

## MSE307 Unit 6—Outline of thermodynamics (A.T.Paxton)

### 1. Closed systems

#### 1.1 State functions

*All thermodynamic thinking begins with a definition of the portion of the universe under study, i.e., the system.*

John O'M. Bockris

I will not start right at the beginning but I will try and introduce what we will need in thermodynamics using just what you have already learned about the first and second laws.

The first law states that for a “closed” system changes in the heat content and the amount of work done *on* the system amount to a change in *internal energy*<sup>†</sup> written as

$$dU = \delta q + \delta w \quad (1.1)$$

If this is combined with the second law then this becomes

$$dU = TdS - p dV \quad (1.2)$$

This is true as long as the only work done involves a change in volume,  $V$ , against an external pressure,  $p$ . The absolute temperature is  $T$  and  $S$  is the entropy. A *closed* system is one that does not exchange matter with its surroundings (although it may transfer heat). We will come on to *open* systems in a while.

Before that, we note that (1.2) is a complete statement of the combined first and second laws for a closed system if only  $pV$ -work is done.<sup>‡</sup> However it may not be the most convenient. For example, we may like to simplify things by doing experiments so that one of the two terms on the right hand side of (1.1) is zero. So if we want to know just the result of the system doing some work, then working with the internal energy as a function of entropy and volume,  $U(S, V)$ , requires us to do experiments adiabatically, that is under the condition  $\delta q = 0$ , and this is not very easy.

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<sup>†</sup> From a mechanical point of view we often state that the total energy of a body, say a sphere of Cu–Ni alloy, is equal to its potential energy,  $E_{\text{pot}}$ , if it's in a gravitational field, say, plus its kinetic energy,  $E_{\text{kin}}$ , if it's moving relative to some inertial frame. This neglects the *internal* state of the body, that is to say, what its atoms are doing and whether any diffusion, phase transformations or chemical reactions are taking place, whether it is expanding or getting hotter or colder. So in thermodynamics as opposed to mechanics we express the total energy as  $E_{\text{tot}} = E_{\text{pot}} + E_{\text{kin}} + U$  and since thermodynamics concerns only *changes* in total energy we consider systems for which the potential and kinetic energies are unchanging, for example that the body is not in motion, and focus purely on the internal energy.

<sup>‡</sup> We have to extend this in cases where there is surface tension, non uniform stress, changes in electric or magnetic state and so on. For example work done on a body by a non hydrostatic stress is  $\sigma_{ij}d\varepsilon_{ij}$ , or work done on a body by increasing the area,  $A$ , of an internal interface of energy  $\gamma$  per unit area (say between the ferrite and austenite phases in steel) is  $\gamma dA$ .

So without making any additional postulates we devise a number of *auxilliary functions*. These are,

$$\begin{aligned} \text{enthalpy,} & \quad H = U + pV \\ \text{Helmholtz function,} & \quad F = U - TS \\ \text{Gibbs function,} & \quad G = H - TS \end{aligned}$$

$G$  is also known as the *free enthalpy* or *Gibbs free energy*;  $F$  is also known as the *free energy* or *Helmholtz free energy*. We are most interested in the Gibbs function so I'll show you how we get it from equation (1.2). We do it in two steps. First we have that  $U$  is a function of  $S$  and  $V$  as indicated by (1.2). Can we find an auxilliary function that depends on  $T$  and  $V$  instead? What is the relation between  $T$  and  $S$ ? From (1.2) we have

$$T = \left( \frac{\partial U}{\partial S} \right)_V$$

We say that  $S$  and  $T$  are “conjugate variables”, and we invent the new function

$$F = U - TS \tag{1.3}$$

that is, the first function,  $U$ , take away the product of the two conjugate variables (the one we are trying to get rid of and replace with the other). Now by taking the total derivative (that means, asking what does a change in  $F$  result in?)

$$\begin{aligned} dF &= dU - d(TS) = dU - TdS - SdT \\ &= -SdT - pdV \end{aligned} \tag{1.4}$$

using (1.2). Now we have a function  $F$  which depends on  $T$  and  $V$  rather than  $U$  which depends on  $S$  and  $V$  so that we can more readily interpret experiments done at constant volume or constant temperature. Suppose we are working at constant pressure rather than constant volume, then we need yet another auxilliary function, which we obtain from  $F$  by replacing the variable  $V$  with its conjugate  $-p$ . Indeed we know from (1.4) that

$$p = - \left( \frac{\partial F}{\partial V} \right)_T$$

so  $-p$  and  $V$  are conjugate variables, meaning that I can find a function that depends on  $p$  and  $T$  by writing down

$$\begin{aligned} G &= F + pV \\ &= H - TS \end{aligned} \tag{1.5}$$

(the original function take away the product of the two conjugate variables<sup>†</sup>). Then similar to before,

$$\begin{aligned} dG &= dF + pdV + Vdp \\ &= dU - TdS - SdT + pdV + Vdp \\ &= TdS - pdV - TdS - SdT + pdV + Vdp \\ &= -SdT + Vdp \end{aligned} \tag{1.6}$$

<sup>†</sup> In mathematics, this is called a *Legendre transformation*. Note that for a pair of conjugate variables, one is intensive and the other extensive.

and is thereby shown to be the required auxilliary function of  $T$  and  $p$ .

## 1.2 Conditions for equilibrium in closed systems

According to the second law, in an *isolated system* (one that can exchange neither matter nor energy with the environment) if any change takes place it must be such that the entropy increases or remains constant,<sup>†</sup>

$$dS \geq 0$$

Strictly in thermodynamics when we write

$$d(\text{something})$$

we really mean

$$\frac{d(\text{something})}{dt}$$

but we accept that the “arrow of time” always runs in the positive direction even if we don’t quite understand why and we leave out the  $dt$  denominator. If the isolated system is made up of one or more parts then we have

$$\sum_m dS_m \geq 0$$

each part being labelled by a subscript  $m$ . So some part may suffer a decrease in entropy as long as the total entropy does not decrease. So we can think of a closed system as an isolated system made up of two parts—the part we are interested in (say, a block of alloy) and a large reservoir of heat at a fixed temperature  $T$ . In this way we can keep our body at constant temperature if it is kept in contact with the reservoir. So if the entropy of our body is  $S$  and that of the reservoir is  $S_r$  then, for a natural process,

$$dS + dS_r \geq 0 \tag{1.7}$$

Now for an infinitesimal change in heat content of the body,  $\delta q$ , at a temperature  $T$ , the change in entropy is  $\delta q/T$ ; <sup>‡</sup> this means that the change in entropy of the reservoir where the heat came from is  $dS_r = -\delta q/T$  (because that amount of heat has been taken out of the reservoir at constant temperature  $T$ ) and so putting this into (1.7) the second law has it that

$$dS - \frac{\delta q}{T} \geq 0$$

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<sup>†</sup> We believe that the Universe is an isolated system, hence the famous statement of Rudolf Clausius, *Die Energie der Welt ist konstant. Die Entropie der Welt strebt einem Maximum zu*: The energy of the world is constant. The entropy of the world is striving to a maximum. This will of course lead to the “heat death” of the universe, but don’t worry the sun will have grown into a red giant and swallowed the earth by then.

<sup>‡</sup> You can think of this as the *definition* of entropy if you like: if an infinitesimal quantity of heat,  $\delta q$ , is added to a body reversibly and at constant temperature  $T$ , then the body’s entropy increases by the amount  $\delta q/T$ .

