Gibbs energy of mixing of perfect gases

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

Gibbs energy of mixing of perfect gases

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

Before mixing $G_i = n_A \mu_{\mathrm{A,i}} + n_B \mu_{\mathrm{B,i}}$

Gibbs energy of mixing of perfect gases

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

Before mixing $G_i = n_A \mu_{\mathrm{A,i}} + n_B \mu_{\mathrm{B,i}}$

$$= n_A \left(\mu_A^{\ominus} + RT \ln p\right) + n_B \left(\mu_B^{\ominus} + RT \ln p\right)$$

Gibbs energy of mixing of perfect gases

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

Before mixing $G_i = n_A \mu_{\mathrm{A,i}} + n_B \mu_{\mathrm{B,i}}$

$$= n_A \left(\mu_A^{\ominus} + RT \ln p\right) + n_B \left(\mu_B^{\ominus} + RT \ln p\right)$$

After mixing $G_{\mathrm{f}} = n_A \mu_{\mathrm{A,f}} + n_B \mu_{\mathrm{B,f}}$

Gibbs energy of mixing of perfect gases

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

Before mixing $G_i = n_A \mu_{\mathrm{A,i}} + n_B \mu_{\mathrm{B,i}}$

$$= n_A \left(\mu_A^{\ominus} + RT \ln p\right) + n_B \left(\mu_B^{\ominus} + RT \ln p\right)$$

After mixing $G_{\mathrm{f}} = n_A \mu_{\mathrm{A,f}} + n_B \mu_{\mathrm{B,f}}$

$$= n_A \left(\mu_A^{\ominus} + RT \ln p_A\right) + n_B \left(\mu_B^{\ominus} + RT \ln p_B\right)$$

Gibbs energy of mixing of perfect gases

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

Before mixing $G_i = n_A \mu_{\mathrm{A,i}} + n_B \mu_{\mathrm{B,i}}$

$$= n_A \left(\mu_A^{\ominus} + RT \ln p\right) + n_B \left(\mu_B^{\ominus} + RT \ln p\right)$$

After mixing $G_{\mathrm{f}} = n_A \mu_{\mathrm{A,f}} + n_B \mu_{\mathrm{B,f}}$

$$= n_A \left(\mu_A^{\ominus} + RT \ln p_A\right) + n_B \left(\mu_B^{\ominus} + RT \ln p_B\right)$$

$$\therefore \Delta_{\mathrm{mix}} G = G_{\mathrm{f}} - G_i$$

$$= n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

Gibbs energy of mixing of perfect gases

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

Before mixing $G_i = n_A \mu_{\mathrm{A,i}} + n_B \mu_{\mathrm{B,i}}$

$$= n_A \left(\mu_A^{\ominus} + RT \ln p\right) + n_B \left(\mu_B^{\ominus} + RT \ln p\right)$$

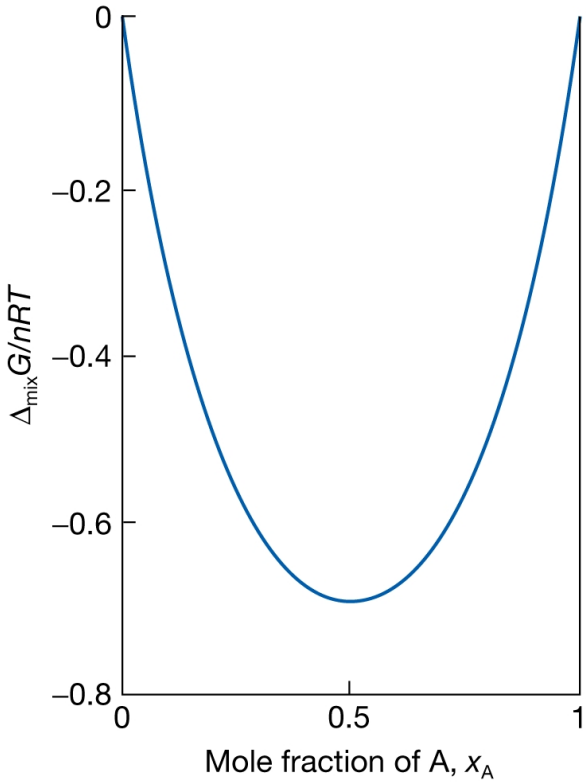
After mixing $G_{\mathrm{f}} = n_A \mu_{\mathrm{A,f}} + n_B \mu_{\mathrm{B,f}}$

$$= n_A \left(\mu_A^{\ominus} + RT \ln p_A\right) + n_B \left(\mu_B^{\ominus} + RT \ln p_B\right)$$

