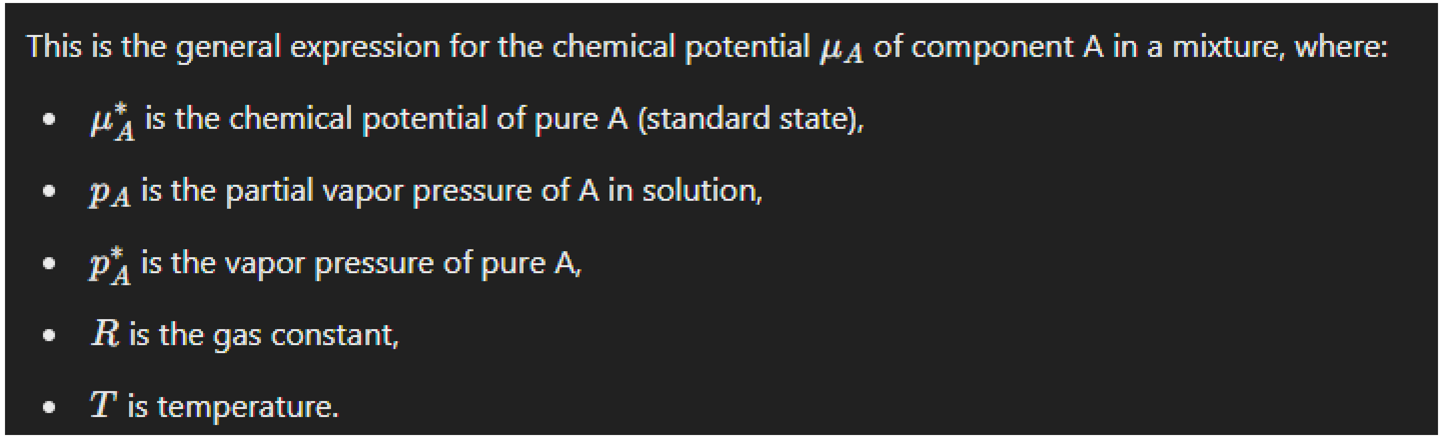
Focus 5: Simple mixtures

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

Solvent (A) activity

$$(\mu_A = \mu_A^* + RT\ln(p_A/p_A^*)$$



This is the general expression for the chemical potential μ_A of component A in a mixture, where:

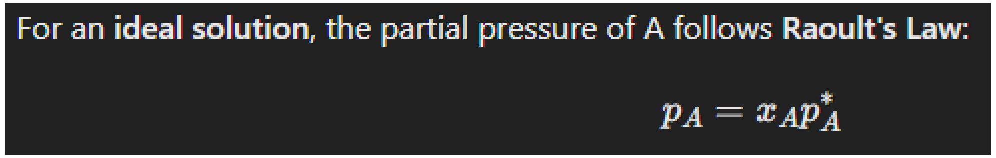
- μ_A^* is the chemical potential of pure A (standard state),
- p_A is the partial vapor pressure of A in solution,
- p_A^* is the vapor pressure of pure A,
- R is the gas constant,
- T is temperature.

Solvent (A) activity

$$\mu_A = \mu_A^* + RT \ln x_A$$

Ideal solution

$$(\mu_A = \mu_A^* + RT \ln(p_A/p_A^*)$$



For an **ideal solution**, the partial pressure of A follows **Raoult's Law:**

$$p_A = x_A p_A^*$$

Solvent (A) activity

$$(\mu_A = \mu_A^* + RT\ln(p_A/p_A^*)$$

$$\mu_A = \mu_A^* + RT\ln x_A$$

Ideal solution

$$\mu_A = \mu_A^* + RT\ln a_A$$

Real solution

Solvent (A) activity

$$(\mu_A = \mu_A^{\star} + RT\ln(p_A/p_A^{\star})$$

$$\mu_A = \mu_A^{\star} + RT\ln x_A$$

Ideal solution

$$\mu_A = \mu_A^{\star} + RT\ln a_A$$

Real solution

$$\Downarrow$$

activity of A

Solvent (A) activity

$$(\mu_A = \mu_A^* + RT\ln(p_A/p_A^*)$$

$$\mu_A = \mu_A^* + RT\ln x_A$$

Ideal solution

$$\mu_A = \mu_A^* + RT\ln a_A$$

Real solution

activity of A

An ‘effective’ mole fraction that accounts for non-ideal behavior.

