ADVANCED THERMODYNAMICS

Handout IV – Calculation and Interpretation of Multi-Component Phase Diagrams

(Gaskell Chapters 10 & 14)

Background

This handout continues on the subject of solution thermodynamics for multi-component systems, but the emphasis is now with its role in the stability of multi-component phase equilibria. The portrayal of stability fields of equilibria in temperature-composition space at constant pressure (1 atm) is known classically in materials as the phase diagram.

With a thermodynamic model assumed for the behavior of each solution phase, coupled with the free energy differences among the various phases of the pure components, the full phase diagram can be calculated, both for complete equilibrium and for meta-stable equilibrium.

The calculated equilibria can be compared to the measured equilibria where amenable to experimentation. The model is not just useful to interpolate and extrapolate among data, but is also immensely helpful in interpreting notable features of the phase diagram for a particular system.

Up to five components are considered in this handout. Alloy systems are stressed over oxide systems, which differ in that the vertices are usually compounds, rather than the pure components.

Introduction to Phase Diagrams

A phase in materials science is any homogeneous part of a thermodynamic system. It is physically distinct – within which, all thermodynamic properties in its bulk are uniform. A system of two or more phases is called heterogeneous.

Phase diagrams are traditionally *maps* in composition-temperature space showing the equilibrium domains of each phase alone, and the domains of more than one phase in mutual co-existence. These are typically at 1 atm pressure, but pressure can be another co-ordinate (as well as molar volume).

Phase diagrams actually pre-date the rigorous development of thermodynamics in the late 19th century. The latter eventually showed - in theory at least – that the phase diagram could, in fact, be calculated if the thermodynamic behavior of each phase (and the difference in the free energies among the various pure phases) were known. With the advent of the computer coupled with activity data, etc., the phase diagram could at last be calculated and compared to the experimentally derived one.

Even the development of the infamous *Gibbs Phase Rule* (GPR) – which actually is thermodynamics at its simplest – didn't really get understood and applied until 1900. Then, it soon became clear that many phase diagrams, as they were presently accepted, actually had numerous errors and internal inconsistencies!

In a sense, phase diagrams are more than maps, which are very useful in themselves – such as in tracking solidification, etc.; they are actually manifestations of the thermodynamic properties of the system at equilibrium (at metastable equilibrium, as well), but are expressed in terms of the composition and temperature variables, rather than the usual thermodynamic variables (such as G). Indeed, *reverse* calculations for the activity, etc. can be made from knowledge of the phase diagram! Today, this endeavor is known as *coupling* phase diagram and thermodynamic measurements, the goal being to arrive at a more accurate assessment of *both* sets of data.

The equilibrium state – defined as one with the lowest global free energy - is, in fact, one of many possible states; hence meta-stable equilibria can also be calculated, as the solution behavior for the meta-stable phase is still governed by the same solution model.

Co-existence of phases occur in the phase diagram only when the partial molar free energies of each component in each phase have the same value (i.e., when they have equal chemical potentials), hence the technique for calculating the phase diagram.

Review of Free Energy and the Activity

The Gibbs Free Energy of mixing of components A and B to form one mole of solution is (noting that the notation for molar M has been dropped for convenience):

 $\Delta G^{mix} + RT(X_A \ln a_A + X_B \ln a_B)$

Conventionally, as the Gibbs Free Energy of a component cannot be measured absolutely, it is assigned a value of zero.

For the ideal solution (where $a_i = X_i$), we have (noting $\Delta H^{ideal} = 0$):

$$\Delta G^{ideal} = RT(X_A \ln X_A + X_B \ln X_B) = -T\Delta S^{ideal}$$

While in the above equation, $\Delta S^{ideal} = R(X_A \ln X_A + X_B \ln X_B)$ is independent of temperature, clearly, the variation of ΔG^{ideal} with composition is dependent directly on temperature.

It is recalled from the previous handout that the tangent to the free energy curve at that composition gives the partial free energy (or, chemical potential) at its intercept with the axis $X_i = 1$.

Now consider the activity of B in the solution of A and B for the three cases depicted in Figure HIV.1.



Figure IV.1 – Activity of Component B in the AB system, showing three cases: (1) ideal behavior; (2) slight positive departure from ideality; and (3) slight negative departure from ideality.

As $a_B = \gamma_B X_B$, we can deduce the following:

$$\gamma_B(2) > \gamma_B(1) = 1 > \gamma_B(3)$$

$$a_B(2) > a_B(ideal) > a_B(3)$$

 $a_B(1, 2, 3) < 1 \text{ at } X_B^*$

For the above equation, it is noted that $a_B \rightarrow 1 \text{ as } X_B \rightarrow 1$.

Figure HIV.2 shows graphically the relationship between the integral molar free energy and the chemical potential for the three cases considered in Figure IV.1.



Figure IV.2 – The molar Gibbs Free Energies of mixing in binary system exhibiting ideal behavior (1), positive deviation from ideal behavior (2), and negative deviation from ideal behavior (3) corresponding to Figure HIV.1.

With departure from ideality $\Delta \overline{G}_i$ will depend not just on temperature, but also on γ_i , which can change with temperature as well for a given composition.

The Regular Solution – Role of Temperature and Parameter α on Phase Separation

Before consideration of the phase diagram – which involves generally more than one phase – we want to consider the simplest case, where, below a critical temperature, a phase separates out into two distinct phases (having the same crystal structure as the parent phase, but differing compositions). Such is the case for a regular solution, depending on the (positive) value of the regular solution parameter (here α). (For convenience, the notation for molar *M* has been dropped.)

For a regular solution, we have:

$$\Delta G^{ex} = \Delta H = RT\alpha X_A X_B = \alpha' X_A X_B = \Omega X_A X_B$$

For the ideal solution, we have:

$$\Delta G^{ideal} = RT(X_A \ln X_A + X_B \ln X_B)$$

The following figure, plotted as dimensionless $\Delta H/RT$ and $\Delta G/RT$ illustrate the big and unusual effect of the regular solution parameter ($\Delta H/RT = \alpha X_A X_B$ for $\alpha = +3$).



Figure HIV.3 – The effect of the magnitude of α on the integral molar heats and integral molar Gibbs Free Energy of formation of a binary solution.

The addition of $\Delta H/RT$ to $-\Delta S^{ideal} / RT$ causes two inflexion points. These result in phase separation, as the equilibrium configuration of the two different phases is a lower free energy than only the original phase.

Compare free energy diagrams for two different levels of α : $\alpha \le 1 \& \alpha = 3$. This is shown in Figure HIV.4.



Figure HIV.4 – Comparison of the molar integral Gibbs Free Energy at two different levels of solution parameter α . (a) At $\alpha \leq 1$; (b) At $\alpha = +3$.

