

Topic : Solution Colligative Properties

Type of Questions		M.M., Min.
Single choice Objective ('-1' negative marking) Q.1 to Q.4	(3 marks, 3 min.)	[12, 12]
Multiple choice objective ('-1' negative marking) Q.5 to Q.6	(4 marks, 4 min.)	[8, 8]
Subjective Questions ('-1' negative marking) Q.7	(4 marks, 5 min.)	[4, 5]
Comprehension ('-1' negative marking) Q.8 to Q.10	(3 marks, 3 min.)	[9, 9]

- A student was assigned a certain task by his teacher in chemistry lab. During the experiment, student dropped the flask containing 250 ml, 3 molar NaOH solution. Due to this 50 ml of solution out of 250 ml, had fallen on the floor. Thinking that teacher may punish him for this mistake, he replenished the left over solution with 50 ml of water. The new molarity of NaOH solution will be.
(A) 2M (B) 3M (C) 2.5 M (D) 2.4 M
- Statement-1** : N_2 gas present in a closed container along with some H_2O (ℓ) at equilibrium has relative humidity = 100%
Statement-2 : At equilibrium, partial pressure of $H_2O(g)$ is equal to aqueous tension at that temperature.
(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
- A mixture of two immiscible liquids at a constant pressure of 1 atm boils at a temperature
(A) equal to the normal boiling point of more volatile liquid
(B) equal to the mean of the normal boiling points of the two liquids
(C) greater than the normal boiling point of either of the liquid
(D) smaller than the normal boiling point of either of the liquid.
- 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
- * 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
- * In which of the following cases van't Hoff factor is greater than three
(A) $AlCl_3$ if $\alpha = 0.8$. (B) $BaCl_2$ if $\alpha = 0.9$.
(C) Na_3PO_4 if $\alpha = 0.9$ (D) $K_4[Fe(CN)_6]$ if $\alpha = 0.7$.

7. Mixture of volatile components A and B has total vapour pressure (in Torr) $p = 265 - 130 x_A$, where x_A is mole fraction of A in mixture. Hence p_A^0 and p_B^0 are (in Torr). Calculate sum of the vapour pressure of pure component A and B. Report your answer as $\frac{1}{100}$ th part of the original sum.

Comprehension # (Q. 8 to Q. 10)

Read the following comprehension regarding **Completely Immiscible Liquids : Steam Distillation** carefully and answer the questions (8 to 10).

It is probably true that no two liquids are absolutely insoluble in each other, but with certain pairs, eg., mercury and water and carbon disulfide and water, the mutual solubility is so small that the liquids may be regarded as virtually immiscible. For systems of this type, each liquid exerts its own vapour pressure, independent of the other, and the total vapour pressure is the sum of the separate vapour pressures of the two components in the pure state at the given temperature. The composition of the vapour can be readily calculated by assuming that the gas laws are obeyed; the number of moles of each constituent in the vapour will then be proportional to its partial pressure, that is to say, to the vapour pressure of the substance in the pure state. If p_A^0 and p_B^0 are the vapour pressures of the pure liquids A and B, respectively, at the given temperature, and n'_A and n'_B are the numbers of moles of each present in the vapour, the total pressure P at the same temperature is given by

$$P = p_A^0 + p_B^0 \quad (1)$$

and the composition of the vapour by
$$\frac{n'_A}{n'_B} = \frac{p_A^0}{p_B^0} \quad (2)$$

To express the ratio of A to B in the vapour in terms of the actual weights w_A and w_B , the numbers of moles must be multiplied by the respective molecular weights M_A and M_B ; hence,

$$\frac{w_A}{w_B} = \frac{n'_A M_A}{n'_B M_B} = \frac{p_A^0 M_A}{p_B^0 M_B} \quad (3)$$

A system of two immiscible liquids will boil, that is, distill freely, when the total vapour pressure P is equal to the atmospheric pressure. The boiling point of the mixture is thus lower than that of either constituent. Further, since the total vapour pressure is independent of the relative amounts of the two liquids, the boiling point, and hence the composition of the vapour and distillate, will remain constant as long as the two layers are present.

The properties just described are utilized in the process of steam distillation, whereby a substance that is immiscible, or almost immiscible, with water, and that has a relatively high boiling point, can be distilled at a much lower temperature by passing steam through it. The same result should, theoretically, be obtained by boiling a mixture of water and the particular immiscible substance, but by bubbling steam through the latter the system is kept agitated, and equilibrium is attained between the vapour and the two liquids. The mixture distills freely when the total pressure of the two components is equal to that of the atmosphere.

It is seen that chlorobenzene, which has a normal boiling point of 132°C , can be distilled with steam at a temperature about 40° lower, the distillate containing over 70 percent of the organic compound.

