

Chemical potential and thermodynamic potentials

We will now onwards use classical thermodynamics concepts. Our formulation will be based upon the following two postulates.

Postulate 1: In processes for which there is no net effect on the environment, all systems with given internal restraints will change in such a way so as to approach one and only one state, referred to as the equilibrium state.

Postulate 2: For each system within given internal restraints, there exist equilibrium states which can be completely characterized by two independently variable properties and the number of moles of each chemical species.

According to postulate 2, any property of a system can be written as a function of any two independently variable properties of the system and the number of moles of all the components present in the system. Consider a system with ' N ' components. We denote the number of moles of i th component as n_i . For any thermodynamic property Z ,

$$Z = f(x, y, n_1, n_2, \dots, n_N) - 1$$

where x and y are independently variable properties.

$$\Rightarrow dz = \left(\frac{\partial f}{\partial x} \right)_{y, n_1, \dots, n_N} dx + \left(\frac{\partial f}{\partial y} \right)_{x, n_1, \dots, n_N} dy + \sum_{i=1}^N \left(\frac{\partial f}{\partial n_i} \right)_{x, y, n_i^*} dn_i$$

where $n_i^* = n_1, n_2, \dots, n_{i-1}, n_{i+1}, \dots, n_N$. Let us choose $x = S$ and $y = V$

$$\Rightarrow dz = \left(\frac{\partial f}{\partial S} \right)_{V, n_1, \dots, n_N} dS + \left(\frac{\partial f}{\partial V} \right)_{S, n_1, \dots, n_N} dV + \left(\frac{\partial f}{\partial n_i} \right)_{S, V, n_i^*} dn_i \quad (1)$$

For a closed system, we write the combined first and second law of thermodynamics as

$$dU = TdS - PdV$$

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, n} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n} dV \quad (2)$$

Comparison of Eqⁿ (1) and (2) and extension gives

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, n_1, \dots, n_N} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n_1, \dots, n_N} dV$$

$$+ \sum_{i=1}^N \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_i^*} dn_i \quad (3)$$

$$\left(\frac{\partial U}{\partial S}\right)_{V, n_1, \dots, n_N} = T$$

$$\left(\frac{\partial U}{\partial V}\right)_{S, n_1, \dots, n_N} = -P$$

$$\left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_j^*} = \mu_i \leftarrow \text{chemical potential of } i\text{th component}$$

$$\Rightarrow dU = TdS - PdV + \sum_{i=1}^N \mu_i dn_i \quad - (4)$$

Therefore, we have a "fundamental equation" for internal energy of the system.

$$U = U(S, V, n_1, n_2, \dots, n_N)$$

Specification of the system in the internal energy framework requires specification of S and V . Both of them are extensive quantities. These "natural coordinates" for internal energy are, however, not very convenient. Hence we would like to systematically change these coordinates. A convenient set would be (T, P) . But

$$T = (\partial U / \partial S)_{V, n_1, \dots, n_N}$$

$$P = -(\partial U / \partial V)_{S, n_1, \dots, n_N}$$

In essence, we need to change the variables from an independent set of variables to the derivative of the function with respect to the original set of variables as the new set of independent variables. This can be done using Legendre transformation.

Let us first consider a two-dimensional case.

