

SOLUTIONS

SINGLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

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- 1. Formation of a solution from two components can be considered as :
 - (i) Solvent \rightarrow separated molecules, ΔH_1
 - (ii) Solute \rightarrow separated molecules, ΔH_2

(iii) Separated solute molecules + separated solvent molecules \rightarrow solution, ΔH_3

An ideal solution will be formed when

- (a) $\Delta H_1 + \Delta H_2 > \Delta H_3$ (b) $\Delta H_1 + \Delta H_2 < \Delta H_3$
- (c) $\Delta H_1 + \Delta H_2 = -\Delta H_3$ (d) $\Delta H_1 + \Delta H_2 + \Delta H_3 \neq 0$
- 2. Two moles of a liquid A $(p_A^o = 100 \text{ torr})$ and 3 moles of

liquid *B* ($p_B^o = 150$ torr) form a solution having vapour pressure of 120 torr. Based upon this observation one can conclude :

- (a) Interactions between like molecules > those between unlike molecules
- (b) Interaction between like molecules < those between unlike molecules
- (c) Interaction between like molecules = those between unlike molecules
- (d) $\Delta S_{\text{mixing}} = 0$

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- 3. At certain temperature, vapour pressure of a solution of acetone ($p^{\circ} = 150$ mm) and chloroform ($p^{\circ} = 120$ mm) in the molar ratio 1 : 4 is found to be 121 mm. The data suggest that partial vapour pressures of both components
 - (a) vary proportionately with the respective mole fractions
 - (b) vary less than proportionately with the respective mole fractions

- (c) vary more than proportionately with the respective mole fractions
- (d) $\Delta H_{\text{soln}} = 0$
- Which of the following statements is *not* true regarding vapour pressure of solvent (p°) and that of the solution (p_{s}) containing non-volatile solute?
 - (a) Both p° and p_s increase on increasing temperature
 - (b) $(p^{\circ}-p_{s})$ increases on increasing temperature
 - (c) $p_s = p^{o_x}$ mole fraction of solvent
 - (d) $\frac{(p^o p_s)}{p^o}$ decreases on increasing temperature
- 5. Liquids A and B form an ideal solution and the former has stronger intermolecular forces. If X_A and X'_A are the mole fractions of A in the solution and vapour in equilibrium, then

a)
$$\frac{X'_A}{X_A} = 1$$
 (b) $\frac{X'_A}{X_A} > 1$

(c)
$$\frac{X'_A}{X_A} < 1$$
 (d) $X'_A + X_A = 1$

The solubility of common salt is 36.0 g in 100 g of water at 20°C. If systems *I*, *II* and *III* contain 40.0, 36.0 and 20.0 g of the salt added to 100.0 g of water in each case, the vapour pressures would be in the order:

a)
$$I < II < III$$
 (b) $I > II > III$

(c)
$$I = II > III$$
 (d) $I = II < III$

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Mark Your	1. abcd	2. abcd	3. abcd	4. abcd	5. abcd
Response	6. abcd				

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- 7. In the above problem if water evaporates, which of the following is correct about the vapour pressure?
 - (a) decreases in all the cases
 - (b) increases in all the cases
 - (c) remains unchanged in I, II and increases in III
 - (d) remains unchanged in I, II and decreases in III
- 8. Vapour pressure (in torr) of an ideal solution of two liquids A and B is given by : $P = 52X_A + 114$

where X_A is the mole fraction of A in the mixture. The vapour pressure (in torr) of equimolar mixture of the two liquids will be :

- (a) 166 (b) 83
- (c) 140 (d) 280
- 9. The vapour pressure (at the standard boiling point of water) of an aqueous solution containing 28% by mass of a non-volatile normal solute (molecular mass = 28) will be
 - (a) 152 torr (b) 608 torr
 - (c) 760 torr (d) 547 torr
- 10. Lowering of vapour pressure of 1.00 m solution of a non-volatile solute in a hypothetical solvent of molar mass 40g at its normal boiling point, is :
 - (a) 29.23 torr (b) 30.4 torr
 - (c) 35.00 torr (d) 40.00 torr
- **11.** Mole fraction of a liquid *A* in an ideal mixture with another

liquid *B* is X_A . If X'_A is the mole fraction of component *A* in the vapour in equilibrium, the total vapour pressure of the liquid mixture is

 $(p_A^\circ = \text{vapour pressure of pure } A : p_B^\circ = \text{vapour pressure of pure } B)$

(a)
$$\frac{p_{A}^{\circ}X_{A}^{'}}{X_{A}}$$
 (b) $\frac{p_{A}^{\circ}X_{A}}{X_{A}^{'}}$

(c)
$$\frac{p_B^{\circ} X'_A}{X_A}$$
 (d) $\frac{p_B^{\circ} X_A}{X'_A}$

12. Dry air was successively passed through an aqueous solution containing 0.5 mole of non-volatile solute and then through pure water. The loss in mass of solution was 1.3500 g and that of pure water was 0.1500 g. The amount of water present in the solution was :

13. Which of the following figures represents correctly the changes in thermodynamic functions during the formation of a binary solution showing positive deviation from ideal behaviour?

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(a)	J mol ⁻¹ O	mole fraction
	-	ΔH _{mix}
		ΔG_{mix}
		TAC

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14. X is the mole fraction of a particular component in a binary azeotropic liquid mixture showing negative deviation. If X' is the mole fraction of the same component in the vapour in equilibrium with the ageotrope, then which of the following is correct?

(a)
$$X > X'$$

(b) $X < X'$
(c) $X = X'$
(d) $\frac{dX}{dt} = \frac{dX'}{dt} \neq 0$

Mark Your	7. abcd	8. abcd	9. abcd	10. abcd	11. abcd
Response	12.abcd	13.abcd	14. abcd		

15. Boiling temperature - composition graphs for a binary solution of liquids *A* and *B* capable of forming an azeotrope with minimum boiling point is shown below. If a liquid mixture of composition *X* is subjected to fractional distillation, which of the following statements is correct?



- (a) Both components *A* and *B* can be obtained in pure states, former as residue and latter as distillate.
- (b) Only *A* can be obtained partially in pure state as residue.
- (c) Only *B* can be obtained partially in pure state as distillate
- (d) Neither A nor B can be obtained in the pure state.
- **16.** Boiling point composition diagram of the liquid-vapour equilibrium for propanol-2 (*A*) and 2-methyl-propanol-1 (*B*) is shown below. If a binary liquid mixture of *A* and *B* is distilled fractionally, which of the following would be correct observation?



- (a) composition of the still (residue) will approach pure liquid *A*
- (b) composition of the distillate will approach pure B
- (c) composition of distillate and residue will approach pure *A* and *B* respectively.
- (d) Neither of the components can be obtained in pure state.

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- 17. 25 ml of an aqueous solution of NaCl required 20 ml of 0.10 *M* AgNO₃ solution for complete precipitation of Cl⁻ ions. The osmotic pressure of NaCl solution at 27°C is expected to be :
 - (a) 1.97 atm (b) 2.46 atm (c) 3.94 atm (d) 0.35 atm
- **18.** CNS⁻ ions give red colour with Fe³⁺ ions in aqueous solution as :

$$\operatorname{Fe}_{(\operatorname{aq})}^{3+} + 3\operatorname{CNS}_{(\operatorname{aq})}^{-} \rightarrow \operatorname{Fe}(\operatorname{CNS})_{3}_{(\operatorname{aq})}_{\operatorname{red}}$$

If 0.1M KCNS solution is separated from 0.1M FeCl₃ solution by means of semipermeable membrane, red colour will appear on:

- (a) FeCl₃ solution side (b) KCNS solution side
- (c) both sides (d) neither side
- When solid SnO₂ is added to an aqueous solution of NaOH, the
 - (a) vapour pressure is lowered
 - (b) vapour pressure is raised
 - (c) osmotic pressure is increased
 - (d) boiling point is raised
- **20.** π_1 , π_2 , π_3 and π_4 atm are the osmotic pressures of 5% (mass/volume) solutions of urea, fructose, sucrose and KCl respectively at certain temperature. The correct order of their magnitudes is :
 - (a) $\pi_1 > \pi_4 > \pi_2 > \pi_3$ (b) $\pi_1 < \pi_4 < \pi_2 < \pi_3$
 - (c) $\pi_4 > \pi_1 > \pi_2 > \pi_3$ (d) $\pi_4 > \pi_1 > \pi_3 > \pi_2$
- **21.** Based upon the technique of reverse osmosis, the approximate pressure required to desalinate sea water containing 2.5% (mass/volume) NaCl at 27°C will be :
 - (a) 10.5 atm (b) 21 atm
 - (c) 2.1 atm (d) 1.05 atm
- **22.** Which of the following pairs of solutions are expected to be isotonic, temperature being the same?
 - (a) 0.1 M glucose and $0.1 M C_6 H_5 N H_3 Cl$
 - (b) 0.1 M NaCl and 0.05 M BaCl₂
 - (c) $0.1 M \text{Na}_2 \text{SO}_4$ and $0.1 M \text{KNO}_3$
 - (d) $0.1 M \text{BaCl}_2$ and $0.075 M \text{FeCl}_3$

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Mark Your	15.@bcd	16. abcd	17. abcd	18. abcd	19. abcd
Response	20. abcd	21. abcd	22. abcd		

- **23.** A living cell contains a solution which is isotonic with 0.3 *M* sugar solution. What osmotic pressure develops when the cell is placed in 0.1*M* NaCl solution at body temperature?
 - (a) 5.08 atm (b) 2.54 atm

(c) 4.92 atm (d) 2.46 atm

- 24. Which of the following has been arranged in the increasing order of freezing point?
 - (a) $0.025M \text{ KNO}_3 < 0.1M \text{ NH}_2\text{CSNH}_2$

$$< 0.05M$$
 BaCl₂ $< 0.1M$ NaCl

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(b) 0.1M NaCl < 0.05M BaCl₂

 $< 0.1M \text{ NH}_2 \text{CSNH}_2 < 0.025M \text{ KNO}_3$

(c) $0.1M \text{ NH}_2\text{CSNH}_2 < 0.1M \text{ NaCl}$

<0.05M BaCl₂ <0.025M KNO₃

(d) $0.025M \text{ KNO}_3 < 0.05M \text{ BaCl}_2$

< 0.1M NaCl < 0.1M NH₂CSNH₂

- 25. 0.010*M* solution an acid *HA* freezes at -0.0205° C. If K_f for water is 1.860 *K* kg mol⁻¹, the ionization constant of the conjugate base of the acid will be (assume 0.010 M=0.010 m)
 - (a) 1.1×10^{-4} (b) 1.1×10^{-3}
 - (c) 9.0×10^{-11} (d) 9.0×10^{-12}
- **26.** At 27°C, 41 ml of ozone dissolves in 100 ml of water at a pressure of 1.00 atm. What mass of ozone dissolves in 200 ml of water at a pressure of 3.00 atm and at the same temperature ?
 - (a) 0.240 g (b) 0.480 g
 - (c) $0.600 \,\mathrm{g}$ (d) $0.720 \,\mathrm{g}$
- 27. 1.0 *M* aqueous solution of $CrCl_3.6H_2O$ freezes at $-5.58^{\circ}C$. Assuming complete ionization of the hydrated complex, which of the following isomers conforms to the observation $(K_r$ for water = $1.86 K \text{ kg mol}^{-1})$?
 - (a) $[Cr(H_2O)_3Cl_3].3H_2O$
 - (b) $[Cr(H_2O)_4Cl_4]Cl_2H_2O$
 - (c) $[Cr(H_2O)_5Cl]Cl_2.H_2O$
 - (d) $[Cr(H_2O)_6]Cl_3$

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28. Assuming degree of ionization to be unity in each case, which of the following equimolal solutions would freeze at the lowest temperature ?

(a)	$[Pt(NH_3)_6]Cl_4$	(b)	[Pt(NH ₃) ₅ Cl]Cl ₃
(c)	$[Pt(NH_3)_4Cl_2]Cl_2$	(d)	[Pt(NH ₃) ₃ Cl ₃]Cl
Ben pho	zene freezes at 5.50°C. If a sphorous in 100g benzen	the fr e is 4	eezing point of 2.48 g of 4.48°C, the atomicity of
pho	sphorus in benzene is (K_f)	benz	ene) = $5.12 K \text{kg mol}^{-1}$):
(a)	1	(b)	3
(c)	4	(d)	8
pН	of 0.1 <i>M</i> BOH (a weak b	base)	is found to be 12. The
solu	tion at temperature TK wi	ll disp	play an osmatic pressure
equ	al to :		

(a)	0.01 <i>RT</i>	(b)	0.01 R7
(c)	0 11 <i>RT</i>	(d)	1.1 RT

31. An aqueous solution of NaCl shows the depression of freezing point of water equal to 0.372 K. The boiling point of BaCl₂ solution of same molality will be $(K_f(H_2O)=1.86 \text{ K kg mol}^{-1}; K_b(H_2O)=0.52 \text{ K kg mol}^{-1})$

- 32. When a solution containing w g of urea in 1kg of water is cooled to -0.372° C, 200g of ice is separated. If K_f for water is 1.86 K kg mol⁻¹, w is :
 - (a) 4.8 g (b) 12.0g
 - (c) 9.6 g (d) 6.0 g
- **33.** One molal solution of a carboxylic acid in benzene shows the elevation of boiling point of 1.518 *K*. The degree of association of the acid in benzene is $(K_b \text{ for benzene} = 2.53 \text{ K kg mol}^{-1})$:
 - (a) 60% (b) 70%
 - (c) 75% (d) 80%
- 34. Equal volumes of 1.0 M KCl and 1.0 M Ag NO₃ are mixed. The depression of freezing point of the resulting solution will be $(K_f(H_2O) = 1.86 K \text{ kg mol}^{-1}, 1M = 1m)$
 - (a) 3.72 K (b) 1.86 K
 - (c) 0.93 K (d) None of these
- **35.** 1.0 molar solution of the complex salt, $CrCl_3$. $6H_2O$, displays an osmotic pressure of 3RT. 0.5L of the same solution on treatment with excess of Ag NO₃ solution will yield (assume $\alpha = 1$);
 - (a) 0.5 mol of AgCl (b) 1.0 mol of AgCl
 - (c) 1.5 mol of AgCl (d) 3.0 mol of AgCl

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NIARK YOUR Response	28.@b©d	29. abcd	30. abcd	31. abcd	32. abcd
	33.abcd	34. abcd	35. abcd		

- 36. The boiling point of 0.1 $m \text{ K}_4[\text{Fe}(\text{CN})_6]$ is expected to be $(K_b \text{ for water} = 0.52 \text{ K kg mol}^{-1})$
 - (a) 100.52°C (b) 100.10°C
 - (c) 100.26°C (d) 102.6°C
- **37.** The vapour pressure of a liquid decreases by 10 torr when a non-volatile solute is dissolved. The mole fraction of the solute in solution is 0.1. What would be the mole fraction of the liquid if the decrease in vapour pressure is 20 torr, the same solute being dissolved :
 - (a) 0.2 (b) 0.9
 - (c) 0.8 (d) 0.6
- **38.** When a solution containing non-volatile solute freezes, which of the following equilibrium would exist?
 - (a) Solid solvent \rightleftharpoons liquid solvent
 - (b) Solid solute \rightleftharpoons solution
 - (c) Solid solute \rightleftharpoons liquid solvent
 - (d) Solid solvent \rightleftharpoons solution
- **39.** The variation of total vapour pressure of an ideal solution of two liquids A and B is depicted below. The total vapour pressure denoted by the point 'X' will be



- (a) 34 mm (b) 46 mm (c) 40 mm (d) 24 mm
- **40.** A solute X has a solubility of 10.0 g in 100 g of water at 25° C. If a solution containing 4.0 g of solute in 50g of water is subjected to evaporation at constant temperature of 25° C, the osmotic pressure of the solution
 - (a) remains unchanged throughout
 - (b) increases continuously
 - (c) increases to constant value
 - (d) decreases to constant value
- **41.** A solid dissolves in water exothermically. If its saturated solution at 20°C is cooled to 0°C, then
 - (a) some solid seperates out
 - (b) some ice separates out

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- (c) both the solid and ice separate
- (d) neither the solid nor the ice separates out

- **42.** When the super cooled liquid starts freezing, the temperature
 - (a) falls to freezing point
 - (b) rises to freezing point
 - (c) fluctuates
 - (d) remains constant
- **43.** Completely miscible liquids *A* and *B* form an azeotropic mixture having minimum vapour pressure. If the liquid *A* is more volatile, then which of the following represents the boiling point-composition diagram?



