

Vapour Pressure of Liquid Solutions

Understanding binary volatile mixtures through Raoult's Law and Vapour-Liquid Equilibrium.

Section 1.4.1

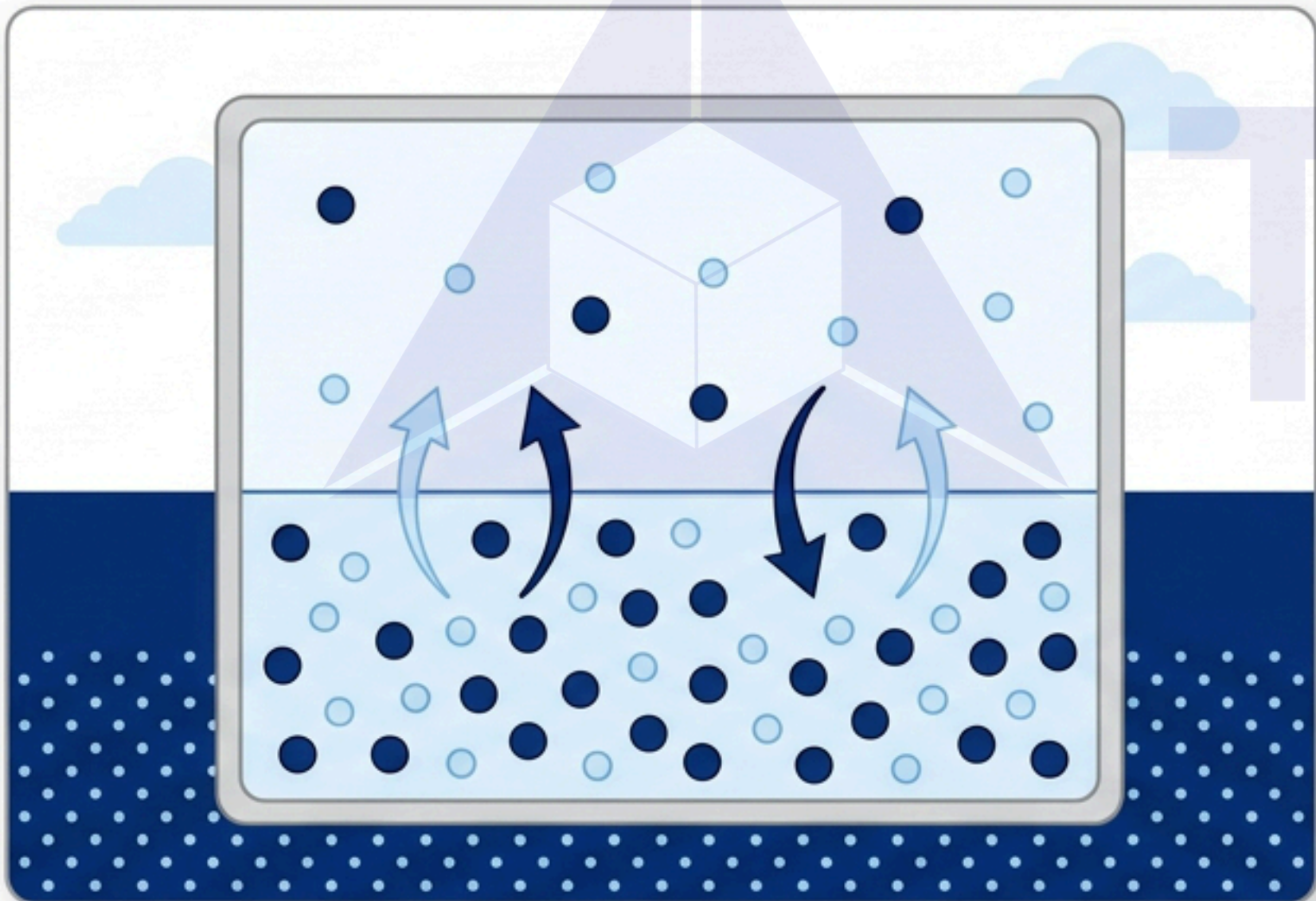


1.0 THE PHYSICAL MODEL

Vapour-Liquid Equilibrium in Binary Solutions



When a binary solution of two volatile liquids is placed in a closed vessel, both components evaporate until a state of dynamic equilibrium is established between the liquid and vapour phases.



The Vapour Phase

Exerts a pressure over the liquid. Each component contributes to the total measurable pressure of the system.

p_1 , p_2 (Partial Pressures) | p_{total} (Total Pressure)

The Liquid Phase

Contains both volatile components. Their physical concentrations are defined by their liquid mole fractions.

x_1 , x_2

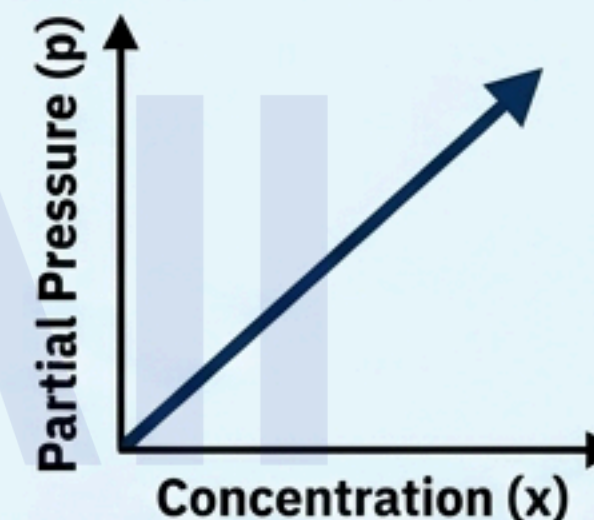
2.0 RAOULT'S LAW



Partial Vapour Pressure of Each Component

Francois Marte Raoult (1886) established the quantitative relationship connecting a liquid's composition to the **vapour pressure** it generates.

