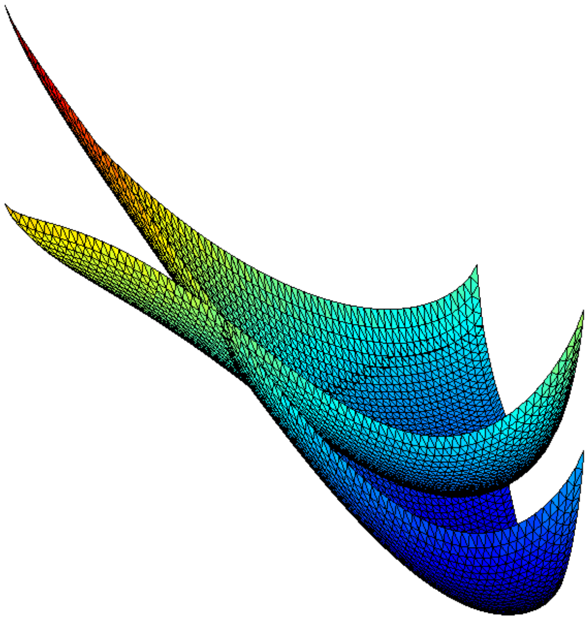
Computerized Thermodynamics for Materials Scientists and Engineers

by

Mats Hillert and Malin Selleby



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Introductory remarks

Basic thermodynamics is simple.
Applications may become very complicated.
Especially if one wants to express relations analytically or evaluate results by analytical methods.
Numerical methods could be even more laborious.
Previously, there was no other alternative.
Today, applications can be greatly simplified by using numerical methods through computer software.
The computer software obeys the rules of basic thermodynamics.
Properties of phases (substances or solutions) are stored as parameters in well defined models.
The models are analytical expressions and are based on physical models, which may be more or less correct.
A thermodynamic data bank contains a set of databases and is equipped with modules for computing equilibria and diagrams.

Introduction

Classical thermodynamics deals with states of equilibrium but is also used to shed light on spontaneous changes between two states. One can compute the state of equilibrium or the driving force for a change by searching for the extremum of a characteristic state function. It is most common to use a function called Gibbs energy, which must be minimized under constant P, T and content of matter in the system under consideration. From this criterion one has derived a large number of equations under various conditions of equilibrium. In applications it is often necessary to solve a set of such equations simultaneously. Modern computers offer a different possibility. Software has been developed for the automatic minimization of Gibbs energy. It is no longer necessary to define or find the proper set of equilibrium equations. It is sufficient to define the conditions for the equilibrium state to be computed. Advanced software is not limited to minimizing the Gibbs energy but makes it possible to use other conditions than constant P, T and content of matter.

In this new situation it seems that students of thermodynamics should not be forced to handle the wealth of formulae common in classical textbooks of thermodynamics. The main emphasis should be on the modelling of the Gibbs energy of various kinds of phases and on different ways of defining the conditions for various kinds of equilibria. This should lead to a new strategy of teaching thermodynamics and it requires close contact with computers. Exercises on the use of equilibrium equations in various situations should be replaced by computer-operated exercises mainly concerned with an analysis of what factors might control the equilibrium conditions in a given situation. The student should thus be required to acquire a better fundamental understanding of thermodynamics and less skill in manipulating formulae.

The present compendium represents a first attempt to present thermodynamics in this new way. Hopefully, the text is self-consistent and logical but much shorter than in textbooks with derivations of many equations and relations between various quantities. However, in order to acquire any working ability in thermodynamics it is necessary for the student to practice repeatedly on a computer as s/he works her/his way through the text.

List of important terms

Associate	Real or hypothetical group of atoms, to be treated as a species
Component	Atom or group of atoms used for representing the composition of the system
Concentration	Amount per volume
Constituent	A species in a certain phase or sublattice
Constitution	Distribution of constituents on the sublattices
Content	Amount in system or phase
Dormant	Sleeping, a phase excluded from taking part in the equilibrium
Excess Gibbs energy	${}^{E}G$, Gibbs energy in excess of a model regarded as ideal
Isobaric	Under constant P
Isobarothermal	Under constant P and T
Isoplethal	Under constant amounts of or ratio between some components
Isothermal	Under constant T
Molar content	Amount (in mole) per mole of phase or system, i.e. a ratio.
Molar Gibbs Energy	G_m, Gibbs energy per mole of atoms or formula units
Mole fraction, x_j	Fraction of a component j in a system. Same as “molar content”
Reciprocal system	A special kind of four-component system
Reference state	Unique state of an element at some selected P and T, used as reference for Gibbs energy
Site fraction, y_j	Fraction of constituent j in a sublattice
Species	Atom or group of atoms of some stability, e.g. molecule
Standard state	State of a pure element at the current P and T
Stoichiometric	Composition/Phase expressible by formula with small integer coefficients
Suspended	Phase/Species/Component/Constituent that is excluded from the system
System	The portion of the universe for which equilibrium is considered

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Chapter 1

Basic Thermodynamics

1.1 First law of thermodynamics

Energy can be transferred to a **system** from the **surroundings** as heat, Q, or work, W. **The first law** of thermodynamics requires that energy cannot be generated nor destroyed and the transferred energy must somehow be stored inside the system. Without analyzing in what way it is stored, one would thus know that the energy of the system has changed by an amount equal to what it has received. One has thus defined a special concept, **the internal energy**, U, and in basic thermodynamics there is no need to discuss its physical nature.

$$dU = dQ + dW \tag{1.1}$$

We will mainly be concerned with work done by an external pressure, P, by compressing the system with an amount of $-dV$, yielding

$$dU = dQ - PdV \tag{1.2}$$

Under constant volume, V, the heat transfer to the system will be

$$dQ = dU \tag{1.3}$$

Under constant pressure, P, the heat transfer will be

$$dQ = dU + PdV \pm VdP = d\left(U + PV\right) - VdP = dH \tag{1.4}$$

We have introduced the notation H for $U + PV$ and that quantity is called **enthalpy**. Eq. 1.4 explains why it is often called heat content but it should be remembered that there is no thermodynamic way of distinguishing heat from work inside the system. In thermodynamics, heat and work are just *different mechanisms of transferring energy* between two systems or between a system and its surroundings. Enthalpy is a very useful property because it is more common to operate under constant P than V. Using Eq. 1.4 one can determine experimentally how H varies with T for various substances and such information is often collected in tables for properties of various substances.

Exercise 1.1.1. Evaluate the heat of melting of 1 mole of pure fcc-Ni at 1 bar. *Hint* 1) The melting point at 1 bar is 1728.25 K. 2) Integration of Eq. 1.4 yields $Q_{melting} = H^{liquid} - H^{fcc}$ because for a pure element the phases retain their properties during the whole melting process when P and T are kept constant.

1.2 Second law of thermodynamics

The **second law** of thermodynamics concerns another quantity, S, called **entropy**. A process or reaction occurring spontaneously inside a system must increase the entropy of the system if there is no heat exchange with the surroundings.

$$d_{ip}S > 0 \quad \text{for spontaneous } \textbf{internal processes} \tag{1.5}$$

An internal process will be infinitely slow if $d_{ip}S = 0$. This is sometimes regarded as a **reversible process**. The symbol d_{ip} means that the change is caused by an internal process and $d_{ip}S$ is regarded as an **internal entropy production**. A heat exchange itself will change the entropy by dQ/T and the total change of S in the system accompanying an internal process would be

$$dS = \frac{dQ}{T} + d_{ip}S > \frac{dQ}{T} \tag{1.6}$$

since $d_{ip}S > 0$. No attempt will here be made to explain entropy or prove the second law. Actually, both laws will be regarded as axioms.

Exercise 1.2.1. Evaluate $\Delta_{ip}S$ for the solidification of 1 mole of liquid Ni in a system at 1720 K and 1 bar.
Hint Solidification of the liquid can be regarded as an internal process of the system. Liquid and fcc Ni are in equilibrium at 1728.25 K. At that temperature liquid Ni will not solidify spontaneously, $d_{ip}S = 0$. At 1720 K the liquid is supercooled and could solidify spontaneously, $d_{ip}S > 0$. The quantity $d_{ip}S$ could be evaluated from Eq. 1.6 in the integrated form, $\Delta_{ip}S = \Delta S - \Delta Q/T$. Eq. 1.4 then yields for one mole $\Delta_{ip}S_m = S_m^{fcc} - S_m^{liq} - \left(H_m^{fcc} - H_m^{liq}\right)/1720$. The molar quantities should here be taken from 1720 K.

1.3 The combined law

Combining Eq. 1.6, rewritten as $TdS = dQ + Td_{ip}S$, with the first law as given by Eq. 1.2 yields the **combined law**,

$$TdS = dQ + Td_{ip}S = dU + PdV + Td_{ip}S > dU + PdV \tag{1.7}$$

We can rearrange the terms in order to introduce P and T as the variables,

$$-Td_{ip}S = dU + PdV - TdS = d\left(U + PV - TS\right) - VdP + SdT \tag{1.8}$$

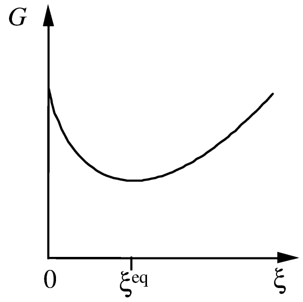


Figure 1.1: For an internal variable, the equilibrium is found by minimizing G if P and T are constant.

Introducing the symbol G for $U + PV - TS$, a quantity called **Gibbs energy**, we obtain

$$dG = VdP - SdT - Td_{ip}S < VdP - SdT \quad \text{for spontaneous internal processes} \tag{1.9}$$

G is of more direct practical use than S because it depends on P and T and one usually considers systems under constant P and T. A system kept under conditions of constant P and T may undergo a change by a spontaneous internal process under exchange of heat and work with the surroundings if it causes a negative change of G.

$$dG = -Td_{ip}S < 0 \quad \text{for spontaneous internal changes under constant } P \text{ and } T \tag{1.10}$$

Exercise 1.3.1. Evaluate $\Delta_{ip}S$ for the solidification of 1 mole of liquid Ni at 1720 K and 1 bar from information on ΔG for solidification. *Hint* ΔG may be obtained from a table of G_m or from a computerized database.

1.4 Driving force and dissipation

Eq. 1.10 may be illustrated with a simple diagram, Fig. 1.1, where the x axis represents the **extent of an internal process**, ξ, in a system kept under constant P and T. In contrast to the **external** variables, which may be controlled from the outside, ξ is an **internal** variable, which can change spontaneously even in a completely isolated system. Starting at $\xi = 0$, the Gibbs energy here decreases as the process proceeds but the process will finally stop when it can no longer decrease the Gibbs energy, i.e. at the point of minimum. If the system were initially on the other side of the minimum, the process would spontaneously proceed in the other direction and approach the same minimum. The minimum thus represents the equilibrium of the system with respect to this internal process and the equilibrium condition under constant P and T is

$$(\partial G/\partial \xi)_{P,T} = 0 \tag{1.11}$$

One may thus determine the state of equilibrium with regard to this internal process if one knows how G varies with ξ under constant P and T. It is evident that G must be a function of ξ in addition to P and T, i.e. $G = G(P, T, \xi)$. The rate of decrease of Gibbs energy, defined from the slope of the G curve in Fig. 1.1, can be regarded as the **driving force** for increasing the ξ variable, denoted D (or DF if there is a need to distinguish it from a diffusion coefficient).

$$D = -\left(\partial G/\partial \xi\right)_{P,T} \tag{1.12}$$

For a transformation between two states, $\alpha \to \beta$, one obtains by integration $D = -\Delta G_m$ where $\Delta G_m = G_m^{\beta} - G_m^{\alpha}$. In view of Eq. 1.11, a system will be in internal equilibrium under constant P and T if $D = 0$ for all possible internal processes. One often assumes that the rate of a process is proportional to its driving force. A process could occur spontaneously only if $D > 0$.

If we consider only one process at a time, then Eq. 1.9 yields under constant P and T

$$D = -\left(\partial G/\partial \xi\right)_{P,T} = T d_{ip} S/d\xi \tag{1.13}$$

We can identify D with $T d_{ip} S/d\xi$ and replace $T d_{ip} S$ by $D d\xi$ in all the previous equations, e.g. Eq. 1.9,

$$dG = V dP - S dT - D d\xi \tag{1.14}$$

In this connection, $D d\xi$ may thus be regarded as the **dissipation** of Gibbs energy and $\int D d\xi$ as the dissipated Gibbs energy for a process. Evidently, an internal process occurring under $D = 0$ would not produce any entropy, nor dissipate any Gibbs energy. However, it is predicted to be infinitely slow. As already mentioned, such a process is sometimes regarded as a **reversible process**. Likewise, a process does not dissipate any Gibbs energy if $d\xi = 0$. Of course, that happens at equilibrium where $D = 0$ but also for a **frozen process**, which could happen if the temperature is low enough to make the rate of the internal processes practically zero. In both cases

$$dG = V dP - S dT \tag{1.15}$$

It would thus be possible to vary P and T of a system without causing an internal process if all possible internal processes are frozen. Eq. 1.15 will be our most useful form of the combined law for a unary system.

Exercise 1.4.1. Find the driving force for the formation of solid Ni from liquid Ni at 1720 K and 1 bar.
Hint The only quantity that changes during isobarothermal solidification of pure Ni is the amounts of solid and liquid Ni. It may thus be convenient to express the extent of solidification, ξ, by the amount of solid Ni, e.g. expressed as moles, N^{sol}. The driving force, D, will have the same value during the whole solidification of a pure substance and we obtain $D = -\Delta G/\Delta\xi = -\left(G^{sol} - G^{liq}\right)/\Delta N^{sol} = G_m^{liq} - G_m^{sol}$.

1.5 Variable Composition

Consider a system for which also the content may change by exchange of matter with the surroundings. By generalizing Eq. 1.14 one obtains

$$dG = VdP - SdT + \sum \mu_i dN_i - Dd\xi \tag{1.16}$$

μ_i enters into this expression as one of several coefficients. They can all be expressed as partial derivatives of G, e.g. $V = (\partial G/\partial P)_{T,N_i,\xi}$ and $\mu_k = (\partial G/\partial N_k)_{T,P,N_j,\xi}$. The subscript N_j indicates that all N_i except N_k are kept constant. If also P and T are kept constant and there is no internal entropy production, one obtains

$$\mu_k = (\partial G/\partial N_k)_{T,P,N_j} \tag{1.17}$$

Due to its definition, μ_k is a partial derivative of G and is often called the **partial Gibbs energy** of component k. P and T and all μ_i are regarded as **external variables** because they can be controlled from the surroundings. V, S and N_i are also external variables but of all those external variables only P, T and all the μ_i are regarded as potentials because at equilibrium they must each have the same value in the whole system. They can be kept constant at fixed values by requiring equilibrium with an infinite reservoir of matter with those values. In addition to be regarded as a partial Gibbs energy, μ_k is also regarded as the **chemical potential** of component k. It is a very important property of the system.

It is also possible to consider the system as a reservoir which can supply the surroundings with matter of the potentials given by Eq. 1.17 because

$$\left(\frac{-\partial G}{-\partial N_k}\right)_{P,T,N_j} = \left(\frac{\partial G}{\partial N_k}\right)_{P,T,N_j} = \mu_k \tag{1.18}$$

The mole fraction $x_k \equiv N_k/\sum N_i = N_k/N$ will now be introduced as a means of expressing composition. From Eq. 1.16, we obtain

$$dG = VdP - SdT + \left(\sum \mu_i x_i\right) dN - Dd\xi \tag{1.19}$$

Consider a large amount of homogeneous matter with uniform P, T and composition. Define a very small volume as the system and extend its limits gradually without really changing anything. At any stage the Gibbs energy will be proportional to the amount of matter.

$$G = \left(\sum \mu_i x_i\right) N = \sum \mu_i N_i \tag{1.20}$$

It should be emphasized that one could often define a large number of internal processes and their driving forces. They are also internal variables. In fact, all that can be used to describe the internal state of a system can be regarded as internal variables.