 $x_{B} = 0$

 $x_A = 0$

Mark Your	36.@bcd	37. abcd	38. abcd	39. abcd	40. abcd
Response	41.abcd	42. abcd	43. abcd		

44. Liquids and vapours curves show the compositions of the solution and vapour in equilibrium at the boiling point of the former. Pick out the correct diagram of the following representing the variation of B.Pt. of solution of two liquids *A* and *B* (*A* being more volatile) with composition.









45. Equimolal solutions of KCl and compound X in water show depressions in freezing point in the ratio of 4 :1. Assuming KCl to be completely ionized, the compound X in solution must

- (a) Dissociate to the extent of 50%
- (b) Hydrolyse to the extent of 80%
- (c) Dimerize to the extent of 50%
- (d) Trimerize to the extent of 75%
- 46. An element X of atomic mass 25.0 exists as X_4 in benzene to the extent of 100%. When 10.30g of saturated solution of X in benzene is added to 20.0 g of benzene, the depression in freezing point of the resulting solution is 0.51 K. If K_f for benzene is 5.1 K kgmol⁻¹, the solubility of X in 100g of benzene will be
 - (a) 2.9 g (b) 3.0 g (c) 0.7 c
 - (c) 0.7 g (d) 0.3 g
- 47. $0.004 M \text{Na}_2 \text{SO}_4$ is iso-osmotic with 0.01M glucose. Degree of ionization of $\text{Na}_2 \text{SO}_4$ is:
 - (a) 25% (b) 50% (c) 75% (d) 85%
- **48.** A 0.2 *M* aqueous solution of a weak acid *(HX)* is 50% ionized. The freezing point of this solution is $(K_f = 1.86 \text{K kgmol}^{-1} \text{ for water})$
 - (a) -0.31° C (b) -0.45° C
 - (c) -0.56° C (d) -0.90° C
- **49.** Increasing amount of solid HgI_2 is added to 1L of an aqueous solution containing 0.1 mol KI. Which of the following graphs does represent the variation of depression in freezing point of the resulting solution with the amount of HgI_2 added?



- 50. What mass of urea be dissolved in 171g of water so as to decrease the vapour pressure of water by 5%
 - (a) 15 g (b) 20 g(c) 25 g (d) 30 g

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Mark Your	44. abcd	45. abcd	46. abcd	47. abcd	48. abcd
Response	49. abcd	50. abcd			

51. Equal masses of a solute are dissolved in equal amount of two solvents A and B, respective molecular masses being M_A and M_B . The relative lowering of vapour pressure of solution in solvent A is twice that of the solution in solvent B. If the solutions are dilute, M_A and M_B are related as

(a)
$$M_A = M_B$$
 (b) $2M_A = M_B$

(c) $M_A = 2M_B$ (d) $M_A = 4M_B$

52. At 20°C and 1.00 atm partial pressure of H_2 , 18 ml of H_2 (STP) dissolves in 1 L of water. If 2 L of water is exposed to a gaseous mixture having a total pressure of 1425 torr (excluding the vapour pressure of water) and containing 80% H_2 by volume, the volume of H_2 (STP) dissolved is

- 53. Henery's law constant K of CO_2 in water at 25°C is 3.0×10^{-2} molL⁻¹atm⁻¹. Calculate the mass of CO_2 present in 100 L of soft drink bottled with a partial pressure of CO_2 of 4 atm at the same temperature
 - (a) 5.28 g (b) 12.0 g
 - (c) 428 g (d) 528 g
- 54. A tube of uniform cross sectional area of 1 cm^2 is fitted with a semipermeable membrane at its one end. An aqueous solution containing 2gL^{-1} of urea is placed inside of the tube which is then placed in pure water at 27°C. The maximum height of vertical solution column developed will be (density of solution = 1gcm^{-3} ; density of Hg = 13.6 g cm⁻³)
 - (a) $0.62 \,\mathrm{m}$ (b) $0.82 \,\mathrm{m}$
 - (c) 8.47 m (d) None of these
- **55.** A beaker containing 18g of glucose in 100 g water and another containing 18 g of urea in 100 g water are placed under a bell jar and air is removed. After a course of time when equilibrium reaches, how much water will be transferred from one beaker to the other?

(a)	20 g	(b)	25 g
(c)	30 g	(d)	50 g

56. At 17°C, the osmotic pressure of sugar solution is 580 torr. The solution is diluted and the temperature is raised to 57°C, when the osmotic pressure is found to be 165 torr. The extent of dilution is:

(a) 2 times	(b)	3 times
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(c) 4 times (d) 5 times

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- 57. At 27° C, the vapour pressure of an ideal solution containing 1 mole of *A* and 1 mole of *B* is 500 mm of Hg. At the same temperature, if 2 mole of *B* is added to this solution, the vapor pressure of solution increases by 50 mm of Hg. The vapour pressure of *A* and *B* in their pure states are respectively
 - (a) 600 mm, 400 mm (b) 400 mm, 600 mm
 - (c) 300 mm, 700 m m (d) 200 mm, 800 mm
- 58. The solubility of gases in liquids (water) is favoured by
 - (a) increase in both pressure and temperature
 - (b) decrease in both pressure and temperature
 - (c) increase in pressure and decrease in temperature
 - (d) decrease in pressure and increase in tempeature
- **59.** The solubility of oxygen in water is $1.25 \times 10^{-3} M$ at a pressure of 1 atm and 298 K. solubility of atomospheric oxygen at sea level and the same temp will be :
 - (a) $1.25 \times 10^{-3} M$ (b) $2.50 \times 10^{-3} M$ (c) $2.5 \times 10^{-4} M$ (d) $1.00 \times 10^{-3} M$
- 60. What mass of 0.5 M solution of sucrose required to be added to 500 g of water so as to obtain 0.2 m solution

(a)	117.1 <i>g</i>	(b)	200 g
(c)	234.2 g	(d)	

- **61.** A solution is 25% by mass of solvent. What is its % by mass of solution?
 - (a) 33.3% (b) 30%
 - (c) 24% (d) 20%
- **62.** ΔH_1 and ΔH_2 are molar enthalpies of vaporisation of solvent from pure state and solution containing non-volatile solute respectively. Corresponding entropy changes are ΔS_1 and ΔS_2 . Select the correct of the following
 - (a) $\Delta H_1 < \Delta H_2$; $\Delta S_1 > \Delta S_2$
 - (b) $\Delta H_1 = \Delta H_2$; $\Delta S_1 > \Delta S_2$
 - (c) $\Delta H_1 > \Delta H_2$; $\Delta S_1 = \Delta S_2$
 - (d) $\Delta H_1 > \Delta H_2$; $\Delta S_1 < \Delta S_2$
- 63. At the freezing point of solution vapour pressures of
 - (a) Solid solvent and liquid solvent are equal
 - (b) Solid solvent and solution are equal
 - (c) Solid solute and solution are the same
 - (d) Solid solute and solid solvent are the same.

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MARK YOUR Response	56.@b©d	57. abcd	58. abcd	59. abcd	60. abcd
	61.abcd	62. abcd	63. abcd		

- 64. Which of the following statements is *not* correct?
 - (a) Entropy of vaporisation of solution is smaller than that of pure solvent
 - (b) Enthlpy of vaporization of solvent from pure state and solution is the same because similar attractive forces between solvent molecules must be overcome in both cases.
 - (c) Solvent in a solution of non-volatile solute has greater tendency to escape into vapour state relative to pure state
 - (d) Solution has less tendency to freeze than the solvent.
- **65.** At the freezing point which of the following equilibria does exist?
 - (a) Solid solvent \rightleftharpoons liquid solvent
 - (b) Solid Solute \rightleftharpoons Solution
 - (c) Solid solvent \rightleftharpoons Solution
 - (d) Solid Solute \rightleftharpoons liquid
- 66. Which of the following terms has units of temperature?

I : <i>K</i>	$I_f \qquad II: mK_f$	f III: iK_f	IV: $\frac{mK_f}{i}$
(a)	I, II	(b) I, III	
(c)	II, III	(d) II, IV	

67. Consider the following statements

I : Osmosis takes place with increase of entropy

II : Osmosis is a non-spontaneous process

III: free energy decreases during Osmosis.

- Which of the above is/are correct?
- (a) I only (b) I and II
- (c) II and III (d) I and III
- **68.** A colligative property of a solution depends upon
 - (a) molecular mass of solute
 - (b) structure of solute molecules
 - (c) nature of particles in solution
 - (d) relative number of molecules of solute and solvent.
- 69. $\Delta T_f/K_f$ has the same value of 1 mol kg⁻¹ for 8% AB_2 and 10% A_2B by mass of solvent, both AB_2 and A_2B being nonelectrolytes. Atomic masses of A and B will be respectively
 - (a) 20,40 (b) 20,50
 - (c) 40,20 (d) 50,40

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- 70. Depression of freezing point of 1 *M* area solution (density $= 1.16 \text{ g ml}^{-1}$) is :
 - (a) 1.86 K (b) 1.80 K(c) 1.69 K (d) 1.61 K
- 71. 0.5 *m* solution of a complex of iron and cyanide ions has the depression of *F*.pt. to be $3.72 K (K_f \text{ for water} = 1.86 \text{ molal}^{-1})$. The formula of the complex is:
 - (a) $K_4[Fe(CN)_6]$ (b) $K_2[Fe(CN)_4]$
 - (c) $K_3[Fe(CN)_6]$ (d) $Fe(CN)_4$
- 72. An aqueous solution of a compound *AB* freezes at -0.48 °C. At this temperature *AB* behaves as a non-electrolyte. The same solution boils at 100.26 °C at a pressure of 1 atm.

(For water $K_f/K_b = 3.7$) We can conclude that the compound *AB* at the boiling point of solution

- (a) behaves as a non-electrolyte
- (b) ionizes to a the extent of 50%
- (c) behaves as a strong electrolyte
- (d) dimerises completely in solution
- **73.** An aqueous solution containing 1 mol of KCl in 324 g of water at 100°C exihibits a lowering of vapour pressure to be:
 - (a) 40 torr (b) 60 torr
 - (c) 70 torr (d) 76 torr
- 74. If $BaCl_2$ in 0.5 *M* solution ionizes to the extent of 90%. The osmolarity of the solution is
 - (a) 1.5 (b) 1.4 (c) 1.3 (d) 1.2
- **75.** Dissolution of 1.28 g of sulphur in 50g of CS₂ causes the freezing point of solvent to be lowered by 0.010°. In CS₂, sulphur molecule could be represented by $(K_f \text{ for } \text{CS}_2 = 0.1 \text{ } K \text{ kg mol}^{-1})$
 - (a) S_2 (b) S_4 (c) S_6 (d) S_8
- 76. An aqueous solution containing 1 mol of a complex $Cu(NH_3)_3 Cl_2$ in 8 mol of water is found to have relative decrease in vapour pressure equal to 0.2. The formula of the complex is:
 - (a) $[Cu(NH_3)_3 Cl] Cl$ (b) $[Cu(NH_3)_3] Cl_2$
 - (c) $[Cu(NH_3)_3 Cl_2]$ (d) none of these

<i>p</i> u					
MenuVoun	64. abcd	65. abcd	66. abcd	67. abcd	68. abcd
NIARK YOUR Response	69. abcd	70. abcd	71. abcd	72. abcd	73. abcd
	74.abcd	75.@bCd	76. abcd		

25 ml of aqueous solution of BaCl₂ required 20 mol of 1*M* AgNO₃ when titrated using K₂CrO₄ indicator.

Assuming 100% ionization, the elevation of boiling point of BaCl₂ solution will be $(K_b \text{ for water} = 0.52 \text{ K molal}^{-1})$

- (a) 0.21 K (b) 0.42 K
- (c) 0.62 K (d) 0.72 K
- 78. Vapour pressure of solution containing 2 mol of liquid A
 - ($p_A^\circ = 80 \text{ torr}$) and 3 mol of liquid *B* ($p_B^\circ = 100 \text{ torr}$) is 87 torr. We can conclude that
 - (a) there is negative deviation from Raoult's law
 - (b) boiling point is higher than that expected for ideal solution
 - (c) molecular attractions between unlike molecules are stronger than those between like molecules
 - (d) All of these statements are correct
- **79.** Relative lowering of vapour pressure of an aqueous solution of KCl is 20%. What is the number of moles of solute dissolved in 144 g of water?
 - (a) $1 \mod (b) 2 \mod c$
 - (c) $3 \mod$ (d) $4 \mod$
- **80.** A mixture of two immiscible liquids at a pressure of 1 atm boils at a temperature
 - (a) equal to normal boiling point of more volatile liquid
 - (b) equal to the normal boiling point of less volatile liquid
 - (c) greater than the normal boiling point of either of the liquids
 - (d) smaller than the normal boiling point of either of the liquids.
- **81.** At a certain temperature the vapour pressure of a solution containing methyl alochol and ethyl alcohol was found to be represented by the following equation,
 - P = 120X + 150

An

Where X is the mole fraction of methyl alcohol and P the total vapour pressure in mm of Hg.

The vapour pressure of pure ethyl alochol at this temperature, is

- (a) 120 mm of Hg (b) 150 mm of Hg
- (c) 135 mm of Hg (d) 30 mm of Hg

- 82. When two liquids A and B are mixed they form an ideal solution. At certain temperature the V.P. of the solution, that contains 3 moles of A and 1 mole of B was found to be 550 mm of Hg. The vapour pressure of a solution containing 4 moles of A and 1 mole of B was found to be 560 mm of Hg. The vapour pressure of pure liquid A is
 - (a) 200mm (b) 300mm
 - (c) 400 mm (d) 600 mm
- 83. The vapour pressure of pure A and pure B are 0.04 and 0.06 bar respectively. The mixture of A and B show an ideal behaviour. If the mole fraction of B in the liquid phase is 0.50, then the mole fraction of B in vapour phase in equilibrium with liquid phase is
 - (a) 0.05 (b) 0.4
 - (c) 0.6 (d) 0.5
- **84.** At 15°C and 1 atmosphere partial pressure of hydrogen, 20 ml of hydrogen measured at STP dissolves in 1 L of water. If water at 15°C is exposed to a gaseous mixture having a total pressure of 1500 mm of Hg (excluding the vapour pressure of water) and containing 80% hydrogen by volumne, then the volume of hydrogen measured at STP that will dissolve in 1 L of water is
 - (a) 20.0 ml (b) 31.6 ml
 - (c) 36.1 ml (d) 26.3 ml
- **85.** The vapour pressure of two pure liquids A and B that form an ideal solution, are 400 and 800 mm of Hg respectively at a temperature $t^{\circ}C$. The mole fraction of A in a solution of Aand B whose boiling point is $t^{\circ}C$ will be
 - (a) 0.4 (b) 0.8
 - (c) 0.1 (d) 0.2
- **86.** When 0.9 g of acid dissolved in 300 ml of water is extracted with 75 ml of ether, it was found on analysis that 0.6 g organic acid goes into the ether layer. The correct ratio representing the solubility of organic acid in ether and water is

(a)
$$\frac{S_{\text{ether}}}{S_{\text{Water}}} = 9$$
 (b) $\frac{S_{\text{ether}}}{S_{\text{Water}}} = 6$

(c)
$$\frac{S_{\text{ether}}}{S_{\text{Water}}} = 7.5$$
 (d) $\frac{S_{\text{ether}}}{S_{\text{Water}}} = 8$

Here I					
Mark Your	77.@bcd	78. abcd	79. abcd	80. abcd	81. abcd
Response	82. abcd	83. abcd	84. abcd	85. abcd	86. abcd

\equiv Comprehension Type \equiv

B

This section contains groups of questions. Each group is followed by some multiple choice questions based on a paragraph. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

3.

