

Chapter  
8

# TEMPERATURE & IDEAL GASES



## Content

- Thermal equilibrium
- Temperature scales
- Equation of state
- Kinetic theory of gases
- Kinetic energy of a molecule

## Learning Outcomes

Candidates should be able to:

- (a) show an understanding that regions of equal temperature are in thermal equilibrium
- (b) explain how empirical evidence leads to the gas laws and to the idea of an absolute scale of temperature (i.e. the thermodynamic scale that is independent of the property of any particular substance and has an absolute zero)
- (c) convert temperatures measured in degrees Celsius to kelvin:  
 $T / K = T / ^\circ C + 273.15$
- (d) recall and use the equation of state for an ideal gas expressed as  $pV = nRT$ , where  $n$  is the amount of gas in moles
- (e) state that one mole of any substance contains  $6.02 \times 10^{23}$  particles and use the Avogadro number  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$
- (f) state the basic assumptions of the kinetic theory of gases
- (g) explain how molecular movement causes the pressure exerted by a gas and hence derive the relationship  $pV = \frac{1}{3}Nm\langle c^2 \rangle$  where  $N$  is the number of gas molecules. (a simple model considering one-dimensional collisions and then extending to three dimensions using  $\frac{1}{3}\langle c^2 \rangle = \langle c_x^2 \rangle$  is sufficient)
- (h) 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 to solve related problems.

**Links  
Between  
Sections  
and Topics**

Concepts such as speed, velocity, force and kinetic energy are carefully defined to make the study of mechanics quantitative. Similarly, there needs to be careful definition of terms like temperature, heat and internal energy, which are used in thermal physics. Understanding thermal physics requires us to approach the concepts from both the macroscopic and microscopic perspectives.

Heat and temperature are often used interchangeably by the lay-person. However, these terms have different and specific meanings in physics. Macroscopically, temperature can be defined in terms of its measurement while heat refers to the energy transferred between two systems at different temperatures. Linking these two ideas is the *zeroth law of thermodynamics*, which states that when two objects at different temperature are placed in thermal contact, there will be energy exchange between them until thermal equilibrium is reached. The zeroth law allows the use of thermometers to measure temperature. When thermal equilibrium is achieved, the thermometer reflects its own temperature which is of the same value as the other body that it is in thermal contact with.

A thermometer is calibrated according to a temperature scale. The *Kelvin* scale has a privileged status, as it is independent of the physical properties of the medium used for temperature measurement. This is unlike the Celsius scale, commonly used in liquid-in-glass thermometers, which is calibrated based on the properties of water. Energy transfer between two substances in thermal contact causes temperature changes in both of them. Heat capacity and specific heat capacity allow for the calculation of temperature changes in interactions involving heat exchanges. Similarly, latent heat is used to calculate the energy required to change the phase of a substance.

Generally, the physical properties of a substance depend on physical quantities such as temperature, pressure and volume. The condition in which a particular material exists is known as its state, and this could be described by such macroscopic physical quantities. We are particularly interested in the study of gases as their volumes can be varied much more dramatically than for typical solids and liquids. At very low pressures, most gases behave in much the same way, which is encapsulated in the the ideal gas model. While the exact properties of real gases are very complex, most gases at room temperature and atmospheric pressure behave approximately like that of ideal gases. The ideal gas equation expresses the relationship between the state variables for an ideal gas.

These concepts lay the foundation for thermodynamics, the study of relationships involving heat, mechanical work, and other aspects of energy and energy transfer. The first law of thermodynamics is central to understanding concepts related to thermodynamic processes. This law is an extension of the principle of conservation of energy through the incorporation of the concept of internal energy.

The kinetic theory of gases links the macroscopic properties such as pressure, volume and temperature of gases, with the microscopic properties such as the mass and speed of the gas molecules. To a good approximation, Newtonian mechanics can be used to model the microscopic motion of gas molecules and concepts from kinematics and dynamics can be applied to analyse the average pressure exerted by the randomly-moving molecules.



**Applications and relevance to daily life**

Many researchers still actively investigate the behaviour of gases using computer simulation and other techniques. Environmental concerns connected with Earth's atmosphere, such as the depletion of the ozone layer, are motivations for such work. A better understanding of the behaviour of gases might lead to an improved characterisation and possible solutions to these problems.

The application of thermodynamics pervades modern society e.g. car engines, air conditioners and power stations. However, an inevitable consequence of this energy conversions in these systems is the discharge of heat. This unwanted release of thermal energy into the environment is known as thermal pollution. One approach to reduce this is the development of alternative sources of energy, e.g. solar power. Another approach is to make things more efficient. Reducing the demand for energy should also be a personal and policy priority.

Links to Core Ideas		
Systems and Interactions	Models and Representations	Conservation Laws
<ul style="list-style-type: none"> <li>Internal energy is the sum of the random distribution of KE and PE associated with the molecules of a system of gas</li> <li>Work done and heat are processes which transfer energy</li> </ul>	<ul style="list-style-type: none"> <li>Kinetic theory of gases</li> <li>Ideal gas law</li> <li>Microscopic versus macroscopic description of a gas</li> <li>Temperature as proportional to the average kinetic energy per particle</li> <li>Common representations: e.g. <math>P</math>-<math>V</math> diagrams</li> <li>Simplifying assumptions: e.g. an ideal gas has no intermolecular forces, negligible heat loss, mean translational KE of a molecule of an ideal gas = <math>\frac{3}{2} kT</math> as a useful approximation</li> </ul>	<ul style="list-style-type: none"> <li>First law of thermodynamics as conservation of energy</li> </ul>

## 8.1

### Temperature and Thermal Equilibrium

**Temperature**

Temperature is a fundamental physical quantity associated with the physiological sense of hotness and coldness. An object that is cold will cause different sensation from one that is warm. These sensations are not reliable enough for scientific work because they are subjective and depend on contrast.

Early attempts in finding a way to measure the "degree of hotness" involved fixing certain values to particular temperatures (at which a particular substance changes phase) and then establishing a scale between them e.g. the Fahrenheit and Centigrade scales. The "degree of hotness" of an object can then be expressed as a number on the scale.

Later in this chapter, you will learn that temperature is a measure of the average kinetic energy possessed by the atoms or molecules of a substance. The greater the average microscopic kinetic energy of the molecules, the higher the temperature of the substance is.

## Heat

A hot cup of coffee left in a room will eventually cool and conversely, a cold pan eventually becomes hot when placed above a stove. What happens is that there is a *transfer of energy*, called **heat**, due to a temperature difference between objects or between an object and its surroundings.

Heat flows from an object at a higher temperature to another at a lower temperature until their temperatures are equal at some intermediate value.

## Thermal Equilibrium

When heat can be exchanged between, the objects are said to be in **thermal contact**. For two objects in thermal contact, the object at the higher initial temperature loses heat and its temperature decreases whereas the object at the lower initial temperature gains heat and its temperature increases.

Some time later, net heat transfer between them ceases i.e. each object gains heat from and loses heat to the other object at the same rate. The two objects are said to be in a state of **thermal equilibrium**.

When there is **no net flow of heat** between two objects in thermal contact, the two objects are in a state of **thermal equilibrium**.

This implies that the **temperatures** of the two objects are equal. In the previous example of the hot cup of coffee, thermal equilibrium is eventually attained between the cup of coffee and its surroundings and both will be at the same temperature.

