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## Colligative properties

These are behaviors of solution which depend on the number of nonvolatile dissolved particles (lons, molecules, atoms etc.) other than the chemical nature of the solute.

They include:

1. Freezing point depression
2. elevation of boiling points
3. lowering of the vapor pressure
4. osmotic pressure

Application of Colligative properties
These properties are used in the determinations of molecular masses of substance.

## Trial 1

(i) Explain the term Colligative property.
(ii) State four Colligative properties of solution.

## 1. Depression of freezing point

When a nonvolatile solute dissolves in a solvent, the freezing point of the solution is lower than that of the solvent.

The difference between the freezing point of the solvent and solution is called freezing point depression, $\Delta \mathbf{t}$.

The depression of freezing point depends on the following rules.
(i) Depression of freezing point of a given mass of solvent is proportional to mass of a solute dissolved; i.e., the more solute dissolved in a solvent, the lower the freezing point of the solution and the bigger the freezing point depression.
(ii) The freezing point depression for a given mass of solvent is inversely proportional to the molecular mass of the solute.

Thus, when the mass ( m ) of a solute of relative molecular mass ( Mr ) dissolved in a given amount of solvent cause a freezing point depression ( $\Delta \mathrm{t}$ ) degrees Celsius
then $\quad \Delta t \propto m-----------------------------------\quad$ a

$$
\Delta \mathrm{t} \propto \frac{1}{M r}------------------------------------\quad \text { b }
$$

or $\quad \Delta \mathrm{t} \propto \frac{m}{M r}$
It follows that depression of freezing point is proportional to the number of moles of a solute and if the same number of moles were present for a different solute, in the same mass of solvent, the freezing point depression would be the same.

## Cryoscopic constant

From b,
$\Delta \mathrm{t}=\mathrm{K}_{\mathrm{F}}^{\mathrm{m} r}$
When $\mathrm{m}=\mathrm{Mr}, \Delta \mathrm{t}=\mathrm{K}_{\mathrm{f}}$
The constant of proportionality $K_{f}$ is called the cryoscopic constant of the solvent.

## Definition

Cryoscopic constant ( $\mathrm{K}_{\mathrm{f}}$ ) is the amount by which the freezing point of 1000 g of a solvent is lowered by 1 mole of solute; assuming rules $a$ and $b$ still hold at this concentrations.

The cryoscopic constants for commonly used solvents are

| Solvent | $\mathrm{K}_{\mathrm{f}} /{ }^{0} \mathrm{Cmol}^{-1}$ |
| :--- | :--- |
| Water | 1.86 |
| Benzene | 5.12 |
| Ethanoic Acid | 3.5 |
| Camphor | 40.0 |

Note: cryoscopic constants are sometimes given for 100 g of solvent. E.g. for 100 g of water $=18.6^{0} \mathrm{Cmol}^{-1}$.

## Determination of cryoscopic constant

The rationale of the experiment is to determine the freezing point of a dilute solution of a nonvolatile solute and the work out the freezing point depression of a solution containing 1 mole of a solute in 1000 g of solvent.

The major problem is that the depression of freezing point of a solvent is usually very small thus, a very sensitive thermometer like Beckmann's thermometer is required.

## A. Beckmann's procedure

1. A given mass of the solvent $\left(m_{1}\right)$ is placed in glass tube $A$ into which a thermometer is immersed. This tube is fitted with a wire stirrer, $s_{1}$, and a side arm, $m$, through which the solute can be introduced.
Apparatus

2. the tube $A$ is surrounded by a wider tube, $B$, which provides an air jacket to ensure uniform cooling
3. The freezing agent is contained in vessel $C$ consisting of a mixture of ice and salt and is kept stirred by stirrer $\mathrm{S}_{2}$.
4. The freezing point of the pure solvent $T_{1}$, is determined by stirring both freezing agent and the solvent and recording the constant temperature at which a liquid turns into a solid.
5. After determining the freezing point of a solvent the solid is warmed to melt.
6. A given mass of solute $m_{2}$ is introduced into the solvent through side arm, $m$, and stirred until completely dissolved.
7. Repeat procedure 4 and note the temperature $\left(T_{2}\right)$ at which pure solvent alone separate out from solution as solid.

Treatment of results
Mass of solvent $=M_{1}$
Mass of solute $\quad=\mathrm{m}_{2}$
$\Delta \mathrm{t} \quad=\left(\mathrm{T}_{1}-\mathrm{T}_{2}\right)$
Molecular mass of solute

$$
=\mathrm{Mr}
$$

Mass of solute in 1000 g of solvent $\quad=\frac{1000 m_{2}}{m_{1}}$
Then,
$\mathrm{K}_{\mathrm{f}}=\frac{\left(T_{1}-T_{2}\right) \times \mathrm{Mrxm}}{1000 m_{2}}$ where $\mathrm{K}_{\mathrm{f}}$ is the cryoscopic constant of a solvent.

## B. Rast's method

This is based on the use of melted camphor as a solvent because it has un usually high cryoscopic constant. An ordinary ( 360 degree) thermometer is used instead of Beckmann's thermometer.


The procedure consists essentially of measuring the melting point of pure camphor and that of the mixture as described in Beckmann's procedure.

## Limitation of the cryoscopic method

A correct value for relative molecular mass (that is a value corresponding to the actual molecular formula) is obtained under the following conditions.

1. When the solution freezes, the pure solvent alone must separate out.
2. There must be no chemical reaction between solute and solvent. For example, the formula mass of phosphorous pentachloride cannot be determined using this method in water because the two react.
3. The dissolved substance must not dissociate or associate appreciably. Thus this method is not suitable for strong electrolytes, acids and bases.

When the solute dissociates the number particles in solution increase causing the apparent molecular mass of the solute to decrease.

