

CHAPTER 17 CHEMICAL THERMODYNAMICS

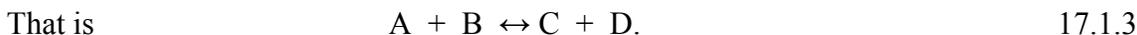
17.1 *Equilibrium Constant*

There are many types of chemical reaction, but to focus our attention we shall consider a reaction involving two reactants A and B which, when mixed, form two resultants C and D. The reaction will proceed at a certain *rate* (fast or slow), and the rate at which the reaction proceeds is part of the subject of *chemical kinetics*, which is outside the scope of this chapter, and to some extent, though by no means entirely, outside the scope of this writer! We shall not, therefore, be concerned with how fast the reaction proceeds, but with what the final state is, and whether the reaction needs some heat to get it going, or whether it proceeds spontaneously and generates heat as it does so.

We shall suppose that the reaction is *reversible*. That is, that either



is possible.



The end result is a dynamic equilibrium in which the rates of forward and backward reaction are the same, and there is an equilibrium amount of A, of B, of C and of D. The question is: How much of A? Of B? Of C? Of D?

Let us suppose that in the equilibrium mixture there are N_A moles of A, N_B of B, N_C of C and N_D of D. If we make the reasonable assumption that the rate of the forward reaction is proportional to $N_A N_B$ and the rate of the backward reaction is proportional to $N_C N_D$, then, when equilibrium has been achieved and these two rates are equal, we have

$$\frac{N_A N_B}{N_C N_D} = \text{"constant"}. \quad 17.1.4$$

The "constant", which is called the *equilibrium constant* for the reaction, is constant only for a particular temperature; in general it is a function of temperature.

A simpler type of reaction is the dissociation-recombination equilibrium of a diatomic molecule:



The *dissociation equilibrium constant* is then

$$\frac{N_A N_B}{N_{AB}}. \quad 17.1.6$$

This “constant” is a function of the temperature and the dissociation energy of the molecule.

A similar consideration obtains for the ionization of an atom:



In this situation,
$$\frac{N_+ N_-}{N_0}, \quad 17.1.8$$

the *ionization equilibrium constant*, is a function of the temperature and the ionization energy. The equilibrium constants can be determined either experimentally or they can be computed from the *partition functions* of statistical mechanics. Some details of how to calculate the dissociation and ionization constants and how to use them to calculate the numbers of atoms, ions and molecules of various species in a hot gas are discussed in *Stellar Atmospheres*, Chapter 8, as well as in papers by the writer in *Publ. Dom. Astrophys. Obs.*, XIII (1) (1966) and by A. J. Sauval and the writer in *Astrophys. J. Supp.*, **56**, 193 (1984).

17.2 Heat of Reaction

In some reactions, heat is *produced* by the reaction, and such reactions are called *exothermic*. If no heat is allowed to escape from the system, the system will become hot. In other reactions, heat has to be *supplied* to cause the reaction. Such reactions are *endothermic*.

The heat of reaction is the heat required to effect the reaction, or the heat produced by the reaction – some authors use one definition, others use the other. Here we shall define the heat of reaction as the heat required *to effect* the reaction, so that it is positive for endothermic reactions and negative for exothermic reactions. (In your own writing, make sure that your meaning is unambiguous – don’t assume that there is some “convention” that everyone uses.) If the reaction is carried out *at constant pressure* (i.e. on an open laboratory bench), the heat required to effect the reaction is the increase of *enthalpy* of the system. In other words, ΔH is positive for an endothermic reaction. If the reaction produces heat, the enthalpy decreases and ΔH is negative. Heats of reaction are generally quoted as molar quantities at a specific temperature (often 25 °C) and pressure (often one atmosphere). The usual convention is to write



One can make it yet clearer by specifying the temperature and pressure at which the enthalpy of reaction is determined, and whether the reactants are solid (s), liquid (l) or gas (g).

If the reaction is carried out *at constant volume* (in a closed vessel), the heat required to effect the reaction is the increase of the *internal energy*, ΔU . In either case, in our convention (which seems to be the most common one) ΔH or ΔU is positive for an endothermic reaction and negative for an exothermic reaction.

The heat of reaction at constant pressure (ΔH) is generally a little larger than at constant volume (ΔU), though if all reactants are liquid or solid the difference is very small indeed and often negligible within the precision to which measurements are made.

17.3 *The Gibbs Phase Rule*

Up to this point the thermodynamical systems that we have been considering have consisted of just a single component and, for the most part, just one phase, but we are now going to discuss systems consisting of more than one phase and more than one component. The Gibbs Phase Law provides a relation between the number of phases, the number of components and the number of degrees of freedom. But Whoa, there! We have been using several technical terms here: *Phase, Component, Degrees of Freedom*. We need to describe what these mean.

The state of a system consisting of a single component in a single phase (for example a single gas – not a mixture of different gases) can be described by three intensive state variables, P , V and T . (Here V is the molar volume – i.e. the reciprocal of the density in moles per unit volume – and is an intensive variable.) That is, the state of the system is described by a point in three-dimensional PVT space. However, the intensive state variables are connected by an *equation of state* $f(P, V, T) = 0$, so that the system is constrained to be on the two-dimensional surface described by this equation. Thus, because of the constraint, only two intensive state variables suffice to describe the state of the system. Just two of the intensive state variables can be independently varied. The system has two degrees of freedom.

Definition. A *phase* is a chemically homogeneous volume, solid, liquid or gas, with a boundary separating it from other phases.

Definition. The number of intensive state variables that can be varied independently without changing the number of phases in a system is called the *number of degrees of freedom* of the system.

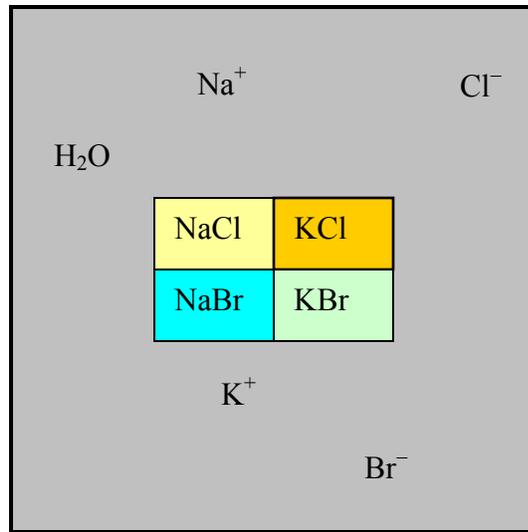
These are easy. Defining the number of *components* in a system needs a bit of care. I give a definition, but what the definition *means* can, I hope, be made a little clearer by giving a few examples.

Definition. The number of *components* in a system is the least number of constituents that are necessary to describe the composition of each phase.

Let us look at a few examples to try and grasp what this means.

First, let us consider an aqueous solution of the chlorides and bromides of sodium and potassium co-existing with the crystalline solids NaCl, KCl, NaBr, KBr, illustrated schematically in figure XVII.1.

FIGURE XVII.1



There are *five phases* – four solid and one liquid – but how many components? There are *six* elements: H, O, Na, K, Cl, B – but the quantities of each cannot be varied independently. There are two constraints: $n(\text{H}) = 2n(\text{O})$, and $n(\text{Na}) + n(\text{K}) = n(\text{Cl}) + n(\text{Br})$. That is, if we know the number of hydrogen atoms, then the number of oxygen atoms is known. And if we know the number of any three of Na, K, Cl or Br, then the fourth is known. Thus the number of constituents that that can be independently varied is *four*. The number of *components* is *four*.

Or again, consider an aqueous solution of a moles of H_2SO_4 in b moles of water. There is just one phase. There are *three* elements: H, O and S. These may be distributed among several species, such as H_2O , H_2SO_4 , H_3O^+ , OH^- , SO_4^{--} , but that doesn't matter. There is just *one* constraint, namely that

$$2(a + b)n(\text{H}) = an(\text{S}) + (4a + b)n(\text{O}).$$

That is, if we know the number of any two of H, O or S, we also know the number of the third. The number of *components* is *two*.

Or again, consider the reversible reaction



If the system is in equilibrium, and we know the numbers of any two of these *three* molecules, the number of the third is determined by the equilibrium constant. Thus the number of *components* is *two*.

In each of these three examples, it was easy to state the number of *phases* and slightly more difficult to determine the number of *components*. We now need to ask ourselves what is the number of *degrees of freedom*. This is what the Gibbs phase law is going to tell us.

