## 16

## Osmosis and Osmotic Pressure

## C H A P TER

CONTENTS

WHAT IS OSMOSIS?
The Egg Experiment
Silica Garden
SEMIPERMEABLE MEMBRANES
Preparation of Cupric ferrocyanide membrane
OSMOTIC PRESSURE
Pfeffer's Method
Berkeley and Hartley's Method
A Modern Osmometer
ISOTONIC SOLUTIONS
THEORIES OF OSMOSIS
Molecular Sieve Theory
Membrane Solution Theory
Vapour Pressure Theory
Membrane Bombardment Theory
REVERSE OSMOSIS
Desalination of Sea Water
LAWS OF OSMOTIC PRESSURE
Boyle-van't Hoff Law for Solutions
Charles'-van't Hoff Law for Solutions
Van't Hoff Equation for Solutions
Avogadro-van't Hoff Law for Solutions
VAN'T HOFF THEORY OF DILUTE SOLUTIONS
CALCULATION OF OSMOTIC PRESSURE
DETERMINATION OF MOLECULAR WEIGHT
RELATION BETWEEN VAPOUR PRESSURE AND OSMOTIC PRESSURE
OSMOTIC PRESSURE OF ELECTROLYTES


## DIFFUSION AND OSMOSIS

Just as a gas can diffuse into vacant space or another gas, a solute can diffuse from a solution into the pure solvent. If you pour a saturated aqueous solution of potassium permanganate with the help of a thistle funnel into a beaker containing water, it forms a separate layer at the bottom. After some time, you will see the permanganate actually diffusing up into water. This continues until a homogeneous solution is obtained.

The diffusion of solute into solvent is, in fact, a bilateral process. It consists of: (1) the solute molecules moving up into solvent; and (2) the solvent molecules moving down into solution. This intermingling of solute and solvent molecules goes on, so that ultimately a solution of uniform concentration results.

It is the tendency to equalise concentration in all parts of the solution which is responsible for the diffusion of the solute.

Thus diffusion of solute will also take place when two solutions of unequal concentrations are in contact. Solvent molecules will pass from the dilute to the concentrated solution and solute molecules will pass from the concentrated to the dilute solution until equality of concentration is achieved.


Figure 16.1
(a) Diffusion consists of solute molecules moving upward into the solvent and solvent molecules moving down into concentrated solution;
(b) Osmosis consists of solvent molecules passing through the semipermeable membrane, while large solute particles are held up.

## WHAT IS OSMOSIS?

Let us consider a pure solvent and solution separated by a membrane which permits the passage to solvent molecules but not to solute molecules. Only the solvent will diffuse through the membrane into solution. A membrane which is permeable to solvent and not to solute, is called a semipermeable membrane.


Figure 16.2
Illustration of the process of osmosis. The solvent molecules can pass through the membrane from either side of the semipermeable membrane. There is a net flow of solvent from the dilute solution to the concentrated solution. It shows up in the rise of level in the concentrated solution compartment.
The flow of the solvent through a semipermeable membrane from pure solvent to solution, or from a dilute solution to concentrated solution, is termed Osmosis (Greek Osmos $=$ to push).

It must be clearly understood that the diffusion of solvent molecules through a semipermeable membrane is taking place in both directions. That is, solvent molecules are passing from solvent to
solution, and also from solution to solvent. But since the diffusion from solvent to solution or from dilute to concentrated solution, is more rapid, the net flow of the solvent is from low to high concentration.


Figure 16.3
Demonstration of Osmosis.
The phenomenon of osmosis can be demonstrated by fastening a piece of animal bladder or cellophane over a thistle funnel as shown in Fig. 16.3. A concentrated aqueous sugar solution is placed inside the thistle funnel which is then immersed in water. The osmosis takes place through the semipermeable membrane from water to the sugar solution. The flow of water into the funnel shows up as the solution is seen rising in the tube remarkably.

## SOME INTERESTING EXPERIMENTS DEMONSTRATING OSMOSIS

Many natural membranes are semipermeable e.g., pig's bladder, skin around white of an egg, membrane around the red blood corpuscle, and the membrane in the cell of the plant. Some interesting experiments demonstrating osmosis are listed below.

## (1) Silica Garden

Crystals of many salts e.g., ferrous sulphate, nickel chloride, cobalt nitrate and ferric chloride are placed in a solution of glass material (sodium silicate). The layers of metallic silicates formed on the surface of crystals by double decomposition are semipermeable. The water from outside enters through these membranes which burst and form what we call a Silica Garden.

## (2) The Egg Experiment

The outer hard shell of two eggs of the same size is removed by dissolving in dilute hydrochloric acid. One of these is placed in distilled water and the other in saturated


Figure 16.4 Silica garden.
salt solution. After a few hours it will be noticed that the egg placed in water swells and the one in salt solution shrinks. In the first case, water diffuses through the skin (a semipermeable membrane) into the egg material which swells. In the second case, the concentration of the salt solution being higher than the egg material, the egg shrinks.


Figure 16.5
Demonstration of osmosis by the Egg experiment. (a) Egg structure; (b) egg without the shell; (c) egg swells in water (d) egg shrinks in salt solution.

## SEMIPERMEABLE MEMBRANES

Animal and vegetable membranes are not completely semipermeable. Cupric ferrocyanide, $\mathrm{Cu}_{2} \mathrm{Fe}(\mathrm{CN})_{6}$, membrane deposited in the walls of a porous pot is perfectly semipermeable and is used for accurate experimental work. All semipermeable membranes have fine holes or capillaries in their structure. These allow passage to solvent molecules but not to larger solute molecules.


Figure 16.6
Some examples of semipermeable membranes.

## Preparation of Cupric Ferrocyanide Membrane

An unglazed porcelain battery pot filled with copper sulphate solution is placed in a solution of potassium ferrocyanide, $\mathrm{K}_{4} \mathrm{Fe}(\mathrm{CN})_{6}$. The two solutions permeate into porous walls of the pot from opposite sides. A gelatinous precipitate of cupric ferrocyanide is formed in the middle of the pores of the walls.

$$
2 \mathrm{Cu}^{2+}+\mathrm{Fe}(\mathrm{CN})_{6}^{4-} \longrightarrow \mathrm{Cu}_{2} \mathrm{Fe}(\mathrm{CN})_{6} \downarrow
$$

The electrical method which gives a more compact and stout membrane in a short time is shown in Fig. 16.8. The resistance of the cell rises as the membrane is completely formed and the bell rings no more.


Figure 16.7
Preparation of semipermeable membrane.


Figure 16.8
Electrical deposition of semipermeable membrane.

## WHAT IS OSMOTIC PRESSURE?

A porous pot with cupric ferrocyanide membrane deposited in its walls is fitted with a rubber stopper having a long glass tube (Fig. 16.9). It is filled with concentrated aqueous sugar solution and immersed in distilled water. The osmosis of water through the membrane from water to the sugar solution takes place. As a result, the solution level in the long tube rises over a period of time. After a few days the level attains a definite maximum value. This marks the stage when the hydrostatic pressure set up due to the column of sugar solution counterbalances the flow of pure water (or osmosis) into the solution.


Figure 16.9
Hydrostatic pressure necessary to stop osmosis is equal to osmotic pressure.


Figure 16.10
The external pressure applied on solution to stop osmosis is equal to osmotic pressure.

The hydrostatic pressure built up on the solution which just stops the osmosis of pure solvent into the solution through a semipermeable membrane, is called Osmotic Pressure.

Osmosis can be counteracted not only by hydrostatic pressure but also by application of external pressure on the solution. The external pressure may be adjusted so as to prevent the osmosis of pure water into solution. This provides another definition of osmotic pressure.

Osmotic pressure may be defined as the external pressure applied to the solution in order to stop the osmosis of solvent into solution separated by a semipermeable membrane.

This definition can be illustrated by means of the apparatus shown in Fig. 16.10. The external pressure on the solution is applied with the help of the piston and the progress of osmosis is shown by the movement of the liquid in the flow indicator. The pressure required just to arrest the movement of the liquid level in the flow indicator, is equal to the osmotic pressure of the solution.