When the solute associate the number of solute molecules in solution decrease, the apparent molecular mass will be greater than the actual value
For example, the apparent relative molecular mass of ethanoic acid in benzene is double because two molecules of ethanoic Acid associate to give one molecules.
4. The solution must be dilute.
5. The freezing point method is not suitable for determining the molecular mass of polymers because the freezing point depression for dilute solution of the polymers is negligible.

Example 1
0.55 g of nitrobenzene in 22 g of ethanoic acid depresses the freezing point of the latter by $0.78^{\circ} \mathrm{C}$. Calculate the relative molecular mass of nitrobenzene. [The cryoscopic constant for 1000 g of ethanoic acid is $3.90^{\circ} \mathrm{Cmol}^{-1}$ ]

## Solution

Mass of nitrobenzene in 1000 g of ethanoic acid
22 g of benzene contain 0.55 g of nitrobenzene
1000 g of benzene will contain $\frac{0.55 \times 1000}{22}=25 \mathrm{~g}$

Formula mass of nitrobenzene
A depression of $0.78^{\circ} \mathrm{C}$ is caused by
25 g of nitrobenzene
Thus, $3.90^{\circ} \mathrm{C}$ will be caused by $\frac{25 \times 3.90}{0.78}=125$
Therefore, molecular mass nitrobenzene $=125 \mathrm{~g}$.

Example 2
0.72 g of a compound $X$ was dissolved in 80 g of water and the resultant solution had a freezing point of $-0.14^{\circ} \mathrm{C}$. When 2.9 g of the same compound was dissolved in 11 g of benzene, the depression was $6^{\circ} \mathrm{C}$. [ $\mathrm{K}_{\mathrm{f}}$ for water is
$1.86{ }^{0} \mathrm{Cmol}^{-1} \mathrm{~kg}^{-1}$ and $\mathrm{K}_{\mathrm{f}}$ for benzene is $5.5^{0} \mathrm{Cmol}^{-1} \mathrm{~kg}^{-1}$.)
(a) Calculate the apparent molecular mass of $X$ in
(i) water
(ii) Benzene
(b) comment on the results

## Solution

(a) (i) mass of $X$ in 1000 g of water

80 g of water contain 0.72 g of $X$
1000 g of water will contain $\frac{0.72 \times 1000}{80}=9 \mathrm{~g}$

$$
\begin{aligned}
\text { Freezing Point depression } & =0-(-.14) \\
& =0.14^{\circ} \mathrm{C}
\end{aligned}
$$

Formula mass of $X$

Depression of $0.14^{\circ} \mathrm{C}$ is caused by 9 g of X
$\therefore 1.86^{\circ} \mathrm{C}$ will be caused by $\frac{1.86 \times 9}{0.14}=120 \mathrm{~g}$
$\therefore$ the apparent molecular mass of X in water

$$
=120 \mathrm{~g}
$$

(b) (a)(ii) mass of $X$ in 1000 g of benzene

11 g of benzene contain 2.9 g of $X$
1000 g of water will contain $\frac{2.9 \times 1000}{8011}=263 \mathrm{~g}$
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Freezing Point depression =6 员
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Formula mass of $X$
Depression of $6^{\circ} \mathrm{C}$ is caused by 263 g of $X$
$\therefore 5.5^{\circ} \mathrm{C}$ will be caused by $\frac{5.5 \times 263}{6}=241 \mathrm{~g}$
$\therefore$ the apparent molecular mass of X in benzene

$$
=241 \mathrm{~g}
$$

(b) the apparent molecular mass is X is in benzene is double that in water probably because two molecules of $X$ associate in benzene to give one molecule. Or one molecule of $X$ dissociates into two particles in water.

## 2. Elevation of Boiling point

When a substance a nonvolatile solute is dissolved in a solvent, the boiling point of the solution is raised above the boiling point of the solvent in accordance to the following rules:
(i) Elevation of boiling point of a given mass of solvent is proportional to mass of a solute dissolved.
(ii) Elevation of boiling point for a given mass of solvent is inversely proportional to the molecular mass of the solute.
Thus, is the mass ( m ) of a solute of relative molecular mass ( Mr ) dissolved in a given amount of solvent cause a freezing point depression $(\Delta t)$ degrees Celsius

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then }\Deltat\propto
(a)
\Deltat}\propto\frac{1}{Mr

It follows that elevation of boiling point is proportional to the number of moles of a solute and if the same number of moles were present for a different solute, in the same mass of solvent, the Elevation of boiling point would be the same.

\section*{Ebullioscopic/boiling point constant Kb}

From (a) and (b),
\(\Delta t=\mathrm{K}_{\mathrm{b}} \frac{m}{M r}\)
When \(\mathrm{m}=\mathrm{Mr}, \Delta \mathrm{t}=\mathrm{K}_{\mathrm{b}}\)
The constant of proportionality \(\mathrm{K}_{\mathrm{b}}\) is called the boiling point constant of the solvent.

\section*{Definition}

Boiling point constant \(\left(K_{b}\right)\) is the amount by which the boiling point of 1000 g of a solvent is raised by 1 mole of solute; assuming rules (a) and (b) still hold at this concentration.

The boiling point constants for commonly used solvents are
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Solvent \(\mathrm{K}_{f}{ }^{0} \mathrm{Cmol}^{-1}\)

Water 0.51

Benzene 2.67

Ethanoic Acid

Limitation of this method in determination of the relative molecular masses of substance
1. Solution must be dilute
2. Solute should not react with solvent
3. Solute must not associate or dissociate in solution
4. Substance must be stable at boiling point of the solution and non-volatile
5. It is not suitable for determination of molecular masses of polymers because dilute solutions of polymers, produce negligible boiling point elevation.

