The Helmholtz free energy, the enthalpy, and the Gibbs free energy

In this article, we will introduce the Helmholtz free energy, the enthalpy, and the Gibbs free energy.

First, recall the following basic thermodynamic relation.

$$dU = TdS - PdV \tag{1}$$

This shows

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S \tag{2}$$

Here, the subscript V and S mean that they are held constant respectively i.e., $dV = 0$ and $dS = 0$. If V is constant, we can write

$$dU = TdS = dQ \tag{3}$$

where Q is the heat transferred under a constant volume. Thus, if we let the molar specific heat at constant volume by C_v, then we can write

$$dU = TdS = dQ = nC_v dT \tag{4}$$

which implies

$$C_v = \frac{1}{n}\frac{dU}{dT} \tag{5}$$

The energy U is a function of S and V in (1). It satisfies $dU = 0$ when $dS = 0$ and $dV = 0$, i.e., when S and V are held constant. However, we do not always maintain S constant. Sometimes, it is easier to hold T constant. Could we define a quantity that is more convenient when T and V are maintained constant?

In this context, let's define the Helmholtz free energy F by

$$F = U - TS \tag{6}$$

Let's consider its differential dF. Using (1), we have

$$dF = dU - TdS - SdT = -PdV - SdT \tag{7}$$

which implies

$$P = -\left(\frac{\partial F}{\partial V}\right)_T, \qquad S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{8}$$

Now, F is a function of V and T and $dF = 0$ when V and T are constant.

Similarly, let us introduce a quantity that is more convenient when P and S are constant. We define the enthalpy H by

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

which implies

$$dH = dU + PdV + VdP = TdS + VdP \tag{10}$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P, \qquad V = \left(\frac{\partial H}{\partial P}\right)_S \tag{11}$$

If the system is in a constant pressure, we have $dP = 0$. Then, we can write

$$dH = TdS = dQ \tag{12}$$

where Q is the heat transferred under a constant pressure. Thus, if we let the molar specific heat at constant pressure by C_p, then we can write

$$dH = TdS = dQ = nC_p dT \tag{13}$$

which implies

$$C_p = \frac{1}{n}\frac{dH}{dT} \tag{14}$$

Thus, we see that H is a natural quantity for energy when the system is in a constant pressure. Most chemical reactions in a laboratory are performed in such a situation. Thus, enthalpy is often used in chemistry. When I first encountered enthalpy, I thought that it was some kind of variation of entropy as it sounds similar. No, it isn't. It is some kind of energy.

Finally, a quantity that is convenient when we deal with a constant pressure and a constant temperature: The Gibbs free energy is defined by

$$G = U - TS + PV \tag{15}$$

which implies (**Problem 1.** Check this!)

$$dG = VdP - SdT \tag{16}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T, \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \tag{17}$$

We see that we have $dG = 0$ when $dP = 0$ and $dT = 0$ are satisfied.

Now, let's come to our earlier conclusion slightly differently. Recall that S is maximized (i.e., $dS = 0$) for a closed system. Similarly, what is maximized or minimized when the system has a constant volume (i.e., $dV = 0$), but is in an outside thermal contact with infinite thermal reservoir of temperature T? This is when the system is in a constant T. In other words, even though the system emits or absorbs energy from the thermal reservoir, the thermal reservoir has such a big heat capacity that its temperature doesn't change. Given this, we will now show that $dF = 0$ when they reach a thermal equilibrium. As we have $dT = 0$ in such a case, we have

$$dF = dU - TdS - SdT = dU - TdS \tag{18}$$

However, if we plug in (2) to the above equation, we get $dF = 0$.

Actually, we can show that F is minimum. Let's call the energy of the system by U_{sys} and the energy of the reservoir by U_{res}, and their entropy by S_{sys} and S_{res} respectively. Then, the total energy is

$$U = U_{\text{res}} + U_{\text{sys}} \tag{19}$$

Given this, the total entropy is given by

$$S = S_{\text{res}} + S_{\text{sys}} = S_{\text{res}}(U - U_{\text{sys}}) + S_{\text{sys}}(U_{\text{sys}}) \tag{20}$$

$$= S_{\text{res}}(U) - U_{\text{sys}} \left(\frac{\partial S_{\text{res}}}{\partial U_{\text{res}}} \right)_V + S_{\text{sys}}(U_{\text{sys}}) \tag{21}$$

$$= S_{\text{res}}(U) - U_{\text{sys}} \frac{1}{T} + S_{\text{sys}}(U_{\text{sys}}) \tag{22}$$

$$= S_{\text{res}}(U) - \frac{F_{\text{sys}}}{T} \tag{23}$$

Notice that $S_{\text{res}}(U)$ is just a constant, because U is a constant as the total energy of the reservoir and the system is conserved. As the entropy S is always maximized, we see that F has to be minimized.

Problem 2. Show that $C_p = C_v + R$ is satisfied for an ideal gas by using (5), (9) and (14).

Problem 3. From the fact that partial derivative commute, i.e.,

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial S \partial V} \tag{24}$$

by using (2), derive the following relation

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \tag{25}$$

Notice also that we can obtain three more similar relations from (2), (8) and (11).

There was a tacit assumption in this article. That the system doesn't exchange the actual particles with the outside world, even though they may exchange energy (in case of the Hemlholtz free energy, and the Gibbs free energy) or the volume changes (in case of the enthalpy and the Gibbs free energy). In a later article, we will see what happens if we relax this condition.

Summary

- The Helmholtz free energy is defined by

$$F = U - TS$$

- The enthalpy is defined by

$$H = U + PV$$

- The Gibbs free energy is defined by

$$G = U - TS + PV$$

- We can express their differentials dF, dH, dG in terms of the thermodynamic quantities by using the relation $dU = TdS - PdV$.

- Just as $dS = 0$ is satisfied when a closed system reaches the equilibrium, $dF = 0$ is satisfied when an otherwise closed system with a thermal contact in thermal reservoir reaches the equilibrium. Similarly, $dH = 0$ is satisfied when an otherwise closed system provided with a constant pressure reaches the equilibrium, and $dG = 0$ is satisfied when an otherwise closed system with a thermal contact in thermal equilibrium with constant outside pressure reaches the equilibrium