Detailed Solutions

1. Number of moles of solute dissolved in one litre solution is called molarity. It is denoted by M.

$$M = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litre}}$$

2. Mole fraction is the ratio of number of moles of solute or solvent and total number of moles of solution. It is denoted by x.

$$x_{\text{solute}} = \frac{n_2}{n_1 + n_2},\ x_{\text{solvent}} = \frac{n_1}{n_1 + n_2}$$

3. Molality of a solution can be defined as the number of moles of solute dissolved in one kg solvent. It is denoted by m.

$$m = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} = \frac{n_2}{W_1}$$

4. Molality is independent of temperature, whereas molarity is a function of temperature.

5. Mass of solute = 9.8 g

Mass of solution = 100 g

Density of solution = 1.02 g mL^{-1}

$$\therefore \quad \text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}}$$

$$= \frac{100\text{ g}}{1.02\text{ g mL}^{-1}} = 98.039\text{ mL}$$

$$= 0.098\text{ L}$$

$$\text{Number of moles of solute, } n = \frac{9.8\text{ g}}{98\text{ g}} = 0.1\text{ mol}$$

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$$

$$= \frac{0.1\text{ mol}}{0.098\text{ L}} = 1.02\text{ M}$$

6.

Molarity	**Molality**
Number of moles of solute dissolved in one litre solution is called molarity.	Number of moles of solute dissolved in one kg solvent is called molality.
$M = \dfrac{\text{No. of moles of solute}}{\text{Volume of solution in litre}}$	$m = \dfrac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$
Molarity depends on temperature as volume depends on temperature. Molarity decreases with rise in temperature.	Molality is independent of temperature as mass does not change with temperature.

7. (i) *Refer to answer 2.*

(ii) *Refer to answer 3.*

8. Mass of solution = 100 g

Mass of solute = 10 g

$$\text{Mass of solvent} = 100 - 10 = 90\text{ g} = \frac{90}{1000}\text{ kg} = 0.09\text{ kg}$$

$$\text{Number of moles of solute, } n = \frac{10}{180} = 0.055\text{ mol}$$

$$m = \frac{0.055\text{ mol}}{0.09\text{ kg}} = 0.61\text{ m}$$

9. *Refer to answer 6.*

10. *Refer to answer 6.*

If M_B is the molar mass of solute, d is the density of solution then molarity (M) value of a solution can be converted into its molality (m) by using the following formula,

$$m = \frac{1000 \times M}{(1000 \times d) - (M \times M_B)}$$

11. *Refer to answer 1.*

Disadvantage in using molarity as the unit of concentration is that it depends upon temperature.

12. Mass of the solute, $C_2H_4(OH)_2$ = 222.6 g

Molar mass of solute, $C_2H_4(OH)_2$ = 62 g mol^{-1}

$$\therefore \quad \text{Moles of the solute} = \frac{222.6\text{ g}}{62\text{ g mol}^{-1}} = 3.59$$

Mass of the solvent = 200 g = 0.200 kg

$$\text{Volume of solution} = \frac{422.6\text{ g}}{1.072\text{ g mL}^{-1}} = 394.2\text{ mL} = 0.3942\text{ L}$$

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} = \frac{3.59}{0.2} = 17.95\text{ m}$$

$$\text{Molarity} = \frac{3.59\text{ moles}}{0.3942\text{ L}} = 9.11\text{ mol L}^{-1}$$

13. Given : Mass of solute, $W_2 = 10$ g
Mass of solvent, $W_1 = 90$ g
Molar mass of solute, $M_2 = 180$ g mol^{-1}
Density of solution = 1.2 g mL^{-1}

(i) Molality $= \dfrac{W_2 \times 1000}{M_2 \times W_1} = \dfrac{10 \times 1000}{180 \times 90}$

$= 0.62$ mol kg^{-1}

(ii) Volume of solution $= \dfrac{\text{mass}}{\text{density}} = \dfrac{100\,\text{g}}{1.2\,\text{g mL}^{-1}}$

$$\text{Molarity} = \frac{w_2 \times 1000}{M_2 \times V}$$

$$M = \frac{10 \times 1000}{180 \times \frac{100}{1.2}} = \frac{10 \times 1000 \times 1.2}{180 \times 100} = 0.66 \text{ mol L}^{-1}$$

14. According to Henry's law, the solubility of a gas is inversely proportional to the Henry's law constant (K_H) for that gas. Hence, gas (B) being less soluble, would have a higher K_H value.

15. Henry's law states that, the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.

$p = K_H \cdot x$ where, K_H = Henry's law constant. Different gases have different K_H values at the same temperature.

16. *Refer to answer 15.*

17. *Refer to answer 15.*

Applications of Henry's law :
(i) To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
(ii) To minimise the painful effects of decompression sickness in deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.

18. Increase in temperature decreases the solubility of oxygen in water. As a result, amount of dissolved oxygen decreases. It becomes more difficult to breathe as oxygen is less. Hence, the aquatic species are not comfortable in warm water.

19. Henry's law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

Refer to answers 17.

20. Applying the relationship,
$m = K_H \times p$
In the first case, 6.56×10^{-2} g $= K_H \times 1$ bar
or, $K_H = 6.56 \times 10^{-2}$ g bar^{-1}

In the second case,
5.0×10^{-2} g $= (6.56 \times 10^{-2}$ g bar$^{-1}) \times p$

$$p = \frac{5.0 \times 10^{-2}\ \text{g}}{6.56 \times 10^{-2}\ \text{g bar}^{-1}} = 0.762 \text{ bar}$$

21. According to Henry's law, $p_{N_2} = K_H \times x_{N_2}$

$$x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{0.987 \text{ bar}}{76480 \text{ bar}} = 1.29 \times 10^{-5}$$

If n moles of N_2 are present in 1 L (*i.e.*, 55.55 moles),

$$x_{N_2} = \frac{n}{n + 55.55} \simeq \frac{n}{55.55} \text{ of water}$$

$$\therefore \quad \frac{n}{55.55} = 1.29 \times 10^{-5}$$

or $\quad n = 1.29 \times 10^{-5} \times 55.55$ moles
$= 71.659 \times 10^{-5}$ moles = 0.716 millimoles

