SOLVED EXAMPLES

Ex.1 Mixture of volatile components A and B has total vapour pressure (in torr) :

$P = 254 - 119\,x_A$

Where x_A is mol fraction of A in mixture.

Hence P_A° and P_B° are (in torr)

(A) 254, 119 **(B)** 119, 254 **(C)** 135, 254 **(D)** 154, 119

Sol. **(C)**

when $x_A = 0, x_B = 1$

$\therefore$ $P = P_B^\circ$

$\therefore$ $P_B^\circ = 254,$

when $x_A = 1, x_B = 0$

$\therefore$ $P_A^\circ = P = 254 - 119 = 135$

Ex.2 When mango is placed in dilute aqueous solution of hydrochloric acid, it ?

(A) Shrinks **(B)** Swells **(C)** Brusts **(D)** Nothing happens

Sol. **(A)**

The H^+ ion concentration in the medium is lower than that of H^+ concentration present in the mango juice, therefore osmotic pressure inside the mango is higher than that of aqueous hydrochloric acid. Therefore, H_2O will be passes out from the mango into aqueous hydrochloric acid. Therefore mango shrinks.

Ex.3 Heptane and octane form ideal solution. At 373 K, the vapour pressures of the two liquids are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure, in bar, of a mixture of 25g of heptane and 35 g of octane ?

Sol. **(A)** Heptane C_7H_{16} $m_A = 100$

(B) Octane C_8H_{18} $m_B = 114$

$$n_A = \frac{w_A}{m_A} = \frac{25}{100} = 0.25\,; \qquad n_B = \frac{35}{114} = 0.3$$

$$x_A = \frac{0.25}{0.25 + 0.30} = 0.45 \qquad x_B = \frac{0.3}{0.25 + 0.30} = 0.55$$

$$= 0.45$$

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= 105.2 \times 0.45 + 46.8 \times 0.55$$

$$= 47.34 + 25.74 = 73.08 \text{ kPa}$$

Ex.4 A certain substance 'A' tetramerises in water to the extent of 80%. A solution of 2.5 g of A in 100 g of water lowers the freezing point by 0.3°C. The molar mass of A is :

(A) 122 **(B)** 31 **(C)** 244 **(D)** 62

Sol. **(D)**

$$\alpha = \frac{1 - i}{1 - \frac{1}{n}}$$

$$0.8 = \frac{1 - i}{1 - \frac{1}{n}}; i = 0.4$$

$$\Delta T = iK_f \times m$$

$$0.3 = 0.4 \times 1.86 \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.3 = 0.4 \times 1.86 \times \frac{2.5 \times 1000}{m_B \times 100}$$

$$m_B = 62$$

Ex.5 Which of the following solutions will exhibit highest boiling point ?

(A) 0.01 M Na_2SO_4 **(B)** 0.01 M KNO_3 **(C)** 0.015 M urea **(D)** 0.015 M glucose

Sol. **(A)**

$\Delta T = i \times K_b \times m$

$i \times m$ of Na_2SO_4 is highest, hence its boiling point will also be highest.

Na_2SO_4	$i \times m = 3 \times 0.01 = 0.03$
KNO_3	$i \times m = 2 \times 0.01 = 0.02$
Urea	$i \times m = 1 \times 0.015 = 0.015$
Glucose	$i \times m = 1 \times 0.015 = 0.015$

Ex.6 What is the osmotic pressure of 12% solution of can sugar (mol. wt. 342) at 17°C.

Sol. 12 g. sugar is dissolved in 100 mL thus 342 g. sugar is dissolved in

8 litres

Now, $\pi V = ST \; \{\because \; n = 1\}$

$$\pi = \frac{ST}{V} = \frac{0.0821 \times 290}{2.85} = 8.35 \text{ atm}$$

Ex.7 A dilute solution contains m mol of solute A in 1 kg of a solvent with molal elevation constant K_b. The solute dimerises in solution as $2A \rightleftharpoons A_2$. Show that equilibrium constant for the dimer formation is

$$K = \frac{K_b(K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2}$$

where ΔT_b is the elevation of the boiling point for the given solution. Assume molarity = molality

Sol.

$2A$	$\rightleftharpoons$	A_2	
m		0	initially
$(m - m\alpha)$		$\frac{m\alpha}{2}$	after dimerization
$m(1-\alpha)$		$\frac{m\alpha}{2}$	

Where α is the degree of dimerization and m is molality which is also molarity (given). Hence due to dimerization, final molality = m

$$m(1-\alpha) + \frac{m\alpha}{2} = m\left(1 - \frac{\alpha}{2}\right)$$

$$i = 1 + (n-1)\alpha$$

$$= 1 + \left(\frac{1}{2} - 1\right)\alpha$$

$$= \left(1 - \frac{\alpha}{2}\right)$$

$$\Delta T_b = K_b \times m \times i = K_b \times m\left(1 - \frac{\alpha}{2}\right)$$

$$\therefore \quad \alpha = \frac{2(K_b m - \Delta T_b)}{K_b m}$$

equilibrium constant K for the dimer formation is

$$K = \frac{[A_2]}{[A]^2} = \frac{\frac{m\alpha}{2}}{m^2(1-\alpha)^2} = \frac{\alpha}{2m(1-\alpha)^2}$$

$$K = 2\left[\frac{K_b m - \Delta T_b}{K_b m}\right] \bigg/ 2m\left[1 - \frac{2(K_b m - \Delta T_b)}{K_b m}\right]^2$$

$$K = \frac{K_b(K_b m - \Delta T_b)}{(K_b m - 2K_b m + 2\Delta T_b)^2}$$

$$K = \frac{K_b(K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2} \qquad \textbf{Proved}$$

Ex.8 Distribution coefficient of an organic acid between water and benzene is 4.1 in favour of C_6H_6. If 5 g of acid is distributed in between 50 mL of benzene and 100 mL of water, calculate the concentration of acid in two solvents.

Sol. Let the amount of organic acid in

C_6H_6 layer = a g

volume of C_6H_6 = 50 mL

$\therefore$ concentration of acid in $C_6H_6 = \frac{a}{50}$ g mL^{-1}

since total amount of acid = 5 g

$\therefore$ Amount of acid in H_2O layer = (5 – a) g

and volume of H_2O = 100 mL

$\therefore$ Conc. of acid in $H_2O = \left(\frac{5-a}{100}\right)\frac{g}{mL}$

$$\text{Now,} \quad K = \frac{\text{Conc. of acid in } C_6H_6}{\text{Conc. of acid in } H_2O}$$

$$= \frac{a}{50} \times \frac{100}{(5-a)}$$

$$\therefore \quad 4.1 = \frac{a}{50} \times \frac{100}{(5-a)}$$

or a = 3.361 g.

$\therefore$ Amount of acid in 50 mL

C_6H_6 = 3.361 g

$\therefore$ acid concentration in $C_6H_6 = \frac{3.361}{50} \times 1000 = 67.22$ g/L

Also, amount of acid in 100 mL $H_2O = 5 - a = 5 - 3.361 = 1.639$ g

$\therefore$ acid concentration in $H_2O = \frac{1.639}{100} \times 1000 = 16.39$ g/L

Ex.9 The freezing point depression of 0.001 m $K_x[Fe(CN)_6]$ is 7.10×10^{-3} K. Determine the value of x. Given, $K_f = 1.86$ K kg mol^{-1} for water.

Sol. $$\Delta x = i \times K_f \times m$$

$$7.10 \times 10^{-3} = i \times 1.86 \times 0.001$$

$$i = 3.817$$

$$\alpha = \frac{i-1}{n-1}$$

$$1 = \frac{3.817-1}{(x+1)-1}$$

$$x = 2.817 \approx 3$$

$\therefore$ Molecular formula of the compound is $K_3[Fe(CN)_6]$.

Ex.10 The composition of vapour over a binary ideal solution is determined by the composition of the liquid. If x_A and y_A are the mole fractions of A in the liquid and vapour, respectively find the value of x_A for which $(y_A - x_A)$ has maximum. What is the value of the pressure at this composition ?

Sol. Since

$$y_A = \frac{x_A P_A^\circ}{P_B^\circ + (P_A^\circ - P_B^\circ)x_A}$$

Substracting x_A from both the sides, we get

$$y_A - x_A = \frac{x_A P_A^\circ}{P_B^\circ + (P_A^\circ - P_B^\circ)x_A} - x_A$$

Differentiating this with respect to x_A, we get

$$\frac{d(y_A - x_A)}{dx_A} = \frac{P_A^\circ}{P_A^\circ + (P_A^\circ - P_B^\circ)x_A} - \frac{x_A P_A^\circ \left(P_A^\circ - P_B^\circ\right)}{\left\{P_B^\circ + (P_A^\circ - P_B^\circ)x_A\right\}^2} - 1$$

The value of x_A at which $y_A - x_A$ has a maximum value can be obtained by setting the above differential equal to zero. Thus, we have

$$\frac{P_A^\circ}{P_A^\circ + (P_A^\circ - P_B^\circ)x_A} - \frac{x_A P_A^\circ \left(P_A^\circ - P_B^\circ\right)}{\left\{P_B^\circ + (P_A^\circ - P_B^\circ)x_A\right\}^2} - 1 = 0$$

Solving for x_A, we get $x_A = \dfrac{\sqrt{P_A^\circ P_B^\circ} - P_B^\circ}{P_A^\circ - P_B^\circ}$

The value of P at this composition is

$$P = x_A P_A^\circ + x_B P_B^\circ$$

or $P = P_B^\circ + (P_A^\circ - P_B^\circ)\, x_A$

or $P = P_B^\circ + (P_A^\circ - P_B^\circ)\left(\dfrac{\sqrt{P_A^\circ P_B^\circ} - P_B^\circ}{P_A^\circ - P_B^\circ}\right)$

or $P = \sqrt{P_A^\circ P_B^\circ}$

Exercise # 1

[Single Correct Choice Type Questions]

1. We have 100 mL of 0.1 M KCl solution. To make it 0.2 M,

(A) evaporate 50 mL water
(B) evaporate 50 mL solution
(C) add 0.1 mol KCl
(D) add 0.01 mol KCl

2. Persons are medically considered to have lead poisoning if they have a concentration greater than 10 micrograms of lead per decilitre of blood. Concentration in parts per billion is :

(A) 1000
(B) 100
(C) 10
(D) 1

3. Which of the following concentration factors can be calculated if the mole fraction and density of an aqueous solution of HCl are known ?

(A) Molality
(B) Molarity
(C) Percent by mass
(D) Normality

4. Which statement best explains the meaning of the phrase "like dissolves like " ?

(A) A Solute will easily dissolve a solute of similar mass
(B) A solvent and solute with similar intermolecular forces will readily form a solution
(C) The only true solutions are formed when water dissolves a non-polar solute
(D) The only true solutions are formed when water dissolves a polar solute

5. An ionic compound that attracts atmospheric water so strongly that a hydrate is formed is said to be :

(A) Dilute
(B) Hygroscopic
(C) Immiscible
(D) Miscible

6. The vapour pressure of water depends upon :

(A) Surface area of container
(B) Volume of container
(C) Temperature
(D) All

7. A liquid is kept in a closed vessel. If a glass plate (negligible mass) with a small hole is kept on top of the liquid surface, then the vapour pressure of the liquid in the vessel is :

(A) More than what would be if the glass plate were removed
(B) Same as what would be if the glass plate were removed
(C) Less than what would be if the glass plate were removed
(D) Cannot be predicted

8. At higher altitudes, water boils at temperature < 100ºC because

(A) temperature of higher altitudes is low
(B) atmospheric pressure is low
(C) the proportion of heavy water increases
(D) atmospheric pressure becomes more.

9. Among the following substances, the lowest vapour pressure is exerted by :

(A) Water
(B) Mercury
(C) Kerosene
(D) Rectified spirit

10. When a liquid that is immiscible with water was steam distilled at 952ºC at a total pressure of 748 torr, the distillate contained 1.25 g of the liquid per gram of water. The vapour pressure of water is 648 torr at 95.2ºC, what is the molar mass of liquid?

(A) 7.975 g/mol
(B) 166 g/mol
(C) 145.8 g/mol
(D) None of these

11. Two liquids X and Y are perfectly immiscible. If X and Y have molecular masses in ratio 1 : 2, the total vapour pressure of a mixture of X and Y prepared in weight ratio 2 : 3 should be ($P_x^0 = 400$ torr, $P_y^0 = 200$ torr)

(A) 600 torr
(B) 400 torr
(C) 800 torr
(D) 1000 torr

12. An ideal solution contains two volatile liquids A ($p^o = 100$ torr) and B ($p^o = 200$ torr). If mixture contain 1 mole of A and 4 mole of B then total vapour pressure of the distillate is:

(A) 150
(B) 180
(C) 188.88
(D) 198.88

13.. The vapour pressure of two pure liquids A and B, that form an ideal solution are 100 and 900 torr respectively at temperature T. This liquid solution of A and B is composed of 1 mole of A and 1 mole of B. What will be the pressure, when 1 mole of mixture has been vaporized ?
(A) 800 torr
(B) 500 torr
(C) 300 torr
(D) None of these

14. For a binary ideal liquid solution, the total pressure of the solution is given as :
(A) $P_{total} = P^o_A + (P^o_A - P^o_B)\, X_B$
(B) $P_{total} = P^o_B + (P^o_A - P^o_B)\, X_A$
(C) $P_{total} = P^o_B + (P^o_B - P^o_A)\, X_A$
(D) $P_{total} = P^o_B + (P^o_B - P^o_A)\, X_B$

15. Given at 350 K $p_A{}^\circ = 300$ torr and $p_B{}^\circ = 800$ torr, the composition of the mixture having a normal boiling point of 350 K is
(A) $X_A = 0.08$
(B) $X_A = 0.06$
(C) $X_A = 0.04$
(D) $X_A = 0.02$

16. Two liquids A and B have P^o_A and P^o_B in the ratio of 1 : 3 and the ratio of number of moles of A and B in liquid phase are 1 : 3 then mole fraction of 'A' in vapour phase in equilibrium with the solution is equal to :
(A) 0.1
(B) 0.2
(C) 0.5
(D) 1.0

17. Which of the following will form non-ideal solution ?
(A) C_2H_5OH and water
(B) HNO_3 and water
(C) $CHCl_3$ and CH_3COCH_3
(D) C_6H_6 and $C_6H_5CH_3$

18. A maxima or minima obtained in the temperature composition curve of a mixture of two liquids indicates
(A) an azeotropic mixture
(B) an eutectic formation
(C) that the liquids are immiscible with one another
(D) that the liquids are partially miscible at the maximum or minimum

19. A solution of sulphuric acid in water exhibits :
(A) Negative deviations from Raoult's law
(B) Positive deviations from Raoult's law
(C) Ideal properties
(D) The applicability of Henry's law

20. For chloroform and acetone or for a solution of chloroform and acetone if p_s (observed (actual)) is compared with p_s (Theoretical (Raoult)) then which of the following is /are true ?
(A) $p_{s(actual)} < p_{s(raoult)}$
(B) $\overset{\text{Limit}}{X_{\text{chloroform}}} \longrightarrow 0\ (p^o_{acetone} - p_{s\ actual}) = 0$
(C) $\overset{\text{Limit}}{X_{\text{acetone}}} \longrightarrow 0\ (p^o_{chloroform} - p_{s(actual)}) = 0$
(D) $p^o_{acetone} > p^o_{chloroform}$ near room temperature

21. The vapour pressure of the solution of two liquids A(p^o = 80 mm) and B(p^o = 120 mm) is found to be 100 mm when $x_A = 0.4$. The result shows that
(A) solution exhibits ideal behaviour
(B) solution shows positive deviations
(C) solution shows negative deviations
(D) solution will show positive deviations for lower concentration and negative deviations for higher concentrations.