\section*{Method for determining the boiling point elevation}

The main difficult for finding molecular masses by this method arises from super heating of the liquid above its true boiling point. This can be minimized by the following methods.
A. Cottrell's method

1. The solvent is heated in a wide tube, \(A\), fitted with a side arm leading to a reflux condenser which condenses the vapor of the boiling solvent and returns it to the boiling tube.
2. \(A\) is closed by a stopper, through which passed a second tube \(B\), open at the lower end. \(B\) contains a Beckmann thermometer.
3. The bulb of the thermometer is above the liquid and protected by the inner tube from drops of condensed liquid falling to it from the side arm.
4. Partially immersed in liquid is the Cottrell's 'pump', C, consisting of small inverted glass funnels with a step which divides into two narrow tubes. These are bending around at the top so that, when the liquid boils,
the vapor forces the liquid to rise up the narrow tube and spray the bulb of the thermometer. This prevents super heating, and as further precaution is a platinum wire sealed through the bottom of the tube A at D . Heating is by micro burner, which is shielded from draught.
5. First, we read the Beckmann thermometer for boiling point \(\left(T_{0}\right)\) a known mass \(\left(m_{s} g\right)\) of solvent. Then we introduce a weighed solute (mass \(\mathrm{M}_{2} \mathrm{~g}\) ) through the side arm and determine the boiling point ( \(\mathrm{T}_{1}\) ) of the solution.

This method can be used to determine the molecular mass of benzoic acid dissolved in acetone or that of naphthalene dissolved in chloroform.

\section*{Treatment of results}
\begin{tabular}{ll} 
Mass of solvent & \(=m_{s}\) \\
Mass of solute & \(=m_{2}\) \\
\(\Delta t\) & \(=\left(T_{1}-T_{0}\right)\) \\
Molecular mass of solute & \(=M r\) \\
Mass of solute in 1000 g of solvent & \(=\frac{1000 m_{2}}{m_{s}}\)
\end{tabular}

Then,
\(\mathrm{K}_{\mathrm{b}}=\frac{\left(T_{1}-T_{0}\right) \times M r \times m_{s}}{1000 m_{2}}\)
where \(K_{b}\) is the boiling point constant of a solvent.

\section*{Lands Berger's method}

1. The solvent is boiled in a separate flask. The vapor passes into the solution which is contained in a graduated tube; surrounded by a second tube.
2. The solution is raised to its boiling point by the latent heat of condensation of the solvent vapor.

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3. When the solution boils the solvent vapor passes through the solution without condensing. It passes through a hole, E , in the boiling tube so that the latter becomes jacketed with the vapor of boiling solvent. Thus reducing radiation to the minimum.
4. The bulb B on the inner tube prevent a liquid from being splashed through \(E\).
5. The boiling point \(\left(T_{0}{ }^{0} \mathrm{C}\right)\) of pure solvent is first found and then a known mass of a solute ( \(\mathrm{m}_{2} \mathrm{~g}\) and formula mass Mr ) is introduced and the boiling point \(\left(\mathrm{T}_{1}{ }^{0} \mathrm{C}\right)\) of solution is found.
6. The final volume of the liquid in the graduated tube is read of and from the density of the solvent the mass \(\left(m_{s} g\right)\) of the solvent into which a solute is dissolved is calculated.

Then the boiling point constant Kb is given by
\[
\mathrm{Kb}=\frac{\left(T_{1}-T_{0}\right) \times M r \times m_{s}}{1000 m_{2}}
\]

NB. The reason why steam at \(100^{\circ} \mathrm{C}\) raises the temperature of the solution above \(100^{\circ} \mathrm{C}\) is that steam at \(100^{\circ} \mathrm{C}\) has a higher vapor than a solution at the same temperature, it forms a layer above the solution condensing at the surface of the solution and the latent heat evolved would increase the temperature of the solution. The same situation exists when steam is bubbled through the solution.

\section*{Example 3}

The boiling of ethanol is \(78^{\circ} \mathrm{C}\). Calculate the boiling point of the solution containing 2.7 g of ethanamide \(\left(\mathrm{CH}_{3} \mathrm{CONH}_{2}\right)\) in 75 g of ethanol. (Boiling point elevation constant for 1000 g of ethanol \(=1.15^{0} \mathrm{Cmol}^{-1} \mathrm{~kg}^{-1}\) )

\section*{Solution}

Mass of ethanamide in 1000 g of ethanol
75 g of ethanol contain 2.7 g of ethanamide
1000 g of water will contain \(\frac{2.7 \times 1000}{75}=36 \mathrm{~g}\)

Formula mass of \(\mathrm{CH}_{3} \mathrm{CONH}_{2}=59\)

\section*{Boiling Point elevation}

59 g of ethanamide cause elevation of \(1.15^{\circ} \mathrm{C}\)
\(\Rightarrow 36 \mathrm{~g}\) of ethanamide cause \(\frac{1.15 \times 36}{59}=0.7^{\circ} \mathrm{C}\)
The boiling point of the solution \(=(78+0.7)(b p t\) of solution is higher than that of solvent by \(\Delta t)\)
\[
=78.7^{\circ} \mathrm{C}
\]

\section*{3. Lowering of vapor pressure}

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

The vapor pressure of a solution of a nonvolatile solute is usually less than that of pure solvent at a given temperature; because the nonvolatile solute particles occupy part of the solvent surface reducing the escaping tendency of the solvent molecules

\section*{Laws of vapor pressure of solution}

As with freezing point depression and boiling point elevation; lowering of the vapor pressure of a solvent by a nonvolatile solute at a given temperature is directly proportional to the concentration of the solute and inversely proportional to the formula mass (RFM).

More important than the actual lowering of the vapor pressure is the relative lowering of vapor pressure, \(\frac{P-P \prime}{P}\) or \(\frac{\Delta P}{P}\) at the same temperature.
Where, \(\mathrm{P}=\) vapor pressure of the solvent
\(\mathrm{P}^{\prime}=\) vapor pressure of the solution

The relative lowering of vapor pressure is
(i) independent of temperature
(ii) proportional to the concentration of solute
(iii) Constant if the number of molecules of different solute is dissolved in the same mass of solvent.

