

# 3

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## Reverse Osmosis

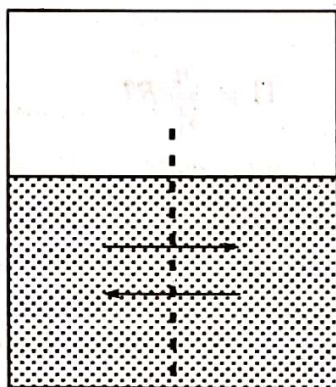
Reverse osmosis (RO), less commonly known as hyperfiltration, is a high pressure, energy efficient technique for dewatering process streams, concentrating low molecular weight substances in solution, or purifying wastewater. It has the ability to concentrate dissolved as well as suspended solids. RO is widely used in the desalination of brackish water. To desalinate water, it is required to create a flow through a membrane, causing the water to leave the salty side of the membrane, passing into the unsalted side. To achieve this, pressure must be created upon the water column on the salt side of the membrane; firstly, to remove the natural osmotic pressure and secondly, to create extra pressure on the water column in order to push the water through the membrane. As the name suggests, reverse osmosis is osmosis in reverse. Therefore, to describe reverse osmosis, it is first necessary to understand the phenomenon of osmosis.

### 3.1 CONCEPT OF OSMOSIS

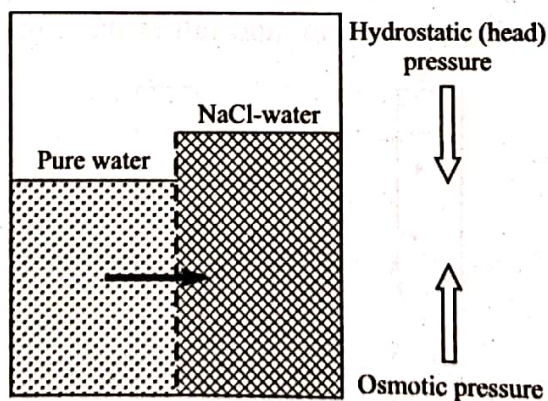
The word 'osmosis' is originated from the Greek word *osmos* which means 'to push'. Osmosis is a natural phenomenon, most commonly observed in plants. If we do not water our plants they wilt. A plant cell is a semipermeable (water flows through the membrane but salts do not) membrane with the living stuff inside in a salt solution. Water is drawn into the cell from outside because pure water moves across a semipermeable membrane to dilute the higher concentration of salt inside. This is how water is drawn in from the ground when we water our plants. On the other hand, if we add salt to plants (over fertilize or spill some salt on the grass), the plant wilts because the salt concentration outside of the cell becomes higher than inside and then water moves across the membrane from inside to outside.

Osmosis may be defined as the physical movement of a solvent through a semipermeable membrane based on a difference in chemical potential between two solutions separated by that semipermeable membrane.

Let us take a simple example to demonstrate osmosis. A beaker of water as shown in Figure 3.1 is divided through the centre by a semipermeable membrane. The thick dotted line represents the semipermeable membrane. We will define this semipermeable membrane as lacking the capacity to diffuse anything other than the solvent, in this case water molecules. Now, if we add a small amount of common salt (NaCl) to the solution on one side of the membrane (Figure 3.2), the salt water solution will be having a higher chemical potential than the water solution on the other side of the membrane. Therefore, in an effort to equilibrate the difference in chemical potential, water begins to diffuse through the membrane from the water side to the salt water side. This movement is osmosis. The pressure exerted by this mass transfer is known as osmotic pressure.



**Figure 3.1** A simplified diagram of osmotic equilibrium.



**Figure 3.2** Osmosis process at work.

The diffusion of water will continue until one of the two constraints is met. One constraint would be that the solutions essentially equilibrate, at least to the extent that the remaining difference in chemical potential is offset by the resistance or pressure loss of diffusion through the membrane. The other constraint is that the rising column of salt water exerts sufficient hydrostatic



pressure to limit further diffusion. By observation, then, we can measure the osmotic pressure of a solution by noting the point at which the head pressure impedes further diffusion.

### 3.1.1 Determination of Osmotic Pressure

The thermal movement of a solute molecule within a solvent is overdamped by the solvent molecules that surround it. The solute movement is wholly determined by fluctuations of thermal collisions with nearby solvent molecules. However, the average thermal velocity of the solute molecule is the same had it been free in a gas phase, without nearby solvent molecules.

