

Osmotic Pressure

Water can be transported across semi-permeable membranes which separate compartments containing different concentrations of solutes. The membrane must be impermeable to the solute but permeable for water (hence semi-permeable). This process, called osmosis, has enormous significance for living organisms, although an understanding of the phenomenon at the molecular level has remained obscure. The archetypal experiment to demonstrate osmosis, which is also responsible for the development of the term ‘osmotic pressure’ is the rise of water in a U tube apparatus.

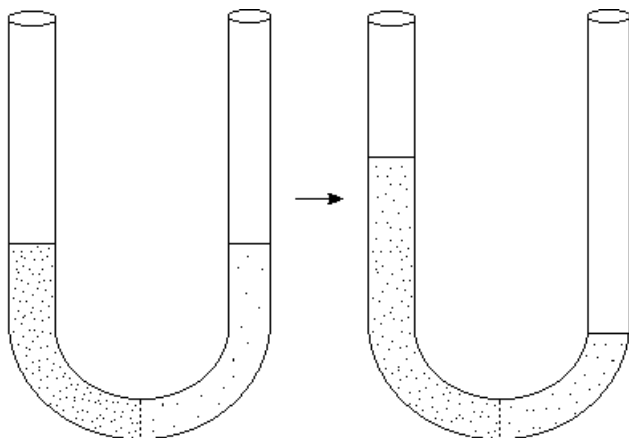


Fig. 4.2.1

The water moves across the semi-permeable membrane from the solution containing a low concentration of solute to the solution with a high concentration of solute until the weight of the column of water is sufficient to stop any further transport. Thus, the pressure exerted on the membrane by the raised column of water at equilibrium is said to be equal and opposite to the ‘osmotic pressure’ of the solution.

Thermodynamics:

In thermodynamics we talk about energy balance. The energy can take several forms; kinetic energy (heat), gravitational potential energy, chemical energy, and so on. The chemical potential energy (μ) represents the free energy per mole of solvent. Thus for water, we can express it as

$$\mu_w = \mu_w^0 + VP + RT \ln(a_w) \quad (4.2.1)$$

where μ_0 is the chemical potential of water at its standard state, V_{bar} is the molal volume, P is the hydrostatic pressure and a_w is the activity of the water.

If we consider the U tube apparatus shown above, then the osmotic pressure (P) is the hydrostatic pressure required to stop the osmotic flow. Although we’ve shown it as an increase in hydrostatic pressure (due to the gravitational potential of the raised column of solution) it could just as easily be a negative hydrostatic pressure (tension) on the opposite side of the membrane.

At this pressure, the change in chemical potential of the solution (in this case the osmotic potential) is equal to the hydrostatic pressure difference across the membrane.

If we consider that the activity of the water is reduced by adding solutes, then we can relate the decrease in chemical potential to the increase in hydrostatic pressure needed to obtain equilibrium. For a situation in which a semi-permeable membrane separates pure water from a solution, then

$$\pi = P - 1 = -\left(\frac{RT}{V}\right)\ln(a_w) \quad (4.2.2)$$

For a solution in which there are no interactions between the solvent and the solute (an ideal solution), the activity can be described by the mole fraction of solvent molecules (X_w)

$$a_w = X_w = \frac{n_w}{n_w + n_s} \quad (4.2.3)$$

where n_w is the number of water molecules and n_s is the number of solute molecules. If $n_w \gg n_s$ then we can use the approximation

$$-\ln \frac{n_w}{n_w + n_s} \approx \frac{n_s}{n_w + n_s} \quad (4.2.4)$$

we can get an expression for the osmotic pressure

$$\pi \approx RT \frac{X_s}{V} = RTm \approx RTc \quad (4.2.5)$$

where X_s is the mole fraction of solute, m is the molal concentration of solute, and c is the molar concentration of solute. This is the van't Hoff relation for osmotic pressure.