The molar Gibbs energy is defined as

$$G_m \equiv G/N = \sum \mu_i x_i \tag{1.21}$$

The definition of chemical potential is illustrated for a binary solution phase by the molar Gibbs energy diagram in Fig. 1.2.

In order to explain the diagram we shall soon need the following partial derivatives for $x_A = N_A/N$ and $x_B = N_B/N$

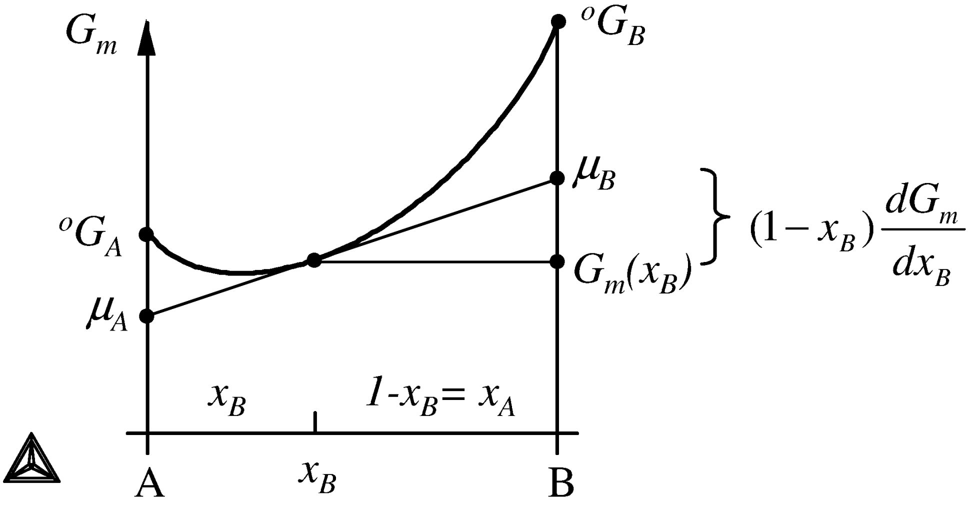


Figure 1.2: The chemical potentials of a binary alloy of composition x_A, x_B are found from the intercepts made on the axes by the tangent.

$$\left(\frac{\partial x_A}{\partial N_B}\right)_{N_A} = \frac{N \cdot 0 - N_A \cdot 1}{N^2} = \frac{-x_A}{N} \tag{1.22}$$

$$\left(\frac{\partial x_B}{\partial N_B}\right)_{N_A} = \frac{N \cdot 1 - N_B \cdot 1}{N^2} = \frac{1-x_B}{N} \tag{1.23}$$

It is evident from Eq. 1.18 that the chemical potential of each component must have the same value everywhere in a system at equilibrium. Otherwise, the Gibbs energy could decrease spontaneously by some material moving into the region with the lower value. The driving force for such a reaction would be

$$D = \mu_i' - \mu_i'' \tag{1.24}$$

This is why the chemical potential is regarded as a potential. The same applies to P and T, which are also potentials. There is one exception. P will have different values on the two sides of a curved interface with a specific interfacial energy, σ $\left[\mathrm{J/m^2}\right]$. For a spherical interface a simple mass balance shows that

$$\Delta P = 2\sigma/V_m \tag{1.25}$$

One usually regards the elements A and B as a set of two independent components in a binary system because one can vary the amount of one without changing the amount of the other. However, one can define the set of two independent components differently. It may be convenient to regard a combination of A and B as one of the independent components. When A is replaced by A_aB_b but B is retained, Eq. 1.20 for a binary system can be rearranged

$$\begin{aligned} G = \sum \mu_i N_i = N_A\mu_A + N_B\mu_B = N_A\mu_A + N_B\mu_B \pm (b/a)N_A\mu_B \\ = N_A(\mu_A + (b/a)\mu_B) + (N_B - (b/a)N_A)\mu_B = N'_{A_aB_b}\mu_{A_aB_b} + N'_B\mu_B \end{aligned} \tag{1.26}$$

where

$$\mu_{A_aB_b} = a\mu_A + b\mu_B \tag{1.27}$$

and $N'_{A_aB_b} = N_A/a$ and $N'_B = N_B - (b/a)N_A$. The coefficients, a and b are usually small numbers but may be replaced by the mole fractions, x_A and x_B. It should be emphasized that $\mu_{A_aB_b}$ may be a useful quantity even without defining a new independent component. When A_aB_b molecules are actually present in a solution phase, then Eq. 1.27 expresses their chemical potential at internal equilibrium between the three species. For a frozen state, all three chemical potentials depend on their actual amounts. Eq. 1.27 can be applied only for a real or assumed equilibrium.

Exercise 1.5.1. (Advanced) Use Eq. 1.17 to derive μ_A for a system composed of a mixture of two stoichiometric A-B phases.
*Hint*Remember that Gibbs energy is an additive quantity. How can one then keep N_B constant when one varies N_A?

1.6 Expressing chemical potentials through the molar Gibbs energy

In order to apply the definition of μ_B, obtained from Eq. 1.17 for a binary system, to Fig. 1.2 we shall introduce the molar Gibbs energy $G_m = G/N$, which should really be described as a function of x_A or x_B but is often given with an expression containing both mole fractions. It is then implied that $x_A = 1 - x_B$ for a binary system. As long as we obey Eqs. 1.22 and 1.23 we may treat G_m as a function of both x_A and x_B, regarded as independent variables, which is often practical. We may thus derive expressions for the slope of the tangent, dG_m/dx_B , and chemical potentials.

$$dG_m = \frac{\partial G_m}{\partial x_A}dx_A + \frac{\partial G_m}{\partial x_B}dx_B = \left(\frac{\partial G_m}{\partial x_B} - \frac{\partial G_m}{\partial x_A}\right)dx_B \tag{1.28}$$

$$\frac{dG_m}{dx_B} = \left(\frac{\partial G_m}{\partial x_B} - \frac{\partial G_m}{\partial x_A}\right) \tag{1.29}$$

Using Eqs. 1.22 and 1.23 we obtain

$$\begin{aligned}
G_B \equiv \mu_B \equiv \left(\frac{\partial G}{\partial N_B}\right)_{N_A} &= \left(\frac{\partial\left(N G_m\right)}{\partial N_B}\right)_{N_A} \\
&= G_m\left(\frac{\partial N}{\partial N_B}\right)_{N_A} + N\frac{\partial G_m}{\partial x_A}\cdot\left(\frac{\partial x_A}{\partial N_B}\right)_{N_A} + N\frac{\partial G_m}{\partial x_B}\cdot\left(\frac{\partial x_B}{\partial N_B}\right)_{N_A} \\
&= G_m - x_A\frac{\partial G_m}{\partial x_A} + \left(1 - x_B\right)\frac{\partial G_m}{\partial x_B} \\
&= G_m + x_A\left(\frac{\partial G_m}{\partial x_B} - \frac{\partial G_m}{\partial x_A}\right) \\
&= G_m + x_A\frac{dG_m}{dx_B}
\end{aligned} \tag{1.30}$$

The chemical potentials can thus be obtained from the intersections of the tangent with the component axes in Fig. 1.2. Taking the difference between Eq. 1.30 and a similar equation for μ_A we obtain for the slope of the tangent

$$\begin{aligned}
&\mu_B - \mu_A = G_m + x_A\left(\frac{\partial G_m}{\partial x_B} - \frac{\partial G_m}{\partial x_A}\right) - G_m - x_B\left(\frac{\partial G_m}{\partial x_A} - \frac{\partial G_m}{\partial x_B}\right) \\
&= \frac{\partial G_m}{\partial x_B} - \frac{\partial G_m}{\partial x_A} = \frac{dG_m}{dx_B}
\end{aligned} \tag{1.31}$$

This relation is also illustrated by Fig. 1.2. Finally, it should be mentioned that one can in the same way derive an expression for the chemical potentials in a multicomponent solution. It is preferable to express it as follows.

$$G_B \equiv \mu_B = G_m + \frac{\partial G_m}{\partial x_B} - \sum x_i\frac{\partial G_m}{\partial x_i} \tag{1.32}$$

It is evident that this reduces to the third line of Eq. 1.30 for the binary case. In connection to Eq. 1.18 it was mentioned that the chemical potential of a component could be regarded as its partial molar Gibbs energy. Partial quantities of other molar properties can be defined in a similar way according to the general relation,

$$A_k \equiv \left(\frac{\partial A}{\partial N_k}\right)_{P,T,N_j} = A_m + \frac{\partial A_m}{\partial x_k} - \sum x_i\frac{\partial A_m}{\partial x_i} \tag{1.33}$$

As an example, by inserting H in place of A one obtains the partial enthalpy of component k in the solution, usually called **heat of solution of component k**.

Since each potential must have the same value in all parts of a system at equilibrium, two phases in equilibrium must have the same values for P, T and all the chemical potentials. In a molar Gibbs energy diagram for which P and T are kept constant it is thus necessary that the compositions of two phases in equilibrium are such that there is a **common tangent** and from the intersections on the component axes one can read the chemical potentials of the two-phase equilibrium. See Fig. 1.3.

A binary compound ϕ with constant composition is represented with a single point in the molar Gibbs energy diagram but it is convenient to represent it with a very narrow parabola which is consistent with the difficulty to vary its composition. Fig. 1.4 demonstrates that the chemical potentials of the components are not uniquely defined in such a phase.

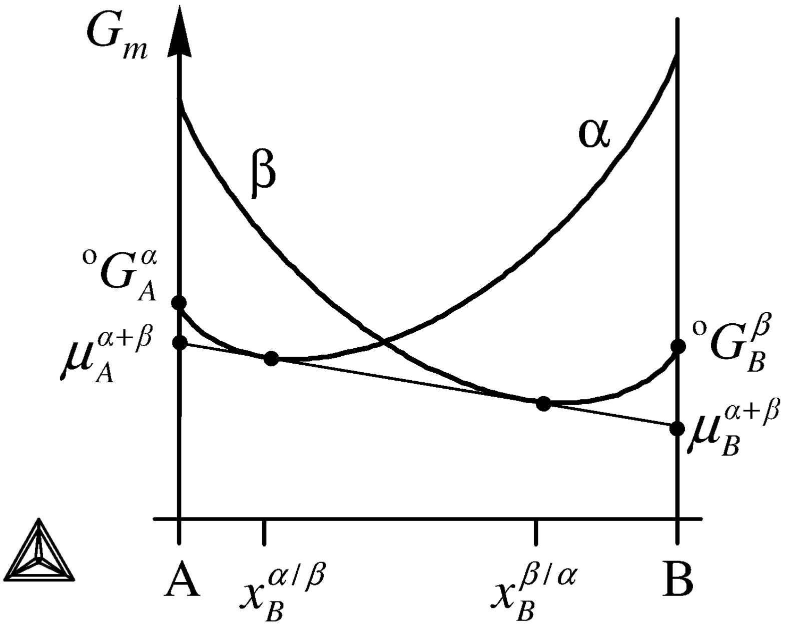


Figure 1.3: The equilibrium between binary phases is found from the common tangent. Its intercepts on the axes give the chemical potentials.

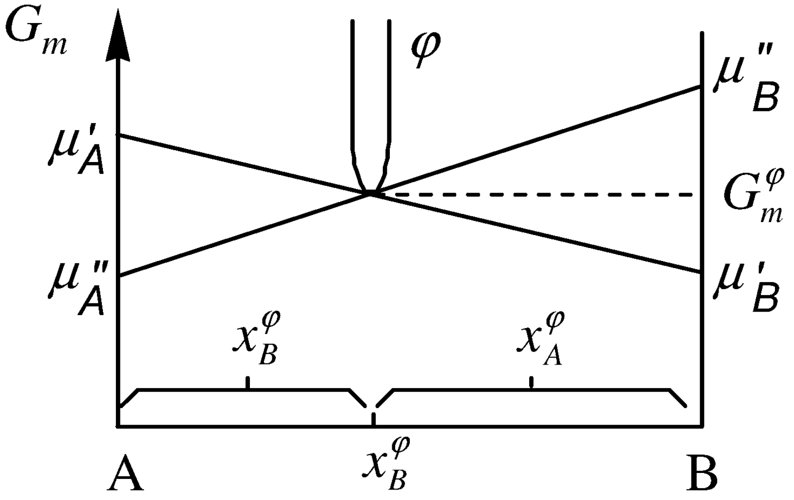


Figure 1.4: The chemical potentials are not defined by a phase of constant composition, a so-called stoichiometric phase. It is here approximated by a very sharp parabola.

Exercise 1.6.1. Use Eq. 1.17 for evaluating the chemical potentials of Ag and Cu at equilibrium in an Ag-Cu melt of 40 mass-% Cu at 1200 K and 1 bar.
Hint When you can define the conditions for a state of equilibrium in your software then it should be possible to make your software evaluate most properties of the state. Find out if it can evaluate μ_{Ag} and μ_{Cu} as partial derivatives, i.e. as $(dG/dN_i)_{P,T,N_j}$.

1.7 Gibbs–Duhem relation

In Fig. 1.4 one can give the tangent any slope through the point representing φ, a so-called stoichiometric phase. This demonstrates that the chemical potentials are not defined for such a phase alone. Two possibilities are shown in Fig. 1.4. They are identified by $'$ and $''$, respectively. However, the μ_A, μ_B pair can be chosen in an infinite number of ways but according to Eq. 1.21 it must obey the relation

$$G_m^{\phi} = x_A^{\phi}\mu_A + x_B^{\phi}\mu_B \tag{1.34}$$

This relation can also be verified geometrically from Fig. 1.4. Since x_A^{ϕ} and x_B^{ϕ} are constant and G_m^{ϕ} has a fixed value for this phase, we find

$$x_A^{\phi}d\mu_A + x_B^{\phi}d\mu_B = dG_m^{\phi} = 0 \tag{1.35}$$

Actually, one can prove that this relation also holds for a solution phase where the composition can vary, as long as the variation in composition is small. It is called the **Gibbs–Duhem relation** and its general form is

$$\sum x_i d\mu_i - V_m dP + S_m dT = 0 \tag{1.36}$$

Multiplying by N we obtain an alternative form of the Gibbs–Duhem relation.

$$\sum N_i d\mu_i - V dP + S dT = 0 \tag{1.37}$$

It should be emphasized that we have derived the Gibbs–Duhem relation only for a system containing a single phase. In fact, it only applies to each phase separately if there are more than one phase in the system.

Exercise 1.7.1. Consider the equilibrium between an A-rich phase and a stoichiometric A_3B_2 compound. Use Eq. 1.34 to illustrate how μ_B can be obtained from a molar Gibbs energy diagram.
Hint Remember that the molar Gibbs energy of all phases is expressed per mole of atoms in the molar Gibbs energy diagram, not per formula unit.

Exercise 1.7.2. The chemical potentials of A and B in an A-B solution phase can be changed by adding some B or by exchanging some A for the same amount of B. Check the validity of the Gibbs–Duhem relation at constant P and T for these two cases numerically on a solid Ag-Cu alloy with 5 atom-% Cu at 1 bar and 1100 K.
Hint For these two cases the Gibbs-Duhem relation yields

$$N_{Cu}\left(\partial\mu_{Cu}/\partial N_{Cu}\right)_{N_{Ag},P,T} + N_{Ag}\left(\partial\mu_{Ag}/\partial N_{Cu}\right)_{N_{Ag},P,T} = 0$$
$$N_{Cu}\left(\partial\mu_{Cu}/\partial N_{Cu}\right)_{N,P,T} + N_{Ag}\left(\partial\mu_{Ag}/\partial N_{Cu}\right)_{N,P,T} = 0$$

An advanced thermodynamic program can give all these derivatives directly. If that is not available to you, consider 1 mole of the alloy, first evaluate the chemical potentials directly, then add a small amount of Cu, e.g. 0.01 mole, and evaluate the new chemical potentials, and apply Eq. 1.37 to the differences obtained and, finally, do the same after also removing the same amount of A.

