SIO 224

Thermodynamics of phase transitions

1. The Gibbs Free Energy

When discussing phase transformations, we usually work in the P, T domain in which G, the Gibbs free energy is the most useful function. In a system such as the mantle consisting of several minerals in different phases, we have $G = G(P, T, N_1, N_2, ...)$ where N_i is the number of moles of the *i*'th mineral phase present. A general expression for the change in G is then given by (equation 43 of the thermo notes):

$$dG = -SdT + VdP + \sum_{i} \mu_i dN_i \tag{1}$$

where

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N_1,N_2...}$$
$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,N_1,N_2...}$$

and

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

is called the chemical potential of the *i*'th species (usually taken to be "per mole" so that N_i is the number of moles of the *i*'th component). In general, the Gibbs free energy is given by (equation 45 of the thermo notes)

$$G = \sum_{i} \mu_i N_i \tag{2}$$

If only one component is present, we see that the chemical potential of a pure substance is just the Gibbs free energy per mole. A system will always change towards the state with the lowest Gibbs free energy. Thus, as pressure and temperature change, a new phase may have a lower possible free energy. In equilibrium, the Gibbs free energy of a system is a minimum. This has some important consequences as we discuss in the next section. Since $G = \sum_{i} \mu_i N_i$, we get

$$dG = \sum_{i} d\mu_i N_i + \sum_{i} \mu_i dN_i \tag{3}$$

and combining with equation (1) gives

$$\sum_{i} d\mu_i N_i = -SdT + VdP \tag{4}$$

which is called the Gibbs-Duhem equation (equation 24 of the thermo notes) and is used in a discussion of phase boundaries. For a single component system, equation (4) gives

$$\left(\frac{\partial\mu}{\partial T}\right)_P = -\frac{S}{N} \quad \text{and} \quad \left(\frac{\partial\mu}{\partial P}\right)_T = \frac{V}{N}$$
(5)

2. The Clapeyron equation

Consider a one component system in which dN moles go from phase α to phase β at a particular P and T. As T and P are fixed, then equation (1) becomes

$$dG^{\alpha} = -\mu^{\alpha} dN \quad \text{and} \quad dG^{\beta} = \mu^{\beta} dN$$
(6)

i.e. dN moles are removed from phase α and added to phase β . The total change in the Gibbs free energy of the system must be zero for the system to be in equilibrium so

$$dG = dG^{\alpha} + dG^{\beta} = (\mu^{\beta} - \mu^{\alpha})dN = 0$$
(7)

whence

$$\mu^{\alpha} = \mu^{\beta} \tag{8}$$

i.e. the chemical potentials of the two phases are the same. In a system of many components, this argument generalizes to give

$$\mu_i^{\alpha} = \mu_i^{\beta} \tag{9}$$

Suppose now we perturb the P and T conditions of our single component system such that the two phases remain in equilibrium. From equation 5, we have (using molar quantities)

$$d\mu^{\alpha} = -S^{\alpha}dT + V^{\alpha}dP \quad \text{and} \quad d\mu^{\beta} = -S^{\beta}dT + V^{\beta}dP \tag{10}$$

but, for equilibrium, $d\mu^{\alpha} = d\mu^{\beta}$ so that the chemical potentials of the the phases stay the same and combining the above equations gives

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{S^{\beta} - S^{\alpha}}{V^{\beta} - V^{\alpha}} \tag{11}$$

which is Clapeyron's equation for the gradient of the P - T curve separating two phases of a single component system . ΔS and ΔV are the discontinuitues in molar entropy and volume associated with the phase transformation. Clapeyron's equation is sometimes written in terms of the molar latent heat of the transition L (the amount of heat released by a mole of material undergoing the phase transformation) where $L = T\Delta S$, i.e.

$$\frac{dP}{dT} = \frac{L}{T\Delta V} \tag{12}$$

At high T and P, ΔS tends to be relatively independent of temperature and pressure and of the order the gas constant, R. Also, ΔV tends to be a slowly decreasing function of pressure. This is particularly true of liquid–solid phase transitions since at high pressures the volumes of the liquid and solid tend to become the same, so $dT/dP \rightarrow 0$.

