

# THERMODYNAMICS & THERMOCHEMISTRY

## SYNOPSIS :

Some important terms, their types and their meaning in Thermodynamics;

- **System; Closed, open & isolated.**
- **Process: Isobaric( $\Delta P = 0$ ), Isochoric ( $\Delta V = 0$ ), Adiabatic( $\Delta q = 0$ ).**
- **Work( $w$ ), heat( $q$ ) & their sign conventions**

$$W_{(\text{irrev})} = - P_{(\text{ext})} \Delta V.$$

- $W_{(Rev)} = -2.303nRT \log V_2/V_1$   
 $= -2.303nRT \log P_1/P_2.$

- Internal energy: (U or E) & Enthalpy (H)

$$H = U + PV$$

$$\Delta H = \Delta U + P\Delta V \text{ or } \Delta H = \Delta U + RT\Delta n.$$

- 1<sup>st</sup> Law of thermodynamics:

$$\Delta U = q + w$$

- Exothermic reactions:  $H_p < H_R$  ;

$$\Delta H = H_p - H_R = -Ve$$

- Endothermic reaction:  $H_p > H_R$  ;

$$\Delta H = H_p - H_R = +Ve$$

- Enthalpy of reaction ( $\Delta H_{\text{reaction}}$ )

$$= \sum \Delta H_p - \sum \Delta H_R.$$

- $(\Delta H_{\text{reaction}}) = \sum \text{Bond energies of reactants}$   
 $- \sum \text{Bond energies of products.}$

## Various forms of heat of reactions and their calculations;

1. Heat of formation ( $\Delta H_f$ ): Lesser the value of  $\Delta H_f$  of a compound greater the stability.
2. Heat of combustion.
3. Heat of solution.
4. Heat of transition.
5. Heat of phase change

## 6. Heat of neutralization:

- Constant =  $-57.1\text{kJ}$  or  $-13.4\text{kCal}$  for strong acids and bases
- For weak acids or bases

$$= -57.3 + \Delta H_{(\text{Dissociation})}$$

- Laws of thermo chemistry: Lavoiser & Laplace law and Hess's Law and their applications in calculation of  $\Delta H_{(\text{reaction})}$

➤ **Entropy(S):**

**Measure of disorderness; entropy increases from solid → liquid → gases.**

$$\Delta S = \frac{q}{T} \quad q \text{ in Joules \& } T \text{ in Kelvin}$$

- **Gibb's free energy(G)  $G = H - TS$   
 $\Delta G = \Delta H - T \Delta S$ .**
- **Prediction of spontaneity of reactions based on above equation**

- If  $\Delta G^0 = -Ve$                       **Spontaneous**
- If  $\Delta G^0 = +Ve$                       **Non Spontaneous**
- If  $\Delta G^0 = 0$                         **Equilibrium.**
- For exothermic reactions at lower temperature  $\Delta G^0$  becomes  $-Ve$
- For endothermic reactions at higher temperature  $\Delta G^0$  becomes  $-Ve$
- $\Delta G^0 = -2.303 RT \log K_p$
- $\Delta G^0 = -nFE^0_{(Cell)}$

# QUESTIONS

1. Which of following value of  $\Delta H_f^0$  represents that product is least stable?

1.  $-94.0 \text{ kJmol}^{-1}$

2.  $-231.6 \text{ kJmol}^{-1}$

3.  $+21.4 \text{ kJmol}^{-1}$

4.  $+64.8 \text{ kJmol}^{-1}$

Larger the value of  $\Delta H_f$  of a compound lesser the stability.

Ans : (4)



2. The heat of combustion of yellow and red phosphorus are  $-9.91 \text{ kJmol}^{-1}$  and  $-8.78 \text{ kJmol}^{-1}$  respectively. The heat of formation of yellow P to red P is

- |                        |                       |
|------------------------|-----------------------|
| 1. $-18.69 \text{ kJ}$ | 2. $+1.13 \text{ kJ}$ |
| 3. $+18.69 \text{ kJ}$ | 4. $-1.13 \text{ kJ}$ |

For Combustion of  $\text{P}_{\text{yellow}} = \Delta H = -9.91$

For Combustion of  $\text{P}_{\text{red}} = \Delta H = -8.78$

$$\text{P}_{\text{yellow}} \rightarrow \text{P}_{\text{red}} = [-9.9 - (-8.78)]$$

$$= -9.9 + 8.78 = -1.13 \text{ kJ}$$

Ans : (4)

3. If enthalpy of vaporisation of water is  $186.5 \text{ J mol}^{-1}$  at  $100^{\circ}\text{C}$  then its entropy of vaporisation will be