\section*{Raoult's vapor pressure law}

The relative lowering of vapor pressure is equal to the mole fraction of the solute. If \(n_{1}\) and \(n_{2}\) are the number of moles of solute and solvent

Then, \(\quad \frac{P-P \prime}{P}=\frac{n_{1}}{n_{1}+n_{2}}\)
In a dilute solution, \(n_{1}\), is negligible compared to \(n_{2}\), hence \(n_{1}+n_{2} \approx n_{2}\).
Then, \(\frac{P-P P^{\prime}}{P}=\frac{n_{1}}{n_{2}}\) \(\qquad\)
In \(\mathrm{m}_{1}\) is the mass of the solute in the solvent of mass \(\mathrm{m}_{2}\), and \(\mathrm{Mr}_{1}\) and \(\mathrm{Mr}_{2}\) are the relative molecular massed of the solute and solvent respectively

Then, \(\quad \mathrm{n}_{1}=\frac{m_{1}}{M r_{1}}\) and \(\mathrm{n}_{2}=\frac{m_{2}}{M r_{2}}\)

Substituting for \(\mathrm{n}_{1}\) and \(\mathrm{n}_{2}\) in equation (2)
\(\frac{P-P^{\prime}}{P}=\frac{m_{1} / M r_{1}}{m_{2} / M r_{2}}=\frac{m_{1} M r_{2}}{m_{2} M r_{1}}\)

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The vapor pressure law (3) holds true if only the solute is non volatile, the solution is dilute; and the solute does not dissociate or associate appreciably.

\section*{Example 4}

The vapor pressure of water at \(50^{\circ} \mathrm{C}\) is 12333 Pa . At this temperature, a solution of 9.14 g of carbamide (urea) in 150.0 g of water has a vapor pressure of 12106 Pa . Find the relative molecular formula of the carbamide.

From, \(\frac{P-P I}{P}=\frac{m_{1} M r_{2}}{m_{2} M r_{1}}\)
(iv) \(\frac{12333-12106}{12333}=\frac{9.14 \times 18}{150 \times M r(\text { carbamide })}\)
\(\therefore\) Formula mass of carbamide (Mr (carbamide)
\(=59.6\)
4. Osmotic pressure method for determining the relative molecular masses of substance.

\section*{Definitions}

Osmosis is the movement of the solvent molecules from the region where they are highly concentrated to the region of their low concentration through a semi-permeable membrane.

Suppose the solution and solvent are contained in the limbs of a U-tube and a semi-permeable membrane separates a solution from a solvent and that a movable piston is placed on a limb containing the solution. The piston would be observed to rise as the solvent passes through the membrane to the solution. The rise may be prevented by applying just the right external pressure to the piston.

The osmotic pressure of the solution is the minimum pressure which must be applied to the solution to balance the tendency of the solvent to flow from the solvent to the solution side of the semi-permeable membrane.

Laws of osmotic pressure
The Dutch scientist Vant Hoff found out that there is a close resemblance between the osmotic pressure and the gas law
\[
P V=n R T
\]

Since the law analogous to Charles and Boyles law apply to osmotic pressure and an expression similar to gas equation \(\pi V=n R^{\prime} T\) can be deduced for a dilute solution. Where \(\pi=\) osmotic pressure, \(\mathrm{V}=\) volume of the solution, \(\mathrm{R}^{\prime}=\) constant which is very close to the gas constant and T is temperature of the solution in Kelvin.

Calculations on the osmotic pressure method are chiefly used to find RFM of polymers that have high molecular mass.

Example 5
An aqueous solution of sucrose containing 19.15 g of sugar per \(\mathrm{dm}^{-3}\) has osmotic pressure of \(136,300 \mathrm{~Pa}\). Find the Relative Formula mass of sucrose.

Treating the sugar as a gas,
Method 1
We find the volume, V , the gas would occupy at s.t.p.
From \(\frac{P V}{T}=\) constant
\(\frac{136,300 \times 1}{(273+20)}=\frac{101325 \times V}{273}\)
\(V=1.254 \mathrm{dm}^{3}\)

The molar volume of a gas at s.t.p \(=22.4 \mathrm{dm}^{3}\).
then, \(1.254 \mathrm{dm}^{3}\) of sugar weigh 19.15 g
\(22.4 \mathrm{dm}^{3}\) of sugar will weigh \(\frac{19.15 \times 22.4}{1.254}\)
\[
=342.3
\]
\(\therefore\) Molecular mass of sucrose \(\mathbf{=} \mathbf{3 4 2 . 3}\)

\section*{Method II}

From \(\pi V=n R^{\prime} T\), we find the moles of sugar solution in 19.15 g ,
NB: Pressure must be in Pascal, Volume in \(\mathrm{m}^{3}\), and temperature in Kelvin
\(\pi=136,300 \mathrm{~Pa}\)
\(V=1 \mathrm{dm}^{3}=1 \times 10^{-3} \mathrm{~m}^{3}\)
\(\mathrm{R}=8.31\)
\(\mathrm{T}=(273+20) \mathrm{K}\)
Then, \(\mathrm{n}=\frac{\pi V}{R T}=\frac{136300 \times 1 \times 10^{3}}{8.31 \times 293}=0.056 \mathrm{moles}\)

Thus, 0.056 moles weigh 19.15
1mole weigh \(\frac{19.15}{0.056}=342\)