4.

PASSAGE-1

The solubility of an ionic solid in a polar solvent like water depends on two factors :

- (a) Lattice energy (ΔH_{latt}) of the ionic solid which keeps the constitutent ions held together tightly in the ionic crystal; lattice energy is the energy released when 1 mole of the ionic solid is formed from the constituent ions in the gaseous state.
- (b) Solvation energy $(\Delta H_{solv.})$ of the ionic solid, which is the energy released when the ions interact with solvent dipoles (water dipoles) to form solvated (hydrated) ions.

The former factor opposes the solubility whereas the latter favours it. Thus, the enthalpy of solution of the ionic solid is given by

$$\Delta H_{\rm soln.} = \Delta H_{\rm solv.} - \Delta H_{\rm latt}$$

From the formal definitions of the two quantities it is seen that $\Delta H_{\text{latt.}}$ and $\Delta H_{\text{solv.}}$ are negative. Factors that affect the two competiting quantities do so in the same way. Firstly, the smaller the ion, the closer will be its association with the opposite ion in the crystal lattice, or with water molecules and more negative will be $\Delta H_{\text{latt.}}$ and $\Delta H_{\text{solv.}}$. Secondly, the greater the charge on the ion, the greater will be electrostatic forces of attraction between itself and the other ions or water molecules, resulting in more negative values of both the quantities. In a particular group (up and down) $\Delta H_{\text{latt.}}$ and $\Delta H_{\text{solv.}}$ for the ionic solids with the same anion undergo similar changes but usually $\Delta H_{\text{solv.}}$ is more pronounced than $\Delta H_{\text{latt.}}$. This can be seen from the solubility changes of carbonates of alkaline earths (II group elements) listed in the table.

Group II Carbonate	Solubility (mol L ⁻¹)
MgCO ₃	1.30×10^{-3}
CaCO ₃	0.13×10^{-3}
SrCO ₃	0.07×10^{-3}
BaCO ₃	0.09×10^{-3}

However, there is one exception to these general rules. If the cation and the anion of the salt have approximately the same size, the packing of the ions in the crystal lattice is more efficient to give more stable lattice and more negative $\Delta H_{\text{latt.}}$. In the dissolution of the solid solute, increase in randomness always favours the process.

- 1. The CO_3^{2-} anion has nearly the same size as
 - (a) Ba^{2+} (b) Sr^{2+} (c) Ca^{2+} (d) Mg^{2+}
- 2. $\Delta H_{\text{solv.}}$ for doubly charged anion X²⁻ was found to be more negative than for the CO₃²⁻ anion. Which of the following is most likely the explanation?
 - (a) X^{2-} anion is larger CO_3^{2-} than anion
 - (b) X^{2-} is smaller than CO_3^{2-} anion
 - (c) X^{2-} anion has the same size as the CO_3^{2-}
 - (d) $\Delta H_{\text{latt.}}$ for the salt MX is greater than for MCO₃
 - $Ca(OH)_2$ has approximately the same solubility product as $CaSO_4$. Pick out the correct one of the following
 - (a) Molarity of saturated solution of $Ca(OH)_2$ is greater than that of $CaSO_4$
 - (b) Molarity of saturated solution of $Ca(OH)_2$ is smaller than that of $CaSO_4$
 - (c) Molarities of both the solutions are the same
 - (d) The relation between the molarities of the two solutions depends on the temperature at the time.
 - A solution of $MgCO_3$ in water boils at a temperature more than 100°C at 1 atm. Why is this?
 - (a) Density of solution is greater than that of water
 - (b) Vapor pressure of solution exceeds that of water
 - (c) Vapour pressure of solution is smaller than that of water
 - (d) Dissolution of $MgCO_3$ lowers down the surface tension of water
- 5. Enthalpy of solution of HgCl₂ has a positive value of 83.8 kJmol⁻¹. Yet it is soluble in water. Which of the following accounts for this?
 - (a) Endothermic dissolution is favoured energetically
 - (b) Hydration energy of the solid exceeds its lattice energy
 - (c) The entropy factor $T\Delta S_{soln}$ exceeds ΔH_{soln}
 - (d) Both ΔH_{soln} and $T\Delta S_{soln}$ favour the dissolution

Mark Your Response	1. abcd	2. abcd	3. abcd	4. abcd	5. abcd

- 6. Solubility of sulphates of second group metals decrease down the group. This is due to the reason that both the lattice and hydration energies
 - (a) become more negative down the group, the former having the profound effect
 - (b) become less negative down the group, the latter having the profound effect
 - (c) become less negative down the group, the former having the profound effect
 - (d) tend to become equal

A system of greater disorder of molecules is more probable. The disorder of molecules is reflected by the entropy of the system. A liquid vaporises to form a more disordered gas. When a solute is present, there is additional contribution to the entropy of the liquid due to increased randomness. As the entropy of solution is higher than that of pure liquid, there is weaker tendency of it to form the gas. Thus, a solute (non-volatile) lowers the vapour pressure of a liquid, and hence a higher boiling point of the solution.

Similarly, the greater randomness of the solution opposes the tendency to freeze. In consequence, a lower temperature must be reached for achieving the equilibrium between the solid (frozen solvent) and the solution.

Elevation of B.Pt. (ΔT_b) and depression of F.Pt. (ΔT_f) of a solution are the colligative properties which depend only on the concentration of particles of the solute, not upon their identity. For dilute solutions, ΔT_b and ΔT_f are proportional to the molality of the solute in the solution.

$$\Delta T_b = K_b m$$
 $K_b = \text{Ebullioscopic constant} = \frac{R T_b^{\circ 2} M}{1000 \,\Delta H_{vap}}$

And
$$\Delta T_f = K_f m$$
 $K_f = \text{Cryoscopic constant} = \frac{RT_f^{\circ 2}M}{1000 \Delta H_{fus}}$

(M =molecular mass of the solvent)

The values of K_b and K_f do depend on the properties of the solvent.

- 7. Depression of freezing point of which of the following solutions does represent the cryoscopic constant of water?
 - (a) 6% by mass of urea is aqueous solution
 - (b) 100g of aqueous solution containing 18 g of glucose
 - (c) 59 g of aqueous solution containing 9 g of glucose
 - (d) 1 M KCl solution in water
- **8.** Dissolution of a non-volatile solute into a liquid leads to the
 - (a) decrease of entropy
 - (b) increase in tendency of the liquid to freeze
 - (c) increase in tendency to pass into the vapour phase
 - (d) decrease in tendency of the liquid to freeze.
- **9.** To aqueous solution of NaI, increasing amounts of solid HgI₂ is added. The vapor pressure of the solution
 - (a) decreases to a constant value
 - (b) increases to a constant value
 - (c) increases first and then decreases
 - (d) remains constant because HgI₂ is sparingly soluble in water.
- **10.** A liquid possessing which of the following characteristics will be most suitable for determining the molecular mass of a compound by cryoscopic measurements?
 - (a) That having low freezing point and small enthalpy of freezing
 - (b) That having high freezing point and small enthalpy of freezing
 - (c) That having high freezing point and small enthalpy of vaporisation
 - (d) That having large surface tension

PASSAGE-3

Measurement of colligative properties of dilute solutions of many of substances may be used to determine their molecular masses. However, in some cases the calculated values differ considerably from the normal values. Their departure from the normal values is owing to the change of molecular state of the solute in the solution. The ratio of normal molecular mass to the observed value called Van't Hoff factor, *i*, reflects the kind of change of molecular state of the dissolved substance.



- **11.** Which of the following structural changes will not be reflected by the Van't Hoff factor of a dissolved solute?
 - (a) Association (b) Ionization
 - (c) Micellization (d) Isomerization
- **12.** Which of the following substances will not show the abnormal colligative properties in solutions ?
 - (a) Aqueous solution of sodium oleate
 - (b) Aqueous solution of

$$CH_{2}OH$$

$$C_{15}H_{31}COOCH_{2} - C - CH_{2}OH$$
 above CMC
$$|$$

$$CH_{2}OH$$

- (c) Phenol in benzene
- (d) Aqueous solution of thiourea
- 13. Molal cryoscopic constant of water is $1.80 K \text{ kg mole}^{-1}$. A solution containing 6.00 g of pure acetic acid in 1 kg of water will show a depression of freezing point to be
 - (a) 0.18*K*
 - (b) 0.36*K*
 - (c) Slightly greater than 0.18 K
 - (d) Slightly less than 0.36 K

Binary liquid solutions, many times, exhibit maxima or minima in their vapour pressure-composition plots. A liquid mixture having the maximum vapour pressure will boil at the minimum temperature, lower of course than the boiling point of either liquid. On the other hand, mixture having a minimum vapour pressure will boil at a temperature, highest for all other compositions. Such liquid mixtures are called azeotropes. At constant pressure an azeotrope boils at a constant temperature, the composition of the azeotrope remaining unchanged throughout. However, the composition of an azeotrope alters on changing the external pressure.

14. Select the correct statement of the following

- (a) Composition of an azeotrope remains unchanged on continued boiling at a fixed pressure whereas the distillate has varying composition
- (b) Compositions of an azeotrope and distillate obtained do not change on continuous distillation.
- (c) An azeotrope is a compound as is indicated by its fixed composition at a given pressure
- (d) components of an azeotrope can be separated by fractional distillation at a fixed pressure.

- **15.** Rectified spirit boils at a constant temperature of 78.18°C at 1 atm. Select the correct statements of the following.
 - (a) The two components form ideal solution as both of them associate through *H*-bonding.
 - (b) The two components exhibit negative deviations from Raoult's law
 - (c) The two components show positive deviations from ideal behaviour.
 - (d) The components can be separated by fractional distillation



A set *A* of glass bulbs contain a solution of 1 mol of glucose in 24 mol of water. Another set *B* of bulbs contain pure water. All bulbs are maintained at the same temperature and are interconnected as shown in the figure. A current of dry air is passed successively through the solution in set *A* and then through pure water in set *B*. The solution is found to suffer a mass loss of $W_1 g$ and water a mass loss of $W_2 g$ after certain period of time.

- 16. If P_s and P° are the vapour pressures of solution and water respectively at the temperature of experiment, then which of the following is correct?
 - (a) $w_1 \alpha p^{\circ}$ (b) $w_1 \alpha (p^{\circ} p_s)$
 - (c) $w_2 \alpha (p^{\circ} p_s)$ (d) $(w_1 + w_2) \alpha (p^{\circ} + p_s)$
- 17. The relative lowering of vapour pressure of solution is given by

(a)
$$\frac{w_1}{w_2}$$
 (b) $\frac{w_1}{w_1 + w_2}$

(c)
$$\frac{w_2 - w_1}{w_1 + w_2}$$
 (d) $\frac{w_2}{w_1 + w_2}$

18. If vapour pressure of water is 50 mm Hg at the temperature of experiment, the vapour pressure of solution will be:

(a) $2 \operatorname{mm} \operatorname{Hg}$ (b) $4 \operatorname{mm} \operatorname{Hg}$

(c) 46 mm Hg (d) 48 mm Hg

Mark Your	11. abcd	12. abcd	13. abcd	14. abcd	15. abcd
Response	16.abcd	17. abcd	18. abcd		

Vapour pressure of a liquid is the function of temperature. On increasing temperature, greater number of liquid molecules acquire kinetic energy sufficient to overcome the molecular attractions and pass into the vapour state. Hence vapour pressure increases, with increase in temperature, to a limiting value equal to the external pressure, usually 1 atmosphere in an open vessel. The corresponding temperature also attains a limiting value so long external pressure is fixed. However the vapour pressure of a liquid is altered on adding a foreign substance soluble in the former, it may be raised or lowered.

Vapour pressure-temperature plots for pure water, 0.5 m glucose and 0.5 *m* methanol are depicted in the figure as shown.



- 19. Boiling points of methanol and glucose solutions are respectively

 - (a) T_1 and T_2 (b) T_2 and T_3 (c) T_1 and T_3 (d) none of these
- Elevation of boiling point of glucose solution is 20.

(a) $T_3 - T_1$	(b)	$T_2 - T_1$
-----------------	-----	-------------

- (c) $T_2 T_3$ (d) $T_3 - T_2$
- 21. Addition of methanol to water leads to
 - (a) decrease in vapour pressure of solution
 - (b) increase in vapour pressure of solution
 - (c) increase in boiling point
 - (d) no change of entropy

E

PASSAGE-7

Properties such as boiling point, freezing point and vapour pressure of pure solvent change when solute molecules are added to get solution. The changes in these properties are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing mixture in the radiater of automobiles.

A solution *M* is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

Given: K_f for water = 1.86 K Kg mol⁻¹; K_f for ethanol = 2.0 K Kg mol^{-1} ; K_b for water = 0.52 K Kg mol⁻¹; K_b for ethanol = 1.2 K Kg mol^{-1} ; standard freezing point and boiling point of water = 273 K and 373 K; standard freezing point and boiling point of ethanol = 155.7 K and 351.5 K respectively; vapour pressure of pure ethanol = 40 mm Hg, molecular weight of water = 18 g mol^{-1} , molecular weight of ethanol = 46 g mol^{-1}

In answering the following questions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

22. The freezing point of the solution *M* is

(a)	268.7 <i>K</i>	(b)	268.5 K
(c)	234.2 <i>K</i>	(d)	150.9 <i>K</i>

- The vapour pressure of the solution M is 23.
 - (a) 39.3 mm Hg (b) 36.0 mm Hg
 - (c) 29.5 mm Hg (d) 28.8 mm Hg
- 24. Water is added to the solution *M* such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is

(a)	380.4 <i>K</i>	(b)	376.2 <i>K</i>
(c)	375 5 K	(b)	354 7 K

PASSAGE-8

The freezing point of a solution of sulphur in naphthalene, in which 3.95 g of sulphur are dissolved in 100 g of naphthalene, was found to be 80.0°C.

[**Given** : K_f for naphthalene = 6.5°K kg mol⁻¹; m.p. of pure naphthalene $= 81.0^{\circ}C$]

- The mass of sulphur needed to cause a depression in freez-25. ing point of 1 kg by this amount, is
 - (a) 3.95 g (b) 395 g
 - (d) 0.395 g (c) 39.5g

MARK YOUR	19.@bcd	20. abcd	21. abcd	22. abcd	23. abcd
Response	24. abcd	25. abcd			

- **26.** The mass of sulphur needed to cause a depression of 6.5°C in 1 kg?
 - (a) 32 g (b) 25.6 g
 - (c) 100 g (d) 256.75 g
- **27.** The number of moles of sulphur present in a solution in problem 2 above and atomicity of sulphur are respectively
 - (a) 1,8 (b) 2,4
 - (c) 4,4 (d) 8,8

To account for all abnormal cases (i.e., those of association or dissociation of solute molecules when dissolved in a solvent), van't Hoff introduced a factor, i, known as van't Hoff factor.

$$i = \frac{\text{Number of particles after association or dissociation}}{\text{Number of normal solute particles}}$$

The ratio of van't Hoff factor (*i*) to the number of ions furnished by one molecule of solute is known as osmotic coefficient 'g'

i.e.,
$$g = \frac{i}{n} = \frac{\text{van't Hoff factor}}{n}$$

Consider 0.5% aqueous soluion of potassium chloride which was found to freeze at 272.76 K. [Given K_f of water = 1.86 K kg mol⁻¹) and answer the following questions.

