DPP-4 [Ideal & Non-ideal Solution] – SOLUTIONS

Chapter: Solution

"Everyone wants marks. Very few want to sit and solve."

TYPE–1 : Ideal Solution Basics

1. **Among the following that forms an ideal solution?**
   (1) water and methanol
   (2) acetone and ethanol
   (3) benzene and toluene
   (4) water and HCl

Explanation

An **ideal solution** is formed when the solute-solute, solvent-solvent, and solute-solvent interactions are **nearly identical**. This happens when both components have:

- Similar molecular size
- Similar molecular structure
- Similar polarity
- Similar intermolecular forces

Approach

Benzene (C_6H_6) and **Toluene** ($C_6H_5CH_3$) are both non-polar aromatic hydrocarbons with similar structures. They have nearly identical intermolecular forces (London dispersion forces), so they form an ideal solution.

Other options fail because:

- Water + Methanol: H-bonding difference → slight deviation
- Acetone + Ethanol: Different functional groups
- Water + HCl: Ionic interaction → strong negative deviation

Answer

Option (3) benzene and toluene

2. **The mixture of n-hexane and n-heptane is an example of**
   (1) ideal solution
   (2) non-ideal solution
   (3) dilute solution
   (4) none

Explanation

n-Hexane (C_6H_{14}) and **n-Heptane** (C_7H_{16}) are both straight-chain alkanes (saturated hydrocarbons). They have:

- Same type of intermolecular forces (weak van der Waals)
- Similar molecular structure (differ by only one $-CH_2^-$ unit)
- Non-polar nature

Approach

When two liquids have **similar structure and similar intermolecular forces**, they form an ideal solution because:

$$A\text{-}A \approx B\text{-}B \approx A\text{-}B \text{ interactions}$$

This means $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$.

Answer

Option (1) ideal solution

3. **Among the following, that does not form an ideal solution is:**
   (1) C_6H_6 and $C_6H_5CH_3$
   (2) C_2H_5Cl and C_6H_5OH
   (3) C_6H_5Cl and C_6H_5Br
   (4) C_2H_5Br and C_2H_5I

Explanation

For ideal solution formation, both components must have **similar properties**. Let's analyze:

- C_6H_6 (Benzene) + $C_6H_5CH_3$ (Toluene) → Both aromatic, similar
- C_2H_5Cl (Ethyl chloride) + C_6H_5OH (Phenol) → Very different!
- C_6H_5Cl (Chlorobenzene) + C_6H_5Br (Bromobenzene) → Both haloarenes, similar
- C_2H_5Br (Ethyl bromide) + C_2H_5I (Ethyl iodide) → Both haloalkanes, similar

Approach

C_2H_5Cl is a **small polar haloalkane** while C_6H_5OH (phenol) is a **polar aromatic compound with strong H-bonding capability**.

Their intermolecular forces are completely different:

- Ethyl chloride: Dipole-dipole interactions
- Phenol: Strong hydrogen bonding + aromatic interactions

This mismatch leads to **non-ideal behavior**.

Answer

Option (2) C_2H_5Cl and C_6H_5OH

4. **Which condition is not satisfied by an ideal solution**

   (1) $\Delta H_{\text{mixing}} = 0$
   (2) $\Delta V_{\text{mixing}} = 0$
   (3) $\Delta S_{\text{mixing}} = 0$
   (4) Obeyance of Raoult's law

Explanation

Properties of an **Ideal Solution**:

- $\Delta H_{\text{mix}} = 0$ (No heat absorbed or released)
- $\Delta V_{\text{mix}} = 0$ (No volume change)
- Obeys Raoult's Law: $P_A = P_A^\circ \cdot x_A$
- $\Delta S_{\text{mix}} > 0$ (Entropy **increases** due to mixing!)

Approach

Think of it like shuffling two decks of cards together:

- No energy change (cards don't heat up) $\rightarrow \Delta H = 0$
- No size change (same total cards) $\rightarrow \Delta V = 0$
- But **disorder increases** (cards are now mixed!) $\rightarrow \Delta S > 0$

Entropy of mixing is **always positive** because mixing increases randomness.

Answer

Option (3) $\Delta S_{\textbf{mixing}} = 0$

This is **NOT** satisfied because $\Delta S_{\text{mix}} > 0$ (positive) for ideal solutions.

5. **Which one of the following is incorrect for ideal solution?**

   (1) $\Delta P = P_{\text{obs}} - P_{\text{calculated by Raoult's law}} = 0$
   (2) $\Delta G_{\text{mix}} = 0$
   (3) $\Delta H_{\text{mix}} = 0$
   (4) $\Delta U_{\text{mix}} = 0$

Explanation

For ideal solutions:

- $\Delta P = 0 \rightarrow$ Obeys Raoult's law exactly
- $\Delta H_{\text{mix}} = 0 \rightarrow$ No heat change
- $\Delta U_{\text{mix}} = 0 \rightarrow$ No internal energy change
- $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$

Approach

Since $\Delta H_{\text{mix}} = 0$ and $\Delta S_{\text{mix}} > 0$:

$$\Delta G_{\text{mix}} = 0 - T(\text{positive}) = \text{negative}$$

So $\Delta G_{\text{mix}} < 0$ (not zero!)
This makes sense because mixing is a **spontaneous process** (things naturally mix), and spontaneous processes have negative ΔG.

