

CHAPTER 24

KINETIC THEORY OF GASES

24.1 INTRODUCTION

We have seen in the previous chapter that the pressure p , the volume V and the temperature T of any gas at low densities obey the equation

$$pV = nRT,$$

where n is the number of moles in the gas and R is the gas constant having value $8.314 \text{ JK}^{-1}\text{mol}^{-1}$. The temperature T is defined on the absolute scale. We define the term *ideal gas* to mean a gas which always obeys this equation. The real gases available to us are good approximation of an ideal gas at low density but deviate from it when the density is increased.

Any sample of a gas is made of molecules. A molecule is the smallest unit having all the chemical properties of the sample. The observed behaviour of a gas results from the detailed behaviour of its large number of molecules. The kinetic theory of gases attempts to develop a model of the molecular behaviour which should result in the observed behaviour of an ideal gas.

24.2 ASSUMPTIONS OF KINETIC THEORY OF GASES

1. All gases are made of molecules moving randomly in all directions.
2. The size of a molecule is much smaller than the average separation between the molecules.
3. The molecules exert no force on each other or on the walls of the container except during collision.
4. All collisions between two molecules or between a molecule and a wall are perfectly elastic. Also, the time spent during a collision is negligibly small.
5. The molecules obey Newton's laws of motion.
6. When a gas is left for sufficient time, it comes to a steady state. The density and the distribution of molecules with different velocities are independent of position, direction and time. This assumption may be justified if the number of molecules is very large.

The last assumption needs some explanation. Suppose there are 2×10^{19} molecules in a particular

1 cm^3 . Our assumption means that there are 2×10^{19} molecules in any other 1 cm^3 in the container and this number does not change as time passes. Similarly, if there are 400 molecules having velocities nearly parallel to the x -axis in a particular 1 cm^3 , there are 400 molecules having velocities in this direction in any other 1 cm^3 and this number does not change with time. Also, there are 400 molecules in 1 cm^3 that are going in y -direction. The fact that the distribution of molecules does not change with time has an interesting consequence. Consider a molecule in a small volume ΔV having a velocity \vec{v} . A collision occurs and the velocity of this molecule changes. But the number of molecules in ΔV having velocity \vec{v} should not depend on time. So there must be another collision which results in a nearby molecule taking up velocity \vec{v} . Effectively, we may neglect both the collisions and say that the molecule continues with the same velocity \vec{v} . This greatly simplifies calculations.

The assumptions of kinetic theory are close to the real situation at low densities. The molecular size is roughly 100 times smaller than the average separation between the molecules at 0.1 atm and room temperature. The real molecules do exert electric forces on each other but these forces may be neglected as the average separation between the molecules is large as compared to their size. The collisions between real molecules are indeed elastic if no permanent deformation is caused to a molecule. This is true when the temperature is not too high. The collisions with the walls are elastic if the temperature of the walls is the same as the temperature of the gas. If the gas is left in the container for sufficient time, this assumption will be valid. The fact that the motion of molecules may be described by Newton's laws may be taken as a pure chance for the time being. The last assumption is very nearly true if the number of molecules is very large. As there are about 6×10^{23} molecules per mole, this condition is almost always true in a practical situation.

24.3 CALCULATION OF THE PRESSURE OF AN IDEAL GAS

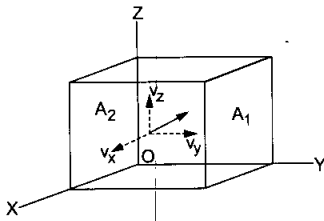


Figure 24.1

Consider an ideal gas enclosed in a cubical vessel of edge L . Take a corner of the vessel as the origin O and the x -, y -, z - axes along the edges (figure 24.1). Let A_1 and A_2 be the parallel faces perpendicular to the x -axis. Consider a molecule moving with velocity \vec{v} . The components of the velocity along the axes are v_x , v_y and v_z . When the molecule collides with the face A_1 , the x -component of the velocity is reversed whereas the y - and the z -components remain unchanged. This follows from our assumption that the collisions of the molecules with the wall are perfectly elastic. The change in momentum of the molecule is

$$\Delta p = (-mv_x) - (mv_x) = -2mv_x.$$

As the momentum remains conserved in a collision, the change in momentum of the wall is

$$\Delta p' = 2mv_x. \quad \dots (i)$$

After rebound, this molecule travels towards A_2 with the x -component of velocity equal to $-v_x$. Any collision of the molecule with any other face (except for A_2) does not change the value of v_x . So, it travels between A_1 and A_2 with a constant x -component of velocity which is equal to $-v_x$. Note that we can neglect any collision with the other molecules in view of the last assumption discussed in the previous section.

The distance travelled parallel to the x -direction between A_1 and A_2 is L . Thus, the time taken by the molecule to go from A_1 to A_2 is L/v_x . The molecule rebounds from A_2 , travels towards A_1 and collides with it after another time interval L/v_x . Thus, the time between two consecutive collisions of this molecule with A_1 is $\Delta t = 2L/v_x$. The number of collisions of this molecule with A_1 in unit time is

$$n = \frac{1}{\Delta t} = \frac{v_x}{2L}. \quad \dots (ii)$$

The momentum imparted per unit time to the wall by this molecule is, from (i) and (ii),

$$\begin{aligned} \Delta F &= n\Delta p' \\ &= \frac{v_x}{2L} \times 2mv_x = \frac{m}{L} v_x^2. \end{aligned}$$

This is also the force exerted on the wall A_1 due to this molecule. The total force on the wall A_1 due to all the molecules is

$$\begin{aligned} F &= \sum \frac{m}{L} v_x^2 \\ &= \frac{m}{L} \sum v_x^2. \end{aligned} \quad \dots (iii)$$

As all directions are equivalent, we have

$$\begin{aligned} \sum v_x^2 &= \sum v_y^2 = \sum v_z^2 \\ &= \frac{1}{3} \sum (v_x^2 + v_y^2 + v_z^2) \\ &= \frac{1}{3} \sum v^2. \end{aligned}$$

$$\text{Thus, from (iii), } F = \frac{1}{3} \frac{m}{L} \sum v^2.$$

If N is the total number of molecules in the sample, we can write

$$F = \frac{1}{3} \frac{mN}{L} \frac{\sum v^2}{N}.$$

The pressure is force per unit area so that

$$\begin{aligned} p &= \frac{F}{L^2} \\ &= \frac{1}{3} \frac{mN}{L^3} \frac{\sum v^2}{N} \\ &= \frac{1}{3} \frac{M}{L^3} \frac{\sum v^2}{N} = \frac{1}{3} \rho \frac{\sum v^2}{N}, \end{aligned}$$

where M is the total mass of the gas taken and ρ is its density. Also, $\sum v^2/N$ is the average of the speeds squared. It is written as $\overline{v^2}$ and is called *mean square speed*. Thus, the pressure is

$$p = \frac{1}{3} \rho \overline{v^2} \quad \dots (24.1)$$

$$\text{or, } pV = \frac{1}{3} M \overline{v^2} \quad \dots (24.2)$$

$$\text{or, } pV = \frac{1}{3} N m \overline{v^2} \quad \dots (24.3)$$

24.4 RMS SPEED

The square root of mean square speed is called *root-mean-square speed* or *rms speed*. It is denoted by the symbol v_{rms} . Thus,

$$v_{rms} = \sqrt{\sum v^2 / N}$$

$$\text{or, } v^2 = (v_{rms})^2.$$

Equation (24.1) may be written as

$$p = \frac{1}{3} \rho v_{rms}^2$$

so that
$$v_{rms} = \sqrt{\frac{3p}{\rho}} = \sqrt{\frac{3pV}{M}}.$$

Example 24.1

Calculate the rms speed of nitrogen at STP (pressure = 1 atm and temperature = 0°C). The density of nitrogen in these conditions is 1.25 kg m^{-3} .

Solution : At STP, the pressure is $1.0 \times 10^5 \text{ N m}^{-2}$. The rms speed is

$$\begin{aligned} v_{rms} &= \sqrt{\frac{3p}{\rho}} \\ &= \sqrt{\frac{3 \times 10^5 \text{ N m}^{-2}}{1.25 \text{ kg m}^{-3}}} \\ &= 490 \text{ m s}^{-1}. \end{aligned}$$

Translational Kinetic Energy of a Gas

The total translational kinetic energy of all the molecules of the gas is

$$K = \sum \frac{1}{2} m v^2 = \frac{1}{2} m N \frac{\sum v^2}{N} = \frac{1}{2} M v_{rms}^2. \quad \dots (24.4)$$

The average kinetic energy of a molecule is

$$K/N = \frac{1}{2} \frac{M}{N} v_{rms}^2 = \frac{1}{2} m v_{rms}^2.$$

From equation (24.2),

$$pV = \frac{2}{3} \cdot \frac{1}{2} M v_{rms}^2$$

or,

$$pV = \frac{2}{3} K$$

or,

$$K = \frac{3}{2} pV.$$

24.5 KINETIC INTERPRETATION OF TEMPERATURE

We know that a hotter body has larger internal energy than an otherwise similar colder body. Thus, higher temperature means higher internal energy and lower temperature means lower internal energy. According to the kinetic theory of gases, the internal energy of an ideal gas is the same as the total translational kinetic energy of its molecules which is, from equation (24.4),

$$K = \frac{1}{2} M v_{rms}^2.$$

Thus, for a given sample of a gas, higher temperature means higher value of v_{rms} and lower temperature means lower value of v_{rms} . We can write,

$$T = f(v_{rms})$$

for a given sample of a gas.

Let p and v be the pressure of the gas and the rms speed of the molecules at temperature T respectively. Let p_{tr} and v_{tr} be the values of these quantities at

temperature 273.16 K , keeping the volume V the same as that at T .

From equation (24.2),

$$pV = \frac{1}{3} M v^2$$

and

$$p_{tr}V = \frac{1}{3} M v_{tr}^2.$$

Thus,

$$\frac{p}{p_{tr}} = \frac{v^2}{v_{tr}^2}. \quad \dots (i)$$

From the definition of absolute temperature scale,

$$\frac{p}{p_{tr}} = \frac{T}{273.16 \text{ K}}. \quad \dots (ii)$$

From (i) and (ii),

$$T = \left(\frac{273.16 \text{ K}}{v_{tr}^2} \right) v^2. \quad \dots (24.5)$$

Now, v_{tr} is the rms speed of the molecules at 273.16 K and hence is a constant for a given gas. Equation (24.5) shows that *the absolute temperature of a given gas is proportional to the square of the rms speed of its molecules*. As the total translational kinetic energy of the molecules is $K = \frac{1}{2} M v_{rms}^2$, we see that $T \propto K$ for a given sample of a gas.

Thus, *the absolute temperature of a given sample of a gas is proportional to the total translational kinetic energy of its molecules*.

Now consider a mixture of two gases A and B . Let m_1 be the mass of a molecule of the first gas and m_2 be that of the second. As the molecules collide with each other, they exchange energy. On an average, the molecules with higher kinetic energy lose energy to those with lower kinetic energy. In thermal equilibrium, the average kinetic energy of all molecules are equal. If v_1 and v_2 be the rms speeds of the molecules of A and B respectively,

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2. \quad \dots (24.6)$$

We find that for different kinds of gases, it is not the rms speed but average kinetic energy of individual molecules that has a fixed value at a given temperature. The heavier molecules move with smaller rms speed and the lighter molecules move with larger rms speed.

Example 24.2

If the rms speed of nitrogen molecules is 490 m s^{-1} at 273 K , find the rms speed of hydrogen molecules at the same temperature.

Solution : The molecular weight of nitrogen is 28 g mol^{-1} and that of hydrogen is 2 g mol^{-1} . Let m_1, m_2 be the

masses and v_1, v_2 be the rms speeds of a nitrogen molecule and a hydrogen molecule respectively. Then $m_1 = 14m_2$. Using equation (24.6),

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2$$

$$\text{or, } v_2 = v_1 \sqrt{m_1/m_2} = 490 \text{ m s}^{-1} \times \sqrt{14} \approx 1830 \text{ m s}^{-1}.$$

24.6 DEDUCTIONS FROM KINETIC THEORY

Boyle's Law

At a given temperature, the pressure of a given mass of a gas is inversely proportional to its volume. This is known as Boyle's law.

From equation (24.3), we have

$$pV = \frac{1}{3} mN v_{rms}^2 \quad \dots (i)$$

As for a given gas $v_{rms}^2 \propto T$, the value of v_{rms}^2 is constant at a given temperature. Also, for a given mass of the gas, m and N are constants. Thus, from (i),

$$pV = \text{constant}$$

$$\text{or, } p \propto \frac{1}{V}$$

which is Boyle's law.