1.  $0.5 \text{ JK}^{-1} \text{ mol}^{-1}$

2.  $1.0 \text{ JK}^{-1} \text{ mol}^{-1}$

3.  $1.5 \text{ JK}^{-1} \text{ mol}^{-1}$

4.  $2.0 \text{ JK}^{-1} \text{ mol}^{-1}$

$$\Delta S = \frac{\Delta H_{\text{vap}}}{T_{\text{b.p}}} = \frac{186.5}{373} = 0.5 \text{ JK}^{-1} \text{ mol}^{-1}$$

Ans : (1)

4. According to the reaction  $\text{C}_6\text{H}_6 + \frac{15}{2}\text{O}_2 \rightarrow 3\text{H}_2\text{O} + 6\text{CO}_2$   $\Delta H = -3264.6 \text{ KJ mol}^{-1}$ , the energy evolved when 3.0 g of benzene is burnt in air will be

1.  $163.23 \text{ KJ mol}^{-1}$

2.  $326 \text{ KJ mol}^{-1}$

3.  $32.64 \text{ KJ mol}^{-1}$

4.  $3.264 \text{ KJ mol}^{-1}$



$$78\text{g} \rightarrow -3264.6 \text{ KJ mol}^{-1}$$

$$3\text{g} \rightarrow \frac{-3264.6 \times 3}{78}$$

$$= -163.23 \text{ KJ mol}^{-1}$$

**Ans (1)**

5. In general exothermic reaction to be spontaneous

1. Temperature should be high
2. Temperature should be zero
3. Temperature should be low
4. Temperature has no effect

According to  $\Delta G^0 = \Delta H^0 - T\Delta S$

Exothermic reaction ( $\Delta H = -ve$ ) are favoured by low temperature.

Endothermic reaction ( $\Delta H = +ve$ ) are favoured by high temperature.

**Ans (3)**

6. The heat of neutralisation of strong base and strong acid is  $-57.0$  KJ. The heat released when  $0.5$  mol of  $\text{HNO}_3$  solution is added to  $0.2$  mol. of  $\text{NaOH}$  solution is

1.  $57.0$  KJ

2.  $11.40$  KJ

3.  $28.5$  KJ

4.  $34.945$  KJ

$0.2$  mol of  $\text{NaOH}$  is limiting reagent.

Heat liberated for  $0.2$  mol of  $\text{NaOH}$

$$= 0.2 \times 57.0 \text{ kJ} = 11.40 \text{ kJ}$$

**Ans (2)**

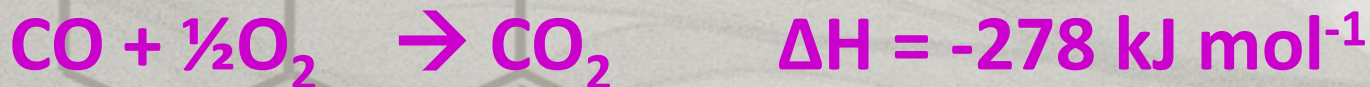
7. The enthalpies of combustion of carbon and carbon monoxide are  $-390 \text{ kJ mol}^{-1}$  and  $-278 \text{ kJ mol}^{-1}$  respectively. The enthalpy of formation of carbon monoxide is

1.  $668 \text{ kJ mol}^{-1}$

2.  $112 \text{ kJ mol}^{-1}$

3.  $-112 \text{ kJ mol}^{-1}$

4.  $-668 \text{ kJ mol}^{-1}$



$$= -390 + 278$$

$$= -112 \text{ kJ mol}^{-1}$$

**Ans (3)**

8. The bond dissociation energy of  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 104, 58 and 103 kCal respectively. The enthalpy of formation of  $\text{HCl}$  gas will be

1. -44 kCal
2. -88 kCal
3. -22 kCal
4. -11 kCal



$$\begin{aligned}\Delta H_{(\text{reaction})} &= (\frac{1}{2}\text{B.E. of H}_2 + \frac{1}{2} \text{B.E of Cl}_2) - \text{B.E. of HCl} \\ &= (\frac{1}{2} \times 104 + \frac{1}{2} \times 58) - 103 \\ &= 52 + 29 - 103 \\ &= -22 \text{ kCal}\end{aligned}$$