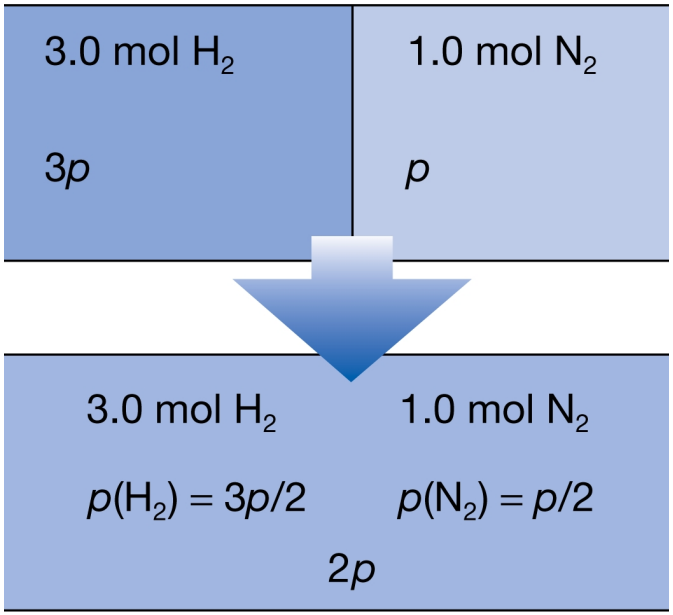
$$\therefore \Delta_{\mathrm{mix}} G = G_{\mathrm{f}} - G_i$$

$$= n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

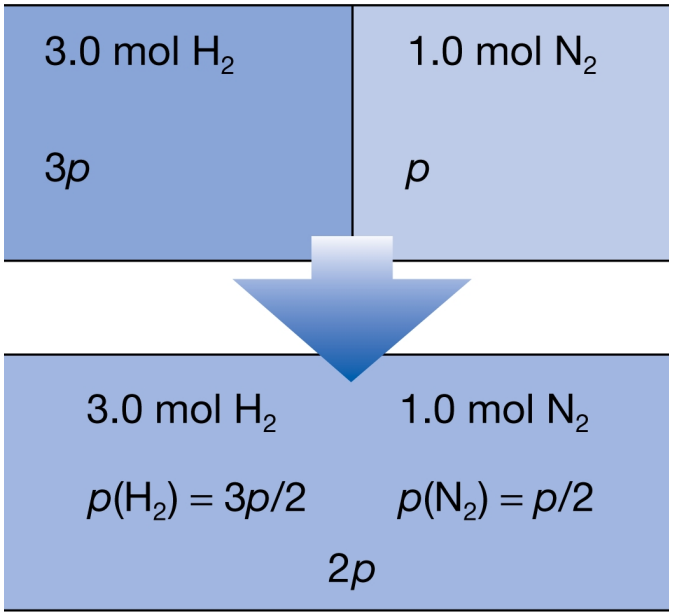
$$= nRT \left(x_A \ln x_A + x_B \ln x_B\right)$$



Ex. : initial pressures not the same :

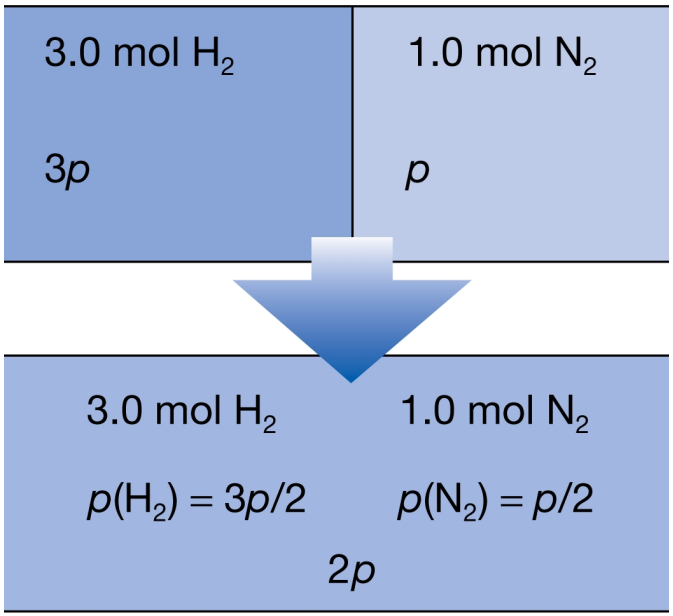


Ex. : initial pressures not the same :



$$G_i = 3\left(\mu^{\ominus}_{H_2} + RT \ln 3p\right) + 1\left(\mu^{\ominus}_{N_2} + RT \ln p\right)$$

Ex. : initial pressures not the same :



$$G_i = 3\left(\mu^{\ominus}_{H_2} + RT \ln 3p\right) + 1\left(\mu^{\ominus}_{N_2} + RT \ln p\right)$$

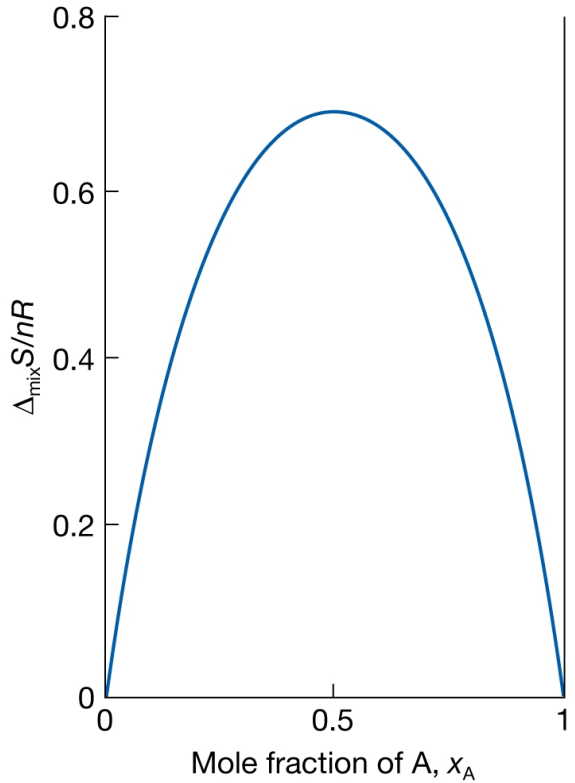
$$G_f = 3\left(\mu^{\ominus}_{H_2} + RT \ln \tfrac{3}{2}p\right) + n_B\left(\mu^{\ominus}_{N_2} + RT \ln \tfrac{p}{2}\right)$$