22. $T = 25°C + 273 = 298$ K
Total pressure (P_{total}) = 1 atm
p_{N_2} = mol fraction of N_2 in air $\times P_{total} = 0.78 \times 1$ atm
= 0.78 atm = 0.78 × 760 mm = 592.8 mm
As K_H is in the units of M(mm)$^{-1}$, Henry's law is applied in the form :
Conc. in solution $= K_H\, p_{N_2} = 8.42 \times 10^{-7}$ M (mm)$^{-1}$ $\times 592.8$ mm
$= 4.99 \times 10^{-4}$ M

23. **Raoult's law :** For a solution of volatile liquids, the partial pressure of each component in the solution is directly proportional to its mole fraction. Thus, for any component, partial vapour pressure,
$p \propto x \Rightarrow p = p°.\, x$
where $p°$ = vapour pressure of pure component
x = mole fraction of that component

24. *Refer to answer 23.*

25. *Refer to answer 23.*

26. *Refer to answer 23.*

Henry's law : If gas is the solute and liquid is the solvent, then according to Henry's law,

$p = K_H \cdot x$

i.e., partial pressure of the volatile component (gas) is directly proportional to the mole fraction of that component (gas) in the solution.
Hence, Raoult's law and Henry's law has been identical except that their proportionality constant are different. It is equal to $p°$ for Raoult's law and K_H for Henry's law.
Therefore, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to vapour pressure of pure component $p°$.

27. *Refer to answer 23.*

Let a solution consists of two volatile liquids *A* and *B* with their mole fraction x_A and x_B respectively. If p_A and p_B are their partial vapour pressures,

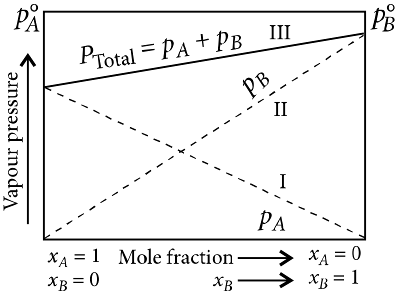
then,

$p_A \propto x_A \Rightarrow p_A = p_A^\circ x_A$ and $p_B \propto x_B \Rightarrow p_B = p_B^\circ x_B$

where p_A° and P_B° represent the vapour pressures of pure liquid components *A* and *B*.

$P_{\text{total}} = p_A + p_B$

A plot of p_A or p_B against x_A or x_B for a solution will be a straight line.



Ideal solutions obey Raoult law at all concentrations and temperature.

28. *Refer to answer 23.*

Raoult's law for solution containing non-volatile solute : It states that partial vapour pressure of a solution of non-volatile solute, p_{solution} is directly proportional to the mole fraction of the solvent in the solution.

Mathematically,

$p_{\text{solution}} = p^\circ_{\text{solvent}} \times x_{\text{solvent}}$

where p°_{solvent} = vapour pressure of the pure solvent at the given temperature.

or, $\dfrac{p^\circ - p_{\text{sol}}}{p^\circ} = x_2$

29. Given : p_A° = 450 mm Hg, p_B° = 700 mm Hg, P_{Total} = 600 mm Hg, x_A = ?

Applying Raoult's law, $p_A = x_A \times p_A^\circ$

$p_B = x_B \times p_B^\circ = (1 - x_A)p_B^\circ$

$P_{\text{Total}} = p_A + p_B = x_A \times p_A^\circ + (1 - x_A)p_B^\circ$

$= p_B^\circ + (p_A^\circ - p_B^\circ)x_A$

Substituting the given values, we get

$600 = 700 + (450 - 700)x_A$ or, $250x_A = 100$

or $x_A = \dfrac{100}{250} = 0.40$

Thus, composition of the liquid mixture will be

$x_A = 0.40$

$x_B = 1 - 0.40 = 0.60$

Calculation of composition in the vapour phase,

$p_A = x_A \times p_A^\circ = 0.40 \times 450$ mm Hg = 180 mm Hg

$p_B = x_B \times p_B^\circ = 0.60 \times 700$ mm Hg = 420 mm Hg

Mole fraction of *A* in the vapour phase

$$= \frac{p_A}{p_A + p_B} = \frac{180}{180 + 420} = 0.30$$

Mole fraction of *B* in the vapour phase = 1 – 0.30
= 0.70

30. Non-ideal solutions that show negative deviation from Raoult's law form maximum boiling azeotropes.

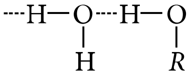
31. Azeotropes are the binary mixtures of solutions that have the same composition in liquid and vapour phases and that have constant boiling points.

It is not possible to separate the components of azeotropes by fractional distillation.

32. *Refer to answer 31.*

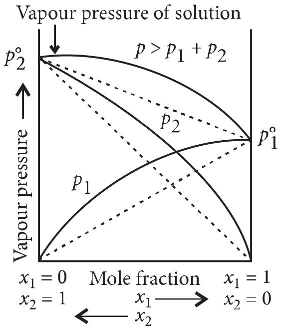
33. A solution which obeys Raoult's law at all concentrations and temperatures is called an ideal solution.

34. Both alcohol and water are polar in nature hence, they are miscible in all proportions. Water and ethanol molecules attract each other because of the formation of H-bonds. This property also makes them miscible.



$$\cdots \text{H}-\underset{\text{H}}{\underset{|}{\text{O}}}\cdots\text{H}-\underset{R}{\underset{|}{\text{O}}}$$

35. Positive deviation : For non-ideal solutions, if the vapour pressure is higher, then it is said to exhibit positive deviation. *A*—*B* interactions are weaker than *A*—*A* or *B*—*B* interactions. Due to this, vapour pressure increases which results in positive deviation. In positive deviation, intermolecular force decreases, volume increases, vapour pressures increases. enthalpy increases. Therefore, ΔH_{mix} = +ve, ΔV_{mix} = + ve. *e.g.*, ethanol + acetone and carbon disulphide + acetone show positive deviation.

