

THERMODYNAMICS & MOLECULAR INTERACTIONS

1.5 Ideal and Non-ideal Solutions

Decoding the causal relationship between microscopic forces and macroscopic thermodynamic behaviours.

[A-A]

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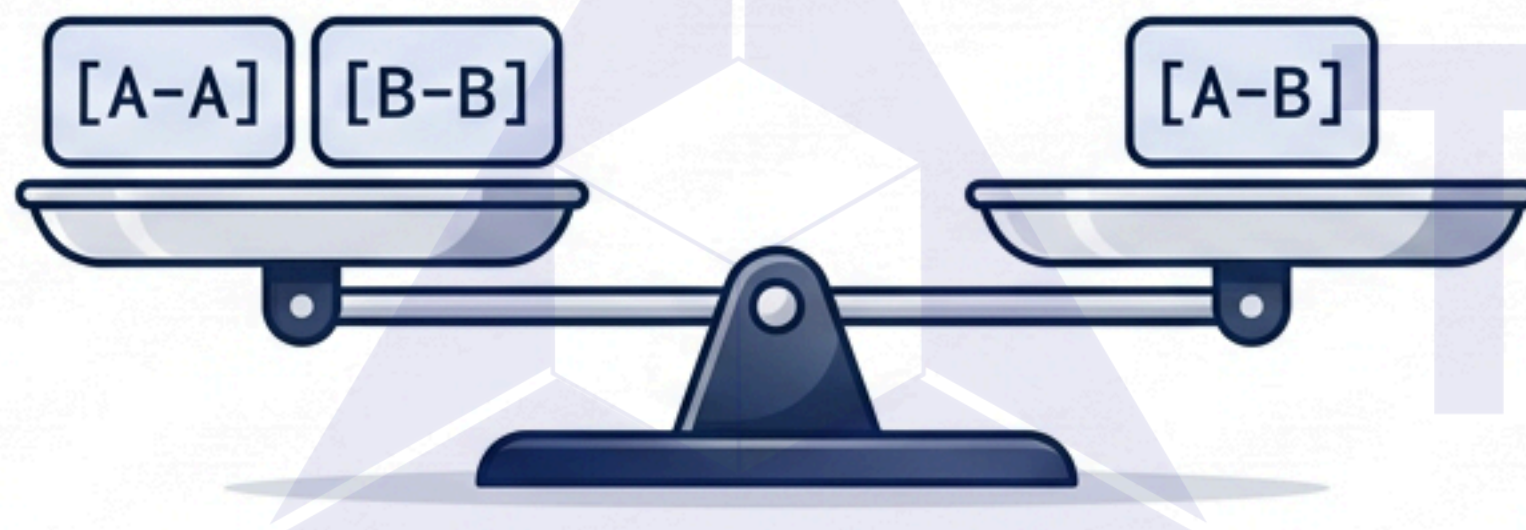
[B-B]

$\rightleftharpoons$

[A-B]

What Makes a Solution Ideal

Perfect Balance



Intermolecular attractive forces between solute-solute and solvent-solvent are nearly equal to solute-solvent interactions. The solution obeys Raoult's law over the entire range of concentration.

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

No heat is absorbed or evolved

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

Volume equals the sum of pure components

$$p_i = p_i^0 x_i$$

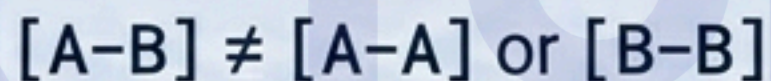
Strict adherence to Raoult's Law

Common Ideal Pairs: n-hexane & n-heptane | bromoethane & chloroethane | benzene & toluene

What Makes a Solution Non-Ideal

A non-ideal solution does not obey Raoult's law over the entire range of concentration.

$$\Delta_{\text{mix}}H \neq 0 \quad \Delta_{\text{mix}}V \neq 0$$



Vapour pressure is higher than predicted (Positive Deviation).



Vapour pressure is lower than predicted (Negative Deviation).

