CHEM3520 - Spring 2023

Focus 1: Properties of gases

Focus 2: The First Law

Focus 3: The Second and Third Laws

Focus 4: Physical transformation of pure substances

Focus 5: Simple mixtures

Focus 6: Chemical equilibrium

Focus 16: Molecules in motion

Focus 17: Chemical kinetics

Focus 18: Reaction dynamics

Focus 5: Simple mixtures

- TD description of mixtures
- Properties of solutions
- Phase diagrams of binary systems
- Phase diagrams of ternary systems
- Thermodynamic activity

Chemical potential of liquids

$$\mu = \mu^{\ominus} + RT \ln \frac{p}{p^{\ominus}}$$

Variation of chemical potential with pressure [perfect gas]

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Variation of chemical potential with pressure [perfect gas]

Pure A

vapour

$$\underbrace{\mu_A^{\ominus}(g) + RT\ln p_A^{*}}_{\text{vapour}}$$

$p_A^{*}/p^{\ominus}$

* => pure substances

Chemical potential of liquids

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$\downarrow$

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↓ $p_A^*/p^\ominus$

A and a solute B

$$\mu_A(l) = \mu_A^\ominus(g) + RT \ln p_A$$

In a mixture

↓ Partial pressure

Chemical potential of liquids

Pure A

liquid vapour

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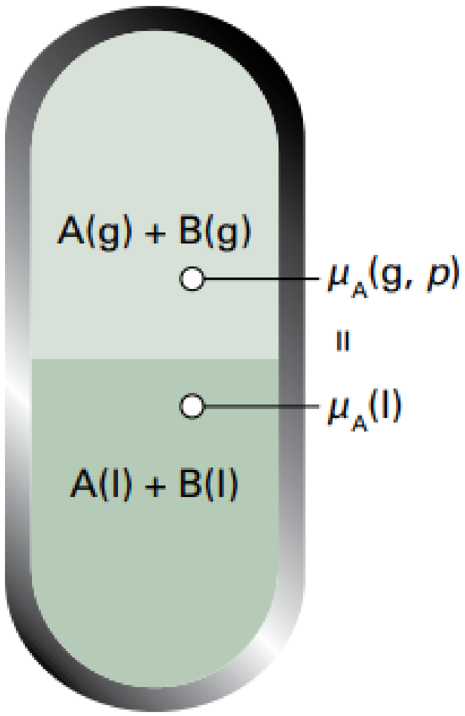
Partial pressure



At equilibrium, the chemical potential of the gaseous form of substance A is equal to the chemical potential of its condensed phase. This equality is preserved even if a solute is present.

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partial vapor pressure

vapor pressure when present as the pure liquid

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partial vapor pressure

vapor pressure when present as the pure liquid

From Raoult's Law:

$$\mu_A(l) = \mu_A^*(l) + RT\ln x_A$$

Chemical potential [ideal solution]

Raoult's Law

Raoult's Law

By François Raoult (1830 – 1901)

$$p_A = x_A p_A^*$$

Mole fraction in the liquid phase

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

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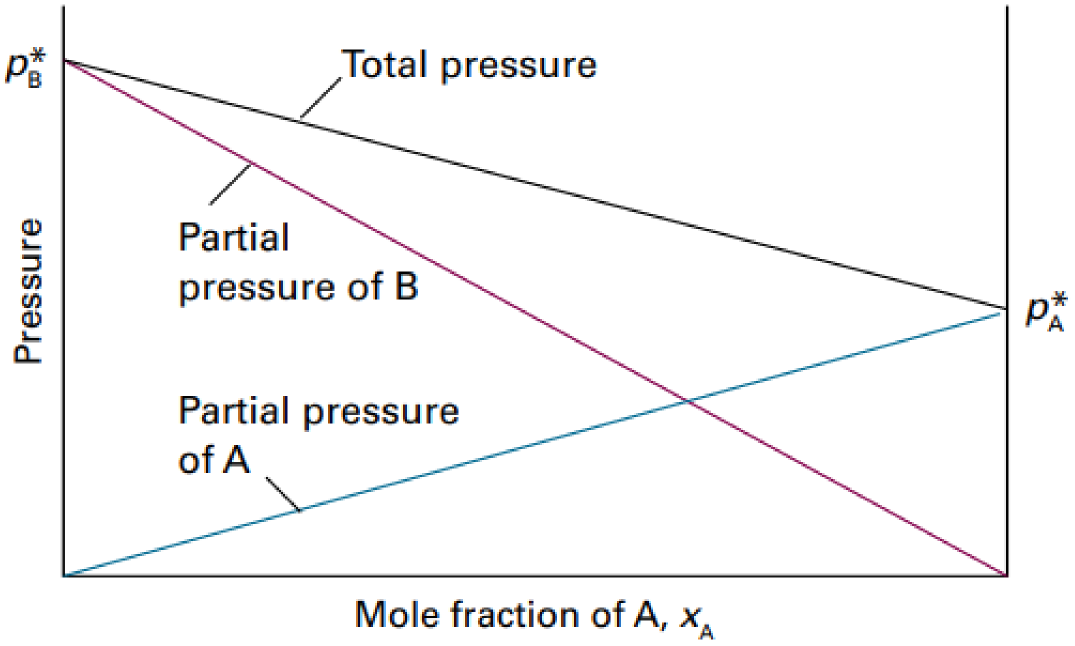

Vapor Pressure Diagram

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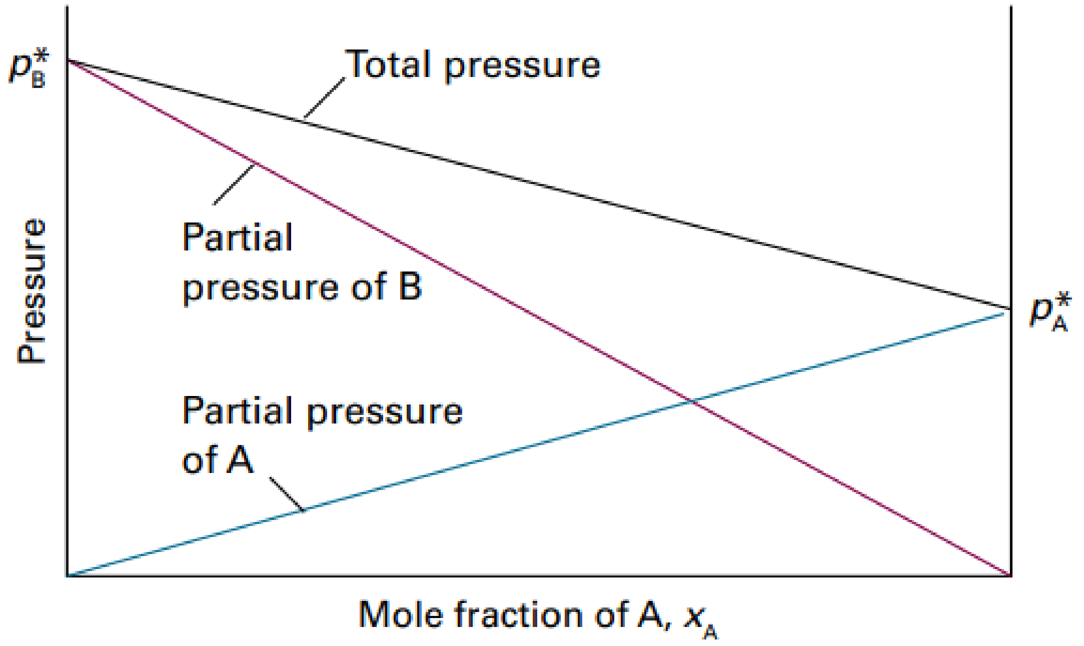