If there are C *components* in a system, the composition of *a particular phase* is fully described if we know the mole fraction of $C - 1$ of the components, since the sum of the mole fractions of all the components must be 1. This is so for each of the P *phases*, so that there are in all $P(C - 1)$ mole fractions to be specified, as well as any two of the intensive state variables P , V and T . Thus there are $P(C - 1) + 2$ intensive state variables to be specified. (The mole fraction of each component is an intensive state variable.) But not all of these can be independently varied, because the *molar Gibbs functions* of each component are the same in all phases. (To understand this important statement, re-read this argument in Chapter 14 on the Clausius-Clapeyron equation.) For each of the C components there are $P - 1$ equations asserting the equality of the specific Gibbs functions in all the phases. Thus the number of intensive state variables that can be varied independently without changing the number of phases – i.e. the number of degrees of freedom, F – is $P(C - 1) + 2 - C(P - 1)$, or

$$F = C - P + 2. \quad 17.3.1$$

This is the *Gibbs Phase Rule*.

In our example of the sodium and potassium salts, in which there were $C = 4$ components distributed through $P = 5$ phases, there is just one degree of freedom. No more than one intensive state variable can be changed without changing the number of phases.

In our example of sulphuric acid, there was one phase and two components, and hence three degrees of freedom.

In the calcium carbonate system, there were three phases and two components, and hence just one degree of freedom.

If we have a pure gas, there is one phase and one component, and hence two degrees of freedom. (We can vary any two of P , V or T independently.)

If we have a liquid and its vapour in equilibrium, there are two phases and one component, and hence $F = 1$. We can vary P or T , but not both independently if the system is to remain in equilibrium. If we increase T , the pressure of the vapour that

remains in equilibrium with its liquid increases. The system is constrained to lie on a line in PVT space.

If we have a liquid, solid and gas co-existing in equilibrium, there are three phases and one component and hence no degrees of freedom. The system exists at a single point in PVT space, namely the triple point.

I have often been struck by the similarity of the Gibbs phase rule to the topological relation between the number of faces F , edges E and vertices V of a solid polyhedron (with no topological holes through it).

This relation is $F = E - V + 2$. E.g.

	E	V	F
Tetrahedron:	6	4	4
Cube:	12	8	6
Octahedron:	12	6	8

As far as I know there is no conceivable connection between this and the Gibbs phase rule, and I don't even find it useful as a mnemonic. I think we just have to put it down as one of life's little curiosities.

Since writing this section, I have added some additional material on binary and ternary alloys, which provide additional examples of the Gibbs phase rule. I have added these at the end of the chapter, as sections 17.9 and 17.10.

17.4 Chemical Potential

It is a truth universally acknowledged that, if we add some heat reversibly to a closed thermodynamic system at constant volume, its internal energy will increase by

$\left(\frac{\partial U}{\partial S}\right)_V dS$; or, if we allow it to expand without adding heat, its internal energy will

increase by $\left(\frac{\partial U}{\partial V}\right)_S dV$. (In most cases the derivative $\left(\frac{\partial U}{\partial V}\right)_S$ is negative, so that an

increase in volume results in a decrease of internal energy.) If we do both, the increase in internal energy will be

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV. \quad 17.4.1$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dU = TdS - PdV. \quad 17.4.2$$

Likewise, it is a truism that, if we add some heat reversibly to a closed thermodynamic system at constant pressure, its enthalpy will increase by $\left(\frac{\partial H}{\partial S}\right)_P dS$; or, if we increase

the pressure on it without adding heat, its enthalpy will increase by $\left(\frac{\partial H}{\partial P}\right)_S dP$. If we do both, the increase in internal energy will be

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP. \quad 17.4.3$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dH = TdS + VdP. \quad 17.4.4$$

Likewise, it is a truism that, if we increase the temperature of a closed thermodynamic system at constant volume, its Helmholtz function will increase by $\left(\frac{\partial A}{\partial T}\right)_V dT$; or, if we allow it to expand at constant temperature, its Helmholtz function will increase by $\left(\frac{\partial A}{\partial V}\right)_T dV$. (In most cases both of the derivatives are negative, so that an increase in temperature at constant volume, or of volume at constant temperature, results in a decrease in the Helmholtz function.) If we do both, the increase in the Helmholtz function will be

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV. \quad 17.4.5$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dA = -SdT - PdV. \quad 17.4.6$$

Likewise, it is a truism that, if we increase the temperature of a closed thermodynamic system at constant pressure, its Gibbs function will increase by $\left(\frac{\partial G}{\partial T}\right)_P dT$. (In most cases the derivative $\left(\frac{\partial G}{\partial T}\right)_P$ is negative, so that an increase in temperature at constant pressure results in a decrease in the Gibbs function.) If we increase the pressure on it at constant

temperature, its Gibbs function will increase by $\left(\frac{\partial G}{\partial P}\right)_T dP$. If we do both, the increase in Gibbs function will be

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP. \quad 17.4.7$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dG = -SdT + VdP. \quad 17.4.8$$

So much, we are already familiar with.

However, we can increase any of these thermodynamical functions of a system without adding any heat to it or doing any work on it – merely by adding more matter. You will notice that, in the above statements, I referred to a “closed” thermodynamical system. By a “closed” system, I mean one in which no matter is lost or gained by the system. But, if the system is not closed, adding additional matter to the system obviously increases the (total) thermodynamical functions. For example, consider a system consisting of several components. Suppose that we add dN_i moles of component i to the system at constant temperature and pressure, by how much would the Gibbs function of the system increase?

We might at first make the obvious reply: “ dN_i times the molar Gibbs function of component i ”. This might be true if the component were entirely inert and did not interact in any way with the other components in the system. But it is possible that the added component might well interact with other components. It might, for example, shift the equilibrium position of a reversible reaction $A + B \leftrightarrow C + D$. The best we can do, then, is to say merely that the increase in the (total) Gibbs function of the system would

be $\left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j} dN_i$. Here, N_j refers to the number of moles of any component other than i .

In a similar manner, if dN_i moles of component were added at constant volume without adding any heat, the increase in the internal energy of the system would be

$\left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j} dN_i$. Or if dN_i moles of component were added at constant pressure without

adding any heat, the increase in the enthalpy of the system would be $\left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_j} dN_i$. Or

if dN_i moles of component were added at constant temperature and volume, the increase

in the Helmholtz function of the system would be $\left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j} dN_i$. If we added a little bit more of *all* components at constant temperature and volume, the increase in the Helmholtz function would be $\sum \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j} dN_i$, where the sum is over all components.

Thus, if the system is not closed, and we have the possibility of adding or subtracting portions of one or more of the components, the formulas for the increases in the thermodynamic functions become

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_i} dV + \sum \left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j} dN_i, \quad 17.4.9$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,N_i} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N_i} dP + \sum \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_j} dN_i, \quad 17.4.10$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,N_i} dT + \left(\frac{\partial A}{\partial V}\right)_{T,N_i} dV + \sum \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j} dN_i, \quad 17.4.11$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N_i} dP + \sum \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j} dN_i. \quad 17.4.12$$

The quantity $\left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j}$ is the same as $\left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_j}$ or as $\left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j}$ or as $\left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j}$, and it is called the *chemical potential* of species *i*, and is usually given the

symbol μ_i . Its SI units are J kmole⁻¹. (We shall later refer to it as the “partial molar Gibbs function” of species *i* – but that is jumping slightly ahead.) If we make use of the symbol μ_i , and the other things we know from application of the first and second laws, we can write equations 17.4.9 to 17.4.12 as

$$dU = TdS - PdV + \sum \mu_i dN_i, \quad 17.4.13$$

$$dH = TdS + VdP + \sum \mu_i dN_i, \quad 17.4.14$$

$$dA = -SdT - PdV + \sum \mu_i dN_i \quad 17.4.15$$

and

$$dG = -SdT + VdP + \sum \mu_i dN_i. \quad 17.4.16$$

It will be clear that

$$\begin{aligned} \left(\frac{\partial U}{\partial S}\right)_{V,N_i} &= T; & \left(\frac{\partial U}{\partial V}\right)_{S,N_i} &= -P; & \left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j} &= \mu_i; \\ \left(\frac{\partial H}{\partial S}\right)_{P,N_i} &= T; & \left(\frac{\partial H}{\partial P}\right)_{S,N_i} &= V; & \left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_j} &= \mu_i; \\ \left(\frac{\partial A}{\partial T}\right)_{V,N_i} &= -S; & \left(\frac{\partial A}{\partial V}\right)_{T,N_i} &= -P; & \left(\frac{\partial A}{\partial N_i}\right)_{V,T,N_j} &= \mu_i; \\ \left(\frac{\partial G}{\partial T}\right)_{P,N_i} &= -S; & \left(\frac{\partial G}{\partial P}\right)_{T,N_i} &= V; & \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_j} &= \mu_i. \end{aligned} \quad 17.4.17-28$$