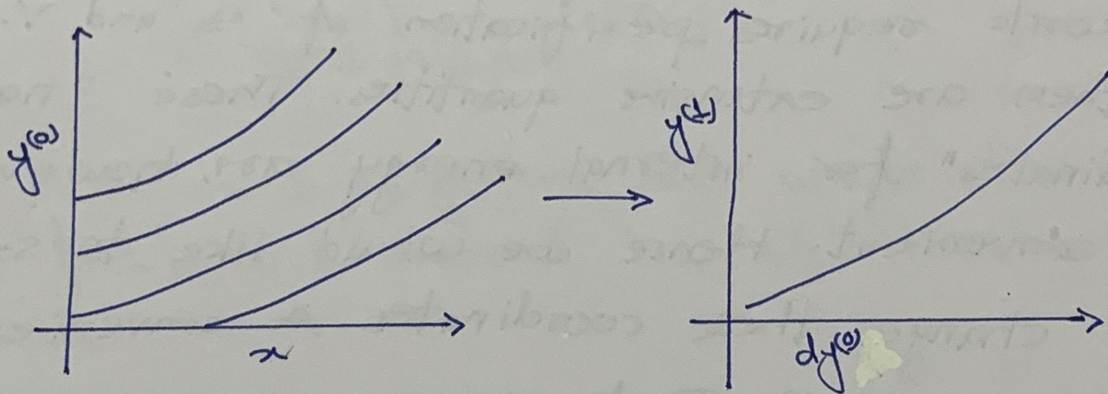
$$y^{(0)} = y^{(0)}(x)$$

The superscript (0) signifies the untransformed system. If the derivative is defined as

$$\xi_1 = \frac{dy^{(0)}}{dx}$$

then we require a transformation $y^{(1)} = y^{(1)}(\xi_1)$.

A direct transformation using the derivative is not useful as it will not give a unique transformation. Transformation for a family of curves will be the same.

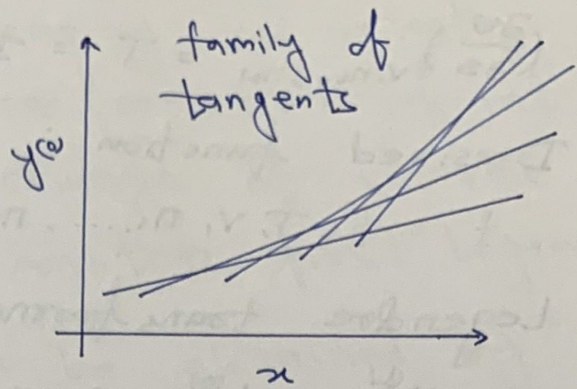
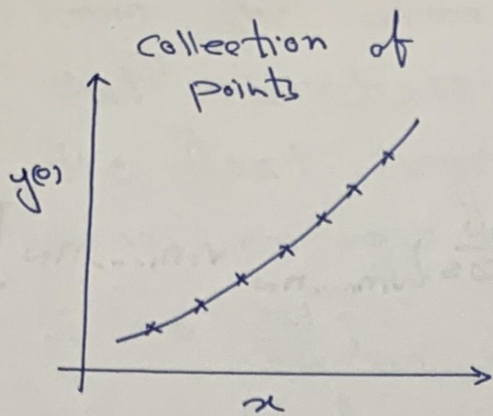


There are two ways of describing a curve:

(1) as $y = y(x)$

(2) as y as an envelop of a family of tangents.

In the second representation, the transformation can be uniquely obtained by specifying both slopes as well as corresponding intercept of the tangents.



If the slope is ξ_1 and the intercept of the tangent on y -axis is given by $y^{(1)}$ then

$$y^{(1)} = y^{(1)}(\xi_1)$$

For a point $(x, y^{(0)})$, the slope and intercept are related as

$$y^{(0)} = \xi_1 x + y^{(1)}$$

$$\Rightarrow y^{(1)} = y^{(0)} - \xi_1 x \quad - (4)$$

Eqⁿ (4) gives the Legendre transformation. In higher dimensions,

$$y^{(n)} = y^{(0)} - \sum_{i=1}^n \xi_i x_i \quad - (5)$$

Using the above transformation, a unique function can be obtained which is free from the original variable x and gives a new function which contain the transformed variable ξ . We will now use this technique and apply the transformation to thermodynamic potentials

$$U = U(S, V, n_1, n_2, \dots, n_N) = y^{(0)}$$

$$\left(\frac{\partial U}{\partial S}\right)_{V, n_1, \dots, n_N} = T = T_1$$

Desired function :

$$f = f(T, V, n_1, \dots, n_N) = f\left\{\left(\frac{\partial U}{\partial S}\right)_{V, n_1, \dots, n_N}, V, n_1, \dots, n_N\right\}$$