In (a) in this figure, this is the situation with a small value for α ($\alpha \le 1$), in which separation of the solution into two phases (identical in structure) of compositions $X'_B \& X''_B$ cannot happen because the total free energy of the system at Point *c* is higher than at Point *d*, where thereby resulting in only one phase of a 50/50 mix of A and B.

In (b) in this figure, the total free energy is at a minimum at the common tangent (Point *m* at X'_B and Point *q* at X''_B , thereby resulting in two phases forming at $X'_B \& X''_B$. Between points n & p, the homogeneous solution has a greater free energy than the separate phases.

Since we have a common tangent between $\Delta G(X'_B)$ and $\Delta G(X''_B)$, we have equal chemical potentials, and therefore, equal activities:

$$\overline{G}_A - G_A^o(@X'_B) = \overline{G}_A - G_A^o(@X''_B)$$

Or
$$RT \ln a_A (@X'_B) = RT \ln a_A (@X''_B)$$

Because temperature is a parameter as well as α , for a given value (e.g., $\alpha = 3$), temperature can be varied to compensate for the effect of α on causing the inflexion Points *m* and *q*. The *critical temperature* T^{cr} occurs, where $X'_B \leftrightarrow X''_B$, above which there is only a single homogeneous solution.

In order to evaluate T^{cr} , we explore the inflexion Points m & q, where:

$$\frac{\partial^2 \Delta G}{\partial X_B^2} = 0$$

At *T^{cr}*, we have:

$$\frac{\partial \Delta G}{\partial X_B} = \frac{\partial^2 \Delta G}{\partial X_B^2} = \mathbf{0} \Rightarrow X'_B = X''_B = X_B$$

Thus, we have:

$$T^{cr} = \frac{2X_B^*(1-X_B^*)\Omega}{R}$$

It is clear that Ω must be positive for T^{cr} to be positive. The value of X_B^* that maximizes T^{cr} is $X_B^* = 0.5$, therefore:

$$T^{cr}=\frac{\Omega}{2R}$$

From the QC model, a positive value for Ω means repulsion of A & B, and a tendency to phase separation. The larger is Ω , the higher is T^{cr} . This is illustrated in Figure HIV.5.



Figure HIV.5 - (a) The effect of temperature on the molar Gibbs Free Energy of mixing a binary solution for which $\Omega = 4000$ cal; (b) The loci of the double tangent ponts in (a), which generate the phase diagram for the system; and (c) The activities of component B derived from (a).

Conditions of Heterogeneous Phase Equilibrium

Consider one phase consisting of n_A moles of A and n_B moles of B. This system has an (extensive) free energy G', then:

$$\mu_{A} = \left(\frac{\partial G'}{\partial n_{A}}\right)_{T,P,n_{B}}$$
And
$$\mu_{B} = \left(\frac{\partial G'}{\partial n_{B}}\right)_{T,P,n_{A}}$$

Now, consider a heterogeneous, closed system of two phases $\alpha \& \beta$. The change in the free energy for each phase due to a reversible change in mass is:

$$dG'^{lpha}_{T,P} = \mu^{lpha}_A dn^{lpha}_A + \mu^{lpha}_B dn^{lpha}_B$$

And
 $dG'^{eta}_{T,P} = \mu^{eta}_A dn^{eta}_A + \mu^{eta}_B dn^{eta}_B$

Now, consider a change of the amount of A atoms in each of the two phases. Let dn_A atoms be transferred to the α -phase from the β -phase, keeping the number of B atoms in each phase constant, as shown in Figure HIV.6:

$$dn^{lpha}_B=dn^{eta}_B=0$$



Figure HIV.6 – Schematic diagram showing transfer of dn_A atoms of A to the α -phase from the β -phase, keeping the number of B atoms in each phase constant.

As a result of the transfer of dn_A atoms from β to α :

$$dG'^{lpha}_{T,P} = \mu^{lpha}_A dn^{lpha}_A$$

And
 $dG'^{eta}_{T,P} = \mu^{eta}_A dn^{eta}_A$

The total free energy change of the system of these two phases is the sum of the free energy change for each of the individual phases:

$$dG'^{sys}_{T,P} = dG'^{\alpha}_{T,P} + dG'^{\beta}_{T,P} = \mu^{\alpha}_A dn^{\alpha}_A + \mu^{\beta}_B dn^{\beta}_A$$

However, the system is closed, and the amount of A lost by the β -phase is equal to the amount of A gained by the α -phase:

$$dn^{lpha}_A = -dn^{eta}_A \Longrightarrow$$

 $dG'^{sys}_{T,P} = (\mu^{lpha}_A - \mu^{eta}_A)dn^{eta}_A$

Since the transfer of A was done reversibly, we have:

$$dG'^{sys}_{T,P}=0$$

Thus, we have:

$$(\mu_A^{\alpha}-\mu_A^{\beta})dn_A^{\alpha}=0$$

Finally, we can say, at equilibrium:

$$\mu_A^{lpha} = \mu_A^{eta}$$

And
 $\mu_B^{lpha} = \mu_B^{eta}$

We can generalize the above equations for a heterogeneous system consisting of N components and S co-existing phases, at constant T, P:

$$\mu_i^S = \mu_i^1 = \mu_i^2 = \cdots \mu_{i|i=1,2,\dots N \text{ components } \& j=1,2\dots(S-1) \text{ phases}}^j$$

In the above equation, it is recalled that $\mu = f(X_i, T, P)$.

Mass Balance Constraints on a Closed System at Equilibrium - The Lever Rule

Reconsider the system AB consisting of n_A^{α} , n_A^{β} , n_B^{α} and n_B^{β} . If this system is closed, the following equations describe this constraint. Let X_i^{o} be the overall or total composition of the entire system of the two phases and X_i^{ϕ} be the composition of *i* in the individual phases ($\phi = \alpha, \beta$). Finally, let f^{ϕ} be the fraction of each phase ϕ . Thus, we have the following set of mass balances:

$$X_{i}^{o} = \sum_{\phi=1}^{S} f^{\phi} X_{i}^{\phi}$$
$$\sum X_{i}^{o} = 1$$
$$\left[\sum_{i}^{N} X_{i}^{\phi} = 1\right]_{\phi=1,2,\dots,S}$$
And
$$\sum_{\phi=1}^{S} f^{\phi} = 1$$

The above set of mass balance equations is known as the *Lever Rule* (LR). This is a mechanical analogue to a lever force balance in the phase diagram (constant temperature) where the relative distance in composition space between the total composition and the composition of the individual phases of an equilibrium gives the fraction of each phase. The LR is illustrated for the two-phase equilibrium ($l \rightleftharpoons s$) in Binary System AB in Figure HIV.7.



Figure HIV.7 – Illustration of the Lever Rule applied to the two-phase equilibrium in a binary system.

A specific calculation of the fraction liquid in the Pb-rich side of the Pb-Sn system at various temperatures is made in Figure HIV.8.