Since the four thermodynamical functions are functions of state, their differentials are exact and their mixed second partial derivatives are equal. Consequently we have the following twelve Maxwell relations:

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_{S,N_i} &= -\left(\frac{\partial P}{\partial S}\right)_{V,N_i}; & \left(\frac{\partial T}{\partial N_i}\right)_{S,V,N_j} &= +\left(\frac{\partial \mu_i}{\partial S}\right)_{V,N_i}; & \left(\frac{\partial P}{\partial N_i}\right)_{S,V,N_j} &= -\left(\frac{\partial \mu_i}{\partial V}\right)_{S,N_i}; \\ \left(\frac{\partial T}{\partial P}\right)_{S,N_i} &= +\left(\frac{\partial V}{\partial S}\right)_{P,N_i}; & \left(\frac{\partial T}{\partial N_i}\right)_{S,P,N_j} &= +\left(\frac{\partial \mu_i}{\partial S}\right)_{P,N_i}; & \left(\frac{\partial V}{\partial N_i}\right)_{S,P,N_j} &= +\left(\frac{\partial \mu_i}{\partial P}\right)_{S,N_i}; \\ \left(\frac{\partial S}{\partial V}\right)_{T,N_i} &= +\left(\frac{\partial P}{\partial T}\right)_{V,N_i}; & \left(\frac{\partial S}{\partial N_i}\right)_{T,V,N_j} &= -\left(\frac{\partial \mu_i}{\partial T}\right)_{V,N_i}; & \left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j} &= -\left(\frac{\partial \mu_i}{\partial V}\right)_{T,N_i}; \\ \left(\frac{\partial S}{\partial P}\right)_{T,N_i} &= -\left(\frac{\partial V}{\partial T}\right)_{P,N_i}; & \left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_j} &= -\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N_i}; & \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j} &= +\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N_i}. \end{aligned} \quad 17.4.29-40$$

Refer to equations 17.4.13 to 17.4.16, and we understand that:

If we add dN_1 moles of species 1, dN_2 moles of species 2, dN_3 moles of species 3, etc., in a insulated constant-volume vessel (dS and dV both zero), the increase in the internal energy is

$$dU = \sum \mu_i dN_i. \quad 17.4.41$$

If we do the same in an insulated vessel at constant pressure (for example, open to the atmosphere, but in a time sufficiently short so that no significant heat escapes from the system, and dS and dP are both zero), the increase in the enthalpy is

$$dH = \sum \mu_i dN_i. \quad 17.4.42$$

If we do the same in a closed vessel (e.g. an autoclave or a pressure cooker, so that $dV = 0$) in a constant temperature water-bath ($dT = 0$), the increase in the Helmholtz function is

$$dA = \sum \mu_i dN_i. \quad 17.4.43$$

If we do the same at constant pressure (e.g. in an open vessel on a laboratory bench, so that $dP = 0$) and kept at constant temperature (e.g. if the vessel is thin-walled and in a constant-temperature water bath, so that $dT = 0$), the increase in the Gibbs free energy is

$$dG = \sum \mu_i dN_i. \quad 17.4.44$$

We have called the symbol μ_i the *chemical potential* of component i – *but in what sense is it a “potential”?* Consider two phases, α and β , in contact. The Gibbs functions of the two phases are G^α and G^β respectively, and the chemical potential of species i is μ_i^α in α and μ_i^β in β . Now transfer dN_i moles of i from α to β . The increase in the Gibbs function of the system is $\mu_i^\beta dN_i - \mu_i^\alpha dN_i$. But for a system of two phases to be in chemical equilibrium, the increase in the Gibbs function must be zero. In other words, the condition for chemical equilibrium between the two phases is that $\mu_i^\beta = \mu_i^\alpha$ for all species, just as the condition for thermal equilibrium is that $T^\alpha = T^\beta$, and the condition for mechanical equilibrium is that $P^\alpha = P^\beta$.

Students of classical mechanics may see an analogy between equation 17.4.44 and the principle of Virtual Work. One way of finding the condition of static equilibrium in a mechanical system is to imagine the system to undergo an infinitesimal change in its geometry, and then to calculate the total work done by all the forces as they are displaced by the infinitesimal geometrical alteration. If the system were initially in equilibrium, then the work done by the forces, which is an expression of the form $\sum F_i dx_i$, is zero, and this gives us the condition for mechanical equilibrium. Likewise, if a system is in chemical equilibrium, and we make infinitesimal changes dN_i , at constant temperature and pressure, in the chemical composition, the corresponding change in the Gibbs function of the system, $\sum \mu_i dN_i$, is zero. At chemical equilibrium, the Gibbs function is a minimum with respect to changes in the chemical composition.

17.5 Partial and Mean Molar Quantities, and Partial Pressure

Consider a single phase with several components. Suppose there are N_i moles of component i , so that the total number of moles of all species is

$$N = \sum N_i. \quad 17.5.1$$

The *mole fraction* of species i is

$$n_i = \frac{N_i}{N}, \quad 17.5.2$$

and of course $\sum n_i = 1$.

Let V be the volume of the phase. What will be the increase in volume of the phase if you add dN_i moles of component i at constant temperature and pressure? The answer, of course, is

$$dV = \left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j} dN_i. \quad 17.5.3$$

If you increase the number of moles of all species at constant temperature and pressure, the increase in volume will be

$$dV = \sum \left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j} dN_i. \quad 17.5.4$$

The quantity $\left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j}$ is called the *partial molar volume* of species i :

$$v_i = \left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j} \quad 17.5.5$$

Let us suppose that the volume of a phase is just proportional to the number of moles of all species in the phase. It might be thought that this is always the case. It would indeed be the case if the phase contained merely a mixture of ideal gases. However, to give an example of a non-ideal case: If ethanol C_2H_5OH is mixed with water H_2O , the volume of the mixture is less than the sum of the separate volumes of water and ethanol. This is because each molecule has an electric dipole moment, and, when mixed, the molecules

attract each other and pack together more closely than in the separate liquids. However, let us go back to the ideal, linear case.

In that case, if a volume V contains N moles (of all species) and you add N_i moles of species i at constant temperature and pressure, the ratio of the new volume to the old is given by

$$\frac{V + dV}{V} = \frac{N + dN_i}{N}, \quad 17.5.6$$

and hence
$$\frac{dV}{V} = \frac{dN_i}{N}, \quad 17.5.7$$

or
$$\left(\frac{\partial V}{\partial N_i} \right)_{P,T,N_j} = v_i = \frac{V}{N}. \quad 17.5.8$$

Example. (You'll need to think long and carefully about the next two paragraphs fully to appreciate what are meant by *molar volume* and *partial molar volume*. You'll need to understand them before you can understand more difficult things, such as partial molar Gibbs function.)

A volume of 6 m^3 contains 1 mole of A, 2 moles of B and 3 moles of C. Thus the *molar volumes* (not the same thing as the *partial molar volumes*) of A, B and C are respectively 6, 3 and 2 m^3 .

Assume that the mixing is *ideal*. In *that case*, equation 17.5.8 tells us that the *partial molar volume* of each is the total volume divided by the total number of moles. That is, the *partial molar volume* of each is 1 m^3 . You could imagine that, before the component were mixed (or if you were to reverse the arrow of time and un-mix the mixture), we had 1 mole of A occupying 1 m^3 , 2 moles of B occupying 2 m^3 and 3 moles of C occupying 3 m^3 , the molar volume of each being 1 m^3 .

The *mean molar volume per component* is

$$\bar{v} = \frac{V}{N}. \quad 17.5.9$$

If the components are ideal, each component has the same partial molar volume, and hence the mean molar volume is equal to the partial molar volume of each – but this would not necessarily be the case for nonideal mixing.

The total volume of a phase, whether formed by ideal or nonideal mixing, is

$$V = \sum N_i v_i. \quad 17.5.10$$

If you divide each side of this equation by N , you arrive at

$$\bar{v} = \sum n_i v_i . \quad 17.5.11$$

Note that the partial molar volume of a component is not just the volume occupied by the component divided by the number of moles. I.e. the partial molar volume is not the same thing as the molar volume. In our ideal example, the molar volume of the three components would be, respectively, 6, 3 and 2 m³.

Another way of looking at it: In the mixture, N_i moles of species i occupies the entire volume V , as indeed does every component, and its *molar volume* is V/N_i . The pressure of the mixture is P . Now remove all but species i from the mixture and then compress it so that its pressure is still P , it perforce must be compressed to a smaller volume, and the volume of a mole *now* is its *partial molar volume*.

Let Φ be any extensive quantity (such as S, V, U, H, A, G).

Establish the following notation:

Φ = total extensive quantity for the phase;

ϕ_i = partial molar quantity for component i ;

$\bar{\phi}$ = mean molar quantity per component.