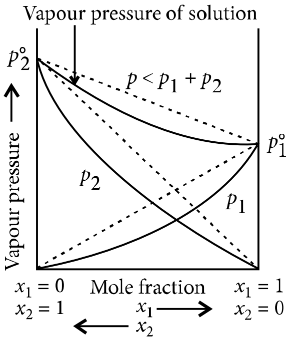


Plot for non-ideal solution showing positive deviation

36. *Refer to answer 31.*

A minimum boiling azeotrope is formed by solutions showing a large positive deviation from Raoult's law at a specific composition. For example an ethanol-water mixture containing approximately 95% ethanol by volume.

37. **Negative deviation :** For non-ideal solution, if the vapour pressure is lower, then it is said to exhibit negative deviation. $A—B$ interactions are stronger than $A—A$ and $B—B$ interactions. Due to this, vapour pressure decreases which results in negative deviation. In negative deviation, intermolecular force increases, volume decreases, vapour pressure decreases and heat is released. Therefore, $\Delta H_{mix} = -\text{ve}$, $\Delta V_{mix} = -\text{ ve}$ Example, phenol + aniline and chloroform + acetone show negative deviation.



Plot for non-ideal solution showing negative deviation

38. *Refer to answer 31.*

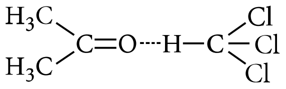
A maximum boiling azeotrope is formed by solutions showing a large negative deviation from Raoult's law at a specific compostion.

For example Chloroform – acetone mixture.

39. A mixture of ethanol and acetone shows positive deviation from Raoult's law. Pure ethanol possesses hydrogen bonding. Introduction of acetone between the molecules of ethanol results in breaking of some of these hydrogen bonds. Due to weakening of interactions, the solution shows positive deviation from Raoult's law.

40. *Refer to answers 35 and 37.*

41. A mixture of chloroform and acetone shows negative deviation from Raoult's law because chloroform molecule forms H-bonding with acetone molecule. As a result of this $A—B$ interaction becomes stronger than $A—A$ and $B—B$ interactions. This leads to the decrease in vapour pressure and resulting in negative deviation.



42. *Refer to answers 35 and 37.*

43. (i) *n*-Hexane and *n*-octane : London dispersion forces as both the molecules are non-polar.

(ii) Methanol and acetone : Dipole-dipole interactions as both the molecules are polar.

44. *Refer to answers 23, 35 and 37.*

45. *Refer to answer 37.*

46. Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.

47. Molal elevation constant may be defined as the elevation in boiling point when the molality of the solution is unity (*i.e.*, 1 mole of the solute is dissolved in 1 kg (1000 g) of the solvent). The units of K_b are therefore, degree/molality *i.e.*, K/m or °C/m or K kg mol^{-1}.

48. When a non-volatile solute is added to a solvent, the vapour pressure of the solvent (above the resulting solution) is lower than the vapour pressure above the pure solvent.

49. Osmotic pressure is the extra pressure which is applied on the solution to just prevent the flow of solvent into the solution through a semi-permeable membrane.

50. *Refer to answer 46.*

51. Ebullioscopic constant is the boiling point elevation constant when one mole of solute is dissolved in 1000 g of solvent. It is denoted by K_b.

52. Colligative properties are the properties of solution which depend upon the number of solute particles and not upon the nature of the solute.

53. Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution side.

54. (i) The elevation in boiling point of a solution is a colligative property which depends on the number of moles of solute added. Higher the concentration of solute added, higher will be the elevation in boiling point. Thus, 2 M glucose has higher boiling point than 1 M glucose solution.

(ii) When the external pressure applied becomes more than the osmotic pressure of solution then the solvent molecules from the solution pass through the semipermeable membrane to the solvent side and the process is called reverse osmosis.

55. (i) 1.2% sodium chloride solution is hypertonic with respect to 0.9% sodium chloride solution or blood cells thus, on placing blood cells in this solution exosmosis takes place that results in shrinking of cells.

(b) 0.4% sodium chloride solution is hypotonic with respect to 0.9% sodium chloride solution or blood cells thus, on placing blood cells in this solution endosmosis takes place that results in swelling of cells.

56. The boiling point of the solution is always higher than that of the pure solvent. As the vapour pressure of the solution is lower than that of the pure solvent and vapour pressure increases with increase in temperature. Hence, the solution has to be heated more to make the vapour pressure equal to the atmospheric pressure.

Elevation of boiling point is a colligative property because it depends on number of solute particles present in a solution.

57. Given : $W_2 = ?$, $M_2 = 256\text{ g mol}^{-1}$, $\Delta T_f = 0.48\text{ K}$
$W_1 = 75\text{ g}$, $K_f = 5.12\text{ K kg mol}^{-1}$

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_f \times M_2 \times W_1}{K_f \times 1000} = \frac{0.48 \times 256 \times 75}{5.12 \times 1000} = 1.8\text{ g}$$

58. Given $W_1 = 1\text{ kg} = 1000\text{ g}$, $W_2 = 18\text{ g}$,
$M_2 = 180\text{ g mol}^{-1}$
$T_b^{\circ} = 373.15\text{ K}$, $K_b = 0.52\text{ K Kg mol}^{-1}$, $T_b = ?$
Using formula,

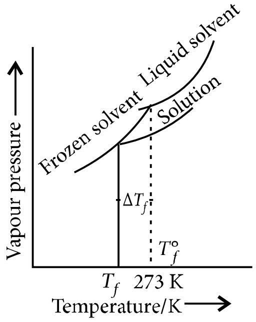
$$\Delta T_b = K_b \times \frac{W_2 \times 1000}{M_2 \times W_1}$$

or $$\Delta T_b = \frac{0.52\text{ K} \times 18 \times 1000}{180 \times 1000} = 0.052\text{ K}$$

$$\Delta T_b = T_b - T_b^{\circ}$$
$$0.052 = T_b - 373.15$$
$$T_b = 373.15 + 0.052 = 373.202\text{ K}$$

59. When a non-volatile solute is added to a solvent, the freezing point of the solution is always lower than that of pure solvent as the vapour pressure of the solvent decreases in the presence of non-volatile solute.

Plot for the lowering in freezing point of water when NaCl is added to it is shown as :



60. **Osmosis :** The spontaneous movement of the solvent molecules from the pure solvent or from a dilute solution to a concentrated solution through a semi-permeable membrane is called osmosis.