Exercise 1.7.3. It is common to express the chemical potential of oxygen in a gas through the partial pressure of the O_2 molecules. Of course, the value of this quantity is directly related to the chemical potential of O_2. Show that it is also related to the chemical potential of O. The result may seem absurd if there are no O atoms present. Some condition must be fulfilled. Which one?
Hint Apply Eq. 1.27.

1.8 Phases

A homogeneous system or portion of a system is regarded as a **phase** and is often denoted by a Greek letter, e.g. α, β, γ, δ etc. Many phases can have a variable composition and can then be regarded as **solution phases**. Phases are thus identified not by their composition but by their structure, e.g. body-centered cubic (bcc) or liquid (L). Many phases have an almost or practically constant composition, which can be represented by a chemical formula with small integers as coefficients, e.g. Al_2O_3. They are regarded as **stoichiometric phases**.

V, U and S are all **extensive** properties and are additive in the sense that the value for a composite system is the sum of the values of the parts, e.g.

$$V = V^\alpha + V^\beta \tag{1.38}$$

For a homogeneous system, the value of an additive property is proportional to the size of the system, N, and for all extensive properties one can define the **molar quantity**

$$V_m = V/N \tag{1.39}$$

The subscript m indicates that the size is here measured as the total number of mole of atoms, N. Tables with properties of substances always give molar properties. Molar properties can be regarded as **intensive** because they have the same value everywhere in a homogeneous system. However, they are not potentials like P, T and μ_i, which must have the same value everywhere in the whole system at equilibrium.

G is also an additive property *but only for systems with uniform P and T* because they are external variables. The molar Gibbs energy of a pure element A could be denoted $^\circ G^\alpha_m(A)$ but is usually abbreviated $^\circ G^\alpha_A$. From Eq. 1.17 it is evident that μ_A for a pure element in the α state is equal to $^\circ G^\alpha_A$ because $N = N_k$ and $G = N \cdot {}^\circ G^\alpha_A$. For a stoichiometric phase like Al_2O_3 one may define the molar Gibbs energy per mole of formula units, $^\circ G_{Al_2O_3}$, i.e. for five moles of atoms.

Exercise 1.8.1. Find the total Gibbs energy of a system containing 0.5 kg of Al_2O_3 and 1 kg of CaO at 1 bar and 1500 K. Suppose the two substances have not reacted with each other. Check the law of additivity.
Hint The system is not really in internal equilibrium since the two oxides have a tendency to react with each other. To avoid that they react with each other, you could simply omit all other phases from the set of data fetched from the database. To check the law of additivity, evaluate the total G and G of the Al_2O_3 phase and G of the CaO phase separately and add them.

1.9 Gibbs phase rule

The value of a potential in a system can be changed to a new value by bringing the system in contact with a large reservoir at another value. There are $c + 2$ such independent potentials, basically P, T and the chemical potentials for c components. It may seem that one has the freedom to vary all $c + 2$ potentials, i.e., one has $c + 2$ degrees of freedom. However, the Gibbs-Duhem relation states that a phase cannot remain in a system under changed conditions unless the variations of all the independent potentials are somehow related. The degrees of freedom to vary the conditions are thus reduced to $c + 2 - p$ where p is the number of phases one wants to be present in the system because the Gibbs-Duhem relation is different for all the phases. One also says that the variance for a system with p prescribed phases is

$$v = c + 2 - p \tag{1.40}$$

When applied to a phase diagram v is the dimensionality of phase fields but it should be realized that the rule was derived by considering potential variables. Consequently, it applies only to phase diagrams with potential axes. Fig. 1.5 illustrates this difference with an example from the Ag-Cu system, One degree of freedom has already been consumed by requiring that the pressure is always 1 bar, yielding a remaining variance of $v = c + 2 - p - 1 = 3 - p$. The first diagram has two potential axes and one-phase fields are two-dimensional, two-phase fields are linear and the three-phase field is the point of intersection in agreement with the rule. The other phase diagram has a two-phase field that is two-dimensional in conflict with the rule. The reason is the use of a molar axis which is not a potential.

Exercise 1.9.1. Sometimes one plots the phase diagram for a system with different sets of axes in order to illustrate different aspects. Fig. 1.5 shows the Ag-Cu phase diagram at a pressure of 1 bar, plotted in two ways. Locate the fcc+L phase field in both diagrams and try to apply the Gibbs phase rule. Explain the results.
Hint In this system there are two fcc phases. Choose one of them. Remember under what conditions the rule was derived.

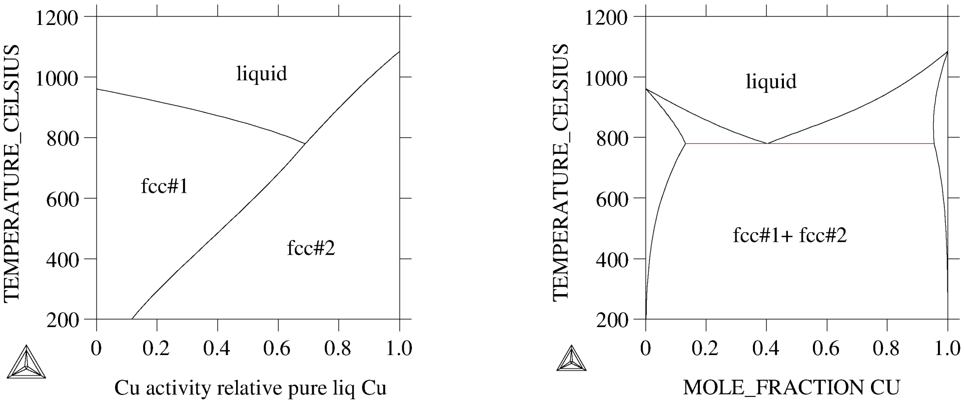


Figure 1.5: The Ag-Cu phase diagram at 1 bar.

Exercise 1.9.2. Eq. 1.16 has some terms with a potential as variable and some with an extensive quantity. Which one is intensive and which one is extensive in the term $Dd\xi$?
Hint You may for instance consider the solidification of a pure metal as the internal process.

1.10 Introduction of new components

In Section 1.5 it was shown how one could define a new component for a particular purpose. A common case is a solution phase containing associates between the basic components, e.g. a gas phase with two components, H and O elements or H_2 and O_2 molecules, which may react to form H_2O molecules. According to Eq. 1.27, equilibrium for the reaction requires that

$$\mu_{H_2O} = 2\mu_H + \mu_O \tag{1.41}$$

It could also be written

$$\mu_{H_2O} = \mu_{H_2} + 0.5\mu_{O_2} \tag{1.42}$$

because $\mu_{H_2} = 2\mu_H$ and $\mu_{O_2} = 2\mu_O$ at equilibrium, again according to Eq. 1.27 but now with $a = 2$ and $b = 0$. The driving force for the reaction $H_2 + 0.5O_2 \rightarrow H_2O$, before equilibrium has been established, can be written as

$$D = \mu_{H_2} + 0.5\mu_{O_2} - \mu_{H_2O} \tag{1.43}$$

where all the chemical potentials are evaluated from the actual amounts of the species.

One could thus define a new set of components in any way provided that the Gibbs phase rule is satisfied by the number of **independent** components being correct. As an example where a new set of components may be convenient one can mention a system obtained by mixing several stoichiometric oxides. Oxygen and the primary oxides may then be used as the set of independent components instead of the set of elements. At equilibrium one can directly obtain the chemical potentials for one set in terms of those in the other set using Eq. 1.27. However, if all the oxides were stoichiometric and formed from different elements, there should be no way of varying the oxygen content independently. Eq. 1.17 could not be applied to oxygen and the oxygen potential could not be defined, nor the potentials of the other elements, only the potentials of the oxides.

Stoichiometric phases may be taken as an example. From a database one may obtain some thermodynamic properties of an oxide MO by tabulation, e.g. the molar Gibbs energy of a particular crystalline structure, ${}^{\circ}G^{\varphi}_{MO}$. Other pieces of information may be obtained be calculations from the basic information. If a general kind of software for thermodynamic calculations is available it probably requires that the degrees of freedom are reduced to zero by the specification of conditions. For a system with only the MO phase one obtains $v = c + 2 - p = 2 + 2 - 1 = 3$. Two further conditions could be prescribed values of P and T. It will be necessary to introduce one more condition. It could be another phase formed by one or both of the components, e.g. metallic M or gaseous O_2 or the oxygen potential. One can use any such condition as long as one is interested in only the properties of MO, e.g. its heat capacity or enthalpy. For a system with oxides of two different metals, MO and LO, the situation will be the same and also the remedy.

Exercise 1.10.1. For the Ca-O-Si system it may be natural to use the three elements as components. However, suppose you are only interested in the reactions between the two primary oxides, CaO and SiO_2, and you like to compute the CaO-SiO_2 phase diagram, which is really a quasibinary section of the ternary one. Should you expect any problem? If so, try to solve it.
Hint A thermodynamic program normally treats the elements as components and for a ternary system there are three. In the present case it may seem natural to define CaO and SiO_2 as the components but the program may still require a third component. You have to introduce a third component that is not situated on the CaO-SiO_2 line. It may seem most logical to select O as the third component. To avoid that other phases in the CaO-O-SiO_2 system appear in the calculation it may be convenient to use a very low O activity, e.g. 10^{-10}.

1.11 Gibbs energy of formation

Consider an A-B system consisting of pure A and pure B which are not soluble in each other. The values of μ_A and μ_B are thus established as ${}^{\circ}G^{\alpha}_{A}$ and ${}^{\circ}G^{\beta}_{B}$. Then, suppose A and B atoms in the correct amounts form one mole of a new stoichiometric phase, the ϕ phase. The change of the molar Gibbs energy of the system will be

$$\Delta G_m = G^{\phi}_m - x^{\phi}_A \mu_A - x^{\phi}_B \mu_B = G^{\phi}_m - x^{\phi}_A \, {}^{\circ}G^{\alpha}_A - x^{\phi}_B \, {}^{\circ}G^{\beta}_B \tag{1.44}$$

The formation of ϕ is illustrated with a molar Gibbs energy diagram in Fig. 1.6. In this case the compound forms under a decrease of the Gibbs energy and the driving force is thus positive, $D = -\Delta G_m$.

The formula of a compound is usually given with the coefficients a and b as small integers and the Gibbs energy per mole of formula unit is $G^{\phi}_{A_aB_b} = (a + b)\, G^{\phi}_m$. The change per formula unit of the new phase ϕ when formed from pure A and pure B will be,

$$\Delta_f^\circ G^\phi_{A_aB_b} = {}^\circ G^\phi_{A_aB_b} - a{}^\circ G^\alpha_A - b{}^\circ G^\beta_B = -(a+b)\,D \tag{1.45}$$

The superscript ° indicates that a quantity refers to a pure component or stoichiometric compound. The quantity $\Delta_f^\circ G^\phi_m$ is regarded as the **standard Gibbs energy of formation** of the ϕ phase if ${}^\circ G^\alpha_A$ and ${}^\circ G^\beta_B$ have been chosen as the molar Gibbs energies of pure A and B in their most stable states at the same P and T, their standard states. See Section 1.14. This quantity is thus negative for all compounds that can form spontaneously from the standard states of the elements.

The magnitude of the driving force of a phase with variable composition depends on the exact composition of the phase as it precipitates (in this specific case, the phase is stoichiometric, i.e. always the same composition) but also on the composition of the parent phase if it is a solution phase. The largest value is obtained with a parallel tangent construction in Fig. 1.7(a) which illustrates the precipitation from a solution phase. The composition of that phase, $(x_A^{\alpha\circ}; x_B^{\alpha\circ})$, controls the chemical potentials of both components and this phase acts as a reservoir of both components. Instead of the molar Gibbs energies of the pure components one should here introduce the chemical potentials of the parent solution phase in Eqs. 1.44 and 1.45 obtaining

$$D = x^\phi_A \mu^{\alpha\circ}_A + x^\phi_B \mu^{\alpha\circ}_B - G^\phi_m \tag{1.46}$$

G^ϕ_m in Eq. 1.46 is defined for 1 mole of atoms. Multiplying Eq. 1.46 with $a+b$, rearranging and inserting the value for ${}^\circ G^\phi_{A_aB_b}$ from Eq. 1.45 and knowing that $x^\phi_A = a/(a+b)$ and $x^\phi_B = b/(a+b)$, we obtain

$$(a+b)\,D = a\left(\mu^{\alpha\circ}_A - {}^\circ G^\alpha_A\right) + b\left(\mu^{\alpha\circ}_B - {}^\circ G^\beta_B\right) - \Delta_f^\circ G^\phi_{A_aB_b} \tag{1.47}$$

The composition of the solution phase will change gradually as the precipitation proceeds and the driving force will thus decrease until it approaches zero as a final equilibrium is established when the parallel tangents coincide. Fig. 1.7(a) thus shows the initial driving force and Fig. 1.7(b) shows the total driving force for the complete process. It is expressed per mole of the precipitated phase because it comes from a molar Gibbs energy diagram. It may be called integrated driving force and may sometimes be denoted D_{int} since it is obtained by integration over the whole process. It should be emphasized that an integrated driving force can be evaluated only between two states of the same composition. In a molar Gibbs energy diagram they must fall on the same vertical line.

Thermodynamic information of compounds is often tabulated in the form of standard Gibbs energy of formation i.e. defined relative to the standard states at the current P and T. However, in computerized databases it is preferable to store the properties of substances as functions of temperature and it is then more convenient to have references at a fixed temperature. See Section 1.14.

Exercise 1.11.1. Evaluate the standard Gibbs energy of formation of $Cr_{23}C_6$ at 1 bar and 1000 K from your data bank system.
Hint Find the Gibbs energy for 1 mole of formula units of $Cr_{23}C_6$. Start by changing the references of Cr and C to bcc-Cr and graphite at 1 bar and 1000 K.

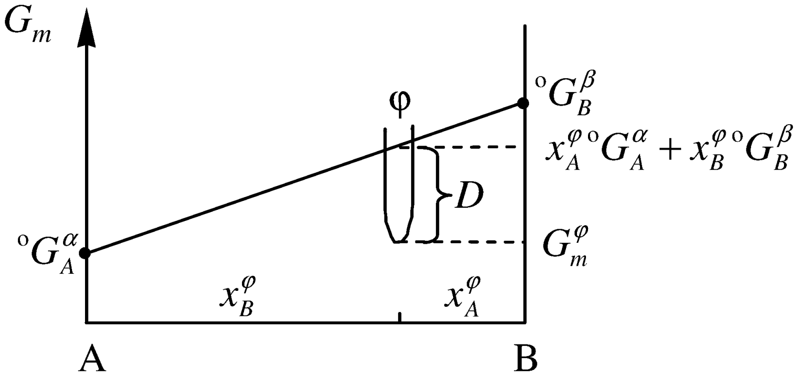


Figure 1.6: Construction to find the driving force to form one mole of a binary phase from the pure components.

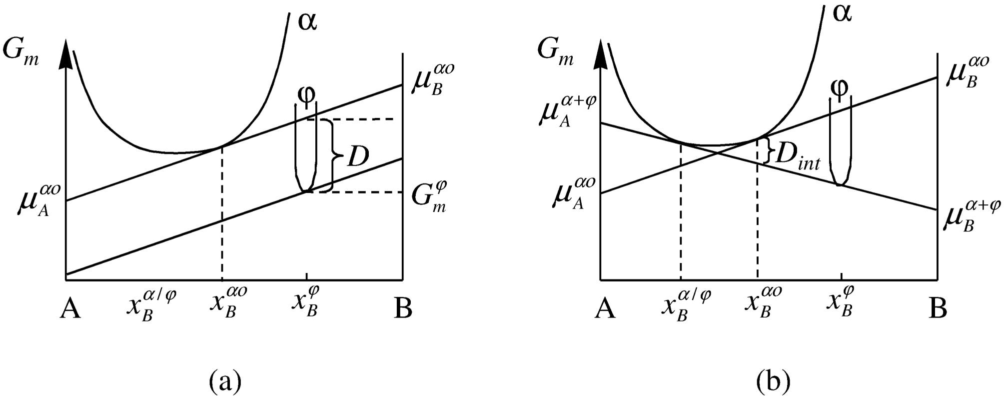


Figure 1.7: (a) Construction to find the initial driving force D for precipitating a binary ϕ phase from a solution phase of an initial composition $x_B^{\alpha\circ}$. (b) Diagram showing the final composition, $x_B^{\alpha/\phi}$, of the parent phase at the $\alpha + \phi$ equilibrium. D_{int} is the integrated driving force for the complete precipitation process.