Kinetic Theory:

If we consider osmotic equilibrium from a kinetic point of view, then the difference in kinetic energy must be due to the difference in solvent concentration between the two compartments. Liquid molecules are in perpetual motion and collide with each other as well as with the membrane. The pressure developed from this kinetic energy is given by

$$P = \frac{RT}{V} \quad (4.2.6)$$

For water at 20°C, this pressure would be over 1300 atmospheres if there were no intermolecular forces. Obviously the forces between water molecules are appreciable. If we consider the semi-permeable membrane to be constructed of water filled pores, then the mole fraction of water on the solute side will drop from 1 to X_w at the pore openings. Since the solute molecules will not be

able to transfer their momentum to the water molecules inside the pores, then those water molecules at the pore openings will be bombarded by fewer water molecules from the solution side than from the pure water side. This will give a pressure on the solution side of

$$P = \frac{RT}{V} X_w \quad (4.2.7)$$

Thus the osmotic pressure is given by the difference in kinetic pressure in the pore openings

$$\pi = \frac{RT}{V} - \frac{RT}{V} X_w = \frac{RT}{V} X_s \approx RTc \quad (4.2.8)$$

Intermolecular Forces:

The equation given above clearly works well, but we must ask why the intermolecular forces are not relevant to the osmotic pressure of a solution. We can't help but notice the similarity between the equation for osmotic pressure and the ideal gas law ($PV=nRT$), so as a first approximation, let's recall how intermolecular forces result in a departure from the ideal gas law for real gases.

The gas equation of van der Waals takes two factors into account. First, the volume occupied by the molecules of the gas reduces the total volume by a certain amount (the constant b represents the volume of the gas molecules, so we have $P(V-b)=nRT$). Second, the intermolecular forces reduce the momentum that the molecules impart to the walls of the container through collisions. This second fact is due to the attraction between a molecule about to collide with the container wall and the other gas molecules within the container.

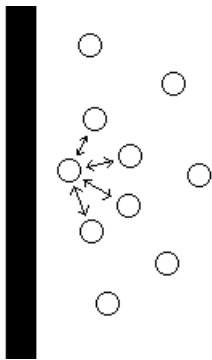


Fig. 4.2.2

Since this attractive force only counteracts momentum transfer to the walls of the container (within the bulk of the gas, the attractive forces are symmetrical and therefore cancel), the pressure will be reduced by an amount inversely proportional to the square of the volume. Van der Waals equation is

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \quad (4.2.9)$$

where a and b are constants (a is not related to the thermodynamic activity).

We can extend this reasoning to the case for a liquid by considering the intermolecular forces between solvent molecules and between solvent and solute molecules. The equipartition theorem says that solvent and solute molecules will have the same mean kinetic energy; the important difference being that the membrane is impermeable for the solute. At the surfaces, the intermolecular forces are such that there is no transfer of momentum from the molecules to the container. Within the liquid, symmetry guarantees that each molecule is attracted equally on all sides. Thus the kinetic pressure does not have a component corresponding to P in the van der Waals equation and is only given by a/V^2 . If we consider the membrane pores to be so small that water molecules must pass single-file, then we can see that symmetry once again eliminates the intermolecular forces.

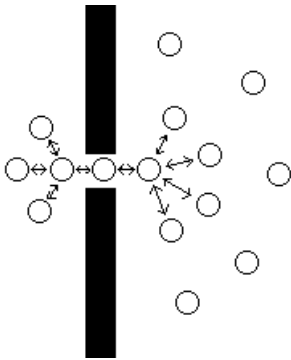


Fig. 4.2.3

In an ideal solution, the volume is given by the sum of the volume of solvent and the volume of solute, thus the volume correction for the space taken up by solute molecules is already included in the molal volume of water. So we can see why the equation for osmotic pressure corresponds better with the equation for an ideal gas than does the equation for the pressure of a real gas. It is because the momentum deficiency which causes flow is only important at the pore openings where the intermolecular forces are canceled by symmetry.

