General Approach

Reminder on nomenclature: , n-component system

$\underline{B}$ extensive property - function of n+2 variables

B intensive property - function of n+1 intensive vars.

Common variable sets:

$\underline{B} = f(T, P, N_1, \dots N_n)$ or, $x_i = \frac{N_i}{N}$ (mole fractions)

$\underline{B} = f(T, P, x_1, \dots x_{n-1}, N)$

$B = f(T, P, x_1 \dots x_{n-1})$

T and P are easy to control experimentally, hence the importance of $\underline{G}$ or G which has T and P as the natural variables

A very important derivative for mixtures is the partial molar quantity (over bar!)

$$\overline{B_i} \equiv \left(\frac{\partial \underline{B}}{\partial N_i}\right)_{T, P, N_j[i]}$$ intensive property

$$d\underline{B} = \left.\frac{\partial \underline{B}}{\partial T}\right)_{P,N_i} dT + \left.\frac{\partial \underline{B}}{\partial P}\right)_{T,N_i} dP + \Sigma \left.\frac{\partial \underline{B}}{\partial N_i}\right)_{T,P,N_j(i)} dN_i \Rightarrow$$

Euler integrate

$$\boxed{\underline{B} = \sum_i \overline{B_i} N_i} \leftarrow$$

or

$$\boxed{B = \sum_i \overline{B_i} x_i} \leftarrow$$

partial molar quantities are the "contributions" of each component to the total properties

Of particular interest is the partial molar Gibbs energy,

$$\bar{G}_i = \left.\frac{\partial G}{\partial N_i}\right)_{T,P,N_j[i]} = \mu_i$$

Skip §92, which refers to $P\underline{V}TN$ EoS for mixtures → all that we need to know is that one can obtain mixture properties by expressing the parameters in EoS in terms of the composition.

Relationships among partial molar properties

Consider $\underline{A} = \underline{U} - T\underline{S}$ or $A = U - TS$

is $\bar{A}_i = \bar{U}_i - T\bar{S}_i$? $\boxed{\text{YES}}$

Proof: $\underline{A} = \underline{U} - T\underline{S} \Rightarrow \left.\frac{\partial \underline{A}}{\partial N_i}\right)_{T,P,N_j[i]} =$

$$= \left.\frac{\partial \underline{U}}{\partial N_i}\right)_{T,P,N_j[i]} - T \left.\frac{\partial \underline{S}}{\partial N_i}\right)_{T,P,N_j[i]} \Rightarrow \bar{A}_i = \bar{U}_i - T\bar{S}_i$$

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

Differential forms are a little harder:

$$d\underline{G} = -\underline{S}\,dT + \underline{V}\,dP + \sum_{m=1}^{n} \mu_m\, dN_m \Rightarrow$$

$$d\bar{G}_i = -\bar{S}_i\,dT + \bar{V}_i\,dP + \sum_{m=1}^{n} \left.\frac{\partial \mu_m}{\partial N_i}\right)_{T,P,N_j[i]} dN_m$$

Note that, as an intensive property, $\bar{B}_i$ is a function only of n+1 intensive properties, e.g. $T, P, x_1, \ldots x_{n-1}$

$$d\bar{B}_i = \left.\frac{\partial \bar{B}_i}{\partial T}\right)_{P,x} dT + \left.\frac{\partial \bar{B}_i}{\partial P}\right)_{T,x} dP + \sum_{j=1}^{n-1} \left(\frac{\partial \bar{B}_i}{\partial x_j}\right)_{T,P,x[j,n]} dx_j$$

How does one evaluate $\bar{B}_i$ given:

(a) $\underline{B} = f(T, P, N_1 \ldots N_n)$

(b) $B = f(T, P, N_1 \cdots N_n)$

(c) $B = f(T, P, x_1, \cdots x_{i-1}, x_{i+1}, \cdots x_n)$ ← note that x_i is "missing"

?

(a) is immediate $\bar{B}_i = \left.\frac{\partial \underline{B}}{\partial N_i}\right)_{T,P,N_j[i]}$

(b) $\left.\frac{\partial \underline{B}}{\partial N_i}\right)_{T,P,N_j[i]} = \bar{B}_i = \left.\frac{\partial (N \cdot B)}{\partial N_i}\right)_{T,P,N_j[i]} =$

$$= B + N \left.\frac{\partial B}{\partial N_i}\right)_{T,P,N_j[i]}$$

(c) is harder: $dB = \left(\frac{\partial B}{\partial T}\right)_{P,x} dT + \left(\frac{\partial B}{\partial P}\right)_{T,x} dT + \sum_{\substack{m=1 \\ m \neq i}}^{n} \left.\frac{\partial B}{\partial x_m}\right)_{T,P,x[m,i]} dx_m$

$$\Rightarrow \left.\frac{\partial B}{\partial N_i}\right)_{T,P,N_j[i]} = \sum_{m \neq i} \left.\frac{\partial B}{\partial x_m}\right)_{T,P,x[m,i]} \left.\frac{\partial x_m}{\partial N_i}\right)_{N_j[i]}$$