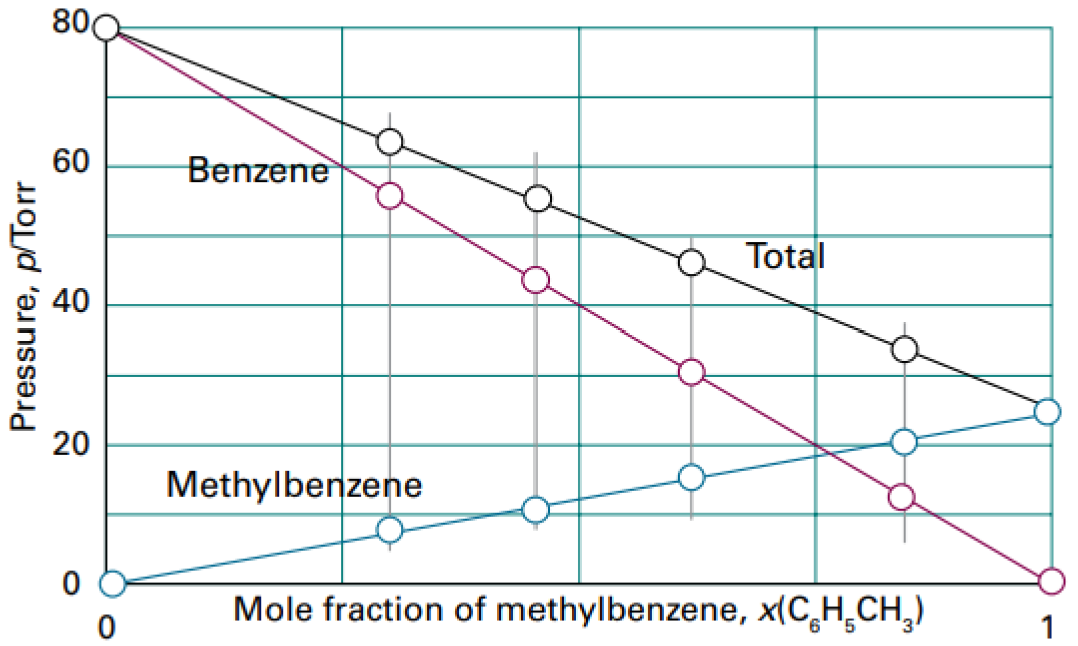

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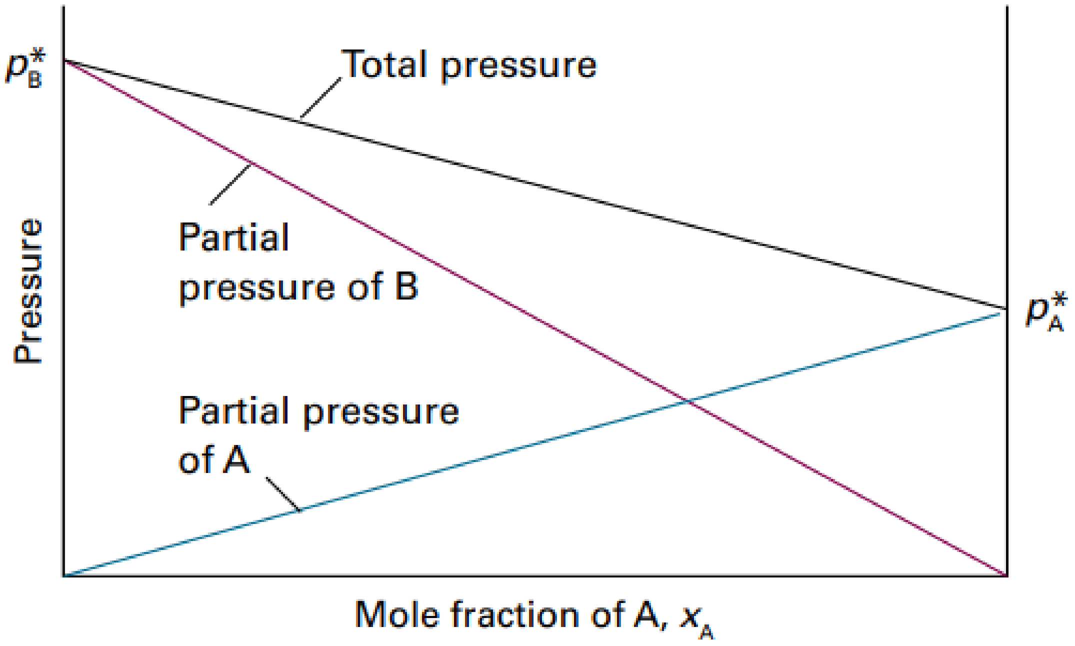
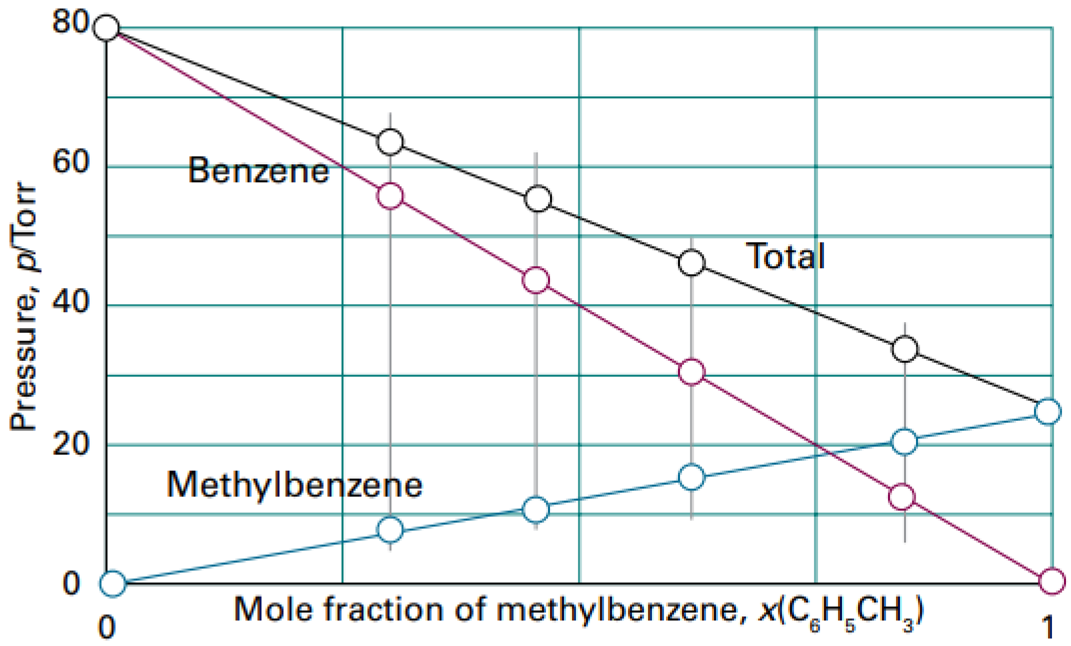
For ideal liquid mixtures (ideal solutions)!





