

## Intermediate Thermodynamics

### Homogeneous Mixtures

#### Property relationship for system of variable composition

Let's start with the *fundamental relation* in energy representation, which expresses that in a simple system the state of a system is fixed by  $n+2$  variables, where  $n$  is the number of components:

$$U = U(S, V, N_1, N_2, \dots, N_n) \quad (1)$$

where  $N_i$  is the number of moles of the chemical species  $i$  in a system in equilibrium. Notice that all the variables are extensive. The total differential of  $U$  is given by:

$$dU = \left. \frac{\partial U}{\partial S} \right|_{V, N} dS + \left. \frac{\partial U}{\partial V} \right|_{S, N} dV + \sum_{i, j \neq i} \left. \frac{\partial U}{\partial N_i} \right|_{S, V, N_j} dN_i \quad (2)$$

The first  $Tds$  equation states that  $Tds - PdV = du$ , so at constant composition ( $dN_i=0$ ) we can write:

$$T = \left. \frac{\partial U}{\partial S} \right|_{V, N}, \quad P = - \left. \frac{\partial U}{\partial V} \right|_{S, N} \quad (3)$$

for the third term on the RHS of Eq. (2) we define the *chemical potential*  $\mu_i$ , first introduced by J. W. Gibbs as:

$$\mu_i = \left. \frac{\partial U}{\partial N_i} \right|_{S, V, N_j, j \neq i} \quad (4)$$

The chemical potential is interpreted as the internal energy change that occurs when we change the number of moles of component  $i$  in one unit. Using Eqs. (3) and (4), we can write Eq. (2) as:

$$dU = T dS - P dV + \sum_i \mu_i dN_i \quad (5)$$

Similarly with what was done for Eq. (1), we may propose a fundamental relation in terms of the Gibbs function in an entirely equivalent manner:

$$G = G(P, T, N_1, N_2, \dots, N_n) \quad (6)$$

that has the advantage of being a function only of measurable quantities. The differential results:

$$dG = \left. \frac{\partial G}{\partial P} \right|_{T,N} dP + \left. \frac{\partial G}{\partial T} \right|_{P,N} dT + \sum_{i, j \neq i} \left. \frac{\partial G}{\partial N_i} \right|_{P,T,N_j} dN_i \quad (7)$$

and using the fourth Gibbsian equation  $dg = v dP - s dT$  we can write:

$$dG = V dP - S dT + \sum_{i, j \neq i} \left. \frac{\partial G}{\partial N_i} \right|_{P,T,N_j} dN_i \quad (8)$$

If we note that  $G = H - TS = U + PV - TS$ , using Eqs. (5) and (8) we can conclude that:

$$dG = V dP - S dT + \sum_i \mu_i dN_i \quad (9)$$

which implies that the chemical potential is:

$$\mu_i = \left. \frac{\partial G}{\partial N_i} \right|_{P,T,N_j, j \neq i} \quad (10)$$

Expressions of the chemical potential can be derived also in terms of the enthalpy or the Helmholtz function:

$$\mu_i = \left. \frac{\partial H}{\partial N_i} \right|_{S,P,N_j, j \neq i} \quad (11)$$

$$\mu_i = \left. \frac{\partial A}{\partial N_i} \right|_{T,V,N_j, j \neq i} \quad (12)$$

and the corresponding differentials:

$$dH = T dS + V dP + \sum_i \mu_i dN_i \quad (13)$$

$$dA = -S dT - P dV + \sum_i \mu_i dN_i \quad (14)$$

### **Partial Molar Properties**

As in the case of the Gibbs function, Eq. (7), changes in any extensive property can be expressed in terms of changes in pressure, temperature and composition:

$$dY = \left. \frac{\partial Y}{\partial P} \right|_{T,N} dP + \left. \frac{\partial Y}{\partial T} \right|_{P,N} dT + \sum_{i, j \neq i} \left. \frac{\partial Y}{\partial N_i} \right|_{P,T,N_j} dN_i \quad (15)$$

where we define the partial molar property, sometimes called partial molal property, as:

$$\bar{y}_i = \left. \frac{\partial Y}{\partial N_i} \right|_{P,T,N_j} \quad (16)$$

therefore, a change in the extensive property  $Y$  can be written as:

$$dY = \left. \frac{\partial Y}{\partial P} \right|_{T,N} dP + \left. \frac{\partial Y}{\partial T} \right|_{P,N} dT + \sum_i \bar{y}_i dN_i \quad (17)$$

Let's apply the Euler theorem on homogeneous functions to the partial molar properties. An extensive property can be expressed as:

$$Y = Y(P, T, N_1, N_2, \dots, N_i) \quad (18)$$

Because of spatial composition homogeneity, we can write:

$$k Y(P, T, N_1, N_2, \dots, N_i) = Y(P, T, k N_1, k N_2, \dots, k N_i) \quad (19)$$

which means that we get  $k$  times the original property  $Y$  if we have  $k$  times more mass of each component. Mathematically,  $Y$  is a homogeneous function of first degree in  $N_i$ . Differentiating respect to  $k$  we obtain:

$$Y(P, T, N_1, N_2, \dots, N_i) = N_1 \frac{\partial Y}{\partial k N_1} + N_2 \frac{\partial Y}{\partial k N_2} + \dots + N_i \frac{\partial Y}{\partial k N_i} \quad (20)$$