Answer

Option (2) $\Delta G_{\textbf{mix}} = 0$
This is incorrect because $\Delta G_{\text{mix}} < 0$ (negative) for ideal solutions.

6. **For an ideal solution of A and B which statement is incorrect:-**
   (1) The enthalpy change of mixing of A and B is zero
   (2) The volume change of solution A and B is zero
   (3) The intermolecular forces of A and B is same as that of A–A and B–B
   (4) The entropy change of mixture of A and B is zero

Explanation

This is similar to Question 4. For ideal solutions:

- $\Delta H_{\text{mix}} = 0 \rightarrow$ Option (1) is correct
- $\Delta V_{\text{mix}} = 0 \rightarrow$ Option (2) is correct
- $A\text{-}B \approx A\text{-}A \approx B\text{-}B \rightarrow$ Option (3) is correct
- $\Delta S_{\text{mix}} > 0 \rightarrow$ Option (4) is **incorrect**

Approach

Remember the **card shuffling analogy**:
When you mix two liquids, even if they're identical twins chemically, you still create **more disorder** (entropy). The molecules that were once organized in separate containers are now randomly distributed.
$\Delta S_{\text{mix}} = -R(n_A \ln x_A + n_B \ln x_B) > 0$ always!

Answer

Option (4) The entropy change of mixture of A and B is zero

7. **For an ideal solution, the correct option is** [NEET-2019]
   (1) $\Delta_{\text{mix}} S = 0$ at constant T and P
   (2) $\Delta_{\text{mix}} V \neq 0$ at constant T and P
   (3) $\Delta_{\text{mix}} H = 0$ at constant T and P
   (4) $\Delta_{\text{mix}} G = 0$ at constant T and P

Explanation

Let's verify each option for ideal solutions:

- Option (1): $\Delta S_{\text{mix}} = 0$? **NO!** $\Delta S_{\text{mix}} > 0$
- Option (2): $\Delta V_{\text{mix}} \neq 0$? **NO!** $\Delta V_{\text{mix}} = 0$
- Option (3): $\Delta H_{\text{mix}} = 0$? **YES!**
- Option (4): $\Delta G_{\text{mix}} = 0$? **NO!** $\Delta G_{\text{mix}} < 0$

Approach

Quick memory trick for ideal solutions:

"H and V are Zero Heroes, S is Positive, G is Negative"

- $\Delta H = 0$ (Zero)
- $\Delta V = 0$ (Zero)
- $\Delta S > 0$ (Positive - disorder increases)
- $\Delta G < 0$ (Negative - spontaneous mixing)

Answer

Option (3) $\Delta_{\text{mix}} H = 0$ at constant T and P

8. **Which one is not equal to zero for an ideal solution:-**

(1) ΔS_{mix}

(2) ΔV_{mix}

(3) $\Delta P = P_{\text{observed}} - P_{\text{Raoult}}$

(4) ΔH_{mix}

Explanation

For ideal solutions:

- $\Delta S_{\text{mix}} > 0 \rightarrow$ **NOT zero**
- $\Delta V_{\text{mix}} = 0 \rightarrow$ Zero
- $\Delta P = 0 \rightarrow$ Zero (obeys Raoult's law)
- $\Delta H_{\text{mix}} = 0 \rightarrow$ Zero

Approach

Only **entropy of mixing** is non-zero for ideal solutions.
Why? Because when you mix anything, you create disorder. Even if you mix identical balls of two colors, the arrangement becomes more random.

Answer

Option (1) ΔS_{mix}
$\Delta S_{\text{mix}} > 0$ for ideal solutions.

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

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

Explanation

Summary for ideal solutions:

- $\Delta H_{\text{mix}} = 0$ (not less than zero)
- $\Delta V_{\text{mix}} = 0$ (not less than zero)
- $\Delta G_{\text{mix}} < 0$ (negative!)
- $\Delta S_{\text{mix}} > 0$ (positive, not negative)

Approach

Using the Gibbs equation:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

$$\Delta G_{\text{mix}} = 0 - T(\text{positive}) = \text{negative}$$

Mixing is always **spontaneous** (you don't need to force liquids to mix), so $\Delta G < 0$.

Answer

Option (C) ΔG_{mix}
$\Delta G_{\text{mix}} < 0$ because mixing is a spontaneous process.

10. **Which condition is not satisfied by an ideal solution?**
(1) $\Delta_{\text{mix}} H = 0$
(2) $\Delta_{\text{mix}} V = 0$
(3) $\Delta_{\text{mix}} S = 0$
(4) Obeyance to Raoult's Law

Explanation

This is a repeat concept. The key point:
Entropy ALWAYS increases when mixing occurs.
Even for ideal solutions, $\Delta S_{\text{mix}} > 0$ because randomness increases.