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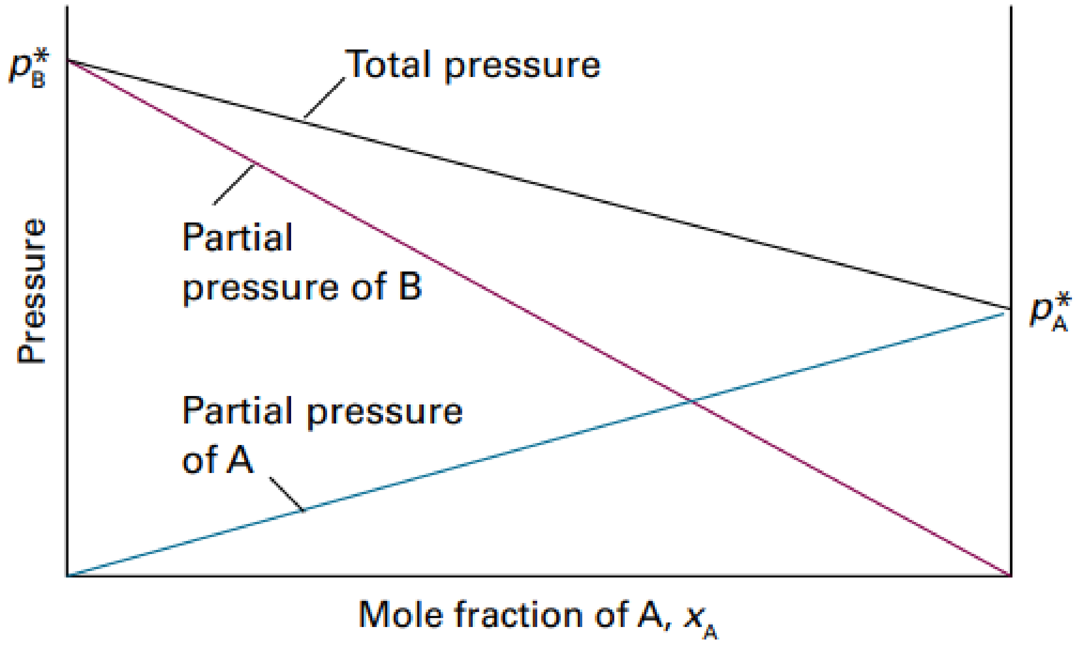
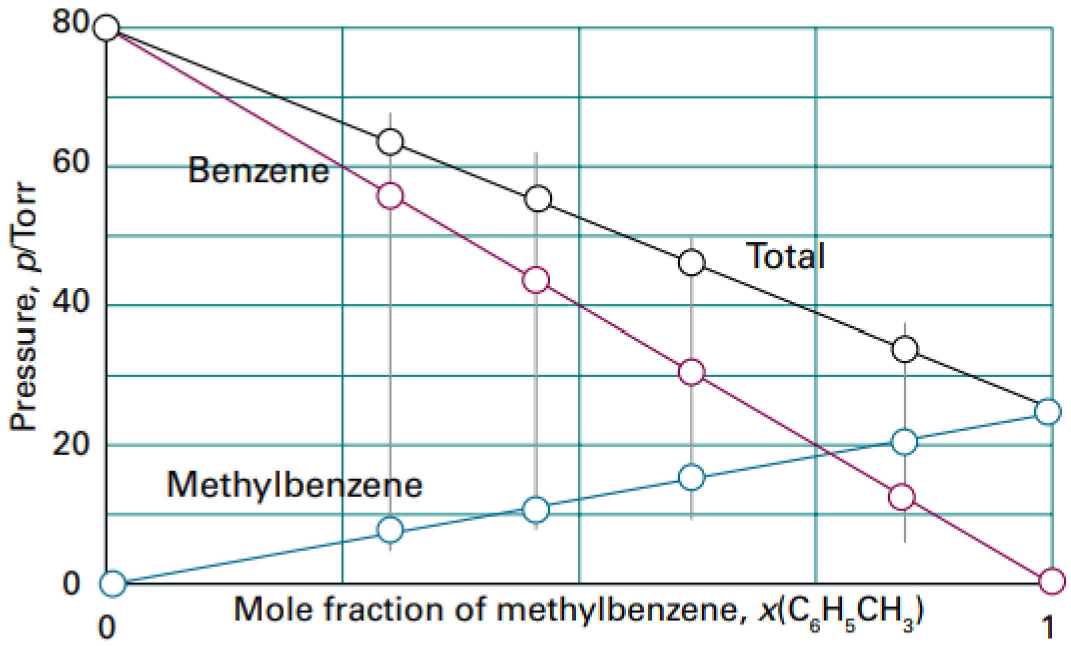
For ideal liquid mixtures (ideal solutions)!

$P_A < P_A^*$





Ideal solutions (ideal mixtures)

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Mixing

$$H_{products} - H_{reactants} = \Delta H_{soln}.$$

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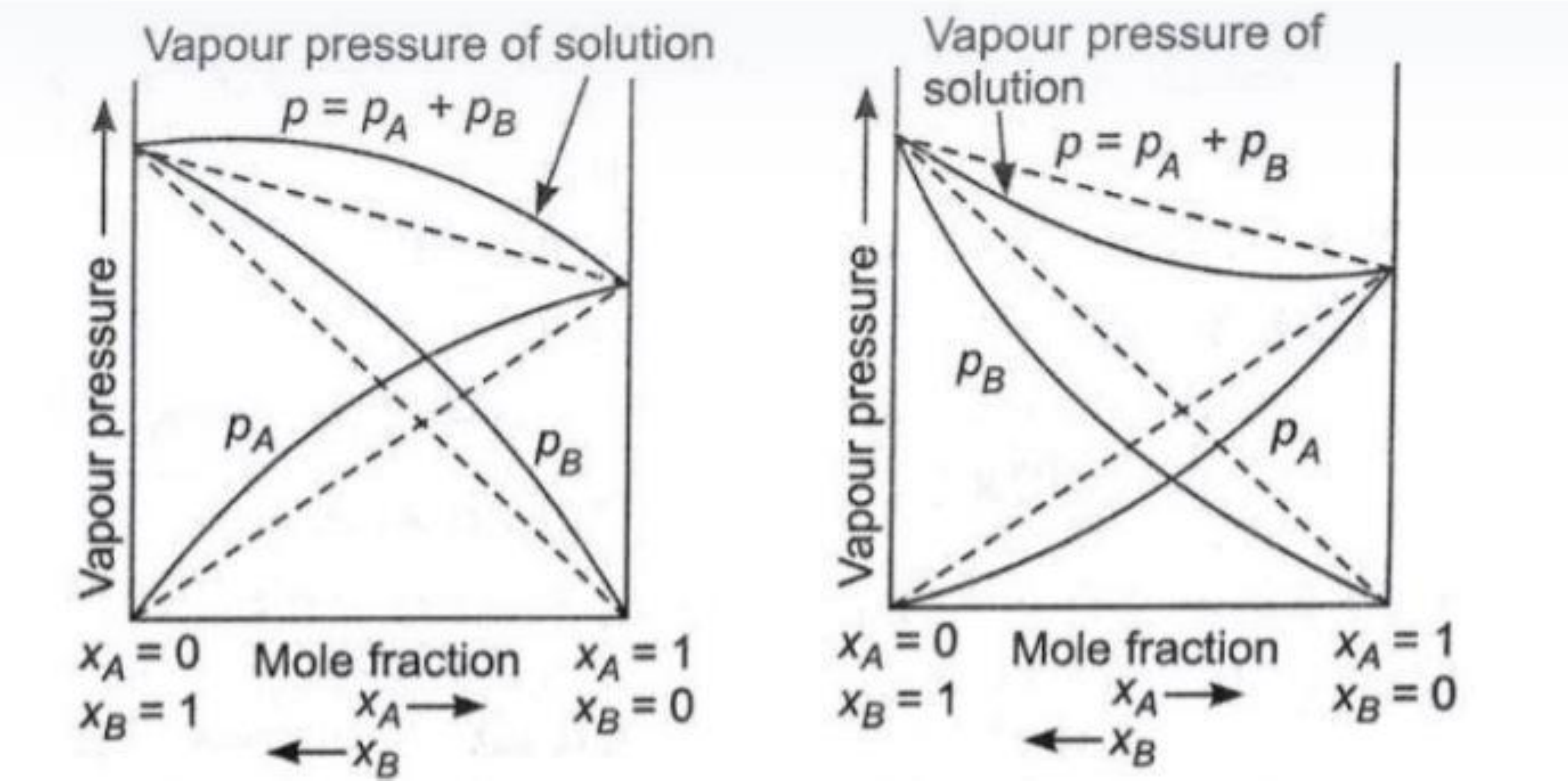
For an ideal solution $\Delta H_{soln} = 0$

The solvent-solvent and solute-solute intermolecular forces are approximately as strong as the solvent-solute interaction

