

COLLIGATIVE PROPERTIES

Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic.

Those solutions whose properties do not depend on the chemical nature/ identity of the solute are called colligative properties.

Colligative property is a physical property of a dilute solution that does not depend on the chemical nature of a solute but depends on the number of moles of a non-volatile solute dissolved in a given amount of a solvent.

In other words, all solutes, regardless of their physical or chemical identity, would have the same effect when equal amounts are dissolved in the same amount of the same or different solvents. Colligative properties include:

- Lowering of vapour pressure of the solvent.
- Boiling point elevation of the solvent.
- Freezing point depression of the solvent.
- Osmotic pressure of a solution.

Limitations of colligative properties

- The solution must be sufficiently dilute.
- The solute must be non-volatile
- The solute should not dissociate in the solvent.
- The solute should not associate when added to the solvent.
- There should be no chemical reaction between the solute and the solvent.

Lowering of vapour pressure.

If the space above the liquid is a closed one, the molecules escaping from the surface of the liquid (referred to as vapour molecules) will go on collecting in the empty space when the liquid is being heated. After sometime it is observed that a constant pressure is registered.

This pressure is due to the vapour molecules of the liquid and hence it is known as the vapour pressure of the liquid.

Since this pressure is constant, it follows that there must be a constant number of molecules in the space above the liquid.

Thus, there is a two-way process i.e. the molecules are leaving the liquid (when they gain enough kinetic energy) and are simultaneously coming back to it (when they lose the kinetic energy). Otherwise, the pressure in the space would continue to increase.

We get a state of dynamic equilibrium when the rate of evaporation of the liquid molecules is equal to the rate of condensation of the vapour molecules thus;

The vapour pressure of a liquid is the pressure exerted by the vapour when it is in equilibrium with the liquid at a given temperature.

The vapour pressure of a solution of a non-volatile solute is always lower than that of a pure solvent.

The addition of a solute to the solvent lowers the vapour pressure of the solvent because the molecules of the solute on the surface of solvent tends to hinder the escape of the solvent molecules into the vapour phase.

The lowering of vapour pressure is directly proportional to the concentration of the solution i.e. how much solute is added to a solvent.

Task

The vapour pressure of a solution is lower than that of a pure solvent at a given temperature. Briefly explain this observation.

If P is the vapour pressure of a solution and P^0 is the vapour pressure of a pure solvent, then P is less than P^0 .

The lowering of vapour pressure is given by $\Delta P = P^0 - P$

The lowering of vapour pressure is generally expressed in terms of Raoult's law.

Raoult's law of relative lowering of vapour pressure states that the relative lowering of vapour pressure of a pure solvent is equal to the mole fraction of the non-volatile solute dissolved in a given amount of a solvent at a given temperature.

$$\frac{P^0 - P}{P^0} = X$$

Where; X is the mole fraction of a non-volatile solute denoted by $X = \frac{n_2}{n_1 + n_2}$; where n_1 and n_2 are the number of moles of pure solvent and a non-volatile solute respectively.

$$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1 + n_2}$$

For a very dilute solution, the assumption is that the number of moles of a non-volatile solute is far much less than that of number of moles of a pure solvent. i.e. $n_1 \gg n_2$

This implies that; $n_1 + n_2 \approx n_1$;

$$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1}$$

NOTE:

- The lowering of vapour pressure of a solvent is directly proportional to the concentration of the solute in the solvent.
- The lowering of vapour pressure is a constant if the same number of moles of different solutes is dissolved in the same mass of the same solvent.

Examples:

1. The vapour pressure of water at 50°C is 12.27 kPa. A solution containing 18.1g of a non-volatile solute X in 100g of water has a vapour pressure of 11.6 kPa at the same temperature. Calculate the relative molecular mass of X.

Solution

$$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1}$$

$$Rfm \text{ of glucose, } C_6H_{12}O_6; = (12 \times 6) + (1 \times 12) + (16 \times 6) = 180$$

$$Rfm \text{ of water, } H_2O; = (1 \times 2) + 16, = 18$$

$$\frac{12.27 - 11.60}{12.27} = \left(\frac{18.1}{Rfm} \right) \div \left(\frac{100}{18} \right)$$

$$Rfm = 59.67 \cong 60$$

2. The Vapour pressure of water at 293K is 17.5 mmHg. Calculate the vapour pressure of water at 293K when 30 g of glucose, $C_6H_{12}O_6$, is dissolved in 540 g of water.

Solution

$$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1}$$

$$Rfm \text{ of glucose, } C_6H_{12}O_6; = (12 \times 6) + (1 \times 12) + (16 \times 6) = 180$$

$$Rfm \text{ of water, } H_2O; = (1 \times 2) + 16, = 18$$

$$\frac{17.5 - P}{17.5} = \left(\frac{30}{180} \right) \div \left(\frac{540}{18} \right)$$

$$P = 17.40 \text{ mmHg}$$

3. Vapour pressure of pure water at 298K is 23.8 mmHg. 50g of urea (NH_2CONH_2) is dissolved in 850g of water. Calculate the vapour pressure of water for this solution and its relative lowering.

Solution

$$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1}$$

$$Rfm \text{ of Urea, } NH_2CONH_2; = (14 \times 2) + (1 \times 4) + 12 + 16 = 60$$

$$Rfm \text{ of water, } H_2O; = (1 \times 2) + 16, = 18$$

$$\frac{23.8 - P}{23.8} = \left(\frac{50}{60} \right) \div \left(\frac{850}{18} \right)$$

$$P = 23.38 \text{ mmHg}$$

The relative lowering of vapour pressure is given by $\frac{P^0 - P}{P^0}$

$$\frac{P^0 - P}{P^0} = \frac{23.8 - 23.38}{23.8} = 0.018$$

4. The vapour pressure of pure water was reduced from 22.50 to 22.39 mmHg when 1.5 g of a solute was dissolved in 24.5 g of water. Determine the molar mass of the solute.

Solution

$$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1}$$

Rfm of solvent (water), H_2O ; = $(1 \times 2) + 16$, = 18

$$\frac{22.5 - 22.39}{22.5} = \left(\frac{1.5}{M_r}\right) \div \left(\frac{24.5}{18}\right)$$

$$M_r = 225$$

The molar mass of the solute is 225 g mol^{-1}

5. The vapour pressure of pure water at 298K is 3160 Nm^{-2} and the vapour pressure of solution containing 5.30g of solute per 100g of water at 298K is 3110 Nm^{-2} . Calculate the molar mass of solute.

Solution

$$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1}$$

Rfm of solvent (water), H_2O ; = $(1 \times 2) + 16$, = 18

$$\frac{3160 - 3110}{3160} = \left(\frac{5.30}{M_r}\right) \div \left(\frac{100}{18}\right)$$

$$M_r = 60.2929 \approx 60$$

The molar mass of the solute is 60 g mol^{-1}

Task

1. Calculate the vapour pressure above a solution containing 6.4g of naphthalene, $C_{10}H_8$ in 78.0g of benzene, C_6H_6 . (Vapour pressure of pure benzene is $12,685.89 \text{ Nm}^{-2}$).
[Answer: 12051.60 Nm^{-2}]
2. The vapour pressure of a solution containing 108.2g of a compound X in 1000g of water at 20°C was reduced by 24.79 Pa. The vapour pressure of water at the same temperature is 2338 Pa. Calculate the relative molecular mass of X.

3. A solution of 100g of a solute in 1 litre of water has a saturated vapour pressure of $2.27 \times 10^3 \text{ Nm}^{-2}$ at 20°C . The saturated vapour pressure of water at 20°C is $2.34 \times 10^3 \text{ Nm}^{-2}$. Calculate the relative molecular mass of the solute.

[Answer=60.17]

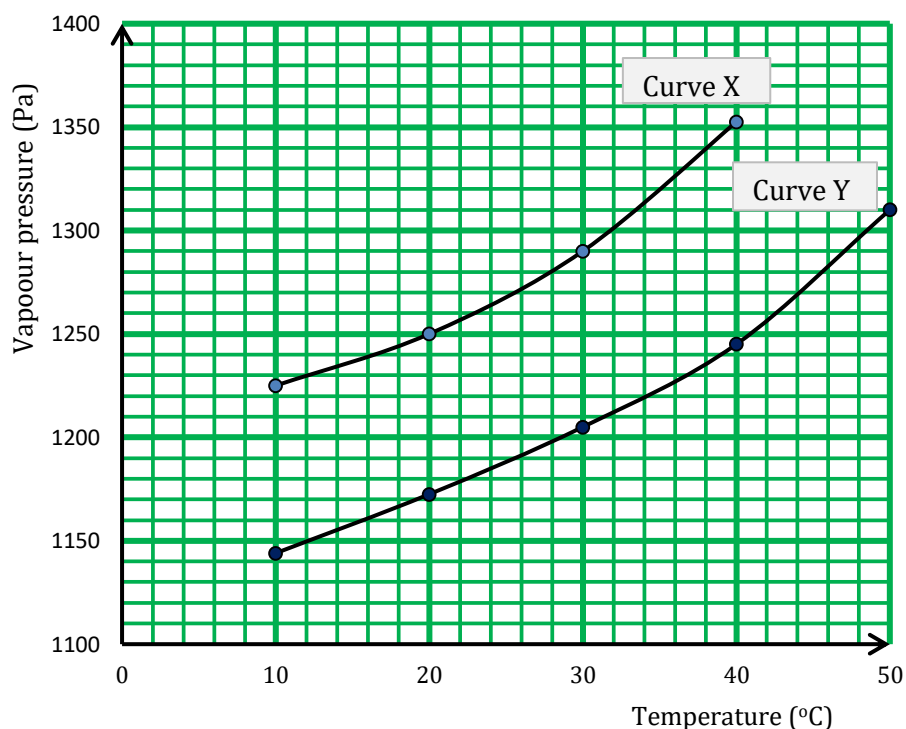
4. The vapour pressure of water at 50°C is 12333Pa. At this temperature, the solution of 9.14g of urea in 150g of water has a vapour pressure of 12106 Pa. calculate the relative molecular mass of urea.

[Answer= 60]

5. The vapour pressure of benzene is $9.97 \times 10^3 \text{ Nm}^{-2}$ at 20°C . What is the vapour pressure of the solution if 1.8g of C_4H_{10} is dissolved in 100g of benzene, C_6H_6 ?