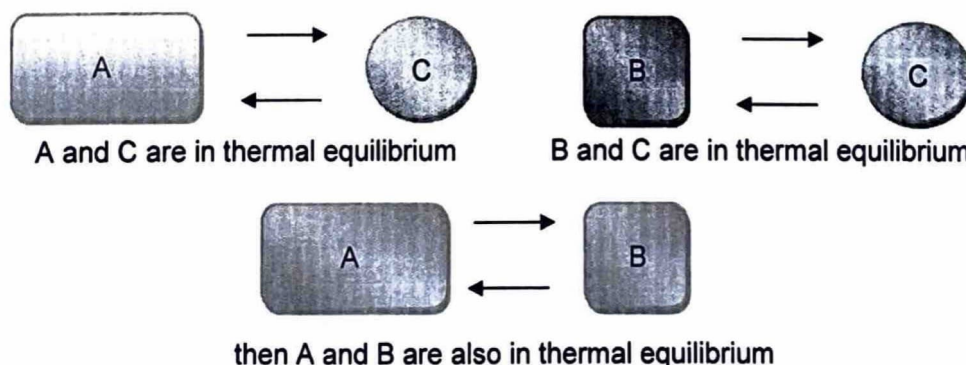
Two objects are in thermal equilibrium if and only if they are at the same temperature.

Hence temperature can be thought of as the property that determines whether an object is in thermal equilibrium with other objects.

## The Zeroth Law of Thermodynamics

The concept of objects in thermal equilibrium being at the same temperature is formalised in the **Zeroth Law of Thermodynamics** which can be stated as follows:

If objects A and B are each separately in thermal equilibrium with a third object C, then A and B are also in thermal equilibrium with each other.



In summary, if  $T_A = T_C$  and  $T_B = T_C$ , then  $T_A = T_B$ , where  $T_A$ ,  $T_B$  and  $T_C$  are the temperatures of objects A, B and C respectively.



One may use object C as a **thermometer** to measure the temperatures of objects A and B separately. If the results of the two separate measurements yield the same value for objects A and B, then it can be inferred that they will be in thermal equilibrium with each other if they are to be brought into thermal contact i.e. there will not be any net heat transfer between them as their temperatures are the same.

The importance of this law was recognised only after the first and second laws of thermodynamics had been established. Since it is most fundamental, the name "zeroth" seemed appropriate.

## 8.2

### Temperature Scales

#### Temperature Scales and Empirical Celsius Scale

As this is a recap of 'O' level concepts, please refer to Appendix for details.

#### Example 1

A resistance thermometer has a resistance of  $25.40\ \Omega$  at ice point,  $27.34\ \Omega$  at steam point and  $26.95\ \Omega$  at the melting point of a certain solid.

- Calculate the temperature of its melting point on the Celsius scale of the resistance thermometer.
- State an assumption made in your calculations.

(a) Using  $\theta = \frac{(R_\theta - R_0)}{(R_{100} - R_0)} \times 100$

The temperature of melting point of solid,  $\theta = \frac{(26.95 - 25.40)}{(27.34 - 25.40)} \times 100 = 79.9\ ^\circ\text{C}$

- (b) The resistance of the metal varies linearly with temperature.

#### Constant-Volume Gas Thermometer

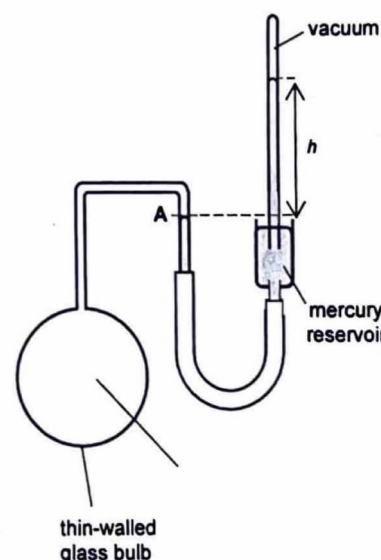
The thermometric property of a gas thermometer is the pressure of a fixed mass of gas at constant volume. The bulb may contain dry air like those found in in school models or hydrogen, helium or nitrogen, in more accurate versions.

As the temperature increases, the gas in the bulb expands, pushing the mercury level in the capillary tube below 'A'. The level of the reservoir is adjusted until the level of the mercury reaches the level 'A' again to ensure constant volume of gas.

Height  $h$  is then measured and the pressure of the gas can be found using  $p = h\rho g$ , where  $\rho$  is the density of mercury.

If calibrated at the ice and steam points, it gives readings on the Celsius scale and the temperature can be determined from the equation

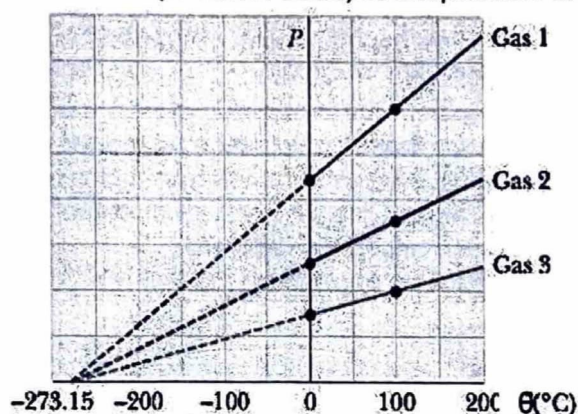
$$\theta = \frac{(p_\theta - p_0)}{(p_{100} - p_0)} \times 100\ ^\circ\text{C}.$$



A constant volume gas thermometer

Experiments using gas thermometers show that the thermometer readings are nearly independent of the type of gas used particularly when pressure is low. This is because the lower the pressure of a real gas, the closer it approaches a linear relationship between the variation of pressure or volume with temperature, as the behaviour of real gases approaches that of an **ideal gas** (ideal gas will be discussed in a later section).

If empirical Celsius scales for different gases are set up by obtaining the pressures of the gas at the ice point and steam point, and the graph of pressure  $p$  against temperature  $\theta$  is extrapolated to zero pressure, the temperature tends to a value of  $-273.15^\circ\text{C}$  regardless of the type of gas used or the value of the low starting pressures. This suggests that this particular temperature value is universal in importance because it does not depend on the properties of any particular substance. This temperature is known as the **absolute zero** and is used as the lower fixed point on the **thermodynamic scale** (or Kelvin Scale) of temperature in the next section.



#### The Celsius Scale

The Celsius scale is defined based on the ice point ( $0^\circ\text{C}$ ) and steam point ( $100^\circ\text{C}$ ) of water at a pressure of 1 atm. This allows the scale to be easily calibrated as water is easily accessible.

However, a better scale will be one which does not depend on any particular substance and hence make the definition of scales more universal.

#### Thermodynamic Temperature Scale (Absolute Temperature Scale)

**The absolute scale of temperature or the thermodynamic scale of temperature is one that is independent of the property of any substance and has an absolute zero.**

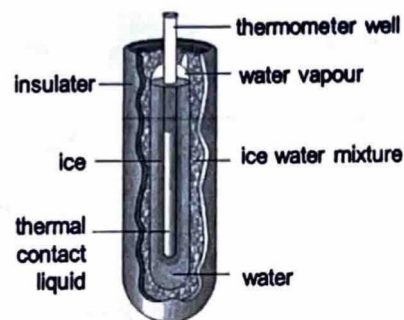
**Absolute zero** is defined as the zero point (0 K) of the thermodynamic temperature scale and the temperature at which all substances have a minimum internal energy.

