

Recapitulation and today's lecture

In our recent discussions of Thermodynamics, we developed inquiries into independent and dependent chemical species. We concluded that *the number of independent species is equal to the total number of species extant in the model minus the number of independent mass balance equations*. Moreover, we also discussed the equilibrium conditions for charges species–electrochemical equilibrium.

From lectures of statistical physics, we mentioned stability criterion of Gibbs-Duhem and Gibbs phase rules (29 April) without giving a rationale for their origins. Today, we will introduce molar and partial molar quantities, and the Gibbs phase rule that is deduced from Gibbs-Duhem relations and conditions for equilibrium. In addition, we will discuss *very important* graphical constructions that determines the equilibrium composition of phases in equilibrium and the chemical potentials of each independent species–*the common tangent construction*.

Molar and Partial Molar Quantities

We often need to distinguish between the *amount of an extensive quantity per mole of all species* (for molar quantities) and the *rate at which an extensive quantity changes with the addition of a species*.

Total amounts of extensive quantities depend on the size of a system; they are not interesting for describing the properties of a material (just as mass is not useful for describing the properties of gold and lead: the relevant comparison is density). The molar volume of an ideal gas is about 22 liters per mole of gas species.

Partial molar quantities are used to define extensive variables per mole of each component indicate how a particular extensive quantity changes. For example, consider how the volume of a free-standing sponge change with the addition of water: the partial molar volume of water in the sponge is

$$V_{\text{H}_2\text{O}}^{\text{sponge}} = \left(\frac{\partial V^{\text{sponge}}}{\partial N_{\text{H}_2\text{O}}} \right)_{\text{all other variables}} \quad (1)$$

is clearly *not* simply related to the molar volume of pure water. (Note that, the superscript-subscript notation has the same convention as μ_i^j .)

Extra Information and Notes

Potentially interesting but currently unnecessary

Extensive quantities are homogeneous-degree-one functions of their extensive variables—triple each of the variables and the value of the function triples. Therefore, partial molar quantities must be homogeneous-degree-zero functions of their associated chemical species. In other words, the partial molar quantities are *material properties* and not system properties.

Molar Quantities

A molar quantity can be defined for each phase by dividing an extensive quantity, \mathcal{E} , by the total number of atoms in that phase:

$$\overline{\mathcal{E}}^\alpha (= e^\alpha) \equiv \frac{\mathcal{E}^\alpha}{\sum_i N_i^\alpha} = \frac{\mathcal{E}^\alpha}{N_{\text{total}}^\alpha} = \frac{\mathcal{E}^\alpha}{|\vec{N}^\alpha|} \quad (2)$$

I like to use the “overbar” notation $\overline{\mathcal{E}}$; Denbigh uses a lower case letter, e . $\overline{G}^\alpha = g^\alpha$, $\overline{S}^\alpha = s^\alpha$, and $\overline{V}^\alpha = v^\alpha$ are molar quantities for Gibb’s free energy, entropy, and volume. For example,

$$\overline{G}^\alpha = g^\alpha = \frac{G^\alpha}{\sum_i N_i^\alpha} \quad (3)$$

We could also define a molar quantity for an entire system by summing over all of the phases contained in the system; for example:

$$G = \sum_j G^j = \sum_j \sum_i N_i^j \overline{G}^j \quad (4)$$

dividing by $N_{\text{total}}^{\text{system}}$

$$\overline{G} = \frac{G}{\sum_i \sum_j N_i^j} = \frac{\sum_j \sum_i N_i^j \overline{G}^j}{\sum_i \sum_j N_i^j} = \sum_j f^j \overline{G}^j \quad (5)$$

where the phase fractions f^j

$$f^j \equiv \frac{\sum_i N_i^j}{\sum_i \sum_j N_i^j} \quad (6)$$

are the fractions of atoms in each phase.

If we divide the internal energy by the total number of atoms present in the system, we get the differential relation between the changes in the entire system.

$$\begin{aligned} \frac{dU}{\sum_i N_i} &= \frac{TdS - PdV + \sum_i \mu_i dN_i}{\sum_i N_i} \\ d\overline{U} &= Td\overline{S} - Pd\overline{V} + \sum_i \mu_i d\overline{N}_i \\ d\overline{U} &= Td\overline{S} - Pd\overline{V} + \sum_i \mu_i dX_i \end{aligned} \quad (7)$$

where a new symbol for the molar composition $X_i = N_i/N_{\text{total}} \equiv \overline{N}_i$ is introduced because it is used so often.

