Solutions — Why so important

- Residents living in cold climate add antifreeze to water in cooling system of automobiles in winter. Why? We learn in this chapter.
- Body fluids of a dehydrated person can not be restored by pure water. Solution having a correct value of osmotic pressure is administered by intravenous drip. Why is it so? We understand in this chapter.

In this unit we learn the various type of solutions and how we express solution concentration. This is followed by knowing the factors which affect solubility.

Thereafter we explore several solution properties viz., vapour pressure, boiling point, freezing point etc. Whose values depend on solution concentration and lastly we study the colligative properties of electrolytic solutions.

A solution is a homogenous mixture of 2 or more substances.
- The solute is(are) the substance(s) present in smaller amount(s).
- The solvent is the substance present in larger amount(s).

A saturated solution contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature.
- An unsaturated solution contains less solute than the solvent has the capacity to dissolve at a specific temperature.

A supersaturated solution contains more solute than is present in a saturated solution at a specific temperature.
- Sodium acetate crystals rapidly form when a seed crystal is added to a supersaturated solution of sodium acetate.

Solution terminology
- Miscible / immiscible: Two liquids are miscible in each other if they readily mix to form a uniform solution (alcohol and water). Two immiscible liquids will always separate out into two distinct layers (oil and water).

General properties of solutions
1. A solution is a homogeneous mixture of two or more components.
2. It has variable composition.
3. The dissolved solute is molecular or ionic in size.
4. A solution may be either colored or colorless but is generally transparent.
5. The solute remains uniformly distributed throughout the solution and will not settle out through time.
6. The solute can be separated from the solvent by physical methods.

Steps in Solution Formation

Step 1 - Expanding the solute
Step 2 - Expanding the solvent
Step 3 - Allowing the solute and solvent to interact to form a solution

\[ \Delta H_{\text{soln}} = \Delta H_{\text{step 1}} + \Delta H_{\text{step 2}} + \Delta H_{\text{step 3}} \]

The formation of a liquid solution can be divided into three steps: (1) expanding the solute, (2) expanding the solvent, and (3) combining the expanded solute and solvent to form the solution.

The driving factor that favors the process of solution formation is an increase in disorder.

The energy terms for various types of solutes and solvents

<table>
<thead>
<tr>
<th>Solvent Type</th>
<th>( \Delta H_1 )</th>
<th>( \Delta H_2 )</th>
<th>( \Delta H_3 )</th>
<th>( \Delta H_{\text{soln}} )</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polar solvent, polar solute</td>
<td>Large</td>
<td>Large</td>
<td>Large, negative</td>
<td>Small</td>
<td>Solution forms</td>
</tr>
<tr>
<td>Nonpolar solvent, nonpolar solute</td>
<td>Small</td>
<td>Large, positive</td>
<td>Small</td>
<td>No solution forms</td>
<td></td>
</tr>
<tr>
<td>Nonpolar solvent, polar solute</td>
<td>Small</td>
<td>Small</td>
<td>Large, positive</td>
<td>No solution forms</td>
<td></td>
</tr>
</tbody>
</table>

Factor Affecting Solubility

1. Structure
2. Pressure
3. Temperature

Two substances with similar intermolecular forces are likely to be soluble in each other.

- Non-polar molecules are soluble in non-polar solvents \( \text{CCl}_4 \) in \( \text{C}_6\text{H}_6 \)
- Polar molecules are soluble in polar solvents \( \text{C}_2\text{H}_5\text{OH} \) in \( \text{H}_2\text{O} \)
- Ionic compounds are more soluble in polar solvents \( \text{NaCl} \) in \( \text{H}_2\text{O} \) or \( \text{NH}_3 \) (l)

The molecular structures of (a) vitamin A (nonpolar, fat-soluble) and (b) vitamin C (polar, water-soluble). The circles in the structural formulas indicate polar bonds. Note that vitamin C contains far more polar bonds than vitamin A.

Pressure Effects

- Pressure has little effect on solids and liquids.
- It increases the solubility of gases.
Slide 16

(a) A gaseous solute in equilibrium with a solution.
(b) The piston is pushed in, increasing the pressure of the gas and number of gas molecules per unit volume. This causes an increase in the rate at which the gas enters the solution, so the concentration of dissolved gas increases.
(c) The greater gas concentration in the solution causes an increase in the rate of escape. A new equilibrium is reached.