1.12 Properties of the Gibbs energy function

As already discussed, it is possible to express all the thermodynamic properties of a substance through its Gibbs energy. This is accomplished by the use of various partial derivatives of the characteristic state function $G(P, T, N_i)$. Eq. 1.17 is just one example. In the same way one obtains

$$V = (\partial G/\partial P)_{P,T,N_i} \tag{1.48}$$

$$S = -(\partial G/\partial T)_{P,N_i} \tag{1.49}$$

$$H \equiv U + PV = G + TS = G - T(\partial G/\partial T)_{P.N_i} = (\partial (G/T)/\partial (1/T))_{P,N_i} \tag{1.50}$$

One defines the **heat capacity** as the capability of a system to receive heat under a given increase of T, dQ/dT. It used to be called specific heat. Under constant P we obtain

$$C_P = (\partial H/\partial T)_{P,N_i} = -T\left(\partial^2 G/\partial T^2\right)_{P,N_i} = T(\partial S/\partial T)_{P,N_i} \tag{1.51}$$

The molar heat capacity is defined as C_P/N. Furthermore, one defines the **isothermal compressibility** and **thermal expansion** as

$$\kappa_T = -(\partial V/\partial P)_{T,N_i}/V = -\left(\partial^2 G/\partial P^2\right)_{T,N_i}/(\partial G/\partial P)_{T,N_i} \tag{1.52}$$

$$\alpha = (\partial V/\partial T)_{P,N_i}/V = \left(\partial^2 G/\partial T \partial P\right)_{N_i}/(\partial G/\partial P)_{T,N_i} \tag{1.53}$$

The definitions of k_T and α can be applied to the molar volume without change of the numerical value but the results of Eq. 1.51 is proportional to the size. It is usually applied to the molar Gibbs energy and the result is called molar heat capacity.

These three quantities are particularly important properties and can be determined experimentally for various substances. Such information is compiled into tables that have been the primary source for the evaluation of other thermodynamic data, mainly for Gibbs energy. In recent years one has started to collect evaluated functions of $G(P, T, N_i)$ from such information and store them into computerized databases. One may use automatic procedures based on the above relations and similar ones to directly obtain all the properties needed for a practical application. With advanced software it may not even be necessary to inspect or handle the values of those properties. They may be directly applied to the practical situation and the output could give the answer to a technical question.

Exercise 1.12.1. Evaluate the enthalpy of pure Mo at 2000 K relative 25°C and 1 bar.
Hint You may not need to use Eq. 1.50 because most kinds of thermodynamic software have special procedures for the evaluation of the properties based on the first derivatives of G.

Exercise 1.12.2. Evaluate the thermal expansion of an alloy of Fe with 0.5 mass-% C at 1300 K and 1 bar from stored information on G for the fcc phase, which is the stable phase under those conditions.
Hint Again you need the kind of software that can evaluate partial derivatives.

1.13 Adiabatic changes

We can rearrange the second law from Eq. 1.6 using Eq. 1.13,

$$dS = dQ/T + d_{ip}S = dQ/T + (1/T)\, Dd\xi \tag{1.54}$$

During a very rapid compression of a material one may imagine that there is no time for heat conduction nor for an internal process. The first condition means that the compression is **adiabatic**, $dQ = 0$, and the second condition means that the compression is reversible, because there is not sufficient time for an internal process, $d\xi = 0$. Eq. 1.54 shows that these conditions make $dS = 0$. An adiabatic and reversible change is **isentropic**. The change of temperature during this kind of compression can be expressed as $(\partial T/\partial P)_S$.

Exercise 1.13.1. Consider a shock wave traveling through a plate of iron, which initially is at 20°C. Evaluate dT/dP.
Hint A shock wave is very fast and there is very little time for heat conduction. It may happen that there is time for some dislocation movements and the wave may leave the material slightly deformed. Neglecting such effects one can approximate the compression and the release of pressure on the back side of the wave as isentropic. One could then obtain dT/dP when the wave is approaching as $(\partial T/\partial P)_S$. It is directly obtainable from an advanced data bank system for thermodynamics. If such a system is not available one must express the partial derivative in terms of the properties available in tables, i.e. C_P, α and κ_T, which are second derivatives of G with respect to P and T. In that case you should thus transform $(\partial T/\partial P)_S$ to derivatives where P and T are the variables. Since S is also involved you should consider a function $S(T, P)$.

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

For $dS = 0$

$$0 = \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S + \left(\frac{\partial S}{\partial P}\right)_T$$

and using Eqs. 1.51 and 1.53

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial S}{\partial P}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{-\partial^2 G}{\partial P \partial T}\right) \Big/ \left(\frac{-\partial^2 G}{\partial T^2}\right) = \frac{V\alpha}{C_P/T}$$

It should be emphasized that V, α and C_P vary with P and T and detailed information is required in order to integrate this result to higher pressures. That can be obtained from a database but integration is still laborious. Much can be gained by using an advanced data bank system.

1.14 State of reference and standard states

Thermodynamic modeling of the properties of solution phases will be described in Chapter 2. The chemical potentials of the components vary with composition and different models use different functions of the composition variables. The chemical potentials of the pure components are usually given as the molar Gibbs energy of the component in the same crystallographic structure as the solution phase, denoted by $^\circ G_A^\alpha$ where the superscript $^\circ$ indicates that the quantity concerns the component in pure form. $^\circ G_A^\alpha$ is thus used as a reference for the chemical potential of A in the α solution. It may be regarded as a **model-based reference**. When comparing the chemical potential of a component in two different phases one may need a common reference. In Fe-Cr solutions one may like to compare the chemical potential of chromium with the value obtained for pure bcc-Cr at the same P and T, i.e., at the current P and T. This is the most stable form of chromium and it is common practice to use the most stable form of the element as a common reference. It is often regarded as the standard state of the element and may be denoted by $^\circ G_A^{std}$. It is as in the definition of the standard Gibbs energy of formation in Eq. 1.45. The relation between two references is found by applying the fact that the actual chemical potential, μ_A^α, is not affected by the choice of reference made when one wanted to express it with a number.

$$\mu_A^\alpha = {}^\circ G_A^\alpha + f\left(comp\right) = {}^\circ G_A^{std} + \left({}^\circ G_A^\alpha - {}^\circ G_A^{std}\right) + f\left(comp\right) \tag{1.55}$$

One will thus have to add the quantity $\left({}^\circ G_A^\alpha - {}^\circ G_A^{std}\right)$ to the function $f\left(comp\right)$.

There is also a need of references for the description of Gibbs energy as function of P and T. It must be independent of P and T and it is then possible simply to use the most stable state of the element at normalized values of P and T. This may be denoted by $^\circ G_A^{NPT}$ where NPT stands for Normalized P and T. Usually, one uses 298.15 K (25°C) and 1 bar or possibly 1 atm. If there is a need of yet another kind of reference, it may simply be denoted by $^\circ G_A^{ref}$.

The kind of reference, represented by the Gibbs energy of a state, is not sufficient for all purposes because there are two contributions to Gibbs energy, an enthalpy part and an entropy part and each one requires a reference. The enthalpy has no natural reference and it can be chosen arbitrarily but should follow international agreement. One usually uses the enthalpy of the most stable state at 1 bar and 298.15 K. For the entropy there is a natural zero point for the elements at 0 K according to the third law of thermodynamics. The problem is that it is difficult to determine experimentally the difference of entropy between 298.15 K and 0 K. Nevertheless, there is a system called the G-HSER system that uses this zero point. A dataset based on this system should thus be able to return the absolute values of entropy. In practice this may be best satisfied for the most stable phase of the elements. The considerable uncertainty for other states of the elements has practical consequences only at very low temperatures. The enthalpy reference for one mole of an element will be denoted by H_A^{SER} and data are given as $G_A - H_A^{SER}$ for a unary (one component) system and as $G_m - H^{SER}$ for a solution or compound of more than one component where H^{SER} represents an average over the components.

1.15 Duhem's theorem

In the state of equilibrium under given P, T and N_i all the internal variables have obtained their optimum values, which minimize the Gibbs energy of the whole system. In principle, the Gibbs energy of a system *in equilibrium* is thus uniquely defined by a function of variables and, in principle, they may be controlled from the outside, so-called external variables, $G = G\left(P, T, N_i\right)$. This is true independent of how many phases are involved, although the G function is more complicated the more phases there are. For a closed system, i.e. a system with a given content of matter, i.e. all the N_i, the equilibrium state can vary only with P and T. When computing the state of equilibrium using a computer program, one could thus give two conditions, primarily the values of P and T, in addition to all N_i. This is called **Duhem's theorem**. Altogether this makes $2 + c$ conditions and it is interesting to see how the number of necessary conditions is related to the degrees of freedom according to the Gibbs phase rule.

Exercise 1.15.1. Using a thermodynamic data bank system, determine the state of equilibrium of an alloy with 20 mole-% Cu in Ag at 800°C and 1 bar.
Hint The size is not prescribed and you can choose any size, e.g. $N = 1$. With that choice $N_{Cu} = 0.2$ and $N_{Ag} = 0.8$. Or you could enter the condition as $N = 1$ and $x_{Cu} = 0.2$ or even $N_{Cu} = 0.2$ and $x_{Ag} = 0.8$.

Exercise 1.15.2. From the previous exercise you know that there will be two phases, fcc and liquid (L). You will also know the amounts and compositions of the phases. Omit the condition on the value of the temperature and accept the value of the Cu content in L as a new condition for an attempt to determine the temperature.
Hint Of course, you should expect to recreate the same state of equilibrium, i.e. to find $T = 1073\,\mathrm{K}$.

1.16 Characteristic state function and Gibbs energy model

The state of a system can be defined by the values of a sufficient set of variables that describe the conditions for the system. The state of a homogeneous system of a given internal structure can be completely defined with a set of independent state variables. Gibbs energy is one of several functions of such state variables which describe thermodynamic properties of a system. It has the very useful property that all other thermodynamic properties can be expressed through it and its derivatives with respect to the state variables P, T and N_i. The function $G(P, T, N_i)$ may be regarded as a characteristic state function and the Helmholtz energy, $F(V, T, N_i)$, is another example. The sets of variables, P, T, N_i and V, T, N_i, are regarded as their respective set of natural variables.

By measurements and modeling one may hope to construct an equation yielding the value of Gibbs energy as a function of its natural variables, i.e. $G(P, T, N_i)$, containing various numerical parameters. It could be used for calculating values of all thermodynamic properties at fixed values of P, T and N_i.

In the modeling of Gibbs energy of a system, P, T and N_i are all regarded as external variables because their values can be controlled by actions from the surroundings. However, there are also internal variables but their values will spontaneously be adjusted to changes in the external variables until a state of equilibrium has been established. That state represents the Gibbs energy minimum under the given external conditions. In principle, the Gibbs energy function $G(P, T, N_i)$ is thus well-defined through the model under equilibrium conditions. On the other hand, it is often impossible to express that function analytically. In modeling, Gibbs energy is given as an equation with internal variables in addition to the external variables, $G(P, T, N_i, \xi_k)$, and it can thus be evaluated for any set of values, including both kinds of variables. Gibbs energy as a characteristic state function only applies under equilibrium conditions but in an actual calculation one gives start values to the internal variables and gradually adjusts their values until a minimum of G has been found and the initial function has been reduced to the characteristic state function $G(P, T, N_i)$. The modeled form of the Gibbs energy with internal variables is very valuable also away from the states of equilibrium because it can give information on the driving force for the processes that lead to equilibrium. The function $G(P, T, N_i, \xi_k)$ will simply be regarded as a thermodynamic model.

For a system with more than one phase, the model will be composed of functions like $G_m^\alpha\,(P, T, x_i^\alpha, \xi_1^\alpha, \xi_2^\alpha, \ldots)$ for all the possible phases, each one multiplied by the amount of that phase, N^α, which is another internal variable. The equilibrium of the complex system could be obtained by minimizing that complicated expression with respect to all the internal variables. This is what the thermodynamic data bank system does when you ask for the equilibrium to be computed.

It may be noted that phase equilibria and phase diagrams as well as properties of systems at equilibrium can all be described by intensive quantities, i.e. potentials or molar quantities. In principle, it should thus be possible to obtain all such information without involving the size of the system. However, available methods of computation based on minimizing the Gibbs energy normally require access to the size, which may be chosen arbitrarily.

Exercise 1.16.1. For the Ag-Cu system, try to use the condition that fcc and L must be present in an equilibrium at 800°C and 1 bar.
Hint A way to define that both phases are present would be to require a certain amount of each one, e.g. 1 mole. According to Duhem's theorem it then remains to define $2 + c - 2 = c = 2$ conditions, which should be the values of P and T.

Chapter 2

Solution Models

2.1 Constitution and constituents

The basic features of thermodynamics were dealt with in Chapter 1 and the effect of variations in the composition of phases was an important topic. Variations with the change of the content of components were described, often the number of atoms of various elements expressed through the numbers, N_i, or mole fractions, x_i. Chapter 2 will now deal with the modeling of solution phases. Many phases have more than one kind of sites for the atoms. The sites are then divided into **sublattices** and a model may be based on the assumption that atoms of different elements prefer to dissolve in different sublattices. Each atom will have a different effect on the properties of the phase depending on in what sublattice it resides. An essential part of the model can then be described with a formula and $(\mathrm{A,B})_1\,(\mathrm{B,C,D})_2$ is an example with two sublattices of which the second one has twice as many sites as the first one and it can dissolve atoms of the B, C and D elements whereas the first one can dissolve A and B atoms. This situation will be regarded as the **constitution** of the phase. The indices 1 and 2 are the **stoichiometric coefficients** of the phase. A and B are the **constituents** of the first sublattice and B, C and D are the constituents of the second sublattice. B can thus reside in both sublattices and will then be regarded as two different constituents although they are atoms of the same element. The contents of the constituents on each sublattice will be described with their fractions within the sublattice. They are called **site fractions** and are denoted $y_j^{\alpha k}$ for constituent j in the k:th sublattice of phase α. They are defined as $y_j^{\alpha k} = N_j^{\alpha k}/\sum N_i^{\alpha k}$. Naturally, for each sublattice, $\sum y_i^{\alpha k} = 1$. An ionized atom may also occupy a site and is then regarded as a constituent different from the neutral atom of the same element even if they reside in the same sublattice.

It may also happen that atoms combine to form molecules or other kinds of **associates**. When a solution phase is modeled with an associate in the same sublattice as single atoms, they are all regarded as constituents of that sublattice.

A model of a phase with two or more sublattices may be given as an analytical function of the site fractions, not mole fractions. It will normally be possible to evaluate the mole fraction of a phase from information on the site fractions and the stoichiometric coefficients. It should finally be mentioned that anything that can occupy a site is regarded as a **species** irrespective of where it is situated. A, B, C and D in the above example are thus four different species but an A^{+1} ion would not be the same species as the neutral A atom. An $\mathrm{A_1B_2}$ associate (or molecule) would also be regarded as a species if it could occupy a single site according to the model.

Exercise 2.1.1. The mole fractions of the components in a phase can be evaluated from the site fractions if one considers the stoichiometric coefficients. Evaluate the mole fraction of component B in the phase $(\mathrm{A,B})_1(\mathrm{B,C,D})_2$ if $y'_B = 0.2$ and $y''_B = 0.05$.
Hint Apply the definition $x_B = N_B/\sum N_i$ to one formula unit.