Deviation from Raoult's Law



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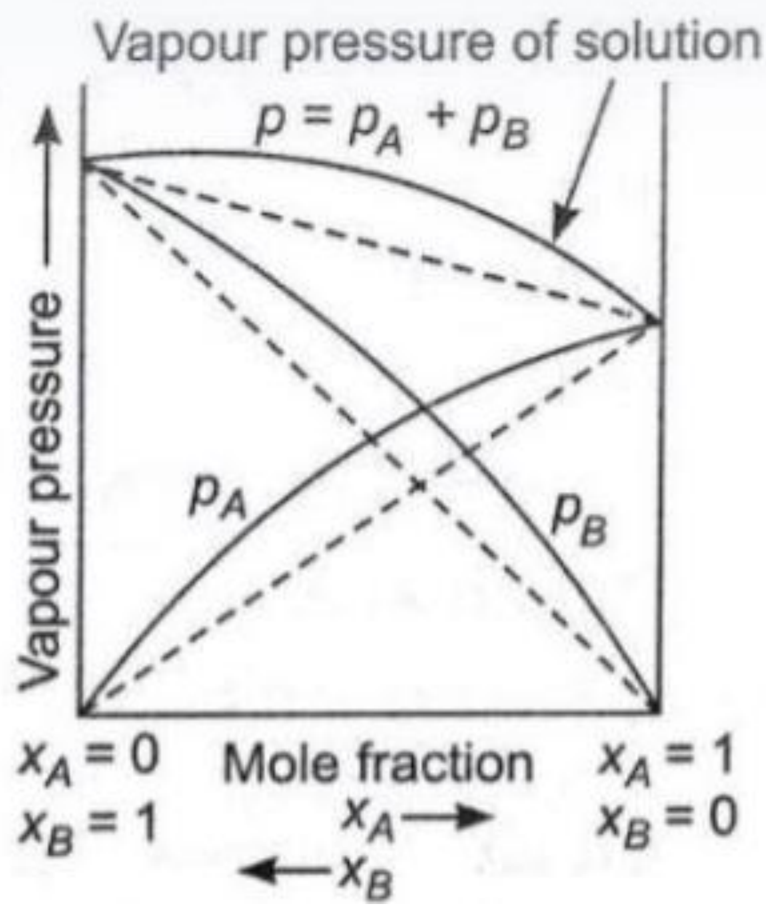
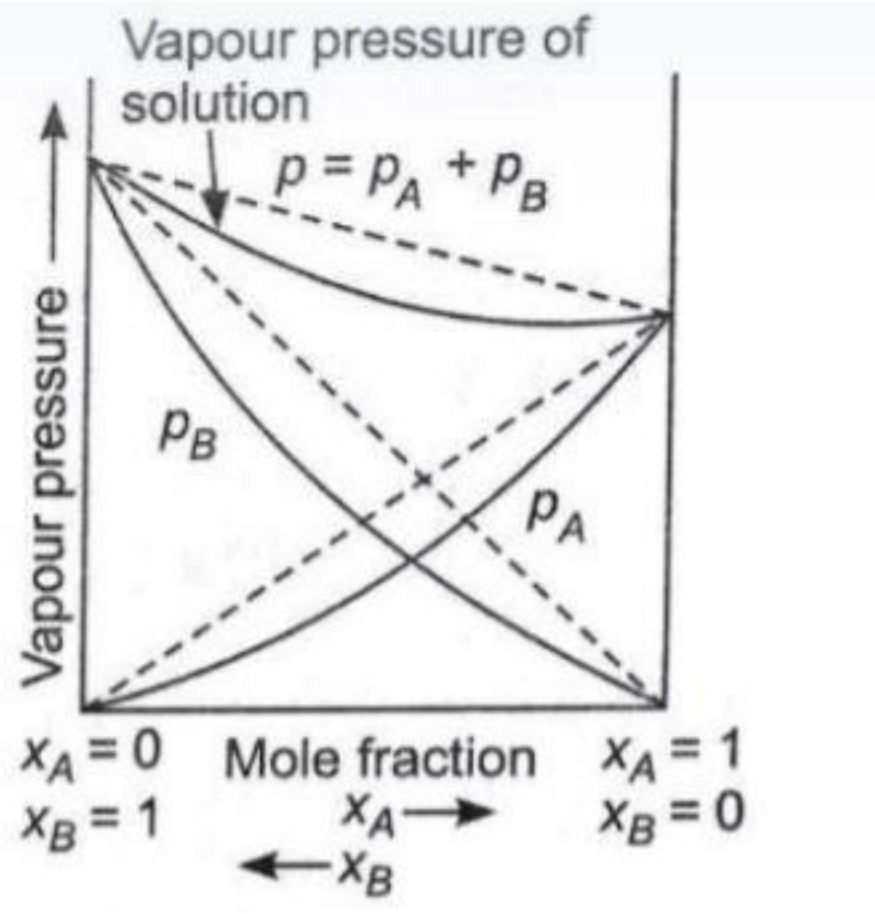
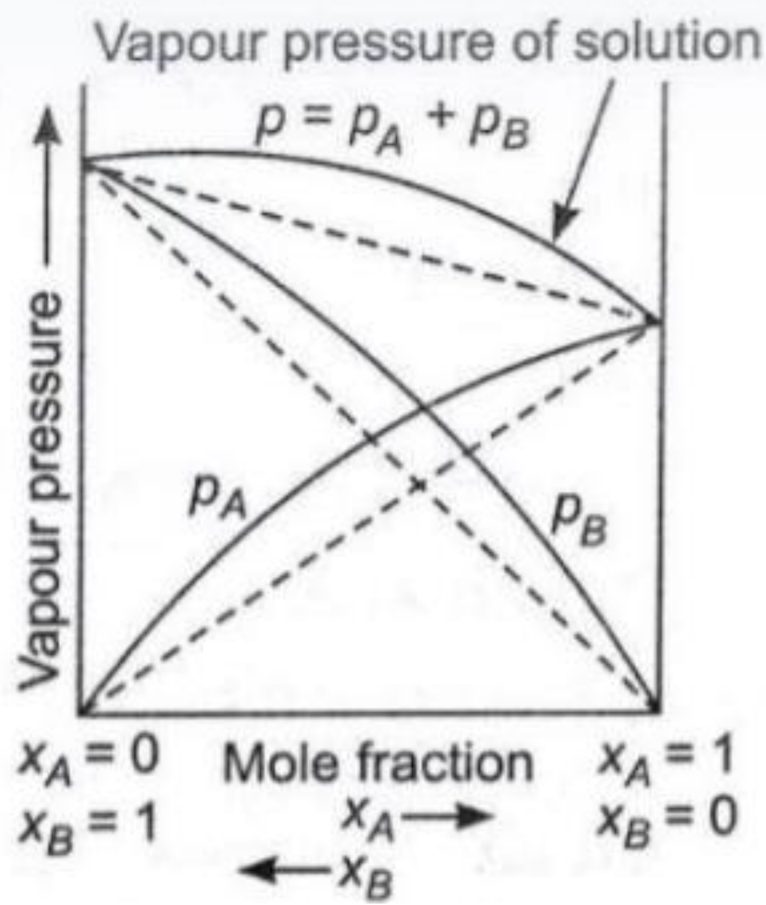




