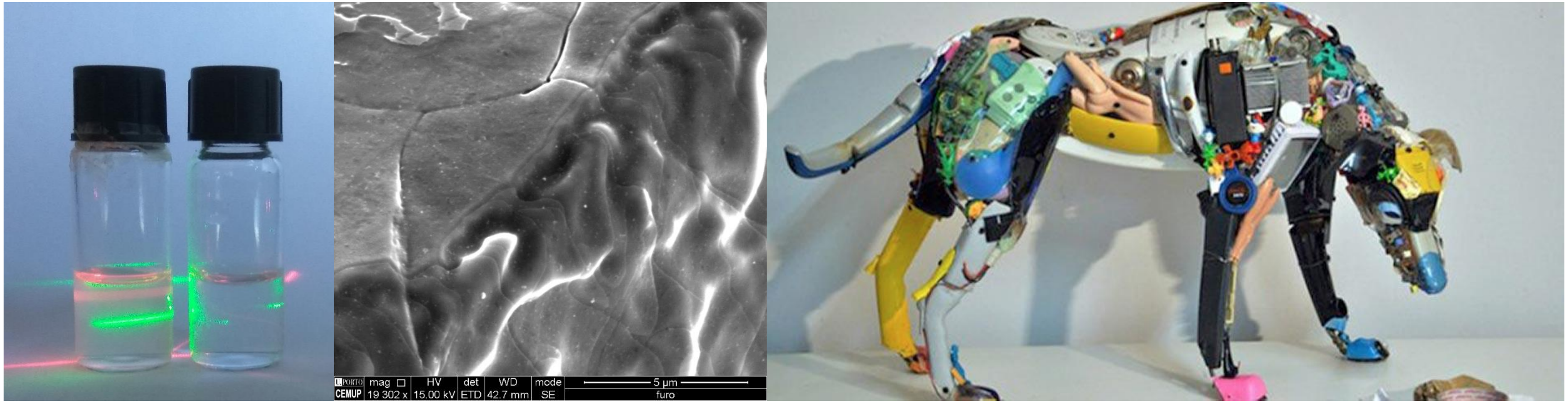
Physical Chemistry

... 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 description of mixtures

State 1

$V(T, p, n_i, n_j)$
$G(T, p, n_i, n_j)$

$\longrightarrow$

State 2

$V(T, p, n_i, n_j) + dV$
$G(T, p, n_i, n_j) + dG$

By changing
T, p, n

Partial molar quantities

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'}$$

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$$

$$G = n_A\mu_A + n_B\mu_B$$

Change of
de **volume**

$$dV = \left(\frac{\partial V}{\partial T}\right)_{p,T,n_i,n_j} . dT + \left(\frac{\partial V}{\partial p}\right)_{p,T,n_i,n_j} . dp + \left(\frac{\partial V}{\partial ni}\right)_{p,T,n_i} . dn_i$$

Temperature effect (Thermal Expansion)

Pressure effect (Isothermal compressibility)

Composition effect

Change of
Gibbs energies

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots$$

Pressure effect

Temperature effect

Composition effect

The thermodynamic description of mixtures

$$G = U + pV - TS$$

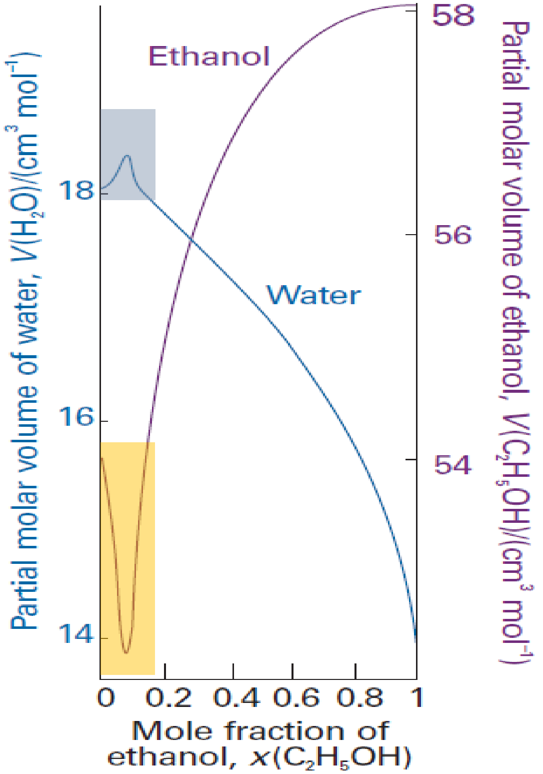
Gibbs–Duhem equation

$$G = n_A\mu_A + n_B\mu_B$$

chemical potential is the contribution of that substance to the **total Gibbs energy** of the mixture

