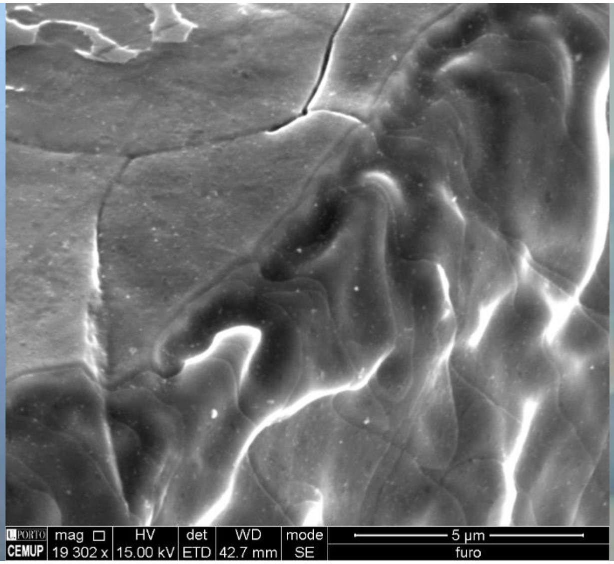
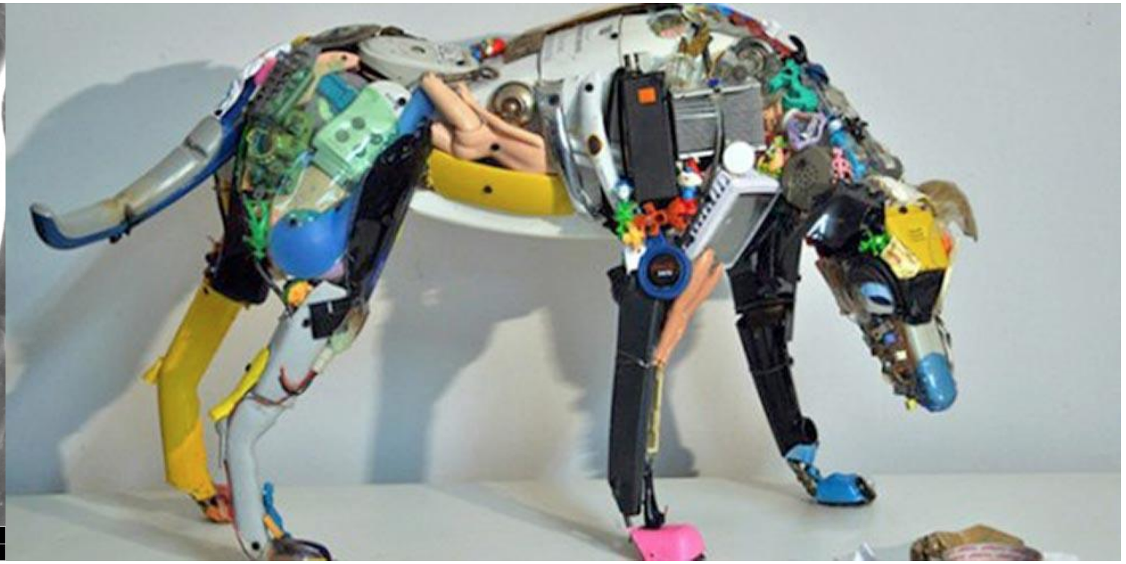
Physical Chemistry

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

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



Gibbs–Duhem equation $G = U + pV - TS$

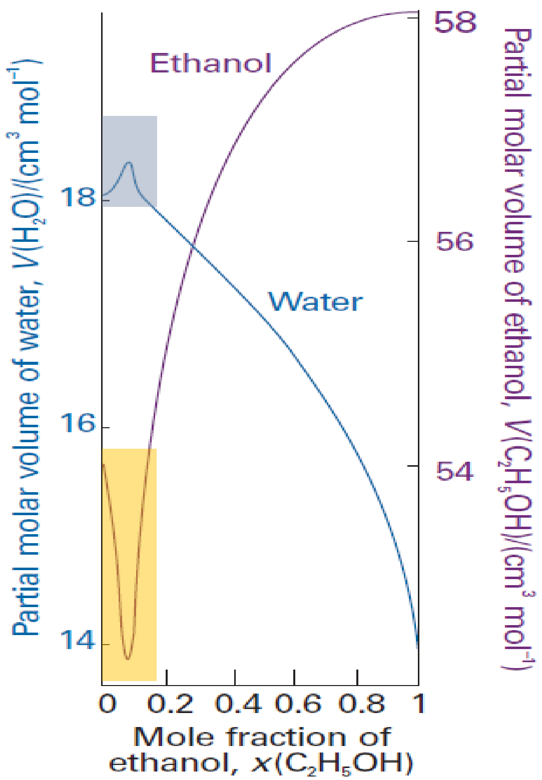
$$G = n_A\mu_A + n_B\mu_B$$

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

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

$$\sum_J n_J d\mu_J = 0$$

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$



Gibbs–Duhem equation |

the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components.