Ethanol + Acetone

Deviation from Raoult's Law



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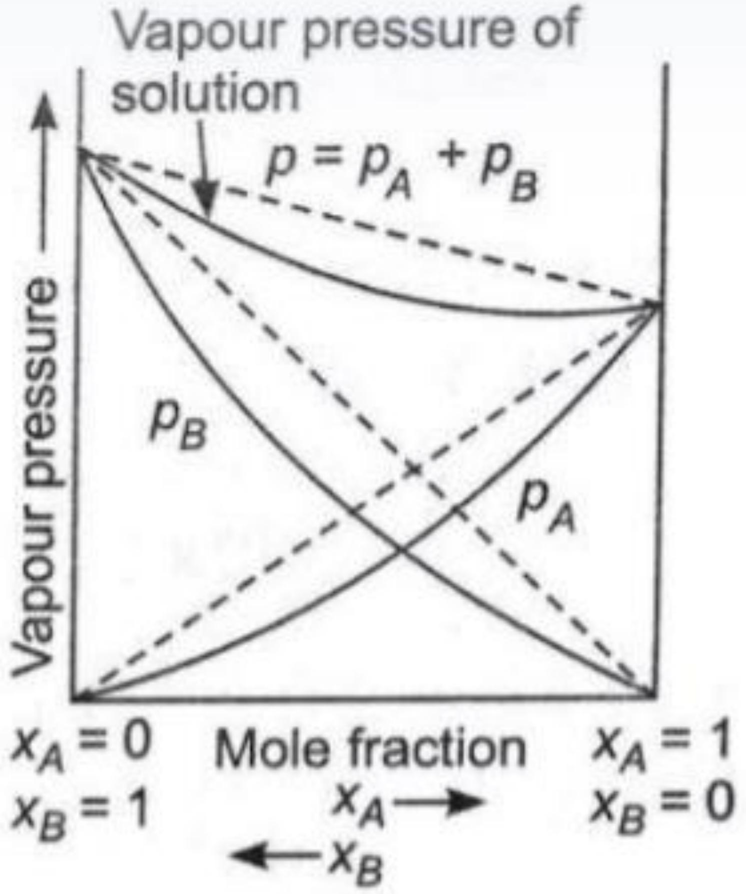
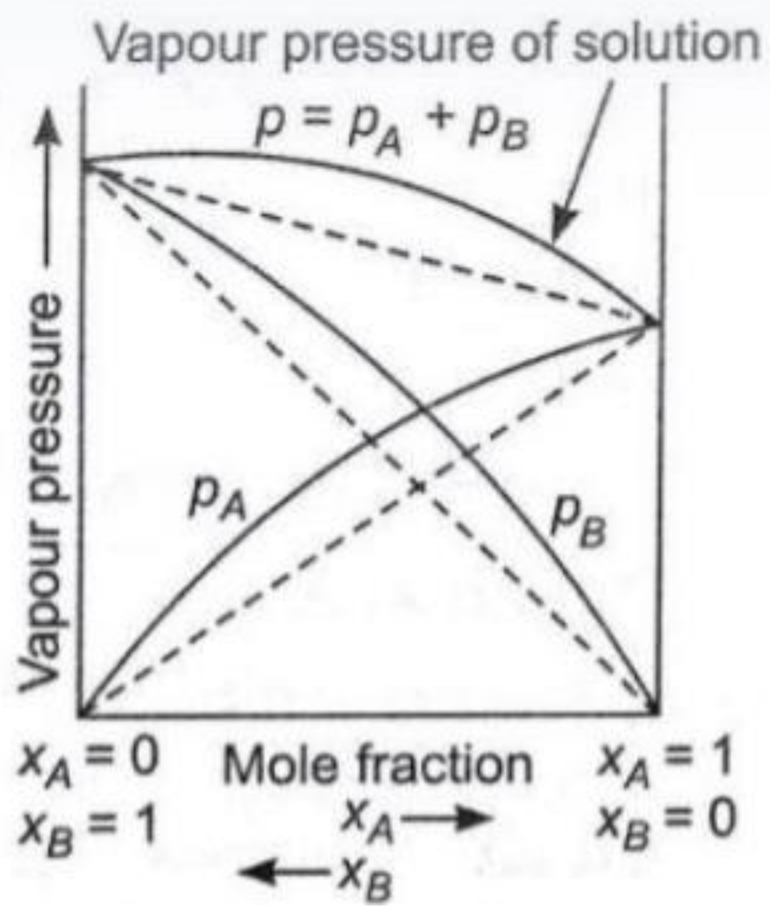