$$\therefore \Delta_{\text{mix}} G = G_f - G_i$$

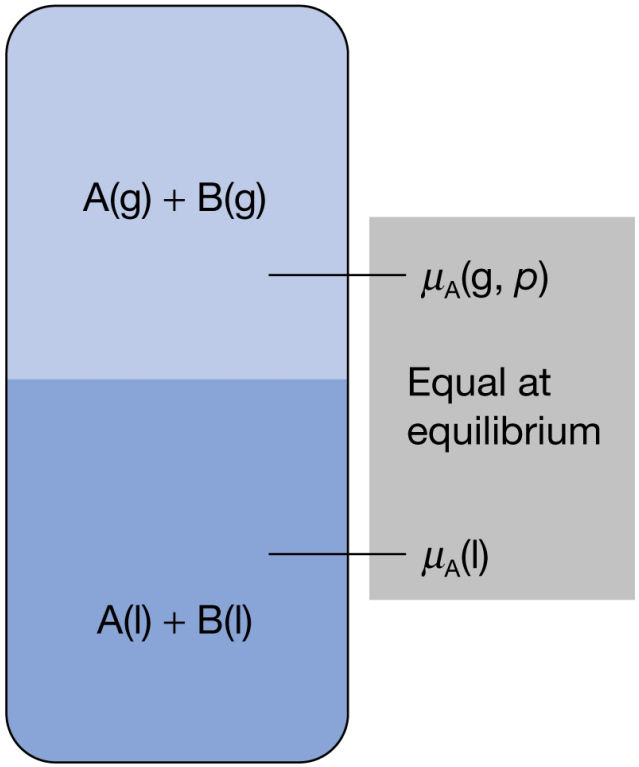
$$= -4RT \ln 2 \overset{T=298}{=} -6.9\text{kJ}$$

for a mixture of perfect gases initially at the same pressure,

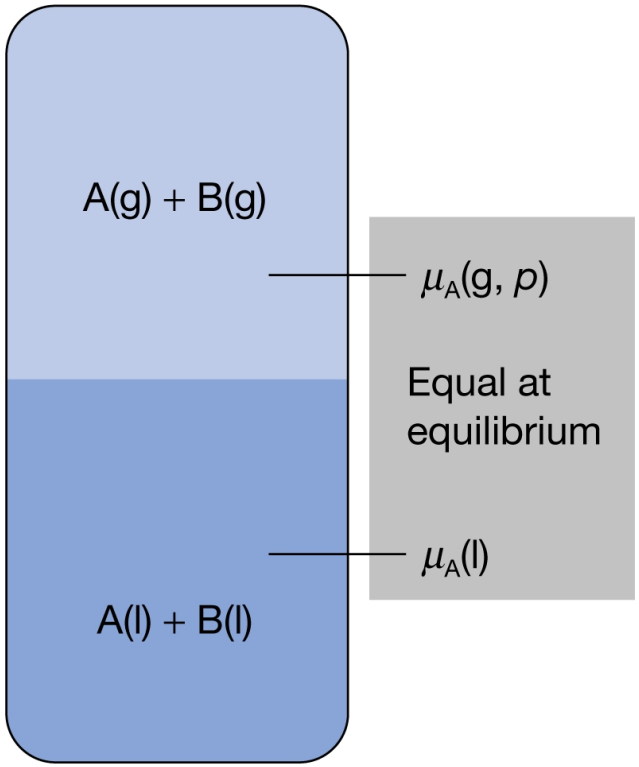
$$\Delta_{\mathrm{mix}} S = -\left(\frac{\partial \Delta_{\mathbf{mix}} G}{\partial T}\right)_{p,n_{\boldsymbol{A}},n_{\boldsymbol{B}}} = -nR\left(x_A \ln x_A + x_B \ln x_B\right)$$