As we go from low to high pressure, phase transformations always have ΔV negative (the high pressure phase is denser) but ΔS can be negative or positive. If it is negative, the clapeyron slope is positive and latent heat is released (exothermic). Thus increasing temperature increases the pressure at which the transformation occurs. A positive ΔS gives a negative clapeyron slope and heat is absorbed (endothermic). The transformation of forsterite (magnesium end member of olivine) to wadsleyite is exothermic and happens at pressures close to that of the 410km discontinuity. The transformation of ringwoodite to perovskite and magnesiowustite is endothermic and occurs close to the pressures of the 660km discontinuity. Thus, it is often loosely stated that the 410 is exothermic and the 660 is endothermic – however, this ignores the fact that we are not dealing a single component system. The mantle is made up of more than olivine and all minerals are solid solutions with iron substituting for magnesium. We now see how this affects possible phase diagrams for mantle minerals.

3. Mixtures

In the mantle, we deal with a mixture of minerals and not a single component. When two substances are mixed together there is generally an expansion or contraction (called the "volume of mixing") so that volumes are not additive. An "ideal" mixture shows no volume change on mixing so that it becomes simple to compute the fraction of the mass which corresponds to each component of the mixture. Consider a mixture of two components A and B. with masses M_A and M_B and occupying volumes V_A and V_B and suppose the mixture has mass M and volume V. Clearly, masses are additive:

$$M = M_A + M_B \tag{13}$$

and in terms of volumes we have

$$V_A = \frac{M_A}{\rho_A}, \quad V_B = \frac{M_B}{\rho_B} \quad \text{and} \quad V = \frac{M}{\rho}$$
 (14)

If volumes are also additive then

$$V = V_A + V_B \tag{15}$$

whence it is easy to show that

$$\frac{1}{\rho} = \frac{1-x}{\rho_A} + \frac{x}{\rho_B} \tag{16}$$

where x is the mass fraction of component B so $x = M_B/M$. Given ρ_a , ρ_B , and ρ , it is trivial to compute x. We usually work with mole fractions rather than mass fractions. A mole fraction, X_i , can easily be converted to a mass fraction, x_i , and vice versa. We have

$$X_i = \frac{n_i}{N} = \frac{n_i}{\sum_i n_i} \tag{17}$$

and the total mass is written as $M = \sum_i m_i$ so the mass fraction of the *i*'th component is given by

$$x_i = \frac{m_i}{M} \tag{18}$$

Now, $n_i = m_i/w_i$ where w_i is the gram molecular weight of the *i*'th component so

$$x_i = \frac{m_i}{M} = \frac{n_i w_i}{\sum n_i w_i} = \frac{X_i w_i}{\sum X_i w_i}$$
(19)

and

$$X_i = \frac{n_i}{N} = \frac{x_i/w_i}{\sum x_i/w_i} \tag{20}$$

In a two component system, this simplifies since $\sum X_i = 1$ and $\sum x_i = 1$ so

$$X_1 = \frac{x_1}{x_1 + \frac{w_1}{w_2}(1 - x_1)} \tag{21}$$

and so on.

Mixtures are divided into several categories. "Perfect" mixtures are those which behave ideally for all values of x. Many solid solutions behave like perfect mixtures. True "ideal" mixtures are those which behave ideally for small values of x and, if x is small enough, most mixtures behave ideally.

4. Chemical potentials

The behavior of a mixture hinges on the behavior of the chemical potential. In a mixture of perfect gases at fixed P and T conditions, the chemical potential of the *i*'th component behaves like

$$\mu_i = \mu_i^* + RT \ln X_i \tag{22}$$

where X_i is the mole fraction of the *i*'th component and μ_i^* is the chemical potential when only the *i*'th component is present. In a perfect mixture, all components have chemical potentials which behave this way but, in a weak mixture, μ_i^* can be interpreted as the chemical potential of the pure solvent when *i* is the solvent component. For other components (solutes) μ_i^* can not be regarded as the chemical potential of the pure solute.