Legendre transformation :

$$y^{(1)} = y^{(0)} - T_1 x$$

$$\Rightarrow y^{(1)} = U - TS = A \rightarrow \text{Helmholtz free energy}$$

$$\Rightarrow A = A(T, V, n_1, n_2, \dots, n_N)$$

$$\begin{aligned} \Rightarrow dA &= \left(\frac{\partial A}{\partial T}\right)_{V, n_1, \dots, n_N} dT + \left(\frac{\partial A}{\partial V}\right)_{T, n_1, \dots, n_N} dV \\ &+ \sum_{i=1}^N \left(\frac{\partial A}{\partial n_i}\right)_{T, V, n_i^*} dn_i \quad - (6) \end{aligned}$$

The coefficients of the differentials can be identified as the following quantities

$$\left(\frac{\partial A}{\partial T}\right)_{V, n_1, \dots, n_N} = -S$$

$$\left(\frac{\partial A}{\partial V}\right)_{T, n_1, \dots, n_N} = -P$$

$$\left(\frac{\partial A}{\partial n_i}\right)_{T, V, n_i^*} = \mu_i$$

The above equation gives another definition of chemical potential. It is important to take care of the quantities which are kept constant.

From the above analysis, it can be seen that Helmholtz free energy is actually the first Legendre transformation of internal energy with a change of variable $S \rightarrow (\frac{\partial U}{\partial S})_{V, n_1, \dots, n_N} = T$. Another first Legendre transformation can be obtained by retaining S and changing V .

$$U = U(S, V, n_1, n_2, \dots, n_N)$$

$$\left(\frac{\partial U}{\partial V}\right)_{S, n_1, \dots, n_N} = -P$$

Desired function :

$$f = f(S, P, n_1, n_2, \dots, n_N) = f\left\{S, \left(\frac{\partial U}{\partial V}\right)_{S, n_1, \dots, n_N}, n_1, \dots, n_N\right\}$$

$$y^{(1)} = y^{(0)} - \sum x$$

$$\Rightarrow y^{(1)} = U + PV = H \rightarrow \text{enthalpy}$$

$$\Rightarrow H = H(S, P, n_1, \dots, n_N)$$

$$\begin{aligned} \Rightarrow dH &= \left(\frac{\partial H}{\partial S}\right)_{P, n_1, \dots, n_N} dS + \left(\frac{\partial H}{\partial P}\right)_{S, n_1, \dots, n_N} dP \\ &+ \sum_{i=1}^N \left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_i^*} dn_i \quad - (7) \end{aligned}$$

The coefficients of the differentials can be identified as follows.

$$\left(\frac{\partial H}{\partial S}\right)_{P, n_1, \dots, n_N} = T$$

$$\left(\frac{\partial H}{\partial P}\right)_{S, n_1, n_2, \dots, n_N} = V$$

$$\left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_i^*} = \mu_i$$

The above equation gives yet another definition of chemical potential. Further, enthalpy can be identified to be obtained as the first Legendre transformation of internal energy with the transformation $V \rightarrow \left(\frac{\partial U}{\partial V}\right)_{S, n_1, \dots, n_N} = P$.

Now we transform by simultaneously changing S and V .

$$U = U(S, V, n_1, n_2, \dots, n_N)$$

$$\left(\frac{\partial U}{\partial S}\right)_{V, n_1, \dots, n_N} = T$$

$$\left(\frac{\partial U}{\partial V}\right)_{S, n_1, \dots, n_N} = -P$$

Desired function :

$$f = f(T, P, n_1, \dots, n_N) = f\left\{\left(\frac{\partial U}{\partial S}\right)_{V, n_1, \dots, n_N}, \left(\frac{\partial U}{\partial V}\right)_{S, n_1, \dots, n_N}, n_1, \dots, n_N\right\}$$

$$y^{(2)} = y^{(0)} - \xi_1 x_1 - \xi_2 x_2$$

$$\Rightarrow y^{(2)} = U - TS + PV = G \rightarrow \text{Gibbs free energy}$$

$$\Rightarrow G = G(P, T, n_1, n_2, \dots, n_N)$$

$$\Rightarrow dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, \dots, n_N} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, \dots, n_N} dP$$

$$+ \sum_{i=1}^N \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_i^*} dn_i \quad - \text{ (2)}$$