Charles's Law

At a given pressure, the volume of a given mass of a gas is proportional to its absolute temperature. This is known as Charles's law.

From (i), if p is constant,

$$V \propto v_{rms}^2$$

As $v_{rms}^2 \propto T$, we get $V \propto T$

which is Charles's law.

Charles's Law of Pressure

At a given volume, the pressure of a given mass of a gas is proportional to its absolute temperature. This is known as Charles's law for pressure.

In fact, this is the definition of the absolute temperature T . If one starts from the fact that $v_{rms}^2 \propto T$ and uses the fact that V is constant, one gets from (i),

$$p \propto v_{rms}^2$$

$$\text{or, } p \propto T.$$

Avogadro's Law

At the same temperature and pressure, equal volumes of all gases contain equal number of molecules. This is known as Avogadro's law.

Consider equal volumes of two gases kept at the same pressure and temperature. Let,

m_1 = mass of a molecule of the first gas

m_2 = mass of a molecule of the second gas

N_1 = number of molecules of the first gas

N_2 = number of molecules of the second gas

p = common pressure of the two gases

V = common volume of the two gases.

From equation (24.3),

$$pV = \frac{1}{3} N_1 m_1 v_1^2$$

$$\text{and } pV = \frac{1}{3} N_2 m_2 v_2^2$$

where v_1 and v_2 are rms speeds of the molecules of the first and the second gas respectively. Thus,

$$N_1 m_1 v_1^2 = N_2 m_2 v_2^2 \quad \dots (i)$$

As the temperatures of the gases are the same, the average kinetic energy of the molecules is same for the two gases (equation 24.6), i.e.,

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2 \quad \dots (ii)$$

From (i) and (ii),

$$N_1 = N_2$$

which proves Avogadro's law.

Graham's Law of Diffusion

When two gases at the same pressure and temperature are allowed to diffuse into each other, the rate of diffusion of each gas is inversely proportional to the square root of the density of the gas. This is known as Graham's law of diffusion.

It is reasonable to assume that the rate of diffusion is proportional to the rms speed of the molecules of the gas. Then if r_1 and r_2 be the rates of diffusion of the two gases,

$$\frac{r_1}{r_2} = \frac{v_{1,rms}}{v_{2,rms}} \quad \dots (i)$$

From equation (24.1),

$$v_{rms} = \sqrt{\frac{3p}{\rho}}$$

If the pressure of the two gases are the same,

$$\frac{v_{1,rms}}{v_{2,rms}} = \sqrt{\frac{\rho_2}{\rho_1}}$$

so that from (i)

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

which is Graham's law.

Dalton's Law of Partial Pressure

Dalton's law of partial pressure says that *the pressure exerted by a mixture of several gases equals*

the sum of the pressures exerted by each gas occupying the same volume as that of the mixture.

In kinetic theory, we assume that the pressure exerted by a gas on the walls of a container is due to the collisions of the molecules with the walls. The total force on the wall is the sum of the forces exerted by the individual molecules. Suppose there are N_1 molecules of gas 1, N_2 molecules of gas 2, etc., in the mixture.

Thus, the force on a wall of surface area A is

$$\begin{aligned} F &= \text{force by } N_1 \text{ molecules of gas 1} \\ &\quad + \text{force by } N_2 \text{ molecules of gas 2} + \dots \\ &= F_1 + F_2 + \dots \end{aligned}$$

Thus, the pressure is

$$p = \frac{F_1}{A} + \frac{F_2}{A} + \dots$$

If the first gas alone is kept in the container, its N_1 molecules will exert a force F_1 on the wall. If the pressure in this case is p_1 ,

$$p_1 = F_1 / A.$$

Similar is the case for other gases.

Thus,

$$p = p_1 + p_2 + p_3 + \dots$$

24.7 IDEAL GAS EQUATION

Consider a sample of an ideal gas at pressure P , volume V and temperature T . Let m be the mass of each molecule and v be the rms speed of the molecules. Also, let v_{tr} be the rms speed of the gas at the triple point 273.16 K. From equation (24.3),

$$pV = \frac{1}{3} N m v^2 \quad \dots (i)$$

and from equation (24.5)

$$T = \left(\frac{273.16 \text{ K}}{v_{tr}^2} \right) v^2$$

$$\text{or,} \quad v^2 = \left(\frac{v_{tr}^2}{273.16 \text{ K}} \right) T.$$

Putting this expression for v^2 in (i),

$$pV = N \left(\frac{1}{3} \frac{m v_{tr}^2}{273.16 \text{ K}} \right) T. \quad \dots (ii)$$

Now $\frac{1}{2} m v_{tr}^2$ is the average kinetic energy of a molecule at the triple point 273.16 K. As the average kinetic energy of a molecule is the same for all gases at a fixed temperature (equation 24.6), $\frac{1}{2} m v_{tr}^2$ is a universal constant. Accordingly, the quantity in bracket in equation (ii) above is also a universal

constant. Writing this constant as k , equation (ii) becomes,

$$pV = NkT. \quad \dots (24.7)$$

The universal constant k is known as the *Boltzmann constant* and its value is

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

up to three significant digits. If the gas contains n moles, the number of molecules is

$$N = n N_A$$

where $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro constant.

Using this, equation (24.7) becomes

$$pV = n N_A k T$$

$$\text{or,} \quad pV = nRT \quad \dots (24.8)$$

where $R = N_A k$ is another universal constant known as the *universal gas constant*. Its value is

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Equation (24.8) is known as the *equation of state* of an ideal gas.

Example 24.3

Calculate the number of molecules in each cubic metre of a gas at 1 atm and 27 °C.

Solution : We have $pV = NkT$

or,

$$N = \frac{pV}{kT}$$

$$\begin{aligned} &= \frac{(1.0 \times 10^5 \text{ N m}^{-2}) (1 \text{ m}^3)}{(1.38 \times 10^{-23} \text{ J K}^{-1}) (300 \text{ K})} \\ &\approx 2.4 \times 10^{25}. \end{aligned}$$

Rms Speed in Terms of Temperature

We are now in a position to write the rms speed of the molecules in terms of the absolute temperature. From equation (24.3),

$$pV = \frac{1}{3} N m v_{rms}^2$$

and from equation (24.7),

$$pV = NkT.$$

From these two,

$$\frac{1}{3} m v_{rms}^2 = kT$$

or,

$$v_{rms} = \sqrt{\frac{3kT}{m}}. \quad \dots (24.9)$$

This may also be written as,

$$v_{rms} = \sqrt{\frac{3kN_A T}{mN_A}}$$

$$= \sqrt{\frac{3RT}{M_o}} \quad \dots (24.10)$$

where $M_o = mN_A$ is the molecular weight.

Average Kinetic Energy of a Molecule

Average kinetic energy of a molecule is

$$\begin{aligned} \frac{1}{2} m v_{rms}^2 &= \frac{1}{2} m \cdot \frac{3kT}{m} \\ &= \frac{3}{2} kT. \end{aligned} \quad \dots (24.11)$$

The total kinetic energy of all the molecules is

$$U = N \left(\frac{3}{2} kT \right) = \frac{3}{2} nRT. \quad \dots (24.12)$$

The average speed $\bar{v} = \Sigma v / N$ is somewhat smaller than the rms speed. It can be shown that

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M_o}}$$

Example 24.4

Find the rms speed of oxygen molecules in a gas at 300 K.

$$\begin{aligned} \text{Solution : } v_{rms} &= \sqrt{\frac{3RT}{M_o}} \\ &= \sqrt{\frac{3 \times (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{32 \text{ g mol}^{-1}}} \\ &= \sqrt{\frac{3 \times 8.3 \times 300}{0.032}} \text{ m s}^{-1} = 483 \text{ m s}^{-1}. \end{aligned}$$

It should be clearly understood that the motion of molecules discussed here is truly random motion. In other words, the centre of mass of the gas is assumed to be at rest and any rotation about the centre of mass is assumed to be absent. Any systematic motion of a gas sample has no effect on temperature. For example, if we place a gas jar in a moving train, the increase in translational kinetic energy does not increase the temperature of the gas.

24.8 MAXWELL'S SPEED DISTRIBUTION LAW

The rms speed of an oxygen molecule in a sample at 300 K is about 480 m s^{-1} . This does not mean that the speed of each molecule is 480 m s^{-1} . Many of the molecules have speed less than 480 m s^{-1} and many have speed more than 480 m s^{-1} . Maxwell derived an equation giving the distribution of molecules in different speeds. If dN represents the number of molecules with speeds between v and $v + dv$ then

$$dN = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} dv \quad \dots (24.13)$$

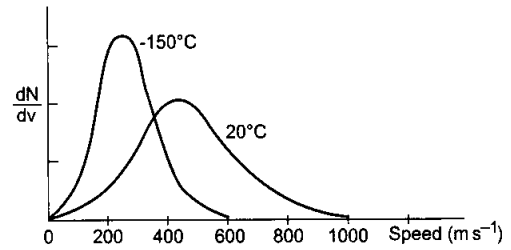


Figure 24.2

Figure (24.2) shows plots of dN/dv against v at two different temperatures. We see that there are some molecules which have speeds many times greater than the mean speed. This fact helps in making nuclear fusion reactions in a laboratory. The speed v_p at which dN/dv is maximum is called the *most probable speed*. Its value is given by

$$v_p = \sqrt{\frac{2kT}{m}} \quad \dots (24.14)$$

24.9 THERMODYNAMIC STATE

A given sample of a substance has a number of parameters which can be physically measured. When these parameters are uniquely specified, we say that the *thermodynamic state* of the system is specified. However, not all of these parameters are independent of each other. For example, we can measure pressure, volume, temperature, internal energy and many other parameters of an ideal gas. But if pressure and volume are specified, the rest of the parameters may be calculated. Thus, a thermodynamic state of a given sample of an ideal gas is completely described if its pressure and its volume are given. When a process is performed on a system, it passes from one thermodynamic state to another.

Equation of State

The pressure, volume and temperature of a given sample of a substance are related to each other. An equation describing this relation is called the *equation of state for that substance*. For an ideal gas it is

$$pV = nRT$$

where the symbols have their usual meanings. For a real gas the equation of state is different. The size of a molecule is not negligible in comparison to the average separation between them. Also, the molecular attraction is not negligible. Taking these two facts into account, van der Waals derived the following equation of state for a real gas:

$$\left(p + \frac{a}{V^2} \right) (V - b) = nRT \quad \dots (24.15)$$

where a and b are small positive constants. The constant a is related to the average force of attraction between the molecules and b is related to the total volume of the molecules.

24.10 BROWNIAN MOTION

We have assumed in kinetic theory of gases that the molecules of a gas are in constant random motion, colliding with each other and with the walls of the container. This is also valid for a liquid. Robert Brown, a botanist, accidentally came across an evidence of this type of molecular motion in 1827. He was observing small pollen grains suspended in water, under a powerful microscope. He observed that although the water appeared to be at complete rest, the grains were moving randomly in the water, occasionally changing their directions of motion. A typical path of a grain looks as shown in figure (24.3). Such a phenomenon is called *Brownian motion*. The molecules strike the particles of the pollen grains and kick them to move in a direction. Another collision with some other molecules changes the direction of the grain.

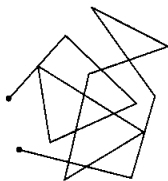


Figure 24.3

The molecules are too small to be directly seen under a normal microscope, but the grains can be seen. A piece of wood floating in water can be seen with naked eyes but its mass is so large that it does not respond quickly to the molecular collisions. Hence, to observe Brownian motion one should have light suspended particles. Brownian motion increases if we increase the temperature. Comparing between different liquids, one with smaller viscosity and smaller density will show more intense Brownian motion.

Einstein developed a theoretical model for Brownian motion in 1905 and deduced the average size of the molecules from it.

24.11 VAPOUR

The kinetic theory of gases described above is strictly valid only for ideal gases. These concepts are also useful in qualitatively understanding several behaviours of nonideal gases, liquids and even solids. We have assumed in kinetic theory that the molecules do not exert a force on each other except at the time of collision. The molecules, in fact, exert an attractive

force on each other. For a gas at a low pressure and a high temperature, the average separation between the molecules is quite large. The molecular attraction is quite small and hence the associated attraction energy is small as compared to the average kinetic energy. If the pressure is increased or the temperature is decreased, the attraction energy gradually becomes more important and finally the gas liquefies. Thus, in general, a gas can be liquefied either by increasing the pressure (by compressing it) or by decreasing the temperature. However, if the temperature is sufficiently high so that the kinetic energy of the molecules is large, no amount of pressure can liquefy the gas. The temperature above which this behaviour occurs is called the *critical temperature* of the substance. A gas below its critical temperature is called *vapour*.