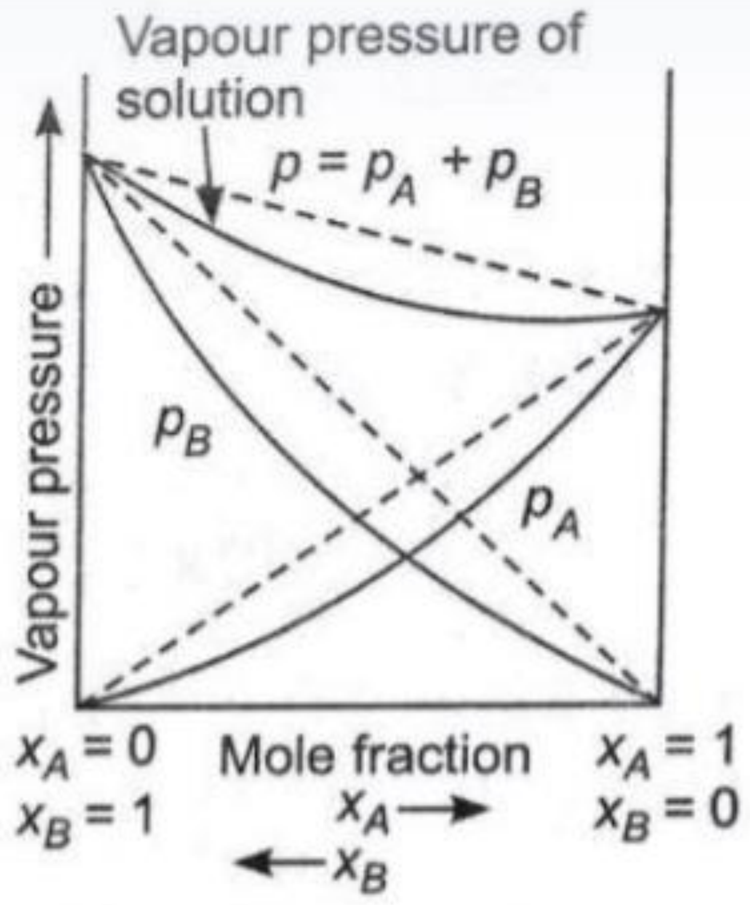
Ethanol + Water

Deviation from Raoult's Law



Ethanol + Acetone

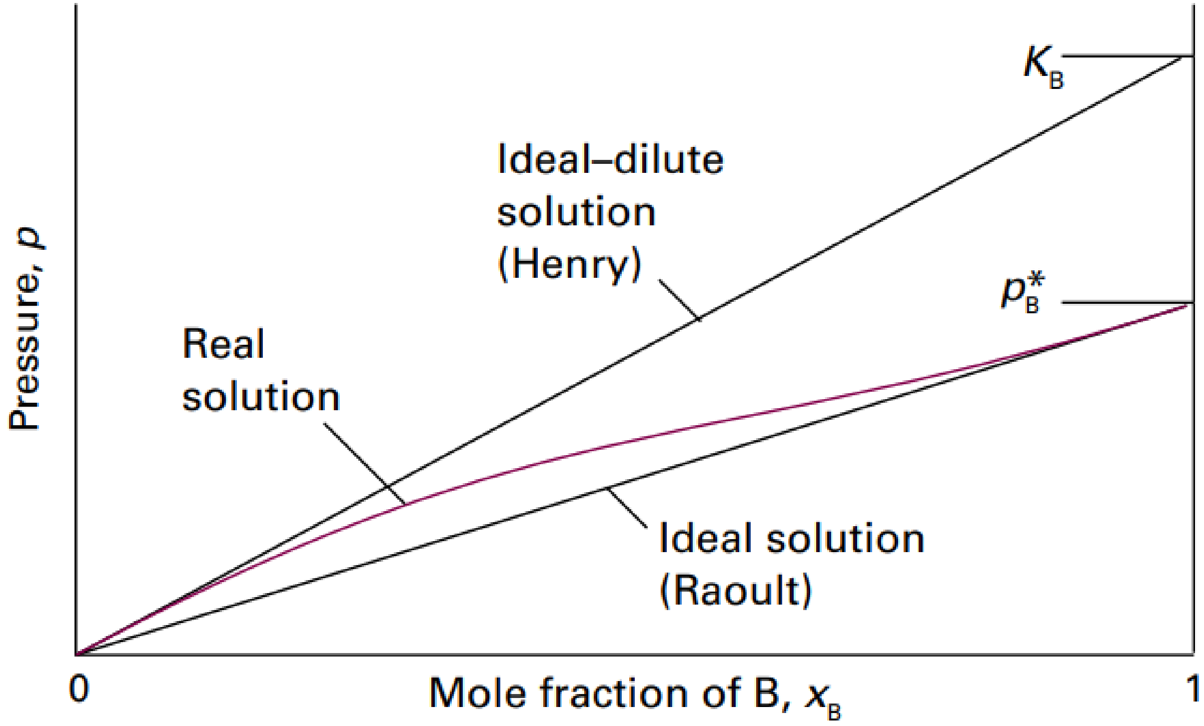
$$H_{mixing} > 0$$



Ethanol + Water

$$H_{mixing} < 0$$

Henry's law

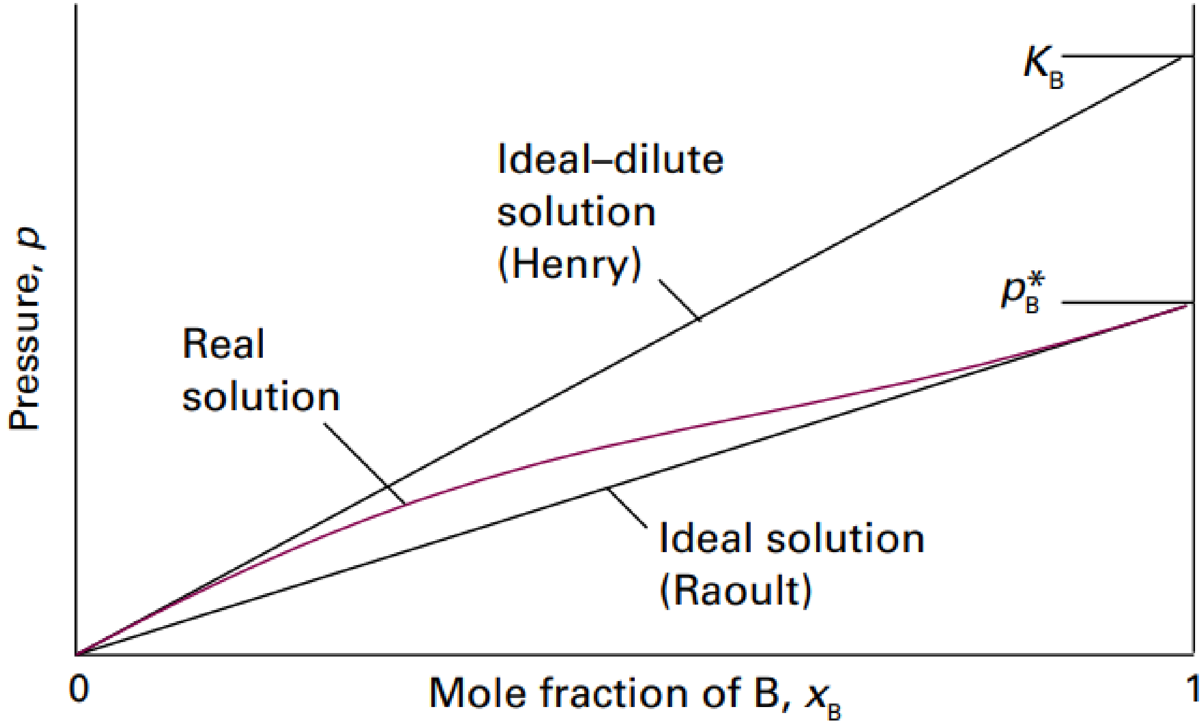


Pressure, p
K_B
Ideal–dilute
solution
(Henry)
p_B^*
Real
solution
Ideal solution
(Raoult)
0
Mole fraction of B, x_B
1

Henry's law

$$p_B = x_B K_B$$

Henry's law
[ideal–dilute solution]

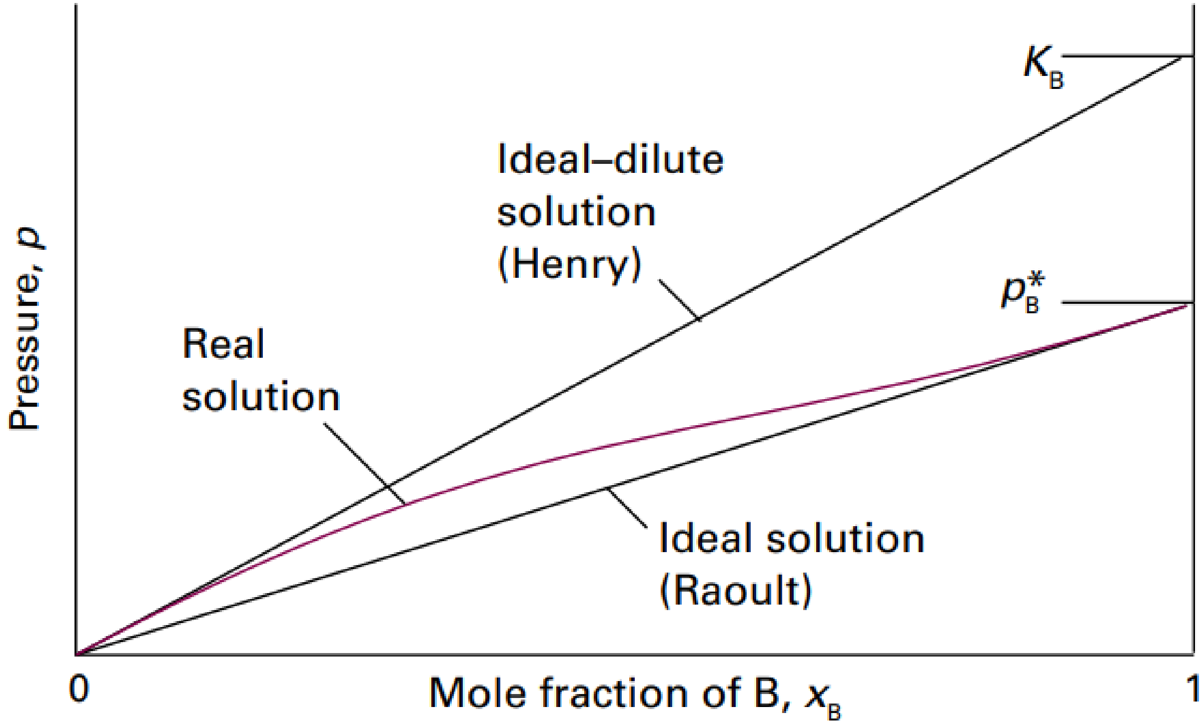


Henry's law

K_B is an empirical constant (with the dimensions of pressure)

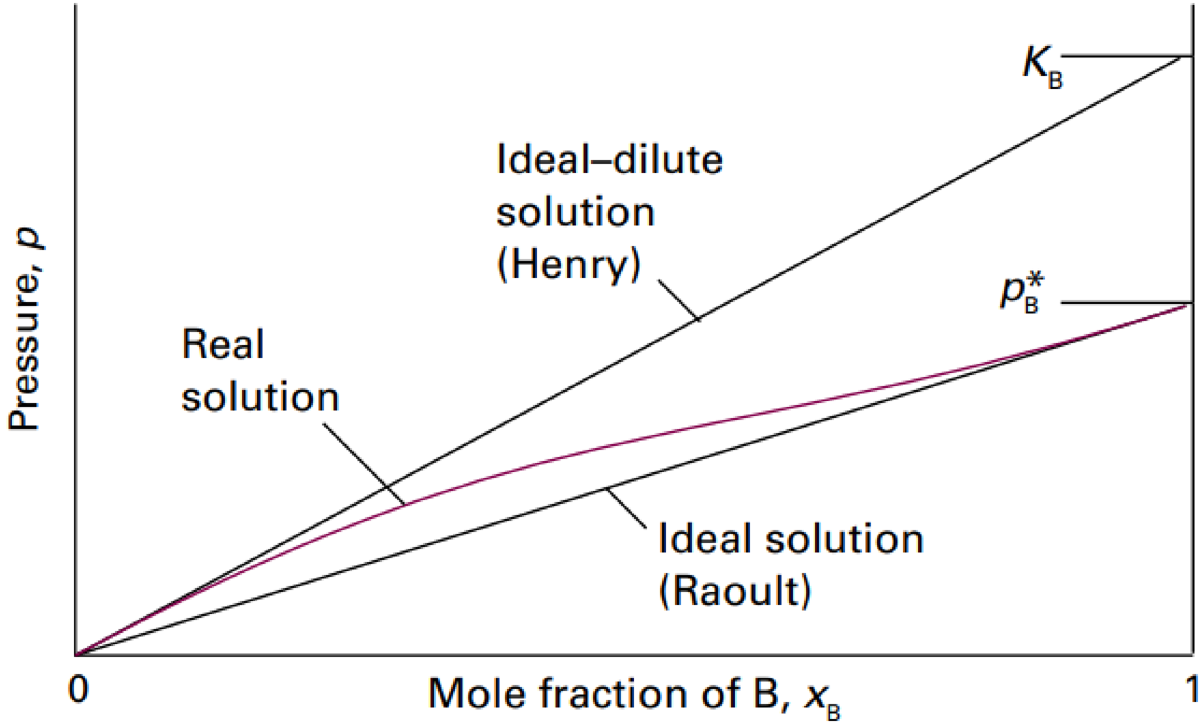
$$p_B = x_B K_B$$

Henry's law
[ideal–dilute solution]



Henry's law constant

K_B is chosen so that the plot of the $V_{p(B)}$ vs X_B is tangent to the experimental curve at $x_B = 0$