- 28. The van't Hoff factor for it is approximately (a) 1 (b) 2 (c) $\frac{1}{2}$ (d) Can't be predicted
- **29.** What is the degree of dissociation (α) in this case?
 - (a) 100% (b) 95% (c) 92.0% (d) 90%
- 30. The value of 'osmotic coefficient' for this is
 (a) 1.92
 (b) 2

(d) 6.9 (c) 0.96 Mark Your 27.(a)(b)(c)(d) 26.(a)(b)(c)(d) 28. (a) (b) (c) (d) 29.(a)(b)(c)(d)30. (a)b)c)d) Response REASONING TYPE \equiv In the following questions two Statement-1 (Assertion) and Statement-2 (Reason) are provided. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct. Mark your responses from the following options: Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1. (a) (b) Both Statement-1 and Statement-2 are true and Statement-2 is not the correct explanation of Statement-1. (c) Statement-1 is true but Statement-2 is false. (d)Statement-1 is false but Statement-2 is true. **Statement - 1** : If hydration energy is greater than lattice 4. Statement - 1 : The vapour pressure of a liquid decreases if 1. some non-volatile solute is dissolved in it. energy, the solid dissolves in liquid. **Statement - 2** : The relative lowering of vapour pressure **Statement - 2** : The solubility of a solid in a liquid depends of a solution containing a non-volatile upon lattice energy and hydration energy. solute is equal to the mole fracton of the 2. Statement - 1 : The solubility of a gas in a liquid increases solute in the solution. with increase of pressure. 5. **Statement - 1** : At the same temperature water has higher Statement - 2 : The solubility of a gas in a liquid is directly vapour pressure than acetic acid. proportional to the pressure of the gas. **Statement - 2** : Hydrogen bonding in water is weaker than 3. Statement - 1 : One molar aqueous solution has always that in acetic acid. 6. Statement - 1 : Molecular mass of polymers cannot be higher concentration than one molal. calculated using boiling point or freezing Statement - 2 : The molality of a solution depends upon point method. the density of the solution whereas Statement - 2 : Polymers solutions do not possess a molarity does not. constant boiling point or freezing point. (A) 1. (a)(b)(c)(d) 2. (a)b)c)d) 3. (a)b)©(d) 4. (a)(b)(c)(d) 5. (a)(b)(c)(d)MARK YOUR Response 6. (a)(b)(c)(d)

7.	Statement - 1	:	If more and more solute is added to a
			solvent, the freezing point of the solution
			keeps on reducing.
	Statement - 2	:	Presence of large amount of the solid solute
			does not allow the solution to freeze.
8.	Statement - 1	:	Camphor is used as solvent in the
			determination of molecular masses of
			naphthalene, anthracene etc.
	Statement - 2	:	Camphor has high molal elevation
			constant.
9.	Statement - 1	:	The boiling point of $0.1 M$ urea solution is
			less than that of 0.1 M KCl solution.
	Statement - 2	:	Elevation of boiling point is directly
			proportional to the number of species
			present in the solution.
10.	Statement - 1	:	NaCl in water and organic acids in benzene
			show abnormal molecular masses.
	Statement - 2	:	Abnormal molecular mass is obtained
			when the substance in the solution
			undergoes dissociation or association.
11.	Statement - 1	:	A liquid boiling at 1 atmospheric pressure
			in a beaker is at equilibrium.
	Statement - 2	:	It refers to open system.
12.	Statement - 1	:	Non-ideal solutions always form
	~		azeotropes.
	Statement - 2	:	Boiling point of an azeotrope may be
			higher or lower than boiling points of both
12	Statement 1		components.
13.	Statement - 1	:	Larger the value of cryoscopic constant
			of the solvent, lesser will be the depression
	Statement 2		For a given solute concentration
	Statement - 2	•	depression of freezing point depends on
			the nature of the solvent
14	Statement _ 1	•	If one component of a solution obeys
17.	Statement - I	•	Raoult's law over a certain range of
			composition the other component will not
			obey Henry's law in that range
	Statement - ?	•	Raoult's law is a special case of Henry's
	~uutoment *2	•	law.

- 15. Statement 1 : If more volatile liquid is added to another liquid, vapour pressure of solution will be greater than that of pure solvent.
 - Statement 2 : Vapour pressure of solution is entirely due to solvent molecules.
- **16. Statement 1** : The solubility of all the solutes, in water, increases with increase in temperature.
 - Statement 2 : The solubility of a solute depends upon temperature.
- 17. Statement 1 : Lowering of vapour pressure is directly proportional to osmotic pressure of the solution.
 - Statement 2 : Osmotic pressure is a colligative property.
- **18.** Statement 1 : Van't Hoff calculated the value of K_f (molal depression constant of a solvent) from thermodynamic considerations using the relation.

$$K_f = \frac{RT_f^2}{1000 L_f}$$

where T_f is the freezing point of pure solvent and L_f is the latent heat of fusion.

- **Statement 2** : The calculated values of K_f for water and benzene were 1.86 K Kg mol⁻¹ and 5.12 K kg mol⁻¹ respectively.
- 19. Statement 1 : The process of mixing of CH₃OH and CCl₄ is accompanied by increase in enthalpy and is a spontaneous process.
 - Statement 2 : When we mix CCl_4 and CH_3OH , we replace weaker forces of attraction by stronger forces of attraction.
- **20.** Statement 1 : Higher the value of molal depression constant of solvent (K_j) used to prepare the solution, lower will be the freezing point of the solution.
 - Statement 2 : Depression in freezing point depends upon the nature of the solvent.

	7. abcd	8. abcd	9. abcd	10. abcd	11. abcd
MARK YOUR Response	12.abcd	13. abcd	14. abcd	15. abcd	16. abcd
	17.abcd	18.abcd	19. abcd	20. abcd	

MULTIPLE CORRECT CHOICE TYPE =

- Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE OR MORE is/are correct.
- 1. Consider two solutions :

I: 0.5 *M* NaCl aqueous solution at 25°C; NaCl is completely ionized.

 $II : 2.0 MC_6H_5COOH$ in benzene at 25°C; the acid dimerizes to the full extent.

Which of the following statement(s) is/are correct?

- (a) Both the solutions display equal osmotic pressures
- (b) Both have equal vapour pressures
- (c) solution *II* is hypertonic
- (d) Solution *II* has greater depression of freezing point than the solution *I*
- 2. In a binary and ideal liquid mixture
 - (a) Partial vapour pressure of each component varies directly with respective mole fraction in the solution
 - (b) $H_{\text{Solution}} = H_A + H_B$
 - (c) $G_{\text{Solution}} = G_A + G_B$
 - (d) $S_{\text{Solution}} = S_A + S_B$
- 3. A binary liquids mixture of two liquids *A* and *B* showing departure from the ideal behaviour :
 - (a) behaves as an ideal solution of *B* into *A* when $X_B \rightarrow 0$
 - (b) behaves as an ideal solution of A into B when $X_A \rightarrow 0$
 - (c) ΔH_{Soln} is always positive
 - (d) $T\Delta S_{\text{Soln}}$ is always positive
- 4. Which of the following is/are correct statement(s) about the Raoult's law applied to a solution of non-volatile solute?
 - (a) Vapour pressure of solution is proportional to mole fraction of solute
 - (b) V.P. of solution is proportional to the mole fraction of solvent
 - (c) Relative lowering of V.P. = mole fraction of solute
 - (d) Lowering of vapour pressure is proportional to the mole fraction of solute.
- 5. Which pair(s) of liquids on mixing are expected to show no net volume change and no heat effect
 - (a) acetone and ethanol

(An

- (b) chlorobenzene and bromobenzene
- (c) chloroform and benzene
- (d) n-butyl chloride and n-butyl bromide

6. A liquid mixture having composition corresponding to point *M* in the figure shown is subjected to distillation at constant pressure. Which of the following statement(s) is/are correct about the process?



- (a) The boiling point goes on changing
- (b) The composition of the solution and distillate are the same throughout
- (c) The composition of distillate differs from that of the mixture
- (d) The mixture has lowest vapour pressure than for any other composition
- 7. Solid HgI₂ is gradually added to KI solution; which of the following statements is/are correct?
 - (a) Freezing point increases and then becomes constant
 - (b) Freezing point decreases constantly
 - (c) Boiling point decreases and then becomes constant
 - (d) Vapour pressure increases to a constant value
- 8. Composition of an azeotrope
 - (a) is independent of external pressure because it is a compound
 - (b) alters on changing the external pressure as it is not a compound
 - (c) remains unchanged during distillation at a constant external pressure
 - (d) fluctuates even at constant pressure

-					
Mark Your	1. abcd	2. abcd	3. abcd	4. abcd	5. abcd
Response	6. abcd	7. abcd	8. abcd		

- 9. When a solution of non-volatile solute is frozen and cooling is continued, then
 - (a) freezing point remains constant
 - (b) freezing point goes on decreasing
 - (c) freezing point goes on increasing
 - (d) nothing can be said
- **10.** In a binary liquid mixture of components *A* and *B*, the former has greater tendency to escape into the vapour state than demanded by Raoult's law. Indicate the correct statement(s)
 - (a) Component *A* shows positive deviation and the component *B* negative deviation
 - (b) Both components show positive deviations
 - (c) Component *A* shows negative deviation and the component *B* positive deviation
 - (d) The component B has also greater tendency to escape into the vapour state than demanded by Raoult's law
- 11. Colligative properties are similar in that they all
 - (a) were discovered in college laboratories
 - (b) are due to solvent molecules linked together
 - (c) have no harmful side effects
 - (d) depend on the concentration of solute particles in solution
- **12.** Which of the following is/are not linked to the lowering of vapour pressure by a non-volatile solute
 - (a) boiling point elevation
 - (b) freezing point depression
 - (c) solubility
 - (d) surface tension
- **13.** The molecular mass of benzoic acid as determined by depression in freezing point method corresponds to
 - (a) ionization of benzoic acid
 - (b) dimerization of the acid
 - (c) trimerization of the acid
 - (d) solvation of the acid

An

14. The diagram given below depicts the boiling point as the function of composition of the mixture of CCl₄ and SiCl₄. Which of the following statements about the diagram is/ are true ?



- (a) The point *a* represents the composition of solution and the point *b* that of the vapour in equilibrium
- (b) The proportion of CCl_4 in the solution is smaller than that in the vapour in equilibrium
- (c) bc represents the condensation of the vapour
- (d) The point *c* represents the composition of solution and the point *b* that of the vapour in equilibriums





Semipermeable membrane

- (a) A white precipitate of AgCl is formed on AgNO₃ side
- (b) A white precipitate of AgCl is formed on BaCl₂ side
- (c) No precipitate is formed on either side
- (d) Meniscus of $BaCl_2$ solution rises and that of $AgNO_3$ solution falls in due course of time
- 16. If p° is the vapour pressure of pure solvent and p_s that of solution containing a non-volatile solute, then on raising the temperature
 - (a) Both p° and p_s increase to the same extent
 - (b) p° increases much more rapidly than p_{\circ}
 - (c) The difference $(p^{\circ} p_s)$ and p° increase to the same extent
 - (d) $\frac{p^{\circ} p_s}{p^{\circ}}$ remains unchanged

<i>p</i> === 2					
MARK YOUR	9. abcd	10. abcd	11. abcd	12. abcd	13. abcd
Response	14.abcd	15.abcd	16. abcd		

- 17. In which of the following solutions, $Cu_2[Fe(CN)_6]$ permits the solvent molecules to pass through?
 - (a) Benzoic acid in benzene (b) Urea in acetone
 - (c) Urea in water (d) Thiourea in water
- **18.** Molal depression constant of a solvent can be calculated from $(L_f = \text{latent heat of fusion of solid solvent, } \Delta H_f \text{ molar}$

heat of fusion, $T_{\rm f}^{\circ}$ = F. Pt. of solvent)

(a)
$$K_{\rm f} = \frac{RT_{\rm f}^{2}}{100L_{\rm f}}$$
 (b) $\frac{RT_{\rm f}^{2}}{100\,\Delta H_{\rm f}}$

(c)
$$\frac{RT_{\rm f}^{o^2}}{1000 L_{\rm f}}$$
 (d) $\frac{RT_{\rm f}^{o^2} M}{1000 \Delta H_{\rm f}}$

- 19. Dry air is passed though a set of inter-connected air tight vessels containing a solution of non-volatile solute and then through another set of vessels containing pure solvent. If the solution and the solvent suffer losses of mass to be w_1 and w_2 g respectively, then
 - (a) $w_1 \propto p_s$ (b) $w_2 \propto p^\circ$
 - (c) $w_2 \propto (p^\circ p_s)$ (d) $(w_1 + w_2) \propto p^\circ$
- **20.** Vapour pressure temperature curves of pure solvent and a solution cantaining a non-volatile solute are depicted in the figure aside. Select the correct statements(s) of the following



Å.

- (a) Curve I represents variation vapour pressure of solution and II that of solvent with temperature
- (b) Curves I and II represent the variation of vapour pressures of solvent and solution respectively with temperature
- (c) Gap *ab* represents $K_b m$ for the solution
- (d) Gap *ab* represents $K_c m$ for the solution
- **21.** At certain temperature a solution of 3 mol of a liquid $A (p^\circ = 500 \text{ torr})$ and 1 mol of liquid $B (p^\circ = 340 \text{ torr})$ has a vapour pressure of 435 torr, we can conclude that
 - (a) a solution of 50 mL of A and 50 mL of B must have a volume of 100 mL.
 - (b) the solution shows negative deviation from Raoult's law
 - (c) on mixing the two liquids heat must be given out so as to obtain solution at the same temperature
 - (d) entropy of mixing is zero
- 22. The ebulioscopic constant depends upon
 - (a) the molar mass of the solute in the solution
 - (b) the molar mass of the solvent in the solution
 - (c) the enthalpy of vaporisation of the solvent
 - (d) the boiling point of solvent
- **23.** Consider 0.1 *m* solutions of KCl urea, aniline hydrochloride and K₂SO₄. Which of the following statement (s) is/are correct ?
 - (a) The urea solution has the highest freezing point
 - (b) The K_2SO_4 solution has the highest boiling point
 - (c) KCl and aniline hydrochloride solutions are isotonic
 - (d) Urea solution has the lowest osmotic pressure.
- 24. Which of the following represents the behaviour of ideal binary liquid solution? $(X_A = \text{mole fraction of } A)$
 - (a) Plot of $P_{\text{Total}} vs X_A$ is linear passing through the origin
 - (b) Plot of $P_{\text{Total}} vs X_A$ is linear having an intercept p_B°
 - (c) Plot of $P_{\text{Total}} vs X_A$ is linear having an intercept p_A°
 - (d) Plot of P_{Total} vs X_A is non-linear

Je I					
Mark Your	17.@bcd	18. abcd	19. abcd	20. abcd	21. abcd
Response	22. abcd	23. abcd	24. abcd		