Applies to all partial molar quantities !!!

The thermodynamic mixing

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

ENTROPY of mixing

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

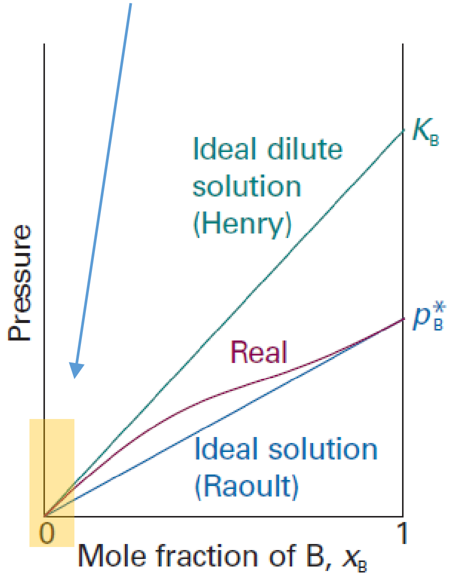
Enthalpy of mixing

$$\Delta_{mix}H = 0$$ **perfect gases**

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,

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

	K/(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*.

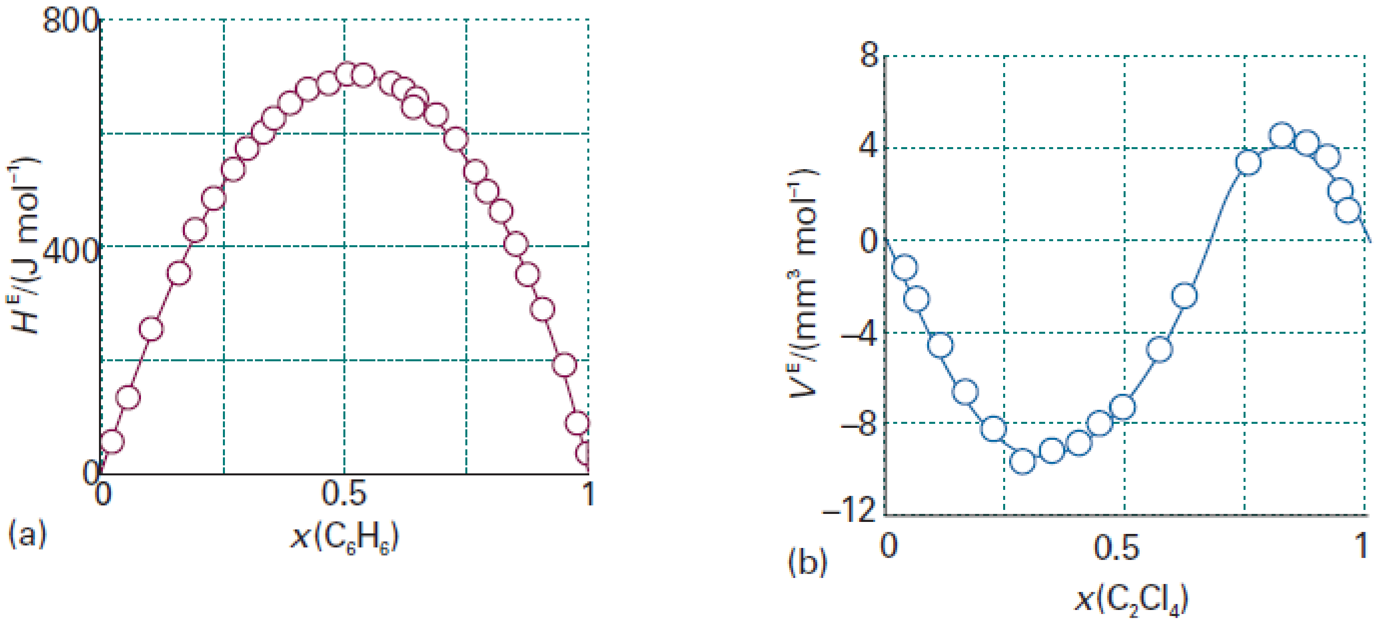
$$\Delta_{mix}G = nRT\{x_A \ln x_A + x_B \ln x_B\}$$