22. Consider a binary mixture of volatile liquids. If at $X_A = 0.4$ the vapour pressure of solution is 580 torr then the mixture could be ($p_A{}^\circ = 300$ torr, $p_B{}^\circ = 800$ torr) :
(A) $CHCl_3 - CH_3COCH_3$
(B) $C_6H_5Cl - C_6H_5Br$
(C) $C_6H_6 - C_6H_5CH_3$
(D) $nC_6H_{14} - n\,C_7H_{16}$

23. The solubility of N_2(g) in water exposed to the atmosphere, when the partial pressure is 593 mm is 5.3×10^{-4} M. Its solubility at 760 mm and at the same temperature is :
(A) 4.1×10^{-4} M
(B) 6.8×10^{-4} M
(C) 1500 M
(D) 2400 M

24. The solubility of gases in liquids :
(A) increases with increase in pressure and temperature
(B) decreases with increase in pressure and temperature
(C) Increases with increase in pressure and decrease in temperature
(D) decreases with increase in pressure and increase in temperature

25. Select correct statements :
(A) Gases which have high value of Van der Waals constant ‘a’ are easily liquefied
(B) Easily liquefiable gases are water soluble
(C) Ions forming gases in a solvent are soluble in that solvent
(D) Under same conditions, NH_3 has low solubility than that of CO_2.

26. Some of the following gases are soluble in water due to formation of their ions :
I : CO_2 ; II : NH_3 ; III : HCl ; IV : CH_4 ; V : H_2
Water insoluble gases can be :
(A) I, IV , V **(B)** I, V **(C)** I, II, III **(D)** IV, V

27. In which of the following pairs of solutions will the values of the vant Hoff factor be the same?
(A) 0.05 M $K_4[Fe(CN)_6]$ and 0.10 M $FeSO_4$
(B) 0.10 M $K_4[Fe(CN)_6]$ and 0.05 M $FeSO_4\,(NH_4)_2SO_4 . 6H_2O$
(C) 0.20 M NaCl and 0.10 M $BaCl_2$
(D) 0.05 M $FeSO_4\,(NH_4)_2SO_4 . 6H_2O$ and 0.02 M $KCl . MgCl_2 . 6H_2O$

28. One mole of a solute A is dissolved in a given volume of solvent. The association of the solute take place as follows:

$$nA \rightleftharpoons A_n$$

If α is the degree of association of A, the van’t Hoff factor i is expressed as:
(A) $i = 1 - \alpha$ **(B)** $i = 1 + \frac{\alpha}{n}$ **(C)** $i = \frac{1 - \alpha + \frac{\alpha}{n}}{1}$ **(D)** $i = 1$

29. If M_{normal} is the normal molecular mass and α is the degree of ionization of $K_3[Fe(CN)_6]$, then the abnormal molecular mass of the complex in the solution will be :
(A) $M_{normal}\,(1 + 2\alpha)^{-1}$ **(B)** $M_{normal}\,(1 + 3\alpha)^{-1}$ **(C)** $M_{normal}\,(1 + \alpha)^{-1}$ **(D)** equal to M_{normal}

30. The vapour pressure of a solution of a non-volatile solute B in a solvent A is 95% of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of the solute, what is the ratio of weight of solvent to solute.
(A) 0.15 **(B)** 5.7 **(C)** 0.2 **(D)** none of these

31. If P_0 and P are the vapour pressures of a solvent and its solution respectively and N_1 and N_2 are the mole fractions of the solvent and non-volatile solute respectively, then correct relation is :
(A) $P = P_0N_2$ **(B)** $P = P_0N_1$ **(C)** $P_0 = PN_1$ **(D)** $P = P_0(N_1/N_2)$

32. A complex of iron and cyanide ions is 100% ionised at 1m (molal). If its elevation in b.p. is 2.08. Then the complex is ($K_b = 0.52°\ mol^{-1}\ kg$) :
(A) $K_3[Fe(CN)_6]$ **(B)** $Fe(CN)_2$ **(C)** $K_4[Fe(CN)_6]$ **(D)** $Fe(CN)_4$

33. A solution of x moles of sucrose in 100 grams of water freezes at -0.2^0C. As ice separates the freezing point goes down to 0.25^0C. How many grams of ice would have separated?
(A) 18 grams **(B)** 20 grams **(C)** 25 grams **(D)** 23 grams

34. Sea water is found to contain 5.85 % NaCl and 9.50% $MgCl_2$ by weight of solution. Calculate its normal boiling point assuming 80% ionisation for NaCl and 50% ionisation of $MgCl_2$ ($K_b(H_2O) = 0.51\ kgmol^{-1}\ K$).
(A) $T_b = 101.9°C$ **(B)** $T_b = 104.9°C$ **(C)** $T_b = 108.5°C$ **(D)** $T_b = 110.3°C$

35. $PtCl_4 . 6H_2O$ can exist as a hydrated complex 1 molal aq. solution has depression in freezing point of 3.72°. Assume 100% ionisation and $K_f(H_2O) = 1.86°\ mol^{-1}$ kg, then complex is -

(A) $[Pt(H_2O)_6]Cl_4$
(B) $[Pt(H_2O)_4Cl_2]Cl_2 . 2H_2O$
(C) $[Pt(H_2O)_3Cl_3]Cl . 3H_2O$
(D) $[Pt(H_2O)_2Cl_4] . 4H_2O$

36. How many moles of sucrose should be dissolved in 500 gms of water so as to get a solution which has a difference of 104°C between boiling point and freezing point. ($K_f = 1.86$ K Kg mol^{-1}, $K_b = 0.52$ K Kg mol^{-1})

(A) 1.68 **(B)** 3.36 **(C)** 8.40 **(D)** 0.840

37. Which of the following has been arranged in order of decreasing freezing point?

(A) 0.05 M KNO_3 > 0.04 M $CaCl_2$ > 0.140 M sugar > 0.075 M $CuSO_4$
(B) 0.04 M $BaCl_2$ > 0.140 M sucrose > 0.075 M $CuSO_4$ > 0.05 M KNO_3
(C) 0.075 M $CuSO_4$ > 0.140 M sucrose > 0.04 M $BaCl_2$ > 0.05 M KNO_3
(D) 0.075 M $CuSO_4$ > 0.05 M $NaNO_3$ > 0.140 M sucrose > 0.04 M $BaCl_2$

38. Consider following cases :
I : 2M CH_3COOH solution in benzene at 27°C where there is dimer formation to the extent of 100%
II : 0.5 M KCl aq. solution at 27°C, which ionises 100%
Which is/are true statements(s) :

(A) both are isotonic **(B)** I is hypertonic **(C)** II is hypotonic **(D)** none is correct

39. Select correct statement :

(A) Osmosis, like all colligative properties, results from an increase in entropy as pure solvent passes through the membrane and mixes with the solution
(B) Desalination of sea-water is done by reverse osmosis
(C) Both are correct statements
(D) None is correct statement

40. Osmotic pressure of 30% solution of glucose is 1.20 atm and that of 3.42% solution of cane sugar is 2.5 atm. The osmotic pressure of the mixture containing equal volumes of the two solutions will be

(A) 2.5 atm **(B)** 3.7 atm **(C)** 1.85 atm **(D)** 1.3 atm.

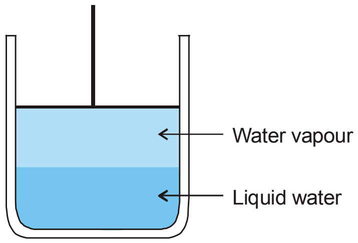
41. The dissolving process is exothermic when :

(A) The energy released in solvation exceeds the energy used in breaking up solute-solute and solvent-solvent interactions.
(B) The energy used in solvation exceeds the energy released in breaking up solute-solute and solvent-solvent interactions.
(C) The energy released in solvation is about the same as the energy used in breaking up solute-solute and solvent-solvent interactions.
(D) The energy used in solvation is about the same as the energy used in breaking up solute-solute and solvent-solvent interactions.

42. A sample of air is saturated with benzene (vapor pressure = 100 mm Hg at 298 K), 750mm Hg pressure. If it is isothermally compressed to one third of its initial volume, the final pressure of the system is

(A) 2250 torr **(B)** 2150 torr **(C)** 2050 torr **(D)** 1950 torr

43. The vapour pressure of water at 20°C is 17.54 mmHg. What will be the vapour pressure of the water in the apparatus shown after the piston is lowered, decreasing the volume of the gas above the liquid to one half of its initial volume (assume temperature is constant).



(A) 8.77 mmHg
(B) 17.54 mmHg
(C) 35.08 mmHg
(D) between 8.77 and 17.54 mmHg

44. All of the water in a 0.20 M solution of NaCl was evaporated and a 0.150 mol of NaCl was obtained. What was the original volume of the sample ?

(A) 30 mL **(B)** 333 mL **(C)** 750 mL **(D)** 1000 mL

45. A 20.0 mL sample of $CuSO_4$ solution was evaporated to dryness, leaving 0.967 g of residue. What was the molarity of the original solution ? (Cu = 63.5)

(A) 48.4 M **(B)** 0.0207 M **(C)** 0.0484 M **(D)** 0.303 M

46. When KCl dissolves in water (assume endothermic dissolution), then :

(A) $\Delta H = +$ ve, $\Delta S = +$ ve, $\Delta G = +$ ve **(B)** $\Delta H = +$ ve, $\Delta S = -$ ve, $\Delta G = -$ ve

(C) $\Delta H = +$ ve, $\Delta S = +$ ve, $\Delta G = -$ ve **(D)** $\Delta H = -$ ve, $\Delta S = -$ ve, $\Delta G = +$ ve

47. Water and chlorobenzene are immiscible liquids. Their mixture boils at 89ºC under a reduced pressure of 7.7×10^4 Pa. The vapour pressure of pure water at 89ºC is 7×10^4 Pa. Weight per cent of chlorobenzene in the distillate is:

(A) 50 **(B)** 60 **(C)** 78.3 **(D)** 38.46

48. If two liquids A (P^o_A =100 torr) and B (P^o_B = 200 torr) are completely immiscible with each other, each one will behave independently of the other, are present in a closed vessel. The total vapour pressure of the system will be:

(A) less than 100 torr **(B)** greater than 200 torr

(C) between 100 to 200 torr **(D)** 300 torr

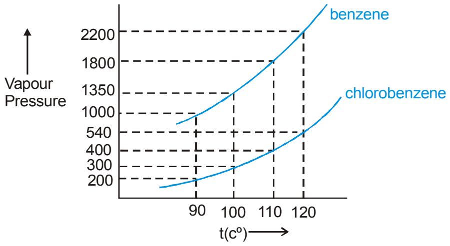
49. The vapor pressures of benzene, toluene and a xylene are 75 Torr, 22 Torr and 10 Torr respectively at 20ºC. Which of the following is **not** a possible value of the vapor pressure of an equimolar binary/ternary solution of these at 20ºC ? Assume all form ideal solution with each other.

(A) $48\frac{1}{2}$ **(B)** 16 **(C)** $35\frac{2}{3}$ **(D)** $53\frac{1}{2}$

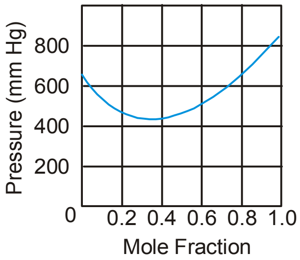
50. Assuming the formation of an ideal solution, determine the boiling point of a mixture containing 1560 g benzene (molar mass = 78) and 1125 g chlorobenzene (molar mass = 112.5) using the following against an external pressure of 1000 Torr.

(A) 90ºC **(B)** 100ºC

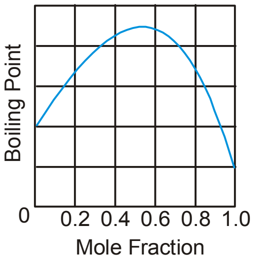
(C) 110º **(D)** 120ºC



51. Given P-x curve for a non-ideal liquid mixture (Fig.). Identify the correct T-x curve for the same mixture.



(A)



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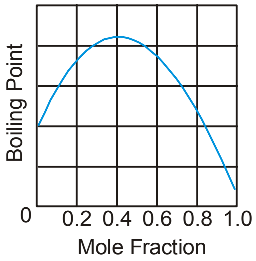

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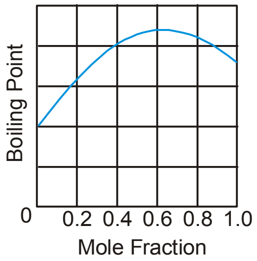

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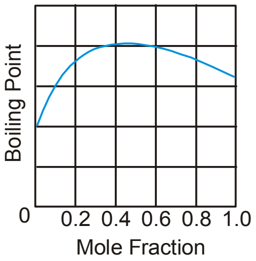


52. If vapour pressures of pure liquids 'A' & 'B' are 300 and 800 torr respectively at 25°C. When these two liquids are mixed at this temperature to form a solution in which mole percentage of 'B' is 92, then the total vapour pressure is observed to be 0.95 atm. Which of the following is true for this solution.

(A) $\Delta V_{mix} > 0$ **(B)** $\Delta H_{mix} < 0$ **(C)** $\Delta V_{mix} = 0$ **(D)** $\Delta H_{mix} = 0$

53. At 323 K, the vapour pressure in millimeters of mercury of a methanol-ethanol solution is represented by the equation $p = 120\,X_A + 140$, where X_A is the mole fraction of methanol. Then the value of $\lim_{x_A \to 1} \frac{p_A}{X_A}$ is :

(A) 250 mm **(B)** 140 mm **(C)** 260 mm **(D)** 20 mm

54. Consider two liquids A & B having pure vapour pressures P_A° & P_B° forming an ideal solution. The plot of $\frac{1}{X_A}$ v/s $\frac{1}{Y_A}$ (where X_A and Y_A are the mole fraction of liquid A in liquid and vapour phase respectively) is linear with slope and Y intercepts respectively :

(A) $\frac{P_A^{\circ}}{P_B^{\circ}}$ and $\frac{(P_A^{\circ} - P_B^{\circ})}{P_B^{\circ}}$

(B) $\frac{P_A^{\circ}}{P_B^{\circ}}$ and $\frac{(P_B^{\circ} - P_A^{\circ})}{P_B^{\circ}}$

(C) $\frac{P_B^{\circ}}{P_A^{\circ}}$ and $\frac{(P_A^{\circ} - P_B^{\circ})}{P_B^{\circ}}$

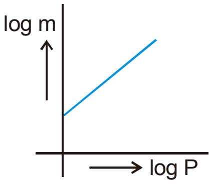
(D) $\frac{P_B^{\circ}}{P_A^{\circ}}$ and $\frac{(P_B^{\circ} - P_A^{\circ})}{P_B^{\circ}}$

55. Which of the following is less than zero for ideal solutions ?

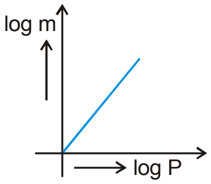
(A) ΔH_{mix} **(B)** ΔV_{mix} **(C)** ΔG_{mix} **(D)** ΔS_{mix}

56. Which of the following curves represents the Henry's law ?

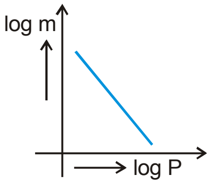
(A)



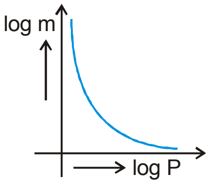
(B)



(C)



(D)



57. According to Henry's law, the solubility of a gas in a given volume of liquid increases with increase in :

(A) Temperature **(B)** Pressure **(C)** Both **(A)** and **(B)** **(D)** None of these