Ideal solutions



Ideal solutions

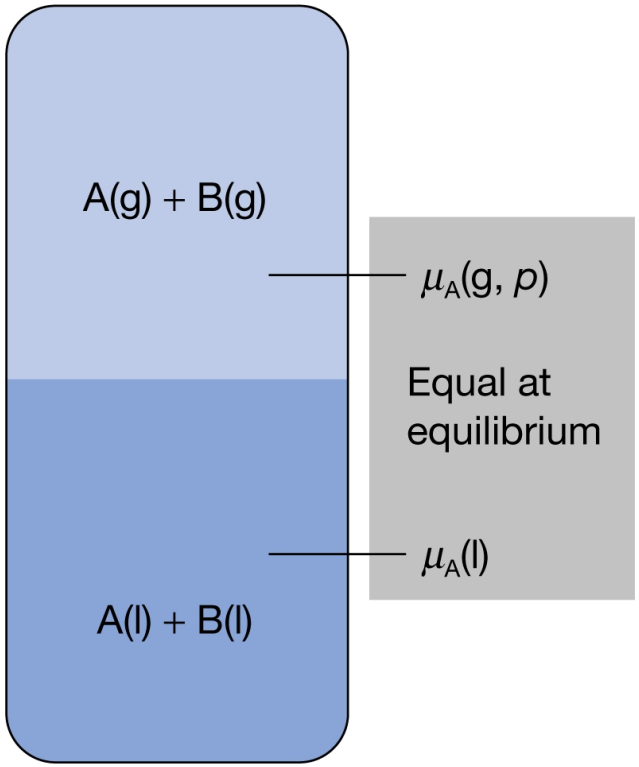


$* \equiv$ pure substance

μ_A^* = chemical potential of pure A

$\mu_A^*(l)$ = chemical potential of pure liquid A

Ideal solutions



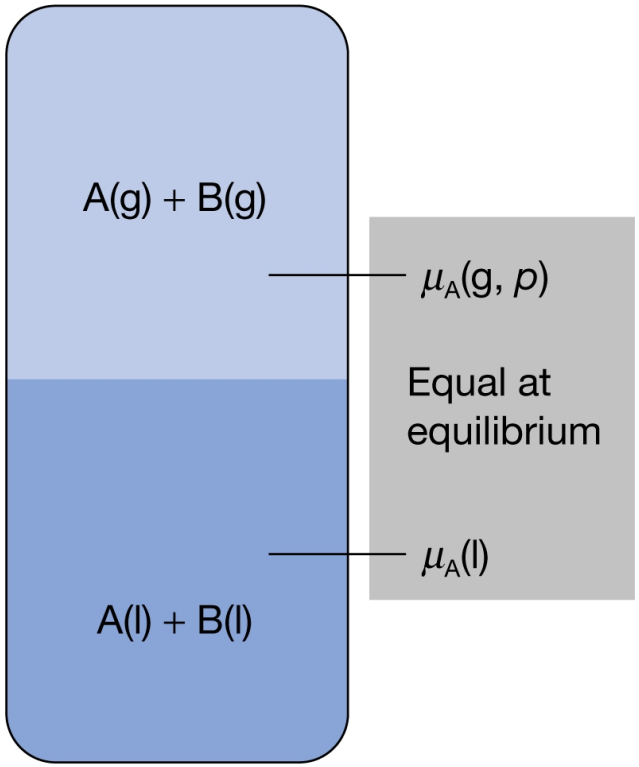
$* \equiv$ pure substance

μ_A^* = chemical potential of pure A

$\mu_A^*(l)$ = chemical potential of pure liquid A

$$\mu_A^* = \mu_A^{\ominus} + RT \ln p_A^*$$

Ideal solutions



$* \equiv$ pure substance

μ_A^* = chemical potential of pure A

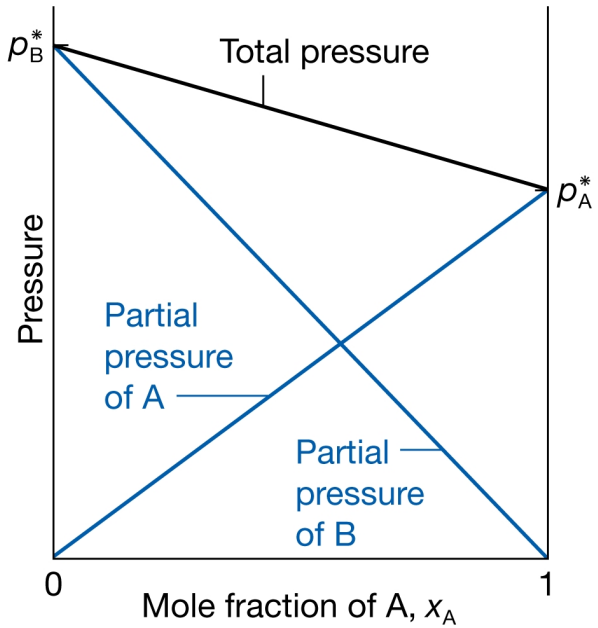
μ_A^*(l) = chemical potential of pure liquid A

