

Chapter 4

Solution Theory

In the first chapters we dealt primarily with closed systems for which only heat and work is transferred between the system and the environment. In this chapter, we study the thermodynamics of systems that can also exchange matter with other systems or with the environment, and in particular, systems with more than one component. First we focus on homogeneous systems called solutions. Next we consider heterogeneous systems with emphasis on the equilibrium between different multi-component phases.

4.1 WHAT IS A SOLUTION?

A *solution* in thermodynamics refers to a system with more than one chemical component that is mixed homogeneously at the molecular level. A well-known example of a solution is salt water: The Na^+ , Cl^- and H_2O ions are intimately mixed at the atomic level. Many systems can be characterized as a dispersion of one phase within another phase. Although such systems typically contain more than one chemical component, they do not form a solution. Solutions are not limited to liquids: for example air, a mixture of predominantly N_2 and O_2 , forms a *vapor* solution. *Solid* solutions such as the solid phase in the Si-Ge system are also common. Figure 4.1. schematically illustrates a binary solid solution and a binary liquid solution at the atomic level.

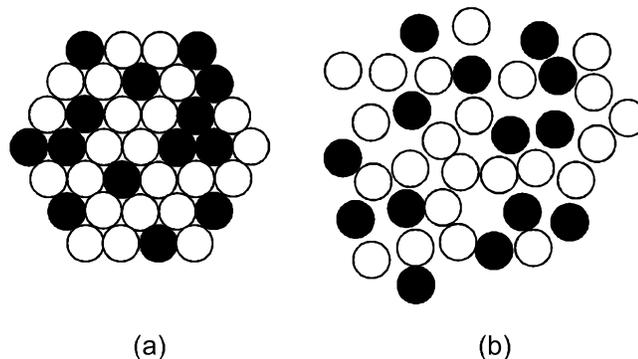


Figure 4.1: (a) The (111) plane of the fcc lattice showing a cut of a binary A-B solid solution whereby A atoms (empty circles) are uniformly mixed with B atoms (filled circles) on the atomic level. (b) A two-dimensional cut through a binary liquid solution showing a uniform distribution of A and B atoms on the atomic level.

To characterize a solution, it is necessary to introduce variables specifying the composition of the different chemical components of the solution. Several composition variables are often used, each having particular advantages in different applications. The first composition variables of importance are the **mole numbers**. For a system with N components, we will refer to the number of moles of each component i as n_i . When specifying the composition of a multi-component system in a phase diagram, more practical composition variables are **mole fraction** and **weight fraction**. The mole fraction of component i , denoted by x_i , refers to the number of mole n_i of i in the solution divided by the total number of mole n_{tot} in the solution. Similarly, the weight fraction, w_i , of component i is the ratio of the weight of component i , W_i , in solution to the total weight of solution, W_{tot} . Weight fractions are often used in practical applications, where a mixture having a particular weight fraction can easily be prepared by weighing the pure components before mixing them. Mole fractions are useful when viewing the solution within a theoretical framework where details of the solution at the atomic level become important. Closely related to mole fraction is the **atomic percent** of component i which is often denoted by $(at\%)_i$ and equals 100 times the mole fraction x_i . A fourth important composition variable is the **concentration** C_i of component i , defined as the number of moles of i divided by the volume V of the solution. This variable is often implemented in the study of irreversible processes, since the concentration is a natural variable in Fick's differential equations describing diffusion. As an overview, the four concentration variables are summarized in table 1.

Mole Fraction:	$x_i \equiv \frac{n_i}{n_{tot}}$	with	$n_{tot} = \sum_i n_i$
Atomic Percent:	$(at\%)_i \equiv 100\% \times x_i$		
Weight Fraction:	$w_i \equiv \frac{W_i}{W_{tot}}$	with	$W_{tot} = \sum_i W_i$
Concentration:	$C_i = \frac{n_i}{V}$	or sometimes	$C_i = \frac{W_i}{V}$

Table 1: Definitions of important composition variables in solutions.

4.2 PARTIAL MOLAR QUANTITIES

In previous chapters, we saw that the state of a single phase, single component system that is subjected to only P - V work is completely specified once two independent variables such as P and T are fixed. Thermodynamic variables such as the equilibrium volume V or the Gibbs free energy G are then uniquely determined once particular values of P and T have been imposed on the system and we sometimes remind ourselves of this functional dependence by explicitly writing the volume as $V(T,P)$ and the Gibbs free energy as $G(T,P)$.

In solutions, this functional dependence is no longer complete. A multi-component system subjected to only P - V work has added degrees of freedom due to the fact that we can change its composition. To fully characterize the equilibrium state of a multi-component system, it is therefore necessary to also specify, in addition to P and T , the number of moles n_i of the different components i in the solution. Now the equilibrium volume of the solution should be written as $V(P,T,n_1, \dots, n_N)$ and the Gibbs free energy as $G(P,T,n_1, \dots, n_N)$, where n_i , $i=1, \dots, N$, denotes the number of moles of each of the N components of the solution.

As a result of the added dependence on n_i , the perfect differential of thermodynamic quantities like V and G take the forms

$$dV = \left(\frac{\partial V}{\partial T} \right)_{P, n_i} dT + \left(\frac{\partial V}{\partial P} \right)_{T, n_i} dP + \sum_i \left(\frac{\partial V}{\partial n_i} \right)_{P, T, n_{j \neq i}} dn_i \quad (1)$$

and

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_i} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_i} dP + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{P, T, n_{j \neq i}} dn_i. \quad (2)$$

The subscripts n_i on the partial derivatives indicate that the number of moles of all components is kept constant. Expressions for the partial derivatives with respect to T and P follow from the results obtained for closed systems. Indeed, if we impose the constraint that the multi-component system is closed, it cannot exchange matter with the environment and the dn_i are all zero. Then the differential expressions for V and G reduce to those for closed systems studied in previous chapters and the partial derivatives with respect to T and P become by comparison

$$\begin{aligned} \left(\frac{\partial V}{\partial T} \right)_{P, n_i} &= V\alpha & \left(\frac{\partial V}{\partial P} \right)_{T, n_i} &= -V\beta \\ \left(\frac{\partial G}{\partial T} \right)_{P, n_i} &= -S & \left(\frac{\partial G}{\partial P} \right)_{T, n_i} &= V \end{aligned}$$

where α is the thermal expansion coefficient and β is the isothermal coefficient of compressibility.