Now using (1.2) we have

$$dS - \frac{dU - \delta w}{T} \geq 0$$

I multiply through by  $T$ , rearrange and note that since this change is at constant temperature  $d(U - TS) = dU - TdS$  and I get

$$d(U - TS) \leq \delta w \quad (1.8)$$

By comparison with (1.3) we have  $dF \leq \delta w$  so that if the body does work ( $\delta w < 0$ ) then the Helmholtz function may increase, but otherwise and especially if no work is done either by or on the body, then the Helmholtz function can only decrease during a natural change, or remain constant. Thus when all changes have happened and the body is in equilibrium then the Helmholtz free energy is at a minimum. This is a condition for equilibrium.

I can add  $d(pV)$  to both sides of equation (1.8) and I get

$$d(U + pV - TS) = dG \leq \delta w + d(pV)$$

If as well as working at constant temperature, my body is maintained under a constant external pressure,  $p$ , then  $d(pV) = pdV$  and so if I define  $\delta w' = \delta w + pdV$  as the work done not including work done,  $pdV$ , by the body against the external pressure<sup>†</sup> then the condition for equilibrium is that the Gibbs free energy of a body at constant temperature and pressure is a minimum if no work other than that either *against* or *by* the external pressure is done either on or by the body,

$$dG \leq \delta w' \quad \text{in a closed system}$$

If no such work is done ( $\delta w' = 0$ ) then  $dG \leq 0$  in which case the Gibbs free energy can only decrease or remain constant. This means that when all changes have happened that are going to happen the system is in equilibrium and  $G$  is a minimum,  $dG = 0$ . This is the condition for equilibrium of a closed system at constant temperature and pressure.

In metallurgy when we deal with solids the amount of work done say by the thermal expansion of a body against atmospheric pressure is so tiny as to be negligible, and we can regard the Helmholtz and Gibbs functions to be interchangeable and both minimal at equilibrium; but since we usually work at constant pressure and not constant volume the focus is always on the Gibbs free energy.

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<sup>†</sup> In these notes  $\delta w$  is the work done on the body, not the work done by the body. The latter convention is commonly used by engineers who are interested in, say, an internal combustion engine for which  $pdV$  is the work done by the explosion of a fuel moving a piston against the external pressure  $p$ . So for us, if the body does work against the external pressure then the work done *on* the body is  $-pdV$ . So  $\delta w' = \delta w - (-pdV) = \delta w + pdV$ .

## 2. Open systems, chemical potential

An “open” system, such as the lump of metal that we have been thinking about, can exchange both energy and matter with its surroundings. Under these circumstances we must modify our statement of the combined first and second laws (1.2). We have to ask about the chemical composition of our body and to identify how many different “components” it is made up from. It is sufficient for our purposes to identify each chemical element as one of the components, so that for example a piece of Cu–Ni alloy has two components. In addition to components the body may be divided into phases. For example a piece of Fe–C alloy at equilibrium within the  $\alpha + \gamma$  field of the Fe–C phase diagram may have a certain volume fraction of ferrite, having a very small concentration of carbon and a certain volume fraction of austenite with a much larger concentration of dissolved carbon. These two phases will be intimately in contact sharing one or more interfaces which divide the body into its phases. For now we consider a homogeneous, single phase body having  $N$  components and we will use a subscript  $i$  to label these in our mathematical formulas. The internal energy is now no longer a function of only the two variables  $S$  and  $V$  it is also a function of the number of moles,<sup>†</sup>  $n_i$ , of each component that currently make up the body,

$$U = U(S, V, n_1, n_2 \cdots n_N)$$

The total differential of the internal energy is, now,

$$dU = \left( \frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left( \frac{\partial U}{\partial V} \right)_{S, n_i} dV + \sum_{i=1}^N \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}} dn_i \quad (2.1)$$

In the case of constant composition, this is obviously still valid, and so from (1.2)

$$\left( \frac{\partial U}{\partial S} \right)_{V, n_i} = T \quad (2.2)$$

and

$$\left( \frac{\partial U}{\partial V} \right)_{S, n_i} = -p \quad (2.3)$$

We now define the *chemical potential* of component  $i$  as the term under the summation sign in (2.1)

$$\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}} \quad (2.4)$$

and here the partial derivative is taken of  $U$  with respect to the number of moles of component  $i$  while keeping all other variables constant: namely the volume and entropy

<sup>†</sup> If you’re a physicist you tend to think in terms of the number of particles or number of atoms of each component, but since we deal with macroscopically sized bodies, in metallurgy and chemistry we use the number of moles to keep the numbers of reasonable size. A mole is nothing other than an Avogadro number of objects and the Avogadro number is  $N_A = 6.023 \times 10^{23}$ . Physicists use the Boltzmann constant,  $k_B$ , while we use the gas constant  $R = N_A k_B$ .

and the numbers of moles of all the other components. You might ask how can I do this in practice? The answer is to imagine that to the body in question you take an infinitesimal number of moles of component  $i$  (from a reservoir in which its chemical potential has some standard value—more on that later) and add it to the body. While the body's volume necessarily changes you readjust that by application of an infinitesimal increase in pressure. Since the added quantity of matter may bring with it some heat, to ensure that the entropy doesn't change in this process it is necessary then to remove that heat, say by placing it in contact with a heat bath at the appropriate temperature.

Maybe you'd like to think of the chemical potential as the reversible work done in bringing an infinitesimal amount of matter from a reservoir to the body in question. Sometimes I like the analogy with electrostatics; the *electric potential* is the work done in taking a positive test charge from infinity (the reservoir) to a place in space where there is an electric field—that is, the influence of other charges. Loosely speaking if the electric potential is large and negative then positive charges are attracted to that place and the work done in bringing the test charge from infinity is negative; conversely, if the electric potential  $\phi(\mathbf{r})$  is positive at position  $\mathbf{r}$ , then I need to do work to bring in extra positive charges. In this vein if the chemical potential of, say, carbon in Fe–C is large and positive then I need to expend energy to increase its concentration. If the concentration, or rather the chemical potential, of C in Fe varies from place to place then if the carbon is mobile it will diffuse from regions of high chemical potential to regions of low chemical potential. This is rather obvious if we equate chemical potential with concentration. Later we'll see how these two are actually related. Whereas in standard diffusion theory you are told that the carbon will travel down a concentration gradient, to be properly precise you should say that it diffuses down the gradient in *chemical potential*.

In view of equations (2.1)–(2.4) we have for the total differential of the internal energy of a body,

$$dU = TdS - pdV + \sum_{i=1}^N \mu_i dn_i \quad (2.5)$$

which is the modification of the combined first and second laws (1.2) for the case of an open system.

Now let me begin this argument again, but this time starting with the modification of the Gibbs function (1.5) for an open system. The Gibbs free energy is a function of temperature, pressure and the numbers of moles of each of the components,

$$G = G(T, p, n_1, n_2 \cdots n_N)$$

and so its total differential is

$$dG = \left( \frac{\partial G}{\partial T} \right)_{p, n_i} dT + \left( \frac{\partial G}{\partial p} \right)_{T, n_i} dp + \sum_{i=1}^N \left( \frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}} dn_i \quad (2.6)$$

We now define the *chemical potential* of component  $i$  as

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}} \quad (2.7)$$

and (2.6) being still valid in the special case of all the  $dn_i$  being zero (that is, fixed composition) equation (1.6) gives

$$\left(\frac{\partial G}{\partial T}\right)_{p,n_i} = -S \quad ; \quad \left(\frac{\partial G}{\partial p}\right)_{T,n_i} = V \quad (2.8)$$

which when put into (2.6) results in

$$dG = -SdT + Vdp + \sum_{i=1}^N \mu_i dn_i \quad (2.9)$$

with  $\mu_i$  defined by equation (2.7). This is the modification of (1.6) for an open system. Have I now made two different definitions of the chemical potential? That would be a real mess. Well, luckily, no! If I add to both sides of (2.5) the quantity  $d(pV - TS)$  then this equation is transformed into equation (2.9) by virtue of the fact that  $G = U + pV - TS$ .

