

Henry's law is one of the gas laws formulated by William Henry in 1803 and states:

"At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."

An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid:

$$C = kP_{gas}$$

where

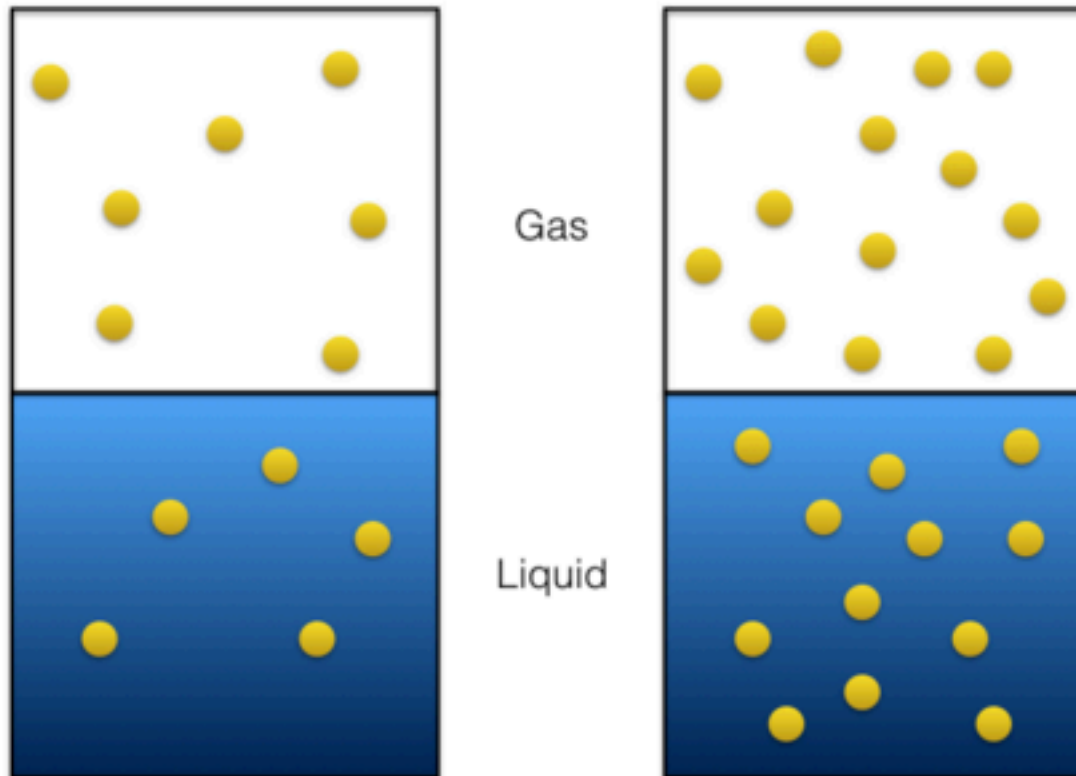
- C is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L)
- k is Henry's law constant (often in units of M/atm)
- P_{gas} is the partial pressure of the gas (often in units of atm)

