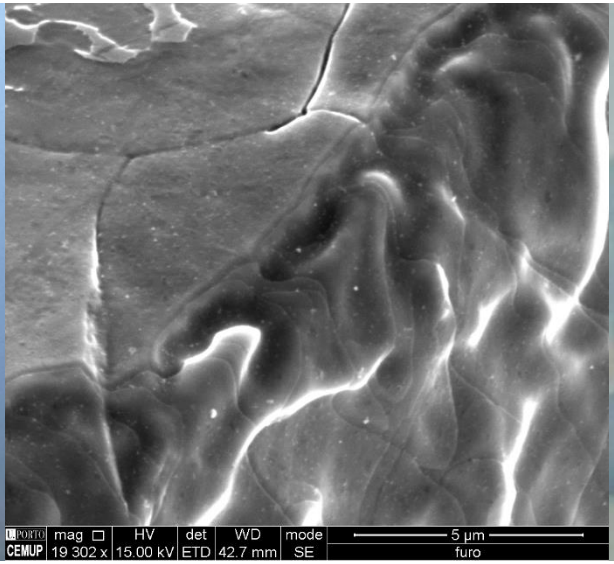
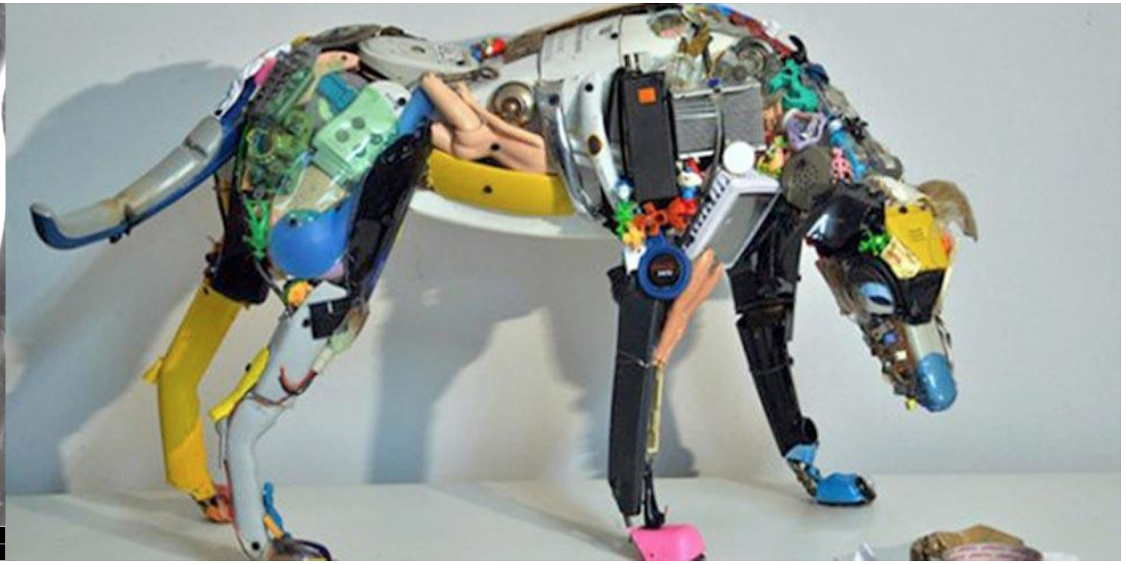
Physical Chemistry

... iremos explorar, refletir, aprender ?..

Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.



