12 TEMPERATURE & IDEAL GASES

H2 Physics 9478

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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 degrees Celsius to kelvin: $T/\mathrm{K} = \theta/^{\circ}\mathrm{C} + 273.15$.

(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 $N_A = 6.02 \times 10^{23}\ \mathrm{mol}^{-1}$ as well as the relationship $Nk = nR$ between the Boltzmann constant and the molar gas constant (n is the amount of substance in moles).

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

(f) explain how the random motion of gas particles exert 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 use the relationship that the mean translational kinetic energy of a particle of an ideal gas is (directly) proportional to the thermodynamic temperature (i.e., $\frac{1}{2}m\langle c^2 \rangle = \frac{3}{2}kT$) to solve problems.

Temperature and Ideal Gases – An Overview

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 using a thermometer, while heat refers to the energy transferred between two systems due to a temperature difference between them.

A thermometer is used to measure temperature and it 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.

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 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.

A key focus of this topic is to model the ideal gas with the kinetic theory of gases, which 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. The collective macroscopic properties of a system therefore come from taking suitable averages of physical quantities from single-particle mechanics.

A crucial area where the investigation into the behaviour of gases will be the environment. Extensive modelling of the atmosphere and relevant large-scale systems is needed to characterise and deal with climate change. Even the simplest models will involve and incorporate many aspects of physics. Tackling climate change is an existential question for human society – a huge issue that provides plenty of scope for discussion and possible action at global and local scales, at policy and personal levels.

12.1 Temperature scales

❖ 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 dependent 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.

❖ Thermometer Temperature Scales

In order to measure temperature reliably, many temperature scales have been developed. A temperature scale is a system of measuring temperature. Most of them rely on measuring the changes in some physical property of a substance that varies with temperature. This is known as **thermometric property**.

Thermometer	Thermometric Substance	Thermometric Property
liquid-in-glass	fix mass of liquid in a capillary tube	length of liquid
platinum resistance	fixed length of platinum wire	resistance of wire
constant volume gas	fixed mass of gas at constant volume	pressure of a gas
thermocouple	two junctions of dissimilar metals	e.m.f. between the junctions

Extra: A good thermometric property should satisfy the following criteria:

1. It **varies continuously and uniquely** with temperature i.e., different values of the thermometric property for different temperatures.
2. The value of the thermometric property at any temperature within its working range must be **reproducible**.

3. The change in the property must be large enough to enable accurate measurements of temperature. If changes in the thermometric property of a substance with temperature is small, then the **sensitivity** of the thermometer is said to be low.
4. It responds quickly to changes in temperature. The **responsiveness** of a thermometer is different from its sensitivity; sensitivity tells us how much the quantity changes per unit temperature change, while responsiveness is how quickly the quantity changes to a change in temperature.

Example 12.1

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

(a) Calculate the temperature of the solid on the Celsius scale of the resistance thermometer.

(b) State an assumption made in your calculation.

Solutions:

❖ **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 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 $p = p_{atm} + h\rho g$, where ρ is the density of mercury.

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

$$\theta = \frac{(p_\theta - p_0)}{(p_{100} - p_0)} \times 100\ ^\circ\text{C} = \frac{(h_\theta - h_0)}{(h_{100} - h_0)} \times 100\ ^\circ\text{C}$$

Experiments using gas thermometers show that the thermometer readings are nearly independent of the type of gas used particularly when pressure is low. At lower the pressures for a real gas, the variation of pressure or volume with temperature approaches a linear relationship, i.e., the behaviour of real gases approaches that of an ideal gas (ideal gas will be discussed in a later section).

