Chemical potential...

high chemical potential

low chemical potential

Le moyen-age en jeu, Eidôlon, 86 Presses Univer. Bordeaux (2009)

Exemple :

Wikipedia (article chemical potential 2013)

"In thermodynamics, chemical potential, also known as partial molar free energy (wrong), is a form of potential energy (wrong) that can be absorbed or released during a chemical reaction (wrong) […] At chemical equilibrium or in phase equilibrium the total sum of chemical potentials is zero (wrong or at least too vague)

Not so easy !

In thermodynamics

Closed system (constant energy E volume V number of particles N)

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E + \frac{P}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N \quad \left(\Leftrightarrow \mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N\right)$$

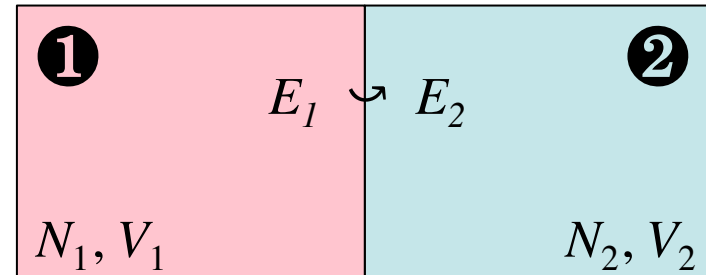☞ $$\frac{\mu}{T} = -\frac{\partial S}{\partial N}\bigg)_{E,V}$$

Physical meaning ?

Thermal equilibrium

Energy exchange between 1 and 2

$$E_1 + E_2 = E^{\text{tot}} \Rightarrow dE_2 = -dE_1$$

At equilibrium, entropy S is maximum

$$dS = dS_1 + dS_2 \quad = \frac{\partial S_1}{\partial E_1} dE_1 + \frac{\partial S_2}{\partial E_2} dE_2$$

$$= \frac{\partial S_1}{\partial E_1} dE_1 - \frac{\partial S_2}{\partial E_2} dE_1$$

$$\Longrightarrow \quad dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 \geq 0$$

If $T_1 > T_2$ then $1/T_1 - 1/T_2 < 0$ so that $dE_1 \leq 0$

Energy tends to flow from a system with a high value of T to a system with a low value of T. This energy transfer continues until $T_1 = T_2$

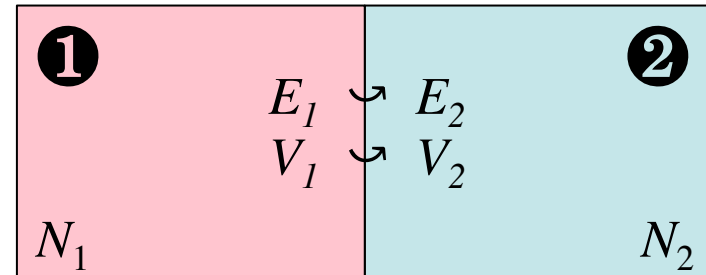Physical meaning of temperature = tendency of a system to give energy

Mechanical equilibrium

Volume exchange between 1 and 2

$$\mathrm{d}E_2 = -\mathrm{d}E_1 \ \text{ and } \ \mathrm{d}V_2 = -\mathrm{d}V_1$$

At equilibrium, entropy S is maximum

$$\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2 = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) \mathrm{d}E_1$$
$$+ \left(\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} \right) \mathrm{d}V_1$$

$$\Longrightarrow \quad \mathrm{d}S = \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) \mathrm{d}V_1 \geq 0 \quad (\text{if } T_1 = T_2 = T)$$

$$\text{If } P_1 > P_2, \ \mathrm{d}V_1 \geq 0$$

Volume tends to be transferred from a system with a low value of P to a system with a high value of P. This volume change continues until $P_1 = P_2$

