DPP–5 [Azeotropes] – SOLUTIONS

Chapter: Solution

"No one fails because the paper is tough. They fail because preparation was weak."

1. **An azeotropic mixture of two liquids has b.p. lower than either of them when it :-**

   (1) shows a (+ve) deviation from Raoult's law

   (2) shows no deviation from Raoult's law

   (3) shows (+ve) deviation from Henry's law

   (4) shows (–ve) deviation from Henry's law

Explanation

Azeotropes are constant boiling mixtures that cannot be separated by simple distillation.

Two types of azeotropes:

- **Minimum boiling azeotrope**: BP lower than both components → Positive deviation
- **Maximum boiling azeotrope**: BP higher than both components → Negative deviation

Approach

Think of it like a party:

- **Positive deviation**: A and B don't like each other → They want to escape quickly → Easier to boil → **Lower boiling point**
- **Negative deviation**: A and B love each other → They want to stay together → Harder to boil → **Higher boiling point**

Lower BP than both components = Minimum boiling azeotrope = Positive deviation

Answer

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

2. **Azeotropic mixture are :**

   (1) Mixture of two solids

   (2) Those which boil at different temperatures

   (3) Those which can be fractionally distilled

   (4) Constant boiling mixtures

Explanation

The word **"Azeotrope"** comes from Greek:

- *a* = no/without
- *zeo* = boil
- *tropos* = change

Meaning: "No change on boiling" — the composition remains constant during boiling.

Approach

Key properties of azeotropes:

- They are **liquid mixtures** (not solids)
- They boil at a **constant temperature** (not different temperatures)
- They **cannot** be separated by fractional distillation
- The vapour has the **same composition** as the liquid

That's why they're called "constant boiling mixtures"!

Answer

Option (4) Constant boiling mixtures

3. **An azeotropic mixture of two liquids boil at a lower temperature than either of them when**

(1) It is saturated
(2) It does not deviate from Raoult's law
(3) It shows negative deviation from Raoult's law
(4) It shows positive deviation from Raoult's law

Explanation

This is the same concept as Question 1.

Minimum boiling azeotrope characteristics:

- Boiling point **lower** than both pure components
- Shows **positive deviation** from Raoult's law
- Vapour pressure **higher** than expected
- A-B interactions are **weaker** than A-A and B-B

Approach

Memory trick:

Property	Positive Dev.	Negative Dev.
Vapour Pressure	Higher ↑	Lower ↓
Boiling Point	Lower ↓	Higher ↑
Azeotrope type	Minimum BP	Maximum BP

VP and BP are **inversely related**!

Answer

Option (4) It shows positive deviation from Raoult's law

4. **The azeotropic mixture of water (B.P 100.15°C) and HCl (B.P. –85°C) boils at 108.5°C. When this mixture is distilled, it is possible to obtain :**
   (1) Pure HCl
   (2) Pure water
   (3) Pure water as well as HCl
   (4) Neither HCl nor H_2O in their pure states

Explanation

Given data:

- BP of water = 100.15°C
- BP of HCl = –85°C
- BP of azeotrope = 108.5°C

Since 108.5°C > 100.15°C > –85°C, the azeotrope boils at a **higher temperature** than both components.

This is a **Maximum boiling azeotrope**!

Approach

Key property of azeotropes:

An azeotrope **cannot be separated** by simple or fractional distillation because the vapour has the same composition as the liquid.

When you try to distill:

- The mixture boils together at constant temperature
- Both components come out together in fixed ratio
- You can NEVER get pure components by distillation

It's like trying to separate best friends who always go everywhere together!

Answer

Option (4) Neither HCl nor H_2O in their pure states

Azeotropes cannot be separated by distillation.

5. **Minimum boiling azeotropes and Maximum boiling azeotropes respectively on the examples of**
   (1) Non-ideal solution following +ve deviation and ideal solution
   (2) Ideal solution and non-ideal solution following negative deviation
   (3) Both are ideal solution
   (4) Non-ideal solution showing positive deviation and Non-ideal solution showing negative deviation

Explanation

Both types of azeotropes are non-ideal solutions!