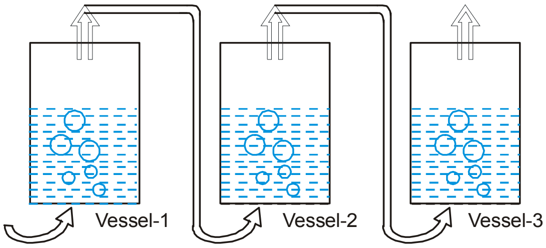
58. The degree of dissociation of an electrolyte is α and its van't Hoff factor is i. The number of ions obtained by complete dissociation of 1 molecule of the electrolyte is:

(A) $\frac{i + \alpha - 1}{\alpha}$ **(B)** $i - \alpha - 1$ **(C)** $\frac{i - 1}{\alpha}$ **(D)** $\frac{i + 1 + \alpha}{1 - \alpha}$

59. Dry air is slowly passed through three solutions of different concentrations, c_1, c_2 and c_3 ; each containing (non volatile) NaCl as solute and water as solvent, as shown in the Fig. If the vessel 2 gains weight and the vessel 3 loses weight, then :

(A) $c_1 > c_2$ **(B)** $c_1 < c_2$

(C) $c_1 < c_3$ **(D)** $c_2 > c_3$



60. Pressure cooker reduces cooking time because
(A) the heat is more evenly distributed inside the cooker
(B) a large flame is used
(C) boiling point of water is elevated
(D) whole matter is converted into steam

61. A solute'S' undergoes a reversible trimerization when dissolved in a certain solvent. The boiling point elevation of its 0.1 molal solution was found to be identical to the boiling point elevation in case of a 0.08 molal solution of a solute which neither undergoes association nor dissociation. To what percent had the solute 'S' undergone trimerization?
(A) 30% **(B)** 40% **(C)** 50% **(D)** 60%

62. Barium ions, CN^- and Co^{2+} form an ionic complex. If that complex is supposed to be 75% ionised in water with vant Hoff factor ' i ' equal to four, then the coordination number of Co^{2+} in the complex can be :
(A) Six **(B)** Five **(C)** Four **(D)** Six and Four both

63. Relative decrease in vapour pressure of an aqueous solution containing 2 moles $[Cu(NH_3)_3Cl]Cl$ in 3 moles H_2O is 0.50. On reaction with $AgNO_3$, this solution will form(assuming no change in degree of ionisation of substance on adding $AgNO_3$)
(A) 1 mol AgCl **(B)** 0.25 mol AgCl **(C)** 0.5 mol AgCl **(D)** 0.40 mol AgCl

64. In the following aqueous solutions
(A) 1 m sucrose
(B) 1 m potassium ferricyanide
(C) 1 m potassium sulphate
maximum value of vapour pressure of solution is that of :
(A) A **(B)** B **(C)** C **(D)** equal

65. When only a little quantity of $HgCl_2(s)$ is added to excess KI(aq) to obtain a clear solution, which of the following is true for this solution? (no volume change on mixing)
(A) Its boiling and freezing points remain same **(B)** Its boiling point is lowered
(C) Its vapour pressure become lower **(D)** Its boiling point is raised
(E) Its freezing point is lowered.

66. The freezing point of aqueous solution that contains 3% urea, 7.45% KCl and 9% of glucose is (given K_f of water = 1.86 and assume molarity = molality).
(A) 290 K **(B)** 285.5 K **(C)** 267.42 K **(D)** 250 K

67. x mole of KCl and y mole of $BaCl_2$ are both dissolved in 1 kg of water. Given that $x + y = 0.1$ and K_f for water is 1.85 K/molal, what is the observed range of ΔT_f, if the ratio of x to y is varied ?
(A) 0.37^0 to 0.505^o **(B)** 0.185^0 to 0.93^0 **(C)** 0.56^0 to 0.93^0 **(D)** 0.37^0 to 0.93^0

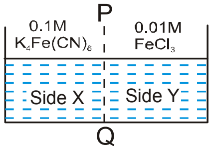
68. Two beakers, one containing 20 ml of a 0.05 M aqueous solution of a non volatile, non electrolyte and the other, the same volume of 0.03 M aqueous solution of NaCl, are placed side by side in a closed enclose. What are the volumes in the two beakers when equation is attached ? Volume of the solution in the first and second beaker are respectively.
(A) 21.8 mL and 18.2 mL **(B)** 18.2 mL and 21.8 mL
(C) 20 mL and 20 mL **(D)** 17.1 mL and 22.9 mL

69. Osmotic pressure of blood is 7.40 atm at 27°C. Number of moles of glucose to be used per litre for an intravenous injection that is to have the same osmotic pressure as blood is :
(A) 0.3 **(B)** 0.2 **(C)** 0.1 **(D)** 0.4

70. For a solution of 0.849 g of mercurous chloride in 50 g of $HgCl_2(\ell)$ the freezing point depression is 1.24ºC. K_f for $HgCl_2$ is 34.3. What is the state of mercurous chloride in $HgCl_2$? (Hg – 200, Cl – 35.5)
(A) as Hg_2Cl_2 molecules **(B)** as HgCl molecules
(C) as Hg^+ and Cl^- ions **(D)** as Hg_2^{2+} and Cl^- ions

71. At a constant temperature, ΔS will be maximum for which of the following processes :
(A) Vaporisation of a pure solvent
(B) Vaporisation of solvent from a solution containing nonvolatile and nonelectrolytic solute in it
(C) Vaporisation of solvent from a solution containing nonvolatile but electrolytic solute in it
(D) Entropy change will be same in all the above cases

72. $FeCl_3$ on reaction with $K_4[Fe(CN)_6]$ in aq. solution gives blue colour. These are separated by a semipermeable membrane PQ as shown. Due to osmosis there is-
(A) blue colour formation in side X
(B) blue colour formation in side Y
(C) blue colour formation in both of the sides X and Y
(D) no blue colour formation



73. The solubility of gases in liquids :
(A) increases with increase in pressure and temperature
(B) decreases with increase in pressure and temperature
(C) Increases with increase in pressure and decrease in temperature
(D) decreases with increase in pressure and increase in temperature

74. Colligative properties have many practical uses, some of them may be :
I : Melting of snow by salt
II : Desalination of sea water
III : Determination of molar mass
IV : Determination of melting point and boiling point of solvent
Actual practical uses are :
(A) I, II **(B)** III, IV **(C)** I, II, III **(D)** II, III, IV

75. Select correct statement(s) :
(A) When solid $CaCl_2$ is added to liquid water, the boiling temperature rises
(B) When solid $CaCl_2$ is added to ice at 0°C, the freezing temperature falls
(C) Both **(A)** and **(B)**
(D) None of the above

76. The concentration of pollutant in ppm (w/w), that has been measured at 450 mg per 150 kg of sample is :
(A) 3 ppm **(B)** 6 ppm **(C)** 3000 ppm **(D)** 330 ppm

77. Available are 1L of 0.1 M NaCl and 2L of 0.2 M $CaCl_2$ solutions. Using **only these two solutions** what maximum volume of a solution can be prepared having $[Cl^-] = 0.34$ M exactly. Both electrolytes are strong
(A) 2.5 L **(B)** 2.4 L C) 2.3 L **(D)** None of these

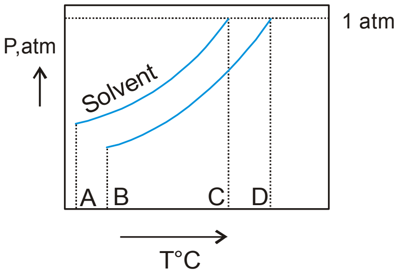
78. Mole fraction of $C_3H_5(OH)_3$ in a solution of 36 g of water and 46 g of glycerine is :
(A) 0.46 **(B)** 0.36 **(C)** 0.20 **(D)** 0.40

79. A complex containing K^+, Pt(IV) and Cl^- is 100% ionised giving i = 3. Thus, complex is :
(A) $K_2[PtCl_4]$ **(B)** $K_2[PtCl_6]$ **(C)** $K_3[PtCl_5]$ **(D)** $K[PtCl_3]$

80. In which case, van't Hoff factor i remains unchanged ? [Assume common complexes of these ions]
(A) $PtCl_4$ reacts with KCl
(B) aq. $ZnCl_2$ reacts with aq. NH_3
(C) aq. $FeCl_3$ reacts with aq. $K_4[Fe(CN)]_6$
(D) $KMnO_4$ reduced to MnO_2 in alkaline medium (MnO_2 a black ppt)

81. If $pK_a = -\log K_a = 4$, and $K_a = Cx^2$ then Van't Hoff factor for weak monobasic acid when C = 0.01 M is :
(A) 1.01 **(B)** 1.02 **(C)** 1.10 **(D)** 1.20

82. What is the normal boiling point of the solution represented by the phase diagram ?



(A) A **(B)** B **(C)** C **(D)** D

83. Select correct statement ?

(A) Heats of vaporisation for a pure solvent and for a solution are similar because similar intermolecular forces between solvent molecules must be overcome in both cases

(B) Entropy change between solution and vapour is smaller than the entropy change between pure solvent and vapour

(C) Boiling point of the solution is larger than that of the pure solvent

(D) All are correct statements

84. Ratio of $\Delta T_b / K_b$ of 6% AB_2 and 9% A_2B (AB_2 and A_2B both are non-electrolytes) is 1 mol/kg in both cases. Hence, atomic masses of A and B are respectively :

(A) 60, 90 **(B)** 40, 40 **(C)** 40, 10 **(D)** 10, 40

85. Consider following terms (m = molality) :

I : mK_b ; **II :** $mK_b i$ **III :** $\frac{\Delta T_b}{i}$ **IV :** K_b

Terms which can be expressed in degree (temperature) are

(A) III, IV **(B)** I, II **(C)** I, II, IIII **(D)** I, III

86. Elevation in b.p. of an aqueous urea solution is 0.52°. (K_b = 0.52° mol^{-1} kg) Hence, mole-fraction of urea in this solution is :

(A) 0.982 **(B)** 0.567 **(C)** 0.943 **(D)** 0.018

87. Insulin $(C_2H_{10}O_5)_n$ is dissolved in a suitable solvent and the osmotic pressure π of the solution of various concentration (in kg/m^3) is measured at 20ºC. The slope of a plot of π against c is found to be 8.134×10^{-3} (SI units) The molecular weight of the insulin (in kg/mol) is :

(A) 4.8×10^5 **(B)** 9×10^5 **(C)** 293×10^3 **(D)** 8.314×10^5

88. An aqueous solution of a solute AB has b.p. of 101.08°C (AB is 100% ionised at boiling point of the solution) and freezes at – 1.80°C. Hence, AB (K_b / K_f = 0.3)

(A) is 100% ionised at the f.p. of the solution **(B)** behaves as non-electrolyte at the f.p. of the solution

(C) forms dimer **(D)** none of the above

89. Density of 1M solution of a non-electrolyte $C_6H_{12}O_6$ is 1.18 g/mL. If K_f (H_2O) is 1.86° mol^{-1} kg, solution freezes at :

(A) – 1.58°C **(B)** – 1.86°C **(C)** – 3.16°C **(D)** 1.86°C

90. Mole fraction of a non-electrolyte in aqueous solution is 0.07. If K_f is 1.86° mol^{-1} kg, depression in f.p., ΔT_f, is:

(A) 0.26° **(B)** 1.86° **(C)** 0.13° **(D)** 7.78°

91. Total vapour pressure of mixture of 1 mol of volatile component A ($p_A°$ = 100 mmHg) and 3 mol of volatile component B ($p_B°$ = 60 mmHg) is 75 mm. For such case :

(A) there is positive deviation from Raoult's low

(B) boiling point has been lowered

(C) force of attraction between A and B is smaller than that between A and A or between B and B

(D) all the above statements are correct

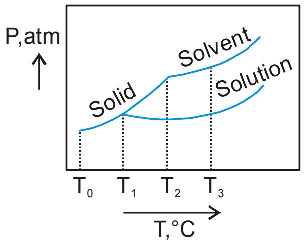
92. Water and chlorobenzene are immiscible liquids. Their mixture boils at 90°C under a reduced pressure of 7.82×10^4 Pa. The vapour pressure of pure water at 90°C is 7.03×10^4 Pa. On weight percent basis, chlorobenzene in the distillate is equal to (mol. wt. of chlorobenzene is 112.5 g mol^{-1})

(A) 50 **(B)** 60 **(C)** 70 **(D)** 80

93. Relative decrease in vapour pressure of an aqueous NaCl is 0.167. Number of moles of NaCl present in 180g of H_2O is

(A) 2 mol **(B)** 1 mol **(C)** 3 mol **(D)** 4 mol

94. What is the normal freezing point of the solution represented by the phase diagram ?



(A) T_1 **(B)** T_2 **(C)** T_3 **(D)** T_0

95. Select correct statement :

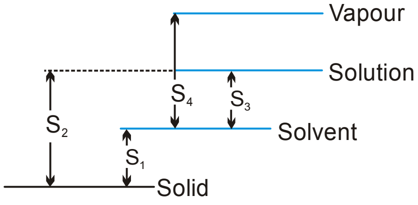
(A) Solution has more molecular randomness than a pure solvent has, the entropy change between solution and solid is larger than the entropy change between pure solvent and solid

(B) Heats of fusion of solution and solvent are similar since similar forces of intermolecular forces are involved

(C) Sugar containing solution freezes at a lower temperature than pure water

(D) All are correct statements

96. Some entropy change are represented in figure. Select correct entropy change.



(A) $\Delta S_1, \Delta S_2, \Delta S_3$ **(B)** $\Delta S_1, \Delta S_2, \Delta S_4$ **(C)** $\Delta S_1, \Delta S_2, \Delta S_3, \Delta S_4$ **(D)** ΔS_2 and ΔS_4

97. Which statement comparing solutions with pure solvent is not correct

(A) A solution containing a non-volatile solute has a lower vapour pressure than pure solvent

(B) A solution containing a non-volatile solute has a lower boiling point than pure solvent

(C) A solution containing a non-volatile solute has a lower freezing point than pure solvent

(D) A solution will have a greater mass than an equal volume of pure solvent if the solute has a molar mass greater than the solvent

98. A colligative property of a solution depends on the :

(A) arrangement of atoms in solute molecule **(B)** total number of molecules of solute and solvent

(C) number of molecules of solute in solution **(D)** mass of the solute molecules

99. Which has maximum freezing point ?

(A) 6g urea solution in 100 g H_2O **(B)** 6g acetic acid solution in 100g H_2O

(C) 6g sodium chloride in 100 g H_2O **(D)** All have equal freezing point

100. Mole fraction of the toluene in the vapour phase which is in equilibrium with a solution of benzene (p° = 120 Torr) and toluene (p° = 80 Torr) having 2.0 mol of each is :

(A) 0.50 **(B)** 0.25 **(C)** 0.60 **(D)** 0.40

101. The vapour pressure of pure benzene, C_6H_6 at 50°C is 268 Torr. How many moles of non-volatile solute per mol of benzene is required to prepare a solution of benzene having a vapour pressure of 167 Torr at 50°C ?

