The Chemical Potential and Open Systems

(Lecture 9)

1st semester, 2021

Advanced Thermodynamics (M2794.007900)

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(*) Some materials in this lecture note are borrowed from the textbook of Ashley H. Carter.

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The Chemical Potential

- For open systems, we need to include the change of mass (or mole) in our fundamental equation of thermodynamics!

$$U = U(S, V, n)$$

$$\rightarrow dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn$$

$$\rightarrow dU = TdS - PdV + \bar{\mu} dn$$

Chemical potential!

For multiple components,

$$dU = TdS - PdV + \sum_{j=1}^{m} \bar{\mu}_j dn_j \quad \text{where} \quad \bar{\mu}_j = \left(\frac{\partial U}{\partial n_j}\right)_{S,V,n_k(\neq n_j)}$$

The Chemical Potential

- Gibbs' definition
  - If to any homogeneous mass in a state of hydrostatic stress we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and *its entropy and volume remaining unchanged*, *the increase of the energy of the mass* divided by the quantity of the substance added is the *potential* for that substance in the mass considered.
- Particles tend to move from areas of higher chemical potential to lower chemical potential
  - The difference (or gradient) in chemical potential = driving force!
  - Diffusions, Reactions, Phase changes, ...

$$\bar{\mu}_i = \left.\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left.\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \left.\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} = \left.\frac{\partial F}{\partial n_i}\right)_{T,V,n_j}$$

$\rightarrow \bar{g}_i$ (partial molal Gibbs function)

The Chemical Potential

➔ The chemical potential is associated with intermolecular forces!

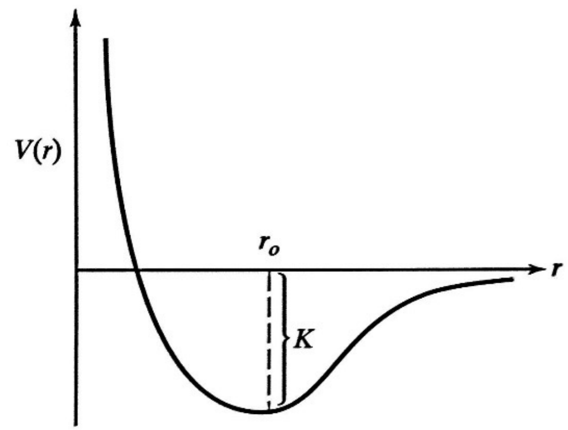
As new particle approaches its neighbor,

1. It gains kinetic energy while losing potential energy.
2. Kinetic energy is dissipated through collisions with other particles.
3. The system gains internal energy in the process!

$$E = K + V(r)$$

$$(\text{where } E: \text{total E}, \ K: \text{kinetic E}, \ V: \text{potential E})$$

$$\text{Set arbitrarily, } E = 0 \ \text{ at } \ r = \infty$$



Then, by energy conservation,

$$E = 0 = K + V(r_0) \quad \text{or} \quad K = -V(r_0) \sim \mu$$

The Chemical Potential – Osmosis (Example)

- For osmosis process, chemical potential drives the water through membrane!