We will use equation (2.7) as our expression for the chemical potential (numerically it is identical to (2.4), but we are concerned in metallurgy with the Gibbs function whose independent variables are  $p$  and  $T$  which are easily controlled—it's not easy to measure let alone control the entropy!). In the case of there being a single component then the chemical potential is the "partial free energy per mole". Usually for all extensive state functions we define a partial amount, being the amount per mole. We use lower case for these. In this way, we have for a single component homogeneous body,

partial molar volume,	$v = V/n$
partial molar enthalpy,	$h = H/n$
partial molar free energy,	$f = F/n$
partial molar free enthalpy,	$g = G/n$

Equation (2.7) is the more general expression of the partial free enthalpy of component  $i$  when it finds itself in a body having mole numbers  $n_1, n_2, \dots, n_N$ .

Finally in this section let's find a way to express the total Gibbs free energy of a body in terms of the mole numbers and chemical potentials of the components, equation (2.10) below. Now, the Gibbs free energy is an *extensive* property so if I know  $G(T, p, n_1, n_2, \dots, n_N)$  for a body and then I assemble some number  $\lambda$  of these bodies together then  $p$  and  $T$  do not change as these are intensive properties and the mole numbers are all multiplied by  $\lambda$  and the total Gibbs free energy is also multiplied by  $\lambda$  (because it is an extensive property),

$$G(T, p, \lambda n_1, \lambda n_2, \dots, \lambda n_N) = \lambda G(T, p, n_1, n_2, \dots, n_N)$$

(actually  $\lambda$  does not need to be a whole number—if I extend the body by an amount  $\lambda$  then the free energy is increased in the same ratio). We now invoke Euler's theorem for homogeneous functions of first order. Suppose a function  $f$  of  $N$  variables satisfies

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_N) = \lambda f(x_1, x_2, \dots, x_N)$$

We first exchange left and right hand sides and write  $u_i = \lambda x_i$

$$\lambda f(x_1, x_2, \dots, x_N) = f(u_1, u_2, \dots, u_N)$$

then differentiate each side with respect to  $\lambda$ , using the rule for differentiating a function of a function for the right hand side,

$$\begin{aligned} f(x_1, x_2, \dots, x_N) &= \sum_{i=1}^N \frac{\partial f}{\partial u_i} \frac{du_i}{d\lambda} \\ &= \sum_{i=1}^N \frac{\partial f}{\partial u_i} x_i \\ &= \sum_{i=1}^N \frac{1}{\lambda} \frac{\partial f}{\partial x_i} x_i \end{aligned}$$

This is true for any  $\lambda$  but if I choose  $\lambda = 1$  then I get

$$f(x_1, x_2, \dots, x_N) = \sum_{i=1}^N \frac{\partial f}{\partial x_i} x_i$$

This is Euler's theorem which I now apply to the Gibbs function,

$$G(T, p, n_1, n_2, \dots, n_N) = \sum_{i=1}^N \left( \frac{\partial G}{\partial n_i} \right)_{T, p, n_j \neq i} n_i$$

and by comparison with (2.7) I get

$$G = \sum_{i=1}^N \mu_i n_i \quad (2.10)$$

This states that the total free energy of a phase having  $N$  components is equal to the sum of the number of moles of each component times its chemical potential.

From this I can obtain the famous *Gibbs-Duhem equation*. If I take the total differential of (2.10),

$$dG = \sum_{i=1}^N \mu_i dn_i + \sum_{i=1}^N n_i d\mu_i$$

and if I compare this with (2.9) there results

$$-SdT + Vdp - \sum_{i=1}^N n_i d\mu_i = 0$$

This is the Gibbs-Duhem equation which you can use to prove the *Gibbs phase rule* which is central to the interpretation of phase diagrams (but for brevity I'll leave that out of these notes). At constant  $T$  and  $p$ , we then find

$$\sum_{i=1}^N n_i d\mu_i = 0 \quad (2.11)$$

## 2.1 Conditions for equilibrium in open systems

Possibly the most significant statement in metallurgical thermodynamics that you need to remember is this, *in equilibrium the chemical potential of each component is the same in all phases*. That is to say, if the body comprises more than one phase (and we will label the phases with subscripts  $\alpha, \beta, \dots$ ) and the components are distributed among the phases so that the number of moles of component  $i$  in phase  $\alpha$  is  $n_{i\alpha}$ , then as long as the phases are in contact and each component can diffuse throughout the body, then at equilibrium the chemical potential  $\mu_i$  for component  $i$  is the same in each phase. This makes sense because it implies that if the chemical potential of component  $i$  is the same everywhere then there's no gradient to drive diffusion and so all atoms stay where they are—equilibrium is reached. For example a piece of Fe–C alloy at equilibrium within the  $\alpha + \gamma$  field of the Fe–C phase diagram has a particular volume fraction of ferrite, having a very small concentration of carbon and a certain volume fraction of austenite with a large concentration of dissolved carbon. The concentrations of C in the two phases is very different because of the big difference in solubility of C in  $\alpha$ -Fe and  $\gamma$ -Fe, but in equilibrium  $\mu_{C\alpha} = \mu_{C\gamma}$ —the chemical potential of carbon is the same everywhere.

For the curious, I will try and prove this for you. Suppose in a multiphase, multicomponent body I take an infinitesimal amount of component  $i$ ,  $dn_{i\alpha}$ , from phase  $\alpha$  and transfer it reversibly into phase  $\beta$ .<sup>†</sup> The amount of increase of component  $i$  in the  $\beta$  phase is, rather obviously,  $dn_{i\beta} = dn_{i\alpha}$  while the change of mole number of component  $i$  in phase  $\alpha$  is negative *viz.*,  $-dn_{i\alpha}$ . If I do this at constant temperature and pressure, then according to equation (2.9) the change in Gibbs free energy is

$$dG = -\mu_{i\alpha}dn_{i\alpha} + \mu_{i\beta}dn_{i\beta} = (\mu_{i\beta} - \mu_{i\alpha})dn_{i\alpha}$$

since (2.9) must hold separately in each phase as each phase may be regarded as an open system and a part of the whole body. If the system was originally in equilibrium and the transfer is done reversibly then

$$dG = 0 = (\mu_{i\beta} - \mu_{i\alpha})dn_{i\alpha}$$

and so, since  $dn_{i\alpha} \neq 0$ , it must be true that

$$\mu_{i\alpha} = \mu_{i\beta}$$

<sup>†</sup> For example I could have some Fe–C at the temperature at which austenite and ferrite are in equilibrium (at the “no name” line in the Fe–C phase diagram). Then keeping  $T, p$  and the carbon concentrations fixed, I could take  $dn_{\text{Fe}\alpha}$  moles of body centred cubic Fe (ferrite) and transfer them across the  $\alpha / \gamma$  interface and rearrange them into the face centred cubic austenite. Alternatively I could reversibly move the  $\alpha / \gamma$  interface in such a way that  $dn_{\text{Fe}\alpha}$  moles of ferrite are rearranged into austenite. Actually there is a complication in this thought experiment because once I have transformed some ferrite into austenite I will have to also transfer an amount of carbon so that the austenite retains the carbon concentration appropriate to the tie line in the phase diagram; I gloss over this somewhat here, but as long as the amount I am transferring is *infinitesimal* in the sense of the differential calculus then I can neglect the need to re-equilibrate the carbon in this process.

if the two phases are in equilibrium. We can extend this argument to any number of phases.