Method III
From \(\pi V=n R^{\prime} T\), we find the moles of sugar solution in 19.15g,
NB: Pressure must be in atmospher, Volume in \(\mathrm{dm}^{3}\), and temperature in Kelvin, \(R=0821\)
\(\pi=136,300 \mathrm{~Pa}=136300 / 101325=1.345 \mathrm{~atm}\)
\(\mathrm{V}=1 \mathrm{dm}{ }^{3}\)
\(R=0.0821\)
\(\mathrm{T}=(273+20) \mathrm{K}\)
Then, \(\mathrm{n}=\frac{\pi V}{R T}=\frac{1.345 \times 1}{0.0821 \times 293}=0.056 \mathrm{~mol}\) les

Thus, 0.056 moles weigh 19.15
1 mole weigh \(\frac{19.15}{0.056}=342\)

NB. The only problem with the second method is that, there is a need to convert units to standard units of Pressure ( \(\mathrm{Nm}^{-2} /\) Pascal), Volume, \(\left(\mathrm{m}^{3}\right)\), and temperature (Kelvin)

\section*{Precautions to osmotic law}
- the solution must be dilute
- the solute should not dissociate or associate in solution
- the solute should not react with the solvent
- the temperature should not be very high of very low.

Method of determination of Relative formula mass of a substance by osmotic pressure method

1. cylindrical tube between the solvent and solution is porous/semi-permeable
2. Pressure is applied to the solution and adjusted until there no flow of solvent into solution.
3. Capillary tube indicates movement of solvent into the solution.
4. Osmotic pressure obtained from the pressure gauge.

\section*{Exercise}

\section*{Freezing point depression}

Trial 1
(a) A solution containing 4.50 g of solute B dissolved in 125 g of water freezes at \(-0.372{ }^{\circ} \mathrm{C}\). Calculate the formula mass of \(B\) ( Kf for water is \(1.86^{\circ} \mathrm{Cmol}^{-1}\) per 1000 g ) (4marksk)
(b) How do you expect the formula mass of \(B\) to change it ionized in water explain your answer?(2mk)

\section*{Trial 2}
(b)(i) Describe how the molecular mass of a substance can be determined using the depression of the freezing point method.
(ii) State two limitations of the method
(c) Calculate the freezing point of an aqueous solution of urea \(\left(\mathrm{CO}\left(\mathrm{NH}_{2}\right)_{2}\right)\) of concentration \(12.0 \mathrm{gdm}^{-3}\) at a pressure of 101.3 kPa . Assume that the volume of the solute is negligible compared to that of the solution. [the freezing point depression constant is \(1.86^{0} \mathrm{Cmol}^{-1} \mathrm{~kg}^{-1}, \mathrm{C}=12, \mathrm{H}=1, \mathrm{O}=16, \mathrm{~N}=14\) )

\section*{Trial 3}
(a)(i) Describe how the molecular formula of a substance can be determined using freezing point depression method (Diagram not required)
(07mks)
(ii) Explain why the method you described in (a)(i) not suitable for determining the molecular mass of a polymer (02marks)
(b) Calculate the freezing point of a solution containing 4.2 g of ethane-1,2-diol (molecular mass \(=62\) ) in 30 g of water. ( \(\mathrm{K}_{\mathrm{f}}\) of water \(1.86^{0} \mathrm{Cmol}^{-1} \mathrm{~kg}^{-1}\) ) ( 04 mks )

\section*{Trial 4}
(a) Define the term freezing point constant of a substance?
( \(11 / 2 \mathrm{mk}\) )
(b) A solution containing 1.54 g of Naphthalene \(\left(\mathrm{C}_{10} \mathrm{H}_{8}\right)\) in 18 g of camphor freezes at \(148.3^{\circ} \mathrm{C}\). Calculate the freezing point constant of camphor. [The freezing point of camphor is \(175^{\circ} \mathrm{C}\) ) ½mks)
Trial 5
(a) One of the limitations of determining relative molecular mass by freezing point method is that the solute should not associate or dissociate in solution
(i) State three other limitation of determining molecular mass by freezing point method. (1 \(1 / 2\) marks)
(ii) Explain how association of solute in solution affects the molecular mass determined by freezing point method ( \(31 / 2\) marks)
(b) A solution 0.142 g of naphthalene in 20.25 of benzene caused a lowering of freezing point of \(0.284^{\circ} \mathrm{C}\). Calculate the molecular mass of naphthalene. (Cryoscopic constant Kf of benzene is \(5.120 \mathrm{Cmol}^{-1} \mathrm{~kg}^{-1}\) )

Trial 6
A solution containing 28.145 g of R in 250 g of water froze at \(-3.49^{\circ} \mathrm{C}\). Determine the molecular mass of \(R\). (freezing point constant, Kf of water is \(1.86^{\circ} \mathrm{C} \mathrm{mol}^{-1}\) per 1000 g )

\section*{Trial 7}

The cooling curve of a solution containing 1.2 g of sulphur in 20 g of carbon disulphide and that of pure carbon disulphide are shown in figure below

(a) (i) identify the curve X and Y (1mark)
(ii) State what is represented by the points \(A\) and B. (01mark)
(b) Calculate the relative molecular mass of sulphur in carbon disulphide. (The freezing point depression constant for carbon disulphide is \(6.10^{0} \mathrm{Cmol}^{-1} \mathrm{~kg}^{-1}\) and freezing point depression of carbon disulphide was \(1.43^{\circ} \mathrm{C}\) ).