Solvent (A) activity

$$(\mu_A = \mu_A^* + RT\ln(p_A/p_A^*)$$

$$\mu_A = \mu_A^* + RT\ln x_A$$

Ideal solution

$$\mu_A = \mu_A^* + RT\ln a_A$$

Real solution

activity of A

$$a_A = \frac{p_A}{p_A^*}$$

An ‘effective’ mole fraction that accounts for non-ideal behavior.

Solvent (A) activity

$$(\mu_A = \mu_A^* + RT\ln(p_A/p_A^*)$$

$$\mu_A = \mu_A^* + RT\ln x_A$$

Ideal solution

$$\mu_A = \mu_A^* + RT\ln a_A$$

Real solution

activity of A

$$a_A = \frac{p_A}{p_A^*}$$

An ‘effective’ mole fraction that accounts for non-ideal behavior.

It adjusts the mole fraction to reflect how the intermolecular environment alters the molecule’s escaping tendency!

Solvent activity

The vapour pressure of 0.500 mol dm^{-3} KNO_3(aq) at 100 °C is 99.95 kPa, and the vapour pressure of pure water at this temperature is 1.00 atm (101 kPa). It follows that the activity of water in this solution at this temperature is

$$\mu_A = \mu_A^* + RT \ln a_A$$

Real solution

activity of A

An 'effective' mole fraction

$$a_A = \frac{p_A}{p_A^*}$$

Solvent activity

The vapour pressure of 0.500 mol dm^{-3} KNO_3(aq) at 100 °C is 99.95 kPa, and the vapour pressure of pure water at this temperature is 1.00 atm (101 kPa). It follows that the activity of water in this solution at this temperature is

$$a_{\mathrm{A}} = \frac{99.95\ \mathrm{kPa}}{101\ \mathrm{kPa}} = 0.990$$

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{\star} + RT \ln a_{\mathrm{A}}$$