It is the theoretical temperature at which the molecules of a substance have the lowest energy and hence the substance has minimum internal energy (discussed in later section).

Also known as the Kelvin temperature scale (named after Lord Kelvin who proposed it in 1848), it is based on the theoretical efficiency of a perfectly reversible heat engine (not in the syllabus). The symbol for the temperature on this scale is  $T$  and the unit is the kelvin (K).



In 1954, the International Committee on Weights and Measures adopted the **absolute zero** as the lower fixed point on the thermodynamic temperature scale with a value of 0 K. The upper fixed point was taken as the **triple point of water**, which is the single temperature and pressure at which water, water vapour and ice can co-exist in equilibrium in an enclosed cell like the one shown on the right.



The triple point of water occurs at a temperature of 0.01 °C and is therefore assigned a value of 273.16 K on the thermodynamic scale (at a pressure of 611.2 Pa). One kelvin (1 K) is defined such that a change in thermodynamic temperature  $T$  results in a change of energy  $kT$ , where  $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$  is the Boltzmann constant.

Using the constant volume gas thermometer to measure the pressures  $p$  at an unknown temperature  $T$  and  $p_r$  at triple point,  $T$  can be determined from

$$T = 273.16 \left( \frac{p}{p_r} \right).$$

Hence on the thermodynamic temperature scale, the temperature in kelvin is directly proportional to the pressure of the gas.

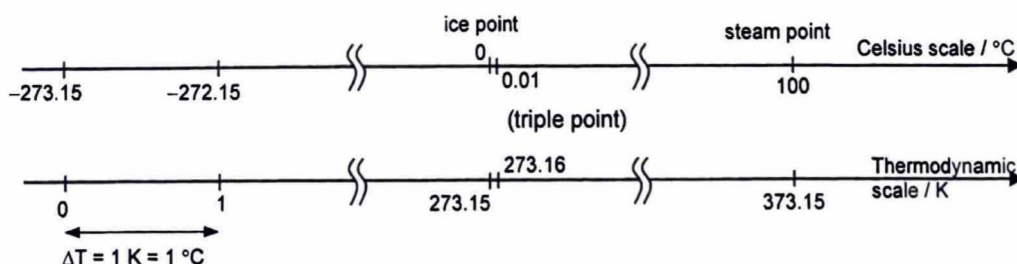
**Relationship between the Celsius Scale and the Thermodynamic Scale (Absolute Temperature Scale)**

The kelvin has been defined in such a way as to make the size of one unit on the Kelvin scale (one kelvin) identical to the size of one degree on the Celsius scale i.e. an interval of 1 K is equal to an interval of 1 °C.

The absolute zero (0 K) and triple point of water (273.16 K) temperatures on the Kelvin scale correspond to -273.15 °C and 0.01 °C on the Celsius scale respectively. This implies the ice point at 0 °C and steam point at 100 °C on the Celsius scale correspond to thermodynamic temperature values of 273.15 K and 373.15 K respectively. This makes a temperature interval of 1 K the same as 1 °C.

The Celsius temperature  $\theta$  is therefore shifted from the thermodynamic temperature  $T$  according to

$$T / \text{K} = \theta / ^\circ\text{C} + 273.15$$



## 8.3

### Equation of State - The Ideal Gas Equation

#### Ideal Gas

A system of gas consists of molecules moving about freely and randomly in space. The molecules in a gas are relatively far apart and interact only very weakly except during collisions. The forces between molecules, known as van der Waals forces, decreases rapidly with separation.

An **ideal gas** is an idealisation of the real gas in which the potential energy of interaction between molecules is zero. This is due to the absence of intermolecular forces as the molecules are assumed to be very far apart and do not interact. The behaviour of a real gas can be approximated to that of an ideal gas at sufficiently low pressures and at temperatures well above their liquefaction points.

A state of a system is the set of variables that characterises it. We define an ideal gas in terms of the equation of state that it obeys.

An **ideal gas** is a gas which obeys the equation of state  $pV = nRT$  at all pressures, volumes and temperatures

where  $p$  is the pressure of the gas,  $V$  is the volume of the gas,  $n$  is the amount of gas in moles,  $R$  is the molar gas constant and  $T$  is the thermodynamic temperature (in kelvin) of the gas.

$p$ ,  $V$ , and  $T$  are the state variables that characterise the state of a fixed amount of the system.

#### Empirical Gas Laws

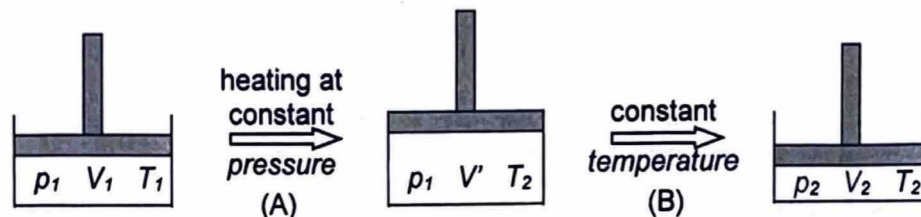
The ideal gas equation can be derived from the following empirical gas laws:

	Boyle's Law	Charles' Law	The Pressure Law
Relationship	$p \propto \frac{1}{V}$	$V \propto T$	$p \propto T$
Constants	$n, T$	$n, p$	$n, V$



**The Ideal Gas Equation (Derivation)**

Consider changing the volume of a fixed mass of ideal gas through two processes:  
(A) Heating the gas at constant pressure (thus allowing the gas to expand)  
(B) Compressing the gas at constant temperature (and allowing heat exchange)



Consider process (A) i.e. constant pressure heating where  $V \propto T$ , hence

$$\frac{V_1}{T_1} = \frac{V'}{T_2} \quad \dots (1)$$

Consider process (B) i.e. constant temperature compression where  $p \propto \frac{1}{V}$ , hence

$$p_1 V' = p_2 V_2$$

$$\Rightarrow V' = \frac{p_2 V_2}{p_1} \quad \dots (2)$$

Substituting (2) into (1),  $\frac{V_1}{T_1} = \frac{\left(\frac{p_2 V_2}{p_1}\right)}{T_2} \Rightarrow \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} = \text{constant}$

The above equation is simply a combination of the empirical gas laws relating the state variables and we expect the constant to be proportional to the amount of gas  $n$  in moles

$$\frac{pV}{T} \propto n$$

If we use S.I. units for all the quantities, the constant of proportionality is a constant known as **molar gas constant**,  $R$

$$\Rightarrow \frac{pV}{T} = nR$$

where  $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ .

Hence, the ideal gas equation (or the equation of state for ideal gas) can be expressed as

$$pV = nRT$$

where the unit of each quantity is in its respective SI unit.

**Avogadro's Constant & the Mole**

Avogadro's constant ( $N_A$ ) is defined as exactly  $6.02 \times 10^{23}$  particles per mole,  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ .

The mole is defined as the amount of matter containing the number of particles (atoms, ions or molecules) equal to exactly  $6.02 \times 10^{23}$  particles.

The mole establishes a connection between a macroscopic amount of matter with the number of microscopic particles within it.

**Ideal Gas Equation – Alternative Forms**

Below are alternative expressions of the equation of state for an ideal gas:

for 1 mole:

$$pV_m = RT$$

where  $V_m = \frac{V}{n}$  is the molar volume

for  $N$  molecules:

$$pV = \left( \frac{N}{N_A} \right) RT$$

where  $N_A$  is the Avogadro constant

$\Rightarrow$

$$pV = NkT$$

where  $k = \frac{R}{N_A}$  is the Boltzmann constant with a value of  $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ .

These two are alternative forms of the equation of state, and we may use them depending on which quantities are given in the question. However, if you were to state the ideal gas equation it will be  $pV = nRT$ .

**Example 2**

An oxygen tank of volume  $50.0 \times 10^{-3} \text{ m}^3$  experiences a pressure change from  $21.4 \times 10^5 \text{ Pa}$  to  $7.8 \times 10^5 \text{ Pa}$  when some oxygen is drawn out. In the process, the temperature drops from  $30.0^\circ \text{C}$  to  $10.0^\circ \text{C}$ .

Determine the number of moles of molecules drawn out during the process.

$$pV = nRT$$

$$(21.4 \times 10^5)(50.0 \times 10^{-3}) = n_1(8.31)(30 + 273.15)$$

$$n_1 = 42.5 \text{ mol}$$

$$pV = nRT$$

$$(7.8 \times 10^5)(50.0 \times 10^{-3}) = n_2(8.31)(10 + 273.15)$$

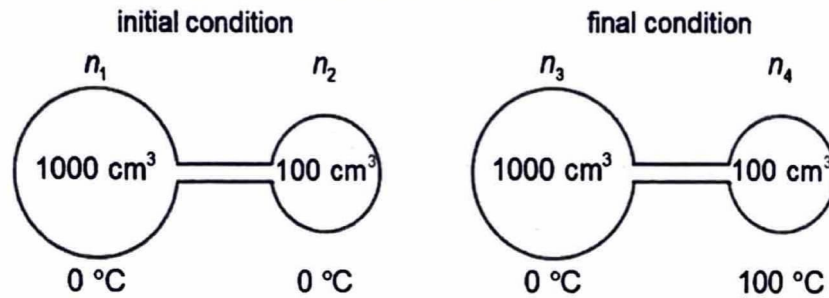
$$n_2 = 16.6 \text{ mol}$$

$$n_1 - n_2 = 42.5 - 16.6 = 25.9 \text{ mol}$$



**Example 3**

Two gas containers with volumes of  $100 \text{ cm}^3$  and  $1000 \text{ cm}^3$  are connected by a tube of negligible volume, and contain air at a pressure of  $1000 \text{ mmHg}$ . If both vessels have an original temperature of  $0^\circ\text{C}$ , what is the new pressure in  $\text{mm Hg}$  when the temperature of the smaller container is raised to  $100^\circ\text{C}$ ?



$$pV = nRT \Rightarrow n = \frac{pV}{RT}$$

By conservation of mass,  $n_1 + n_2 = n_3 + n_4$

$$\frac{p_1 V_1}{RT_1} + \frac{p_2 V_2}{RT_2} = \frac{p_3 V_3}{RT_3} + \frac{p_4 V_4}{RT_4}$$

The pressure in the containers will equalize, so  $p_1 = p_2 = p$  &  $p_3 = p_4 = p'$

$$\frac{1000 \times 1000}{273.15} + \frac{1000 \times 100}{273.15} = \frac{p' \times 1000}{273.15} + \frac{p' \times 100}{100 + 273.15}$$

$$p' = 1025 \text{ mm Hg}$$

## 8.4

### Kinetic Theory of Gases - Kinetic Energy of a Molecule

#### Microscopic Model of an Ideal Gas

In this section, a microscopic model for an ideal gas is developed by considering an ideal gas in an enclosed container. The following are assumptions of the kinetic theory of gases that are made in developing the model:

1. The gas consists of a large number of molecules in random motion (so that only the average behaviour is considered).
2. The molecules exert no intermolecular forces on one another except during collisions (i.e. microscopic potential energy = 0)
3. Collisions between the molecules and the container are perfectly elastic.
4. The duration of an intermolecular collision is negligible compared with the duration between collisions.
5. The volume of the molecules is negligible compared with the volume occupied by the gas.

An ideal gas satisfies the above assumptions.

In the following derivations, it is further assumed that the walls of the container are rigid and that the container is massive such that it does not move when hit by the molecules.

#### Derivation

Consider a cube of side  $d$  containing  $N$  molecules of an ideal gas. Let the mass of each molecule be  $m$ .

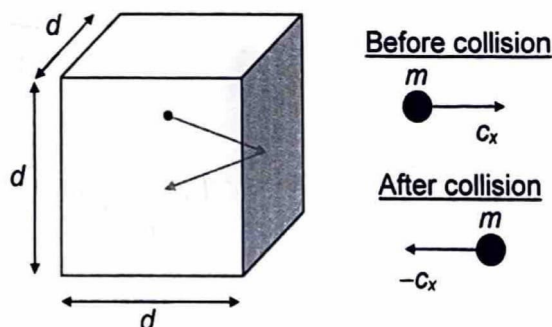
Consider a molecule with velocity  $c_x$  in the  $x$ -direction. Upon elastically colliding with the wall, its velocity changes from  $c_x$  to  $-c_x$ . The change in momentum for this molecule is then

$$\begin{aligned}\Delta P &= \text{final momentum} - \text{initial momentum} \\ &= (-mc_x) - mc_x = -2mc_x\end{aligned}$$

The next time this same molecule collides with the same wall, it would then have travelled a total distance of  $2d$  along the  $x$ -direction (across the container and back).

Hence, on average, over the duration of time  $\Delta t$ , the molecule collides with the wall once where

$$\Delta t = \frac{2d}{c_x}$$





Therefore, the average rate of change of momentum for this molecule, which by Newton's 2<sup>nd</sup> Law is equal to the average force that the wall acts on the molecule, is given by

$$F_{\text{on molecule}} = \frac{\Delta P}{\Delta t} = -2mc_x \times \frac{c_x}{2d} = -\frac{mc_x^2}{d}$$

Hence, by Newton's 3<sup>rd</sup> Law, the average force that the molecule acts on the wall is

$$F_{\text{on wall}} = -F_{\text{on molecule}} = \frac{mc_x^2}{d}$$

By considering all the  $N$  number of molecules, the total force acting on the wall,

$F_{\text{tot}}$ , is given by

$$F_{\text{tot}} = \frac{mc_{x1}^2}{d} + \frac{mc_{x2}^2}{d} + \frac{mc_{x3}^2}{d} + \dots + \frac{mc_{xN}^2}{d} = \frac{m}{d}(c_{x1}^2 + c_{x2}^2 + c_{x3}^2 + \dots + c_{xN}^2)$$

where  $c_{xN}^2$  is the square of the  $x$ -velocity of the  $N^{\text{th}}$  molecule.

The mean-square-speed of all molecules in the  $x$ -direction is defined as

$$\langle c_x^2 \rangle = \frac{c_{x1}^2 + c_{x2}^2 + c_{x3}^2 + \dots + c_{xN}^2}{N}$$

Hence

$$F_{\text{tot}} = \frac{Nm}{d} \langle c_x^2 \rangle.$$

The total pressure  $p$  on the wall is therefore

$$P = \frac{F_{\text{tot}}}{d^2} = \frac{Nm}{d^3} \langle c_x^2 \rangle = \frac{Nm}{V} \langle c_x^2 \rangle,$$

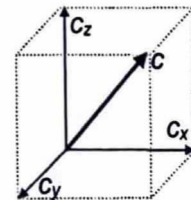
where the volume of the cubic container is  $V = d^3$ .