Approach

Think of it this way:

- Before mixing: Liquid A in one container, Liquid B in another (organized)
- After mixing: A and B molecules randomly scattered (disordered)

More disorder = More entropy = $\Delta S > 0$

Answer

Option (3) $\Delta_{\textbf{mix}} S = 0$

11. **Which of the following statement about the composition of the vapour over an ideal 1 : 1 molar mixture of benzene and toluene is correct? Assume that the temperature is constant at 25°C. (Given: Vapour Pressure Data at 25°C, benzene = 12.8 kPa, Toluene = 3.85 kPa)**
    (1) The vapour will contain a higher percentage of benzene
    (2) The vapour will contain a higher percentage of toluene
    (3) The vapour will contain equal amounts of benzene and toluene
    (4) Not enough information is given to make a prediction

Explanation

For an ideal solution, using Raoult's Law:

- $P_{\text{benzene}} = P^{\circ}_{\text{benzene}} \times x_{\text{benzene}} = 12.8 \times 0.5 = 6.4$ kPa
- $P_{\text{toluene}} = P^{\circ}_{\text{toluene}} \times x_{\text{toluene}} = 3.85 \times 0.5 = 1.925$ kPa

Approach

In the vapour phase, the mole fraction is proportional to partial pressure:

$$y_{\text{benzene}} = \frac{P_{\text{benzene}}}{P_{\text{total}}} = \frac{6.4}{6.4 + 1.925} = \frac{6.4}{8.325} = 0.77$$

Since benzene has **higher vapour pressure**, it evaporates more readily.
Rule: The component with higher vapour pressure will have a higher percentage in the vapour phase.

Answer

Option (1) The vapour will contain a higher percentage of benzene
Benzene (12.8 kPa) has higher VP than Toluene (3.85 kPa), so benzene dominates the vapour.

TYPE–2 : Non-ideal Solution & Deviations

1. **If solute-solvent interactions are more than solute-solute and solvent-solvent interactions then**
    (1) It is ideal solution
    (2) It is non-ideal solution with positive deviation
    (3) It is non-ideal solution with negative deviation
    (4) None of these

Explanation

Types of deviations:

- **Ideal:** A-B = A-A = B-B (all forces equal)
- **Positive deviation:** A-B < A-A and B-B (weaker new bonds)
- **Negative deviation:** A-B > A-A and B-B (stronger new bonds)

Approach

Think of it like friendships:

- **Positive deviation:** A and B don't like each other much → they want to escape (higher VP)
- **Negative deviation:** A and B become best friends → they want to stay together (lower VP)

When solute-solvent interactions are **stronger**, molecules hold each other tightly → fewer escape to vapour → **lower vapour pressure** → **negative deviation**.

Answer

Option (3) It is non-ideal solution with negative deviation

2. **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

Explanation

When H_2SO_4 dissolves in water:

- Strong **ion-dipole interactions** form between H^+/SO_4^{2-} and water
- **Hydrogen bonding** increases significantly
- The reaction is highly **exothermic** (releases heat)

Approach

$H_2SO_4 + H_2O$ forms very strong interactions:

$$H_2SO_4 \longrightarrow {}_2H^+ + SO_4^{2-}$$

These ions are heavily hydrated by water molecules. The A-B interaction is much stronger than A-A or B-B.

Strong new bonds → Molecules don't want to escape → Lower VP → **Negative deviation**

Answer

Option (A) Negative deviations from Raoult's law

3. **On mixing 10 mL of acetone with 40 mL of chloroform, the total volume of the solution is**
   (1) < 50 mL
   (2) > 50 mL
   (3) $= 50$ mL
   (4) Cannot be predicted

Explanation

Acetone (CH_3COCH_3) and Chloroform ($CHCl_3$) form a **hydrogen bond**:

$$CHCl_3 — H \cdots O{=}C(CH_3)_2$$

The slightly acidic H of $CHCl_3$ forms H-bond with the carbonyl oxygen of acetone.

Approach

Since A-B interactions are **stronger** than A-A and B-B:

- Molecules come **closer together**
- Volume **decreases** ($\Delta V_{\text{mix}} < 0$)
- This is **negative deviation**

Real volume = 10 + 40 - (some shrinkage) < 50 mL

Answer

Option (1) < 50 **mL**

Acetone + Chloroform shows negative deviation → Volume contracts.

4. **On mixing 10 ml of ethanol with 10 ml of benzene the total volume of the solution is**
   (1) > 20 ml
   (2) < 20 ml
   (3) $= 20$ ml
   (4) Can't be predicted

Explanation

Ethanol (C_2H_5OH) has **strong hydrogen bonding** within itself.

Benzene (C_6H_6) is **non-polar** with no H-bonding capability.

When mixed, ethanol's H-bonds are **broken** but no new strong bonds form with benzene.