## KIDNEY DIALYSIS



A hospital patient whose kidneys have ceased to function receives dialysis. In this process, the patient's blood is pumped through a dialysis machine, where it is filtered to remove waste products, then returned to the patient's body through a vein.


Scheme of semipermeable membrane during kidney dialysis, where red is blood, blue is the dialysing fluid, and yellow is the membrane.

Kidney Dialysis, also known as hemodialysis, is a medical treatment used to remove waste materials from the blood of patients lacking renal function. Blood from an artery is pumped through a dialyzer, or artificial kidney, where it flows past a semipermeable membrane. Dialysis fluid passing on the other side of the membrane removes unwanted elements in the blood by diffusion. The blood is then returned to the body through a vein.

## DETERMINATION OF OSMOTIC PRESSURE

The osmotic pressure of a given solution can be determined experimentally by the methods detailed below. The apparatus used for the purpose is often referred to as osmometer.
(1) Pfeffer's Method

The apparatus used by Pfeffer (1877) for determination of osmotic pressure is shown in Fig. 16.11. It consists of a porous pot with copper ferrocyanide membrane deposited in its walls and having a
glass top cemented to it. The glass top has an open tube and a closed mercury manometer in the side.
The apparatus is filled with a solution under examination through the tube which is then sealed off. The pot is now placed in pure water maintained at constant temperature. The water passes across the membrane into the solution and develops a pressure on the manometer. The highest pressure registered by the manometer gives the osmotic pressure of the solution. The Pfeffer's method suffers from two disadvantages :
(a) It is slow and it takes a few days before the highest pressure is reached.
(b) It cannot be used for measuring high osmotic pressures as the ferrocyanide membrane being weak ruptures.

Morse and Frazer (1910) used essentially the same method but deposited the copper ferrocyanide membrane electrolytically. The membrane so produced being more stout, they were able to measure osmotic pressures up to about 300 atmospheres.


■ Figure 16.11
Pfeffer's apparatus for measuring osmotic pressure.

## (2) Berkeley and Hartley's Method

Berkeley and Hartley (1904-1909) employed the technique of applying external pressure on the solution just enough to prevent osmosis. The osmometer used by them is illustrated in Fig. 16.12. A porcelain tube with copper ferrocyanide membrane deposited in its walls is enclosed in a metallic jacket. The tube is fitted with a reservoir of pure solvent (water) at one end and a capillary tube at the other. Mechanical pressure can be applied on the solution with a piston connected to a pressure gauge.

Procedure. The inner porcelain tube is filled with pure solvent and the jacket with the solution whose osmotic pressure is to be determined. The level of the solvent meniscus in the capillary tube will tend to move down as solvent flows into the solution across the membrane. Pressure is then applied through the piston so that the meniscus becomes stationary. It indicates that osmosis has been stopped and now the pressure recorded by the pressure gauge gives the osmotic pressure of the solution.


■ Figure 16.12
Berkeley and Hartley's osmometer.
This method is superior to the older method of pfeffer in as much as :
(a) It is quick and accurate.
(b) It can be used for determining high osmotic pressures. The osmotic pressure being balanced by the external pressure, there is no strain left on the membrane and the danger of its bursting is eliminated.
(3) AModern Osmometer

A modern apparatus for the determination of osmotic pressure is shown in Fig. 16.13.


Figure 16.13
Stainless steel cell of a modern osmometer.
It consists of a stainless steel cell with a rigid fixed semipermeable membrane. The membrane divides the cell into solute and solvent compartments. A flexible diaphragm is fixed in the solvent compartment.

When the solution and the solvent compartments are filled and the taps closed, osmosis occurs. The solvent flows into the solution across the semipermeable membrane. This reduces the pressure in the solvent compartment, causing the diaphragm to distort. Eventually the pressure becomes low enough to stop the occurrence of osmosis. The degree of diaphragm distortion is related to the osmotic pressure of the solution. The diaphragm distortion is measured by a device called strain gauge. The strain gauge provides an electric current that is proportional to the extent of distortion. The gauge is calibrated to give osmotic pressure directly.

## ISOTONIC SOLUTIONS

When two solutions are separated by a semipermeable membrane and there is no flow of water across the membrane, the solutions are said to be Isotonic. If the membrane is completely semipermeable, isotonic solutions are also iso-osmotic i.e., have the same osmotic pressure since osmotic pressure depends on the number of molecules. The isotonic solutions have equimolar concentrations.


Figure 16.14
Osmotic effects in the red blood cells.
Of the two solutions separated by a semipermeable membrane if one is of lower osmotic pressure, it is said to be hypotonic relative to the second solution. If it has a higher osmotic pressure than the second solution, it is said to be hypertonic relative to the second solution. Thus when red blood cells are placed in distilled water (hypotonic medium), water flows into the cells and they swell or burst. If, on the other hand, they are placed in $5 \% \mathrm{NaCl}$ solution (hypertonic medium), water comes out of the cells and they shrink. A 0.16 M sodium chloride solution ( $0.95 \%$ ) is isotonic with blood cells and they neither swell nor shrink as no osmosis takes place. However, since the membrane of the cells is not completely semipermeable and is leaky, the medium outside the cell and the inner fluid, although isotonic, is not necessarily iso-osmotic.

## THEORIES OF OSMOSIS

Several theories have been advanced to explain the action of a semipermeable membrane. It is probable that the mechanism depends on the particular type of membrane used and also on the nature of the solute and solvent. Some of the more important theories of osmosis across a membrane are outlined below :

## (1) The Molecular Sieve Theory

According to this theory, the membrane contains lots of fine pores and acts as a sort of 'molecular sieve'. Smaller solvent molecules can pass through the pores but the larger molecules cannot. Solvent molecules flow from a region of higher solute concentration to one of lower concentration across such a membrane. But since some membranes can act as sieves even though the solute molecules are smaller than the solvent molecules, this theory remains in doubt.


Figure 16.15
A semipermeable membrane can separate particles on the basis of size. It allows the passage of small $\mathrm{H}_{2} \mathrm{O}$ molecules in both directions. But it prevents the passage of glucose molecules which are larger than water molecules. (IIlustration of Sieve theory)
Recently it has been shown that the pores or capillaries between the protein molecules constituting an animal membrane are lined with polar groups ( $-\mathrm{COO}^{-},-\mathrm{NH}_{3}^{+},-\mathrm{S}^{2-}$, etc.). Therefore, the membrane acts not simply as a sieve but also regulates the passage of solute molecules by electrostatic or 'chemical interactions'. In this way even solute molecules smaller than solvent molecules can be held back by the membrane.
(2) Membrane Solution Theory

Membrane proteins bearing functional groups such as $-\mathrm{COOH},-\mathrm{OH},-\mathrm{NH}_{2}$, etc., dissolve water molecules by hydrogen bonding or chemical interaction. Thus membrane dissolves water from the pure water (solvent) forming what may be called 'membrane solution'. The dissolved water flows into the solution across the membrane in a bid to equalise concentrations. In this way water molecules pass through the membrane while solute molecules being insoluble in the membrane do not.
(3) Vapour Pressure Theory

It suggests that a semipermeable membrane has many fine holes or capillaries. The walls of these capillaries are not wetted by water (solvent) or solution.


Figure 16.16
Water vapours diffuse into solution across the gas in a capillary of the membrane.

Thus neither solution nor water can enter the capillaries. Therefore each capillary will have in it solution at one end and water at the other, separated by a small gap. Since the vapour pressure of a solution is lower than that of the pure solvent, the diffusion of vapour will occur across the gap from water side to solution side. This will result in the transfer of water into the solution. The vapour theory offers a satisfactory explanation of the mechanism of osmosis in most cases.
(4) Membrane Bombardment Theory

This theory suggests that osmosis results from an unequal bombardment pressure caused by solvent molecules on the two sides of the semipermeable membrane. On one side we have only solvent molecules while on the other side there are solute molecules occupying some of the surface area. Thus there are fewer bombardments per unit area of surface on the solution side than on the solvent side. Hence the solvent molecules will diffuse more slowly through the membrane on the solution side than on the solvent side. The net result causes a flow of the solvent from the pure solvent to the solution across the membrane.