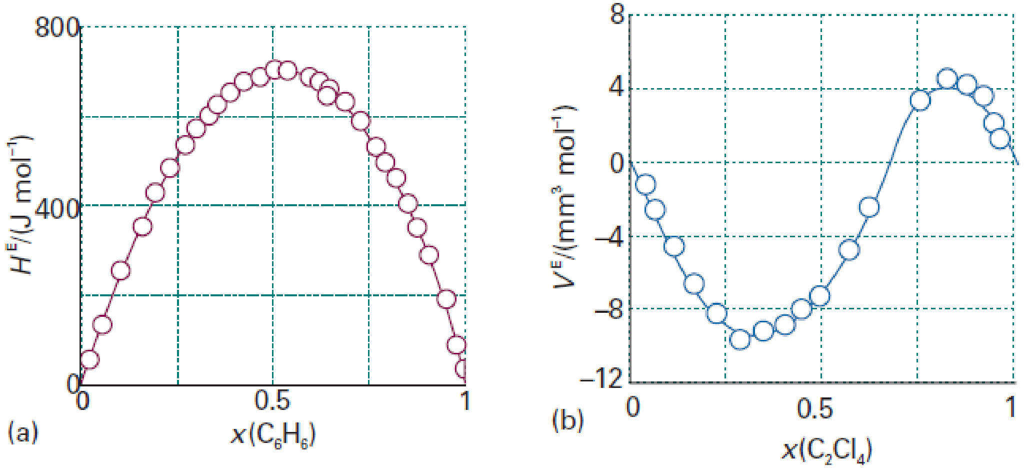


The thermodynamic mixing |Excess properties Solutions

Excess functions, X^{E},

$$\boldsymbol{X}^{E} = X^{\text{real}} - X^{\text{ideal}}$$

$$S^{E} = \Delta_{\text{mix}}S - \Delta_{\text{mix}}S^{\text{ideal}}$$



Ideal properties of mixing

$$\Delta_{\text{mix}}H = 0$$

$$\Delta_{\text{mix}}S = -nR\{x_A \ln x_A + x_B \ln x_B\}$$

$$\Delta_{\text{mix}}G = nRT\{x_A \ln x_A + x_B \ln x_B\}$$

Real properties of mixing

$$H^{E} = n\beta RTx_A x_B$$

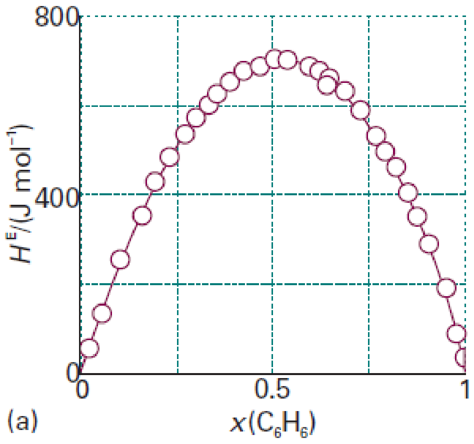
β is a dimensionless parameter that is a measure of the energy of **AB** interactions relative to that of the **AA** and **BB** interactions.

The thermodynamic mixing |Excess properties Solutions

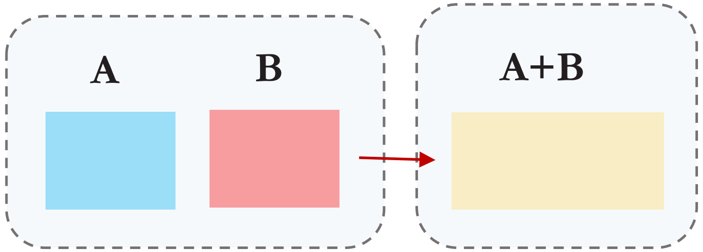
Excess functions, X^E,

$$\boldsymbol{X}^E = X^{\text{real}} - X^{\text{ideal}}$$

$$H^E = H^{\text{real}} - 0$$



$$S^E = \Delta_{\text{mix}}S - \Delta_{\text{mix}}S^{\text{ideal}}$$



A-A
B-B

→

A-B
A-A
B-B

Simple model |*cohesive interactions*

$H^E > 0$	A-B	Weaker than overall B-B A-A
$H^E < 0$	A-B	Stronger than overall B-B A-A

Ideal properties of mixing

$$\Delta_{\text{mix}}H = 0$$

$$\Delta_{\text{mix}}S = -nR\{x_A \ln x_A + x_B \ln x_B\}$$

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Real properties of mixing

$$H^E = n\beta RTx_Ax_B$$

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The thermodynamic mixing |Excess properties Solutions

