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(Electro)Chemical Potential

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

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

$1/T$ — thermal equilibrium; p/T — 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)

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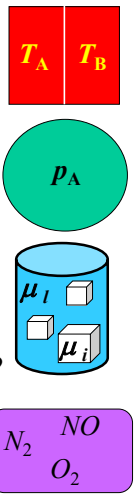
Chemical/Phase Equilibrium

- Two systems in thermal equilibrium have same?
  - ***T***
- Two systems in mechanical equilibrium (with no body or external forces) 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 and NO

    $N_2+O_2 \rightarrow 2NO \Rightarrow \mu_{N_2}+\mu_{O_2}=2\mu_{NO}$



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Relationship to Gibbs Free Energy

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

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

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

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

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} \qquad -S = \left(\frac{\partial G}{\partial T}\right)_{p,n_i} \qquad \boxed{\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}}}$$

also written $\hat{\mu}_i$ *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 Single Phase Mixture

- Since G extensive

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

- This requires that

$$\sum_i \left.\frac{\partial G(p, T, \lambda n_1, ..., \lambda n_k)}{\partial(\lambda n_i)}\right|_{p,T,n_{j\neq i}} n_i = G(p, T, n_1, ..., n_k)$$

- True for all λ, including λ=1

$$G(p, T, n_1, ..., n_k) = \sum_i \left.\frac{\partial G}{\partial n_i}\right|_{p,T,n_{j\neq i}} n_i \quad \Rightarrow \quad \boxed{G = \sum_i n_i \mu_i}$$

- For single phase, pure substance (1 component)

$$\mu = \frac{G}{n} = \hat{g}$$

Molar (intensive) Gibbs Free Energy

Chemical Potential and Equilibrium

- We previously showed
  - for isolated system; ***U,V* constant**

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

  - for **constant *T, V*** system

$dF = dU - SdT - TdS$

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

  - for **constant *T, P*** system

$dG = dU + d(pV) - SdT - TdS$

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

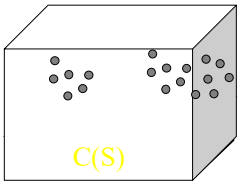
$$\Rightarrow \sum \mu_i dn_i \leq 0$$

- 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 $\sum \mu_i dn_i = 0$
    - $\mu_{C(s)} dn_{C(s)} + \mu_{C(g)} dn_{C(g)} = 0 \quad \Rightarrow \mu_{C(s)} = \mu_{C(g)}$

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



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

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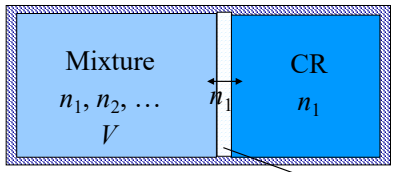
Evaluating μ_i in Mixture

- Define Constituent Reservoir (CR) as holder of uniform, pure substance (single phase) that is internally reversible



- Consider isolated system made up of single-phase mixture in contact with CR through membrane
  - rigid (V_M, V_{CR} constant), nonadiabatic (Q allowed), semi-permeable (only passes 1 component)
- Equilibrium
  - $T_M = T_{CR}$, $p_M \neq p_{CR}$ and $\mu_{1M} = \mu_{CR} = \hat{g}_{CR}(p_{CR}, T_{CR})$

CR pure, single phase

- So, we have $\boxed{\mu_i = \hat{g}_i(p^*, T)}$

for ideal gas mixture, p=partial pressure*

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, H_2, I_2 (and only these) that can react with each other

stoichiometric coefficients (ν)

- Can write this "reaction" as $\underline{2}HI \leftrightarrow \underline{1}H_2 + \underline{1}I_2$

LHS **RHS**

  - why this way?
  - for these three molecules, this is the only way to conserve mass = "atoms" (nuclei) must "balance"
  - mathematically $\sum_i \nu_i M_i = 0$
    - ν_i: stoich. coeff. for ith species (+) RHS; (–) LHS
    - M_i: ith species (e.g., HI or H_2 or I_2 in our example)

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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)

$2HI \leftrightarrow H_2 + I_2$

η=0 =1

- Then $d\eta = \dfrac{dn_i}{\nu_i}$ $\qquad d\eta \begin{cases} > 0 & \rightarrow \\ < 0 & \leftarrow \end{cases}$

$$\sum_i \mu_i dn_i = \sum_i \mu_i (\nu_i d\eta) = \left(\sum_i \mu_i \nu_i \right) d\eta$$

- General equilibrium requirement $\sum_i \mu_i dn_i \le 0$

$$\underbrace{-\left(\sum_i \mu_i \nu_i \right)}_{\equiv \text{Affinity}} d\eta \ge 0 \qquad -\sum_i \nu_i \mu_i \begin{cases} > 0 & \rightarrow \\ < 0 & \leftarrow \\ = 0 & equil! \end{cases}$$

≡ Affinity (sign tells in which direction reaction will go)

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Single Chemical Reaction Example

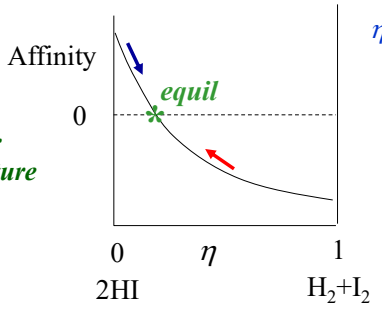
- For our example Affinity=$-\{(\mu_{H_2}+\mu_{I_2})-2\mu_{HI}\}$

$2HI \leftrightarrow H_2 + I_2$

η=0 =1

reason μ called chemical potential

reaction proceeds to lower chemical potential of mixture



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