The cause for these deviations lies strictly in the nature of interactions at the molecular level.



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$$E=mc^2$$



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Positive and Negative Deviations



Positive Deviation



(highlighting weaker bonds)

Mechanism:

Molecules find it easier to escape.
Vapour pressure increases.

Real-world Example:

Ethanol + Acetone

Acetone molecules get between host molecules and break existing hydrogen bonds.

Negative Deviation



(highlighting stronger bonds)

Mechanism:

Decreases escaping tendency.
Vapour pressure decreases.

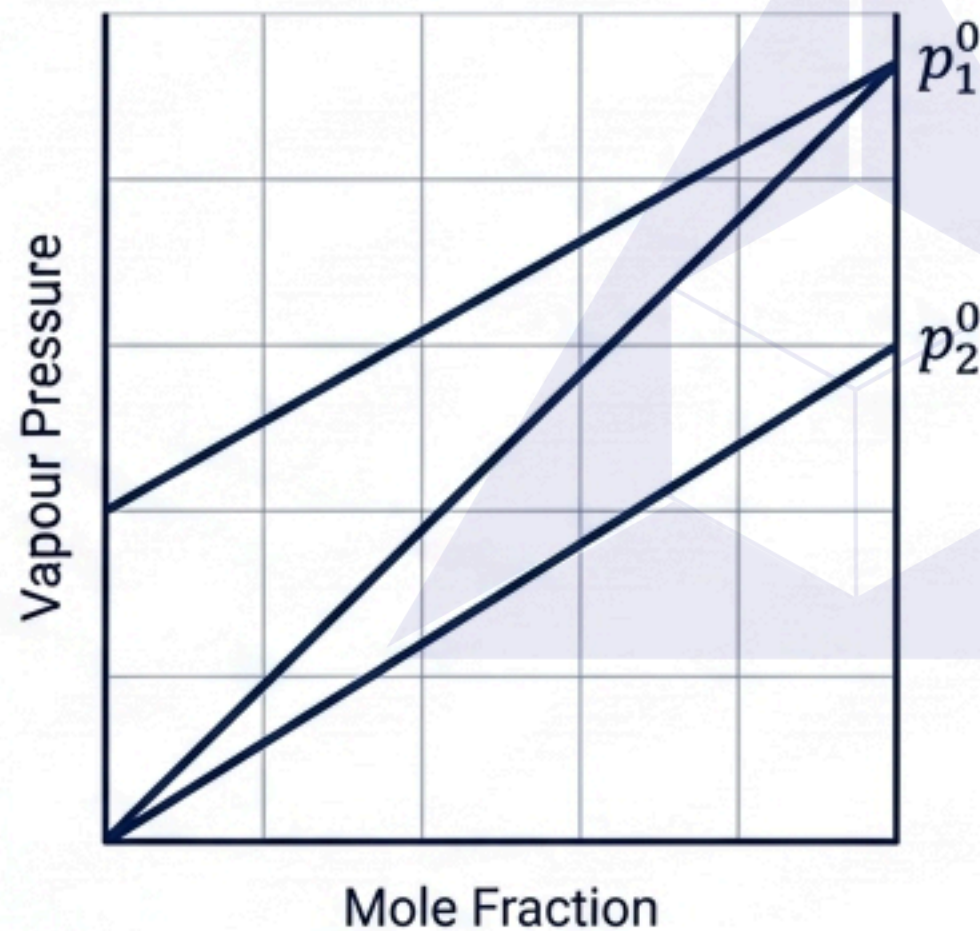
Real-world Example:

Chloroform + Acetone

The two molecules form new intermolecular hydrogen bonds, holding them in the liquid phase. (Also: Phenol + Aniline).