(A) 0.377 **(B)** 0.605 **(C)** 0.623 **(D)** 0.395

102. An azeotropic solution of two liquids has a boiling point lower than either of them when it :

(A) shows negative deviation from Raoult's law
(B) shows positive deviation from Raoult's low
(C) shows ideal behaviour
(D) is saturated

103. Van't Hoff factors of aqueous solutions of X, Y, Z are 1.8, 0.8 and 2.5. Hence, their (assume equal concentrations in all three cases)

(A) b.p. : $X < Y < Z$ **(B)** f. p. $Z < X < Y$
(C) osmotic pressure : $X = Y = Z$ **(D)** v. p. : $Y < X < Z$

104. Select correct statements :

(A) The fundamental cause of all colligative properties is the higher entropy of the solution relative to that of the pure solvent
(B) The freezing point of hydrofluoride solution is larger than that of equimolal hydrogen chloride solution
(C) 1M glucose solution and 0.5 M NaCl solution are isotonic at a given temperature
(D) All are correct statements

105. The vapour pressure of a pure liquid A is 40 mmHg at 310 K. The vapour pressure of this liquid in a solution with liquid B is 32 mmHg. Mole fraction of A in the solution, if it obeys Raoult's law is :

(A) 0.8 **(B)** 0.5 **(C)** 0.2 **(D)** 0.4

106. Depression of freezing point of 0.01 molal aq. CH_3COOH solution is 0.02046°. 1 molal urea solution freezes at – 1.86°C. Assuming molality equal to molarity, pH of CH_3COOH solution is :

(A) 2 **(B)** 3 **(C)** 3.2 **(D)** 4.2

107. If relative decrease in vapour pressure is 0.4 for a solution containing 1 mol NaCl in 3 mol H_2O, NaCl is .... % ionised.

(A) 60% **(B)** 50% **(C)** 100% **(D)** 40%

108. Which of the following azeotropic solutions has the b.p. less than b.p. of the constituents A and B ?

(A) $CHCl_3$ and CH_3COCH_3 **(B)** CS_2 and CH_3COCH_3
(C) CH_3CH_2OH and CH_3COCH_3 **(D)** CH_3CHO and CS_2

109. Vapour pressure of CCl_4 at 25°C is 143 mmHg. 0.5 g of a non-volatile solute (molar mass = 65 mol^{-1}) is dissolved in 100 mL of CCl_4 (density = 1.538 g mL^{-1}). Vapour pressure of solution is

(A) 141.9 mmHg **(B)** 94.4 mmHg **(C)** 99.3 mmHg **(D)** 144.1 mmhg

110. A 0.50 molal solution of ethylene glycol in water is used as coolant in a car. If the freezing point constant of water is 1.86° per molal, at which temperature will the mixture freeze ?

(A) 1.56°C **(B)** – 0.93°C **(C)** – 1.86°C **(D)** 0.93°C

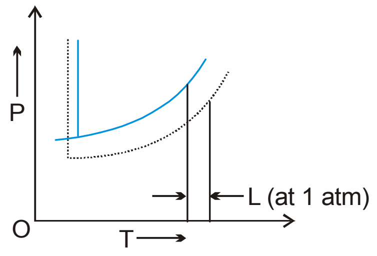
111. The depression of freezing points of 0.05 molal aqueous solution of the following compounds are measured.

1. NaCl **2.** K_2SO_4 **3.** $C_6H_{12}O_6$ **4.** $Al_2(SO_4)_3$

Which one of the above compounds will exhibit the maximum depression of freezing point ?

(A) 3 **(B)** 2 **(C)** 4 **(D)** 1

112. The phase diagrams for the pure solvent (solid lines) and the solution (non-volatile solute, dashed line) are recorded below :



The quantity indicated by L in the figure is :

(A) Δp **(B)** ΔT_f **(C)** $K_b m$ **(D)** $K_f m$

113. The total concentration of dissolved particles inside red blood cells is approximately 0.30 M and the membrane surrounding the cells is semipermeable. What would be the osmotic pressure (in atmosphere) inside the cells become if the cells were removed from the blood plasma and placed in pure water at 298 K ?

(A) 7.34 atm **(B)** 1.78 atm **(C)** 2.34 atm **(D)** 0.74 atm

114. The fundamental cause of ΔT (depression is) :

(A) higher entropy of the solution relative to that of pure solvent
(B) lower entropy of the solution relative to that of pure solvent
(C) higher enthalpy of the solution relative to that of pure solvent
(D) lower enthalpy of the solution relative to that of pure solvent

115. Assuming each salt to be 90% dissociated which of the following will have highest osmotic pressure ?

(A) Decimolar $Al_2(SO_4)_3$
(B) Decimolar $BaCl_2$
(C) Decimolar Na_2SO_4
(D) A solution obtained by mixing equal volumes of (B) and (C) and filtering.

116. The boiling point of an azeotropic mixture of water and ethyl alcohol is less than that of theoretical value of water and alcohol mixture. Hence , the mixture shows :

(A) That solution is highly saturated **(B)** Positive deviation from Raoult's law
(C) Negative deviation from Raoult's law **(D)** Nothing can be said

117. On mixing 10 mL of acetone with 40 mL of chloroform , the total volume of the solution is :

(A) < 50 mL **(B)** > 50 mL **(C)** $= 50$ mL **(D)** Cannot be predicted

118. For an ideal binary solution with P_A^0 / P_B^0 which relation between X_A (mole fraction of A in liquid phase) and Y_A (mole fraction of A in vapour phase) is correct , X_B and Y_B are mole fraction of B in liquid and vapour phase respectively:
(Given : $P_A^0 > P_B^0$)

(A) $X_A = Y_A$ **(B)** $X_A > Y_A$

(C) $\frac{X_A}{X_B} < \frac{Y_A}{Y_B}$ **(D)** X_A, Y_A, X_B and Y_B cannot be correlated

119. What will be the molecular weight of NaCl determined experimentally from elevation in the boiling point or depression in freezing point method ?

(A) < 58.5 **(B)** > 58.5 **(C)** $= 58.5$ **(D)** None of these

120. Which characterises the weak intermolecular forces of attraction in a liquid ?

(A) High boiling point **(B)** High vapour pressure
(C) High critical temperature **(D)** High heat of vaporization

121. A teacher one day pointed out to his students the preculia fact that water is unique liquid which freezes exactly at 0^0 C and boils exactly at 100^0 C. He asked the students to find the correct statement based on this fact :
(A) Water dissolves anything however sparingly the dissolution may be
(B) Water is a polar molecule
(C) Boiling and freezing temperatures of water were used to define a temperature scale
(D) Liquid water is denser than ice

122. When an ideal binary solution is in equilibrium with its vapour , molar ratio of the two components in the solution and in the vapour phase is :
(A) Same
(B) Different
(C) May or may not be same depending upon volatile nature of the two components
(D) None of the above

123. The melting points of most of the solid substances increases with an increase of pressure acting on them. However, ice melts at a temperature lower than its usual melting point , when the pressure increases. This is because :
(A) Ice is less denser than water **(B)** Pressure generates heat
(C) The bonds break under pressure **(D)** Ice is not a true solid

124. Which of the following liquid pairs shows a positive deviation from Raoult's law ?
(A) Acetone – chloroform **(B)** Benzene – methanol
(C) Water – nitric acid **(D)** Water – hydrochloric acid

125. The relationship between osmotic pressure at 273 K when 10 g glucose (P_1) ,10 g urea (P_2) and 10 g sucrose (P_3) are dissolved in 250 mL of water is :
(A) $P_1 > P_2 > P_3$ **(B)** $P_3 > P_1 > P_2$ **(C)** $P_2 > P_1 > P_3$ **(D)** $P_2 > P_3 > P_1$

126. The amount of ice that will separate out on cooling a solution containing 50 g of ethylene glycol in 200 g water to – 9.3^0C is : ($K_f' = 1.86$ K molality^{-1})
(A) 38.71 g **(B)** 38.71 mg **(C)** 42 g **(D)** 42 mg

127. A liquid is in equilibrium with its vapours at its boiling point. On the average the molecules in the two phases have equal :
(A) Potential energy **(B)** Total energy **(C)** Kinetic energy **(D)** Intermolecular forces

128. On the basis of intermolecular forces predict the correct order of decreasing boiling points of the compounds:
(A) $CH_3OH > H_2 > CH_4$ **(B)** $CH_3OH > CH_4 > H_2$
(C) $CH_4 > CH_3OH > H_2$ **(D)** $H_2 > CH_4 > CH_3OH$

129. During depression of freezing point in a solution the following are in equilibrium :
(A) Liquid solvent, solid solvent
(B) Liquid solvent, solid solute
(C) Liquid solute, solid solute
(D) Liquid solute, solid solvent

Exercise # 2 Part # I [Multiple Correct Choice Type Questions]

1. For the given electrolyte A_xB_y, the degree of dissociation 'α' can be given as

(A) $\alpha = \frac{i-1}{x+y-1}$ **(B)** $i = (1-\alpha) + x\alpha + y\alpha$ **(C)** $\alpha = \frac{1-i}{1-x-y}$ **(D)** None

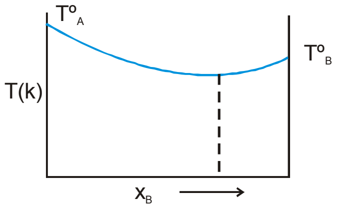
2. A graph plotted between $\frac{P}{d}$ vs d (where P is osmotic pressure of solution of a solute of mol. wt. m and d is its density at temperature T. Pick out the correct statements about the plots :

(A) $\left[\frac{P}{d}\right]_{d\to 0} = \frac{ST}{m}$ **(B)** The intercept of the plot $\frac{ST}{m}$

(C) The intercept of the plot $= \left[\frac{P}{d}\right]_{d\to 0}$ **(D)** $\left[\frac{P}{d}\right]_{d\to 0}$ is independent of temperature

3. Which of the following is/are correct for an ideal binary solution of two volatile liquids (eg. benzene & toluene)?
(A) Its vapour is always richer in the more volatile component (compared to the liquid).
(B) The liquid will gradually become richer in the less volatile component if such a mixture is boiled (distilled).
(C) The P_T (ie. the total pressure) above the solution will be the sum of the vapor pressures of the two pure components.
(D) The boiling point of the solution will be less than the boiling points of the two components.

4. The diagram given below represents boiling point composition diagram of solution of component A and B, which is/are incorrect among the following?



(A) The solution shows negative deviation
(B) A-B-interactions are stronger than A-A and B-B
(C) The solution is ideal solution
(D) The solution shows positive deviation.

5. According to Henry's law , the partial pressure of gas (P'_g) is directly proportional to mole fraction of gas in dissolved state , i.e., $P_{gas}' = K_H . X_{gas}$ where K_H is Henry's constant. Which are correct ?
(A) K_H is characteristic constant for a given gas–solvent system
(B) Higher is the value of K_H , lower is solubility of gas for a given partial pressure of gas
(C) K_H has temperature dependence
(D) K_H increases with temperature

6. Which of the following concentration factors can be calculated if the mole fraction and density of an aqueous solution of HCl are known ?

(A) Molality **(B)** Molarity **(C)** Percent by mass **(D)** Normality

7. Consider following solutions :
I : 1 M aqueous glucose solution
II : 1M aqueous sodium chloride solution
III : 1M aqueous ammonium phosphate solution
IV : 1M benzoic acid in benzene
Select correct statements for the above solutions :
(A) All are isotonic solutions
(B) III is hypertonic of I, II and IV
(C) IV is hypotonic of I, II and III
(D) II is hypotonic of III but hypertonic of I and IV

8. Which combination of (I) vapour pressure, (II) intermolecular forces and (III) ΔH_{vap} (latent heat of vaporisation) is matched correctly

	I	II	III
(A)	high	weak	small
(B)	high	strong	large
(C)	low	weak	large
(D)	low	strong	small

9. Which is/are true about ideal solutions ?

(A) The volume of mixing is zero
(B) The enthalpy of mixing is zero
(C) The entropy of mixing is zero
(D) The enthalpy of mixing is negative

10. Freezing point lowering expression is

$\Delta T_f = K_f m$ (molality)

Which of the following assumptions are considered for the validity of above equation ?

(A) The solution is dilute
(B) The ΔH_f (latent heat of fusion of solvent) is independent of temperature between the actual and normal freezing point
(C) The solid-phase consists of pure solvent when solution is allowed to cool
(D) ΔT_f is not equal to $3K_f$ for 3 mol L^{-1} solution

11. At 35°C, the vapour pressure of CS_2 is 512 mmHg, and of acetone is 344 mmHg. A solution of CS_2 and acetone in, which the mole fraction of CS_2 is 0.25, has a total vapour pressure of 600mmHg. Which of the following statements is/are correct ?

(A) A mixture of 100 mL of acetone and 100 mL of CS_2 has a volume of 200 mL
(B) When acetone and CS_2 are mixed at 35°C, heat must be absorbed in order to produce a solution at 35°C
(C) Process of mixing is exothermic
(D) Entropy of mixing is zero

12. Which is/are correct statement(s) ?

(A) When mixture is more volatile, there is positive deviation from Raoult's law
(B) When mixture is less volatile, there is negative deviation from Raoult's law
(C) Ethanol and water form ideal solution
(D) $CHCl_3$ and water form ideal solution

13. At 40°C, vapour pressure in Torr of methanol and ethanol solution is $P = 119x + 135$ where x is the mole fraction of methanol. Hence

(A) vapour pressure of pure methanol is 119 Torr
(B) vapour pressure of pure ethanol is 135 Torr
(C) vapour pressure of equimolar mixture of each is 127 Torr
(D) mixture is completely immiscible

14. Which one of the statements given below concerning properties of solutions, describes a colligative effect ?

(A) Boiling point of pure water decreases by the addition of ethanol
(B) Vapour pressure of pure water decreases by the addition of nitric acid
(C) Vapour pressure of pure benzene decreases by the addition of naphthalene
(D) Boiling point of pure benzene increases by the addition of toluene

15. For a dilute solution having molality m of a given solute in a solvent of mol.wt. M , b.pt. T_b and heat of vaporisation per mole ΔH ; $\left[\frac{\partial T_b}{\partial m}\right]_{m\to 0}$ is equal to :

(A) Molal elevation constant of solvent

(B) $\frac{RT_b^2 M}{\Delta H_{vap}}$; where M in kg ΔH_{vap} and R in J mol^{-1}

(C) $\frac{RT_b^2 M}{\Delta S_{vap}}$; where M in kg ; ΔS_{vap} and R in J mol^{-1}

(D) $\frac{RT_b^2 M}{1000\Delta H_{vap}}$; where M in g ; R and ΔH_{vap} expressed in same unit of heat.

16. Which facts are true when we use van't Hoff equation PV = CST for osmotic pressure P of dilute solutions ?

(A) The equation is identical to that of ideal gas equation

(B) The solute particles in solution are analogous to the gas molecules and the solvent is analogous to the empty space between the gas molecules

(C) Solute molecules are dispersed in the solvent the way the gas molecules are dispersed in empty space

(D) The equation is not identical to that of ideal gas equation

17. Which statements are correct about antifreeze mixtures to use to melt ice or snow on roads ?

(A) Antifreeze mixture of $CaCl_2$ + water (f.pt. – 50^0 C) is preferred over KCl + water (f.pt. – 10^0 C)

(B) The low freezing point of aq. $CaCI_2$ solution is due to its vant Hoff factor i = 3.

(C) The use of antifreeze for salt solutions causes major problems of corrosion of steel car bodies and reinforcement bars in concrete road structures.

(D) More is the amount of salt spreaded on road, easier is melting of ice.

18. The vapour pressure of a dilute solution of a solute is influenced by :

(A) Temperature of solution

(B) Mole fraction of solute

(C) M.pt. of solute

(D) Degree of dissociation of solute

19. In the depression of freezing point experiment , it is found that the :

(A) Vapour pressure of the solution is less than that of pure solvent

(B) Vapour pressure of the solution is more than that of pure solvent

(C) Only solute molecules solidify at the freezing point

(D) Only solvent molecules solidify at the freezing point

20. Which of the following statements are correct for van't Hoff factor 'i' for a solution of weak electrolyte A_xB_y ?

(A) i = 1 – a + Xa + Ya

(B) i > 1 at normal dilution

(C) i increases more rapidly with dilution and attains a limiting value of (x + y) at infinite dilution

(D) The increase in 'i' with dilution is due to increase in molality of solution with dilution

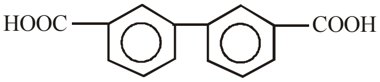
Part # II [Assertion & Reason Type Questions]

Directions : Each question has 5 choices (A), (B), (C), (D) and (E) out of which only one is correct.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.
(E) Both Statements are False.