To see how equation 22 arises, we consider the simple olivine solid solution. For mantle solid solutions, it is not always obvious how to designate the "components" which are being mixed. For olivine, it is pretty obvious that we should use forsterite and fayalite, but it is not always that obvious. The way to approach such solutions is to use the "mixing-on-sites" (MOS) model, which assumes that all ions occupying a given crystallographic site mix independently (and randomly in the ideal case) on that site. The ideal model implies that ions in the solution show no preferential interactions as a result of mixing, i.e., there is no heat of mixing.

The key to quantifying the MOS model is to identify the number of available configurations of ions in the crystal, W, and then compute the "configurational entropy". Consider the mixing of two different ions (e.g. Mg²⁺ and Fe²⁺) on the same crystallographic site. Suppose the number of ions mixed are N_1 and N_2 respectively, then the question is: how many ways can N_1 and N_2 ions be distributed over $N_1 + N_2$ sites. From probability, we have

$$W = \frac{(N_1 + N_2)!}{N_1! N_2!}$$

The configurational entropy is just given by $S = k \ln W$ for each mixing site. If there are *n* sites that mixing can take place on (per mineral formula unit) then the total entropy is $S = nk \ln W$. Thus

$$S = nk \left[\ln (N_1 + N_2)! - \ln N_1! - \ln N_2! \right]$$

Since all the N's are very large, we can use Stirling's approximation $(\ln n! = n \ln n - n)$ and rewrite this as

$$S = -nk\left[N_1 \ln\left(\frac{N_1}{N_1 + N_2}\right) + N_2 \ln\left(\frac{N_2}{N_1 + N_2}\right)\right]$$

If we deal with a mole of exchangeable sites then $N_1 + N_2 = N$ where N is Avogadros number and R = Nk so giving

$$S = -nR(X_1 \ln X_1 + X_2 \ln X_2) = -nR\Sigma_i X_i \ln X_i$$

where, in the last term, we have generalized to the case of more than two different ions.

The free energy of mixing is given by

$$\Delta G = \Delta H - T\Delta S$$

but, for ideal mixtures, there is no heat of mixing so $\Delta H = 0$ The free energy of the ideal solution is then the sum of the free energies of the end members plus the free energy of mixing

$$G = X_1 \mu_1^* + X_2 \mu_2^* + nRT \left(X_1 \ln X_1 + X_2 \ln X_2 \right)$$

We can also write this in terms of the chemical potentials of the individual components:

$$G = X_1\mu_1 + X_2\mu_2$$

which leads to

$$\mu_1 = \mu_1^* + nRT \ln X_1$$
 and $\mu_2 = \mu_2^* + nRT \ln X_2$

which is in the form of equation 22. (For more complicated mixing geometries, we find that (for perfect mixing)

$$S = -R\Sigma_j n_j \Sigma_i X_{i,j} \ln X_{i,j}$$

where n_j is the total number of crystallographic sites (expressed in terms of atoms per formula unit) on which mixing takes place, and $X_{i,j}$ is the mole fraction of the *i*'th atom on the *j*'th site.)

The equation for the chemical potential is generalized to include non-ideal behavior by introducing the "activity", a_i with

$$\mu_i = \mu_i^* + RT \ln a_i \tag{23}$$

Comparison with our equation above indicates that $a_i = X_i^n$ for our ideal solution. For simplicity in what follows, we shall assume there is just one mixing site so n = 1. Sometimes the activity is written as a coefficient (the activity coefficient) times the ideal solution activity which means the ideal part in equation 23 can be separated from the "excess" part due to non-ideal behavior.