Whenever a solute movement is blocked by the membrane it will transfer momentum to it and, therefore, generate pressure on it. Since the velocity is the same as that of a free molecule, the pressure will be the same as the pressure of an ideal gas of the same molecular concentration. Hence, the osmotic pressure  $\Pi$ , is given by the Van't Hoff formula, which is identical to the pressure formula of an ideal gas:

$$\Pi = \frac{n}{\bar{V}_w} RT \quad (3.1)$$

where  $n$  is the number of kg mol of solute,  $\bar{V}_w$  the molar volume of pure solvent water in  $\text{m}^3$  associated with  $n$  kg mol of solute,  $R$  is the gas constant ( $82.057 \times 10^3 \text{ m}^3 \cdot \text{atm/kg mol} \cdot \text{K}$ ), and  $T$  is the absolute temperature in  $\text{K}$ . The osmotic pressure does not depend on the solute type, or its molecular size, but only on its molar concentration, as the formula states.

Figure 3.3 shows connected vessels separated by a semipermeable membrane. If there is only water in the device, the level will be the same at both arms. When solute molecules are added to one arm, water will start to flow into it, so that its level will rise at this arm, and fall at the other arm.

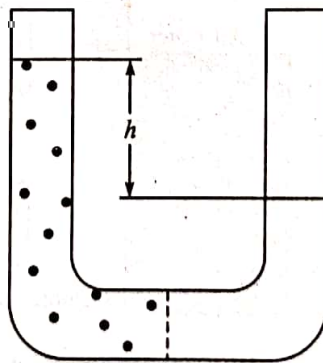


Figure 3.3 Demonstration of osmotic pressure.

The system will stabilize when the osmotic pressure is balanced by the hydrostatic pressure generated by the difference  $h$  in the water levels. This can be given by the following expression:

$$cRT = \rho h \quad (3.2)$$

where  $\rho$  is the specific gravity of water. The physical significance of osmotic pressure is well known in biological and clinical situations. Germination of seeds to burst open their protective layer, transportation of water from the soil to the root system in plants and activation of dormant cells in a solution of lower osmotic pressure are all due to the difference of osmotic pressure. Even relatively small concentrations of dissolved solutes can develop fairly large osmotic pressures. Table 3.1 shows osmotic pressure of various dilute aqueous solutions of NaCl at 25°C.

**Table 3.1** Osmotic pressure of various dilute aqueous solutions of NaCl at 25°C

$\frac{\text{gmol NaCl}}{\text{kg H}_2\text{O}}$	Density (Kg/m <sup>3</sup> )	Osmotic pressure (atm)
0	997.0	0
0.01	997.4	0.47
0.10	1001.1	4.56
0.50	1017.2	22.55
1.00	1036.3	45.80
2.00	1072.3	96.2

**EXAMPLE 3.1** Calculate the osmotic pressure of a solution containing 0.10 g mol KCl/1000 g H<sub>2</sub>O at 25°C. Given that density of water at 25°C is 997 kg/m<sup>3</sup>.

**Solution:** Since KCl dissociates to give two ions,  $n = 2 \times 0.10 \times 10^{-3}$   
 $= 2.00 \times 10^{-4} \text{ kg mol}$

The volume of pure solvent water  $V_m = (1.00)/(997) \text{ m}^3$

$$\begin{aligned} \text{Therefore, by Eq. (3.1)} \quad \Pi &= \frac{n}{V_w} RT \\ &= \frac{(2.00 \times 10^{-4})(82.057 \times 10^{-3})(298.15)}{1.000/997.0} \\ &= 4.88 \text{ atm} \end{aligned}$$

### 3.1.2 Thermodynamic Consideration of Osmosis

Reversibility is a fundamental idea of thermodynamics. Osmosis is a reversible thermodynamic process. This implies that the direction of water flow through the membrane can be reversed at any moment by proper control of the external pressure on the solution. Contrary to this, mixing a teaspoon full of sugar in a cup of tea is an irreversible thermodynamic process of sugar diffusion within water. There is no way to reverse the process at any given moment and unmix the sugar back to the spoon. Osmosis phenomenon can also be explained in the light of Gibb's free energy.

Gibbs free energy equation in its simplest form can be written as

$$G \equiv H - TS \quad (3.3)$$



where  $G$  = Gibb's free energy;  $H$  = Enthalpy;  $T$  = absolute temperature; and  $S$  = entropy.