Real solution

activity of A

An ‘effective’ mole fraction

$$a_{\mathrm{A}} = \frac{p_{\mathrm{A}}}{p_{\mathrm{A}}^{\star}}$$

Activity Coefficient

$$a_{\mathrm{A}} = \gamma_{\mathrm{A}} x_{\mathrm{A}}$$

Activity Coefficient

$$\gamma_A \to 1 \text{ as } x_A \to 1$$

$$a_A = \gamma_A x_A$$

Activity Coefficient

$$\gamma_\mathrm{A} \rightarrow 1 \text{ as } x_\mathrm{A} \rightarrow 1$$

$$a_\mathrm{A} = \gamma_\mathrm{A} x_\mathrm{A}$$

$$a_\mathrm{A} \rightarrow x_\mathrm{A} \text{ as } x_\mathrm{A} \rightarrow 1$$

Solvent activity

$$(\mu_A = \mu_A^* + RT\ln(p_A/p_A^*)$$

$$\mu_A = \mu_A^* + RT\ln x_A$$

Ideal solution

$$\mu_A = \mu_A^* + RT\ln a_A$$

Real solution

$$a_A = \gamma_A x_A$$

Solvent activity

$$(\mu_A = \mu_A^{*} + RT\ln(p_A/p_A^{*})$$

$$\mu_A = \mu_A^{*} + RT\ln x_A$$

Ideal solution

$$\mu_A = \mu_A^{*} + RT\ln a_A$$

Real solution

$$a_A = \gamma_A x_A$$

$$\mu_A = \mu_A^{*} + RT\ln x_A + RT\ln \gamma_A$$

Solvent activity

$$(\mu_A = \mu_A^* + RT\ln(p_A/p_A^*)$$

$$\mu_A = \mu_A^* + RT\ln x_A$$

Ideal solution

$$\mu_A = \mu_A^* + RT\ln a_A$$

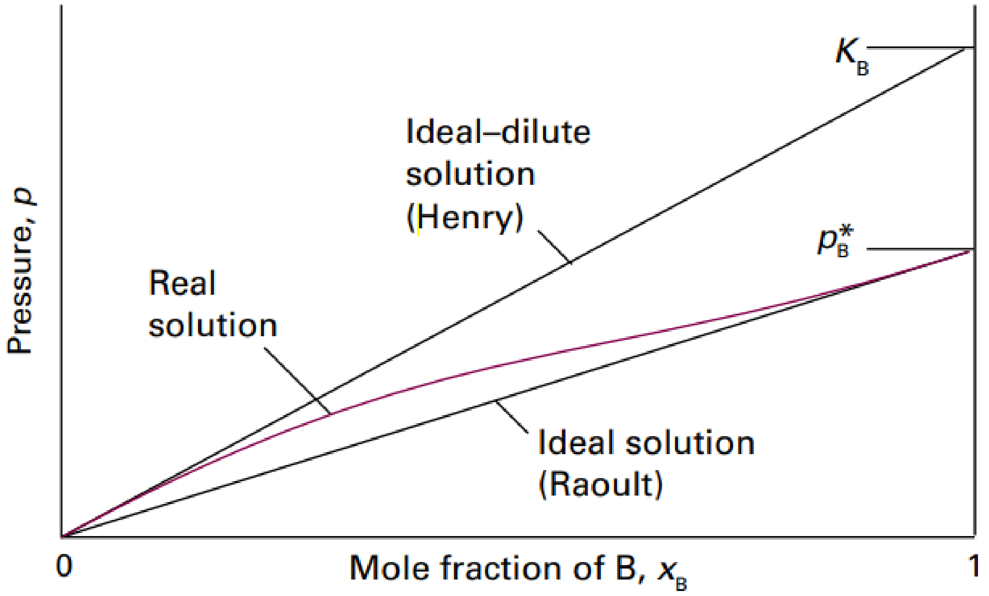
Real solution

$$a_A = \gamma_A x_A$$

$$\mu_A = \underbrace{\mu_A^* + RT\ln x_A}_{\text{Ideal solution}} + RT\ln \gamma_A$$

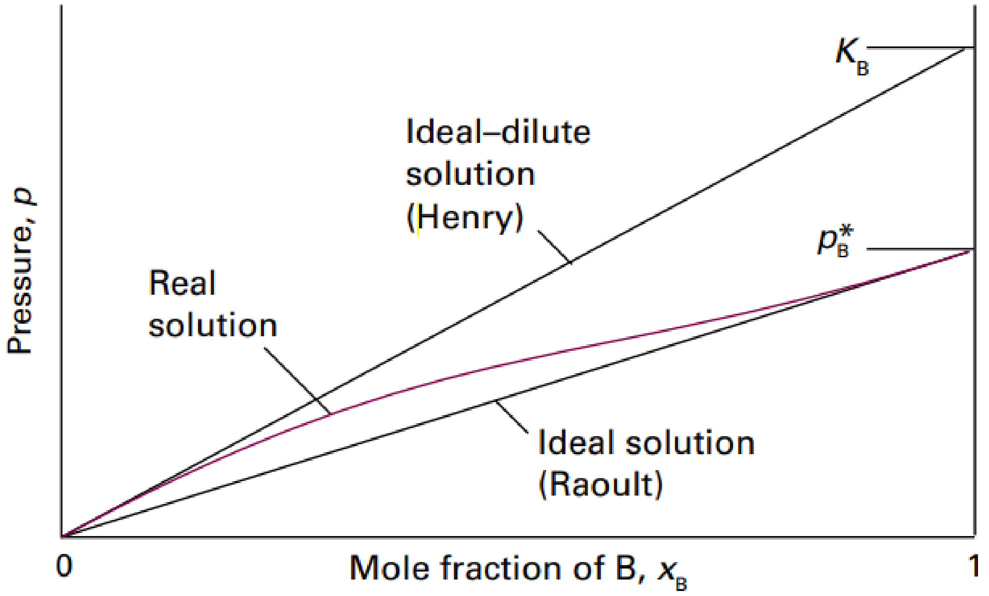
Solute (B) activity

Solute activity in ideal-dilute solutions



Solute activity in ideal-dilute solutions

$$\mu_B = \mu_B^* + RT\ln\frac{p_B}{p_B^*}$$



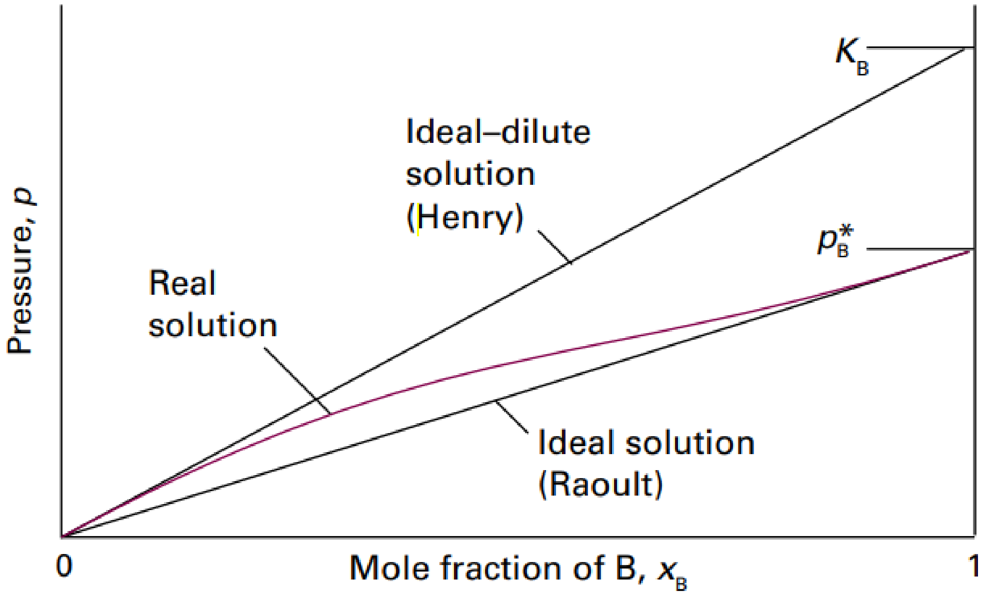
Solute activity in ideal-dilute solutions