Osmotic Pressure : The minimum excess pressure that has to be applied on the solution to prevent the passage of solvent molecules into it through semipermeable membrane is called osmotic pressure.

Osmotic pressure is a colligative property because it depends on the number of solute particles and not on their nature.

61. (i) Number of particles of solute
(ii) Association or dissociation of solute
(iii) Concentration of solute
(iv) Temperature

62. *Refer to answer 60.*

The osmotic pressure method has the advantage over other methods because

(i) osmotic pressure can be measured at room temperature and the molarity of the solution is used instead of molality.

(ii) its magnitude is large as compared to other colligative properties even for very dilute solutions.

63. The egg placed in pure water will swell because the concentration of proteins is high inside the egg as compared to water. Therefore, endosmosis occurs and water diffuses through the semipermeable membrane. The egg which is placed in sodium chloride solution will shrink due to osmosis of water out of the egg.

64. Given, $W_2 = 0.520\text{ g}$,
$W_1 = 80.2\text{ g}$, $K_b = 0.52\text{ K m}^{-1}$
M_2 of $C_6H_{12}O_6 = 6 \times 12 + 12 \times 1 + 6 \times 16$
$= 180\text{ g mol}^{-1}$

$$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{0.52 \times 0.520 \times 1000}{180 \times 80.2} = 0.019\text{ K}$$

Boiling point of solution, $T_b = T_b^\circ + \Delta T_b$

$= 373\text{ K} + 0.019\text{ K} = 373.019\text{ K}$

65. *Refer to answer 49.*

Relation between osmotic pressure and molar mass,

$$\pi V = n_2 RT$$

$$\pi V = \frac{W_2 RT}{M_2} \qquad \left[\because\ n_2 = \frac{W_2}{M_2}\right]$$

$$M_2 = \frac{W_2 RT}{\pi V}$$

where π is osmotic pressure and

M_2 is molar mass of solute.

66. Mass of ethylene glycol ($C_2H_6O_2$), $W_2 = 31$ g

Mass of water, $W_1 = 500$ g

M_2 (Mol. mass of $C_2H_6O_2$) = 62 g mol^{-1},

$K_f = 1.86\text{ K kg mol}^{-1}$, $T_f = ?$

Using formula, $\Delta T_f = K_f \times \dfrac{W_2 \times 1000}{M_2 \times W_1}$

$$= 1.86 \times \frac{31 \times 1000}{62 \times 500} = 1.86\text{ K}$$

$$\Delta T_f = T_f^\circ - T_f$$

or $T_f = T_f^\circ - \Delta T_f = 273 - 1.86 = 271.14\text{ K}$

67. Mass of urea = 15 g

Molar mass of urea = 60 g mol^{-1}

Molar mass of glucose = 180 g mol^{-1}

Mass of glucose = ?

For isotonic solution, osmotic pressure, $\pi_1 = \pi_2$

$n_1 = n_2$ (when volume is same)

or $\dfrac{W_1}{M_1} = \dfrac{W_2}{M_2} \Rightarrow \dfrac{15}{60} = \dfrac{W_2}{180}$

$\Rightarrow \quad W_2 = \dfrac{15 \times 180}{60} = 45\text{ g}$

68. Mass of $CaCl_2$ (W_2) = 10 g

Mass of water (W_1) = 200 g

Molar mass of $CaCl_2$ (M_2) = 111 g mol^{-1}

Molal Elevation constant = 0.512 K kg mol^{-1}

$$m = \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$m = \frac{10}{111} \times \frac{1000}{200} = 0.450\text{ m}$$

$\Delta T_b = K_b\, m = 0.512 \times 0.450 = 0.2306\text{ K}$

69. (i) *Refer to answer 61.*

(ii) *Refer to answer 52.*

70. $T_f = -15°\text{C}$, $K_f = 1.86\text{ K kg mol}^{-1}$

$\Delta T_f = T_f^\circ - T_f = 0 - (-15°\text{C}) = 15°\text{C} = 288\text{ K}$

$\Delta T_f = K_f \times m$

$$288 = 1.86 \times \frac{W_2}{0.062 \times 5}$$

$W_2 = 48$ kg

$\Delta T_b = K_b \times m$

$$\Delta T_b = 0.52 \times \frac{48}{0.062 \times 5}$$

$\Delta T_b = 80.51$ K

$\Delta T_b = T_b - T_b^\circ$

$80.51 = T_b - 373$

$T_b = 80.51 + 373 = 453.51$ K

71. $W_2 = 1.00$ g, $W_1 = 50$ g, $K_f = 5.12\text{ K kg mol}^{-1}$,

$\Delta T_f = 0.40$ K

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$M_2 = \frac{K_f \times W_2 \times 1000}{W_1 \times \Delta T_f} = \frac{5.12 \times 1 \times 1000}{50 \times 0.40}$$

$= 256\text{ g mol}^{-1}$

72. Molality of sugar solution

$$= = \frac{W_2 \times 100}{M_2 \times W_1} = \frac{5}{342} \times \frac{1000}{95} = 0.154\text{ m}$$

$\Delta T_f = T_f^\circ - T_f = 273.15 - 271 = 2.15\text{ K}$

$\Delta T_f = K_f \times m \quad \therefore\ K_f = \dfrac{\Delta T_f}{m} = \dfrac{2.15}{0.154}$

Molality of glucose solution

$$= = \frac{W_2 \times 100}{M_2 \times W_1} = \frac{5}{180} \times \frac{1000}{95} = 0.292\text{ m}$$

$\therefore \quad \Delta T_f(\text{Glucose}) = K_f \times m = \dfrac{2.15}{0.154} \times 0.292 = 4.08$

$\therefore \quad$ Freezing point of glucose solution =

$= 273.15 - 4.08 = 269.07$ K

73. $W_1 = 500$ g

Boiling point of solution (T_b) = 100.42°C

K_b for water = 0.512 K kg mol^{-1}

$M_2(C_3H_8O_3) = (3 \times 12) + (8 \times 1) + (3 \times 16)$

$= 92\text{ g mol}^{-1}$

$\Delta T_b = T_b - T_b^\circ$

$= 373.42\text{ K} - 373\text{ K} = 0.42\text{ K}$

$$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_b \times M_2 \times W_1}{K_b \times 1000} = \frac{0.42 \times 92 \times 500}{0.512 \times 1000} = 37.73 \text{ g}$$