Applying the Pythagoras Theorem to the 3-D velocity vector for a molecule leads to

$$c^2 = c_x^2 + c_y^2 + c_z^2.$$

Taking the average on both sides of the equation,

$$\langle c^2 \rangle = \langle c_x^2 \rangle + \langle c_y^2 \rangle + \langle c_z^2 \rangle.$$



However, since  $N$  is large and the molecules are moving randomly, with no preference in any direction,  $\langle c_x^2 \rangle = \langle c_y^2 \rangle = \langle c_z^2 \rangle$ .

$$\Rightarrow \langle c^2 \rangle = 3\langle c_x^2 \rangle$$

$$\therefore \langle c_x^2 \rangle = \frac{1}{3} \langle c^2 \rangle$$

Substituting  $\langle c_x^2 \rangle = \frac{1}{3} \langle c^2 \rangle$  into  $p = \frac{Nm}{V} \langle c_x^2 \rangle$  leads to  $p = \frac{1}{3} \frac{Nm}{V} \langle c^2 \rangle$ :

$$pV = \frac{1}{3} Nm \langle c^2 \rangle$$

where  $N$  is the number of gas molecules,  
 $m$  is the mass of one gas molecule,  
 $\langle c^2 \rangle$  is the mean-square-speed of the gas molecules.

Using  $p = \frac{1}{3} \frac{Nm}{V} \langle c^2 \rangle$  and  $p = \frac{m_{total}}{V} = \frac{Nm}{V}$ ,

$$p = \frac{1}{3} \rho \langle c^2 \rangle$$

The root-mean-square  $c_{rms}$  is defined as

$$c_{rms} = \sqrt{\langle c^2 \rangle} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_N^2}{N}}$$

By combining  $pV = NkT$  and  $pV = \frac{1}{3} Nm \langle c^2 \rangle$ ,

$$\frac{1}{3} Nm \langle c^2 \rangle = NkT$$

$$\Rightarrow \frac{1}{2} m \langle c^2 \rangle = \frac{3}{2} kT$$

The left-hand side of the equation is **the average (or mean) translational microscopic kinetic energy**  $\langle E_k \rangle$  of one gas molecule. Thus,

$$\langle E_k \rangle = \frac{1}{2} m \langle c^2 \rangle = \frac{1}{2} m c_{rms}^2 = \frac{3}{2} kT$$

This equation tells us that temperature is a direct measure of the average microscopic kinetic energy, with proportionality constant  $\frac{3}{2} k$ .

In fact,  $\frac{3}{2} kT$  is the microscopic kinetic energy possess by each monatomic particle. For non-monatomic particles, the microscopic kinetic energy will be higher due to rotational and vibrational kinetic energies.



**Example 4**

A Helium-Neon laser contains a mixture of Helium and Neon gases, the atomic masses of which are  $4u$  and  $20u$ , respectively. What is the ratio of the root-mean-square speed of Helium atoms to that of the Neon atoms?

Assuming that the Helium and Neon gases are in thermal equilibrium, they are at the same temperature. Hence the average kinetic energies of the two types of gas molecules are equal:

$$\begin{aligned} \frac{1}{2} m_{\text{He}} \langle c_{\text{He}}^2 \rangle &= \frac{1}{2} m_{\text{Ne}} \langle c_{\text{Ne}}^2 \rangle \Rightarrow \frac{\langle c_{\text{He}}^2 \rangle}{\langle c_{\text{Ne}}^2 \rangle} = \frac{m_{\text{Ne}}}{m_{\text{He}}} \\ \Rightarrow \frac{c_{\text{rms}}^{\text{He}}}{c_{\text{rms}}^{\text{Ne}}} &= \sqrt{\frac{\langle c_{\text{He}}^2 \rangle}{\langle c_{\text{Ne}}^2 \rangle}} = \sqrt{\frac{m_{\text{Ne}}}{m_{\text{He}}}} = \sqrt{\frac{20u}{4u}} = 2.24 \end{aligned}$$

**Example 5**

In an ideal gas at  $600^\circ\text{C}$ , the mean kinetic energy of the gas molecules is  $1.8 \times 10^{-20} \text{ J}$ . When its molecules are, on average, travelling at half the speed, what are the values for the temperature of the gas and the mean kinetic energy of the molecules?

When the speed is halved,

$$\langle E_K \rangle = \frac{1}{2} m \left\langle \left( \frac{1}{2} v \right)^2 \right\rangle = \frac{1}{4} \times \frac{1}{2} m \langle v^2 \rangle = \frac{1}{4} (1.8 \times 10^{-20}) = 4.5 \times 10^{-21} \text{ J}$$

$$\langle E_K \rangle \propto T \Rightarrow \frac{\langle E_{K2} \rangle}{\langle E_{K1} \rangle} = \frac{T_2}{T_1}$$

$$\begin{aligned} T_2 &= \frac{\langle E_{K2} \rangle}{\langle E_{K1} \rangle} \times T_1 = \frac{1}{4} \times (600 + 273.15) \\ &= 218.29 \text{ K} = -54.9^\circ\text{C} \end{aligned}$$

## APPENDIX

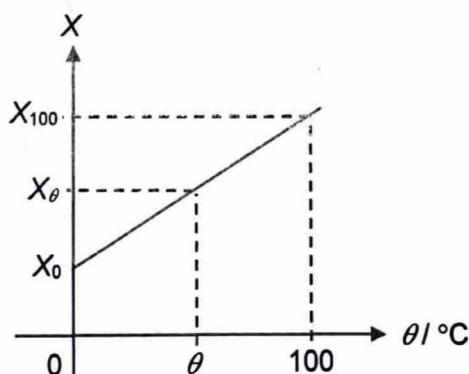
### Empirical Celsius Scale

Each type of thermometer can be used to establish its own temperature scale based on the thermometric property of the substance used. An **empirical scale** of temperature can be established for a particular thermometer by taking the values of its thermometric property at two fixed points i.e. the lower and upper fixed points where a specific substance undergoes changes in phase and subsequently dividing the range of values into a number of equal steps (or degrees).

For the empirical **Celsius** scale of temperature, the lower fixed point is the ice point i.e. the temperature of pure ice in equilibrium with water at standard atmospheric pressure of 101.3 kPa and it is assigned the value of 0 °C. The upper fixed point is the steam point i.e. the temperature at which steam and pure boiling water are in equilibrium at standard atmospheric pressure and is assigned the value of 100 °C.

The following steps are taken in setting up an empirical Celsius scale.

1. Measure the thermometric property  $X$  at the two fixed points;  $X_0$  for the value at ice point and  $X_{100}$  for the value at steam point.
2. Divide the interval of  $(X_{100} - X_0)$  into 100 divisions so that each division corresponds to an interval of one degree of temperature.
3. Assume that the thermometric property  $X$  varies linearly with temperature. On a calibration graph of  $X$  versus temperature  $\theta$ , it means joining the points (0 °C,  $X_0$ ) and (100 °C,  $X_{100}$ ) with a straight line.