This last point shows why osmosis is unique to the liquid state. Osmotic flow only occurs if there is some mechanism for generating tension within the solvent. The cohesive intermolecular forces that exist in a liquid pull the solvent molecules through the pores like a train. Thus although the intermolecular forces do not create the osmotic potential, they are essential for flow to occur in response to that potential.

Thermodynamic Relation:

We can obtain an equation for the thermodynamic relationship between osmotic pressure and the lowering of the vapor pressure above a solution by considering the following perpetual motion machine.

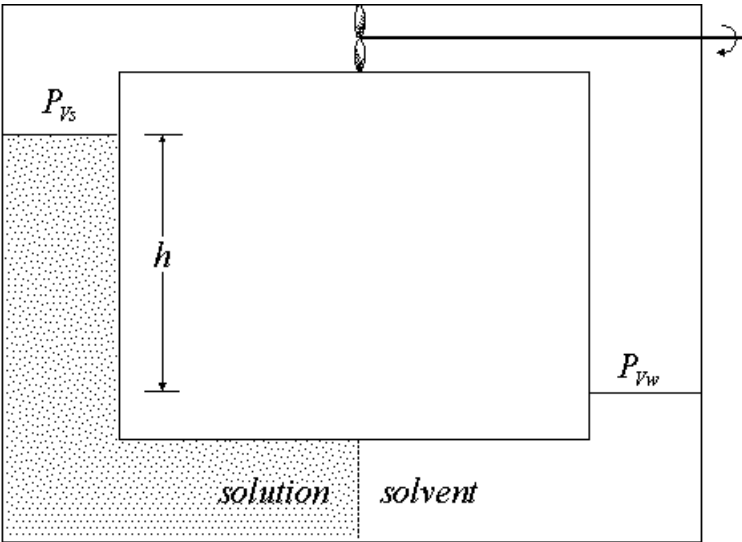


Fig. 4.2.4

A semipermeable membrane separates a solution, on the left side of the apparatus, from pure solvent on the right side. A pressure difference is then set up to balance the osmotic pressure across the membrane. Since the vapour pressure above the pure solvent is higher than the vapour pressure above the solution (eq. 4.12), there is a pressure gradient in the top of the apparatus between the left and right sides. This gradient will drive a flow of vapour from the right side to the left which is used to drive a turbine blade. The vapour condenses on the surface of the solution on the left side, thereby diluting that solution and reducing its osmotic pressure. This causes solvent to flow back through the semi-permeable membrane into the right side to restore the original concentration. Thus we extract energy from the machine without having to put anything in.

[Stop here and think about this before proceeding]

The hydrostatic pressure of the column of solution on the left hand side is given by

$$P = \frac{M}{V} gh \quad (4.2.13)$$

The column of vapor that exists over the solvent on the right hand side is given by the difference in vapor pressure between the top and bottom of the column

$$P_{Vw} - P_{Vs} = \frac{M}{V} gh \quad (4.2.14)$$

where M/V is the density of the water vapor. If water vapor obeys the ideal gas law then we can combine these relations to get an equation for the pressure

$$P = \frac{RT}{V} \left(\frac{P_{Vw} - P_{Vs}}{P_{Vw}} \right) \quad (4.2.15)$$

If we recall that Raoult's law states

$$\left(\frac{P_{Vw} - P_{Vs}}{P_{Vw}} \right) = X_s \quad (4.2.16)$$

leaving us with

$$P = \frac{RT}{V} X_s \quad (4.2.17)$$

However, we can refine this by noting that the gas above the water column is not incompressible, and will hence vary in density as the height is increased. This means that the weight of this column should be given by

$$\int_{P_{Vs}}^{P_{Vw}} \left(\frac{1}{P} \right) dP = \ln \frac{P_{Vw}}{P_{Vs}} \quad (4.2.18)$$