- **25.** Consider 0.1 *M* solutions of two solutes *X* and *Y*. The solute *X* behaves uni-univalent strong electrolyte while the solute *Y* dimerises completely in solution. Which of the following statements are correct regarding these solutions?
 - (a) The solution of Y is hypotonic to that of X
 - (b) Lowering of vapour pressure of solution of *X* is higher than that of *Y*
 - (c) The depression of freezing point of solution *X* is four times that of solution *Y*
 - (d) The escaping tendency of solvent into the vapour state from solution *X* is higher that that from solution *Y*
- **26.** Which of the following is/are correct for binary liquid solutions :
 - (a) Water ethanol; $\Delta H_{sol} > 0; \Delta V_{sol} > 0$
 - (b) Water HCl; $\Delta H_{sol} > 0; \Delta V_{sol} < 0$
 - (c) Acetone-chloroform : $\Delta H_{sol} < 0; \Delta V_{sol} = 0$
 - (d) Benzene toluene : $\Delta H_{sol} = 0; \Delta V_{sol} = 0$
- 27. If liquids *A* and *B* form an ideal solution
 - (a) The entropy of mixing is zero
 - (b) The free energy of mixing is negative
 - (c) The enthalpy of mixing is zero
 - (d) The free energy of mixing is zero
- **28.** The total vapour pressure of a binary solution is given by the relation

 $P_s = (110.X_A + 125 X_B) \text{ mm of Hg}$

where $X_A =$ mole fraction of component A in solution

 X_B = mole fraction of component *B* in solution

From the above, we can say that

12 m

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- (a) the V.P. of solution (P_s) containing equal number of mole of both the components (i.e., $X_A = X_B$) is less than the vapour pressure of pure component *B* (i.e., P_B°)
- (b) the V.P. of solution (P_s) containing equal number of moles of both the components (i.e., $X_A = X_B$) is more than the V.P. of pure component A (i.e. P_A°)
- (c) $P_A^{\circ} = 110 \text{ mm of Hg and } P_B^{\circ} = 125 \text{ mm of Hg}$
- (d) $P_A^{\circ} = 125 \text{ mm of Hg and } P_B^{\circ} = 110 \text{ mm of Hg}$
- **29.** For a 0.1 *m* solutions each of two solutes *X* and *Y* in which solute *X* behaves as a univalent electrolyte and *Y* dimerises in solution. The correct statement (s) are
 - (a) The b.p. of solution of solute *X* will be higher than that of *Y*.
 - (b) The osmotic pressure of the solution of solute *Y* will be lower than that of *X*.
 - (c) The freezing point of solution of solute *X* will be lower than that of *Y*.
 - (d) The relative lowering of V.P. of solution of solute *X* will be same as that of *Y*.
- **30.** In many a cases it has been observed that the boiling point of a solution is higher as compared to that of the pure solvent. For such an observation choose the correct statement(s)
 - (a) It is due to positive Gibb's free energy
 - (b) It is due to negative Gibbs free energy
 - (c) It is due to higher ΔH_{vap} for pure solvent than that of solvent in solution
 - (d) It is due of smaller ΔS_{vap} for solution as compared to that of pure solvent.

-					
Mark Your	25.abcd	26. abcd	27. abcd	28. abcd	29. abcd
Response	30.@bcd				

MATRIX-MATCH TYPE

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labeled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column -I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example: If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.



1. Solubility of a solid solute into water increases as the temperature is raised. Match the processes listed in Column I with the changes in appropriate properties listed in Column II. (m = molality) Column II Column I (A) Gas + water \rightarrow Solution $\Delta H > 0, \Delta S > 0$ p. (B) Solid + water \rightarrow Solution $\Delta H = 0, \Delta m = 0$ q. (C) Saturated solution + Solid solute $\Delta H < 0, \Delta m < 0$ r. (D) Super saturated solution + Solid solute $\Delta H < 0, \Delta S < 0$ s. Dry air is passed repeatedly through a solution of a non-volatile solute in water and then through pure water at the same 2. temperature. Given that : Loss in mass of solution = w_1g Vapour pressure of solution = p_s Loss in mass of water = $w_2 g$ Vapour pressure of water $= p^{o}$ Column II Column I $(p^{o} - p_{s})$ (A) $W_1 \propto$ p. (B) $w_2 \propto$ q. p_s $(p^{o} - p_{s})/p^{o}$ (C) $(w_1 + w_2) \propto$ r. p^o (D) $w_2 / (w_1 + w_2) \propto$ s. 3. $M_n =$ Normal molecular mass of solute M_{o} = Observed molecular mass of solute from colligative property measurement Match the following : Column I **Column II** $0.1 M CH_3 COOH$ in benzene (A) $M_o < M_n$ p. (B) $M_o' \approx M_n/3$ 0.1 M urea in water q. (C) $M_o > M_n$ r. 0.05 M barium chloride in water 0.1 MCH₃COOH in water (D) $M_o = M_n$ s. ΔH_f = Molar heat of fusion of ice; L_f = Latent heat of fusion of ice (g⁻¹) 4. ΔH_v = Molar heat of vaporisation of water; L_v = Latent heat of vaporisation of water (g⁻¹) Match the following appropriately : Column II Column I $18 \times 373 \times 373 \times R$ (A) Molal depression constant of water p. $1000 \Delta H_{v}$ $373 \times 373 \times R$ (B) Molal elevation constant of water q. $1000 L_{v}$ $18 \times 273 \times 273 \times R$ (C) ΔT_f of solution containing 9.0 g of glucose in 50g of water r. $1000 \Delta H_f$ $273 \times 273 \times R$ (D) ΔT_h of solution containing 3.0g of urea in 50g of water s. $1000 L_{f}$ - 🖾 pqrs pqrs pqrs pqrs 2. 3. 4. 1. (P)(T)(S)(P)(T)(S)(P)(T)(S)PARS A А A Α MARK YOUR В PP В $\mathbb{P}(\mathbb{Q})$ в (P)(q)(r)(s)в PPIS Response С С $(\mathbf{p}(\mathbf{q}))$ С PQTS С (p)(q)(r)(s (p)(q)(r)(s)D $\mathbb{P}(\mathbb{Q})$ D $\mathbb{P}(\mathbb{Q})$ D (\mathbb{P}) D (P)

5. Match the following at a constant pressure of 1 atm.

Column-I (System)

- (A) Mixture of two immiscible liquids
- (B) Solution of two miscible liquids following Raoult's law
- (C) Maximum B. pt. azeotrope
- (D) Minimum B. pt azeotrope

Column-II (B. Pt.)

Composition dependent p.

- Constant, independent of relative q. amounts of the liquids
- Constant alongwith composition r.
- Constant, composition of solution and s. vapour being identical

A solution of liquids A and B exhibits a maximum in vapour pressure - composition plot, composition of maximum vapour being 6. 40% by mass of A.

The solutions (i) 30% by mass of A and (ii) 60% by mass of A are subjected to fractional distillation separately. Match the entries in column I correctly with those in column II.

		Column I		Column II
	(A)	Distillate of (i)	p.	Pure A
	(B)	Distillate of (ii)	q.	Pure B
	(C)	Residue of (i)	r.	Azeotrope
	(D)	Residue of (ii)	s.	40% by mass of A
7.	Mat	tch the following entries in column I with those in column II		
		Column I		Column II
	(A)	Supercooled solution is stirred	p.	Freezing point of water is decreased
	(B)	Super saturated solution is seeded	q.	Boiling point of water is lowered
	(C)	Urea is added to water	r.	Solid solvent is separated
	(D)	Methanol is added to water	S.	Solid solute is separated
8.		Column A-(Property)		Column B - (Characteristics)
	(A)	Relative lowering of vapour pressure	p.	αί
	(B)	Elevation in boiling point	q.	α molality(<i>m</i>)
	(C)	Freezing point	r.	α molarity (M)
	(D)	Osmotic pressure	S.	Indirectly proportional to loweirng of
				vapour pressure

9. Column A

.

- (A) Depression in freezing point
- (B) Relative lowering in vapour pressure
- (C) Osmotic pressure
- (D) Elevation in boiling point

- Column B
- p. a colligative property
- Ebullioscopic constant q.
- Berkeley-Heartley method r.
- Ostwald and Walker method s.

Mark Your Response	5.	6.	7. pqrs A @@^C\$ B @@^\$ C @@^\$ D @@C\$	8.	9. P q r s A P Q r s B P Q r s C P Q r s D P Q r s

 NUMERIC/INTEGER ANSWER TYPE The answer to each of the questions is either numeric (eg. 304, 40, 3010, 3 etc.) or a fraction (2/3, 23/7) or a decimal (2.35, 0.546). The appropriate bubbles below the respective question numbers in the response grid have to be darkened. For example, if the correct answers to question X, Y & Z are 6092, 5/4 & 6.36 respectively then the correct darkening of bubbles will look like the following. For single digit integer answer darken the extreme right bubble only. 	X Y Z 0
--	---

- 1. Two liquids A and B are miscible in all proportions and form ideal solution. At 350 K the vapour pressure of pure A is 24.0 kPa and that of pure B is 12.0 kPa. A mixture of 60% (by mole) of A and 40% of B is distilled at this temperature. A small amount of distillate is collected and redistilled at the same temperature. What will be the mole percent of A in the second distillate at initial stage?
- 2. 0.400 g of an acid HA (mol. mass = 80) was dissolved in 100g of water. The solution showed a depression of freezing point of 0.12 K. Compute dissociation constant (in multiple 10⁻³) of the acid at about 0°C, given K_f (water) = 1.86 K Kg mol⁻¹. Assume molarity of solution \approx molality
- 3. An element X (Atomic mass = 25) exists as X_4 is benzene. 51g of saturated solution of X in benzene was added to 50.0 g of pure benzene. The resulting solution showed a depression of freezing point of 0.55 K. Calculate the solubility of X per 100 g of benzene. (K_f for benzene = 5.5 K kg mol⁻¹)
- 4. 23.5 g of phenol was dissolved in 500 g of a solvent having depression constant K_f of 12.0 K Kg mol⁻¹. If the depression in freezing point of solution was found to be 3.60 K, calculate percent dimerization of phenol in the solvent.
- 5. A 0.01 *m* solution of Pt(NH₃)₄Cl₄ in water had the freezing point of -0.056° C. Assuming 100% ionization of the complex in solution, find the formula of the complex ion; given K_f (water) = 1.86 K kg mole⁻¹.



SINGLE CORRECT CHOICE TYPE

1.	с	2.	b	3.	b	4.	d	5.	c	6.	d	7.	d	8.	с	9.	b	10.	а
11.	b	12.	d	13.	b	14.	с	15.	b	16.	с	17.	с	18.	d	19.	b	20.	с
21.	b	22.	d	23	b	24.	b	25.	с	26.	b	27.	с	28.	а	29.	с	30.	с
31.	d	32.	с	33.	d	34.	b	35.	b	36.	с	37.	с	38.	d	39.	а	40	с
41	d	42	b	43	а	44	d	45	d	46	b	47	с	48	с	49	с	50	d
51	с	52	b	53	d	54	с	55	d	56	с	57	b	58.	с	59.	с	60.	с
61.	d	62.	b	63.	b	64.	с	65.	с	66.	d	67.	d	68 .	с	69.	с	70.	с
71.	с	72.	с	73.	d	74.	b	75.	d	76	а	77.	с	78.	d	79.	а	80.	с
81.	b	82.	d	83.	с	84.	b	85.	с	86.	d								

A

$\mathbf{B} \equiv$ Comprehension Type =====

1	(b)	4	(c)	7	(c)	10	(b)	13	(c)	16	(c)	19	(c)	22	(d)	25	(c)	28	(b)
2	(b)	5	(c)	8	(d)	11	(d)	14	(b)	17	(d)	20	(d)	23	(a)	26	(d)	29	(c)
3	(a)	6	(b)	9	(b)	12	(d)	15	(c)	18	(d)	21	(b)	24	(d)	27	(a)	30	(c)

 $\mathbf{C} \models \text{Reasoning Type} \blacksquare$

1	(a)	4	(b)	7	(c)	10	(a)	13	(d)	16	(d)	19	(d)
2	(a)	5	(a)	8	(c)	11	(d)	14	(b)	17	(b)	20	(a)
3	(b)	6	(c)	9	(a)	12	(d)	15	(c)	18	(b)		

MULTIPLE CORRECT CHOICE TYPE

1.	a,d	2.	a,b	3.	a,b,d	4.	b,c,d	5.	b,d	6.	b,d	7.	a,c,d	8.	b,c	9.	b	10.	b,d
11.	d	12.	c,d	13.	b	14.	a,b,c	15.	c,d	16.	b,c,d	17.	c,d	18.	c,d	19.	a,c,d	20.	b,c
21.	b,c	22.	b,c,d	23.	a,b,c,d	24.	b	25.	a,b,c	26.	a,d	27.	b,c	28.	a,b,c	29.	a,b,c	30.	d

E MATRIX-MATCH TYPE

D

- 1. A-s; B-p; C-q; D-r
- 3. A-r, s; B-r; C-p; D-q
- 5. A-q; B-p; C-r, s; D-r, s
- 7. A-r; B-s; C-p; D-p, q
- 9. A-p; B-p, s; C-p, r; D-p, q
- **NUMERIC/INTEGER ANSWER TYPE** F
 - 5.92 2 0.8 85.7 3 4 2

- 2. A-q; B-p; C-s; D-r
- 4. A-r, s; B-p, q; C-r, s; D-p, q
- 6. A-r, s; B-r, s; C-q; D-p
- 8. A-p; B-p, q; C-s; D-p, r

Dolutions

13.

Α

SINGLE CORRECT CHOICE TYPE

- 1. (c) For the formation of an ideal solution, $\Delta H = 0$; ΔH_1 and ΔH_2 are positive and ΔH_3 is negative.
- **2.** (b) Total V.P.

$$= P_A^{\circ} X_A + P_B^{\circ} X_B = 100 \times \frac{2}{5} + 150 \times \frac{3}{5} = 130 \text{ torr}$$

The observed vapour pressure is smaller than that calculated from Raoult's law (negative deviation). Hence, interactions A - B > A - A or B - B.

3. **(b)** Total vapour pressure = $150 \times \frac{1}{5} + 120 \times \frac{4}{5} = 126$ mm

> observed value (121 mm); hence negative deviation from Raoult's law.

4. (d) Relative lowering of vapour pressure,
$$\frac{\Delta p}{p^{\circ}}$$
 is independent of temperature.

5. (c)
$$X'_A = \frac{p_A}{p} = \frac{p^\circ_A X_A}{p} \Rightarrow \frac{X'_A}{X_A} = \frac{p^\circ_A}{p} < 1$$
 (since the

liquid A is less volatile, $p_A^o < P$)

- 6. (d) Solutions in cases *I* and *II* are saturated and that in *III* is unsaturated.
- 7. (d) In cases *I* and *II*, solution remains saturated althrough (no change in concentration) but in case *III* concentration increases due to evaporation.

8. (c) Total V.P.,
$$P = P_A^{\circ} X_A + P_B^{\circ} X_B = P_A^{\circ} X_A + P_B^{\circ} (1 - X_A)$$

 $= (P_A^{\circ} - P_B^{\circ}) X_A + P_B^{\circ}$
Thus, $P_B^{\circ} = 114$ torr; $P_A^{\circ} - P_B^{\circ} = 52$

or $P_A^\circ = 166$ torr

Hence
$$P = 166 \times \frac{1}{2} + 114 \times \frac{1}{2} = 140$$
 torr

9. **(b)** Moles of solute
$$=\frac{28}{28}=1$$
;

moles of water =
$$\frac{100-28}{18} = 4$$

V.P. of solution

$$= P_{\rm H_2O}^{\circ} \times X_{\rm H_2O} = 760 \times \frac{4}{5} = 608 \text{ torn}$$

10. (a)
$$P_{\text{solvent}}^{\circ} = 760 \text{ torr (at the B. pt.)}; \quad n_{\text{solute}} = 1$$

 $n_{\text{solvent}} = \frac{1000}{40} = 25;$
 $\Delta P = 760 \times X_{\text{solute}} = \frac{760}{26} \text{ torr}$

26

11. **(b)**
$$X'_{\rm A} = \frac{P_{\rm A}}{P_{\rm total}} = \frac{P^{\circ}_{\rm A}X_{\rm A}}{P_{\rm total}}$$
, or $P_{\rm total} = \frac{P^{\circ}_{\rm A}X_{\rm A}}{X'_{\rm A}}$

12. (d)
$$\frac{\Delta P}{P^o} = \frac{\text{Loss in mass of solvent}}{\text{Total loss in mass}} = \frac{0.1500}{0.1500 + 1.3500} = \frac{1}{10}$$

But
$$\frac{\Delta P}{P^o} = \frac{1}{10} = X_{\text{solute}} = \frac{0.5}{0.5 + n_{\text{H2O}}}$$
;

$$n_{\rm H_2O} = 4.5 \Longrightarrow 81.0 {\rm g}$$

- (b) During mixing entropy increases to maximum, free energy decreases to minimum; for positive deviation, $\Delta H_{\text{mix}} > 0$.
- 14. (c) The compositions of an azeotrope and the vapour in equilibrium are the same and do not change with distillation.
- 15. (b) In case of minimum boiling point azeotrope, only the component present in excess than azeotropic proportion will be obtained partially in pure state as residue (still). The distillate will be azeotrope.
- **16.** (c) The distillate would be the pure component which is more volatile.