## REVERSE OSMOSIS

When a solution is separated from pure water by a semipermeable membrane, osmosis of water occurs from water to solution. This osmosis can be stopped by applying pressure equal to osmotic pressure, on the solution. If pressure greater than osmotic pressure is applied, osmosis is made to proceed in the reverse direction to ordinary osmosis i.e., from solution to water.


Normal osmosis


Reverse osmosis

Figure 16.17
Reverse osmosis versus ordinary osmosis.
The osmosis taking place from solution to pure water by application of pressure greater than osmotic pressure, on the solution, is termed Reverse Osmosis.
Desalination of Sea Water by Hollow-fibre Reverse Osmosis
Reverse osmosis is used for the desalination of sea water for getting fresh drinking water. This is done with the help of hollow fibres (nylon or cellulose acetate) whose wall acts as semipermeable membrane. A hollow-fibre reverse osmosis unit is shown in Fig. 16.18.


Figure 16.18
Desalination of sea water by reverse osmosis in a hollow fibre unit.

## NANOTUBE MEMBRANES

## Nanotube Membranes Offer Possibility of Cheaper Desalination

A nanotube membrane on a silicon chip the size of a rupee coin may offer a cheaper way to remove salt from water.

Researchers at Lawrence Livermore National Laboratory (USA) have created a membrane made of carbon nanotubes and silicon that may offer, among many possible applications, a less expensive desalinization.

The nanotubes, special molecules made of carbon atoms in a unique arrangement, are hollow and more than 50,000 times thinner than a human hair. Billions of these tubes act as the pores in the membrane.


Molecules flowing through a carbon nanotube less than two nanometers in diameter. The super smooth inside of the nanotubes allow liquids and gases to rapidly flow through, while the tiny pore size can block larger molecules. This previously unobserved phenomenon opens a vast array of possible applications.

Membranes that have carbon nanotubes as pores could be used in desalination. Salt removal from water, commonly performed through reverse osmosis, uses less permeable membranes, requires large amounts of pressure and is quite expensive. However, these more permeable nanotube membranes could reduce the energy costs of desalination by up to 75 percent compared to conventional membranes used in reverse osmosis.

Water is introduced under pressure around the hollow fibres. The fresh water is obtained from the inside of the fibre. In actual practice, each unit contains more than three million fibres bundled together, each fibre is of about the diameter of a human hair.

## LAWS OF OSMOTIC PRESSURE

From a study of the experimental results obtained by Pfeffer, van't Hoff showed that for dilute solutions :
(a) The osmotic pressure of a solution at a given temperature is directly proportional to its concentration.
(b) The osmotic pressure of a solution of a given concentration is directly proportional to the absolute temperature.
From the above findings, van't Hoff (1877) established the laws of osmotic pressure and pointed out that these were closely related to the gas laws.

## (1) Boyle-van't Hoff Law for Solutions

If $\pi$ is the osmotic pressure and $C$ its concentration, from ( $a$ ) we can write $\pi \propto C$, if temperature is constant.

If the concentration of the solute is expressed in moles per litre and $V$ is the volume of the solution that contains 1 mol of solute,

Thus

$$
\begin{aligned}
& C=\frac{1}{V} \\
& \pi \propto \frac{1}{V} \text { at constant temperature }
\end{aligned}
$$

This relationship is similar to the Boyle's law for gases and is known as the Boyle-van't Hoff law for solutions.
(2) Charles-van't Hoff Law for Solutions

If T is the absolute temperature, from the statement $(b)$, we can write

$$
\pi \propto T \text {, if temperature is constant }
$$

This relationship is similar to the Charles'Law for gases and is known as Charles-van't Hoff law for solutions.
(3) Van't Hoff Equation for Solutions

As shown above the osmotic pressure $(\pi)$ of a dilute solution is inversely proportional to the volume $(V)$ containing 1 mole of the solute and is directly proportional to the absolute temperature $(T)$. This is,

$$
\begin{align*}
\pi & \propto \frac{1}{V}  \tag{1}\\
\pi & \propto T \tag{2}
\end{align*}
$$

Combining (1) and (2) van't Hoff gave the general relationship

$$
\begin{equation*}
\pi V=R^{\prime} T \tag{3}
\end{equation*}
$$

where $R^{\prime}$ is a constant. He showed that this equation was parallel to the general Gas Equation ( $P V=R T$ ), as the value of $R^{\prime}$ calculated from the experimental values of $\pi$, $V$, and $T$ came out to be almost the same as of the Gas constant, $R$.

It is noteworthy that the van't Hoff Equation (3) was derived for 1 mole of solute dissolved in $V$ litres. If $n$ moles of solute are dissolved in $V$ litres of solution, this equation assumes the form

$$
\pi V=n R T
$$

SOLVED PROBLEM 1. A solution of cane-sugar (mol mass $=342$ ) containing 34.2 g litre ${ }^{-1}$ has an osmotic pressure of 2.4 atm at $20^{\circ} \mathrm{C}$. Calculate the value of $R$ in litre-atmospheres.

SOLUTION
From van’t Hoff equation

$$
\begin{equation*}
R=\frac{\pi V}{T} \tag{1}
\end{equation*}
$$

where $\pi=$ osmotic pressure, $V=$ volume of solution in litres containing 1 mole of solute, $T=$ absolute temperature.

In the present case,

$$
\begin{aligned}
\pi & =2.4 \mathrm{~atm} \\
V & =\frac{1}{34.2} \times 342=10 \text { litres } \\
T & =20+273=293 \mathrm{~K}
\end{aligned}
$$

Substituting the values in the expression (1),

$$
R=\frac{2.4 \times 10}{293}=\mathbf{0 . 0 8 1 9} \text { litre }- \text { atmosphere } K^{-\mathbf{1}} \mathrm{mol}^{-\mathbf{1}}
$$

SOLVED PROBLEM 2. Experiment shows that 10 g of cane sugar (mol mass $=342$ ) in $1 \times 10^{-3} \mathrm{~m}^{3}$ of solution produces an osmotic pressure of $6.68 \times 10^{4} \mathrm{~N} \mathrm{~m}^{-2}$ at 273 K . Calculate the value of $R$ in $S I$ units.

SOLUTION

$$
R=\frac{\pi V}{T}
$$

...van't Hoff equation
In this case,

$$
\begin{aligned}
& \pi=6.68 \times 10^{4} \mathrm{~N} \mathrm{~m}^{-2} \\
& V=\frac{1 \times 10^{-3} \times 342}{10}=3.42 \times 10^{-2} \mathrm{~m}^{3}
\end{aligned}
$$

Substituting the values in van't Hofff equation,

$$
\begin{aligned}
R & =\frac{6.68 \times 10^{4} \times 3.42 \times 10^{-2}}{273} \\
& =\mathbf{8 . 3 6} \mathbf{~ J ~ m o l}^{-1} \mathbf{K}^{\mathbf{1}}
\end{aligned}
$$

(4) Avogadro-van't Hoff Law for Solutions

Writing Van't Hoff equation for two different dilute solutions,

$$
\begin{align*}
& \pi_{1} V_{1}=n_{1} R T_{1}  \tag{1}\\
& \pi_{2} V_{2}=n_{2} R T_{2} \tag{2}
\end{align*}
$$

where $n_{1}$ and $n_{2}$ are the number of moles (molecules) of the solute in $V_{1}$ and $V_{2}$ litres of the two solutions.

If $\pi_{1}=\pi_{2}$ and $T_{1}=T_{2}$, it follows from (1) and (2) that

$$
\frac{n_{1}}{V_{1}}=\frac{n_{2}}{V_{2}}
$$

Hence when osmotic pressure and temperature are the same, equal volumes of solutions would contain equal number of moles (molecules) of the solute. This relationship is analogous to Avogadro's law of gases and is referred to as Avogadro-van't Hoff law for solutions. Alternatively, this law may be stated as:

Isotonic solutions at the same temperature have equimolar concentrations.

## VAN'T HOFF THEORY OF DILUTE SOLUTIONS

Van't Hoff noted the striking resemblance between the behaviour of dilute solutions and gases. Dilute solutions obeyed laws analogous to the gas laws. To explain it van't Hoff visualised that gases consist of molecules moving in vacant space (or vacuum), while in solutions the solute particles are moving in the solvent. The exact parallelism between solutions and gases is illustrated by experimental demonstration shown in Fig. 16.19.