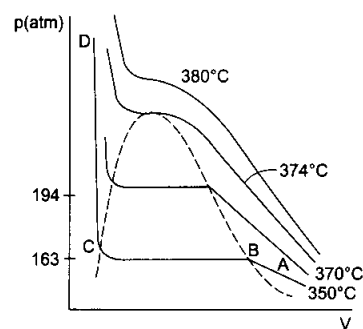


Figure 24.4

Figure (24.4) shows the gas-liquid transition of water in a p - V diagram. Each solid curve represents the variation in pressure with the volume of a sample of water while the temperature is kept fixed. It, therefore, represents an isothermal process and is called an *isotherm*. The dotted curve represents the region where the transition actually takes place. Consider the isotherm $ABCD$. Suppose the water is in its gas form at 350°C and its pressure and volume are represented by the point A . We say that the state of the system is represented by A . As the pressure is increased keeping the temperature fixed, the state changes to B where it enters the region bounded by the dotted curve. Liquefaction starts at 350°C at 163 atm of pressure and the volume rapidly decreases. When the entire water is converted to liquid phase, the state is represented by the point C . Now, a large increase in pressure is needed for even a small compression so that the part CD is very steep.

At 370°C , liquefaction starts at a higher pressure that is around 194 atm. If the temperature is higher than 374.1°C (say 380°C), the isotherm does not enter the region bounded by the dotted curve. This means water cannot be liquefied at a temperature greater

than 374.1°C , no matter how large the pressure is. Thus, 374.1°C is the critical temperature of water. Water in its gas form at a temperature lower than 374.1°C is called *water vapour* and that above 374.1°C is *water gas*.

So, a vapour is a gas which can be liquefied by increasing the pressure without changing the temperature. Vapour obeys Dalton's law of partial pressure. Thus, the pressure exerted by the vapour present in air is the same as what it would be if the vapour were alone in the space with the same density and at the same temperature.

24.12 EVAPORATION

Let us take equal amounts of ether in three identical vessels. One is closed by a lid, one by a big jar and one is left open to air.

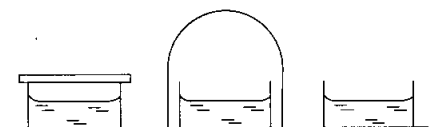


Figure 24.5

If we examine the vessels after a few hours, we shall find that the quantity of ether in the first vessel is almost the same, that in the second is reduced to some extent and that in the third has almost vanished. This can be explained with the help of kinetic theory. The molecules of ether move with random speeds and in random directions. A molecule collides frequently with other molecules and the container walls to change its direction and speed. Occasionally, a molecule starting in upward direction near the surface of the liquid may escape collisions and move out of the liquid. This process is called *evaporation*. Thus, *evaporation is a process in which molecules escape slowly from the surface of a liquid*.

We can now understand why the first vessel contains almost the same amount of ether as time passes. Surface molecules still move out of the liquid, but they cannot move very far away because of the lid. These molecules collide with the lid, with the air molecules, with the surface of the water and among themselves. Some of these molecules may be directed back into the liquid. The number going back depends on the density of the escaped molecules which keeps on increasing as more and more evaporation takes place. An equilibrium is reached when the number of molecules escaping from the liquid per second equals the number returning to the liquid. The volume of the liquid then becomes constant.

The same process takes place in the vessel covered by the jar. But now there is much more space for the escaped molecules to move around and many more

molecules must escape before the equilibrium is reached.

In the vessel open to air, there is no restriction on the escaped molecules. They can go far away and never return. Occasionally, some molecules may return after colliding with an air molecule but the number escaped is always greater than the number returned. Thus, the liquid will keep on evaporating till the entire liquid is evaporated. If air blows over the liquid surface in the open vessel, the number of returning molecules is further reduced. This is because any molecule escaping from the surface is blown away from the vicinity of the liquid. This increases the rate of net evaporation. This is why clothes dry faster when a wind is blowing.

When a molecule comes out of the liquid surface, it has to oppose the attraction of the surface molecules it is leaving behind. This needs extra energy. Thus, only those molecules can escape which have kinetic energy sufficiently larger than the average. The average kinetic energy of the remaining liquid decreases and hence, its temperature goes down. This effect is used in cooling water in pitchers having porous walls.

24.13 SATURATED AND UNSATURATED VAPOUR: VAPOUR PRESSURE

Let us consider the vessel of figure (24.5) closed by the jar. After sufficient time an equilibrium is reached when the volume of the liquid becomes constant. The rate of transformation from liquid to vapour equals the rate of transformation from vapour to liquid. If we inject some vapour from outside into the space above the liquid, the rate of the returning molecules will increase while the rate of evaporation will still be the same. The net result is that the extra amount of vapour will convert into liquid. Thus, the space cannot contain more than a certain maximum amount of vapour. If the amount of vapour is less than this, the return rate is less than the rate of evaporation and the amount of vapour will increase to its maximum value.

When a space actually contains the maximum possible amount of vapour, the vapour is called *saturated*. If the amount is less than the maximum possible, the vapour is called *unsaturated*.

This maximum amount depends on the temperature. If we increase the temperature of the vessel, the liquid molecules will have higher average speed and the chances of escaping increases. Thus, the rate of evaporation increases and equilibrium is reached after more vapour has gone in the space provided.

The pressure exerted by a saturated vapour is called *saturation vapour pressure*. We shall denote it by the symbol SVP. The saturation vapour pressure of a substance is constant at a given temperature. It increases when the temperature is increased. Figure (24.6) shows the saturation vapour pressure as a function of temperature for methyl alcohol and water.

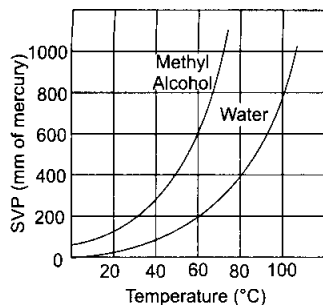


Figure 24.6

Table (24.1) gives the saturation vapour pressure of water at different temperatures.

Table 24.1 : Saturation vapour pressure of water

T °C	Vapour pressure torr (mmHg)	T °C	Vapour pressure torr (mmHg)
0	4.58	100	760
5	6.51	120	1490
10	8.94	140	2710
15	12.67	160	4630
20	17.5	180	7510
40	55.1	200	11650
60	149	220	17390
80	355		

The concept of saturated vapour is valid even if there is no liquid below. Consider a closed vessel in which we gradually inject vapour. When the amount of vapour is small, on an average, the molecules are far apart. The average attraction energy is much smaller than the average kinetic energy. As the amount is increased, the average separation decreases and the attraction energy becomes more and more important. At a certain state, the attraction becomes sufficient to draw several molecules close enough to form liquid. Thus, the vapour starts condensing. This is the case of saturation. Any vapour further injected will condense and the pressure inside the container will remain equal to the saturation vapour pressure.

In atmosphere, air and vapour are mixed with each other. If a given volume contains maximum amount of

vapour possible, the air is called saturated with vapour. Otherwise, it is called unsaturated.

24.14 BOILING

The energy of a certain amount of substance is more in its vapour state than in its liquid state. This is because energy has to be supplied to separate the molecules against the attractive forces operating in the liquid phase. If we heat the liquid, the average kinetic energy of the entire liquid increases and at a certain stage the energy becomes sufficient to break the molecular attraction. The molecules anywhere in the liquid can form vapour bubbles. These bubbles float to the surface of the liquid and finally come out of the liquid. This phenomenon is called *boiling* and the temperature at which boiling occurs is called *boiling point*. Thus, in evaporation, only the molecules near the surface which have kinetic energy greater than the average escape from the liquid, whereas, in boiling, the molecules all over the liquid gain enough energy to become vapour.

The boiling point of a liquid depends on the external pressure over its surface. In fact, boiling occurs at a temperature where the SVP equals the external pressure. Thus, from figure (24.6), the boiling point of water at 1 atm (760 mm of mercury) is 100°C but at 0.5 atm it is 82°C.

Example 24.5

At what external pressure will water boil at 140°C? Use table (24.1) for vapour pressure data and express the answer in atm.

Solution : The saturation vapour pressure of water at 140°C is 2710 mm of Hg. Thus, water will boil at 140°C at this pressure. Now 760 mm of Hg = 1 atm.

Thus, 2710 mm of Hg = $\frac{2710}{760}$ atm = 3.56 atm.

The pressure inside a pressure cooker is of this order when it whistles. So, the temperature inside is of the order of 140°C which helps in cooking the food much faster.

24.15 DEW POINT

Table (24.1) gives the saturation vapour pressure of water as a function of temperature. Suppose air at temperature 20°C contains some vapour which exerts a pressure of 8.94 mm of mercury. The air is unsaturated because a vapour pressure of 17.5 mm of mercury is needed to saturate the air at 20°C. If we decrease the temperature from 20°C to 10°C, the air will become saturated with vapour because at 10°C the saturated vapour pressure is 8.94 mm of mercury.

The temperature at which the saturation vapour pressure is equal to the present vapour pressure is called the *dew point*.

If the temperature is decreased below the dew point, some of the vapour condenses.

24.16 HUMIDITY

The amount of water vapour present in a unit volume of air is called the *absolute humidity* of air. It is generally mentioned in terms of g m^{-3} . The ratio of the amount of water vapour present in a given volume to the amount of water vapour required to saturate the volume at the same temperature is called the *relative humidity*. Thus, relative humidity is defined as

$$RH = \frac{\text{Amount of water vapour present in a given volume of air at a given temperature}}{\text{Amount of water vapour required to saturate the same volume of air at the same temperature}} \quad \dots (24.16)$$

Relative humidity is generally expressed as a percentage. Thus, if the above ratio is 0.6, the relative humidity is 60%. If the air is already saturated, the relative humidity is 100%.

As the pressure exerted by the vapour is directly proportional to the amount of vapour present in a given volume, the relative humidity may also be defined as

$$RH = \frac{\text{Vapour pressure of air}}{\text{SVP at the same temperature}} \quad \dots (24.17)$$

The vapour pressure of air at the actual temperature is equal to the saturation vapour pressure at the dew point. Thus, the relative humidity may be redefined as

$$RH = \frac{\text{SVP at the dew point}}{\text{SVP at the air-temperature}} \quad \dots (24.18)$$

Example 24.6

The vapour pressure of air at 20°C is found to be 12 mm of Hg on a particular day. Find the relative humidity. Use the data of table (24.1).

Solution : The saturation vapour pressure of water at 20°C is 17.5 mm of Hg. Thus, the relative humidity is

$$\begin{aligned} & \frac{\text{vapour pressure of air}}{\text{SVP at the same temperature}} \\ &= \frac{12 \text{ mm of Hg}}{17.5 \text{ mm of Hg}} = 0.69, \end{aligned}$$

that is, 69%.

24.17 DETERMINATION OF RELATIVE HUMIDITY

A simple method to measure the relative humidity is to find the dew point and then use equation (24.18). We describe below the Regnault's hygrometer to find the dew point.

The apparatus consists of two test tubes *A* and *B* fitted with a hollow stand *C*. The test tube *A* can communicate with the hollow space in *C* but the tube *B* cannot. Both the tubes have silvered outer surfaces in the lower part. A hollow tube *D* goes into the test tube *A*. The other end of the tube *D* is open to the atmosphere. Sensitive thermometers T_1 and T_2 are inserted in the test tubes. The hollow space of the stand is connected to a vessel *E* through a rubber tube. The vessel has an outlet.

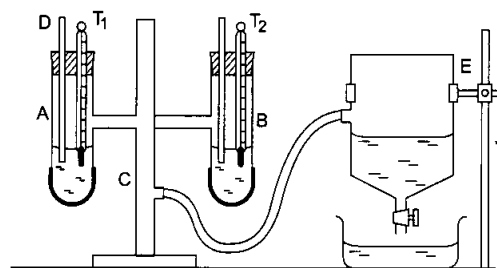


Figure 24.7

Some ether (about half the test tube) is taken in the test tube *A* and the vessel *E* is filled with water. The outlet below the vessel *E* is opened so that the water slowly comes out of the vessel. As a partial vacuum is created over the water surface, air is sucked through the tube *D*, the hollow stand and the rubber tube. Thus, air passes through the ether and evaporates it in the process. The temperature of the test tube *A* gradually decreases and becomes equal to the dew point at a certain time. The vapour in the air near the silvered surface of the test tube *A* starts condensing. Tiny water droplets in the form of *dew* appear on the silvered surface. This surface becomes hazy while the silvered surface of the test tube *B* remains shining. Both the surfaces are continuously observed from a distance (a telescope may be used for the purpose). As soon as the difference in shine is observed, the temperature of the test tube *A* is noted with the thermometer T_1 . The reading of T_2 gives the air-temperature.