### 3. Activity

Next, we need to know how does the chemical potential relate to the concentration. Obviously we design and process metal alloys using concentrations of the components but as we have seen what controls the thermodynamics and the kinetics at the fundamental level is the chemical potential. The best way to start this is simply to write down the answer. The chemical potential of component  $i$  in a particular phase (I'll leave out the subscript  $\alpha$  unless it's needed) is

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (3.1)$$

$\mu_i^\circ$  is the chemical potential in some “standard state” (mathematically it's an integration constant) and depends only on temperature and pressure; and  $a$  is the “activity”. Where does this equation come from? At the most shallow level it's simply a *definition* of activity, and still we need to find the connection between activity,  $a_i$  and concentration,  $x_i$ . This is most generally expressed like this,

$$a_i = \gamma_i x_i$$

which may be a very complicated function since the so called “activity coefficient”  $\gamma_i$  is a function of the concentrations of all the components, not just component  $i$ ,

$$\gamma_i = \gamma_i(x_1, x_2, \dots, x_N)$$

Thermodynamics can tell us nothing about how the activity depends on the concentrations. Ultimately it is up to experiment or detailed atomic-scale theory to determine the relationship. For example, it follows from the Gibbs-Helmholtz equation that<sup>†</sup>

$$R \left( \frac{\partial \ln \gamma_i}{\partial (1/T)} \right)_{p, n_j \neq i} = h_i - h_i^\circ \quad (3.2)$$

where  $h_i^\circ$  is the partial molar enthalpy in the same standard state as is applied to  $\mu_i^\circ$ . For an ideal solution,  $\gamma = \text{constant}$  and so the left hand side is zero, implying that the enthalpy of the component in solution is the same as in the pure substance at the same  $T$  and  $p$ , if the pure substance standard state is used. By integration of the

<sup>†</sup> Combine (1.5) with (2.8),

$$G = H + T \left( \frac{\partial G}{\partial T} \right)_{p, n_i}$$

which can be recast as follows,

$$\left( \frac{\partial(G/T)}{\partial T} \right)_{p, n_i} = -\frac{H}{T^2}$$

which is the Gibbs-Helmholtz equation. Just divide  $G$  and  $H$  by the number of moles and insert (3.1) with  $a_i = \gamma_i x_i$  to get (3.2).

Gibbs-Helmholtz equation, activity coefficients can be inferred from measured heats of solution.

The results of such experiments are shown in figure 1. You can see that the activity does not at all show a straightforward relationship to the concentration, except to say that as the concentration increases so does the activity. However you see two very clear limits: for large concentrations we see that

$$a_i = x_i \quad (x_i \rightarrow 1)$$

meaning that in the concentrated limit the activity of the *solvent* is equal to its concentration, the activity coefficient being one; and

$$a_i = \gamma_i x_i \quad (x_i \rightarrow 0)$$

with  $\gamma_i$  constant, that is, in the dilute limit the activity of the *solute* is proportional to its concentration. In this limit the activity coefficient is a proportionality constant. These two limits are the metallurgical statements of, respectively, Raoult's law and Henry's law (first stated to refer to the partial pressures of gasses).

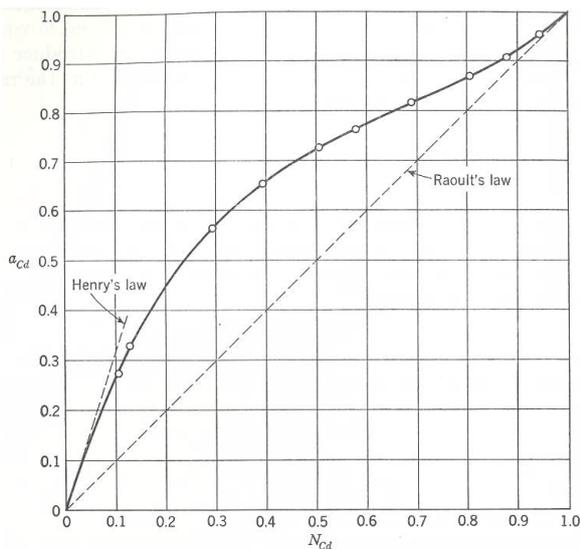


FIG. 10-5. Activity of cadmium in the Cd-Pb system at 500°C.

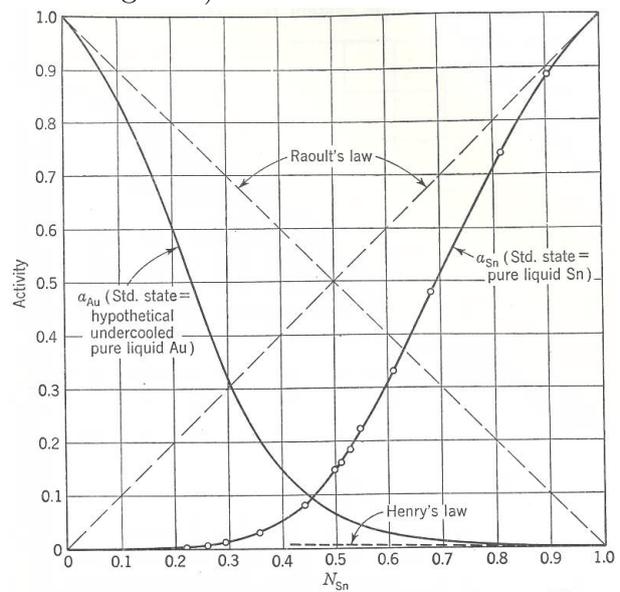


FIG. 10-10. Activity of tin and gold in the Sn-Au system at 600°C.

Figure 1. Activity for some liquid binary alloys as functions of concentration. The left hand figure shows a *positive* deviation from Raoult's law and the right hand figure shows *negative* deviation. When the concentration of a component tends to one we then call this component the *solvent* for obvious reasons.

In solid solutions with positive deviation,  $a_i > x_i$ , the solute behaves as if it were in a greater concentration than it actually is, and *vice versa*. Equation (3.2) indicates that if  $a_i > x_i$  (activity coefficient greater than one) then the mixing of the solute in the solvent is endothermic, meaning that the solute doesn't want to form a solid solution

and the mixture has a tendency to phase separation or possibly spinodal decomposition. Conversely if  $\gamma_i < 1$  then the mixing is exothermic, very roughly meaning that the component  $i$  likes to form bonds with the atoms of the solvent.

Incidentally a consequence of the Gibbs-Duhem equation (2.11) is that

$$\sum_{i=1}^N x_i d \ln a_i = 0$$

This can often be used to find the activity of one component if the activity of the others is known.