Of central importance in the study of solutions are the partial derivatives with respect to the n_i . These partial derivatives measure the variations of extensive thermodynamic properties as chemical components are added or removed from the system. We call these partial derivatives **partial molar quantities**. In general, the partial molar quantity of the extensive variable Y with respect to component i , is denoted by the symbol \bar{Y}_i . The partial molar volume for example is then written as

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_{j \neq i}} \quad (3)$$

This is the partial derivative of V with respect to n_i holding constant T , P and the number of moles of all other components j not equal to i . One exception to this notation is the partial molar quantity of thermodynamic potentials such as the Gibbs free energy. These are referred to as **chemical potentials** and are denoted by

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} \quad (4)$$

Putting everything together, the perfect differentials (1) and (2) become

$$dV = \alpha V dT - \beta V dP + \sum_i \bar{V}_i dn_i$$

$$dG = -S dT + V dP + \sum_i \mu_i dn_i.$$

At constant T and P , a partial molar quantity measures the amount by which the extensive thermodynamic quantity changes when an infinitesimal amount of a particular component is added or removed from the solution. For example, we may be interested to know how much the volume of ferritic steel (primarily iron in a bcc structure with a dilute composition of carbon residing in the interstitial sites) changes when the carbon composition is increased. Under typical circumstances, where T and P are the controlling variables, the volume of a block of steel in equilibrium will depend on T , P , n_{Fe} and n_C . Working at constant T and P and keeping the amount of iron fixed, the change of volume of the steel when an amount dn_C of carbon is added is simply

$$dV = \bar{V}_C \cdot dn_C.$$

Carbon is a small atom in comparison to iron, and furthermore it resides in interstitial sites while iron forms the substitutional framework of the bcc structure. This knowledge about the atomic structure of the solid already gives us an important clue that \bar{V}_C will be smaller than \bar{V}_{Fe} since addition of iron extends the frame-work of the bcc crystal while

carbon simply fills some of the numerous open spaces already present within the structure. (figure 4.2.) While in general, partial molar volumes are positive, many examples exist where the partial molar volume is actually negative. Addition of a component with a negative partial molar volume causes the solution to shrink. This happens for example in $\text{Li}_{0.5}\text{CoO}_2$ where addition of Li results in a reduction of the volume of the crystal.

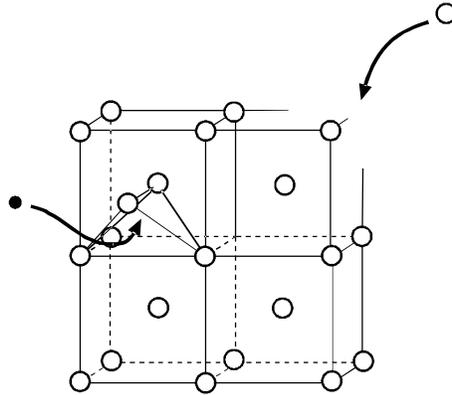


Figure 4.2: In steel, Fe (large empty circles) forms a bcc crystal structure and C (small filled circle) resides in the interstitial sites. The partial molar volume of Fe is larger than that of C because the former extends the bcc crystal structure while the latter fills empty interstitial space.

4.3 PROPERTIES OF EXTENSIVE QUANTITIES

Experimental observation has established that thermodynamic quantities such as a system's volume V , enthalpy H , and Gibbs free energy G are extensive properties, that is they are proportional to the size of the system. For example, doubling the number of moles of each component results in the doubling of the equilibrium volume of the system. The same holds for other extensive quantities like H , S , G , etc. In general, if we increase the number of moles of each component by a factor λ at constant T and P the following relation can be written for any extensive quantity Y

$$Y(\lambda n_1, \lambda n_2, \dots, \lambda n_N) = \lambda Y(n_1, n_2, \dots, n_N) \quad (5)$$

(We have omitted the explicit dependence of Y on T and P because we are assuming them fixed). The fact that extensive quantities are state functions that satisfy equation (5) has two important implications. First it leads, as will be shown below, to an important relation between an extensive quantity and its partial molar quantities, namely that

$$Y = \sum_i n_i \bar{Y}_i \quad (6)$$

at constant T and P . Secondly it leads to the Gibbs-Duhem relation which is useful in surface thermodynamics and in applications involving ionic diffusion in non-homogenous solutions.

To derive equation (6), we start by setting $v_i = \lambda n_i$. Differentiating equation (5) with respect to λ yields

$$\sum_{i=1}^N \frac{\partial Y(v_1, v_2, \dots, v_N)}{\partial v_i} \cdot \frac{\partial v_i}{\partial \lambda} = \lambda Y(n_1, n_2, \dots, n_N)$$

or

$$\sum_{i=1}^N n_i \cdot \frac{\partial Y(\lambda n_1, \lambda n_2, \dots, \lambda n_N)}{\partial (\lambda n_i)} = \lambda Y(n_1, n_2, \dots, n_N)$$

Noting that the operation $\partial Y / \partial v_i$ is equivalent to $\partial Y / \partial n_i$ we obtain after setting $\lambda=1$

$$\sum_{i=1}^N n_i \cdot \frac{\partial Y(n_1, n_2, \dots, n_N)}{\partial n_i} = Y(n_1, n_2, \dots, n_N)$$

which, when using the definition of partial molar quantities, reduces to equation (6). For the volume V of a multi-component solution, equation (6) becomes

$$V = \sum_{i=1}^N n_i \cdot \bar{V}_i \quad (7)$$

while for the Gibbs free energy, equation (6) becomes

$$G = \sum_{i=1}^N n_i \cdot \mu_i \quad (8)$$

Equation (6) (along with equations (7) and (8)) shows that partial molar quantities are not only useful to indicate how extensive properties change with variations in composition, but can also be used to describe the total value of the extensive property.