1. **Statement -1 :** The molar mass obtained for benzoic acid in benzene is found to be nearly 244.

Statement -2 : Benzoic acid has the formula



2. **Statement-1 :** The difference in the boiling points of equimolar solution of HCl and HF decreases as their molarity is decreased.

Statement-2 : The extent of dissociation decreases steadily with increasing dilution.

3. **Statement-1 :** When 'a' mL of a 0.1 molal urea solution is mixed with another 'b' mL of 0.1 molal glucose solution, the boiling point of the solution is no different from the boiling points of the samples prior to mixing but if 'a' mL of 0.1 molal urea is mixed with 'b' mL of 0.1 molal HF the boiling point of the mixture is different from the boiling points of the separate samples .

Statement-2 : HF is an electrolyte (weak) whereas glucose is a non electrolyte.

4. **Statement-I :** 0.02 m solutions of urea and sucrose will freeze at same temperature.

Statement-II : Freezing point of a solution is inversely proportional to the conc. of solution.

5. **Statement-I :** When mercuric iodide is added to the aqueous solution of KI, the freezing point is raised.

Statement-II : HgI_2 reacts with KI forming complex ion $[HgI_4]^{2-}$.

6. **Statement-I :** 1 M solution of Glauber's salt is isotonic with 1 M solution of KNO_3.

Statement-II : Solutions having same molar concentration of solute may or may not have same osmotic pressure.

7. **Statement-I :** 0.1 M solution of NaCl has greater osmotic pressure than 0.1 M solution of glucose at same temperature.

Statement-II : In solution, NaCl dissociates to produce more number of particles.

8. **Statement-I :** Relative lowering of vapour pressure is equal to mole fraction of the solvent.

Statement-II : Relative lowering of vapour pressure is a colligative property.

9. **Statement-I :** Molal elevation constant depends on the nature of solvent.

Statement-II : Molal elevation constant is the elevation in boiling point when 1 mole of the solute is dissolved in 1 kg of solvent.

10. **Statement-I :** If decimolal solution of sodium chloride boils at 101.2°C, then decimolal solution of calcium chloride will also boil at the same temperature.

Statement-II : For same molal concentration of aqueous solutions of electrolytes, the elevation of boiling point may not be same.

Exercise # 3

Part # I [Matrix Match Type Questions]

1. Assuming all the solutes are non volatile and all solutions are ideal and neglect the hydrolysis of cation and anion.

Column – I	Column – II
(A) 10 ml 0.1 M NaOH aqueous solution is added to 10 ml 0.1 M HCl aqueous solution	**(p)** Osmotic pressure of solution increases
(B) 10 ml 0.1 M NaOH aqueous solution is added to 10 ml 0.1 M CH_3COOH aqueous solution	**(q)** Vapour pressure of solution increases
(C) 10 ml 0.1 M HCl aqueous solution is added to 10 ml 0.1 M NH_3 aqueous solution	**(r)** Boiling point of solution increases
(D) 10 ml 0.1 M HCl aqueous solution is added to 10 ml 0.1 M KOH aqueous solution	**(s)** Freezing point of solution increases

2.

Column I	Column II
(A) Acetone + $CHCl_3$	**(p)** $\Delta S_{mix.} > 0$
(B) Ethanol + Water	**(q)** $\Delta V_{mix.} > 0$
(C) $C_2H_5Br + C_2H_5I$	**(r)** $\Delta H_{mix.} < 0$
(D) Acetone + Benzene	**(s)** Maximum boiling azeotropes
	(t) Minimum boiling azeotropes

3.

Column-I (Properties)	Column-II (Affecting factors)
(A) Relative lowering of vapour pressure	**(p)** Directly proportional to van't Hoff factor, i
(B) Elevation in boiling point	**(q)** Directly proportional to molality
(C) Freezing point	**(r)** Directly proportional to molarity
(D) Osmotic pressure	**(s)** Indirectly proportional to lowering of vapour pressure

Part # II [Comprehension Type Questions]

Comprehension # 1

Addition of non–volatile solute to a solvent always increases the colligative properties such as osmotic pressure, ΔP , ΔT_b and ΔT_f. All these colligative properties are directly proportional to molality if solutions are dilute. The increases in colligative properties on addition of non–volatile solute is due to increase in number of solute particles.

1. For different aqueous solutions of 0.1 N NaCI, 0.1 M urea , 0.1 N Na_2SO_4 and 0.1 N Na_3PO_4 solution at 27^0 C. The correct statements are :

1. The order of osmotic pressure is, NaCl > Na_2SO_4 > Na_3PO_4 > urea

2. $\pi = \dfrac{\Delta T_b}{K_b} \times ST$ for urea solution

3. Addition of salt on ice increases its melting point

4. Addition of salt on ice brings in melting of ice earlier

(A) 2 , 3 ,4 **(B)** 2, 4 **(C)** 1 , 2 , 3 **(D)** 3 , 4

2. 1 g mixture of glucose and urea present in 250 mL aqueous solution shows the osmotic pressure of 0.74 atm at 27^0 C. Assuming solution to be dilute , which are correct ?

1. Percentage of urea in mixture is 17.6.

2. Relative lowering in vapour pressure of this solution is 5.41×10^{-4}.

3. The solution will boil at 100.015^0 C , if K_b of water is 0.5 K molality^{-1}.

4. If glucose is replaced by same amount of sucrose, the solution will show higher osmotic pressure at 27^0C.

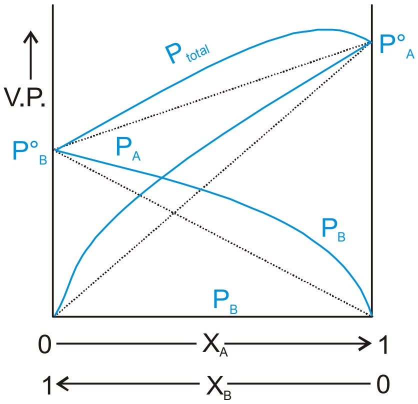
5. If glucose is replaced by same amount of NaCl, the solution will show lower osmotic pressure at 27^0C.

(A) 1 , 2 , 3 **(B)** 1 , 2 , 3 , 5 **(C)** 2 , 4 , 5 **(D)** 1 , 4 , 5

Comprehension # 2

Answer the questions (given below) which are based on the following diagram.

Consider some facts about the above phase diagram :



Vapour pressure diagram for real solutions of two liquids A and B that exhibit a positive deviation from Raoult's law. The vapour pressure of both A and B are greater than predicted by Raoult's law. The dashed lines represented the plots for ideal solutions.

1. **A :** This is observed when A...B attractions are greater than average of A...B and B...B attraction:

B : $\Delta H_{mix} = +ve, \Delta V_{mix} = +ve$

C : Boiling point is smaller than expected such that vaporisation is increased

D : Mixture is called azeotropic mixture

Select correct facts

(A) A, B, C **(B)** B, C, D **(C)** A, C, D **(D)** A, B, C, D

2. Total vapour pressure of mixture of 1 mol of volatile component A ($p°_A$ = 100 mmHg) and 3 mol of volatile component B ($p°_B$ = 60 mmHg) is 75 mm. For such case :

(A) There is positive deviation from Raoult's law

(B) Boiling point has been lowered

(C) Force of attraction between A and B is smaller than that between A and A or between B and B.

(D) All the above statements are correct.

Comprehension # 3

Following passage explains effect of temperature on the vapour pressure of liquid. Answer the questions given at the end.

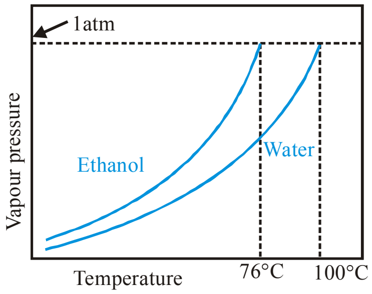
Effect of temperature on Vapour pressure

The quantity of heat required to evaporate a given liquid at constant temperature is defined as the heat of vaporisation. Variation of vapour pressure with temperature is given by

Clausius-Clapeyron equation.

$$\log_e P = -\frac{\Delta H_{vap}}{RT} + \log_e A$$

A liquid is said to be at its boiling temperature if its vapour pressure is equal to external pressure. Therefore, the boiling point of water in particular and of liquids in general decreases as altitude of a place increases where the external pressure is less than 1 atmosphere (normal b.p. of water is 373.15 K at 1 atmosphere)



On top of Mount Everest, for example, where the atmospheric pressure is only about 260 mm Hg, water boils at approximately 71°C. Conversely, if the external pressure on a liquid is greater than 1 atm., the vapour pressure necessary for boiling than normal boiling is reached later, and the liquid boils at a temperature greater than normal boiling point.

1. Clausius-Clapeyron equation can be written in the following form :

(A) $P = Ae^{-\Delta H_{vap}/RT}$

(B) $\frac{d\log_{10}P}{dT} = \frac{\Delta H_{vap}}{2.303RT^2}$

(C) $\frac{d\log_e P}{dT} = -\frac{\Delta H_{vap}}{RT^2}$

(D) $P = Ae^{\Delta H_{vap}/RT}$

2. For a given liquid at a given temperature vapour pressure is given by :

$$\log_{10} P\ (\text{mm}) = -\frac{400(K)}{T} + 10$$

Vapour pressure of the liquid at 400 K is :

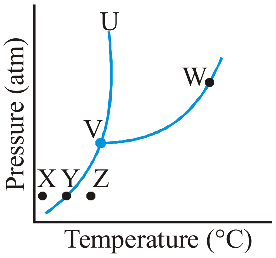
(A) 9 mm **(B)** –9 mm **(C)** 10^9 mm **(D)** 10^{-9} mm

3. Latent heat of vaporisation of the above case in the given temperature range is :

(A) –400 R **(B)** 400 R

(C) –400 × 2.303 R **(D)** 400 × 2.303 R

Comprehension # 4



The phase diagram for a pure substance is shown above. Use this diagram and your knowledge about changes of phase to answer the following questions.

1. What does point V represent :

(A) point of equilibrium **(B)** point of fusion **(C)** point of vaporisation **(D)** Triple point

2. What characteristics are specific to the system only at point V?

(A) Liquid $\rightleftharpoons$ Solid

(B) Solid $\rightleftharpoons$ Vapour

(C) Liquid $\rightleftharpoons$ Vapour

(D) Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour

3. What happens if temperature is increased from X to Y at 1.0 atm ?

(A) solid is competely vaporised

(B) solid and vapour are in equilibrium

(C) solid and liquid are in equilibrium

(D) liquid and vapour are in equilibrium

4. Select correct statement (s) :

(A) curve VU is solid-liquid equilibrium curve

(B) curve VU has a positive slope

(C) curve VW is vapour pressure curve for liquid substance

(D) In the solid - liquid mixture of the substance, solid will float

5. If the given substance is water then :

(A) curve VU would have negative slope

(B) in ice $\rightleftharpoons$ water liquid mixture, ice will float

(C) as the temperature increases, pressure at which solid and liquid are in equilibrium, decreases

(D) increase in pressure at constant temperature causes ice to be converted to liquid water

6. If the triple point pressure of a substance is greater than 1 atm, we expect :

(A) the solid to sublime without melting

(B) the boiling point temperature to be lower than the triple point temperature

(C) the melting point of the solid to come at a lower temperature than the triple point

(D) that the substance cannot exist as a liquid

7. In a phase change (say solid to liquid or liquid to solid) $\Delta G = \Delta H - T\Delta S$ where :

(A) ΔH is the enthalpy change associated with making or breaking the intermolecular attractions that hold solid and liquid together and ΔS is associated with change in disorder between the various phases.

(B) ΔH is associated with change in disorder while ΔS is associated with energy change

(C) both are associated with change in disorder

(D) both are associated with change in energy

Exercise # 4

[Subjective Type Questions]

1. **(a)** The vapour pressure of n-hexane and n-heptane at 273 K are 45.5 mm Hg and 11.4 mm Hg, respectively. What is the composition of a solution of these two liquids if its vapour pressure at 273 K is 37.3 mm Hg.

(b) The mole fraction of n-hexane in the vapour above a solution of n-hexane and n-heptane is 0.75 at 273 K. What is the composition of the liquid solution.

2. A solution containing 30 g of a nonvolatile solute in exactly 90 g water has a vapour pressure of 21.85 mm Hg at 25°C. Further 18 g of water is then added to the solution. The resulting solution has vapour pressure of 22.18 mm Hg at 25°C. Calculate **(a)** molar mass of the solute, and **(b)** vapour pressure of water at 25°C.

3. The freezing point of ether was lowered by 0.60°C on dissolving 2.0 g of phenol in 100 g of ether. Calculate the molar mass of phenol and comment on the result. Given : K_f(ether) = 5.12 K kg mol^{-1}.

4. The vapour pressure of ethanol and methanol are 44.5 mm Hg and 88.7 mm Hg, respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol and 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour.

5. The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molar mass of the solid substance?

6. Addition of 0.643 g of a compound to 50 mL of benzene (density : 0.879 g mL^{-1}) lower the freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 K kg mol^{-1}, calculate the molar mass of the compound.

7. A solution contains 3.22 g of $HClO_2$ in 47.0 g of water. The freezing point of the solution is 271.10 K. Calculate the fraction of $HClO_2$ that undergoes dissociation to H^+ and ClO_2^-. Given : K_f(water) = 1.86 K kg mol^{-1}.

8. A 0.1 molar solution of NaCl is found to be isotonic with 1% urea solution. Calculate **(a)** Van't Hoff factor, and **(b)** degree of dissociation of sodium chloride. Assume density of 1% urea equal to 1 g cm^{-3}.

9. The addition of 3 g of a substance to 100 g CCl_4 (M = 154 g mol^{-1}) raises the boiling point of CCl_4 by 0.60°C. If K_b (CCl_4) is 5 K mol^{-1} kg, calculate **(a)** the freezing point depression **(b)** the relative lowering of vapour pressure **(c)** the osmotic pressure at 298 K and **(d)** the molar mass of the substance. Given : K_f(CCl_4) = 31.8 K kg mol^{-1} and ρ (solution) = 1.64 g cm^{-3}.

10. A solution containing 0.122 kg of benzoic acid in 1 kg of benzene (b. pt. 353 K) boils at 354.5 K. Determine the apparent molar mass of benzoic acid (which dimerizes) in the solution and the degree of dimerization. Given : $\Delta_{vap}H_{1m}$ (benzene) = 394.57 J g^{-1}.

11. A solution containing 0.011 kg of barium nitrate in 0.1 kg of water boils at 100.46°C. Calculate the degree of ionization of the salt. K_b (water) = 0.52 K kg mol^{-1}.

12. When 3.24 g of mercuric nitrate $Hg(NO_3)_2$ dissolved in 1 kg of water, the freezing point of the solution is found to be – 0.0558°C. When 10.84 g of mercuric chloride $HgCl_2$ is dissolved in 1 kg of water, the freezing point of the solution is –0.0744°C. K_f = 1.86 mol^{-1} K kg. Will either of these dissociate into ions in an aqueous solution ?

13. To 500 cm^3 of water 3.0×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression of freezing point? K_f and density of water are 1.86 K kg mol^{-1} and 0.997 g cm^{-3}, respectively.