Slide 17

Henry’s Law

- The amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution.
  \[ \text{C} = k \times \text{P} \]
  \[ \text{C} = \text{concentration of dissolved gas} \]
  \[ \text{P} = \text{partial pressure of gaseous solute above the solution} \]
  \[ k = \text{a constant} \]

Slide 18

Henry’s Law Applied for

- Dilute solutions
- Gases that do not dissociate or react with solvent:
  - O$_2$/water: Applied
  - HCl/water: Is not applied

Slide 19

Temperature Effect on Gases

- The solubilities of several gases in water as a function of temperature at a constant pressure of 1 atm of gas above the solution.

Slide 20

The solubilities of several solids as a function of temperature

Slide 21

General Solubility Rules for aqueous solutions

- Disclaimer: these rules do not address slightly soluble salts.
- All Na$^+$, K$^+$, and NH$_4^+$ salts are soluble.
- All NO$_3^-$ and most C$_2$H$_5$O$_2^-$ are soluble.
- The Halides are soluble except Ag$^+$, Hg$_2^{2+}$, & Pb$^{2+}$.
- Sulfates are soluble except Ba$^{2+}$, Sr$^{2+}$, and Pb$^{2+}$.
- CO$_3^{2-}$, OH$^-$, & S$^{2-}$ are insoluble of Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$; Al$^{3+}$, Cr$^{3+}$, Fe$^{3+}$ and Pb$^{2+}$, Cu$^{2+}$, Bi$^{3+}$, Hg$^{2+}$ etc. respectively.
Solution Composition

1. Molarity (M) = \( \frac{\text{moles of solute}}{\text{liters of solution}} \)
2. Mass (weight) percent = \( \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \)
3. Mole fraction \( (\chi_A) = \frac{\text{moles of solute}}{\text{total moles in solution}} \)
4. Molality \( (m) = \frac{\text{moles of solute}}{\text{kilograms of solvent}} \)

Calculating concentration of solutions

1. Mass Percent = \( \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \)
2. Parts per million = \( \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \)
3. Mass/volume percent = \( \frac{\text{mass of solute}}{\text{mL solution}} \times 100 \)
4. Volume percent = \( \frac{\text{mL solute}}{\text{mL solution}} \times 100 \)
5. Molarity = moles solute / L solution
6. Molality = moles of solute / kg solvent

Concentration Units

- The concentration of a solution is the amount of solute present in a given quantity of solvent or solution.

**Percent by Mass**

\[ \% \text{ by mass} = \frac{\text{mass of solute}}{\text{mass of solution} + \text{mass of solute}} \times 100\% \]

**Mole Fraction \( (X) \)**

\[ X_A = \frac{\text{moles of } A}{\text{sum of moles of all components}} \]

Concentration Units Continued

**Molarity (M)**

\[ M = \frac{\text{moles of solute}}{\text{liters of solution}} \]

**Molality (m)**

\[ m = \frac{\text{moles of solute}}{\text{mass of solvent} \times \text{liters of solution}} \]

Normality (N)

\[ N = \frac{\text{number of equivalents}}{\text{liters of solution}} \]

Number of equivalents

- Acid-Base reaction: is the amount needed to accept one mole of H\(^+\)
  \[ \text{Equivalent mass of } H_2SO_4 = \frac{MM}{2} \]
  \[ \text{Equivalent mass of } Ca(OH)_2 = \frac{MM}{2} \]

Redox reaction: is the amount needed to accept exactly one mole e\(^-\)

\[ MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O \]

Equivalent mass of KMnO\(_4\) = \( \frac{MM}{5} \)

The Molar Mass, Equivalent Mass, and Relationship of Molarity and Normality for Several Acids and Bases

<table>
<thead>
<tr>
<th>Acid or Base</th>
<th>Molar Mass</th>
<th>Equivalent Mass</th>
<th>Relationship of Molarity and Normality</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>36.5</td>
<td>36.5</td>
<td>1 ( M = 1 \ N )</td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>98</td>
<td>98</td>
<td>1 ( M = 2 \ N )</td>
</tr>
<tr>
<td>NaOH</td>
<td>40</td>
<td>40</td>
<td>1 ( M = 1 \ N )</td>
</tr>
<tr>
<td>Ca(OH(_2))</td>
<td>74</td>
<td>74</td>
<td>1 ( M = 2 \ N )</td>
</tr>
</tbody>
</table>