An additional thermodynamic relation, often referred to as the Gibbs-Duhem equation, can be obtained by taking the total differential of equation (6) at constant T and P . This yields

$$\sum_{i=1}^N \left(\frac{\partial Y}{\partial n_i} \right)_{T, P, n_{j \neq i}} dn_i = \sum_{i=1}^N n_i d\bar{Y}_i + \sum_{i=1}^N \bar{Y}_i dn_i$$

which can be rewritten as

$$\sum_{i=1}^N \bar{Y}_i dn_i = \sum_{i=1}^N n_i d\bar{Y}_i + \sum_{i=1}^N \bar{Y}_i dn_i$$

Canceling like terms we obtain the Gibbs-Duhem relation

$$\sum_{i=1}^N n_i d\bar{Y}_i = 0 \quad (9).$$

The Gibbs-Duhem relation for the Gibbs free energy becomes

$$\sum_{i=1}^N n_i d\mu_i = 0 \quad (10).$$

This equation states that not all chemical potentials can be varied independently. In a binary solution for example,

$$n_A d\mu_A + n_B d\mu_B = 0.$$

Hence a variation of μ_A by $d\mu_A$ causes μ_B to change by

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A = -\frac{x_A}{x_B} d\mu_A \quad (11)$$

Equation (11) also shows that if the chemical potential of one of the components in a binary solution is known as a function of composition it is possible to obtain the chemical potential of the other component by integration. The integral, though, is not straightforward since it extends from $\mu_A = -\infty$ when $x_A=0$ and diverges as x_B approaches zero (see for example “Chemical Thermodynamics of Materials” by C. H. P. Lupis for more details).

4.4. QUANTITIES OF MIXING

Partial molar quantities tell us how a thermodynamic property of a solution changes when adding or removing an infinitesimal amount of a given chemical component. Often, though, we are also interested in the change of thermodynamic quantities when going from the unmixed state to the mixed state. For example, it may be important to know by how much the volume of a binary solution differs from the combined volumes of the two chemical species before they are mixed. This difference in

volume is called the *volume of mixing*. We may also want to know by how much the enthalpy changes of a binary solution when going from the unmixed state to the mixed state. As was shown in a previous chapter, the change in enthalpy at constant T and P associated with an irreversible change of state (such as mixing) is equal to the heat exchanged between the system and the environment. Hence, the *enthalpy of mixing* at constant T and P tells us how much heat will be released or absorbed when combining chemical species.

Before, further specifying quantities of mixing, it is useful to introduce the concept of *molar quantities*. A molar quantity refers to an extensive thermodynamic variable that has been divided by the total number of moles in the system. The molar quantity associated with the extensive variable Y is denoted by \underline{Y} and is given by

$$\underline{Y} = \frac{Y}{n_{tot}} \quad (12)$$

where n_{tot} is the total number of moles in the system. For binary systems, molar quantities are often plotted as a function of the mole fraction x_i of one of the two components. This is illustrated in figure 4.3 where the molar volume of a binary mixture of Ti and Al is plotted as a function of the Al mole fraction x_{Al} .

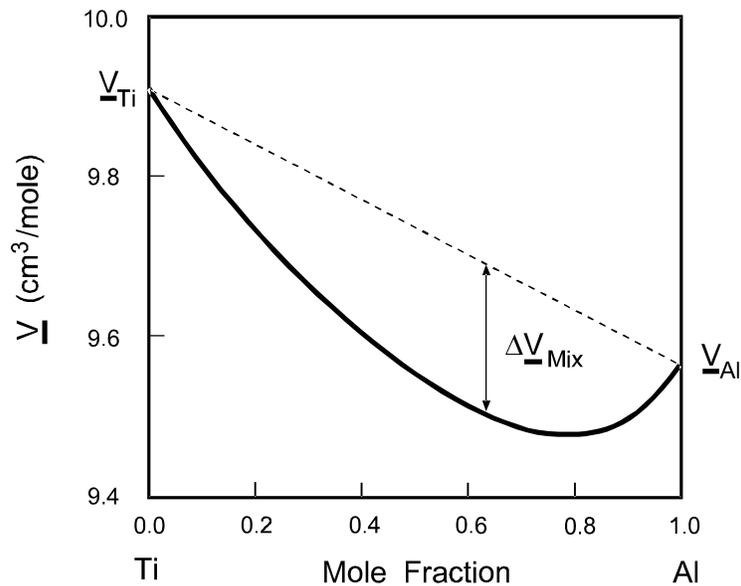


Figure 4.3: Molar volume of a Ti-Al solution plotted as a function of the Al mole fraction.

Plots such as the one illustrated in figure 4.3 are useful to graphically display quantities of mixing. As an illustration, consider the volume change associated with mixing n_{Al} moles of pure Al and n_{Ti} moles of pure Ti. Before mixing Al and Ti, the combined volume of the two pure components is simply

$$n_{Al} \underline{V}_{Al} + n_{Ti} \underline{V}_{Ti}$$

where \underline{V}_{Al} and \underline{V}_{Ti} are the molar volumes of pure Al and Ti respectively. Dividing this premixing volume by $n_{tot}=n_{Al}+n_{Ti}$ yields the molar volume before mixing

$$\frac{n_{Al}\underline{V}_{Al} + n_{Ti}\underline{V}_{Ti}}{n_{Al} + n_{Ti}} = x_{Al}\underline{V}_{Al} + x_{Ti}\underline{V}_{Ti}$$