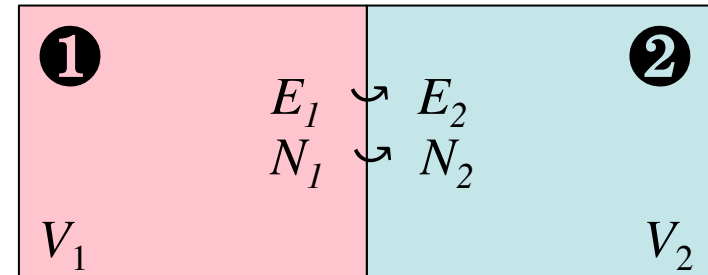*Physical meaning of pressure = tendency of a system to take volume*

Chemical equilibrium

Particles exchange between 1 and 2

$$dE_2 = -dE_1 \text{ and } dN_2 = -dN_1$$

At equilibrium, entropy S is maximum

$$dS = dS_1 + dS_2 = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right)dE_1$$
$$+ \left(\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right)dN_1$$

$\Longrightarrow$ $dS = \left(-\dfrac{\mu_1}{T_1} + \dfrac{\mu_2}{T_2}\right)dV_1 \geq 0$ (if $T_1 = T_2 = T$

If $\mu_1 > \mu_2$, $dN_1 \leq 0$

Particles tends to flow from a system with a high value of μ to a system with a high value of μ. This particle transfer continues until $\mu_1 = \mu_2$

Physical meaning of chemical potential
= tendency of a system to give particles

Chemical potential...

high chemical potential

low chemical potential

Chemical potential...

high chemical potential

not because she is rich…

because she is generous!!!

low chemical potential

not because he is poor…

Because he is willig to receive money!!!

In chemistry also, you can be very rich but not very generous (attractive forces)…

Le moyen-age en jeu, Eidôlon, 86 Presses Univer. Bordeaux (2009)

Exemples of chemical potential

> *Physical meaning of chemical potential*
> *= tendency of a system to give particles*

Chemical potential of a proton (H^+) : pH

$$pH = \left(\mu^0_{H+} - \mu_{H+} \right) / RT \ln 10$$

pH : tendency of a solution to take H^+

Chemical potential of water moleculaes : humidity

$$\ln P_{\text{water}} / P^0 = \left(\mu_{\text{water}} - \mu^0_{\text{water}} \right) / RT$$

humidity : tendency of an atmosphere to give water molecules – further units exists following the context (hydric potential, etc…)

Chemical potential of electrons : Nernst potential

$$E = E^0 + \left(\frac{RT}{nF} \right) \ln \frac{a_{Ox}}{a_{Red}} = -\frac{\mu_{e-}}{F} + \text{Cte}$$

E : tendency of system to take electrons

Further exemples : pC, pOH, etc…

Chemical potential

$$\mu_i = \mu_i^0 + k_B T \ln a_i = \mu_i^0 + k_B T \ln a_i^{\text{ideal}} + k_B T \ln(\gamma_i)$$

Standard term μ_i^0

gives the mass action law constant

$$-RT \ln K^0 = \sum_i \nu_i \mu_i^0$$

Activity coefficient γ_i

depends on *N* body effects

Role of the standard state

The standard state 0 is such that the activity coefficient and the ideal activity are both equal to 1.

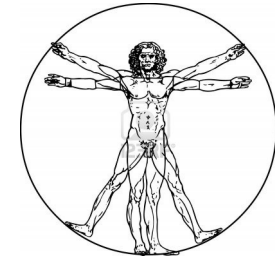It depends on the choice of the ideal activity expression a_i^{ideal}

- **Gas phase** : infinitely dilute pure gas with $P = P^0 = 1$ bar $\quad a_i^{\text{ideal}} = \dfrac{P_i}{P^0}$

- **Liquid or solid mixtures** : pure system $\quad a_i^{\text{ideal}} = x_i$

- **Solutions (convention)** :