\section*{Boiling point elevations}

Trial 8
5.5 g of a non-volatile substance was dissolved in 125 g of a solvent. The vapor pressure curves for the solution and pure solvent at constant pressure \(P\) are shown below:

(a) Indentif \({ }^{\text {Temperature }}\left({ }^{\circ} \mathrm{C}\right.\) ) ution
(b) Calculate the molecular mass of B [the boiling point elevation constant for the solvent \(\mathrm{K}=0.52^{\circ} \mathrm{Cmol}^{-}\) \({ }^{1} \mathrm{~kg}^{-1}\) )
(c) State two limitation of your calculation in (b)

Trial 9
(a) State Raoult's law (2marks)
(b) Explain what is meant by the term 'Colligative property' (3marks)
(c) A substance was dissolved in a solvent \(X\). the graph below shows how the vapor pressure of the solution and that of pure \(X\) vary with temperature

(i) State what points \(A, B, C, D, E\) and line \(A B\) and \(A C\) represent
(ii) Show how the graph can be used to derive an expression for calculating the molecular mass of a solute (12marks)
(d) A solution was prepared by dissolving 7.5 g of propan-1,2,3-triol, \(\mathrm{C}_{3} \mathrm{H}_{8} \mathrm{O}_{3}\) in 200 g of water at \(25^{\circ} \mathrm{C}\).Calculate the boiling point of the solution at atmospheric pressure ( \(\mathrm{Kb}=0.52^{\circ} \mathrm{C}\) )

Trial 10

A solution contains 50 g of ethane-1,2-diol and 40 g of water
(a) Calculate the boiling point of the solution ( \(\mathrm{H}=1, \mathrm{O}=16, \mathrm{C}=12, \mathrm{~K}_{\mathrm{b} \text { (water) }}=0.52 \mathrm{Kmol}^{-1} \mathrm{~kg}^{-1}\) ) (4marks)
(b) State any assumption you made in the calculation
(2marks)

Trial 11
1.455 g of a compound Y was dissolved in 80 g of ethanol. The boiling point of the solution was \(78.97^{\circ} \mathrm{C}\) while that of ethanol was \(78.8^{\circ} \mathrm{C}\) ( Kb for ethanol is \(1.15^{\circ} \mathrm{C}\) for 1 mole in 1000 g ). Calculate the molecular mass of \(Y\) in ethanol
(4marks)

\section*{Trial 12}
(a) State what meant by the term boiling point constant of a liquid. (2marks)
(b) Describe an experiment that can be used to determine the relative molecular mass of a compound using the method of elevation of the boiling point of a liquid. Draw a labeled diagram of the apparatus used. (12marks)
(c) Explain why the method you have described in (b) is not suitable for determination of the relative molecular mass of ethanoic acid in aqueous solution.
(03marks)
(d) A solution of 2.8 g of cadmium (II) iodide in 20 g of water boiled at 100.20 C at normal pressure. Calculate the relative molecular mass of cadmium II iodide and comment on your results. [The boiling point elevation constant for water is \(0.52^{\circ} \mathrm{Cmol}^{-1} \mathrm{~kg}^{-1}\) ) (03marks)

\section*{Lowering of vapor pressure}

Trial 13
(i) A solvent Y of molecular mass 62 has a vapor pressure of \(1.0 \times 10^{4} \mathrm{Nm}^{-2}\) at 298 K .23 .3 g of a non volatile solute of molecular mass 270 was added to 100 g of Y at 298 K . Calculate the vapor pressure of solution
(ii) State and explain the effect of increasing the concentration of the solute on the boiling point of Y .

\section*{Trial 14}
(a) the vapor pressure of a solution containing 108.2 g of a substance Y in 1000 was reduced by 0.186 mmHg of water at \(20^{\circ} \mathrm{C}\)
(The vapor pressure of water at 200 C is 17.54 mmHg . Calculate the relative molecular mass of substance Y. (04marks)
(b) State four assumptions made in (a)
(c) Explain why the vapor pressure of the solution containing a nonvolatile solute is less than the vapor pressure of a pure solvent.

\section*{Osmotic pressure}

\section*{Trial 15}
(a) Define the term osmotic pressure (2 marks)
(b) The osmotic pressure of a solution containing \(42 \mathrm{~g} / \mathrm{I}\) of a substance is \(5.62 \times 10^{5} \mathrm{Nm}^{-2}\) at \(20^{\circ} \mathrm{C}\). Calculate the relative molecular mass of \(y\).
( \(21 / 2 \mathrm{mks}\) )

\section*{Trial 16}
(c) the osmotic pressure of various concentration of a solute in methylbenzene at 200C are given in the table below
\begin{tabular}{|l|l|l|l|l|l|l|}
\hline Conc. \(\mathrm{g} / \mathrm{dm}^{3}\) & 1.0 & 2.0 & 3.0 & 4.0 & 5.0 & 6.0 \\
\hline \begin{tabular}{l} 
Osmotic \\
pressure \(/ \mathrm{Nm}^{-2}\)
\end{tabular} & 23 & 37 & 53 & 75 & 92 & 109 \\
\hline
\end{tabular}
(i) Plot a graph of osmotic pressure against concentration
(ii) Use the graph you have drawn to determine the molecular mass \(X\left(R=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}\right)\)

Trial 17
(a) Solution containing20 g of a polymer X in 11 of solution exert an osmotic pressure of 1.4 mmHg at \(25{ }_{0} \mathrm{C}\)
(i) Explain what is meant by the term osmosis. (2mks)

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(ii) Calculate the molecular mass of \(X\)
(iii) The molecular formula of the monomer of \(X\) is \(\left(\mathrm{CH}_{2}=\mathrm{CHCN}\right)\). Determine the number of monomers of \(X\) (2mks)
(iv) Draw the general formula of \(X\) (1mk)
(v) Explain why the freezing point depression method is not suitable for determining the molecular mass of a polymer (2mks)
(b) (i)Describe how the molecular mass of a substance can be determined by the freezing point depression method. (06marks)
(ii) Calculate the freezing point depression of the solvent in (a)