Since $x_{Al}+x_{Ti}=1$, the molar volume before mixing becomes

$$x_{Al}\underline{V}_{Al} + (1 - x_{Al})\underline{V}_{Ti} \quad (13)$$

This expression for the premixing molar volume represents the dashed line of figure 4.3 connecting \underline{V}_{Ti} at $x_{Al}=0$ and \underline{V}_{Al} at $x_{Al}=1$. When Ti and Al are mixed and form a solution, the molar volume changes from that of the weighted average of the pure components given by equation (13) to the volume given by $\underline{V}(x_{Al})$ (full curve in figure 4.3). The change in volume upon mixing is, therefore, the difference between the dashed line and the curve $\underline{V}(x_{Al})$ as illustrated in figure 3. This can be written as

$$\Delta\underline{V}_{mix} = \underline{V}(x_{Al}) - (x_{Al}\underline{V}_{Al} + (1 - x_{Al})\underline{V}_{Ti}) \quad (14)$$

Other important quantities of mixing are the mixing enthalpy, entropy and Gibbs free energy. These can be written as follows for a binary A-B solution.

$$\Delta\underline{H}_{mix} = \underline{H}(x_B) - (x_B\underline{H}_B + (1 - x_B)\underline{H}_A) \quad (15)$$

$$\Delta\underline{S}_{mix} = \underline{S}(x_B) - (x_B\underline{S}_B + (1 - x_B)\underline{S}_A) \quad (16)$$

$$\Delta\underline{G}_{mix} = \underline{G}(x_B) - (x_B\underline{G}_B + (1 - x_B)\underline{G}_A) \quad (17)$$

As noted, the enthalpy of mixing $\Delta\underline{H}_{mix}$ is equal to the heat exchanged with the environment upon mixing a total of one mole of pure components A and B at concentration x_B . When $\Delta\underline{H}_{mix}$ is negative, heat is released and mixing is said to be exothermic. When the enthalpy of mixing is positive, heat is absorbed and mixing is said to be endothermic. (See figure 4.4 a and b)

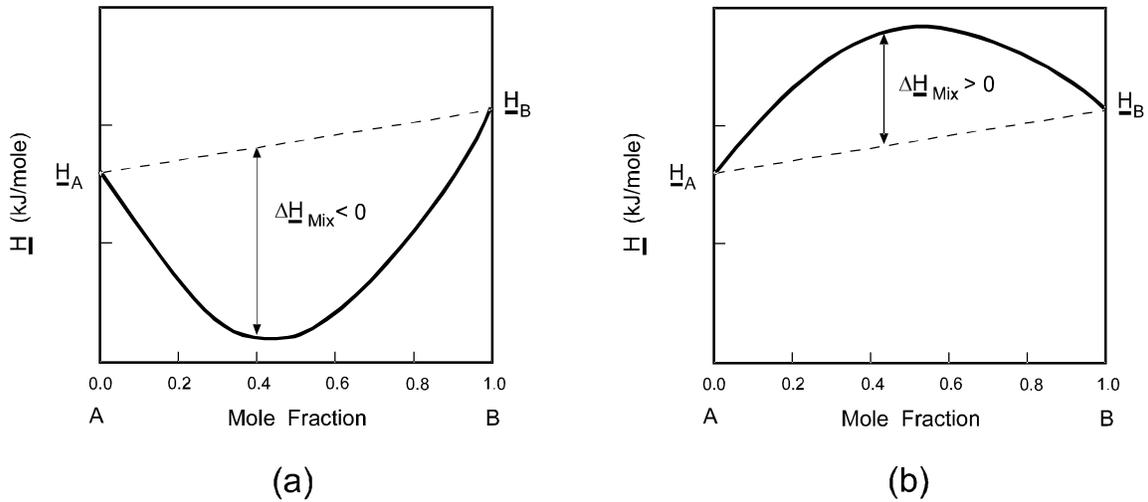


Figure 4.4: Enthalpies of mixing for a hypothetical binary A-B solution. A negative enthalpy of mixing (a) means that heat is released upon mixing (exothermic) while a positive enthalpy of mixing (b) means that heat is absorbed upon mixing (endothermic).

The value of ΔG_{mix} is an important quantity as its sign determines whether mixing will occur or not. A negative Gibbs free energy of mixing means that there is a thermodynamic driving force for mixing and the pure components when brought in contact will spontaneously form a solution. A positive Gibbs free energy of mixing means that the components are immiscible and will not form a solution when brought together, but rather a two phase dispersion of a pure A phase mixed with a pure B phase. (figure 4.5 a and b).

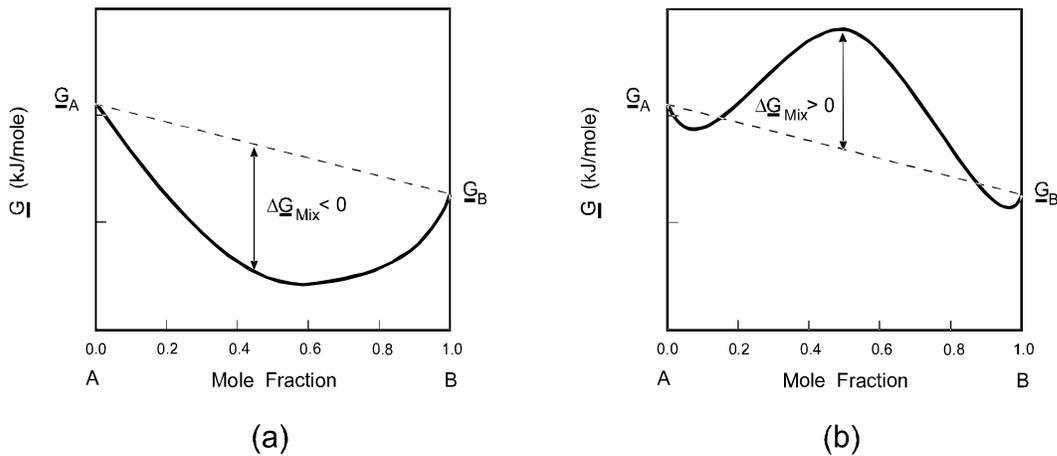


Figure 4.5: Gibbs free energies of mixing for a hypothetical binary A-B solution. A negative free energy of mixing (a) means that there is a thermodynamic driving force for mixing to occur (i.e. it will occur spontaneously), while a positive free energy of mixing (b) means that the pure components will not mix.