Again

$$H = E + PV \quad (3.4)$$

where  $E$  = internal energy;  $P$  = pressure; and  $V$  = volume.

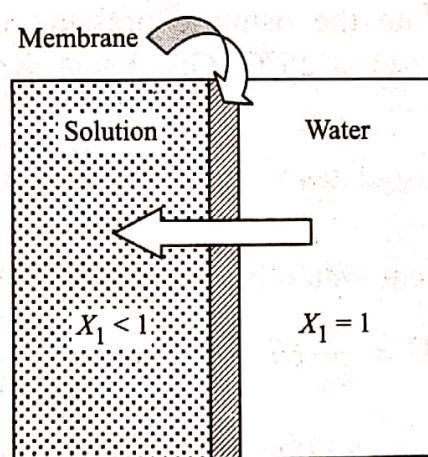
In differential form, these equations can be expressed as

$$dG = dH - TdS - SdT$$

$$dH = dE + PdV + VdP \quad (3.5)$$

or 
$$dG = dE + PdV + VdP - TdS - SdT \quad (3.6)$$

Chemical potential ( $\mu$ ) is essentially a driving force expressed as a result of change in the composition of the system. The standard chemical potential is defined as the free energy per mol of substance formed, consumed or transferred from one phase to the other in its standard state, which corresponds to 1 atm pressure at particular temperature (usually 20°C). Consider Figure 3.4, which shows that two chambers are separated by a semipermeable membrane. The right one contains a very dilute solution or the pure solvent and the other contains a solute dissolved in the solvent.



**Figure 3.4** Osmotic flow from a region of higher chemical potential to that of lower chemical potential.

Pure solvent in the right compartment containing a mol fraction of water ( $x_1$ ) of 1 would have a chemical potential designated by  $\mu_1^\circ$ , while the solution compartment with a mol fraction of water less than 1, would have a lower chemical potential of  $\mu_1$ .

Physically speaking, the highest energy form of water is when it is in pure state. Adding any material or solute (here salt) to it results in the increases of its entropy. A disorder is created in a system when solute is added. Since  $S$  is increased,  $G$  will reduce, according to Eq. (3.1). This means that water is flowing from higher Gibb's free energy region to lower Gibb's free energy region. In other words, the chemical potential of water in a solution is always lower than when it is in a pure state. This indicates that the water in the right compartment has a greater chemical potential than the water in the left

compartment. Since the two compartments are separated by a semipermeable membrane, which, in the ideal case, is permeable only to the water and not to the solute, the natural tendency would be for the water to flow in the downward direction of the driving force. This is the phenomenon of osmosis, the movement of solvent from the dilute solutions to the more concentrated solution. Table 3.2 gives the osmotic pressure of various compounds at 25°C.

**Table 3.2** Osmotic pressure of various compounds at room temperature (25°C) [Cheryan 1989]

<i>Compounds</i>	<i>Concentration</i>	<i>Osmotic pressure (psi)</i>
Milk	9% solid-not-fat	100
Whey	6% total solids	100
Orange juice	11% total solids	230
Apple juice	15% total solids	300
Grape juice	16% total solids	300
Coffee extract	28% total solids	500
Lactose	5% w/v	55
Sodium chloride	1% w/v	125
Lactic acid	1% w/v	80
Sweet potato waste water	22% total solids	870

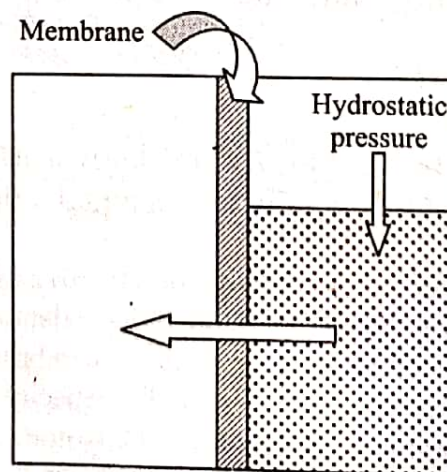


inside and outside of the cell. Water molecules flow in and out at an equal rate by osmosis, causing the cell size to stay the same. As a result, it will not lose or gain any solutes. Plant cells in an isotonic environment are flaccid, and they will wither. The equilibrium of water movement is unable to provide plant cells with internal pressure for structural support, and therefore, plants prefer to live in a hypotonic environment. In this situation, the concentration of solutes inside plant cells is higher than outside, and the plants use active transport to transport solutes in. This also ensures that the concentration of water will be higher outside plant cells than inside which insures plant health.