[Answer = 9860.642 Nm^{-2}]

6. 28.6g of a non-volatile substance B was dissolved in 100g of water. The variation of vapour pressure for the solution, pure solvent with temperature is given below.



- Identify curve X and Y.
- Explain why curve Y has a lower vapour pressure than X at any temperature.
- Calculate the mole fraction of substance B in the solution at 30°C .
- Calculate the relative molecular mass of substance B.

NOTE: The determination of relative molecular mass by use of vapour pressures is not an accurate method since it is not easy to accurately measure pressure.

However, lowering of vapour pressure of a solvent leads to elevation of boiling point and a depression in freezing point of the solvent, both of which are easier to determine experimentally.

Boiling point elevation (Ebullioscopy).

Relationship between boiling point and vapour pressure:

When a liquid is being heated, its vapour pressure increases with increase in temperature since more molecules will gain more kinetic energy and escape to the vapour phase constituting the vapour pressure.

When the vapour pressure becomes equal to the external atmospheric pressure bubbles of vapour are formed within the liquid which rise upwards and escape to the surface; at this point, the liquid has started boiling.

The boiling point of a liquid is defined as the constant temperature at which the liquid vapour pressure becomes equal to the external atmospheric pressure.

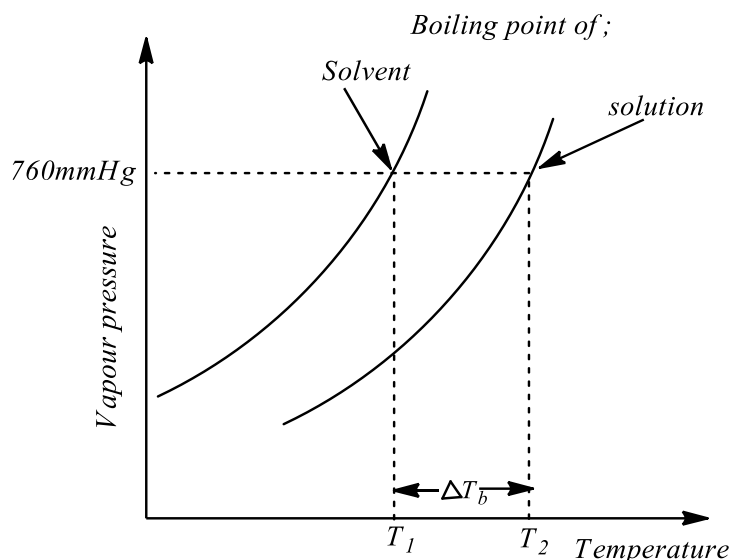
Boiling point is a characteristic property of liquids and is a criterion to check the purity of liquids.

When a pure solvent is heated, the molecules of the solvent acquire kinetic energy and those molecules which have enough kinetic energy escape into the space above the liquid in the vapour phase.

As heat is increased, more molecules of the solvent will increase in the vapour phase and when the vapour pressure of the solvent becomes equal to the atmospheric pressure, the pure solvent boils at a temperature $T_1^{\circ}C$.

When a non-volatile solute is added to the solvent to form a solution, the solute particles introduced in the solvent tend to prevent the molecules of the solvent from escaping into the vapour phase. This reduces the total vapour pressure of the solution.

In order for the solution to boil, the solution has to be heated to a higher temperature i.e. there is an increase (elevation) in boiling point.



The elevation in Boiling point is given by; $\Delta T_b = T_2 - T_1$

Task

A solution containing glucose in ethanol boils at a higher temperature compared to pure ethanol at the same pressure. Briefly explain this observation.

The elevation in boiling point is directly proportional to the number of moles of a non-volatile solute dissolved in a given mass of a solvent i.e.

$$\Delta T_b \propto n$$

$$\Delta T_b = K_b n$$

Where K_b is the boiling point constant/ Ebullioscopic constant. By definition;

Boiling point constant is the elevation in boiling point when one mole of a non-volatile solute is dissolved in 1000g of a pure solvent.

Boiling point constants are characteristic properties that depend on the identity of the solvent.

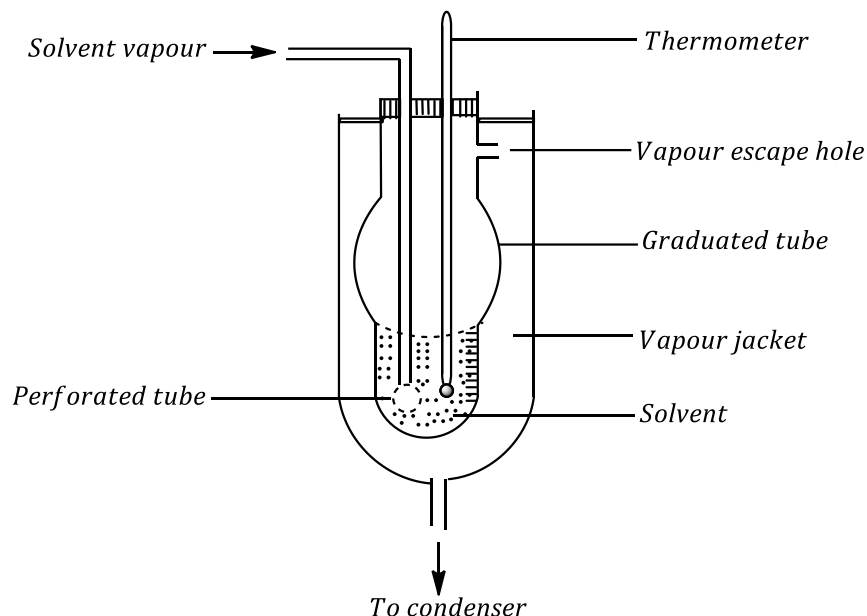
The boiling point constant for some common solvents are shown in the table below;

Solvent	Bpt (°C)	K_b (°Cmol ⁻¹ Kg ⁻¹)
Water	100	0.52
Benzene	80	2.70
Ethanol	79	1.15
Propanone	56	1.70

The molar mass of a solute can be determined by measuring the elevation in the boiling point of a solvent when a specific amount of the solute is dissolved in a known mass of the solvent.

The determination of molar mass from boiling point elevation is called ebullioscopy.

Determination of relative molecular mass using boiling point elevation method (Land's Berger's method)



Procedure;

- A known mass of a pure solvent (a grams) is put in a graduated tube.
- The solvent vapour is then directed into the solvent in the graduated tube until the pure solvent boils.
- The constant boiling temperature of the pure solvent ($T_1^{\circ}C$) is noted.
- The solvent is then allowed to cool.
- A known quantity of a solute (b grams) is added into the solvent in the graduated tube.
- More vapour of the pure solvent is directed into the solution until it boils and its constant boiling temperature is noted ($T_2^{\circ}C$)

Treatment of results:

- Let K_b be the boiling point constant of the solvent
- $\Delta T_b = (T_2 - T_1)^{\circ}C$
- a grams of solvent dissolves b grams of the solute
- 1000g of the solvent dissolves $\left(\frac{1000b}{a}\right)$ g of the solute
- ΔT_b is the elevation in boiling point when 1000g of a solvent dissolves $\left(\frac{1000b}{a}\right)$ g of the solute

- K_b is the elevation in boiling point when 1000g of a solvent dissolves $\left(\frac{1000b \times K_b}{a \times \Delta T_b}\right)$ g of the solute.
- Where $\left(\frac{1000b \times K_b}{a \times \Delta T_b}\right)$ is the relative molecular mass of the solute.

Examples:

1. The dissolution of 0.5g substance *P* in 50g of benzene at 298K raises the boiling point by 0.6°C. Calculate the relative formula mass of substance *P*. (K_b of benzene is 2.7°Cmol⁻¹Kg⁻¹).

Solution

50g of benzene dissolves 0.5g of *P*

1000g of benzene dissolves $\left(\frac{1000}{50} \times 0.5\right) = 10$ g of *P*

Elevation in boiling point, $\Delta T_b = 0.6^\circ\text{C}$

0.6°C is the elevation in boiling point caused by 10g of *P*.

2.7°C is the depression caused by $\left(\frac{2.7}{0.6} \times 10\right) = 45$ g of *P*.

Therefore, the relative molar mass of *P* is 45

2. 18g of glucose, C₆H₁₂O₆, is dissolved in 500g of water in a saucepan. At what temperature will this solution boil? (K_b of water is 0.52°Cmol⁻¹Kg⁻¹ and the boiling point of pure water is 100°C).

Solution

500g of water dissolves 18g of glucose

1000g of water dissolves $\left(\frac{1000}{500} \times 18\right) = 36$ g

Rfm of glucose, C₆H₁₂O₆; = (12 × 6) + (1 × 12) + (16 × 6) = 180

180g of glucose causes an elevation of 0.52 °C

36g of glucose causes an elevation of $\left(\frac{36 \times 0.52}{180}\right) = 0.104^\circ\text{C}$

Boiling point of the solution is equal to (100+0.104)°C

Therefore, the boiling point of the solution is 100.104°C

3. Calculate the boiling point of the solution made by dissolving 6.0g of urea, NH₂CONH₂, in 200g of water. (K_b of water is 0.52°Cmol⁻¹Kg⁻¹ and the boiling point of pure water is 100°C).