Initially,

$$\bar{\mu}_{H_2O,Left}(T,P) > \bar{\mu}_{H_2O,Right}(T,P,x_{H_2O,Right})$$

At equilibrium (at constant T),

Osmotic pressure

$$\bar{\mu}_{H_2O,Left}(T,P) = \bar{\mu}_{H_2O,Right}(T,P+\Pi,x_{H_2O,Right})$$

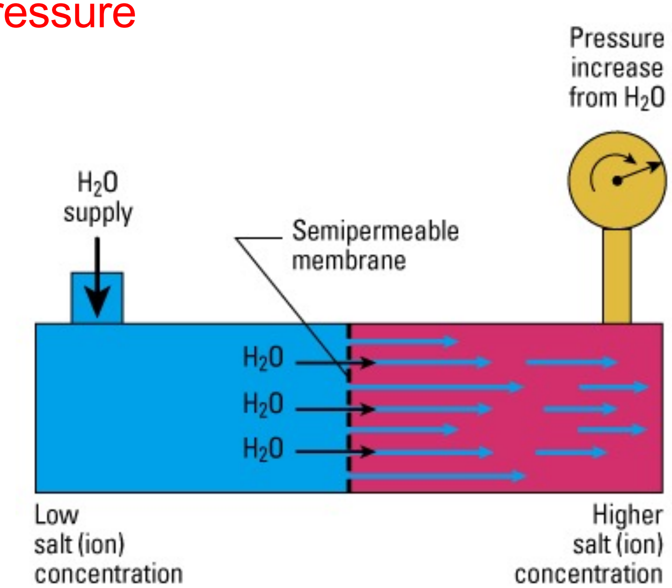
For an ideal solution,

$$\bar{\mu}_i(T,P) = \bar{g}_i(T,P) = \hat{g}_i(T,P)$$

Partial molal property Molar property

$$\longrightarrow \hat{g}_{H_2O,Left}(T,P) = \hat{g}_{H_2O,Right}(T,P+\Pi,x_{H_2O,Right})$$

$$= \hat{g}_{H_2O,Right}(T,P+\Pi) + \hat{R}T\ln x_{H_2O,Right}$$



Osmotic Pressure Cell

(source: wikipedia.org)

The Chemical Potential

- Let's derive Gibbs-Duhem equation!

Using Euler's theorem for homogeneous functions,

$$\lambda f(x,y,z) = f(\lambda x, \lambda y, \lambda z) \quad (f \ : \text{homogeneous function})$$

Differentiating by λ ,

$$f = x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z}$$

Similarly,

$$U = U(S, V, n_1 \ldots n_m) \ : \ \text{homogeneous function}$$

$$\text{e.g.} \quad 2U = U(2S, 2V, 2n_1 \ldots 2n_m)$$

Then,

$$U = S\left(\frac{\partial U}{\partial S}\right)_{V,n_k} + V\left(\frac{\partial U}{\partial V}\right)_{S,n_k} + \sum_{j=1}^{m} n_j \left(\frac{\partial U}{\partial n_j}\right)_{S,V,n_k}$$

$$= ST - PV + \sum_{j=1}^{m} n_j \bar{\mu}_j$$

The Chemical Potential

- Continue on. $$U = ST - PV + \sum_{j=1}^{m} n_j \bar{\mu}_j$$

Here, Gibbs function (G) is given by,

$$G = \sum_{j=1}^{m} n_j \bar{g}_j = U - ST + PV = \sum_{j=1}^{m} n_j \bar{\mu}_j \quad \text{or} \quad \bar{\mu}_j = \bar{g}_j$$

Differentiating the internal energy (U),

$$dU = TdS + SdT - PdV - VdP + \sum_{j=1}^{m} dn_j \bar{\mu}_j + \sum_{j=1}^{m} n_j d\bar{\mu}_j$$

$$SdT - VdP + \sum_{j=1}^{m} n_j d\bar{\mu}_j = 0$$

Gibbs-Duhem equation

Relationship between changes in “intensive” properties!

The Chemical Potential

- Continue on.

Differentiating the Gibbs function (G),

$$G = \sum_{j=1}^{m} n_j \bar{\mu}_j \quad \text{or} \quad dG = \sum_{j=1}^{m} dn_j \bar{\mu}_j + \sum_{j=1}^{m} n_j d\bar{\mu}_j$$

At constant temperature and pressure,

$$S\cancel{dT} - V\cancel{dP} + \sum_{j=1}^{m} n_j d\bar{\mu}_j = 0$$

Then,

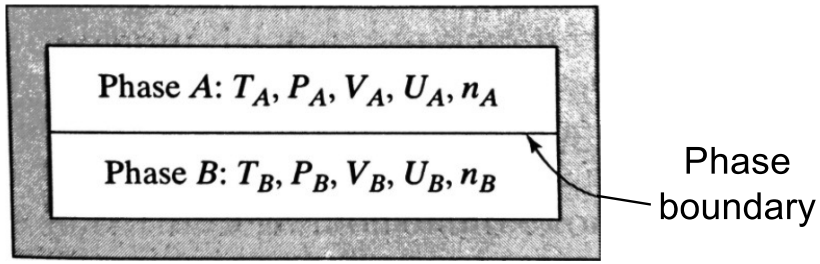
$$(dG)_{T,P} = \sum_{j=1}^{m} \bar{\mu}_j dn_j$$

The final equation is quite useful in many interesting processes in nature!

