LECTURE

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Open Systems and Chemical Potential

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Limitations of the Fundamental Equation of Chemical Thermodynamics:

$$\boxed{dG = Vdp - SdT}$$

Does not apply

- When composition is changing due to exchange of matter with surroundings (open system)
- Irreversible chemical reaction
- Irreversible inter-phase transport of matter

For one phase and multi-component system, in thermal and mechanical equilibrium but not in material equilibrium, $G = f(T, p, n_1, n_2, ...)$,

$$(T, p, n_1, n_2, \ldots.) \xrightarrow{\text{Irreversible}} (T+dT, p+dp, n_1+dn_1, n_2+dn_2, \ldots.)$$

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,\, n_i} dp + \left(\frac{\partial G}{\partial T}\right)_{p,\, n_i} dT + \left(\frac{\partial G}{\partial n_1}\right)_{T,\, p,\, n_j \neq n_1} dn_1 + \ldots + \left(\frac{\partial G}{\partial n_i}\right)_{T,\, p,\, n_j \neq n_i} dn_i$$

$$dG = Vdp - SdT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,\, p,\, n_j \neq n_i} dn_i$$

G is state function, dG is same if the process was reversible

Chemical Potential

$$dG = Vdp - SdT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,\, p,\, n_j \neq n_i} dn_i$$

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

$$\mu_i = f\left(T, p, n_1, n_2, ...\right)$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{J\#i}}$$

For pure substance

$\boxed{\mu \text{ (Chemical Potential)} = G_m = G/n}$

Applicable to single phase, multi component system at thermal and mechanical equilibrium but *not material equilibrium.*

$$dG_{p,T} = \sum_i \mu_i dn_i$$

$$dw_{\text{add, max}} = \sum_i \mu_i dn_i$$

Maximum additional work that can arise from changing the components of the system.

Fundamental Equations of Thermodynamics or Gibbs Equations - Revisited

$$dU = TdS - pdV + \sum_{i=1}^{n} \mu_i dn_i \quad \text{where, } \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j}$$

$$dH = TdS + Vdp + \sum_{i=1}^{n} \mu_i dn_i \quad \text{where, } \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j}$$

$$dA = -SdT - pdV + \sum_{i=1}^{n} \mu_i dn_i \quad \text{where, } \mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}$$

$$dG = -SdT + Vdp + \sum_{i=1}^{n} \mu_i dn_i \quad \text{where, } \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}$$

Applicable to single phase multi-component open system in thermal and mechanical equilibrium and pV work only.

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

Multi-phase Multi-Component System:

$$dG^{\alpha} = V^{\alpha}dp - S^{\alpha}dT + \sum_i \mu_i^{\alpha} dn_i^{\alpha}$$

For one phase (α) system, in thermal and mechanical equilibrium pV work only

For multiple phases

$$dG = \sum_{\alpha} dG^{\alpha} = \sum_{\alpha} V^{\alpha}dp - \sum_{\alpha} S^{\alpha}dT + \sum_{\alpha}\sum_i \mu_i^{\alpha} dn_i^{\alpha}$$

$$\mu_i^{\alpha} = \left(\frac{\partial G^{\alpha}}{\partial n_i^{\alpha}}\right)_{p,T,n_{j\neq i}^{\alpha}}$$

Since, S and V are extensive properties,

$$\boxed{dG = Vdp - SdT + \sum_{\alpha}\sum_i \mu_i^{\alpha} dn_i^{\alpha}}$$

Thermal and mechanical equilibrium. p-V work only

Material Equilibrium

$$\boxed{dG = Vdp - SdT + \sum_{\alpha}\sum_{i}\mu_i^{\alpha} dn_i^{\alpha}}$$

Thermal and mechanical equilibrium. *p*-*V* work only

For a liquid and vapor mixture of water and acetone,

$$dG = Vdp - SdT + \mu_{\mathrm{w}}^{\mathrm{v}} dn_{\mathrm{w}}^{\mathrm{v}} + \mu_{\mathrm{ac}}^{\mathrm{v}} dn_{\mathrm{ac}}^{\mathrm{v}} + \mu_{\mathrm{w}}^{\mathrm{l}} dn_{\mathrm{w}}^{\mathrm{l}} + \mu_{\mathrm{ac}}^{\mathrm{l}} dn_{\mathrm{ac}}^{\mathrm{l}}$$

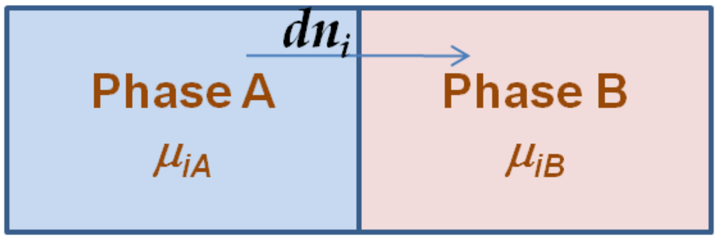
$$dG_{p,T} = \sum_{\alpha}\sum_{i}\mu_i^{\alpha} dn_i^{\alpha}$$

Thermal and mechanical equilibrium and constant *T* and *p*. *p*-*V* work only

At complete equilibrium (thermal, mechanical, and material) at constant *T* and *p*, *pV* work only, $dG = 0$.

$$\sum_{\alpha}\sum_{i}\mu_i^{\alpha} dn_i^{\alpha} = 0$$

Chemical Potential and Phase Equilibrium



Change taking place
at constant T, p

$$dG^A = \mu_{i,A}(-dn_i) \text{ and } dG^B = \mu_{i,B}dn_i$$

$$dG = dG^A + dG^B = (\mu_{i,B} - \mu_{i,A})dn_i$$

If $\mu_{i,A} > \mu_{i,B}$, then $dG < 0$	•Spontaneous transport of i from phase A to phase B
If $\mu_{i,A} < \mu_{i,B}$, then $dG > 0$	•Spontaneous transport of i from phase B to phase A
If $\mu_{i,A} = \mu_{i,B}$, then $dG = 0$	•Phase Equilibrium

•Substance i flows spontaneously from a phase with higher chemical potential to a phase with lower chemical potential .

Gibbs-Duhem Equation

$$G_{p,T} = n_1\mu_1 + n_2\mu_2 + \cdots = \sum_i n_i\mu_i$$

$$dG_{p,T} = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$$

$$dG_{p,T} = \sum_i \mu_i dn_i$$

At thermal and mechanical equilibrium.

At constant p and T

$$\boxed{\sum_i n_i d\mu_i = 0}$$

Gibbs-Duhem Equation

For a binary mixture, $n_1\, d\mu_1 + n_2\, d\mu_2 = 0$

Hence, $d\mu_1 = -\,(n_2/n_1)\, d\mu_2$

If $n_2 > n_1$, a small change in μ_2 causes a large change in μ_1

Chemical potential of one component of a mixture can not change independently of the chemical potentials of other components.