\section*{Trial 18}
(a) Explain what is meant by the following terms
\begin{tabular}{lll} 
(i) Osmosis & \((3 \mathrm{mks})\) \\
(ii) & Osmotic
\end{tabular}
(b) State the significance of osmosis (1mk)
(c) Describe a method which can be used to determine the osmotic pressure of a solution ( 7 mks )
(d) state the conditions under which solutions do not obey the laws of osmotic pressure (3mk)
(e) The osmotic pressure of a solution containing \(1.24 \%\) of a polymer is \(3.1 \times 10^{-3}\) atmospheres at \(25^{\circ} \mathrm{C}\). Determine the relative formula mass of the polymer. ( \(\mathrm{R}-0.0821\) )
Trial 19
The osmotic pressure of a solution containing 4 g per litre of a polymer is \(65 \mathrm{Nm}^{-2}\) at 298 K . Calculate the approximate molecular mass of the polymer. (02marks)

Trail 20
The osmotic pressure of a solution containing \(2 \mathrm{gdm}^{-3}\) of nylon 6.10 at \(25^{\circ} \mathrm{C}\) is 0.155 mmHg . Calculate the relative molecular mass of nylon \(6,10 .\left[R=0.0821 \mathrm{~atm}^{-10} \mathrm{Cmol}^{-1}\right]\)

\section*{Solutions to the trials in the chapter 3}

Trial 1
(a)(i) formula mass of \(B=180 \mathrm{~g}\)
(a)(ii) the apparent molecular mass reduces because the number of particles in solution increase.

\section*{Trial 2}
(b)(i) Choose between Beckmann's procedure and Rast's procedures
(ii) Any two limitation cryoscopic methods
(c) We are required to determine the freezing point depression and then subtract it from the freezing point of water (which is \(0^{\circ} \mathrm{C}\) at 101.3 kPa , i.e. pressure here is quoted because it affects freezing point of the liquids) to get the freezing point of the solution
Begin with
- determination molecular mass of urea
\[
\begin{aligned}
& =12+16+2(14+2) \\
& =60
\end{aligned}
\]
- determination freezing point depression

60 g of urea cause a depression of \(1.86^{\circ} \mathrm{C}\)
12 g of urea cause \(\frac{12 \times 1.86}{60}=0.372^{\circ} \mathrm{C}\)
- determining freezing point of solution
\(\begin{aligned}= & \begin{array}{l}\text { Freezing point } \\ \\ \text { of water }\end{array} \\ = & (0-0.372)^{\circ} \mathrm{C} \\ = & -0.372^{\circ} \mathrm{C}\end{aligned}\)
Trial 3
(a)(i) A given mass \(\mathrm{X} g\) of a solute of molecular mass, Mr , is dissolves in Yg of solvent whose freezing point is \(\mathrm{T}_{0}{ }^{0} \mathrm{C}\) and freezing point depression constant Kf . The freezing point of the solution \(\mathrm{T}^{0} \mathrm{C}\) is determined.
\(\Rightarrow\) Calculation
Freezing point depression \(=\left(\mathrm{T}_{0}-\mathrm{T}\right){ }^{0} \mathrm{C}\)
Mass of solute in 1000 g of solvent
Y g of solvent contain X g of solute
Therefore, 1000 g of solvent contain \(\left[\frac{1000 X}{Y}\right] \mathrm{g}\)
\(\Rightarrow\left[\frac{1000 X}{Y}\right] \mathrm{g}\) of solute cause a depression of \(\left(\mathrm{T}_{0}-\mathrm{T}\right){ }^{\circ} \mathrm{C}\).
\(\Rightarrow M r g\) cause freezing point depression of Kf
\(\Rightarrow M r=\frac{1000 X \cdot K_{f}}{Y\left(T_{0}-T\right)}\)
(ii) Dilute solution of a polymer has negligible freezing point depression
(c) freezing point \(=-4.2^{\circ} \mathrm{C}\)

Trial 4
(a) Freezing point constant is the freezing point depression caused by one of solute dissolved in 1000 g of solvent.
(b) Formula mass of naphthalene \(=12 \times 10+8\)
\[
=128
\]

Freezing point depression \(=175-148.3\)
\[
=26.7^{\circ} \mathrm{C}
\]

Mass of naphthalene in 1000 g of camphor
18 g of camphor contain 1.54 g of naphthalene
\(\therefore 1000 \mathrm{~g}\) of camphor contain \(\frac{1.54 \times 1000}{18}=85.56 \mathrm{~g}\)

\section*{Freezing point constant}
85.56 g of camphor cause a depression of \(26.7^{\circ} \mathrm{C}\)
\(\therefore 128 \mathrm{~g}\) of naphthalene cause \(\frac{26.7 \times 128}{85.56}=39.94^{\circ} \mathrm{C}\)
\(\therefore\) the freezing constant of camphor
\[
=39.94^{0} \mathrm{Cmol}^{-1} \mathrm{~kg}^{-1}
\]

\section*{Trial 5}
(a)(ii) association increases relative molecular mass of a solute because it reduces the number of particles in solution.
(b) 126

Trial 6

60

Trial 7
(a)(i) \(\mathrm{X}=\) solvent, \(\mathrm{Y}-\) solution
(ii) A- freezing point of solvent
\(B\) - freezing point of solution
(b) 256

Trial 8
(a) curve y
(b) 164 (note that \(\Delta t=(100.139-100)=0.139^{\circ} \mathrm{C}\) from the graph.)
(c) any two of the limitations of the boiling point method; except that of \(B\) being nonvolatile because this is already mentioned in the question.