For a solution of volatile liquids, the partial vapour pressure of each component is directly proportional to its mole fraction present in the solution.



$$p_1 = p_1^\circ \cdot x_1$$

$$p_2 = p_2^\circ \cdot x_2$$

p_1, p_2 : Partial vapour pressure of the component in the solution

p_1°, p_2° : Vapour pressure of the pure component at the same temperature

x_1, x_2 : Mole fraction of the component in the physical liquid phase



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$$E=mc^2$$



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3.0 SYSTEM INTEGRATION

Total Vapour Pressure of the Solution

According to Dalton's law of partial pressures, the total pressure over the solution phase is the sum of the individual partial pressures.

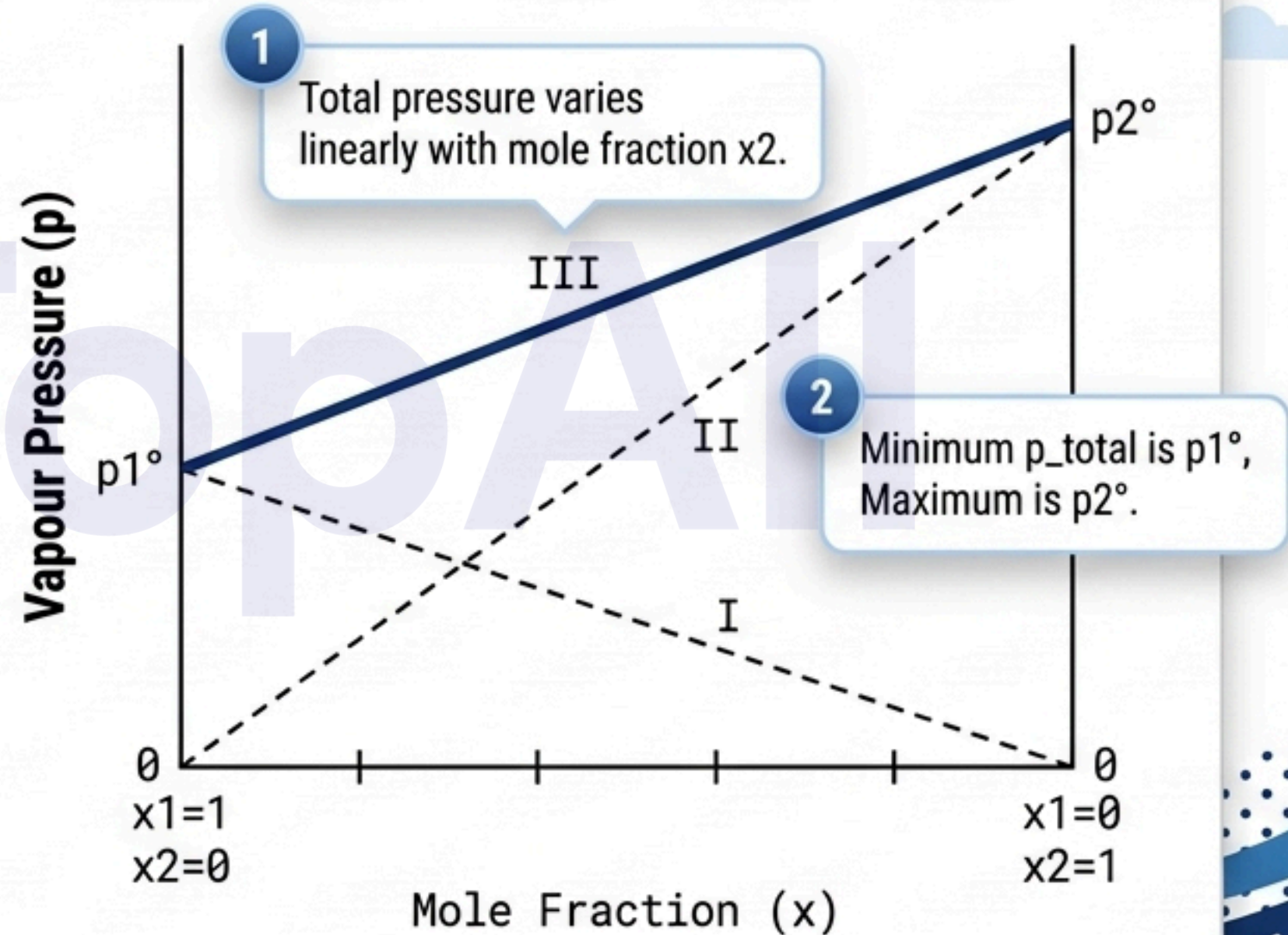
Step 1: $p_{\text{total}} = p_1 + p_2$

Step 2: Substitute Raoult's Law

$$p_{\text{total}} = x_1 \cdot p_1^\circ + x_2 \cdot p_2^\circ$$

Step 3: Relate to a single component
(Since $x_1 = 1 - x_2$)

