5.1: Thermodynamic Potentials

The second law leads to the result $dQ = TdS$, so that, for a gaseous system, the first law may be written as

$$dU = TdS - pdV \tag{5.1.1}$$

More generally, we have

$$dU = TdS - pdV - \sigma dA - MdB \tag{5.1.2}$$

where σ is the surface tension, A is the area, M is the magnetization, B is the magnetic field, etc.

Returning to the case of a gaseous system, we now define a number of quantities related to U. These are called thermodynamic potentials and are useful when considering different processes. We have already seen that the enthalpy H is useful for considering processes at constant pressure. This follows from

$$dH = d(U + pV) = dQ + Vdp \tag{5.1.3}$$

so that for processes at constant pressure, the inflow or outflow of heat may be seen as changing the enthalpy

The Helmholtz free energy is defined by

$$F = U - TS \tag{5.1.4}$$

Taking differentials and comparing with the formula for dU, we get

$$dF = -SdT - pdV \tag{5.1.5}$$

The Gibbs free energy G is defined by

$$G = F + pV = H - TS = U - TS + pV \tag{5.1.6}$$

Evidently,

$$dG = -SdT + Vdp \tag{5.1.7}$$

Notice that by construction, H, F and G are functions of the state of the system. They may be expressed as functions of p and V, for example. They are obviously extensive quantities.

So far, we have considered the system characterized by pressure and volume. If there are a number of particles, say, N which make up the system, we can also consider the N-dependence of various quantities. Thus we can think of the internal energy U as a function of S, V and N, so that

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN \equiv TdS - pdV + \mu dN \tag{5.1.8}$$

The quantity μ which is defined by

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{5.1.9}$$

is called the chemical potential. It is obviously an intensive variable. The corresponding equations for H, F and G are

$$\begin{aligned} dH &= TdS + Vdp + \mu dN \\ dF &= -SdT - pdV + \mu dN \\ dG &= -SdT + Vdp + \mu dN \end{aligned} \tag{5.1.10}$$

Thus the chemical potential μ may also be defined as

$$\mu = \left(\frac{\partial H}{\partial N}\right)_{S,p} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,p} \tag{5.1.11}$$

Since U is an extensive quantity and so are S and V, the internal energy has the general functional form

$$U = Nu\left(\frac{S}{N}, \frac{V}{N}\right) \tag{5.1.12}$$

where u depends only on $\frac{S}{N}$ and $\frac{V}{N}$ which are intensive variables. In a similar way, we can write

$$\begin{gathered} H = N\, h\left(\frac{S}{N}, p\right) \\ F = N\, f\left(T, \frac{V}{N}\right) \\ G = N\, g(T, p) \end{gathered} \tag{5.1.13}$$

The last equation is of particular interest. Taking its variation, we find

$$dG = N\left(\frac{\partial g}{\partial T}\right)_p dT + N\left(\frac{\partial g}{\partial p}\right)_T dT + g\, dN \tag{5.1.14}$$

Comparing with Equation 5.1.10, we get

$$S = -N\left(\frac{\partial g}{\partial T}\right)_p, \quad V = N\left(\frac{\partial g}{\partial p}\right)_T, \quad \mu = g \tag{5.1.15}$$

The quantity g is identical to the chemical potential, so that we may write

$$G = \mu N \tag{5.1.16}$$

We may rewrite the other two relations as

$$S = -N\left(\frac{\partial \mu}{\partial T}\right)_p dT, \quad V = N\left(\frac{\partial \mu}{\partial p}\right)_T \tag{5.1.17}$$

Further, using $G = \mu N$, we can rewrite the equation for dG as

$$N d\mu + SdT - V dp = 0 \tag{5.1.18}$$

This essentially combines the previous two relations and is known as the Gibbs-Duhem relation. It is important in that it provides a relation among the intensive variables of a thermodynamic system.