**Ans (3)**

9. The cell reaction is spontaneous if the cell potential is

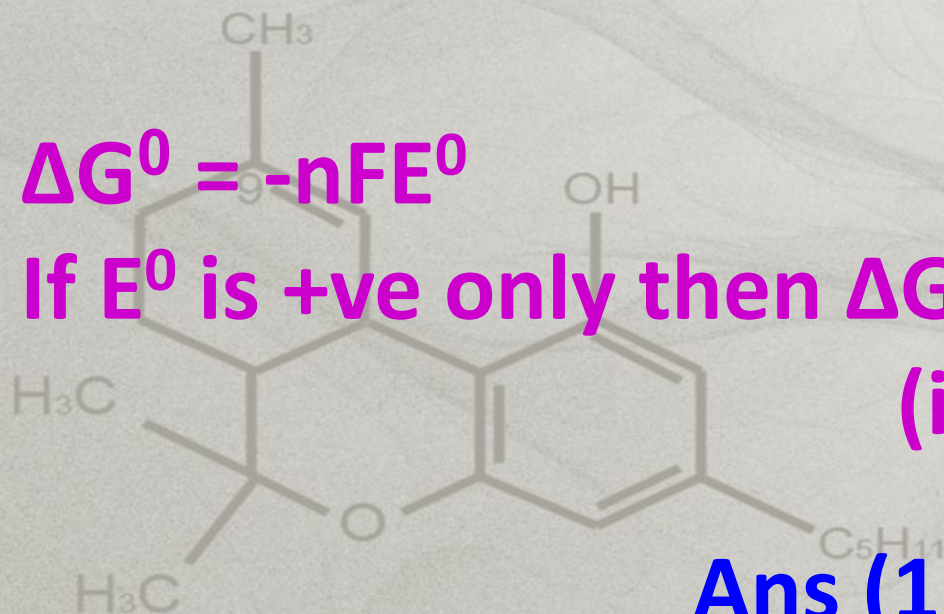
- |             |             |
|-------------|-------------|
| 1. Positive | 2. Negative |
| 3. Zero     | 4. Infinite |

$$\Delta G^0 = -nFE^0$$

If  $E^0$  is +ve only then  $\Delta G = -ve$

(i.e. spontaneous)

**Ans (1)**





**10. Intensive property among the following is**

**1. Volume**

**2. Mass**

**3. Density**

**4. Energy**

**Intensive property does not depend on the amount of the substance.**

H<sub>3</sub>C

H<sub>3</sub>C

**Ans (3)**

C<sub>5</sub>H<sub>11</sub>

11. A gas absorbs 250 J of heat and expands from 1 litre to 10 litre against the pressure of 0.5 atm at controlled temperature. The value of  $q$ ,  $w$  and  $\Delta E$  are

1. +250J, -455J, -205J    2. +250J, 455J, 205J  
3. -250J, 205J, 455J    4. -205J, -250J, -455J

Here gas absorbs 250J of Heat

Therefore,  $q$  is +ve i.e., 250J

$$w = -P_{\text{ext}} (V_2 - V_1) = -0.5 (10-1) = -4.5 \text{ Litre atm.}$$
$$= -4.5 \times 1.0132 \times 10^2 \text{ J} = -455 \text{ J}$$

$$\Delta E = q + w = 250 - 455 = -205 \text{ J} \quad \text{Ans (1)}$$

**12. When a solid change to liquid, the entropy becomes**

**1. Zero**

**2. Becomes minimum**

**3. increases**

**4. remains same**

**When solid  $\rightarrow$  liquid  $\rightarrow$  Gas  
randomness increases.**

**Therefore entropy increases**

**Ans (3)**

13. In a reaction involving only solids and liquids which of the following is true

1.  $\Delta H < \Delta E$

2.  $\Delta H = \Delta E$

3.  $\Delta H > \Delta E$

4.  $\Delta H = \Delta E + RT \Delta n$

$$\Delta H = \Delta E + P\Delta V$$

If only solids and liquids are involved  
no change in volume  $\Delta V = 0$

Therefore,  $\Delta H = \Delta E$

Ans (2)

14. One mole of a perfect gas expands isothermally to ten times its original volume. The change in entropy is

1. 0.1 R    2. 2.303R    3. 10.0 R    4. 100.0R

$$q_{\text{rev}} = -W = -2.303 nRT \log \frac{V_2}{V_1}$$

$$q_{\text{rev}} = +2.303 R \times T \log 10$$

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{2.303 RT}{T} = 2.303 R$$

**Ans (2)**

15. When enthalpy and entropy change for a chemical reaction are  $-2.5 \times 10^3$  Cals and  $7.4 \text{ Cals deg}^{-1}$  respectively. Predict that reaction at 298K is

1. spontaneous
2. reversible
3. irreversible
4. non spontaneous

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= -2.5 \times 10^3 - 298 \times 7.4 \\ &= -4.705 \times 10^3 \text{ Cals} = -ve\end{aligned}$$

Ans (1)

# THEORY OF DILUTE SOLUTION

## Synopsis

- Colligative properties:  $\alpha$  to number of solute particles, but not on their nature.

Eg: osmotic pressure, relative lowering of vapor pressure, elevation in boiling point, depression in freezing point.

