

Ideal and Non-Ideal Solutions

JEE Weightage: High

The graph JEE Advanced always draws —
and always asks you to explain.

The Baseline: Ideal Solutions

Before exploring deviations, we must define the baseline. Ideal solutions perfectly obey Raoult's law over the entire range of concentration because intermolecular forces (A-A and B-B) are nearly identical to (A-B).

FORMULA BANK

$$\Delta_{mix}H = 0$$

$$\Delta_{mix}V = 0$$

(ideal solutions only)

Positive Deviation

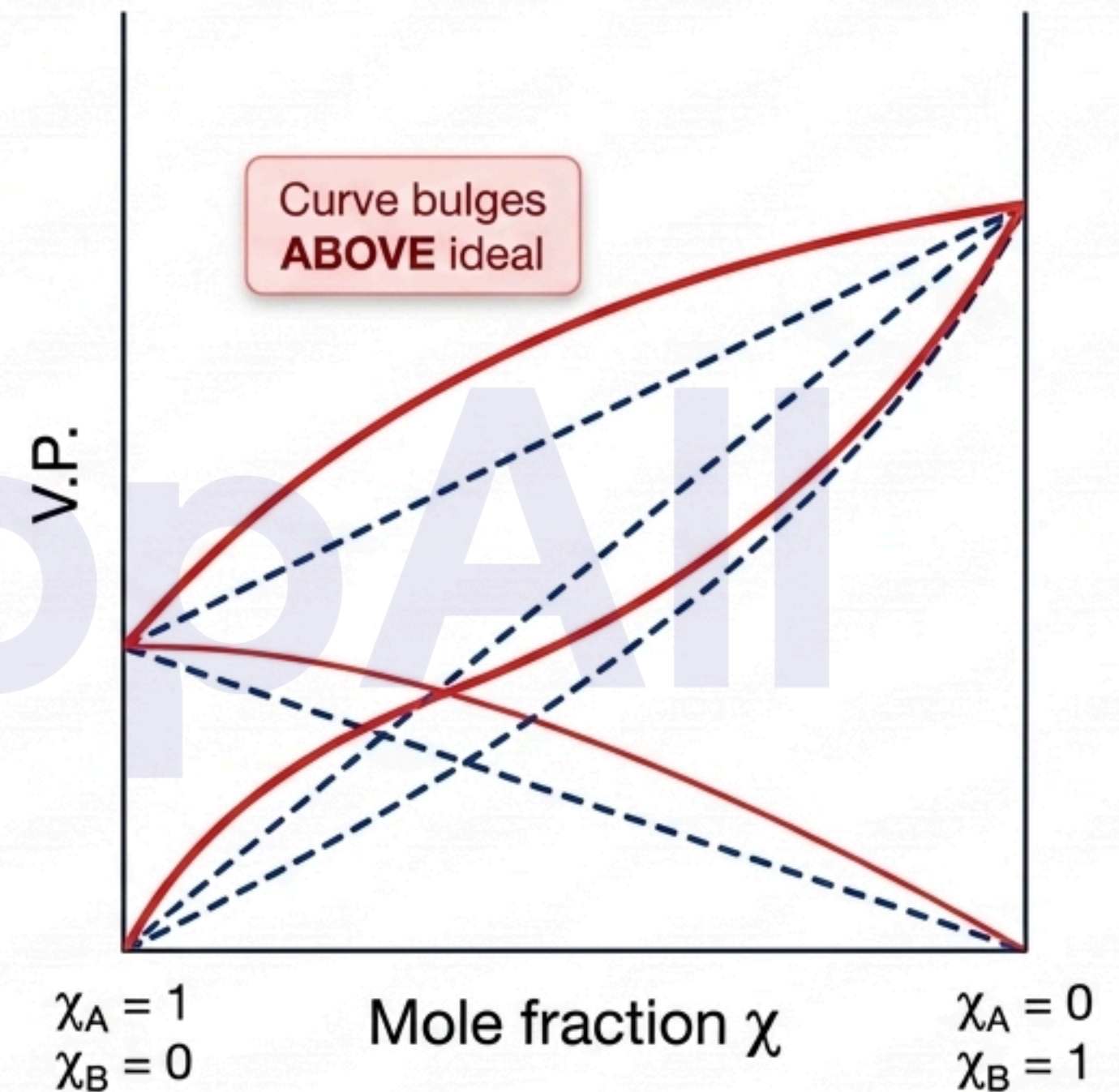
Vapour pressure is higher than predicted by Raoult's law.