Henry's law

$$\boxed{p_B = K_B x_B}$$

$$\mu_B = \mu_B^* + RT\ln\frac{p_B}{p_B^*}$$

$$= \mu_B^* + RT\ln\frac{K_B x_B}{p_B^*}$$

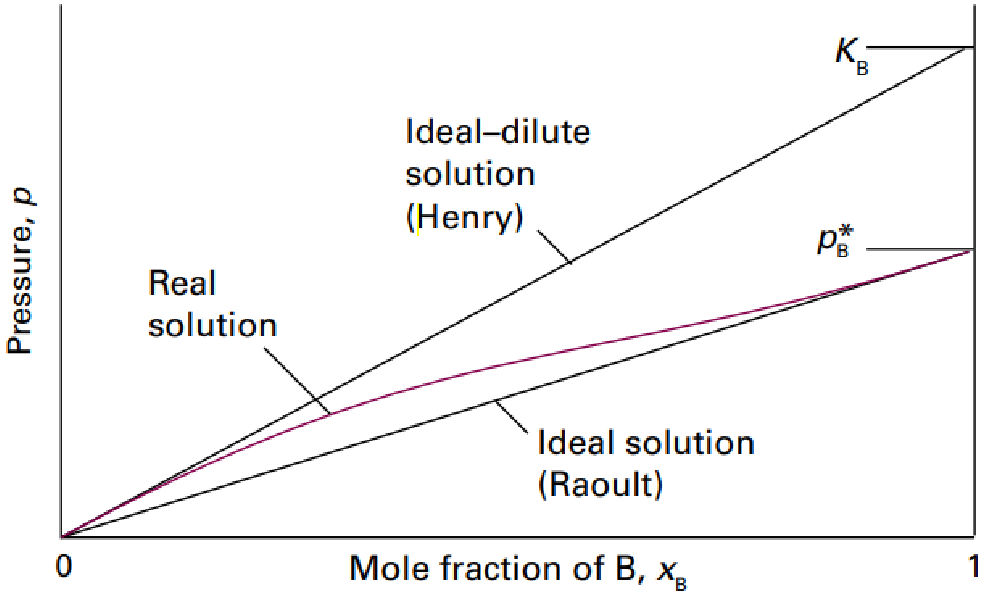


Solute activity in ideal-dilute solutions

Henry's law

$p_B = K_B x_B$

$$\mu_B = \mu_B^* + RT\ln\frac{p_B}{p_B^*} = \mu_B^* + RT\ln\frac{K_B x_B}{p_B^*} = \mu_B^* + RT\ln\frac{K_B}{p_B^*} + RT\ln x_B$$



Solute (B) activity in ideal-dilute solutions

Henry's law

$p_{\mathrm{B}} = K_{\mathrm{B}} x_{\mathrm{B}}$

$$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}^{*} + RT\ln\frac{p_{\mathrm{B}}}{p_{\mathrm{B}}^{*}} = \mu_{\mathrm{B}}^{*} + RT\ln\frac{K_{\mathrm{B}} x_{\mathrm{B}}}{p_{\mathrm{B}}^{*}} = \overbrace{\mu_{\mathrm{B}}^{*} + RT\ln\frac{K_{\mathrm{B}}}{p_{\mathrm{B}}^{*}}}^{\mu_{\mathrm{B}}^{\ominus}} + RT\ln x_{\mathrm{B}}$$