What is the molality of a 5.86 M ethanol (C\(_2\)H\(_5\)OH) solution whose density is 0.927 g/mL?

\[ m = \frac{\text{moles of solute}}{\text{mass of solvent} \times \text{liters of solution}} \]

Assume 1 L of solution:

5.86 moles ethanol = 270 g ethanol

927 g of solution (1000 mL x 0.927 g/mL)

mass of solvent = mass of solution – mass of solute

\[ = 927 \text{ g} - 270 \text{ g} = 657 \text{ g} = 0.657 \text{ kg} \]

\[ m = \frac{\text{moles of solute}}{\text{mass of solvent} \times \text{liters of solution}} = \frac{5.86 \text{ moles C}_2\text{H}_5\text{OH}}{0.657 \text{ kg solvent}} = 8.92 \text{ m} \]

Properties whose values depend only on the concentration of solute particles in solution and not on what the solute is called colligative properties. Some of these properties are:

- Lowering in vapour pressure
- Elevation in boiling point
- Depression in freezing point
- Osmotic pressure
Vapour Pressure:
- The pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature is called vapour pressure of the liquid.

Raoult’s law

(A) For Non-volatile solute
- The vap. Pressure of solution containing non-volatile solute is less than the vapour pressure of pure solvent.
- If $p_1$ is the vapour pressure of solvent in solution and $p_1' - p_1 = p_1' - p_1 x_1$
  (since $x_1 = x_1 p_1'$)
  or $p_1' = p_1 (1 - x_1)$

(B) Solution of two volatile liquids
- Two volatile liquids A and B.
  $P_A \propto X_A$ Or $P_A = P_A^\circ X_A$
  $P_B \propto X_B$ Or $P_B = P_B^\circ X_B$
  $P_A^\circ$ and $P_B^\circ$ are vapour pressure of pure components A and B respectively.
Molecular interactions are responsible for those deviations.

- For positive deviation \( A - B < A - A \) or \( B - B \).
- Examples are ethanol and acetone or carbon disulphide and acetone.

- For negative deviation \( A - B > A - A \) or \( B - B \).
- Phenol and aniline; chloroform and acetone are examples of this type.

Some liquid solutions form azeotropes which are binary mixtures.

- These have the same composition in the liquid and vapour phase and boil at a constant temperature.

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

Azeotropes can be minimum or maximum boiling.

Ethanol-water mixtures show a large positive deviation and form a minimum boiling azeotrope.

- This azeotrope contains approx 95% ethanol and 5% water,
- Similarly nitric acid and water have less vapour pressure than the ideal value and show a negative deviation and form a maximum boiling azeotrope.
- It contains almost 68 percent nitric acid and 32% water by mass.

Elevation in boiling point

- The temperature at which the vapour pressure becomes equal to the atmospheric pressure is called boiling point.
- On dissolving a non-volatile solute in the solvent, the boiling temperature of the solution goes up.
- The following figure depicts the boiling point of pure solvent and solution.

Experiments have shown that for dilute solution
\[ \Delta T_b \propto m \]

or
\[ \Delta T_b = K_b \cdot m \]

\( K_b = \frac{R \cdot M \cdot T_b^2}{1000 \cdot \Delta H_{vap.}} \) is called molal elevation constant or molal ebullioscopic constant.

Here \( R \) is gas constant, \( M \) is molar mass of solvent, \( T_b \) is boiling point of pure solvent, \( \Delta H_{vap.} \) is enthalpy of vapourisation.