Exercise 2.1.2. Give the formula showing the constitution of an $\mathrm{A_1B_2}$ phase if one has been able to decrease the mole fraction of B to 0.5 by some A atoms entering as a second constituent of the second sublattice.
Hint Express the formula in a general way as $\mathrm{A_1(A_{1-z}B_z)_2}$ and apply $x_B = N_B/\sum N_i$.

2.2 Ideal solutions and related non-ideal solutions

In a **substitutional** solution all the components can **substitute** for each other because they occupy the same kind of lattice sites. With statistical methods one can show that already the physical mixing of the components in a substitutional solution contributes to the molar entropy by the amount $-R\sum x_i \ln x_i$ if the mixing is random. The effect on the molar Gibbs energy will thus be $-TS = +RT\sum x_i \ln x_i$. If this is the only thermodynamic effect of the mixing, then the chemical potential of each component in a phase α is given as

$$\mu_i^\alpha = {}^\circ G_i^\alpha + RT\ln x_i^\alpha \tag{2.1}$$

This is **the ideal solution model**, x_i^α is the mole fraction of component i and ${}^\circ G_i^\alpha$ is the molar Gibbs energy of pure component i of the same structure (phase) as the solution and *at the current P and T*. Pure i is often regarded as one of the end-members of the solution phase and ${}^\circ G_i^\alpha$ is a model-based reference for component i in the phase α. It may be selected in a different way by applying another model. This will always happen if the solution cannot be extended all the way to pure i. Inserting μ_i^α in Eq. 1.21 we find for the molar Gibbs energy of this solution,

$$G_m^\alpha = \sum x_i^\alpha \mu_i^\alpha = \sum x_i^\alpha\, {}^\circ G_i^\alpha + RT\sum x_i^\alpha \ln x_i^\alpha \tag{2.2}$$

The first summation of terms on the right hand side represents the average of the references for the components and this summation may thus be regarded as the frame of reference for the mixture. For a binary solution it may be regarded as a line of reference. That is illustrated in Fig. 2.1, which shows the same case as Fig. 1.2 .

The last summation in Eq. 2.2 is recognizes as the effect of the ideal entropy of mixing in the Gibbs energy. All the terms are negative because all mole fractions are less than unity. This summation represents the distance of the G_m curve below the line of reference. Fig. 2.2 illustrates the same situation for a ternary solution phase. The triangle at the top represents the model-based plane of reference, $\sum x_i\, {}^\circ G_i$.

In reality, one should always expect some deviation from ideality and it is often expressed with an excess Gibbs energy, ${}^E G_m^\alpha$, defined from

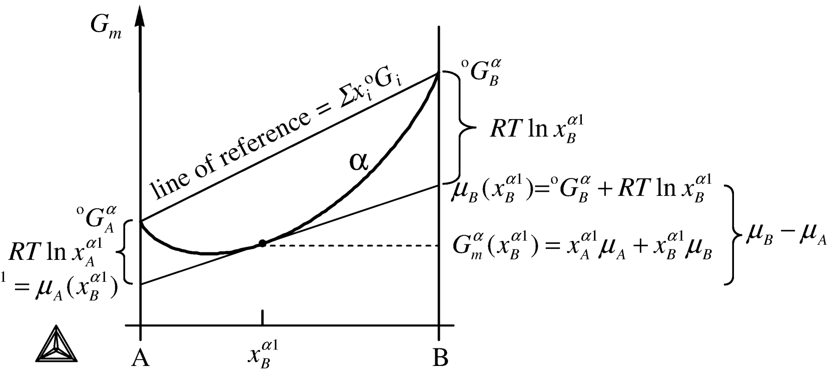


Figure 2.1: Molar Gibbs energy diagram for an ideal binary α phase, illustrating the line of reference and the construction to obtain the chemical potentials for a given composition.

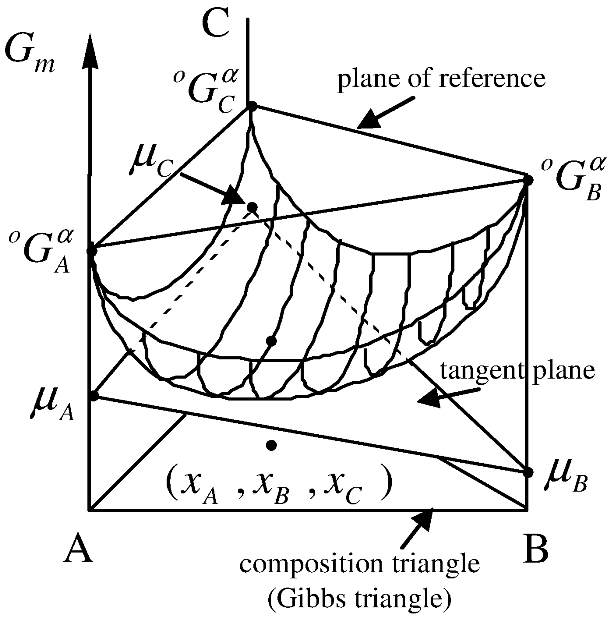


Figure 2.2: Molar Gibbs energy diagram for a ternary phase, illustrating the plane of reference and the construction to obtain the chemical potentials for a given composition.

$$G_m^\alpha = \sum x_i^\alpha \mu_i^\alpha = \sum x_i^\alpha \, {}^\circ G_i^\alpha + RT \sum x_i^\alpha \ln x_i^\alpha + {}^E G_m^\alpha \tag{2.3}$$

Of course, ${}^E G_m^\alpha$ depends on the composition and several models have been proposed. By definition, ${}^E G_m^\alpha \Rightarrow 0$ as the composition approaches a pure component, e.g. one of the three corners in Fig. 2.2. Deriving an expression for the chemical potential of a component i, we obtain instead of Eq. 2.1,

$$\mu_i^\alpha = {}^\circ G_i^\alpha + RT \ln x_i^\alpha + {}^E G_i^\alpha \tag{2.4}$$

${}^E G_i^\alpha$ is the **partial excess Gibbs energy** for component i in the α phase and is obtained by applying Eq. 1.30 to G_m^α from Eq. 2.3. If an analytical expression has been chosen for ${}^E G_m^\alpha$ as function of composition, then one can derive an expression for ${}^E G_i^\alpha$ by applying Eq. 1.33 to ${}^E G_m^\alpha$. An example will be presented in Section 2.5.

There are many special models. When states of equilibrium or values of thermodynamic properties at equilibrium are calculated with computer, then the time and cost depend only marginally on whether the data are expressed with the simple ideal solution model or more sophisticated ones. However, it can make an enormous difference if one calculates by hand or even with a hand calculator. The ideal solution model was used extensively before the advent of the computer. It still predominates in teaching where exact results are not as important as the demonstration of how various factors may affect the results. This is particularly true for reactions between molecules in a solution, which will be considered in the next section.

Numerical values can be obtained only relative to references, e.g. as the differece $\mu_i^\alpha - {}^\circ G_i^\alpha$ from Eq. 2.4 or as $\mu_i^\alpha - {}^\circ G_i^{\mathrm{ref}}$ by introducing another reference. One may then obtain numerical values of

$$\mu_i^\alpha - {}^\circ G_i^{\mathrm{ref}} = \mu_i^\alpha - {}^\circ G_i^\alpha + \Delta_{\mathrm{ref}} {}^\circ G_i^\alpha \tag{2.5}$$

where $\Delta_{\mathrm{ref}}^{\circ} G_i^\alpha = {}^\circ G_i^\alpha - {}^\circ G_i^{\mathrm{ref}}$. This is identical to Eq. 1.45 when applied to a single component. The molar Gibbs energy of the α phase can thus be stored as the numerical values of $\Delta_{\mathrm{ref}}^{\circ} G_i^\alpha$ in addition to the excess parameter ${}^E G_m^\alpha$.

Exercise 2.2.1. In the regular solution model of a binary A-B system one assumes that ${}^E G_m = L_{AB} x_A x_B$. Evaluate the partial excess Gibbs energy of component B. *Hint* You can apply Eq. 1.32 directly by neglecting the other terms in G_m or Eq. 1.33 by identifying A_m with ${}^E G_m$.

2.3 Chemical activity and activity coefficient

Each kind of solution requires its own kind of model. Many models have similarities with the ideal solution model in Eq. 2.1 but the mole fraction is replaced by a quantity called activity or chemical activity, a_B. Thermodynamically it is defined by its relation to the chemical potential.

$$\mu_B = {}^\circ G_B + RT \ln a_B \tag{2.6}$$

$^\circ G_B$ can here be the Gibbs energy of any real or hypothetical state of pure B, selected for expressing the activity. It defines the numerical values of the activity by making $\ln a_b = 0$, i.e $a_B = 1$ when $\mu_B = {}^\circ G_B$ and it is thus a reference for the activity.

Let us now consider the case where $^\circ G_B$ is chosen as $^\circ G_B^\alpha$, the value for pure B of the same phase. Then $a_B = x_B$ if the solution is ideal as defined by Eq. 2.1. Real solutions deviate from the ideal behaviour and one may write $a_B = f_B x_B$ where f_B is the **activity coefficient**. It may be regarded as a correction factor to x_B and is normally a function of composition. Eq, 2.6 yield

$$\begin{aligned}\mu_B &= {}^\circ G_B^\alpha + RT \ln a_B^\alpha \\ &= {}^\circ G_B^\alpha + RT \ln f_B^\alpha + RT \ln x_B^\alpha\end{aligned} \tag{2.7}$$

Comparison with 2.4 yields the relation between the two approaches

$$RT \ln f_B = {}^E G_B^\alpha \text{ i.e. } f_B^\alpha \equiv \exp\left({}^E G_B^\alpha / RT\right) \tag{2.8}$$

We will soon discuss the modelling of $^E G_m^\alpha$.

When comparing with other phases it is essential to use common references for the chemical potentials, e.g. by chosing standard states for the elements at the current P and T or global references at a particular pressure and temperature, the SER reference being an example. See Section 1.14. We will here use the notation G_B^{ref} for any such reference. When combining pieces of thermodynamic information on a system from different sources it is essential to check that they are based on the same set of references. If that is not the case, it is necessary to transform the data, which were given relative to a local set of references, e.g. as $\Delta G_m^\alpha \equiv G_m^\alpha - \sum x_i^\alpha \, {}^\circ G_i^{local}$, into $\Delta^{ref} G_m^\alpha$, where the superscript ref now indicates that values refer to any set of agreed references. It is obtained as

$$\Delta^{ref} G_m^\alpha \equiv G_m^\alpha - \sum x_i^\alpha \, {}^\circ G_i^{ref} = \Delta G_m^\alpha + \sum x_i^\alpha \left({}^\circ G_i^{local} - {}^\circ G_i^{ref}\right) \tag{2.9}$$

$^\circ G_i^{local} - {}^\circ G_i^{ref}$ is the difference in Gibbs energy of pure i in the two states of reference. When comparing the activity of an element B in two different solution phases, one often finds that the reference for pure B in each phase has been taken from the end-member B in that phase, i.e. $^\circ G_B^\alpha$ and $^\circ G_B^\beta$, respectively. It is then common to prefer the most stable state as the common reference, say α. See Section 1.14. The difference $^\circ G_B^\alpha - {}^\circ G_B^\beta$ is regarded as the **lattice stability** of pure B in the less stable β state relative to the most stable state. It is thus negative by definition.

Exercise 2.3.1. One has studied solutions of Mn in fcc Fe-Ni and bcc Fe-Cr alloys at 1200 K and has expressed the Mn activity using pure fcc-Mn and pure bcc-Mn, respectively, as references. For both alloys, Fe-Mn-Ni and Fe-Mn-Cr, one obtained $a_{Mn} = 0.03$. What alloy had the highest activity?
Hint To answer this question you must use a common reference and you may use any state as the common reference, say fcc-Mn. With a data bank system you can simply ask for the activity relative fcc-Mn instead of bcc-Mn as long as you have kept data for the fcc phase. Of course, you could just as well solve the problem analytically by changing to the fcc reference using $a_{Mn}^{fcc-ref} = a_{Mn}^{bcc-ref} \cdot \exp\left[\left({}^\circ G_{Mn}^{bcc} - {}^\circ G_{Mn}^{fcc}\right)/RT\right]$ but then you must first evaluate the difference for Mn in the two states at 1200 K.

2.4 Excess Gibbs energy

${}^{E}G_{B}^{\alpha}$ in Eq. 2.7 was defined in Eq. 2.4. It is regarded as the partial excess Gibbs energy for component B. For a binary A-B solution there would be partial excess Gibbs energies for both components and they are not independent of each other. That will automatically be taken care of by starting from an expression for the excess molar Gibbs energy, ${}^{E}G_{m}^{\alpha}$, defined in Eq. 2.3 and deriving expressions for the various partial excess Gibbs energies by applying Eq. 1.33 to ${}^{E}G_{m}^{\alpha}$. Naturally ${}^{E}G_{m}^{\alpha} = 0$ for all the pure elements if all the references have been chosen from the pure elements in the phase under consideration, here to be denoted by ${}^{\circ}G_{j}^{\alpha}$. For this choice, the simplest approach for a binary A-B solution would be

$$ {}^{E}G_{m}^{\alpha} = L x_{A}^{\alpha} x_{B}^{\alpha} \tag{2.10} $$

With $L = 0$ this model degenerates to the ideal solution model, with L independent of composition but not of temperature. This is called the **regular solution model**. Some more complicated solution models describe L as a power series in $x_{A}^{\alpha} - x_{B}^{\alpha}$.

When applied to ${}^{E}G_{m}^{\alpha}$ from Eq. 2.10, Eq. 1.33 yields ${}^{E}G_{A}^{\alpha} = L(x_{B}^{\alpha})^{2}$ and

$$ \begin{aligned} \mu_{A}^{\alpha} &= {}^{\circ}G_{A}^{\alpha} + RT\ln a_{A}^{\alpha} \\ &= {}^{\circ}G_{A}^{\alpha} + RT\ln x_{A}^{\alpha} + {}^{E}G_{A}^{\alpha} \\ &= {}^{\circ}G_{A}^{\alpha} + RT\ln x_{A}^{\alpha} + L\left(x_{B}^{\alpha}\right)^{2} \end{aligned} \tag{2.11} $$

$$ \begin{aligned} \mu_{B}^{\alpha} &= {}^{\circ}G_{B}^{\alpha} + RT\ln a_{B}^{\alpha} \\ &= {}^{\circ}G_{B}^{\alpha} + RT\ln x_{B}^{\alpha} + {}^{E}G_{B}^{\alpha} \\ &= {}^{\circ}G_{B}^{\alpha} + RT\ln x_{B}^{\alpha} + L\left(x_{A}^{\alpha}\right)^{2} \end{aligned} \tag{2.12} $$

Eq. 2.3 yields

$$ f_{B}^{\alpha} = e^{[L(x_{A}^{\alpha})^{2}/RT]} \tag{2.13} $$

$$ a_{B}^{\alpha} = f_{B}^{\alpha} x_{B}^{\alpha} = x_{B}^{\alpha} e^{[L(x_{A}^{\alpha})^{2}/RT]} \tag{2.14} $$

It is easy to see that $G_{m} = x_{A}\mu_{A} + x_{B}\mu_{B}$ will contain the excess term given by Eq. 2.10.

Fig. 2.3 a illustrates the effect of various values of the regular solution parameter on the molar Gibbs energy in a binary solution and Figs. 2.3 b and 2.3 c present the corresponding variations of the chemical activities when the pure elements in the same phase have been chosen as standard states for the activities.

