Chemical potential...
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 $N$)

$$
\begin{align*}
d S &= \frac{1}{T} d E + \frac{P}{T} d V - \frac{\mu}{T} d N \\
& \iff d E = T d S - P d V + \mu d N
\end{align*}
$$

$$
\frac{\mu}{T} = - \left( \frac{\partial S}{\partial N} \right)_{E,V}
$$

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

\[
\begin{align*}
    dS &= dS_1 + dS_2 \\
    &= \frac{\partial S_1}{\partial E_1} dE_1 + \frac{\partial S_2}{\partial E_2} dE_2 \\
    &= \frac{\partial S_1}{\partial E_1} dE_1 - \frac{\partial S_2}{\partial E_2} dE_1
\end{align*}
\]

\[
    dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 \geq 0
\]

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
\[ dE_2 = -dE_1 \text{ and } dV_2 = -dV_1 \]

At equilibrium, entropy \( S \) is maximum
\[
\text{d}S = \text{d}S_1 + \text{d}S_2 = \left( \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) \text{d}E_1 + \left( \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} \right) \text{d}V_1
\]

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

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 \( P_1 = P_2 \)
Chemical equilibrium

Particles exchange between 1 and 2

\[ dE_2 = -dE_1 \text{ and } dN_2 = -dN_1 \]

At equilibrium, entropy \( S \) is maximum

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

\[
\rightarrow dS = \left( -\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2} \right) dV_1 \geq 0 \quad (\text{if } T_1 = T_2 = T)
\]

If \( \mu_1 > \mu_2 \), \( dN_1 \leq 0 \)

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

Physical meaning of chemical potential

= tendency of a system to give particles
Chemical potential...

Chemical potential...

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

Exemples of chemical potential

**Physical meaning of chemical potential**

= tendency of a system to give particles

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

\[
pH = \left( \mu_{H^+}^0 - \mu_{H^+} \right) / RT \ln 10
\]

pH : tendency of a solution to take \(H^+\)

Chemical potential of water moleculaes : humidity

\[
\ln P_{\text{water}} / P^0 = \left( \mu_{\text{water}}^0 - \mu_{\text{water}} \right) / RT
\]

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

Chemical potential of electrons : Nernst potential

\[
E = E^0 + \left( \frac{RT}{nF} \right) \ln \frac{a_{\text{ox}}}{a_{\text{red}}} = -\frac{\mu_e}{F} + \text{Cte}
\]

\(E\) : tendency of system to take electrons

Further exemples : pC, pOH, etc…
Significance of the standard term

**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 \(\mu_i^0\)
- gives the mass action law constant

Activity coefficient \(\gamma_i\)
- 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 \(a_i^{\text{ideal}}\)

- **Gas phase**: infinitely dilute pure gas with \(P = P^0 = 1\) bar \(\quad a_i^{\text{ideal}} = \frac{P_i}{P^0}\)
- **Liquid or solid mixtures**: pure system \(\quad a_i^{\text{ideal}} = x_i\)
- **Solutions (convention)**:
  - Solvent: pure solvent \(\quad a_i^{\text{ideal}} = x_i\)
  - 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 \(x_i\)

\[-RT \ln K^0 = \sum_i \nu_i \mu_i^0\]
Typically:  
\[ a_i^{\text{ideal}} = x_i = \frac{N_i}{N_{\text{tot}}} \]  
(sometimes with a prefactor)

This formula is exact only for an ideal mixture.

Ideal activity represents a mixing configurationnal entropy.

\[ \Omega = \binom{N_1 + N_2}{N_2} = \frac{(N_1 + N_2)!}{N_1!N_2!} \]

Ideal mixture = similar molecules (same microscopic configurations)

if mixing, there is only one difference.
the number of states is multiplied by  \( \Omega \)

\[ S^{\text{mix}} = k_B \ln \Omega = k_B \ln \left( \frac{(N_1 + N_2)!}{N_1!N_2!} \right) \approx -k_B \left( N_1 \ln(x_1) + N_2 \ln(x_2) \right) \]

Corresponding mixing chemical potential:

\[ \mu_i^{\text{mix}} = \frac{\partial G^{\text{mix}}}{\partial N_i} = -T \frac{\partial S^{\text{mix}}}{\partial N_i} = k_B T \ln x_i \]
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

**Free energy calculation**

\[ c = \text{typical concentration of solutes} \quad n = \text{aggregation number} \]

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

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

If the solutes are diluted (small \( c \)), \( \Delta G \) becomes infinitely high.

**association becomes not stable** – at high dilution entropy always wins
Configurational entropy

Configurational entropy cost for aggregation

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

\[ \frac{\Delta G}{N} \approx -RT \ln c + \frac{\Delta G^0}{N} \]

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

\[ \frac{\Delta G}{N} \approx -RT \ln c + \frac{\Delta G^0}{N} \]

\[ \begin{cases} 
  c \geq 10^{24} \Rightarrow \frac{\Delta G^0}{N} \leq 50 \ k_B T \approx 100 \ kJ.mol^{-1} \\
  c \geq 10^{12} \Rightarrow \frac{\Delta G^0}{N} \leq 25 \ k_B T \approx 50 \ kJ.mol^{-1}
\end{cases} \]

Weak forces are forces that can be overcome by configurational entropy
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)
Standard term

Gas phase $\mu_i^0$

Noble gas: molecule = a single atom

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

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

Consequence for the standard chemical potential

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

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

$$\mu_{\text{elect}} = -k_B T \ln \left[ \omega_0 + \omega_1 \exp \left( -\frac{\varepsilon_1}{k_B T} \right) + \ldots \right]$$

degeneracy and energy of the electronic levels

Experimental validation for the entropy

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<th>Element</th>
<th>exp.</th>
<th>calc.</th>
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<tbody>
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<td>Ne</td>
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<td>Ar</td>
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<td>Xe</td>
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<td>Hg</td>
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<td>41.78</td>
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</table>
**Gas phase** \( \mu^0_i \)

Polyatomic molecules (ex: O\(_2\), N\(_2\), UF\(_6\), etc…)

\[
H = H_{\text{nucl}} + H_{\text{elect}}
\]

\[
H_{\text{nucl}} = H_{\text{internal}} + H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}}
\]

\[
\mu^0 = \mu_{\text{int}} + \mu_{\text{trans}} + \mu_{\text{rot}} + \mu_{\text{vib}} + \mu_{\text{elect}}
\]

**Quantum transition for rotation and vibration**

- Low temperature: fundamental state (\(\mu_{\text{rot}}, \mu_{\text{vib}}\) constant)
- High temperature: rotation or vibration (\(\mu_{\text{rot}}, \mu_{\text{vib}}\) depends on \(T\))

<table>
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<tr>
<th></th>
<th>H(_2)</th>
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<th>I(_2)</th>
<th>O(_2)</th>
<th>N(_2)</th>
<th>CO</th>
<th>NO</th>
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<td>(T_{\text{vib}})</td>
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(in kelvin)
Ortho and para

Quantum states of the nuclei

\[ \Delta E = k_B \times 175 \text{ K} \]

- \( s^{\text{tot}} = 1 \):
  - 3 states
  - Ortho \( \text{H}_2 \)

- \( s^{\text{tot}} = 0 \):
  - 1 state
  - Para \( \text{H}_2 \)

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

Mass action law

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

Low \( T \): only para \( \text{H}_2 \)

High \( T \): \( \frac{1}{4} \) para \( \text{H}_2 \) \( \frac{3}{4} \) ortho \( \text{H}_2 \)
Conclusion

**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…