Solution

200g of water dissolves 6.0g of urea

Advanced Level Physical Chemistry

1000g of water dissolves $\left(\frac{1000}{200} \times 6.0\right) = 30g$

Rfm of urea, NH_2CONH_2 ; = $(14 \times 2) + (1 \times 4) + 12 + 16 = 60$

60g of urea causes an elevation of $0.52^\circ C$

30g of urea causes an elevation of $\left(\frac{30 \times 0.52}{60}\right) = 0.26^\circ C$

Boiling point of the solution is equal to $(100 + 0.26)^\circ C$

Therefore, the boiling point of the solution is $100.26^\circ C$

Task

1. A compound **P** contains 66.7% by mass of carbon, 11.1% by mass of hydrogen and 22.2% by mass of oxygen.
(a) Determine the empirical formula of compound P.
(b) 3.6g of **P** when dissolved in 124g of water causes the boiling point of water to elevate by $0.21^\circ C$. Determine the molecular formula of compound P. (K_b for water is $0.52^\circ C mol^{-1} Kg^{-1}$).
[Answer; C_4H_8O]
2. The boiling point of pure water is $100^\circ C$ at 760 mmHg pressure. At the same pressure, a solution containing 1.576g of potassium chloride in 100g of water boils at $100.11^\circ C$. calculate the boiling point constant, K_b for water.
3. The addition of 2.01g of glucose, $C_6H_{12}O_6$, to 25g of benzene causes the boiling point elevation of $1.204^\circ C$ while the boiling point elevation caused by addition of 2.04g of solid X to 20g of benzene was $2.413^\circ C$. calculate the;
(a) K_b for benzene. [Answer: $2.7^\circ C mol^{-1} kg^{-1}$]
(b) Relative molecular mass of solid X. [Answer: 114.13]
4. Boiling point of water at 750 mmHg is $99.63^\circ C$. How much sucrose ($C_{12}H_{22}O_{11}$) is to be added to 500g of water such that it boils at $100^\circ C$. (Boiling point constant for water is $0.52^\circ C mol^{-1} Kg^{-1}$).
[Answer = 121.67g]
5. The boiling point of ethanol is $78^\circ C$. Calculate the boiling point of a solution containing 2.7g of ethanamide, CH_3CONH_2 , in 75g of ethanol. (K_b of ethanol is $1.15^\circ C mol^{-1} Kg^{-1}$, C=12, N=14, H=1, O=16).
[Answer: $78.7^\circ C$]
6. Find the boiling point of a solution containing 0.520g of glucose, ($C_6H_{12}O_6$) dissolved in 80.2g of water. Boiling point constant of water is $0.52^\circ C mol^{-1} Kg^{-1}$.
[Answer = 100.0187]

Freezing point depression (Cryoscopy).

The freezing point of a substance is defined as the constant temperature at which the solid is in equilibrium with the pure liquid.

It is also defined as the constant temperature at which the liquid is converted to a solid.

The freezing point of a solution is less than that of a pure solvent at the same pressure. When a non-volatile solute dissolves in a liquid, the freezing point of the liquid is lowered.

If the T_1 is the freezing point of the pure solvent and T_2 is the freezing point of the solution, then $(T_1 - T_2)$ is the depression in freezing point i.e. $\Delta T_f = T_1 - T_2$.

The depression in freezing point is directly proportional to the amount (mass) of the non-volatile solute dissolved in a given mass of a solvent. Therefore;

$$\Delta T_f \propto n \dots \dots \dots (i)$$

Where; n is the number of moles of a non-volatile solute.

Removing the proportionality sign from equation (i), yields; $\Delta T_f = K_f n$

$$\text{Therefore, } \Delta T_f = K_f \frac{m}{M_r} \dots \dots \dots (ii)$$

Where:

m is a given mass of a solute

M_r is the molar mass of the solute

K_f is the freezing point constant or the cryoscopic constant.

Equation (ii) shows that the depression in freezing point, ΔT_f is inversely proportional to the relative formula mass of the solute.

By definition, freezing point constant is the depression in freezing point when one mole of a non-volatile solute is dissolved in 1000g of a pure solvent.

The freezing point constant for some common solvents are shown in the table below:

Solvent	Freezing point (°C)	Kf (°Cmol ⁻¹ Kg ⁻¹)
Water	0.0	1.86
Benzene	5.5	5.12
Ethanol	-114.6	1.99

The molar mass of a substance can be determined by measuring the freezing point depression of a solvent when a known amount of the solute is dissolved in it. This process is called cryoscopy.

NOTE:

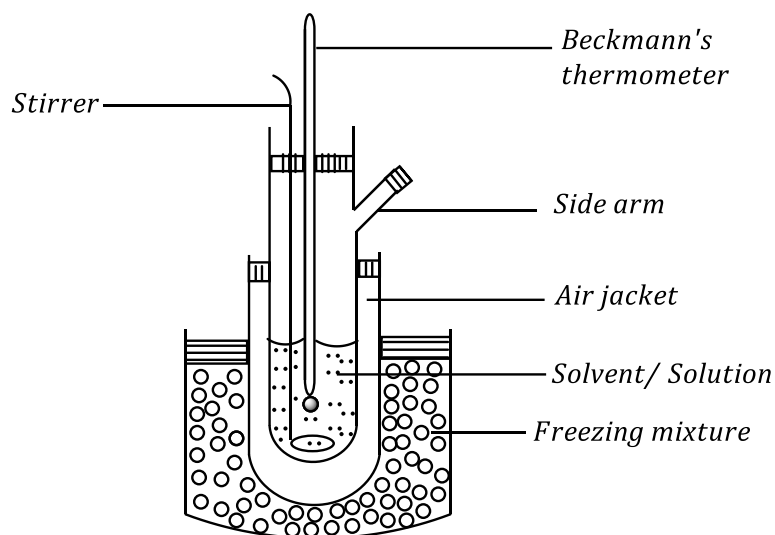
- One advantage of freezing point depression method over boiling point elevation method is that the freezing point method is less affected by pressure unlike the boiling point method which depends majorly on atmospheric pressure.
- Depression in freezing point is not suitable for determination of relative molecular masses of polymers.

Polymers have got very high relative molar masses which cause a very small depression in freezing point (changes in temperature) which is difficult to measure using the thermometer. Since the depression in freezing point (a colligative property) is inversely proportional to the relative molecular mass, the relative molecular mass obtained is higher than the expected value.

Therefore, the relative molecular masses of polymers are accurately determined using osmotic pressure method.

Experimental determination of molar mass by freezing point depression method

Set up



Procedure:

- A known mass (a grams) of a pure solvent is placed in an inner tube with a side arm. It is fitted with a stirrer and a thermometer. The inner tube is then fitted into an empty tube to act as an air jacket. The air jacket is to prevent super cooling i.e. ensure uniform cooling.
- The whole set up is then placed in the freezing mixture that is kept stirred. The solvent is allowed to cool while being stirred. The constant/ steady temperature at which the solvent solidifies is noted as $T_1^{\circ}C$.
- The tube with the side arm is then removed from the air jacket and warmed to melt the solvent.

- A known mass (**b** grams) of the non-volatile solute is added to the solvent through the side arm and stirred to dissolve to form a solution. The solution is then put back in the air jacket.
- The solution is allowed to cool while stirring. The constant temperature $T_2^{\circ}\text{C}$ at which the solution solidifies is noted. This is the freezing point of the solution.

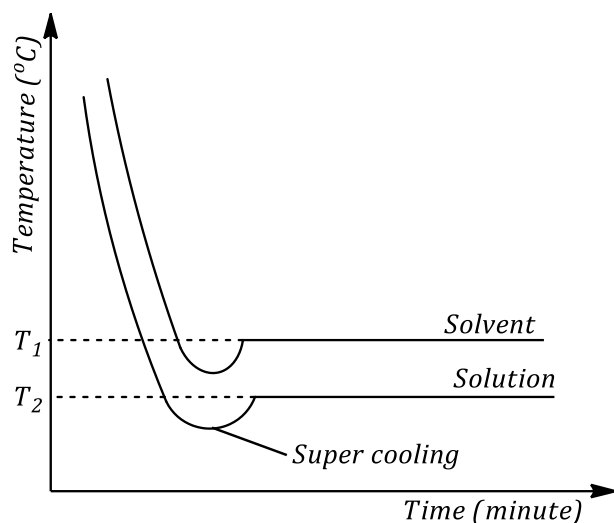
Treatment of results:

- Let K_f be the freezing point constant of the solvent
- The depression in freezing point, $\Delta T_f = (T_1 - T_2)^{\circ}\text{C}$
- a grams of solvent dissolves b grams of the solute
- 1000g of the solvent dissolves $\left(\frac{1000b}{a}\right)$ g of the solute
- ΔT_f is the depression in freezing point when 1000g of a solvent dissolves $\left(\frac{1000b}{a}\right)$ g of the solute
- K_f is the depression in freezing point when 1000g of a solvent dissolves $\left(\frac{1000b \times K_f}{a \times \Delta T_f}\right)$ g of the solute
- Where $\left(\frac{1000b \times K_f}{a \times \Delta T_f}\right)$ is the relative molecular mass of the solute

Alternative method (Using the cooling curve):

Procedure

- ❖ A known mass of a solvent (**a** g) is placed in the inner tube and directly put in the freezing mixture.
- ❖ The solvent is stirred constantly and its temperature is recorded at regular intervals of time until it solidifies at a constant temperature, $T_1^{\circ}\text{C}$.
- ❖ The inner tube is then removed from the freezing mixture and the solid is melted by heating.
- ❖ A known mass of the solute (**b** g) is added to the solvent, stirred to dissolve and placed back into the freezing mixture.
- ❖ The solution is constantly stirred and its temperature recorded at regular intervals of time until it solidifies at a constant temperature, $T_2^{\circ}\text{C}$.
- ❖ A graph of temperature against time is plotted for the pure solvent and the solution on the same axes.



Treatment of results

- Let K_f be the freezing point constant of the solvent
- The depression in freezing point, $\Delta T_f = (T_1 - T_2)^{\circ}\text{C}$
- a grams of solvent dissolves b grams of the solute
- 1000g of the solute dissolves $\left(\frac{1000b}{a}\right)$ g of the solute
- ΔT_f is the depression in freezing point when 1000g of a solvent dissolves $\left(\frac{1000b}{a}\right)$ g of the solute
- K_f is the depression in freezing point when 1000g of a solvent dissolves $\left(\frac{1000b \times K_f}{a \times \Delta T_f}\right)$ g of the solute
- Where $\left(\frac{1000b \times K_f}{a \times \Delta T_f}\right)$ is the relative molecular mass of the solute

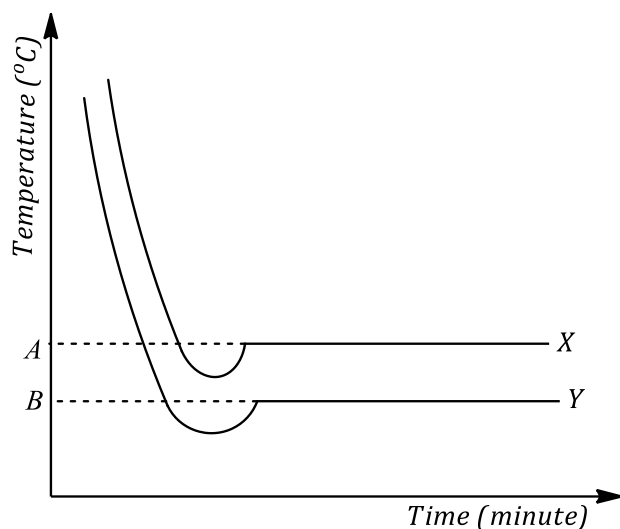
NOTE: One advantage of freezing point depression method over boiling point method is that the freezing point method is less affected by pressure unlike the boiling point method which majorly depends on atmospheric pressure.