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

Excess functions, X^E,

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

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



Ideal Enthalpy of mixing

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

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

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},

$$X^{E} = X^{real} - X^{ideal}$$

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

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

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

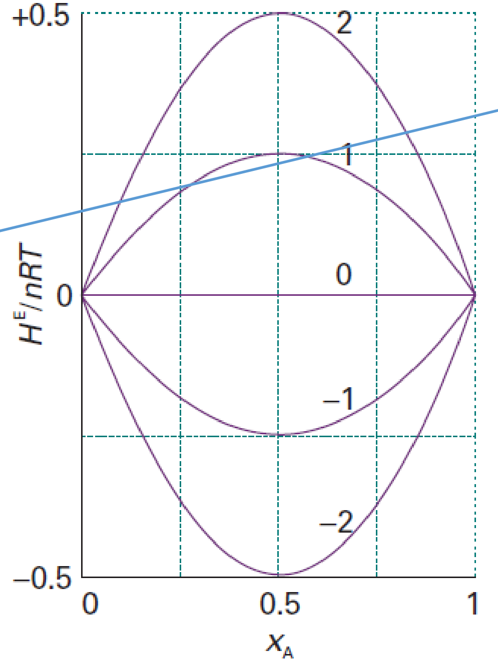
$$\Delta_{mix}G = nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B\}$$