$$\mu_A^* = \mu_A^{\ominus} + RT \ln p_A^*$$

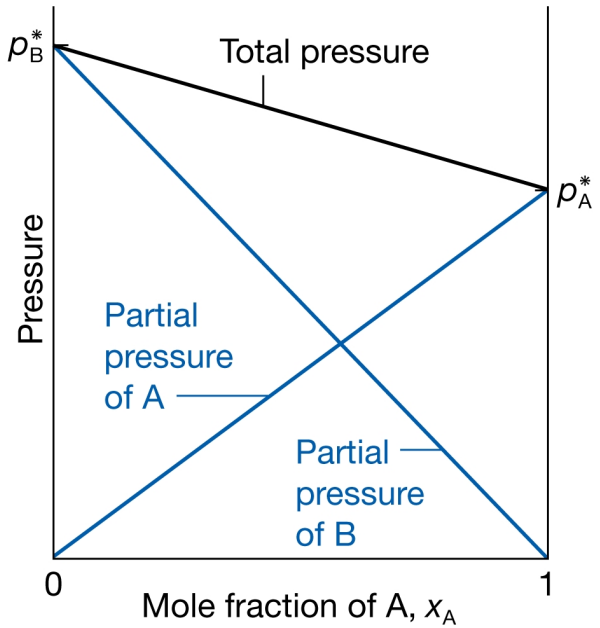
soln. : $\mu_A = \mu_A^{\ominus} + RT \ln p_A$

or, $\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$

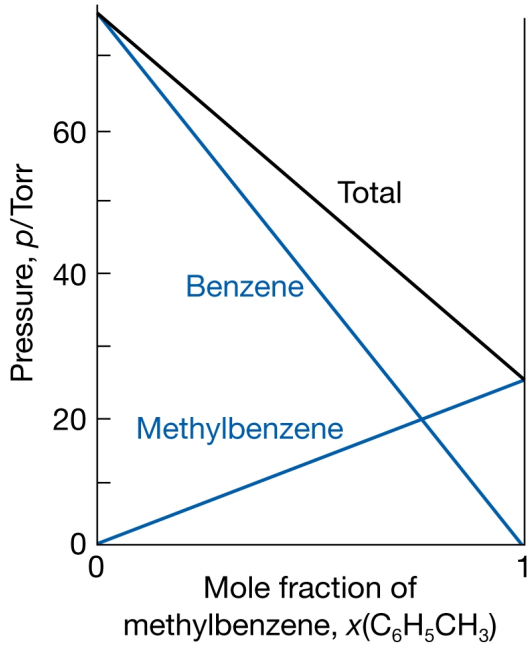
Ideal solutions - Raoult's law: $p_A = x_A p_A^* \Longrightarrow \mu_A = \mu_A^* + RT \ln x_A$



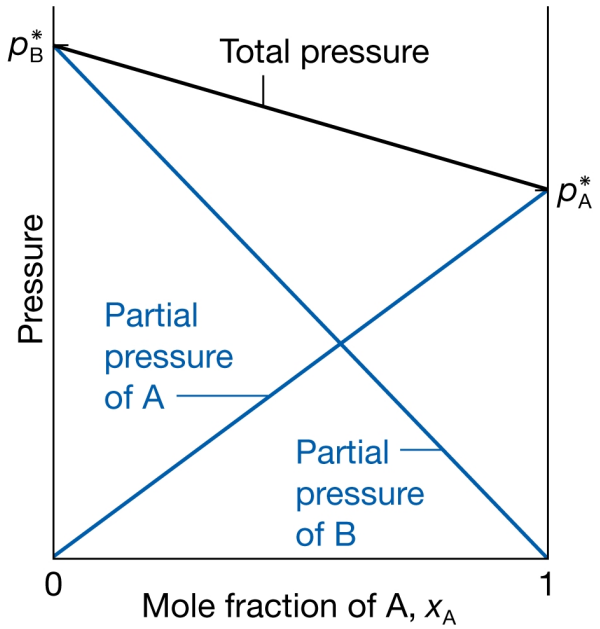
Ideal solutions - Raoult's law: $p_A = x_A p_A^* \Longrightarrow \mu_A = \mu_A^* + RT \ln x_A$



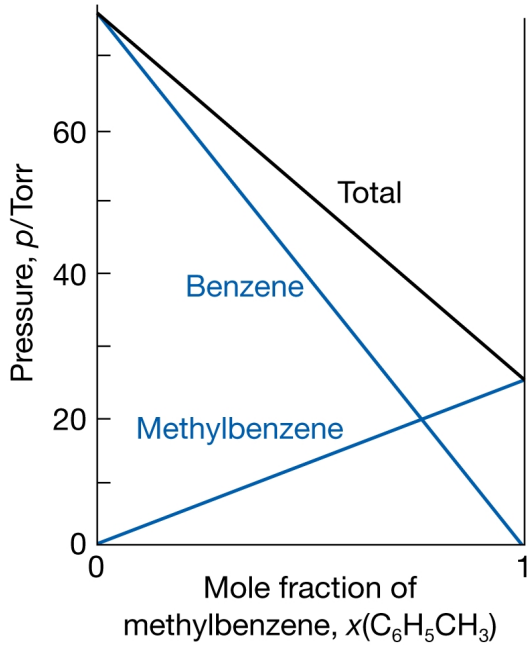
Some mixtures obey Raoult's law very well especially when the components are structurally similar



Ideal solutions - Raoult's law: $p_A = x_A p_A^* \Longrightarrow \mu_A = \mu_A^* + RT \ln x_A$



Some mixtures obey Raoult's law very well especially when the components are structurally similar