The coefficients of the differentials can be identified as follows:

$$\left(\frac{\partial G}{\partial T}\right)_{P, n_1, \dots, n_N} = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_{T, n_1, \dots, n_N} = V$$

$$\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j^*} = \mu_i$$

Again, we get another definition of chemical potential. Further, the Gibbs free energy is obtained as the second Legendre transformation of the internal energy with change of coordinates as $S \rightarrow T$ and $V \rightarrow P$.

To summarize, we get the following definitions of chemical potential

$$\begin{aligned} \mu_i &= \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_j^*} = \left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_j^*} = \left(\frac{\partial A}{\partial n_i}\right)_{T, V, n_j^*} \\ &= \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j^*} \end{aligned} \quad - (9)$$

Further,

$$dU = Tds - PdV + \sum_{i=1}^N \mu_i dn_i \quad - (10)$$

$$dH = Tds + VdP + \sum_{i=1}^N \mu_i dn_i \quad - (11)$$

$$dA = -SdT - PdV + \sum_{i=1}^N \mu_i dn_i \quad - (12)$$

$$dG = -SdT + VdP + \sum_{i=1}^N \mu_i dn_i \quad - (13)$$

Integration of fundamental equations:

Eq's (10)-(13) need to be integrated to obtain explicit expressions for the thermodynamic potentials. For this, we need Euler integration.

Consider a function $f(a, b, x, y)$ which is "homogeneous" in degree 'h' in x and y and degree zero in a and b . This means that if x and y are each multiplied by a factor k then

$$f(a, b, kx, ky) = k^h f(a, b, x, y) \quad - (14)$$

For functions satisfying this condition,

$$x \left\{ \frac{\partial f(a, b, x, y)}{\partial x} \right\}_{a, b, y} + y \left\{ \frac{\partial f(a, b, x, y)}{\partial y} \right\}_{a, b, x} = hf(a, b, x, y) \quad - (15)$$

Now we apply the above technique to the thermodynamic potentials.

Internal energy:

$$U = U(S, V, n_1, n_2, \dots, n_N)$$

All the independent variables in the above equation have first order dependence i.e.

$$U(kS, kV, kn_1, \dots, kn_N) = k U(S, V, n_1, \dots, n_N)$$

Application of Euler theorem to the above equation gives

$$S \left(\frac{\partial U}{\partial S} \right)_{V, n_1, \dots, n_N} + V \left(\frac{\partial U}{\partial V} \right)_{S, n_1, \dots, n_N} + \sum_{i=1}^N n_i \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}} = U(S, V, n_1, n_2, \dots, n_N)$$

$$\Rightarrow U = TS - PV + \sum_{i=1}^N \mu_i n_i \quad - (16)$$

Enthalpy :

$$H = H(S, P, n_1, \dots, n_N)$$

Pressure is an intensive property and has zero order dependence.

$$\Rightarrow S \left(\frac{\partial H}{\partial S} \right)_{P, n_1, \dots, n_N} + \sum_{i=1}^N n_i \left(\frac{\partial H}{\partial n_i} \right)_{S, P, n_{j \neq i}} = H(S, P, n_1, \dots, n_N)$$

$$\Rightarrow H = TS + \sum_{i=1}^N \mu_i n_i \quad - (17)$$

Note that the final expression does not contain pressure which is an intensive property.