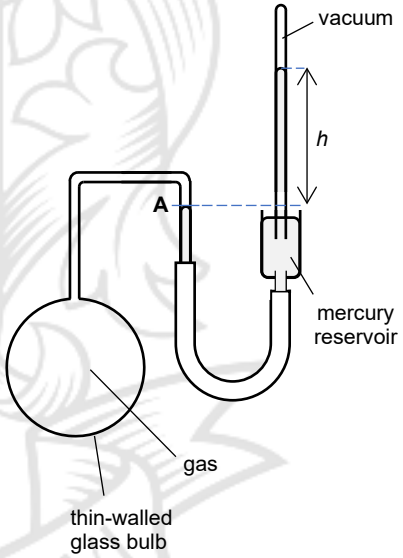


Fig. 12.1 A constant volume gas thermometer

If empirical Celsius scales for different gases are set up by obtaining the pressures of the gases at the ice point and steam point, and the graphs of pressure *p* against temperature θ are extrapolated to zero pressure, the temperatures tend to a value of $-273.15\,°C$ regardless of the type of gas used as shown in Fig. 12.2.

This suggests that **this particular temperature** is universal in importance because it **does not depend on the properties of any substance**. This temperature **is known as the absolute zero** and is used as the lower fixed point on the thermodynamic scale of temperature in the next section.

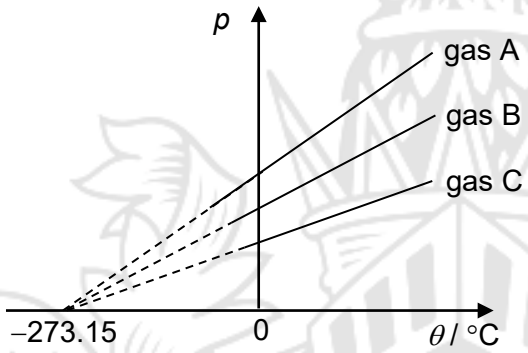


Fig. 12.2 Pressure *p* against temperature θ graph for different gases

❖ Thermodynamic Temperature Scale or Kelvin Temperature Scale (An Absolute Temperature Scale)

The Celsius scale is defined based on the ice point (0 °C) and the steam point (100 °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.

The thermodynamic scale of temperature has an absolute zero and is independent of the property of any particular substance.

Definition of 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 particles of a substance have the lowest 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).

Explore the scientific history of the Kelvin scale.

https://go.gov.sg/iwnodc

The requirement of an absolute thermodynamic scale.

https://go.gov.sg/m6focv

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 temperature and pressure at which water, water vapour and ice can co-exist in thermal equilibrium in an enclosed cell like the one shown on Fig. 12.3.

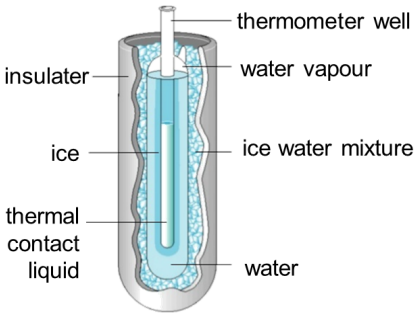


Fig. 12.3 Water, water vapour and ice coexisting in thermal equilibrium

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 $k = 1.38 \times 10^{-23}$ J K^{-1} is the Boltzmann constant.

If an ideal gas is used in the constant-volume gas thermometer to measure the pressure p at an unknown temperature T and the pressure p_{tr} at triple point of water, T can be determined from

$$T = 273.16\left(\frac{p}{p_{tr}}\right)$$

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

❖ Relationship between the Celsius Temperature Scale and the Thermodynamic Scale (or the Kelvin Temperature Scale)

The kelvin is defined in such a way as to make the size of one unit on the Kelvin temperature scale identical to the size of one unit on the Celsius temperature 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) on the Kelvin temperature scale correspond to 273.15 °C and 0.01 °C on the Celsius temperature scale, respectively. The ice point (0 °C) and steam point (100 °C) on the Celsius temperature scale correspond to 273.15 K and 373.15 K on the Kelvin scale, respectively.