An examination of the calculation shows that the high proportion by weight of chlorobenzene in the steam distillate is due largely to the high molecular weight of this substance, viz., 112.5 as compared with that of water. In addition this case is a particularly favorable one because chlorobenzene has a relatively high vapour pressure in the region of 90° to 100°C. In order that a liquid may be distilled efficiently in steam, it should therefore be immiscible with water, it should have a high molecular weight, and its vapour pressure should be appreciable in the vicinity of 100°C. A liquid which is partially miscible with water, such as aniline, may be effectively distilled in steam, provided the solubility is not very great. In calculating the composition of the distillate, however, the pressures p_A^0 and p_B^0 in equation (3) would have to be replaced by the actual partial pressures. Attention may be called to the fact that equation (3) can be employed to determine the approximate molecular weight of a substance that is almost immiscible with water. This can be done provided the composition of the steam distillate and the vapour pressures of the two components are known.

8. The hydrocarbon terpinene was found to distil freely in steam at a temperature of 95°C, when the atmospheric pressure was 744 mm; the vapour pressure of pure water at this temperature is 634 mm.

The distillate contains 55 per cent by weight of terpinene; calculate its molecular weight.

- (A) 127 (B) 121 (C) 132 (D) 120

9. Which of the following cannot be efficiently steam distilled ?

- (A) ethanol (B) chlorobenzene (C) aniline (D) *o*-nitrophenol

10. Following is the variation of vapour pressure with temperature for (1) water and (2) a substance to be steam distilled. At what temperature will the mixture of water and that substance boil under a pressure of 740 mm Hg?

T(°C)	p_{water}^0 (mm Hg)	$p_{\text{substance}}^0$ (mm Hg)
98	707.27	7.62
98.5	720.15	7.80
99.0	733.24	7.97
99.5	746.52	8.15
100.0	760.00	8.35

- (A) 98.45°C (B) 98.95°C (C) 99.25°C (D) 99.75°C



Answer Key

PHYSICAL CHEMISTRY

DPP No. # 1

- | | | | | | | | |
|-----|---------|-----|---------|----|-----|----|-----|
| 1. | (D) | 2. | (A) | 3. | (D) | 4. | (C) |
| 5.* | (A,B,D) | 6.* | (A,C,D) | 7. | 3 | 8. | (A) |
| 10. | (B) | | | | | 9. | (A) |

Hints & Solutions

PHYSICAL / INORGANIC CHEMISTRY

DPP No. # 1

1. $M = \frac{0.2 \times 3}{\left(\frac{250}{1000}\right)} = 2.4 \text{ M.}$
2. Vapour pressure is depend upon temperature
So at equilibrium, partial pressure of $\text{H}_2\text{O}(\text{g})$ is equal to aqueous tension at that temperature.
3. The vapour pressure of a mixture of two immiscible liquids is the sum of their vapour pressures in the pure states, independent of their relative amounts. Hence, B.Pt. of the mixture will be less than that of either of the liquids, remaining constant throughout.
4. Mole fraction of more volatile substance is greater in vapour phase.
- 5.* Temperature \uparrow , vapour pressure \uparrow .
- 6.* (A) $i = 1 + (n - 1) \alpha$
 $i = 1 + (4 - 1) \cdot 0.8 = 3.4$
(B) For BaCl_2 , $i = 1 + (3 - 1) \times 0.9 = 2.8$
(C) For Na_3PO_4 , $i = 1 + (4 - 1) \times 0.9 = 3.7$
(D) For $\text{K}_4[\text{Fe}(\text{CN})_6]$, $i = 1 + (5 - 1) \times 0.7 = 3.8$
7. $P = X_A P_A^0 + X_B P_B^0 = (P_A^0 - P_B^0) X_A + P_B^0$
So $P_B^0 = 265$
 $P_A^0 - P_B^0 = -130$ $P_A^0 = 135$
 $P_A^0 + P_B^0 = 300.$
 $(P_A^0 + P_B^0) / 100 = 3.$
8. If terpinene is designated by A, and water by B, it follows that at 95°C , the boiling point of the mixture, p_B^0 is 634 mm, and hence p_A^0 is equal to $P - p_B^0$, i.e.,
 $744 - 634 = 110 \text{ mm.}$
now using equation (3), $\frac{55}{45} = \frac{110 \times M_A}{634 \times 18} \Rightarrow M_A = 127$
9. Only immiscible liquids are efficiently steam distilled ethanol dissolves in water.
10. $P_{t^\circ\text{C}} = P_{\text{water}, t^\circ\text{C}}^0 + P_{\text{subs.}, t^\circ\text{C}}^0$
 $P_{t=98.5^\circ\text{C}} = 720.15 + 7.8 = 727.95 \text{ mm of Hg}$
 $P_{t=99^\circ\text{C}} = 733.24 + 7.97 = 741.21 \text{ mm of Hg}$
temp. at which $P_t = 740 \text{ mm of Hg} = 98.5 + \frac{(740 - 727.95)}{(741.21 - 727.95)} \times 0.5 = 98.95^\circ\text{C}.$