In particular, for unit  $k$  we get:

$$Y(P, T, N_1, N_2, \dots, N_i) = N_1 \frac{\partial Y}{\partial N_1} + N_2 \frac{\partial Y}{\partial N_2} + \dots + N_i \frac{\partial Y}{\partial N_i} \quad (21)$$

if the function is the internal energy in terms of the composition, total entropy and volume we can write:

$$U = S \left. \frac{\partial U}{\partial S} \right|_{V, N_i} + V \left. \frac{\partial U}{\partial V} \right|_{S, N_i} + \sum_i N_i \left. \frac{\partial U}{\partial N_i} \right|_{S, V, N_j} \quad (22)$$

Using Eqs. (3) and (4) we obtain:

$$U = TS - PV + \sum_i N_i \mu_i \quad (23)$$

which is known as the *Euler equation*. Eq. (21) introduces a form to calculate mixture (extensive) properties in terms of the partial molar (or molal) properties, defined by Eq. (16). For example, if  $Y$  is the volume we write:

$$V = \sum_i N_i \left. \frac{\partial V}{\partial N_i} \right|_{P, T, N_j} = \sum_i N_i \bar{v}_i \quad (24)$$

Eq. (24) is in general applicable to any extensive property. In terms of intensive properties, we can write:

$$y_m = \sum_i x_i \bar{y}_i \quad (25)$$

where  $y_m$  is the *specific molar property* or *proper molal property* and  $x_i$  is the mole fraction of component  $i$ . Molar fractions are defined as:

$$x_i = \frac{N_i}{N}, \quad N = \sum_i N_i, \quad \sum_i x_i = 1 \quad (26)$$

It is then implied that for a single component substance:

$$y_i = \bar{y}_i \quad (27)$$

The change in an extensive property due to mixing can be evaluated from the difference between the total property before and after mixing:

$$\Delta Y = \sum_i N_i (\bar{y}_i - y_i) \quad (28)$$

frequently  $\bar{y}_i \neq y_i$ , thus there is a change of total property due to mixing. For example, the volume and the enthalpy change due to mixing, defined as:

$$\Delta V = \sum_i N_i (\bar{v}_i - v_i) \quad (29)$$

$$\Delta H = \sum_i N_i (\bar{h}_i - h_i) \quad (30)$$

are in general non-zero.  $\Delta H$  is the *enthalpy or heat of mixing*, either positive or negative. The entropy of mixing is defined as:

$$\Delta S = \sum_i N_i (\bar{s}_i - s_i) \quad (31)$$

must be always positive since mixing is an irreversible process.

**Example:** the partial molar volumes of ethyl alcohol and water in a 59 % ethyl alcohol mixture in weight are 57.3 and 17.15  $\text{cm}^3/\text{gmol}$  at 25 °C. Determine the volume of 100 g of mixture and the change due to mixing.

We have

$$\text{Ethyl alcohol: } \frac{59 \text{ g}}{46.07 \text{ g / gmol}} = 1.282 \text{ gmol}$$

$$\text{Water: } \frac{41 \text{ g}}{18.02 \text{ g / gmol}} = 2.275 \text{ gmol}$$

$$V = \sum_i N_i \bar{v}_i = 1.282 \cdot 57.3 + 2.275 \cdot 17.15 = 112.4 \text{ cm}^3$$

From tables, the specific volumes of ethyl alcohol and water are 1.27377 and 1.00293  $\text{cm}^3/\text{g}$ , respectively. Thus:

$$\Delta V = V - \sum_i V_i = 59 \cdot 1.27377 + 41 \cdot 1.00293 = 112.4 - 116.3 = -3.9 \text{ g}$$

The application of Eq. (21) to the Gibbs function yields:

$$G = \sum_i N_i \bar{g}_i \quad (32)$$

Differentiation at constant pressure and temperature of Eq. (32) results in:

$$dG|_{P,T} = \sum_i N_i d\bar{g}_i + \sum_i \bar{g}_i dN_i \quad (33)$$

where the partial molar gibbs function and the chemical potential are related using Eq. (21)

$$G = \sum_i N_i \left. \frac{\partial G}{\partial N_i} \right|_{P,T,N_j} = \sum_i N_i \bar{g}_i = \sum_i N_i \mu_i \quad (34)$$

Using Eq. (9) we then can write:

$$dG|_{P,T} = \sum_i \bar{g}_i dN_i = \sum_i \mu_i dN_i \quad (35)$$

thus, comparing Eqs. (33) and (35) we obtain the Gibbs-Duhem equation:

$$\sum_i N_i d\mu_i = 0 \quad (36)$$

Applying the test of exactness to Eq. (9) we obtain two important relations:

$$\left. \frac{\partial \mu_i}{\partial T} \right|_{P,N} = - \left. \frac{\partial S}{\partial N_i} \right|_{T,P,N_j} = -\bar{s}_i \quad (37)$$

$$\left. \frac{\partial \mu_i}{\partial P} \right|_{T,N} = \left. \frac{\partial V}{\partial N_i} \right|_{T,P,N_j} = \bar{v}_i \quad (38)$$