The high activity values in Figs. 2.3 b and c obtained with large L, cannot represent stable states. There would even be a positive driving force for the formation of pure B from a solution with $a_{B} > 1$. To examine this problem we should go back to Fig. 2.3 a and draw a double tangent to one of the curves for large L values. Fig. 2.4 illustrates that all states on the curve between the tangent points could decrease their Gibbs energy by separating into two phases with compositions on those points. The average Gibbs energy of such a "mechanical mixture" will

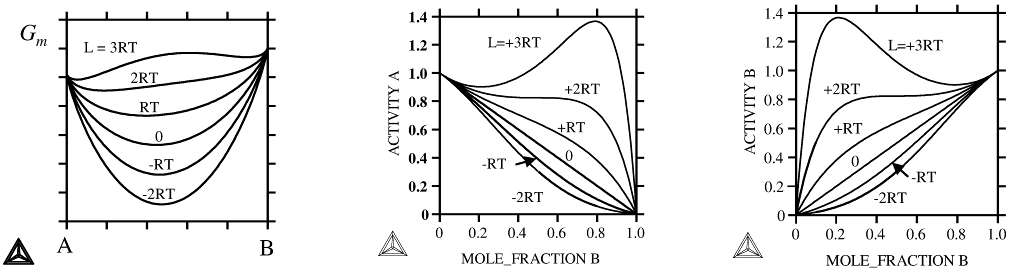


Figure 2.3: a) The binary regular solution model for a series of values of the interaction energy. b) The activity of A in the regular solutions illustrated in a). c) The activity of B in the regular solutions illustrated in a).

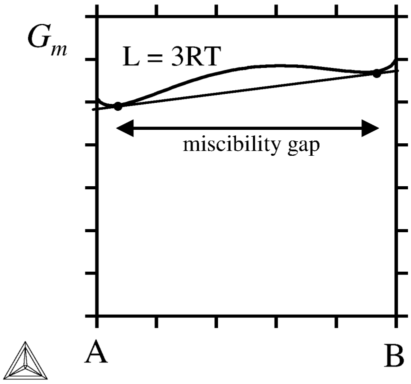


Figure 2.4: Gibbs energy diagram illustrating the construction to find a miscibility gap. The Gibbs energy curve is taken from Fig. 2.3

fall on the tangent. There is thus a miscibility gap between those points. For all alloys within the miscibility gap there is a positive driving force for decomposition into two phases, one rich in A and the other rich in B. Compare with Fig. 1.3.

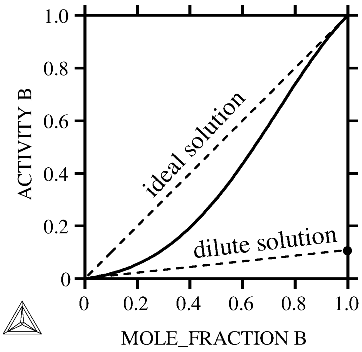
For a ternary solution the regular solution model yields

$$G_m^\alpha = \sum x_i \,{}^\circ G_i^\alpha + RT \sum x_i \ln x_i + L_{AB} x_A x_B + L_{BC} x_B x_C + L_{CA} x_C x_A \tag{2.15}$$

$$\mu_A^\alpha \equiv G_A^\alpha = {}^\circ G_A^\alpha + RT \ln x_A + L_{AB} x_B \left(1 - x_A\right) - L_{BC} x_B x_C + L_{CA} x_C \left(1 - x_A\right) \tag{2.16}$$

$$\mu_B^\alpha \equiv G_B^\alpha = {}^\circ G_B^\alpha + RT \ln x_B + L_{AB} x_A \left(1 - x_B\right) + L_{BC} x_C \left(1 - x_B\right) - L_{CA} x_C x_A \tag{2.17}$$

$$\mu_C^\alpha \equiv G_C^\alpha = {}^\circ G_C^\alpha + RT \ln x_C - L_{AB} x_A x_B + L_{BC} x_B \left(1 - x_C\right) + L_{CA} x_A \left(1 - x_C\right) \tag{2.18}$$



$\leftarrow \exp[{}^{E}G_B(x_B \rightarrow 0)/RT] = \exp(L/RT)$

Figure 2.5: Comparison between the ideal and dilute solution models for a regular solution with $L = -2RT$. The dilute solution model is based on the tangent at infinite dilution, i.e. Henry's law.

Exercise 2.4.1. An A-B solution phase can be approximated as a regular solution with $L_{AB} = 20$ kJ/mol at 800°C. Evaluate the activity coefficient for B at $x_B = 0.40$. *Hint* You must solve this exercise analytically if you cannot create your own database for the regular solution model. Having evaluated the activity coefficient, f_B, you should also evaluate a_B.

2.5 Dilute solutions

For a discussion of methods to treat information on activities at the two ends of a binary solution, the curve for $L = -2RT$ from Fig. 2.3 c is again shown in Fig. 2.5. It is interesting to note that the modelled activity of B approaches the ideal solution model close to pure B. That is called **Raoult's law**. For small x_A^α, i.e., x_B^α close to 1, it is demonstrated by Eqs. 2.12 and 2.14 which yields

$$\mu_B^\alpha \cong {}^\circ G_B^\alpha + RT \ln x_B^\alpha + 0 \tag{2.19}$$

$$a_B^\alpha \cong x_B^\alpha e^0 = x_B^\alpha \tag{2.20}$$

By extending the initial tangent to the activity curve in Fig. 2.5, one obtains **Henry's law** for dilute solutions. It is also demonstrated by Eqs. 2.12 and 2.14 for x_A^α close to 1, i.e. for small x_B^α,

$$\mu_B^\alpha \cong {}^\circ G_B^\alpha + RT \ln x_B^\alpha + L \tag{2.21}$$

$$a_B^\alpha \cong x_B^\alpha exp(L/RT) = f_B^\alpha x_B^\alpha \tag{2.22}$$

$$\text{where } f_B^\alpha = exp(L/RT) \tag{2.23}$$

There are many cases where one has information only from a dilute range of a solution and information may then be described with Henry's law using $^\circ G_B^\alpha$ as a reference for the chemical potential of B. L can thus be evaluated from the initial slope of the B activity and be inserted in Eq. 2.12 to yield a regular solution extrapolation to higher B contents. However, $^\circ G_B^\alpha$ would not be known if there is no information on pure B in the α state. The combination $^\circ G_B^\alpha + L$ in Eq. 2.21 instead of L would then be the unknown parameter which could be evaluated from Henry's law. If one notices some deviation from Henry's law at the highest B contents available, then one can separate $^\circ G_B^\alpha$ and L to obtain the best fit of the limited information and again apply Eq. 2.12 for some extrapolation to higher B contents.

By tradition it is common to apply Henry's law with any convenient measure of B content, e.g. mole % or mass % or even molality. Denoting mass % with w_B one writes Henry's law as $a_B^\alpha = \gamma_B^\alpha w_B^\alpha$. In this case one usually uses the standard state of B as the reference.

$$\mu_B^\alpha \equiv {}^\circ G_B^{std} + RT \ln a_B^\alpha \cong {}^\circ G_B^{std} + RT \ln w_B^\alpha + RT \ln \gamma_B^\alpha \tag{2.24}$$

The activity coefficient has here been denoted by γ_B^α to make it evident that it differs from f_B^α. If w_B^{eq} is the B content in equilibrium with pure B in its standard state, i.e., at the activity 1, then $\gamma_B^\alpha = 1/w_B^{eq}$ if Henry's law applies.

Exercise 2.5.1. The experimental information on many terminal solutions is very limited and often one only gives an ideal solution description based on the Gibbs energy of the solute element in a hypothetical state with the same structure as the solvent. On the other hand, there are methods to estimate that energy relative to the stable state of the solute element in pure form. Study the description of the solution of Si in fcc-Al in your data bank.

1. Plot the activity of Si in the fcc solution (suspend all other phases) at 500°C all the way to pure Si using fcc-Si as reference.
2. Change the reference state to the stable state of Si at the current T and plot the diagram again.
3. From the activity of pure Si obtained from the first diagram compared to the second one, you may calculate the difference in Gibbs energy between the two reference states.

Hint

2. To find the stable state of Si you may for instance calculate the binary phase diagram.
3. Applying the definition of the chemical potential for the two cases you get $\mu_{Si} = {}^\circ G_{Si}^{(1)} + RT \ln a_{Si}^{(1)} = {}^\circ G_{Si}^{(2)} + RT \ln a_{Si}^{(2)}$.

2.6 Phases with sublattices

There are many cases where all the lattice sites are not equivalent. Then one distinguishes between two or more sublattices and various elements may prefer different sublattices. One may define an ideal solution for such phases by requiring that there is random mixing within each sublattice and no excess Gibbs energy term. For a solution phase $(A,B)_a(C,D)_b$ there will be four **end-members**, A_aC_b, B_aC_b, A_aD_b and B_aD_b. The ideal entropy of mixing is determined by the fractions of the elements within each sublattice, the so-called **site fractions** y_i, defined for each sublattice separately. Quantities related to the sublattices can be identified by $'$ and $''$. Since $\left(N_A + N_B\right)/a = \left(N_C + N_D\right)/b$ we obtain $\left(x_A + x_B\right)/a = \left(x_c + x_D\right)/b$ by dividing with the total number of atoms, N. The relation to the ordinary mole fractions is

$$y'_B = \frac{N_B}{N_A + N_B} = \frac{x_B}{x_A + x_B} \tag{2.25}$$

$$y''_C = \frac{N_C}{N_C + N_D} = \frac{(a/b)\,N_C}{N_A + N_B} = \frac{(a/b)\,x_C}{x_A + x_B} \tag{2.26}$$

A simple sublattice solution model without any excess terms is defined for one mole of formula units,

$$G_m = \sum\sum y'_i y''_j \, {}^{\circ}G_{i_a j_b} + aRT\sum y'_i \ln y'_i + bRT\sum y''_j \ln y''_j \tag{2.27}$$

${}^{\circ}G_{i_a j_b}$ represents a model-based reference for the $i_a j_b$ component compound and it is regarded as a compound energy of an end-member. The double summation of terms is a weighted average of all the compound energies and may be regarded as a model-based surface of reference. $y'_i y''_j$ is the fraction of ij bonds between the two sublattices, assuming random mixing within each sublattice and one can show that $\sum\sum i_a j_b = 1$ since $y'_A + y'_B = 1$ and $y''_C + y''_D = 1$. The other two terms represent the entropy contributions caused by random mixing within each sublattice.

This model is regarded as the ideal compound energy model. It provides a basis for more complicated and sophisticated models and in that connection it is called the **Compound Energy Formalism**, CEF. The chemical potentials of the elements cannot be defined for such a phase alone because Eq. 1.17 cannot be applied when there is a stoichiometric constraint, in this case $(N_A + N_B)/a = (N_C + N_D)/b$. One component cannot be varied when all the others are kept constant. Instead of regarding the constituents as the components of the system one may thus regard the end-member compounds as components. For their chemical potentials one can derive an equation with some resemblance to Eq. 1.32.

$$\mu_{A_aC_b} = G_m + \frac{\partial G_m}{\partial y'_A} + \frac{\partial G_m}{\partial y''_C} - y'_A\frac{\partial G_m}{\partial y'_A} - y'_B\frac{\partial G_m}{\partial y'_B} - y''_C\frac{\partial G_m}{\partial y''_C} - y''_D\frac{\partial G_m}{\partial y''_D} \tag{2.28}$$

Without any excess terms, the result will be

$$\mu_{A_aC_b} = {}^{\circ}G_{A_aC_b} + y'_B y''_D \Delta^{\circ}G_{A_aC_b+B_aD_b} + aRT\ln y'_A + bRT\ln y''_C \tag{2.29}$$

where

$$\Delta^{\circ}G_{A_aC_b+B_aD_b} = {}^{\circ}G_{A_aD_b} +^{\circ} G_{B_aC_b} -^{\circ} G_{A_aC_b} -^{\circ} G_{B_aD_b} \tag{2.30}$$

This quantity is often regarded as the Gibbs energy of the reciprocal reaction between pure compounds, $A_aC_b + B_aD_b \rightarrow A_aD_b + B_aC_b$. Fig. 2.6 illustrates the model-based surface of reference for a reciprocal solution phase $\sum y'_i y''_j \, {}^{\circ}G_{i_a j_b}$ and it should be emphasized that this surface is not planar as the one in Fig. 2.2 unless $\Delta^{\circ}G_{A_aC_b+B_aD_b} = 0$ in Eq. 2.30, i.e. ${}^{\circ}G_{A_aD_d} +^{\circ} G_{B_aC_b} = {}^{\circ}G_{A_aC_b} +^{\circ} G_{B_aD_b}$. To save the properties of the reciprocal phase it is thus sufficient to

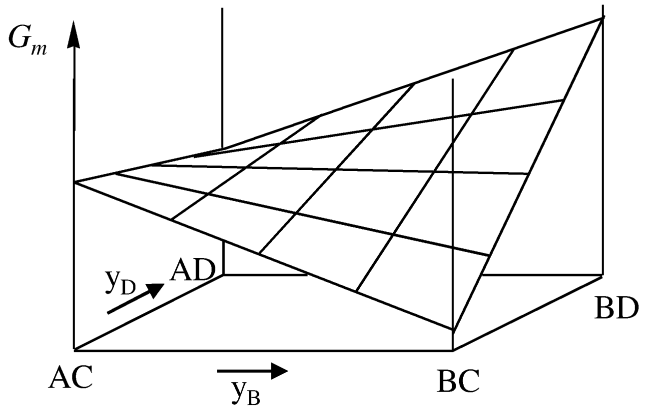


Figure 2.6: Surface of reference for a reciprocal phase in a quaternary system.

store information on the four end-member compounds, which is done as described for $\Delta^{\text{ref}}G^{\phi}_{A_aB_b}$ in Eq. 1.45.

Through Eq. 2.29 and three similar equations one can thus evaluate four chemical potentials, $\mu_{A_aC_b}$, $\mu_{A_aD_b}$, $\mu_{B_aC_b}$ and $\mu_{B_aD_b}$. However, by combining them, two and two, one can show that

$$\mu_{A_aC_b} + \mu_{B_aD_b} = \mu_{A_aD_b} + \mu_{B_aC_b} \tag{2.31}$$

Actually, this relation can be derived directly by applying Eq. 1.27 since each side of Eq. 2.31 will then be equal to $a\mu_A + a\mu_B + b\mu_C + b\mu_D$. This kind of system is regarded as a reciprocal system and due to the Gibbs–Duhem relation, applied to the elements, it behaves as a ternary system although it contains four elements. Only three of them can be regarded as independent of each other. There is thus a compositional constraint and the number of components in the Gibbs phase rule should be decreased by subtracting the number of constraints. This fact is illustrated by the composition tetrahedron in Fig. 2.7 where the reciprocal solution phase is restricted to the planar square. Only three of the chemical potentials in Eq. 2.31 can be independent. The composition square in Figs. 2.6 and 2.7 can thus be compared with the composition triangle in Fig. 2.2.

If one would like to consider the chemical potentials of the elements then one must fix one of them to a constant value that may be chosen arbitrarily, say μ_D. Eq. 1.27 then yields

$$a\mu_A = \mu_{A_aD_b} - b\mu_D \tag{2.32}$$

$$a\mu_B = \mu_{B_aD_b} - b\mu_D \tag{2.33}$$

$$b\mu_C = \mu_{A_aC_b} - \mu_{A_aD_b} + b\mu_D \tag{2.34}$$

One can insert Eq. 2.29 and three similar equations in order to obtain analytical expressions for the chemical potentials of the elements. One may regard μ_D as a reference because the other three

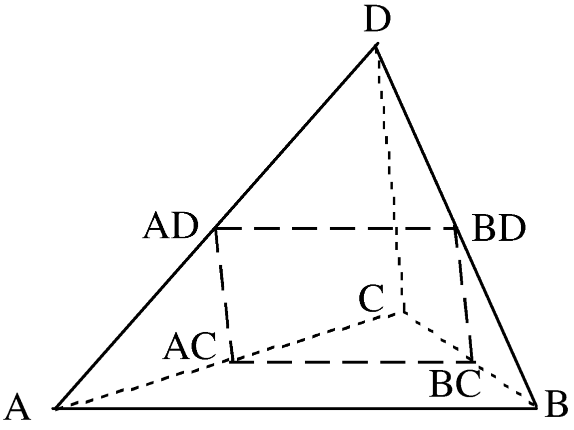


Figure 2.7: Composition tetrahedron for a quaternary system with the composition square for a reciprocal solution phase, $(A, B)_1 (C, D)_1$.

chemical potentials are given relative to μ_D and it is even possible that μ_D is fixed by interaction with the surrounding. The component D may for instance be oxygen and the surrounding may be a gas phase of a given oxygen pressure. All the other three chemical potentials are then defined by the composition of the reciprocal phase.