  ✓ Solvant : pure solvant $\quad a_i^{\text{ideal}} = x_i$

  ✓ Solutes : infinitely dilute solute with $C = C^0 = 1$ mol.L^{-1} or $m = m^0 = 1$ mol.kg^{-1} or $x = 1$ (depending on the choice of the standard state) $\quad a_i^{\text{ideal}} = C_i / C^0$ or m_i / m^0 or x_i
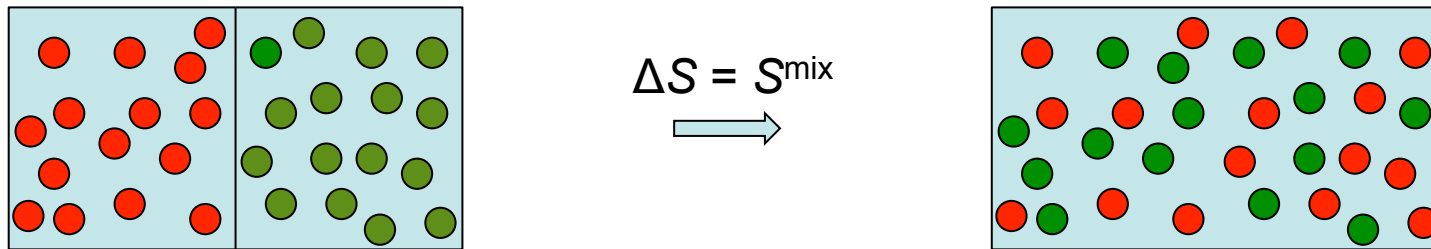
Typically : $\quad a_i^{\text{ideal}} = x_i = \dfrac{N_i}{N_{tot}}$ (sometimes with a prefactor)

This formula is exact only for an ideal mixture.

Ideal activity represents a mixing configurationnal entropy.

$\Delta S = S^{\text{mix}}$

Ideal mixture = similar molecules (same microscopic configurations)

if mixing, there is only one difference.
the number of states is multiplied by Ω

$$\Omega = \begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = \dfrac{(N_1 + N_2)!}{N_1! \, N_2!}$$

$$\Longrightarrow \quad S^{\text{mix}} = k_B \ln \Omega = k_B \ln \dfrac{(N_1 + N_2)!}{N_1! \, N_2!} \approx -k_B \left(N_1 \ln(x_1) + N_2 \ln(x_2) \right)$$

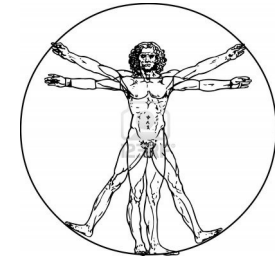Corresponding mixing
chemical potential :
$$\mu_i^{\text{mix}} = \dfrac{\partial G^{\text{mix}}}{\partial N_i} = -T \dfrac{\partial S^{\text{mix}}}{\partial N_i} = k_B T \ln x_i$$

Ideal term

Ideal terms are typically valid

① For ideal mixtures (perfect gas, etc…)

② At low concentration (gas, solute particles)

③ At high concentration (solvent, liquid or solid mixtures)

Typically :

- Valid for ① and ② because the interactions between the particles are not important

- Valid for ③ because of Gibbs-Duhem relation

Activity coefficients represent the interactions between the particles that are not included in the standard term.
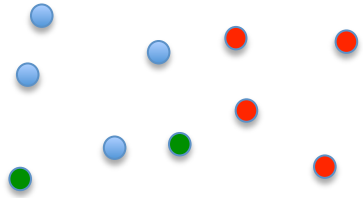
- solute/solute interactions for solutions

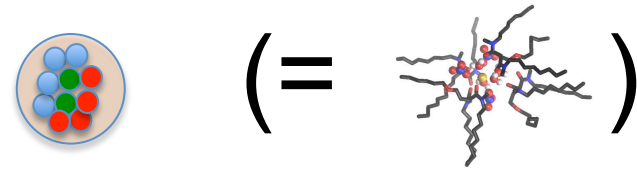- intermolecular interactions for gas

Entropy cost for aggregation

dissociated solutes

associated solutes (complexation aggregation, molecules, etc…)

$$(= \quad)$$

dispersed solutes in their phase (whatever it is)

Organized solutes in a supra molecular aggregate

Free energy calculation

c = typical concentration of solutes n = agregation number

$$G^{\text{init}} = \sum_i \mu_i^0 + NRT \ln \frac{c}{c^0} \qquad G^{\text{final}} = \mu_{\text{agg}}^0 + RT \ln \frac{c}{c^0}$$