Figure IV.8 – Calculation of fraction of liquid phase in the Pb-rich Pb-Sn system.

The Gibbs Phase Rule

The system of equations in i and j give W independent relationships, as follows, where S is the total number of phases of an equilibrium, and N is the number of components:

$$W = N(S-1)$$

What is the number of independent variables Q? Since the phase diagram itself as well as the chemical potentials are expressed in terms of the (intensive) composition variables, we have the following mass balance constraints:

$$X_1^j + X_2^j + \cdots X_N^j = \mathbf{1}_{|j=1,2\dots S}$$

So, we have Q = S(N - 1) + 2 independent variables, including T,P. (The quantity (N - 1) is because the N^{th} component composition is calculated from $X_N = 1 - \sum_{i=1}^{N-1} X_i$.) Thus, the degrees of freedom F of this system of equations describing an equilibrium is:

$$F = Q - W = S(N - 1) - N(S - 1) + 2$$

This becomes the infamous Gibbs Phase Rule (GPR):

$$F = N - S + 2$$

The degrees of freedom F is the number of variables (composition, T & P) that can be varied while remaining in an equilibrium.

(It is to be noted that, unlike for the LR for a specific equilibrium, at a specific temperature, the chemical potential is generally *not* a function of the fraction of a phase, nor of the total composition of the system, so that for the GPR, only the mass balance for the phases *j* apply individually (as in $X_1^j + X_2^j + \cdots X_N^j = \mathbf{1}_{|j=1,2\dots S}$).)

Application of the GPR is made here with reference to Figure HIV.9.



Figure HIV.9 – Application of the *Gibbs Phase Rule* (GPR) in the binary system exhibiting a eutectic equilibrium at constant pressure.

Complications with application of the GPR can arise when chemical reactions are involved and when there is an inert gas to control pressure. This is discussed further in the subsequent handout.

Phase Stabilities

So far, we have not been concerned with different standard states for the chemical potential. This was easily circumvented in the discussion of phase separation, as the new phases continued to have the same crystal structure as the parent phase.

The topic of standard states can be somewhat complicated, especially where calculation of phase diagrams is concerned, because there are more than one phases at issue, and the chemical potential may be referenced to any of the pure phases as its standard state. Usually (but not always) the standard state for a chemical potential of a component in a phase is the phase of the pure component. But sometimes, the phase is metastable in the pure component! Other times, activity for the chemical potential may be measured relative to some other, more convenient standard state. The general topic of standard states is handled in the subsequent handout. For the present discussion, the issue is consistency in the handling of the different standard states corresponding to the variety of phases encountered when calculating phase diagrams.

We now revisit the conditions of equilibrium using the example of the two-phase ($l \rightleftharpoons s$) equilibrium in a multi-component system (constant pressure), where i = A, B, ...:

$$\Delta \mu_i^l = \Delta \mu_i^s + \Delta \mu_i^{o,l \to s}$$
$$\Delta \mu_i^{o,l \to s} = \mu_i^{o,s} - \mu_i^{o,l} = \Delta G_i^{o,l \to s}$$
And
$$\Delta \mu_i^{\phi} = RT \ln a_i^{\phi}|_{\phi=l,s}$$

In the above set of equations, $\Delta \mu_i^{o,l \to s} = \mu_i^{o,s} - \mu_i^{o,l} = \Delta G_i^{o,l \to s}$ are known as the *phase* stability of pure *i*, here, between pure liquid and pure solid *i*.

If the activity of a component in a phase has the same phase as the standard state, it is noted as such:

$$\Delta \mu^{\phi}_i = \mu^{\phi}_i - \mu^{o,\phi}_i = RT \ln a^{relative \, to \, pure \, i \, in \, phase \, \phi}_i = a^{\phi}_i$$

For example, say an activity for *i* is known (i.e., measured) in the liquid phase, *relative to the pure liquid i*, we write:

$$\Delta \mu_i^l = \mu_i^l - \mu_i^{o,l} = RT \ln a_i^{relative \ to \ pure \ liquid \ i} = a_i^l$$

Similarly, for the solid phase, we write:

$$\Delta \mu_i^s = \mu_i^s - \mu_i^{o,s} = RT \ln a_i^{relative to pure solid i} = a_i^s$$

Insertion of the above two equations into our original statement of equilibrium between the liquid and solid phase results in the following system of equations (I = A, B, ...):

$$\Delta \mu_i^l = \Delta \mu_i^s + \Delta \mu_i^{o,l \to s}$$
$$\mu_i^l - \mu_i^{o,l} = \mu_i^s - \mu_i^{o,s} + \mu_i^{o,s} - \mu_i^{o,l} \Rightarrow$$
$$\mu_i^l = \mu_i^s$$
$$Or$$
$$\Delta \mu_i^l = \Delta \mu_i^s$$

In so doing, we have changed the activity of *i* in the solid phase, so that it is now referenced to the liquid phase. In many textbooks, the equality of chemical potentials is given in the form of the equation stated above. This simple form belies the subtlety that in so doing, *the chemical potential of i in the solid is in the same standard state as it is for i in the liquid*!

On the other hand, suppose the activities a_i^l and a_i^s are already given relative to *the same* phase, say, the liquid phase, we may write:

$$\Delta \mu_i^l = \mu_i^l - \mu_i^{o,l} = RT \ln a_i^{relative to pure liquid i} = a_i^l$$
$$\Delta \mu_i^s = \mu_i^s - \mu_i^{o,l} = RT \ln a_i^{relative to pure liquid i} = a_i^l$$

In the above equation, note that the standard state for solid *i* is the pure liquid *i*!

When the standard states for a set of co-existing phases are given relative to the same standard state, a simple set of equations result, where there is no need for phase stabilities, in which case we write:

$$\Delta \mu_i^l = \Delta \mu_i^s$$

In general, the set of phase stabilities are (where ϕ can be any of the *j* phases, j = 1, 2, ...*S*; and i = 1, 2 ... N):

$$\Delta \mu_i^{o,\phi_1 \to \phi_2} = \Delta G_i^{o,\phi_1 \to \phi_2}$$

Calculation of Binary Phase Diagrams – Graphical Approach

By *graphical approach*, we mean establishing the chemical potentials as *tangents* to the integral (molar) free energy curves for each phase, whence, equality of all tangents establishes the compositions for the equilibrium at issue at a given temperature (constant pressure). The systematic change in temperature establishes new tangents, and therefore a new set of compositions for the equilibrium, thereby mapping out the phase diagram. Today, this approach is replaced by a numerical procedure, but it is, nevertheless, instructive.

First, we need to briefly review the relationship between the integral (molar) free energy and the chemical potential (partial molar free energy) discussed earlier. This is illustrated in Figure HIV.10 for the ϕ -phase in AB binary system.

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Figure HIV.10 – Relationship between the molar free energy and the chemical potential in a binary system.