Solute (B) activity in ideal-dilute solutions

Henry's law

$p_{\mathrm{B}} = K_{\mathrm{B}} x_{\mathrm{B}}$

$$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}^{*} + RT\ln\frac{p_{\mathrm{B}}}{p_{\mathrm{B}}^{*}} = \mu_{\mathrm{B}}^{*} + RT\ln\frac{K_{\mathrm{B}} x_{\mathrm{B}}}{p_{\mathrm{B}}^{*}} = \overbrace{\mu_{\mathrm{B}}^{*} + RT\ln\frac{K_{\mathrm{B}}}{p_{\mathrm{B}}^{*}}}^{\mu_{\mathrm{B}}^{\ominus}} + RT\ln x_{\mathrm{B}}$$

$$= \mu_{\mathrm{B}}^{\ominus} + RT\ln x_{\mathrm{B}}$$

Solute (B) activity in ideal-dilute solutions

$$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}^{*} + RT\ln\frac{p_{\mathrm{B}}}{p_{\mathrm{B}}^{*}}$$

Henry's law

$$\boxed{p_{\mathrm{B}} = K_{\mathrm{B}}x_{\mathrm{B}}}$$

$$= \mu_{\mathrm{B}}^{*} + RT\ln\frac{K_{\mathrm{B}}x_{\mathrm{B}}}{p_{\mathrm{B}}^{*}}$$

$$= \overbrace{\mu_{\mathrm{B}}^{*} + RT\ln\frac{K_{\mathrm{B}}}{p_{\mathrm{B}}^{*}}}^{\mu_{\mathrm{B}}^{\ominus}} + RT\ln x_{\mathrm{B}}$$

$$= \mu_{\mathrm{B}}^{\ominus} + RT\ln x_{\mathrm{B}}$$

Where, $$\mu_{\mathrm{B}}^{\ominus} = \mu_{\mathrm{B}}^{*} + RT\ln\frac{K_{\mathrm{B}}}{p_{\mathrm{B}}^{*}}$$

Solute (B) activity in ideal-dilute solutions

Henry's law

$\boxed{p_B = K_B x_B}$

$$\mu_B = \mu_B^* + RT\ln\frac{p_B}{p_B^*} \qquad = \mu_B^* + RT\ln\frac{K_B x_B}{p_B^*} \qquad = \overbrace{\mu_B^* + RT\ln\frac{K_B}{p_B^*}}^{\mu_B^\ominus} + RT\ln x_B$$

$$= \mu_B^\ominus + RT\ln x_B$$

Where, $\mu_B^\ominus = \mu_B^* + RT\ln\dfrac{K_B}{p_B^*}$

$\Big\downarrow$ If the solution is ideal, $K_B = p_B^*$ (Raoult's law)

$$\mu_B^\ominus = \mu_B^*$$

Solute activity in real solutes

$\mu_B = \mu_B^\ominus + RT \ln x_B$ In ideal-dilute solutions

Solute activity in real solutes

$$\mu_B = \mu_B^\ominus + RT \ln x_B$$

In ideal-dilute solutions

$$\mu_B = \mu_B^\ominus + RT \ln a_B$$

In real solutions

Solute activity in real solutes

$$\mu_B = \mu_B^\ominus + RT\ln x_B$$

In ideal-dilute solutions

$$\mu_B = \mu_B^\ominus + RT\ln a_B$$

In real solutions

⬇

$$a_B = \gamma_B x_B$$

$$a_B = \frac{p_B}{K_B}$$

Example

Use the following information to calculate the activity and activity coefficient of trichloromethane (chloroform, C) in propanone (acetone, A) at 25 °C, treating it first as a solvent and then as a solute.

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

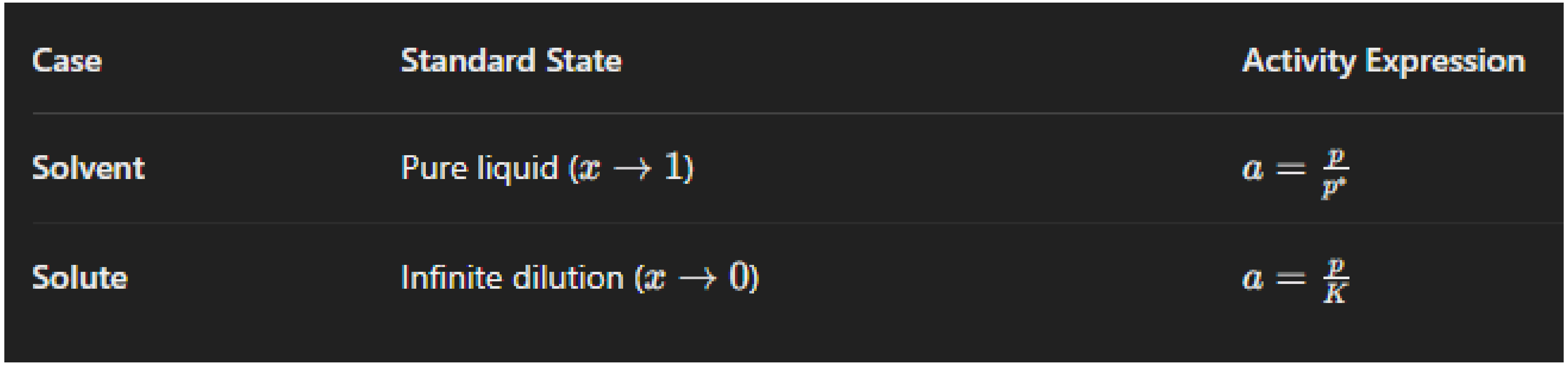
$p_C^* = 36.4\,\text{kPa}$ and $K_C = 23.5\,\text{kPa}$