17. (c)
$$\operatorname{NaCl}_{(aq)} + \operatorname{AgNO}_{3(aq)} \rightarrow \operatorname{NaNO}_{3(aq)} + \operatorname{AgCl}_{(s)}$$

$$[\text{NaCl}] = \frac{0.1 \times 20}{25} = 0.08 \text{ mol } L^{-1} ; \qquad i = 2 ;$$

$$\pi = iCRT = 2 \times 0.08 \times 0.082 \times 300$$
 atm

(d) Only solvent molecules and not the solute molecules or ions can pass through the semipermeable membrane. Hence, Fe³⁺ and CNS⁻ ions do not come in contact on either side.

19. (b)
$$2Na^+_{(aq)} + 2OH^-_{(aq)} + SnO_{2(s)} \rightarrow 2Na^+_{(aq)}$$

$$+\operatorname{SnO}_{3(aq)}^{2-}+\operatorname{H}_2\mathrm{O}$$

The number of ions decreases in the ratio of 4 to 3, and so also the colligative property.

20. (c) Moles of urea =
$$\frac{5}{60}$$
; moles of fructose = $\frac{5}{180}$;

moles of sucrose = $\frac{5}{342}$;

moles of KCl(effective) =
$$2 \times \frac{5}{74.5} = \frac{5}{37.25}$$

21. (b)
$$\pi = iCRT = \frac{2 \times 2.5 \times 1000 \times 0.082 \times 300}{58.5 \times 100} = 21.02$$
 atm

- 22. (d) Effective molarity of $BaCl_2 = 3 \times 0.1 = 0.3$; effective molarity of $FeCl_3 = 4 \times 0.075 = 0.3$
- 23. **(b)** $\pi = (i_1C_1 i_2C_2)RT = (1 \times 0.3 2 \times 0.1) \times 0.082 \times 310$ = 2.54 atm
- 24. (b) Greater is the effective molarity $(i \times C)$, higher the ΔT_f value and lower the freezing point.

25. (c)
$$\Delta T_f$$
 (normal) = $K_f m = 1.86 \times 0.01 = 0.0186$;

$$i = \frac{\Delta T_{f(\text{obs})}}{\Delta T_{f(\text{nor})}} = \frac{0.0205}{0.0186} = 1.10 = 1 + \alpha \quad ; \quad \alpha = 0.1$$
$$K_{a} = \frac{C\alpha^{2}}{1 - \alpha} = \frac{0.01 \times 0.1^{2}}{1 - 0.1} = \frac{1}{9} \times 10^{-3} \quad ;$$
$$K_{b} = \frac{K_{w}}{K_{a}} = 1.0 \times 10^{-14} \times 9 \times 10^{3} = 9 \times 10^{-11}$$

26. (b) V_{O_3} dissolved in 100g water = 41 ml at 300 K, 1 atm

 V_{O_3} dissolved in 200g water = 2 × 41 ml at 300 K, 3 atm

Mol of O₃ =
$$\frac{PV}{RT} = \frac{3 \times 82 \times 10^{-3}}{0.082 \times 300} = 0.01$$

Mass of O_3 dissolved = $0.01 \times 48 = 0.48$ g

27. (c)
$$i = \frac{5.58}{1.86} = 3$$
;
[Cr(H₂O)₅Cl]Cl₂.H₂O \rightarrow [Cr(H₂O)₅Cl]²⁺ + 2Cl⁻

28. (a)
$$[Pt(NH_3)_6]Cl_4 \rightarrow [Pt(NH_3)_6]^{4+} + 4Cl^-;$$

 $i = 1 + 4 = 5 \text{ (maximum)}$

29. (c) Molecular mass of phosphorous =
$$\frac{1000K_f W_{\text{solute}}}{\Delta T_f W_{\text{benzene}}}$$

$$= \frac{1000 \times 5.12 \times 2.48}{1.02 \times 100} = 124.5 = (P)_x$$

or, $x = \frac{124.5}{31} = 4$

30. (c) pH = 12, pOH = 14 - 12 = 2, $[OH^{-}] = 10^{-2}$ = $0.10 \times \alpha \Rightarrow \alpha = 0.1$ $i = 1 + (n - 1)\alpha = 1 + (2 - 1) \times 0.1 = 1.1$ $\pi = iCRT = 1.1 \times 0.1 \times RT = 0.11 RT$

31. (d)
$$\frac{\Delta T_f}{\Delta T_b} = \frac{i_1 K_f m}{i_2 K_b m} = \frac{2 \times 1.86}{3 \times 0.52}$$
; $\Delta T_f = 0.372$

Hence, $\Delta T_b = 0.156^{\circ} \text{C}$

32. (c) Mass of water present in the solution at the F. pt. = 1000 - 200 = 800 g

$$\Delta T_f = 0.372 = \frac{1000 \ K_f W}{60 \times 800} = \frac{1000 \times 1.86 \times W}{60 \times 800}$$

35.

33. (d)
$$\Delta T_b(\text{normal}) = K_b m = 2.53 \times 1 = 2.53 K;$$

$$i = \frac{\Delta T_{b(\text{obs})}}{\Delta T_{b(\text{nor})}} = \frac{1.518}{2.53} = 0.6$$

$$i = 0.6 = 1 - \left(1 - \frac{1}{n}\right)\alpha = 1 - \left(1 - \frac{1}{2}\right)\alpha$$
; $\alpha = 0.8$

34. (b)
$$\operatorname{KCl}_{(aq)} + \operatorname{AgNO}_{3(aq)} \rightarrow \operatorname{AgCl}_{(s)} + \operatorname{KNO}_{3(aq)}$$

$$[KNO_3] = \frac{1 \times V}{2V} = 0.5 \text{ mol } L^{-1} ;$$

$$\Delta T_f = iK_f m = 2 \times 1.86 \times 0.5 = 1.86K$$

(b)
$$\pi = iCRT$$
, $C = 1 \mod L^{-1}$; $i = 3 = 1 + (n-1)\alpha$;
For the salt $\alpha = 1$, hence $n = 3$

$$[Cr(H_2O)_5Cl]Cl_2.H_2O + 2AgNO_3$$

$$\rightarrow$$
 [Cr(H₂O)₅Cl]²⁺ + 2AgCl_(s)

$$0.5L$$
 of 1M salt = $0.5 \times 2 = 1.0$ mol of AgCl

36. (c)
$$i = 1 + (n-1)\alpha = 1 + (5-1) \times 1 = 5$$
;
 $\Delta T_b = i K_b m = 5 \times 0.52 \times 0.1 = 0.26K$

37. (c) $\frac{\Delta p_1}{\Delta p_2} = \frac{X_I(\text{solute})}{X_2(\text{solute})}, \quad X_{2(\text{solute})} = \frac{20}{10} \times 0.1 = 0.2;$ $X_{\text{solvent}} = 1 - 0.2 = 0.8$

39. (a)
$$P_{total} = P_A^o X_A + P_B^o X_B = 50 \times 0.2 + 30 \times 0.8 = 34$$
mm

40. (c) The given solution is unsaturated (saturated one contains 5g of solute in 50g of water). On evaporation, concentration of solution increases to saturation and thereafter becomes constant due to excess solid separating out. Hence, osmotic pressure first increases and then becomes constant.

- 41. (d) In case of exothermic dissolution, the solubility of the solid increases on lowering the temperature. On cooling, the solution becomes unsaturated and solid solute does not separate. At 0°C, water in the solution does not freeze.
- 42. (b) Super cooled liquid has temperature below its freezing point. On commencement of freezing, the latent heat of freezing evolves causing the temperature to rise to F.Pt. (temperature of liquid-solid equilibrium).
- **43.** (a) Since the vapour pressure of A > that of B, the boiling point $T_A^\circ < T_B^\circ$; the azeotrope has the maximum B.pt.
- 44. (d) The mole fraction of more volatile compound (having lower B.Pt.) in the vapour must always exceed that in the solution in equilibrium.

45. (d)
$$\frac{\Delta T_f(KCl)}{\Delta T_f(X)} = \frac{4}{1} = \frac{i(KCl)}{i(X)} = \frac{2}{i(X)} \implies i(X) = 0.5$$

For association of 3 molecules,

$$i(X) = 1 - \left(1 - \frac{1}{n}\right)\alpha = 1 - \left(1 - \frac{1}{3}\right)\alpha = 0.5 \implies \alpha = 0.75$$

46. (b) Molar mass of $X_4 = 4 \times 25 = 100 \text{ g}$;

$$\Delta T_{\rm f} = \frac{1000K_{\rm f}W_{solute}}{M_{solute} \times W_{solvent}}$$

Mass of solute X in 10.3 g solution = Wg; Mass of benzene = (10.3 - W)g. Total mass of benzene in final solution = 20.0 + 10.3 - W = (30.3 - W)g

Hence,
$$\Delta T_f = 0.51 = \frac{1000 \times 5.1 \times W}{100 \times (30.3 - W)} \implies W = 0.3 g$$

Solubility
$$S = \frac{0.3 \times 100}{(10.3 - 0.3)} = 3.0 g$$

47. (c) Effective molarity of Na₂SO₄ solution = $0.004 \times i$ = $0.004 [1 + (n-1)\alpha] = 0.004 [1 + (3-1)\alpha] = 0.004 (1 + 2\alpha)$ = 0.01 (given for glucose, i = 1) $\Rightarrow \alpha = 0.75$

48. (c)
$$\Delta T_f = iK_f m = [1+(n-1)\alpha] \times 1.86 \times 0.2 = [1+(2-1) \times 0.5] \times 1.86 \times 0.2 = 0.56 \text{K}$$
 F. Pt. = -0.56°C

49. (c)
$$2KI_{(aq)} + HgI_{2(s)} \longrightarrow K_2[HgI_4]_{(aq)}$$

or
$$2K^+ + 2I^- + HgI_{2(s)} \longrightarrow 2K^+ + (HgI_4)^{2-1}$$

As a result of complex ion formation the number of mole particles in the solution decreases in the ratio

4 : 3. So, ΔT_f decreases until all the I⁻ ions are

consumed. Excess of HgI_{2(s)} > $\frac{0.1}{2}$ (= 0.05 mole)

remains insoluble, hence F.pt of solution becomes constant.

50. (d)
$$\frac{\Delta p}{p_s} = \frac{M_A W_B}{M_B W_A}$$
 $\frac{5}{100-5} = \frac{18 \times W_B}{60 \times 171}$
 $\Rightarrow W_B = 30 \text{ g} \ (B = \text{solute})$

51. (c) For dilute solution,
$$\frac{\Delta p}{p^{\circ}} \Rightarrow \frac{n_{solute}}{n_{solvent}}$$

For solution in
$$A$$
, $\frac{\Delta p_A}{p_A^\circ} = \frac{W/M}{W_A/M_A} = \frac{W}{M} \times \frac{M_A}{W_A}$(i)

For solution in B,
$$\frac{\Delta p_B}{p_A^\circ} = \frac{W}{M} \times \frac{M_B}{W_B}$$
(ii)

From (i) and (ii),
$$\frac{\Delta p_A/p_A^\circ}{\Delta p_B/p_B^\circ} = 2 = \frac{M_A W_B}{M_B W_A} = \frac{M_A}{M_B}$$
$$(W_A = W_B)$$

52. (b)
$$V_{dissolved} = K P_{H_2}$$

 P_{H_2} in the mixture = $X_{H_2}P = \frac{80 \times 1425}{100} = 1140$ torr

$$=\frac{1140}{760}=1.5$$
 atm

Hence, $V_{dissolved}$ in 2L of water = $2 \times K \times P_{H_2}$ = $2 \times 18 \times 1.5 = 54$ ml

53. (d) Moles of CO_2 disolved

$$= K \times P_{CO_2} V_{drink} = 3 \times 10^{-2} \times 4 \times 100 = 12;$$

Mass of
$$CO_2 = 12 \times 44 = 528 \text{ g}$$

54. (c) O.P.,
$$\pi = CRT = \frac{2}{60} \times 0.082 \times 300 = 0.82$$
atm

Height of solution column = $0.82 \times 0.76 \times 13.6 = 8.47$ m

55. (d) Water in the form of vapour will be transferred from solution of lower osmotic pressure to that of higher one until both become equal. Let w g of water be transferred from glucose solution to urea solution (higher concentration)

$$\pi_{\text{glucose}} = \frac{18 \times 1000 \times RT}{180 \times (100 - w)} = \pi_{\text{urea}} = \frac{18 \times 1000 \times RT}{60 \times (100 + w)}$$
$$\implies w = 50 \text{ g}$$

56. (c)
$$\pi_1 = \frac{nRT_1}{V_1}, \quad \pi_2 = \frac{nRT_2}{V_2}$$

Hence,
$$\frac{\pi_1}{\pi_2} = \frac{580}{165} = \frac{V_2 T_1}{V_1 T_2} = \frac{V_2 \times 290}{V_1 \times 330}$$

$$\Rightarrow \frac{V_2}{V_1} = 4$$

57. (b) Initially, $0.5p_A^\circ + 0.5p_B^\circ = 500$

or
$$p_A^{\circ} + p_B^{\circ} = 1000$$
(i)

On adding 2 mole of *B*, $\frac{1}{4}p_A^\circ + \frac{3}{4}p_B^\circ = 550$

or $p_A^{\circ} + 3p_B^{\circ} = 2200$ (ii)

From (i) and (ii), $p_A^\circ = 400 \text{ mm}$, $p_B^\circ = 600 \text{ mm}$

- 58. (c) Dissolution of gases in liquids is generally an exothernic process accompanied by a large decrease in volume. Follow Le chatelier's principle.
- **59.** (c) Solubility of gas α partial pressure of gas (Henry's law), partial pressure of O₂ in atmosphere at sea level

 $\simeq \frac{1}{5} \times 1 = 0.2$ atm

Hence, solubility = $1.25 \times 10^{-3} \times 0.2 = 2.5 \times 10^{-4} M$

60. (c) Mass of sucrose (mol. mass = 342 g) required to prepare

$$0.2 m = \frac{0.2 \times 342 \times 500}{1000} = 34.2g$$

Mass of 0.5m solution containing 34.2g

$$=\frac{(1000+171)}{171}\times34.2=234.2g$$

61. (d) 25% solution by mass of solvent = 25 + 100 = 125 g of solution

Hence, % by mass of solution $=\frac{25}{125} \times 100 = 20$

62. (b) $\Delta H_1 = \Delta H_2$, because similar attractive forces between solvent molecules in pure state and solution must be overcome for vaporisation. Due to increase in randomness during mixing of solute and solvent, $S_{\text{solution}} > S_{\text{solvent}}$. Hence $(S_{\text{vapour}} - S_{\text{solvent}}) > (S_{\text{vapour}} - S_{\text{solvent}})$.