5. Computing phase equilibria in the mantle

The Gibbs free energy of a multiphase assemblage is given by

$$G(P,T,n_i) = \sum_i n_i \mu_i(P,T,n_i)$$
(24)

where

$$\mu_i = \mu_i^* + RT \ln a_i$$

 a_i is the activity of the i'th species and μ_i^* is the chemical potential of the pure i'th species and so is the same as the Gibbs free energy of that component:

$$\mu_i^* = G_i(P,T) = F_i(V_i,T) + PV_i$$

We already have an equation of state for F(V,T) based on the Mie-Gruneisen EOS (though we need to include the Helmholtz free energy of formation, F_0 so that

$$F(V,T) = F_0 + F_c(V,T_0) + F_{th}$$

where F_c is the cold part (given by finite strain therory) and F_{th} is the thermal part given by Debye theory. We need such an equation of state for each possible component of the mantle (which is specified by 10 numbers if we include the shear velocity). The only other thing we need is a model for the activity of the *i*th species (equation 23). For nearly ideal solutions, this will be dominated by the ideal part which we partially discussed in the previous section. More complete treatments include a non-ideal part through an activity coefficient which is not equal to 1. This leads to a contribution to μ_i called the "excess" part. Treatment of non-ideality is beyond the scope of this course but the interested reader can consult the paper by Stixrude et al (2011).

Our task is now to find the n_i which minimize equation 24 subject to the constraint of a fixed bulk composition and subject to non negativity of the amounts of all species. This is a difficult numerical problem and the paper by Stixrude gives some detail on how to solve it. The phase diagram of the upper mantle according to this calculation is given in the following figure. This diagram forms the basis of discussion of the upper mantle discontinuities that are observed seismically.



Figure 16. Phase diagram of a model pyrolite composition computed from our model showing phase boundaries and the zero-pressure density of the assemblage according to the scale bar at the top. Phase boundaries are shown as thin black lines except those among the olivine polymorphs (brown lines), and the reactions forming st and fp in the transition zone (bold black lines). Also plotted (bold red) is the 1600 K isentrope.

6. The Gibbs phase rule

Multicomponent systems exhibit much more complicated phase diagrams than single component systems because of the ability of more than one phase to coexist at a variety of temperature and pressures. The Gibbs phase rule governs this behavior and can be derived as follows.

The condition for equilibrium of different phases of different components is that the chemical potentials of the *i*'th component in the α and β phases be equal:

$$\mu_i^{\alpha} = \mu_i^{\beta} \tag{25}$$

If we have k components in n phases in equilibrium, the conditions that the chemical potentials be equal give k(n-1) constraints on the system. The number of variables describing the system are 2 (temperature and pressure) plus n(k-1) numbers describing the composition of each phase. (Suppose we use mole fraction, X_i to describe the composition of the *i*'th component in the *n*'th phase, then the composition of the phase is determined by $k X_i$'s but because the sum of all the X_i 's is one, we have only k-1 numbers describing the composition of the system is therefore

$$f = n(k-1) + 2 - k(n-1) = k - n + 2$$
(26)

This is called the "variance" of the system. Suppose we have a phase change in a one component system so that k = 1, n = 2 giving f = 1 when two phases are in equilibrium. This is called a univariant system. If we specify one variable (e.g. pressure) then the others (e.g. temperature) are completely specified by the condition of equilibrium. Thus, for a univariant system, there is a unique P - T curve specifying the equilibrium condition of two phases. Now suppose we have a two component system. The number of degrees of freedom when two phases are in equilibrium is two. This is called a divariant system. If we specify temperature, there are still an infinite number of pressure-composition combinations that allow two phases to be in equilibrium.