Mixtures that obey the law throughout from pure A to pure B are called

ideal solutions

molecular origin of Raoult's law :

molecular origin of Raoult's law : effect of solute on entropy of solution

molecular origin of Raoult's law : effect of solute on entropy of solution

- pure solvent : molecules have a certain disorder and corresponding entropy

molecular origin of Raoult's law : effect of solute on entropy of solution

- pure solvent : molecules have a certain disorder and corresponding entropy
- vapour pressure represents tendency to reach a higher entropy

molecular origin of Raoult's law : effect of solute on entropy of solution

- pure solvent : molecules have a certain disorder and corresponding entropy
- vapour pressure represents tendency to reach a higher entropy
- solution : has a greater disorder than pure solvent because we cannot be sure that a molecule chosen at random will be a solvent molecule

molecular origin of Raoult's law : effect of solute on entropy of solution

- pure solvent : molecules have a certain disorder and corresponding entropy
- vapour pressure represents tendency to reach a higher entropy
- solution : has a greater disorder than pure solvent because we cannot be sure that a molecule chosen at random will be a solvent molecule
- $\because S_{\text{soln.}} > S_{\text{pure solvent}}$ $\therefore$ solution has lower tendency to acquire an even higher entropy by solvent vaporizing

molecular origin of Raoult's law : effect of solute on entropy of solution

- pure solvent : molecules have a certain disorder and corresponding entropy
- vapour pressure represents tendency to reach a higher entropy
- solution : has a greater disorder than pure solvent because we cannot be sure that a molecule chosen at random will be a solvent molecule
- $\because S_{\text{soln.}} > S_{\text{pure solvent}}$ $\therefore$ solution has lower tendency to acquire an even higher entropy by solvent vaporizing
- $\therefore$ vapour pressure of solvent in solution $<$ that of pure solvent

Ideal-dilute solutions

Ideal-dilute solutions

although vapour pressure of solute
$\propto$ mole fraction
constant of proportionality
$\neq$ vapour pressure of pure substance

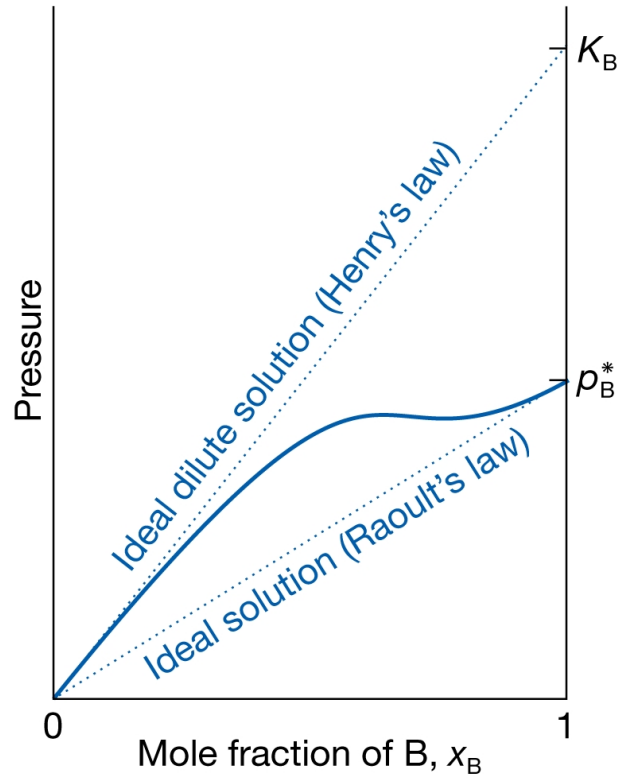
Ideal-dilute solutions

although vapour pressure of solute
$\propto$ mole fraction
constant of proportionality
$\neq$ vapour pressure of pure substance
Henry's law : $p_B = x_B K_B$

Ideal-dilute solutions

although vapour pressure of solute
$\propto$ mole fraction
constant of proportionality
$\neq$ vapour pressure of pure substance
Henry's law : $p_B = x_B K_B$
For practical applications, expressed in terms of molality, b,

$$p_B = b_B K_B$$



Mixtures for which solute obeys Henry's law and solvent obeys Raoult's law are called ideal-dilute solutions

Mixtures for which solute obeys Henry's law and solvent obeys Raoult's law are called ideal-dilute solutions

why this difference in behaviour of solute and solvent at low concentrations?

Mixtures for which solute obeys Henry's law and solvent obeys Raoult's law are called ideal-dilute solutions

why this difference in behaviour of solute and solvent at low concentrations?