Important: *there is one less degree of freedom in the composition \vec{X} than the total numbers of atoms \vec{N} , because $|\vec{X}| = \sum_i X_i = 1$ and therefore $d\sum_i X_i = 0$ (i.e., we can solve for any one of the dX_k in terms of the other dX_i).*

These quantities could also be written per phase:

$$d\overline{U}^j = Td\overline{S}^j - Pd\overline{V}^j + \sum_i \mu_i dX_i^j \quad (8)$$

and these could be related to the total molar quantities through the phase fractions f^j defined above. Here, are all the principle thermodynamic differential energies in terms of molar quantities, written on a per-phase basis:

$U^\alpha = TS^\alpha - PV^\alpha + \vec{\mu} \cdot \vec{N}^\alpha$	$dU^\alpha = TdS^\alpha - PdV^\alpha + \vec{\mu} \cdot d\vec{N}^\alpha$
$\overline{U}^\alpha = T\overline{S}^\alpha - P\overline{V}^\alpha + \vec{\mu} \cdot \vec{X}^\alpha$	$d\overline{U}^\alpha = Td\overline{S}^\alpha - Pd\overline{V}^\alpha + \vec{\mu} \cdot d\vec{X}^\alpha$
$H^\alpha = U^\alpha + PV^\alpha$	$dH^\alpha = TdS^\alpha + V^\alpha dP + \vec{\mu} \cdot d\vec{N}^\alpha$
$\overline{H}^\alpha = \overline{U}^\alpha + P\overline{V}^\alpha$	$d\overline{H}^\alpha = Td\overline{S}^\alpha + \overline{V}^\alpha dP + \vec{\mu} \cdot d\vec{X}^\alpha$
$F^\alpha = U^\alpha - TS^\alpha$	$dF^\alpha = -S^\alpha dT - PdV^\alpha + \vec{\mu} \cdot d\vec{N}^\alpha$
$\overline{F}^\alpha = \overline{U}^\alpha - T\overline{S}^\alpha$	$d\overline{F}^\alpha = -\overline{S}^\alpha dT - Pd\overline{V}^\alpha + \vec{\mu} \cdot d\vec{X}^\alpha$
$G^\alpha = U^\alpha - TS^\alpha + PV^\alpha$	$dG^\alpha = -S^\alpha dT + V^\alpha dP + \vec{\mu} \cdot d\vec{N}^\alpha$
$\overline{G}^\alpha = \overline{U}^\alpha - T\overline{S}^\alpha + P\overline{V}^\alpha$	$d\overline{G}^\alpha = -\overline{S}^\alpha dT + \overline{V}^\alpha dP + \vec{\mu} \cdot d\vec{X}^\alpha$