If pure A and pure B are in the same standard state (for example, if a solid, having the same crystal structure, such as BCC, FCC, HCP, etc.) then $\mu_A^o = \mu_B^o$ and $\Delta G^o = 0$ for the un-mixed components. For simplicity in this case, μ_A^o and μ_B^o can be arbitrarily set to zero, so ΔG^o can be represented by a horizontal line at the origin on the y-axis.

More often the case, pure A and pure B do *not* have the *same* standard state at a given temperature. Then, this line for ΔG^o is tilted. Each pure component must be in have an equilibrium standard state, but in this case, they are not the same, so the tilt reflects the difference between the standard states for the components from their equilibrium standard states.

This is more easily seen by plotting two curves of the integral (molar) free energy of mixing – one for the phase that is stable for the pure Component A, and the other for the phase that is stable for Component B.

We will consider the case, where $T_A^{mp} > T_B^{mp}$, so, at an intermediary temperature, pure A is solid, but pure B is liquid.

The common tangency between these two curves generates the liquidus and solidus of the phase diagram (by systematically varying temperature). This is shown schematically in Figure HIV.11, with explanation.

$$A_{A}^{ma} = A_{A}^{na} = A_{A}^{na} = T_{A}^{na} = A_{A}^{na} = A_{$$

Figure HIV.11 – Establishment of the location of the liquidus and solidus compositions for a temperature intermediary between the melting point of A and that of B, by the technique of common tangents to the integral free energy curves for each phase.

Figure HIV.12, in turn, shows application of the common tangency technique at a series of temperatures, where the integral free energy curves for the liquid and solid phases shift positions, generating different locations of the solidus and liquidus, depending on temperature.



Figure HIV.12 – Generation of the liquidus and solidus for the phase diagram of the AB system by the common tangent technique at several temperatures.

Finally, Figure HIV.13 shows the eutectic system comprised by the $l \leftrightarrow \alpha, \alpha \leftrightarrow \beta$ and $l \leftrightarrow \beta$ equilibria, and the corresponding integral free energy curves for each phase at a series of temperatures, where the common tangents to each set of curves locate the compositions of each equilibrium.



Figure HIV.13 – Illustration of the common tangent method for establishing the phase diagram, here, a eutectic involving the $l \leftrightarrow \alpha, \alpha \leftrightarrow \beta$ and $l \leftrightarrow \beta$ equilibria.

Calculation of Binary Phase Diagrams – Numerical Approach

It is customary, unless otherwise stated, to assume that the activity of a component in a phase is in the standard state consisting of the pure component in that phase. Complications can arise when a phase that is stable for a portion of the phase diagram may not be stable in one of the pure components. An example is the Fe-Cr system, which has the FCC phase protruding from the iron rich side into the binary, resulting in the well-known gamma-loop. But, the FCC phase is meta-stable in pure Cr. For calculation of this feature in the Fe-Cr system, the free energy difference between FCC and BCC chromium is needed. How to obtain this, if FCC Cr is not s stable phase? There are two approaches: (1) this is inferred (i.e., back-calculated) from details of equilibria in the binary system; or (2) this is estimated from fundamental considerations and correlations with other known phase stabilities, depending on characteristics, such as position in the Periodic Chart.

Generally, before proceeding with calculating a phase diagram, a solution model needs to be assumed for each solution phase appearing anywhere in the diagram, and the phase stabilities of the pure components of all participating phases.

In the following procedure, it is assumed that the standard state is the pure component in each phase. For example, for the $l \leftrightarrow s$ equilibrium in the AB system, a_A^l and a_B^l have the pure liquid A and pure liquid B as the standard states, respectively, and a_A^s and a_B^s have pure solid A and pure solid B as the standard states, respectively.

Here, we designate the (two) phases as $\phi_1 = l$ and $\phi_2 = s$, so the following two equations are solved for an equilibrium of two phases:

$$\Delta \mu_A^l = \Delta \mu_A^s + \Delta \mu_A^{o, l \to s}$$
And
$$\Delta \mu_B^l = \Delta \mu_B^s + \Delta \mu_B^{o, l \to s}$$

For the above two equations, T is specified and two of the four composition X_A^l, X_A^s, X_B^l and X_B^s variables are unknown, so there are zero degrees of freedom, and a unique solution.

For *Component A*, we have, on insertion for the activity, taking, say, X_A^l as one of the two composition variables ($X_B^l = 1 - X_A^l$) and taking X_A^s as the other composition variable ($X_B^s = 1 - X_A^s$):

$$\Delta \mu_A^l = \mu_A^l - \mu_A^{o,l} = RT \ln a_A^l = f(X_A^l)$$
$$\Delta \mu_A^s = \mu_A^s - \mu_A^{o,s} = RT \ln a_A^s = f(X_A^s)$$
And
$$\Delta \mu_A^{o,l \to s} = \mu_A^{o,s} - \mu_A^{o,l} = -\Delta \mathbf{G}_A^{\text{melting}} = -(\Delta \mathbf{G}_A^{\text{melting}} - \mathbf{T} \Delta \mathbf{G}_A^{\text{melting}})$$

For *Component B*, we have, on insertion for the activity, taking the same variables, X_A^l as one of the two composition variables $(X_B^l = 1 - X_A^l)$ and taking the same X_A^s as the other composition variable $(X_B^s = 1 - X_A^s)$:

$$\Delta \mu_B^l = \mu_B^l - \mu_B^{o,l} = RT \ln a_B^l = f(X_A^l)$$
$$\Delta \mu_B^s = \mu_B^s - \mu_B^{o,s} = RT \ln a_B^s = f(X_A^s)$$
And
$$\Delta \mu_B^{o,l \to s} = \mu_B^{o,s} - \mu_B^{o,l} = -\Delta G_B^{\text{melting}} = -(\Delta G_B^{\text{melting}} - T\Delta G_B^{\text{melting}})$$

In the above equations $f(X_A^l)$ and $f(X_A^s)$ are from a specific solution model of the integral (molar) free energy, such as the QC model, where, for i = A, B, and ϕ is l, s:

$$\begin{split} \mu_{i}^{\phi} - \mu_{i}^{o,\phi} &= \Delta G^{\phi} + \left(1 - X_{i}^{\phi}\right) \frac{\partial \Delta G^{\phi}}{\partial X_{i}^{\phi}} \bigg|_{i=A,B} \\ \text{Where (if QC model)} \\ \Delta G^{\phi} &= f(\Omega, T, X_{i}^{\phi}) \end{split}$$

The above set of equations is, in general, transcendental, and cannot be solved analytically. Today, it is easily solved using software for solving a system of equations numerically, such as an EXCEL macro.

Calculation of Binary Eutectic or Peritectic Equilibria

Consider the following figure (HIV.14) for the AB binary. In each case, we have an invariant equilibrium, where there are three phases in mutual equilibrium.



