Chemical Potential

1 Overview

When two systems in **thermal equilibrium**, they have same **temperature**. When two systems in **mechanical equilibrium**, they have same **pressure**. When two systems in **phase equilibrium** and **chemical equilibrium**, what are the same? We need to define a new variable, called **chemical potential** μ for this situation.

2 Definition

2.1 From Entropy

Assume simple compressible substance, for **pure** substance, entropy is a function of two variables:

$$S = S(U, V) \tag{1}$$

If now we have a mixture of k simple compressible substances, then **entropy now** is a function of two variables and composition:

$$S = S(U, V, n_1, n_2, ..., n_k)$$
⁽²⁾

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,n_i} dU + \left(\frac{\partial S}{\partial V}\right)_{U,n_i} dV + \sum_{i}^{k} \left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_{j\neq i}} dn_i \tag{3}$$

Recall the thermodynamic definition of temperature:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,n_i} \tag{4}$$

Therefore the first term represents the **thermal equilibrium**. Recall the thermodynamic definition of pressure:

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,n_i} \tag{5}$$

So the second term represents the **mechanical equilibrium**. Now we introduce the thermodynamic definition of **chemical potential**:

$$-\frac{\mu_i}{T} = \left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_{j\neq i}} \tag{6}$$

So the third term represents the **chemical equilibrium**.

2.2 From Gibbs Energy

Besides entropy, we can also get the definition of chemical potential from Gibbs energy. Rearrange previous equation:

$$TdS = dU + pdV - \sum_{i=1}^{k} \mu_i dn_i \tag{7}$$

Recall the definition of Gibbs Energy:

$$G = H - TS \tag{8}$$

$$H = U + pV \tag{9}$$

$$dG = dU + pdV + Vdp - TdS - SdT$$
⁽¹⁰⁾

Plug in the term TdS:

$$dG = Vdp - SdT + \sum_{i=1}^{k} \mu_i dn_i \tag{11}$$

Therefore, we can get the following expressions:

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} \tag{12}$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_{p,n_i} \tag{13}$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} \tag{14}$$

In other way:

$$G = \sum_{i} n_i \mu_i \tag{15}$$

For single component, pure phase:

$$\mu = \frac{G}{n} = \hat{g} \tag{16}$$

Where \hat{g} is the molar Gibbs free energy.

2.3 From Internal Energy

Similarly we have:

$$dU = TdS - pdV + \sum_{i=1}^{k} \mu_i dn_i \tag{17}$$

So:

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_{j \neq i}} \tag{18}$$

2.4 From Enthalpy

$$dH = dU + pdV + Vdp \tag{19}$$

Recall that:

$$dU = TdS - pdV + \sum_{i=1}^{k} \mu_i dn_i \tag{20}$$

Then:

$$dH = TdS + Vdp + \sum_{i=1}^{k} \mu_i dn_i \tag{21}$$

Therefore:

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S, p, n_{j \neq i}} \tag{22}$$

2.5 From Helmholtz Energy

Recall the definition:

$$F = U - TS \tag{23}$$

Then:

$$dF = dU - TdS - SdT \tag{24}$$

$$dF = -pdV - SdT + \sum_{i=1}^{k} \mu_i dn_i \tag{25}$$

So:

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_{j\neq i}} \tag{26}$$

3

2.6 Summary

Therefore, chemical potential could be interpreted as:

- 1. Amount of Gibbs energy added to system by adding one mole of species i keeping T, p constant.
- 2. Amount of internal energy added to system by adding one more of species i keeping S, V constant.
- 3. Amount of enthalpy added to system by adding one more of species i keeping S, p constant.
- 4. Amount of Helmholtz energy added to system by adding one more of species i keeping T, V constant.
- 5. Chemical potential of one species also depends all other species

3 Relations with Equilibrium

Recall the Auxiliary Function chapter, we know the conditions for equilibrium include:

- 1. Isolated System: $dS \ge 0$
- 2. Constant T and V: $dF \leq 0$
- 3. Constant T and P: $dG \leq 0$

Based on previous discussion, we can see that all of them pointing to single expression:

$$\sum \mu_i dn_i \le 0 \tag{27}$$

Conclusion: Minimizing this term is a general equilibrium requirement for multicomponent systems, either phases or chemical reactions

4 Phase Equilibrium



Figure 1: Phase Equilibrium

Consider case of equilibrium between solid and gaseous carbon. Then, because of thermal and mechanical equilibrium:

$$T_{(s)} = T_{(g)}, p_{(s)} = p_{(g)}$$
(28)

For phase equilibrium:

$$\sum \mu_i dn_i = 0 \tag{29}$$

Therefore:

$$\mu_s dn_s + \mu_g dn_g = 0 \tag{30}$$

The amount of mole reduced from gas will be the same as the amount increasing in solid. Therefore:

$$dn_s = -dn_q \tag{31}$$

$$\mu_s = \mu_g \tag{32}$$

Conclusion: μ_i of component i must have same value in every phase at equilibrium.

5 Relations with Chemical Reactions

Choose one chemical reaction as an example:

$$2HI \to H_2 + I_2 \tag{33}$$

Here, we define a progress variable η to see how far we progress between pure LHS (2HI, $\eta = 0$) and pure RHS ($\eta = 1$)

Recall the general chemical reaction expression:

$$\sum_{i=1}^{n} v_i' M_i \to \sum_{i=1}^{n} v_i'' M_i \tag{34}$$

Here, we define:

$$v_i = v'_i - v''_i (35)$$

So (+) means the species are in RHS, (-) means the species are in LHS. M_i is the moles of i^{th} species. Re-arrange, we get:

$$\sum v_i M_i = 0 \tag{36}$$

Then we define:

$$d\eta = \frac{dn_i}{v_i} \tag{37}$$

Intuitively we know:

- 1. $d\eta > 0$, the reaction will approach RHS.
- 2. $d\eta < 0$, the reaction will approach LHS.

Then the chemical potential could be expressed as:

$$\sum_{i} \mu_{i} dn_{i} = \sum_{i} \mu_{i} (v_{i} d\eta) = \left(\sum_{i} \mu_{i} v_{i}\right) d\eta$$
(38)

Recall the equilibrium requirement:

$$\sum \mu_i dn_i \le 0 \tag{39}$$

Therefore, we have:

$$-(\sum \mu_i v_i) d\eta \ge 0 \tag{40}$$

So for the term $-(\sum \mu_i v_i)$, which is called **affinity**, we have 3 conditions:

- 1. > 0, then the reaction will approach RHS
- 2. < 0, then the reaction will approach LHS
- 3. = 0, then the reaction is at equilibrium

For further discussion, again we start from the example. Then the affinity in this case is defined as:

$$-[(\mu_{H_2} + \mu_{I_2}) - 2\mu_{HI}] \tag{41}$$

We can also show this in the graph:



Figure 2: Affinity

If at first affinity is greater than 0, which means:

$$2\mu_{HI} > \mu_{H_2} + \mu_{I_2} \tag{42}$$

So the reaction will proceed from high chemical potential to low chemical potential, so 2HI to H_2 and I_2 . That's why μ is called chemical potential. When the affinity reaches zero, the reaction reaches equilibrium, will not proceed anymore.

Similarly, if at first affinity is less than 0, the reaction will proceed to HI, affinity increases until zero.