74. $W_1 = 450$ g, $W_2 = 15.0$ g

$\Delta T_f = T_f^\circ - T_f = 273 \text{ K} - 272.66 \text{ K} = 0.34 \text{ K}$

$K_f = 1.86 \text{ K kg mol}^{-1}$

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1}$$

$$M_2 = \frac{1.86 \times 15 \times 1000}{0.34 \times 450} = 182.35 \text{ g mol}^{-1}$$

75. The relative lowering of vapour pressure is given by the following expression,

$(p^\circ_{\text{solvent}} - p_{\text{solution}})/p^\circ_{\text{solvent}} = n_2/(n_1 + n_2)$

for dilute solutions, $n_2 << n_1$, therefore

$(p^\circ_{\text{solvent}} - p_{\text{solution}})/p^\circ_{\text{solvent}} = n_2/n_1$

$= (W_2 \times M_1)/(M_2 \times W_1)$

$(p^\circ_{\text{solvent}} - 2.8)/p^\circ_{\text{solvent}} = (30 \times 18)/(M_2 \times 90)$

$(p^\circ_{\text{solvent}} - 2.8)/p^\circ_{\text{solvent}} = 6/M_2$ ...(1)

Similarly for second case we get,

$(p^\circ_{\text{solvent}} - 2.9)/p^\circ_{\text{solvent}} = (30 \times 18)/(M_2 \times 108)$

$(p^\circ_{\text{solvent}} - 2.9)/p^\circ_{\text{solvent}} = 5/M_2$ ...(2)

On solving eq. (1) and (2), we get

$(p^\circ_{\text{solvent}} - 2.8)/(p^\circ_{\text{solvent}} - 2.9) = 6/5$

$\therefore \quad p^\circ_{\text{solvent}} = 3.4 \text{ k}P_a$

i.e., vapour pressure of water at 298 K is 3.4 kp_a

Substituting the value of p°_{solvent} in (1) we get,

$(3.4 - 2.8)/3.4 = 6/M_2$

or $\quad 0.6/3.4 = 6/M_2$

$\therefore \quad M_2 = 34$ g

76. $i = 2$, $K_b = 0.512 \text{ K kg mol}^{-1}$, $W_B = 15$ g

$M_B = 58.44 \text{ g mol}^{-1}$, $W_A = 250$ g

$$\Delta T_b = \frac{i \times K_b \times W_B \times 1000}{M_B \times W_A}$$

$$\Delta T_b = \frac{2 \times 0.512 \times 15 \times 1000}{58.44 \times 250} = 1.05 \text{ K}$$

Therefore, boiling point of aqueous solution,

$T_b = T_b^\circ + \Delta T_b = 373.15 \text{ K} + 1.05 \text{ K} = 374.20 \text{ K}$

77. $W_B = 8.95 \text{ mg} = 8.95 \times 10^{-3}$ g,

$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$, $V = 35 \times 10^{-3}$ L

$T = (25 + 273) \text{ K} = 298 \text{ K}$, $\pi = \frac{0.335}{760}$ atm

Substituting these values in the equation,

$$M_B = \frac{W_B \times R \times T}{\pi \times V}$$

$$M_B = \frac{8.95 \times 10^{-3} \text{ g} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{\frac{0.335}{760} \text{ atm} \times 35 \times 10^{-3} \text{ L}}$$

$M_B = 14193 .29 \text{ g mol}^{-1}$

78. $W_2 = 6.21$ g, $W_1 = 24.0$ g

$T_b = 68.04$ °C, $T_b^\circ = 61.7$ °C

and $K_b = 3.63$ °C/m

$\Delta T_b = T_b - T_b^\circ = 68.04 \text{ °C} - 61.7 \text{ °C} = 6.34 \text{ °C}$

$$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1}$$

or $$M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$$

$$M_2 = \frac{3.63 \text{°C m}^{-1} \times 6.21 \text{ g} \times 1000}{6.34 \text{°C} \times 24.0 \text{ g}} = 148.15 \text{ g mol}^{-1}$$

79. $W_1 = 65.0$ g, $\Delta T_f = 7.50$°C,

$K_f = 1.86$°C/m, $i = 1.87$ and $M_2 = 58.5 \text{ g mol}^{-1}$

$$\Delta T_f = \frac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_f \times M_2 \times W_1}{i \times K_f \times 1000} = \frac{7.50 \text{°C} \times 58.5 \text{ g mol}^{-1} \times 65 \text{ g}}{1.87 \times 1.86 \text{°C/m} \times 1000}$$

$= 8.199$ g

80. *Refer to answer 63.*

81. Concentration of the solution = 1 molar

Density of the solution = 1.06 g mL^{-1}

M_2, molar mass of KBr = 39 + 80 = 119 g mol^{-1}

K_b for H_2O = $0.52 \text{ K kg mol}^{-1}$

Molality, $$m = \frac{M \times 1000}{1000 \times d - M \times M_2}$$

$$m = \frac{1 \times 1000}{1000 \times 1.06 - 1 \times 119} = 1.0626 \text{ mol kg}^{-1}$$

$\Delta T_b = K_b m = 0.52 \text{ K kg mol}^{-1} \times 1.0626 \text{ mol kg}^{-1}$

$\Delta T_b = 0.5525 \text{ K} \approx 0.553 \text{ K}$

$T_b = T_b^\circ + \Delta T_b = 373 \text{ K} + 0.553 \text{ K} = 373.553 \text{ K}$

82. $W_2 = 1.25$ g, $W_1 = 99.0$ g

$\Delta T_b = T_b - T_b^\circ = (80.31 - 80.10)\text{°C} = 0.21\text{°C} = 0.21 \text{ K}$

$\Delta T_b = K_b \cdot m$

$$\Delta T_b = K_b \times \frac{W_2 \times 1000}{M_2 \times W_1}, \quad M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$$

$$= \frac{2.53 \times 1.25 \times 1000}{0.21 \times 99} = \frac{3162.5}{20.79} = 152.11 = 152 \text{ g mol}^{-1}$$