$$n_A d\mu_A + n_B d\mu_B = 0 \quad \rightarrow$$

$$\sum_J n_J d\mu_J = 0 \quad \rightarrow \quad d\mu_B = -\frac{n_A}{n_B} d\mu_A$$



Gibbs–Duhem equation |
the chemical potential of one component of a mixture cannot change independently
the chemical potentials of the other components.

Applies to all partial molar quantities !!!

The Gibbs energy of mixing of perfect gases

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

μ^{o} is the **standard chemical potential**

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

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

$$(G_f - G_i) = \Delta_{mix}G = n_A RT\ln\frac{p_A}{p} + n_B RT\ln\frac{p_B}{p}$$

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

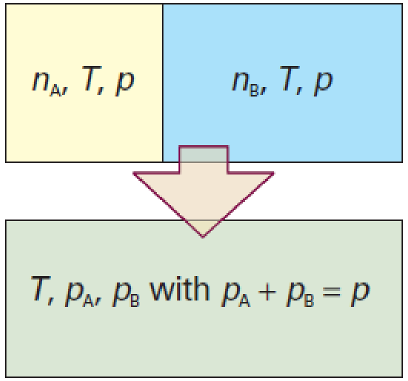
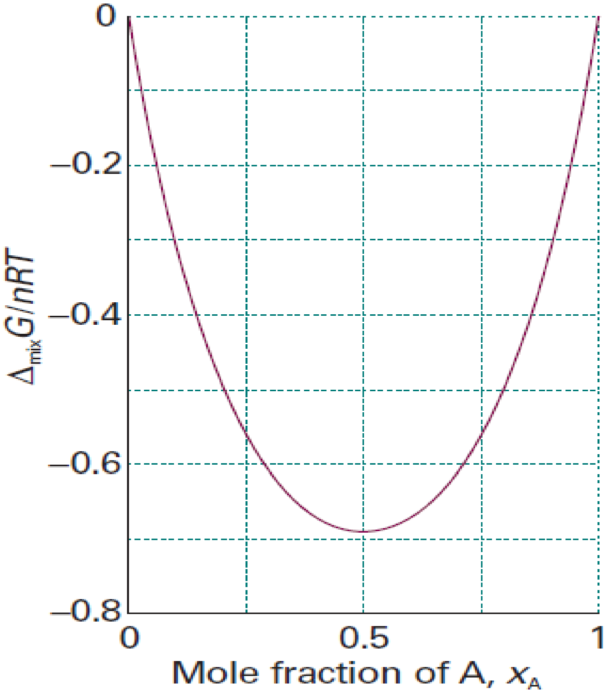


Fig. 5.6 The arrangement for calculating the thermodynamic functions of mixing of two perfect gases.



The Gibbs energy of mixing of perfect gases

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

$$\Delta_{\text{mix}}G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

A container is divided into two equal compartments (Fig. 5.8). One contains 3.0 mol $H_2(g)$ at 25°C; the other contains 1.0 mol $N_2(g)$ at 25°C. Calculate the Gibbs energy of mixing when the partition is removed. Assume perfect behaviour.

$$G_i = (3.0\ \text{mol})\{\mu^\ominus(H_2) + RT \ln 3p\} + (1.0\ \text{mol})\{\mu^\ominus(N_2) + RT \ln p\}$$

$$G_f = (3.0\ \text{mol})\{\mu^\ominus(H_2) + RT \ln \tfrac{3}{2}p\} + (1.0\ \text{mol})\{\mu^\ominus(N_2) + RT \ln \tfrac{1}{2}p\}$$

$$\begin{aligned}\Delta_{\text{mix}}G &= (3.0\ \text{mol})RT \ln\left(\frac{\frac{3}{2}p}{3p}\right) + (1.0\ \text{mol})RT \ln\left(\frac{\frac{1}{2}p}{p}\right)\\ &= -(3.0\ \text{mol})RT \ln 2 - (1.0\ \text{mol})RT \ln 2\\ &= -(4.0\ \text{mol})RT \ln 2 = -6.9\ \text{kJ}\end{aligned}$$