### 3.1 Ideal mixture

The “ideal mixture” or ideal solution, or ideal solid solution, like the ideal gas, is an idealisation but which fits the facts in many cases. They are characterised by a special form of the entropy of mixing, namely this: if the two components are initially separated into two containers and subsequently allowed to mix at constant temperature then the change in entropy is

$$\begin{aligned} \Delta S &= R \sum_{i=1}^N n_i \ln \frac{n}{n_i} \\ &= R \left( n \ln n - \sum_{i=1}^N n_i \ln n_i \right) \end{aligned} \quad (3.3)$$

Here,  $n$  is the total number of moles and  $n_i$  is the number of moles of component  $i$ . For an ideal gas, we have from the ideal gas law (Dalton’s Law) that  $n/n_i = p/p_i$  where  $p$  is the total pressure and  $p_i$  is the partial pressure of component  $i$ . So you can define the ideal solution as one whose entropy of mixing is taken by analogy with the ideal gas. You can see (3.3) derived in a textbook on thermodynamics (look up “Gibbs’s paradox”).<sup>†</sup>

<sup>†</sup> In the case of a binary mixture you can derive (3.3) from a statistical point of view. If the  $N$  atoms are arranged on the lattices of two perfect crystals then the number of ways of arranging the atoms into two separated bodies is exactly **one**. When the atoms are randomly mixed on a common lattice in the alloy body then the number of ways of arranging the  $N_a$  A-atoms and the  $N_b$  B-atoms is

$$W = \frac{(N_a + N_b)!}{N_a! N_b!} = \frac{N!}{N_a! N_b!}$$

So from the Boltzmann formula for the entropy,  $S = k_B \ln W$  the entropy of mixing is

$$\begin{aligned} \Delta S &= k_B \ln \frac{W}{\mathbf{one}} = k_B (\ln N! - \ln N_a! - \ln N_b!) \\ &= -k_B \left( N_a \ln \frac{N_a}{N} - N_b \ln \frac{N_b}{N} \right) \end{aligned}$$

using Sterling’s approximation  $\ln x! \approx x \ln x - x$  for large  $x$ , and this is consistent with (3.3).

So when I take  $n_i$  moles of each of  $N$  components in the pure state at a given temperature and pressure, and I mix them to produce an *ideal* homogeneous single phase mixture of atoms, then the total Gibbs free energy of the body that I have created is the sum of the numbers of moles times the molar free energies,  $\mu_i^{\alpha,0}$ , of the pure substances in phase  $\alpha$  plus the free enthalpy of mixing which is  $-T\Delta S$  since the solution is ideal. Hence, see equation (4.1) below,

$$G(T, p) = \sum_{i=1}^N n_i \left( \mu_i^{\alpha,0}(T, p) - RT \ln \frac{n}{n_i} \right)$$

By comparison with equation (2.10) I see that the chemical potential of component  $i$  in the ideal mixture is

$$\begin{aligned} \mu_i &= \mu_i^{\alpha,0}(T, p) + RT \ln \frac{n_i}{n} \\ &= \mu^\circ + RT \ln \frac{n_i}{n} \end{aligned} \quad (3.4)$$

so that  $\mu^\circ$  is the chemical potential of component  $i$  in its reference state: that is, in the pure substance in phase  $\alpha$  (presumably but not necessarily the crystal structure adopted by the pure substance) at the temperature and pressure specified. So you can at least see where the structure of (3.1) comes from:  $x_i$  is  $n_i/n$  and we replace  $x_i$  with  $a_i$  to recognise that not all mixtures are ideal in real life. In the case of the ideal gas it is usual, as you may know, to write

$$\mu = \bar{\mu} + RT \ln p$$

where  $\bar{\mu}$  is the chemical potential in the standard state of one bar pressure and temperature in question, and the pressure  $p$  is measured in units of one bar.

### 3.2 Non ideal mixture

After (3.4) you saw that  $n_i/n = x_i$  the concentration of component  $i$  in the mixture!† So equation (3.4) is that same as (3.1) for the case that the activity coefficient is one at all concentrations,

$$\gamma_i = 1 \quad \longleftarrow \quad \text{ideal solution}$$

† When I use  $x_i$  for concentration I mean the ratio of the number of moles or number of atoms of component  $i$  to the total number of moles or number of atoms in the mixture. If I write for the concentration  $c_i$  then I mean the number of moles per unit volume. I hope it doesn't confuse you that I use the word concentration for both. Probably for  $x_i$  I should write "mole fraction," or "atom fraction." The relation between the two is

$$\frac{c_i}{x_i} = \frac{\rho(n_0 + \sum n_i)}{M_0 n_0 + \sum M_i n_i}$$

Here we imagine a number of solutes  $i$  dissolved in a solvent, labelled with the subscript 0;  $\rho$  is the density in  $\text{kg m}^{-3}$  and  $M$  is the molar mass in  $\text{kg mole}^{-1}$  (easily confused with relative molar mass which is one thousand times smaller).

The reason that we write for the chemical potential for component  $i$  in a mixture,

$$\mu_i = \mu_i^\circ + RT \ln \gamma_i x_i = \mu_i^\circ + RT \ln a_i \quad (3.5)$$

is firstly that it has the familiar mathematical form as for the ideal solution and secondly that in certain limiting cases the dependence of  $\gamma_i$  on  $x_i$  is especially simple (figure 1). For example it is known experimentally and is also intuitively reasonable on physical grounds that in the case that the concentration tends to one, that is in the limit that the mixture tends to pure component  $i$ ,  $\gamma_i$  tends to one, and

$$\mu_i = \mu_i^\circ + RT \ln \gamma_i x_i \rightarrow \underbrace{\mu_i = \mu_i^\circ + RT \ln x_i}_{\text{Raoult's law}} \quad (x_i \rightarrow 1) \quad (3.6)$$

At  $x_i = 1$ , the last term is zero ( $\log 1 = 0$ ) and so  $\mu_i = \mu_i^\circ$  which identifies  $\mu_i^\circ$  as the chemical potential of pure substance  $i$  at the temperature and pressure of interest.

At the *dilute limit*,  $x_i \rightarrow 0$ , the activity coefficient becomes a constant, independent of concentration.<sup>†</sup>

$$\underbrace{\mu_i = \mu_i^\circ + RT \ln \gamma_i x_i}_{\text{Henry's law}}, \quad \gamma_i \text{ constant} \quad (x_i \rightarrow 0) \quad (3.7)$$

In between these limits the activity coefficient generally has a complicated dependence on the concentration of  $i$  (Figure 1) and indeed all the other components. On the other hand  $\mu_i^\circ$  depends only on temperature and pressure.

Note that figure 1 concerns liquid mixtures, not solids. Figures 2 and 3 show some measurements very relevant to us of the carbon activity in pure austenite and Fe-Mo alloy.

### 3.3 Henrian activity

The most convenient choice of standard state is the so-called Raoultian standard state (3.6) in which  $\mu_i^\circ$  is the free enthalpy per mole of pure substance of  $i$ . This is the standard state chosen even in figures 2 and 3 although it poses an awkward problem. If in the case of carbon dissolved in austenite we want to write

$$\mu_{C\gamma} = \mu_{C\gamma}^\circ + RT \ln a_{C\gamma}$$

and we want to focus, as in figures 2 and 3, on the dilute limit then the Raoultian standard chemical potential has to be imagined as the free enthalpy per mole of a fictitious substance obtained by continually increasing the concentration of carbon until its concentration approaches one. But this thought experiment is impossible to carry

<sup>†</sup> The mathematically astute will notice that as  $x_i$  goes to zero so  $\mu_i$  goes to minus infinity. I'll touch on this again on page 18 in connexion with figure 5.

out in practice. Very quickly you will exceed the solubility limit and in the limit of pure carbon the crystal structure is no longer fcc, it must be graphite. In the case of nitrogen the pure substance is a gas! So equation (3.6) is useful in order to be able to equate the activity with the concentration but it leads to an unrealisable choice of standard state. Instead we exploit Henry's law (3.7) and after writing down the chemical potential as in equation (3.5)

$$\mu_i = \mu_i^\circ + RT \ln \gamma_i x_i$$

but given that in the dilute limit  $\gamma_i$  is a constant, that depends only on temperature and pressure we can fold it in with the standard chemical potential by writing

$$\begin{aligned} \mu_i &= \mu_i^\circ + RT \ln \gamma_i x_i \\ &= \mu_i^\circ + RT \ln \gamma_i + RT \ln x_i \\ &= \mu_i^h + RT \ln x_i \end{aligned}$$

where  $\mu_i^h = \mu_i^\circ + RT \ln \gamma_i$  is the chemical potential of component  $i$  in the solution in its "Henrian standard state." It's best not to try and make a picture of the solute in that state, but just think of  $\mu_i^h$  as standard chemical potential that depends only on temperature and pressure and which allows you to equate activity with concentration, as in (3.6), but in the opposite limit.