For example colligative property of same molar concentrations of  $\text{NaCl} < \text{BaCl}_2 < \text{AlCl}_3 < \text{K}_4[\text{Fe}(\text{CN})_6]$

## 1) Osmotic pressure:

- **Osmosis: Flow of solvent molecules from dilute solution**
- **Osmotic pressure: External pressure required to stop the flow of solvent molecules**
- **Isotonic solutions: Two solutions having equal molar concentration, having equal osmotic pressure.**

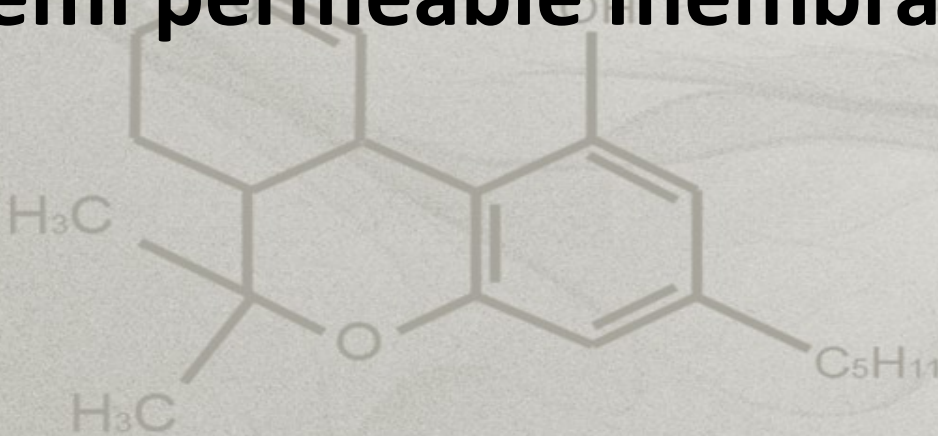


**Hypotonic (lower osmotic pressure) sol<sup>n</sup>**

**Hypertonic (higher osmotic pressure) sol<sup>n</sup>.**

**Reverse osmosis: Flow from concentrated solution to dilute solution**

**Semi permeable membranes and Examples.**



# Factors affecting osmotic pressure

$$\pi V = nCRT$$

$$\text{Or } \pi V = \frac{W}{M} CRT$$

$$\text{Or } \pi = \frac{W}{MV} RT$$

For isotonic solution

$$\frac{W_1}{M_1} = \frac{W_2}{M_2} \quad \text{'W' in mass/litre}$$

## 2. Relative lowering of vapour pressure

$$\text{RLVP} = \frac{p^0 - p}{p^0}$$

$$\text{Raoult's law} = \frac{p^0 - p}{p^0} = \frac{n_2}{n_1 + n_2}$$

$$\text{Molecular mass } M_2 = \frac{W_2 M_1}{W_1 (\text{RLVP})}$$

By Ostwald Walker Method

$$M_2 = \frac{W_2 M_1}{W_1} \frac{(\text{Gain in mass of CaCl}_2 \text{ tube})}{(\text{Loss in mass of Solvent tube})}$$

### 3. Elevation in Boiling point ( $\Delta T_b$ )

Boiling point of solution is  $>$  that of solvent

$$\Delta T_b = k_b m = \frac{1000 k_b W_2}{W_1 M_2} \quad (\text{Weights are in gram})$$

### 4. Depression in freezing point ( $\Delta T_f$ )

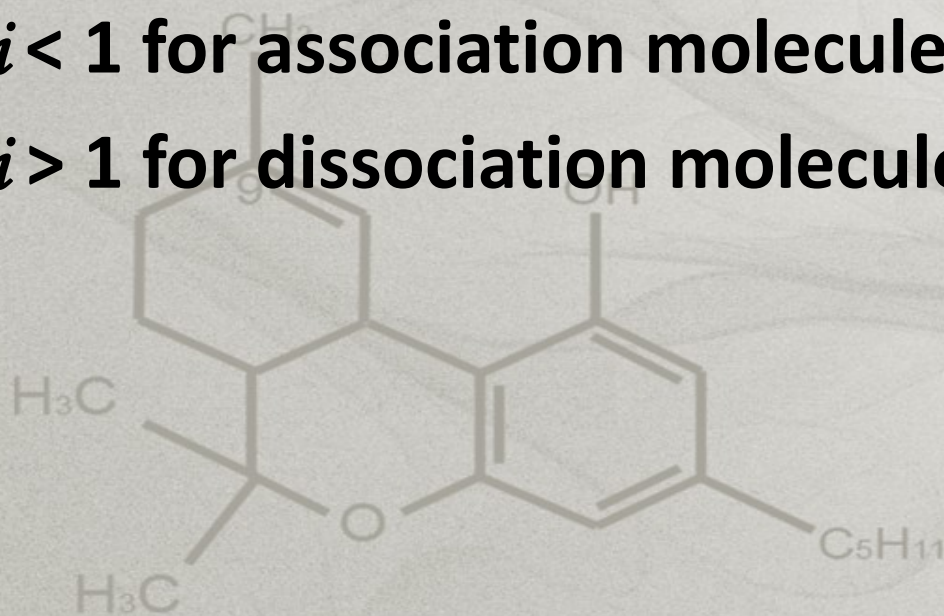
Freezing point of solution  $<$  that of solvent

$$\Delta T_f = k_f m = \frac{1000 k_b W_2}{w_1 M_2} \quad (\text{Weights are in gram})$$

$$\text{Van't Hoff's Factor } (i) = \frac{M_{\text{normal}}}{M_{\text{Observed}}}$$
$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