Suppose we consider a mixture of Forsterite and Fayalite undergoing a phase transition from phase α to phase β (e.g. olivine to wadsleyite). At a fixed P and T we have

$$\mu_{Fo}^{\alpha} = \mu_{Fo}^{\beta} \quad \text{and} \quad \mu_{Fa}^{\alpha} = \mu_{Fa}^{\beta} \tag{27}$$

where we can write

$$\mu_{Fa}^{\alpha} = \mu_{Fa}^{*\alpha} + RT \ln a_{Fa}^{\alpha} \quad \text{and} \quad \mu_{Fa}^{\beta} = \mu_{Fa}^{*\beta} + RT \ln a_{Fa}^{\beta}$$
(28)

with similar equations for Forsterite. Here, $\mu_{Fa}^{*\alpha}$ is the chemical potential of Fayalite if only this component is present. Thus, at equilibrium

$$RT\ln\left(\frac{a_{Fa}^{\beta}}{a_{Fa}^{\alpha}}\right) = \mu_{Fa}^{*\alpha} - \mu_{Fa}^{*\beta}$$
⁽²⁹⁾

We can consider the effect of pressure on the phase transition at constant temperature by differentiating with respect to pressure at constant temperature and using the fact the $(\partial \mu / \partial P)_T = V$. This gives

$$\left(\frac{\partial}{\partial P}\ln\left(\frac{a_{Fa}^{\beta}}{a_{Fa}^{\alpha}}\right)\right)_{T} = \frac{\Delta V_{Fa}}{RT}$$
(30)

where ΔV_{Fa} is the volume change in the pure Fayalite $\alpha \rightarrow \beta$ transition. This is $V_{\alpha} - V_{\beta}$ which is almost always positive – the volume of the higher pressure phase is smaller. If ΔV is independent of pressure, we can integrate this equation from P_{Fa} to P (i.e. from the pressure at which pure Fayalite transforms to the pressure at which the Fayalite in the mixture transforms):

$$\ln\left(\frac{a_{Fa}^{\beta}}{a_{Fa}^{\alpha}}\right) = \frac{\Delta V_{Fa}}{RT}(P - P_{Fa}) \tag{31}$$

A similar equation can be derived for Forsterite:

$$\ln\left(\frac{a_{Fo}^{\beta}}{a_{Fo}^{\alpha}}\right) = \frac{\Delta V_{Fo}}{RT}(P - P_{Fo})$$
(32)

Solid solutions are usually nearly perfect mixtures so we will take a = X. Let $a_{Fa}^{\beta} = X_{\beta}$ and $a_{Fa}^{\alpha} = X_{\alpha}$, then $a_{Fo}^{\beta} = 1 - X_{\beta}$ and $a_{Fo}^{\alpha} = 1 - X_{\alpha}$. Thus

$$\ln\left(\frac{X_{\beta}}{X_{\alpha}}\right) = \frac{\Delta V_{Fa}}{RT}(P - P_{Fa}) \quad \text{and} \quad \ln\left(\frac{1 - X_{\beta}}{1 - X_{\alpha}}\right) = \frac{\Delta V_{Fo}}{RT}(P - P_{Fo}) \tag{33}$$

If we know the pressures at which pure Forsterite and pure Fayalite transform and we know the volume changes associated with these transformations, we can solve for X_{α} and X_{β} at a particular value of *P*. The result of doing this looks like:



and we end up with a phase loop. The main point is that there is a finite range of pressure over which there is a mixed phase region.

A way to interpret the phase loop is to consider a solid solution with composition X_{Fo} in the α phase. As pressure in increased and the phase loop is entered we find that, at a pressure P^* , a mixture with X_1 in the α phase is in equilibrium with a mixture with X_2 in the β phase. Finally, we end up with a composition X_{Fo} in the β phase.

When we have more than two possible phases in the system, things get a little more complicated. In the olivine phase diagram, we have α , β , and γ phases at low pressures – see figure on next page. We have three possible phase loops: $\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$, and $\alpha \rightarrow \gamma$ but, in general, the phase loops will intersect. At the intersection of two mixed phase regions, we have a unvariant system. Consider the intersection of the $\alpha + \gamma$ and $\beta + \gamma$ mixed phase regions. Now k = 2, n = 3 so f = 1. If we fix temperature then, for equilibrium of these three phases, all other variables (including pressure) are fixed. Thus it is possible to get a sharp univariant transition in a mixed phase region. Note how the phase diagram moves up in pressure as temperature increases – this is because of the exothermic nature of all the end member components. Note also that, in the Earth, we are interested in materials which are about 90% magnesium and about 10% iron so we are on the left side of the diagram (to the left of the univariant transformation) so we might expect the 410 "discontinuity" to be distributed over a pressure range.