### 3.2 THE PHENOMENON OF REVERSE OSMOSIS

To reverse the natural process of osmosis, it is required to overcome the osmotic pressure equilibrium across the membrane because the flow is naturally from dilute to concentrate. We want more pure water, and so, we must increase the salt content in the cell (concentrate side of the membrane). To do this we increase the pressure on the salty side of the membrane and force the water across. The amount of pressure is determined by the salt concentration. As we force water out, the salt concentration increases requiring even greater pressure to get more pure water.

By exerting a hydraulic pressure greater than the sum of the osmotic pressure difference and the pressure loss of diffusion through the membrane, we can cause water to diffuse in the opposite direction (Figure 3.5), into the more concentrated solution. This is reverse osmosis. The greater the pressure applied, the more rapid will be the diffusion. It follows that if other variables are kept constant, the water flow rate becomes proportional to the net pressure. Using reverse osmosis we are able to concentrate various solutes, either dissolved or dispersed, in a solution. It has the separation range of 0.0001 to 0.001  $\mu\text{m}$  (i.e. 1 to 10  $\text{\AA}$ ) particle size.



**Figure 3.5** Hydrostatic pressure causing reverse osmosis.



### 3.2.1 Pressure Requirement

Reverse osmosis is a liquid driven membrane process; with the membranes capable of passing water whilst rejecting the microsolute such as salts or low molecular weight organics ( $< 1000$  daltons). Pressure driving force (1 to 10 MPa) is needed to overcome the force of osmosis that cause the water to flow from dilute permeate to concentrated feed. The pressure required is dependent on the concentration of the salt solution on the reject (concentrate) side of the membrane. Running as system at 1100 ppm on the concentrate side requires the application of over 200 psi pressures. Sea water systems at 33,000+ ppm generally run at 800+ psi. Reverse osmosis system in household appliances usually run at 50 to 70 psi. Some basic information on reverse osmosis process is presented in Table 3.3.

**Table 3.3** Some basic information on reverse osmosis

Driving force	Chemical potential gradient (pressure gradient 15 to 100 bar)
Transport mechanism	Diffusion
Separation principle	Solution-diffusion, preferential sorption
Size of retained species	1 – 10 Å
Type of membrane	Asymmetric or thin film composite (flat sheets or hollow fibres)
Membrane materials	Cellulose acetate, aromatic polyamide, polyether urea
Pore size	$< 2$ nm
Type of modules	Spiral wound (74%) and hollow fibre (26%)
Typical flux (in commercial installation)	10 – 30 gal/(ft <sup>2</sup> )(day) [ $5 \times 10^{-6}$ – $1.5 \times 10^{-5}$ (m <sup>3</sup> /m <sup>2</sup> ·s)]

### 3.2.2 High Pressure and Low Pressure RO

High pressure reverse osmosis (HPRO) is the one where osmotic pressure consideration is significant. In general the term 'high pressure RO' includes units designed for feed side operating pressures exceeding 100 bar. Striving for high water recoveries in waste water treatment RO systems are developed operating at transmembrane pressure difference of 120 and 200 bar. These pressure differences enable sufficient net driving forces for the separation of water from brine with high osmotic pressure. On the other hand, low pressure RO (TMP  $< 100$  bar) is used for preparation of electronic grade water where high separation of salt/low molecular weight organic solute is required from very dilute solutions (even in ppb range).

### 3.2.3 Advantages of Reverse Osmosis

Reverse osmosis is the most important process of desalination of brackish (1000–5000 ppm salt) or sea water (about 35,000 ppm or 3.5% salt). Its potential was identified in the 1950s. But commercial exploitation was not



possible until the 1960s when the high flux asymmetric cellulose acetate membrane was developed by the phase inversion technique of Loeb and Sourirajan. Reverse osmosis enjoys several advantages over the conventional separation processes. Some of these are as follows:

1. Since RO is a pressure driven process, no energy intensive phase change or potentially expensive solvents or adsorbents are needed for RO separations.
2. It is inherently simpler to design and operate than many traditional separation processes.
3. Simultaneous separation and concentration of both inorganic and organic compounds are possible using RO process
4. It can be combined with conventional separation processes such as distillation to provide a hybrid process.