Resulting in

$$P = \frac{RT}{V} \ln \frac{P_{Vw}}{P_{Vs}} \quad (4.2.19)$$

Now we invoke the laws of thermodynamics to tell us that perpetual motion machines don't work so we realize that the pressure at equilibrium must be equal to the osmotic pressure

$$\pi = \frac{RT}{V} \ln \frac{P_{Vw}}{P_{Vs}} \quad (4.2.20)$$

Non-Ideal Solutions:

An ideal solution is defined as one in which there is no interaction between the solvent and solute molecules. The expressions that we have derived so far for the reduction in vapor pressure and the osmotic pressure have depended on this assumption holding true. If there are intermolecular bonds which form between solvent and solute, then we might expect some departure in the behavior of the solutions from the equations that we have derived so far. In thermodynamics, the activity parameter (defined as the ratio of vapor pressures with and without solute) is introduced to deal with non-ideal solutions, however, this is merely an empirical parameter which is not a property of the solvent or solute (it changes with changing concentration of solute).

If we assume that each solute molecule binds a certain number of solvent molecules (α) which are then removed from the mole fraction of solvent molecules, we can derive an expression relating this factor to the mole fraction of solvent that is available for the osmotic potential. The

number of solvent molecules is thus reduced from n_w to $(n_w - \alpha n_s)$, so the equation for X_w now becomes

$$X_w = \frac{n_w - \alpha n_s}{n_w - \alpha n_s - n_s} \quad (4.2.21)$$

Resulting in an expression for the osmotic pressure.

$$\pi = -\frac{RT}{V} \ln \left[\frac{n_w - \alpha n_s}{n_w - \alpha n_s - n_s} \right] \quad (4.2.22)$$

Unlike the thermodynamic parameter activity, which is dependent on concentration, the binding constant has no such dependencies (i.e. it's specific for a given solute) and describes osmotic pressure for any solution.

The Osmotic Coefficient

The more common method of dealing with departures from ideal dilute solutions is to use the osmotic coefficient. With the osmotic coefficient, the Van't Hoff equation is written as:

$$\pi = \phi RTm \quad (4.2.23)$$

Where ϕ is the molal osmotic coefficient. For non-electrolytes (e.g. glucose), ϕ 1 in 'ordinary' concentrations. For electrolytes, $\phi < 1$ due to the electrical interactions between the ions (e.g. NaCl at physiological concentrations has an osmotic coefficient of 0.93). For macromolecules, the deviation becomes much more dramatic; hemoglobin, for example, has an osmotic coefficient of 2.57.

Osmoles

The term osmole was developed to describe the osmotic pressure of a solution in a manner that does not vary with temperature. The osmotic pressure in osmoles is defined as π / RT . One osmole is thus the osmotic pressure of a 1m solution of an ideal solute (a solution that has a freezing point depression of 1.86°C).

Osmosis in Cells

The most important and most widely occurring process for water transfer into and out of living cells is osmosis. We can apply the equations of osmotic phenomena to living cells if we assume that: 1. The plasma membrane is effectively semipermeable; and 2. That the cell is normally in a state of osmotic equilibrium (the osmotic pressure of the cytoplasm is equal to that of the external medium).

If we consider the cell to be a spherical semipermeable membrane that holds water and solutes, then we can write:

$$V = V_w + b \quad (4.2.24)$$

Where b is the non-solvent component of the cytoplasm or "osmotically inactive volume". We can define the osmotic pressure of the cytoplasm using the Van't Hoff equation:

$$\pi_i = \phi_i RT m_i \approx \phi_i RT \frac{n_i}{V_w} \quad (4.2.25)$$

Noting that the change from molality to molarity introduces a temperature dependence. Substituting:

$$\pi_i \approx \phi_i RT \frac{n_i}{(V - b)} \quad (4.2.26)$$

At constant temperature,

$$\pi_i (V - b) = \phi RT n_i = k \quad (4.2.27)$$

Where k is a constant. Under isotonic (normal) conditions, we can write:

$$\pi_0 (V_0 - b) = k \quad (4.2.28)$$

If we change the external osmotic conditions, we will get water movement until $\pi_i = \pi_e$, so:

$$\pi_i (V - b) = \pi_e (V - b) = k = \pi_0 (V_0 - b) \quad (4.2.29)$$

So

$$\pi_e (V - b) = \pi_0 (V_0 - b) \quad (4.2.30)$$

This equation was first developed by Lucke and McCutcheon in 1932.