$i < 1$  for association molecules

$i > 1$  for dissociation molecules



# Types of Binary Solution

Ideal	Non ideal showing +ve deviation	Non ideal showing -ve deviation
Interaction forces $A-A=B-B= A-B$	Interaction forces $A-A \text{ or } B-B > A-B$	Interaction forces $A-A \text{ or } B-B < A-B$
$P_{\text{total}} = P_A^0 + P_B^0$	$P_{\text{total}} > P_A^0 + P_B^0$	$P_{\text{total}} < P_A^0 + P_B^0$
$\Delta H_{\text{mix}} = 0$	$\Delta H_{\text{mix}} > 0$	$\Delta H_{\text{mix}} < 0$
$\Delta V_{\text{mix}} = 0$	$\Delta V_{\text{mix}} > 0$	$\Delta V_{\text{mix}} < 0$
Eg: benzene+toluene, chloro benzene + bromo benzene etc.	Eg: Chloroform + carbon tetra chloride, ethanol + acetone, Benzene + acetone	Eg: Chloroform + acetone, HCl + H <sub>2</sub> O, etc.

## QUESTIONS

- 1) During osmosis flow of water through semi permeable membrane is
- 1) from both sides of S.P.M. with unequal flow rates
  - 2) from solution having lower concentration only
  - 3) from solution of higher concentration only
  - 4) from both sides of S.P.M. with equal flow rate

**During osmosis solvents flows from lower concentration, reverse in reverse osmosis.**

**Ans (2)**

2) Percentage of glucose which is isotonic with 1.5% urea is

1) 1.5%

2) 3.0%

3) 4.5%

4) 6.0%

$$\text{M of 1.5\% urea} = \frac{1.5 \times 1000}{100 \times 60} = 0.25\text{M}$$

$$0.25 \text{ M glucose} = \frac{0.25 \times 180 \times 100}{1000} = 4.5\%$$

**Ans (3)**



3) At 25°C the highest osmotic pressure is exhibited by 0.1M solution of

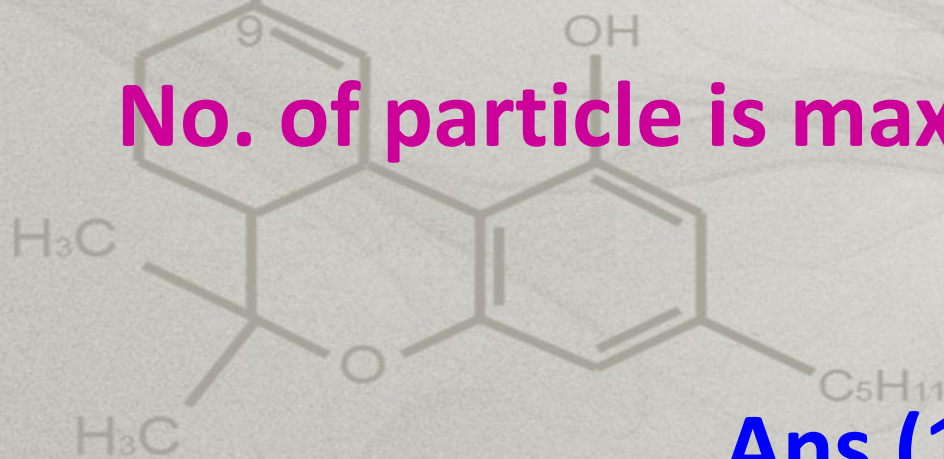
1)  $\text{CaCl}_2$

2) KCl

3) Glucose

4) Urea

No. of particle is maximum in  $\text{CaCl}_2$



Ans (1)

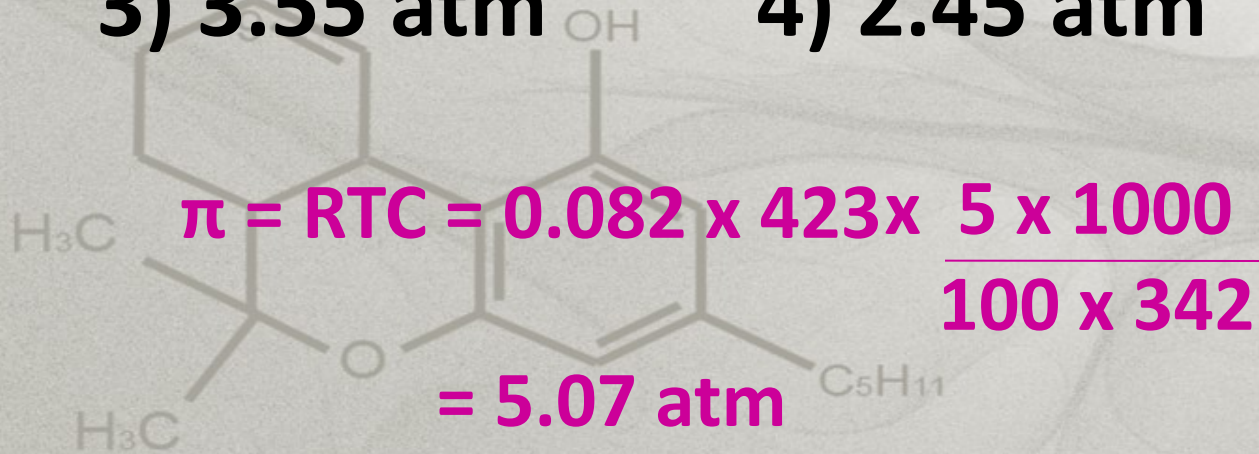
4) The osmotic pressure of 5% solution of cane sugar at 150°C (molar mass = 342) is