Approach

This is **positive deviation**:

- Original ethanol H-bonds (strong) are broken
- New ethanol-benzene interactions (weak) form
- Net: A-B $<$ A-A and B-B
- Molecules move **apart** → Volume **increases**

$\Delta V_{\text{mix}} > 0 \rightarrow$ Total volume > 20 ml

Answer

Option (1) > 20 ml
Ethanol + Benzene shows positive deviation → Volume expands.

5. **Which of the following is correct for a solution showing positive deviation from Raoult's law?**
   (1) $\Delta V_{\text{mix}} > 0$, $\Delta H_{\text{mix}} > 0$
   (2) $\Delta V_{\text{mix}} < 0$, $\Delta H_{\text{mix}} < 0$
   (3) $\Delta V_{\text{mix}} = 0$, $\Delta H_{\text{mix}} = 0$
   (4) $\Delta V_{\text{mix}} > 0$, $\Delta H_{\text{mix}} < 0$

Explanation

Positive Deviation Properties:

Property	**Positive Dev.**	**Negative Dev.**
A-B vs A-A, B-B	Weaker	Stronger
ΔH_{mix}	> 0 (endothermic)	< 0 (exothermic)
ΔV_{mix}	> 0 (expansion)	< 0 (contraction)
Vapour Pressure	Higher than expected	Lower than expected
Boiling Point	Lower (min. BP azeotrope)	Higher (max. BP azeotrope)

Approach

For **positive deviation**:

- Weaker A-B bonds → molecules escape easily → need energy to break original bonds
- $\Delta H_{\text{mix}} > 0$ (heat absorbed - endothermic)
- Molecules spread out → $\Delta V_{\text{mix}} > 0$ (volume increases)

Answer

Option (1) $\Delta V_{\text{mix}} > 0$, $\Delta H_{\text{mix}} > 0$

6. **Which of the following is correct about a solution showing positive deviation?**
   (1) Vapour pressure observed will be the less than that calculated from Raoult's law
   (2) Minimum boiling azeotrope will be formed
   (3) $\Delta H_{\text{mix}} < 0$
   (4) $\Delta V_{\text{mix}} < 0$

Explanation

For **positive deviation**:

- VP observed > VP calculated → Option (1) is wrong
- Minimum boiling azeotrope forms → Option (2) is **correct**
- $\Delta H_{\text{mix}} > 0$ → Option (3) is wrong
- $\Delta V_{\text{mix}} > 0$ → Option (4) is wrong

Approach

Azeotrope connection:

- **Positive deviation** → Higher VP → Easier to boil → **Minimum boiling point** azeotrope
- **Negative deviation** → Lower VP → Harder to boil → **Maximum boiling point** azeotrope

Example: Ethanol-Water forms minimum boiling azeotrope at 78.1°C.

Answer

Option (2) Minimum boiling azeotrope will be formed

7. **Which of the following mixture will show positive deviation from ideal behaviour?**
   (1) $H_2O + C_2H_5OH$
   (2) $H_2O + HNO_3$
   (3) $CHCl_3 + CH_3COCH_3$
   (4) All of these

Explanation

Let's analyze each:

- $H_2O + C_2H_5OH$: Water H-bonds break, weaker new bonds → **Positive**
- $H_2O + HNO_3$: Strong ion formation → **Negative**
- $CHCl_3 + CH_3COCH_3$: New H-bond forms → **Negative**

Approach

Only **Water + Ethanol** shows positive deviation because:

- Both have strong H-bonding individually
- When mixed, some H-bonds are disrupted
- The ethanol-water H-bond is weaker than water-water H-bond
- Net result: weaker interactions → positive deviation

Answer

Option (1) $H_2O + C_2H_5OH$

8. **A mixture of liquid showing positive deviation in Raoult's law is:-**
   (1) $(CH_3)_2CO + C_2H_5OH$
   (2) $(CH_3)_2CO + CHCl_3$
   (3) $(C_2H_5)_2O + CHCl_3$
   (4) $(CH_3)_2CO + C_6H_5NH_2$

Explanation

- Acetone + Ethanol: Both polar, some H-bond breaking → **Positive**
- Acetone + Chloroform: New H-bond forms → **Negative**
- Ether + Chloroform: New H-bond forms → **Negative**
- Acetone + Aniline: Both polar, interact well → Nearly ideal/slight negative

Approach

Acetone + Ethanol shows positive deviation because:

- Ethanol has strong O-H$\cdots$O hydrogen bonding
- Acetone disrupts this H-bonding network
- New acetone-ethanol interaction is weaker
- Result: A-B $<$ A-A, B-B → Positive deviation

Answer

Option (1) $(CH_3)_2CO + C_2H_5OH$ (Acetone + Ethanol)

9. **Which of the following mixtures will show positive deviation from ideal behaviour?**
   (1) H_2O and HNO_3
   (2) H_2O and C_2H_5OH
   (3) $CHCl_3$ and CH_3COCH_3
   (4) n-hexane and n-heptane

Explanation

Analysis:

- $H_2O + HNO_3$: Strong ionic interactions → **Negative**
- $H_2O + C_2H_5OH$: H-bond disruption → **Positive**
- $CHCl_3$ + Acetone: New H-bond → **Negative**
- n-hexane + n-heptane: Similar molecules → **Ideal**