Phase Equilibrium

- Let's find the equilibrium condition for two subsystems having two phases of the same substance. Particles are exchanged through the phase boundary.

$$n_A + n_B = n = const \quad \text{(conservation of mass)}$$
$$V_A + V_B = V = const \quad \text{(conservation of volume)}$$
$$U_A + U_B = U = const \quad \text{(conservation of energy)}$$
$$S_A + S_B = S \quad \text{(maximum at equilibrium)}$$



$$dU_A = T_A dS_A - P_A dV_A + \bar{\mu}_A dn_A \quad \text{or} \quad dS_A = \frac{1}{T_A}\left(dU_A + P_A dV_A - \bar{\mu}_A dn_A\right)$$

in the same way,

$$dS_B = \frac{1}{T_B}\left(dU_B + P_B dV_B - \bar{\mu}_B dn_B\right)$$

For an isolated system, $dS = dS_A + dS_B \geq 0$

Phase Equilibrium

➔ Continue on. $dS = dS_A + dS_B = \frac{1}{T_A}\left(dU_A + P_A dV_A - \bar{\mu}_A dn_A\right) + \frac{1}{T_B}\left(dU_B + P_B dV_B - \bar{\mu}_B dn_B\right) \geq 0$

Here, $dn_B = -dn_A,\ dV_B = -dV_A,\ dU_B = -dU_A$

Then, $dS = dS_A + dS_B = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)dU_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)dV_A - \left(\frac{\bar{\mu}_A}{T_A} - \frac{\bar{\mu}_B}{T_B}\right)dn_A \geq 0$

Before the equilibrium is achieved,

$$\text{if } T_A > T_B \text{, then } dU_A < 0 \ \text{(heat flow from A to B)}$$

$$\text{At } T_A = T_B \text{, if } P_A > P_B \text{, then } dV_A > 0 \ \text{(volume expansion of A)}$$

$$\text{At } T_A = T_B \text{, if } \bar{\mu}_A > \bar{\mu}_B \text{, then } dn_A < 0 \ \text{(mass flow from A to B)}$$

At equilibrium,

$$T_A = T_B \ \text{(thermal equilibrium)}$$

$$P_A = P_B \ \text{(mechanical equilibrium)}$$

$$\bar{\mu}_A = \bar{\mu}_B \ \text{(chemical equilibrium)}$$

Chemical Reactions

➔ Let's find the equilibrium condition for chemical reaction.

Consider the following chemical reaction at constant T and P.

$$2H_2 + O_2 \rightarrow 2H_2O \quad \text{or} \quad 0 \rightarrow 2H_2O - 2H_2 - O_2$$

which can be expressed in,

$$0 \rightarrow \sum_{j=1}^{m} \nu_j M_j \quad (\nu : \text{stoichiometric coeff.}, \quad M : \text{species})$$

$$\text{where } \nu_{H_2} = -2,\ \nu_{O_2} = -1,\ \nu_{H_2O} = 2$$

Then, the change in the number of moles by the reaction is given by,

$$dn_{H_2} : dn_{O_2} : dn_{H_2O} = \nu_{H_2} : \nu_{O_2} : \nu_{H_2O} = -2 : -1 : +2$$

At chemical equilibrium at fixed T and P,

$$(d\mathrm{G})_{T,P} = \sum_{j=1}^{m} \bar{\mu}_j dn_j = 0 \rightarrow \sum_{j=1}^{m} \bar{\mu}_j \nu_j = 0$$

Finally,

$$2\bar{\mu}_{H_2O} - 2\bar{\mu}_{H_2} - \bar{\mu}_{O_2} = 0 \quad \text{or} \quad \bar{\mu}_{H_2O} = \frac{1}{2}\left(2\bar{\mu}_{H_2} + \bar{\mu}_{O_2}\right)$$

Mixing Processes

- Let's consider mixing of two ideal gases at constant T and P(=P_{tot}).