Molecules find it easier to escape the liquid phase because the new bonds formed are weaker than the original bonds.

A-B interactions **WEAKER** than A-A / B-B

Example:
Ethanol +
Acetone

Fig 1.6(a) Positive Deviation





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$$E=mc^2$$



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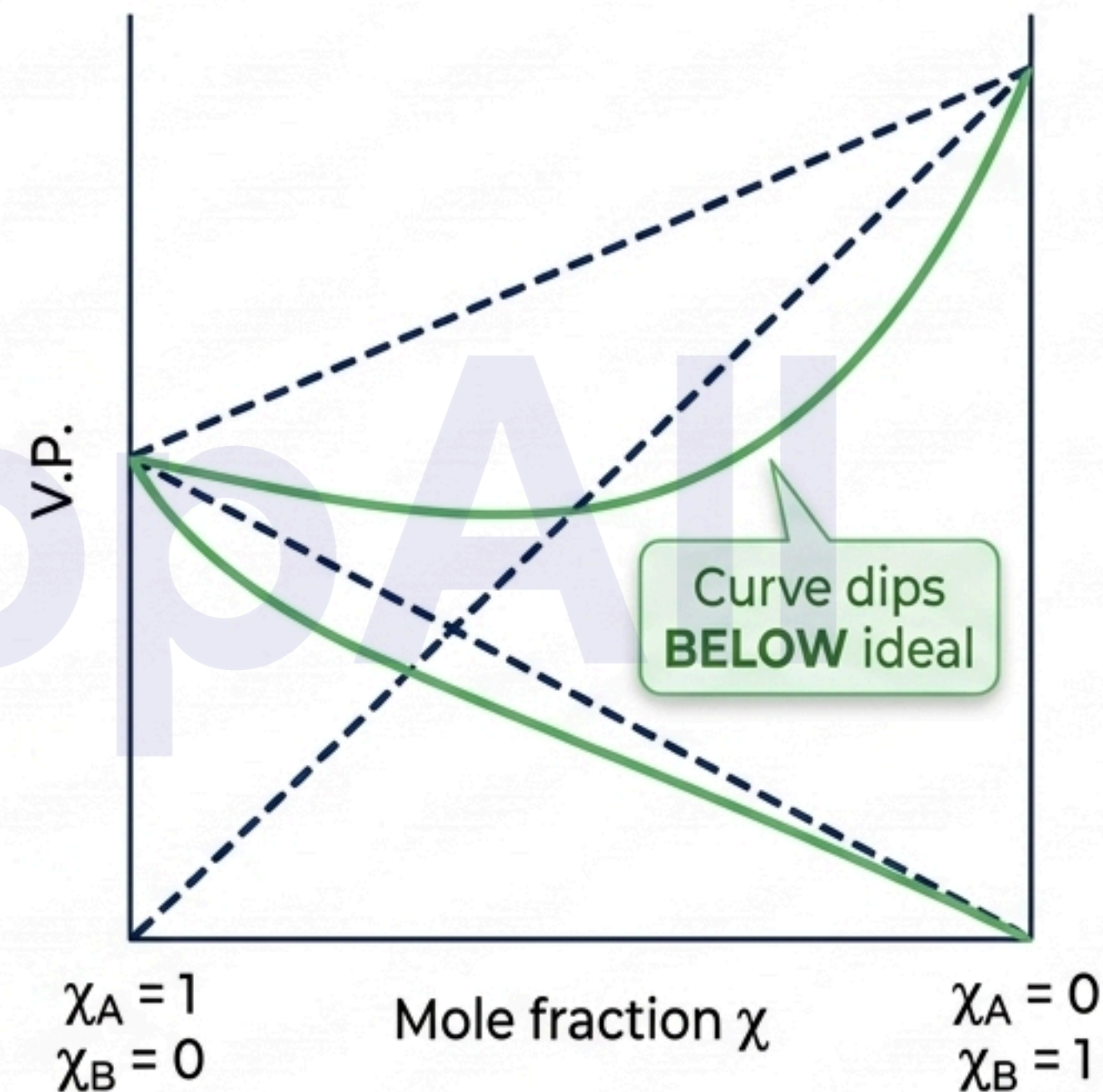
Negative Deviation