Approach

Remember the pattern:

- **Alcohol + Non-polar/weakly polar** → Usually positive deviation
- **Acid + Water** → Usually negative deviation (ionic interaction)
- **Similar alkanes** → Ideal solution

Answer

Option (2) H_2O and C_2H_5OH

10. **Which of the following statements is correct regarding a solution of two components A and B exhibiting positive deviation from ideal behaviour?** [NEET-2019 (Odisha)]
   (1) Intermolecular attractive forces between A-A and B-B are equal to those between A-B

(2) Intermolecular attractive forces between A-A and B-B are stronger than those between A-B
(3) $\Delta_{\text{mix}}H = 0$ at constant T and P
(4) $\Delta_{\text{mix}}V = 0$ at constant T and P

Explanation

For **positive deviation**:

- A-B interactions are **weaker** than A-A and B-B
- This means A-A and B-B are **stronger** than A-B

Approach

Think of it as:

- A molecules prefer to be with A (strong A-A)
- B molecules prefer to be with B (strong B-B)
- A and B don't like each other much (weak A-B)
- So they try to escape → Higher VP → Positive deviation

Answer

Option (2) Intermolecular attractive forces between A-A and B-B are stronger than those between A-B

11. **A solution of acetone in ethanol**

(1) shows a positive deviation from Raoult's law
(2) behaves like a near ideal solution
(3) Obeys Raoult's law
(4) shows a negative deviation from Raoult's law

Explanation

Acetone (CH_3COCH_3) and Ethanol (C_2H_5OH):

- Ethanol has strong O-H hydrogen bonding
- Acetone can only accept H-bonds (C=O), cannot donate
- When mixed, ethanol's H-bonding network is disrupted

Approach

The new acetone-ethanol interactions are **weaker** than original ethanol-ethanol H-bonds:

- Ethanol-Ethanol: O-H$\cdots$O-H (strong)
- Acetone-Ethanol: O-H$\cdots$O=C (weaker)

Result: Positive deviation

Answer

Option (1) shows a positive deviation from Raoult's law

12. **Which of the following liquid pairs show a positive deviation from Raoult's law?** [NCERT Pg. 47]
  (1) Water – Hydrochloric acid
  (2) Ether – Chloroform
  (3) Water – Nitric acid
  (4) Benzene – Acetone

Explanation

Analysis:

- Water + HCl: Strong ionic interaction → **Negative**
- Ether + $CHCl_3$: H-bond formation → **Negative**
- Water + HNO_3: Strong ionic interaction → **Negative**
- Benzene + Acetone: Polar + Non-polar mismatch → **Positive**

Approach

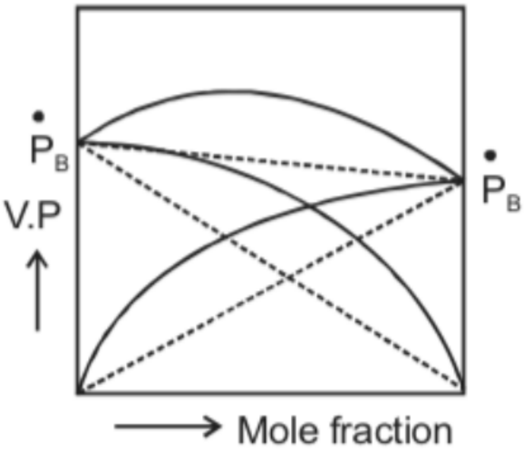
Benzene (non-polar) and **Acetone** (polar):

- Benzene: Only has weak London dispersion forces
- Acetone: Has dipole-dipole interactions
- When mixed: The interactions don't match well
- A-B < A-A and B-B → Positive deviation

Answer

Option (4) Benzene – Acetone

13. **The graph plotted vapour pressure vs mole fraction is the graph for which of the following example**



  (1) Hexane and Heptane
  (2) Ethyl bromide and Ethyl chloride
  (3) Ethanol and Water
  (4) Chloroform and Acetone

Explanation

The graph shows curves **above** the ideal straight line (dashed), indicating **positive deviation**. The VP is higher than expected from Raoult's law.

Approach

From the options:

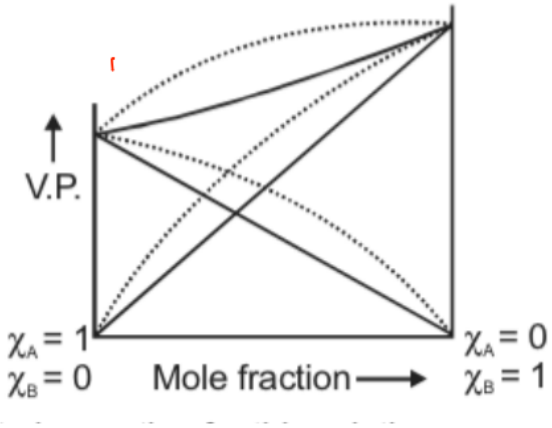
- Hexane + Heptane → Ideal (similar alkanes)
- Ethyl bromide + Ethyl chloride → Nearly ideal (similar halides)
- Ethanol + Water → **Positive deviation**
- Chloroform + Acetone → Negative deviation

Only Ethanol-Water shows positive deviation (curve above ideal line).

