

(Electro)Chemical Potential

- For “pure” (1 constituent), simple compressible substance, we know
 - S function of two variables, $S=S(U,V)$
- Consider mixture of k simple compressible substances
 - S now function of two variables and composition, $S=S(U,V,n_1,n_2,\dots,n_k)$

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,n_i}}_{1/T} dU + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{U,n_i}}_{p/T} dV + \sum_{i=1}^k \underbrace{\left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_{j \neq i}}}_{-\frac{\mu_i}{T}} dn_i$$

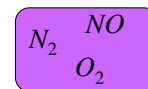
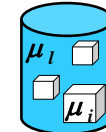
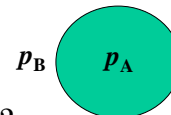
thermal equilibrium mechanical equilibrium chemical/phase equilibrium $-\frac{\mu_i}{T} \equiv \left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_{j \neq i}}$ μ_i : **Chemical Potential (intensive)**

Chemical Potential 1
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Chemical/Phase Equilibrium

- Two systems in **thermal equilibrium** have same?
 - T
- Two systems in **mechanical equilibrium** have same?
 - p
- Two systems in **phase equilibrium** have same?
 - μ
 - e.g., liquid and solid water $\Rightarrow \mu_{liq} = \mu_{ice}$
- Two systems in **chemical equilibrium** have same?
 - μ
 - e.g., $N_2 + O_2 \rightarrow 2NO \Rightarrow \mu_{N_2} + \mu_{O_2} = 2\mu_{NO}$



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Relationship to Gibbs Free Energy

- From definition of $G (=H-TS)$

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$dG = Vdp - SdT + \sum_{i=1}^k \mu_i dn_i \quad G = G(p, T, n_1, \dots, n_k)$$

$$TdS = dU + pdV - \sum_{i=1}^k \mu_i dn_i$$

$$V = \left(\frac{\partial G}{\partial p} \right)_{T, n_i} \quad -S = \left(\frac{\partial G}{\partial T} \right)_{p, n_i} \quad \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}} \quad \text{also written } \hat{\mu}_i \text{ since "per mole"}$$

- μ_i for i^{th} substance in mixture; depends in some way on all other n_j

- Can be shown $\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}} = \left(\frac{\partial H}{\partial n_i} \right)_{S, P, n_{j \neq i}} = \left(\frac{\partial F}{\partial n_i} \right)_{T, V, n_{j \neq i}}$

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Evaluating μ_i for Pure Substance

- Since G extensive

$$G(p, T, \lambda n_1, \dots, \lambda n_k) = \lambda G(p, T, n_1, \dots, n_k)$$

- So $\sum_i \frac{\partial G(p, T, \lambda n_1, \dots, \lambda n_k)}{\partial (\lambda n_i)} \Big|_{p, T, n_j \neq n_i} n_i = G(p, T, n_1, \dots, n_k)$

- True for all λ , including $\lambda=1$

$$G(p, T, n_1, \dots, n_k) = \sum_i \frac{\partial G}{\partial n_i} \Big|_{p, T, n_j \neq n_i} n_i \Rightarrow G = \sum_i n_i \mu_i$$

- For single component, pure phase

$$\mu = \frac{G}{n} = \hat{g} \quad \text{Molar (inten.) Gibbs Free Energy}$$

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Chemical Potential and Equilibrium

- Recall for isolated system; **U, V constant**

$$dS \geq 0 \Rightarrow dU + pdV - \sum_{i=1}^k \mu_i dn_i \geq 0$$

- For **constant T, V** system

$$dF \leq 0 \Rightarrow -SdT - pdV + \sum_{i=1}^k \mu_i dn_i \leq 0 \Rightarrow \sum \mu_i dn_i \leq 0$$

- For **constant T, P** system

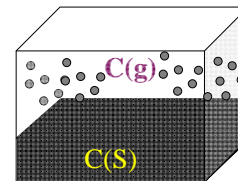
$$dG \leq 0 \Rightarrow Vdp - SdT + \sum_{i=1}^k \mu_i dn_i \leq 0$$

- Minimizing this term is a general equilibrium requirement for multicomponent systems
 - phases and/or chemical reactions

Phase Equilibria Example

- Consider case of equilibrium between solid and gaseous carbon

- e.g., graphitic soot $C(s)$ and $C(g)$ in a high T box
- thermal and mechanical equilibria



- $T_{C(s)} = T_{C(g)}$

- $p_{C(s)} = p_{C(g)}$

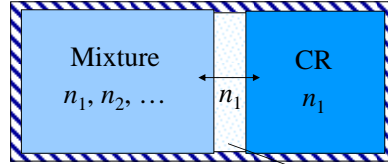
- phase equilibrium $\Rightarrow \sum \mu_i dn_i = 0$

- $\frac{\mu_{C(s)}}{T_{C(s)}} dn_{C(s)} = \frac{\mu_{C(g)}}{T_{C(g)}} dn_{C(g)} \Rightarrow \mu_{C(s)} = \mu_{C(g)}$

- μ_i of component i (same chemical formula) must have same value in every phase at equilibrium

Evaluating μ_i in Mixture

- Define Constituent Reservoir (CR) as holder of uniform, pure substance (single phase) with no internal irrev.
- Consider isolated system made up of single-phase mixture in contact with CR through membrane
 - flexible ($V \neq \text{const}$), diathermal (Q allowed), semi-permeable (only passes 1 component)
- Equilibrium
 - $T_M = T_{CR}$, $p_M = p_{CR}$ and $\mu_{1M} = \mu_{CR} = \hat{g}_{CR}(p_{CR}, T_{CR})$
- So, we have $\mu_i = \hat{g}_i(T, p^*)$ *p^* pressure that would exist in pure phase of i @ equil. in contact with mixture (through our membrane)*



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Single Chemical Reaction Example

- Consider 3 species: HI, H₂, I₂ (and only these) that can react with each other *stoichiometric coefficients (v)*
- Can write this “reaction” as $\underline{2}\text{HI} \leftrightarrow \underline{1}\text{H}_2 + \underline{1}\text{I}_2$
 - why this way?
 - for these three molecules, this is the only way to conserve mass = “atoms” (nuclei) must “balance”
 - mathematically $\sum v_i M_i = 0$
 - v_i : stoich. coeff. for i^{th} species (+) RHS; (-) LHS
 - M_i : mass of i^{th} species

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Single Chemical Reaction Example

- Now define progress variable: η
 - how far we progress between pure LHS (2HI) and pure RHS (H_2+I_2)
- Then $d\eta = \frac{dn_i}{v_i}$

$$\sum_i \mu_i dn_i = \sum_i \mu_i (v_i d\eta) = \left(\sum_i \mu_i v_i \right) d\eta$$
- General equil. requirement $\sum_i \mu_i dn_i \leq 0$

$$-\left(\sum_i \mu_i v_i \right) d\eta \geq 0 \quad -\sum_i v_i \mu_i \begin{cases} > 0 & \rightarrow \\ < 0 & \leftarrow \\ = 0 & \text{equil!} \end{cases}$$

= Affinity (sign tells direction rxn. will go in)

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Single Chemical Reaction Example

- For our example Affinity = $-\{(\mu_{H_2} + \mu_{I_2}) - 2\mu_{HI}\}$
- reason μ called chemical potential*
rxn proceeds from high to low potential
- $2\mu_{HI} > \mu_{H_2} + \mu_{I_2}$
-

Differences in μ sometimes regarded as origin of diffusion processes, which tend to create a mixture of uniform (electro)chemical potential

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