The outlet to the vessel *D* is closed. The evaporation stops and the temperature of *A* which had gone below the dew point, starts rising. As it just crosses the dew point, the surface again starts shining. The temperature of T_1 at which the two silvered surfaces start looking similar, is noted. The average of the two readings of T_1 is taken as the dew point.

If f and F be the saturation vapour pressures at the dew point and at the air-temperature respectively, the relative humidity is

$$\frac{f}{F} \times 100\%.$$

Example 24.7

In an experiment with Regnault's hygrometer, dew appears at 10°C when the atmospheric temperature is 40°C . Using table (24.1), find the relative humidity.

Solution : The dew point is 10°C . The saturation vapour pressure at this temperature is 8.94 mm of Hg from table (24.1). Also, the saturation vapour pressure of air at 40°C is 55.1 mm of Hg. The relative humidity expressed in percentage

$$= \frac{\text{vapour pressure at the dew point}}{\text{SVP at the air-temperature}} \times 100\%$$

$$= \frac{8.94}{55.1} \times 100\% = 16.2\%.$$

24.18 PHASE DIAGRAMS : TRIPLE POINT

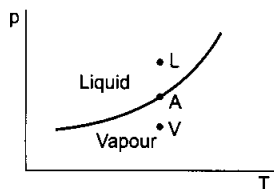


Figure 24.8

When a liquid and its vapour remain together in equilibrium, the vapour is saturated. The saturation vapour pressure depends on temperature. Figure (24.8) shows a curve representing the saturation vapour pressure as a function of temperature. If the vapour pressure and the temperature of a liquid-vapour system are represented by a point on the curve, such as A, the vapour is saturated. The liquid and the vapour can coexist in this case. Now suppose, the vapour pressure is increased by injecting more vapour into the space so that the situation is represented by the point L in figure (24.8). As the vapour is already saturated, the extra vapour will condense into liquid and the system will return to the point A. Similarly, suppose the vapour pressure is decreased by taking out some vapour from the space so that the situation is represented by the point V in figure (24.8). The vapour will become unsaturated and some liquid will evaporate to take the system back to the point A.

Thus, the liquid phase and the vapour phase can coexist only along the curve shown. At points above this curve a pure liquid can exist in equilibrium and at points below this curve a pure vapour can exist in equilibrium.

At the boiling point, the saturation vapour pressure equals the external pressure. The curve in figure (24.8), therefore, also represents the boiling point as a function of external pressure. The horizontal axis then represents the boiling point and the vertical axis represents the external pressure.

Similar curves also exist for solid-liquid transition and for solid-vapour transition. Figure (24.9) shows qualitatively these curves for water and carbon dioxide. The curve PB represents solid-liquid transition and PC represents solid-vapour transition. Solid and liquid phases may coexist along the curve PB and solid and vapour phases can coexist along PC. These curves also represent, respectively, the melting point as a function of pressure and sublimation point as a function of pressure. Thus, the p - T space is divided in three regions labelled solid, liquid and vapour.

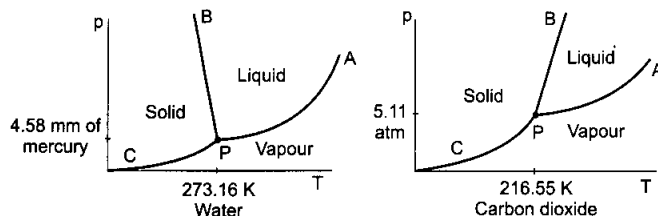


Figure 24.9

The three curves meet at one point labelled P. At the pressure and temperature corresponding to this point, all the three phases may remain together in equilibrium. This point is known as the *triple point*. For water, the triple point occurs at the pressure 4.58 mm of mercury and temperature 273.16 K .

For carbon dioxide, the temperature at the triple point is 216.55 K and the corresponding pressure is 5.11 atm. Thus, at atmospheric pressure it can remain either in solid phase or in vapour phase (figure 24.9). When solid CO_2 , open to atmosphere, is heated, it becomes vapour directly without passing through the liquid phase. It is, therefore, called *dry ice*.

24.19 DEW AND FOG

In winter nights, the atmospheric temperature goes down. The surfaces of windowpanes, flowers, grass, etc., become still colder due to radiation. The air near them becomes saturated and condensation begins. The droplets condensed on such surfaces are known as *dew*.

If the temperature falls further, the whole atmosphere in that region may become saturated. Small droplets then condense on the dust particles present in the air. These droplets keep floating in the air and form a thick mist which restricts visibility. This thick mist is called *fog*.

Worked Out Examples

1. A vessel of volume $8.0 \times 10^{-3} \text{ m}^3$ contains an ideal gas at 300 K and 200 kPa. The gas is allowed to leak till the pressure falls to 125 kPa. Calculate the amount of the gas (in moles) leaked assuming that the temperature remains constant.

Solution : As the gas leaks out, the volume and the temperature of the remaining gas do not change. The number of moles of the gas in the vessel is given by $n = \frac{pV}{RT}$. The number of moles in the vessel before the leakage is

$$n_1 = \frac{p_1 V}{RT}$$

and that after the leakage is

$$n_2 = \frac{p_2 V}{RT}$$

Thus, the amount leaked is

$$\begin{aligned} n_1 - n_2 &= \frac{(p_1 - p_2) V}{RT} \\ &= \frac{(200 - 125) \times 10^3 \text{ N m}^{-2} \times 8.0 \times 10^{-3} \text{ m}^3}{(8.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} \\ &= 0.24 \text{ mol}^{-1}. \end{aligned}$$

2. A vessel of volume 2000 cm^3 contains 0.1 mol of oxygen and 0.2 mol of carbon dioxide. If the temperature of the mixture is 300 K, find its pressure.

Solution : We have $p = \frac{nRT}{V}$.

The pressure due to oxygen is

$$p_1 = \frac{(0.1 \text{ mol}) (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K})}{(2000 \times 10^{-6} \text{ m}^3)} = 1.25 \times 10^5 \text{ Pa}.$$

Similarly, the pressure due to carbon dioxide is

$$p_2 = 2.50 \times 10^5 \text{ Pa}.$$

The total pressure in the vessel is

$$\begin{aligned} p &= p_1 + p_2 \\ &= (1.25 + 2.50) \times 10^5 \text{ Pa} = 3.75 \times 10^5 \text{ Pa}. \end{aligned}$$

3. A mixture of hydrogen and oxygen has volume 2000 cm^3 , temperature 300 K, pressure 100 kPa and mass 0.76 g. Calculate the masses of hydrogen and oxygen in the mixture.

Solution : Suppose there are n_1 moles of hydrogen and n_2 moles of oxygen in the mixture. The pressure of the mixture will be

$$p = \frac{n_1 RT}{V} + \frac{n_2 RT}{V} = (n_1 + n_2) \frac{RT}{V}$$

$$\text{or, } 100 \times 10^3 \text{ Pa} = (n_1 + n_2) \frac{(8.3 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K})}{2000 \times 10^{-6} \text{ m}^3}$$

$$\text{or, } n_1 + n_2 = 0.08 \text{ mol.} \quad \dots (i)$$

The mass of the mixture is

$$n_1 \times 2 \text{ g mol}^{-1} + n_2 \times 32 \text{ g mol}^{-1} = 0.76 \text{ g}$$

or, $n_1 + 16n_2 = 0.38 \text{ mol.} \quad \dots (ii)$
from (i) and (ii),

$$n_1 = 0.06 \text{ mol and } n_2 = 0.02 \text{ mol.}$$

The mass of hydrogen = $0.06 \times 2 \text{ g} = 0.12 \text{ g}$ and the mass of oxygen = $0.02 \times 32 \text{ g} = 0.64 \text{ g}$.

4. A mercury manometer (figure 24-W1) consists of two unequal arms of equal cross section 1 cm^2 and lengths 100 cm and 50 cm. The two open ends are sealed with air in the tube at a pressure of 80 cm of mercury. Some amount of mercury is now introduced in the manometer through the stopcock connected to it. If mercury rises in the shorter tube to a length 10 cm in steady state, find the length of the mercury column risen in the longer tube.

Solution : Let p_1 and p_2 be the pressures in centimetre of mercury in the two arms after introducing mercury in the tube. Suppose the mercury column rises in the second arm to l_0 cm.

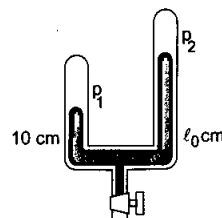


Figure 24-W1

Using $pV = \text{constant}$ for the shorter arm,
 $(80 \text{ cm}) (50 \text{ cm}) = p_1 (50 \text{ cm} - 10 \text{ cm})$

$$\text{or, } p_1 = 100 \text{ cm.} \quad \dots (i)$$

Using $pV = \text{constant}$ for the longer arm,

$$(80 \text{ cm}) (100 \text{ cm}) = p_2 (100 - l_0) \text{ cm.} \quad \dots (ii)$$

From the figure,

$$p_1 = p_2 + (l_0 - 10) \text{ cm.}$$

Thus by (i),

$$100 \text{ cm} = p_2 + (l_0 - 10) \text{ cm}$$

$$\text{or, } p_2 = 110 \text{ cm} - l_0 \text{ cm.}$$

Putting in (ii),

$$(110 - l_0) (100 - l_0) = 8000$$

$$\text{or, } l_0^2 - 210l_0 + 3000 = 0$$

$$\text{or, } l_0 = 15.5.$$

The required length is 15.5 cm.

5. An ideal gas has pressure p_0 , volume V_0 and temperature T_0 . It is taken through an isochoric process till its

pressure is doubled. It is now isothermally expanded to get the original pressure. Finally, the gas is isobarically compressed to its original volume V_0 . (a) Show the process on a p - V diagram. (b) What is the temperature in the isothermal part of the process? (c) What is the volume at the end of the isothermal part of the process?

Solution : (a) The process is shown in a p - V diagram in figure (24-W2). The process starts from A and goes through ABCA.

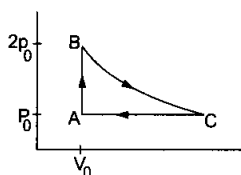


Figure 24-W2

(b) Applying $pV = nRT$ at A and B,

$$p_0 V_0 = nRT_0$$

and $(2p_0)V_0 = nRT_B$.

Thus, $T_B = 2T_0$.

This is the temperature in the isothermal part BC.

(c) As the process BC is isothermal, $T_C = T_B = 2T_0$.

Applying $pV = nRT$ at A and C,

$$p_0 V_0 = nRT_0$$

and $p_0 V_C = nR(2T_0)$

or, $V_C = 2V_0$.

6. A cyclic process ABCA shown in the V - T diagram (figure 24-W3) is performed with a constant mass of an ideal gas. Show the same process on a p - V diagram. In the figure, CA is parallel to the V -axis and BC is parallel to the T -axis.

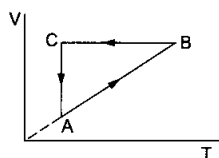


Figure 24-W3

Solution : The p - V diagram is shown in figure (24-W4).

During the part AB of figure (24-W3), V is proportional to T . Thus, $\frac{V}{T}$ is constant. Using $\frac{pV}{T} = nR$, we see that the pressure p is constant in this part. This is represented by the part A'B' in the p - V diagram. During

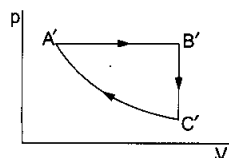


Figure 24-W4

the part BC, volume is constant. Thus, $\frac{p}{T}$ is constant. As the temperature decreases, pressure also decreases. This is represented by the part B'C' in the p - V diagram. During the part CA, the temperature remains constant so that $pV = \text{constant}$. Thus, p is inversely proportional to V . This is represented by the part C'A' in the p - V diagram.

7. Two closed vessels of equal volume contain air at 105 kPa, 300 K and are connected through a narrow tube. If one of the vessels is now maintained at 300 K and the other at 400 K, what will be the pressure in the vessels?