Fig. 8. Calculated boundaries of $\alpha - \beta - \gamma$ transitions at 1473 and 1873 K. Experimentally determined boundaries below 10 GPa at 1473 K by *Akimoto* [1987] are also shown by dashed curves.

Sometimes phase loops can be very narrow and a candidate transformation for the 660 km discontinuity exhibits this (ringwoodite to perovskite plus magnesiowustite). Again we are interested in the left hand side of the figures. Note how the diagram shifts down in pressure as temperature increases because of the endothermic nature of the transformation in the magnesium end member. The pressure in the Earth at a depth of 660km is about 23.45GPa (some models have the discontinuity at 670km with a pressure of about 23.84GPa) so this figure suggests the temperature in the Earth at the 660 is somewhat lower than 1870K. I should point out that there are experimental uncertainties in both temperature and pressure in these figures.



[The phase rule can be extended to include chemical reactions as long as we keep track of the number of independent equilibrium conditions and we are careful by what we mean by independent components. When r independent reactions are occurring, we have

$$f = (k - r) - n + 2 \tag{34}$$

A discussion of this can be found in Kern and Weisbrod (Thermodynamics for Geologists)]

7. Sharpness and shape of phase loops

Since there is no univariant phase transformation candidate for either the 410km discontinuity or the 660 km discontinuity, it is of interest to see how properties behave through a phase loop. Following Stixrude (1997), we introduce the "partition coefficient", K, where

$$K = \frac{X_{\alpha}(1 - X_{\beta})}{(1 - X_{\alpha})X_{\beta}} \tag{35}$$

and, using equation(33) above, we have

$$\ln K = \frac{\Delta V_{Fo}}{RT} (P - P_{Fo}) - \frac{\Delta V_{Fa}}{RT} (P - P_{Fa})$$
(36)

To a reasonable approximation we can take $\Delta V \simeq \Delta V_{Fa} \simeq \Delta V_{Fo}$ (which is positive) and we find that K is independent of pressure:

$$K = \exp\left(-\frac{\Delta P \Delta V}{RT}\right) \tag{37}$$

where $\Delta P = P_{Fo} - P_{Fa}$ and is positive. Remember that ΔV is positive so that as T increases or ΔV decreases (or ΔP is small), K will tend to 1 and we will have a narrow phase loop. Conversely, for small T or large ΔV , K tends to zero and we get a broad phase loop (see figure below).



Now define the normalized pressure, $\Pi = (P - P_{Fa})/\Delta P$ so that $\Pi - 1 = (P - P_{Fo})/\Delta P$, then equation (33) can be written in terms of K:

$$\frac{X_{\alpha}}{X_{\beta}} = K^{\Pi}$$
 and $\frac{1 - X_{\alpha}}{1 - X_{\beta}} = K^{\Pi - 1}$

Rearranging gives

$$X_{\alpha} = \frac{K^{\Pi} - K}{1 - K} \quad \text{and} \quad X_{\beta} = \frac{1 - K^{1 - \Pi}}{1 - K}$$
(38)

The width of the phase loop at a particular value of X can now be derived. Let P_{α} be the pressure at the bottom of the phase loop at composition X and P_{β} be the pressure at the top of the phase loop at composition X. The width, $W(X) = P_{\beta}(X) - P_{\alpha}(X) = (\Pi_{\beta} - \Pi_{\alpha})\Delta P$, can be written in terms of X and K using equation (38). Note that $X = X_{\alpha}$ at P_{α} so we use the first of equation 38 to compute Π_{α} . Similarly, $X = X_{\beta}$ at $P = P_{\beta}$ so we use the second of eq. (38) to compute Π_{β} . The result is

$$W(X) = \Delta P \left\{ 1 - \frac{\ln \left[K + X(1 - X)(1 - K)^2 \right]}{\ln K} \right\}$$
(39)