Figure HIV.14 – System of equations to be solved to calculate the invariant eutectic or peritectic equilibrium in the binary system.

Analytical Calculations of Binary Systems - Selected Cases

Analytical calculations of features in binary systems can be made for certain limiting cases. These are useful for seeing directly what controls the calculation.

Analysis of the Gibbs Free Energy of mixing for condensed phases (liquids and solids) reveals three limiting cases.

For such phases, we have:

$$\Delta G^{mix} = \Delta H^{mix} - T \Delta S^{mix}$$

- *Ideal Entropy of Mixing* In this case, $\Delta S^{mix} \rightarrow R(X_A \ln X_A + X_B \ln X_B)$. The enthalpy of mixing is still finite, as in a regular solution, where $\Delta H^{mix} = \Omega X_A X_B$.
- *Ideal Solution* In this case, $\Delta H^{mix} = 0$, but we still have $\Delta S^{mix} \rightarrow R(X_A \ln X_A + X_B \ln X_B)$. Unlike the following case, we still have intimate atomic (completely random) mixing.
- *Immiscible Solutions* Here, there is no intimate atomic mixing or interacting of the components, so all mixing is a mechanical mixture of phases of pure components, so that both the enthalpy and entropy of mixing are zero, so that $\Delta G^{mix} = \mathbf{0}$.

Case I - Ideal Solutions in Both Phases

Consider, say, the equilibrium between liquid and solid in the binary system, where both phases are ideal. We can write at T_1 :

$$\Delta \mu_A^l = \mu_A^l - \mu_A^{o,l} = RT \ln X_A^l$$
$$\Delta \mu_A^s = \mu_A^s - \mu_A^{o,s} = RT \ln X_A^s$$
$$\Delta \mu_B^l = \mu_B^l - \mu_B^{o,l} = RT \ln X_B^l$$
$$\Delta \mu_B^s = \mu_B^s - \mu_B^{o,s} = RT \ln X_B^s$$

This results in a liquidus and solidus that extends completely from one component to the other (i.e., complete miscibility). This is shown in Figure IV.15.



Figure HIV.15 – Schematic binary phase diagram that results if both condensed phases are ideal.

At equilibrium, the chemical potentials are equal, so we can write:

$$\mu_A^{o,l} + RT \ln X_A^l = \mu_A^{o,s} + RT \ln X_A^s$$
$$\mu_B^{o,l} + RT \ln X_B^l = \mu_B^{o,s} + RT \ln X_B^s$$

Thus, we have, on re-arranging:

$$RT_{1}\ln\frac{X_{A}^{s}}{X_{A}^{l}} = \mu_{A}^{o,l} - \mu_{A}^{o,s} = \Delta G_{A}^{melting} \Rightarrow \frac{X_{A}^{l}}{X_{A}^{s}} = \exp{-\frac{\Delta G_{A}^{melting}}{RT_{1}}}$$
$$RT_{1}\ln{\frac{1-X_{A}^{s}}{1-X_{A}^{l}}} = \mu_{B}^{o,l} - \mu_{B}^{o,s} = \Delta G_{B}^{melting} \Rightarrow \frac{1-X_{A}^{l}}{1-X_{A}^{s}} = \exp{-\frac{\Delta G_{B}^{melting}}{RT_{1}}}$$

Solving for X_A^l and X_A^s gives the following equations:

$$X_{A}^{s} = \frac{1 - \exp\left(-\frac{\Delta G_{B}^{melting}}{RT_{1}}\right)}{\exp\left(-\frac{\Delta G_{A}^{melting}}{RT_{1}}\right) - \exp\left(-\frac{\Delta G_{B}^{melting}}{RT_{1}}\right)}$$
$$X_{A}^{l} = \frac{\left[1 - \exp\left(-\frac{\Delta G_{B}^{melting}}{RT_{1}}\right)\right] \left[\exp\left(-\frac{\Delta G_{A}^{melting}}{RT_{1}}\right)\right]}{\exp\left(-\frac{\Delta G_{A}^{melting}}{RT_{1}}\right) - \exp\left(-\frac{\Delta G_{B}^{melting}}{RT_{1}}\right)}$$

Compositions for the liquidus and solidus are thus obtained for this limiting case analytically, by the above equations for each temperature specified. Systematic variation of the temperature generates the entire liquidus and solidus.

Note that for this special case – where both phases of the two-phase equilibrium are ideal – that the shape of both the liquidus and the solidus is controlled directly by $\Delta G_i^{melting}$, or, assuming $\Delta S_i^{melting} \approx \Delta H_i^{melting}/T_i^{mp}$, by $\Delta H_i^{melting}$ and T_i^{mp} .

Case II – Complete Miscibility in One Phase and Complete Immiscibility in the Other Phase

Here, we want to calculate γ_i^{ϕ} from the two-phase equilibrium in a binary system, or vice-versa. Consider the liquid-solid equilibrium for this case, where the liquid phase is completely miscible in A and B, but the two eutectic solid phases are completely immiscible (in which case, the two solid phases are essentially pure A and pure B). This is shown schematically in Figure HI.16.



Figure IV.16 – Binary eutectic phase diagram for complete miscibility in the liquid phase, but complete immiscibility for the solid phases.

At T_1 , we have the following set of equations:

$$\Delta \mu_A^l = \mu_A^l - \mu_A^{o,l} = RT_1 \ln a_A^l$$
$$\Delta \mu_A^\alpha = \mu_A^\alpha - \mu_A^{o,\alpha} = RT_1 \ln a_A^\alpha = RT_1 \ln 1 = 0 \Rightarrow \mu_A^\alpha = \mu_A^{o,\alpha}$$

At equilibrium, we have:

 $\boldsymbol{\mu}_A^l = \boldsymbol{\mu}_A^\alpha$

$$\mu_A^{o,l} + RT_1 \ln a_A^l = \mu_A^{o,\alpha} \Rightarrow$$

$$-RT_1 \ln a_A^l = \mu_A^{o,l} - \mu_A^{o,\alpha} = \Delta G_A^{melting} - RT_1 \ln(\gamma_A^l X_A^l)$$

Finally, on re-arranging, we get:

$$RT_1\ln(\gamma_A^l) = -\Delta G_A^{melting} - RT_1\ln(1 - X_B^l)$$

In the above equation, both $\Delta G_A^{melting}$ and X_B^l are functions of T_1 , so given X_B^l , γ_A^l is calculated at that temperature, or vice-versa.

Case III – Calculation of the Eutectic Temperature for Case II, but Assuming Ideal Liquid Phase

Figure HIV.17 illustrates the phase diagram for this case.



Figure IV.17 - Binary eutectic phase diagram for complete ideality in the liquid phase, but complete immiscibility for the solid phases.

Case IV – Calculation of the Henrian Coefficient From the Two-Phase Equilibrium in the Binary System

This is the situation, where, if the solubility is sufficiently dilute for the dilute phase, and if the other phase is essentially pure (i.e., the two phases are almost immiscible), then the Henrian coefficient for the dilute phase can be calculated. This situation is illustrated schematically in Figure HIV.18.