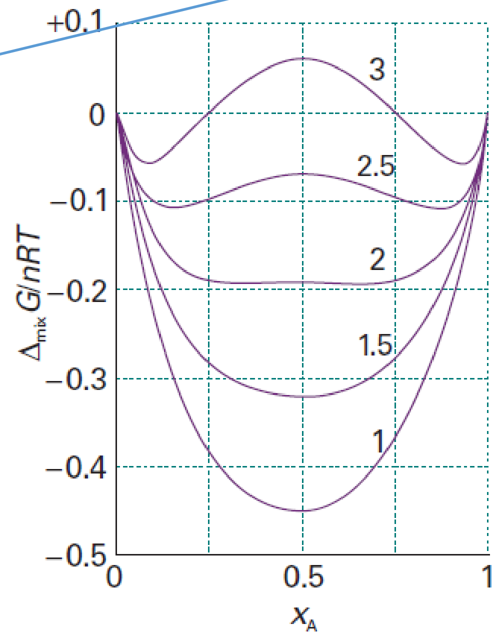
Ideal Enthalpy of mixing

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

$$H^{E} = n\beta RT x_A x_B$$

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





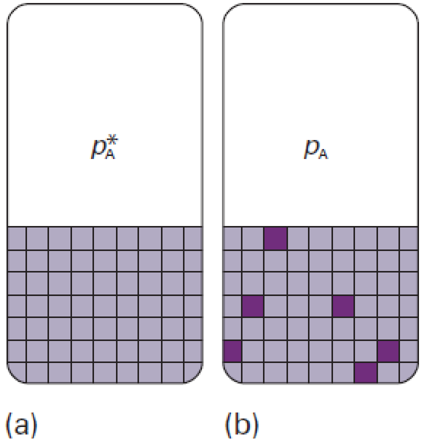
The thermodynamic mixing

Coligative Properties

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

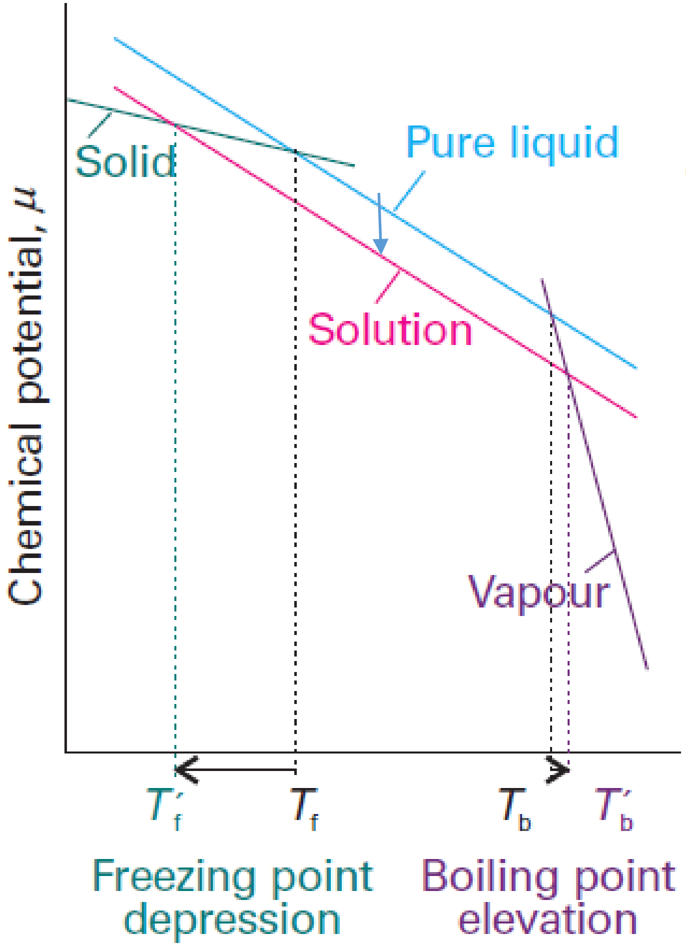
Properties:

1. **lowering of vapour pressure;**
2. **elevation of boiling point;**
3. **depression of freezing point;**
4. **osmotic pressure .**



The chemical potential of a solvent in the presence of a solute.

The lowering of the liquid's chemical potential has a greater effect on the freezing point than on the boiling point because of the angles at which the lines intersect.



The thermodynamic mixing

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

2. elevation of boiling point;

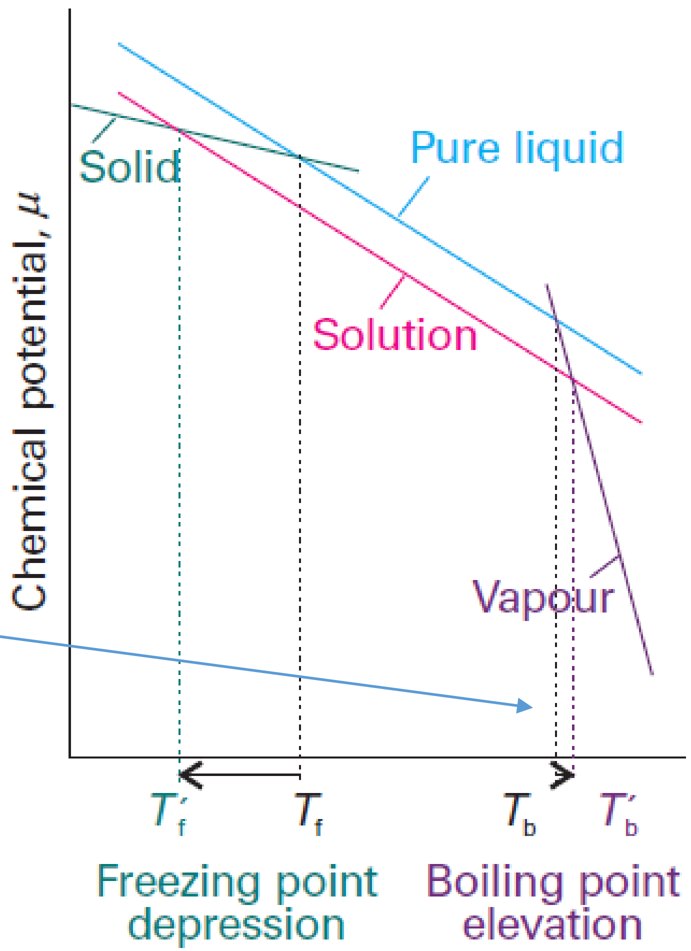
Normal boiling point from T^*

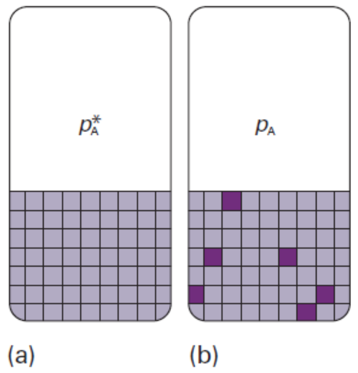
$$\Delta T = Kx_B \qquad K = \frac{RT^{*2}}{\Delta_{vap}H}$$

$$\Delta T = K_b b$$

molality, b, in the solution

where K_b is the empirical **boiling-point constant** of the solvent





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

3. depression of freezing point;