Calculation of Molecular mass. The molality \( m \) of solution is:

\[ m = \frac{W_B}{M_B} \times \frac{1000}{W_A} \]

Here \( W_B \) and \( M_B \) and \( W_A \) are weight and molar mass of solute and \( W_A \) is weight of solvent

\[ \Delta T_b = K_b \cdot m = K_b \frac{W_B}{M_B} \times \frac{1000}{W_A} \]

or

\[ m = \frac{K_b \times W_B \times 1000}{W_A \times \Delta T_b} \]

Depression in freezing point

- Freezing point is defined as the temperature at which its solid and liquid phase have the same vapour pressure.
\[ \Delta T_f \propto m \]
\[ \Delta T_f = K_f \times m \]

Where \( K_f \) is the molal depression constant or cryoscopic constant.\[ K_f = \frac{R \cdot M \cdot T_f^2}{1000 \cdot \Delta H_{\text{ fus.}}} \]

Here \( R \) is gas constant, \( M \) is molar mass of solvent, \( T_f \) is freezing point of solvent and \( \Delta H_{\text{ fus.}} \) is enthalpy of fusion.

---

### Slide 49

**Calculation of Molecular Mass.** The molality of solution \( m \) is:

\[ m = \frac{W_B \times 1000}{M_B \times W_A} \]

or \[ \Delta T_f = K_f \times \frac{W_B \times 1000}{M_B \times W_A} \]

or \[ m = \frac{K_f \times W_B \times 1000}{W_A \times \Delta T_f} \]

---

### Slide 50

**Osmosis and osmotic pressure**

- The osmotic pressure of the solution at a particular temperature may be defined as the excess hydrostatic pressure that builds up when the solution is separated from the solvent by a semi-permeable membrane. \((\pi)\)
- **Isotonic**: Two solutions having same osmotic pressure.
- **Hypertonic solution**: Solutions having higher osmotic pressure in comparison to others is said to be hypertonic w.r.t. other.

---

### Slide 51

**Osmosis**

- The semipermeable membrane should allow only the movement of solvent molecules.
- Therefore, solvent molecules move from pure solvent to solution.

---

### Slide 52

- Equilibrium is reached when pressure produced by extra solution —
  - the **OSMOTIC PRESSURE**, \( \pi \)
  - \( \pi = cRT \) (where \( c \) is conc. in mol/L)
  - counterbalances pressure of solvent molecules moving thru the membrane.

---

### Slide 53

**Abnormal Colligative Properties**

- Colligative properties depend on the number of particles present in solution.
- If the solute undergoes dissociation or association in solution, the number of particles change and the observed values of the colligative properties would also change.

---

### Slide 54

- Vant Hoff introduced a factor \( i \) known as van’t Hoff factor to account for the extent of dissociation or association. Thus

\[ i = \frac{\text{Total number of particles after dissociation or association}}{\text{Total number of particles before dissociation or association}} \]

\[ i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}} \]

\[ i = \frac{\text{Normal molarmass}}{\text{Observed molarmass}} \]

---

### Slide 55

- In the case of association or dissociation of solute particles the expressions are:

\[ \Delta p = \frac{i \cdot n_2}{n_1} \]

\[ \Delta T_f = i K_f \cdot m \]

\[ \pi = i n_1 R T / V \]

\[ n_2 = \text{moles of solute and } n_1 = \text{mole of solvent} \]
CURRICULUM BASED WORKSHEET

Topics for Worksheet - I

- Concentration of solutions
- Henry’s law
- Vapour-pressure of Liquid-Liquid solutions
- Raoult’s law.

Worksheet - I

1. How many grams of H\textsubscript{2}SO\textsubscript{4} are required to prepare 250 ml of 0.2 molar solution?
2. Define an ‘ideal solution’.
3. Prove that the relative lowering of vapour pressure is equal to the mole fraction of nonvolatile solute in the solution.
4. Which type of deviation is shown by the solution formed by mixing cyclohexane and ethanol?
5. Why does the molality of a solution remains unchanged with temperature?
7. List the factors on which the Henry’s constant depends.
8. Henry’s law constant for the molality of methane in benzene is 4.27 \times 10^{5} \text{mmHg}. Calculate the solubility of methane in benzene at 298 K under 760 mmHg.
9. Calculate the mol fraction of ethyl alcohol (C\textsubscript{2}H\textsubscript{5}OH) and water in a solution in which 46 g of ethyl alcohol and 90 g of water have been mixed.
10. What is the molarity and molality of a 13% solution (by weight) of sulphuric acid? Its density is 1.020 g cm\textsuperscript{-3} (Atomic masses: H = 1, O = 16, S = 32 amu)
11. The vapour pressure of a dilute aqueous solution of glucose is 750 mm Hg at 373 K. Calculate the mole fraction of solute. The vapour pressure of pure water is 760 mm Hg at 373 K.
12. State Raoults’s law. State giving suitable examples the factors responsible for deviations from this law.
13. The vapour pressure of pure benzene at 25°C is 639.7 mm Hg and the vapour pressure of a solution of a nonvolatile solute in benzene at the same temperature is 631.9 mm Hg. Calculate the mole fraction of the solute.
14. The vapour pressure of benzene and toluene at 293 K are 75 mm and 22 mm Hg respectively. 23.4 g of benzene and 64.4g of toluene are mixed. If the two form and ideal solution, calculate the mole fraction of benzene in vapour phase assuming that the vapours are in equilibrium with the liquid mixture at this temperature.