Applications of freezing point depression

- Preventing melting ice from refreezing
- Making ice cream.
- Determining the formulas masses of non-volatile solutes

Examples:

1. The cooling curves of a solution containing 1.2g of sulphur in 20g of carbon disulphide are shown in the figure below.



- (a) Identify the curves X and Y.

Solution

X: cooling curve for pure carbon disulphide.

Y: cooling curve for the solution

- (b) State what is represented by the points A and B.

Solution

A: Freezing point of pure carbon disulphide.

B: Freezing point of the solution.

- (c) Calculate the relative molecular mass of sulphur in carbon disulphide. (The freezing point depression constant for carbon disulphide is $6.10^{\circ}\text{Cmol}^{-1}\text{kg}^{-1}$ and the freezing point depression of carbon disulphide was 1.43°C).

Solution

20g of carbon disulphide dissolves 1.2g of sulphur

1000g of carbon disulphide dissolves $\left(\frac{1000}{20} \times 1.2\right) = 60\text{g}$ of sulphur

Depression in freezing point, $\Delta T_f = 1.43^{\circ}\text{C}$

1.43°C is a depression caused by 60g of sulphur.

6.10°C is the depression caused by $\left(\frac{6.10}{1.43} \times 60\right) = 256\text{g}$ of sulphur.

Therefore, the relative molar mass of sulphur is 256

2. A solution of 0.50g of ethanoic acid in 50g of benzene freezes at 5.05°C . Determine the molar mass of ethanoic acid. (Freezing point of benzene is 5.50°C and K_f for benzene is $5.12^{\circ}\text{Cmol}^{-1}\text{Kg}^{-1}$).

Solution

50g of benzene dissolves 0.50g of ethanoic acid

1000g of benzene dissolves $\left(\frac{1000}{50} \times 0.50\right) = 10\text{g}$ of ethanoic acid

Depression in freezing point, $\Delta T_f = (5.50 - 5.05) = 0.45^\circ\text{C}$

0.45°C is a depression caused by 10g of ethanoic acid

5.12°C is the depression caused by $\left(\frac{5.12}{0.45} \times 10\right) = 113.78$

Therefore, the molar mass of ethanoic acid is 114g

3. 15g of compound R when dissolved in 300g of water causes the solution to freeze at -0.34°C . Determine the relative molecular mass of compound R. (K_f of water is $1.86^\circ\text{Cmol}^{-1}\text{kg}^{-1}$).

Solution

300g of water dissolves 15g of R

1000g of water dissolves $\left(\frac{1000}{300} \times 15\right) = 50\text{g}$ of R

Depression in freezing point, $\Delta T_f = 0 - (-0.34) = 0.34^\circ\text{C}$

0.34 is a freezing point depression caused by 50g of R

1.86°C is the freezing point depression caused by $\left(\frac{1.86}{0.34} \times 50\right) = 273.5$

Therefore, the relative molecular mass of compound R is 274

4. Determine the freezing point of a solution containing 0.30g of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, dissolved in 60g of water. (The freezing point constant for water is $1.86^\circ\text{Cmol}^{-1}\text{kg}^{-1}$).

Solution

60g of water dissolves 0.30g of glucose

1000g of water dissolves $\left(\frac{1000}{60} \times 0.30\right) = 5.00\text{g}$

Rfm of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$; $= (12 \times 6) + (1 \times 12) + (16 \times 6) = 180$

180g of glucose causes a depression of 1.86°C

5.00g of glucose causes a depression of $\left(\frac{5.00}{180} \times 1.86\right) = 0.052^\circ\text{C}$

Freezing point of solution $= (0 - 0.052) = -0.052^\circ\text{C}$

5. 5.0g of a non-volatile solute P when dissolved in 250g of benzene lowered the freezing point of benzene by 0.40°C . Determine the molar mass of the solute. (K_f for benzene is $5.12^\circ\text{Cmol}^{-1}\text{Kg}^{-1}$).

Solution

250g of benzene dissolves 5.0g of P

1000g of benzene will dissolve $\left(\frac{1000}{250} \times 5.0\right) = 20g$ of P

Freezing point depression, $\Delta T_f = 0.40^\circ C$

$0.40^\circ C$ is the freezing point depression caused by 20g of P

$5.12^\circ C$ is the freezing point depression caused by $\left(\frac{5.12}{0.40} \times 20\right) = 256$

The relative molecular mass of solute P is 256

6. A solution contains 1.80g of naphthalene in 3.0g of camphor. Calculate the melting point of the solution. (the relative molecular mass of naphthalene = 128; Melting point of pure camphor = $177^\circ C$; The freezing point constant, K_f for camphor = $40^\circ C$ per mole per 100g).

Solution

3.0g of camphor dissolves 1.8g of naphthalene.

100g of camphor dissolves $\left(\frac{100 \times 1.8}{3}\right) = 60g$.

128g of Naphthalene depresses freezing point by $40^\circ C$.

60g of naphthalene depresses freezing point by $\left(\frac{60 \times 40}{128}\right)^\circ C = 18.75^\circ C$

Freezing point, $\Delta T_f = (177 - 18.75) = 158.25^\circ C$.

Therefore, the melting point of the solution is $158.25^\circ C$.

7. 24.0g of a non-volatile solute Q is dissolved in 500g of water. Calculate the freezing point of the solution given the molar mass of non-volatile solute Q is 241. (K_f of water is $1.86^\circ C \text{ mol}^{-1} \text{ kg}^{-1}$).

Solution

500g of water dissolves 24.0g of Q

1000g of water dissolves $\left(\frac{1000 \times 24.0}{500}\right) = 48g$.

241g of Q causes a freezing depression of $1.86^\circ C$

48g of water will cause a depression in freezing point of $\left(\frac{48}{241} \times 1.86\right) = 0.37^\circ C$

$T_{\text{solution}} = (0 - 0.37) = -0.37$

The freezing point for the solution is $-0.37^\circ C$

8. An organic compound **W** contains 22.8% N, 28% O, 8.5% H and the rest carbon.

(a) Calculate the empirical formula of **W**.

Solution

$$\text{Mass of C} = 100 - (22.8 + 28 + 8.5) = 40.7$$

Elements	C	H	N	O
% composition	40.7	8.5	22.8	28
Moles	$\frac{40.7}{12}$	$\frac{8.5}{1}$	$\frac{22.8}{14}$	$\frac{28}{16}$
(Dividing by atomic number)	=3.392	=8.5	=1.629	=1.75
Mole ratio	$\frac{3.392}{1.629}$	$\frac{8.5}{1.629}$	$\frac{1.629}{1.629}$	$\frac{1.75}{1.629}$
(Dividing by the smallest quotient)	=2	=5	=1	=1

Empirical formula of **W** is C_2H_5NO

- (b) 0.5g of **W** dissolves in 80g of water forming a solution that freezes at -0.197°C . Calculate the molecular formula of **W**. (Cryoscopic constant for water $= 1.86^\circ\text{C mol}^{-1}$ per 1000g of water).

Solution

80g of water dissolve 0.5g of **W**

$$1000\text{g of water dissolves } \left(\frac{0.5}{80} \times 1000\right) = 6.25$$

$$\Delta T_f = 0 - (-0.197) = 0.197^\circ\text{C}$$

0.197°C is the freezing point depression caused by 6.25g of **W**

$$1.86^\circ\text{C is the freezing point depression caused by } \left(\frac{1.86}{0.197} \times 6.25\right) = 59$$

Molar mass of **W** = 59g

$$[C_2H_5NO]n = 59$$

$$[(12 \times 2n) + 5n + 14n + 16n] = 59$$

$$59n = 59; n = 1$$

The molecular formula of **W** is C_2H_5NO

- (c) When **W** was refluxed with potassium hydroxide, ethanoic acid and ammonia was produced. Identify **W**.

Solution

W is ethanamide, CH_3CONH_2

9. A compound **Q** contains 76.32% carbon, 6.38% hydrogen and the rest being oxygen. A solution of **Q** in water is acidic but does not liberate carbon dioxide from carbonates.

A solution of 1.50 g of **Q** in 20.90 g of benzene freezes at 1.3°C while pure benzene freezes at 5.50°C. Determine the;

(a) determine the empirical formula of **Q**.

(b) the molecular formula and write the structural formula of **Q**. (*K_f of benzene is 5.49°C per 1000 g mol⁻¹*)

Solution

(a) %age Mass of O = 100 – (76.32 + 6.38) = 17.3

Elements	C	H	O
% composition	76.32	6.38	17.3
Moles	$\frac{76.32}{12}$	$\frac{6.38}{1}$	$\frac{17.3}{16}$
(Dividing by atomic number)	=6.36	=6.38	=1.08125
Mole ratio	$\frac{6.36}{1.08125}$	$\frac{6.38}{1.08125}$	$\frac{1.08125}{1.08125}$
(Dividing by the smallest quotient)	=6	=6	=1

Empirical formula of Q is C_6H_6O

(b) 20.90g of Benzene dissolve 1.5g of Q

$$1000g \text{ of Benzene dissolves } \left(\frac{1.5}{20.9} \times 1000 \right) = 71.77g$$

$$\Delta T_f; = (5.5 - 1.3) = 4.2^\circ C$$

4.2°C is the freezing point depression caused by 71.77g of Q

$$5.49^\circ C \text{ is the freezing point depression caused by } \left(\frac{5.49}{4.2} \times 71.77 \right) = 93.8 \cong 94$$