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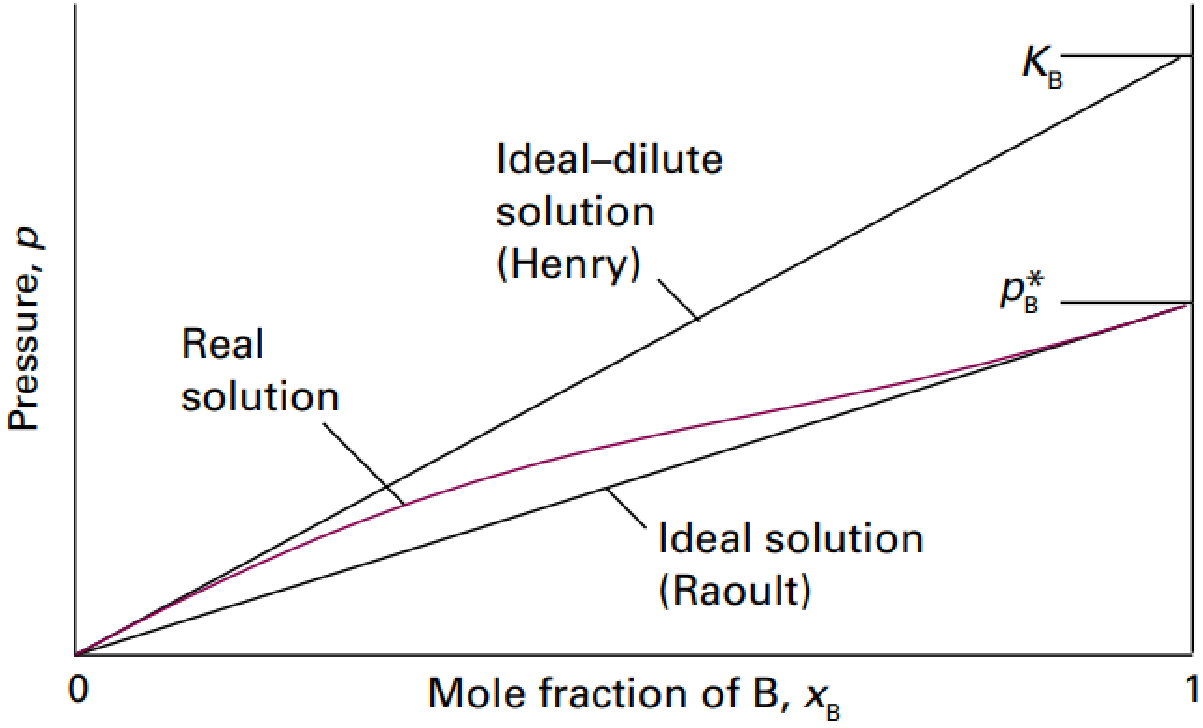
Limiting laws:

Henry's Law achieving reliability as $x_B \rightarrow 0$

Raoult's Law achieving reliability as $x_B \rightarrow 1$



Ideal-dilute solutions

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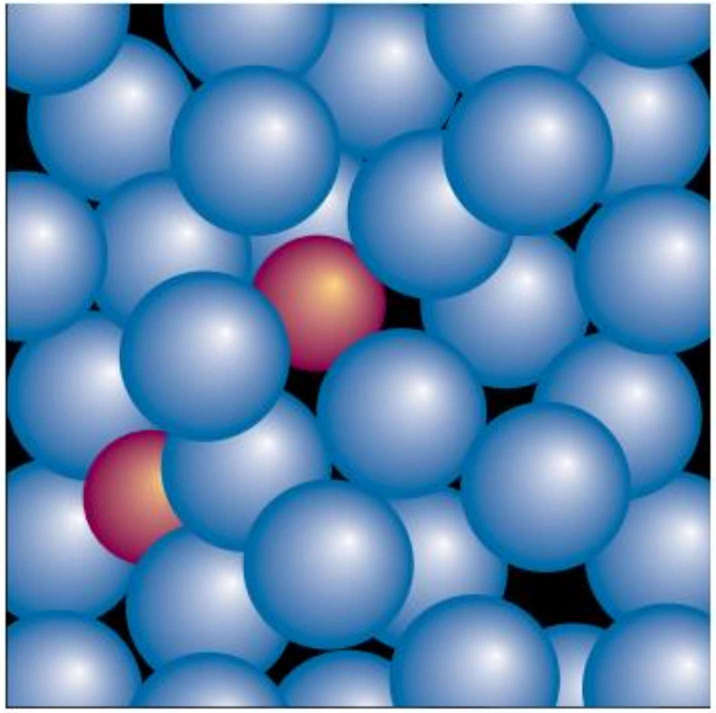

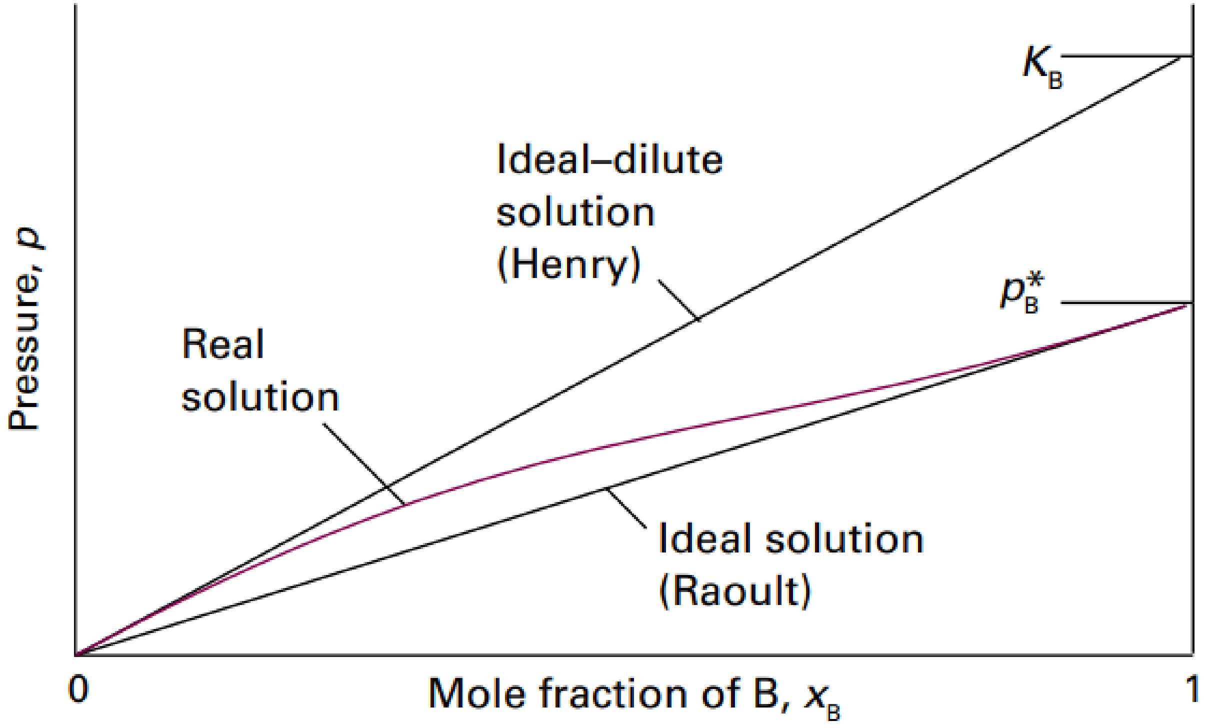

Henry's law constants

Henry's law constants for gases in water at 298 K

	$K/(\text{kPa kg mol}^{-1})$
CO_2	3.01×10^3
H_2	1.28×10^5
N_2	1.56×10^5
O_2	7.92×10^4

For practical applications, Henry's Law can be expressed in terms of molality instead of pressure.

Example- Henry's law

estimate the molar solubility of oxygen in water at 25 °C and a partial pressure of 21 kPa

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$$[O_2] = b_{O_2}\rho = (2.9\times10^{-4}\,\text{mol kg}^{-1})\times(0.997\,\text{kg dm}^{-3})$$

$$= 0.29\,\text{mmol dm}^{-3}$$

Example

The vapour pressures of each component in a mixture of propanone (acetone, A) and trichloromethane (chloroform, C) were measured at 35 °C with the following results:

x_C	0	0.20	0.40	0.60	0.80	1
p_C/kPa	0	4.7	11	18.9	26.7	36.4
p_A/kPa	46.3	33.3	23.3	12.3	4.9	0

Confirm that the mixture conforms to Raoult's law for the component in large excess and to Henry's law for the minor component. Find the Henry's law constants.