Partial Molar Quantities

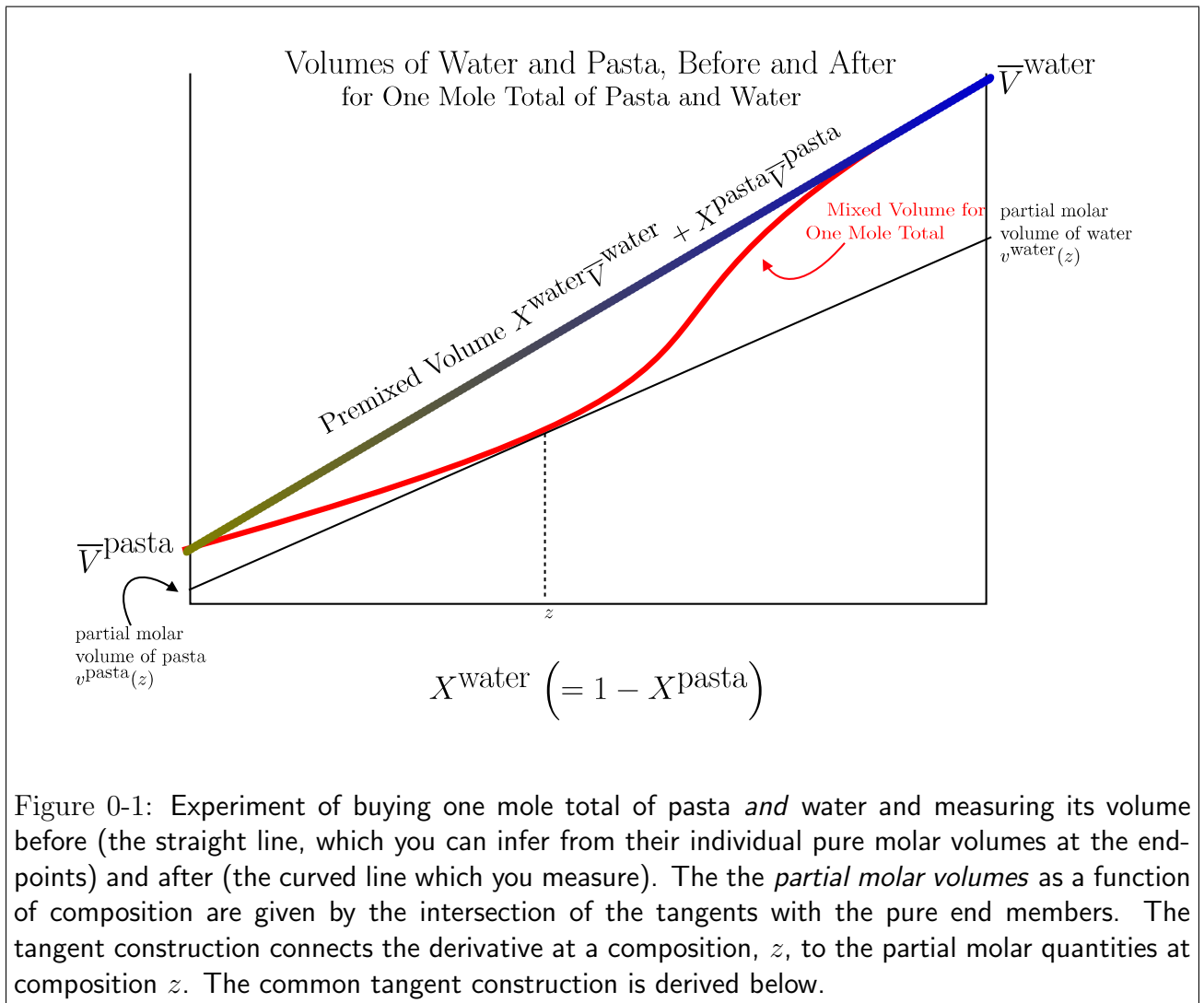
Partial molar quantities are material properties relating the change of an extensive quantity with respect to the change of a chemical species. Here is the definition, written for phase j .

$$\mathcal{E}_i^j \equiv \left(\frac{\partial \mathcal{E}^j}{\partial N_i} \right)_{\text{all other quants.}} \quad (9)$$

Important: Watch the notation difference between the molar quantity, $\overline{\mathcal{E}}_i^j$ (or e_i^j in Denbigh's notation), which is a number density, and a partial molar quantity \mathcal{E}_i^j (which is an intrinsic material property).

To reiterate this:

- You could deduce a molar quantity without doing an experiment at all: you buy N_A atoms from the store that sells A species; you walk down the street and buy N_B moles at the B -store. Even before getting home and mixing it up, you know the *molar* composition will be $X_A = N_A/(N_A + N_B)$. You bake a cake—you know ahead of time what the weight fraction of chocolate will be (but not the volume fraction—that depends on the chef, the environment, and the other ingredients).
- To find a partial molar quantity, you must do an experiment (or look up data from someone else's experiment). You go to the pasta store and buy 40 moles of tortellini which occupies (excluding the air) a volume of 2 standard boxes; you go to the water store and you buy 12 moles of water which has a volume of 1 standard box. You mix 'em up in a (hermetically sealed) bowl and let the water absorb and the pasta swell; you find that the total volume is 2.125 standard boxes. What happened to the other volume? Is this some kind of Sicilian conspiracy? Now, suppose you want to know how bad this consumer fraud is and if it gets worse. So you add $12 + \epsilon$ moles of water which has a volume of $(12 + \epsilon)\overline{V}$, you do the experiment of putting it a bowl and so forth, and you measure the change in total volume: $V_{\text{total}}(12 + \epsilon) = V_{\text{total}}(12) + \mathcal{V}_{\text{water}}^{\text{noodles}} \epsilon$. That's the partial molar quantity.