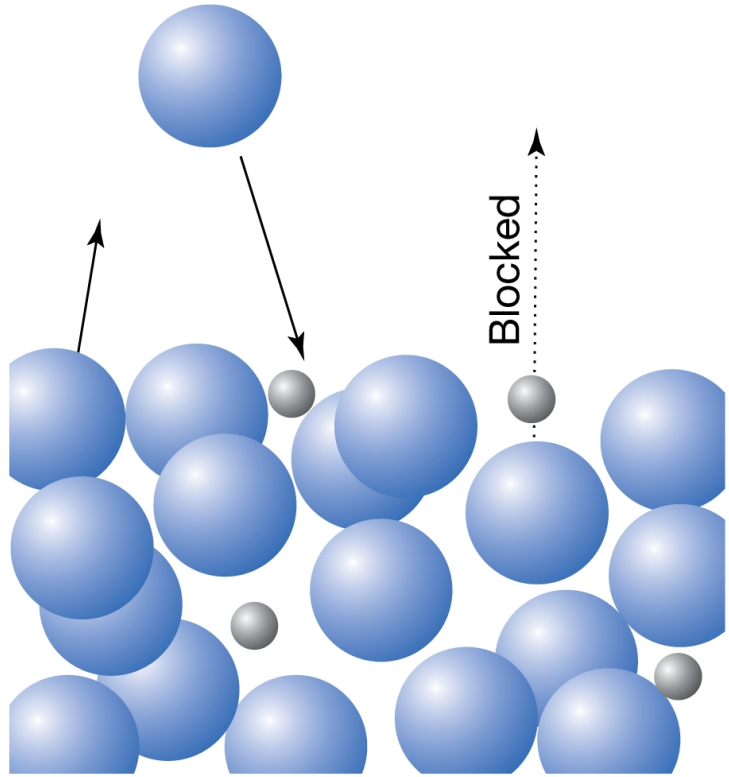
solute molecules are surrounded by solvent molecules, which is entirely different from their environment when pure

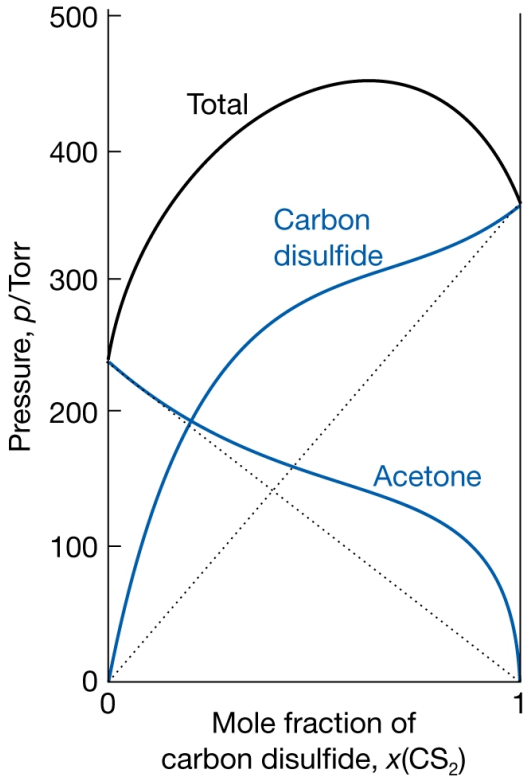
Mixtures for which solute obeys Henry's law and solvent obeys Raoult's law are called ideal-dilute solutions

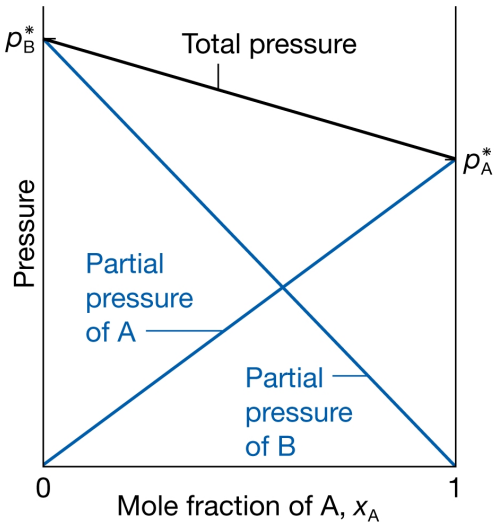
why this difference in behaviour of solute and solvent at low concentrations?

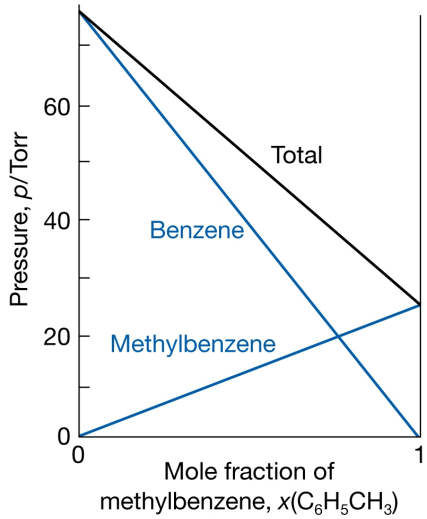
solute molecules are surrounded by solvent molecules, which is entirely different from their environment when pure

solvent behaves like a slightly modified pure liquid, but the solute behaves entirely differently from its pure state unless the solvent and solute molecules happen to be very similar