Example

Use the following information to calculate the activity and activity coefficient of trichloromethane (chloroform, C) in propanone (acetone, A) at 25 °C, treating it first as a solvent and then as a solute.

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

$$p_C^* = 36.4\,\text{kPa} \text{ and } K_C = 23.5\,\text{kPa}$$



Case	Standard State	Activity Expression
Solvent	Pure liquid ($x \to 1$)	$a = \frac{p}{p^*}$
Solute	Infinite dilution ($x \to 0$)	$a = \frac{p}{K}$

Example

Use the following information to calculate the activity and activity coefficient of trichloromethane (chloroform, C) in propanone (acetone, A) at 25 °C, treating it first as a solvent and then as a solute.

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

$p_C^* = 36.4\,\text{kPa}$ and $K_C = 23.5\,\text{kPa}$

$$a = \frac{p_A}{p_A^*}$$

Example

Use the following information to calculate the activity and activity coefficient of trichloromethane (chloroform, C) in propanone (acetone, A) at 25 °C, treating it first as a solvent and then as a solute.

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

$p_C^* = 36.4\,\text{kPa}$ and $K_C = 23.5\,\text{kPa}$

From Raoult's law (chloroform regarded as the solvent): (Use Raoult's law as the reference behavior)

x_C	0	0.20	0.40	0.60	0.80	1
a_C	0	0.13	0.30	0.52	0.73	1.00

← $a = \dfrac{p_A}{p_A^*}$

Example

Use the following information to calculate the activity and activity coefficient of trichloromethane (chloroform, C) in propanone (acetone, A) at 25 °C, treating it first as a solvent and then as a solute.

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

$p_C^* = 36.4\,\text{kPa}$ and $K_C = 23.5\,\text{kPa}$

From Raoult's law (chloroform regarded as the solvent): (Use Raoult's law as the reference behavior)

x_C	0	0.20	0.40	0.60	0.80	1
a_C	0	0.13	0.30	0.52	0.73	1.00

← $a = \dfrac{p_A}{p_A^*}$

$$a = \gamma_A x_A$$

Example

Use the following information to calculate the activity and activity coefficient of trichloromethane (chloroform, C) in propanone (acetone, A) at 25 °C, treating it first as a solvent and then as a solute.

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

$p_C^* = 36.4\,\text{kPa}$ and $K_C = 23.5\,\text{kPa}$

From Raoult's law (chloroform regarded as the solvent): (Use Raoult's law as the reference behavior)

x_C	0	0.20	0.40	0.60	0.80	1
a_C	0	0.13	0.30	0.52	0.73	1.00
γ_C		0.65	0.75	0.87	0.92	1.00

$$\leftarrow \quad a = \frac{p_A}{p_A^*}$$

$$\leftarrow \quad a = \gamma_A x_A$$

Example

Use the following information to calculate the activity and activity coefficient of trichloromethane (chloroform, C) in propanone (acetone, A) at 25 °C, treating it first as a solvent and then as a solute.

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

$p_C^* = 36.4\,\text{kPa}$ and $K_C = 23.5\,\text{kPa}$

From Henry's law (chloroform regarded as the solute): (Use Henry's law as the reference behavior)

$$a_B = \frac{p_B}{K_B}$$

$$a_B = \gamma_B x_B$$

Example

Use the following information to calculate the activity and activity coefficient of trichloromethane (chloroform, C) in propanone (acetone, A) at 25 °C, treating it first as a solvent and then as a solute.