1) 4 atm

2) 5.07 atm

3) 3.55 atm

4) 2.45 atm



**Ans (2)**

5) A solution containing 10g per dm<sup>3</sup> of urea (Molar mass = 60) is isotonic with a 5% solution of non volatile solute. The molar mass of the non-volatile solute is

1. 350      2. 200      3. 250      4. 300

$$\frac{W_1}{M_1} = \frac{W_2}{M_2}$$

$$M_2 = \frac{5 \times 1000 \times 60}{100 \times 10} = 300$$

**Ans (4)**

- 6) A solution of acetone in ethanol
1. behaves like a near ideal solution
  2. obeys Raoult's law
  3. shows negative deviation from Raoult's law
  4. shows positive deviation from Raoult's law

It is an example of Non-ideal solution showing -ve deviation

Ans (3)

7) 4g of a non-volatile solute is dissolved in 36g of water produces the relative lowering of vapor pressure of 0.1. the molar mass of the solute is

1. 40

2. 20

3. 80

4. 100

$$M_2 = \frac{W_2 M_1}{W_1 (\text{RLVP})} = \frac{4 \times 18}{36 \times 0.1} = 20$$

Ans (2)

8) On mixing 10ml ethanol with 40ml water, the resulting solution will be

1. 50ml
2. more than 50 ml
3. less than 50ml
4. data is insufficient to decide

Ethanol + water is non-ideal solution showing +ve deviation.  $\Delta V_{(mix)}$  +ve, volume increases.

**Ans (2)**

9) vant Hoff's factor for  $K_4[Fe(CN)_6]$  in very dilute solution is

1. 1

2. 10

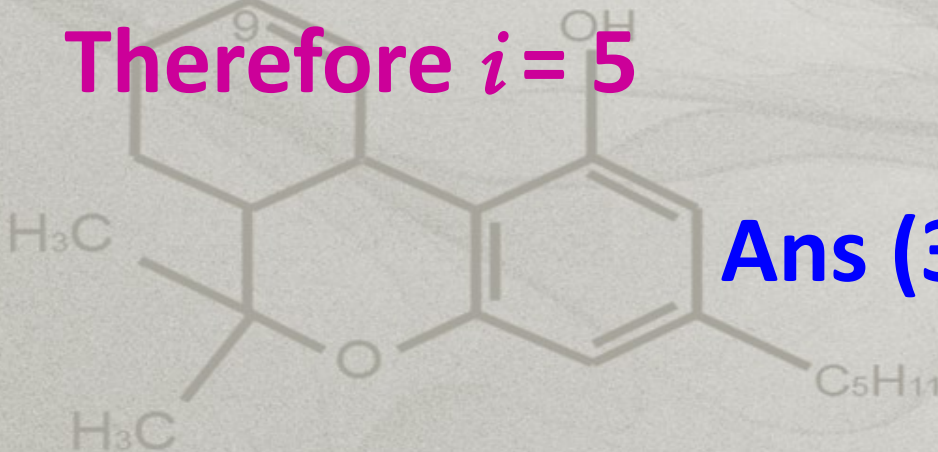
3. 5

4. 1/5

$K_4[Fe(CN)_6]$  Dissociates to 5 particles,

Therefore  $i = 5$

Ans (3)



10) In a solution A and B components shows negative deviation as

1.  $\Delta V_{\text{mix}} > 0$

2.  $\Delta H_{\text{mix}} < 0$

3. A-B interactions is weaker than A-A and B-B interactions

4. none of the above

For negative deviation solutions

$\Delta H = -ve \text{ or } < 0$

Ans (2)



11) Osmotic pressure of 6% urea is  $\pi_1$  and that of glucose is  $\pi_2$ , then  $\pi_1$  and  $\pi_2$  are related as