As shown in Fig. 16.19(a), the pure solvent flows into the solution by osmosis across the semipermeable membrane. The solute molecules striking the membrane cause osmotic pressure and the sliding membrane is moved towards the solvent chamber. In case of a gas (Fig. 16.19b), the gas molecules strike the piston and produce pressure that pushes it towards the empty chamber. Here it is the vacuum which moves into the gas. This demonstrates clearly that there is close similarity between a gas and a dilute solution.

Thinking on these lines, van't Hoff propounded his theory of dilute solution. The van't Hoff theory of dilute solutions states that : a substance in solution behaves exactly like a gas and the osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature occupying the same volume as the solution.

(a)


Figure 16.19
(b)

The analogy between osmotic pressure and gas pressure.
Suppose a dilute sugar solution to be contained in an exactly full, covered beaker. Then suppose the water to vanish, leaving the sugar molecules suspended in otherwise empty space. The sugar would then function as a gas, exerting pressure equal to its former osmotic pressure.

According to the van't Hoff theory of dilute solutions, all laws or relationship obeyed by gases would be applicable to dilute solutions.

From van't Hoff theory it follows that just as 1 mole of a gas occupying 22.4 litres at $0^{\circ} \mathrm{C}$ exerts 1 atmosphere pressure, so, $\mathbf{1}$ mole of any solute dissolved in 22.4 litres would exert $\mathbf{1}$ atmosphere osmotic pressure.


Osmotic pressure = of solution

Pressure of solute if it were gas

Figure 16.20
Illustration of van't Hoff theory of dilute solutions.
van't Hoff theory holds only for dilute solutions and if there is no dissociation or association of the solute molecules.

## CALCULATION OF OSMOTIC PRESSURE

As shown above, all gas laws may be considered to apply to dilute solutions rigidly. This gives an easy solution to problems on osmotic pressure.

SOLVED PROBLEM 1. Calculate the osmotic pressure of a $5 \%$ solution of glucose ( $\mathrm{mol} \mathrm{wt}=180$ )
at $18^{\circ} \mathrm{C}$.
SOLUTION $\quad \pi V=n R T \quad$...van't Hoff Equation where $\pi=$ osmotic pressure in atmospheres; $V=$ volume in litres; $n=$ number of moles of solute ( $w / M$ ), $w$ being the weight in grams and $M$ its molecular weight; $R=$ gas constant.

In this case :

$$
\begin{aligned}
\pi & =? \\
V & =100 \mathrm{ml}=\frac{1}{10} \text { litre } \\
n & =\frac{5}{M}=\frac{5}{180} \\
R & =0.0821 \text { litre-atmosphere } \mathrm{deg}^{-1} \mathrm{~mole}^{-1} \\
T & =273+18=291 \mathrm{~K}
\end{aligned}
$$

Substituting the values in van't Hoff Equation

$$
\begin{aligned}
\pi \times \frac{1}{10} & =\frac{5}{180} \times 0.0821 \times 291 \\
\pi & =6.64 \mathrm{~atm}
\end{aligned}
$$

SOLVED PROBLEM 2. Find the osmotic pressure in millimetres of mercury at $15^{\circ} \mathrm{C}$ of a solution of naphthalene $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right)$ in benzene containing 14 g of naphthalene per litre of solution.

SOLUTION

$$
\pi V=n R T
$$

...vant Hoff equation
Here,

$$
\pi=\text { ? atmosphere }
$$

$$
V=1 \text { litre }
$$

$$
n=\frac{14}{128}(\text { mol mass of naphthalene }=128)
$$

$$
R=0.0821 \text { litre-atmosphere } K^{-1} \mathrm{~mol}^{-1}
$$

$$
T=15+273=288 \mathrm{~K}
$$

Substituting values in van't Hoff equation,

$$
\begin{aligned}
\pi \times 1 & =\frac{14}{128} \times 0.0821 \times 288 \\
\pi & =2.586 \mathrm{~atm} \\
& =2.586 \times 760=\mathbf{1 9 6 5} \mathbf{~ m m}
\end{aligned}
$$

SOLVED PROBLEM 3. Calculate the osmotic pressure of solution obtained by mixing (a) 100 ml of 3.4 per cent solution of urea (mol mass $=60$ ) and $(b) 100 \mathrm{ml}$ of 1.6 per cent solution of cane sugar (mol mass $=342$ ) at $20^{\circ} \mathrm{C}$.

SOLUTION
Osmotic pressure of urea

$$
\pi V=n R T
$$

$$
\begin{aligned}
\pi & =? \text { atmosphere } \\
V & \left.=\frac{200}{1000} \text { litres (After mixing total vol }=200 \mathrm{ml}\right) \\
n & =\frac{3.4}{60} \\
R & =0.0821 \text { litre-atmosphere } \\
T & =20+273=293 \mathrm{~K}
\end{aligned}
$$

Substituting values in van't Hoff equation

$$
\begin{aligned}
\pi \times \frac{200}{1000} & =\frac{3.4}{60} \times 0.0821 \times 293 \\
\pi & =\mathbf{6 . 8 1} \mathbf{~ a t m}
\end{aligned}
$$

where
Osmotic pressure of cane sugar

$$
\begin{aligned}
\pi V & =n R T \\
V & =\frac{200}{1000} \text { litres } \\
n & =\frac{1.6}{342} \\
R & =0.0821 \\
T & =20+273=293 \mathrm{~K}
\end{aligned}
$$

Substituting values

$$
\begin{aligned}
\pi \times \frac{200}{1000} & =\frac{1.6}{342} \times 0.0821 \times 293 \\
\pi & =0.56 \mathrm{~atm}
\end{aligned}
$$

whence
According to the van't Hoff theory of dilute solutions, dissolved substances behave like gases. Thus they obey Dalton's Law of Partial Pressures. Hence the total osmotic pressure of the mixture

$$
=6.81+0.56=7.37 \mathrm{~atm}
$$

## DETERMINATION OF MOLECULAR WEIGHT FROM OSMOTIC PRESSURE

Osmotic pressure measurements are less accurate and difficult to carry out. Therefore, this method is not widely used in the determination of molecular weights. The chief use of this method is in finding molecular weights of polymers e.g., plastics, proteins, and starch, which have very high molecular weights.

Knowing the osmotic pressure of a given solution, the molecular weight of the solute can be calculated as follows from van't Hoff equation.

$$
\begin{aligned}
\pi V & =n R T \\
& =\frac{w}{M} R T \\
M & =\frac{w R T}{\pi V} \\
M & =\text { molecular mass of the solute } \\
w & =\text { amount of solute in grams } \\
R & =0.0821 \text { litre-atmosphere } \\
T & =\left(t^{\circ} \mathrm{C}+273\right) \mathrm{K} \\
\pi & =\text { osmotic pressure in atmospheres } \\
V & =\text { volume of solution in litres }
\end{aligned}
$$

or
where

SOLVED PROBLEM 1. Morse and Frazer observed that a solution of glucose containing 18 grams per litre had an osmotic pressure of 2.39 atmospheres at $23^{\circ} \mathrm{C}$. Find the molecular weight of glucose.

SOLUTION
We know that:

$$
M=\frac{w R T}{\pi V}
$$

Here,

$$
\begin{aligned}
w & =18 \mathrm{~g} \\
R & =0.0821 \text { litre-atmosphere } \\
T & =23+273=296 \mathrm{~K} \\
\pi & =2.39 \text { atmospheres } \\
V & =1 \text { litre }
\end{aligned}
$$

Substituting these values in relation (1)

$$
\begin{aligned}
M & =\frac{18 \times 0.0821 \times 296}{2.39 \times 1} \\
& =\mathbf{1 8 3 . 0}
\end{aligned}
$$

SOLVED PROBLEM 2. A solution of glycol containing 1.821 g per litre has an osmotic pressure of 51.8 cm of mercury at $10^{\circ} \mathrm{C}$. What is the molecular mass of glycol?