Solution : Let the initial pressure, volume and temperature in each vessel be $p_0 (= 105 \text{ kPa})$, V_0 and $T_0 (= 300 \text{ K})$. Let the number of moles in each vessel be n . When the first vessel is maintained at temperature T_0 and the other is maintained at $T' = 400 \text{ K}$, the pressures change. Let the common pressure become p' and the number of moles in the two vessels become n_1 and n_2 . We have

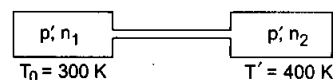


Figure 24-W5

$$p_0 V_0 = nRT_0 \quad \dots (i)$$

$$p' V_0 = n_1 RT_0 \quad \dots (ii)$$

$$p' V_0 = n_2 RT' \quad \dots (iii)$$

$$\text{and } n_1 + n_2 = 2n. \quad \dots (iv)$$

Putting n , n_1 and n_2 from (i), (ii) and (iii) in (iv),

$$\frac{p' V_0}{RT_0} + \frac{p' V_0}{RT'} = 2 \frac{p_0 V_0}{RT_0}$$

$$\text{or, } p' \left(\frac{T' + T_0}{T_0 T'} \right) = \frac{2p_0}{T_0}$$

$$\text{or, } p' = \frac{2p_0 T'}{T' + T_0}$$

$$= \frac{2 \times 105 \text{ kPa} \times 400 \text{ K}}{400 \text{ K} + 300 \text{ K}} = 120 \text{ kPa}.$$

8. A vessel contains 14 g of hydrogen and 96 g of oxygen at STP. (a) Find the volume of the vessel. (b) Chemical reaction is induced by passing electric spark in the vessel till one of the gases is consumed. The temperature is brought back to its starting value 273 K. Find the pressure in the vessel.

Solution : (a) The number of moles of hydrogen = $14 \text{ g} / 2 \text{ g} = 7$ and the number of moles of oxygen = $96 \text{ g} / 32 \text{ g} = 3$. The total number of moles in the vessel = $7 + 3 = 10$. The pressure is $1 \text{ atm} = 1.0 \times 10^5 \text{ N m}^{-2}$ and the temperature = 273 K.

$$\text{Now } pV = nRT \quad \dots (i)$$

$$\begin{aligned} \text{or, } V &= \frac{nRT}{p} \\ &= \frac{(10 \text{ mol}) \times (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})}{1.0 \times 10^5 \text{ N m}^{-2}} \\ &= 0.23 \text{ m}^3. \end{aligned}$$

(b) When electric spark is passed, hydrogen reacts with oxygen to form water (H_2O). Each gram of hydrogen reacts with eight grams of oxygen. Thus, 96 g of oxygen will be totally consumed together with 12 g of hydrogen. The gas left in the vessel will be 2 g of hydrogen which is $n' = 1$ mole.

Neglecting the volume of the water formed,

$$p'V = n'RT. \quad \dots \text{ (ii)}$$

From (i) and (ii),

$$\frac{p'}{p} = \frac{n'}{n} = \frac{1}{10}$$

$$\begin{aligned} \text{or, } p' &= p \times 0.10 \\ &= 0.10 \text{ atm.} \end{aligned}$$

9. A barometer reads 75 cm of mercury. When 2.0 cm^3 of air at atmospheric pressure is introduced into the space above the mercury level, the volume of this space becomes 50 cm^3 . Find the length by which the mercury column descends.

Solution : Let the pressure of the air in the barometer be p . We have,

$$p \times 50 \text{ cm}^3 = (75 \text{ cm of mercury}) \times (2.0 \text{ cm}^3)$$

$$\text{or, } p = 3.0 \text{ cm of mercury.}$$

The atmospheric pressure is equal to the pressure due to the mercury column plus the pressure due to the air inside. Thus, the mercury column descends by 3.0 cm.

10. A barometer tube is 1 m long and 2 cm^2 in cross section. Mercury stands to a height of 75 cm in the tube. When a small amount of oxygen is introduced in the space above the mercury level, the level falls by 5 cm. Calculate the mass of the oxygen introduced. Room temperature = 27°C , $g = 10 \text{ m s}^{-2}$ and density of mercury = 13600 kg m^{-3} .

Solution : The pressure of oxygen in the space above the mercury level = 5 cm of mercury

$$\begin{aligned} &= 0.05 \text{ m} \times 13600 \text{ kg m}^{-3} \times 10 \text{ m s}^{-2} \\ &= 6800 \text{ N m}^{-2}. \end{aligned}$$

$$\begin{aligned} \text{The volume of oxygen} &= (2 \text{ cm}^2) \times (25 \text{ cm} + 5 \text{ cm}) \\ &= 60 \text{ cm}^3 = 6 \times 10^{-5} \text{ m}^3. \end{aligned}$$

$$\text{The temperature} = (273 + 27) \text{ K} = 300 \text{ K.}$$

The amount of oxygen is

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

$$\begin{aligned} &= \frac{(6800 \text{ N m}^{-2}) \times 6 \times 10^{-5} \text{ m}^3}{(8.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} \\ &= 16.4 \times 10^{-5} \text{ mol.} \end{aligned}$$

The mass of oxygen is

$$\begin{aligned} &(16.4 \times 10^{-5} \text{ mol}) \times (32 \text{ g mol}^{-1}) \\ &= 5.24 \times 10^{-3} \text{ g.} \end{aligned}$$

11. Figure (24-W6) shows a vertical cylindrical vessel separated in two parts by a frictionless piston free to move along the length of the vessel. The length of the cylinder is 90 cm and the piston divides the cylinder in the ratio of 5:4. Each of the two parts of the vessel contains 0.1 mole of an ideal gas. The temperature of the gas is 300 K in each part. Calculate the mass of the piston.

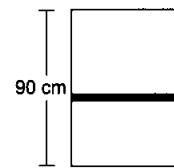


Figure 24-W6

Solution : Let l_1 and l_2 be the lengths of the upper part and the lower part of the cylinder respectively. Clearly, $l_1 = 50 \text{ cm}$ and $l_2 = 40 \text{ cm}$. Let the pressures in the upper and lower parts be p_1 and p_2 respectively. Let the area of cross section of the cylinder be A . The temperature in both parts is $T = 300 \text{ K}$.

Consider the equilibrium of the piston. The forces acting on the piston are

(a) its weight mg

(b) $p_1 A$ downward, by the upper part of the gas

and (c) $p_2 A$ upward, by the lower part of the gas.

$$\text{Thus, } p_2 A = p_1 A + mg \quad \dots \text{ (i)}$$

Using $pV = nRT$ for the upper and the lower parts

$$p_1 l_1 A = nRT \quad \dots \text{ (ii)}$$

$$\text{and } p_2 l_2 A = nRT. \quad \dots \text{ (iii)}$$

Putting $p_1 A$ and $p_2 A$ from (ii) and (iii) into (i),

$$\frac{nRT}{l_2} = \frac{nRT}{l_1} + mg.$$

$$\text{Thus, } m = \frac{nRT}{g} \left[\frac{1}{l_2} - \frac{1}{l_1} \right]$$

$$= \frac{(0.1 \text{ mol}) (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K})}{9.8 \text{ m s}^{-2}} \left[\frac{1}{0.4 \text{ m}} - \frac{1}{0.5 \text{ m}} \right]$$

$$= 12.7 \text{ kg.}$$

12. Figure (24-W7) shows a cylindrical tube of volume V_0 divided in two parts by a frictionless separator. The walls of the tube are adiabatic but the separator is conducting. Ideal gases are filled in the two parts. When the separator is kept in the middle, the pressures are p_1 and p_2 in the

left part and the right part respectively. The separator is slowly slid and is released at a position where it can stay in equilibrium. Find the volumes of the two parts.



Figure 24-W7

Solution : As the separator is conducting, the temperatures in the two parts will be the same. Suppose the common temperature is T when the separator is in the middle. Let n_1 and n_2 be the number of moles of the gas in the left part and the right part respectively. Using ideal gas equation,

$$p_1 \frac{V_0}{2} = n_1 RT$$

and

$$p_2 \frac{V_0}{2} = n_2 RT.$$

Thus,

$$\frac{n_1}{n_2} = \frac{p_1}{p_2} \quad \dots (i)$$

The separator will stay in equilibrium at a position where the pressures on the two sides are equal. Suppose the volume of the left part is V_1 and of the right part is V_2 in this situation. Let the common pressure be p' . Also, let the common temperature in this situation be T' . Using ideal gas equation,

$$p' V_1 = n_1 R T'$$

and

$$p' V_2 = n_2 R T'$$

or,

$$\frac{V_1}{V_2} = \frac{n_1}{n_2} = \frac{p_1}{p_2} \quad [\text{using (i)}]$$

Also,

$$V_1 + V_2 = V_0.$$

$$\text{Thus, } V_1 = \frac{p_1 V_0}{p_1 + p_2} \text{ and } V_2 = \frac{p_2 V_0}{p_1 + p_2}.$$

13. A thin tube of uniform cross section is sealed at both ends. It lies horizontally, the middle 5 cm containing mercury and the parts on its two sides containing air at the same pressure p . When the tube is held at an angle of 60° with the vertical, the length of the air column above and below the mercury pellet are 46 cm and 44.5 cm respectively. Calculate the pressure p in centimetres of mercury. The temperature of the system is kept at 30°C .

Solution : When the tube is kept inclined to the vertical, the length of the upper part is $l_1 = 46$ cm and that of the lower part is $l_2 = 44.5$ cm. When the tube lies horizontally, the length on each side is

$$l_0 = \frac{l_1 + l_2}{2} = \frac{46 \text{ cm} + 44.5 \text{ cm}}{2} = 45.25 \text{ cm}.$$

Let p_1 and p_2 be the pressures in the upper and the lower parts when the tube is kept inclined. As the temperature is constant throughout, we can apply Boyle's law. For the upper part,

$$p_1 l_1 A = p l_0 A$$

or,

$$p_1 = \frac{p l_0}{l_1} \quad \dots (i)$$

Similarly, for the lower part,

$$p_2 = \frac{p l_0}{l_2} \quad \dots (ii)$$

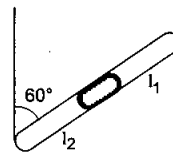


Figure 24-W8

Now consider the equilibrium of the mercury pellet when the tube is kept in inclined position. Let m be the mass of the mercury. The forces along the length of the tube are

(a) $p_1 A$ down the tube

(b) $p_2 A$ up the tube

and (c) $mg \cos 60^\circ$ down the tube.

$$\text{Thus, } p_2 = p_1 + \frac{mg}{A} \cos 60^\circ.$$

Putting from (i) and (ii),

$$\frac{p l_0}{l_2} = \frac{p l_0}{l_1} + \frac{mg}{2A}$$

$$\text{or, } p l_0 \left(\frac{1}{l_2} - \frac{1}{l_1} \right) = \frac{mg}{2A}$$

$$\text{or, } p = \frac{mg}{2A l_0 \left(\frac{1}{l_2} - \frac{1}{l_1} \right)}$$

If the pressure p is equal to a height h of mercury,

$$p = h \rho g.$$

$$\text{Also, } m = (5 \text{ cm}) A \rho$$

$$\text{so that } h \rho g = \frac{(5 \text{ cm}) A \rho g}{2A l_0 \left(\frac{1}{l_2} - \frac{1}{l_1} \right)}$$

$$\begin{aligned} \text{or, } h &= \frac{(5 \text{ cm})}{2(45.25 \text{ cm}) \left(\frac{1}{44.5 \text{ cm}} - \frac{1}{46 \text{ cm}} \right)} \\ &= 75.39 \text{ cm}. \end{aligned}$$

The pressure p is equal to 75.39 cm of mercury.

14. An ideal monatomic gas is confined in a cylinder by a spring-loaded piston of cross section $8.0 \times 10^{-3} \text{ m}^2$. Initially the gas is at 300 K and occupies a volume of $2.4 \times 10^{-3} \text{ m}^3$ and the spring is in its relaxed state (figure 24-W9). The gas is heated by a small heater until the piston moves out slowly by 0.1 m. Calculate the final temperature of the gas. The force constant of the spring is 8000 N m^{-1} , and the atmospheric pressure is $1.0 \times 10^5 \text{ N m}^{-2}$. The cylinder and the piston are

thermally insulated. The piston and the spring are massless and there is no friction between the piston and the cylinder. Neglect any heat-loss through the lead wires of the heater. The heat capacity of the heater coil is negligible.

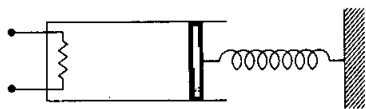


Figure 24-W9

Solution : Initially the spring is in its relaxed state. So, the pressure of the gas equals the atmospheric pressure.