For example, if all of the intrinsic properties are held fixed, then

$$d\mathcal{E}^\alpha = \sum_i \frac{\partial \mathcal{E}^\alpha}{\partial N_i} dN_i = \sum_i \mathcal{E}_i^\alpha dN_i \quad (10)$$

Because \mathcal{E} is homogeneous-degree-one in the \vec{N} , we can (Euler) integrate:

$$\mathcal{E}^\alpha = \sum_i \mathcal{E}_i^\alpha N_i^\alpha \quad (11)$$

In particular for the Gibbs free energy,

$$\begin{aligned}
 \mu_i^\alpha &= \left(\frac{\partial G^\alpha}{\partial N_i} \right)_{P,T,\text{other } N_j \neq i} \\
 G^\alpha &= \sum_i \mu_i^\alpha N_i^\alpha \\
 \overline{G}^\alpha &= \sum_i \mu_i^\alpha X_i^\alpha \\
 G &= \sum_i \mu_i N_i \\
 \overline{G} &= \sum_i \mu_i X_i
 \end{aligned} \tag{12}$$

Comparing this to the last entry in the table, we have the Gibbs-Duhem relations:

$$\begin{aligned}
 0 &= S^\alpha dT - V^\alpha dP + \sum_i N_i^\alpha d\mu_i^\alpha \\
 0 &= \overline{S}^\alpha dT - \overline{V}^\alpha dP + \sum_i X_i^\alpha d\mu_i^\alpha
 \end{aligned} \tag{13}$$

which can be conveniently written as follows

$$0 = \vec{\mathcal{E}} \cdot d\vec{\mathcal{I}} \tag{14}$$

We will discuss this equation's geometry and its application to the Gibbs phase rule in following section.¹

Application of Gibbs-Duhem relation

Below it will be shown, for a multiphase system, that the chemical potential in each phase must be uniform and equal.

Consider the following simple multiphase system:

¹At equilibrium $\vec{x} \cdot d\vec{F} = 0$: for equilibrium the changes in force are constrained to be *normal* to the state vector, \vec{x} . If all the possible states of the system are represented by a surface x , then the tangent plane of that surface (i.e., the plane that touches at a single point) defines the constraint on the equilibrium changes in F .

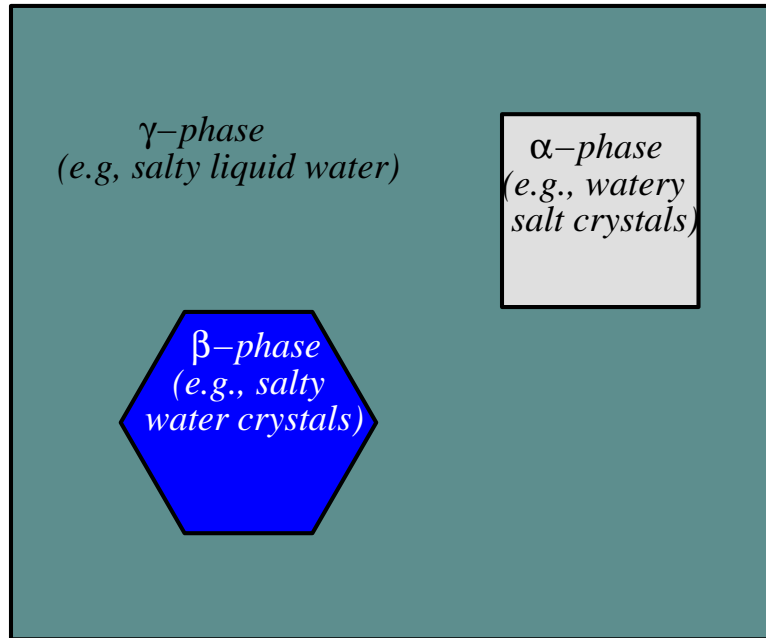


Figure 0-2: An example of a multiphase system. P and T are constant and equilibrium with a reservoir.

Application of the conditions of internal equilibrium to the entire system considering that it is composed of f phases:

$$\begin{aligned}
 dG &= -SdT + VdP + \sum_{i=1}^C \sum_{j=1}^f \mu_i^j dN_i^j \\
 &= -SdT + VdP \\
 &\quad + \mu_1^\alpha dN_1^\alpha + \mu_2^\alpha dN_2^\alpha + \cdots + \mu_C^\alpha dN_C^\alpha \\
 &\quad + \mu_1^\beta dN_1^\beta + \mu_2^\beta dN_2^\beta + \cdots + \mu_C^\beta dN_C^\beta \\
 &\quad + \cdots \\
 &\quad + \mu_1^\zeta dN_1^\zeta + \mu_2^\zeta dN_2^\zeta + \cdots + \mu_C^\zeta dN_C^\zeta
 \end{aligned} \tag{15}$$

μ_i^j is the chemical potential of chemical species i in phase j .