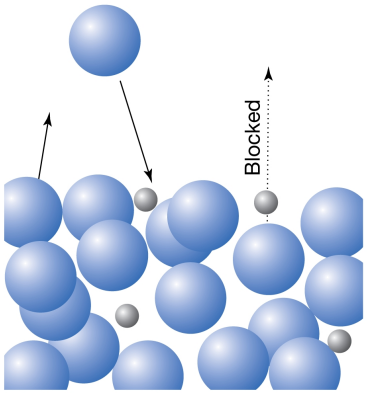


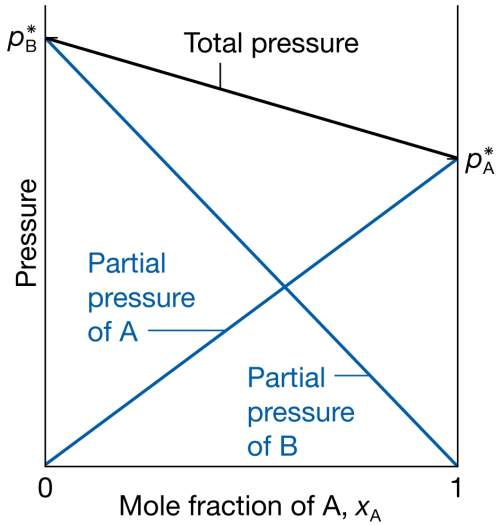

500
400
300
200
100
0
Pressure, p/Torr
Total
Carbon
disulfide
Acetone
0
1
Mole fraction of
carbon disulfide, x(CS2)

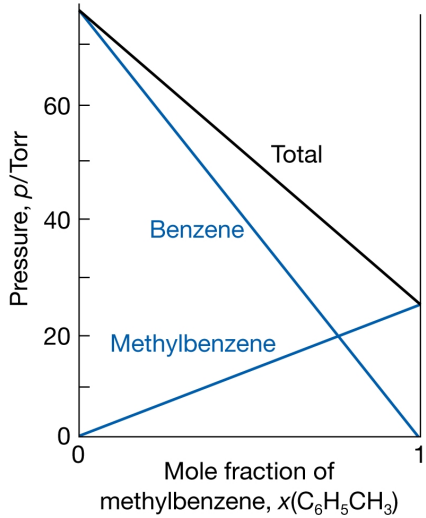




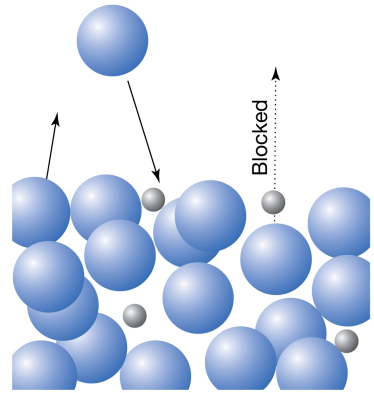
vaporisation (blocked by solute)
& condensation (not hindered)

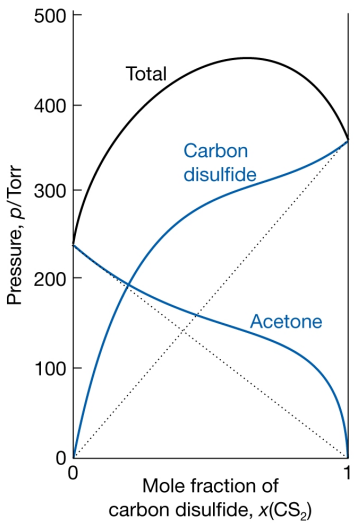


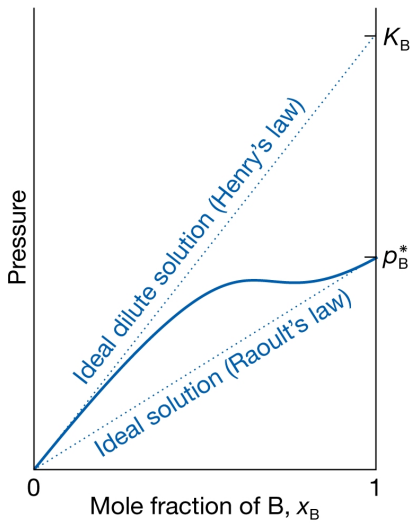


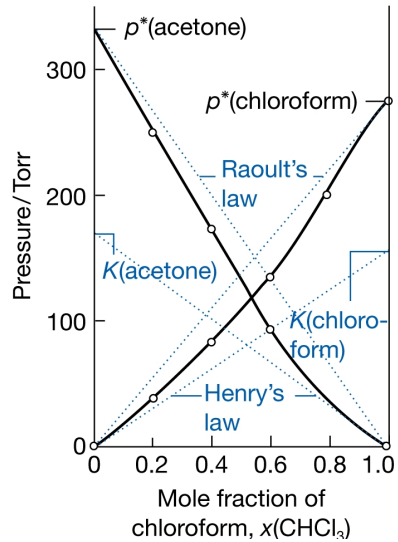


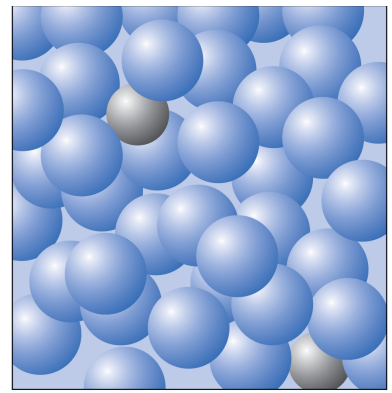
vaporisation (blocked by solute)
& condensation (not hindered)











dilute solution
solvent mols - similar environ as pure liq.
solute mols - very different environ