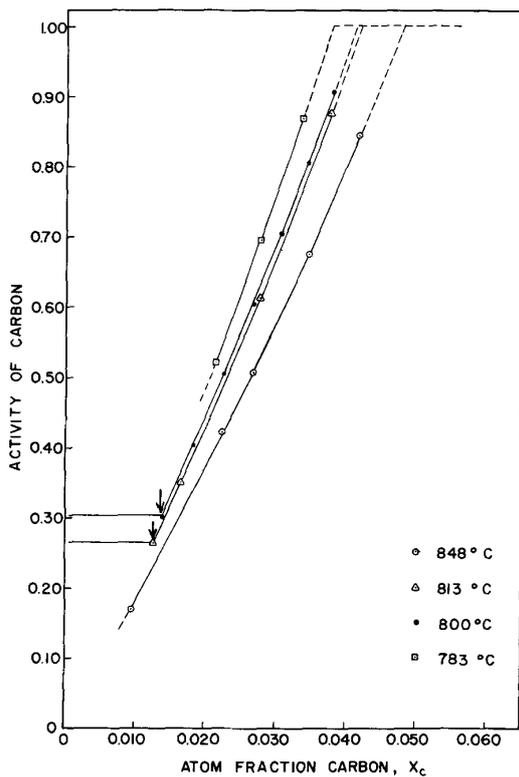


Fig. 2—The activity of carbon in austenite in relation to the atom fraction of carbon.

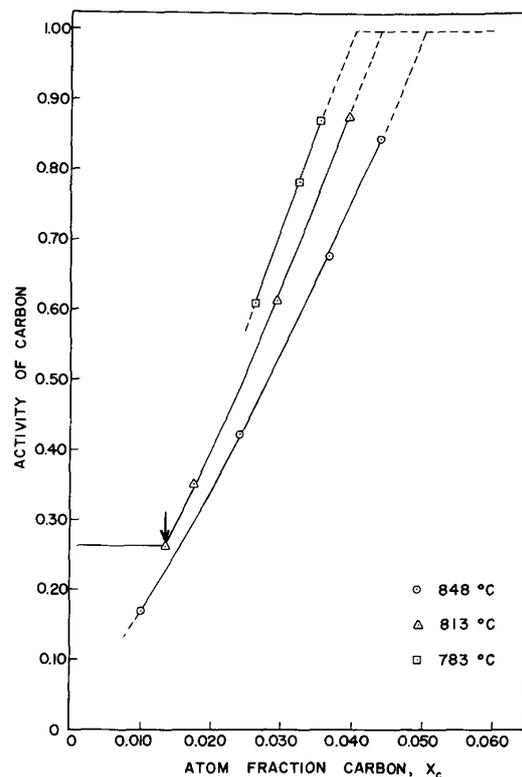


Fig. 4—The activity of carbon in austenitic Fe-1.16 wt pct Mo in relation to the atom fraction of carbon.

Figure 2: Activity of carbon in austenite. Note a very strong positive deviation from the ideal solution ( $a_C \gg x_C$ ;  $\gamma_C \approx 10$ ), and a small positive deviation from Henry's law ( $\gamma_C$  not constant). C in austenite acts as if there is more there than there actually is.

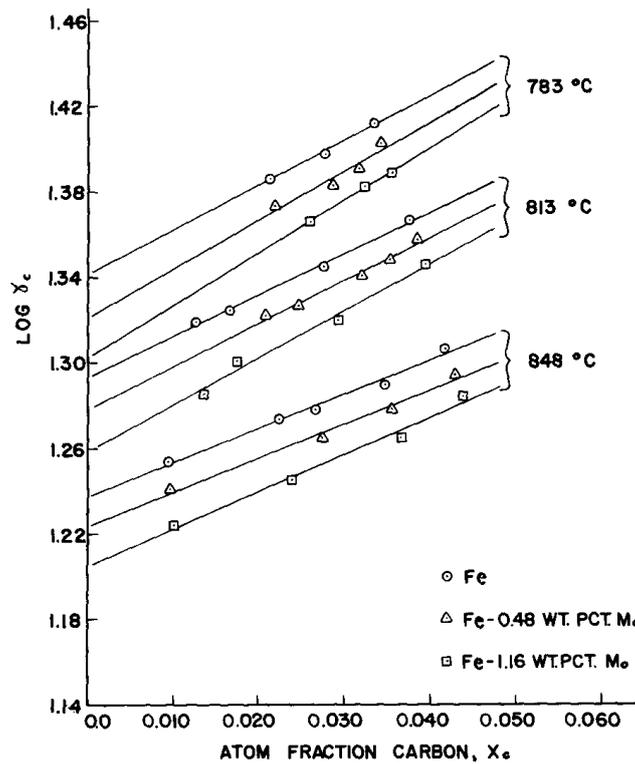


Fig. 6—Activity coefficient of carbon as a function of fraction of carbon for austenite and austenitic iron-carbon-molybdenum alloys.

Figure 3: Activity coefficient of carbon in austenite. Note that even at this very low concentration, Henry's law does not hold as  $\gamma_C$  is clearly not constant.

#### 4. Solid solutions

We consider here a binary A–B solid solution and ask what is its free enthalpy per mole in the  $\alpha$ -phase,  $g^\alpha$ , compared to the free enthalpies of the numbers of moles of A and B in their pure states in the same  $\alpha$  phase as the solid solution.<sup>†</sup> If  $g^\alpha$  is smaller than the sum of the two pure state free enthalpies per mole, weighted by the mole fractions, then the two pure phases will tend to form a solid solution in equilibrium. Relative to some arbitrary zero of energy these pure substance free enthalpies per mole are  $\mu_A^{\alpha,0}$  and  $\mu_B^{\alpha,0}$ . So if a mole of solid A–B solution is made of  $x$  moles of B and  $1 - x$  moles of A then

$$g^\alpha = (1 - x)\mu_A^{\alpha,0} + x\mu_B^{\alpha,0} + \Delta^{\text{mix}} g^\alpha \quad (4.1)$$

and  $\Delta^{\text{mix}} g^\alpha$  is the free enthalpy of mixing or free enthalpy of formation of the  $A_{1-x}B_x$  alloy measured from the standard state of the pure, unmixed A and B components. Figure 4 is a schematic illustration of this, showing the free enthalpy per mole of a

<sup>†</sup> This may be problematic if either A or B or both do not actually exist in the phase  $\alpha$  of the solid solution in question. For example we may be interested in a bcc Mg–Li alloy in which case since Mg does not exist in a bcc modification, the quantity  $\mu_{\text{Mg}}^{\text{bcc},0}$  is unknown.

binary solid solution as a function of the composition at a particular temperature and pressure.