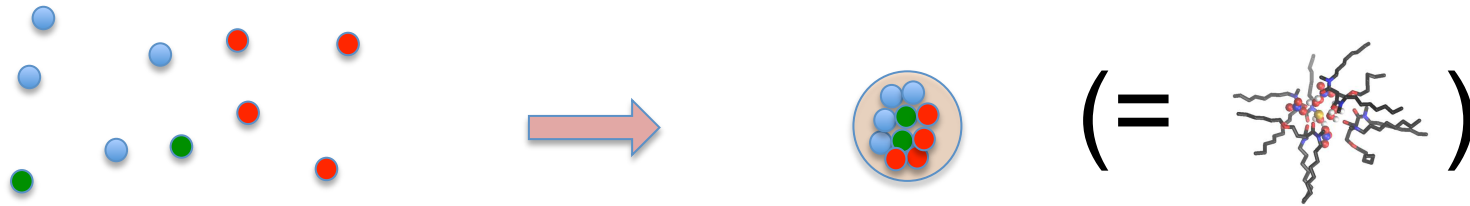Difference $\Delta G = (1 - N)RT \ln c + \text{Cte}$

If the solutes are diluted (small c), ΔG becomes infinitely high.

association becomes not stable – at high dilution entropy always wins

Configurationnal entropy cost for aggregation

$$\Delta G = (1 - N)RT \ln c + \text{Cte}$$

$$\frac{\Delta G}{N} \approx -RT \ln c + \Delta G^0 / N$$

No supramolecular organisation for infinite dilute systems

- Ostwald law (weak acids or electrolytes become strong if dilute)

- critical micellar concentration : micelles do not exist if dilute

- re-extraction from dilution (add solvent for re-extraction)

- no molecules in an infinite space

$$\frac{\Delta G}{N} \approx -RT \ln c + \Delta G^0 / N \quad \begin{cases} c \geq 10^{24} \Rightarrow \Delta G^0 / N \leq 50 \ k_{\text{B}}T \approx 100 \ \text{kJ.mol}^{-1} \\ c \geq 10^{12} \Rightarrow \Delta G^0 / N \leq 25 \ k_{\text{B}}T \approx 50 \ \text{kJ.mol}^{-1} \end{cases}$$

weak forces are forces that can be overcome by configurationnal entropy

Standard term $\quad \mu_i^0$
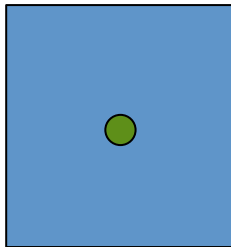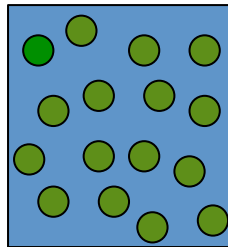
Molar free enthalpy of a particle at the standard state, i.e.

- gas phase : one single molecule (because dilute)

- liquid mixture, solid mixture and solvent : pure system

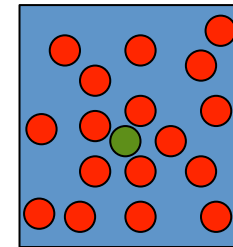- solute particles : one single solute particle dispersed in the solvent

☞ relatively easy evaluation (no correlation)

gas: internal
degrees of freedom

liquids, solids:
anything but
pure system

solute:
solvation

Gas phase μ_i^0

Noble gas: molecule = a single atom

Hamiltonian (energy) of one single atom
(Born-Oppenheimer approx.)

$$H = H_{\text{nucl}} + H_{\text{elect}} = H_{\text{nucl}}^{\text{internal}} + H_{\text{nucl}}^{\text{trans}} + H_{\text{elect}}$$