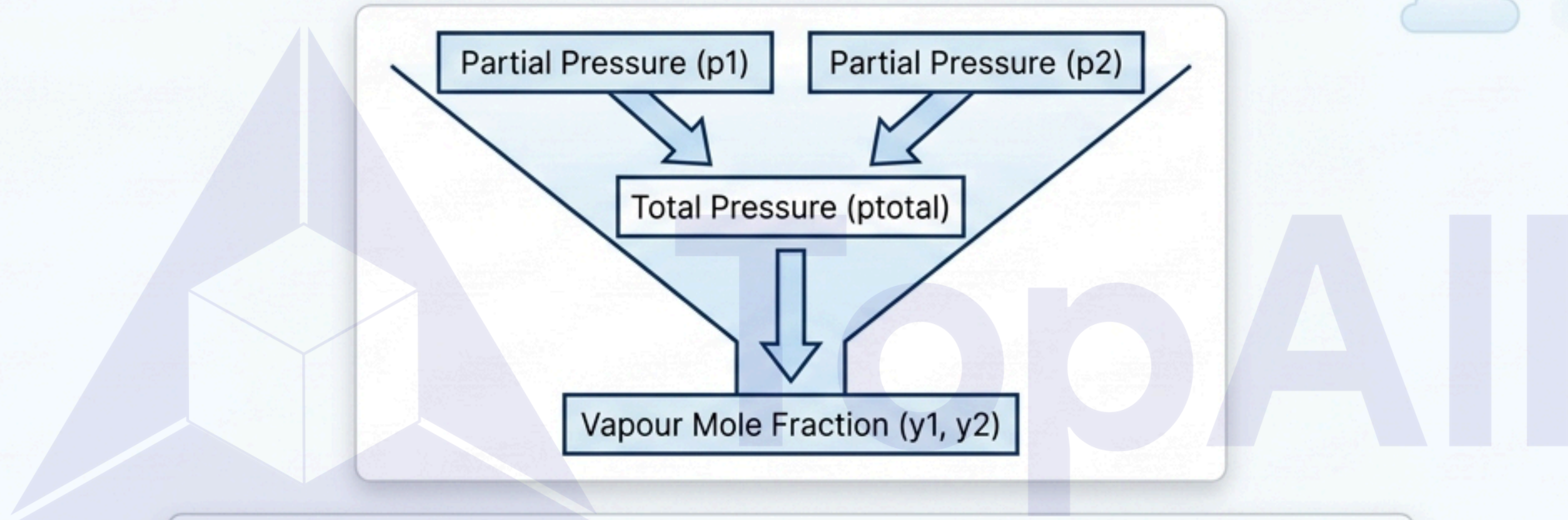
$$p_{\text{total}} = p_1^\circ + (p_2^\circ - p_1^\circ)x_2$$



4.0 THE VAPOUR PERSPECTIVE

Composition of the Vapour Phase

The physical composition of the vapour cloud hovering in equilibrium with the liquid solution is determined by the partial pressures of its components.



$$y_1 = p_1 / p_{\text{total}} \quad y_i = p_i / p_{\text{total}}$$

— y_i represents the mole fraction of component i strictly in the vapour phase.

The Volatility Rule

At equilibrium, the vapour phase will always be richer in the component which is more volatile.
(e.g., If pure $p_2^\circ > p_1^\circ$, the vapour will contain a higher proportion of Component 2 than the liquid does).

5.0 SYNTHESIS



Connecting the Phases: x_i vs. y_i

Liquid composition and vapour composition are intimately related, but they are not identical unless the pure vapour pressures of both liquids are exactly equal.

The Liquid Phase

Liquid Composition (x_i)

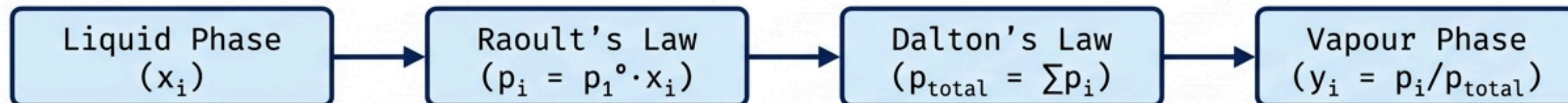
- Represents molecules physically pooled in the solution.
- Sum always equals 1: $x_1 + x_2 = 1$
- Drives partial pressure generation via Raoult's Law.

The Vapour Phase

Vapour Composition (y_i)

- Represents molecules floating in the gas space above.
- Sum always equals 1: $y_1 + y_2 = 1$
- Driven by partial pressures via Dalton's Law.

The Complete Calculation Pathway





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