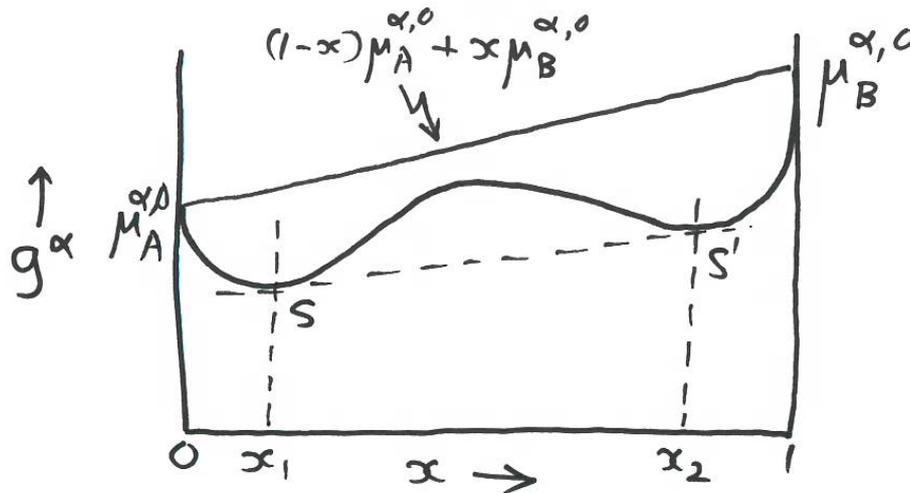


Figure 4

You can see from figure 4 that the free energy is everywhere smaller than the weighted sum of the free energies of the two components. This is because in the case sketched here the free enthalpy of mixing is negative for every concentration. In the case of an ideal solution, we would have

$$\Delta^{\text{mix}} g = RT \{ (1-x) \ln(1-x) + x \ln x \} \quad \leftarrow \text{ideal solution} \quad (4.2)$$

which is negative since  $0 < x < 1$ . This means that for all concentrations the free enthalpy is reduced if the two components mix together rather than remaining as pure A and pure B phases. As long as  $g^\alpha$  has positive curvature then the two substances A and B will form a single phase solid solution. On the other hand if  $g^\alpha$  has a negative curvature, within the so called *spinodal* which is indicated as lying between concentrations at points  $S$  and  $S'$  in figure 4, then the single phase solid solution can further lower its free energy by separating into two phases, namely  $\alpha$ -solid solutions (that is, the same crystal structure) but having concentrations given by the ends of the common tangent to the  $g^\alpha$  curve. If these concentrations are  $x_1$  and  $x_2$  then since the slope is common,

$$\left. \frac{\partial g^\alpha}{\partial x} \right|_{x=x_1} = \left. \frac{\partial g^\alpha}{\partial x} \right|_{x=x_2} = \frac{g^\alpha(x_2) - g^\alpha(x_1)}{x_2 - x_1} \quad (4.3)$$

(The notation of a vertical bar means evaluate the derivative at  $x = x_1$  etc.) Actually the slope of the straight line joining  $\mu_A^{\alpha,0}$  with  $\mu_B^{\alpha,0}$  is arbitrary in the sense that absolute values of  $\mu_A^{\alpha,0}$  and  $\mu_B^{\alpha,0}$  depend on the choice of energy zero as discussed earlier.  $\mu_A^{\alpha,0}$  and  $\mu_B^{\alpha,0}$  do depend on temperature and figure 4 is drawn for one particular temperature. We could have chosen this to be the temperature for which  $\mu_A^{\alpha,0} = \mu_B^{\alpha,0}$ . This amounts to saying that figure 4 is essentially a plot of  $\Delta^{\text{mix}} g^\alpha$  arbitrarily tilted so that the condition (4.3) is equivalent to the statement that

$$\left. \frac{\partial \Delta^{\text{mix}} g^\alpha}{\partial x} \right|_{x=x_1} = \left. \frac{\partial \Delta^{\text{mix}} g^\alpha}{\partial x} \right|_{x=x_2}$$

This equation gives us the *limits of solubility*  $x_1$  and  $x_2$ . For example starting with a dilute solid solution of component B in A, as I add more B (increase  $x$  from zero) the equilibrium mixture is a single  $\alpha$  phase until I reach  $x = x_1$  after which in equilibrium there will appear a phase mixture of one solid solution of composition  $A_{1-x_1}B_{x_1}$  and another of composition  $A_{1-x_2}B_{x_2}$ . The amounts of each will be given by the lever rule.

The hump in the free enthalpy of mixing arises from non ideality. Equation (4.2) is sketched in figure 5 and this would not give rise to a hump. The matter of deciding what is the enthalpy of mixing comes down to questions, roughly speaking, of whether A atoms like to be neighbours of B atoms and at what concentrations. Thermodynamics can tell us nothing of this and it is necessary to resort to experiment or first principles theory to resolve the matter. It is obvious from (4.2), and should be evident in figure 5 if I've sketched it properly that at both  $x = 0$  and  $x = 1$  the slope of the ideal entropy of mixing is infinite. This has been used in the past as an argument that a pure substance cannot exist in equilibrium in contact with one or more other components because the addition of just one B atom, say, to otherwise pure A is bound to lower the free enthalpy; the one B atom having infinitely negative chemical potential. This is not an admissible argument but nonetheless it is true that entropy effects prevent the existence of absolutely pure substances.

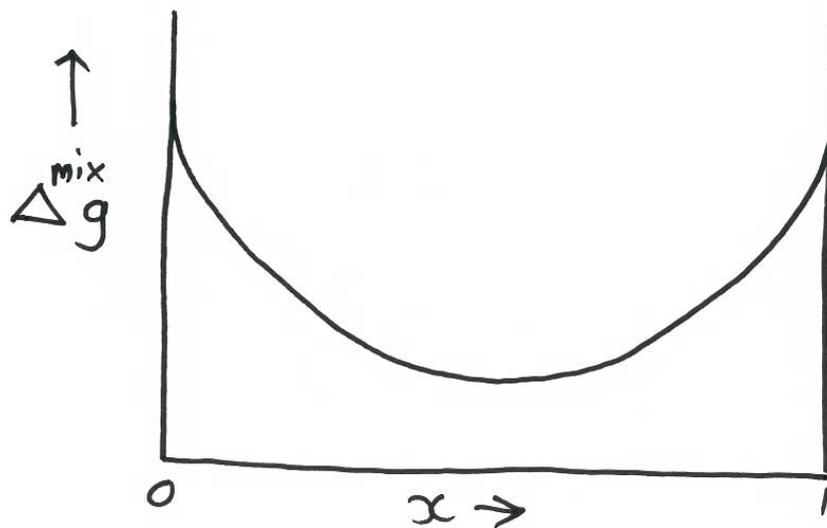


Figure 5

Now we ask, what is the chemical potential,  $\mu_A^\alpha$ , of the component A (or B) in a particular solid solution at a particular composition, temperature and pressure. If the number of moles of A is  $n_A$  and the number of moles of B is  $n_B$  and the total free enthalpy is  $G$  then, if  $n = n_A + n_B$ , from (4.1)

$$\mu_A^\alpha = \frac{\partial G}{\partial n_A} = \mu_A^{\alpha,0} + \frac{\partial (n \Delta^{\text{mix}} g^\alpha)}{\partial n_A}$$

and similarly for B, just by replacing A with B. From equation (2.10) it follows that

$$g^\alpha = (1 - x)\mu_A^\alpha + x\mu_B^\alpha \quad (4.4)$$

therefore

$$\frac{\partial g^\alpha}{\partial x} = \mu_B^\alpha - \mu_A^\alpha$$

This important relation is illustrated in figure 6. In words, at any particular composition of a solid solution, the tangent to the free energy per mole curve intersects the  $x = 0$  and  $x = 1$  axes at the chemical potentials of the two components. We saw an example of this in Unit 2C, slide 10. Figure 6 is sketched for the simpler case of a solution without a spinodal region, but if you look back at figure 4 you see immediately that the common tangent  $S-S'$  leads to the relations

$$\begin{aligned}\mu_A^\alpha(x_1) &= \mu_A^\alpha(x_2) \\ \mu_B^\alpha(x_1) &= \mu_B^\alpha(x_2)\end{aligned}$$

which, as you know, are the conditions for equilibrium (see section 2.1).