  To evaluate the changes in Gibbs function and entropy during mixing,

$$ds = c_P \frac{dT}{T} - R\frac{dP}{P} \rightarrow s = c_P \ln T - R\ln P + s_0 \quad (\text{const } c_P)$$

$$dh = c_P dT \rightarrow h = c_P T + h_0 \quad (\text{const } c_P)$$

$$g = h - Ts = c_P T - c_P T\ln T + RT\ln P - Ts_0 + h_0 = RT(\ln P + \phi(T))$$

Then, the total Gibbs energy in initial state,

$$G_i = n_1 g_{1i} + n_2 g_{2i} = n_1 RT(\ln P + \phi_1) + n_2 RT(\ln P + \phi_2)$$

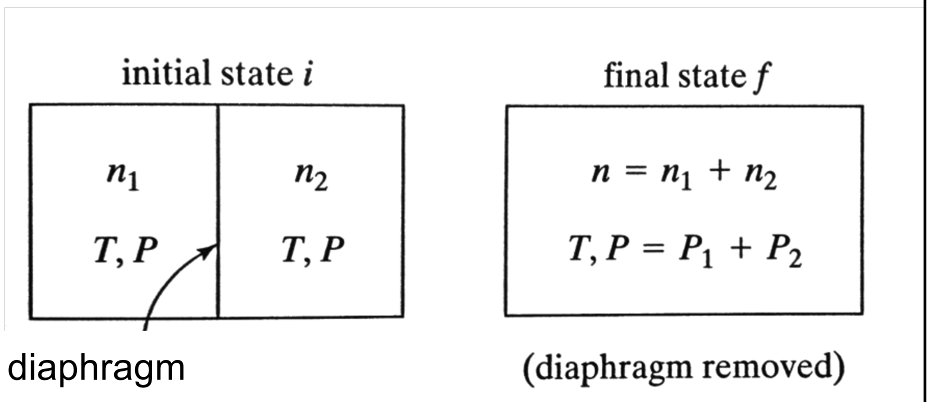
For final state,

$$G_f = n_1 RT(\ln P_1 + \phi_1) + n_2 RT(\ln P_2 + \phi_2)$$

where,

$$P_1 = x_1 P$$

$$P_2 = x_2 P \quad (\text{Dalton's law})$$



Mixing Processes

➔ Continue on.

Then, the change in Gibbs energy is given by,

$$\Delta G = G_f - G_i = n_1 RT(\ln P_1 + \phi_1) + n_2 RT(\ln P_2 + \phi_2) - n_1 RT(\ln P + \phi_1) - n_2 RT(\ln P + \phi_2)$$

$$= n_1 RT \ln\left(\frac{P_1}{P}\right) + n_2 RT \ln\left(\frac{P_2}{P}\right) = RT\left(n_1 \ln x_1 + n_2 \ln x_2\right) = nRT\left(x_1 \ln x_1 + x_2 \ln x_2\right)$$

For the change in entropy,

$$dG = -SdT + VdP \;\rightarrow\; S = -\left(\frac{\partial G}{\partial T}\right)_P \;\rightarrow\; \Delta S = -\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$$

$$\Delta S = -nR\left(x_1 \ln x_1 + x_2 \ln x_2\right) \text{ (always positive)}$$

For the case of $n_1 = n_2$,

$$\Delta S = -nR\left(\tfrac{1}{2} \ln \tfrac{1}{2} + \tfrac{1}{2} \ln \tfrac{1}{2}\right) = nR \ln 2$$

What if you are mixing the same kinds of ideal gases? → Gibbs paradox!