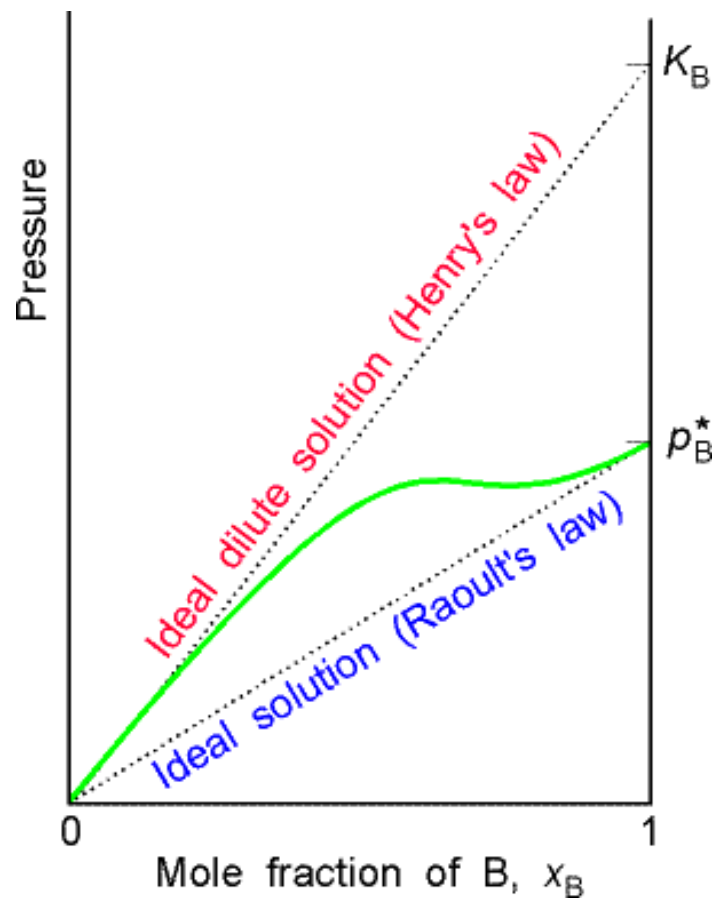
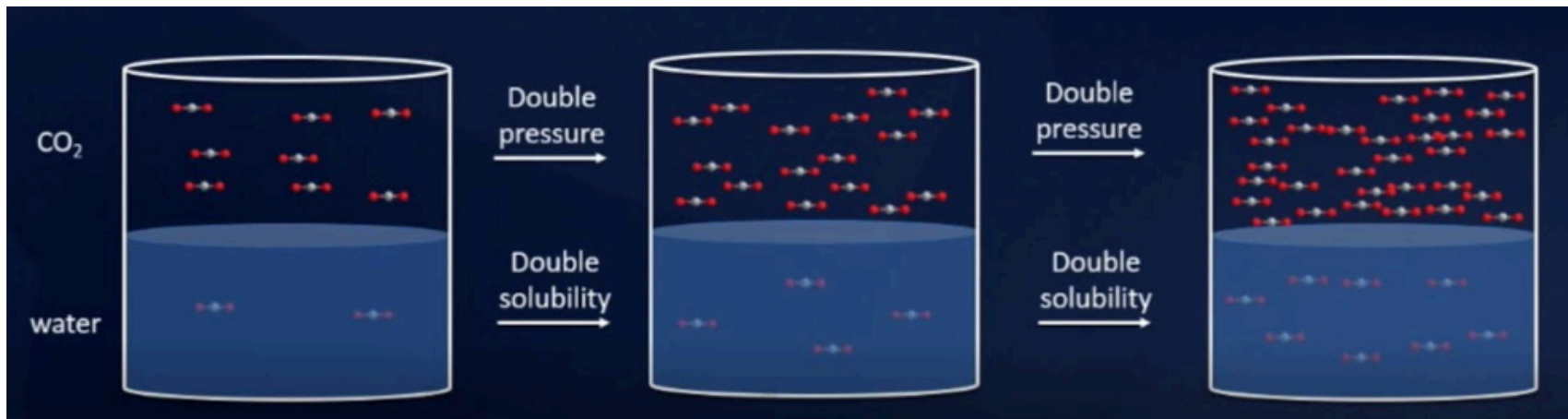


1774 - 1836

Henry's Law

At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.





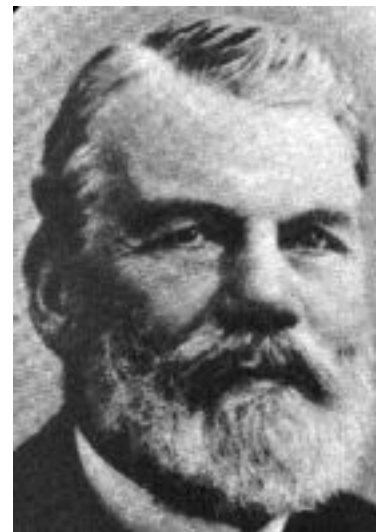
In the 1880s, French chemist **François-Marie Raoult** discovered that when a substance is dissolved in a solution, the vapor pressure of the solution will generally decrease. This observation depends on two variables:

- 1) the mole fraction of the amount of dissolved solute present and
- 2) the original vapor pressure (pure solvent).

At any given temperature for a particular solid or liquid, there is a pressure at which the vapor formed above the substance is in dynamic equilibrium with its liquid or solid form. This is the **vapor pressure** of the substance at that temperature. At equilibrium, the rate at which the solid or liquid evaporates is equal to the rate that the gas is condensing back to its original form. All solids and liquids have a vapor pressure, and this pressure is constant regardless of how much of the substance is present.