4. Measure the thermometric property at the unknown temperature  $\theta$  and call it  $X_\theta$ . The unknown temperature  $\theta$  in °C is then computed from

$$\theta = \frac{(X_\theta - X_0)}{(X_{100} - X_0)} \times 100 \text{ } ^\circ\text{C}$$



The following table gives the equations to determine the unknown temperature  $\theta$  based on the empirical Celsius scale for the different types of thermometers corresponding to the different thermometric properties

Thermometer	Thermometric Property	Empirical Equations
Liquid-in-glass	Length of liquid in a column ( $L$ )	$\theta = \frac{(L_{\theta} - L_0)}{(L_{100} - L_0)} \times 100$
Platinum resistance	Resistance of platinum wire ( $R$ )	$\theta = \frac{(R_{\theta} - R_0)}{(R_{100} - R_0)} \times 100$
Thermocouple	E.M.F between thermocouple junctions ( $E$ )	$\theta = \frac{(E_{\theta} - E_0)}{(E_{100} - E_0)} \times 100$

Formula

**The choice of different thermometric substances and thermometric properties would lead to a different scale. Agreement between scales occurs only at the two fixed points. This happens because the thermometric properties may not vary linearly with temperature.**

For example, when the temperature of some water in a beaker is measured using both a mercury-in-glass thermometer and a resistance thermometer, the readings of the thermometers differ as the two thermometric properties vary in different manners with temperature. Nevertheless, all types of thermometers, irrespective of the thermometric property used, give the same readings at the fixed points.

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

## THE IDEAL GAS TEMPERATURE SCALE

The thermodynamic scale is based on the theoretical efficiency of a perfectly reversible heat engine. As such, it is impossible to put it into practice, since a perfectly reversible heat engine does not exist.

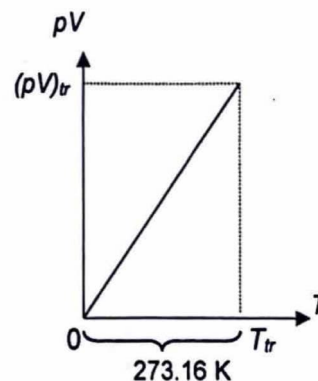
The ideal gas temperature scale provides us a way to obtain the thermodynamic temperature. It uses the properties of an ideal gas, which obeys the equation

$$pV = nRT$$

where  $n$  is the number of moles and  $R$  is the molar gas constant.

Hence for a fixed mass of gas  $pV \propto T$ .

See Section 8.3 for more discussion.



Taking the thermometric property as  $pV$ , the thermodynamic temperature can be calculated using the equation

$$\frac{(pV)_T}{T} = \frac{(pV)_{tr}}{273.16 \text{ K}} = \text{gradient},$$

where  $(pV)_{tr}$  is taken at the triple point of water, at which point  $T = 273.16 \text{ K}$ .

Real gases at low pressure behave nearly as ideal gases. Using a real gas in a constant volume gas thermometer, the ideal gas temperature (and hence the thermodynamic temperature) can be obtained by extrapolating the results to zero pressure. Hence if a real gas is used, the thermodynamic temperature is given by

$$T = \lim_{p_{tr} \rightarrow 0} \frac{(pV)_T}{(pV)_{tr}} \times 273.16 \text{ K}$$

To obtain the ideal gas temperature using a constant-volume gas thermometer:

1. Place the bulb of a constant-volume gas thermometer in the triple-point cell and obtain the pressure  $p_{tr}$ .
2. Remove the bulb from the triple point cell and immerse it a constant temperature bath of unknown temperature  $T$ . Obtain the pressure  $p_T$  at this temperature.
3. Calculate the temperature provisionally from the formula

$$T = \frac{p_T}{p_{tr}} \times 273.16 \text{ K}.$$

4. Remove some of the gas inside the bulb so that the pressure  $p_{tr}$  is reduced. Obtain the new values of  $p_{tr}$  and  $p_T$ . Another provisional value of  $T$  is calculated using these new values of  $p_{tr}$  and  $p_T$  in the formula

$$T = \frac{p_T}{p_{tr}} \times 273.16 \text{ K}.$$

This value will be closer to the true value of  $T$  on the ideal gas temperature than the previous one.

5. Step 4 is repeated for further values of  $p_{tr}$ ,  $p_T$  and  $T$ .

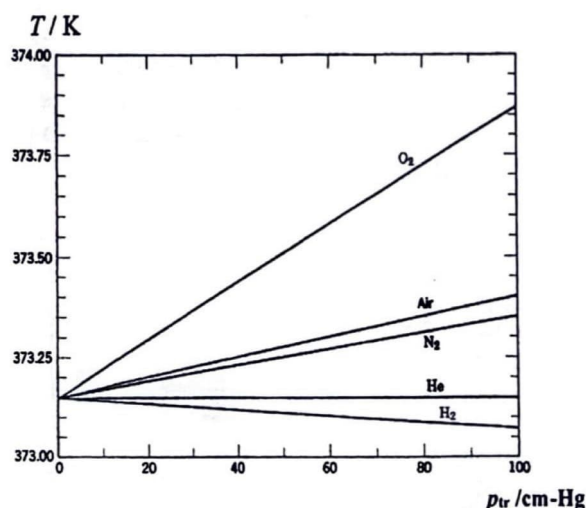


6. A graph of  $T$  is plotted against  $p_{tr}$  and the line is extrapolated to zero pressure.  
The intercept on the vertical axis when  $p_{tr} = 0$  gives the value of the ideal gas temperature of the unknown temperature.

Fig. A1 shows the graphs obtained from the procedure for constant-volume gas thermometers of different gases.

Note that at a particular  $p_{tr}$ , the values of  $T$  given by different gas thermometers differ. However, as the amount of gas in the thermometer reduces and  $p_{tr}$  falls, the temperature readings of constant-volume gas thermometers using different gases get closer to one another. The gas is approaching the ideal gas.

If the graphs are extrapolated to  $p_{tr} = 0$ , they all meet at a point. This point gives the value of the ideal gas temperature and is **independent** of the gas used as all gases becomes ideal at  $p_{tr} = 0$ .

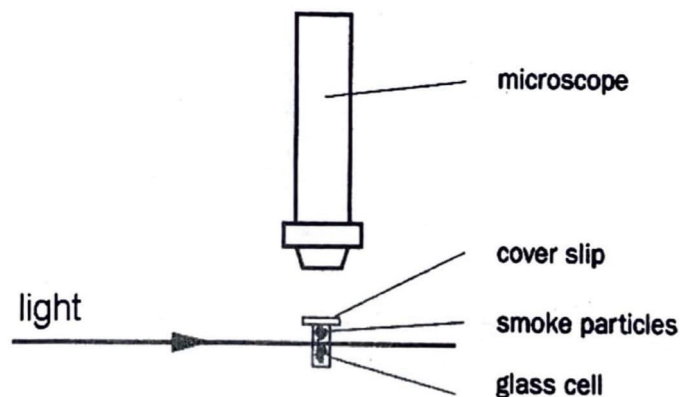


**Fig. A1** The readings of a constant-volume gas thermometer for the temperature  $T$  of condensing steam as a function of  $p_{tr}$ , when different gases are used.

## BROWNIAN MOTION

Jan Ingenhousz made some observations of the irregular motion of carbon dust on alcohol in 1765 but Brownian motion is generally regarded as having been discovered by the botanist Robert Brown in 1827. The story goes that Brown was studying pollen particles floating in water under the microscope. He then observed minute particles within vacuoles in the pollen grains executing the jittery motion that now bears his name. By doing the same with particles of dust, he was able to rule out that the motion was due to pollen being "alive", but it remained to explain the origin of the motion. The first to give a theory of Brownian motion was Louis Bachelier in 1900 in his PhD thesis "The theory of speculation".