$$\Delta_{\text{mix}}S = -nR\{x_A \ln x_A + x_B \ln x_B\}$$

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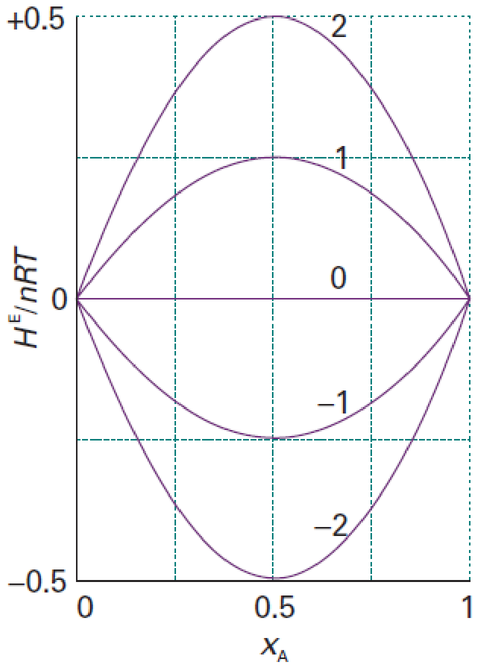
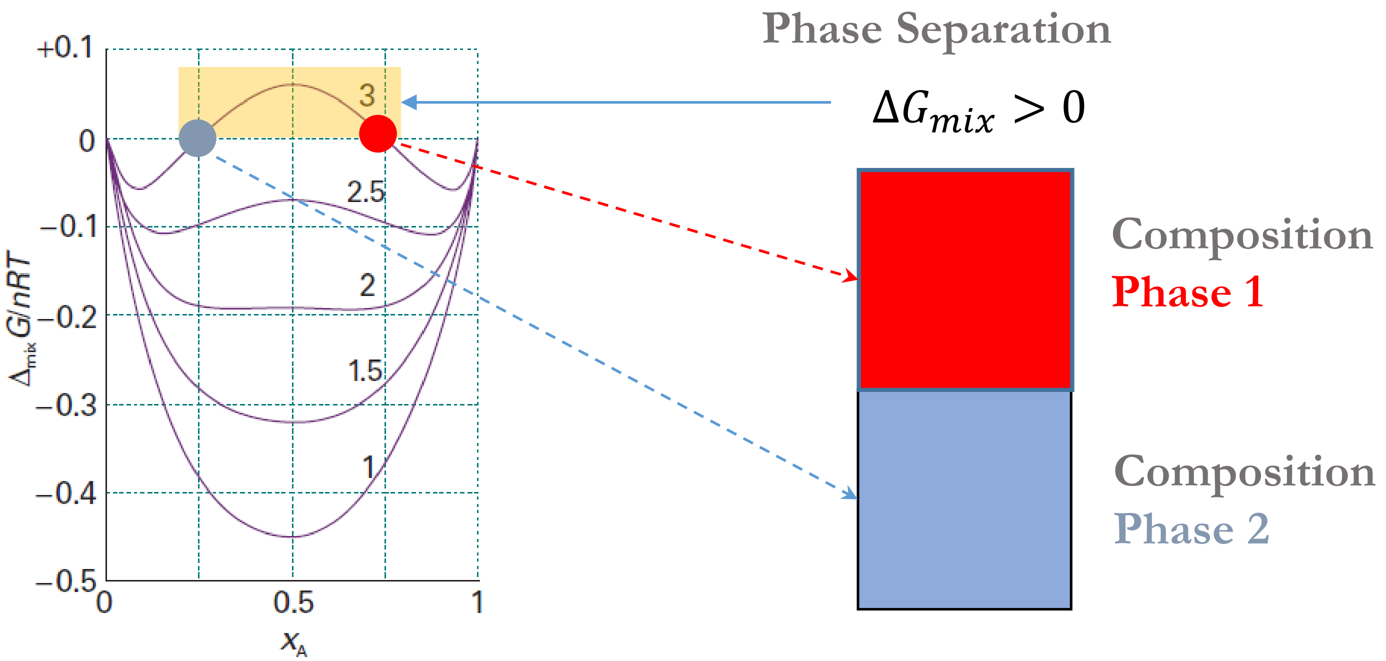
Excess functions, X^E,

$$\boldsymbol{X}^E = X^{\text{real}} - X^{\text{ideal}}$$

$$S^E = \Delta_{\text{mix}}S - \Delta_{\text{mix}}S^{\text{ideal}}$$

$$\Delta_{\text{mix}}G = nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B\}$$





Phase Separation

$$\Delta G_{mix} > 0$$

Composition
Phase 1

Composition
Phase 2

The thermodynamic mixing

Coligative Properties

(arising from the presence of a solute in a solvent)

2. elevation of boiling point;

$$\Delta T = K_b b$$

3. depression of freezing point;