Finally, we are interested in the *yield* of the high pressure phase for composition X as a function of pressure. Yield is defined as

$$f_{\beta} = \frac{X - X_{\alpha}}{X_{\beta} - X_{\alpha}} \tag{40}$$

and can be written in terms of K and X using equation (38):

$$f_{\beta} = \frac{X(1-K) - K^{\Pi} + K}{1 - K^{1-\Pi} - K^{\Pi} + K}$$
(41)



Plotting this for various values of K and X gives the result shown in the figure above. The shape of f is sigmoidal. For large values of X, much of the change occurs in the low pressure part of the phase loop while, at small values of X, most of the change occurs in the high pressure part of the phase loop. This means that the effective (as seen by seismology) width of the loop may be much less than the total width given by equation (39). Stixrude estimates that the effective width of a phase transformation may be as little as 1/10 of the total width when K = 0.01. This may be the case for the garnet-perovskite transformation which is illustrated below (note that this isn't the only phase transformation going on at the 660)



For the olivine to wadsleyite transformation, $K \simeq 0.5$ and the sigmoidal behavior is less pronounced so the width and effective width of the transformation is similar (see figure below).



Stixrude also considers the effect of many complications (multicomponent phase transformations, nonideality, etc) but we refer the reader to the original paper (JGR, 102, p14,835, 1997). There is also a contribution to the phase loop width from latent heat which leads to a finite transition width even in single component systems. This is discussed in Jeanloz and Thompson (1983) and is included in the calculations of Weidner and Wang (2000).

8. Mantle discontinuities

Weidner and Wang discuss the effect of including the pyroxene component of pyrolite on the phase transformations which dominantly occur in the olivine component of pyrolite (see accompanying ppt). It is common for the pyroxene/garnet and olivine components of upper mantle mineralogy to be considered in isolation – but this is not valid. The reason is that partitioning of elements such as iron is a function of the overall mineralogy. In general terms, garnet takes Fe from olivine or wadsleyite and pyroxenes tend to give Fe to olivine. The amount of garnet is strongly dependent on the aluminum content so, even though there is not much Al in the mantle, it can have a big effect on the overall properties of the system. Garnet has a high density and high seismic velocities, so a small amount of aluminum (which stabilizes garnet) can change the seismic properties of the assemblage as well as changing the pressure and width of the olivine/wadsleyite transition.

The 520km discontinuity is often ascribed to the wadsleyite/ringwoodite transition which is fairly broad – so explaining why the 520 often only appears in the analysis of long period body waves. Another explanation is that calcium-silicate perovskite begins to dissolve out of the garnet at this pressure and, in fact, garnet is expected to be almost calcium-free by the bottom of the transition zone. This leads to the possibility of multiple discontinuities at the 520km discontinuity which have been observed (see ppt). The clapeyron slope for the wads/ring transition is positive while the clapeyron slope for the gt/capv transition is probably negative. Thus, lateral changes in temperature can split the discontinuity into two.

The 660km discontinuity could be very complex. Depending on temperature (and aluminum content), the dominant transition could be ringwoodite to perovskite + magnesiowustite or there could be an intermediate transformation from ringwoodite to garnet + magnesiowustite then to perovskite + magnesiowustite. The transition from ringwoodite to garnet is exothermic and has a large change in density so, if the latter transformation occurs, the 660 might actually promote convection rather than being a barrier to convection as would be the case in the olivine-only system. Certainly, lateral variations in aluminum content and temperature could change the character of this seismic discontinuity substantially – possibly leading to a double transformation in certain places as may be observed (see ppt).