Write this out for a three ($f = 3$) phase system composed of two ($C = 2$) species W and B :

For a closed system,

$$dN_B^\alpha + dN_B^\beta + dN_B^\gamma = 0 \tag{16}$$

this follows for each possible species i , therefore:

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma \tag{17}$$

In other words, the chemical potentials of any chemical species is equal in all the present phases.

Or if we number the species $i = 1, 2, \dots, C$ and the number of phases $j = I, II, \dots, f$:

$$\begin{aligned}
\mu_1^I &= \mu_1^{II} = \mu_1^{III} = \cdots = \mu_1^f \\
\mu_2^I &= \mu_2^{II} = \mu_2^{III} = \cdots = \mu_2^f \\
&\vdots \\
\mu_C^I &= \mu_C^{II} = \mu_C^{III} = \cdots = \mu_C^f
\end{aligned}
\tag{18}$$

Each row has $f - 1$ equal signs; i.e. $f - 1$ equations. So in the above there are $C(f - 1)$ equations.

In addition we have, via the Gibbs-Duhem equation for each phase, another relation between the variables:

$$\begin{aligned}
0 &= S^I dT - V^I dP + \sum_{i=1}^C N_i^I d\mu_i^I \\
0 &= S^{II} dT - V^{II} dP + \sum_{i=1}^C N_i^{II} d\mu_i^{II} \\
&\vdots \\
0 &= S^f dT - V^f dP + \sum_{i=1}^C N_i^f d\mu_i^f
\end{aligned}
\tag{19}$$

that gives us another f equations. Therefore,

Let the number of free variables be D (degrees of freedom). Then,

$$D = (Cf + 2) - [C(f - 1) + f] \tag{20}$$

or:

$$D + f = C + 2 \tag{21}$$

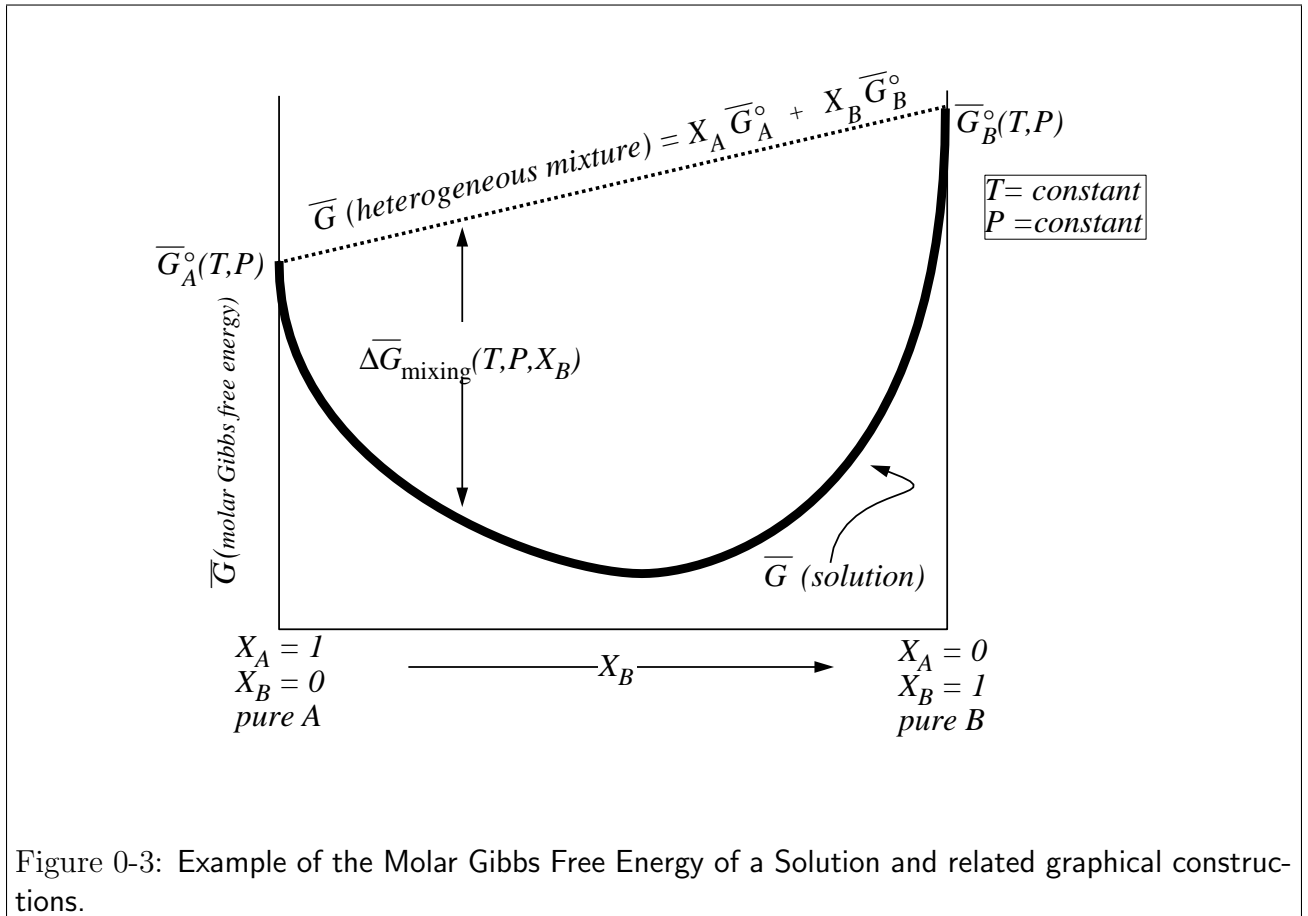
This is a relation between the number of degrees of freedom in a system and the number of components. Commonly, one can think of the number of degrees of freedom in a system as the number of phases that can co-exist, or $D = P$.