SOLUTION
We know that from van't Hoff equation

$$
M=\frac{w R T}{\pi V}
$$

In this case,

$$
\begin{aligned}
w & =1.821 \mathrm{~g} \\
R & =0.0821 \text { litre-atmosphere } \\
T & =10+273=283 \mathrm{~K} \\
\pi & =\frac{51.8}{76} \text { atmosphere } \\
V & =1 \text { litre }
\end{aligned}
$$

Substituting these values in expression (1),

$$
\begin{aligned}
M & =\frac{1.821 \times 0.0821 \times 283 \times 76}{51.8 \times 1} \\
& =62.07
\end{aligned}
$$

## relation between vapour pressure and osmotic pressure

Consider an aqueous solution contained in a tube closed at the lower end by a semipermeable membrane and immersed in pure water (Fig. 16.21). The whole apparatus is enclosed under a bell-jar which is evacuated. When the osmotic equilibrium is reached, the bell jar is saturated with water vapour. Let the height of solution in the tube be $h \mathrm{~cm}$. If the solution is sufficiently dilute, the density of the solution will be approximately the same as that of the pure solvent, $d$.

Since at equilibrium, the osmotic pressure of solution $(\pi)$ is exactly balanced by hydrostatic pressure due to $h \mathrm{~cm}$ column of solution of density $d$, we can write,

$$
\begin{equation*}
\pi=h \times d \tag{1}
\end{equation*}
$$



Figure 16.21
Vapour pressure and osmotic pressure.
If $p$ is the vapour pressure of the solvent at the given temperature and $p$, the vapour pressure of the solution, the pressure at all points on a level with $A$ will be $p$ and at all points on a level with $B$ will be $p_{s}$. Now, the pressure at $A$ is greater than at $B$ due to the weight of the column of solvent vapour of height $h$. Thus,

$$
\begin{equation*}
p-p_{s}=h D \tag{2}
\end{equation*}
$$

where $D=$ density of solvent vapour at pressure $p$.
Dividing (1) by (2), we have

$$
\begin{equation*}
\frac{\pi}{p-p_{s}}=\frac{h d}{h D}=\frac{d}{D} \tag{3}
\end{equation*}
$$

At a given temperature, $d$ and $D$ are constant. That is

$$
\frac{\pi}{p-p_{s}}=\text { constant }
$$

or

$$
\pi=\text { constant } \times\left(p-p_{s}\right)
$$

or

$$
\pi \propto\left(p-p_{s}\right)
$$

This shows that osmotic pressure is directly proportional to the lowering of vapour pressure.

## Relative Lowering of Vapour Pressure and Osmotic Pressure

When the osmotic equilibrium is established in apparatus shown in Fig. 16.21, we have

$$
\begin{align*}
\pi & =h \times d, \text { for dilute solution }  \tag{1}\\
p-p_{s} & =h \times D, \text { for solvent vapour } \tag{2}
\end{align*}
$$

Dividing (2) by (1) and simplifying

$$
\begin{equation*}
p-p_{s}=\pi \times \frac{D}{d} \tag{3}
\end{equation*}
$$

where $D$ is the density of the solvent vapour and $d$ is the density of the solution.
From the gas equation for one mole of the solvent vapour $(p V=R T)$,

$$
\begin{equation*}
p=\frac{R T}{V} \tag{4}
\end{equation*}
$$

If $M$ is the molecular mass of the solvent vapour, its density
or

$$
\begin{aligned}
D & =\frac{M}{V} \\
V & =\frac{M}{D}
\end{aligned}
$$

Substituting the value of $V$ in equation (4)

$$
\begin{equation*}
p=\frac{R T D}{M} \tag{5}
\end{equation*}
$$

Dividing (3) by (5)
or

$$
\begin{align*}
\frac{p-p_{s}}{p} & =\pi \times \frac{D}{d} \times \frac{M}{R T D} \\
\frac{p-p_{s}}{p} & =\pi \times \frac{M}{d R T} \tag{6}
\end{align*}
$$

At a fixed temperature $d$ is constant and hence the factor $\frac{M}{d R T}$ has a constant value. Therefore we can write

$$
\frac{p-p_{s}}{p} \propto \pi
$$

That is, relative lowering of vapour pressure is directly proportional to osmotic pressure.

## DERIVATION OF RAOULT'S LAW

According to van't Hoff equation for solutions,

$$
\pi V=n R T
$$

where $V=$ volume of solution and $n=$ number of moles of solute.
Hence,

$$
\pi=\frac{n R T}{V}
$$

Substituting the values of $\pi$ in (6)
or

$$
\frac{p-p_{s}}{p}=\frac{n R T}{V} \times \frac{M}{d R T}=\frac{n}{V d / M}
$$

$$
\frac{p-p_{s}}{p}=\frac{n}{N}
$$

where $N=$ number of moles of the solvent.
This is the Raoult's law equation in which $n$ is the denominator is ignored when the solution is very dilute.

## OSMOTIC PRESSURE OF ELECTROLYTES

Like other colligative properties, observed osmotic pressure of electrolytes ( $\pi$ ) in aqueous solutions is higher than the value calculated using van't Hoff equation, $\pi_{0} V=n R T$. Expressing in terms of van't Hoff factor $\boldsymbol{i}$,

$$
\frac{\pi}{\pi_{0}}=i
$$

## 61216 physical chemistry

Consequently, the van't Hoff equation for solutions of electrolytes assumes the form

$$
\pi V=i n R T
$$

Since electrolytes are ionized in solution, total number of particles increases as compared to the number of particles if no ionization had taken place. The osmotic pressure of solution being proportional to the number of particles in solution, we can write

$$
\frac{\pi}{\pi_{0}}=\frac{\text { actual number of particles on ionization }}{\text { number of particles if no ionization occurred }}
$$

For example, if NaCl is ionized completely as at infinite dilution, one mole of NaCl will give two moles of particles ( $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$, one mole each). Therefore, the observed osmotic pressure will be twice the calculated value for no ionization. That is,

$$
\frac{\pi}{\pi_{0}}=2
$$

Similarly, the value of $i$ for $\mathrm{CaCl}_{2}$ at infinite dilution will be 3 ; for $\mathrm{FeCl}_{3}$ it will be 4 .
Ordinarily, electrolytes are practically ionized in aqueous solution. If $\alpha$ be the degree of ionization for a salt $A B$,

$$
\underset{1-\alpha}{\mathrm{AB}} \rightleftharpoons \underset{\alpha}{\mathrm{~A}^{+}}+\underset{\alpha}{\mathrm{B}^{-}}
$$

The total number of moles of particles in aqueous solution will be $1-\alpha+2 \alpha=1+\alpha$ as compared to 1 mole of salt for no ionization.

Therefore,

$$
\frac{\pi}{\pi_{0}}=\frac{1+\alpha}{1}
$$

Thus the value of $i$ will be more than 1 and less than 2.
SOLVED PROBLEM 1. The osmotic pressure of a 0.01 m solution of $\mathrm{CaCl}_{2}$ and sucrose at 298.15 K are 0.605 atm and 0.224 atm respectively. Calculate the van't Hoff factor and degree of dissociation of $\mathrm{CaCl}_{2}$.