The Celsius temperature θ is therefore shifted from the thermodynamic temperature T according to

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

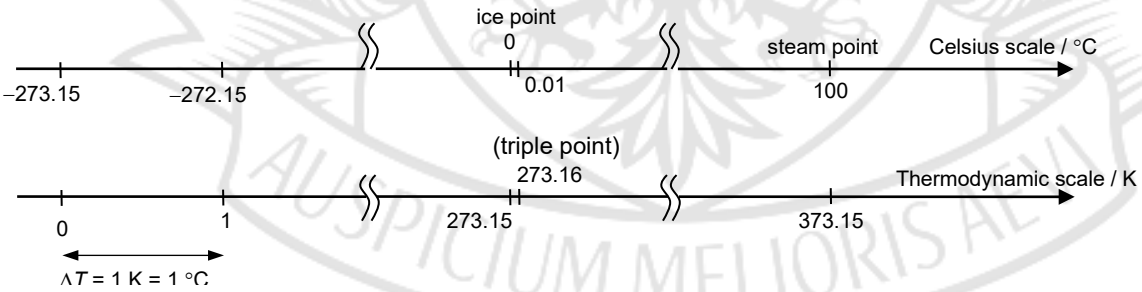


Fig. 12.4 Comparison of Celsius and Thermodynamic temperature scales

12.2 Equation of State for an Ideal Gas

❖ 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 a 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 they 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.

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

Definition of Ideal Gas

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

where p is the pressure of the gas, V is the volume of the gas, N is the number of particles, k is the Boltzmann 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**	**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

Consider changing the volume of a fixed mass of ideal gas as shown in Fig. 12.5 through two processes:

(A) Heating the gas at constant pressure (thus allowing the gas to expand)
(B) Compressing the gas at constant temperature (thus allowing heat exchange)

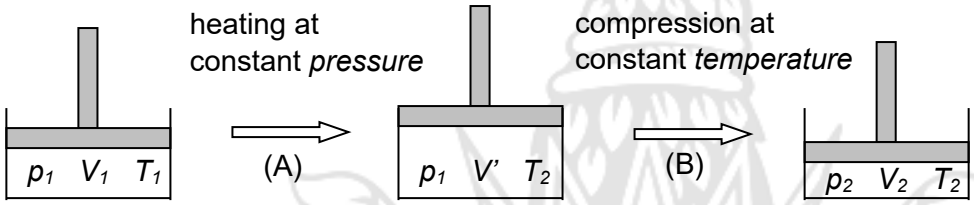


Fig. 12.5 changing the volume of a gas through two processes

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

$$\frac{V_1}{T_1} = \frac{V'}{T_2} \qquad \text{..... (1)}$$

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

$$p_1 V' = p_2 V_2$$

$$\Rightarrow V' = \frac{p_2 V_2}{p_1} \qquad \text{..... (2)}$$

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 number of gas particles N

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

If we use S.I. units for all the quantities, the constant of proportionality is a constant known as **Boltzmann constant**, k

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

where $k = 1.38 \times 10^{-23}$ J K^{-1}.

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

$$\boxed{pV = NkT}$$

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

Investigate the relationship between the properties of an ideal gas such as pressure, volume, temperature and the number of moles

https://go.gov.sg/3u05d0

❖ The Mole & Avogadro Constant

Definition of The Mole

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

Definition of Avogadro Constant

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

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

Explore the scientific history of the Avogadro constant.

❖ Relationship between Boltzmann constant and molar gas constant

Since the number of particles in one mole of any substance is 6.02×10^{23} particles, so we can express the number of particles N using

$$N = nN_A$$

Substituting the above equation into $pV = NkT$, we have

$$pV = nN_Ak T$$

We introduce another constant of proportionality known as the molar gas constant, R, to replace N_Ak,

$$\Rightarrow \boxed{pV = nRT}$$

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

This is an alternative form of the equation of state for an ideal gas. We may use either form of the equation of state depending on which quantities are given in the question.

Thus, the relationship between the Boltzmann constant and the molar gas constant is

$$\boxed{Nk = nR}$$

Example 12.2

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

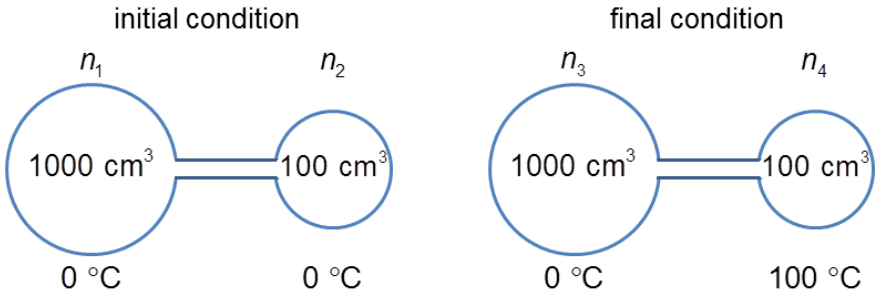
Determine the number of molecules drawn out during the process.