4.5. RELATION BETWEEN MOLAR QUANTITIES AND PARTIAL MOLAR QUANTITIES (THE INTERCEPT RULE)

Molar quantities are normalized extensive variables. In general, it is more practical to work with molar quantities than with the actual extensive variables that pertain to a particular system. Tabulations of thermodynamic properties such as enthalpies, free energies etc. are often expressed per mole. Furthermore, molar quantities of solutions are typically plotted as a function of the mole fraction of the components in the system. There exists a convenient graphical construction to derive partial molar quantities from plots of molar quantities versus mole fractions. This graphical construction is referred to as the *intercept rule*. We will illustrate the intercept rule for a binary system.

Figure 4.6 schematically illustrates the molar free energy for a binary A-B solution plotted as a function of the mole fraction of B. Consider a solution with composition x_B' . The molar free energy of the solution is $\underline{G}(x_B')$. The intercept rule states that μ_A is equal to the intercept of the tangent to \underline{G} at x_B' with the axes at $x_B = 0$ while μ_B is equal to the intercept of the same tangent at $x_B = 1$. This is illustrated in figure 4.6. Notice that the intercepts change as the composition of the solution is changed; As with \underline{G} , μ_A and μ_B are all functions of x_B .

It is a straightforward matter to derive the intercept rule. Starting from the total differential of \underline{G}

$$d\underline{G} = \mu_A dx_A + \mu_B dx_B$$

and using the fact that $dx_A = -dx_B$ we obtain

$$\frac{d\underline{G}}{dx_B} = \mu_B - \mu_A \quad (18)$$

Combining equation (18) with

$$\underline{G} = x_A \mu_A + x_B \mu_B$$

(which is simply equation (8) divided by the total number of moles in the system) to solve for μ_A and μ_B yields

$$\mu_A = \underline{G} - x_B \frac{d\underline{G}}{dx_B} \quad (19a)$$

$$\mu_B = \underline{G} + (1 - x_B) \frac{d\underline{G}}{dx_B} \quad (19b)$$

Equation (19a) and (19b) are the mathematical expression of the intercept rule as illustrated in figure 6.

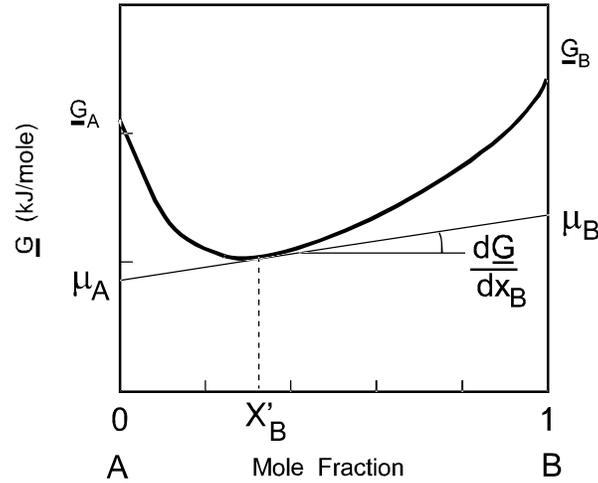


Figure 4.6: Illustration of the intercept rule applied to the molar Gibbs free energy (see text).

It is important to recognize the difference between equation (19) and equation (4). In equation (19), the chemical potentials are obtained from the molar Gibbs free energy \underline{G} while in equation (4) the chemical potentials are obtained from the extensive Gibbs free energy G . It is a common error to set the chemical potential of a component equal to the derivative of the molar Gibbs free energy with respect to the mole fraction of that component.

It is also possible to apply the intercept rule to a plot of the molar Gibbs free energy of mixing (equation 17). Now though, the intercepts are no longer the chemical potentials but rather $\mu_A - \underline{G}_A$ and $\mu_B - \underline{G}_B$ (see figure 7). In this context, \underline{G}_A and \underline{G}_B are often denoted by μ_A^o and μ_B^o respectively. This notation stems from the fact that μ_A^o is the chemical potential of pure A (when $x_A = 1$) and μ_B^o is the chemical potential of pure B when ($x_B = 1$).

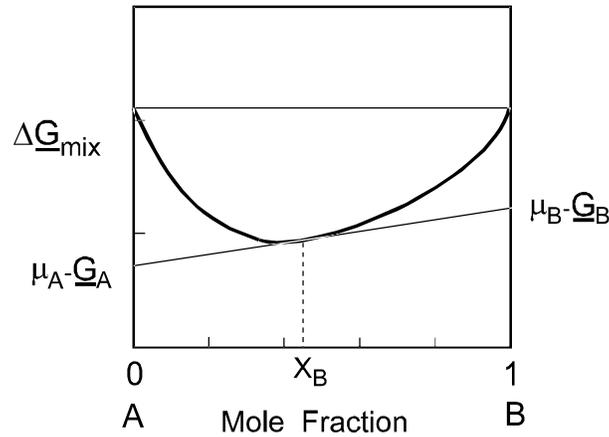


Figure 4.7: Illustration of the intercept rule applied to the molar Gibbs free energy of mixing (see text).

In an analogous way as with the molar Gibbs free energy, the intercept rule can be applied to any molar quantity. The partial molar volumes for example can be obtained from the molar volume using

$$\bar{V}_A = \underline{V} - x_B \frac{d\underline{V}}{dx_B} \quad (20a)$$

$$\bar{V}_B = \underline{V} + x_A \frac{d\underline{V}}{dx_B} = \underline{V} + (1 - x_B) \frac{d\underline{V}}{dx_B} \quad (20b).$$

Figure 4.8 illustrates the intercept rule as applied to the molar volume of a binary A-B solution. It also graphically illustrates the different terms that appear in the expressions for the molar volumes in equations 20.