- **Minimum boiling azeotrope** → Positive deviation → Non-ideal
- **Maximum boiling azeotrope** → Negative deviation → Non-ideal

Ideal solutions **NEVER** form azeotropes because they follow Raoult's law perfectly.

Approach

Classification:

Azeotrope Type	Deviation	Example
Minimum BP	Positive (+ve)	Ethanol + Water
Maximum BP	Negative (–ve)	HCl + Water

Both are **non-ideal** solutions. Ideal solutions (like benzene + toluene) don't form azeotropes.

Answer

Option (4) Non-ideal solution showing positive deviation and Non-ideal solution showing negative deviation

6. **The mixture that forms maximum boiling azeotrope is** [NEET-2019]

(1) Water + Nitric acid
(2) Ethanol + Water
(3) Acetone + Carbon disulphide
(4) Heptane + Octane

Explanation

Maximum boiling azeotrope forms when:

- Solution shows **negative deviation**
- A-B interactions are **stronger** than A-A and B-B
- Usually involves **new bond formation** (like H-bonding)

Approach

Let's analyze each option:

- **Water + HNO_3**: Strong ionic/H-bond interaction → **Negative deviation** → Maximum BP azeotrope
- **Ethanol + Water**: H-bond disruption → Positive deviation → Minimum BP azeotrope
- **Acetone + CS_2**: Non-polar + polar mismatch → Positive deviation
- **Heptane + Octane**: Similar alkanes → **Ideal solution** (no azeotrope)

Water + HNO_3 forms very strong interactions (like H_2O + HCl).

Answer

Option (1) Water + Nitric acid

Forms maximum boiling azeotrope at 120.5°C (68% HNO_3)

7. **Consider the following statement**

I. If one component in a binary solution shows positive deviation, the second component would also show positive deviation.

II. The gases which are easily liquefied, are more soluble in common solvents.

III. Maximum boiling azeotrope is formed by positive deviation.

Choose the correct statement

(1) I & III

(2) II & III

(3) I & II

(4) I, II & III

Explanation

Let's verify each statement:

Statement I: If one component shows positive deviation, the other also shows positive deviation.

- **TRUE** — Deviation is a property of the **solution**, not individual components. Both components in the same solution show the same type of deviation.

Statement II: Gases which are easily liquefied are more soluble.

- **TRUE** — Easily liquefied gases (like NH_3, CO_2, SO_2) have stronger intermolecular forces, making them more soluble in solvents.

Statement III: Maximum boiling azeotrope is formed by positive deviation.

- **FALSE** — Maximum BP azeotrope is formed by **negative deviation**, not positive!

Approach

Why Statement I is true:

Deviation depends on the interaction between A and B molecules. If A-B interaction is weaker than average of A-A and B-B, BOTH components will have higher vapour pressure than expected.

It's like saying "if the room is hot, everyone feels hot" — it's a property of the environment, not individuals.

Why Statement II is true:

Gases that liquefy easily → Strong intermolecular forces → Can interact well with solvent molecules → Higher solubility

Example: NH_3 is highly soluble in water; H_2 is almost insoluble.

Answer

Option (3) I & II

Statement III is wrong (Maximum BP azeotrope → Negative deviation)

8. **The boiling point of an azeotropic mixture of water and ethyl alcohol is less than that of theoretical value of water and alcohol mixture. Mixture shows**

(1) Solution is highly saturated

(2) Positive deviation from Raoult's law

(3) Negative deviation from Raoult's law
(4) Nothing can be said

Explanation

Given information:

- BP of azeotrope < BP of water (100°C)
- BP of azeotrope < BP of ethanol (78.4°C)
- Actually, ethanol-water azeotrope boils at 78.1°C

This is a **Minimum boiling azeotrope**.