Since $x_m = \frac{N_m}{N}$ $\left.\frac{\partial x_m}{\partial N_i}\right)_{N_j[i]} = -\frac{N_m}{N^2} = -\frac{x_m}{N}$

$$\Rightarrow \left.\frac{\partial B}{\partial N_i}\right)_{T,P,N_j[i]} = -\frac{1}{N} \sum_{m \neq i} x_m \left(\frac{\partial B}{\partial x_j}\right)_{T,P,x[j,i]}$$

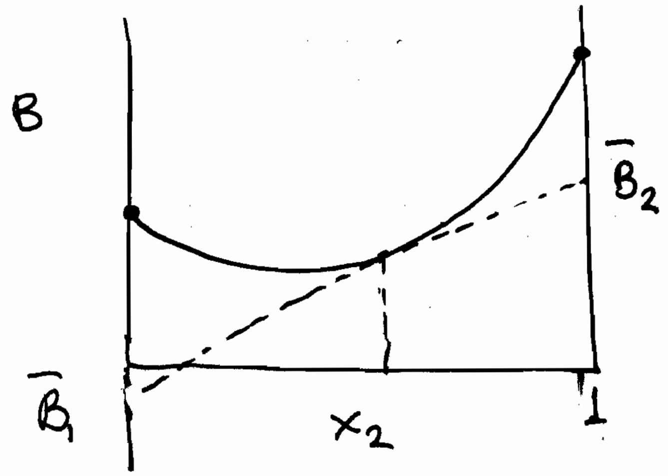
Substituting into the result for (b),

$$\bar{B}_j = B - \sum_{j \neq i} x_j \left(\frac{\partial B}{\partial x_j}\right)_{T,P,x[j,i]}$$

This expression becomes particularly simple for a binary systemof components 1 and 2:

$$\bar{B}_1 = B - x_2 \left(\frac{\partial B}{\partial x_2}\right)_{T,P} \qquad \bar{B}_2 = B - x_1 \left(\frac{\partial B}{\partial x_1}\right)_{T,P}$$

Schematic:



Gibbs-Duhem Relations for Mixtures

These are important because they provide ways to link the partial molar properties of each component to those of other components.

Start from $\underline{U} = y^{(0)} = \underline{U}(\underline{S}, \underline{V}, N_1, N_2, \ldots N_n)$

Gibbs-Duhem: $y^{(n+2)} = y^{(0)} - \sum_{i=1}^{n+2} \xi_i X_i = 0$

↑ this is not mole fractions; $X_1 = \underline{S}$, $X_2 = \underline{V}$ etc

Start from any extensive property $\underline{B} = \underline{B}(N_1, N_2, \ldots N_n, T, P)$

Gibbs-Duhem: $y^{(n)} = y^{(0)} - \sum_{i=1}^{n} \xi_i N_i = 0$

In this case, $\beta_i = \left.\frac{\partial B}{\partial N_i}\right)_{T,P,N_j[i]} = \bar{B}_i$

Differential form of total transform:

$$dy^{(n)} = -N_1 d\bar{B}_1 - N_2 d\bar{B}_2 - \dots - N_n d\bar{B}_n + \left.\frac{\partial B}{\partial T}\right)_{P,N_i} dT + \left.\frac{\partial B}{\partial P}\right)_{T,N_i} dP = 0$$

$$\Rightarrow \boxed{\sum_{i=1}^{n} N_i d\bar{B}_i = \left.\frac{\partial B}{\partial T}\right)_{P,N_j} dT + \left.\frac{\partial B}{\partial P}\right)_{T,N_j} dP} \qquad (9\text{-}60)$$

Divide by total moles N:

$$\boxed{\sum_{i=1}^{n} x_i d\bar{B}_i = \left.\frac{\partial B}{\partial T}\right)_{P,N_j} dT + \left.\frac{\partial B}{\partial P}\right)_{T,N_j} dP} \qquad (9\text{-}61)$$

The most useful form of (9-61) is one in which the derivatives of $\bar{B}_i$ with respect to one of the component mole fractions are obtained at constant T and P:

$$(9\text{-}61) \Rightarrow \quad \sum_{i=1}^{n} x_i \left(\frac{\partial \bar{B}_i}{\partial x_j}\right)_{T,P,x[j,k]} = 0 \qquad (9\text{-}67)$$

↳ cannot vary a single mole fraction!

Example 9.4

Given $\bar{H}_1$ as a function of composition, determine $\bar{H}_2$ and H. [Data are at constant T and P].

From Gibbs-Duhem relationship, (9-67):

$$x_1 \left.\frac{\partial \bar{H}_1}{\partial x_1}\right)_{T,P} + x_2 \left.\frac{\partial \bar{H}_2}{\partial x_1}\right)_{T,P} = 0$$