At that time the atomic nature of matter was still a controversial idea. Albert Einstein and Marian Smoluchowski observed that, if the kinetic theory of fluids was right, then the molecules of water would move at random and so a small particle would receive a random number of impacts of random strength and from random directions in any short period of time. This random bombardment by the molecules of the fluid would cause a sufficiently small particle to move in exactly the way described by Brown. Theodor Svedberg made important demonstrations of Brownian motion in colloids and Felix Ehrenhaft, of particles of silver in air. Jean Perrin carried out experiments to test the new mathematical models, and his published results finally put an end to the century-long dispute about the reality of atoms and molecules.



The random motion of smoke particles in air can be observed by means of a microscope. This is due to the continuous bombardment of a tiny smoke particle by numerous air molecules all round it. The air molecules move with different velocities in different directions. The resultant force on the smoke particle is therefore unbalanced and irregular in magnitude and direction.



# Tutorial 8 TEMPERATURE & IDEAL GASES



## Self-Check Questions

- S1** Two bodies are in thermal equilibrium. What does this statement mean?
- S2** By reference to heat transfer, explain what is meant by
- (i) two bodies having the same temperature,
  - (ii) body H having a higher temperature than body C.
- S3** State the *zeroth law of thermodynamics* and explain its importance in relation to the use of a thermometer to measure temperature.
- S4** Explain the concept of absolute zero and its relation to the thermodynamic temperature scale.
- S5** State what is meant by an "absolute temperature scale".
- S6** What is Avogadro's constant? Explain its significance.
- S7** State the ideal gas equation which uses
- (i) number of moles
  - (ii) number of molecules
- Explain the symbols used.
- S8** Derive the ideal gas equation from empirical laws.
- S9** State the assumptions used for the derivation of the microscopic model of an ideal gas.
- S10** State the equation that relates pressure  $p$ , number density  $n$ , mass of an molecule  $m$ , and mean-square speed  $\langle c^2 \rangle$ .
- S11** State how the thermodynamic temperature of an ideal gas is related to the average microscopic kinetic energy of the molecules of the gas.

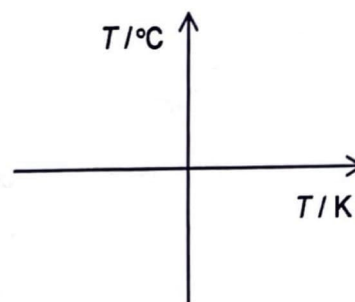
### Self-Practice Questions

#### *Temperature*

**SP1** Express  $40^{\circ}\text{C}$  and  $20^{\circ}\text{C}$  as temperatures measured on the thermodynamic scale. Hence, comment on the statement "Today the temperature is  $40^{\circ}\text{C}$  and yesterday was  $20^{\circ}\text{C}$ . So it is twice as hot today as it was yesterday".

**SP2** A student draws a linear graph on the axes shown in order to convert temperatures in Kelvins to temperatures in degrees Celsius. What is the intercept on the vertical axis and the gradient of the line?

	Intercept	Gradient
<b>A</b>	0	$1/273$
<b>B</b>	$-273$	1
<b>C</b>	$+273$	1
<b>D</b>	0	273



#### *Ideal Gas (Equation of State)*

**SP3** Determine the approximate number of atoms in one cubic metre of ideal gas at a temperature of  $27^{\circ}\text{C}$  and a pressure of  $1.0 \times 10^5 \text{ Pa}$ .

**SP4** An ideal gas at pressure  $P$  (in pascal) and temperature  $T$  (in kelvin) has  $X$  molecules per unit volume. If the pressure of the gas is reduced to  $0.5P$  and its temperature is increased to  $2T$ , what is the number of molecules per unit volume of the gas in terms of  $X$ ?

**SP5** The  $x$ -velocities of several particles are given as follow:

$x$ -velocity / $\text{m s}^{-1}$	$-8.0$	$5.5$	$2.4$	$-3.1$	$6.0$
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Calculate the average  $x$ -velocity, the mean-square speed and the root-mean-square speed in the  $x$ -direction.

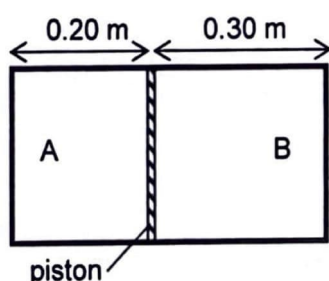


**Discussion Questions**

- D1** An oven has a volume of  $0.064 \text{ m}^3$ . The pressure and temperature of the air in the oven is  $1.0 \times 10^5 \text{ Pa}$  and  $27^\circ\text{C}$  respectively. The mass of one mole of air is  $0.030 \text{ kg}$ . The air behaves as an ideal gas.

- (a) Calculate the mass of air in the oven. [3]
- (b) The oven is heated to a temperature of  $180^\circ\text{C}$ . The oven door is opened. Calculate the mass of air that must escape from the oven for the pressure in the oven to return to  $1.0 \times 10^5 \text{ Pa}$ . [2]

- D2** A cylinder,  $0.50 \text{ m}$  long and of cross-sectional area  $S$ , is closed at each end and fitted with a smooth thermally insulating piston so as to contain an ideal gas in each end A and B as shown.



Initially, the piston is in equilibrium at a distance of  $0.20 \text{ m}$  from one end of the cylinder, and the gas in each compartment is at a temperature of  $27^\circ\text{C}$ .

Now compartment A is submerged in a heat bath of  $177^\circ\text{C}$ , while the gas in B is maintained at  $27^\circ\text{C}$ . The piston moves through a displacement of  $x$  until a new position of equilibrium is obtained.

Determine  $x$ .

- D3** A solid iron cube of side  $20 \text{ mm}$  has a mass of  $6.3 \times 10^{-3} \text{ kg}$ . One mole of the iron atom has a mass of  $5.6 \times 10^{-2} \text{ kg}$ .

- (a) How many iron atoms are there in the cube?
- (b) Hence find the maximum volume that an iron atom could occupy in the solid state.
- (c) Use your answer in (b) to estimate the diameter of an iron atom and state any assumptions made.

- D4** (a) A spherical balloon of volume  $4000 \text{ cm}^3$  contains helium at a pressure of  $1.20 \times 10^5 \text{ Pa}$ . How many moles of helium are in the balloon if the average kinetic energy of the helium atoms is  $3.60 \times 10^{-22} \text{ J}$ ?
- (b) Determine the ratio of the total translational kinetic energy of the molecules in  $1.0 \text{ mol}$  of an ideal gas at room temperature ( $25^\circ\text{C}$ ) to the average kinetic energy of a sprinter, of mass  $70 \text{ kg}$  while running  $100 \text{ m}$  in  $10 \text{ s}$ .