Approach

Ethanol-Water system:

- Both have strong H-bonding individually
- When mixed, H-bonding network is disrupted
- New ethanol-water interaction is weaker than original bonds
- Result: **Positive deviation**

Connection:

Lower BP than expected → Higher VP than expected → Positive deviation

The 95.6% ethanol + 4.4% water azeotrope is why you can't make 100% pure ethanol by distillation!

Answer

Option (2) Positive deviation from Raoult's law

9. **A mixture of two liquids A and B having boiling point of A is 70°C, and boiling point of B is 100°C, distills at 101.2°C as single liquid, hence this mixture is** [NSEC-2002]

(1) Ideal solution
(2) Non ideal solution showing +ve deviation
(3) Non ideal solution showing –ve deviation
(4) Immiscible solution

Explanation

Given data:

- BP of A = 70°C
- BP of B = 100°C
- BP of mixture = 101.2°C

The mixture boils at 101.2°C, which is **higher than both** components!

This is a **Maximum boiling azeotrope**.

Approach

Analysis:

- $BP_{mixture}$ (101.2°C) > BP_A (70°C)
- $BP_{mixture}$ (101.2°C) > BP_B (100°C)

Higher boiling point means:

- Molecules are held more tightly
- Stronger A-B interactions
- Lower vapour pressure than expected
- **Negative deviation** from Raoult's law

Also, it "distills as single liquid" confirms it's an azeotrope.

Answer

Option (3) Non ideal solution showing –ve deviation

10. **Azeotropes are :**

(A) liquid mixtures which distil unchanged in composition

(B) liquids which can mix with each other in all proportions

(C) solids which form solid solutions of definite compositions

(D) gases which can be separated

Explanation

Definition of Azeotrope:

An azeotrope is a mixture of two or more liquids whose proportions **cannot be altered** by simple distillation.

When an azeotrope boils:

- The vapour has the **same composition** as the liquid
- The mixture behaves like a **single pure compound**
- Composition remains **unchanged** during distillation

Approach

Let's eliminate wrong options:

- (B) "mix in all proportions" — This describes **miscible liquids**, not specifically azeotropes
- (C) "solids" — Azeotropes are **liquid** mixtures
- (D) "gases" — Azeotropes are **liquid** mixtures

Only (A) correctly describes the key property: unchanged composition during distillation.

Answer

Option (A) liquid mixtures which distil unchanged in composition

11. **Which of the following azeotropic solutions has the boiling point more than boiling**

point of the constituents A and B ?

(1) CH_3CH_2OH and CH_3COCH_3
(2) CS_2 and CH_3COCH_3
(3) $CHCl_3$ and CH_3COCH_3
(4) CH_3CHO and CS_2

Explanation

We need to find a **Maximum boiling azeotrope**, which forms due to **negative deviation**. Negative deviation occurs when A-B interactions are **stronger** than A-A and B-B interactions. This typically happens when **new hydrogen bonds** form between the components.

Approach

Let's analyze each pair:

(1) Ethanol + Acetone:
- Ethanol has H-bonding, acetone disrupts it
- **Positive deviation** (Minimum BP azeotrope)

(2) CS_2 + Acetone:
- CS_2 is non-polar, acetone is polar
- **Positive deviation** (Minimum BP azeotrope)

(3) $CHCl_3$ + Acetone:
- $CHCl_3$ has acidic H, acetone has C=O (H-bond acceptor)
- **NEW H-bond forms:** $Cl_3C–H \cdots O=C(CH_3)_2$
- **Negative deviation** (Maximum BP azeotrope)

(4) Acetaldehyde + CS_2:
- Different polarities, no new strong bonds
- **Positive deviation**

Answer

Option (3) $CHCl_3$ and CH_3COCH_3 (Chloroform and Acetone)
They form H-bond → Negative deviation → Maximum BP azeotrope

— END OF SOLUTIONS —

Keep practicing! Azeotropes can't be separated, but you can separate yourself from the crowd with hard work!