1.  $\pi_1 > \pi_2$

2.  $\pi_1 < \pi_2$

3.  $\pi_1 = \pi_2$

4.  $\pi_1 = 1/\pi_2$

$$\text{M. of 6\% urea} = \frac{6 \times 1000}{100 \times 60} = 1$$

$$\text{M. of 6\% glucose} = \frac{6 \times 1000}{100 \times 180} = 0.33$$

Therefore,  $\pi_1 > \pi_2$

**Ans (1)**

12) The vapour pressure of pure liquid is 0.80 atm. When a non-volatile solute is added to this liquid the vapour pressure drops to 0.6 atm. The mole fraction of the solute in the solution is

1. 0.75                      2. 0.20    3. 0.25                      4. 0.85

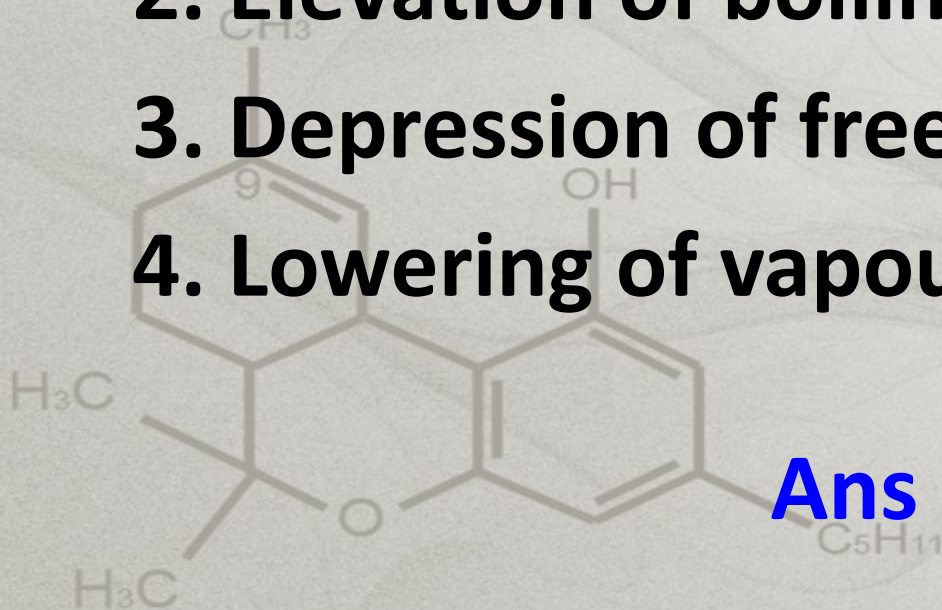
$$\frac{p^0 - p}{p^0} = X_2 = \frac{0.8 - 0.6}{0.8} = 0.25$$

**Ans (3)**

**13) Which of the following is not a colligative property?**

- 1. Osmotic pressure**
- 2. Elevation of boiling point**
- 3. Depression of freezing point**
- 4. Lowering of vapour pressure**

**Ans (4)**



14) 1g of non-volatile solute (molar mass=250) was dissolved in 51.2g of benzene. If  $K_f$  of benzene is  $5.12\text{K kg mol}^{-1}$ , the depression in freezing point of benzene will be

1. 0.5 K      2. 0.2K      3. 0.4K      4) 0.3 K

$$\Delta T_f = \frac{1000 \times k_f \times w_B}{w_A \times M_B}$$

$$= \frac{1000 \times 5.12 \times 1}{51.2 \times 250}$$

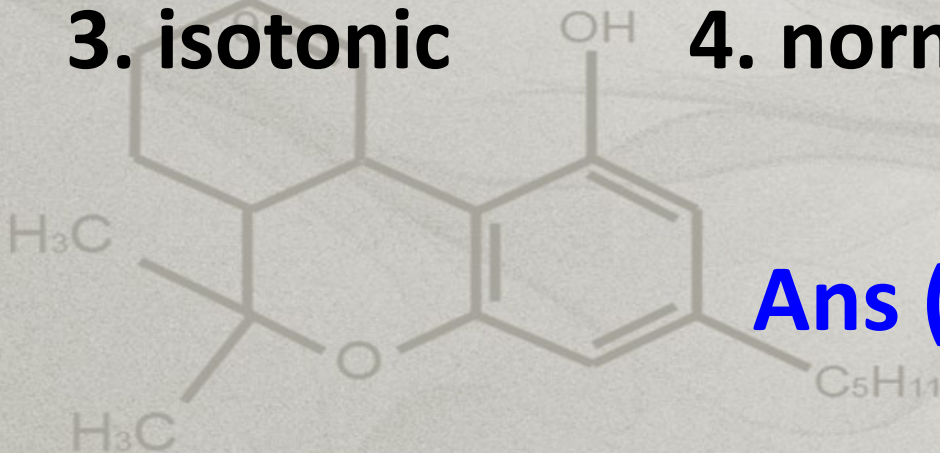
$$= 0.4 \text{ K}$$

**Ans (3)**

**15) Solutions having same osmotic pressure are called**

- 1. hypertonic      2. hypotonic**  
**3. isotonic        4. normal**

**Ans (3)**



16) The rise in boiling point of a solution containing 1.8 g of glucose in 100 g of a solvent is  $0.1^{\circ}\text{C}$ . The molal elevation constant of the liquid is