Deviations from ideal behaviour can be described with excess Gibbs energy terms containing regular solution parameters representing interactions between atoms on the same sublattice. In the present case the terms would be of the following type $y'_A y''_C y''_D L_{A:C,D}$. Higher order terms can also be introduced.

If all elements can dissolve in both sublattices, at least to some degree, then one must include many more compound energies e.g. ${}^{\circ}G_{A:B}$. The model could thus turn very complicated. However, with a computer program there should be no practical problem once all the parameter values have been evaluated.

It should be noted that the chemical potentials of all the elements can be evaluated from the model if at least one element, e.g. A, dissolves in both sublattices because $\mu_{A:A}$ is equal to the chemical potential of the end-member A_aA_b which is $a+b$ atoms of A in the particular structure of A_aC_b. One may then define a model-based reference ${}^{\circ}G_A^{\text{ref}} = {}^{\circ}G_{A:A}/(a+b)$

When the compound energy formalism is applied to a solution between two compounds, which differ on one sublattice only, e.g. A_aC_b and A_aD_b, the result will be much simpler because $y'_A = 1$. Without any excess terms Eqs. 2.27 and 2.29 will give

$$G_m = y''_C \, {}^{\circ}G_{A_aC_b} + y''_D \, {}^{\circ}G_{A_aD_b} + bRT \left(y''_C \ln y''_C + y''_D \ln y''_D \right) \tag{2.35}$$

$$\mu_{A_aC_b} = {}^{\circ}G_{A_aC_b} + bRT \ln y''_C \tag{2.36}$$

The compound energy formalism thus reduces to the ordinary ideal solution model by the site fraction y''_i playing the role of the mole fraction x_i. One may thus regard the compound energy formalism, CEF, as a generalization of the ordinary solution model. Numerical values of the chemical potentials of component compounds can be defined as $\mu_{A_aC_b} - a\,{}^\circ G_A^\alpha - b\,{}^\circ G_C^\gamma$ or as $\mu_{A_aC_b} - a\,{}^\circ G_A^{\mathrm{ref}} - b\,{}^\circ G_C^{\mathrm{ref}}$.

It should be emphasized that with the CEF, the site fractions are defined for the elements A, B etc., which are the constituents, whereas the thermodynamic quantities are defined for the end-member compounds.

Exercise 2.6.1. Suppose $a = b = 1$ and ${}^\circ G_{AC} = 10$, ${}^\circ G_{AD} = 8$, ${}^\circ G_{BC} = 2$, ${}^\circ G_{BD} = 20$ (kJ/mol) in Eq. 2.27. Derive an equation for the line of reference along the AD-BC diagonal using y'_B as the variable.
Hint Start by expressing y'_A, y''_C and y'_D as functions of y'_B along the diagonal.

2.7 Interstitial solutions

Interstitial solutes reside in sites between the host atoms. One may define those sites as belonging to an interstitial sublattice, which is initially occupied by vacancies. Such solutions can be described with the compound energy formalism and the vacancies may be regarded as an additional species and constituent. We may identify the vacancies with the D species in section 2.3 and the interstitials with the C species. The $\mathrm{A_aVa_b}$ compound will simply be a moles of A with all interstitial sites vacant, i.e. a moles of pure A. From Eq. 1.27 we have

$$\mu_{A_aVa_b} = a\mu_A + b\mu_{Va} \tag{2.37}$$

and we find that $\mu_{Va} = 0$. For a simple interstitial solution $A_a\left(C, Va\right)_b$ we get

$$\mu_{A_aC_b} = a\mu_A + b\mu_C \tag{2.38}$$

$$\mu_{A_aC_b} - \mu_{A_aVa_b} = a\mu_A + b\mu_C - a\mu_A - b\mu_{Va} = b\mu_C \tag{2.39}$$

$$\begin{aligned}\mu_C &= (1/b)\left(\mu_{A_aC_b} - \mu_{A_aVa_b}\right)\\ &= (1/b)\left({}^\circ G_{A_aC_b} + bRT\ln y''_C - {}^\circ G_{A_aVa_b} - bRT\ln y''_{Va}\right)\\ &= (1/b)\left({}^\circ G_{A_aC_b} - a\,{}^\circ G_A + bRT\ln\left(y''_C/\left(1 - y''_C\right)\right)\right)\end{aligned} \tag{2.40}$$

For the solvent we obtain

$$\mu_A = (1/a)\,\mu_{A_aVa_b} = (1/a)\left[{}^\circ G_{A_aVa_b} + bRT\ln\left(1 - y''_C\right)\right] \tag{2.41}$$

Exercise 2.7.1. The interstitial solution of C in fcc-Fe can be represented by the formula $Fe_1\left(Va,C\right)_1$. Using a database compute and plot μ_C and a_C as functions of the C content at 1200 K and 1 bar from 0 to 1.5 mass-% C, using graphite as reference. Use the mole fraction of C, not y''_C.
Hint Of course, the computer can directly evaluate x_C and plot the diagram.

2.8 The ideal gas model

For a monatomic species the ideal gas model predicts that

$$\mu_J = K_J + RT\ln P_J \tag{2.42}$$

P_J is regarded as the partial pressure of species J but is actually defined as $y_J P$ where y_J is the fraction of J relative to all other species in the gas and P is the total pressure. Eq. 2.42 can thus be written as

$$\mu_J = K_J + RT\ln P + RT\ln y_J \tag{2.43}$$

The ideal gas thus behaves as an ideal solution of the species but $K_J + RT\ln P$ contains a much stronger pressure dependence through $RT\ln P$ than $^\circ G_i$ in Eq. 2.1 does for condensed phases. For a gas species one usually defines the pure species at a pressure of 1 bar as the reference at the current temperature, i.e. the standard state. Then K_J is identical to $^\circ G_J\left(1\,\mathrm{bar}, T\right)$. With that reference Eq. 2.42 can thus be written as

$$\mu_J = {}^\circ G_J\left(1\,\mathrm{bar}, T\right) + RT\ln P_J \tag{2.44}$$

Of course, this requires that one expresses partial pressures in bar, not pascal, which is normally required. For gaseous species we will let ° indicate that the species is in pure gaseous form, at 1 bar and at the current temperature. We will thus omit the information "(1 bar)" from that notation. We get a similar expression for diatomic J_2 species,

$$\mu_{J_2} = {}^\circ G_{J_2} + RT\ln P_{J_2} \tag{2.45}$$

where $^\circ G_{J_2}$ is the Gibbs energy of one mole of the J_2 species at 1 bar and the current temperature. Between monatomic and diatomic species we have $\mu_{J_2} = 2\mu_J$ at equilibrium according to Eq. 1.27 with $a = 2$ and $b = 0$. From information on P_{J_2} one can then evaluate

$$\mu_J = 0.5\left({}^\circ G_{J_2} + RT\ln P_{J_2}\right) \tag{2.46}$$

We could thus evaluate the equilibrium value of P_J from the current value of P_{J_2} by combining Eqs. 2.44 and 2.46.

$$P_J^2 = P_{J_2}\exp\left[\left({}^\circ G_{J_2} - 2\,{}^\circ G_J\right)/RT\right] \tag{2.47}$$

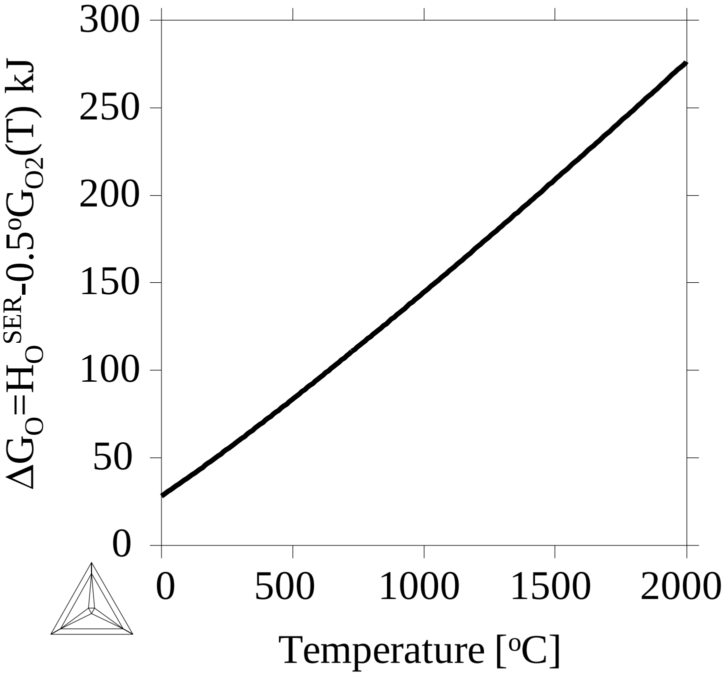


Figure 2.8: Difference between the SER reference and the reference for oxygen based on pure O_2 gas at the current temperature. The difference depends strongly on the temperature.

For the gaseous elements hydrogen, nitrogen and oxygen, the diatomic species is much more abundant than the monatomic species. In these cases one often prefers to use $0.5\,{}^\circ G_{J_2}$ as standard state for the element J and use it also when it appears in other phases. In such cases P_{J_2} is the partial pressure in an imagined atmosphere where *J and J_2 are in equilibrium.* On the other hand, in tables and computerized databases it is common to use the state of reference defined at 1 bar and 25°C, e.g. the SER system for which $G_J^{ref} = H_J^{SER}\,(1\,\mathrm{bar}, 298.15\,\mathrm{K})$. It is often necessary to transform from the $0.5\,{}^\circ G_{J_2}$ reference to another one and that is done by adding $\Delta G_J = G_J^{ref} - 0.5\,{}^\circ G_{J_2}\,(T)$. This transformation term varies with temperature as illustrated in Fig. 2.8 for changing the values of oxygen to the SER system.

When applying the law of mass action to a gas, it is advantageous to insert partial pressures instead of y_i fractions, which cannot be used without information on the total pressure. As an example, for the gaseous reaction $\mathrm{CO} + 0.5\mathrm{O}_2 \rightleftharpoons \mathrm{CO}_2$ we obtain the equilibrium from $\mu_{CO_2} = \mu_{CO} + 0.5\mu_{O_2}$ and inserting expressions for the chemical potentials according to Eq. 2.43 we would get

$$\frac{y_{CO_2}}{y_{CO}\sqrt{y_{O_2}}} = \sqrt{P}\exp\left(-\Delta^\circ G^{reaction}/RT\right) = K^y\,(P) \tag{2.48}$$

where

$$\Delta^\circ G^{reaction} = {}^\circ G_{CO_2} - {}^\circ G_{CO} - 0.5^\circ G_{O_2} \tag{2.49}$$

All the $^\circ G$ values are here given for 1 bar and the current temperature. The equilibrium "constant" would thus depend on the total pressure, P. By instead using expressions according to Eq. 2.44 we would eliminate the $\sqrt{P}$ factor and get

$$\frac{P_{CO_2}}{P_{CO}\sqrt{P_{O_2}}} = \exp\left(-\Delta^\circ G^{reaction}/RT\right) = K^P \tag{2.50}$$

Exercise 2.8.1. What is the partial pressure of monatomic H in a hydrogen gas when in internal equilibrium at 1 bar and 2000 K?

Exercise 2.8.2. Evaluate $\mu_O - H_O^{SER}$ and $\mu_O - 0.5{}^\circ G_{O_2}(T)$ for air with 20% O_2 at 1 bar and 1000 K.

Exercise 2.8.3. Find the value of the standard Gibbs energy of formation of monatomic O from O_2 at 1000 K.

2.9 Vapour pressure

Even a solid element M may have a vapour pressure, although usually very low. In that case, the standard state used for the gas would be based on the solid state at 1 bar and the current T and the chemical potential of the monatomic species in the gas, given by the ideal law for gases through Eq. 2.44, would be

$$\mu_M = {}^\circ G_M^{gas} + RT\ln P_M \pm {}^\circ G_M^{std} = {}^\circ G_M^{std} + \Delta_f^\circ G_M^{gas} + RT\ln P_M \tag{2.51}$$

$$P_M = \exp\left[\left(\mu_M - {}^\circ G_M^{std} - \Delta_f^\circ G_M^{gas}\right)/RT\right] \tag{2.52}$$

where $\Delta_f^\circ G_M^{gas} = {}^\circ G_M^{gas} - {}^\circ G_M^{std}$ is the standard Gibbs energy of formation of the monatomic M species in a gas from solid M if ${}^\circ G_m^{ref}$ is chosen as ${}^\circ G_M^{solid}$ at the current temperature. Similarly, the partial pressure of the M_2 constituent in the gas is

$$P_{M_2} = \exp\left[\left(\mu_{M_2} - 2\,{}^\circ G_M^{std} - \Delta_f^\circ G_{M_2}^{gas}\right)/RT\right] \tag{2.53}$$

where $\Delta_f^\circ G_{M_2}^{gas} = {}^\circ G_{M_2}^{gas} - 2\,{}^\circ G_M^{std}$. There may even be more complex species. It is not self-evident whether one should define the vapour pressure of an element M as the sum of the partial pressures of all species or as a measure of the total content of M in the gas. As an example, Fig. 2.9 illustrates the partial pressures of various gas species of sulphur over pure liquid sulphur.

Exercise 2.9.1. Find the partial pressures of Fe_1 and Fe_2, respectively, in equilibrium with solid fcc-Fe and bcc-Fe, respectively, at 1750 K. Suppose the solid phase is under a pressure of 1 bar caused by an inert atmosphere. From the results, decide whether bcc or fcc Fe is most stable.

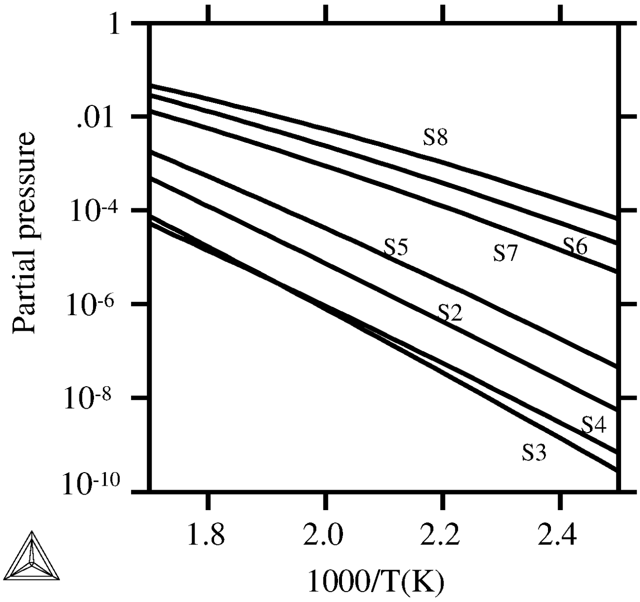


Figure 2.9: The equilibrium partial pressures of various sulphur species over liquid sulphur. S_8 is the most abundant species. Monatomic S is very rare and falls below the diagram.