The partial molar quantity ϕ_i for component i is defined as

$$\phi_i = \left(\frac{\partial \Phi}{\partial N_i} \right)_{P, T, N_{j \neq i}} . \quad 17.5.12$$

The total value of Φ is given by

$$\Phi = \sum N_i \phi_i , \quad 17.5.13$$

and the mean value per component is

$$\bar{\phi} = \sum n_i \phi_i . \quad 17.5.14$$

If the extensive quantity Φ that we are considering is the Gibbs function G , then equation 17.5.12 becomes

$$g_i = \left(\frac{\partial G}{\partial N_i} \right)_{P, T, N_{j \neq i}} \quad 17.5.15$$

Then we see, by comparison with equation 17.4.28 that the *chemical potential* μ_i of component i is nothing other than its *partial molar Gibbs function*.

Note that this is not just the Gibbs function per mole of the component, any more than the partial molar volume is the same as the molar volume.

Recall (Chapter 14 on the Clausius-Clapeyron equation) that, when we had just a single component distributed in two phases (e.g. a liquid in equilibrium with its vapour), we said that the condition for thermodynamic equilibrium between the two phases was that the specific or *molar Gibbs functions* of the liquid and vapour are equal. In Section 17.5 of this chapter, when we are dealing with several components distributed between two phases, the condition for chemical equilibrium is that the *chemical potential* μ_i of component i is the same in the two phases. Now we see that the chemical potential is synonymous with the partial molar Gibbs function, so that the condition for chemical equilibrium between two phases is that the partial molar Gibbs function of each component is the same in each phase. Of course, if there is just one component, the partial molar Gibbs function is just the same as the molar Gibbs function.

Although pressure is an intensive rather than an extensive quantity, and we cannot talk of “molar pressure” or “partial molar pressure”, opportunity can be taken here to define the *partial pressure* of a component in a mixture. The partial pressure of a component is merely the contribution to the total pressure made by that component, so that the total pressure is merely

$$P = \sum p_i, \quad 17.5.16$$

where p_i is the partial pressure of the i th component,

Dalton's Law of Partial Pressures states that for a mixture of ideal gases, the partial pressure of component j is proportional *mole fraction* of component j . That is, for a mixture of ideal gases,

$$\frac{p_j}{P} = \frac{p_j}{\sum p_i} = \frac{N_j}{N} = \frac{N_j}{\sum N_i} = n_j. \quad 17.5.17$$

That is,
$$p_j = n_j P. \quad 17.5.18$$

17.6 The Gibbs-Duhem Relation

In a mixture of several components kept at constant temperature and pressure, the chemical potential μ_i of a particular component (which, under conditions of constant T and P , is also its partial molar Gibbs function, g_i) depends on how many moles of each species i are present. The Gibbs-Duhem relation tells us how the chemical potentials of the various components vary with composition. Thus:

We have seen that, if we keep the pressure and temperature constant, and we increase the number of moles of the components by N_1, N_2, N_3 , the increase in the Gibbs function is

$$dG = \sum \mu_i dN_i. \quad 17.6.1$$

We also pointed out in section 17.5 that, provided the temperature and pressure are constant, the chemical potential μ_i is just the partial molar Gibbs function, g_i , so that the total Gibbs function is

$$G = \sum g_i N_i = \sum \mu_i N_i, \quad 17.6.2$$

the sum being taken over all components. On differentiation of equation 17.6.2 we obtain

$$dG = \sum \mu_i dN_i + \sum N_i d\mu_i. \quad 17.6.3$$

Thus for any process that takes place at constant temperature and pressure, comparison of equations 17.6.1 and 17.6.3 shows that

$$\sum N_i d\mu_i = 0, \quad 17.6.4$$

which is the *Gibbs-Duhem* relation. It tells you how the chemical potentials change with the chemical composition of a phase.

17.7 Chemical Potential, Pressure, Fugacity

Equation 12.9.11 told us how to calculate the change in the Gibbs function of a mole of an ideal gas going from one state to another. For N moles it would be

$$\Delta G = N \int C_p dT - NT_2 \int C_p d(\ln T) + NRT_2 \ln(P_2 / P_1) - NS(T_2 - T_1), \quad 17.7.1$$

where C_p and S are molar, and G is total.

Since we know now how to calculate the absolute entropy and also know that the entropy at $T = 0$ is zero, this can be written

$$G(T, P) = N(RT \ln P + \text{constant}) \quad 17.7.2$$

The “constant” here depends on the temperature, but is not a function of the pressure, being in fact the value of the molar Gibbs function extrapolated to the limit of zero pressure. Sometimes it is convenient to write equation 17.7.2 in the form

$$G = NRT(\ln P + \phi), \quad 17.7.3$$

where ϕ is a function of temperature.

If we have a mixture of several components, the total Gibbs function is

$$G(T, P) = \sum_i N_i(RT \ln p_i + \text{constant}) \quad 17.7.3\frac{1}{2}$$

We can now write this in terms of the partial molar Gibbs function of the component i – that is to say, the chemical potential of the component i , which is given by $\mu_i = (\partial G / \partial N_i)_{P, T, N_{j \neq i}}$, and the *partial pressure* of component i . Thus we obtain

$$\mu_i = \mu_i^0(T) + RT \ln p_i. \quad 17.7.4$$

or

$$\mu_i = RT(\ln p_i + \phi_i). \quad 17.7.5$$

Here I have written the “constant” as $\mu_i^0(T)$, or as $RT\phi_i$. The constant $\mu_i^0(T)$ is the value of the chemical potential at temperature T extrapolated to the limit of zero pressure. If the system consists of a mixture of ideal gases, the partial pressure of the i th component is related to the total pressure simply by *Dalton’s law of partial pressures*:

$$p_i = n_i P, \quad \text{see equation 17.5.18}$$

where n_i is the mole fraction of the i th component. In that case, equation 17.7.4 becomes

$$\mu_i = \mu_i^0(T) + RT \ln n_i + RT \ln P. \quad 17.7.6$$

and equation 17.7.5 becomes

$$\mu_i = RT(\ln n_i + \ln P + \phi_i). \quad 17.7.7$$

However, in a common deviation from ideality, volumes in a mixture are not simply additive, and we write equation 17.7.4 in the form

$$\mu_i = \mu_i^0(T) + RT \ln f_i, \quad 17.7.8$$

or equation 17.7.5 in the form

$$\mu_i = RT(\ln f_i + \phi_i). \quad 17.7.9$$

where f_i is the *fugacity* of component i .

17.8 Entropy of Mixing and Gibbs' Paradox

In Chapter 7, we defined the increase of entropy of a system by supposing that an infinitesimal quantity dQ of heat is added to it at temperature T , and that no irreversible work is done on the system. We then asserted that the increase of entropy of the system is $dS = dQ/T$. If some irreversible work is done, this has to be added to the dQ .

We also pointed out that, in an isolated system any spontaneous transfer of heat from one part to another part was likely (*very likely!*) to be from a hot region to a cooler region, and that this was likely (*very likely!*) to result in an increase of entropy of the closed system – indeed of the Universe. We considered a box divided into two parts, with a hot gas in one and a cooler gas in the other, and discussed what we likely (*very likely!*) to happen if the wall between the parts were to be removed. We considered also the situation in which the wall were to separate two gases consisting of red molecules and blue molecules. The two situations seem to be very similar. A flow of heat is not the flow of an “imponderable fluid” called “caloric”. Rather it is the mixing of two groups of molecules with initially different characteristics (“fast” and “slow”, or “hot” and “cold”). In either case there is likely (*very likely!*) to be a spontaneous mixing, or increasing randomness, or increasing disorder or increasing *entropy*. Seen thus, entropy is seen as a measure of the degree of disorder. In this section we are going to calculate the increase on entropy when two different sorts of molecules become mixed, without any reference to the flow of heat. This concept of entropy as a measure of disorder will become increasingly apparent if you undertake a study of *statistical mechanics*.

Consider a box containing two gases, separated by a partition. The pressure and temperature are the same in both compartments. The left hand compartment contains N_1 moles of gas 1, and the right hand compartment contains N_2 moles of gas 2. The Gibbs function for the system is

$$G = RT[N_1(\ln P + \phi_1) + N_2(\ln P + \phi_2)]. \quad 17.8.1$$

Now remove the partition, and wait until the gases become completely mixed, with no change in pressure or temperature. The partial molar Gibbs function of gas 1 is

$$\mu_1 = RT(\ln p_1 + \phi_1) \quad 17.8.2$$

and the partial molar Gibbs function of gas 2 is

$$\mu_2 = RT(\ln p_2 + \phi_2). \quad 17.8.3$$

Here the p_i are the partial pressures of the two gases, given by $p_1 = n_1P$ and $p_2 = n_2P$, where the n_i are the mole fractions.