1.  $0.01 \text{ K/m}$

2.  $0.1 \text{ K/m}$

3.  $1 \text{ K/m}$

4.  $10 \text{ K/m}$

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

$$0.1$$

$$0.01$$

$$= 10$$

$$m = \frac{1.8}{180} = 0.01$$

**Ans (4)**

17) The osmotic pressure of solution of benzoic acid dissolved in benzene is less than expected because

1. Benzoic acid is an organic solute

2. Benzene is non polar solvent

3. Benzoic acid gets associated in benzene

4. Benzoic acid dissociates in benzene

**Benzoic acid associates &**

**No of particle decreases**

**Ans (3)**

18) The elevation in boiling point of 0.1m aqueous solution of NaCl, CuSO<sub>4</sub>, and Na<sub>2</sub>SO<sub>4</sub> are in the ratio

1. 1: 1: 1

2. 1: 2: 3

3. 1: 1: 1.5

4. 2: 6: 7.

Van, Hoff's factor for NaCl is 2, for CuSO<sub>4</sub> is 2 and Na<sub>2</sub>SO<sub>4</sub> is 3

Ratio = 2:2:3 = 1:1: 1.5

**Ans (3)**



- 19) The plant cell shrinks when placed in
1. a solution isotonic with cell sap
  2. water
  3. Hypertonic solution
  4. Hypotonic solution

**Hypertonic solution- Higher osmotic pressure solution**

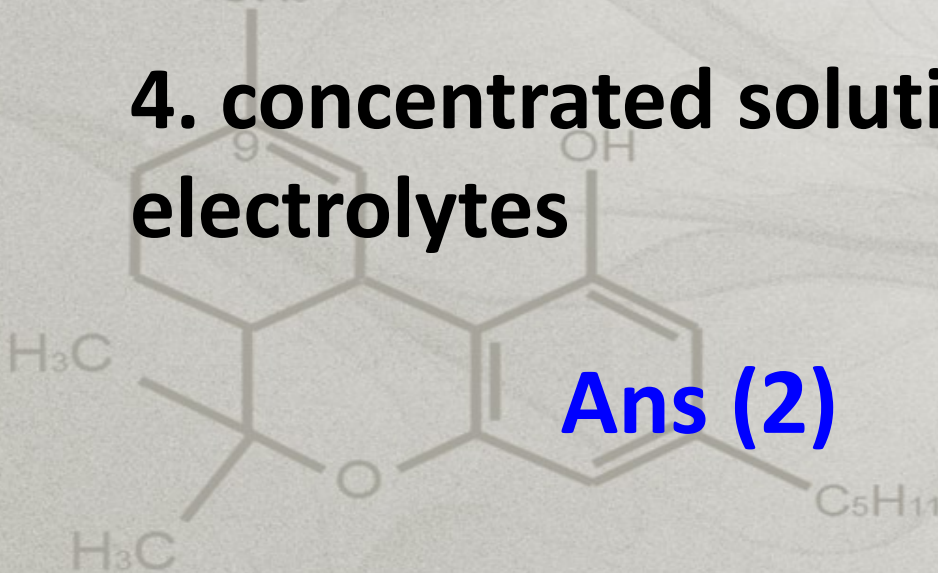
**Water from plant sap come out due to osmosis- Shrinks**

**Ans (3)**

20) For determination of molecular masses Raoult's law is applicable only to

1. Dilute solutions of electrolytes
2. Dilute solutions of non electrolytes
3. concentrated solutions of electrolytes
4. concentrated solutions of non electrolytes

**Ans (2)**



**21. Second law of thermodynamics points out that**

**1. All spontaneous process are thermodynamically irreversible.**

**2. Entropy of universe is continuously increases**

**3. Both 1) & 2) are correct**

**4. Only option (1) is correct**

**Ans (3)**

22. The amount of heat evolved when 500 cm<sup>3</sup> of 0.1M HCl is mixed with 200 cm<sup>3</sup> of 0.2M NaOH is

1. 2.292 kJ

2. 1.292 kJ

3. 0.292 kJ

4. 3.392 kJ

$$500 \text{ cm}^3 \text{ of } 0.1\text{m HCl} = \frac{500 \times 0.1}{1000} = 0.05 \text{ mol}$$

$$200 \text{ cm}^3 \text{ of } 0.2\text{m NaOH} = \frac{200 \times 0.2}{1000} = 0.04 \text{ mol}$$

Limiting reagent is 0.04 mol NaOH

$$\text{Heat released} = 0.04 \times 57.3 = 2.292$$

**Ans (1)**