Note that the total differential of  $\mu_i$  is:

$$d\mu_i = \left. \frac{\partial \mu_i}{\partial T} \right|_{P,x_j} dT + \left. \frac{\partial \mu_i}{\partial P} \right|_{T,x_j} dP + \sum_{j \neq i} \left. \frac{\partial \mu_i}{\partial x_j} \right|_{T,P,x_k} dx_j \quad (39)$$

then, using Eqs. (37) and (38) we get:

$$d\mu_i = -\bar{s}_i dT + \bar{v}_i dP + \sum_{j \neq i} \left. \frac{\partial \mu_i}{\partial x_j} \right|_{T,P,x_k} dx_j \quad (40)$$

Consider a binary mixture with molar fractions  $x_1=x$  and  $x_2=1-x$ . Applying Eq. (17) at constant pressure and temperature we can write:

$$dX = \bar{x}_1 dN_1 + \bar{x}_2 dN_2 \quad (41)$$

and dividing by the total number of moles  $N$ :

$$dx_m = \bar{x}_1 dx_1 + \bar{x}_2 dx_2 = (\bar{x}_1 - \bar{x}_2) dx \quad (42)$$

or

$$\left. \frac{\partial x_m}{\partial x} \right|_{T,P} = \bar{x}_1 - \bar{x}_2 \quad (43)$$

In addition, using Eq. (25) and dividing by  $N$  we can write:

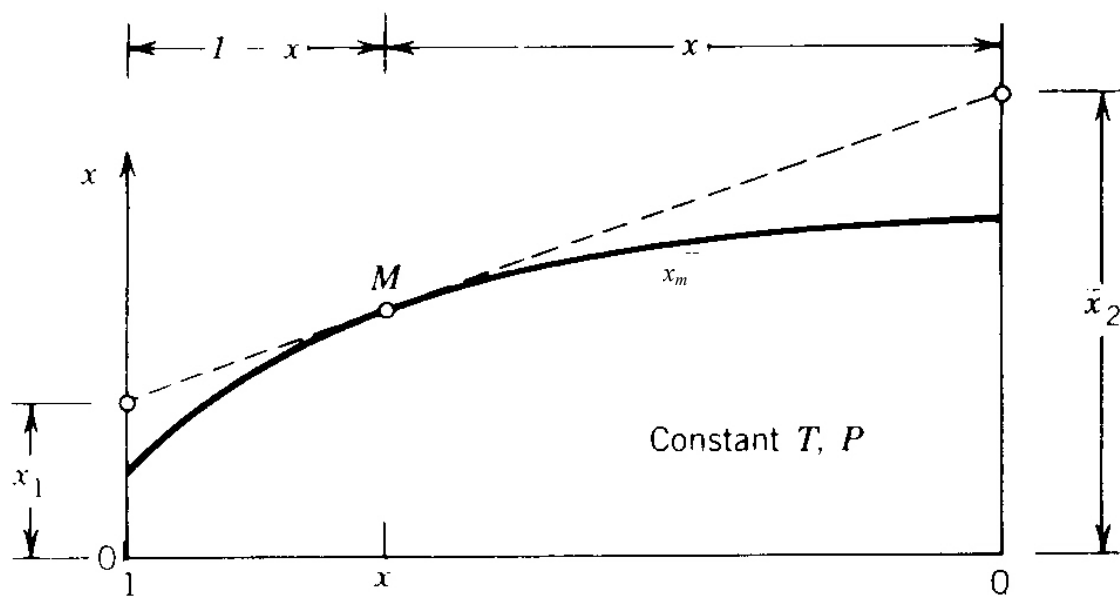
$$x_m = x \bar{x}_1 + (1-x) \bar{x}_2 \quad (44)$$

that we can solve for  $\bar{x}_1$  and  $\bar{x}_2$  to get:

$$\bar{x}_1 = x_m + (1-x) \left. \frac{\partial x_m}{\partial x} \right|_{T,P} \quad (45)$$

$$\bar{x}_2 = x_m - x \left. \frac{\partial x_m}{\partial x} \right|_{T,P} \quad (46)$$

Fig. 1 shows a plot of the proper molal property  $x_m$  at constant pressure and temperature as a function of the concentration. The curve shows Eq. (44) under different concentrations. At a given state  $M$  the tangent line with slope  $(\partial x_m / \partial x)_{T,P}$  is shown. It is easy to see from Eqs. (45) and (46) that the intersections of the tangent with the vertical axis at  $x=0$  and  $x=1$  give the values of the partial molar quantities  $\bar{x}_2$  and  $\bar{x}_1$ , respectively. This method can be used to determine the partial molar quantities with better precision than directly from the definition, Eq. (16), since the numerical differentiation of experimental data can be very noisy.



**Figure 1:** proper molal and partial molar properties for a binary mixture.