The D" region at the base of the mantle may also show evidence of a phase transformation(s) which are now thought to be due to the post-perovskite transformation. This transformation is very dependent on chemistry and apparently has a strong effective positive clapeyron slope. This means that ppv will probably

exist in cold parts of the lowermost mantle but may not exist in hotter regions. It is even possible that the geotherm in the boundary layer could intersect the phase boundary twice (see ppt)

9. Melting

The review paper by Boehler discusses melting of both mantle and core materials and reviews the experimental techniques used to study melting in the DAC. Usually, we end up extrapolating melting curves to higher pressures and some simple melting "laws" are used to do this. Most of these are based on the Lindemann Law of melting. This simple theory of melting views the process as an instability within a crystal when the rms amplitude of atomic vibrations reaches some critical fraction of the interatomic spacing. A crude derivation is as follows.

Suppose we view a solid as 3N harmonic oscillators. If we neglect anharmonic effects (!), in the high temperature regime, the thermal energy of an oscillator is simply proportional to temperature. This will be proportional to the kinetic energy of the oscillation:

$$T \propto \frac{1}{2} m \omega^2 (\delta a)^2$$

where ω is the frequency of the oscillator, m is its mass, and δa is the amplitude of the oscillations.

Suppose melting takes place when δa is some critical fraction, f, of the interatomic spacing, a at melting. Taking averages over all modes of vibration:

$$T_m = K \frac{\langle \delta a^2 \rangle}{a^2} \cdot a^2 = K f^2 a^2$$

where K is a constant. Now a is proportional to volume to the one third power to

$$T_m = C V_m^{2/3}$$

where V_m is the volume at melting. The factor C implicitly includes an average over squared mode frequences and so will be a function of volume. Differentiating with respect to volume gives:

$$\frac{d \ln T_m}{d \ln V_m} = \frac{2}{3} + \frac{d \ln C}{d \ln V_m}$$

If C is proportional to $<\omega^2 >$ then we might crudely write

$$\frac{d \ln C}{d \ln V_m} = 2 \frac{d \ln < \omega >}{d \ln V_m} = -2\hat{\gamma}$$

(Recall that $\hat{\gamma}$ is the average of $-\partial \ln \omega_i / \partial \ln V$). We end up with the Lindemann formula:

$$\frac{d \ln T_m}{d \ln V_m} = \frac{2}{3} - 2\hat{\gamma}$$

where $\hat{\gamma}$ is the harmonic Gruneisen parameter.

This formula has been used extensively in the geophysical literature but it is not clear that it is a good representation of melting – certainly, this formula doesn't work particularly well for the melting of many low pressure minerals.

Some other simple melting "laws" can be derived from the Lindemann formula. If we write it as a difference equation:

$$\frac{\Delta T_m}{T_m^0} = \frac{T_m - T_m^0}{T_m^0} = (\frac{2}{3} - 2\hat{\gamma})\frac{\Delta V}{V_0}$$

we get the empirical Kraut-Kennedy relation:

$$T_m = T_m^0 \left[1 + D \frac{\Delta V}{V_0} \right]$$
 where $D = (2\hat{\gamma} - \frac{2}{3})$

(remember, ΔV is negative). The Lindemann law can also be used to derive the Simon melting equation – yet another empirical melting law. To do this, convert to an equation for pressure:

$$K_T \frac{d \ln T_m}{dP} = 2\hat{\gamma} - \frac{2}{3} = D$$

and approximate K_T as $K_T = K_0 + K'_0(P - P_0)$. Rearranging and integrating gives

$$\frac{P-P_0}{a} = \left(\frac{T_m}{T_m^0}\right)^c - 1$$

(the usual form for Simon's equation) with $c = K'_0/D$ and $a = K_0/K'_0$.

All of these equations have been used to extrapolate melting curves to higher pressures which, given the approximations, is probably a dangerous thing to do. Now, there is melting data for many constituents across the pressure range of the mantle so extrapolation is not so necessary. The same is not true for the core (next lecture) so all of these equations are still in active use.

The data indicate that the melting temperature (solidus) of mantle material is about 4000K at the CMB which could be close to the actual temperature. This leads to the possibility that there are partially molten regions at the CMB. There is seismic evidence to support this (see ppt).

10. Melting temperatures of the lower mantle

See accompanying power point