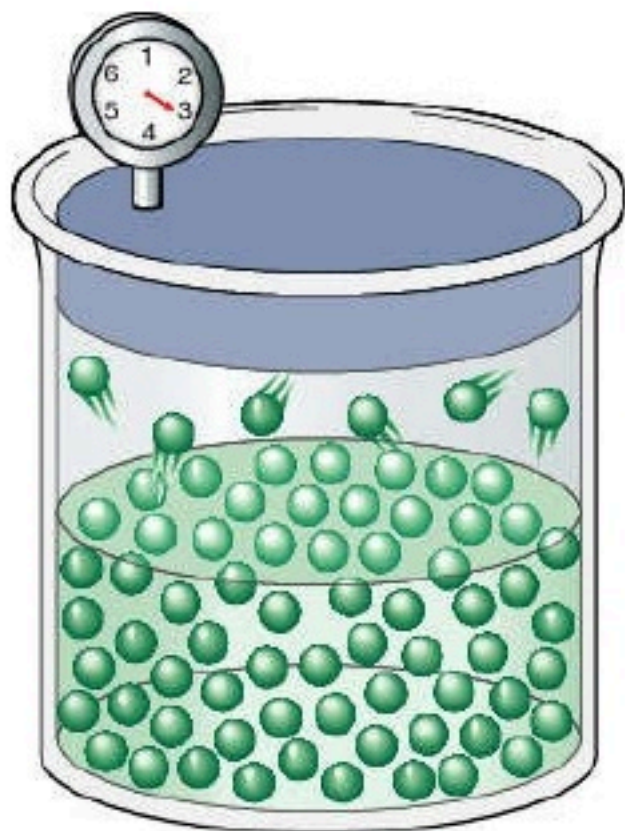
Raoult's law states that the vapor pressure of a solvent above a solution is equal to the vapor pressure of the pure solvent at the same temperature scaled by the mole fraction of the solvent present:

$$P_{\text{solution}} = \chi_{\text{solvent}} P_{\text{solvent}}^{\circ}$$

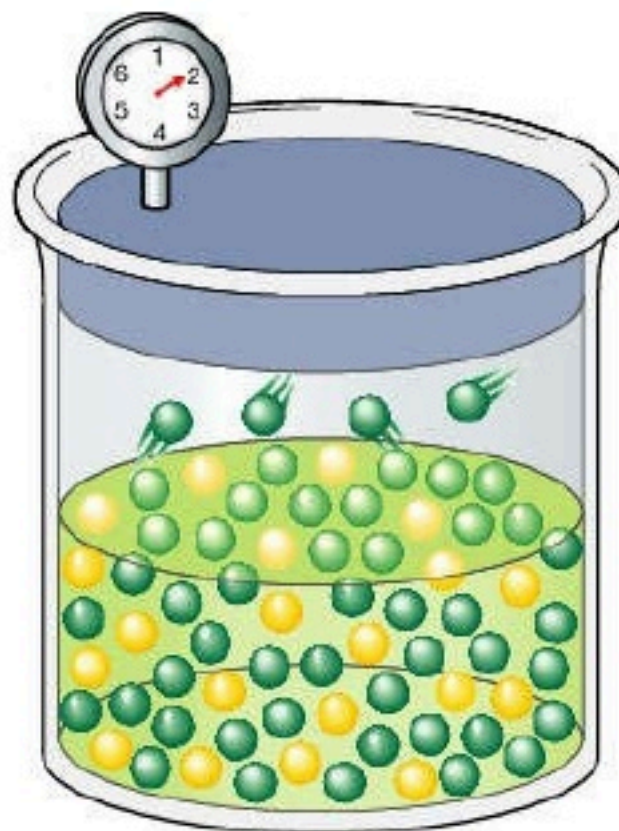


François Raoult
(1830-1901)

Vapor Pressure Lowering



Pure solvent



Solution with a
nonvolatile solute

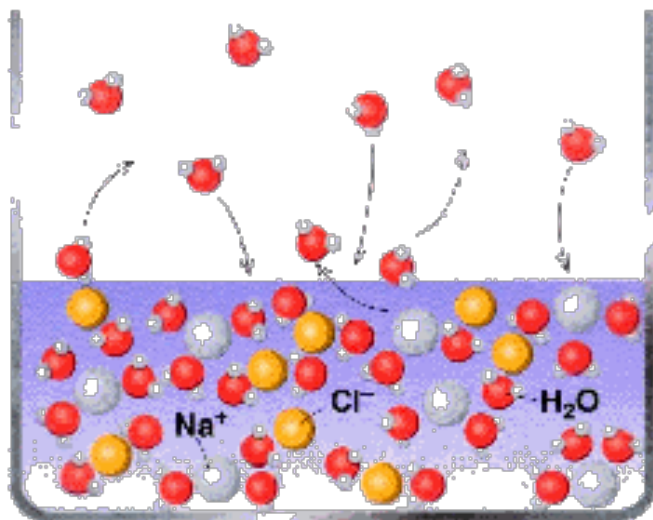
The presence of a non-volatile solute means that fewer solvent particles are at the solution's surface, so less solvent evaporates!