Figure HIV.18 – The α - β equilibrium in the AB binary system, with limited solubility of B in α and β being essentially pure B, allowing calculation of the Henrian coefficient for the dilute solubility of B in the α -phase.

The key assumptions are that α is dilute in Solute B, and that For Solute B on the α -side of the phase diagram (where γ_B^o is the Henrian coefficient): is essentially pure B.

For Solute B on the α -side of the phase diagram (where γ_B^o is the Henrian coefficient):

$$\mu_B^{\alpha} = \mu_B^{o,\beta} + RT \ln a_B^{\alpha,relative to pure B in the \beta-phase} \Rightarrow \mu_B^{o,\beta} + RT \ln \gamma_B^o X_B$$

For Solute B on the β -side of the phase diagram (where β is taken to be pure B):

$$\mu_B^\beta = \mu_B^{o,\beta} + RT \ln a_B^{\beta,relative to pure B in the \beta-phase} \Rightarrow \mu_B^{o,\beta} + RT \ln X_B$$

Thus, we have, on setting equal chemical potentials (noting the same standard states for the activity of B in either phase):

$$\mu_B^\alpha = \mu_B^\beta$$

$$\mu_{B}^{o,\beta} + RT \ln \gamma_{B}^{o} X_{B}^{\alpha \ (at \ saturation)} = \mu_{B}^{o,\beta} + RT \ln X_{B}^{\beta \ (at \ saturation)} \Rightarrow$$

$$RT\ln\gamma_B^o = RT\ln\frac{X_B^{\beta\ (at\ saturation)}}{X_B^{\alpha\ (at\ saturation)}} \Rightarrow$$

$$\ln \gamma_B^o = \ln \frac{X_B^{\beta \ (at \ saturation)}}{X_B^{\alpha \ (at \ saturation)}}$$

Role of the Solution Parameter *Q* in Shaping the Phase Diagram

If we assume regular solution behavior in the liquid in the AB binary system, we have:

$$-\Delta G_A^{melting} = RT \ln X_A^l + \Omega \left(1 - X_A^l\right)^2$$

Of interest is the role of increasing parameter Ω from, say, zero (i.e., the ideal solution). For this analysis, we need to specify $\Delta G_A^{melting}$. Consider a hypothetical system, where $\Delta H_A^{melting} = 10$ KJ, and $T_A^{mp} = 2000$ °K. Then, we have:

$$-10000 + 5T = RT \ln X_A^l + \Omega (1 - X_A^l)^2$$

2

This is illustrated in Figure HIV.19.



Figure HIV.19 – The liquidus of a hypothetical system, where $\Delta H_A^{melting} = 10$ KJ, $T_A^{mp} = 2000 \text{ }^{\circ}\text{K} \text{ and } \Omega \ge \mathbf{0}.$

An inflexion is seen in this liquidus; this occurs when the second and third derivatives of the integral free energy of mixing is zero:

$$\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B) + RT\alpha X_A X_B$$

$$\frac{\partial \Delta G^{mix}}{X_B} = RT \left[\ln \frac{X_B}{X_A} + \alpha (X_A - X_B) \right]$$

$$\frac{\partial^2 \Delta G^{mix}}{X_B^2} = RT \left[\frac{1}{X_A} + \frac{1}{X_B} - 2\alpha \right]$$
$$\frac{\partial^3 \Delta G^{mix}}{X_B^3} = RT \left[\frac{1}{X_A^2} - \frac{1}{X_B^2} \right]$$

The third derivative can equal zero only at $X_A = X_B = 0.5$. Thus, from the second derivative, $\alpha = 2$. Therefore, the value for , above which phase separation must occur is:

$$\Omega = RT\alpha \Rightarrow$$
$$T^{critical} = \frac{\Omega^{critical}}{2R}$$

For the hypothetical system A-B considered, $\boldsymbol{\Omega}^{critical} = 25.3 \text{ KJ} \Rightarrow T^{critical} = 1413 \text{ }^{\circ}\text{K}.$

The following phase diagram (Figure HIV.20) is for the hypothetical system, where $\Omega > \Omega^{critical} = 30$ KJ.



Figure HIV.20 – Hypothetical phase diagram for regular solution parameter $\boldsymbol{\Omega} > \boldsymbol{\Omega}^{critical} = 30$ KJ.

It is seen that the liquidus curve changes into an immiscibility gap – where two liquids, each at a different composition, are in equilibrium, depending on temperature. The phase separation begins at $T^{critical} = 1804$ °K. At the monotectic temperature (1640 °K), we have $l_1 \rightarrow A + l_2$.

The following figure (HIV.21) shows how features of the phase diagram change as values for regular solution parameters $\boldsymbol{\Omega}$ for the liquid and for the solid phases change in a systematic way.



Figure HIV.21 – Calculated series of binary phase diagrams for a systematic chance in regular solution parameter Ω for each of the two phases (here, liquid and solid phases).

Finally, Figure HIV.22 shows examples of how features of the phase diagram change as ΔH^l and ΔH^{α} change systematically.



Figure HIV.22 – Example of how features of the calculated binary phase diagram change as ΔH^l and ΔH^{α} are changed systematically.

TOPOLOGY OF TERNARY AND HIGHER-ORDER PHASE DIAGRAMS

Because of the nature of mole fractions totally unity, $X_A + X_B + X_C = 1$ for the ternary system, it is convenient to represent its co-ordinates as the vertices of an equilateral triangle, the so-called *Gibbs Triangle*. This is in contrast to the perpendicular axes used normally for three variables. Figure HIV.23 illustrates the relationship between the Gibbs Triangle and the Cartesian co-ordinates x-y-z. In the Gibbs triangle, all three compositions can be read directly, as $X_A + X_B + X_C = 1$ at all times.



Figure HIV.23 – The Gibbs triangle used to represent composition of the ternary system in relation to Cartesian co-ordinates.

As one might expect, since the limiting boundaries of the Gibbs Triangle are the three binary systems that make up the ternary system, any equilibria existing in the

binary systems at a given temperature must extend into the ternary system. A tieline in a binary system at constant temperature (and constant pressure) becomes a continuum of tie-lines in the Gibbs Triangle because there is now an additional degree of freedom, afforded by the third component.

The Lever Rule, previously introduced for the two-phase equilibrium in the binary system, applies as well in the Gibbs Triangle. Figure HIV.24 shows one of a continuum of tie-lines in the Gibbs Triangle.



Figure HIV.24 – Application of the Lever Rule to a tie-line of an equilibrium between two phases in the Gibbs Triangle.