$$\Delta T = K_f b$$

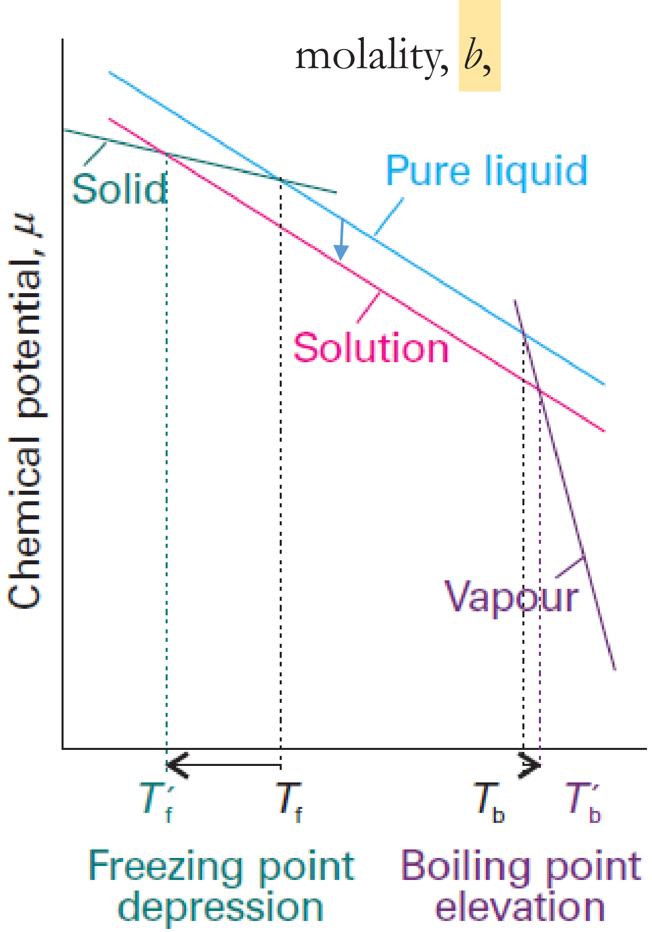
molality, b, in the solution

Synoptic Table 5.2* Freezing-point and boiling-point constants

	K_f/(K kg mol^{-1})	K_b/(K kg mol^{-1})
Benzene	5.12	2.53
Camphor	40	
Phenol	7.27	3.04
Water	1.86	0.51

A solution of **1 molal** (b=1) >

- 1.86 K of boiling point increase
- 0.51 K of freezing point decrease



The thermodynamic mixing

Solubility

$$\mu_B = \mu_B^*(l) + RT \ln x_B$$

we can write

$$\mu_B^*(s) = \mu_B^*(l) + RT \ln x_B$$

$$\ln x_B = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right)$$

If $T = T_f$ $> X_B = 1$

Total Solubility

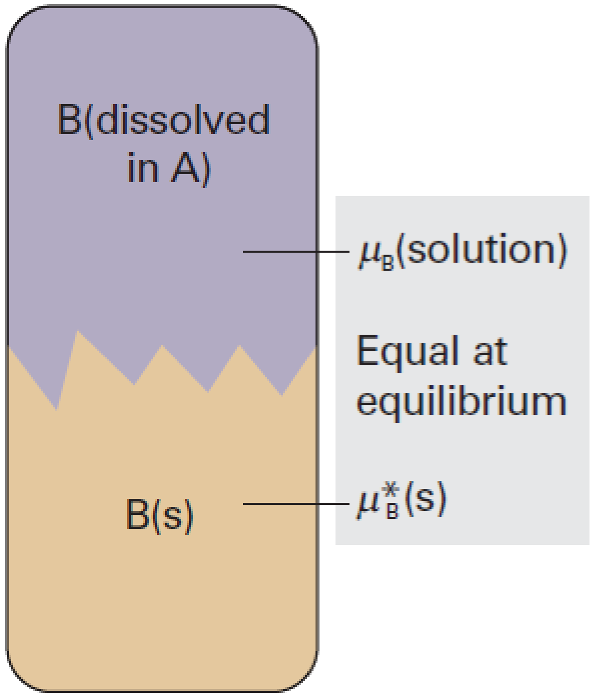
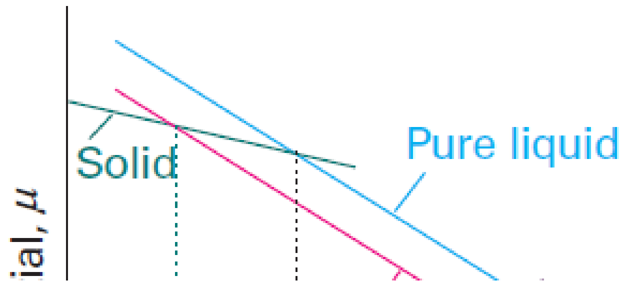


Fig. 5.25 The heterogeneous equilibrium involved in the calculation of the solubility is between pure solid B and B in the mixture.