Colligative Properties -- Raoult's Law

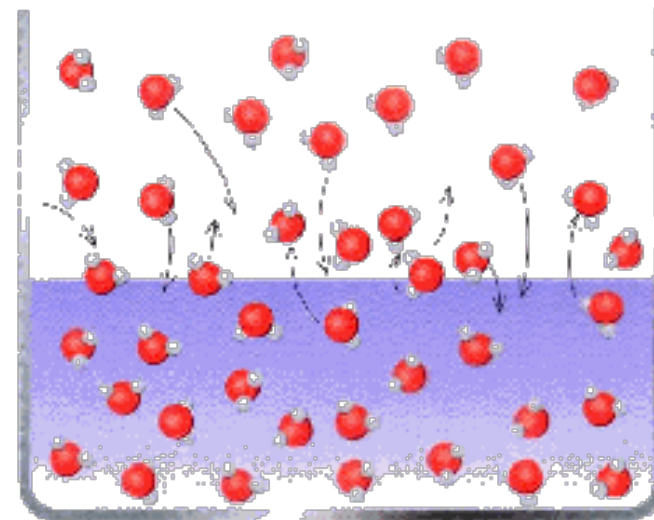
- The Vapor Pressure of the solvent is proportional to its mole fraction

$$- P_{\text{solvent}} \propto X_{\text{solvent}} \quad \text{or} \quad P_{\text{solvent}} = K X_{\text{solvent}}$$

Where K is the vapor pressure of the pure solvent

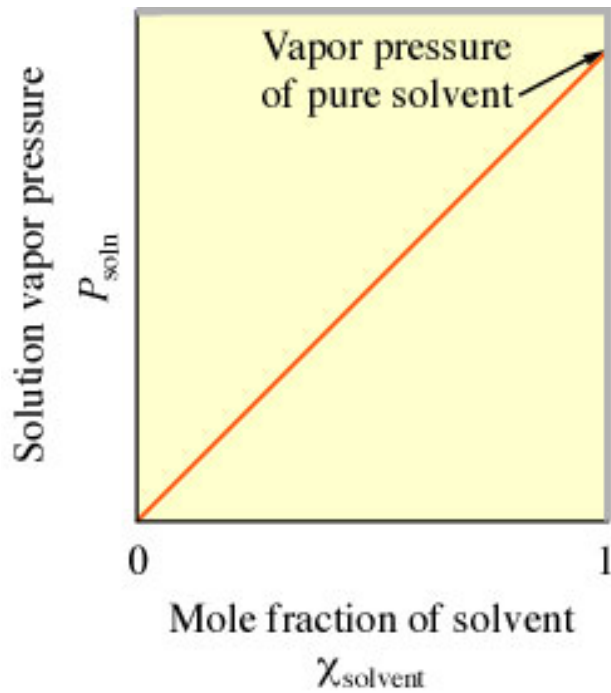


(a) Sea water



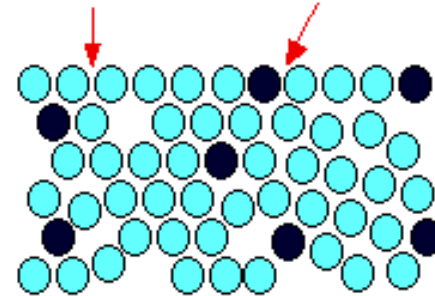
(b) Pure water

Raoult's Law only works for ideal solutions.