83. M_2 (ethylene glycol) = 62 g mol^{-1},
$W_1 = 5.50$ kg = 5500 g, $\Delta T_f = T_f^\circ - T_f = 0°\text{C} - (-10°\text{C})$
$= 10°\text{C} = 10$ K

and $K_f = 1.86$ K kg mol^{-1}

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_f \times M_2 \times W_1}{K_f \times 1000} = \frac{10 \times 62 \times 5500}{1.86 \times 1000} = 1833.33 \text{ g}$$
$$= 1.833 \text{ kg}$$

84. $W_2 = 100$ mg = 0.1 g,
$V = 10.0$ mL = 0.01 L,

$$\pi = 13.3 \text{ mm Hg} = \frac{13.3}{760} \text{atm}$$

$T = 25°\text{C} = 273 + 25 = 298$ K
$R = 0.0821$ L atm mol^{-1} K^{-1}

$$\pi V = \frac{W_2}{M_2} RT$$

$$M_2(\text{Protein}) = \frac{W_2 RT}{\pi V}$$

$$= \frac{0.1 \text{ g} \times 0.0821 \text{ L atm mol}^{-1}\text{K}^{-1} \times 298 \text{ K}}{\frac{13.3}{760} \text{ atm} \times 0.01 \text{ L}}$$

$M_2 = 13980.45$ g mol^{-1}

85. $W_1 = 1$ kg = 1000 g, $\Delta T_f = 3$ K
$K_f = 1.86$ K kg mol^{-1}
$M_2(\text{NaCl}) = 23 + 35.5 = 58.5$ g mol^{-1}

$$\Delta T_f = \frac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_f \times M_2 \times W_1}{i \times K_f \times 1000}$$

[For NaCl, $i = 2$ because 1 mole of NaCl on dissociation gives 2 moles of ions]

$$W_2 = \frac{3 \times 58.5 \times 1000}{2 \times 1.86 \times 1000} = 47.18 \text{ g}$$

86. Total moles in solution

$$= \frac{x}{200} + 0.05 \times 2 = \frac{x}{200} + 0.1 \qquad (\because i = 2 \text{ for NaCl})$$

$pV = nRT$

$$n = \frac{\pi V}{RT}$$

$$\frac{x}{200} + 0.1 = \frac{4.92 \text{ atm} \times 1 \text{ L}}{0.082 \text{ L atm K}^{-1}\text{mol}^{-1} \times 300 \text{ K}} = 0.20$$

$$\frac{x}{200} = 0.20 - 0.1 = 0.1$$

$x = 0.1 \times 200 = 20$ g

87. Molar mass of glucose, $C_6H_{12}O_6$
$= 6 \times 12 + 12 \times 1 + 6 \times 16 = 180$ g mol^{-1}
Molar mass of sucrose, $C_{12}H_{22}O_{11}$
$= 12 \times 12 + 22 \times 1 + 11 \times 16 = 342$ g mol^{-1}

$$n_{\text{glucose}} = \frac{18}{180} = 0.1, \quad n_{\text{sucrose}} = \frac{68.4}{342} = 0.2$$

Total moles of solute, $n_2 = 0.1 + 0.2 = 0.3$

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$\Delta T_f = \frac{K_f \times n_2 \times 1000}{W_1}$$

$$= \frac{1.86 \text{ K m}^{-1} \times 0.3 \text{ mol} \times 1000}{200 \text{ g}} = 2.79 \text{ K}$$

Freezing point of aqueous solution, $T_f = T_f^\circ - \Delta T_f$
$= 273 - 2.79 = 270.21$ K

88. M_2 (glucose, $C_6H_{12}O_6$) = 180 g mol^{-1}
$W_2 = 54$ g, $W_1 = 250$ g, $K_f = 1.86$ K kg mol^{-1}

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{1.86 \times 54 \times 1000}{180 \times 250} = 2.23 \text{ K}$$

Freezing point of solution, $T_f = T_f^\circ - \Delta T_f$
$= 273 \text{ K} - 2.23 \text{ K} = 270.77$ K

89. $T_b = 36.86°\text{C}$, $T_b^\circ = 35.60°\text{C}$
$\Delta T_b = T_b - T_b^\circ = 36.86 - 35.60 = 1.26°\text{C}$

$$m = \frac{W_2}{M_2} \times \frac{1000}{W_1} = \frac{8}{M_2} \times \frac{1000}{100} = \frac{80}{M_2}$$

$\Delta T_b = K_b \cdot m$

$$1.26 = 2.02 \times \frac{80}{M_2}$$

$$M_2 = \frac{80 \times 2.02}{1.26} = 128.25 \text{ g mol}^{-1}$$

90. Molality = 0.1539 m,
$\Delta T_f = T_f^\circ - T_f = 273.15 - 271 = 2.15$ K

$$\therefore \quad \Delta T_f = K_f \cdot m \text{ or } K_f = \frac{\Delta T_f}{m} = \frac{2.15}{0.1539}$$

Again mass of solute, $W_2 = 5$ g
Molar mass of solute, $M_2 = 180$ g mol^{-1}
Mass of solution = 100 g
∴ Mass of solvent, $W_1 = 95$ g

Using, $$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{2.15 \times 5 \times 1000}{0.1539 \times 180 \times 95} = 4.08 \text{ K}$$

∴ Freezing point of solution, $T_f = T_f^{\circ} - \Delta T_f$
$= 273.15 - 4.08 = 269.07$ K

91. **van't Hoff factor :** It is defined as the ratio of the experimental value of colligative property to the calculated value of the colligative property and is used to find out the extent of dissociation or association. Mathematically, it is represented as

$$i = \frac{\text{Experimental (or observed value) of colligative property}}{\text{Calculated (or normal value) of colligative property}}$$

92. *Refer to answer 91.*
(i) van't Hoff factor (i) > 1 for solutes undergoing dissociation
(ii) van't Hoff factor (i) < 1 For soutes undergoing association