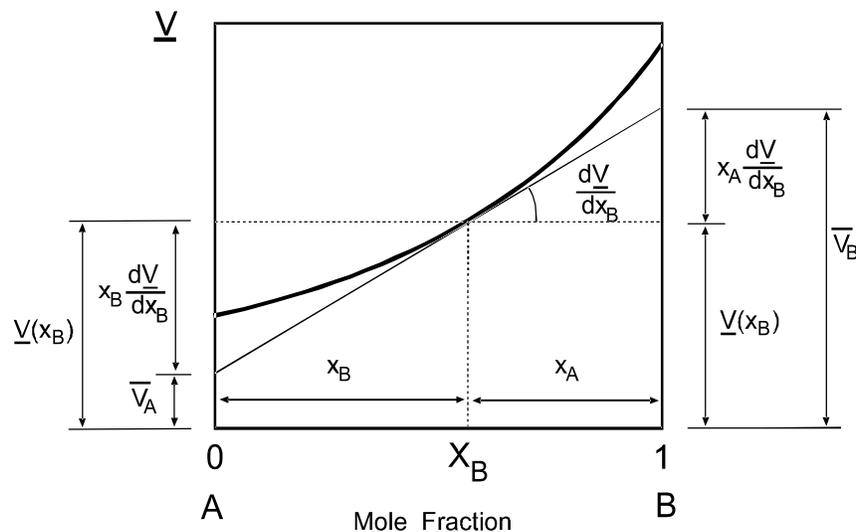


Figure 4.8: Illustration of the intercept rule applied to the molar volume of a binary A-B solution. The different terms appearing in equations 20 are also illustrated.

4.6 PHASE EQUILIBRIUM BETWEEN SOLUTIONS

The thermodynamics of solutions, introduced in the previous sections, is a powerful tool to study the equilibrium of a heterogeneous mixture of homogeneous phases. For example, one may be interested in understanding the equilibrium of solid silicon with trace amounts of iron in contact with a melt containing predominantly aluminum. This equilibrium is of importance during the fabrication of solar cells where an aluminum-rich layer is plated on the back surface of a silicon wafer. During heat treatment, the aluminum-rich layer serves as a gettering sink for unwanted transition metal ions such as iron in the silicon wafer. This example illustrates how the equilibrium characteristics between a liquid Al-Si-Fe phase and a solid Si-Fe-Al phase can be exploited to engineer the composition of the silicon wafer.

In this section we derive the thermodynamic conditions of multi-phase equilibrium. For simplicity, we restrict ourselves to binary systems, yet it is a straightforward task to generalize the treatment of this section to systems with more than two components.

Consider a binary A-B system at constant T and P with two phases α and β as illustrated in figure 4.9. The phases α and β could each be in the solid, liquid or vapor form and for generality, we assume that both phases are solutions containing A and B atoms. The number of moles of A and B in the α phase is denoted by n_A^α and n_B^α and in the β phase by n_A^β and n_B^β . Although in the analysis of equilibrium, we will allow n_A^α , n_B^α , n_A^β and n_B^β to vary, we assume that the total number of moles of each component in the system (defined as the combination of the α and β phases) is fixed. That is

$$n_A = n_A^\alpha + n_A^\beta = \text{constant} \quad (21a)$$

$$n_B = n_B^\alpha + n_B^\beta = \text{constant} \quad (21b)$$

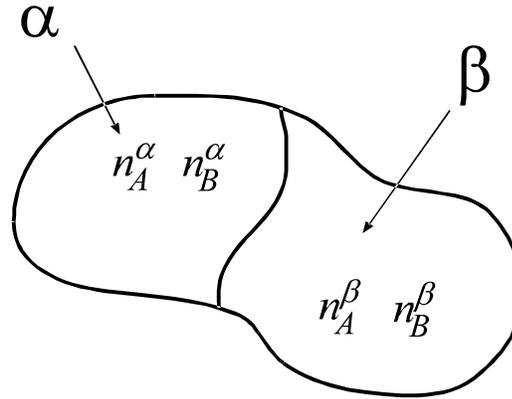


Figure 4.9: Schematic illustration of two different phases α and β in thermodynamic equilibrium.

The Gibbs free energy is the characteristic potential for a system constrained to have constant T , P , and total number of moles of n_A and n_B . Equilibrium of a system under these externally imposed constraints is characterized by that state which minimizes the Gibbs free energy $G(T, P, n_A, n_B)$ of the system. Before continuing, let us elaborate on the meaning of the “state that minimizes the Gibbs free energy”. While in our two phase system of figure 4.9, the temperature, pressure and total number of A and B atoms are fixed, there still remain several internal degrees of freedom. The compositions of A and B atoms in each of the two phases separately are not constrained. All that is required is that the total number of mole of each component remains constant (i.e. equations (21) a and b are satisfied). Hence, if the number of moles of A in α is increased by an amount dn_A^α , then the number of moles of A in β must be reduced by $dn_A^\beta = -dn_A^\alpha$. Each set of values for n_A^α , n_B^α , n_A^β and n_B^β that simultaneously satisfy equations (21) a and b are possible states of the system under the constraint of constant T , P , n_A and n_B . And for each one of these states, a value for the Gibbs free energy exists. Indeed, since the Gibbs free energy is an extensive quantity, it can be written as the sum of the Gibbs free energies of the separate phases α and β according to

$$G^{\text{tot}}(T, P, n_A, n_B) = G^\alpha(T, P, n_A^\alpha, n_B^\alpha) + G^\beta(T, P, n_A^\beta, n_B^\beta) \quad (22)$$

where G^{tot} is the free energy of the whole system, G^α is the free energy of the α phase and G^β is the free energy of the β phase. (In equation 22, we are assuming that the α and β phases are large enough such that surface effects can be neglected). In equilibrium, the system chooses those values of n_A^α , n_B^α , n_A^β and n_B^β that simultaneously minimize G^{tot} and satisfy the constraints of equations (21).