Answer

Option (3) Ethanol and Water

14. **Vapour phase diagram for a solution is given below if dotted line represents deviation**



Correct observation for this solution

(1) ΔH_{mix} : +ve
(2) ΔS_{mix} : +ve
(3) ΔV_{mix} : +ve
(4) All of these

Explanation

The graph shows the actual curve **above** the ideal line, indicating **positive deviation**.
For positive deviation:

- $\Delta H_{\text{mix}} > 0$ (endothermic)
- $\Delta S_{\text{mix}} > 0$ (always positive for mixing)
- $\Delta V_{\text{mix}} > 0$ (expansion)

Approach

All three conditions are satisfied for positive deviation:

- Heat is absorbed ($\Delta H > 0$) because bonds are broken
- Volume increases ($\Delta V > 0$) because molecules spread out
- Entropy increases ($\Delta S > 0$) - this is true for ANY mixing!

Answer

Option (4) All of these

TYPE–3 : JEE Main & Advanced PYQs

1. **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, 4/144]
   (1) The solution is non-ideal, showing +ve deviation from Raoult's Law.
   (2) The solution in non-ideal, showing –ve deviation from Raoult's Law.
   (3) n-heptane shows +ve deviation while ethanol shows –ve deviation from Raoult's Law.
   (4) The solution formed is an ideal solution.

Explanation

n-Heptane (C_7H_{16}): Non-polar alkane with only London dispersion forces
Ethanol (C_2H_5OH): Polar with strong hydrogen bonding
These are very different molecules!

Approach

When mixed:

- Ethanol's H-bonds are broken (needs energy)
- n-Heptane cannot form H-bonds with ethanol
- New A-B interactions are much weaker than original A-A, B-B
- Result: **Positive deviation**

Note: Option (3) is wrong because deviation is a property of the **solution**, not individual components.

Answer

Option (1) The solution is non-ideal, showing +ve deviation from Raoult's Law.

2. **For an ideal solution of two components A and B, which of the following is true?** [JEE(Main) 2014 Online (19-04-14), 4/120]
   (1) $\Delta H_{\text{mixing}} < 0$ (zero)
   (2) $\Delta H_{\text{mixing}} > 0$ (zero)
   (3) A–B interaction is stronger than A–A and B–B interactions

(4) A–A, B–B and A–B interactions are identical

Explanation

For an **ideal solution**, the fundamental condition is:
A-A = B-B = A-B interactions
When all intermolecular forces are equal, there's no preference for any particular interaction.

Approach

Think of it like this:

- If A likes A as much as it likes B
- And B likes B as much as it likes A
- Then mixing doesn't change anything energetically
- Result: $\Delta H = 0$, $\Delta V = 0$, Obeys Raoult's law

Answer

Option (4) A–A, B–B and A–B interactions are identical

3. **Total vapour pressure of mixture of 1 mol of volatile component A ($p^\circ_A = 100$ mmHg) and 3 mol of volatile component B ($p^\circ_B = 60$ mmHg) is 75 mm. For such case:**
   (1) there is positive deviation from Raoult's law
   (2) boiling point has been lowered
   (3) force of attraction between A and B is smaller than that between A and A or between B and B
   (4) all the above statements are correct

Explanation

First, let's calculate the **expected** VP using Raoult's law:

- $x_A = \frac{1}{1+3} = 0.25$
- $x_B = \frac{3}{4} = 0.75$
- $P_{\text{ideal}} = P^\circ_A \cdot x_A + P^\circ_B \cdot x_B$
- $P_{\text{ideal}} = 100(0.25) + 60(0.75) = 25 + 45 = 70$ mmHg

Approach

Comparison:

- $P_{\text{observed}} = 75$ mmHg
- $P_{\text{ideal}} = 70$ mmHg
- $P_{\text{obs}} > P_{\text{ideal}} \rightarrow$ **Positive deviation**

For positive deviation:

- A-B < A-A and B-B
- Higher VP → Lower boiling point
- All statements are correct

Answer

Option (4) all the above statements are correct

4. **Which characterises the weak intermolecular forces of attraction in a liquid?**
   (1) High boiling point
   (2) High vapour pressure
   (3) High critical temperature
   (4) High heat of vaporization

Explanation

Weak intermolecular forces mean molecules don't hold each other strongly.
Effects:

- Easy to escape to gas phase → **High vapour pressure**
- Easy to boil → Low boiling point
- Low critical temperature
- Low heat of vaporization

Approach

Think of a crowded room:

- Strong forces = People holding hands tightly → Hard to leave → Low VP
- Weak forces = People barely touching → Easy to leave → High VP

High BP, high critical temp, high heat of vaporization all indicate **strong** forces.