93. Molecular mass of $Na_2SO_4 \cdot 10H_2O$
$= [2 \times 23 + 32 + 16 \times 4 + 10 \times (2 \times 1 + 16)]$
$= (46 + 32 + 64 + 180)$ g mol^{-1} = 322 g mol^{-1}
$Na_2SO_4 \cdot 10H_2O$ ionises as :
$Na_2SO_4 \cdot 10H_2O \rightleftharpoons 2Na^+ + SO_4^{2-} + 10H_2O$
⇒ $i = 3$

$$m = \frac{n_B}{W_A} = \frac{W_B}{M_B \times W_A} = \frac{6.00 \text{ g}}{322 \text{ g mol}^{-1} \times 0.1 \text{ kg}}$$
$= 0.186$ mol kg^{-1} = 0.186 m

Also, $\Delta T_f = i\, K_f \cdot m$
$= 3 \times 1.86$ K m^{-1} × 0.186 m = 1.04 K
⇒ $T_f = T_f^{\circ} - \Delta T_f = (273 - 1.04)$ K = 271.96 K

94. Molality of solution, $m = 1.00$ m
Boiling point of solution, $T_b = 100.18$°C = 373.18 K
Boiling point of water (solvent), $T_b^{\circ} = 100.00$°C = 373 K
$\Delta T_b = T_b - T_b^{\circ} = 373{\cdot}18$ K − 373 K = 0·18 K
$\Delta T_b = i\, K_b \cdot m$
0.18 K = $i \times K_b \cdot m$
0.18 K = $i \times 0.512$ K kg mol^{-1} × 1 mol kg^{-1}

$$i = \frac{0.18 \text{ K}}{0.512 \text{ K kg mol}^{-1} \times 1 \text{ mol kg}^{-1}} = 0.35$$

95. *Refer to answer 91 and 92 (i).*

96. $\Delta T_f = iK_f \cdot m$
i for $MgCl_2 = 3$

Molality, $$m = \frac{W_2 \times 1000}{M_2 \times W_1} = \frac{1.9 \times 1000}{95 \times 50} = 0.4 \text{ m}$$

$\Delta T_f = 3 \times 1.86 \times 0.4 = 2.232$ K
Freezing point of solution, , $T_f = T_f^{\circ} - \Delta T_f$
$= 273 - 2.232$ K = 270.77 K

97. $W_2 = 2.56$ g, $W_1 = 100$ g, $\Delta T_f = 0.383$ K
$K_f = 3.83$ K kg mol^{-1}, $\Delta T_f = K_f \times m$

$$\Rightarrow \quad \Delta T_f = K_f \times \frac{W_2}{M_2} \times \frac{1000}{W_1}$$

$$\Rightarrow \quad M_2 = \frac{W_2 \times 1000}{\Delta T_f \times W_1} \times K_f = \frac{2.56 \times 1000}{0.383 \times 100} \times 3.83$$
$= 256$ g mol^{-1}

$$\because \quad i = \frac{\text{Normal atomic mass}}{\text{Observed atomic mass}} = \frac{32}{256} = \frac{1}{8}$$

Sulphur exists as S_8.

98. $W_2 = 4$ g, $M_2 = 120$ g mol^{-1}
$W_1 = 100$ g, $K_b = 0.52$ K kg mol^{-1}
For complete dissociation, $i = 2$
Using formula, $\Delta T_b = iK_b m$

$$\text{or} \quad \Delta T_b = \frac{i \times K_b \times W_2 \times 1000}{M_2 \times W_1} = 2 \times 0.52 \times \frac{4 \times 1000}{120 \times 100}$$
$= 0.34$ K

∴ $T_b = T_b^{\circ} + \Delta T_b = 100 + 0.34 = 100.34$°C

99. $W_2 = 3.9$ g, $W_1 = 49$ g, $\Delta T_f = 1.62$ K, $M_2 = 122$ g mol^{-1}, $K_f = 4.9$ K kg mol^{-1}

$$\Delta T_f = i\, K_f m = i \times K_f \times \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$\Rightarrow \quad 1.62 = \frac{i \times 4.9 \times 3.9 \times 1000}{122 \times 49}$$

$$\Rightarrow \quad i = \frac{1.62 \times 122 \times 49}{4.9 \times 3.9 \times 1000} = 0.506$$

As $i < 1$, solute is associated.

100. $$\Delta T_f = iK_f m = \frac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$2 = \frac{2 \times 1.86 \times W_2 \times 1000}{58.5 \times 37.2}$$

⇒ $W_2 = 1.17$ g

101. Mass of K_2SO_4, $W_2 = 2.5 \times 10^{-2}$ g
Molar mass of K_2SO_4, $M_2 = 174$ g mol^{-1}
$V = 2$ L, $T = 25°C = 298$ K
$R = 0.0821$ L atm K^{-1} mol^{-1}

We know, osmotic pressure, $\pi = \dfrac{W_2RT}{M_2V}$

$$\pi = \frac{2.5\times10^{-2}\times0.0821\times298}{174\times2}$$
$$= \frac{61.1645\times10^{-2}}{348} = 0.1758\times10^{-2} \text{ atm}$$

102. $\Delta T_f = 2$ K, $K_f = 1.86$ K kg mol^{-1},
$W_1 = 1$ kg, $\Delta T_f = i\,K_f m$, M_2(KCl) $= 74.5$ g mol^{-1}

$i = 2$ for KCl

$$\Delta T_f = \frac{i\times K_f\times W_2\times1000}{M_2\times W_1}$$
$$2 = \frac{2\times1.86\times W_2\times1000}{74.5\times1000}$$
$\Rightarrow$ $W_2 = 40.05$ g

103. $W_2 = 10.50$ g, $W_1 = 200$ g
$M_2(MgBr_2) = 184$ g mol^{-1}
$K_f = 1.86$ K kg mol^{-1}
$MgBr_{2(aq)} \longrightarrow Mg^{2+}_{(aq)} + 2Br^-_{(aq)}$, $i = 3$

$$\Delta T_f = iK_f m,\quad \Delta T_f = \frac{i\times K_f\times W_2\times1000}{M_2\times W_1}$$
$$\Delta T_f = \frac{3\times1.86\times10.50\times1000}{184\times200} = 1.592 \text{ K}$$
Freezing point of solution, $T_f = T_f^\circ - \Delta T_f = 273 - 1.592$
$= 271.408$ K