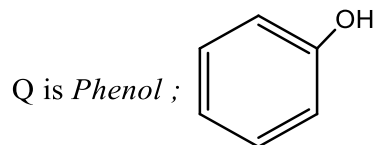
Molar mass of Q = 94g

$$[C_6H_6O]n = 94$$

$$[(12 \times 6n) + (1 \times 6n) + 16n] = 94$$

$$94n = 94; n = 1$$

The molecular formula of W is C_6H_6O



Task

- 0.55g of nitrobenzene in 22g of ethanoic acid depresses the freezing point of ethanoic acid by 0.79°C . Calculate the relative formula mass of nitrobenzene. (K_f for ethanoic acid is $3.9^{\circ}\text{C mol}^{-1}\text{Kg}^{-1}$). [Answer= 123]
- Calculate the melting point of a solution made by dissolving 0.36 g of naphthalene C_{10}H_8 in 6.0 g of camphor. The melting point of camphor is 177°C and the K_f for camphor is 40°C for 1 mole in 1000 g.
- Two aqueous solutions containing 2.0g of ethanamide, CH_3CONH_2 in 50g of water and 6.0g of a non-electrolyte Z in 100g of water freeze at the same temperature. Calculate;
 - Freezing point of the solution. (K_f for water is $18.6^{\circ}\text{C mol}^{-1}$ per 100g).
 - Molar mass of Z. [Answer= 89]
- On dissolving 0.25 g of a non-volatile substance in 30 cm^3 benzene (density 0.8 g / cm^3), its freezing point decreases by 0.40°C . Calculate the molecular mass of non-volatile substance. ($K_f = 5.12^{\circ}\text{C kg}^{-1}\text{ mol}^{-1}$). [Answer=133.33]
- The freezing point of pure benzene is 5.49°C , and its freezing point constant, $K_f = 5.0^{\circ}\text{C}$. A sample of a crystalline unknown was made up such that it contained 0.0187g of unknown per 1.000 g of benzene. The freezing point of the resulting solution was found to be 4.76°C . What was the molar mass M of the unknown? [Answer=130]
- The freezing point of pure benzene is 5.53°C . When 0.775g of an allotrope of phosphorous was dissolved in 50.0g of benzene the solution froze at 4.89°C . [K_f for benzene = $5.12^{\circ}\text{C mol}^{-1}\text{Kg}^{-1}$]
 - Calculate the molecular mass of phosphorous.
 - Deduce the molecular formula of phosphorous in benzene. [P=31]
- A solution of 3.136g of sulphur in 100g of naphthalene ($M_{pt.} 80.1^{\circ}\text{C}$) showed a lowering of freezing point of 0.830°C while a solution of 3.123g of iodine in 100g of naphthalene gave a depression of 0.848°C . If the molecular formula of iodine in naphthalene solution is I_2 , obtain that of sulphur. ($I = 127$). [Answer: S_8]
- The freezing point of a sample of pure benzene was found to be 5.481°C . A solution of 0.321g of naphthalene (C_{10}H_8) in 25g of benzene began to freeze at 4.971°C . A solution of 0.305g of benzoic acid in 25g of benzene began to freeze at 5.226°C . Calculate;
 - the K_f for 1000g of benzene. [Answer: $5.1^{\circ}\text{C mol}^{-1}\text{Kg}^{-1}$]
 - the R.F.M of benzoic acid in benzene. [Answer: 244]
- A compound Q contains 60.0% carbon, 13.3% hydrogen and the rest being oxygen.
 - Calculate the simplest formula of Q. [Answer: $\text{C}_3\text{H}_8\text{O}$]

(b) When 0.698g of Q was dissolved in 100g of a solvent, there was 0.19°C depression in freezing point of the solution. (K_f of the solvent = $1.63^\circ\text{C mol}^{-1}\text{kg}^{-1}$). Calculate;

- (i) the molecular mass of Q. [Answer: 60 g mol^{-1}]
 (ii) the molecular formula of Q. [Answer: $\text{C}_3\text{H}_8\text{O}$]

Graphical determination of relative molecular masses

This can be done in three ways i.e.

- ❖ Plotting a graph of freezing point against concentration
- ❖ Plotting a graph of freezing point depression against concentration.
- ❖ Plotting a graph of boiling point elevation against concentration.

A graph of freezing point depression against concentration.

The freezing point depression, ΔT_f is directly proportional to the number of moles, n of a non-volatile solute added in a given amount of a solvent.

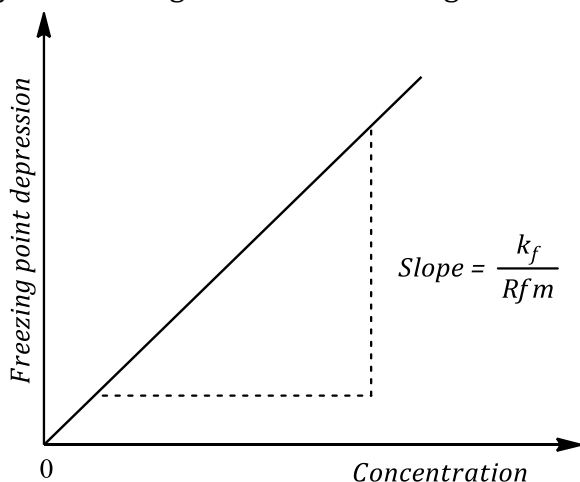
$$\Delta T_f \propto n$$

$$\Delta T_f = K_f n$$

$$\Delta T_f = K_f \frac{m}{Rfm}$$

$$\Delta T_f = \frac{K_f}{Rfm} \times m$$

Plotting a graph of freezing point depression (ΔT_f) against concentration (m) yields a straight line from the origin with a positive slope.



The slope of the graph is equal to $\frac{K_f}{Rfm}$.

Knowing the slope from the graph and the value of the freezing point constant (K_f), the relative molecular mass of the non-volatile solute can be determined.

A graph of freezing point against concentration.

The freezing point depression, ΔT_f is directly proportional to the number of moles, n of a non-volatile solute added in a given amount of a solvent.

$$\Delta T_f \propto n$$

$$(T_1 - T_2) \propto n$$

$$(T_1 - T_2) = K_f n$$

Where;

T_1 is the freezing point of the solvent and

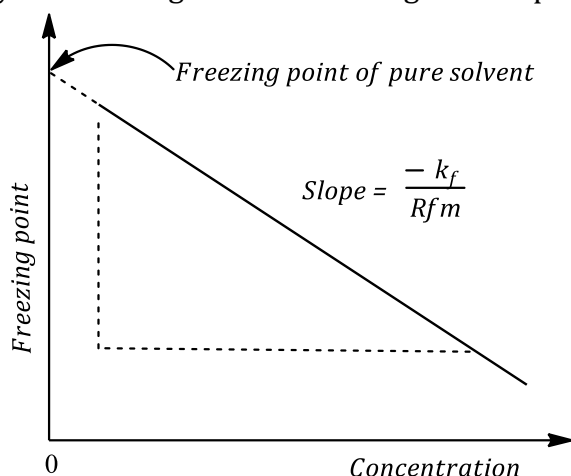
T_2 is the freezing point of the solution.

$$(T_1 - T_2) = K_f \frac{m}{Rfm}$$

$$T_2 = -K_f \frac{m}{Rfm} + T_1$$

$$T_2 = -\frac{K_f}{Rfm} \times m + T_1$$

Plotting a graph of freezing point of the solution (T_2) against concentration (m) yields a straight line with a negative slope.



The y-intercept gives the freezing point of a pure solvent (T_1) when the concentration is zero.

The slope of the graph is equal to $-\frac{K_f}{Rfm}$.

Knowing the slope from the graph and the value of the freezing point constant (K_f), the relative molecular mass of the non-volatile solute can be determined.

1. The table below shows the freezing point of various concentrations of a non-volatile solute D in water at 760mmHg.

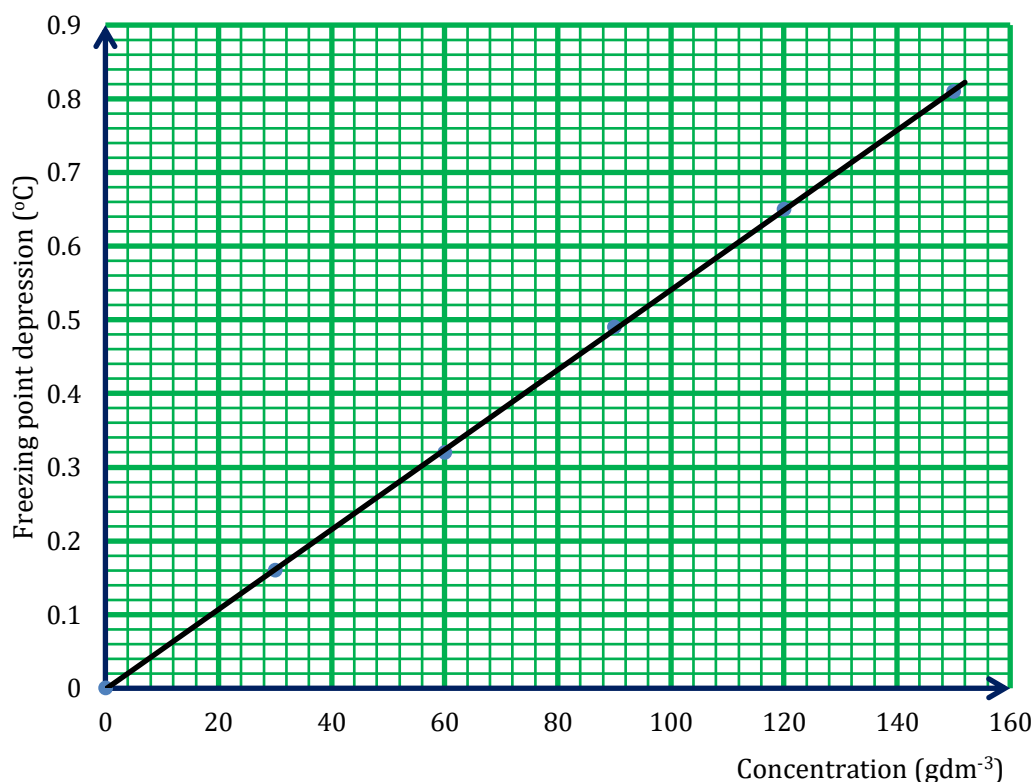
Concentration (gdm ⁻³)	0	30	60	90	120	150
Freezing point (°C)	0	-0.16	-0.32	-0.49	-0.65	-0.81

- (a) Plot a graph of freezing point depression against concentration.
 (b) Use the graph you have drawn to determine the relative molecular mass of D.
 (K_f for water = $1.86^\circ\text{Cmol}^{-1}\text{kg}^{-1}$).