Topics for Worksheet – II

- Elevation in boiling point
- Depression in freezing point
- Osmotic pressure
- Abnormal colligative properties.

Worksheet - II

1. What properties depend on the number of particles dissolved in solution rather than their chemical identity? Name two such properties.
2. Which has the highest freezing point:
   (a) 1 M glucose
   (b) 1 M NaCl
   (c) 1 M CaCl\textsubscript{2}
   (d) 1 M AlF\textsubscript{3}?
3. If \(\pi\) is the osmotic pressure and \(V\) is the volume in litres of solution containing one gm mol of solute, what would be the value of \(\pi V\) at 273 K.
4. Before giving intravenous injection what care is generally taken and why?
5. The freezing point of pure nitrobenzene is 278.8 K. When 2.5 g of unknown substance is dissolved in 100 g of nitrobenzene, the freezing point of solution is found to be 276.8 K. If the freezing point depression constant of nitrobenzene is 8.0 K kg mol\textsuperscript{-1}, what is the molar mass of unknown substance?
6. One litre aqueous solution of sucrose (molar mass = 342 g mol\textsuperscript{-1}) weighing 1015 g is found to record an osmotic pressure of 4.82 atm at 293 K. What is the molality of the sucrose solution?
7. A solution containing 12.5 g of a non electrolyte substance in 175 g of water gave a boiling point elevation of 0.70 K. Calculate the molar mass of the substance. (Elevation constant for water is \(K_b = 0.52\ \text{K kg mol}^{-1}\))
8. To 500 cm\textsuperscript{3} of water, 3.0 \times 10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be depression in freezing point? \(K\) and density of water are 1.86 K kg mol\textsuperscript{-1} and 0.997 g cm\textsuperscript{-3} respectively.
9. 45 g of ethylene glycol, C\textsubscript{2}H\textsubscript{6}O\textsubscript{2} is mixed with 600 g of water. Calculate the freezing point depression and the freezing point of the solution.
10. A 5% solution (by mass) of cane sugar in water has freezing point 271 K. Calculate the freezing point of a 5% glucose in water if freezing point of pure water is 273.15 K.
11. What is the molar concentration of solute particles in human blood if the osmotic pressure is 7.2 atm at the body temperature of 37°C? (R = 0.0821 L atm K⁻¹ mol⁻¹)
12. How much glucose must be dissolved in one litre of an aqueous solution so that its osmotic pressure is 2.57 atm at 300 K? (R = 0.0821 L atm K⁻¹ mol⁻¹)
13. What is reverse osmosis? Give its one use.
14. What are antifreeze solutions? Which substance is generally used in it?
15. A solution of a non volatile solute in water freezes at –14°C. What is the formula of the solute?

2 Marks Questions

1. For which of the following van’t Hoff factor cannot be greater than unity:
   (a) Kₐ[Fe(CN)₆]⁻
   (b) AlCl₃
   (c) NH₃CONH₂
   (d) KNO₃?
2. Osmotic pressure of a solution containing 7 g of dissolved protein per 100 cm³ of the solution is 20 mm Hg at 310 K. Calculate the molar mass of protein. [R = 0.082 L atm K⁻¹ mol⁻¹]
3. An electrolyte AB is 50% ionized in aqueous solution. Calculate the freezing point of 1 molal aqueous solution.
4. What is molar concentration of solute particles in a human blood if the osmotic pressure is 7.2 atm at the body temperature of 37°C?
5 Marks Questions

16. An antifreeze solution is prepared from 222.6 g of ethylene glycol (C₄H₈O₂), and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g/mL, then what is the molarity of the solutions?