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

$p_C^* = 36.4$ kPa and $K_C = 23.5$ kPa

From Henry's law (chloroform regarded as the solute): (Use Henry's law as the reference behavior)

x_C	0	0.20	0.40	0.60	0.80	1
a_C	0	0.20	0.47	0.80	1.14	1.55
γ_C		1.00	1.17	1.34	1.42	1.55

$$\leftarrow \quad a_B = \frac{p_B}{K_B}$$

$$\leftarrow \quad a_B = \gamma_B x_B$$

Regular solutions

$$H^{E} \neq 0 \text{ but } S^{E} = 0.$$

A measure of A-B interactions
compared to A-A and B-B

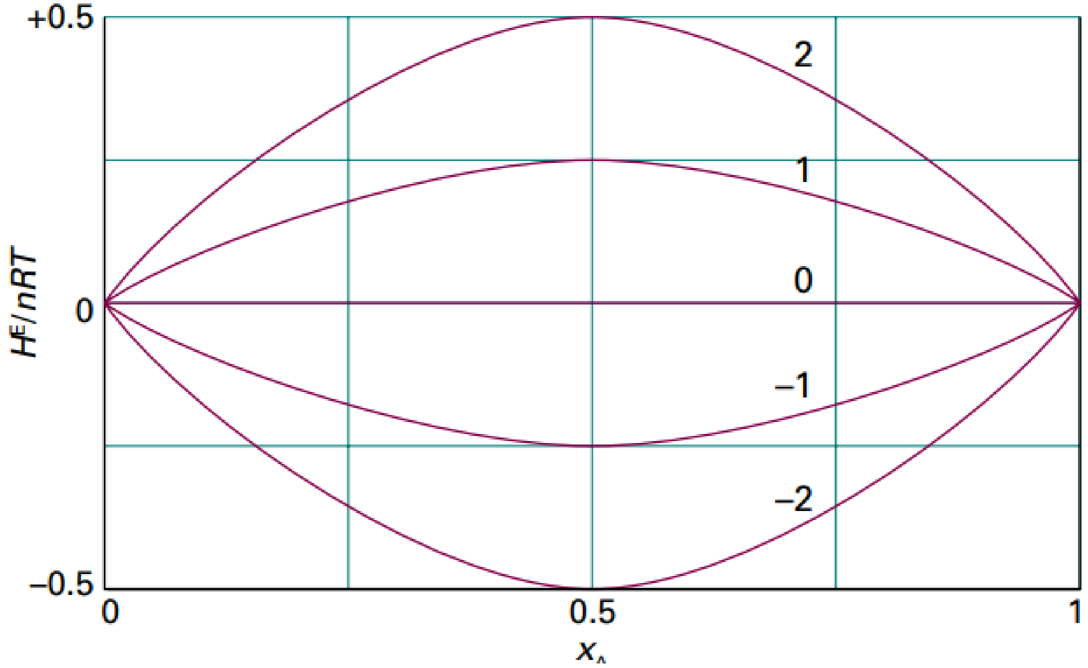
$$H^{E} = n\xi RT x_{A} x_{B}$$

$\xi > 0,$
mixing is endothermic.

A-A and B-B interactions are more favorable

$\xi < 0,$
mixing is exothermic

A–B interactions are more favorable



Activities of regular solutions

$$\ln \gamma_A = \xi x_B^2$$

- The activity of a component is reduced (or enhanced) depending on how much of the other component is present.

Activities of regular solutions

$$\ln \gamma_A = \xi x_B^2$$

- The activity of a component is reduced (or enhanced) depending on how much of the other component is present.
- Has a quadratic dependence (x^2), deviations are small at low concentrations but then increase sharply

Activities of regular solutions

$$\ln \gamma_A = \xi x_B^2$$

- The activity of a component is reduced (or enhanced) depending on how much of the other component is present.

- Has a quadratic dependence (x^2), deviations are small at low concentrations but then increase sharply

- When $x_B=0$, $\ln \gamma_A=0 \Rightarrow \gamma A=1$; behaves ideally!

Activities of regular solutions

$$\ln \gamma_A = \xi x_B^2$$

- The activity of a component is reduced (or enhanced) depending on how much of the other component is present.
- Has a quadratic dependence (x^2), deviations are small at low concentrations but then increase sharply
- When $x_B=0$, $\ln \gamma_A=0 \Rightarrow \gamma A=1$; behaves ideally!