Answer

Option (2) High vapour pressure

5. **Which of the following liquid pairs shows a positive deviation from Raoult's law?**
   (1) Acetone – chloroform
   (2) Benzene – methanol
   (3) Water – nitric acid
   (4) Water – hydrochloric acid

Explanation

Analysis:

- Acetone + Chloroform: H-bond forms → **Negative**
- Benzene + Methanol: Non-polar + H-bonding liquid → **Positive**
- Water + HNO_3: Strong ionic → **Negative**
- Water + HCl: Strong ionic → **Negative**

Approach

Benzene (non-polar) + **Methanol** (polar, H-bonding):

- Methanol's H-bonds are broken
- Benzene can't form H-bonds
- Weaker A-B interaction → Positive deviation

This is similar to ethanol + benzene case.

Answer

Option (2) Benzene – methanol

6. **Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are):** [JEE(Advanced) 2013, 4/120]
   (A) ΔG is positive
   (B) ΔS_{system} is positive
   (C) $\Delta S_{\text{surroundings}} = 0$
   (D) $\Delta H = 0$

Explanation

For an **ideal solution**:

- $\Delta H_{\text{mix}} = 0 \rightarrow$ Option (D) is **correct**
- $\Delta S_{\text{mix}} > 0 \rightarrow$ Option (B) is **correct**
- $\Delta G_{\text{mix}} < 0 \rightarrow$ Option (A) is wrong
- Since $\Delta H = 0$, no heat exchange with surroundings $\rightarrow \Delta S_{\text{surr}} = 0$

Approach

For surroundings: $\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T}$
Since $\Delta H_{\text{sys}} = 0$ for ideal solution:

$$\Delta S_{\text{surr}} = -\frac{0}{T} = 0$$

This is a multi-correct question. Correct options are B, C, and D.

Answer

Options (B), (C), and (D) are correct

- (B) $\Delta S_{\text{system}} > 0$
- (C) $\Delta S_{\text{surroundings}} = 0$
- (D) $\Delta H = 0$

7. **Mixture(s) showing positive deviation from Raoult's law at 35°C is(are)** [JEE(Advanced) 2016, 4/124]
   (A) carbon tetrachloride + methanol

(B) carbon disulphide + acetone
(C) benzene + toluene
(D) phenol + aniline

Explanation

Analysis of each:

- CCl_4 + CH_3OH: Non-polar + H-bonding → **Positive**
- CS_2 + Acetone: Non-polar + polar → **Positive**
- Benzene + Toluene: Similar aromatics → **Ideal**
- Phenol + Aniline: Both can H-bond, form new H-bonds → **Negative**

Approach

Pattern recognition:

- **Non-polar + Polar/H-bonding** → Usually positive deviation
- **Similar molecules** → Ideal
- **New H-bond formation possible** → Negative deviation

Phenol-Aniline can form intermolecular H-bond between OH and NH_2 groups.

Answer

Options (A) and (B) are correct

- (A) CCl_4 + methanol
- (B) CS_2 + acetone

8. **100 ml of liquid A and 25 ml of liquid B is mixed to give a solution which does not obey Raoult's law. The volume of the solution**

(1) Will be 125 ml
(2) Can be > or < than 125 ml
(3) Can be >, = or < than 125 ml
(4) Will be less than 125 ml

Explanation

The solution **does not obey Raoult's law**, meaning it's a **non-ideal solution**.

Non-ideal solutions can show:

- **Positive deviation**: $\Delta V > 0$ → Volume > 125 ml
- **Negative deviation**: $\Delta V < 0$ → Volume < 125 ml

Approach

Since we only know it's non-ideal (doesn't obey Raoult's law), but we don't know **which type** of deviation:

- Could be positive → V > 125 ml
- Could be negative → V < 125 ml

We cannot predict the exact outcome without knowing the specific liquids.

Answer

Option (2) Can be $>$ or $<$ than 125 ml

(Note: It cannot be exactly 125 ml because that would mean $\Delta V = 0$, which is for ideal solutions)

TYPE–4 : Numerical & Calculation Based

1. **The vapour pressure of the solution of two liquids A($p^\circ = 80$ mm) and B($p^\circ = 120$ 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.

Explanation

Calculate ideal VP using Raoult's law:

$$
\begin{aligned}
x_A &= 0.4, \quad x_B = 0.6 \\
P_{\text{ideal}} &= P_A^\circ \cdot x_A + P_B^\circ \cdot x_B \\
P_{\text{ideal}} &= 80(0.4) + 120(0.6) \\
P_{\text{ideal}} &= 32 + 72 = 104 \text{ mm}
\end{aligned}
$$

Approach

Comparison:

- $P_{\text{observed}} = 100$ mm
- $P_{\text{ideal}} = 104$ mm
- $P_{\text{obs}} < P_{\text{ideal}}$

Lower observed VP than expected → **Negative deviation**

(Molecules are held more tightly than expected → fewer escape)

Answer

Option (C) solution shows negative deviations

2. **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) $nC_6H_{14} - nC_7H_{16}$

Explanation

Calculate ideal VP:

$$x_A = 0.4, \quad x_B = 0.6$$
$$P_{\text{ideal}} = 300(0.4) + 800(0.6)$$
$$P_{\text{ideal}} = 120 + 480 = 600 \text{ torr}$$

Approach

Comparison:

- $P_{\text{obs}} = 580$ torr
- $P_{\text{ideal}} = 600$ torr
- $P_{\text{obs}} < P_{\text{ideal}} \rightarrow$ **Negative deviation**

Which pair shows negative deviation?