2.10 Thermal vacancies

In a solid metal all the atoms are located in lattice sites but some sites are vacant. The number of vacancies increases with increasing temperature and one talks about **thermal vacancies**. In a simple thermodynamic model one considers the vacancies as a substitutional solute because they can substitute for the atoms. The formula for one mole of lattice sites will thus be written as $(A, Va)_1$ and the following model for the Gibbs energy per mole of formula units as obtained from the regular solution model will be

$$G_m = y_A\,{}^\circ G_A + y_{Va}\,{}^\circ G_{Va} + RT\left(y_A \ln y_A + y_{Va} \ln y_{Va}\right) + y_A y_{Va} L_{A,Va} \tag{2.54}$$

y_j is defined as mole j per mole of formula units, i.e. mole per mole of lattice sites. When examining this model one must realize that it concerns a unary system with A as the only component. The site fraction y_{Va} is thus an internal variable. To find its value at equilibrium one could study a partial derivative for which the content of A is kept constant. It is then necessary to use an expression of Gibbs energy as function of N_A and N_{Va}. It is related to Eq. 2.54 through $G_m = G\left(N_A, N_{Va}\right) / \left(N_A + N_{Va}\right)$. By further introducing $y_j = N_j / \left(N_A + N_{Va}\right)$ we obtain after omitting the excess term for simplification,

$$\begin{aligned}
G\left(N_A, N_{Va}\right) &= \left(N_A + N_{Va}\right) G_m \\
&= N_A\,{}^\circ G_A + N_{Va}\,{}^\circ G_{Va} + RT\left(N_A \ln \frac{N_A}{N_A + N_{Va}} + N_{Va} \ln \frac{N_{Va}}{N_A + N_{Va}}\right) \\
&= N_A\,{}^\circ G_A + N_{Va}\,{}^\circ G_{Va} \\
&\quad + RT\left[N_A \ln N_A + N_{Va} \ln N_{Va} - \left(N_A + N_{Va}\right) \ln\left(N_A + N_{Va}\right)\right]
\end{aligned} \tag{2.55}$$

Using a partial derivative we can now find the equilibrium.

$$\begin{aligned}\left(\frac{\partial G}{\partial N_{Va}}\right)_{N_A} &= {}^{\circ}G_{Va} + RT\left[\ln N_{Va} - \ln\left(N_A + N_{Va}\right)\right] \\ &= {}^{\circ}G_{Va} + RT\ln y_{Va} = 0\end{aligned} \tag{2.56}$$

$(\partial G/\partial N_{Va})_{N_A}$ looks as a definition of the chemical potential of vacancies and we will indeed accept this. However, since N_{Va} is an internal variable, it belongs to the kind of variables represented by ξ in Section 1.4 for which $D = -\partial G/\partial\xi = 0$ at internal equilibrium. We thus obtain the equilibrium content of vacancies as

$$y_{Va}^{eq} = \exp\left(-{}^{\circ}G_{Va}/RT\right) \tag{2.57}$$

It is not necessary to discuss the nature of ${}^{\circ}G_{Va}$. It is sufficient to accept that it is just an experimental parameter and its numerical value is obtained from information on y_{Va}^{eq} using Eq. 2.57. On the other hand, it is interesting that one can derive the chemical potential of the vacancies directly from the model defined by Eq. 2.54 by applying Eq. 1.32 which can be done if we consider the vacancies as a real component which can be dissolved from a surrounding vacuum. The site fractions will then become mole fractions. Eq. 1.32 will directly yield

$$\mu_{Va} = {}^{\circ}G_{Va} + RT\ln y_{Va} \tag{2.58}$$

This would give the same result as Eq. 2.56 if it is accepted that equilibrium with the surroundings implies that the chemical potential of vacancies has an absolute value of zero. That is a very convenient procedure which is often applied. The present result supports this procedure.

For the regular solution model one obtains

$$\mu_{Va} = {}^{\circ}G_{Va} + RT\ln y_{Va} + y_A^2 L_{AVa} \tag{2.59}$$

However, due to the low vacancy content it is not possible to distinguish experimentally between the effects of ${}^{\circ}G_{Va}$ and L_{AVa}. We can thus introduce a single parameter,

$$y_{Va}^{eq} = \exp\left[-\left({}^{\circ}G_{Va} + y_A^2 L_{AVa}\right)/RT\right] \simeq \exp\left[-E_{AVa}/RT\right] \tag{2.60}$$

It will thus be E_{AVa} that is evaluated from experimental information on y_{Va}^{eq} and it may again be emphasized that it is not necessary to consider its physical interpretation.

For vacancies in a binary phase we obtain by applying the regular solution model to a ternary solution,

$$\begin{aligned}G_m &= y_A\,{}^{\circ}G_A + y_B\,{}^{\circ}G_B + y_{Va}\,{}^{\circ}G_{Va} \\ &\quad + RT\sum y_i\ln y_i + y_A y_B L_{AB} + y_A y_{Va} L_{AVa} + y_B y_{Va} L_{BVa}\end{aligned} \tag{2.61}$$

$$\begin{aligned}\mu_{Va} &= {}^{\circ}G_{Va} + RT\ln y_{Va} - L_{AB} y_A y_B + L_{AVa} y_A\left(1 - y_{Va}\right) + L_{BVa} y_B\left(1 - y_{Va}\right) \\ &\simeq y_A E_{AVa} + y_B E_{BVa} + RT\ln y_{Va}\end{aligned} \tag{2.62}$$

The equilibrium content of vacancies in this approximation is again obtained with $\mu_{Va} = 0$ and it is thus predicted to vary with compositions as

$$y_{Va} = \exp\left[-\left(y_A E_{AVa} + y_B E_{BVa} - y_A y_B L_{AB}\right)/RT\right] \tag{2.63}$$

In a database one prefers to describe phases with the same mathematical model and Eq. 2.61 should thus be used as an expression of when there are thermal vacancies. To make it consistent with Eqs. 2.60 and 2.63 one could simply put $^\circ G_{Va}$ to zero and interpret L_{AVa} and L_{BVa} as E_{AVa} and E_{BVa}.

The vacancies considered in the discussion of interstitial solutions in Section 2.7 are regarded as stoichiometric vacancies. Their number depends directly on the composition, not on the temperature. Also for such vacancies it was shown that one may assume that their chemical potential in equilibrium is equal to zero.

Exercise 2.10.1. Suppose the fraction of vacancies in a pure solid metal is 10^{-3} at the melting point. What should be the fraction at half the melting point?
Hint Of course, half the melting point means half of the absolute melting temperature.

Exercise 2.10.2. Suppose a specimen of pure solid A is equilibrated at the melting point and then quenched to half that temperature. What is the driving force for decreasing the vacancy content at the new temperature? Use the value of $^\circ G_{Va}$ obtained from the preceding exercise.

2.11 Solutions with associates

Non-ideal behaviour of an α solution may be described by assuming that the **species** have a tendency to form more complex species, associates, which are sometimes identical to molecules that appear in another phase. All the species are treated as constituents and the composition variables will be described with the fractions of the constituents, $y_k = N_k/\sum N_i$. This could be called **constituent fraction** but it looks as a special case of the definition of site fraction introduced in Section 2.1, $y_j^{\alpha k} = N_j^{\alpha k}/\sum N_i^{\alpha k}$. It has thus been recommended to use the same symbol, y_i, for both and to apply the term site fraction to both although there are not separate sublattices in the present case. The mole fraction of component d is obtained as

$$x_d^\alpha = \sum_i a_d^i y_i^\alpha / \sum_i \sum_c a_c^i y_i^\alpha \tag{2.64}$$

The first two summations include all constituents i and a_d^i is the stoichiometric coefficient of component d in the constituent i. The third summation includes all components, c, and a_c^i is the stoichiometric coefficient of component c in the constituent i.

In a simple model one assumes that all constituents mix randomly with each other. For a simple A-B solution with free atoms and an A_1B_1 associate one obtains *per mole of constituents*,

$$G_m\left(y_1, y_2, \cdots\right) = y_A\,{}^{\circ}G_A + y_B\,{}^{\circ}G_B + y_{AB}\,{}^{\circ}G_{AB} + RT\sum y_i \ln y_i \tag{2.65}$$

${}^{\circ}G_{AB}$ is the standard Gibbs energy of the AB associate, a quantity that has to be evaluated from the measured properties of the solution. This may be regarded as an ideal solution model for a solution containing associates. Eq. 2.64 yields

$$x_A = \frac{y_A + y_{AB}}{y_A + y_B + y_{AB} + y_{AB}} \tag{2.66}$$

It may seem rather complicated to evaluate the chemical potentials of the components for a state of equilibrium from $G_m\left(y_1, y_2, \cdots\right)$ since this quantity does not apply to a constant number of atoms. This molar Gibbs energy holds for 1 mole of constituents, i.e. 1 mole of lattice sites if the phase is solid. The situation was somewhat similar in the preceding section. It was then shown how the problem can be solved by defining an internal variable and then reformulate the model to an expression in a set of independent variables. However, it was then shown that a more convenient method may be based on the application of Eq. 1.32 by treating all the site fractions as independent mole fractions. That method is often applied to solutions with associates by considering a frozen-in state where the free atoms cannot react to form the associates and their numbers can be controlled by exchange of associates with the surroundings. All the constituents can then be regarded as components. This is often a realistic assumption for aqueous solutions at room temperature where reactions between molecules are very sluggish. One may thus apply Eq. 1.32 to $G_m\left(y_1, y_2, \cdots\right)$ by treating the site fractions, y_i, as if they were mole fractions of the components, x_i, in Eq. 1.32. One may thus express their chemical potentials from Eq. 1.32,

$$\mu_j = G_m + \frac{\partial G_m}{\partial y_j} - \sum y_i \frac{\partial G_m}{\partial y_i} \simeq {}^{\circ}G_j + RT\ln y_j \tag{2.67}$$

This procedure is allowed in two limiting cases, at low temperatures where internal reactions are very sluggish and at high temperatures where internal equilibrium is almost satisfied.

At internal equilibrium, where the situation is not frozen-in, one can relate the chemical potential of an associate to those of its components using Eq. 1.27. In the case of A_1B_1 one can obtain μ_{AB} directly from Eq. 2.67 but also by first evaluating μ_A and μ_B from Eq. 2.67 and then using $\mu_{AB} = \mu_A + \mu_B$.

$$\mu_{AB} = {}^{\circ}G_{AB} + RT\ln y_{AB}^{eq} = {}^{\circ}G_A + RT\ln y_A^{eq} + {}^{\circ}G_B + RT\ln y_B^{eq} \tag{2.68}$$

We may thus calculate the equilibrium content of AB associates from

$$\frac{y_{AB}^{eq}}{y_A^{eq} y_B^{eq}} = \exp\left(-\Delta^{\circ}G_{AB}/RT\right) = K \tag{2.69}$$

where

$$\Delta^{\circ}G_{AB} = {}^{\circ}G_{AB} - {}^{\circ}G_A - {}^{\circ}G_B \tag{2.70}$$

$\Delta^{\circ}G_{AB}$ may be regarded as the standard Gibbs energy of formation of AB associates within the solution phase. It is determined as a fitting parameter to satisfy experimental information.

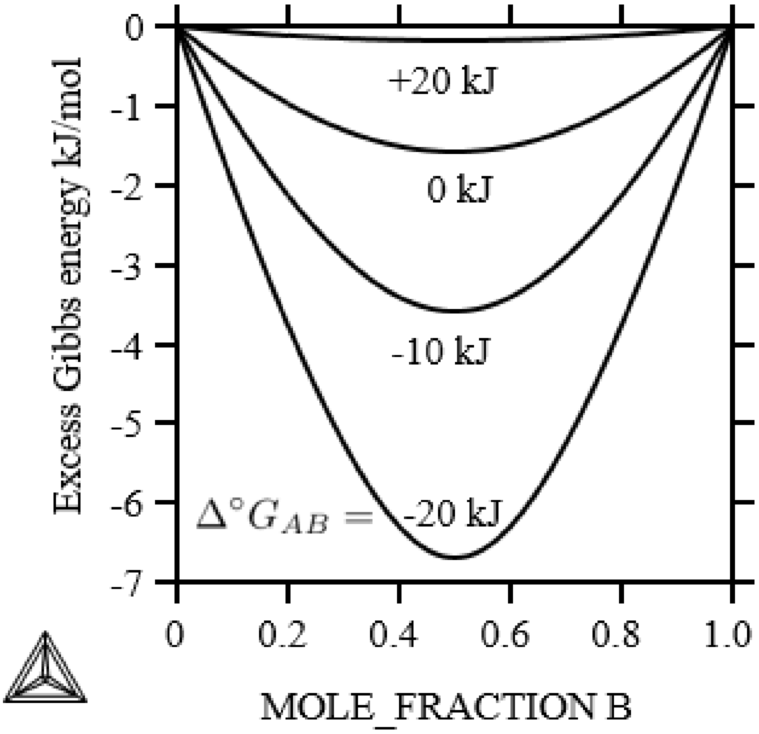


Figure 2.10: Excess Gibbs energy accounted for with the associate solution model using a series of values of the standard Gibbs energy of formation of AB associates.

Eq. 2.69 is an example of the **law of mass action** and K is a temperature dependent coefficient, often called **equilibrium constant**. In many cases such coefficients have been determined experimentally and their values have often been presented in tables without any further thermodynamic analysis. It is common to compute equilibria from such constants using the law of mass action and it should be remembered that it is based on an ideal solution model. The applicability is often restricted to dilute solutions.

For more concentrated solutions the law of mass action cannot be applied and the calculation turns more complicated. On the other hand, with an advanced software for thermodynamic calculations, which can minimize the total Gibbs energy of a system under given conditions, the result may be obtained directly.

The present model for solutions with associates is based on random mixing and could thus be regarded as a kind of ideal solution model if no interactions between the constituents are introduced through an excess Gibbs energy term. However, it should be emphasized that the model is a method of describing a non-ideal behaviour as far as the real components, A and B, are concerned. In some fields it is common to analyse a non-ideal behaviour in terms of hypothesized associates and thus to predict the compositions and contents of associates that are suspected to exist but may not. Fig. 2.10 illustrates the real deviation from ideal behaviour in an A-B system, i.e. the excess Gibbs energy, ${}^EG_m$, predicted with AB associates of various standard Gibbs energy of formation. The curves represent the difference between the associate model and the ideal solution model, i.e.

$$ {}^EG_m = G_m \text{ (associate model, Eq. 2.65)} - G_m \text{ (ideal solution model, Eq. 2.2)} $$

Naturally, the excess Gibbs energy is zero for a pure component.

As already mentioned, it may take time for internal equilibrium in a solution to be established. In such cases one sometimes regards the advance of sluggish internal reactions as extra degrees of freedom but, at the same time, one treats the associates as additional components. The Gibbs phase rule then takes the following form, $(v + rea) = (c + ass) + 2 - p$. Evidently, this is correct only if the number of internal reactions that are considered is equal to the number of associates that are considered. It is advisable to consider only the internal reactions that control the amounts of the associates by formation from the real components and not reactions involving more than one associate. Such reactions could be included if others are excluded but the total number of internal reactions to be considered must be equal to the number of associates. One talks about a set of "independent" reactions.

Before internal equilibrium has been established one could evaluate the chemical potential of an associate from Eq. 2.67 under frozen-in conditions and the driving force for the formation of more of it in a dilute solution is given by

$$\begin{aligned} D &= \mu_A + \mu_B - \mu_{AB} \\ &= {}^{\circ}G_A + RT\ln y_A + {}^{\circ}G_B + RT\ln y_B - {}^{\circ}G_{AB} - RT\ln y_{AB} \\ &= -\Delta^{\circ}G_{AB} + RT\ln\left(y_A y_B / y_{AB}\right) \end{aligned} \tag{2.71}$$

This can be reformulated using Eq. 2.69,

$$D = RT\ln\frac{y_{AB}^{eq} y_A y_B}{y_{AB} y_A^{eq} y_B^{eq}} \tag{2.72}$$

It should be realized that this is actually the driving force for the reaction $A + B \rightarrow A_1B_1$. For thermal vacancies Eq. 2.56 concerned the creation of vacancies with no other constituents involved. The relations derived for AB associates in this section can easily be generalized to more complicated associates and to solutions with several kinds of associates.

Exercise 2.11.1. Analytical expressions for equilibrium constants are usually given through Eq. 2.69 with $\Delta^{\circ}G_{AB} = \alpha + \beta T$ but more exact descriptions could easily be used in computerized databases. Use such a database to check the temperature dependence of $\Delta_f^{\circ}G_{H_2O}$. Make the examination from 0 to 1000°C.
Hint Plot $\Delta^{\circ}G_{H_2O}$ as function of T using the standard states of H_2 and O_2 as references.