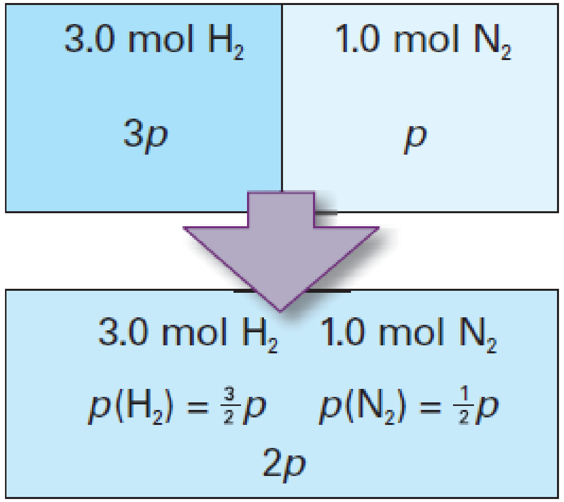


Fig. 5.8 The initial and final states considered in the calculation of the Gibbs energy of mixing of gases at different initial pressures.

The thermodynamic mixing

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

Gibbs energy

$$G = H - TS$$

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

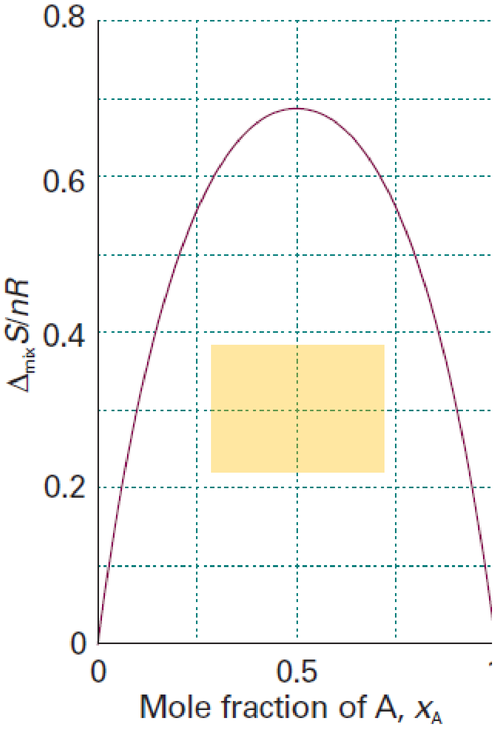
ENTROPY of mixing

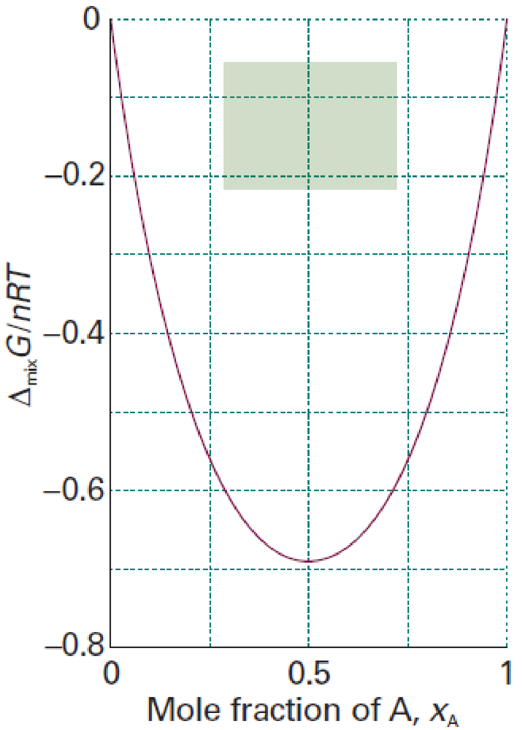
$$\Delta_{\text{mix}}S = -\left(\frac{\partial \Delta_{\text{mix}}G}{\partial T}\right)_{p,n_A,n_B} = -nR(x_A \ln x_A + x_B \ln x_B)$$