SOLUTION

$$
i=\frac{\pi}{\pi_{0}}=\frac{0.605}{0.224}=2.70
$$

If $\alpha$ is the degree of dissociation,

$$
\begin{array}{lrl} 
& \mathrm{CaCl}_{2} & \rightleftharpoons \underset{1-\alpha}{\mathrm{Ca}^{2+}}+\underset{2 \alpha}{2 \mathrm{Cl}^{-}} \\
\therefore & \frac{1+2 \alpha}{1} & =2.70 \\
\text { and } & \alpha & =\mathbf{0 . 8 5}
\end{array}
$$

As shown above the van't Hoff factor $i=2.70$ and the degree of dissociation $(\alpha)=0.85$
SOLVED PROBLEM 2. Find the osmotic pressure of an aqueous solution of $\mathrm{BaCl}_{2}$ at 288 K containing 0.39 g per 60 ml . The salt is $60 \%$ dissociated. $(\mathrm{Ba}=137 ; \mathrm{Cl}=35.5)$

SOLUTION
For an electrolyte solution, van't Hoff equation assumes the form

$$
\begin{equation*}
\pi V=\operatorname{in} R T \text {, where } i \text { is van't Hoff factor } \tag{1}
\end{equation*}
$$

In this case,

$$
V=\frac{60}{1000}=\frac{6}{100} \text { litre }
$$

$$
\begin{aligned}
n & =\frac{0.39}{208} \\
T & =288 \mathrm{~K}
\end{aligned}
$$

## Calculation of $\boldsymbol{i}$

$$
\begin{array}{lrl} 
& \left.\begin{array}{rl}
\mathrm{BaCl}_{2} & \rightleftharpoons \underset{\alpha}{\mathrm{Ba}}+\underset{2 \alpha}{2+} \mathrm{Cl}^{-} \\
\therefore & \\
\text { But } & i
\end{array}\right)=\frac{1-\alpha+\alpha+2 \alpha}{1}=\frac{1+2 \alpha}{1} \\
\therefore & \alpha & =0.60
\end{array}
$$

Substituting values in equation (1)

$$
\begin{aligned}
\pi & =2.2 \times \frac{0.39}{208} \times 0.0821 \times 288 \times \frac{100}{60} \\
& =1.6256 \mathrm{~atm}
\end{aligned}
$$

## EXAMINATION QUESTIONS

1. Define or explain the following terms :
(a) Osmosis
(b) Osmotic pressure
(c) van't Hoff equation
(d) Raoult's law
(e) Isotonic solutions
2. (a) Explain the term 'osmotic pressure'. How is the osmotic pressure of a solution is affected by concentration of a solute and by temperature?
(b) Calculate the osmotic pressure of a $5 \%$ solution of glucose $\left(\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}\right)$ at $18^{\circ} \mathrm{C}$. ( $R=0.082$ atm litre $\mathrm{mol}^{-1} \mathrm{deg}^{-1}$ )
Answer. (b) 6.628 atm
3. (a) State the laws of osmotic pressure. Explain how osmotic pressure is analogous to gas pressure. How can the molecular mass of a substance in solution be determined from its osmotic pressure?
(b) An aqueous solution contains 20 g of glucose per litre. Calculate the osmotic pressure of the solution at $25^{\circ} \mathrm{C}(\mathrm{mol}$. mass of glucose $=180)$.
Answer. 2.715 atm
4. A $1 \%$ solution of potassium chloride is $80 \%$ dissociated. What is its osmotic pressure at 300 K . ( $R=0.082$ lit atm $\mathrm{deg}^{-1} \mathrm{~mol}^{-1} ; \mathrm{K}=39 ; \mathrm{Cl}=35.5$ )
Answer. 5.93 atm
5. Explain : Equimolar aqueous solutions of glucose and potassium nitrate do not have equal osmotic pressures at room temperature.
6. Calculate the molality and osmotic pressure of a $0.5 \%$ solution of urea (Mol. mass 60 ) in water at $0^{\circ} \mathrm{C}$. ( $R=0.082$ lit. atms K ${ }^{-1} \mathrm{~mol}^{-1}$ )
Answer. $0.837 \mathrm{~m} ; 1.86 \mathrm{~atm}$
7. (a) What do you mean by osmosis? State van't Hoff's law of osmotic pressure and deduce osmotic pressure equation $p=C R T$. The symbols have their usual significance.
(b) A solution contains 5 g of urea (mol mass $=60$ ) per 100 g in water. If the density of water at $25^{\circ} \mathrm{C}$ is $0.998 \mathrm{~g} \mathrm{~cm}^{-3}$, calculate the osmotic pressure of the solution at the same temperature ( $R=0.082$ litre atm $\mathrm{deg}^{-1} \mathrm{~mol}^{-1}$ )

## 61416 PHYSICALCHEMISTRY

Answer. (b) 22.34 atm
8. (a) State Raoult's law and show that relative lowering of vapour pressure of a solution is directly proportional to its osmotic pressure.
(b) 3.58 g NaCl was dissolved in 120 g of water at $77^{\circ} \mathrm{C}$. If the osmotic pressure of solution is 26.31 atm ., then calculate the degree of dissociation of NaCl .

Answer. (b) 79.54\%
9. Calculate the concentration (g/litre) of aqueous glucose (molecular mass $=180$ ) which is isotonic with blood (osmotic pressure for blood is 7.65 atm . at $37^{\circ} \mathrm{C}$. and $R=0.0821 \mathrm{~atm}$. lit. $\mathrm{K}^{-1} \mathrm{~mol}^{-1}$ )
Answer. $54.10 \mathrm{~g} / \mathrm{litre}$
10. State and explain the laws of osmosis. Derive the equation relating osmotic pressure and molecular mass of the solute.
11. Given the following solutions at 300 K (a) 0.01 M sucrose; (b) 0.1 M NaCl ; and (c) $0.1 \mathrm{M} \mathrm{BaCl}_{2}$. Which one of these will have highest osmotic pressure? Why?
Answer. None
12. (a) What is osmosis? Derive a relationship between osmotic pressure and concentration of a dissolved solute.
(b) Calculate osmotic pressure of solutions at $25^{\circ} \mathrm{C}$ containing (i) 5.85 g of NaCl , and (ii) 5.0 g of urea per litre of solutions.
Answer. (b) (i) 2.44 atm (ii) 2.038 atm
13. (a) Making use of the concept of chemical potential, derive the van't Hoff equation $p=C R T$, where $p$ is the osmotic pressure of the solution and $C$ is its molar concentration. Also derive a relationship between osmotic pressure and lowering of vapour pressure of an ideal solution.
(b) What are isotonic solutions? Show that for isotonic solutions at the same temperature, the molar concentrations are the same.
(Madurai BSc, 2000)
14. How is relative lowering of vapour pressure of solutions of non-volatile solute and volatile solvent is related to osmotic pressure? Deduce the relationship.
(Gulbarga BSc, 2000)
15. What is the difference between osmosis and diffusion?
(Punjabi BSc, 2000)
16. Derive the relationship between lowering of vapour pressure and osmotic pressure of a solvent.
(Lucknow BSc, 2001)
17. Define osmosis. How molecular weight of a substance can be determined by osmotic pressure method?
(Arunachal BSc, 2002)
18. Write van't Hoff equation for osmotic pressure of a solution. How can it be modified to determine molecular weight of polymers?
(Panjab BSc, 2002)
19. From thermodynamic considerations, obtain the expression; $p=C R T$ for the osmotic pressure.
(Aligarh BSc, 2002)
20. Calculate osmotic pressure of human blood at body temperature $\left(36.9^{\circ} \mathrm{C}\right)$ which shows a freezing depression of $0.558^{\circ} \mathrm{C}$ (assumed to contain no associating or dissociating substances) Molal depression constant of water is equal to $1.86^{\circ} \mathrm{C} \mathrm{kg} \mathrm{mol}^{-1}$.
Answer. 7.623 atm
(Andhra BSc, 2002)
21. Phenol associates in water to form double molecules. When 0.75 g of phenol is dissolved in 45 g of water, the freezing point is depressed by $0.225^{\circ} \mathrm{C}$. Calculate the degree of association of phenol. ( $K_{\mathrm{f}}$ for water is 1.88 per 1000 g )
Answer. 0.647
(Arunachal BSc, 2002)
22. The osmotic pressure $\pi$ of blood is 7.65 atm at 310 K . To inject glucose to a patient intravenously it has to be isotonic with blood. What would be the concentration of glucose solution in g per litre? $\left(M_{\text {glucose }}=180 \mathrm{~g} \mathrm{~mol}^{-1}, R=0.082\right.$ lit atm K $\left.\mathrm{Kml}^{-1}\right)$
Answer. 54.162 g
(Guru Nanak Dev BSc, 2002)
23. A 0.1 M aqueous solution of $\mathrm{KNO}_{3}$ shows an osmotic pressure of 4.5 atm at 300 K while the calculated one is 2.5 atm . What is the van't Hoff factor ' $i$ ' for the solution?
Answer. 0.55
(Guru Nanak Dev BSc, 2002)
24. Discuss the laws of osmotic pressure and van't Hoff's theory. Prove that osmotic pressure is a colligative property.
(Arunachal BSc, 2003)
25. (a) From thermodynamic considerations, derive the expression for osmotic pressure of a solution.
(b) Obtain a relationship between osmotic pressure and elevation in boiling point of a solution.
(Kalyani BSc, 2003)
26. Establish the relationship between osmotic pressure and vapour pressure lowering of an ideal solution.
(Arunachal BSc, 2003)
27. Describe one method for measurement of osmotic pressure.
(Purvanchal BSc, 2003)
28. (a) Define Osmosis and Osmotic pressure. How molecular mass of solute is determined from osmotic pressure measurement?
(b) What is the concentration of cane sugar which is isotonic with solution containing 6 g of urea per litre. (Molecular masses of urea and cane sugar are 60 and 342 respectively).
Answer. $34.2 \mathrm{~g} \mathrm{l}^{-1}$
(Mysore BSc, 2004)
29. How can you determine Osmotic pressure by Berkeley and Hartley's method?