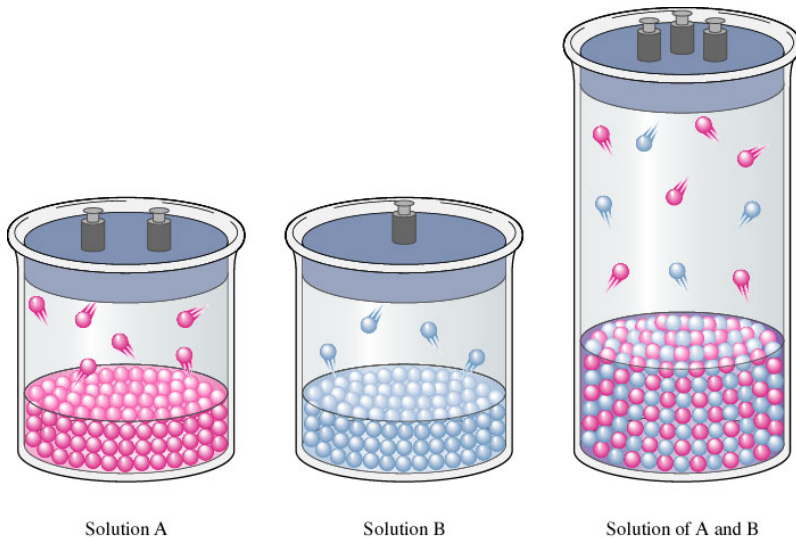


In an ideal solution, the forces between the solvent molecules ...

... are exactly the same as those between solvent and solute.



That means that it takes the same amount of energy for solvent molecules to break away from the surface in either case.