The thermodynamic mixing

Osmotic pressure

$$\mu_A^*(p) = \mu_A(x_A, p + \Pi)$$

$$\mu_A(x_A, p + \Pi) = \mu_A^*(p + \Pi) + RT \ln x_A$$

$$RTx_B = \Pi V_m$$

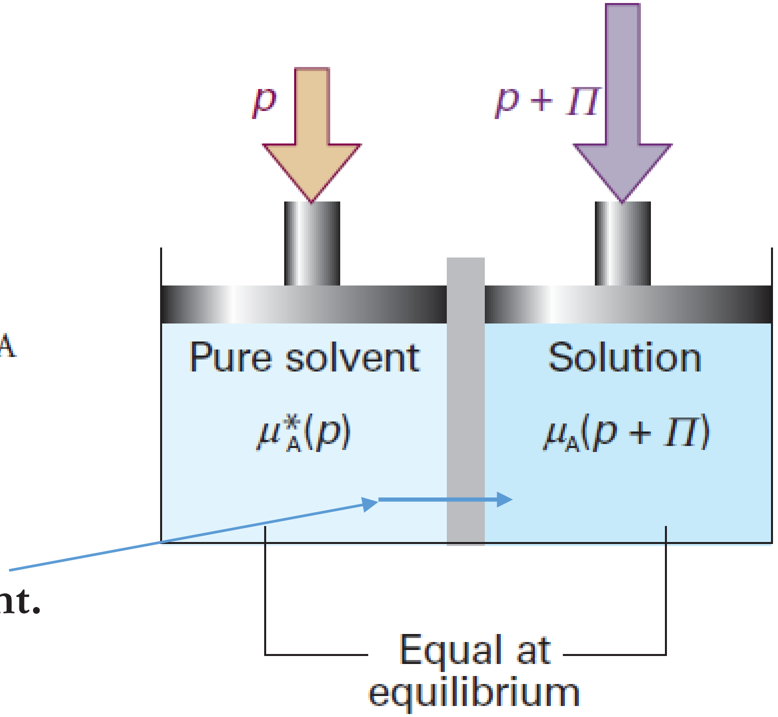


Fig. 5.27 The equilibrium involved in the calculation of osmotic pressure, Π, is between pure solvent A at a pressure p on one side of the semipermeable membrane and A as a component of the mixture on the other side of the membrane, where the pressure is $p + \Pi$.

The **osmotic pressure**, Π,
pressure that must be applied to the solution to stop the **influx of solvent.**

$$\Pi = [B]RT$$

$[B] = n_B/V$ is the molar concentration of the solute

van ’t Hoff equation:

The thermodynamic mixing

The **osmotic pressure**, Π,
pressure that must be applied to the solution to stop the **influx of solvent.**

van ’t Hoff equation:

$\Pi = [\mathrm{B}]RT$ $[\mathrm{B}] = n_\mathrm{B}/V$ is the molar concentration of the solute

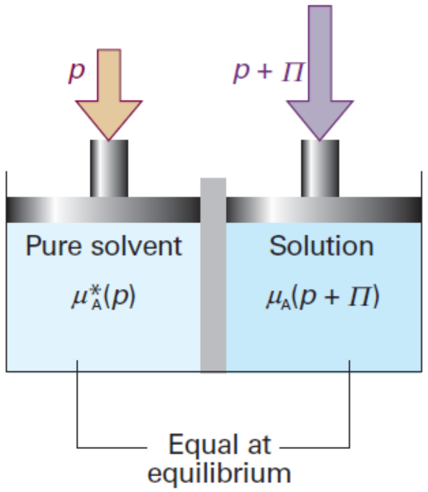


Fig. 5.27 The equilibrium involved in the calculation of osmotic pressure, Π, is

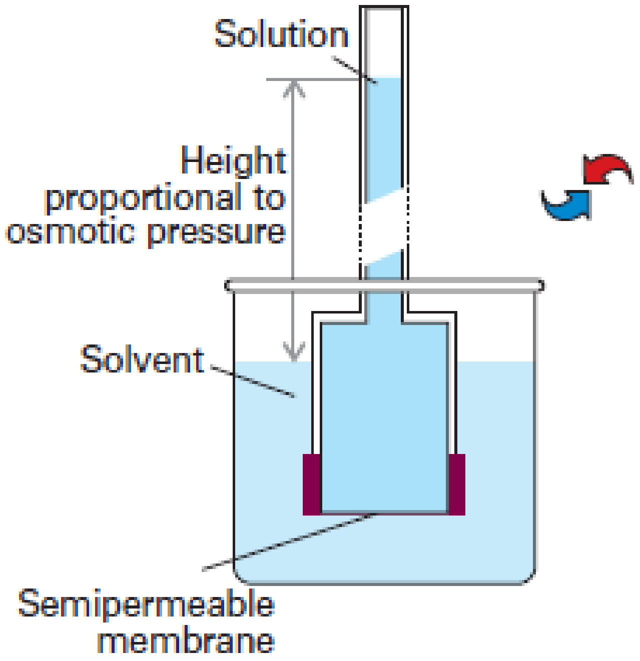


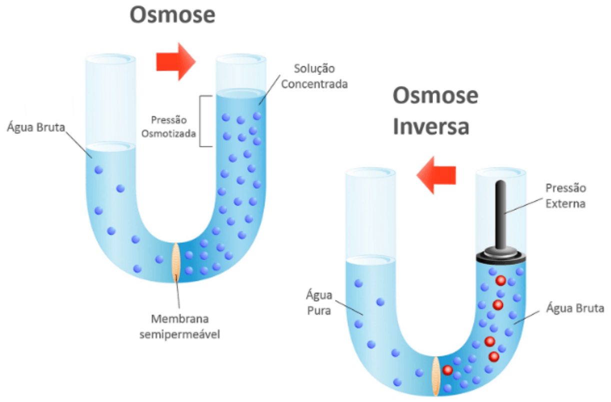
Fig. 5.20 In a simple version of the osmotic pressure experiment, A is at equilibrium on each side of the membrane when enough has passed into the solution to cause a hydrostatic pressure difference.