Solution

Concentration (gdm^{-3})	0	30	60	90	120	150
Freezing point ($^\circ\text{C}$)	0	-0.16	-0.32	-0.49	-0.65	-0.81
Freezing point depression, ΔT_f ($^\circ\text{C}$)	0	0.16	0.32	0.49	0.65	0.81

- (a) A graph of depression in freezing point against concentration



- (b) From the graph, Slope = $0.0054^\circ\text{Cg}^{-1}\text{dm}^3$

$$\text{Slope} = \frac{K_f}{M_r}$$

$$0.0054 = \frac{1.86}{M_r}, \quad M_r = 344.44$$

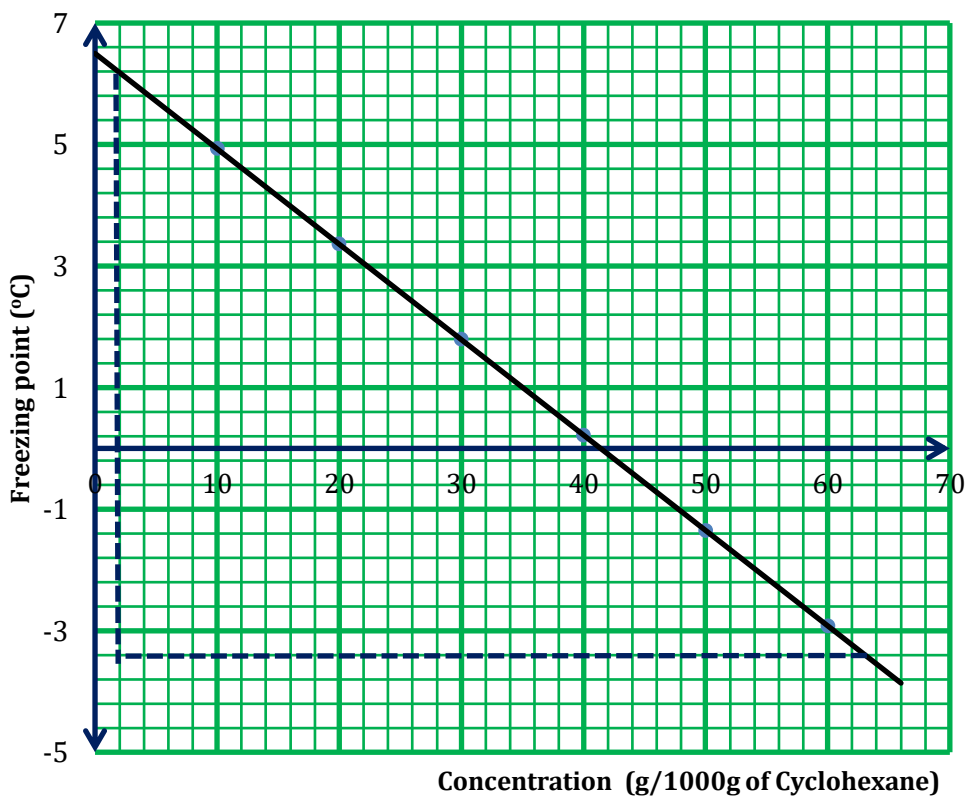
2. The freezing points of solutions of various concentrations of naphthalene in cyclohexane at 760 mmHg are shown in the table below.

Concentration (g/1000g of cyclohexane)	10	20	30	40	50	60
Freezing point ($^\circ\text{C}$)	4.93	3.36	1.79	0.22	-1.35	-2.92

- Plot a graph of freezing point against concentration.
- Use the graph to determine the freezing point of pure cyclohexane.
- Determine the slope of the graph and use it to determine the relative molecular mass of naphthalene. (K_f for cyclohexane = $20.1\text{ }^{\circ}\text{C}/\text{mol}/1000\text{g}$).

Solution

- A graph of freezing point against concentration



- The Y-intercept gives the freezing point.
From the graph, the freezing point is 6.4°C
- Slope of the graph is -0.157

$$\text{Slope} = \frac{-K_f}{Rfm}$$

$$-0.157 = \frac{-20.1}{Rfm}$$

$$Rfm = 128.03$$

The relative molecular mass of naphthalene is 128.03

Task

- The table below shows the freezing points of various solutions of cane sugar in solvent X.

Mass of cane sugar (g per 1000g of solvent X)	26	42	66	78	118	148	173
Freezing point (°C)	5.11	4.87	4.51	4.33	3.73	3.28	2.90

(a) Plot a graph of freezing point against mass of cane sugar and use the graph to determine the;

(b) Freezing point of solvent X. [Hint; *It is the intercept value, 5.50*]

(c) Freezing point constant for solvent X given that the RMM of cane sugar is 342. [Hint; $\text{slope} = \frac{-K_f}{Rfm}$, $\text{slope} = -0.015$; $K_f = 5.13$]

A graph of boiling point elevation against concentration.

The boiling point elevation, ΔT_b is directly proportional to the number of moles, n of a non-volatile solute added in a given amount of a solvent.

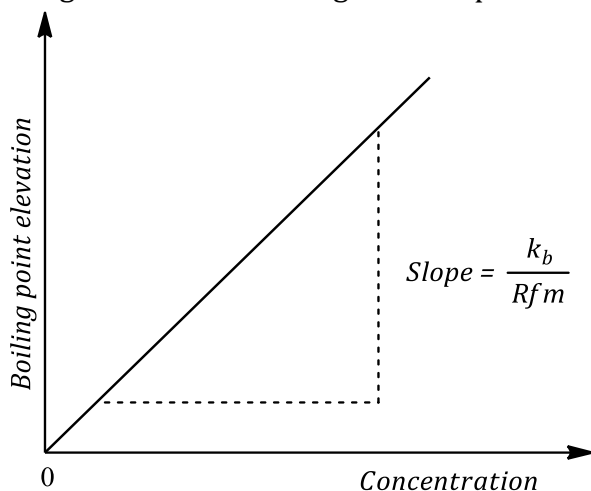
$$\Delta T_b \propto n$$

$$\Delta T_b = K_b n$$

$$\Delta T_b = K_b \frac{m}{Rfm}$$

$$\Delta T_b = \frac{K_b}{Rfm} \times m$$

Plotting a graph of boiling point elevation (ΔT_b) against concentration (m) yields a straight line from the origin with a positive slope.



The slope of the graph is equal to $\frac{K_b}{Rfm}$.

Knowing the slope from the graph and the value of the boiling point constant (K_b), the relative molecular mass of the non-volatile solute can be determined.

Task

1. The table below shows how the boiling point of a certain ketone changes with addition of different concentrations of a non-volatile solute W at constant temperature.

Concentration (g l ⁻¹)	0.0	4.0	8.0	10.0	14.0	16.0
Boiling point (°C)	80.00	80.06	80.15	80.18	80.21	80.24

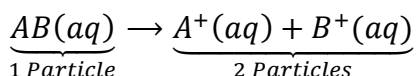
- (a) Plot a graph of boiling point elevation against concentration.
 (b) Use your graph to determine the molecular mass of W. (boiling point elevation constant of the ketone is $2.28^{\circ}\text{C mol}^{-1}\text{kg}^{-1}$)

Anomalous values of relative molecular mass.

Colligative property like elevation of boiling point, depression of freezing point can be used to determine the relative molecular mass. Anomalous values of molar masses are obtained if the solute associates or dissociates in solution.

Effects of dissociation/ ionisation of a solute in a solvent.

Dissociation refers to the splitting of a single ionic solute into two or more solute particles. Consider the ionisation/ dissociation of a solute AB in the solvent;



If a solute dissociates in a solvent, it increases the number of solute particles in the solution. Since depression in freezing point or elevation in boiling point increases with increase in the number of solute particles, the relative molecular mass of the solute will be lower than the true value of relative molecular mass since ΔT_f or $\Delta T_b \propto n \propto \frac{1}{M_r}$.

The freezing point depression of a 0.1M sodium chloride solution is nearly twice that of 0.1M glucose solution.

Sodium chloride is a strong electrolyte which completely dissociates into its ions. One molecule of sodium chloride gives two particles on dissociation, increasing on the number of solute particles. Glucose being a non-electrolyte, does not dissociate and remains as a single molecule in solution.

Example

1. A solution containing 1.4g of cadmium(II) iodide in 10.0g of water boiled at 100.99°C . (K_b of water $= 0.52^{\circ}\text{C mol}^{-1}\text{kg}^{-1}$).
 (a) Calculate the relative formula mass of cadmium(II) iodide in water.

Solution

10.0g of water dissolve 1.4g of cadmium(II) iodide.

$$\begin{aligned} 1000\text{g of water dissolves } \left(\frac{1.4}{10.0} \times 1000 \right) \text{ of cadmium(II) iodide.} \\ = 140\text{g} \end{aligned}$$

$$\Delta T_b; = (100.99 - 100) = 0.99^\circ\text{C}$$

0.99°C is the elevation caused by 140g of cadmium(II) iodide.

$$0.52^\circ\text{C} \text{ is the elevation caused by } \left(\frac{0.52}{0.99} \times 140\right) = 73.5\text{g}$$

Relative formula mass of cadmium(II) iodide = 73.5

(b) Comment on your answer in (a) above.

Solution

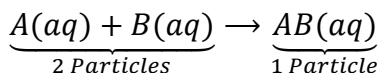
The relative formula mass of cadmium(II) iodide is less than (a fifth) the real value (366) because cadmium(II) iodide dissociates in water.

Task

- (a) A 0.01M aqueous solution of sodium chloride has the same freezing point as a 0.02M aqueous solution of glucose. Briefly explain this observation.
- (b) A solution containing 4.5g of solute B in 125g of water freezes at -0.372°C . (K_f for water = $1.86^\circ\text{Cmol}^{-1}\text{kg}^{-1}$).
- (i) Calculate the formula mass of B.
- (ii) How would you expect the formula mass of B to change if it ionises in water? Explain your answer.

Effects of association of a solute in a solvent

Association refers to the joining of two or more solute particles to form a single solute in solution. Consider substance A and B which undergo association i.e.



From the above, association decreases the number of particles by half making the colligative property to be half its value calculated in the absence of association.

This increases the relative molecular mass by twice the true value e.g. the molecules that form dimers like beryllium chloride, aluminium chloride or molecules which associate through intermolecular hydrogen bonds like carboxylic acids.