17. If N₂ gas is bubbled through water at 293 K, how many millimoles of N₂ gas would dissolve in 1 L of water. Assume that N₂ exerts a partial pressure of 0.987 bar. Given that Henry’s law constant for N₂ at 293 K is 76.48 K bar.

18. At 40°C, methanol and ethanol form nearly an ideal solution with the pressure given by:

\[ p = 119 \times x + 135 \]

Where \( x \) is the mole fraction of methanol and \( P \) is the vapour pressure in torr. What are the vapour pressures of the pure methanol and pure ethanol at this temperature?

19. What is meant by positive and negative deviations from Raoult’s law? How is the sign of \( \Delta H_{\text{mix}} \) related to positive and negative deviations from Raoult’s law?

20. Ethylene glycol (C₄H₈O₂) is used as antifreeze and has density of 1.109 g/cm³. How many litres of ethylene glycol should be used per litre of water to protect it from freezing at –3.7°C?

21. The molal freezing point depression constant of benzene (C₆H₆) is 4.90 K kg mol⁻¹. Selenium exists as a polymer of the type Se₆. When 3.26 g of selenium is dissolved in 226 g of benzene, the observed freezing point is 0.112°C lower than for pure benzene. Deduce the molecular formula of selenium.

22. Assuming complete ionization, calculate the expected freezing point of solution prepared by dissolving 6.00 g of Glauber’s salt, Na₂SO₄·10H₂O in 0.1 kg of H₂O. (Kᵣ for H₂O = 1.86 K kg mol⁻³) [At. mass of Na = 23, S = 32, O = 16, H = 1 u]

### QUESTION BANK FOR COMPETITIONS

1. The solubility of a specific non-volatile salt is 4 g in 100 g of water at 25ºC. If 2.0 g, 4.0 g and 6.0 g of the salt added to 100 g of water at 25ºC, in system X, Y and Z, the vapour pressure would be in the order:

(a) \( X < Y < Z \)  
(b) \( X > Y > Z \)  
(c) \( Z > X = Y \)  
(d) \( X > Y = Z \)

2. The vapour pressure of an aqueous solution of sucrose at 373 K is found to be 750 mm Hg. The molality of the solution at the same temperature will be:

(a) 0.26  
(b) 0.70  
(c) 0.74  
(d) 0.039

3. Equal weight of a solute are dissolved in equal weight of two solvents A and B and these form very dilute solution. The relative lowering of vapour pressure for the solution B has twice the relative lowering of vapour pressure for the solution A. If \( M_A \) and \( M_B \) are the molecular weights of solvents A and B respectively, then:

(a) \( M_A = M_B \)  
(b) \( M_B = 2 \times M_A \)  
(c) \( M_A = 4M_B \)  
(d) \( M_A = 2M_B \)

4. An ideal solution has two components A and B. A is more volatile than B, i.e., \( P_A^0 > P_B^0 \) and also \( P_A^0 > P_{\text{total}}. \) If \( X_A \) and \( Y_A \) are mole fractions of components A in liquid and vapour phases, then:

(a) \( X_A > Y_A \)  
(b) \( X_A > Y_A \)  
(c) \( X_A < Y_A \)  
(d) Data insufficient

5. At 25ºC, the vapour pressure of pure liquid A (mol. Wt. = 40) is 80 torr, while that of pure liquid B is 40 torr, (mol. Wt. = 80). The vapour pressure at 25ºC of a solution containing 20 g of each A and B is:

(a) \( 80 \) torr  
(b) \( 59.8 \) torr  
(c) \( 68 \) torr  
(d) \( 48 \) torr

6. Two liquids A and B have vapour pressure in the ratio \( P_A^0 : P_B^0 = 1 : 3 \) at a certain temperature. Assume A and B form an ideal solution and the ratio of mole fractions of A to B in the vapour phase is 4 : 3. Then the mole fraction of B in the solution at the same temperature is:

(a) \( \frac{1}{5} \)  
(b) \( \frac{2}{5} \)  
(c) \( \frac{4}{5} \)  
(d) \( \frac{1}{4} \)

7. Two liquids A and B have \( P_A^0 \) and \( P_B^0 \) in the ration of 1 : 3 and the ratio of number of moles of A and B in liquid phase are 1 : 3 then mole fraction of ‘A’ in vapour phase in equilibrium with the solution is equal to:

(a) 0.1  
(b) 0.2  
(c) 0.5  
(d) 1.0

8. The vapour pressure curves of the same solute in the same solvent are shown. The curves are parallel to each other and do not intersect. The concentrations of solutions are in order of:

(a) \( I < II < III \)  
(b) \( I = II = III \)  
(c) \( I > II > III \)  
(d) \( I > III > II \)
9. Total vapour pressure of mixture of 1 mole of volatile component A (P_A = 100 mm Hg) and 3 mole of volatile component B (P_B = 80 mm Hg) is 90 mm Hg. For such case:
   (a) There is positive deviation from Raoult’s law
   (b) Boiling point has been lowered
   (c) Force of attraction between A and B is smaller than that between A and A or between B and B
   (d) All the above statements are correct

10. The azeotropic mixture of water (B.P. = 100ºC) and HCl (B.P. = 86ºC) boils at about 120ºC. During fractional distillation of this mixture it is possible to obtain:
   (a) Pure HCl
   (b) Pure H_2O
   (c) Pure H_2O as well as Pure HCl
   (d) Neither H_2O nor HCl

11. Chloroform, CHCl_3, boils at 61.7ºC. If the K_f for chloroform is 3.63ºC/molal, what is the boiling point of a solution of 15.0 kg of CHCl_3 and 0.616 kg of acenaphthalene, C_{12}H_{10}?  
   (a) 61.9
   (b) 62.0
   (c) 52.2
   (d) 62.67

12. A compound has the empirical formula C_{36}H_{6}Fe. A solution of 0.26 g of the compound in 11.2 g of benzene (C_{6}H_{6}) boils at 80.26ºC; the K_b for benzene is 5.12ºC/m. What is the molecular formula of the compound? (B.P. Benzene = 80.10)
   (a) C_{36}H_{6}Fe
   (b) C_{18}H_{3}Fe
   (c) C_{36}H_{2}Fe
   (d) C_{20}H_{10}Fe_{2}

13. One molal solution of a carboxylic acid in benzene shows the elevation of boiling point of 1.518 K. The degree of association for dimerization of the acid in benzene is (K_f for benzene = 2.53 K kg mol^{-1}):  
   (a) 60%
   (b) 70%
   (c) 75%
   (d) 80%

14. The boiling point elevation constant for toluene is 3.32 K kg mol^{-1}. The normal boiling point of toluene is 110.7ºC. The enthalpy of vaporisation of toluene would be nearly:  
   (a) 17.0 kJ mol^{-1}
   (b) 34.0 kJ mol^{-1}
   (c) 51.0 kJ mol^{-1}
   (d) 68.0 kJ mol^{-1}

15. C_{6}H_{6} freezes at 5.5ºC. At what temperature will a solution of 10.44 g of C_{6}H_{10} in 200 g of C_{6}H_{6} freeze? K (C_{6}H_{6}) = 5.12ºC/m
   (a) 4.608ºC
   (b) 0.892ºC
   (c) 5.5ºC
   (d) none of these

16. The freezing point of equimolal aqueous solutions will be highest for:
   (a) C_{6}H_{5}NH_{3}Cl
   (b) Ca(NO_3)_2
   (c) La(NO_3)_2
   (d) C_{6}H_{5}O_6

17. Depression in freezing point of 0.01 molal aqueous HCOOH solution is 0.02046. 1 molal aqueous urea solution freezes at -1.86ºC, assuming molality equal to molarity, pH of HCOOH solution is:
   (a) 2
   (b) 3
   (c) 4
   (d) 5

18. When mercuric iodide is added to the aqueous solution of KI, then the:
   (a) Freezing point is raised
   (b) Freezing point is lowered
   (c) Freezing point does not change
   (d) Boiling point does not change