The total Gibbs function is now $N_1\mu_1 + N_2\mu_2$, or

$$G = RT[N_1(\ln n_1 + \ln P + \phi_1) + N_2(\ln n_2 + \ln P + \phi_2)]. \quad 17.8.4$$

The new Gibbs function minus the original Gibbs function is therefore

$$\Delta G = RT(N_1 \ln n_1 + N_2 \ln n_2) = NRT(n_1 \ln n_1 + n_2 \ln n_2). \quad 17.8.5$$

This represents a *decrease* in the Gibbs function, because the mole fractions are less than 1.

The new entropy minus the original entropy is $\Delta S = -\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$, which is

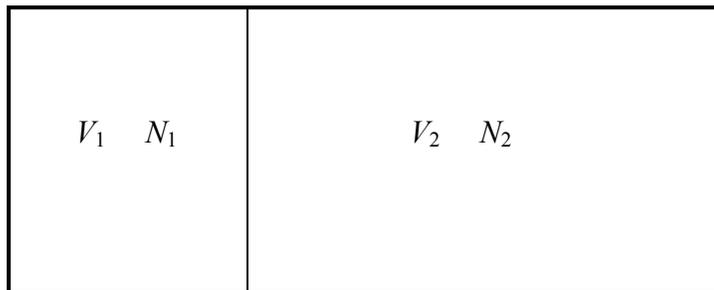
$$\Delta S = -NR(n_1 \ln n_1 + n_2 \ln n_2). \quad 17.8.6$$

This is positive, because the mole fractions are less than 1.

Similar expressions will be obtained for the increase in entropy if we mix several gases.

Here's maybe an easier way of looking at the same thing. (Remember that, in what follows, the mixing is presumed to be ideal and the temperature and pressure are constant throughout.)

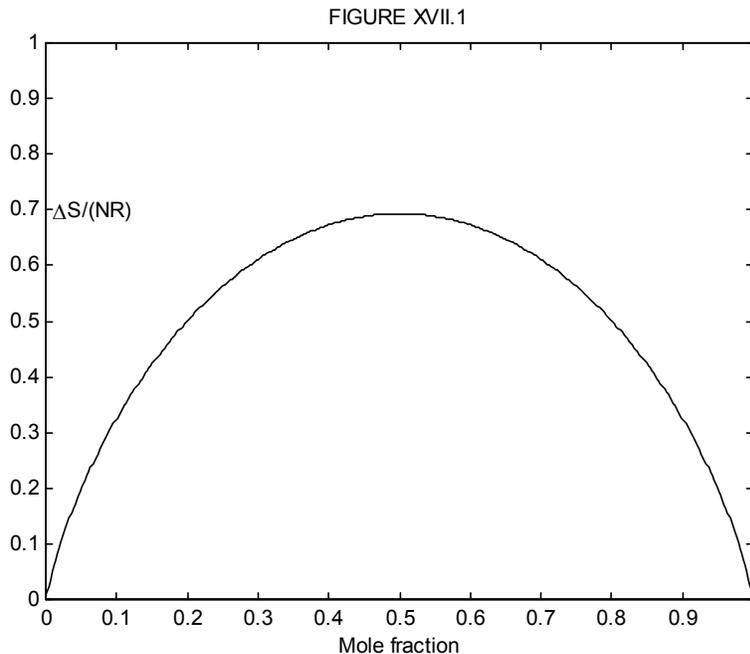
Here is the box separated by a partition:



Concentrate your attention entirely upon the left hand gas. Remove the partition. In the first nanosecond, the left hand gas expands to increase its volume by dV , its internal energy remaining unchanged ($dU = 0$). The entropy of the left hand gas therefore

increases according to $dS = \frac{PdV}{T} = N_1R \frac{dV}{V}$. By the time it has expanded to fill the whole box, its entropy has increased by $RN_1 \ln(V/V_1)$. Likewise, the entropy of the right hand gas, in expanding from volume V_2 to V , has increased by $RN_2 \ln(V/V_2)$. Thus the entropy of the system has increased by $R[N_1 \ln(V/V_1) + N_2 \ln(V/V_2)]$, and this is equal to $RN[n_1 \ln(1/n_1) + n_2 \ln(1/n_2)] = -NR[n_1 \ln n_1 + n_2 \ln n_2]$.

Where there are just two gases, $n_2 = 1 - n_1$, so we can conveniently plot a graph of the increase in the entropy versus mole fraction of gas 1, and we see, unsurprisingly, that the entropy of mixing is greatest when $n_1 = n_2 = \frac{1}{2}$, when $\Delta S = NR \ln 2 = 0.6931NR$.

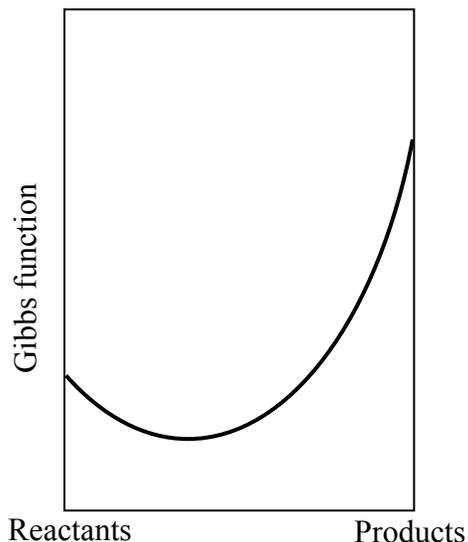


What is n_1 if $\Delta S = \frac{1}{2}NR$? (I make it $n_1 = 0.199710$ or, of course, 0.800290 .)

We initially introduced the idea of entropy in Chapter 7 by saying that if a quantity of heat dQ is added to a system at temperature T , the entropy increases by $dS = dQ/T$. We later modified this by pointing out that if, in addition to adding heat, we did some irreversible work on the system, that irreversible work was in any case degraded to heat, so that the increase in entropy was then $dS = (dQ + dW_{\text{irr}})/T$. We now see that the simple act of mixing two or more gases at constant temperature results in an increase in entropy. The same applies to mixing any substances, not just gases, although the formula $-NR[n_1 \ln n_1 + n_2 \ln n_2]$ applies of course just to ideal gases. We alluded to this in Chapter 7, but we have now placed it on a quantitative basis. As time progresses, two separate gases placed together will spontaneously and probably (*very probably!*) irreversibly mix, and the entropy will increase. It is most unlikely that a mixture of two gases will spontaneously separate and thus decrease the entropy.

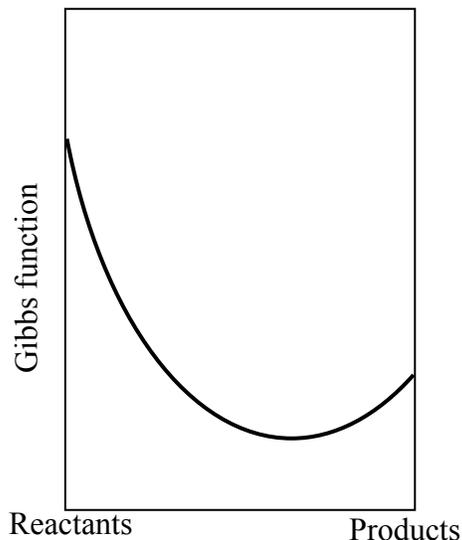
Gibbs' Paradox arises when the two gases are identical. The above analysis does nothing to distinguish between the mixing of two different gases and the mixing of two identical gases. If you have two identical gases at the same temperature and pressure in the two compartments, nothing changes when the partition is removed – so there should be no change in the entropy. Within the confines of classical thermodynamics, this remains a paradox – which is resolved in the study of *statistical mechanics*.

Now consider a reversible chemical reaction of the form $\text{Reactants} \leftrightarrow \text{Products}$ – and it doesn't matter which we choose to call the “reactants” and which the “products”. Let us suppose that the Gibbs function of a mixture consisting entirely of “reactants” and no “products” is less than the Gibbs function of a mixture consisting entirely of “products”. The Gibbs function of a *mixture* of reactants and products will be less than the Gibbs function of either reactants alone or products alone. Indeed, as we go from reactants alone to products alone, the Gibbs function will look something like this:



The left hand side shows the Gibbs function of the reactants alone. The right hand side shows the Gibbs function for the products alone. The equilibrium situation occurs where the Gibbs function is a minimum.