\section*{Trial 9}
(c) (i) A-Vapor pressure of the solvent equal to the atmospheric pressure

B- vapor pressure of the solution at the boiling point of the solvent
C- vapor pressure of the solution equal to atmospheric pressure
D- boiling point of the solvent
E - boiling point of solution
AC- elevation of boiling point of solution
\(A B\) - depression of the vapor pressure of the solution
(ii) Applying principles of lowering vapor pressure

If \(m_{1}\) is the mass of the solute of molecular mass \(\mathrm{Mr}_{1}\) dissolved in \(\mathrm{m}_{s}\) grams of a solvent of molecular mass \(\mathrm{Mr}_{s}\) to form a dilute solution
\[
\begin{aligned}
& \text { then } \frac{m_{1} / M r_{1}}{m_{S} / M r_{s}}=\frac{A B}{A D} \\
& \mathrm{Mr}_{1}=\frac{m_{1} \times M r_{s} \times A D}{M_{s} \times A B}
\end{aligned}
\]

Alternatively, applying principles of elevation of boiling point
If \(m_{1}\) is the mass of the solute of molecular mass \(\mathrm{Mr}_{1}\) dissolved in \(\mathrm{m}_{\mathrm{s}}\) grams of a solvent of boiling point constant \(\mathrm{K}_{\mathrm{b}}{ }^{0} \mathrm{Cmol}^{-1} \mathrm{~kg}^{-1}\) to form a dilute solution

Mass of solute in 1000 g of solvent \(=\frac{1000 m_{1}}{m_{s}}\)
thus, \(\frac{1000 m_{1}}{m_{s}} g\) of solute cause boiling point elevation of (E-D)
\(\mathrm{Mr}_{1} \mathrm{~g}\) cause and elevation \(\mathrm{K}_{\mathrm{b}}\)
\(\therefore \mathrm{Mr}_{1}=\frac{1000 m_{1} K_{b}}{M_{s}(E-D)}\)
(d) \(100.2^{\circ} \mathrm{C}\)

Trial 10
The formula mass ofethane-1,2-diol, \(\mathrm{CH}_{2} \mathrm{CH}_{2}\)
\[
=62
\]

Mass of ethane-1,2-diol in 1000g of water
40 g of water contains 50 g ofethane-1,2-diol
\(\therefore 1000 \mathrm{~g}\) of water contain \(=\frac{50 \times 1000}{40}=1250 \mathrm{~g}\)

\section*{Elevation of the boiling point}

62 g cause boiling point elevation of \(0.52^{\circ} \mathrm{C}\)
1250 g would cause boiling point elevation
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\[
=\frac{1250 \times 0.52}{62}=10.5^{\circ} \mathrm{C}
\]

Boiling point of the solution \(=100+10.5\)
\[
=110.5^{\circ} \mathrm{C}
\]
(b) - ethane-1,2-diol is non volatile
- ethane-1,2-diol does not react with water
- it is stable at the boiling point
- it does not associate or dissociate in water

\section*{Trial 11}

Formula mass of \(Y=123\)
Trial 12
(a) Boiling point elevation constant is elevation of boiling point cause by 1 mole of a solute dissolved in 1000 g of solvent.
(b) A given mass X g of a solute of molecular mass, Mr , is dissolves in Yg of solvent whose boiling point is \(\mathrm{T}_{0}{ }^{0} \mathrm{C}\) and boiling point elevationconstant Kb . The boiling point of the solution \(\mathrm{T}^{0} \mathrm{C}\) is determined.

\section*{Calculation}

Freezing point depression \(=\left(T-T_{0}\right){ }^{0} \mathrm{C}\)
Mass of solute in 1000 g of solvent
Y g of solvent contain X g of solute
Therefore, 1000 g of solvent contain \(\left[\frac{1000 X}{Y}\right] \mathrm{g}\)
\(\left[\frac{1000 X}{Y}\right] \mathrm{g}\) of solute cause a boiling elevation of \(\left(\mathrm{T}-\mathrm{T}_{0}\right)^{\circ} \mathrm{C}\).
\(M r\) g cause boiling point elevation of \(K b\)
\[
M r=\frac{1000 X \cdot K_{b}}{Y\left(T_{0}-T\right)}
\]
(c) it is volatile
it ionizes in water
(d) formula mass \(=364\) (the answer is almost accurate (366) within experimental errors.

\section*{Trial 13}
(i) vapor pressure of solution \(=9464 \mathrm{Nm}^{-2}\)
(ii) it increases the boiling point because a non volatile solute lowers the vapor pressure of the solution such that the solution has to be boiled at a higher temperature to make its vapor pressure equal to that of the atmospheric pressure to boils.
Trial 14
(a) formula mass of \(Y=184\)
(b) - solution is dilute
- solute is non volatile
- solute does not dissociate appreciably
- solute does not react with solvent
- solute does not associate in solution

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(c) The non volatile solute particles occupy part of the solvent surface reducing the escaping tendency of the solvent molecules

Trial 15
(c) Molecular mass of \(y=182\)

Trial 16

\section*{A graph of osmotic pressure against}
(i)

(ii) From \(\mathrm{PV}=\mathrm{nRT}=\frac{m R T}{M r}\)

It implies that \(\mathrm{P}=\frac{R T}{M r} \times \frac{m}{V}\)
Gradient \(\frac{R T}{M r} \quad=\frac{100-18}{5.6-0.4}\)
\[
=17.7
\]

Mr. \(=\frac{8.31 \times 298}{17.7}=140\)
Trial 17
(a)(ii) Molecular mass of \(\mathrm{X}=265471\)
(a)(iii) Number of monomer \(=\frac{265471}{53}=5061\)
(b)(ii) \(3.77 \times 10^{-40} \mathrm{C}\)

\section*{Trial 18}
(e) NB. when \(\mathrm{R}=0.0821\), Pressure used should be in atmospheres and volume in \(\mathrm{dm}^{3}\).

Thus, No. of moles \(=\frac{P V}{R T}=\frac{3.1 \times 10^{-3} \times 0.1}{0.0821 \times 298}\)
\[
=1.267 \times 10^{-5} \text { moles }
\]

Then. \(1.267 \times 10^{-5}\) moles weigh 1.24 g
1 mole will weigh \(\frac{1.24}{1.267 \times 10^{-5}}=97863\)
\(\therefore\) the molecular mass of the polymer \(=97863\)
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Trial 19 :
152466
Trial 20
240000```