- **63.** (b) At the freezing point of solution, solid solvent and solution are in equilibrium.
- 64. (c) Since $S_{\text{solution}} > S_{\text{solvent}}$, the escaping tendency of solvent molecules into vapour state is smaller than that in pure state.
- 66. (d) $mK_f = \Delta T_f$ has the units of temperature . Van't Hoff factor, *i*, is dimensionless quantity.
- 67. (d) Osmosis is a spontaneous process ($\Delta G < 0$) which takes place with $\Delta S > 0$ (due to transfer of solvent in 70 solution)
- 68. (d) Colligative properties depend upon concentration of mol particles in solution, quite independent of the nature, structure and molar mass.
- **69.** (c) Let x and y be the molar masses of A and B respectively.

Then,
$$\frac{\Delta T_f}{K_f} = m = 1 = \frac{8 \times 1000}{(x+2y) \times 100} = \frac{80}{x+2y}$$
 ... (i)

And
$$\frac{\Delta T_f}{K_f} = m = 1 = \frac{10 \times 1000}{(2x \times y) \times 100} = \frac{100}{2x + y}$$
 ... (ii)

Solving (i) & (ii),
$$x = 40$$
; $y = 20$

70.

72

73

(c)
$$1L = 1000 \text{ mL of } 1 M = 1000 \times 1.16 = 1160 g \text{ solution}$$

Molality of urea solution $=\frac{1 \times 1000}{(1160-60)} = \frac{10}{11}$

Hence,
$$\Delta T_f = K_f m = 1.86 \times \frac{10}{11} = 1.69^\circ$$

71. (c)
$$\Delta T_f$$
 (normal) = $K_f m = 1.86 \times 0.5 = 0.93^\circ$

Assuming 100% ionization , i = n = No. of ions per molecule

$$= \frac{\text{Observed }\Delta T_f}{\text{Normal }\Delta T_f} = \frac{3.72}{0.93} = 4$$

$$(c) \quad \frac{\Delta T_f}{\Delta T_b} = \frac{0.48}{0.26} = \frac{mK_f}{mK_b i} = \frac{3.7}{i} \Longrightarrow i = 2$$

Since the compound *AB* at the boiling point of solution ionizes completely.

• (d)
$$\Delta p = p^{\circ} \times \text{solute} = 760 \times \frac{1 \times 2}{18 + 2} = 76 \text{ torr}$$

$$(i = 2 \text{ for KCl});$$
 moles of water = $324/18 = 18$

74. (b) *i* for BaCl₂ = 1 + (*n*-1) α = 1 + (3-1) × 0.9 = 2.8 Hence, osmolarity = *i* × molarity = 2.8 × 0.5 = 1.4

75. (d) Let
$$S_n$$
 be the molecular formula of sulphur in CS_2 .

Then,
$$\Delta T_f = 0.01 = \frac{1000K_f W_{\text{solute}}}{M_{\text{solute}} \times W_{\text{solvent}}}$$
$$= \frac{1000 \times 0.1 \times 1.28}{n \times 32 \times 50} \Longrightarrow n = 8$$

76. (a) Let 1 mol of complex form x mol of cations and anions

Then
$$\frac{\Delta p}{p^{\circ}} = 0.2 = \frac{n_2}{n_1 + n_2} = \frac{x}{8 + x} \Longrightarrow x = 2$$

77. (c) $Cl^- + Ag^+ \rightarrow AgCl_{(s)}$

$$[\text{Cl}^-] = \frac{20 \times 1}{25} = 0.8M$$
; $[\text{BaCl}_2] = 0.4M$

$$\Delta T_b = i K_b m = 3 \times 0.52 \times 0.4 = 0.62K$$

78. (d) For ideal solution vapour pressure of solution

$$= p_{A}^{\circ} X_{A} + p_{B}^{\circ} X_{B}$$
$$= 80 \times \frac{2}{5} + 100 \times \frac{3}{5} = 92 \text{ torr}$$

Since observed vapour pressure of solution < ideal vapour pressure, the solution shows negative deviation.

79. (a)
$$n \text{ water} = \frac{144}{18} = 8$$
; $n = \text{mol of KCl}(i = 2)$
Hence $\frac{\Delta p}{p^{\circ}} = \frac{20}{100} = \frac{n_2}{n_1 + n_2} = \frac{2 \times n}{8 + 2 \times n} \Longrightarrow n = 1$

80. (c) The vapour pressure of a mixture of two immiscible liquids is the sum of their vapour pressures in the pure states, independent of their relative amounts. Hence, *B*. pt. of the mixture will be less than that of either of the liquids, remaining constant until one of the liquids vaporises completely.

81. (b) In pure ethyl alcohol, the mole fraction of methyl alcohol is zero. Thus using the given equation, we get *P* (vapour pressure of pure ethyl alcohol)

$$= 120 \times 0 + 150 = 150 \,\mathrm{mm}\,\mathrm{of}\,\mathrm{Hg}$$

82. (d) From the given data

In case I

3 mole of A + 1 mole of B, V.P. = 550 mm Using the equation

$$P = P_A^{\circ} X_A + P_B^{\circ} X_B$$
, we have

$$550 = P_A^{\circ} \times \frac{3}{4} + P_B^{\circ} \times \frac{1}{4} \quad [X_A = \frac{3}{4}, X_B = \frac{1}{4}]$$

or
$$550 = 0.75 P_A^\circ + 0.25 P_B^\circ$$

In case II

4 mole of A + 1 mole of B; V.P. = 560 mm

$$\therefore 560 = P_A^{\circ} \times 0.80 + P_B^{\circ} \times 0.20$$

$$\left[X_A = \frac{4}{5} \text{ or } 0.8 \text{ and } X_B = \frac{1}{5} = 0.20\right]$$

Solving the above two equations, we get

$$P_A^{\circ} = 600 \,\mathrm{mm}\,\mathrm{of}\,\mathrm{Hg}$$

83. (c) Mole fraction of *B* in vapour phase, $X'_B = \frac{P_B}{P_{\text{total}}}$

$$\frac{0.06}{0.04 + 0.06} = \frac{0.06}{0.1} = 0.60$$

84. (b) From the given data

=

$$P_{H_2} = 1500 \times 0.80$$

= 1200 mm of Hg = $\frac{1200}{760}$ atmosphere = 1.58 atmosphere

If *V*'s are volumes of gas dissolved by same volume of liquid, then from Henry's law

$$\frac{V_2}{V_1} = \frac{P_2}{P_1}$$

or $\frac{V_2}{20} = \frac{1.58}{1.0}$

or $V_2 = 31.60 \text{ ml}$

85. (c) V.P. of solution of A and B at $t^{\circ}C = 760 \text{ mm}$ [at b.p., V.P. of solution =atompheric pressure]

Thus
$$P = P_A^\circ X_A + P_B^\circ X_B$$

or
$$P = P_A X_A + P_B (1 - X_A) [:: X_A + X_B = 1]$$

or
$$760 = 400 X_A + 800 - 800 X_A [:: p = 760 \text{ mm of Hg}]$$

or
$$-800 + 760 = -400$$

or
$$-40 = -400 X_{2}$$

or
$$X_A = \frac{40}{400} = 0.1$$

Thus mole fraction of A in solution is 0.1(1)

86. (d) Solubility of organic acid in water = 0.3g/300 ml [Amount of acid left in water layer = 0.9 - 0.6 = 0.3g] Solubility of acid in ether = 0.6g/75 ml = 2.4g/300 ml

$$\therefore \frac{S_{\text{ether}}}{S_{\text{Water}}} = \frac{2.4}{0.3} = 8 = \text{partition coeff. of organic acid}$$

between ether and water.

COMPREHENSION TYPE

- 1. **(b)** Both ΔH_{latt} and ΔH_{solv} become less negative from BeCO₃ to BaCO₃ due to increase in the cationic size, the latter has the profound effect. Consequently the solubility decreases down the group. However, smaller value of solubility of SrCO₃ than BaCO₃ suggests its greater value of ΔH_{latt} , and hence almost equal size of Sr²⁺ and CO₃².
- 2. (b) The smaller the ion, the greater will be its solvation and more negative will be ΔH_{solv} .
- 3. (a) Solubility = Molarity of saturated solution of

$$\operatorname{Ca(OH)}_{2} = \left(\frac{K_{sp}}{4}\right)^{1/3} \operatorname{mol} \mathrm{L}^{-1}$$

Solubility of $CaSO_4 = (K_{sp})^{1/2} \mod L^{-1}$

Since $K_{sp} < 1$ (for sparingly soluble electrolytes),

solubility of $Ca(OH)_2 > CaSO_4$

- 4. (c) MgCO₃ (salt), being a non volatile solute, lowers down the vapour pressure of water and hence raises the B.Pt.
- 5. (c) For dissolution of a solute into a solvent $\Delta G_{\text{soln}} = \Delta H_{\text{soln}} T\Delta S_{\text{soln}}$ must be negative. Hence, $T\Delta S_{soln} > \Delta H_{soln}$.
- 6. (b) Due to increase in cationic size down the group, both ΔH_{solv} and ΔH_{latt} become less negative; the former must have profound effect.
- 7. (c) Cryoscopic constant $K_f = \Delta T_f$ of solution having unit molality of normal solutes.

Molality of glucose solution in (c) = $\frac{9 \times 1000}{(59-9) \times 180} = 1$

8. (d) Since the solution has greater entropy (disorder) than the pure liquid, so former has lesser tendency to freeze i.e., the temperature has to be lowered to freeze the solution. It has lesser tendency to pass into the vapour phase.

9. **(b)**
$$2Na^{+}_{(aq)} + 2I^{-}_{(aq)} + HgI_{2(s)} \longrightarrow 2Na^{+}_{(aq)} + HgI_{4(aq)}^{2-}$$

The number of mole particles decreases from 4 =

 $(2Na^+ + 2I^-)$ to $3 = (2Na^+ + HgI_4^{2-})$. Hence, the colligative property will decrease or, the vapour pressure will increase to a constant value until NaI is completely consumed.

10. **(b)**
$$K_f = \frac{RT_f^2 M}{1000 \ \Delta H_{fus}}$$
 would be larger for larger value of

 T_f° and smaller value of enthalpy of fusion of the solid solvent.

- 11. (d) Isomerization does not lead to change of concentration of mole particles in the solution
 - (d) In (a) and (b) the solutes undergo micellization in solution and in (c) the solute undergoes dimerization. As a result the observed colligative properties will be lower than the normal values.

(c) Normal value of
$$\Delta T_f = K_f m = 1.80 \times \frac{6}{60} = 0.18^{\circ}$$

Acetic acid is a uni-univalent weak electrolyte and ionizes feebly, hence i is slightly greater than unity.

(c) Rectified spirit is an azeotrope of ethanol and water having minimum boiling point.

Loss of mass of solution, $w_1 \propto p_s$

The air saturated with water vapour at vapour pressure of solution will further absorb vapour from water $(: p^{\circ} > p_s)$ and gets saturated at p° . Hence Loss of mass of solvent (water), $w_2 \propto (p^{\circ} - p_s)$ The total loss of mass $(w_1 + w_2) \propto p^{\circ}$.

18. (d)
$$\frac{\Delta p}{p^{\circ}} = \frac{n_2}{n_1 + n_2} = \frac{1}{24 + 1} \Rightarrow \Delta p = 2 [\because p^{\circ} = 50 \text{ mm Hg}]$$

Hence, $p_s = 50 - 2 = 48 \text{ mm Hg}$

19.

12.

13.

15.

20. (d) 21.

Methanol is more volatile than water hence V. P. of solution is greater than that of pure water. On the other hand, glucose being non-volatile, lowers the vapour pressure. Hence plots I, II and III will be vapour pressure- temperature curves for methanol solution, pure water and glucose solution respectively.

(b)

 T_1 , T_2 and T_3 are the temperatures at which their vapour pressures become 1 atm each i.e., the boiling points.

22. (d) Molality of water in ethanol
$$=\frac{0.1 \times 1000}{0.9 \times 46} = 2.41$$

$$\Delta T_f = K_f m = 2.0 \times 2.41 = 4.82 \,\mathrm{K};$$

Hence, freezing point = 150.7 - 4.82 = 150.9 K

23. (a) Vapour pressure of solution = $X_A P_A^\circ + X_B P_B^\circ$ = $0.9 \times 40 + 0.1 \times 32.8 = 39.3$ torr 24. (d) Water is less volatile than ethanol. Hence boiling point of solution will be greater than the boiling point of pure ethanol and smaller than that of pure water.

 (c) From the given data, Depression in freezing point = (81°C - 80.0°C) = 1°C To cause a depression of 1°C we need 100 g naphthalene and 3.95 g of sulphur.

To cause the same depression in 1 kg (or 1000 g) of naphthalene, we will need sulphur

$$=\frac{3.95}{100}\times1000=39.5\,\mathrm{g}$$

25.

26. (d) The amount of sulphur needed = $39.5 \times 6.5 = 256.75$ g

27. (a) Since $\Delta T_f = K_f (= 6.5^{\circ} \text{K})$, the solution must have unit molality, i.e., 1 mole of sulphur per kg of naphthalene. 1 mole of sulphur molecules = 256.75 kg

Hence, atomicity of sulphur molecule $=\frac{256.75}{32}=8$

[32 = At. mass of S]

30.

4.

5.

6.

7.

8.

9.

Thus, sulphur exists as S_8 . **28.** (b) From the given data, we have

 $w = 0.5 \times 10^{-3} \text{ kg}$ [0.5 % solution] $W = 100 \times 10^{-3} \text{ kg}$

[solvent in water, density = 1 g/km³] $\Delta T_f = 273 - 272.76 = 0.24$

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

$$\therefore M = \frac{1000 \times K_f \times v}{\Delta T_f \times W}$$

$$=\frac{1000\times1.86\times0.5\times10^{-3}}{0.24\times100\times10^{-3}}=38.76$$

C 🗏 REASONING TYPE 🗄

=

- (a) Lattice energy is the amount of energy required to dissociate one mole of an ionic crystal into its ions and hydration energy is the amount of energy released when one mole of ions undergo hydration. So for the solubility of a solid into a liquid (water) hydration energy must be greater than lattice energy.
- (a) This is according to Henry's law which states that the solubility of a gas in given volume of a liquid at a particular temperature is directly proportional to the pressure of gas above the liquid. m ∝ p, m = kp where k = Henry's constant.
- 3. (b) The correct explaination of assertion is that one molar aqueous solution has 1 mole in less than 1000 g of water . Hence 1000 g of water will be associated with more than 1 mole while 1 molal has 1 mole in 1000 g of water.

 \therefore The apparent molecular weight of KCl = 38.76 The molar mass of KCl = 39 + 35.5 = 74.5

 $\therefore i = \frac{\text{Normal molecular weight}}{\text{Apparent molecular weight}}$

$$=\frac{74.5}{38.76}=1.92\approx 2$$

29. (c) In solution KCl dissociates as follows

 $KCl \longrightarrow K^+ + Cl^-$

=

If α is degree of dissociation, then

$$KCl \longrightarrow K^+ + Cl^-$$

 $(1-\alpha)$ α α The number of effective particles is $1-\alpha+\alpha+\alpha$ = $(1+\alpha)$

:.
$$i = \frac{1+\alpha}{1}$$

or $\alpha = i-1$
= 1.92-1 [i=1.92]
= 0.92 or 92.0%

(c) Osmotic coefficient $g = \frac{i}{n}$

$$g = \frac{i}{n} [n = 2, i = 1.92]$$
$$= \frac{1.92}{2} = 9.6$$

- (b) On adding a non-volatile solute in a liquid the vapour pressure decreases. The solution has more randomness (entropy) than the pure liquid and hence has lesser tendency to evapourate.
- (a) Reason is the correct explanation of Assertion.
- (c) The polymer solutions possess very little elevation in boiling point or depression in freezing point.
- (c) The freezing point keeps on becoming lower and lower. Depression in freezing point is a colligative property as it depends on the number of particles present in the solution. The solution will freeze as lower temperature on adding larger amount of solute.
- (c) Camphor has high molal depression constant.
- (a) KCl being an electrolyte provides more number of particles in solution; however urea being a non-electrolyte remains as such in solution.