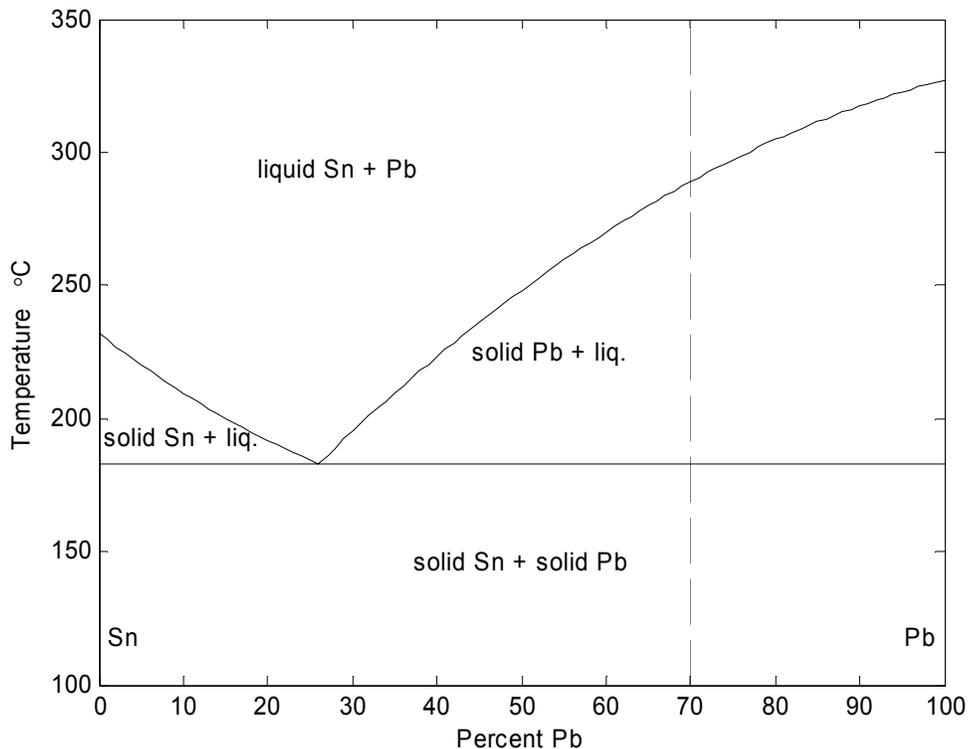
If the Gibbs function of the reactants were greater than that of the products, the graph would look something like:



17.9 Binary Alloys

(This section is a little out of order, and might be better read after Section 17.3.)

If two metals are melted together, and subsequently cooled and solidified, interesting phenomena occur. In this section we look at the way tin and lead mix. I do this in an entirely schematic and idealized way. The details are bit more complicated (and interesting!) than I present them here. For the detailed description and more exact numbers, the reader can refer to the specialized literature, such as *Constitution of Binary Alloys* by M. Hansen and K. Anderko and its subsequent Second Supplement by F. A. Shunk. In my simplified description I am assuming that when tin and lead are melted, the two liquids are completely miscible, but, when the liquid is cooled, the two metals crystallize out separately. The phenomena are illustrated schematically in the figure below, which is a graph of melting point versus composition of the alloy at a given constant pressure (one atmosphere).



The melting point of pure Pb is 327 °C

The melting point of pure Sn is 232 °C

In studying the diagram, let us start at the upper end of the dashed line, where the temperature is 350 °C and we are dealing with a mixture of 70 percent Pb and 30 percent Sn (by mole – that is to say, by relative numbers of atoms, not by relative mass). If you review the definitions of phase, component, and degrees of freedom, and the Gibbs phase rule, from Section 17.3, you will agree that there is just one phase and one component (there's no need to tell me the percentage of Sn if you have already told me the percentage of Pb), and that you can vary two intensive state variables (e.g. temperature and pressure) without changing the number of phases.

Now, keeping the composition and pressure constant, let us move down the *isopleth* (i.e. down the dashed line of constant composition). Even after the temperature is lower than 327 °C, the mixture doesn't solidify. Nothing happens until the temperature is about 289 °C. Below that temperature, crystals of Pb start to solidify. The full curve represents the melting point, or solidification point, of Pb as a function of the composition of the liquid. Of course, as some Pb solidifies, the composition of the liquid changes to one of a lesser percentage of Pb, and the composition of the liquid moves down the melting point curve. As long as the liquid is at a temperature and composition indicated along this curve, there is only one remaining degree of freedom (pressure). You cannot change both the temperature and the composition without changing the number of phases. As the

temperature is lowered further and further, more Pb solidifies, and the composition of the liquid moves further and further along the curve to the left, until it reaches the *eutectic point* at a temperature of 183 °C and a composition of 26% Pb. Below that temperature, both Pb and Sn crystallize out.

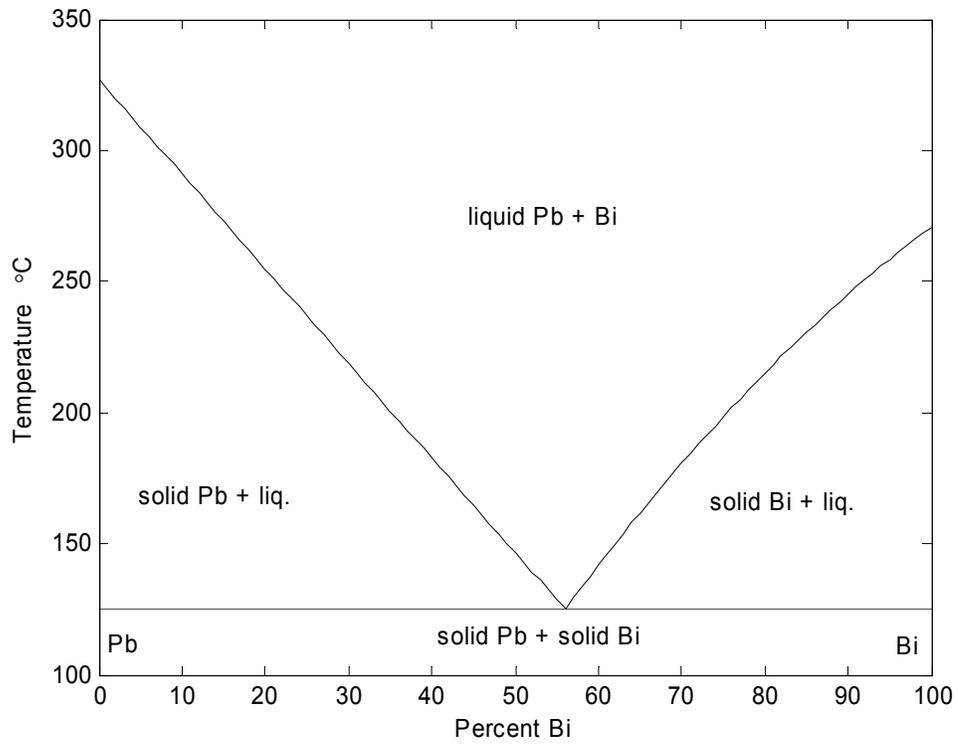
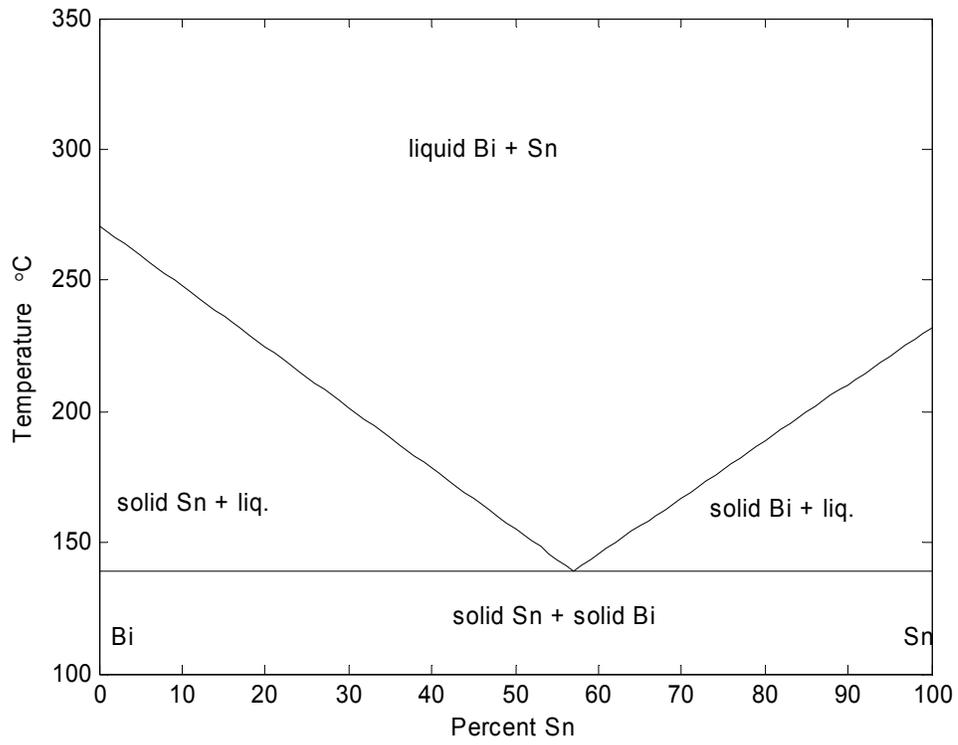
If we had started with a composition of less than 26% Pb, Sn would have started to crystallize out as soon as we had reached the left hand curve, and the composition of the liquid would move along that curve to the right until it had reached the eutectic point.