- (A) $CHCl_3$ + Acetone: Forms H-bond → **Negative**
- (B) Chlorobenzene + Bromobenzene → Ideal
- (C) Benzene + Toluene → Ideal
- (D) n-hexane + n-heptane → Ideal

Answer

Option (A) $CHCl_3 - CH_3COCH_3$ (Chloroform – Acetone)

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

Explanation

Given: $x_B = 0.92$, $x_A = 0.08$

Calculate ideal VP:

$$P_{\text{ideal}} = 300(0.08) + 800(0.92)$$
$$P_{\text{ideal}} = 24 + 736 = 760 \text{ torr} = 1 \text{ atm}$$

Observed: $P_{\text{obs}} = 0.95 \text{ atm} = 722 \text{ torr}$

Approach

$P_{\text{obs}}(722) < P_{\text{ideal}}(760) \rightarrow$ **Negative deviation**

For negative deviation:

- $\Delta H_{\text{mix}} < 0$ (exothermic - heat released)
- $\Delta V_{\text{mix}} < 0$ (volume decreases)

Options (C) and (D) are for ideal solutions. Option (A) is for positive deviation.

Answer

Option (B) $\Delta H_{\textbf{mix}} < 0$

4. **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

Explanation

Given: Dissolution is **endothermic** $\rightarrow \Delta H > 0$ (positive)

When KCl dissolves:

- KCl(s) $\longrightarrow$ K≡(aq) + Cl−(aq)
- Solid (ordered) → Ions in solution (disordered)
- Entropy **increases** $\rightarrow \Delta S > 0$

Approach

Since dissolution **occurs spontaneously**:

- $\Delta G < 0$ (negative) for spontaneous process

This is possible because even though $\Delta H > 0$:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (+) - T(+) = (+) - (+)$$

If $T\Delta S > \Delta H$, then $\Delta G < 0$

This is an **entropy-driven** process!

Answer

Option (C) $\boldsymbol{\Delta H = +}$ **ve,** $\boldsymbol{\Delta S = +}$ **ve,** $\boldsymbol{\Delta G = -}$ **ve**

5. **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.

Explanation

Dissolution involves two steps:

(a) **Breaking bonds** (endothermic - needs energy):
  - Break solute-solute bonds
  - Break solvent-solvent bonds

(b) **Solvation** (exothermic - releases energy):
  - Form solute-solvent bonds

Approach

$\Delta H_{\text{dissolution}} = \text{Energy to break bonds} - \text{Energy from solvation}$

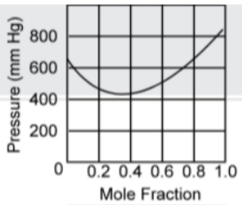
For **exothermic** dissolution ($\Delta H < 0$):

- Energy released in solvation > Energy used in breaking bonds
- More energy comes out than goes in
- Net: Heat is released

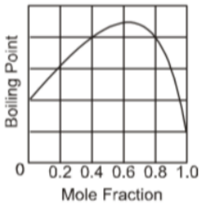
Answer

Option (A) The energy released in solvation exceeds the energy used in breaking up solute-solute and solvent-solvent interactions.

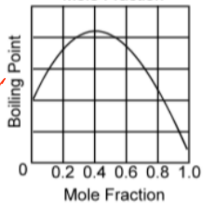
6. **Given P-x curve for a non-ideal liquid mixture (Fig.). Identify the correct T-x curve for the same mixture.**



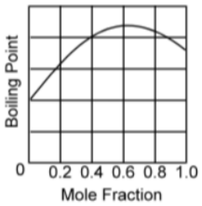
(A)



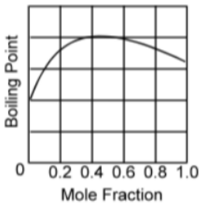
[✓ (B)]



(C)



(D)



Explanation

The P-x curve shows a **minimum** (curve bulges downward), indicating **negative deviation**.
Properties of negative deviation:

- lower VP than expected
- Higher boiling point than expected
- Forms **maximum boiling azeotrope**

Approach

Key relationship:

- P-x curve shows **minimum** → negative deviation
- T-x curve will show **maximum** → Maximum boiling azeotrope

Why? lower VP means molecules escape hardly → Higher temperature needed to boil.
Inverse relationship: Minimum in P-x → Maximum in T-x (and vice versa)

Answer

Option (B) - The curve showing maximum boiling point
(Maximum boiling azeotrope corresponds to negative deviation)

— END OF SOLUTIONS —

Keep practicing! Every problem solved is a step closer to success.