Enthalpy of mixing

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

perfect gases





The thermodynamic mixing

The chemical potentials of liquids

$$\mu_A^* = \mu_A^\ominus + RT\ln p_A^*$$ pure A is written μ_A^*, and as $\mu_A^*(\mathrm{l})$

$$\mu_A^\ominus = \mu_A^* - RT\ln p_A^*$$

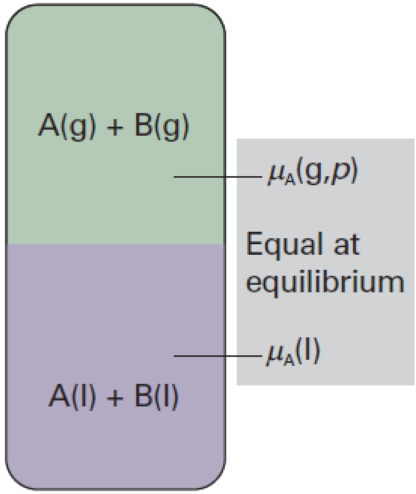
$$\mu_A = \mu_A^\ominus + RT\ln p_A$$ **In the mixture**

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

Raoult's law

$$p_A = x_A p_A^*$$

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



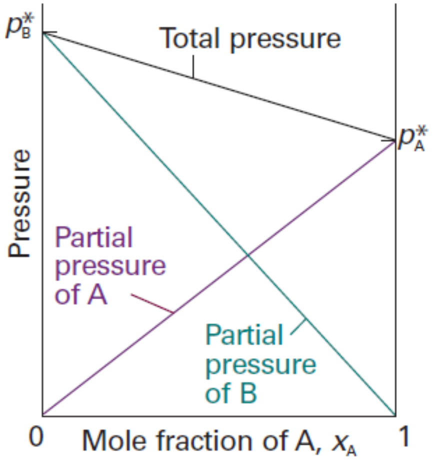
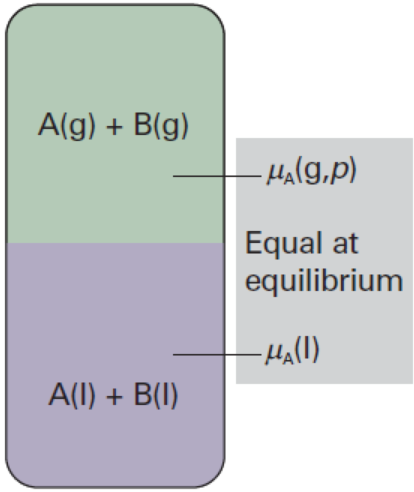


Fig. 5.11 The total vapour pressure and the two partial vapour pressures of an ideal binary mixture are proportional to the mole fractions of the components.