Similarly, for the other component: $\ln \gamma_B = \xi x_A^2$

Activities of regular solutions

$$\ln \gamma_A = \xi x_B^2 \qquad \ln \gamma_B = \xi x_A^2$$

$$\gamma_A \to 1 \text{ as } x_B \to 0 \text{ and } \gamma_B \to 1 \text{ as } x_A \to 0$$

Activities of regular solutions

$$\ln \gamma_A = \xi x_B^2 \qquad \ln \gamma_B = \xi x_A^2$$

$$\gamma_A \to 1 \text{ as } x_B \to 0 \text{ and } \gamma_B \to 1 \text{ as } x_A \to 0$$

$$\boxed{\gamma_A = e^{\xi x_B^2}}$$

$$a_A = \gamma_A x_A = x_A e^{\xi x_B^2}$$

Activities of regular solutions

$$\ln \gamma_A = \xi x_B^2 \qquad \ln \gamma_B = \xi x_A^2$$

$$\gamma_A \to 1 \text{ as } x_B \to 0 \text{ and } \gamma_B \to 1 \text{ as } x_A \to 0$$

$\gamma_A = e^{\xi x_B^2}$

$$a_A = \gamma_A x_A = x_A e^{\xi x_B^2} = x_A e^{\xi(1-x_A)^2}$$

$x_B = 1 - x_A$

Activities of regular solutions

$$\ln \gamma_A = \xi x_B^2 \qquad \ln \gamma_B = \xi x_A^2$$

$$\gamma_A \to 1 \text{ as } x_B \to 0 \text{ and } \gamma_B \to 1 \text{ as } x_A \to 0$$

$$\gamma_A = e^{\xi x_B^2}$$

$$a_A = \gamma_A x_A = x_A e^{\xi x_B^2} = x_A e^{\xi(1-x_A)^2}$$

$$x_B = 1 - x_A$$

$$p_A = p_A^* x_A e^{\xi(1-x_A)^2}$$

Activities of regular solutions

$$\ln \gamma_A = \xi x_B^2 \qquad \ln \gamma_B = \xi x_A^2$$

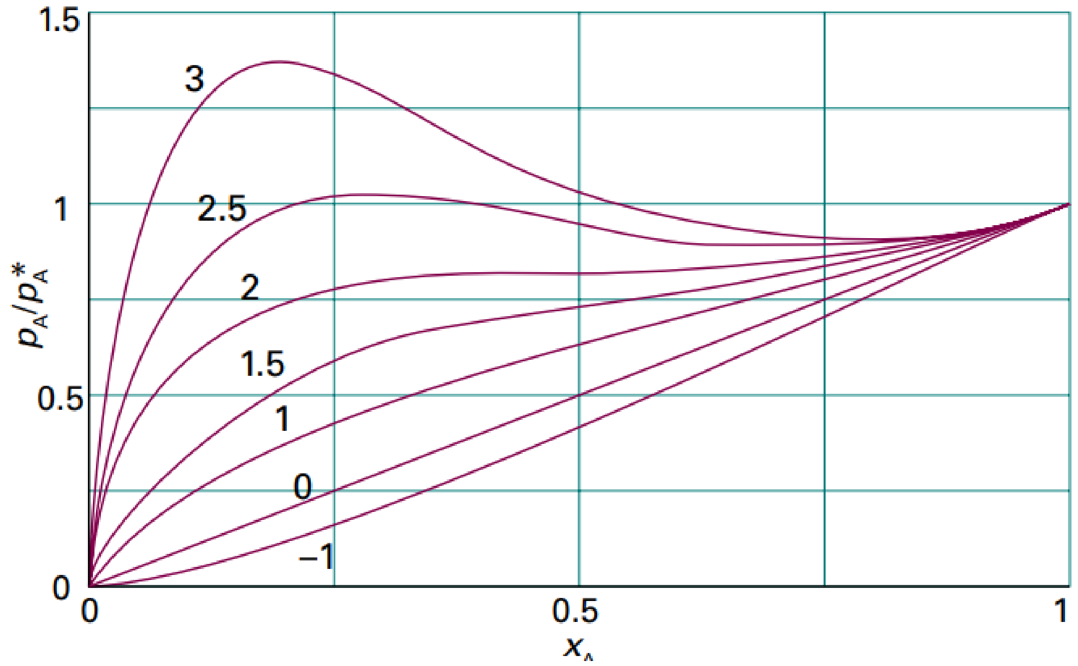
$$\gamma_A \rightarrow 1 \text{ as } x_B \rightarrow 0 \text{ and } \gamma_B \rightarrow 1 \text{ as } x_A \rightarrow 0$$

$$\boxed{\gamma_A = e^{\xi x_B^2}}$$

$$a_A = \gamma_A x_A = x_A e^{\xi x_B^2} = x_A e^{\xi (1-x_A)^2}$$

$$\boxed{x_B = 1 - x_A}$$

$$p_A = p_A^* x_A e^{\xi (1-x_A)^2}$$



Total vapor pressure = $P_A + P_B$