Calculate the osmotic pressure of a 0.01 N solution of cane sugar at $30^{\circ} \mathrm{C}$.
Answer. 0.248 atm
(Dibrugarh BSc, 2004)
30. Calculate the osmotic pressure of $0.745 \%$ solution of KCl at $27^{\circ} \mathrm{C}$ assuming it to be $86 \%$ dissociated. Answer. 4.576 atm
(Goa BSc, 2004)
31. Calculate the osmotic pressure of a solution at $25^{\circ} \mathrm{C}$ obtained by mixing $100 \mathrm{~cm}^{3}$ of $4.6 \%$ of glucose and $200 \mathrm{~cm}^{3}$ of $4.5 \%$ solution of glucose.
Answer. 8.332 atm
(Delhi BSc, 2005)
32. Calculate the osmotic pressure of a glucose solution containing 15 g in 100 ml solution at $27^{\circ} \mathrm{C}$.

Answer. 20.5 atm
(Gulbarga BSc, 2005)
33. The osmotic pressure of blood at $37^{\circ} \mathrm{C}$ is 7.6 atm . A solution that is given intravenously must have the same osmotic pressure as blood. What should be the molarity of a glucose solution to give an osmotic pressure of 7.6 atm at $37^{\circ} \mathrm{C}$ ?
Answer. $0.298 \mathrm{~mol}^{-1}$
(Panjab BSc, 2005)
34. An aqueous solution contains 20 g of glucose in one litre of the solution. Assuming the solution to be ideal, calculate its osmotic pressure at $25^{\circ} \mathrm{C}$.
Answer. 2.718 atm
(Vidyasagar BSc, 2006)
35. The osmotic pressure of a solution containing 2.0 g of protein in 200 ml of aqueous solution is 0.2 atm at 300 K . Calculate the molar mass of the protein. ( $R=0.082 \mathrm{~atm} \mathrm{lit} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$ )
Answer. $1230 \mathrm{~g} \mathrm{~mol}^{-1}$
(Kalyani BSc, 2006)
36. A $1.8 \%$ solution of an unknown solute is isotonic with $10.26 \%$ solution of sugar cane ( molecular mass $=342$ ). Calculate the molar mass of the solute.
Answer. $60 \mathrm{~g} \mathrm{~mol}^{-1}$
(Agra BSc, 2006)
37. Calculate the osmotic pressure of a sugar solution in which 3.42 g of sugar has been dissolved in $100 \mathrm{~cm}^{3}$ of solution at 300 K .
Answer. 2.477 atm
(Baroda BSc, 2006)

## MULTIPLE CHOICE QUESTIONS

1. A semipermeable membrane allows the passage of $\qquad$ through it.
(a) solvent only
(b) solute only
(c) solvent and solute both
(d) either solvent or solute

Answer. (a)
2. The flow of solvent through a semipermeable membrane from pure solvent to solution is called

## 61616 PhYSICALCHEMISTRY

(a) diffusion
(b) osmosis
(c) effusion
(d) none of these

Answer. (b)
3. The flow of solvent molecules can take place from
(a) dilute to concentrated solution
(b) concentrated to dilute solution
(c) anyone solution to the other
(d) none of these

Answer. (a)
4. The external pressure applied to the solution in order to stop the passage of solvent molecules into solution by a semipermeable membrane is called
(a) osmosis
(b) osmotic pressure
(c) optical pressure
(d) none of these

Answer. (b)
5. Osmotic pressure can be measured by an instrument called
(a) manometer
(b) barometer
(c) osmometer
(d) nanometer

Answer. (c)
6. Isotonic solutions have the same
(a) vapour pressure
(b) osmotic pressure
(c) atmospheric pressure
(d) internal pressure

Answer. (b)
7. Which of the following is a colligative property?
(a) atmospheric pressure
(b) critical pressure
(c) osmotic pressure
(d) none of these

Answer. (c)
8. The isotonic solutions have
(a) equimolar concentrations
(b) different osmotic pressure
(c) different colligative properties
(d) same chemical properties

Answer. (a)
9. Two solutions are separated by a semipermeable membrane. The one which is of lower osmotic pressure is called
(a) hypotonic
(b) hypertonic
(c) iso-osmotic
(d) isomorphic

Answer. (a)
10. A hypertonic solution is the one which has $\qquad$ osmotic pressure than the other.
(a) lower
(b) equal
(c) higher
(d) none of these

Answer. (c)
11. The osmosis taking place from solution to pure water by application of pressure greater than osmotic pressure on the solution is called
(a) equilibrium osmosis
(b) irreversible osmosis
(c) reversible osmosis
(d) reverse osmosis

Answer. (d)
12. The osmotic pressure of a solution at a given temperature is directly proportional to
(a) atmospheric pressure
(b) concentration
(c) internal energy
(d) volume of the solution

Answer. (b)
13. The osmotic pressure of a solution of a given concentration is directly proportional to
(a) room temperature
(b) atmospheric pressure
(c) absolute temperature
(d) critical temperature

Answer. (c)
14. The van't Hoff equation for $n$ moles of solute dissolved in $v$ litres of solution is
(a) $\pi=n R T$
(b) $\pi V=n R T$
(c) $\pi P=n R T$
(d) $\pi P=n R T / V$

Answer. (b)
15. When osmotic pressure and temperature are the same, equal volumes of solution would contain equal number of moles (molecules) of the solute. This relationship is called
(a) van't Hoff law for solutions
(b) Avogadro's law for solutions
(c) Boyle's van't Hoff law for solutions
(d) Avogadro-van't Hoff law for solutions

Answer. (d)
16. The osmotic pressure of a solution containing 1 mole of solute in 22.4 litres would be equal to
(a) 1 atm
(b) $1 / 2 \mathrm{~atm}$
(c) 2 atm
(d) 22.4 atm

Answer. (a)
17. Osmotic pressure is directly proportional to
(a) vapour pressure of the pure solvent
(b) lowering of vapour pressure
(c) relative lowering of vapour pressure
(d) none of these

Answer. (c)
18. The molecular mass ' $M$ ' of the solute can be calculated by using the formula
(a) $M=\frac{w R T}{\pi V}$
(b) $\quad M=\frac{w R T}{\pi V^{2}}$
(c) $M=\frac{w R T^{2}}{\pi V}$
(d) $\quad M=\frac{w R T}{\pi^{2} V^{2}}$

Answer. (a)
19. The van't Hoff factor, $i$, is related to the osmotic pressure by the formula
(a) $i=\pi / \pi^{\circ}$
(b) $i=\pi^{\circ} / \pi$
(c) $i=\pi-\pi^{\circ} / \pi^{\circ}$
(d) $i=\pi^{\circ}-\pi / \pi$

Answer. (a)
20. The value of van't Hoff factor, $i$, will be equal to 2 for
(a) urea
(b) glucose
(c) sucrose
(d) NaCl

Answer. (d)
21. The value of van't Hoff factor $i$ for the electrolytes which are partially ionised in aqueous solution will be
(a) equal to 1
(b) less than 1
(c) between 1 and 2
(d) greater than 2

Answer. (c)
22. Two solutions with equal osmotic pressure are called
(a) molar solutions
(b) molal solutions
(c) isotonic solution
(d) isomorphic solutions