$$p_A = \chi_A p_A^\circ$$

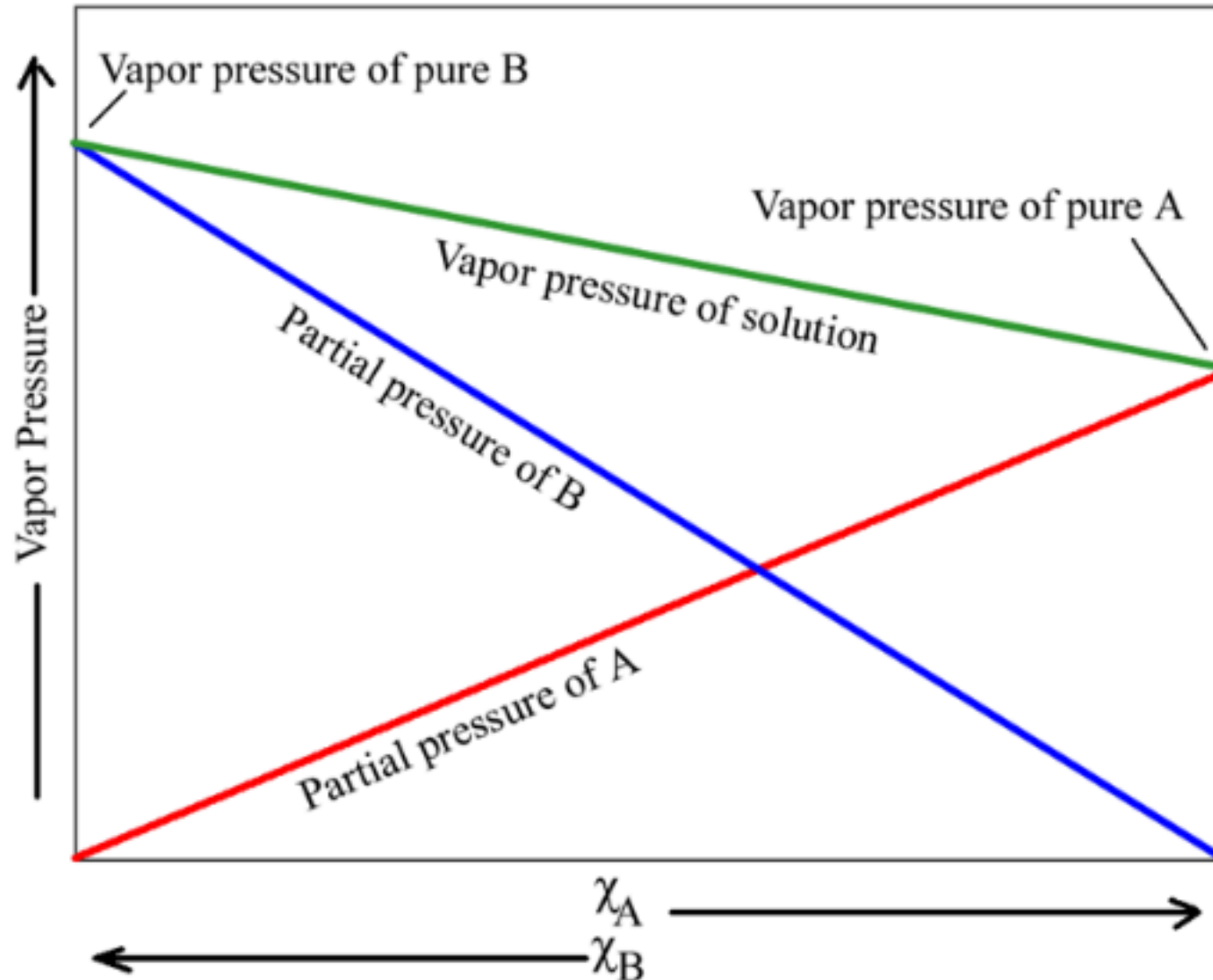
$$p_B = \chi_B p_B^\circ$$

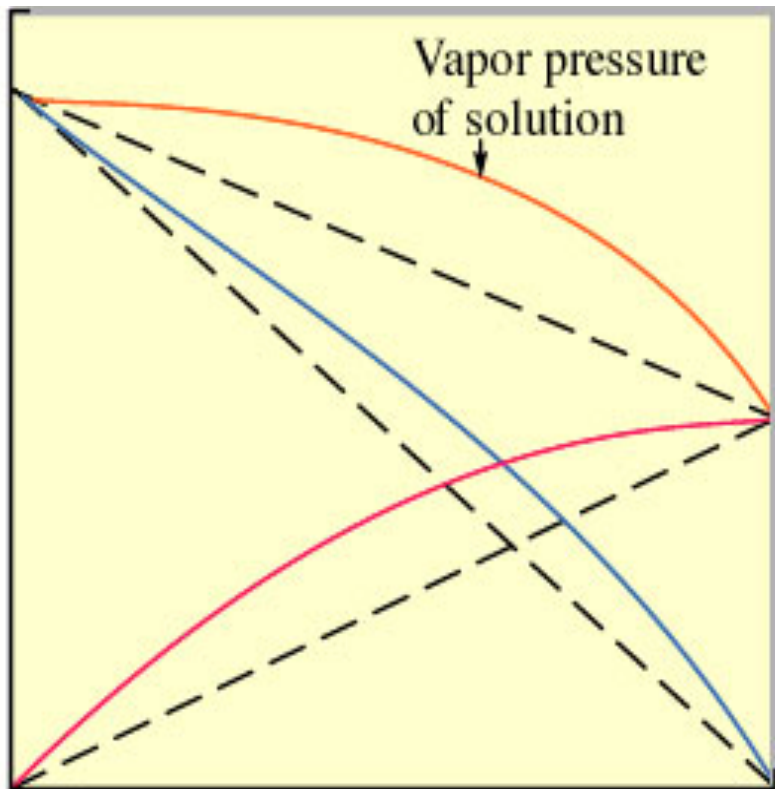
$$p_{\text{tot}} = p_A + p_B$$

$$= \chi_A p_A^\circ + \chi_B p_B^\circ$$

$$\chi_A = \frac{\text{moles of A}}{\text{total number of moles}}$$

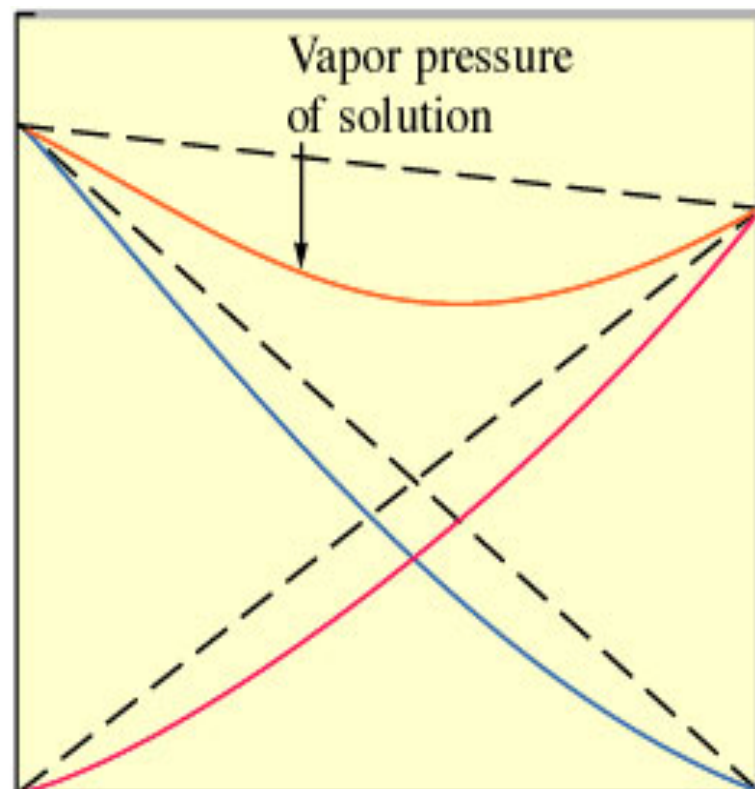
A solution that obeys Raoult's Law is called an ideal solution