Below, we show similar (highly idealized and schematic) eutectic curves for Pb-Bi and for Bi-Sn. (For more precise descriptions, and more exact numbers, see the literature, such as the references cited above). The data for these three alloys are:

For the pure metals:

Melting point	Pb	327 °C
	Bi	271
	Sn	232

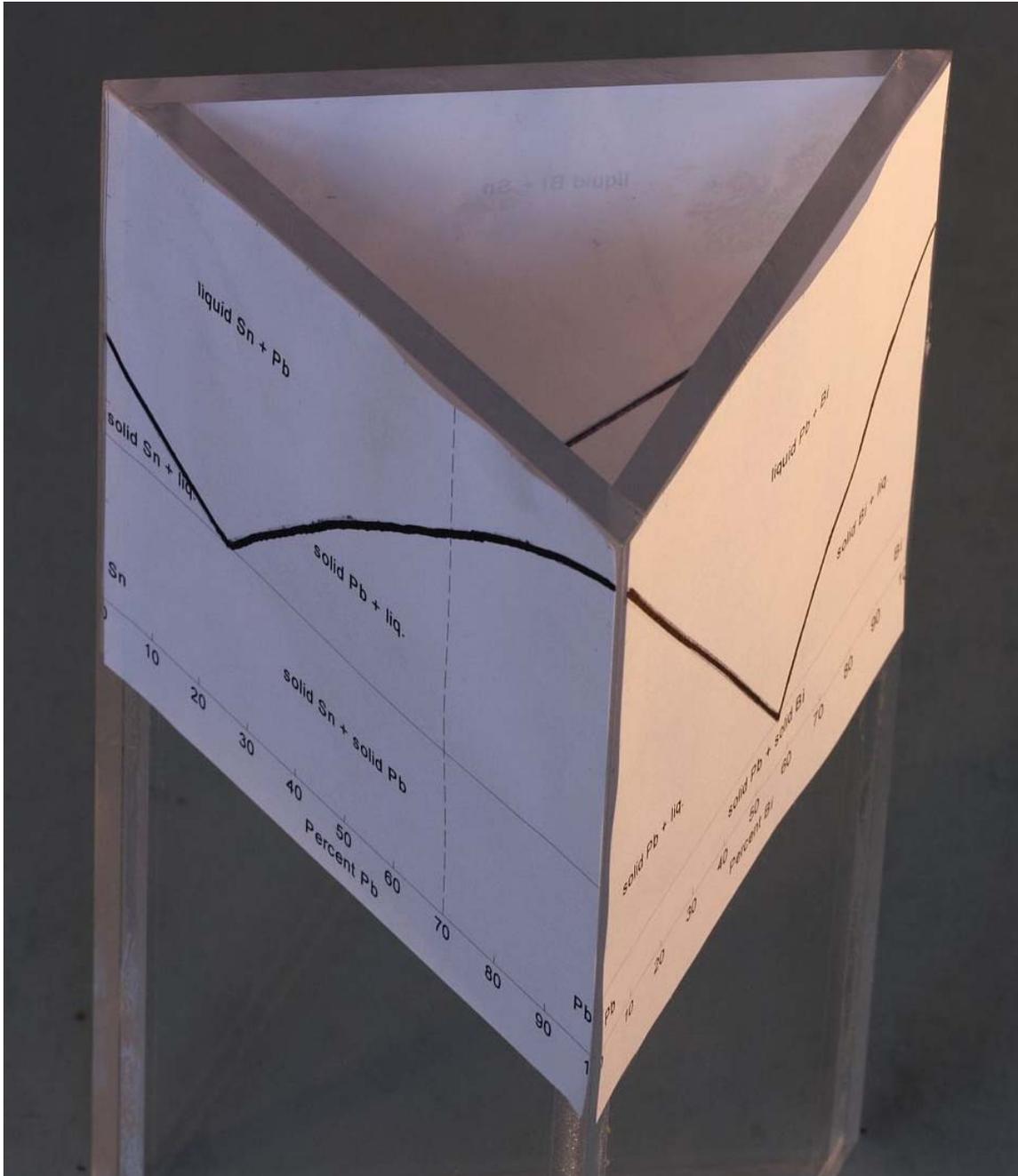
Sn-Pb	Eutectic	183 °C	26% Pb
Pb-Bi	Eutectic	125 °C	56% Bi
Bi-Sn	Eutectic	139 °C	57% Sn