Example

- The boiling point elevation of 0.30g of ethanoic acid in 100g of benzene is 0.0633°C .
 - Calculate the molar mass of acetic acid. (K_b of Benzene is $2.53^\circ\text{CKg}^{-1}\text{Mol}^{-1}$).
 - What conclusion can you draw about the molecular state of the solute in the solution?

Solution

100g of Benzene dissolves 0.30g of ethanoic acid.

$$1000\text{g of Benzene will dissolve } \left(\frac{1000 \times 0.30}{100}\right) = 3.0\text{g}$$

0.0633°C is the elevation caused by 3g of ethanoic acid.

2.53°C will be the elevation caused by $\left(\frac{2.53 \times 3.0}{0.0633}\right) = 119.9$

Rfm of Ethanoic acid in Benzene is $\cong 120$

The actual *Rfm* of ethanoic acid, $CH_3COOH = (12 \times 2) + (4 \times 1) + (16 \times 2) = 60$

The relative molecular mass of ethanoic acid in Benzene is twice the true value. The molecules of the ethanoic acid associate in Benzene through intermolecular hydrogen bonds forming dimers.

2. 0.72g of an organic acid **M** was dissolved in 80g of water and the resultant solution had a freezing point of -0.14°C. When 2.9g of the same compound **M** was dissolved in 11.1g of benzene, C_6H_6 , the freezing point of benzene was depressed by 5.99°C. (K_f for benzene is $5.5^\circ C kg^{-1} mol^{-1}$, K_f for water is $1.86^\circ C mol^{-1} kg^{-1}$)

(a) Calculate the apparent molecular mass of M in;

(i) Water

Solution

80g of water dissolves 0.72g of M.

1000g of water will dissolve $\left(\frac{1000 \times 0.72}{80}\right) = 9.0g$

Freezing point depression, $\Delta T_f = 0 - (-0.14) = 0.14^\circ C$

0.14°C is the freezing point depression caused by 9.0g of M.

1.86°C is the freezing point depression caused by $\left(\frac{1.86 \times 9.0}{0.14}\right) = 119.57$

Rfm of M in water is $\cong 120$

(ii) Benzene

Solution

11.1g of benzene dissolves 2.9g of M.

1000g of benzene will dissolve $\left(\frac{1000 \times 2.9}{11.1}\right) = 261.26g$ of M

Freezing point depression, $\Delta T_f = 5.99^\circ C$

5.99°C is the freezing point depression caused by 261.26g of M.

5.5°C is the freezing point depression caused by $\left(\frac{5.5 \times 261.26}{5.99}\right) = 239.89$

Rfm of M in benzene is $\cong 240$

(b) Explain why the molecular mass of M differ in the two solvents.

Solution

The molecules of M associates in benzene through intermolecular hydrogen bonds forming dimers, making the relative molecular mass to be twice the true value.

Task

1. A solution containing 0.368g of methanoic acid in 50g benzene freezes at 5.093°C.
 (a) Calculate the relative molecular mass of methanoic acid. [The freezing point of pure benzene is 5.533°C and $K_f = 5.5^\circ\text{C mol}^{-1}\text{Kg}^{-1}$].
 (b) Comment on the value obtained in part (a) above.
2. Relative formula mass of aluminium chloride when determined by a method of depression of freezing point of benzene was found to be 267. Briefly explain.

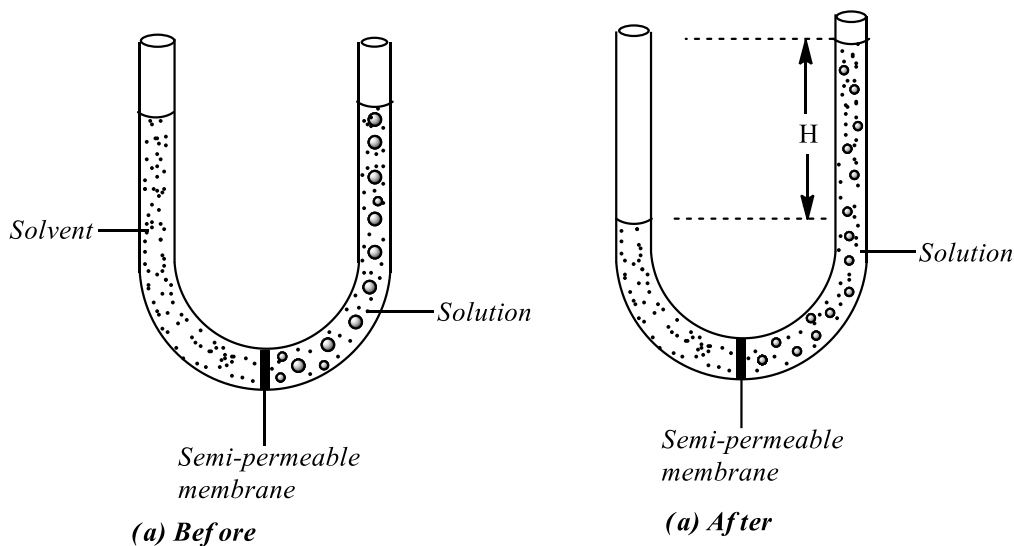
Osmosis and Osmotic pressure of a solution.

When a semipermeable membrane separates a solvent from the solution, the solvent molecules tend to pass to the solution. This is called osmosis.

By definition, Osmosis is the process (tendency) of flow of solvent molecules through a semipermeable membrane from the solvent side to the solution side or from solution of lower concentration to solution of higher concentration.

To prevent such kind of movement, pressure can be applied to the solution and this pressure is called the osmotic pressure of the solution because it is applied on the solution side. By definition;

Osmotic pressure of a solution is that pressure which must be exerted/ applied on the solution to prevent any net movement of the solvent between the solution and its pure solvent, when these are separated by a semi-permeable membrane at a given temperature.



The pressure that must be applied to the solution side to prevent it from rising in the tube is the osmotic pressure. It is also equal to the hydrostatic pressure of the liquid column of the height, H.

NOTE: A semipermeable membrane is a thin layer of material which permits the passage of molecules but not solid particles.

Laws of osmotic pressure;

From experiments, Van't Hoff (1885) established laws of pressure which closely resemble the gas laws.

1. Osmotic pressure of a dilute solution is directly proportional to the concentration of the solute in a given amount of a solvent provided temperature is constant.

$$\pi \propto C$$

But $C \propto \frac{1}{V}$, Where V is the volume of the solution.

$$\Rightarrow \pi \propto \frac{1}{V} \text{ (Compare with } P \propto \frac{1}{V} \text{)}$$

$$\pi V = k \dots \dots \dots (i)$$

2. The osmotic pressure of a solution is directly proportional to the absolute temperature provided concentration is constant.

$$\pi \propto T$$

$$\Rightarrow \pi = kT$$

$$\frac{\pi}{T} = k \dots \dots \dots (ii)$$

Combining laws 1 and 2, we have;

$$\pi \propto \frac{T}{V}$$

$$\pi V = RT \dots \dots \dots (iii)$$

Equation (iii) is for one mole of a solution. For 'n' moles, the equation becomes;

$$\pi V = nRT \dots \dots \dots (iv)$$

The above equation bears a striking resemblance to the ideal gas equation; $PV = RT$.

Equation (iv) is called the Van't Hoff equation. Van't Hoff pointed out that the solute in a dilute solution behave similarly to the ideal gas since its molecules are very widely dispersed throughout the large volume of the solvent.

NOTE

- ❖ From experiments, the constant for osmotic pressure is approximately equal to the universal gas constant, R of ideal gas i.e. $R = 8.314$ or 0.082 .
- ❖ Since the constant is the same as that of an ideal gas, then it means that; one mole of any solute dissolved in 22.4 dm^3 of a solvent at a temperature of 273K exerts an osmotic pressure equal to 1 atmospheres or 760 mmHg or 101325 Pa .

The relationship $\pi V = nRT$ is valid only when;

- ❖ the solute particles have not dissociated or associated in the solution,
- ❖ solute is non-volatile,
- ❖ there is no chemical reaction between the solute and the solvent molecules,
- ❖ the solution is dilute

The expression $\pi V = nRT$ above can be used to work out the relative molecular mass of a non-volatile solute dissolved in a given volume of a solvent.

Examples:

1. The osmotic pressure of a solution containing 42g of solute Y in 100 cm³ of a solvent is 5.62×10^5 Pa at 20°C. Calculate the relative molecular mass of Y.

Solution

$$\begin{aligned}\pi V &= nRT \\ \pi V &= \frac{m}{Rfm} RT \\ Rfm &= \frac{m}{\pi V} RT \\ Rfm &= \frac{42 \times 8.314 \times 293}{5.62 \times 10^5 \times (100 \times 10^{-6})} \\ &= 1820\end{aligned}$$

2. The osmotic pressure of a solution containing 1.24% of a polymer is 3.1×10^{-3} atm at 25°C. Determine the relative molecular mass of the polymer.

Solution

NOTE: 1.24% means 1.24g in 100 cm³ of a solvent.

$$\begin{aligned}\pi V &= nRT \\ \pi V &= \frac{m}{Rfm} RT \\ Rfm &= \frac{1.24 \times 0.082 \times 298}{3.1 \times 10^{-3} \times (100 \times 10^{-3})} = 97,744\end{aligned}$$

3. A solution containing 5.0g of synthetic rubber (polyneoprene) in 200 cm³ of Benzene is found to have an osmotic pressure of 34kPa at 17°C.
(a) Determine the molar mass of polyneoprene.

Solution

$$\begin{aligned}\pi V &= nRT \\ \pi V &= \frac{m}{Rfm} RT \\ Rfm &= \frac{5.0 \times 8.314 \times 290}{34000 \times (200 \times 10^{-6})} = 1773\end{aligned}$$

- (b) The monomer of the polymer above is 2-chlorobuta-1,3-diene. Determine the number of monomers in the polymer.

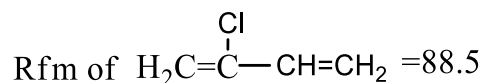
Solution

NOTE: The relative molecular mass of a polymer is theoretically an integral multiple of that monomer i.e. $RMM \text{ of polymer} = n \times RMM \text{ of monomer}$.