- 10. (a) Dissociation results in the increase in the number of particles and hence increase in the value of colligative property and decrease in the molecular mass Association results in the reverse.
- 16. (d) Assertion is false but reason is true. The solubility of some solutes in water decreases on increasing the temperature.
- 17. (b) Both assertion and reason are correct but reason is not the correct explanation of assertion.

The relationship between lowering of vapour pressure and osmotic pressure can be derived as follows:

Van't Hoff equation for dilute solutions is

$$\pi = \frac{n}{V}RT \qquad \dots (1)$$

In case of a dilute solution, the volume of solution can be taken as equal to that of solvent. If N is the number of moles of solvent of molecular weight M and density ρ , the volume V is given by

$$V = \frac{NM}{\rho} \qquad \dots (ii)$$

....(iii)

or

D MULTIPLE CORRECT CHOICE TYPE

 $\frac{n}{N} = \frac{\pi M}{\rho. R. T.}$

1. (a,d) $[NaCl]_{effective} = 2 \times 0.5 = 1.0;$

$$[C_6H_5COOH]_{effective} = 2.0 \times \frac{1}{2} = 1.0 \quad (i = \frac{1}{2})$$
 20.

- (a, b, c) B. pt. of CCl₄ < that of SiCl₄. The vapour must always be richer in more volatile component. Hence, the upper curve represents the composition of the vapour and the lower curve represents the composition of the solution at the corresponding B.pt.
- **15.** (c, d) The solute molecules or ions can not pass through the semipermeable membrane, only the solvent molecules can pass through. Hence no precipitation on either side.

 $M_{\text{effective}}(\text{AgNO}_3) = iC = 2 \times 0.1 = 0.2$

$$M_{\text{effective}}(\text{BaCl}_2) = iC = 3 \times 0.1 = 0.3$$

Osmosis occurs from AgNO₃ side to BaCl₂ side.

From Raoult's law,

$$\frac{P^{\circ} - P}{P^{\circ}} = \frac{n}{N} \qquad \qquad \dots \text{(iv)}$$

$$\frac{P^{\circ} - P}{P^{\circ}} = \frac{\pi M}{\rho RT} \qquad [From (iii) and (iv)]$$

or
$$(P^{\circ} - P) = \frac{\pi M}{\rho RT} \times P^{\circ}$$

The factor $\frac{MP^{\circ}}{\rho RT}$ is constant at constant temperature.

$$\therefore (P^{\circ} - P) \propto \pi$$

18.

19.

or lowering of V.P. \propto osmotic pressure

Thus assertion is correct.

Osmotic pressure is a colligative property is correct.

- (b) Both assertion and reason are correct but reason is not the correct explanation of assertion. It is an application of assertion.
 - (d) Assertion is false but reason is true. The process of mixing of CCl_4 and CH_3OH is accompanied by decrease in enthalpy.
- 20. (a) Both assertion and reason are correct and reason is the correct explanation of assertion.

- 17. (c,d) $Cu_2[Fe(CN)_6]$ acts as semipermeable membrane only for aqueous solutions.
 - (b,c) Vapour pressure of solutin containing non-volatile slute is always smaller than that of solvent points a and b represent the boiling points of solvent and solution respectively (temperatures at which their V.P. = 1 atm each). Hence gap $ab = K_bm =$ elevation of boiling point.
- 21. (b,c) For ideal behaviour $P_{\text{Total}} = X_A p_A^\circ + p_A^\circ$

$$+X_B p_B^{\circ} = \frac{3}{4} \times 500 + \frac{1}{4} \times 340$$

= 460 torr < observed V.P. Hence negative deviation and $\Delta H_{\text{mixing}} < 0$

22. (b,c,d) $K_b = RT_b^{\circ 2}M/1000 \Delta H$ where $T_b^{\circ} =$ boiling point of solvent, $\Delta H =$ molar enthalpy of vaporisation and M = molar mass of solvent 23. (a,b,c,d) The osmolality of Kcl, urea $C_6H_5NH_3^+cl^-$ and K_2SO_4 are 2×0.1 , 1×0.1 , 2×0.1 and 3×0.1

respectively.

24. **(b)**
$$P_{\text{Total}} = X_A p_A^\circ + X_B p_B^\circ = X_A p_A^\circ + (1 - X_A) p_B^\circ$$

$$= p_B + (p_A - p_B) X_A$$

25. (a,b,c) Osmolarity of solution $X = 2 \times 0.1 = 0.2$ (i = 2) Vant Hoff factor for

$$Y = 1 - \left(1 - \frac{1}{n}\right)\alpha = 0.5 \# \# (n = 2; \alpha = 1)$$

Osmolarity of solution $Y = 0.5 \times 0.1 = 0.05$

- Liquid system (a) shows positive deviation and 26. (a,d) Systems (b) and (c) exhibit negative deviations from Raoult's law. System (d) is an ideal solution.
- 27. (d,c) ΔS_{mixing} (for ideal or non-ideal solutions) is always positive and ΔG_{mixing} is always negative

28. (**a**, **b**, **c**) when
$$n_A = n_B$$
, we have $X_A = \frac{n_A}{n_A + n_B} = \frac{1}{2}$

and
$$X_B = \frac{n_B}{n_A + n_B} = \frac{1}{2}$$

Using the given relation, we have

$$P_{S} = (110 \times \frac{1}{2} + 125 \times \frac{1}{2}) \text{ mm of Hg}$$

 $= 117.5 \, \text{mm of Hg}$

In case of pure A or pure B the mole fraction of other component will be zero, then For pure $A; X_A = 1, X_B = 0$ $\therefore P_A = (110 \times 1 + 125 \times 0) \,\mathrm{mm}\,\mathrm{of}\,\mathrm{Hg}$ $=(110+0) \,\mathrm{mm}\,\mathrm{of}\,\mathrm{Hg}$ $= 110 \,\mathrm{mm}\,\mathrm{of}\,\mathrm{Hg}$

Similarly, $P_B^{\circ} = 125 \text{ mm of Hg} [X_B = 1, X_A = 0]$

From the above calculations it is clear that

when $n_A = n_B$: $P_s < P_B^{\circ}$ [$P_S = 117.5$ mm and $P_{R}^{\circ} = 125 \text{ mm}$] $n_A = n_B : P_S > P_A^{\circ} [P_S = 117.5 \text{ mm}]$ and $P_A^\circ = 110 \text{ mm}$]

Also $P_A^{\circ} = 110 \text{ mm of Hg and } P_B^{\circ} = 125 \text{ mm of Hg}$ Statement (d) is incorrect.

29. (a, b, c) Since the solute X behaves as univalent electrolyte in solution, so for this solute, i = 2Since the solute Y dimerises in solution, so for

this solute
$$i = \frac{1}{2}$$

We know that

b.p. $\propto i$, \therefore b.p. of X will be greater than that of Y Osmotic pressure ∞i , \therefore o.p. of X > o.p. of Y

Freezing point
$$\propto \frac{1}{i}$$
; \therefore f.p. of X < f.p. of Y

and relative lawering of V.P. i.e. $\frac{\Delta P}{D^{\circ}} \propto i$

$$\therefore \left(\frac{\Delta P}{P^{\circ}}\right)_{X} > \left(\frac{\Delta P}{P^{\circ}}\right)_{Y}$$

Thus statement (d) is incorrect. All other statements are correct.

We know $\Delta G_{\text{vap}} = \Delta H_{\text{vap}} - T_b$. $\Delta S_{\text{vap}} = 0$ [At equilibrium $\Delta G = 0$; at b.p. the liquid is in equilibrium with vapour] Thus, $\Delta H_{\text{vap}} = T_b \Delta S_{\text{vap}}$

or
$$\frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}} = T_b$$

 $\Delta H_{\rm vap}$ is almost same for solvent and dilute solution. Since b.p. of solution is higher, ΔS_{van} will be lower than that of pure solvent.

МАТКІХ-МАТСН ТҮРЕ 🗮

- 1. A-s; B-p; C-q; D-r
 - (A) All gases dissolve in water exothermically with decrease in randomness. Hence $\Delta H < 0$, $\Delta S < 0$.
 - Since solubility of the given solid in water increases **(B)** on raising temperature, dissolution is endothermic. Hence $\Delta H > 0$ and $\Delta S > 0$ (Increase in disorder on dissolution).
- (C) In a saturated solution, there is no further dissolution of solid. Hence $\Delta H = 0$ and $\Delta m = 0$.
- On adding solid to super saturated solution, excess of (D) solid dissolved separates out with the evolution of heat. Hence $\Delta H < 0$ and $\Delta m < 0$.

30. (d)

2. A-q; B-p; C-s; D-r

- (A) Loss in mass of solution α V.P. of solution (p_s) .
- (B) Loss in mass of solvent α Difference of V.P. of solvent and solution, i.e. $(p^{\circ} p_s)$.
- (C) Since the air is saturated at the V.P. of solvent, so total loss $(w_1 + w_2) \alpha p^0$.
- (D) Relative lowering of V.P. = $\frac{p^{\circ} p_s}{p^{\circ}} = \frac{w_2}{w_1 + w_2}$

3. A-r, s; B-r; C-p; D-q

- (A) In case of ionisation of solute in solution, $M_0 < M_n$.
- (B) $\operatorname{BaCl}_2 \longrightarrow \operatorname{Ba}^{2+} + 2\operatorname{Cl}^-$

Degree of ionization $\alpha = 1$ and i = 3

Hence
$$\frac{M_n}{M_0} = 3 \implies M_0 = \frac{M_n}{3}$$

(C) In case of association of solute in solution, observed colligative property is smaller than the normal value. CH₃COOH dimerises in benzene. Hence $M_0 > M_n$.

(A)
$$K_f = \frac{RT_f^{\circ 2}}{1000 L_f} = \frac{RT_f^{\circ 2} M}{1000 \Delta H_f}$$

$$T_f^{\circ}(\text{water}) = 273K, M = 18$$

(B)
$$K_b = \frac{RT_b^{\circ^2}}{1000 L_v} = \frac{RT_b^{\circ^2} M}{1000 \Delta H_f}$$

$$T_b^{\circ}$$
 (water) = 373 K, M = 18

(C)
$$\Delta T_f = K_f \times m = K_f \times \frac{9 \times 1000}{180 \times 50} = K_f$$

(D)
$$\Delta T_b = K_b \times m = K_b \times \frac{3 \times 1000}{60 \times 50} = K_b$$

9. A-p; B-p, s; C-p, r; D-p, q

All the properties listed in column A are colligative properties. Elevation in boiling point depends upon the value of ebullioscopic constant of the solvent. Osmotic pressure can be determined by Berkeley-Heartley method. Ostwald and Walker method is used for the determination of relative lowering of vapour pressure.

F NUMERIC/INTEGER ANSWER TYPE ==

- 1. Mole fraction of A, $X_A = \frac{60}{100} = 0.60$; $p_A^0 = 24.0 k P_a$ Mole fraction of B, $X_B = \frac{40}{100} = 0.40$; $p_B^0 = 12.0 k P_a$ $p_A =$ Partial vapour pressure of A at 350 K $= p_A^0 X_A = 24 \times 0.60 = 14.4 k P_a$ $p_B =$ Partial vapour pressure of B at 350 K $= p_B^0 X_B = 12 \times 0.40 = 4.8 k P_a$ Mole fraction of A in vapour, i.e., first distillate $X_A' = \frac{p_A}{p_A + p_B} = \frac{14.4}{14.4 + 4.8} = \frac{14.4}{19.2} = 0.75$ Mole fraction of B in first distillate $X_B' = 1 - 0.75 = 0.25$ This distillate is redistilled.
- Mole fraction of A in second distillate = mole fraction of A in the vapour above first distillate

$$=\frac{P_{A}}{P_{A}^{'}+P_{B}^{'}}=\frac{18}{18+3}=0.857$$

Hence, mole % of A in 2nd distillate = 85.7

2. Molality (*m*) of solution $=\frac{0.4 \times 1000}{80 \times 100} = 0.05$

$$\Delta T_f$$
 (normal) = $K_f \times m = 1.86 \times 0.05 = 0.093$ K

Van't Hoff factor,
$$i = \frac{\Delta T_f \text{(observed)}}{\Delta T_f \text{(normal)}} = \frac{0.12}{0.093} = 1.290$$

HA + H₂O
$$\implies$$
 H₃O⁺ + A⁻
 $\alpha = \frac{i-1}{n-1} = \frac{1.290 - 1}{2 - 1} = 0.29$
 $K_a = \frac{C\alpha^2}{1 - \alpha} = \frac{0.05 \times 0.29^2}{1 - 0.29} = 5.92 \times 10^{-3}$

 p'_A = Partial vapour pressure of

$$A = p_A^{o} X_A' = 24 \times 0.75 = 18 k P_a$$

 p_B = Partial vapour pressure of

 $B = p_B^{o} X_B' = 12 \times 0.25 = 3 k P_a$

3. Let x g be the mass of element in 51.0 g of saturated solution.

Mass of benzene in 51.0 g of saturated solution = 51.0 - x g

Total mass of benzene containing x g of solute = 50 + 51 - x = (101 - x) g

$$\Delta T_f = \frac{1000K_f W_B}{M_B W_A} = \frac{1000 \times 5.5 \times x}{4 \times 25 \times (101 - x)} = 0.55 \text{ (given)}$$

$$\Rightarrow x = 1.0g$$

Hence, solubility $= \frac{W_B \times 100}{W_A} = \frac{1}{(51-1)} \times 100 = 2.0 \text{ g}$

4. Molality of solution,
$$m = \frac{23.5 \times 1000}{94 \times 500} = 0.5$$

(mol. mass = 94)

$$2C_6H_5OH \Longrightarrow (C_6H_5OH)_2$$

 $(\alpha = degree of dimerization)$

Van't Hoff factor of phenol,

5.

$$i = \left[1 - \left(1 - \frac{1}{n}\right)\alpha\right] = \left[1 - \left(1 - \frac{1}{2}\right)\alpha\right] = 1 - \frac{\alpha}{2}$$

Hence $\Delta T_f = iK_f m = \left(1 - \frac{\alpha}{2}\right) \times 12.0 \times 0.5 = \left(1 - \frac{\alpha}{2}\right) \times 6.0$
 $3.60 = \left(1 - \frac{\alpha}{2}\right) \times 6.0 \Rightarrow \alpha = 0.80$

 \therefore 80% of phenol is present in dimeric form.

In the complex, $4NH_3$ molecules will be ligands only, i.e. non-ionizable and 4Cl can be ligands or ionisable or both.

Let *n* Cl be the ligands (non-ionisable). Then, number of ionisable Cl = 4 - n

 $[Pt(NH_3)_4Cl_n]Cl_{4-n} = [Pb(NH_3)_4Cl_n]^{(4-n)+} + (4-n)Cl^{-1}$ Van't Hoff factor, $i = 1 + (1 + 4 - n - 1)\alpha = 5 - n$ ($\alpha = 1$)

$$\Delta T_f = iK_f m = (5 - n) \times 1.86 \times 0.01 = 0.056 \text{ (given)}$$

$$\Rightarrow n = 2$$

Hence, formula of the complex ion is $[Pt(NH_3)_4Cl_2]^{2+}$