Solution:

Example 12.3

Two gas containers with volumes of 100 cm^3 and 1000 cm^3 are connected by a tube of negligible volume and contain air at a pressure of 1000 mm Hg. Both containers have an initial temperature of 0 °C.

Determine the new pressure in mm Hg when the temperature of the smaller container is raised to 100 °C.



Solution:

12.3 Kinetic Theory of Gases

❖ 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.

Investigate the motion of a large number of particles in a system.

https://go.gov.sg/bspc7d

In the following derivation, 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 2*d* along the *x*-direction (across the container and back).

Hence, on average, over the duration of time Δt, 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 2nd 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 3rd 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_{tot}, is given by

$$\begin{aligned} F_{\text{tot}} &= \frac{mc_{x1}^{\,2}}{d} + \frac{mc_{x2}^{\,2}}{d} + \frac{mc_{x3}^{\,2}}{d} + \ldots + \frac{mc_{xN}^{\,2}}{d} \\ &= \frac{m}{d}(c_{x1}^{\,2} + c_{x2}^{\,2} + c_{x3}^{\,2} + \ldots + c_{xN}^{\,2}) \end{aligned}$$

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

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

$$\left\langle c_x^{\,2} \right\rangle = \frac{c_{x1}^{\,2} + c_{x2}^{\,2} + c_{x3}^{\,2} + \ldots + c_{xN}^{\,2}}{N}$$

Hence,

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

Since pressure is the force acting per unit area, the total pressure p on the wall is therefore

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

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

$$c^{\,2} = c_x^{\,2} + c_y^{\,2} + c_z^{\,2}$$

Hence, the average value of $c^{\,2}$ is related to the average values of $c_x^{\,2}$, $c_y^{\,2}$ and $c_z^{\,2}$ by the following equation

$$\left\langle c^{\,2} \right\rangle = \left\langle c_x^{\,2} \right\rangle + \left\langle c_y^{\,2} \right\rangle + \left\langle c_z^{\,2} \right\rangle$$

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

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

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

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 $\rho = \frac{m_{total}}{V} = \frac{Nm}{V}$, we get

$$p = \frac{1}{3}\rho\langle c^2 \rangle \text{ or } p = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m\langle c^2 \rangle\right)$$

This shows us that we can increase the pressure exerted by a gas on a container by increasing the number of particles per unit volume in the container or by increasing the average translational kinetic energy of the particles in the container.

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

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

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

The left-hand side of the equation is **the mean or average translational kinetic energy** $\langle E_K \rangle$ of one gas particle. Thus,

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

This equation tells us that the mean **translational** kinetic energy of a particle of an ideal gas is directly proportional to the thermodynamic temperature.

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.

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

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

From $\frac{1}{2}m\langle c^2 \rangle = \frac{3}{2}kT$, we get

$$c_{rms} = \sqrt{\frac{3kT}{m}}$$

This shows that at a given temperature, lighter particles tend to move faster than heavier particles.

Example 12.4

In an ideal gas at 600 °C, the mean kinetic energy of the gas molecules is 1.8×10^{-20} J.

Determine the temperature of the gas and the mean kinetic energy of the molecules when the gas molecules are, on average, travelling at half of their initial speed.

Solution:

Example 12.5

A helium-neon laser contains a mixture of helium and neon gases, the atomic masses of which are 4*u* and 20*u*, respectively.

Determine the ratio of the root-mean-square speed of helium atoms to that of the neon atoms.