From which;

$$n = \frac{RMM \text{ of polymer}}{RMM \text{ of monomer}}$$

Where n is the number of monomers.



$$\text{Number of monomers} = \left(\frac{1773}{88.5} \right) = 20$$

Task

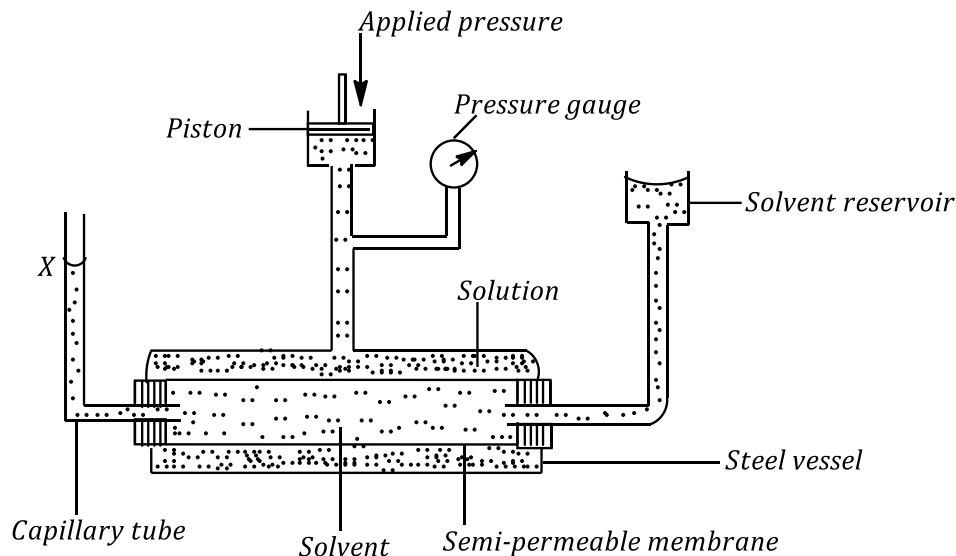
- 0.50 g polystyrene, was dissolved in 250.0 cm³ of water to produce a solution whose osmotic pressure is 60.0 Pa at 27.0°C. Determine the molar mass of the polystyrene, hence calculate the number of styrene molecules in the polymer.
[Ans; $Rfm = 83140$; 800 monomers]
- A solution is made up so as to have a concentration of 1.428g of solute per dm³ in water. The osmotic pressure exerted by the solvent across a semipermeable membrane at 298K was 0.224 atm. What is the molar mass of the solute?
- The osmotic pressure of a solution containing 4g per litre of a polymer is 65Pa at 298K. Calculate the molecular mass of the polymer.
- Calculate the osmotic pressure in Pascal exerted by a solution prepared by dissolving 1.0g of polymer of molar mass 185,000 in 450 cm³ of water at 37°C.
[Answer = 30.98Pa]
- The osmotic pressure of a solution containing 1.4g of a polymer X per 100 cm³ of a solution is 1200Nm⁻² at 25°C. Calculate the relative molecular mass of X.

Importance of osmotic pressure;

- Plants use osmotic pressure to achieve mechanical stability.
- Purification of water/ Desalination of seawater using reverse osmosis. In reverse osmosis, pressure greater than the osmotic pressure is applied to the solution side.
- Used in the process of excretion e.g. filtration in the kidney, gaseous exchange.
- Used in the uptake of water by plants through the roots.

Experimental determination of relative molecular mass of a solute using osmotic pressure method.

Set up



Procedure

- A porous pot (to act as a semipermeable membrane) carrying a capillary tube on one end and a reservoir at the other end is filled with a pure solvent and enclosed in a gun metal casing (steel vessel).
- A known mass of a solute (**a g**) is dissolved in a known volume of a pure solvent (**V cm³**) to form a solution of known concentration.
- The solution is then placed between the porous pot and the metal casing (steel vessel).
- The metal case carrying the piston is connected to the pressure gauge.
- When the setup is left to stand, the level of the solvent in the capillary tube reduces.
- Pressure is slowly applied on the solution via the piston until the level of the solvent balances at point **X**.
- The pressure is noted and recorded as the osmotic pressure of the solution.
- The temperature of the solution when the level of the solution balances at point **x** is also noted and recorded.
- The molecular mass of solute can be calculated from the formula;

$$\pi V = \frac{m}{Rf m} RT$$

NOTE

Depression in freezing point and elevation in boiling point methods are not suitable for determining relative molecular masses of polymers like plastics, proteins.

Polymers have very high relative molecular masses. This causes very small changes in temperature which are difficult to measure on the thermometer. Since a colligative property is inversely proportional to the relative molecular mass i.e. ΔT_f or $\Delta T_f \propto \frac{1}{M_r}$, the relative molecular mass that will be obtained will be higher than the true value.

With osmotic pressure method, the advantage is that measurements can be made at room temperature since many naturally occurring substances such as proteins are temperature sensitive and undergo changes at 0°C and 100°C.

Therefore, relative molecular masses are determined using osmotic pressure method.

Graphical determination of molar masses using osmotic pressure.

Using; $\pi V = \frac{m}{Rfm} RT$

$$\pi = \left(\frac{m}{v}\right) \frac{RT}{Rfm}$$

But $\left(\frac{m}{v}\right) = C$, concentration

$$\pi = \left(\frac{RT}{Rfm}\right) \times C$$

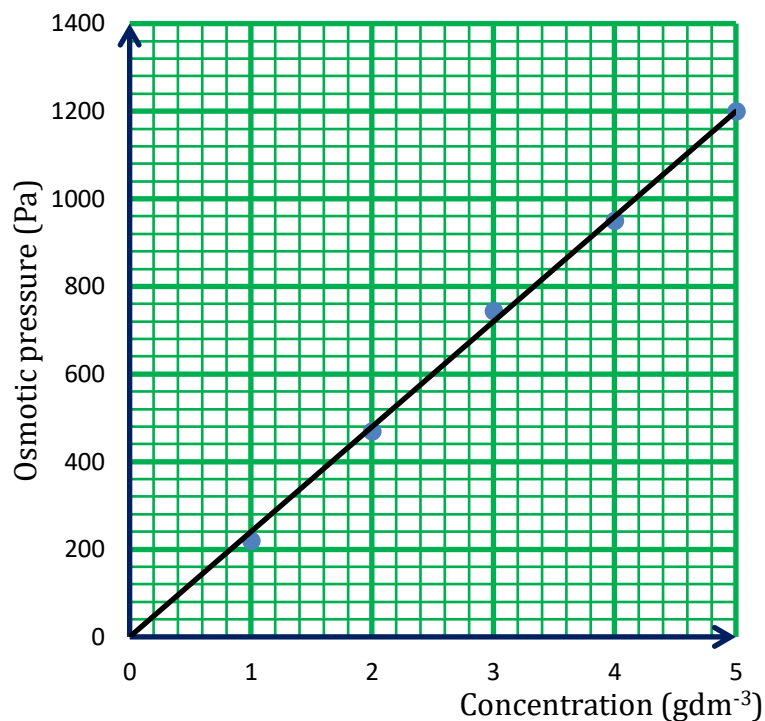
Plotting a graph of osmotic pressure (π) against concentration (C) yields a straight line from the origin with the slope/ gradient equal to $\frac{RT}{Rfm}$

Example;

The osmotic pressure at 25°C for various concentrations of enzyme **Q** in water is given in the table below.

Osmotic pressure (Pa)	Concentration (gdm ⁻³)
220	1.0
470	2.0
745	3.0
950	4.0
1200	5.0

Plotting a graph of osmotic pressure against concentration for the above data yields the graph below;



The slope of the graph is 116.31

$$\text{Slope} = \frac{RT}{Rfm}$$

$$\frac{RT}{Rfm} = 116.31$$

$$\text{But } 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$$

$$Rfm = \frac{(8.314 \times 298)}{(116.31 \times 10^{-3})}$$

$$Rfm = 21,301.45$$

Task

- The table below show the data of how osmotic pressure of solution varies with the amount of polymer Y.

Osmotic pressure/ Nm^{-2}	1.40	4.20	8.40	12.60	15.40	17.50
Concentration gdm^{-3}	49.6	148.7	297.3	446.0	545.1	619.4

(a) Plot a graph of osmotic pressure against concentration

(b) Use the graph to determine the molecular mass of the polymer.

[Answer: 70004]

- (c) The molecular mass of the monomer of Y is 28. Determine the number of monomer units in Y.
[Answer: 2500 monomers]

Assignment

Question one

- Explain what is meant by the term osmotic pressure.
- State two factors that affect the osmotic pressure of a solution.
- Under what conditions are the osmotic pressure laws valid?
- The osmotic pressure of solutions of different concentrations measured at 298K for a polymer are given in the table below.

Osmotic pressure/Pa	Concentration/ gdm^{-3}
118	2.0
480	6.0
1000	10.0
1680	14.0

- Plot a graph of osmotic pressure against concentration.
- Using the graph you have drawn, calculate the molar mass of the polymer. ($R = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$).
[Answer: 1903 gmol^{-1}]

Question two

- A solution containing 1.5% of a polymer was found to have an osmotic pressure of 3.6×10^{-4} atmospheres at 25°C . Calculate the molecular mass of the polymer.
- Explain why in the determination of molecular mass of polymers, osmotic pressure is used instead of ebullioscopic and cryoscopic methods.

Question three

- Explain why the method of depression in freezing point is not suitable for determining the molecular mass of;
 - A polymer.
 - Ethanoic acid in benzene.
 - Phosphorous(V) oxide in water.
- The osmotic pressure of various concentrations of solute X in methyl benzene at 25°C is given in the table below.

Concentration (gdm^{-3})	1.0	2.0	3.0	4.0	5.0	6.0
Osmotic pressure (Nm^{-2})	23	37	53	75	92	109

- Plot a graph of osmotic pressure against concentration.
- Use the graph you have drawn to determine the molecular mass of X. ($R = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$).

Question four

3.4g of an organic compound **Q** on complete combustion produced 5.04 dm^3 of carbon dioxide and 2.70g of water at s.t.p. An aqueous solution of **Q** containing 2.8 g dm^{-3} has an osmotic pressure of 380 mmHg at 25°C . Calculate the:

- (a) empirical formula of **Q**.
- (b) molecular formula of **Q**.
- (c) **Q** burns with a sooty flame and reacts with sodium metal to form a gas that burns with a pop sound but **Q** has no effect on both litmus papers and hot acidified potassium dichromate. Identify **Q**.