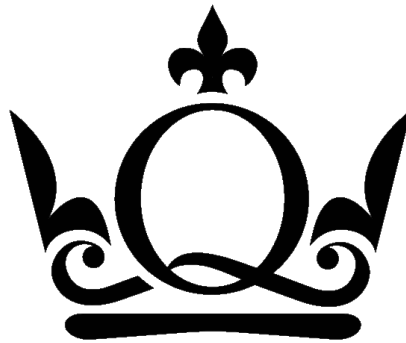


# Thermodynamics of Open System

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May 14, 2015



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The 1st law of thermodynamics gives the following identity:

$$dU = TdS - PdV \quad (1)$$

where it is assumed that the work done to the system is only through the changing of volume. Keeping (1) in mind, also considering the definition of several thermodynamics functions given as following:

$$H = U + PV \quad \rightarrow \text{enthalpy} \quad (2)$$

$$F = U - TS \quad \rightarrow \text{Helmholtz free energy} \quad (3)$$

$$G = U - TS + PV \rightarrow \text{Gibbs free energy} \quad (4)$$

the full derivative of the three basic functions can be given:

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= TdS - PdV + PdV + VdP \\ &= TdS + VdP \end{aligned} \quad (5)$$

$$\begin{aligned} dF &= dU - TdS - SdT \\ &= TdS - PdV - TdS - SdT \\ &= -PdV - SdT \end{aligned} \quad (6)$$

$$\begin{aligned} dG &= dU - TdS - SdT + PdV + VdP \\ &= TdS - PdV - TdS - SdT + PdV + VdP \\ &= VdP - SdT \end{aligned} \quad (7)$$

The full derivative given above is for close system only, which means there is no particle interaction between the system in interest with surroundings. In practice, however, it is always necessary to take into account the influence of particle number. For example, in any chemical reaction process, the particle number of each component taking part in the reaction will definitely change. Therefore, the above four basic functions should be adjusted accordingly to describe the open system. First of all for Gibbs free energy, the full derivative for the open system becomes:

$$dG = -SdT + VdP + \mu dn \quad (8)$$

where we have  $\mu$  is defined as:

$$\mu = \left( \frac{\partial G}{\partial n} \right)_{P,T} \quad (9)$$

and is given the name of *chemical potential*, which actually defines the energy changing corresponding to the changing of particle number. Here it worths pointing out that Gibbs free energy can be thgought of as the 'full' energy of the close system, if taking the volume-changing work interaction with surroundings as part of the energy of the close system. Then taking into account of the particle number related energy term is equivalent as defining Gibbs free energy as the 'full' energy of the open system. And this is why the new term is added to Gibbs free energy but not the three basic functions.

Starting from (8), and considering (4), we have:

$$\begin{aligned} dU &= dG + d(TS) - d(PV) \\ &= -SdT + VdP + \mu dn + TdS + SdT - PdV - VdP \\ &= TdS - PdV + \mu dn \end{aligned} \quad (10)$$

Then we have:

$$\begin{aligned} dH &= dU + d(PV) \\ &= TdS - PdV + \mu dn + PdV + VdP \\ &= TdS + VdP + \mu dn \end{aligned} \quad (11)$$

Similarly for Helmholtz free energy:

$$\begin{aligned} dF &= dU - d(TS) \\ &= TdS - PdV + \mu dn - TdS - SdT \\ &= -SdT - PdV + \mu dn \end{aligned} \quad (12)$$

Then accordingly, we can write down the following identities:

$$U = U(S, V, n) \quad (13)$$

$$H = H(S, P, n) \quad (14)$$

$$F = F(T, V, n) \quad (15)$$

$$G = G(T, P, n) \quad (16)$$

Taking the Gibbs free energy  $G$  as an example, the above identity says  $G$  is explicitly the function of  $T$ ,  $P$  and  $n$ . Furthermore, considering (9), we could have:

$$G = \mu n \quad (17)$$

At first sight, it seems that the number of independent variables of function  $G$  is reduced from 3 ( $T$ ,  $P$  and  $n$ ) to 2 ( $\mu$ ,  $n$ ). However this is not case, since later we will see that  $\mu$  is actually again the function of  $T$  and  $P$ , therefore the actual number of independent variables is still 3 – nothing changes except the explicit expression for  $G$  is given in a more compact form – (17). Furthermore, we have:

$$dG = \mu dn + nd\mu \quad (18)$$

Then by subtracting (18) from (8), we could obtain:

$$nd\mu = -SdT + VdP \quad (19)$$

This is called the *Gibbs-Duhem* equation, from which we can see that  $\mu$  is indeed the function of  $T$  and  $P$ , explicitly.

Finally, another basic function in thermodynamics is defined – the grand potential  $J$ , which is given by:

$$J = F - G = F - \mu n \quad (20)$$

Considering (3) and (4), we could have:

$$J = F - G = -PV \quad (21)$$

Furthermore,

$$\begin{aligned} dJ &= d(-PV) \\ &= dF - dG \\ &= -SdT - PdV + \mu dn - \mu dn - nd\mu \\ &= -SdT - PdV - nd\mu \end{aligned} \quad (22)$$

Therefore we have:

$$J = J(T, V, \mu) \quad (23)$$

which means the grand potential  $J$  is the function of  $T$ ,  $V$  and  $\mu$ , explicitly. And again the number of independent variables is 3. However, from (19), we know that  $\mu$  is actually the function of  $T$  and  $P$ , again explicitly. Does that mean we are now increasing the number of independent variables for  $J$ , since we already have the independent variables  $T$  and  $V$ . The answer is no, since we have an overlapping variable  $T$  here, thus the 'net' number of independent variables is still 3 –  $T$ ,  $P$  and  $V$ . As a matter of fact, we can use the *Gibbs-Duhem* equation given in (19) to express  $J$  as a function of  $T$ ,  $P$  and  $V$ . However, since we are now dealing with the open system, and the variable  $\mu$  – the *chemical potential* – is specifically defined for open system, therefore we choose to use  $T$ ,  $V$  and  $\mu$ , but not  $T$ ,  $V$  and  $P$  as the independent variables.