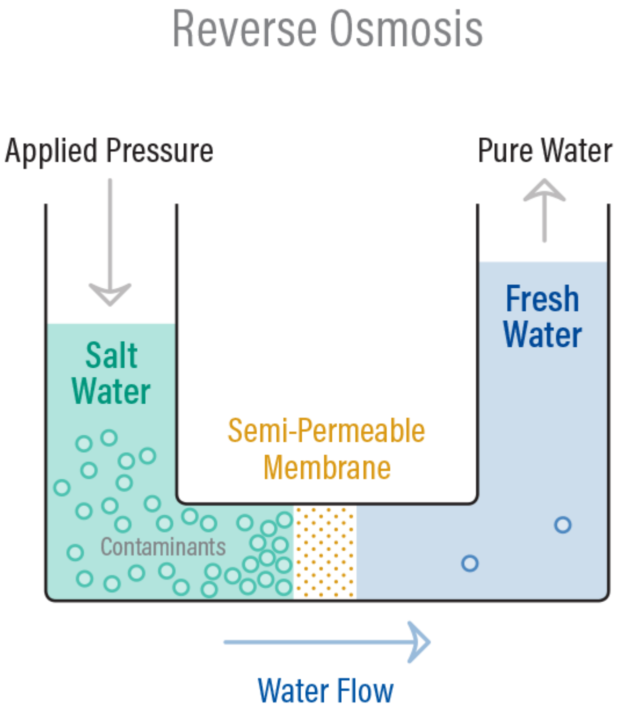
The thermodynamic mixing

The **osmotic pressure**, Π,
pressure that must be applied to the solution to stop the **influx of solvent.**

van ’t Hoff equation:

$$\Pi = [\mathrm{B}]RT \qquad [\mathrm{B}] = n_\mathrm{B}/V \text{ is the molar concentration of the solute}$$





The solvent activity

The quantity a_A is the **activity** of A, a kind **of ‘effective’ mole fraction,**

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

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

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

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

$$a_A \rightarrow x_A \quad \text{as} \quad x_A \rightarrow 1$$

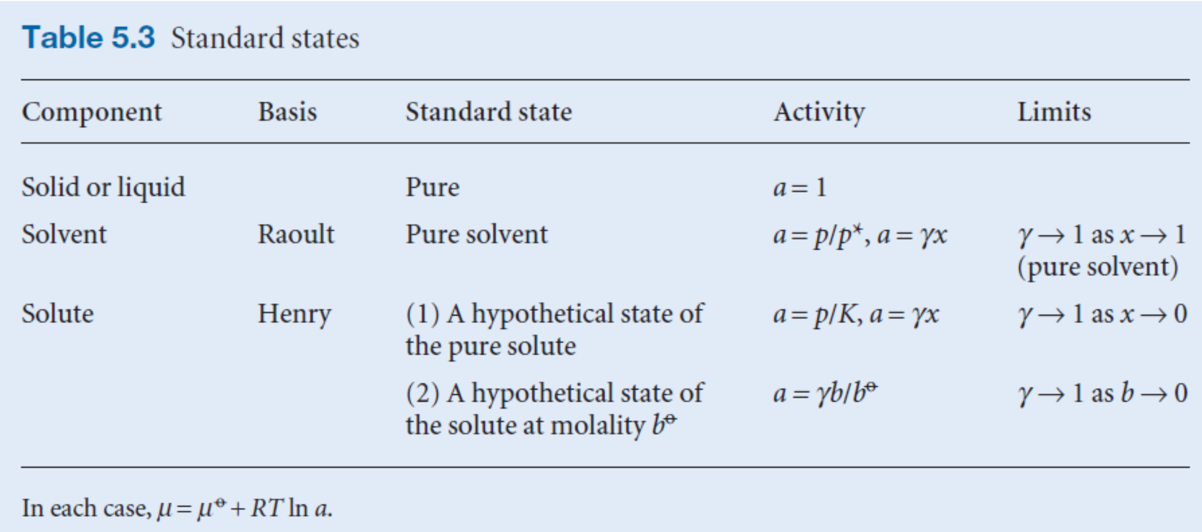


Table 5.3 Standard states

Component	Basis	Standard state	Activity	Limits
Solid or liquid		Pure	$a = 1$	
Solvent	Raoult	Pure solvent	$a = p/p^*$, $a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 1$ (pure solvent)
Solute	Henry	(1) A hypothetical state of the pure solute	$a = p/K$, $a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 0$
		(2) A hypothetical state of the solute at molality $b^\ominus$	$a = \gamma b/b^\ominus$	$\gamma \rightarrow 1$ as $b \rightarrow 0$

In each case, $\mu = \mu^\ominus + RT\ln a$.