104. $m = 0.561$ m, $\Delta T_f = 2.93°C$ and
$K_f = 1.86°C$ kg mol^{-1}
$\Delta T_f = iK_f m$
$$i = \frac{\Delta T_f}{K_f m} = \frac{2.93°C}{1.86°C \text{ kg mol}^{-1}\times0.561\text{ m}} = 2.807$$

105. Here, $n = 2$ because phenol forms dimer on association.
$W_2 = 20$ g, $W_1 = 1$ kg $= 1000$ g, $\Delta T_f = 0.69$ K, $K_f = 5.1$ K m^{-1}
$$\Delta T_f = \frac{K_f\times W_2\times1000}{M_2\times W_1}$$
$$M_2 = \frac{K_f\times W_2\times1000}{\Delta T_f\times W_1} = \frac{5.1\times20\times1000}{0.69\times1000} = 147.82$$
$M_{2(observed)} = 147.82$

$M_{2(calculated)}$
$C_6H_5OH = 6\times12 + 6\times1 + 16 = 94$ g mol^{-1}
$$i = \frac{M_{2(calculated)}}{M_{2(observed)}} = \frac{94}{147.82} = 0.635$$
$$2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$$
$$\alpha = \frac{i-1}{\left(\frac{1}{n}-1\right)} = \frac{0.635-1}{\left(\frac{1}{2}-1\right)} = \frac{0.365}{0.5} = 0.73 = 73\%$$

106. Here, $n = 3$ because 1 molecule of $BaCl_2$ on dissociation gives three ions.
$W_2 = 12.48$ g, $W_1 = 1.0$ kg $= 1000$ g
$T_b = 373.0832$ K, K_b for $H_2O = 0.52$ K m^{-1}
and $M_2(BaCl_2) = 208.34$ g mol^{-1}
$\Delta T_b = T_b - T_b^\circ = 373.0832$ K $- 373$ K $= 0.0832$ K
$$M_{2(observed)} = \frac{K_b\times W_2\times1000}{\Delta T_b\times W_1}$$
$$M_{2(observed)} = \frac{0.52\times12.48\times1000}{0.0832\times1000} = 78$$
$M_{2(observed)} = 78$ g mol^{-1}
$$i = \frac{M_{2(calculated)}}{M_{2(observed)}} = \frac{208.34 \text{ g mol}^{-1}}{78 \text{ g mol}^{-1}} = 2.67$$
$$\alpha = \frac{i-1}{n-1} = \frac{2.67-1}{3-1} = \frac{1.67}{2} = 0.835 = 83.5\%$$

107. $C = \dfrac{1}{10}$ M
$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$
$\therefore$ $n = 5$
Degree of dissociation, $\alpha = \dfrac{50}{100} = 0.5$
$$\alpha = \frac{i-1}{n-1},\ 0.5 = \frac{i-1}{5-1},\ 0.5 = \frac{i-1}{4}$$
$\Rightarrow$ $i - 1 = 2$ $\therefore$ $i = 3$
So, osmotic pressure, $\pi = iCRT$
$$= 3\times\frac{1}{10}\times0.0821\times300 = 90\times0.0821 = 7.389 \text{ atm}$$

108. $$M_2 = \frac{K_b\times W_2\times1000}{\Delta T_b\times W_1} = \frac{2.53\times0.30\times1000}{0.0633\times100}$$
$= 120$ g mol^{-1}
$\therefore$ Molar mass of $CH_3COOH = 60$ g/mol
$$i = \frac{M_{2(calculated)}}{M_{2(observed)}} = \frac{60}{120} = \frac{1}{2} = 0.5$$

Here, $i < 1$, therefore the solute acetic acid is associated in benzene.

109. (i) $M_2 = \dfrac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1} = \dfrac{5.12 \times 0.2 \times 1000}{0.45 \times 20}$

$= 113.77 \text{ g/mol}^{-1}$

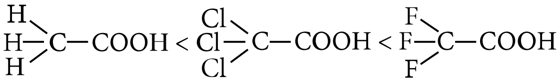
(ii) Molar mass of acetic acid = 60 g/mol

$$i = \frac{M_{2(\text{calculated})}}{M_{2(\text{observed})}} = \frac{60}{113.77} = 0.52$$

$i < 1$, the solute acetic acid is associated in benzene.

110. (i) The depression in freezing point is in the order :

Acetic acid < trichloroacetic < trifluoroacetic acid



$$\mathrm{H_3C{-}COOH} < \mathrm{Cl_3C{-}COOH} < \mathrm{F_3C{-}COOH}$$

Fluorine has the highest electron withdrawing inductive effect ($-I$ effect) so trifluoroacetic acid is the strongest acid and acetic acid is the weakest acid. Therefore, trifluoroacetic acid ionises to the greater extent and acetic acid ionises to the minimum extent. Greater the number of ions produced, greater is the depression in freezing point.

(ii) Molar mass of $CH_3CH_2CHClCOOH$

$= 4 \times 12 + 7 \times 1 + 35.5 + 2 \times 16 = 122.5 \text{ g mol}^{-1}$

Number of moles of $CH_3CH_2CHClCOOH$

$$= \frac{20}{122.5} = 0.1632 \text{ mol}$$

$$\text{Molality of solution} = \frac{\text{Moles of solute} \times 1000}{\text{Mass of solvent (g)}}$$

$$m = \frac{0.1632 \times 1000}{500} = 0.3264 \text{ m}$$

$$CH_3CH_2CHClCOOH_{(aq)} \rightleftharpoons CH_3CH_2CHClCOO^-_{(aq)} + H^+_{(aq)}$$

Initial conc.	C	0	0
Equili. conc.	$C - C\alpha$	$C\alpha$	$C\alpha$

where, α is the degree of dissociation of acid.

$$K_a = \frac{(C\alpha)^2}{C(1-\alpha)} = C\alpha^2 \qquad (\because\ 1 >>> \alpha)$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} = 0.065$$

$$\alpha = \frac{i-1}{n-1} \Rightarrow 0.065 = \frac{i-1}{2-1}$$ [$\because$ For the given acid $n = 2$ because 1 molecule gives 2 particles on dissociation.]

$i = 1 + 0.065 = 1.065$

$\Delta T_f = iK_f m$

$= 1.065 \times 1.86 \times 0.3264$

$\Delta T_f = 0.6465 \approx 0.65$ K