19. The cryoscopic constant of water is 1.86 K kg mol^{-1}. A 0.01 molal acetic acid solution produces a depression of 0.0194ºC in the freezing point. The degree of dissociation of acetic acid is:
   (a) Zero
   (b) 0.043
   (c) 0.43
   (d) 1

20. In a 0.2 molal aqueous solution of weak acid HX the degree of ionization is 0.25. The freezing point of the solution will be nearest to: (K_i = 1.86 K kg mol^{-1})  
   (a) –0.26ºC
   (b) 0.465ºC
   (c) –0.48ºC
   (d) –0.465ºC

21. When some NaCl was dissolved in water, the freezing point depression was numerically equal to twice the molal depression constant. The relative lowering of vapour pressure of the solution is:
   (a) 0.117
   (b) 0.018
   (c) 0.0585
   (d) none of these

22. 0.1 molal aqueous solution of an electrolyte AB_3 is 90% ionized. The boiling point of the solution at 1 atm is:  
   (K_b(H_2O) = 0.52 K Kg mol^{-1})
   (a) 273.19 K
   (b) 374.92 K
   (c) 376.4 K
   (d) 373.19 K

23. A semi permeable membrane used in the measurement of osmotic pressure of a solution allows the passage of:
   (a) Solute molecules through it
   (b) Solvent molecules through it
   (c) Both solvent and solute molecules
   (d) Either solvent or solute molecules

24. A 5% (w/V) solution of cane sugar (molecular weight = 342) is isotonic with 1% (w/V) solution of a substance X. The molecular weight of X is:
   (a) 34.2
   (b) 171.2
   (c) 68.4
   (d) 136.8

25. A 1% (w/vol) KCl solution is ionized to the extent of 80%. The osmotic pressure at 27ºC of the solution will be:
   (a) 6.95 atm
   (b) 5.94 atm
   (c) 2.71 atm
   (d) 3.30 atm

26. The relationship between osmotic pressures (π_a, π_b and π_c) at a definite temperature when 1 g glucose, 1 g urea and 1 g sucrose are dissolved in 1 litre of water is (assume l = 1 for all):
   (a) π_a > π_b > π_c
   (b) π_b > π_a > π_c
   (c) π_b > π_a > π_c
   (d) π_b > π_a > π_c
   (e) π_a > π_b > π_c
27. A solution containing 4.0 g of PVC in 2 litre of dioxane (industrial solvent) was found to have an osmotic pressure $3.0 \times 10^{-4}$ atm at 27ºC. The molecular mass of the polymer will be:
(a) $1.6 \times 10^4$  
(b) $1.6 \times 10^5$
(c) $1.6 \times 10^3$  
(d) $1.6 \times 10^2$

28. The osmotic pressures of 0.010 M solutions of KI and of sucrose ($C_{12}H_{22}O_{11}$) are 0.432 atm and 0.24 atm respectively. The van’t Hoff factor for KI is:
(a) 1.80  
(b) 0.30
(c) 1.2  
(d) 1.0

29. Two breaker A and B are present in a closed vessel. Beaker A contains 152.4 g aqueous solution of urea, containing 12 g of urea. Beaker B contains 196.2 g glucose solution, containing 18 g of glucose. Both solutions are allowed to attain the equilibrium. Determine wt % of glucose in its solution at equilibrium:
(a) 6.71  
(b) 14.49
(c) 16.94  
(d) 20

30. An ideal solution contains two volatile liquids A ($p^o = 100$ torr) and B($p^o = 200$ torr). If mixture contain 1 mole of A and 4 mole of B then total vapour pressure of the distillate is:
(a) 150  
(b) 180
(c) 188.88  
(d) 198.88

31. An aqueous solution boils at 101ºC. What is the freezing point of the same solution? ($K_f = 1.86^\circ$C/m and $K_b = 0.51^\circ$C/m)
(a) 3.674ºC  
(b) -3.647ºC
(c) -0.364ºC  
(d) none of these

32. 0.1 M KI and 0.2 M AgNO$_3$ are mixed in 3 : 1 volume ratio.
The depression of freezing point of the resulting solution will be [$K_f (H_2O) = 1.86$ K kg mol$^{-1}$]:
(a) 3.72 K  
(b) 1.86 K
(c) 0.93 K  
(d) 0.279 K