14. A 0.01 m aqueous solution of $K_3[Fe(CN)_6]$ freezes at –0.062°C. What is the apparent percentage of dissociation? [K_f for water = 1.86]

15. The degree of dissociation of Ca $(NO_3)_2$ in a dilute aqueous solution containing 7 g of the salt per 100 g of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm, calculate the vapour pressure of the solution.

16. The vapour pressure of solution containing 6.69 g of $Mg(NO_3)_2$ dissolved in 100 g of water is 747 Torr at 373 K. Calculate the degree of dissociation of the salt in the solution.

17. At 353 K, the vapour pressure of pure ethylene bromide and propylene bromide are 22.93 and 16.93 k Nm^{-2}, respectively, and these compounds form a nearly ideal solution. 3 mol of ethylene bromide and 2 mole of propylene bromide are equilibrated at 553 K and a total pressure of 20.4 k Nm^{-2}.

(a) What is the composition of the liquid phase?

(b) What amount of each compound is present in the vapour phase?

18. The vapour pressure of two pure liquids, A and B, that form an ideal solution are 300 and 800 torr, respectively, at temperature T. A mixture of the vapour of A and B for which the amount fraction of A is 0.25 is slowly compressed at temperature T. Calculate :

(a) The composition of the first drop of the condensate,

(b) The total pressure when this drop is formed,

(c) The composition of the solution whose normal boiling point is T.

(d) The pressure when only the last bubble of vapour remains.

(e) The composition of the last bubble.

19. A certain mass of a substance, when dissolved in 100 g C_6H_6, lowers the freezing point by 1.28°C. The same mass of solute dissolved in 100 g water lowers the freezing point by 1.40°C. If the substance has normal molecular weight in benzene and is completely ionised in water, into how many ions does it dissociate in water? K_f for H_2O and C_6H_6 are 1.86 and 5.12 K kg mol^{-1}.

20. The cryoscopic constant for acetic acid is 3.6 K kg/mol. A solution of 1 g of a hydrocarbon in 100 g of acetic acid freezes at 16.14°C instead of the usual 16.60°C. The hydrocarbon contains 92.3% carbon. What is the molecular formula?

21. A radiator was filled with 10 L of water to which 2.5 L of methanol (density = 0.8 $g.mL^{-1}$) were added. At 9 : 00 pm, the vehicle is parked outdoors where the temperature is 0°C. The temperature is decreasing at a uniform rate of 0.5°C / min. Upto what time will there be no danger to the radiator of the car. K_f (water) = 1.86 $kg.mol^{-1}$ K. Assume methanol to be non-volatile.

22. Sea water is found to contain 5.85% NaCl and 9.50% $MgCl_2$ by weight of solution. Calculate its normal boiling point assuming 80% ionisation for NaCl and 50% ionisation of $MgCl_2$ [K_b (H_2O) = 0.51 kg mol^{-1} K].

23. Find the freezing point of a glucose solution whose osmotic pressure at 25°C is found to be 30 atm. K_f(water) = 1.86 $kg.mol^{-1}$. K.

24. The latent heat of fusion of ice is 80 calories per gram at 0°C. What is the freezing point of a solution of $KC\ell$ in water containing 7.45 grams of solute 500 grams of water, assuming that the salt is dissociated to the extent of 95%?

25. At 300 K, two solutions of glucose in water of concentration 0.01 M and 0.001 M are separated by semipermeable membrane. Pressure needs to be applied on which solution, to prevent osmosis? Calculate the magnitude of this applied pressure?

26. At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.

27. When cells of the skeletal vacuole of a frog were placed in a series of NaCl solutions of different concentration at 25°C, it was observed microscopically that they remained unchanged in 0.7% NaCl solution, shrank in more cocentrated solutions, and swelled in more dilute solutions. Water freezes from the 0.7% salt solution at –0.406°C. What is the osmotic pressure of the cell cytoplasm at 25°C ? $K_f = 1.86 \text{ kg mol}^{-1}\text{ K}$.

28. An ideal solution of two volatile liquid A and B has a vapour pressure of 402.5 mmHg, the mole fraction of A in vapour & liquid state being 0.35 & 0.65 respectively. What are the vapour pressure of the two liquid at this temperature.

29. Dry air was drawn through bulbs containing a solution of 40 grams of urea in 300 grams of water, then through bulbs containing pure water at the same temperature and finally through a tube in which pumice moistened with strong H_2SO_4 was kept. The water bulbs lost 0.0870 grams and the sulphuric acid tube gained 2.036 grams. Calculate the molecular weight of urea.

30. A 0.1 M solution of potassium ferrocyanide is 46% dissociated at 18°C. What will be its osmotic pressure?

31. At 100°C, benzene & toluene have vapour pressure of 1375 & 558 Torr respectively. Assuming these two form an ideal binary solution that boils at 1 atm & 100°C. What is the composition of vapour issuing at these conditions?

32. Two beaker A and B present in a closed vessel. Beaker A contains 152.4 g aqueous solution of urea, containing 12 g of urea. Beaker B contains 196.2 g glucose solution, containing 18 g of glucose. Both solutions allowed to attain the equilibrium. Determine wt. % of glucose in it's solution at equilibrium :

33. The vapour pressure of two pure liquids A and B, that form an ideal solution are 100 and 900 mm Hg respectively at temperature T. This liquid solution of A and B is composed of 1 mole of A and 1 mole of B. What will be the pressure, when 1 mole of mixture has been vaporized ?

34. The addition of 3 g of substance to 100 g CCl_4 ($M = 154 \text{ g mol}^{-1}$) raises the boiling point of CCl_4 by 0.60°C of K_b (CCl_4) is $5.03 \text{ kg mol}^{-1}\text{ K}$. Calculate :

(a) the freezing point depression

(b) the relative lowering of vapour pressure

(c) the osmotic pressure at 298 K

(d) the molar mass of the substance

Given $K_f(CCl_4) = 31.8 \text{ kg mol}^{-1}\text{ K}$ and ρ (density) of solution = 1.64 g/cm^3.

35. A one litre solution is prepared by dissolving some solid lead-nitrate in water. The solution was found to boil at 100.15°C. To the resulting solution 0.2 mole NaCl was added. The resulting solution was found to freeze at –0.83°C. Determine solubility product of $PbCl_2$. Given $K_b = 0.5$ and $K_f = 1.86$. Assume molality to be equal to molarity in all case.

36. A protein has been isolated as sodium salt with their molecular formula Na_xP (this notation means that xNa^+ ions are associated with a negatively charged protein P^{-x}). A solution of this salt was prepared by dissolving 0.25 g of this sodium salt of protein in 10 g of water and ebulliscopic analysis revealed that solution boils at temperature 5.93×10^{-3} °C higher than the normal boiling point of pure water. K_b of water 0.52 kg mol^{-1}. Also elemental analysis revealed that the salt contain 1% sodium metal by weight. Deduce molecular formula and determine molecular weight of acidic form of protein H_xP.

37. The vapour pressure of two miscible liquids **(A)** and **(B)** are 300 and 500 mm of Hg respectively. In a flask 10 mole of **(A)** is mixed with 12 mole of **(B)**. However, as soon as **(B)** is added, **(A)** starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 minute, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation, and ideal behaviour for the final solution.

38. If 20 mL of ethanol (density = 0.7893 g/mL) is mixed with 40 mL water (density = 0.9971 g/mL) at 25°C, the final solution has density of 0.9571 g/mL. Calculate the percentage change in total volume of mixing. Also calculate the molality of alcohol in the final solution.

39. Mixture of two liquids A and B is placed in cylinder containing piston. Piston is pulled out isothermally so that volume of liquid decreases but that of vapour increases. When negligibly small amount of liquid was remaining, the mole fraction of A in vapour is 0.4. Given $P^\circ_A = 0.4$ atm and $P^\circ_B = 1.2$ atm at the experimental temperature. Calculate the total pressure at which the liquid has almost evaporated. (Assume ideal behaviour)

40. 1.5 g of monobasic acid when dissolved in 150 g of water lowers the freezing point by 0.165°C. 0.5 g of the same acid when titrated, after dissolution in water, requires 37.5 mL of N/10 alkali. Calculate the degree of dissociation of the acid (K_f for water = 1.86° C mol^{-1}).

41. 30 mL of CH_3OH (d = 0.7980 g cm^{-3}) and 70 mL of H_2O (d = 0.9984 g cm^{-3}) are mixed at 25°C to form a solution of density 0.9575 g cm^{-3}. Calculate the freezing point of the solution. $K_f(H_2O)$ is 1.86 kg mol^{-1} K. Also calculate its molarity.

42. Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C is given by P (mm Hg) = 179 X_B + 92, where X_B is the mole fraction of C_6H_6 . A solution is prepared by mixing 936 g benzene and 736 g toluene and if the vapours over this solution are removed and condensed into liquid and again brought to the temperature of 50°C, what would be mole fraction of C_6H_6 in the vapour state ?

43. When the mixture of two immiscible liquids (water and nitrobenzene) boils at 372 K and the vapour pressure at this temperature are 97.7 kPa (H_2O) and 3.6 kPa ($C_6H_5NO_2$). Calculate the weight % of nitrobenzene in the vapour.

44. The molar volume of liquid benzene (density = 0.877 g mL^{-1}) increase by a factor of 2750 as it vaporizes at 20°C and that of liquid toluene (density = 0.867 g mL^{-1}) increases by a factor of 7720 at 20°C solution has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.

45. Calculate the boiling point of a solution containing 0.61 g of benzoic acid in 50 g of carbon disulphide assuming 84% dimerization of the acid. The boiling point and K_b of CS_2 are 46.2°C and 2.3 K kg mol^{-1}, respectively.

46. At 25°C, 1 mol of A having a vapour pressure of 100 torr and 1 mol of B having a vapour pressure of 300 torr were mixed. The vapour at equilibrium is removed, condensed and the condensate is heated back to 25°C. The vapour now formed are again removed, recondensed and analyzed. What is the mole fraction of A in this condensate ?

47. The vapour pressure of a certain liquid is given by the equation :

$$\text{Log}_{10}P = 3.54595 - \frac{313.7}{T} + 1.40655 \log_{10} T$$ where P is the vapour pressure in mm and T = Kelvin Temperature.

Determine the molar latent heat of vaporisation as a function of temperature. Calculate the its value at 80 K.

48. A very dilute saturated solution of a sparingly soluble salt A_3B_4 has a vapour pressure of 20 mm of Hg at temperature T, while pure water exerts a pressure of 20.0126 mm Hg at the same temperature. Calculate the solubility product constant of A_3B_4 at the same temperature.

49. The molar volume of liquid benzene (density = 0.877 g mL^{-1}) increases by a factor of 2750 as it vaporises at 20°C while in equilibrium with liquid benzene. At 27°C when a non - volatile solute (that does not dissociate) is dissolved in 54.6 cm^3 of benzene vapour pressure of this solution, is found to be 98.88 mm Hg. Calculate the freezing point of the solution.

Given : Enthalpy of vaporization of benzene (l) = 394.57 J/g

Molal depression constant for benzene = 5.12 K kg. mol^{-1}

Freezing point of benzene = 278.5 K.

50. The freezing point of 0.02 mol fraction solution of acetic acid **(A)** in benzene **(B)** is 277.4 K. Acetic acid exists partly as a dimer $2A = A_2$. Calculate equilibrium constant for the dimerisation. Freezing point of benzene is 278.4 K and its heat of fusion ΔH_f is 10.042 kJ mol^{-1}.

51. Tritium, T (an isotope of H) combines with fluorine to form weak acid TF, which ionizes to give T^+. Tritium is radioactive and is a β-emitter. A freshly prepared aqueous solution of TF has pT (equivalent of pH) of 1.5 and freezes at –0.372°C. If 600 mL of freshly prepared solution were allowed to stand for 24.8 years, calculate (i) ionization constant of TF. (ii) Number of β-particles emitted.

(Given : K_f for water = 1.86 kg mol K^{-1}, $t_{1/2}$ for tritium = 12.4 years.)

52. An ideal solution was prepared by dissolving some amount of cane sugar (non-volatile) in 0.9 moles of water. The solution was then cooled just below its freezing temperature (271 K), where some ice get separated out. The remaining aqueous solution registered a vapour pressure of 700 torr at 373 K. Calculate the mass of ice separated out, if the molar heat of fusion of water is 96 kJ.

53. The freezing point depression of a 0.109 M aq. solution of formic acid is –0.21°C. Calculate the equilibrium constant for the reaction,

$$HCOOH\,(aq) \rightleftharpoons H^+\,(aq) + HCOO^{\ominus}\,(aq)$$

K_f for water = 1.86 kg mol^{-1} K

54. 10 g of NH_4Cl (mol. weight = 53.5) when dissolved in 1000 g of water lowered the freezing point by 0.637°C. Calculate the degree of hydrolysis of the salt if its degree of dissociation of 0.75. The molal depression constant of water is 1.86 kg mol^{-1} K.

Exercise # 5

Part # I [Previous Year Questions] [AIEEE/JEE-MAIN]

1. 6.02×10^{20} molecules of urea are present in 100 ml of its solution. The concentration of urea solution is : **[AIEEE-2004]**

(A) 0.001 M **(B)** 0.01 M **(C)** 0.02 M **(D)** 0.1 M.

2. Which one of the following aqueous solutions will exhibit highest boiling point ? **[AIEEE-2004]**

(A) 0.01 M Na_2SO_4 **(B)** 0.01 M KNO_3 **(C)** 0.015 M urea **(D)** 0.015 M glucose

3. Equimolar solutions in the same solvent have : **[AIEEE-2005]**

(A) same boiling point but different freezing point **(B)** same freezing point but different boiling point

(C) same boiling and same freezing points **(D)** different boiling and freezing points

4. Two solutions of a substance (non electrolyte) are mixed in the following manner. 480 ml of 1.5 M first solution + 520 mL of 1.2 M second solution. What is the molarity of the final mixture ? **[AIEEE-2005]**

(A) 1.20 M **(B)** 1.50 M **(C)** 1.344 M **(D)** 2.70 M

5. Benzene and toluene form nearly ideal solutions. At 20ºC, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20 ºC for a solution containing 78 g of benzene and 46 g of toluene in torr is : **[AIEEE-2005]**

(A) 50 **(B)** 25 **(C)** 37.5 **(D)** 53.5

6. If α is the degree of dissociation of Na_2SO_4, the vant Hoff's factor (i) used for calculating the molecular mass is : **[AIEEE-2005]**

(A) $1 + \alpha$ **(B)** $1 - \alpha$ **(C)** $1 + 2\alpha$ **(D)** $1 - 2\alpha$.

7. Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is **[AIEEE-2006]**

(A) 3.28 mol Kg^{-1} **(B)** 2.28 mol Kg^{-1} **(C)** 0.44 mol Kg^{-1} **(D)** 1.14 mol Kg^{-1}

8. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be **[AIEEE-2007]**

(A) 700 **(B)** 360 **(C)** 350 **(D)** 300

9. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm^{-3}, molar mass of the substance will be **[AIEEE-2007]**

(A) 105.0 g mol^{-1} **(B)** 210.0 g mol^{-1} **(C)** 90.0 g mol^{-1} **(D)** 15.0 g mol^{-1}

10. The vapour pressure of water at 20° C is 17.5 mm Hg. If 18g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20° C, the vapour pressure of the resulting solution will be **[AIEEE-2008]**

(A) 15.750 mm Hg **(B)** 16.500 mm Hg **(C)** 17.325 mm Hg **(D)** 17.675 mm Hg

11. At 80° C , the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at 80° C and 1 atm pressure, the amount of 'A' in the mixture is (1atm = 760 mm Hg) **[AIEEE-2008]**

(A) 34 mol percent **(B)** 48 mol percent **(C)** 50 mol percent **(D)** 52 mol percent

12. A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statement is correct regarding the behaviour of the solution ? **[AIEEE-2009]**

(A) The solution is non-ideal, showing +ve deviation from Raoult's Law.