((N10/II/5-part, N85/II/3))

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- D5** A certain plasma contains hydrogen ions (protons) and electrons in thermal equilibrium. Both protons and electrons can be assumed to behave as the molecules of an ideal gas. The root-mean-square speed  $c_{\text{rms}}$  of the electrons in the plasma is estimated to be  $3.0 \times 10^6 \text{ m s}^{-1}$ .
- (a) Determine the root-mean-square speed  $c_{\text{rms}}$  of the hydrogen ions given that the mass of a proton is  $1.67 \times 10^{-27} \text{ kg}$  and that of an electron is  $9.11 \times 10^{-31} \text{ kg}$ .
  - (b) Estimate the temperature of the plasma.
- D6** For a fixed amount of ideal gas in a container with fixed walls, explain why pressure is proportional to mean-square speed of the molecules of an ideal gas.
- D7** (a) The temperature  $T$  of an ideal gas at pressure  $p$  is defined by the equation  $p = nkT$ . Identify the quantities  $n$  and  $k$  in this equation.
- (b) Another equation that relates pressure and mean-square speed is  $p = \frac{1}{3} \rho_m \langle c^2 \rangle$ . Identify the quantity  $\rho_m$ .
- D8** One mole of argon has a mass of 40 g. Assuming argon behaves as an ideal gas, calculate:
- (a) the volume occupied by one mole of argon gas when at temperature 273 K and pressure  $1.01 \times 10^5 \text{ Pa}$ ,
  - (b) the density of argon gas at this temperature and pressure
  - (c) the root-mean-square speed of its atoms at 273 K
  - (d) the average kinetic energy of an argon atom.
- (N99/III/4-part modified)
- D9** The following passage is a quotation from the *Cambridge Encyclopedia of Earth Science*.
- In the upper layers of atmosphere, a large fraction of the hydrogen molecules travel so fast that they are able to escape completely from the Earth. It is estimated that about two-thirds of all the hydrogen molecules present in the atmosphere will escape in about one thousand years. There may also be some loss of helium, but for all other heavier molecules escape is negligible.*
- Suggest an explanation for each of the following observations.
- (a) Fast molecules are able to escape the atmosphere.
  - (b) Molecules of small mass are able to escape whereas more massive ones are not.
  - (c) Some molecules escape even though the speed required for escape is very much greater than their root-mean-square speed.
  - (d) Large quantities of hydrogen have remained indefinitely on the Earth as a constituent of water.

(J89/II/10-part)



**Challenging Questions**

- C1** A tiny hole of area  $8.0 \times 10^{-17} \text{ m}^2$  develops in a sealed glass tube of volume  $2.0 \times 10^{-3} \text{ m}^3$ . The original pressure in the tube is  $1.0 \times 10^{-6} \text{ Pa}$ . The air outside the tube has a pressure of  $1.0 \times 10^5 \text{ Pa}$  and a temperature of 300 K.
- (For this question, the mass of an air molecule may be taken as  $5.6 \times 10^{-26} \text{ kg}$ .)
- (a) Given that the rate  $S$  at which gas molecules hit an area  $A$  of the wall of their container is  $S = \frac{1}{4} n \langle c \rangle A$ , where  $n$  is the number density of the gas molecules and  $\langle c \rangle$  is their root-mean-square speed, calculate the rate at which air molecules leak into the tube from outside.
- (b) Determine how long will it take for the pressure in the tube to reach  $5.0 \times 10^{-3} \text{ Pa}$ .

**Answers**

- |   |  |
|---|--|
| <b>D1</b> (a) 0.077 kg (b) 0.026 kg   | <b>D2</b> 0.05 m to the right  |
| <b>D3</b> (a) $6.8 \times 10^{22}$ (b) $1.2 \times 10^{-28} \text{ m}^3$<br>(c) $4.9 \times 10^{-10} \text{ m}$ | <b>D4</b> (a) 3.32 mol (b) 1.1   |
| <b>D5</b> (a) $7.0 \times 10^4 \text{ m s}^{-1}$ (b) $2.0 \times 10^5 \text{ K}$                                | <b>D8</b> (a) $2.25 \times 10^{-2} \text{ m}^3$ (b) $1.78 \text{ kg m}^{-3}$<br>(c) $413 \text{ ms}^{-1}$ (d) $5.65 \times 10^{-21} \text{ J}$ |
| <b>C1</b> (a) $2.28 \times 10^{11} \text{ s}^{-1}$ (b) 2.95 h   |  |

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**Self-Check Questions Suggested Solutions**

- S1** It means that there is no net transfer of heat between the two bodies and the two bodies are at the same temperature.
- S2** (i) There is no net heat transfer between the two bodies.  
(ii) If body H and body C is in thermal contact, then there will be heat transfer from body H to body C.
- S3** Zeroth Law of Thermodynamics states that if objects A and B are each separately in thermal equilibrium with a third object C, then A and B are in thermal equilibrium with each other.  
Zeroth Law of Thermodynamics explains the basis for temperature measurement. The comparison of temperatures of A and B can be done with C without making direct thermal contact between A and B i.e. C acts as a thermometer.
- S4** Absolute zero is the theoretical temperature at which the molecules of all substances have the lowest energy, i.e. all substances have a minimum internal energy at absolute zero. It is also the zero point (0 K) of the thermodynamics temperature scale.
- S5** This means that the temperature on such a scale is not dependent on the thermometric property of any particular substance.
- S6** Avogadro's constant ( $N_A$ ) is defined as exactly  $6.02 \times 10^{23}$  particles per mole.
- S7** (i)  $pV = nRT$                       (ii)  $pV = NkT$   
 $p$  is pressure of the gas,  $V$  is the volume of the gas,  $n$  is the amount of gas in moles,  $N$  is number of molecules in the gas,  $T$  is the thermodynamic temperature,  $R$  is the molar gas constant, and  $k$  is the Boltzmann constant.
- S8** Refer to Pages 10 and 11 of the lecture notes.
- S9** Refer to Page 14 of the lecture notes.
- S10**  $p = \frac{1}{3} \rho m \langle c^2 \rangle$ .
- S11** The average microscopic kinetic energy of a molecule of the gas is proportional to the thermodynamic temperature  $T$  of the gas:  $\langle E_k \rangle = \frac{3}{2} kT$



### Self-Practice Questions Suggested Solutions

**SP1**  $T_{\text{today}} / \text{K} = 40 + 273.15 = 313.15, T_{\text{today}} = 313.15 \text{ K}$

$T_{\text{yesterday}} / \text{K} = 20 + 273.15 = 293.15, T_{\text{yesterday}} = 293.15 \text{ K}$

The statement assumes that the Celsius scale is an absolute scale and hence can be compared in absolute quantities. On the thermodynamic temperature scale, it is wrong to say that 'is is twice as hot today as it was yesterday'.

**SP2** B.  $T / \text{K} = \theta / ^\circ\text{C} + 273.15$ , hence  $\theta / ^\circ\text{C} = T / \text{K} - 273.15$ .

**SP3**  $pV = NkT$

$(1.0 \times 10^5)(1.0) = N(1.38 \times 10^{-23})(27 + 273.15)$

$N = 2.41 \times 10^{25} \text{ atoms/molecules/particles}$

**SP4**  $pV = NkT \Rightarrow X = \frac{N}{V} = \frac{p}{kT}$

$\frac{X_2}{X} = \frac{p_2 / kT_2}{p / kT} = \frac{0.5p / (2T)}{p / T} = \frac{1}{4}$

$X_2 = 0.25 X$

**SP5**  $c_{\text{ave}} = \frac{-8.0 + 5.5 + 2.4 - 3.1 + 6.0}{5} = 0.56 \text{ m s}^{-1}$

$\langle c^2 \rangle = \frac{(-8.0)^2 + (5.5)^2 + (2.4)^2 + (-3.1)^2 + (6.0)^2}{5} = 29 \text{ m}^2 \text{ s}^{-2}$

$c_{\text{rms}} = \sqrt{\langle c^2 \rangle} = \sqrt{29.124} = 5.4 \text{ m s}^{-1}$