Answer. (c)
23. The osmotic pressure of a solution increases if
(a) volume of the solutions is increased
(b) the no. of the solute particles is increased
(c) the no. of solute particles is decreased
(d) the temperature is decreased

Answer. (b)

## 61816 PhYSICALCHEMISTRY

24. The highest osmotic pressure will be observed in
(a) 0.1 M urea
(b) 0.1 M glucose
(c) 0.1 M NaCl
(d) $0.1 \mathrm{M} \mathrm{Al}_{2}\left(\mathrm{SO}_{4}\right)_{3}$

Answer. (d)
25. The ratio of osmotic pressures of $\mathrm{BaCl}_{2}, \mathrm{NaCl}$ and urea will be
(a) 3:2:1
(b) 1:2:3
(c) 2:1:3
(d) 3:1:2

Answer. (a)
26. The osmotic pressure of equimolar solutions of $\mathrm{CaCl}_{2}, \mathrm{NaCl}$ and urea will be in the order
(a) $\mathrm{CaCl}_{2}>\mathrm{NaCl}>$ urea
(b) $\mathrm{CaCl}_{2}<\mathrm{NaCl}<$ urea
(c) urea $>\mathrm{CaCl}_{2}>\mathrm{NaCl}$
(d) urea $<\mathrm{CaCl}_{2}<\mathrm{NaCl}$
Answer. (a)
27. The osmotic pressure of a solution containing 0.02 mole of solute at 300 K will be
(a) $0.02 \times 0.0821 \times 300 \mathrm{~atm}$
(b) $\frac{0.02 \times 0.0821}{300} \mathrm{~atm}$
(c) $\frac{0.02 \times 300}{0.0821} \mathrm{~atm}$
(d) $0.02 \times 0.821 \times 300 \mathrm{~atm}$

Answer. (a)
28. The outer hard shell of two eggs of the same size is removed by dissolving in dil HCl . One is placed in water and other in saturated NaCl solution. It will be observed after few hours that
(a) the first one shrinks while the other swells
(b) the first one swells while the other shrinks
(c) both eggs swell
(d) both eggs shrink

Answer. (b)
29. Blood is isotonic with
(a) 0.16 M sodium chloride solution
(b) 0.31 M sodium chloride solution
(c) 0.40 M sodium chloride solution
(d) 0.80 M sodium chloride solution

Answer. (a)
30. The osmotic pressure of a solution of urea containing $8.6 \mathrm{~g} \mathrm{lit}^{-1}$ is equal to that of $5 \%$ solution of a non-volatile solute. The molecular mass of the solute will be
(a) 349
(b) 34.9
(c) 430
(d) 860

Answer. (a)
31. The osmotic pressure of $2 \%$ solution of urea (mol mass $=60$ ) at $27^{\circ} \mathrm{C}$ would be ( $\alpha$ is the degree of dissociation)
(a) 0.0821 atm
(b) 0.821 atm
(c) 8.21 atm
(d) none of these

Answer. (c)
32. The osmotic pressure of the solution of urea is
(a) $5 \%<3 \%<2 \%<1 \%$
(b) $1 \%<2 \%>3 \%>5 \%$
(c) $1 \%<2 \%<3 \%<5 \%$
(d) $3 \%>2 \%>1 \%>5 \%$

Answer. (c)
33. Which of the following inorganic precipitates acts as a semipermeable membrane?
(a) $\mathrm{Al}(\mathrm{OH})_{3}$
(b) $\mathrm{BaCO}_{3}$
(c) $\mathrm{CuSO}_{4}$
(d) $\mathrm{Cu}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$

Answer. (d)
34. The osmotic pressure of a solution increases if
(a) temperature is lowered
(b) volume is increased
(c) concentration of solute particles is increased (d) solution constant is increased Answer. (c)
35. The concentration in gram per litre of a solution of cane sugar (mol mass $=342$ ) is isotonic with a solution containing 3 gms of urea per litre. The concentration of cane sugar is
(a) $17.1 \mathrm{~g} \mathrm{lit}^{-1}$
(b) $34.2 \mathrm{~g} \mathrm{lit}^{-1}$
(c) $3.42 \mathrm{~g} \mathrm{lit}^{-1}$
(d) $1.71 \mathrm{~g} \mathrm{lit}^{-1}$

Answer. (a)
36. The osmotic pressure of $10 \%$ solution of cane sugar at $69^{\circ} \mathrm{C}$ is
(a) 0.0821 atm
(b) 0.821 atm
(c) 8.21 atm
(d) 16.42 atm

Answer. (c)
37. Osmotic pressure is not determined by
(a) Pfeffer's method
(b) Berkley and Hertley's method
(c) Abbe's refractometer
(d) all of these

Answer. (c)
38. Which of the following is not correct?
(a) in osmosis solvent molecules flow in one direction
(b) in diffusion solute and solvent molecule flow in opposite direction
(c) for osmosis a semipermeable membrane is required
(d) for diffusion, a semipermeable membrane is required

Answer. (d)
39. The osmotic pressure of a solution of cane sugar (mol mass $=342$ ) at $69^{\circ} \mathrm{C}$ is 8.21 atm . The concentration of the solution is
(a) $1 \%$
(b) $2 \%$
(c) $5 \%$
(d) $10 \%$

Answer. (d)
40. The volume of the solution containing one mole of solute that shows an osmotic pressure of 1 atm is
(a) 22.4 litre
(b) 2.24 litre
(c) 0.224 litre
(d) 1.0 litre

Answer. (a)
41. Which of the following types of compounds will have van't Hoff factor $=1$ ?
(a) strong electrolytes
(b) weak electrolytes
(c) non-electrolytes
(d) none of these

Answer. (c)
42. For binary electrolytes of the type $A B$, the abnormal mol. mass is given by ( $\alpha$ is the degree of dissociation)
(a) $\frac{M_{\text {normal }}}{1+\alpha}$
(b) $\frac{M_{\text {normal }}}{1-\alpha}$
(c) $\frac{M_{\text {normal }}}{1+2 \alpha}$
(d) $\frac{M_{\text {normal }}}{1+3 \alpha}$

Answer. (a)
43. Which one of the following is not correct?
(a) the equimolar solutions have same osmotic pressure at different temperatures
(b) the equimolar solutions have same osmotic pressure at same temperatures
(c) the osmotic pressure is directly proportional to the number of moles of solutions
(d) the osmotic pressure is directly proportional to the relative lowering of vapour pressure

## 62016 PhYSICALCHEMISTRY

Answer. (a)
44. Which of the following statements is true?
(a) Osmosis can be reversed by application of pressure on the solution
(b) Beckmann thermometer can be used to measure elevation in boiling point
(c) Osmosis and diffusion are same in solutions
(d) Barometer can be used to measure osmotic pressure

Answer. (a)
45. The van't Hoff factor for dilute aqueous solutions of urea and NaCl respectively are
(a) 1, greater than 1
(b) 1,0
(c) 0,1
(d) greater than 1, 1

Answer. (a)
46. The observed molecular mass in case of electrolytes of the type $A B_{2}$ is
(a) equal to the normal molecular mass
(b) less than the normal molecular mass
(c) greater than the normal molecular mass
(d) none of these

Answer. (b)
47. The compounds which undergo association in solutions have observed molecular mass always
(a) equal to their normal molecular mass
(b) less than their normal molecular mass
(c) greater than their normal molecular mass
(d) none of these

Answer. (c)
48. The van't Hoff factors for urea, sucrose and glucose are in the ratio
(a) 1:2:1
(b) 1:1:2
(c) 2:1:1
(d) 1:1:1

Answer. (d)
49. The value of van't Hoff factor is more than one in dissociation and less than one in association. This statement is
(a) false
(b) true
(c) sometimes false, sometimes true
(d) none of these

Answer. (c)
50. For electrolytes of the type $\mathrm{A}_{2} \mathrm{~B}$ or $\mathrm{AB}_{2}$ the abnormal molecular mass is given by
(a) $\frac{M_{\text {normal }}}{1+\alpha}$
(b) $\frac{M_{\text {normal }}}{1+2 \alpha}$
(c) $\frac{M_{\text {normal }}}{1+3 \alpha}$
(d) $\frac{M_{\text {normal }}}{1-\alpha}$

Answer. (b).