(B) The solution in non-ideal, showing –ve deviation from Raoult's Law.

(C) n-heptane shows +ve deviation while ethanol shows –ve deviation from Raoult's Law.

(D) The solution formed is an ideal solution.

13. Two liquids X and Y form an ideal solution. At 300K, vapour pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mmHg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mmHg. Vapour pressure (in mmHg) of X and Y in their pure states will be, respectively : **[AIEEE-2009]**

(A) 300 and 400 **(B)** 400 and 600 **(C)** 500 and 600 **(D)** 200 and 300

14. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mole of sodium sulphate is dissolved in 1 kg of water, is ($K_f = 1.86$ K kg mol^{-1}) **[AIEEE-2010]**

(A) 0.0372 K **(B)** 0.0558 K **(C)** 0.0744 K **(D)** 0.0186 K

15. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25.0 g of heptane and 35 g of octane will be (molar mass of heptane - 100 g mol^{-1} and of octane = 114 g mol^{-1}) **[AIEEE-2010]**

(A) 72.0 kPa **(B)** 36.1 kPa **(C)** 96.2 kPa **(D)** 144.5 kPa

16. K_f for water is 1.86 K kg mol^{-1}. If your automobile radiator holds 1.0 kg of water, how may grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to –2.8ºC ? **[AIEEE 2012]**

(A) 72 g **(B)** 93 g **(C)** 39 g **(D)** 27 g

17. 18g glucose ($C_6H_{12}O_6$) is added to 178.2 g water. The vapor pressure of water (in torr) for this aqueous solution is: **[Jee (Mains) 2016]**

(A) 76.0 **(B)** 752.4 **(C)** 759.0 **(D)** 7.6

18. The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be : (K_f for benzene = 5.12 K kg mol^{-1}) **[Jee (Mains) 2017]**

(A) 64.6 % **(B)** 80.4 % **(C)** 74.6 % **(D)** 94.6 %

19. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point ? **[Jee (Mains) 2018]**

(A) $[Co(H_2O)_5Cl]Cl_2.H_2O$ **(B)** $[Co(H_2O)_4Cl_2]Cl.2H_2O$ **(C)** $[Co(H_2O)_3Cl_3].3H_2O$ **(D)** $[Co(H_2O)_6]Cl_3$

20. An aqueous solution contains an unknown concentration of Ba^{2+}. When 50 mL of a 1 M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is 1×10^{-10}. What is the original concentration of Ba^{2+} ? **[JEE(Main) 2018]**

(A) 2×10^{-9} M **(B)** 1.1×10^{-9} M **(C)** 1.0×10^{-10} M **(D)** 5×10^{-9} M

Part # II [Previous Year Questions][IIT-JEE ADVANCED]

1. A 0.004 M solution of Na_2SO_4 is isotonic with 0.010 M solution of glucose at same temperature. The apparent percentage dissociation of Na_2SO_4 is : **[JEE 2004]**

(A) 25% **(B)** 50% **(C)** 75% **(D)** 85%

2. 1.22 g of benzoic acid is dissolved in 100 g of acetone and 100 g of benzene separately. Boiling point of the solution in acetone increases by 0.17ºC, while that of, in the benzene increases by 0.13ºC ; K_b for acetone and benzene is 1.7 K kg mol^{-1} and 2.6 K kg mol^{-1}. Find molecular weight of benzoic acid in two cases and justify your answer. **[JEE 2004]**

3. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1kg of water using the following information, will be (Molecular weight of $CuCl_2$ = 134.4 and K_b = 0.52 K molal^{-1}) : **[JEE 2005]**

(A) 0.16 **(B)** 0.05 **(C)** 0.1 **(D)** 0.2

4. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene (K_f = 1.72 K kg mol^{-1}), a freezing point depression of 2 K is observed. The van't Hoff factor (i) is : **[JEE-2007]**

(A) 0.5 **(B)** 1 **(C)** 2 **(D)** 3

Comprehension

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Application of colligative properties are very useful in day-to-day life. One of its example is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles

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

Given : Freezing point depression constant of water (K_f^{water}) = 1.86 K kg mol^{-1}

Freezing point depression constant of ethanol ($K_f^{ethanol}$) = 2.0 K kg mol^{-1}

Boiling point elevation constant of water (K_b^{water}) = 0.52 K kg mol^{-1}

Boiling point elevation constant of ethanol ($K_b^{ethanol}$) = 1.2 K kg mol^{-1}

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg

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, consider the solution to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

5. The freezing point of the solution **M** is **[JEE 2008]**

(A) 268.7 K **(B)** 268.5 K **(C)** 234.2 K **(D)** 150.9 K

6. The vapour pressure of the solution **M** is **[JEE 2008]]**

(A) 39.3 mm Hg **(B)** 36.0 mm Hg **(C)** 29.5 mm Hg **(D)** 28.8 mm Hg

7. 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 **[JEE 2008]**

(A) 380.4 K **(B)** 376.2 K **(C)** 375.5 K **(D)** 354.7 K

8. The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water of 298 K and 5 atm pressure is :

[JEE 2009]

(A) 4×10^{-4} **(B)** 4.0×10^{-5} **(C)** 5.0×10^{-4} **(D)** 4.0×10^{-6}

9. The freezing point (in ºC) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (Mol. Wt. 329) in 100 g of water (K_f = 1.86 K kg mol^{-1}) is : **[JEE 2011]**

(A) -2.3×10^{-2} **(B)** -5.7×10^{-2} **(C)** -5.7×10^{-3} **(D)** -1.2×10^{-2}

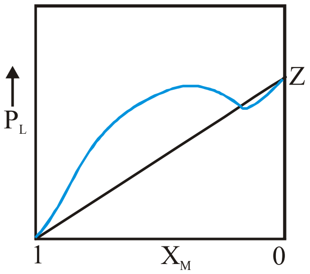
10. For a dilute solution containing 2.5 g of a non- volatile non- electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2ºC. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take $K_b = 0.76$ K kg mol^{-1}) **[IIT 2012]**

(A) 724 **(B)** 740 **(C)** 736 **(D)** 718

11. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm^{-3}. The ratio of the molecular weights of the solute and solvent, $\left(\frac{MW_{solute}}{MW_{solvent}}\right)$,is

[JEE ADVANCED 2016]

12. For a solution formed by mixing liquids L and M, the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure. Here x_L and x_M represent mole fractions of L and M, respectively, in the solution. The correct statement(s) applicable to this system is(are) **[JEE ADVANCED 2017]**



(A) The point Z represent vapour pressure of pure liquid M and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$

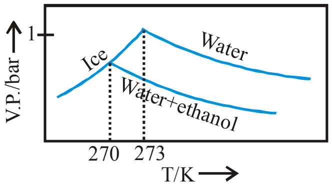
(B) Attractive intermolecular interactions between L–L in pure liquid L and M–M in pure liquid M are stronger than those between L-M when mixed in solution

(C) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L \to 0$

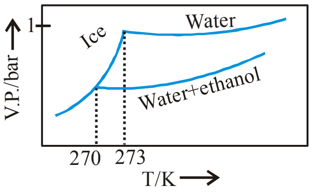
(D) The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \to 1$

13. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol of 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol^{-1}. The figures shown below represent plots of vapour pressure (V.P.) versus temperature (T). [molecular weight of ethanol is 46 g mol^{-1}]
Among the following the option representing change in the freezing point is **[JEE ADVANCED 2017]**

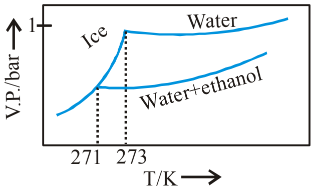
(A)



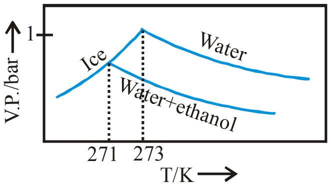
(B)



(C)



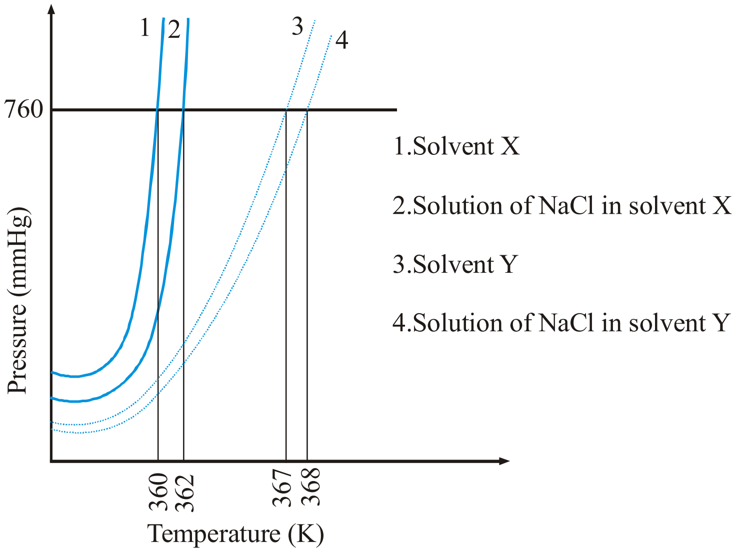
(D)



14. Liquids A and B form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids A and B has vapour pressure 45 Torr. At the same temperature, a new solution of A and B having mole fractions x_A and x_B, respectively, has vapour pressure of 22.5 Torr. The value of x_A / x_B in the new solution is_____. (given that the vapour pressure of pure liquid A is 20 Torr at temperature T) **[JEE(ADVANCED) 2018]**

15. The plot given below shows P–T curves (where P is the pressure and T is the temperature) for two solvents X and Y and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.

[JEE(ADVANCED) 2018]



On additionof equal number of moles of a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solvent S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y, the degree of dimerization in solvent X is ___.

MOCK TEST

SECTION - I : STRAIGHT OBJECTIVE TYPE

1. Three solutions are prepared by adding 'w' gm of 'A' into 1 kg of water, 'w' gm 'B' into another 1kg of water and 'w' gm of 'C' in another 1 kg of water (A,B,C are non electrolytic). Dry air is passed from these solutions in sequence ($A \rightarrow B \rightarrow C$). The loss in weight of solution A was found to be 2gm while solution B gained 0.5 gm and solution C lost 1 gm. Then the relation between molar masses of A,B and C is :

(A) MA : MB : MC = 4 : 3 : 5 **(B)** MA : MB : MC = $\frac{1}{4}:\frac{1}{3}:\frac{1}{5}$

(C) MC > MA > MB **(D)** MB > MA > MC

2. Barium ions, CN– and Co^{+2} form an ionic complex. If this complex is 75% ionised in aqueous solution with Vant Hoff factor (i) equal to four and paramagnetic moment is found to be 1.73 BM(due to spin only) then the hybridisation state of Co(II) in the complex will be :

(A) sp^3d **(B)** d^2sp^3 **(C)** sp^3d^2 **(D)** dsp^3

3. The incorrect statement is :

(A) Vapour pressure of a liquid always increases by increasing the temperature.

(B) Vapour pressure only depends on temperature and not on the nature of the substance.

(C) Vapour pressure does not depend on the quality of the liquid taken and the surface area of the liquid.

(D) Vapour pressure is not a colligative property and is independent of the concentration of a liquid.

4. Relative decrease in in vapour pressure of an aqueous solution containing 2 moles $[Cu(NH_3)_3Cl]Cl$ in 3 moles H_2O is 0.50. On reaction with $AgNO_3$, this solution will form

(A) 1 mol AgCl **(B)** 0.25mol AgCl **(C)** 2 mol AgCl **(D)** 0.40 mol AgCl

5. A solution of x moles of sucrose in 100gms of water freezes at – 0.2°C. As ice separates the freezing point goes down to 0.25°C. How many grams of ice would have separated?

(A) 18 grams **(B)** 20 grams **(C)** 25 grams **(D)** 23 grams

6. A sample of air is saturated with benzene (vapour pressure = 100 mm Hg at 298K) at 298 K, 750mm Hg pressure. If it is isothermally compressed to one third of its initial volume, the final pressure of the system is

(A) 2250 torr **(B)** 2150 torr **(C)** 2050 torr **(D)** 1950 torr

7. Available solutions are 1L of 0.1 M NaCl and 2L of 0.2 M $CaCl_2$. Using only these two solutions what maximum volume of a solution can be prepared having [Cl–]= 0.34 M exactly. Both electrolytes are strong

(A) 2.5L **(B)**2.4L **(C)**2.3L **(D)** None of these

8. Calculate the osmotic pressure of the solution prepared in the above ques T = 300K, (R = 0.082 L atm mol–1 K–1)

(A) 10.8 atm **(B)**12.8 atm **(C)** 5.6 atm **(D)** None of these

9. Consider equimolal aqueous solutions of $NaHSO_4$ and NaCl with ΔTb and $\Delta T'b$ as their respective boiling point elevations. The value of $\underset{m \to 0}{Lt} \frac{\Delta T_b}{\Delta T'_b}$ will be

(A) 1 **(B)** 1.5 **(C)** 3.5 **(D)** 2/3

10. The vapour pressure of benzene, toulene and a xylene are 75 Torr, 22 Torr and 10 Torr at 20°C. Which of the following is not a possible value of the vapour pressure of an equimolar binary/ternary solution of these at 20°C ? Assume all form ideal solution with each other.

(A) 48.5 **(B)** 16 **(C)** $35\frac{2}{3}$ **(D)** 53.5

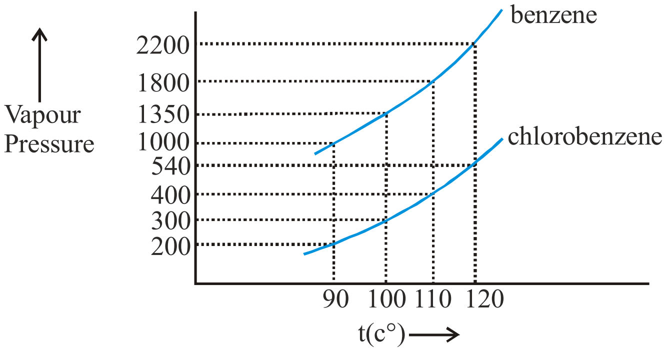
11. 3.24g of $Hg(NO_3)_2$ (molar mass = 324) dissolved in 1000g of water constitutes a solution having a freezing point of –0.0558°C while 21.68 g of $HgCl_2$ (molar mass = 271) in 2000g of water constitutes a solution with a freezing point of –0.0744°C. The Kf for the water is 1.86 $\frac{K-kg}{mol}$. About the state of ionization of these two solids in water it can be inferred that :

(A) $Hg(NO_3)_2$ and $HgCl_2$ both are completely ionized.
(B) $Hg(NO_3)_2$ is fully ionized but $HgCl_2$ is fully unionized.
(C) $Hg(NO_3)_2$ and $HgCl_2$ both are completely unionized.
(D) $Hg(NO_3)_2$ is fully unionized and $HgCl_2$ is fully ionized.

12. For a solution of 0.849 g of mercurous chloride in 50 g og HgCl2 (ℓ) the freezing point depression is 1.24°C. Kf for HgCl2 is 34.3. What is the state of mercurous chloride in HgCl2?
(Hg – 200, Cl – 35.5).