Solution:

12.4 Appendix

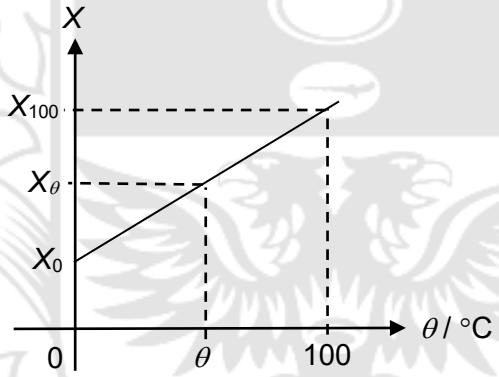
❖ Empirical Celsius Scale

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 thermal 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 thermal 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_o for the value at ice point and X_{100} for the value at steam point.
2. Divide the interval of ($X_{100} - X_o$) 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 θ, it means joining the points (0 °C, X_o) and (100 °C, X_{100}) with a straight line.



4. Measure the thermometric property at the unknown temperature θ and call it X_θ. The unknown temperature θ in °C is then computed from

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

The following table gives the equations to determine the unknown temperature θ 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.

❖ 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 $pV \propto T$, as shown in Fig. 12.6.

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 $T = 273.16$ K.

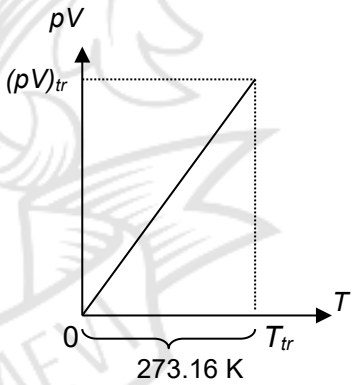


Fig. 12.6 pV vs T graph for a gas

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

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

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

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

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

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

   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. 12.7 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 $p_{tr} = 0$.

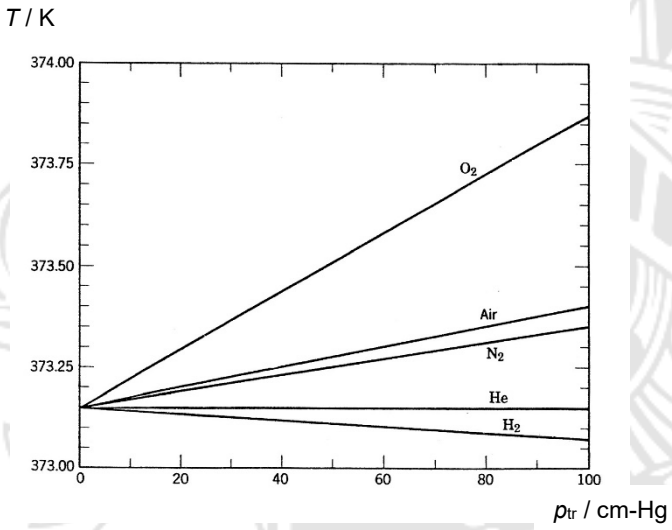
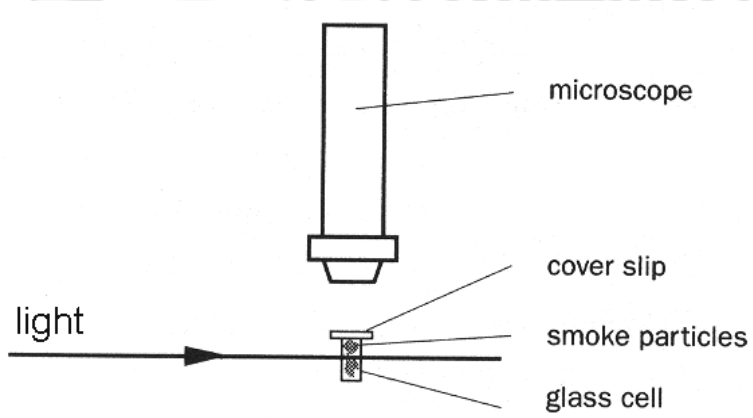


Fig. 12.7 The readings of a constant-volume gas thermometer for the temperature T of condensing steam as a function of p_{tr}, when different gases are used.

❖ 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.