The Gibbs free energy revisited

In the last article, we defined

$$-\frac{\mu_i}{T} \equiv \frac{\partial S}{\partial N_i} \tag{1}$$

where we now introduce the index i to denote the different kinds of particles.

Recall, when the number of particles didn't change, we had

$$dS = \frac{dU}{T} + \frac{P}{T}dV \tag{2}$$

Now, considering (1), this relation is modified to

$$dS = \frac{dU}{T} + \frac{P}{T}dV - \sum_i \frac{\mu_i}{T}dN_i \tag{3}$$

when the number of particles can change. If we re-express the above relation, we have

$$dU = TdS - PdV + \sum_i \mu_i dN_i \tag{4}$$

Thus, we obtain

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V} \tag{5}$$

Let's now consider $U(S, V, N_i)$. We have

$$dU = \frac{\partial U}{\partial S}dS + \frac{\partial U}{\partial V}dV + \sum_i \frac{\partial U}{\partial N}dN_i \tag{6}$$

Given this, notice that U, S, V, N are variables that are proportional to the quantity in contrast to variables like P, T. Therefore, if the quantities of S, V, and N becomes γS, γV, and γN, then U must become γU. If we let $\gamma = 1 + \alpha$ for an infinitesimal α, (6) becomes

$$\alpha U = \frac{\partial U}{\partial S}\alpha S + \frac{\partial U}{\partial V}\alpha V + \sum_i \frac{\partial U}{\partial N}\alpha N_i \tag{7}$$

which implies

$$U = \frac{\partial U}{\partial S}S + \frac{\partial U}{\partial V}V + \sum_i \frac{\partial U}{\partial N}N_i \tag{8}$$

By plugging in the following relation

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T, \qquad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P, \qquad \mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V} \tag{9}$$

which we can see from (4), (8) becomes

$$U = TS - PV + \sum_i \mu_i N_i \tag{10}$$

which implies

$$U - TS + PV = \sum_i \mu_i N_i \tag{11}$$

Thus, we conclude

$$G = \sum_i \mu_i N_i \tag{12}$$

In other words, the chemical potential is the Gibbs free energy per a particle.

In our earlier article on the definition of temperature, we considered two systems that are free to exchange energy each other. There, we saw that the maximization of entropy led to the equality of temperature of the two systems, namely $T_1 = T_2$. We derived this condition from the fact that the total energy was conserved, i.e., the energy lost by the first system was equal to the energy gained by the second system. In another article of ours, we have seen that the condition that the total number of certain particle is conserved led to the concept of chemical potential of that particle. Thus, if we have two systems that can exchange particles, it is very easy to see that the chemical potential of the first system will be equal to the one of the second system, namely $\mu_1 = \mu_2$, when the equilibrium is reached. The calculation is very similar to the case of $T_1 = T_2$.

Then, what happens when the number of each kind of particles is not conserved? This is the case when chemical reactions are taking place. For example, for the following reaction

$$A + B \leftrightarrow C + D \tag{13}$$

the number of each particle A, B, C, D is not conserved separately. Nevertheless, there are certain relations between these numbers. These relations will give a certain condition on the chemial potential at the equilibrium, i.e., when the reaction rate for $A + B \to C + D$ is the same as the one for $A + B \leftarrow C + D$. (Recall that, in our earlier article on temperature, the situation is such that the energy transferred from the first system to the second system is equal to the energy transferred from the second system to the first system, when the equilibrium is reached, i.e., the net energy transfer is zero. We have an analogus situation now.)

So, let's find this relation. Recall that at constant temperature and pressure, we have $dG = 0$. This implies

$$\mu_A \Delta N_A + \mu_B \Delta N_B + \mu_C \Delta N_C + \mu_D \Delta N_D = 0 \tag{14}$$

where ΔN_A denotes the change of the number of particle A, and so on. Given this, observe that (13) implies

$$\Delta N_A = \Delta N_B = -\Delta N_C = -\Delta N_D \tag{15}$$

Plugging this relation to (14), we see that

$$\mu_A + \mu_B = \mu_C + \mu_D \tag{16}$$

Thus, we see that the sum of chemical energy is conserved when the chemical reaction is in equilibrium.

Summary

- The chemical potential is the Gibbs free energy per particle, i.e.,

$$G = \sum_i \mu_i N_i$$

- In chemical equilibrium, the chemical potential is conserved. For example, if we have the following chemical reaction

$$A + B \leftrightarrow C + D$$

  we have

$$\mu_A + \mu_B = \mu_C + \mu_D$$