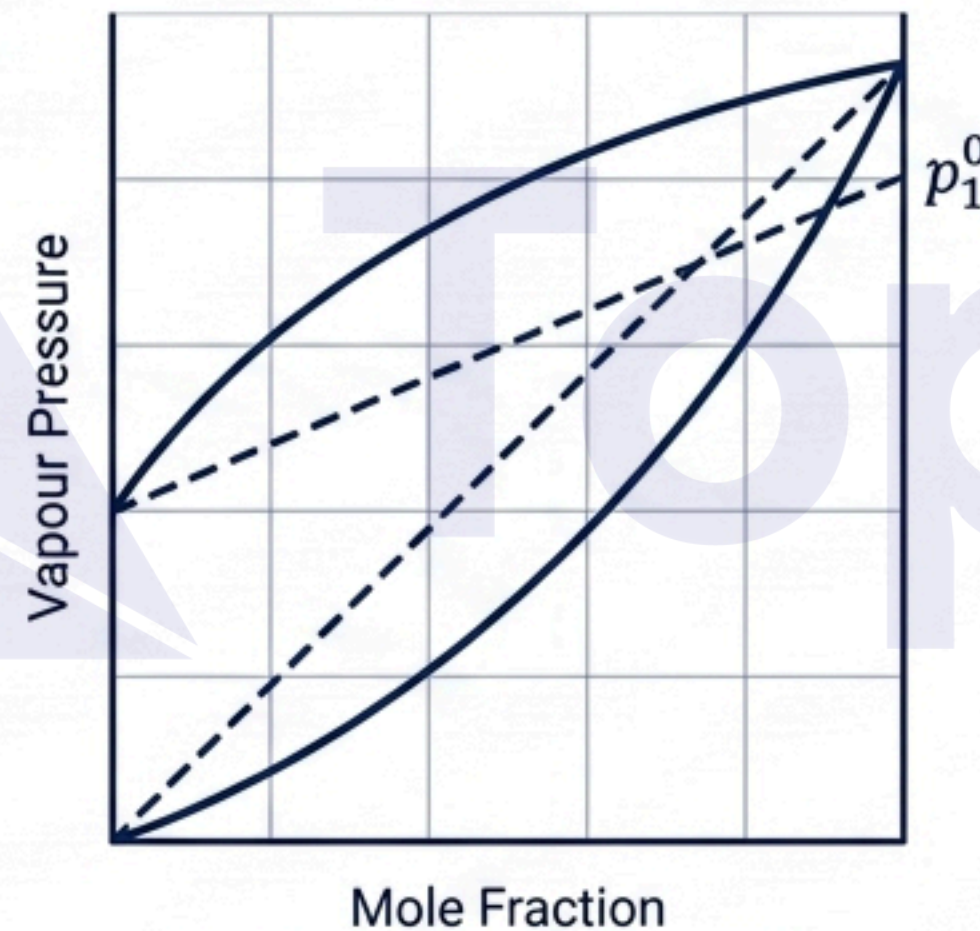
Vapour Pressure Curves

Ideal Solution



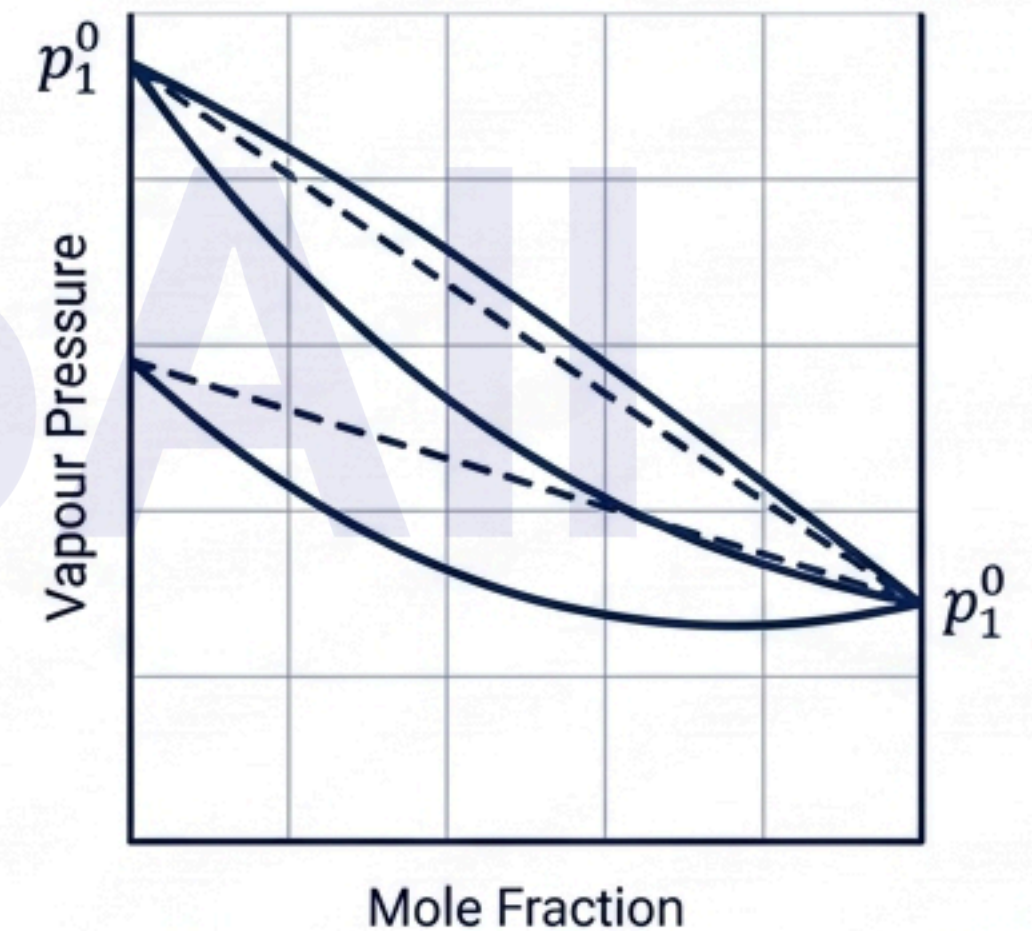
Linear: $p_{total} = p_1 + p_2$

Positive Deviation



Convex: $p_{total} > p_1^0 x_1 + p_2^0 x_2$

Negative Deviation



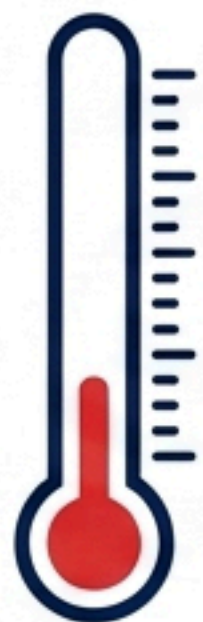
Concave: $p_{total} < p_1^0 x_1 + p_2^0 x_2$

Graphs plot Vapour Pressure (y-axis) vs. Mole Fraction (x-axis) at a constant temperature.

Azeotropes: The Distillation Barrier

Binary mixtures having the same composition in liquid and vapour phase. They boil at a constant temperature, making separation by fractional distillation impossible.

Minimum Boiling Azeotrope



Driven by: Large Positive Deviations.

Classic Example:
Ethanol-Water mixture
(fermentation product).
Reaches azeotropic lock at
~95% ethanol by volume.

Maximum Boiling Azeotrope



Driven by: Large Negative Deviations.

Classic Example:
Nitric Acid-Water.
Reaches azeotropic lock at
68% nitric acid (by mass) at
393.5 K.

Final Recap: Deviation is Driven by Molecular Interactions

Solution Type	Interaction Strength	Enthalpy & Volume	VP Curve Shift	Azeotrope Formed
Ideal	$[A-B] \approx [A-A]$	$\Delta H=0, \Delta V=0$	Linear (Baseline)	None
Positive	$[A-B] < [A-A]$ (Weaker)	$\Delta H > 0, \Delta V > 0$	Convex (Upward)	Minimum Boiling
Negative	$[A-B] > [A-A]$ (Stronger)	$\Delta H < 0, \Delta V < 0$	Concave (Downward)	Maximum Boiling

Master the micro-interactions, predict the macro-behaviour.



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