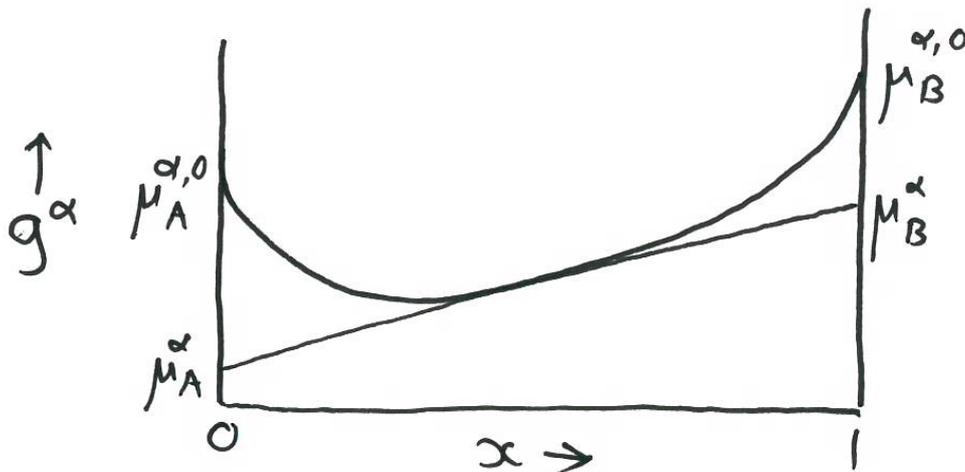


Figure 6: For a given composition, given by the mole fraction,  $x$ , of B-atoms, I can find the chemical potentials of A and B atoms in the solid solution by this construction: I draw a tangent to the curve of  $g^\alpha$  versus  $x$  that touches the curve at the concentration of interest. Where the tangent intersects the ordinate at  $x = 0$  and  $x = 1$ , I read off the chemical potentials  $\mu_A^\alpha$  and  $\mu_B^\alpha$ , respectively. By construction the molar free enthalpy at the concentration  $x$  is  $g^\alpha = (1 - x)\mu_A^\alpha + x\mu_B^\alpha$  which is equation (4.4)

The occurrence of a spinodal is fairly rare, but you are aware that some solid solutions undergo a spontaneous, second order phase transformation known as spinodal decomposition into two phases having the same crystal structure but separate compositions. More common is the case of a single solid solution decomposing into two phases,  $\alpha$  and  $\beta$ , having both different crystal structures and different compositions (concentrations).<sup>†</sup>

<sup>†</sup> An example is hypoeutectoid Fe-C above  $A_1$  but below  $A_3$  which separates into two solid solutions of C in ferrite and C in austenite with solubility limits given by the no-name line and  $A_3$  at the temperature in question, and the volume fractions of each phase given by the tie line depending on the overall C concentration.

As indicated in figure 7 we now have to draw separate free energy curves for each phase as the one does not go over continuously into the other. By analogy with (4.1) the free enthalpy per mole of the  $\beta$  phase is

$$g^\beta = (1 - x)\mu_A^{\beta,0} + x\mu_B^{\beta,0} + \Delta^{\text{mix}}g^\beta$$

The common tangent construction, as shown in figure 7, defines two concentrations  $x_\alpha$  and  $x_\beta$  which are solubility limits. In other words at the given  $T$  and  $p$  of figure 7, as I add component B to a dilute alloy, the single  $\alpha$  phase reaches a limit of solubility at  $x = x_\alpha$  upon which the lowest free enthalpy corresponds to a two phase mixture of  $\alpha$  phase of composition  $x_\alpha$  and  $\beta$  phase of composition  $x_\beta$ . Once the concentration of B reaches  $x_\beta$  then a single  $\beta$  phase will be reverted to. In this sense  $x_\alpha$  and  $x_\beta$  are *solubility limits*. In similar manner as equation (3.3) we can deduce these using

$$\begin{aligned} \left. \frac{\partial g^\alpha}{\partial x} \right|_{x=x_\alpha} &= \left. \frac{\partial g^\beta}{\partial x} \right|_{x=x_\beta} \\ &= \frac{g^\beta(x_\beta) - g^\alpha(x_\alpha)}{x_\beta - x_\alpha} \end{aligned} \quad (4.5)$$

You note of course that in the two phase concentration range between  $x_\alpha$  and  $x_\beta$ , the slope of the molar free enthalpy *is the same* for both phases as you see in (4.5) or by looking at the common tangent. This means that the chemical potentials of the component B are the same in each phase, which is the condition for the two phases to be in equilibrium.

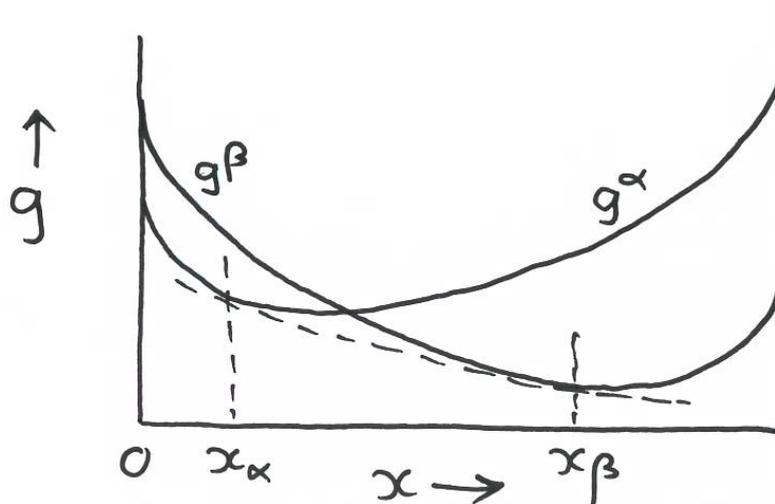


Figure 7

I don't want to take this any further; it is probably revision for you and you know that this is the stepping off point for learning how to construct phase diagrams. There are computer programmes that do this for you, using vast (and expensive) databases of measured, calculated and inferred free enthalpies (see, for example, <http://www.thermocalc.com>). As mentioned in the footnote on page 16 there are severe problems in this approach if the computer needs to estimate the free enthalpy per mole of a pure substance, or indeed alloy, in a crystal structure which is not observed

or is not even mechanically stable. For example you may need to know the molar free enthalpy of bcc Ti below 822°C, or of non magnetic bcc Fe above 920°C. There are indeed unresolved disputes between the electron theorists and the CALPHAD community over such issues.

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