To minimize the Gibbs free energy of the two phase system, we consider the total differential of G^{tot} with respect to its internal degrees of freedom

$$dG^{\text{tot}} = dG^\alpha + dG^\beta \quad (23)$$

where, at constant T and P

$$dG^\alpha = \mu_A^\alpha dn_A^\alpha + \mu_B^\alpha dn_B^\alpha \quad (24a)$$

$$dG^\beta = \mu_A^\beta dn_A^\beta + \mu_B^\beta dn_B^\beta \quad (24b).$$

Combining (23) and (24) along with the constraints that $dn_A^\alpha = -dn_A^\beta$ and $dn_B^\alpha = -dn_B^\beta$ (which follows from (21) a and b) yields

$$dG^{\text{tot}} = (\mu_A^\alpha - \mu_A^\beta) dn_A^\alpha + (\mu_B^\alpha - \mu_B^\beta) dn_B^\alpha \quad (25).$$

In equilibrium, G^{tot} is minimal and the differential of G^{tot} with respect to the internal degrees of freedom, equation (25), must equal zero. This must be true for any infinitesimal positive or negative perturbation dn_A^α or dn_B^α away from equilibrium. Hence, equilibrium is characterized by an equality of chemical potentials of each species in the two phases

$$\mu_A^\alpha = \mu_A^\beta \quad (26a)$$

$$\mu_B^\alpha = \mu_B^\beta \quad (26b).$$

This set of equations constitutes the fundamental conditions of equilibrium in a binary two-phase system.

Equation (25) not only sets the equilibrium criteria for a binary two-phase system, it also indicates how the system evolves when the above equilibrium conditions, equations (26a) and (26b), are not satisfied. To comply with the second law of thermodynamics, a system out of equilibrium will change its state in a direction that decreases the free energy. If for example, the equilibrium conditions (26) a and b are not satisfied and the chemical potential of A in α is less than the chemical potential of A in β , i.e.

$$\mu_A^\alpha < \mu_A^\beta$$

then the system will evolve in a direction for which $dG^{\text{tot}} < 0$. For this example, $dG^{\text{tot}} < 0$ when dn_A^α is positive. In general, atoms flow to the phase where their chemical potential is the lowest. Only when the chemical potentials for each component in the different phases are equal will the system be in equilibrium and remain unchanged over time.

A similar analysis can be performed for a system with more than two components and more than two phases. The general equilibrium criteria for a system with components 1, 2, ..., N and phases $\alpha, \beta, \gamma, \dots$ is

$$\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \dots$$

$$\begin{aligned}
 \mu_2^\alpha &= \mu_2^\beta = \mu_2^\gamma = \dots \\
 &\vdots \\
 &\vdots \\
 \mu_N^\alpha &= \mu_N^\beta = \mu_N^\gamma = \dots
 \end{aligned}
 \tag{27}$$

The conditions of equilibrium, as encapsulated by equation (26) or (27), can be represented graphically by the common tangent method. Figure 10 illustrates a plot containing the free energy curves of two different phases as a function of mole fraction in an A-B system. Using the intercept rule, it is clear that in equilibrium the concentrations in the two phases must be such that the two free energy curves have a common tangent as illustrated in figure 4.10.

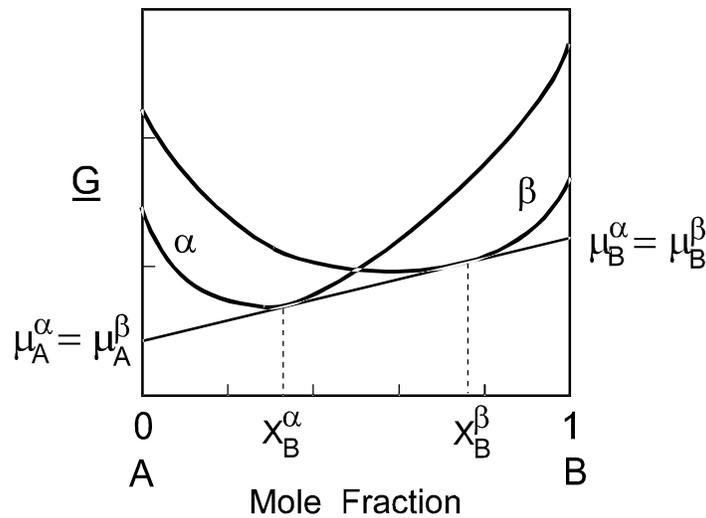


Figure 4.10: Schematic illustration of the common tangent method for a binary system containing an α and β phase.

4.7 PHENOMENOLOGICAL EXPRESSIONS FOR CHEMICAL POTENTIALS.

The Gibbs free energy of a solution is a function of T , P and the number of mole of each of the components in the system. Chemical potentials also depend on T and P . But since chemical potentials, along with all partial molar quantities, are intensive and, therefore, do not depend on the size of the system, it is sufficient to describe their composition dependence with intensive composition variables such as mole fractions x_i .

In previous sections, knowledge of the functional dependence of chemical potentials on T , P and concentration variables was implicitly assumed. In this section, we introduce and motivate a commonly used explicit expression for the chemical potential.

A useful system to start with to derive an expression for the chemical potential is a single component ideal gas. For a one component system, the chemical potential is equal to the molar Gibbs free energy since

$$\mu = \frac{\partial G}{\partial n} = \frac{\partial(n\underline{G})}{\partial n} = \underline{G}$$

where n is the number of mole in the system and \underline{G} is independent of n . From the properties of the Gibbs free energy of single component systems covered in chapter 2 along with the equation of state of an ideal gas, we know that

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \left(\frac{\partial \underline{G}}{\partial P}\right)_T = \underline{V} = \frac{RT}{P}$$

or

$$d\mu = RT \frac{dP}{P} = RT d(\ln P) \quad (28).$$

Integration of equation (28) from a reference state with pressure P° and temperature T , we obtain

$$\mu(P, T) - \mu(P^\circ, T) = RT \ln\left(\frac{P}{P^\circ}\right) \quad (29).$$

Often the reference state is defined as the gas at 1 atmospheric pressure, i.e. $P^\circ=1$ atm. In the reference state, $\mu(P^\circ, T)$ is denoted by $\mu^\circ(T)$. The chemical potential then becomes

$$\mu(P, T) = \mu^\circ(T) + RT \ln(P) \quad (30)$$

where P is measured in atm. So far, no approximations have been made and equation (30) is the exact expression for the chemical potential of a single component ideal gas.