Vapour pressure is **lower** than predicted by Raoult's law.
Molecules are trapped in the liquid phase because the mixture forms new, highly stable intermolecular forces.

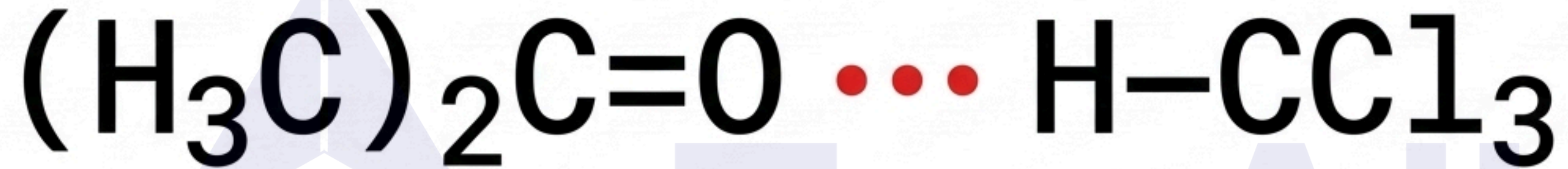
A-B interactions STRONGER than A-A / B-B

Example: Chloroform + Acetone (new H-bond)

Fig 1.6(b) Negative Deviation



Microscopic Cause: The Power of Hydrogen Bonds



✓ **Stronger A-B bond → negative deviation**

The intermolecular H-bond between the chloroform H and the lone pair on acetone's oxygen is stronger than the solute-solute interactions alone. This traps the molecules, lowering vapor pressure.

Macroscopic Effect: Azeotropes

When deviations are extremely large, solutions form binary mixtures that boil at a constant temperature with identical liquid/vapour compositions.

H3: Minimum Boiling Azeotrope

Created by large **POSITIVE** deviation

- Vapor pressure is maximized → boiling point is minimized.
- Example: Ethanol-water (~95% ethanol).

H3: Maximum Boiling Azeotrope

Created by large **NEGATIVE** deviation

- Vapor pressure is minimized → requiring more heat to boil.
- Example: HNO_3 -water (68:32 ratio, b.p. 393.5K).

Exam Strategy



JEE Trap Alert: Swapping which deviation gives which azeotrope type.

Test-makers know your brain wants '**Positive**' to match with 'Maximum'. Vapor pressure and boiling point are inversely related.

- **Positive** deviation → **minimum** boiling.
- **Negative** deviation → **maximum** boiling.

Master this trap; never flip them.

KEY TAKEAWAYS

- **Link** weaker A-B forces to positive deviation, and stronger A-B forces to negative deviation.
- **Memorize** ethanol-water (positive deviation, minimum boiling) and HNO_3 -water (negative deviation, maximum boiling) as your anchor examples.
- **Match** deviation type to azeotrope type perfectly—remember that high vapor pressure (positive) strictly implies low boiling point (minimum).



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