(A) as $Hg2Cl_2$ molecules
(B) As HgCl molecules
(C) As Hg+ and Cl– ions
(D) As Hg_2^{2+} and Cl– ions

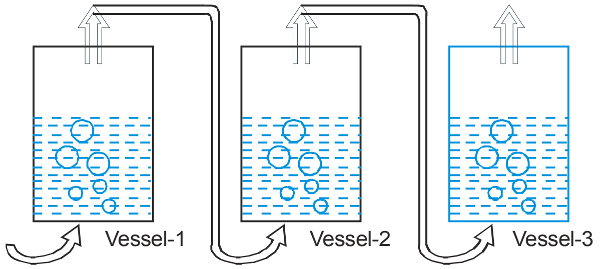
13. Assuming that the formation of an ideal solution, determine the boiling point of a mixture containing 1560 g benzene (molar mass = 78) and 1125 g chlorobenzene (molar mass = 112.5) using the following against an external pressure of 1000 torr.



(A)90°C
(B)100°C
(C)110°C
(D)120°C

SECTION - II : MULTIPLE CORRECT ANSWER TYPE

14. Dry air is slowly passed through three solutions of different concentration , c_1, c_2, c_3 ; each containing (non volatile) NaCl as solute and water as solvent, as shown in the figure. If the vessel 2 gains weight, then



(A) $c_1 > c_2$
(B) $c_1 < c_2$
(C) $c_1 < c_3$
(D) $c_2 > c_3$

15. In which of the following pairs of solution will have the values of Vant hoff factors can be the same?

(A) 0.05 M $K_4[Fe(CN)_6]$ and 0.10 M $FeSO_4$

(B) 0.10 M $K4[Fe(CN)_6]$ and 0.05 M $FeSO_4(NH_4)_2SO_4.6H_2O$

(C) 0.20 M NaCl and 0.10 M $BaCl_2$

(D) 0.05 M $FeSO_4(NH_4)_2SO_4.6H_2O$ and 0.02 M $KCl.MgCl_2.6H_2O$

16. Vapour pressure of solution containing 6g of a non-volatile solute in 180 g water is 20.0 Torr. If 1 mole water is further added vapour pressure increases by 0.02 Torr. Which of the following is true?

(A) The molecular weight of solute is 54g/mol

(B) The vapour pressure of pure water is 20.22 Torr.

(C) Addition of more water in the solution will further raise the vapour pressure of solution.

(D) The vapour pressure of pure water is 22.22 Torr.

SECTION - III : ASSERTION AND REASON TYPE

17. **Statement - 1** When a cell is placed in hypertonic solution, it shrinks.

Statement - 2 Reverse osmosis is used for desalination of water.

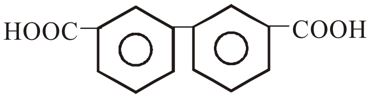
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.

18. **Statement - 1** The difference in the boiling points of equimolar solution of HCl and HF decreases as their molarity is decreased.

Statement - 2 The extent of dissociation decreases steadily with increasing dilution.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.

19. **Statement - 1** The molar mass obtained for benzoic acid in benzene is found to be nearly 244.

Statement - 2 Benzoic acid has the formula 

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.

20. **Statement - 1** When 'a' mL of a 0.1 molal urea solution is mixed with another 'b' mL of 0.1 molal glucose solution, the boiling point of the solution is no different from the boiling points of the samples prior to mixing but if 'a' mL of 0.1 molal urea is mixed with 'b' mL of 0.1 molal HF the boiling point of the mixture is different from the boiling points of the separate samples.

Statement - 2 HF is an electrolyte (weak) whereas glucose is a non electrolyte.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.

SECTION - IV : COMPREHENSION TYPE

Read the following comprehensions carefully and answer the questions.

Ideal Solution at Fixed Temperature

Consider two liquid ‘B’ and ‘C’ that form an ideal solution. We hold the temperature fixed at some value T that is above freezing points of ‘B’ and ‘C’. We shall plot the system’s pressure P against xB, the overall mole fraction of B in the system :

$$xB = \frac{n_{B,total}}{n_{total}} = \frac{n_B^\ell + n_B^v}{n_B^v + n_C^\ell + n_B^\ell}$$

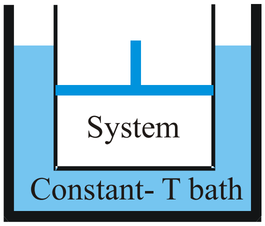
Where n_B^ℓ and n_B^v are the number of moles of B in the liquid and vapor phases, respectively. For a closed system xB is fixed, althoud n_B^ℓ and n_B^v may vary.

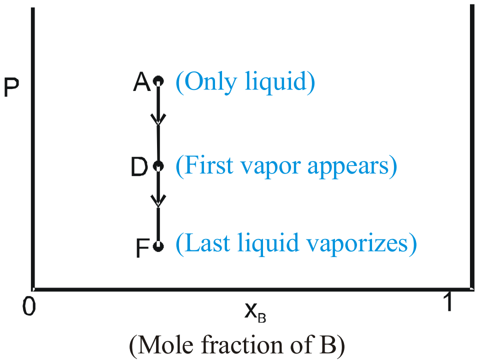
Let the system be enclosed in a cylinder fitted with a piston and immersed in a constant-temperature bath. To see what the P-versus-xB phase diagram looks like, let us initially set the external pressure on the piston high enough for the system to be entirely liquid (point A in figure) As the pressure is lowered below that at A, the system eventually reaches a pressure where the liquid just begins to vaporizes (point D). At point D, the liquid has composition x_B^ℓ where x_B^ℓ at D is equal to the overall mole fraction xB since only an infinitesimal amount of liquid has vapourized.

What is the composition of the first vapour that comes off ? Raoult’s law, $P_B \equiv x_B^v P_B^0$ relates the vapour-phase mole fractions to the liquid composition as follows :

$$x_B^0 = \frac{X_B^\ell P_B^0}{P} \quad \text{and} \quad x_C^v = \frac{x_C^\ell P_C^0}{P} \qquad \text{...(A)}$$

Where P_B^0 and P_C^0 are the vapour pressures of pure ‘B’ and pure ‘C’ at T, where the system’s pressure P equals the sum PB + PC of the partial pressures, where $P_B^\ell = \frac{n_B^\ell}{(n_B^\ell + n_C^\ell)}$, and the vapor is assumed ideal.





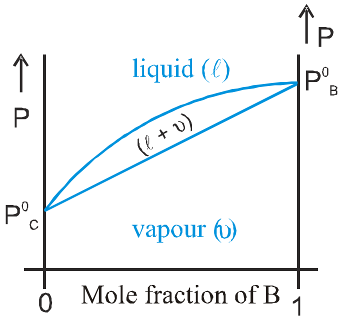
$$\frac{x_B^v}{x_C^v} = \frac{x_B^\ell P_B^*}{x_C^\ell P_C^*} \qquad \text{ideal solution} \qquad \text{...(B)}$$

Let B be the more volatile component, meaning that $P_B^0 > P_C^0$. Above equation then shows that $x_B^v / x_C^v > x_B^\ell / x_C^\ell$. The vapor above an ideal solution is richer than the liquid in the more volatile component. Equations **(A)** and **(B)** apply at any pressure where liquid–vapor equilibrium exists, not just at point D.

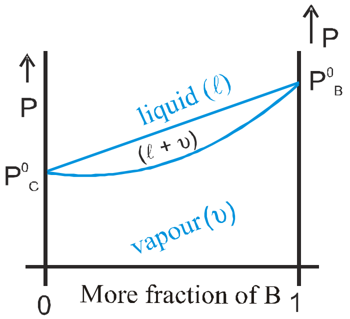
Now let us isothermally lower the pressure below point D, causing more liquid to vaporize. Eventually, we reach point F in the figure, where the last drop of liquid vaporizes. Below F, we have only vapor. For any point on the line between D and F liquid and vapor phases coexist in equilibrium.

21. If the above process is repeated for all other compositions of mixture of C and B. If all the points where vapours start converting into liquid are connected and all the points where vapours get completely converted into liquid are connected obtained graph will look like.

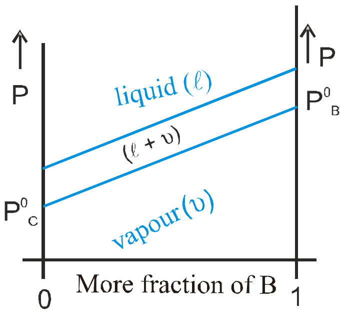
(1)



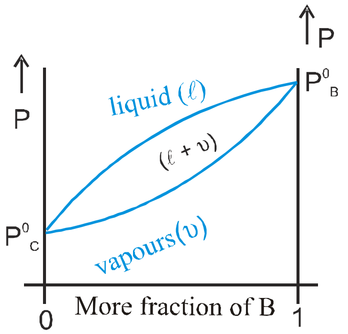
(2)



(3)



(4)



22. The equation of the curve obtained by connecting all those points where the vapors of above mixture (all mixtures of different composition are taken) just start forming will be

(A) $P = P^\circ C + (P^\circ B - P^\circ C)\, X\ell B$

(B) $P = P^\circ B + (P^\circ B - P^\circ C)\, X\ell B$

(C) $P = \dfrac{P^0_B P^0_C}{X^{\upsilon}_B (P^0_C - P^0_B) + P^0_B}$

(D) $P = \dfrac{P^0_B P^0_C}{X^{\ell}_B (P^0_C - P^0_B) + P^0_B}$

23. Two liquids A and B have the same molecular weight and form an ideal solution. The solution has a vapor pressure of 700 Torrs at 80ºC. It is distilled till 2/3rd of the solution (2/3rd moles out of total moles) is collected as condensate. The composition of the condensate is x'A = 0.75 and that of the residue is x"A = 0.30. If the vapor pressure of the residue at 80ºC is 600 Torrs, find the original compositions of the liquid.

(A) XA = 0.5 **(B)** XB = 0.6 **(C)** XA = 0.6 **(D)** XB = 0.3

SECTION - V : MATRIX - MATCH TYPE

24. Match the following :

Column I	Column II
(A) Pyridine + CH_3COOH	**(p)** ΔSmixing = +Ve
(B) $C_6H_5Cl + C_6H6Br$	**(q)** ΔVmixing = +Ve
(C) $CHCl_3 + CCl_4$	**(r)** ΔGmixing = –Ve
(D) $H_2O + HClO_4$	**(s)** ΔHmixing = –Ve

25. Match the following :

Column I	Column II
(A) Relative lowering in vapour pressure	**(p)** negative deviation from ideal behaviour
(B) Depression in freezing point	**(q)** Walker and Ostwald Method
(C) ΔHmix < Zero	**(r)** Beckmann thermometer
(D) Osmotic pressure	**(s)** Berkeley and Hartley's method

SECTION - VI : SUBJECTIVE TYPE

26. Barium ions, CN– and Co^{+2} form a water soluble ionic complex with Ba^{2+} as free cations. For a 0.01 M solution of this complex osmotic pressure is observed to be equal to 0.984 atm and degree of dissociation is found out to be 75%. Then find the coordination number of Co(II) in this complex.

(T = 300K) (R = 0.082 L atm mol-1 K-1).

27. What is the osmotic pressure of a solution (in Torr) made by mixing 20mL of 0.01 M $BaCl_2$ with 30mL of 0.01M NaF at 27°C ? Ksp (BaF_2) = 2.4 × 10–5. R = 0.082 lit atm mol–1 K–1, 1 atm= 760Torr.

28. The composition of vapour over a binary ideal solution is determined by the composition of a liquid. If XA and YA are the mole fractions of A in the liquid and vapour , respectively , find the value of XA for which YA–XA has a maximum value.What is the value of pressure at this composition in terms of P°A and P°B.

29. When 2g of non volatile hydrocarbon containing 94.4 percent carbon is dissolved in 100g benzene, the vapour presure of benzene is lowered from 74.66 torr to 74.01 torr. Determine the molecular formulae for the hydrocarbon.

30. A saturated solution of sparingly soluble salt MCl_2 has a vapour pressure of 31.96 torr while pure water has a vapour pressure of 32.0 torr at the same temperature. Calculate the solubility of the product of MCl_2.

ANSWER KEY

EXERCISE - 1

1. A, B, D **2.** B **3.** A, B, C, D **4.** B **5.** B **6.** C **7.** B **8.** B **9.** B **10.** C **11.** A

12. C **13.** C **14.** B **15.** A **16.** A **17.** A, B, C **18.** A **19.** A **20.** A, B, C, D **21.** C **22.** A **23.** B

24. C **25.** A, C **26.** D **27.** B, D **28.** C **29.** B **30.** B **31.** B **32.** A **33.** B **34.** A **35.** C

36. D **37.** A **38.** A **39.** C **40.** C **41.** A **42.** C **43.** B **44.** C **45.** D **46.** C **47.** D **48.** D

49. D **50.** B **51.** B **52.** B **53.** C **54.** B **55.** C **56.** A **57.** B **58.** A **59.** B, D **60.** C

61. A **62.** B **63.** C **64.** A **65.** B **66.** C **67.** A **68.** B **69.** A **70.** A **71.** A **72.** D **73.** C

74. C **75.** C **76.** A **77.** A **78.** C **79.** B **80.** B **81.** C **82.** D **83.** D **84.** C **85.** C **86.** D

87. C **88.** B **89.** B **90.** D **91.** D **92.** C **93.** B **94.** A **95.** D **96.** C **97.** B **98.** C **99.** A

100. D **101.** A **102.** B **103.** B **104.** D **105.** A **106.** B **107.** C **108.** C **109.** A **110.** B **111.** C **112.** C

113. A **114.** A **115.** A **116.** B **117.** A **118.** C **119.** A **120.** B **121.** C **122.** C **123.** A **124.**B **125.** C

126. A **127.** C **128.** B **129.** A

EXERCISE - 2 : PART # I

1. A, B, C **2.** A, B, C **3.** A, B **4.** A, B, C **5.** A, B, C, D **6.** A, B, C, D

7. B, C, D **8.** A **9.** A, B **10.** A, B, C **11.** B **12.** A, B

13. B **14.** B, C **15.** A, B, D **16.** A, B, C **17.** A, B, C, D **18.** A, B, D

19. A, D **20.** A, B, C

PART # II

1. C **2.** C **3.** A **4.** B **5.** A **6.** D **7.** A **8.** D **9.** B **10.** D

EXERCISE - 3 : PART # I

1. A → q, s, B → q, s, C → q, s, D → q, s **2.** A → p, s, r, B → p, q, t, C → p, D → p, q, t

3. A → p; B → p, q; C → s; D → p, r

PART # II

Comprehension # 1 : **1.** B **2.** A

Comprehension # 2 : **1.** B **2.** D

Comprehension # 3 : **1.** **A, B** **2.** C **3.** D

Comprehension # 4 : **1.** D **2.** D **3.** B **4.** A, B, C **5.** A, B, C, D **6.** A **7.** A

EXERCISE - 5 : PART # I

1. B **2.** A **3.** C **4.** C **5.** A **6.** C **7.** B **8.** C **9.** B **10.** C **11.** C **12.** A **13.** B

14. B **15.** A **16.** B **17.** B **18.** D **19.** C **20.** B

PART # II

1. C **2.** 122, 224 **3.** A **4.** A **5.** D **6.** B **7.** B **8.** A **9.** A **10.** A **11.** 9 **12.** B, D

13. B **14.** 19 **15.** 0.05

MOCK - TEST

1. C **2.** D **3.** B **4.** A **5.** B **6.** C **7.** A **8.** B **9.** B **10.** D **11.** B **12.** A **13.** B

14. B,D **15.** B,D **16.** A,B,C **17.** B **18.** C **19.** C **20.** A **21.** B **22.** A **23.** C

24. A → p,r,s ; B → p,r ; C → p,q,r ; D → p,r,s **25.** A → q ; B → r ; C → p ; D → s