Consequence for the standard chemical potential

$$\mu^0 = \mu_{\text{nucl}}^{\text{int}} + \mu_{\text{nucl}}^{\text{trans}} + \mu_{\text{elect}}$$

$$\mu_{\text{nucl}}^{\text{trans}} = -k_B T \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{k_B T}{P^0}\right]$$

$$\mu_{\text{elec}} = -k_B T \ln\left[\omega_0 + \omega_1 \exp(-\varepsilon_1/k_B T) + ...\right]$$

degeneracy and energy
of the electronic levels

Experimental validation
for the entropy

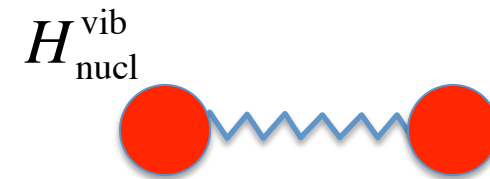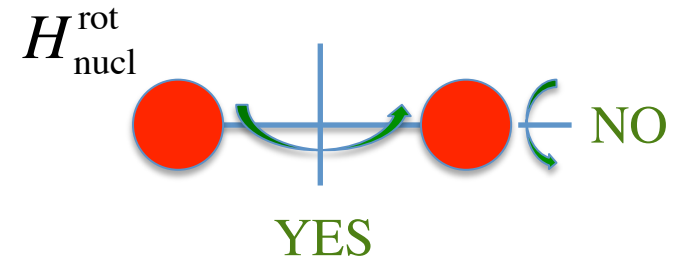|	exp.	calc.
He	30.13	30.11
Ne	34.95	34.94
Ar	36.98	36.97
Kr	39.19	39.18
Xe	40.53	40.52
Hg	41.8	41.78

e.u.

Gas phase μ_i^0

Polyatomic molecules (ex: O_2, N_2, UF_6, etc…)

$$H = H_{\text{nucl}} + H_{\text{elect}}$$

$$H_{\text{nucl}} = H_{\text{nucl}}^{\text{internal}} + H_{\text{nucl}}^{\text{trans}} + H_{\text{nucl}}^{\text{rot}} + H_{\text{nucl}}^{\text{vib}}$$

$$\mu^0 = \mu_{\text{nucl}}^{\text{int}} + \mu_{\text{nucl}}^{\text{trans}} + \mu_{\text{nucl}}^{\text{rot}} + \mu_{\text{nucl}}^{\text{vib}} + \mu_{\text{elect}}$$

$H_{\text{nucl}}^{\text{rot}}$

NO

YES

$H_{\text{nucl}}^{\text{vib}}$

Quantum transition for rotation and vibration
- Low temperature : fundamental state ($\mu_{\text{nucl}}^{\text{rot}}$, $\mu_{\text{nucl}}^{\text{vib}}$ constant)
- High temperature : rotation or vibration ($\mu_{\text{nucl}}^{\text{rot}}$, $\mu_{\text{nucl}}^{\text{vib}}$ depends on T)

	H_2	D_2	I_2	O_2	N_2	CO	NO	HCl	HBr	CO_2	H_2O
T^{rot}	85.3	42.7	0.05	2.07	2.88	2.77	2.45	15.0	12.0	0.56	40 / 21 / 13
T^{vib}	6215	4324	308	2256	3374	3103	2719	4227	3787	3360 954 1890	5360 954 1890

(in kelvin)

Ortho and para

$\mu_{\text{nucl}}^{\text{int}}$: internal energy of nuclei

Quantum states of the nuclei

$s^{\text{tot}} = 1$
3 states   ortho H_2

$\Delta E = k_B \times 175$ K

$s^{\text{tot}} = 0$
1 state   para H_2

$$\mu_{\text{para}}^0 = \mu_{\text{ortho}}^0 - k_B T \ln(3) + \Delta E$$

Mass action law

$$C_{\text{para}} / C_{\text{ortho}} = \frac{1}{3} \exp(\Delta E / k_B T)$$

Low T : only para H_2

High T : ¼ para H_2 ¾ ortho H_2

storage of cold H_2

*chemical potential
= tendency to give particles*

Ideal activity : entropy

Standard term : internal free enthalpy or solvation

Activity coefficients : attraction (<1) or repulsion (>1)
between the particles…