Initial pressure $= p_1 = 1.0 \times 10^5 \text{ N m}^{-2}$.

$$\begin{aligned} \text{Final pressure} &= p_2 = p_1 + \frac{kx}{A} \\ &= 1.0 \times 10^5 \text{ N m}^{-2} + \frac{(8000 \text{ N m}^{-1})(0.1 \text{ m})}{8.0 \times 10^{-3} \text{ m}^2} \\ &= 2.0 \times 10^5 \text{ N m}^{-2}. \end{aligned}$$

Final volume $= V_2 = V_1 + Ax$

$$= 2.4 \times 10^{-3} \text{ m}^3 + 8.0 \times 10^{-3} \text{ m}^2 \times 0.1 \text{ m} = 3.2 \times 10^{-3} \text{ m}^3.$$

$$\text{Using } \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2},$$

$$T_2 = \frac{p_2 V_2}{p_1 V_1} T_1$$

$$\begin{aligned} &= \frac{(2.0 \times 10^5 \text{ N m}^{-2})(3.2 \times 10^{-3} \text{ m}^3)}{(1.0 \times 10^5 \text{ N m}^{-2})(2.4 \times 10^{-3} \text{ m}^3)} \times 300 \text{ K} \\ &= 800 \text{ K}. \end{aligned}$$

15. Assume that the temperature remains essentially constant in the upper part of the atmosphere. Obtain an expression for the variation in pressure in the upper atmosphere with height. The mean molecular weight of air is M .

Solution : Suppose the pressure at height h is p and that at $h + dh$ is $p + dp$. Then

$$dp = -\rho g dh. \quad \dots (i)$$

Now considering any small volume ΔV of air of mass Δm ,

$$p\Delta V = nRT = \frac{\Delta m}{M} RT$$

$$\text{or, } p = \frac{\Delta m}{\Delta V} \frac{RT}{M} = \frac{\rho RT}{M}$$

$$\text{or, } \rho = \frac{M}{RT} p.$$

Putting in (i),

$$dp = -\frac{M}{RT} pg dh$$

$$\text{or, } \int_{p_0}^p \frac{dp}{p} = \int_0^h -\frac{M}{RT} g dh$$

$$\text{or, } \ln \frac{p}{p_0} = -\frac{Mgh}{RT}$$

where p_0 is the pressure at $h = 0$.

$$\text{Thus, } p = p_0 e^{-\frac{Mgh}{RT}}.$$

16. A horizontal tube of length l closed at both ends contains an ideal gas of molecular weight M . The tube is rotated at a constant angular velocity ω about a vertical axis passing through an end. Assuming the temperature to be uniform and constant, show that

$$p_2 = p_1 e^{\frac{M\omega^2 l^2}{2RT}},$$

where p_2 and p_1 denote the pressures at the free end and the fixed end respectively.

Solution : Consider an element of the gas between the cross sections at distances x and $x + dx$ from the fixed end (figure 24-W10). If p be the pressure at x and $p + dp$ at $x + dx$, the force acting on the element towards the centre is Adp , where A is the cross sectional area. As this element is going in a circle of radius x ,

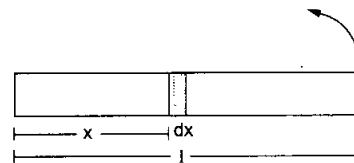


Figure 24-W10

$$Adp = (dm)\omega^2 x \quad \dots (i)$$

where dm = mass of the element. Using $pV = nRT$ on this element,

$$pAdx = \frac{dm}{M} RT$$

$$\text{or, } dm = \frac{MpA}{RT} dx.$$

Putting in (i),

$$Adp = \frac{MpA}{RT} \omega^2 x dx$$

$$\text{or, } \int_{p_1}^{p_2} \frac{dp}{p} = \int_0^l \frac{M\omega^2}{RT} x dx$$

$$\text{or, } \ln \frac{p_2}{p_1} = \frac{M\omega^2 l^2}{2RT}$$

$$\text{or, } p_2 = p_1 e^{\frac{M\omega^2 l^2}{2RT}}.$$

17. A barometer tube contains a mixture of air and saturated water vapour in the space above the mercury column. It reads 70 cm when the actual atmospheric pressure is 76 cm of mercury. The saturation vapour pressure at room temperature is 1.0 cm of mercury. The tube is now lowered in the reservoir till the space above the mercury column is reduced to half its original volume. Find the

reading of the barometer. Assume that the temperature remains constant.

Solution : The pressure due to the air + vapour is 76 cm – 70 cm = 6 cm of mercury. The vapour is saturated and the pressure due to it is 1 cm of mercury. The pressure due to the air is, therefore, 5 cm of mercury.

As the tube is lowered and the volume above the mercury is decreased, some of the vapour will condense. The remaining vapour will again exert a pressure of 1 cm of mercury. The pressure due to air is doubled as the volume is halved. Thus, $p_{\text{air}} = 2 \times 5 \text{ cm} = 10 \text{ cm}$ of mercury. The pressure due to the air + vapour = 10 cm + 1 cm = 11 cm of mercury. The barometer reading is 76 cm – 11 cm = 65 cm.

18. Find the mass of water vapour per cubic metre of air at temperature 300 K and relative humidity 50%. The saturation vapour pressure at 300 K is 3.6 kPa and the gas constant $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$.

Solution : At 300 K, the saturation vapour pressure = 3.6 kPa. Considering 1 m^3 of volume,

$$pV = nRT = \frac{m}{M} RT$$

where m = mass of vapour and M = molecular weight of water.

$$\text{Thus, } m = \frac{MpV}{RT} = \frac{(18 \text{ g mol}^{-1})(3.6 \times 10^3 \text{ Pa})(1 \text{ m}^3)}{(8.3 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})} \approx 26 \text{ g}.$$

As the relative humidity is 50%, the amount of vapour present in 1 m^3 is $26 \text{ g} \times 0.50 = 13 \text{ g}$.

19. The temperature and the relative humidity of air are 20°C and 80% on a certain day. Find the fraction of the mass of water vapour that will condense if the temperature falls to 5°C. Saturation vapour pressures at 20°C and 5°C are 17.5 mm and 6.5 mm of mercury respectively.

Solution : The relative humidity is

$$\frac{\text{vapour pressure of the air}}{\text{SVP at the same temperature}}$$

Thus, the vapour pressure at 20°C

$$\begin{aligned} &= 0.8 \times 17.5 \text{ mm of Hg} \\ &= 14 \text{ mm of Hg.} \end{aligned}$$

Consider a volume V of air. If the vapour pressure is p and the temperature is T , the mass m of the vapour present is given by

$$pV = \frac{m}{M} RT$$

$$\text{or, } m = \frac{MVp}{RT} \quad \dots (i)$$

The mass present at 20°C is

$$m_1 = \frac{MV}{R} \frac{14 \text{ mm of Hg}}{293 \text{ K}}$$

When the air is cooled to 5°C, some vapour condenses and the air gets saturated with the remaining vapour. The vapour pressure at 5°C is, therefore, 6.5 mm of mercury. The mass of vapour present at 5°C is, therefore,

$$m_2 = \frac{MV}{R} \frac{6.5 \text{ mm of Hg}}{278 \text{ K}}$$

The fraction condensed

$$\begin{aligned} &= \frac{m_1 - m_2}{m_1} = 1 - \frac{m_2}{m_1} \\ &= 1 - \frac{6.5}{278} \times \frac{293}{14} = 0.51. \end{aligned}$$

20. A vessel containing water is put in a dry sealed room of volume 76 m^3 at a temperature of 15°C. The saturation vapour pressure of water at 15°C is 15 mm of mercury. How much water will evaporate before the water is in equilibrium with the vapour?

Solution : Water will be in equilibrium with its vapour when the vapour gets saturated. In this case, the pressure of vapour = saturation vapour pressure = 15 mm of mercury

$$\begin{aligned} &= (15 \times 10^{-3} \text{ m})(13600 \text{ kg m}^{-3})(9.8 \text{ m s}^{-2}) \\ &= 2000 \text{ N m}^{-2}. \end{aligned}$$

Using gas law, $pV = \frac{m}{M} RT$

$$\begin{aligned} m &= \frac{MpV}{RT} \\ &= \frac{(18 \text{ g mol}^{-1})(2000 \text{ N m}^{-2})(76 \text{ m}^3)}{(8.3 \text{ J K}^{-1} \text{ mol}^{-1})(288 \text{ K})} \\ &= 1145 \text{ g} = 1.14 \text{ kg}. \end{aligned}$$

Thus, 1.14 kg of water will evaporate.

21. A jar contains a gas and a few drops of water at absolute temperature T_1 . The pressure in the jar is 830 mm of mercury. The temperature of the jar is reduced by 1%. The saturation vapour pressures of water at the two temperatures are 30 mm of mercury and 25 mm of mercury. Calculate the new pressure in the jar.

Solution : At temperature T_1 , the total pressure is 830 mm of mercury. Out of this, 30 mm of mercury is due to the vapour and 800 mm of mercury is due to the gas. As the temperature decreases, the pressure due to the gas decreases according to the gas law. Here the volume is constant, so,

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

$$\text{or, } p_2 = \frac{T_2}{T_1} p_1$$

As T_2 is 1% less than T_1

$$T_2 = 0.99 T_1$$

and hence,

$$p_2 = 0.99 p_1$$

$$= 0.99 \times 800 \text{ mm of mercury} = 792 \text{ mm of mercury.}$$

The vapour is still saturated and hence, its pressure is 25 mm of mercury. The total pressure at the reduced temperature is

$$p = (792 + 25) \text{ mm of mercury} \\ = 817 \text{ mm of mercury.}$$

22. Calculate the mass of 1 litre of moist air at 27°C when the barometer reads 753.6 mm of mercury and the dew point is 16.1°C. Saturation vapour pressure of water at 16.1°C = 13.6 mm of mercury, density of air at STP = 0.001293 g (cc)⁻¹, density of saturated water vapour at STP = 0.000808 g (cc)⁻¹.

Solution : We have $pV = \frac{m}{M} RT$

$$\text{or, } \rho = \frac{m}{V} = \frac{Mp}{RT} \quad \dots (i)$$

The dew point is 16.1°C and the saturation vapour pressure is 13.6 mm of mercury at the dew point. This means that the present vapour pressure is 13.6 mm of mercury.

At this pressure and temperature, the density of vapour will be

$$\rho = \frac{Mp}{RT} \\ = \frac{(18 \text{ g mol}^{-1}) (13.6 \times 10^{-3} \text{ m}) (13600 \text{ kg m}^{-3}) (9.8 \text{ m s}^{-2})}{(8.3 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K})} \\ = 13.1 \text{ g m}^{-3}.$$

Thus, 1 litre of moist air at 27°C contains 0.0131 g of vapour.

The pressure of dry air at 27°C is 753.6 mm – 13.6 mm = 740 mm of mercury. The density of air at STP is 0.001293 g (cc)⁻¹. The density at 27°C is given by equation (i),

$$\frac{\rho_1}{\rho_2} = \frac{p_1/T_1}{p_2/T_2} \\ \text{or, } \rho_2 = \frac{p_2 T_1}{T_2 p_1} \rho_1 \\ = \frac{740 \times 273}{300 \times 760} \times 0.001293 \text{ g (cc)}^{-1} \\ = 0.001457 \text{ g (cc)}^{-1}.$$

Thus, 1 litre of moist air contains 1.145 g of dry air. The mass of 1 litre of moist air is 1.1457 g + 0.0131 g ≈ 1.159 g.

□

QUESTIONS FOR SHORT ANSWER

- When we place a gas cylinder on a van and the van moves, does the kinetic energy of the molecules increase? Does the temperature increase?
- While gas from a cooking gas cylinder is used, the pressure does not fall appreciably till the last few minutes. Why?
- Do you expect the gas in a cooking gas cylinder to obey the ideal gas equation?
- Can we define the temperature of (a) vacuum, (b) a single molecule?
- Comment on the following statement: the temperature of all the molecules in a sample of a gas is the same.
- Consider a gas of neutrons. Do you expect it to behave much better as an ideal gas as compared to hydrogen gas at the same pressure and temperature?
- A gas is kept in a rigid cubical container. If a load of 10 kg is put on the top of the container, does the pressure increase?
- If it were possible for a gas in a container to reach the temperature 0 K, its pressure would be zero. Would the molecules not collide with the walls? Would they not transfer momentum to the walls?
- It is said that the assumptions of kinetic theory are good for gases having low densities. Suppose a container is so evacuated that only one molecule is left in it. Which of the assumptions of kinetic theory will not be valid for such a situation? Can we assign a temperature to this gas?
- A gas is kept in an enclosure. The pressure of the gas is reduced by pumping out some gas. Will the temperature of the gas decrease by Charles's law?
- Explain why cooking is faster in a pressure cooker.
- If the molecules were not allowed to collide among themselves, would you expect more evaporation or less evaporation?
- Is it possible to boil water at room temperature, say 30°C? If we touch a flask containing water boiling at this temperature, will it be hot?
- When you come out of a river after a dip, you feel cold. Explain.