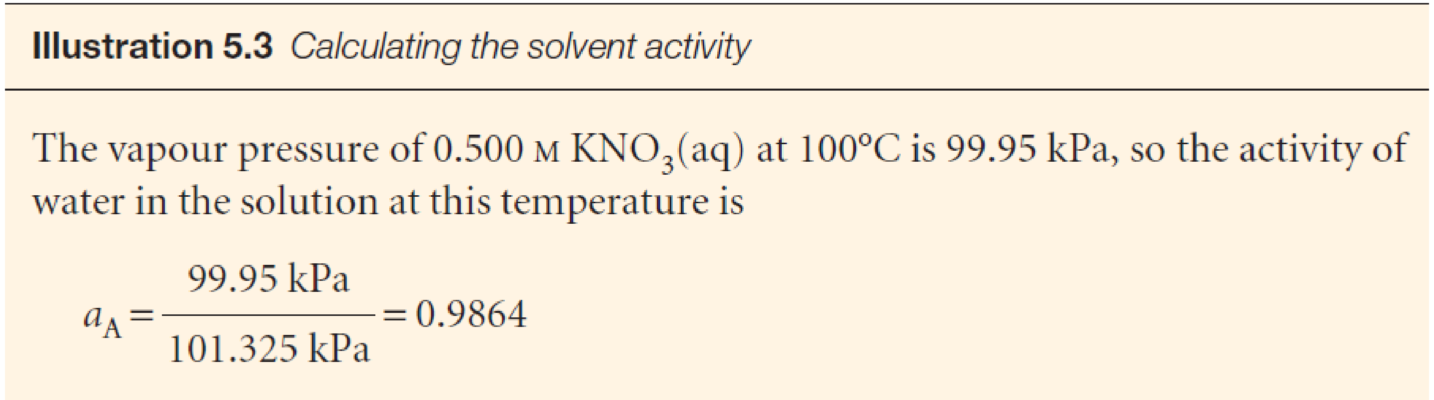


Illustration 5.3 *Calculating the solvent activity*

The vapour pressure of 0.500 M $KNO_3(aq)$ at 100°C is 99.95 kPa, so the activity of water in the solution at this temperature is