Consider a mixture of phases whose compositions are represented by Points p and q in the Gibbs Triangle of Figure HIV.24. The fraction of phase of composition p, and the fraction of phase of composition q are:

$$f_p = rac{rq}{pq}$$
 and $f_q = rac{pr}{pq}$

The distances r-q, p-r and p-q can be conveniently measured/read directly in the Gibbs Triangle, which is, of course, convenient. In point of fact, the fractions f_p and f_q can also be calculated from the prevailing mass balances for a specified total composition $X^o = r$ as discussed earlier.

The Isomorphous Ternary System

Figure IV.25 shows the simplest two-phase equilibrium in the ternary system, analogous to the isomorphous binary system exhibiting complete solubility in both the phases (here, liquid and solid) across the Gibbs Triangle.



Figure IV.25 – The simplest two-phase equilibrium in the ternary system, where each phase has complete solubility in the Gibbs Triangle.

It is instructive to apply the Gibbs Phase Rule (GPR) to all regions of this Gibbs Triangle. Generally, in the ternary system (at constant pressure, P), we have:

$$F=3-\wp+1=4-\wp$$

In this equation, F are the degrees of freedom, and \wp is the number of phases. For the liquid or solid primary (or, single) phase fields, $\wp = 1$, thus, F = 3. If we now fix temperature, then we reduce the degrees of freedom to two. This means that two of the compositions have to be specified (the third composition specified by distance) to completely specify the system, in this case, the location in the primary phase field.

It is clear, extending the above logic, that in the two-phase equilibrium field, the number of phases is increased to two, so that, at constant T, P, the degrees of freedom is now reduced to *one*, meaning one of the six compositions representing each tie-line has to be specified to specify one of the continuum tie-lines of the equilibrium.

As discussed earlier, the Gibbs Phase Rule is none other than the criterion guaranteeing a solution to the system of equations of governing the equilibrium with more than one coexisting phases. Thus, for the two-phase field in the Gibbs Triangle, represented by a continuum of tie-lines, each tie-line is calculated at a specified temperature *and* one of the six composition variables, viz.:

 $\Delta \mu_A^l = \Delta \mu_A^s + \Delta \mu_A^{o,l \to s} = f(X_A^l, X_A^s)$ $\Delta \mu_B^l = \Delta \mu_B^s + \Delta \mu_B^{o,l \to s} = f(X_B^l, X_B^s)$ $\Delta \mu_C^l = \Delta \mu_C^s + \Delta \mu_C^{o,l \to s} = f(X_C^l, X_C^s)$ $X_A^l + X_B^l + X_C^l = 1$ And

$$X_A^s + X_B^s + X_C^s = 1$$

The above system of equations consists of five independent equations (of which three are statements of equal chemical potentials for each of the three components, and two are mass balance equations, one for each phase). However, there are six independent composition variables, so that any *one* of these can be specified to arrive at a unique solution.

So, it should be clear exactly how a the continuum of tie-triangles of a particular equilibrium *at a particular temperature* is generated by calculation – one for each stepwise increment in a composition variable beginning just inside the Gibbs Triangle of one of the binary systems exhibiting the two-phase equilibrium, and exiting the Gibbs

Triangle in one of the other two binary systems, where the two-phase equilibrium is stable. The procedure is repeated for another selected temperature, and so on. This is shown graphically in Figure HIV.26.



Figure HIV.26 – Illustration of the calculation of a continuum of tie-lines of a two-phase equilibrium in a ternary system, by systematically varying one of six composition variables (here, $X_A' = X_A^l \text{ or } X_A^s$) across the Gibbs Triangle for selected temperatures T_1 (a) and T_2 (b).

A very useful diagram results, if the primary phase field, such as a liquidus or solidus – which is a line at constant T,P, but becomes a surface in the Gibbs Triangle when temperature is relaxed – is projected over a range of temperatures onto the basal plane of the Gibbs Triangle (called a *liquidus*, or *solidus* projection). Such a projection is shown in depicted in Figure HIV.27. While information from multiple diagrams is collapsed onto one diagram for such a projection, what is lost is the full tie-line, because only one of the co-ordinates of the tie-line is retained in the projection.



Figure HIV.27 – Example of projection of a primary phase field (here, a liquidus) that exists over a range of temperatures, onto the basal plane of the Gibbs Triangle.

The Three-phase Ternary Equilibrium

When there are three co-existing phases in the ternary system, we have from the GPR, at constant pressure:

$$F = 3 - \wp + 1 = 3 - 3 + 1 = 1$$

If we fix temperature (pressure already is fixed), then we have zero degrees of freedom; this means we have only one unique set of compositions of the three phases of this particular equilibrium. Such a set of unique compositions in the Gibbs Triangle is the *tie-triangle*. The sides of the tie-triangle representing the three-phase equilibrium can be thought of a set of tie-lines for each of the three sub-sets of two-phase equilibria of the three-phase equilibrium. Similarly, the three-phase equilibrium in the binary system (such as at the eutectic/oid, or peritectic/oid temperature) can also be thought of as a *collapsed* tie-triangle, which, then expands into a tie-triangle – one for each temperature – in the ternary system. It is calculated in the ternary system by specifying only temperature (constant pressure already assumed), whence the system of nine equations (three components, three phases) can be solved for a unique solution without specifying any of

the nine composition variables. As temperature is systematically varied, the continuum of tie-triangles in the Gibbs Triangle is generated by this calculation.

The Lever Rule is equally applicable to the three-phase equilibrium in the Gibbs Triangle. The amount of each of the three phases can be calculated when the vertices (i.e., compositions) of each of the three phases is known, as well as the overall composition of the system of three phases. This is illustrated in Figure HIV.28, where f_{α} , f_{β} and f_l can be determined, knowing the positions in the Gibbs Triangle of the vertices *R*, *S* and *L*, and overall composition Point *P*.



Figure HIV.28 – Determination of fractional amounts of each of the three phases of the mutual equilibrium in the Gibbs Triangle from application of the Lever Rule, where $\mathbf{R} = \boldsymbol{\alpha}$ and $\mathbf{S} = \boldsymbol{\beta}$.

There three ways to do this calculation:

- 1. The easiest way to perform this calculation is to read the actual distances directly in the Gibbs Triangle to arrive at the relative distances. For example, for calculating the fractional amount of the α -phase, $f_{\alpha} = PQ/SQ$. This can be done without having to identify numerically any of the compositions of the vertex or overall composition Point P, and the distances can be read off a ruler.
- 2. A far more cumbersome procedure is to work numerically with the actual compositions in the Gibbs Triangle for *R*, *S*, *L*,*P*, etc. to determine the distances between each point in the Gibbs Triangle, so that the relative proportions could

then be determined – this is totally unnecessary, as in the end, the relative distances can be read anyway from the tie-triangle in the Gibbs Triangle without working with the actual numerical values for each point.