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Raoult's law => straight-line $p_J = x_J p_J^*$ in the region in which it is in excess

Henry's => straight line $p_J = X_J K_J$ is tangent to partial vapor pressure curve at low X_J

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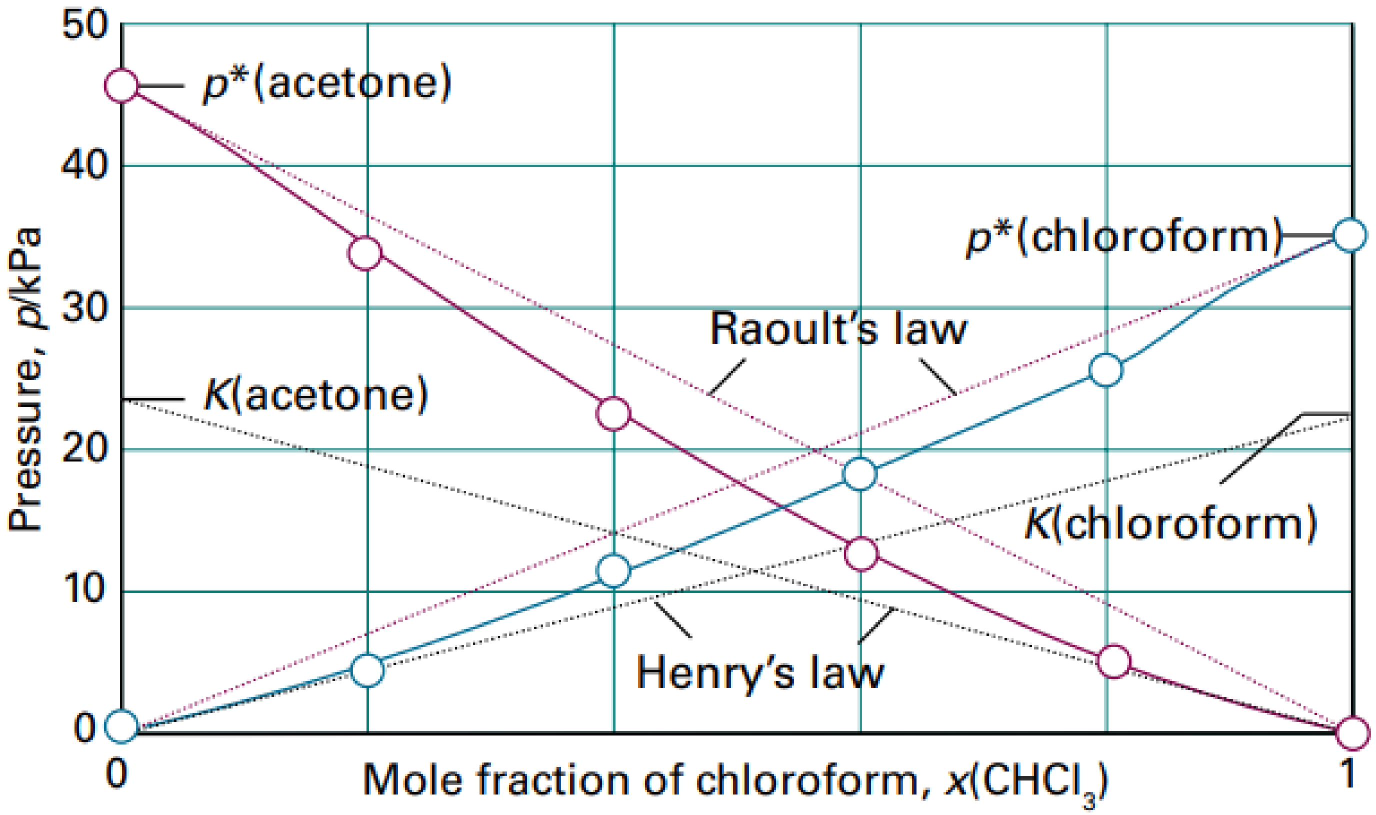

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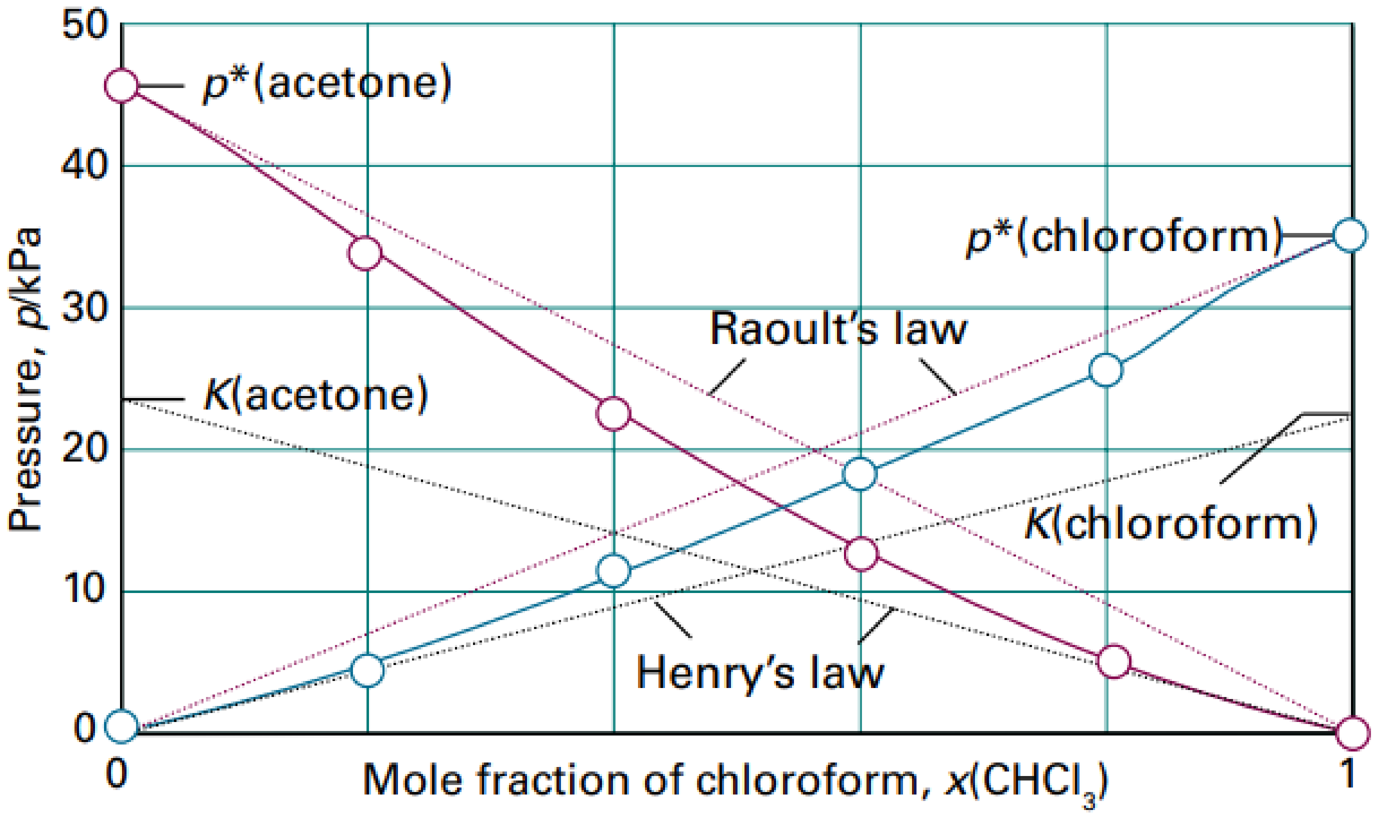

Henry's law constants:

K_A = 24.5 kPa for acetone

K_C = 23.5 kPa for chloroform

Focus 5: Simple mixtures

TD description of mixtures

Properties of solutions

Phase diagrams of binary systems

Phase diagrams of ternary systems

Thermodynamic activity