OBJECTIVE I

- Which of the following parameters is the same for molecules of all gases at a given temperature ?
(a) Mass (b) Speed
(c) Momentum (d) Kinetic energy.
- A gas behaves more closely as an ideal gas at
(a) low pressure and low temperature
(b) low pressure and high temperature
(c) high pressure and low temperature
(d) high pressure and high temperature.
- The pressure of an ideal gas is written as $p = \frac{2E}{3V}$. Here E refers to
(a) translational kinetic energy
(b) rotational kinetic energy
(c) vibrational kinetic energy
(d) total kinetic energy.
- The energy of a given sample of an ideal gas depends only on its
(a) volume (b) pressure (c) density (d) temperature.
- Which of the following gases has maximum rms speed at a given temperature ?
(a) hydrogen (b) nitrogen
(c) oxygen (d) carbon dioxide.
- Figure 24-Q1 shows graphs of pressure vs density for an ideal gas at two temperatures T_1 and T_2 .
(a) $T_1 > T_2$ (b) $T_1 = T_2$
(c) $T_1 < T_2$ (d) Any of the three is possible.
- The mean square speed of the molecules of a gas at absolute temperature T is proportional to
(a) $\frac{1}{T}$ (b) \sqrt{T} (c) T (d) T^2 .
- Suppose a container is evacuated to leave just one molecule of a gas in it. Let v_a and v_{rms} represent the average speed and the rms speed of the gas.
(a) $v_a > v_{rms}$ (b) $v_a < v_{rms}$
(c) $v_a = v_{rms}$ (d) v_{rms} is undefined.
- The rms speed of oxygen at room temperature is about 500 m/s. The rms speed of hydrogen at the same temperature is about
(a) 125 m s^{-1} (b) 2000 m s^{-1} (c) 8000 m s^{-1} (d) 31 m s^{-1} .
- The pressure of a gas kept in an isothermal container is 200 kPa. If half the gas is removed from it, the pressure will be
(a) 100 kPa (b) 200 kPa (c) 400 kPa (d) 800 kPa.
- The rms speed of oxygen molecules in a gas is v . If the temperature is doubled and the oxygen molecules dissociate into oxygen atoms, the rms speed will become
(a) v (b) $v\sqrt{2}$ (c) $2v$ (d) $4v$.
- The quantity $\frac{pV}{kT}$ represents
(a) mass of the gas
(b) kinetic energy of the gas
(c) number of moles of the gas
(d) number of molecules in the gas.
- The process on an ideal gas, shown in figure (24-Q2), is
(a) isothermal (b) isobaric (c) isochoric (d) none of these.

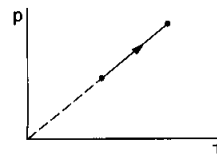


Figure 24-Q2

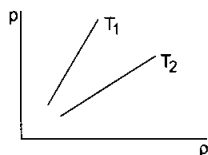


Figure 24-Q1

- There is some liquid in a closed bottle. The amount of liquid is continuously decreasing. The vapour in the remaining part
(a) must be saturated (b) must be unsaturated
(c) may be saturated (d) there will be no vapour.
- There is some liquid in a closed bottle. The amount of liquid remains constant as time passes. The vapour in the remaining part
(a) must be saturated (b) must be unsaturated
(c) may be unsaturated (d) there will be no vapour.
- Vapour is injected at a uniform rate in a closed vessel which was initially evacuated. The pressure in the vessel
(a) increases continuously
(b) decreases continuously
(c) first increases and then decreases
(d) first increases and then becomes constant.
- A vessel A has volume V and a vessel B has volume $2V$. Both contain some water which has a constant volume. The pressure in the space above water is p_a for vessel A and p_b for vessel B.
(a) $p_a = p_b$ (b) $p_a = 2p_b$
(c) $p_b = 2p_a$ (d) $p_b = 4p_a$

OBJECTIVE II

- Consider a collision between an oxygen molecule and a hydrogen molecule in a mixture of oxygen and hydrogen kept at room temperature. Which of the following are

possible ?

- The kinetic energies of both the molecules increase.
- The kinetic energies of both the molecules decrease.

- (c) kinetic energy of the oxygen molecule increases and that of the hydrogen molecule decreases.
 (d) The kinetic energy of the hydrogen molecule increases and that of the oxygen molecule decreases.
2. Consider a mixture of oxygen and hydrogen kept at room temperature. As compared to a hydrogen molecule an oxygen molecule hits the wall
 (a) with greater average speed
 (b) with smaller average speed
 (c) with greater average kinetic energy
 (d) with smaller average kinetic energy.
3. Which of the following quantities is zero on an average for the molecules of an ideal gas in equilibrium ?
 (a) Kinetic energy (b) Momentum
 (c) Density (d) Speed.
4. Keeping the number of moles, volume and temperature the same, which of the following are the same for all ideal gases ?
 (a) Rms speed of a molecule (b) Density
 (c) Pressure
 (d) Average magnitude of momentum.
5. The average momentum of a molecule in a sample of an ideal gas depends on
 (a) temperature (b) number of moles
 (c) volume (d) none of these.
6. Which of the following quantities is the same for all ideal gases at the same temperature ?
 (a) The kinetic energy of 1 mole
 (b) The kinetic energy of 1 g
 (c) The number of molecules in 1 mole
 (d) The number of molecules in 1 g
7. Consider the quantity $\frac{MkT}{pV}$ of an ideal gas where M is the mass of the gas. It depends on the
 (a) temperature of the gas (b) volume of the gas
 (c) pressure of the gas (d) nature of the gas.

EXERCISES

Use $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$ wherever required.

- Calculate the volume of 1 mole of an ideal gas at STP.
- Find the number of molecules of an ideal gas in a volume of 1.000 cm^3 at STP.
- Find the number of molecules in 1 cm^3 of an ideal gas at 0°C and at a pressure of 10^{-5} mm of mercury.
- Calculate the mass of 1 cm^3 of oxygen kept at STP.
- Equal masses of air are sealed in two vessels, one of volume V_0 and the other of volume $2V_0$. If the first vessel is maintained at a temperature 300 K and the other at 600 K , find the ratio of the pressures in the two vessels.
- An electric bulb of volume 250 cc was sealed during manufacturing at a pressure of 10^{-3} mm of mercury at 27°C . Compute the number of air molecules contained in the bulb. Avogadro constant $= 6 \times 10^{23} \text{ mol}^{-1}$, density of mercury $= 13600 \text{ kg m}^{-3}$ and $g = 10 \text{ m s}^{-2}$.
- A gas cylinder has walls that can bear a maximum pressure of $1.0 \times 10^6 \text{ Pa}$. It contains a gas at $8.0 \times 10^5 \text{ Pa}$ and 300 K . The cylinder is steadily heated. Neglecting any change in the volume, calculate the temperature at which the cylinder will break.
- 2 g of hydrogen is sealed in a vessel of volume 0.02 m^3 and is maintained at 300 K . Calculate the pressure in the vessel.
- The density of an ideal gas is $1.25 \times 10^{-3} \text{ g cm}^{-3}$ at STP. Calculate the molecular weight of the gas.
- The temperature and pressure at Simla are 15.0°C and 72.0 cm of mercury and at Kalka these are 35.0°C and 76.0 cm of mercury. Find the ratio of air density at Kalka to the air density at Simla.
- Figure (24-E1) shows a cylindrical tube with adiabatic walls and fitted with a diathermic separator. The separator can be slid in the tube by an external mechanism. An ideal gas is injected into the two sides

at equal pressures and equal temperatures. The separator remains in equilibrium at the middle. It is now slid to a position where it divides the tube in the ratio of 1:3. Find the ratio of the pressures in the two parts of the vessel.



Figure 24-E1

- Find the rms speed of hydrogen molecules in a sample of hydrogen gas at 300 K . Find the temperature at which the rms speed is double the speed calculated in the previous part.
- A sample of 0.177 g of an ideal gas occupies 1000 cm^3 at STP. Calculate the rms speed of the gas molecules.
- The average translational kinetic energy of air molecules is 0.040 eV ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$). Calculate the temperature of the air. Boltzmann constant $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$.
- Consider a sample of oxygen at 300 K . Find the average time taken by a molecule to travel a distance equal to the diameter of the earth.
- Find the average magnitude of linear momentum of a helium molecule in a sample of helium gas at 0°C . Mass of a helium molecule $= 6.64 \times 10^{-27} \text{ kg}$ and Boltzmann constant $= 1.38 \times 10^{-23} \text{ J K}^{-1}$.
- The mean speed of the molecules of a hydrogen sample equals the mean speed of the molecules of a helium sample. Calculate the ratio of the temperature of the hydrogen sample to the temperature of the helium sample.
- At what temperature the mean speed of the molecules of hydrogen gas equals the escape speed from the earth ?

19. Find the ratio of the mean speed of hydrogen molecules to the mean speed of nitrogen molecules in a sample containing a mixture of the two gases.
20. Figure (24-E2) shows a vessel partitioned by a fixed diathermic separator. Different ideal gases are filled in the two parts. The rms speed of the molecules in the left part equals the mean speed of the molecules in the right part. Calculate the ratio of the mass of a molecule in the left part to the mass of a molecule in the right part.

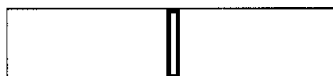


Figure 24-E2

21. Estimate the number of collisions per second suffered by a molecule in a sample of hydrogen at STP. The mean free path (average distance covered by a molecule between successive collisions) = 1.38×10^{-5} cm.
22. Hydrogen gas is contained in a closed vessel at 1 atm (100 kPa) and 300 K. (a) Calculate the mean speed of the molecules. (b) Suppose the molecules strike the wall with this speed making an average angle of 45° with it. How many molecules strike each square metre of the wall per second?
23. Air is pumped into an automobile tyre's tube up to a pressure of 200 kPa in the morning when the air temperature is 20°C . During the day the temperature rises to 40°C and the tube expands by 2%. Calculate the pressure of the air in the tube at this temperature.
24. Oxygen is filled in a closed metal jar of volume $1.0 \times 10^{-3} \text{ m}^3$ at a pressure of $1.5 \times 10^5 \text{ Pa}$ and temperature 400 K. The jar has a small leak in it. The atmospheric pressure is $1.0 \times 10^5 \text{ Pa}$ and the atmospheric temperature is 300 K. Find the mass of the gas that leaks out by the time the pressure and the temperature inside the jar equalise with the surrounding.
25. An air bubble of radius 2.0 mm is formed at the bottom of a 3.3 m deep river. Calculate the radius of the bubble as it comes to the surface. Atmospheric pressure = $1.0 \times 10^5 \text{ Pa}$ and density of water = 1000 kg m^{-3} .
26. Air is pumped into the tubes of a cycle rickshaw at a pressure of 2 atm. The volume of each tube at this pressure is 0.002 m^3 . One of the tubes gets punctured and the volume of the tube reduces to 0.0005 m^3 . How many moles of air have leaked out? Assume that the temperature remains constant at 300 K and that the air behaves as an ideal gas.
27. 0.040 g of He is kept in a closed container initially at 100.0°C . The container is now heated. Neglecting the expansion of the container, calculate the temperature at which the internal energy is increased by 12 J.
28. During an experiment, an ideal gas is found to obey an additional law $pV^2 = \text{constant}$. The gas is initially at a temperature T and volume V . Find the temperature when it expands to a volume $2V$.

29. A vessel contains 1.60 g of oxygen and 2.80 g of nitrogen. The temperature is maintained at 300 K and the volume of the vessel is 0.166 m^3 . Find the pressure of the mixture.
30. A vertical cylinder of height 100 cm contains air at a constant temperature. The top is closed by a frictionless light piston. The atmospheric pressure is equal to 75 cm of mercury. Mercury is slowly poured over the piston. Find the maximum height of the mercury column that can be put on the piston.
31. Figure (24-E3) shows two vessels A and B with rigid walls containing ideal gases. The pressure, temperature and the volume are p_A , T_A , V in the vessel A and p_B , T_B , V in the vessel B. The vessels are now connected through a small tube. Show that the pressure p and the temperature T satisfy

$$\frac{p}{T} = \frac{1}{2} \left(\frac{p_A}{T_A} + \frac{p_B}{T_B} \right)$$

when equilibrium is achieved.