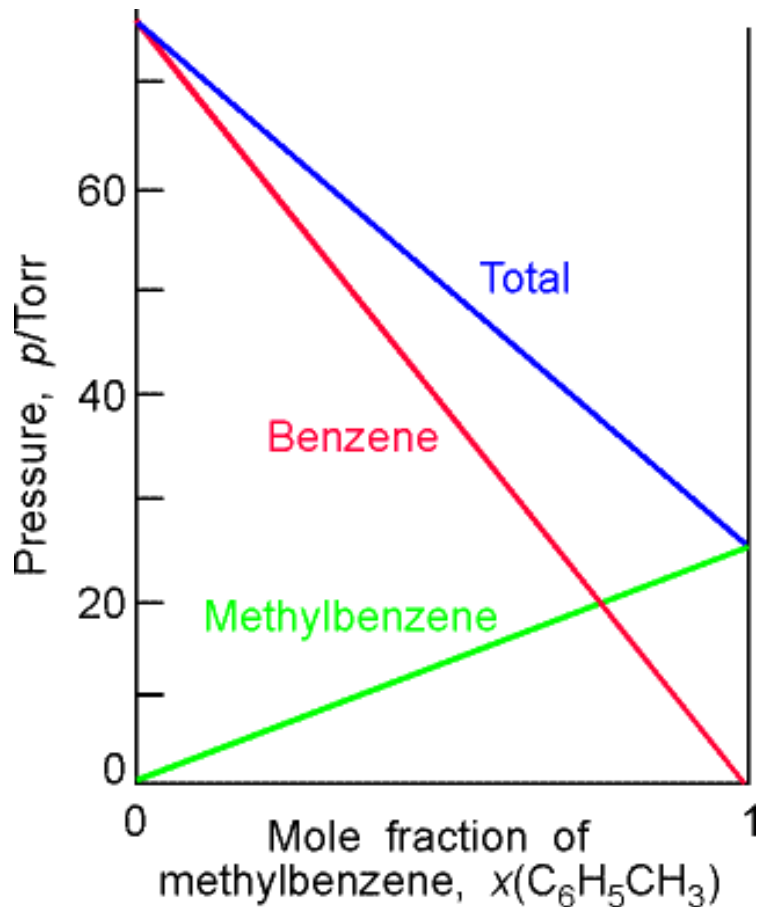
χ_A →
← χ_B

Positive deviation

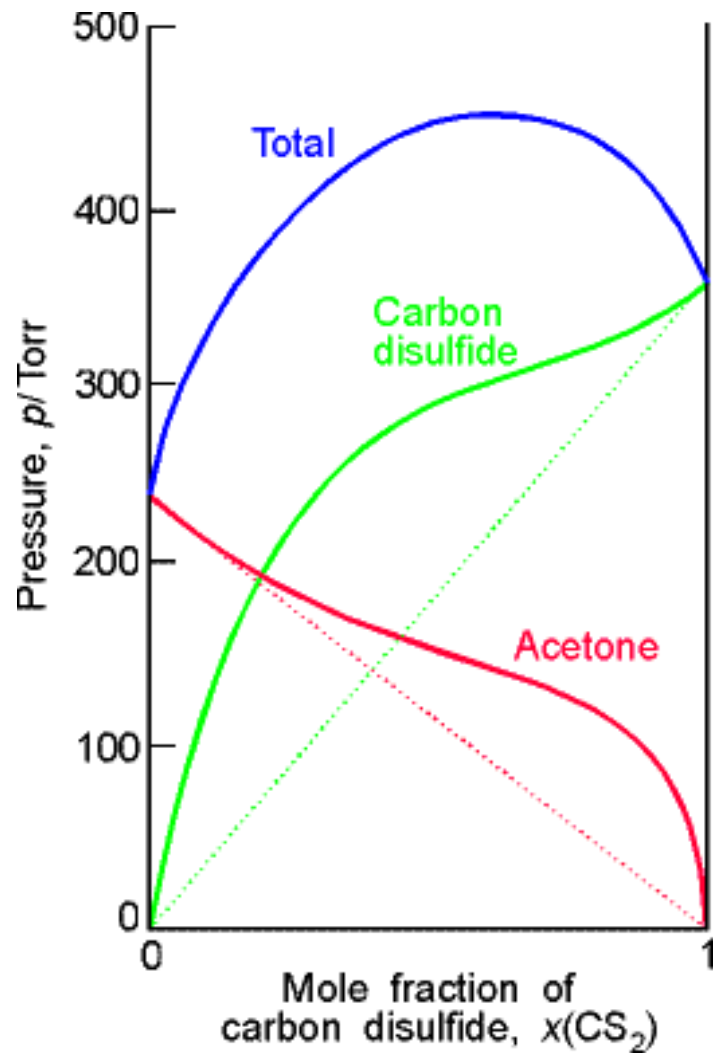


χ_A →
← χ_B

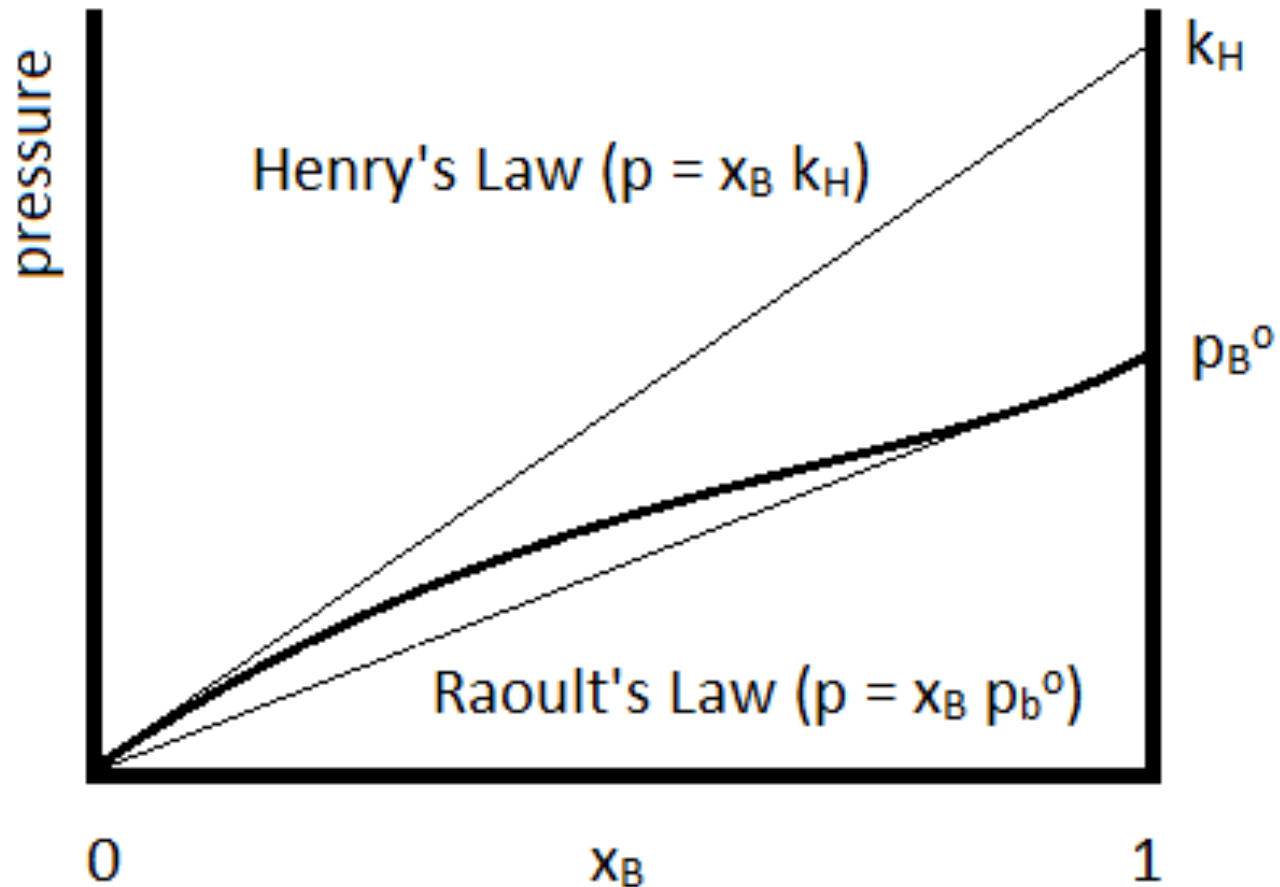
Negative deviation



Ideal solution



Non ideal solution



Positive **non-ideal behavior** of the vapor pressure of a solution follows Henry's Law at low concentrations and Raoult's Law at high concentrations (pure).