The “2” in the Gibbs phase rule is kind of special. It is lonely sitting there as a number-jealous of the other quantities who can take any value that they want—an ugly step-sibling, waiting for its magic pumpkin? Is its fate sealed? Never more than more than itself—and never ever less? Oh, cruel fate!?

No! We hold these truths to be self-evident. The “2” is a place holder for T and P , the temperature and the pressure. This is just an result of our lack of imagination for storing other kinds of work in the system, such as stress-strain, polarization-electric fields. We have liberated “2” from this unjust classist burden and set it free—free to be any other number being equal to the number of different ways we can do work and also change the temperature. We have liberated our friend “2” and set it free—free like the doves, to fly, to fly, unconstrained and to pursue its own happiness. The quality of mercy is not strained, it falls upon the earth as the gentle rain. And where it lands is *twice* bless’d.

The Origin of Common Tangent Construction

A useful graphical construction can be utilized for extracting values of chemical potentials:
Consider that the molar free energy of a solution is plotted as follows:



It would be particularly useful to obtain the chemical potentials of each species in solution as a function of composition. This relationship can be determined as follows:

Starting with an expression for the molar free energy of the solution being a weighted sum of the chemical potentials:

$$\overline{G}_{sol} = X_A \mu_A + X_B \mu_B$$

$$d\overline{G}_{sol} = X_A d\mu_A + X_B d\mu_B + \mu_A dX_A + \mu_B dX_B$$

$d\overline{G}_{sol}$ becomes when using $dX_B = -dX_A$.

$$d\overline{G}_{sol} = X_A d\mu_A + X_B d\mu_B + (\mu_B - \mu_A) dX_B$$

and recall that

$$0 = \vec{\mathcal{E}} \cdot d\vec{\mathcal{I}} \quad (0 = \vec{X} \cdot d\vec{\mu})$$

thus,

$$\frac{\partial \overline{G}_{sol}}{\partial X_A} = \mu_A - \mu_B$$

similarly,

$$\frac{\partial \overline{G}_{sol}}{\partial X_B} = \mu_B - \mu_A$$

Multiplying $\partial \overline{G}/\partial X_B$ by X_B and subtracting it from \overline{G}_{sol} :

$$\overline{G}_{sol} - X_B \frac{\partial \overline{G}_{sol}}{\partial X_B} = X_A \mu_A + X_B \mu_B - (X_B \mu_B - X_B \mu_A) = \mu_A \quad (22)$$

or

$$\begin{aligned} \mu_A &= \overline{G}_{sol} + X_B \frac{\partial \overline{G}_{sol}}{\partial X_A} \\ &= \boxed{\overline{G}_{sol} - X_B \frac{\partial \overline{G}_{sol}}{\partial X_B}} \end{aligned} \quad (23)$$

similarly,

$$\begin{aligned} \mu_B &= \overline{G}_{sol} + X_A \frac{\partial \overline{G}_{sol}}{\partial X_B} \\ &= \boxed{\overline{G}_{sol} - X_A \frac{\partial \overline{G}_{sol}}{\partial X_A}} \end{aligned} \quad (24)$$

These equations can be interpreted with the following figure.