3. Finally, since the LR is just a manifestation of the prevailing mass balances, the fractions f_{α} , f_{β} and f_l are determined by solving the system of equations of the appropriate mass balances; i.e., the mass balances of composition of each component for each phase, and the mass balance among the phases for each component. In this procedure, the calculations are done without recourse to the Gibbs Triangle, other than reading the composition for the vertex corresponding to each phase, and Point *P* if is not already given:

$$X_{i=1,2...N}^{o} = \sum_{\phi=1}^{S} f^{\phi} X_{i=1,2,...N}^{\phi}$$
$$\sum_{i=1}^{N} X_{i}^{o} = 1$$
$$\sum_{i=1}^{N} X_{i}^{\phi} = 1; \phi = 1, 2 \dots S$$
And
$$\sum_{\phi=1}^{S} f^{\phi}$$

Clearly, as with tie-lines, the tie-triangle obeys certain rules that become obvious when calculated: it must be isothermal; they never intersect each other, and it collapses into the three-phase conjugal tie-lines of the binary, three-phase equilibrium on reaching one of the limiting binary systems.

Topology of the Ternary Phase Diagram

Figure HIV.29 shows a schematic example of the ternary system, whose limiting binary systems consists of one isomorphous system and two eutectic systems. Between the two binary systems in the Gibbs Triangle is a continuum of tie-triangles, one for each temperature. This begins at the eutectic temperature in AB binary system, proceeds to

map out the continuum of tie-triangles in the Gibbs Triangle, then exits as a co-incidental tie-lines at the lower eutectic temperature in the AB binary system.



Figure HIV.29 – The three-phase equilibrium in a simple ternary system, consisting of one isomorphous binary and two eutectic binary systems. The three-phase equilibrium begins at the eutectic temperature in the AB system, traverses the Gibbs Triangle as a continuum of tie-triangles, then exist at the lower eutectic temperature in the CB system.

The following figure (HIV.30) is an *exploded* model, where the topological features of each of the fields of stability are shown schematically. While such a diagram is of limited practical use, it does help with understanding the relationship among the various fields to each other.



Figure HIV.30 – Exploded model of the diagram shown in Figure HIV.29.

More useful is the isothermal section, such as shown in Figures HIV.31 and HIV.32 for the same diagram as shown in Figure HIV.29.



Figure HIV.31 – Spatial diagrams showing selection of isotherms T_1 through T_5 of the ternary system shown in Figure HIV.29. Isothermal sections in the Gibbs Triangle are shown in Figure HIV.32.



Figure HIV.32 – Isothermal sections in the Gibbs triangle corresponding to temperatures selected in Figure HIV.31.

Another example of the three-phase equilibrium, but emanating from peritectic equilibria in two of the binaries is shown in Figure HIV.33. Again, we have a continuum of tie-triangles for the three-phase equilibrium in the ternary system, one for each temperature.



Figure HIV.33 – A simple ternary system with a peritectic three-phase equilibrium initiating in the AB system at the binary peritectic temperature, and exiting the ternary system in the CB system at the binary peritectic temperature.

The Ternary Four-Phase Equilibrium

The four-phase can occur in the ternary system when at least one binary system has a eutectic/oid reaction, the others having the peritectic/oid reaction. According to the phase rule, the co-existence of four phases in the ternary system (at constant pressure) can occur at only one (unique) temperature, in which case, the degrees of freedom is zero; viz.: $F = 3 - \wp + 1 = 3 - 4 + 1 = 0$. This means no variable needs to be specified, including temperature, because this equilibrium occurs at one and only one temperature. Figure HIV.34 illustrates this equilibrium in a ternary system.



Figure HIV.34 – Example of the four-phase equilibrium in the ternary system, where the temperatures correspond to the isothermal sections in Figure HIV.32.

It is noted that such an equilibrium requires at least one binary eutectic/oid system, the other two being eutectic/oid, eutectic and peritectic/oid, or both peritectic/oid systems. In Figure HIV.34, it is seen that at the unique ternary eutectic temperature (which is the lowest temperature where liquid is stable) the three sets of tri-triangles emanating from each of the three eutectic equilibria in the binary systems become co-incident and touch at this temperature at the Ternary Eutectic Point in the diagram. Immediately below this temperature, the equilibrium is back to a tie-triangle consisting for the equilibrium among the three solid phases. Figure HIV.35 is an exploded model corresponding to the ternary system depicted in Figure HIV.34.



Figure HIV.35 – Exploded model of ternary system with a four-phase equilibrium shown in Figure HIV.34

Quaternary and Higher-order Systems

It is abundantly clear that visualization of equilibria beyond three components quickly stretches the imagination. Nevertheless, the process of depicting the multi-component phase diagram has its internal logic emanating from the lower-order systems. The compositional phase diagram (constant T and P) is represented by equilateral (Gibbs) polyhedrea. In turn, the equilibria depicted in the polyhedrea has a systematic consistency: each additional component adds another dimension to this representation. For example, the liquidus, which is a point in the binary system, becomes a line in the Gibbs Triangle for the ternary system, a surface in the four-component system, a volume in the five-component system, and so forth.

Figure HIV.36 gives the polyhedrea for up to five components.



Figure HIV.36 – The equilateral polyhedrea used to represent compositions up to five components (constant *T* and *P*).

The structural element that depicts the conjugate compositions of a multi-phase equilibrium in the equilateral polyhedrea is called the *hyper-conode*. These are depicted in Figure HIV.37. For the ternary system, up to three of these are employed: the tie-line, the tie-triangle and the tie-tetrahedron, the latter being collapsed into four co-incident tie-triangles for the four phase equilibrium occurring at one temperature.



Figure HIV.37 – The hyper-conodes used to depict the conjugate compositions of multiphase equilibria.

To include, say, temperature in the depiction of the equilibria, of course, requires another dimension. The technique of polythermal projection is employed to get a representation in two- or three- dimensional space. By this is meant depicting the temperature – composition relationships onto one of the limiting planes of the polyhedrea, for example, projection of the liquidus of a quaternary system onto one of the limiting ternary systems. While visualization of such diagrams can be exceedingly difficult, they produce diagrams that are rather beautiful in themselves, but, are also full of meaning, and can be understood by following the equilibria from the limiting systems into the higher-order system. As the number of components become larger, tracking equilibria, for example, to assist in understanding compositional changes during, say, solidification, is best done by a computer program, where the depiction in a traditional diagram format becomes essentially meaningless. The following figures (HIV.38 and HIV.39) are just two examples of polythermal projection from a quaternary system onto the limiting ternary systems.



Figure HIV.38 – Polythermal projection of the four-phase equilibrium of the type $l \rightarrow \alpha + \beta + \gamma$ in the quaternary system on to the surfaces of the limiting ternary Gibbs triangles of a quadrahedron.



Figure HIV.39 – Polythermal projection of the Bi-Cd-Pb-Sn quaternary system with a five-phase equilibrium of the type $l \rightarrow \alpha + \beta + \gamma + \delta$.