Consider now an ideal gas containing several components. We are interested in the chemical potential of each the components in this ideal gas mixture. For an ideal gas mixture, we introduce partial pressures for each component P_i defined as

$$P_i = x_i P$$

where x_i is the mole fraction of component i and P is the total pressure of the gas mixture. These partial pressures should not be confused with partial molar quantities. They are fictive variables introduced for convenience. For an ideal-like gas mixture, it turns out to be a very good approximation to set the chemical potential of each component i equal to

$$\mu_i(P, T, x_i) = \mu_i^\circ(T) + RT \ln(P_i) = \mu_i^\circ(T) + RT \ln(x_i P) \quad (31).$$

Equation (31) has the same form as equation (30) for a single component ideal gas with the exception that the partial pressure is used instead of the total pressure. For an ideal gas mixture at atmospheric pressure $P=1$ atm, the chemical potential becomes

$$\mu_i = \mu_i^\circ + RT \ln(x_i) \quad (32).$$

The form of the chemical potential in equation (31) is retained even for non-ideal gas mixtures although then x_i is replaced with a fugacity f_i which itself is a function of x_i . In general, gasses deviate from ideality only under extremely high pressures and equation (31) is a good approximation for most gas mixtures around atmospheric pressure. μ_i° in equation (31) and (32) is the chemical potential of i in the standard state. For gasses, the most common standard state is that of pure i in the gas phase at one atmospheric pressure. μ_i° , therefore, only has a temperature dependence.

Equation (32) is also a reasonable approximation for the chemical potentials in liquid and solid solutions. Often though, a more accurate description of the chemical potentials of the components in condensed solutions is obtained after an **activity coefficient** γ_i is introduced inside the logarithm. The chemical potential is then written as

$$\mu_i = \mu_i^\circ + RT \ln(\gamma_i x_i) \quad (33).$$

The product $\gamma_i x_i$ is typically replaced by the variable a_i which is called the **activity** of component i . The chemical potential is then written as

$$\mu_i = \mu_i^\circ + RT \ln(a_i) \quad (34)$$

μ_i° represents the chemical potential of i in the **standard state**. The standard state for solid solutions is chosen as the pure component i in the same phase as the solution at the temperature and pressure of interest. In this standard state, μ_i° is equal to the molar free energy of pure i . Note that due to this definition of the standard state, μ_i° depends both on T and P but is independent of the concentration.

Figure 11 illustrates a schematic plot of an activity in a binary condensed solution. A solution is said to be ideal if

$$a_i = x_i$$

for all the components in the solution (figure 11a). The solution then exhibits what is referred to as **Raoultian behavior**. Usually, the activity does not vary linearly with mole fraction but deviates from it as illustrated in figure 11b for a binary system. Although the concentration dependence of a_i may be complicated, there are two features that are always satisfied in a binary system:

- (i) When i is the solvent, that is as x_i approaches 1, the activity a_i approaches x_i . This is called the Raoultian regime.
- (ii) In the dilute limit when x_i approaches 0, the activity can be written as $a_i = k_i x_i$ where k_i is a constant. This is called Henrian behavior.

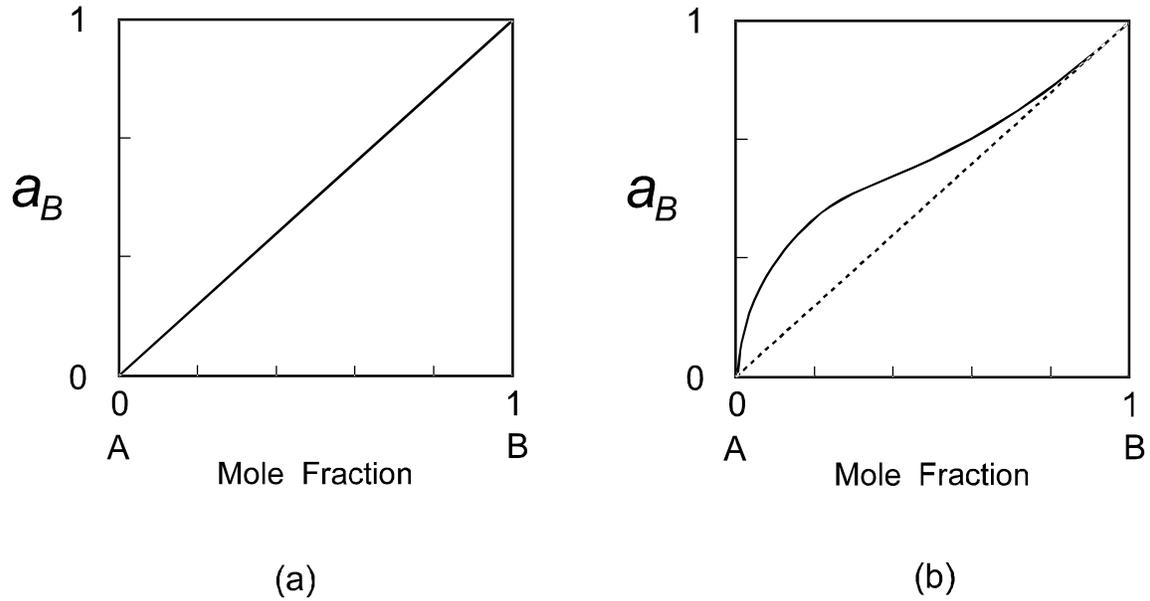


Figure 4.11: The activity of component B in a binary A-B solution. (a) corresponds to an ideal solution and (b) corresponds to a more realistic solution.