$$a_A = \frac{99.95\ \text{kPa}}{101.325\ \text{kPa}} = 0.9864$$

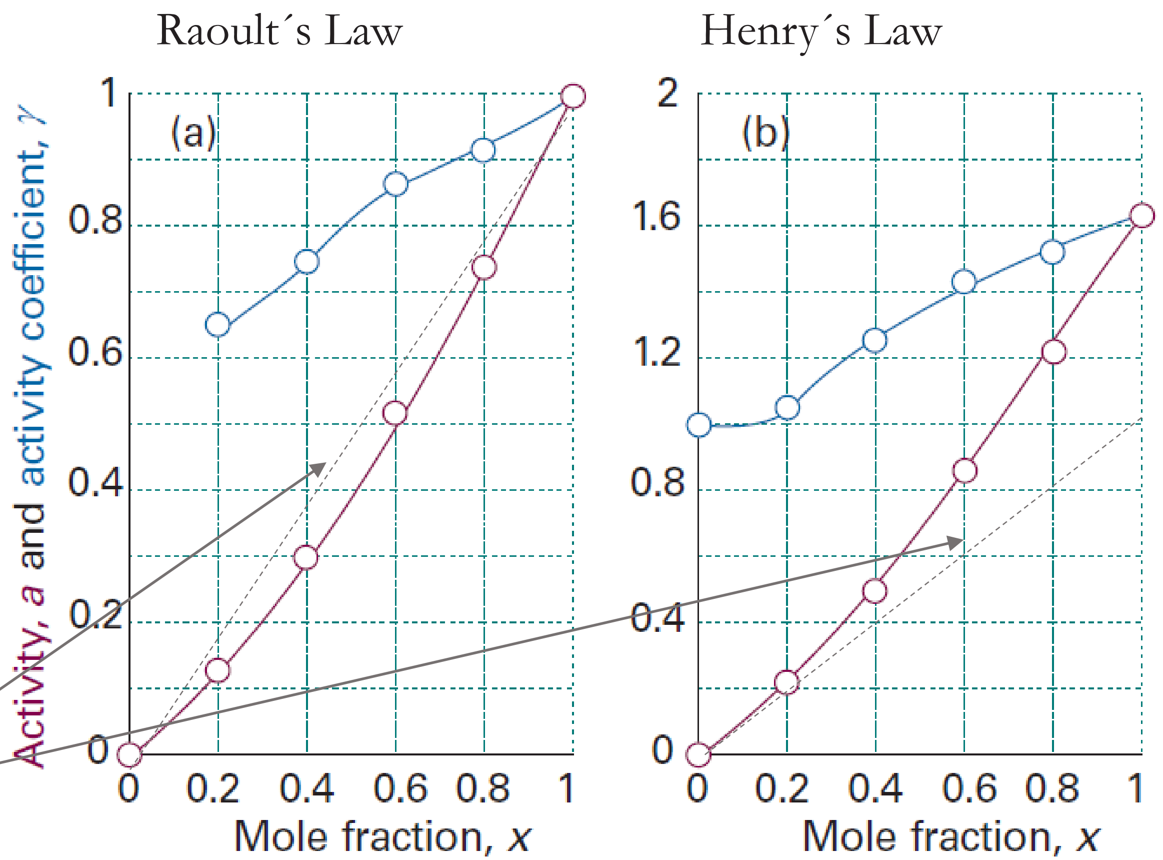
The solvent activity

The quantity a_A is the **activity** of A, a kind of ‘effective’ mole fraction,

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

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

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



Hipotetical a_A **activity**
For activity coefficient = 1

Fig. 5.31 The variation of activity and activity coefficient of chloroform (trichloromethane) and acetone (propanone) with composition according to (a) Raoult’s law, (b) Henry’s law.

The activities of ions in solution

The quantity a_A is the **activity** of A, a kind of 'effective' concentration,

Activities of ions in solution

$$G_m^{ideal} = \mu_+^{ideal} + \mu_-^{ideal}$$

$$G_m = \mu_+ + \mu_- = \mu_+^{ideal} + \mu_-^{ideal} + RT\ln\gamma_+ + RT\ln\gamma_- = G_m^{ideal} + RT\ln\gamma_+\gamma_-$$

$$\gamma_\pm = (\gamma_+\gamma_-)^{1/2}$$

mean activity coefficient

geometric mean of the individual coefficients

$$\mu_+ = \mu_+^{ideal} + RT\ln\gamma_\pm \qquad \mu_- = \mu_-^{ideal} + RT\ln\gamma_\pm$$

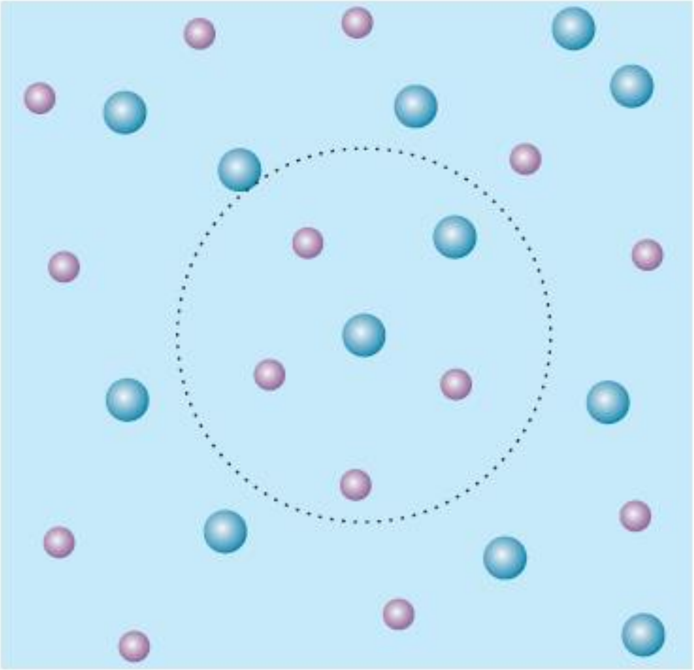
The activities of ions in solution

The quantity a_A is the **activity** of A, a kind of 'effective' concentration,

Debye–Hückel theory of ionic solutions

Describes a **tendency for anions** to be found around cations, and of cations to be found around anions

The chemical potential, central ion is lowered as ***a result of its electrostatic interaction*** with its **ionic atmosphere**.



Debye–Hückel limiting law

$$\log \gamma_\pm = -|z_+z_-|AI^{1/2}$$

$A = 0.509$ for an aqueous solution at 25°C

ionic strength

$$I = \tfrac{1}{2}\sum_i z_i^2(b_i/b^\ominus)$$