The thermodynamic mixing

The chemical potentials of liquids

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



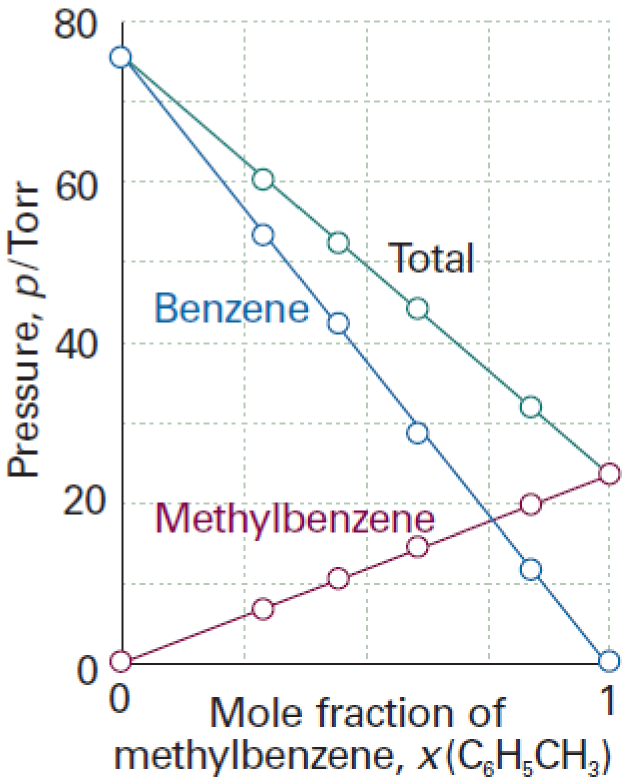


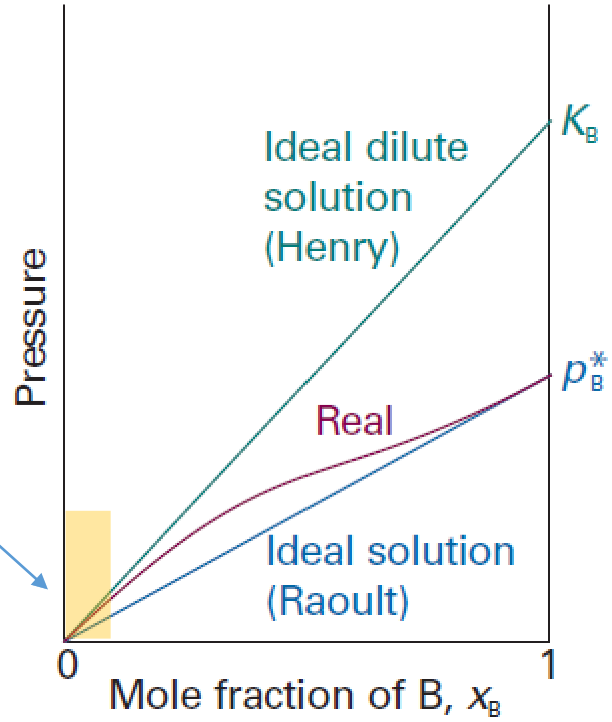
Fig. 5.12 Two similar liquids, in this case benzene and methylbenzene (toluene), behave almost ideally, and the variation of their vapour pressures with composition resembles that for an ideal solution.

The thermodynamic mixing

Henry Law

$$p_B = x_B K_B$$

dilute solutions



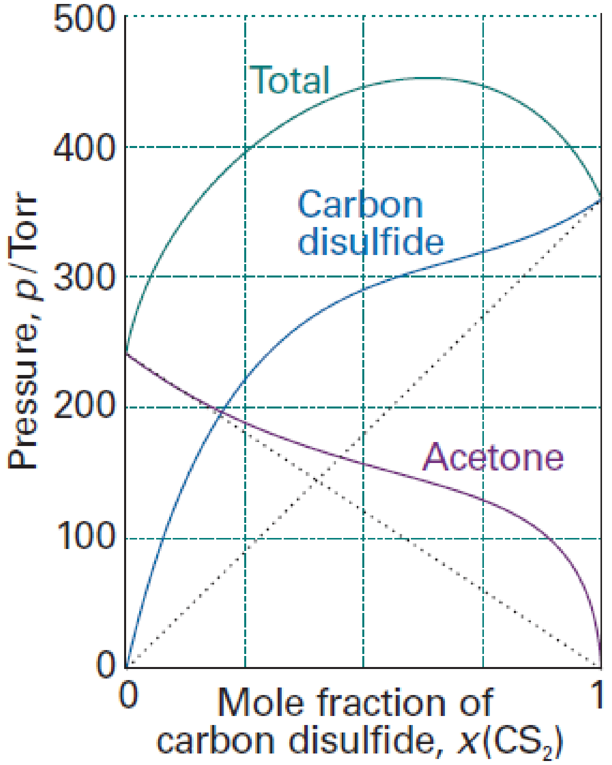


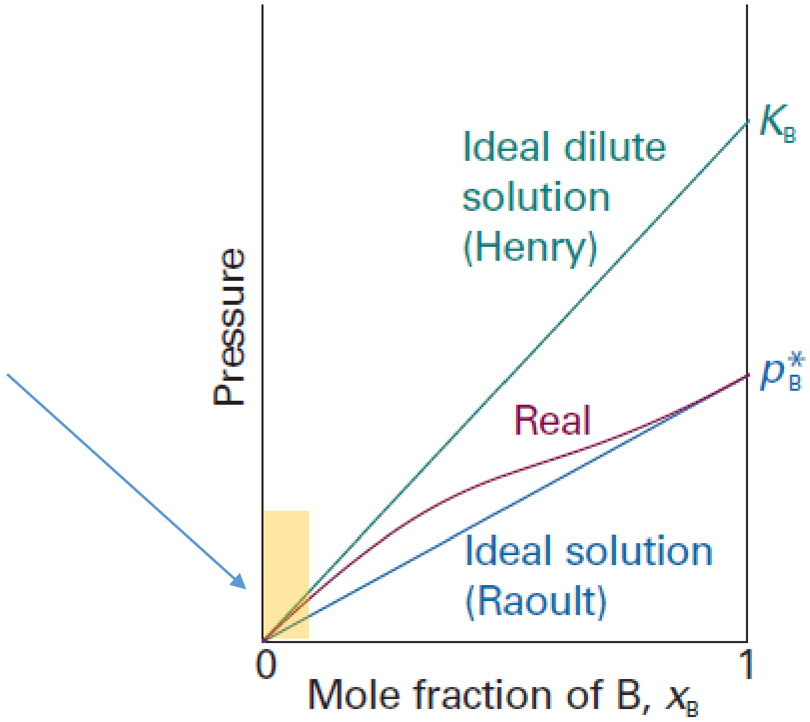
Fig. 5.14 Strong deviations from ideality are shown by dissimilar liquids (in this case carbon disulfide and acetone, propanone).