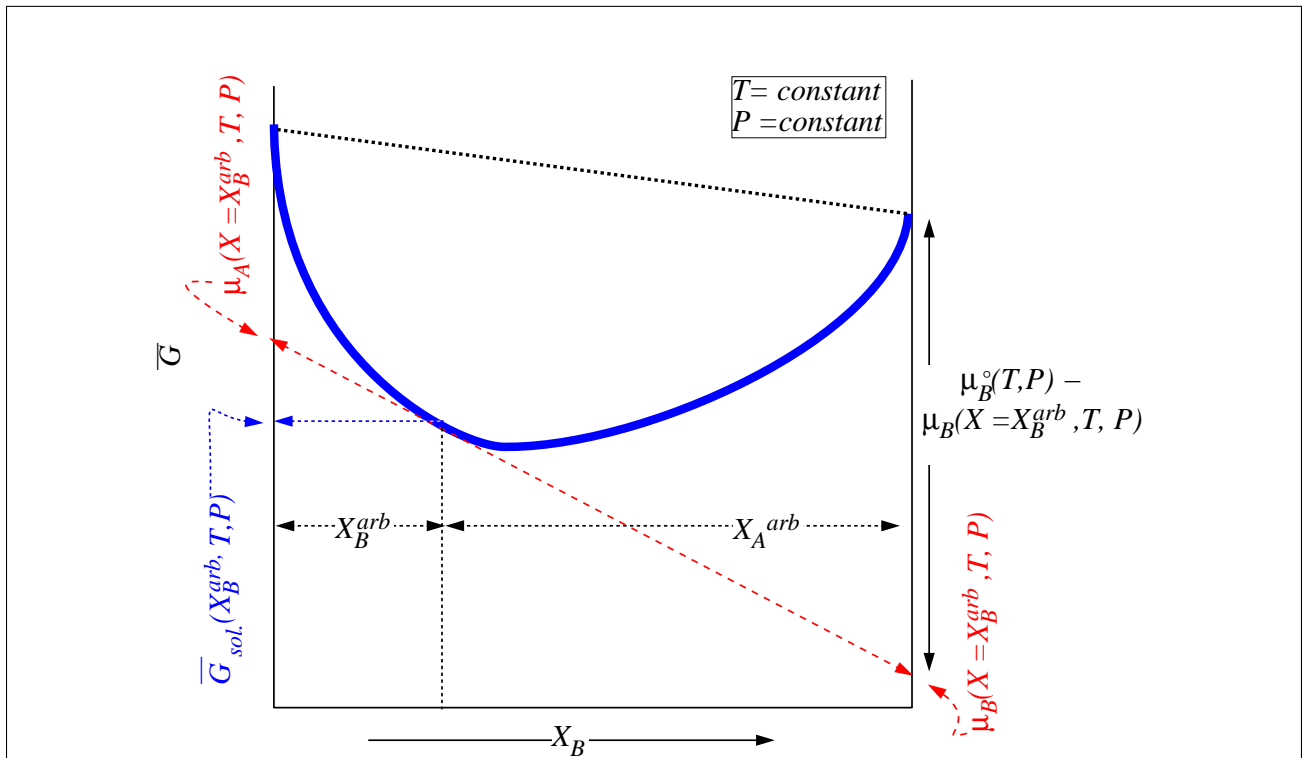


Figure 0-4: Illustration of how to determine the chemical potentials from a graph of $\overline{G}(X_B)$ for a binary alloy. X_B^{arb} is an arbitrary composition where the tangent construction is performed.

Here is the important thing to remember for ever for constructions like the above: *Each point on the solution curve has a tangent: the chemical potentials of each species are given by the intersection of that tangent with the pure axis for that species.* **At the temperature and pressure for which the curve is drawn, T and P , the chemical potentials $\mu_A(X, P, T)$ and $\mu_B(X, P, T)$ are thus determined.**