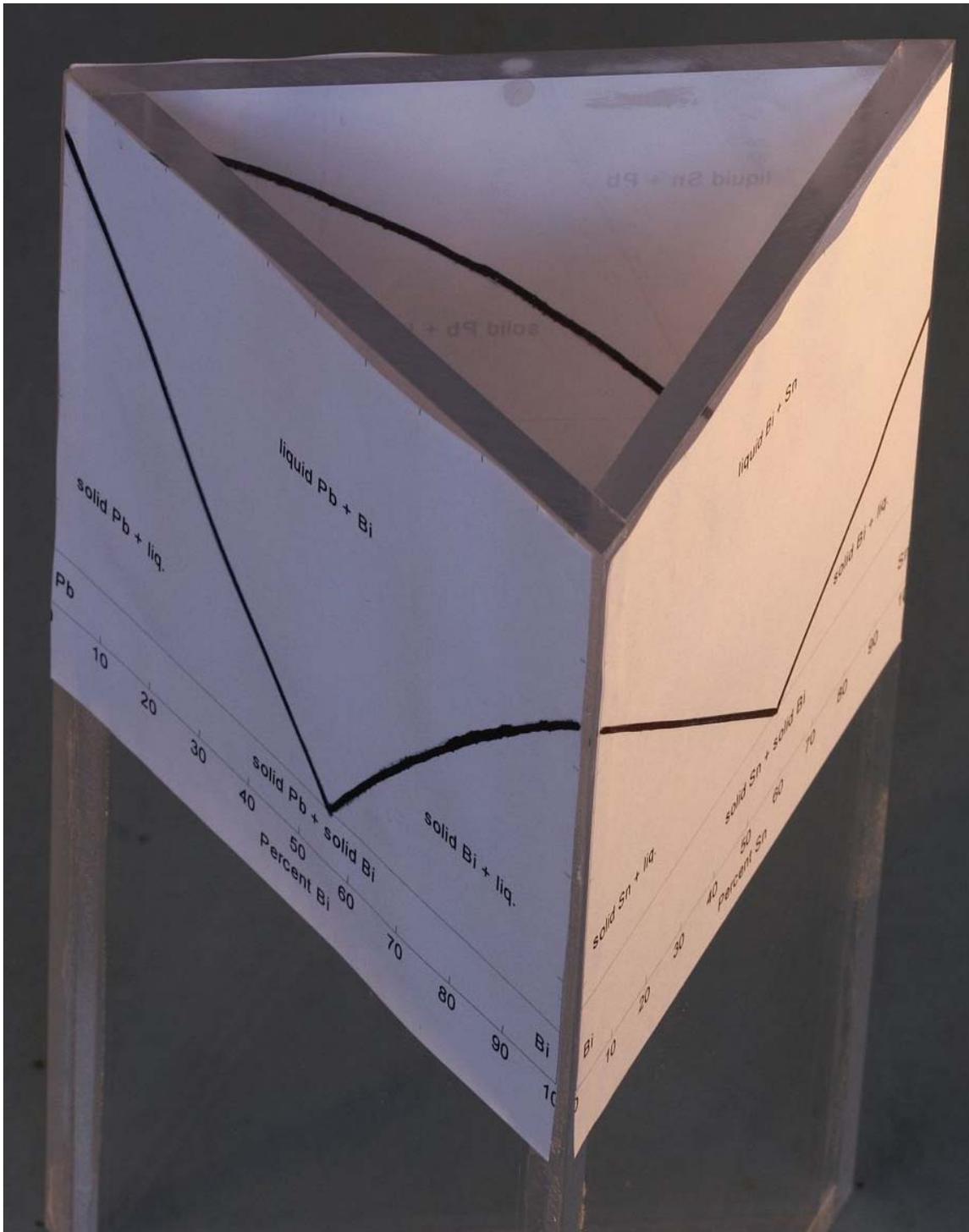


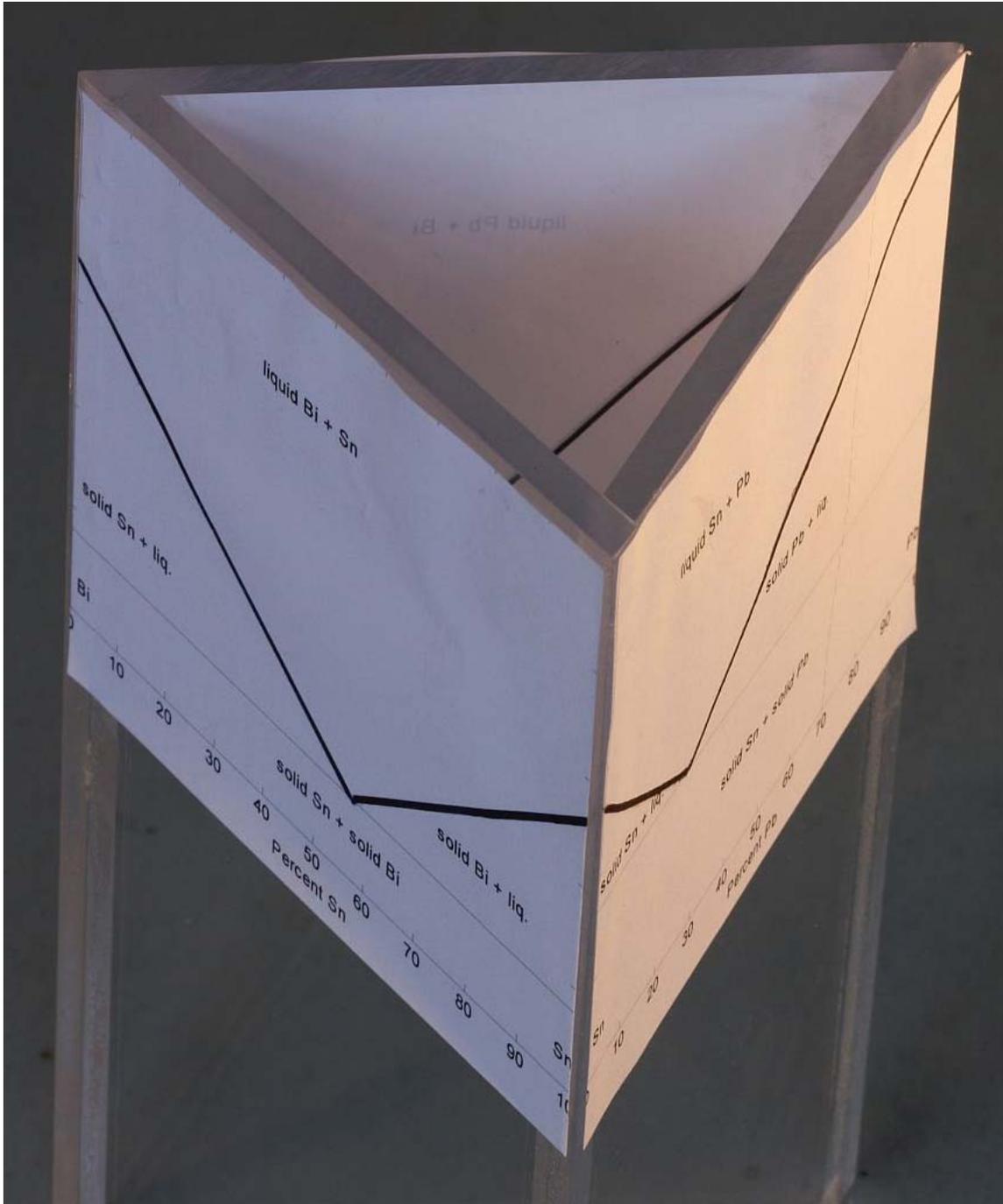
17.10 Ternary Alloys

In this section we look at what happens with an alloy of three metals, and we shall use as an example Pb-Bi-Sn. Our description is merely illustrative of the principles; for more exact details, see the specialized literature.

To illustrate the phase equilibria of an alloy of these three metals, I have pasted the eutectic diagrams of the previous section to the faces of a triangular prism, as shown below. The vertical ordinate is the temperature.

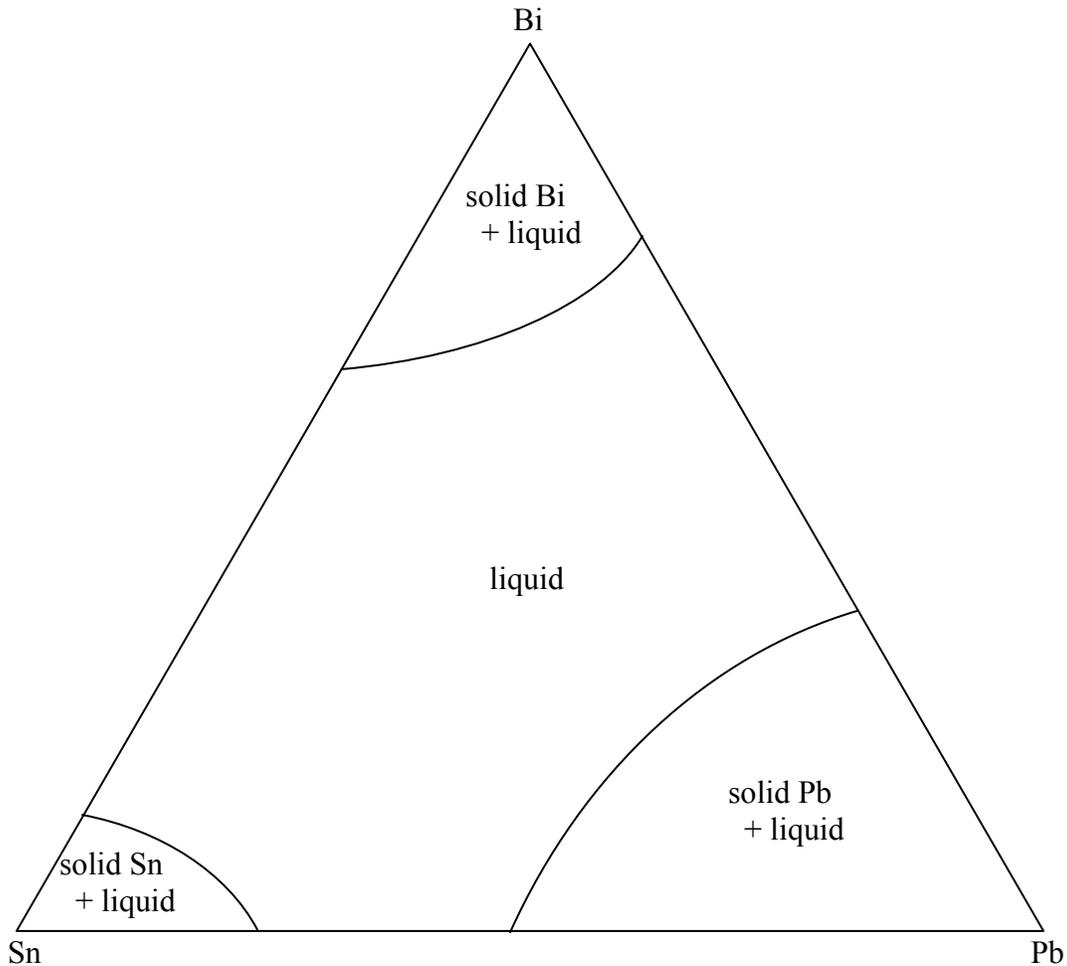






On each of the three faces only two of the metals are present. The situation where all three metals are present on comparable quantities would be illustrated by a surface inside the prism, but creating this inner surface is unfortunately beyond my skills. Anywhere above the surface outlined by the curves on each face is completely liquid. Below it one or other of the constituent metals solidifies. The surface goes down to a deep well, terminating in a eutectic temperature well below the 125 °C of the Pb-Bi eutectic.

In lieu of building a nice three-dimensional model, the next best thing might be to take a horizontal slice through the prism at constant temperature. If I do that at, say, 200°C, the ternary phase diagram might look something like this:



You can imagine what happens as you gradually lower the temperature. First a bit of Pb solidifies out. Then a bit of Bi. Lastly a bit of Sn. You have to try and imagine what this ternary diagram would look like as you lower the temperature. Eventually the solidification parts spread out from the corners of the triangle, and meet at a single

eutectic point where there are no degrees of freedom. Below that temperature, all is solid, whatever the composition.