The thermodynamic mixing

Henry Law

$$p_B = x_B K_B$$

dilute solutions



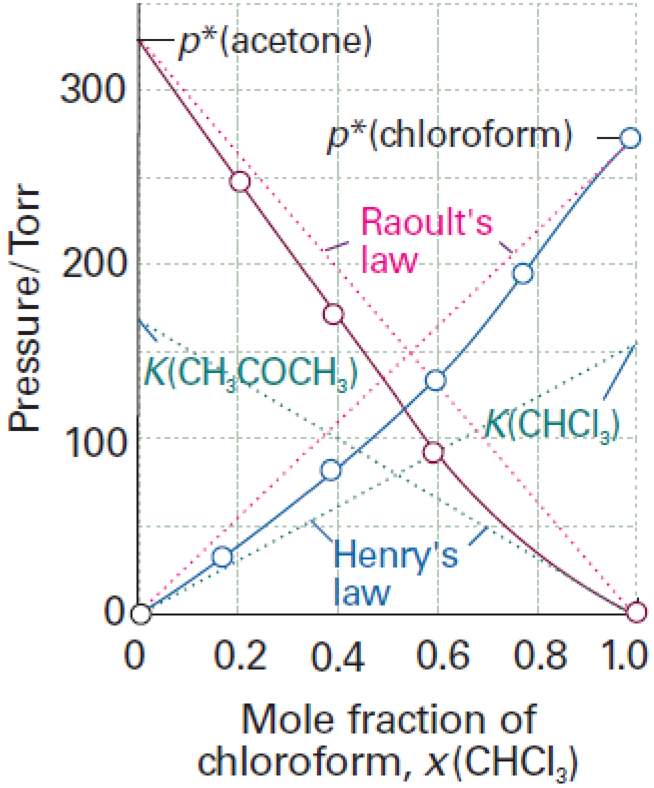
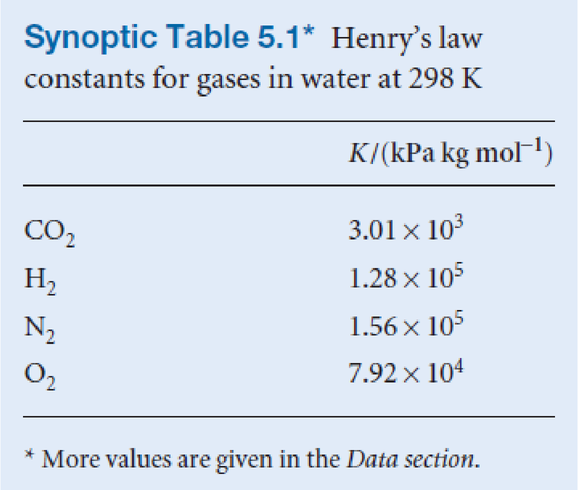


Fig. 5.17 The experimental partial vapour pressures of a mixture of chloroform (trichloromethane) and acetone