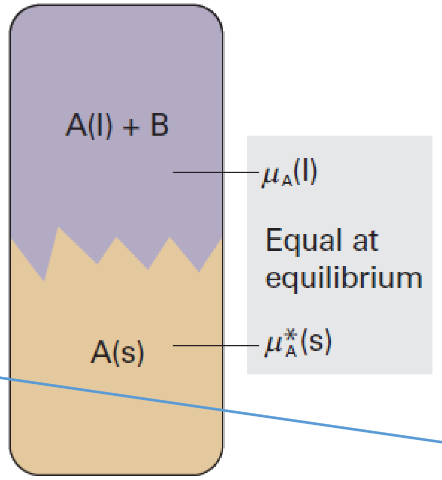
Normal boiling point from T^*

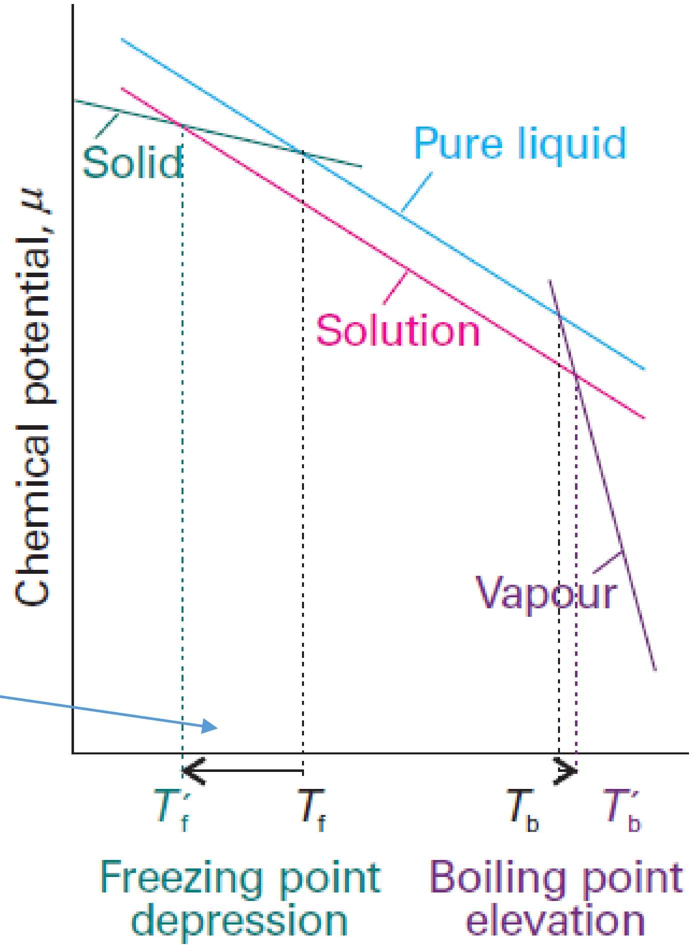
$$\Delta T = K' x_B \qquad K' = \frac{RT^{*2}}{\Delta_{fus}H}$$

$$\Delta T = K_f b$$

molality, b, in the solution

where K_f is the empirical **freezing-point constant**





The thermodynamic mixing

Coligative Properties

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

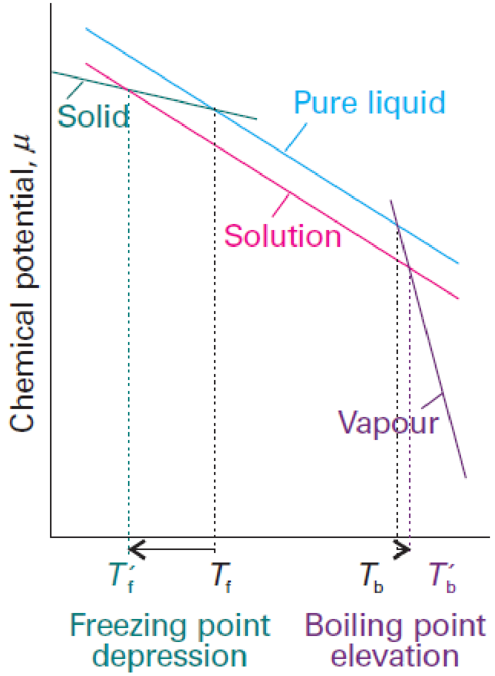
2. elevation of boiling point;

$$\Delta T = K_b b$$

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

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