The Boyle-Van't Hoff Relation

Rearranging the above equation,

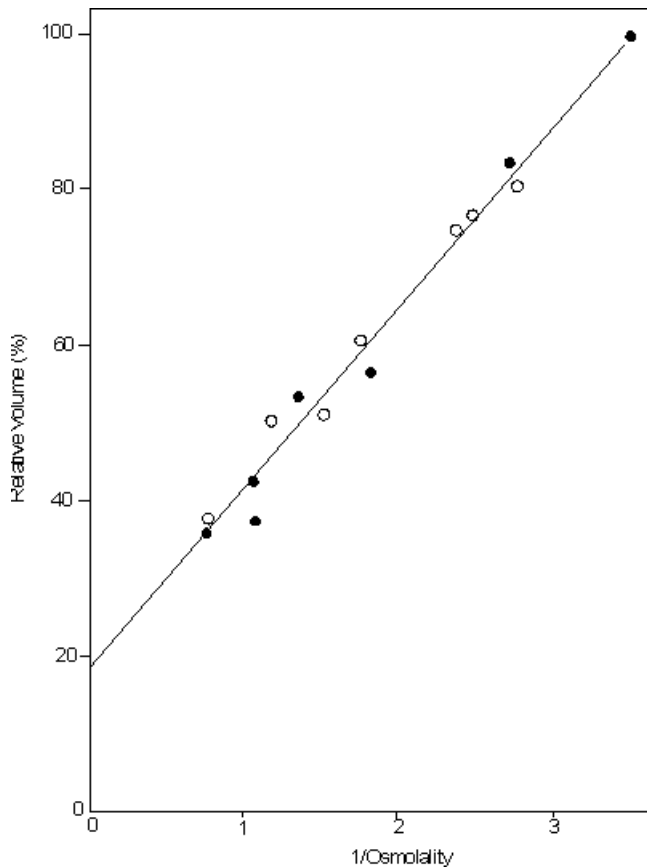
$$V - b = \left(\frac{\pi_0}{\pi_e} \right) (V_0 - b) = \left(\frac{\pi_0}{\pi_e} \right) V_{w0} \quad (4.2.31)$$

Leaving us with the Boyle-Van't Hoff Relation:

$$V = \left(\frac{\pi_0}{\pi_e} \right) (V_{w0} - b) \quad (4.2.32)$$

If we plot the cell volume vs. (π_0/π_e) , we get a straight line in which the y-intercept is the osmotically inactive volume and the slope is the isotonic water volume. Boyle-Van't Hoff plots

are used extensively in cryobiology to determine the osmotic parameters of given cell types. The assumption of constant temperature that is part of the derivation implies that the relation is temperature dependent.



Typical Boyle-Van't Hoff plot showing the relative volume changes of fertilized mouse ova (Leibo S., Water Permeability of Mouse Ova. *J Membrane Biol* **53**: 179-88. 1980.)

Fig. 4.2.5

The water volume that results from this relation has been found to be different from the water volume that results from other methods of measurement, so it is assumed that there is a compartment of water that is "bound" (unavailable for osmotic exchange). It should be noted, however, that any given water molecule within the cell is available for osmosis, but there is always a residual compartment (that is freely exchangeable with bulk water) that does not participate in osmosis.

[\[home\]](#) [\[previous\]](#) [\[next\]](#)

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