The thermodynamic mixing



Synoptic Table 5.1* Henry's law constants for gases in water at 298 K

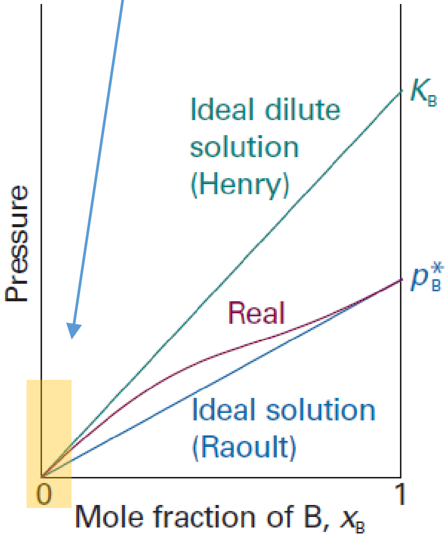
	$K/(\text{kPa kg mol}^{-1})$
CO_2	3.01×10^3
H_2	1.28×10^5
N_2	1.56×10^5
O_2	7.92×10^4

* More values are given in the *Data section*.

Henry Law

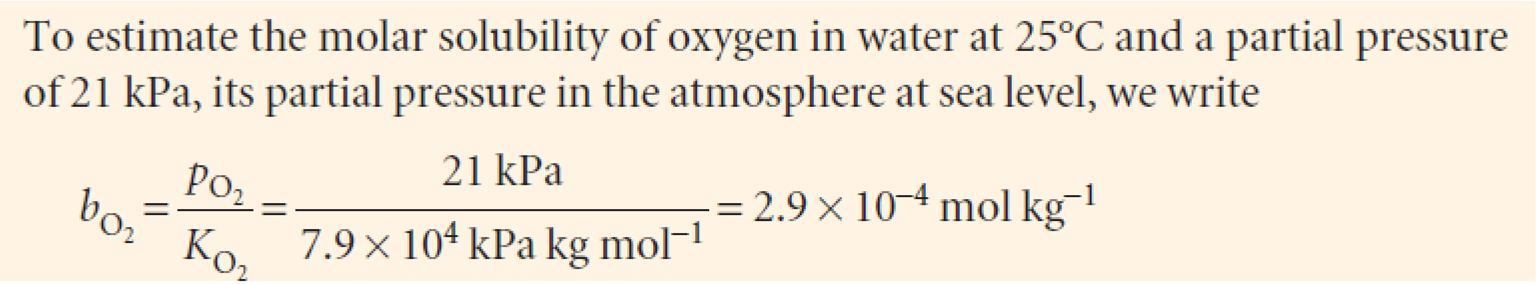
$$p_B = x_B K_B$$

dilute solutions



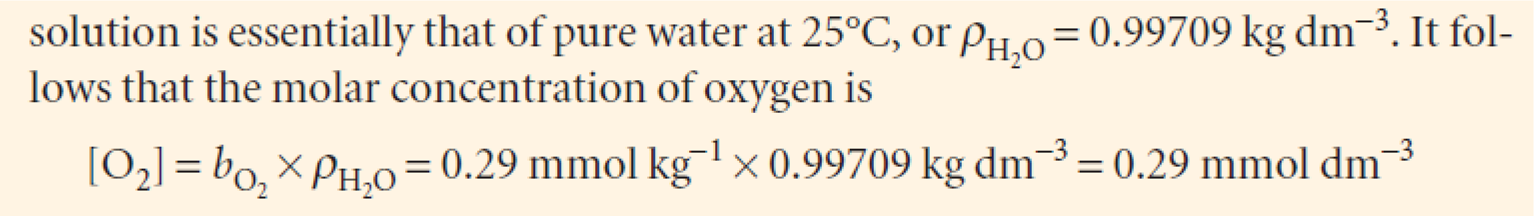
$$p_B = b_B K_B$$

Henry's law is expressed in terms of the molality, *b*, of the solute,



To estimate the molar solubility of oxygen in water at 25°C and a partial pressure of 21 kPa, its partial pressure in the atmosphere at sea level, we write

$$b_{O_2} = \frac{p_{O_2}}{K_{O_2}} = \frac{21\text{ kPa}}{7.9 \times 10^4\text{ kPa kg mol}^{-1}} = 2.9 \times 10^{-4}\text{ mol kg}^{-1}$$



solution is essentially that of pure water at 25°C, or $\rho_{H_2O} = 0.99709\text{ kg dm}^{-3}$. It follows that the molar concentration of oxygen is

$$[O_2] = b_{O_2} \times \rho_{H_2O} = 0.29\text{ mmol kg}^{-1} \times 0.99709\text{ kg dm}^{-3} = 0.29\text{ mmol dm}^{-3}$$