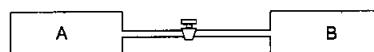


Figure 24-E3

32. A container of volume 50 cc contains air (mean molecular weight = 28.8 g) and is open to atmosphere where the pressure is 100 kPa. The container is kept in a bath containing melting ice (0°C). (a) Find the mass of the air in the container when thermal equilibrium is reached. (b) The container is now placed in another bath containing boiling water (100°C). Find the mass of air in the container. (c) The container is now closed and placed in the melting-ice bath. Find the pressure of the air when thermal equilibrium is reached.
33. A uniform tube closed at one end, contains a pellet of mercury 10 cm long. When the tube is kept vertically with the closed-end upward, the length of the air column trapped is 20 cm. Find the length of the air column trapped when the tube is inverted so that the closed-end goes down. Atmospheric pressure = 75 cm of mercury.
34. A glass tube, sealed at both ends, is 100 cm long. It lies horizontally with the middle 10 cm containing mercury. The two ends of the tube contain air at 27°C and at a pressure 76 cm of mercury. The air column on one side is maintained at 0°C and the other side is maintained at 127°C . Calculate the length of the air column on the cooler side. Neglect the changes in the volume of mercury and of the glass.
35. An ideal gas is trapped between a mercury column and the closed-end of a narrow vertical tube of uniform base containing the column. The upper end of the tube is open to the atmosphere. The atmospheric pressure equals 76 cm of mercury. The lengths of the mercury column and the trapped air column are 20 cm and 43 cm respectively. What will be the length of the air column when the tube is tilted slowly in a vertical plane through an angle of 60° ? Assume the temperature to remain constant.

36. Figure (24-E4) shows a cylindrical tube of length 30 cm which is partitioned by a tight-fitting separator. The separator is very weakly conducting and can freely slide along the tube. Ideal gases are filled in the two parts of the vessel. In the beginning, the temperatures in the parts A and B are 400 K and 100 K respectively. The separator slides to a momentary equilibrium position shown in the figure. Find the final equilibrium position of the separator, reached after a long time.

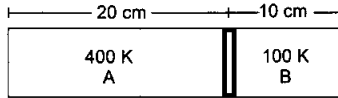


Figure 24-E4

37. A vessel of volume V_0 contains an ideal gas at pressure p_0 and temperature T . Gas is continuously pumped out of this vessel at a constant volume-rate $dV/dt = r$ keeping the temperature constant. The pressure of the gas being taken out equals the pressure inside the vessel. Find (a) the pressure of the gas as a function of time, (b) the time taken before half the original gas is pumped out.
38. One mole of an ideal gas undergoes a process

$$p = \frac{p_0}{1 + (V/V_0)^2}$$

where p_0 and V_0 are constants. Find the temperature of the gas when $V = V_0$.

39. Show that the internal energy of the air (treated as an ideal gas) contained in a room remains constant as the temperature changes between day and night. Assume that the atmospheric pressure around remains constant and the air in the room maintains this pressure by communicating with the surrounding through the windows, doors, etc.
40. Figure (24-E5) shows a cylindrical tube of radius 5 cm and length 20 cm. It is closed by a tight-fitting cork. The friction coefficient between the cork and the tube is 0.20. The tube contains an ideal gas at a pressure of 1 atm and a temperature of 300 K. The tube is slowly heated and it is found that the cork pops out when the temperature reaches 600 K. Let dN denote the magnitude of the normal contact force exerted by a small length dl of the cork along the periphery (see the figure). Assuming that the temperature of the gas is uniform at any instant, calculate $\frac{dN}{dl}$.

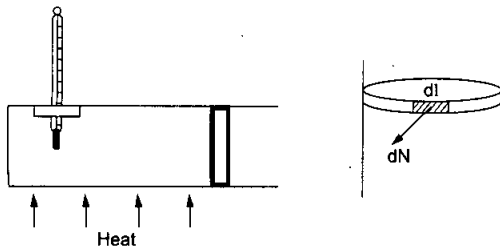


Figure 24-E5

41. Figure (24-E6) shows a cylindrical tube of cross-sectional area A fitted with two frictionless pistons. The pistons are connected to each other by a metallic wire. Initially,

the temperature of the gas is T_0 and its pressure is p_0 which equals the atmospheric pressure. (a) What is the tension in the wire? (b) What will be the tension if the temperature is increased to $2T_0$?

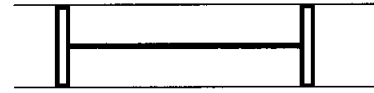


Figure 24-E6

42. Figure (24-E7) shows a large closed cylindrical tank containing water. Initially the air trapped above the water surface has a height h_0 and pressure $2p_0$ where p_0 is the atmospheric pressure. There is a hole in the wall of the tank at a depth h_1 below the top from which water comes out. A long vertical tube is connected as shown. (a) Find the height h_2 of the water in the long tube above the top initially. (b) Find the speed with which water comes out of the hole. (c) Find the height of the water in the long tube above the top when the water stops coming out of the hole.

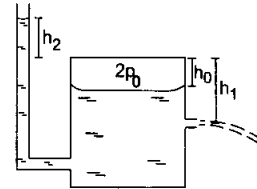


Figure 24-E7

43. An ideal gas is kept in a long cylindrical vessel fitted with a frictionless piston of cross-sectional area 10 cm^2 and weight 1 kg (figure 24-E8). The vessel itself is kept in a big chamber containing air at atmospheric pressure 100 kPa. The length of the gas column is 20 cm. If the chamber is now completely evacuated by an exhaust pump, what will be the length of the gas column? Assume the temperature to remain constant throughout the process.

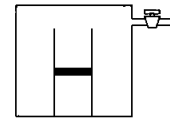


Figure 24-E8

44. An ideal gas is kept in a long cylindrical vessel fitted with a frictionless piston of cross-sectional area 10 cm^2 and weight 1 kg. The length of the gas column in the vessel is 20 cm. The atmospheric pressure is 100 kPa. The vessel is now taken into a spaceship revolving round the earth as a satellite. The air pressure in the spaceship is maintained at 100 kPa. Find the length of the gas column in the cylinder.
45. Two glass bulbs of equal volume are connected by a narrow tube and are filled with a gas at 0°C at a pressure of 76 cm of mercury. One of the bulbs is then placed in melting ice and the other is placed in a water bath maintained at 62°C . What is the new value of the

pressure inside the bulbs? The volume of the connecting tube is negligible.

46. The weather report reads, "Temperature 20°C : Relative humidity 100%". What is the dew point?
47. The condition of air in a closed room is described as follows. Temperature = 25°C , relative humidity = 60%, pressure = 104 kPa. If all the water vapour is removed from the room without changing the temperature, what will be the new pressure? The saturation vapour pressure at 25°C = 3.2 kPa.
48. The temperature and the dew point in an open room are 20°C and 10°C . If the room temperature drops to 15°C , what will be the new dew point?
49. Pure water vapour is trapped in a vessel of volume 10 cm^3 . The relative humidity is 40%. The vapour is compressed slowly and isothermally. Find the volume of the vapour at which it will start condensing.
50. A barometer tube is 80 cm long (above the mercury reservoir). It reads 76 cm on a particular day. A small amount of water is introduced in the tube and the reading drops to 75.4 cm. Find the relative humidity in the space above the mercury column if the saturation vapour pressure at the room temperature is 1.0 cm.
51. Using figure (24.6) of the text, find the boiling point of methyl alcohol at 1 atm (760 mm of mercury) and at 0.5 atm.
52. The human body has an average temperature of 98°F . Assume that the vapour pressure of the blood in the veins behaves like that of pure water. Find the minimum atmospheric pressure which is necessary to prevent the blood from boiling. Use figure (24.6) of the text for the vapour pressures.
53. A glass contains some water at room temperature 20°C . Refrigerated water is added to it slowly. When the temperature of the glass reaches 10°C , small droplets condense on the outer surface. Calculate the relative humidity in the room. The boiling point of water at a pressure of 17.5 mm of mercury is 20°C and at 8.9 mm of mercury it is 10°C .
54. 50 m^3 of saturated vapour is cooled down from 30°C to 20°C . Find the mass of the water condensed. The absolute humidity of saturated water vapour is 30 g m^{-3} at 30°C and 16 g m^{-3} at 20°C .
55. A barometer correctly reads the atmospheric pressure as 76 cm of mercury. Water droplets are slowly introduced into the barometer tube by a dropper. The height of the mercury column first decreases and then becomes constant. If the saturation vapour pressure at the atmospheric temperature is 0.80 cm of mercury, find the height of the mercury column when it reaches its minimum value.
56. 50 cc of oxygen is collected in an inverted gas jar over water. The atmospheric pressure is 99.4 kPa and the room temperature is 27°C . The water level in the jar is same as the level outside. The saturation vapour pressure at 27°C is 3.4 kPa. Calculate the number of moles of oxygen collected in the jar.
57. A faulty barometer contains certain amount of air and saturated water vapour. It reads 74.0 cm when the atmospheric pressure is 76.0 cm of mercury and reads 72.10 cm when the atmospheric pressure is 74.0 cm of mercury. Saturation vapour pressure at the air temperature = 1.0 cm of mercury. Find the length of the barometer tube above the mercury level in the reservoir.
58. On a winter day, the outside temperature is 0°C and relative humidity 40%. The air from outside comes into a room and is heated to 20°C . What is the relative humidity in the room? The saturation vapour pressure at 0°C is 4.6 mm of mercury and at 20°C it is 18 mm of mercury.
59. The temperature and humidity of air are 27°C and 50% on a particular day. Calculate the amount of vapour that should be added to 1 cubic metre of air to saturate it. The saturation vapour pressure at 27°C = 3600 Pa.
60. The temperature and relative humidity in a room are 300 K and 20% respectively. The volume of the room is 50 m^3 . The saturation vapour pressure at 300 K is 3.3 kPa. Calculate the mass of the water vapour present in the room.
61. The temperature and the relative humidity are 300 K and 20% in a room of volume 50 m^3 . The floor is washed with water, 500 g of water sticking on the floor. Assuming no communication with the surrounding, find the relative humidity when the floor dries. The changes in temperature and pressure may be neglected. Saturation vapour pressure at 300 K = 3.3 kPa.
62. A bucket full of water is placed in a room at 15°C with initial relative humidity 40%. The volume of the room is 50 m^3 . (a) How much water will evaporate? (b) If the room temperature is increased by 5°C , how much more water will evaporate? The saturation vapour pressure of water at 15°C and 20°C are 1.6 kPa and 2.4 kPa respectively.

□

ANSWERS

OBJECTIVE I

- | | | | | | |
|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (b) | 3. (a) | 4. (d) | 5. (a) | 6. (a) |
| 7. (c) | 8. (c) | 9. (b) | 10. (a) | 11. (c) | 12. (d) |
| 13. (c) | 14. (b) | 15. (a) | 16. (d) | 17. (a) | |

OBJECTIVE II

- | | | |
|-------------|--------|-------------|
| 1. (c), (d) | 2. (b) | 3. (b) |
| 4. (c) | 5. (d) | 6. (a), (c) |
| 7. (d) | | |

EXERCISES

1. $2.24 \times 10^{-2} \text{ m}^3$
2. 2.685×10^{19}
3. 3.53×10^{11}
4. 1.43 mg
5. 1 : 1
6. 8.0×10^{15}
7. 375 K
8. $1.24 \times 10^5 \text{ Pa}$
9. 28.3 g mol^{-1}
10. 0.987
11. 3 : 1
12. 1930 m s^{-1} , 1200 K
13. 1300 m s^{-1}
14. 310 K
15. 8.0 hour
16. $8.0 \times 10^{-24} \text{ kg m s}^{-1}$
17. 1 : 2
18. 11800 K
19. 3.74
20. 1.18
21. 1.23×10^{10}
22. (a) 1780 m s^{-1} (b) 1.2×10^{28}
23. 209 kPa
24. 0.16 g
25. 2.2 mm
26. 0.14
27. 196°C
28. $T/2$
29. 2250 N m^{-2}
30. 25 cm
32. (a) 0.058 g (b) 0.0468 g (c) 73.0 kPa
33. 15 cm
34. 36.5 cm
35. 48 cm
36. 10 cm from the left end
37. (a) $p = p_0 e^{-\eta/V_0}$ (b) $\frac{V_0 \ln 2}{\gamma}$
38. $\frac{p_0 V_0}{2R} \text{ mol}^{-1}$
40. $1.25 \times 10^4 \text{ N m}^{-1}$
41. (a) zero (b) $p_0 A$
42. (a) $\frac{p_0}{\rho g} - h_0$ (b) $\left[\frac{2}{\rho} (p_0 + \rho g (h_1 - h_0)) \right]^{1/2}$
(c) $-h_1$
43. 2.2 m
44. 22 cm
45. 84 cm of mercury
46. 20°C
47. 102 kPa
48. 10°C
49. 4.0 cm^3
50. 60%
51. 65°C , 48°C
52. 50 mm of mercury
53. 51%
54. 700 g
55. 75.2 cm
56. 1.93×10^{-3}
57. 91.1 cm
58. 9.5%
59. 13 g
60. 238 g
61. 62%
62. (a) 361 g (b) 296 g

□