Helmholtz free energy :

$$A = A(T, V, n_1, \dots, n_N)$$

$$\Rightarrow V \left(\frac{\partial A}{\partial V} \right)_{T, n_1, \dots, n_N} + \sum_{i=1}^N n_i \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_{j \neq i}} = A(T, V, n_1, \dots, n_N)$$

$$\Rightarrow A = -PV + \sum_{i=1}^N \mu_i n_i \quad - (18)$$

Finally, the Gibbs free energy, which has T and P as the coordinates, can be obtained as follows:

$$G = G(T, p, n_1, \dots, n_N)$$

$$\Rightarrow G = \sum_{i=1}^N n_i \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{i \neq i}}$$

$$\Rightarrow G = \sum_{i=1}^N \mu_i n_i \quad - (19)$$

Using Eq's (16) - (19), relationships among the thermodynamic potentials can be easily recovered.

Gibbs - Duhem equation and partial molar properties:

The two fundamental equations for internal energy in integrated and differential forms are:

$$dU = Tds - pdv + \sum_{i=1}^N \mu_i dn_i$$

$$U = TS - PV + \sum_{i=1}^N \mu_i n_i$$

$$\Rightarrow dU = Tds + sdT - pdv - vdp$$

$$+ \sum_{i=1}^N \mu_i dn_i + \sum_{i=1}^N n_i d\mu_i$$

$$\Rightarrow dU = (Tds - pdv + \sum_{i=1}^N \mu_i dn_i) + (sdT - vdp + \sum_{i=1}^N n_i d\mu_i)$$

$$\Rightarrow sdT - vdp + \sum_{i=1}^N n_i d\mu_i \quad - (20)$$

Eqⁿ (10) is referred to as the Gibbs-Duhem equation. When μ_i is defined at constant T and P then

$$\sum_{i=1}^N n_i d\mu_i = 0 \quad - (21)$$

Partial molar property of a system is defined as

$$\bar{B}_i = \left(\frac{\partial B}{\partial n_i} \right)_{T, P, n_i^*} \quad - (22)$$

The overbar is used to emphasize that the quantity is a partial molar property. If B is any property of the system the from postulate 2,

$$B = B(T, P, n_1, \dots, n_N)$$

$$\Rightarrow dB = \left(\frac{\partial B}{\partial T} \right)_{P, n_1, \dots, n_N} dT + \left(\frac{\partial B}{\partial P} \right)_{T, n_1, \dots, n_N} dP + \sum_{i=1}^N \left(\frac{\partial B}{\partial n_i} \right)_{T, P, n_i^*} dn_i$$

$$\Rightarrow dB = \left(\frac{\partial B}{\partial T} \right)_{P, n_1, \dots, n_N} dT + \left(\frac{\partial B}{\partial P} \right)_{T, n_1, \dots, n_N} dP + \sum_{i=1}^N \bar{B}_i dn_i \quad - (23)$$

From Euler's theorem for first order dependence,

$$B = \sum_{i=1}^N n_i \left(\frac{\partial B}{\partial n_i} \right)_{T, P, n_j^*}$$

$$\Rightarrow B = \sum_{i=1}^N n_i \bar{B}_i \quad - (24)$$

Now we can obtain a generalized Gibbs-Duhem equation. From Eqⁿ (24),

$$dB = \sum_{i=1}^N (n_i d\bar{B}_i + \bar{B}_i dn_i) \quad - (25)$$

A comparison of Eqⁿ (23) and (25) yields

$$\left(\frac{\partial B}{\partial T} \right)_{P, n_1, \dots, n_N} dT + \left(\frac{\partial B}{\partial P} \right)_{T, n_1, \dots, n_N} dP - \sum_{i=1}^N n_i d\bar{B}_i = 0 \quad - (25)$$

And at constant T and P ,

$$\sum_{i=1}^N n_i d\bar{B}_i = 0 \quad - (26)$$

It can be easily shown that various partial molar thermodynamic potentials are related following their native relationship i.e.

$$\bar{H}_i = \bar{U}_i + P\bar{V}_i$$

$$\bar{A}_i = \bar{U}_i - T\bar{S}_i$$

$$\bar{G}_i = \mu_i = \bar{U}_i - T\bar{S}_i + P\bar{V}_i$$

$$\bar{G}_i = \bar{\mu}_i = \bar{H}_i + P\bar{V}_i$$