6 Phase Transitions and Phase Equilibria

Phase transitions are part of everyday experience (e.g. the formation of water clouds) and very important in atmospheric dynamics. But they are also very important inside planets... they’re everywhere, as melting to provide volcanism; abrupt changes in density and seismic properties in mantle (the 410 and 660km discontinuity in Earth’s mantle), the formation of Earth’s inner core, etc. They have a profound influence on planet evolution as well as affecting the static structure (density as a function of depth). We’ve already seen one example of a (hypothesized) phase transition in hydrogen; below we examine phase transitions in more detail.

6.1 Why do Phase Transitions Happen?

At a given T, P; a thermodynamic system will seek to minimize the Gibbs energy:

\[ G = E + PV - TS \]

As one increases pressure, this will clearly favor phases of lower volume (more compact packing of constituents). Or as one increases temperature, it will clearly favor phases of higher entropy (more disorder).

\[ \frac{\partial G}{\partial P} _T = V \] and \( \frac{\partial G}{\partial T} _P = -S. \]

Now consider two phases (1 and 2) that are in equilibrium at \( P, T \) and still in equilibrium at \( P + dP, T+dT \).

\[
\begin{align*}
G_1 &= G_2 \text{ and } G_1 + dG_1 = G_2 + dG_2 \Rightarrow dG_1 &= dG_2 \\
\Rightarrow V_1 dP - S_1 dT &= V_2 dP - S_2 dT \\
\Rightarrow (dP/dT)_{ph} &= \frac{(S_2 - S_1)}{(V_2 - V_1)} 
\end{align*}
\]

or, equivalently,
\[ \frac{d\ell}{d\eta} P = \frac{T \Delta S}{P \Delta V} \]  

(6.2)

Note that the RHS is a ratio of energies. The dimensionless derivative on the LHS will be large if the volume change is small and/or the entropy change is large; and small if the volume change is large and/or the entropy change is small. This is a very useful thing to remember because it will enable you to understand phase diagrams better.

This equation will tell you things such as: The pressure dependence of the condensation temperature of a gas (solar nebular thermodynamics), the pressure dependence of the melting point of a solid (e.g., why ice I has a melting point that decreases with pressure), the topography on phase boundaries in Earth’s mantle associated with convective upwellings and downwellings (purportedly detected seismologically), etc.

6.3 Multicomponent systems

This is a big topic, but the main points are these: When two multicomponent phases are in contact and in equilibrium, the chemical potential (specific Gibbs energy) of each species must be equal. The two phases need not have the same composition and in general will not have the same composition. This is an example of the Gibbs phase rule. (See Appendix to this chapter). For example, multimineralic assemblages do not have a melting point (in the sense of a single T at which you transition from completely solid to completely liquid)..... they have a solidus (a T at which melting begins) and a liquidus (at which the material is completely molten). Simple melting (where solidus = liquidus = “melting point”) is the exception rather than the rule in planetary systems (including icy satellites).

6.4 Kinds of Phase Transitions

6.4.1 Electronic

Reorganizations of the electron distribution (nature of the electronic states) can occur. This could be an insulator metal transition or a change in spin states, for example. The major example in our solar system could be

Molecular hydrogen → Metallic hydrogen

and probably involves a substantial volume change (e.g. 10%) but a modest entropy change (e.g. Boltzmann’s constant per proton) implying that the transition pressure is only weakly T-dependent according to the Clausius-Clapeyron equation.

As discussed previously, the hydrogen case is in reality probably more complicated, i.e.

Molecular hydrogen → Metallic molecular hydrogen → Monatomic metal

6.4.2 Structural (Solid→ Solid)

These generally arise because there exists a lower volume structure that can (by lowering the Gibbs energy) exist at higher P. All major mantle transitions in terrestrial planets are driven in this way. Examples:

Olivine → spinel
Spinel or post-spinel $\rightarrow$ Magnesiowustite + Perovskite

although the latter also involves disproportionation (breakdown into new mineral phases that have a different chemical formula.

The 660km discontinuity in Earth corresponds to spinel $\rightarrow$ perovskite and magnesiowustite. The phase boundary is shown below as a composition vs. pressure slice of the phase diagram. Notice (by the Gibbs phase rule) that there must be two lines separating the spinel and pv+mw field. But in this case they’re very close together, which means that the phase transition is sharply defined.

Figure 6.2
Perovskite is the most common mineral in Earth. However, it may transform at still higher pressure:
Figure 6.3
This figure is taken from Oganov et al, *Nature* **411**, 934-937 (2004). The top part shows the crossover in enthalpy (same as Gibbs energy at low T) that favors the new phase above a pressure of ~ 1 megabar, according to two theoretical calculations. The bottom half shows the data (X-ray crystallographic determination of structure) and the inferred phase boundary in T-P space.

**Water ice** undergoes many structural phase transitions as a function of pressure, even in the pressure range encountered in icy satellites.

**Figure 6.4**

Ice I has a density of ~0.92g/cm$^3$ (hence the negative slope of the melting curve.) Ice III has a density of ~1.16g/cm$^3$, ice V has a density of ~1.25, Ice VI a density of ~1.31 and ice VII a density of 1.49. Notice the remarkable differences over a range of only a few tens of kilobars (i.e., much more compressible than rock).

At still higher pressures, water symmetrizes (i.e. hydrogen bond and covalent bonds have same length and strength). This is ice X (way beyond the pressures of icy satellites). At that stage you should no longer think of “separate” water molecules. Here is a recent phase diagram for ice at higher pressure [Lin JF, Gregoryanz E, Struzhkin VV, et al. Melting behavior of H2O at high pressures and temperatures *GEOPHYSICAL RESEARCH LETTERS* 32 (11): Art. No. L11306 JUN 10 2005]. The dash-dot line is their suggested extrapolation for the melting curve beyond the triple point they find at T~1000K, P~35GPa. They suggest that this might even lead to freezing of water in the hot interiors of massive planets such as Earth or Uranus (as indicated by the insert showing possible T and P inside planets.)
Water ice has such complexity that the existence of “exotic” phases has even been featured in literature. In Kurt Vonnegut’s novel, *Cat’s Cradle*, Ice IX is a phase of ice that could spontaneously cause all of Earth’s oceans to freeze. This was an actual scientific claim (albeit incorrect) known as “polywater”. The “phase” was only seen in capillary tubes and the experimental evidence was subsequently attributed to small amounts of silica dissolved in the water. Ice IX really exists (see above diagram); it was found after the novel was written but does not have the properties attributed to it by Vonnegut.
6.4.3 *Structural (Order → Disorder, especially solid → liquid, liquid → gas)*

Transitions can also be driven by entropy.... as you increase T, a higher entropy phase is favored. The most striking example is melting, where the liquid is disordered and thus has higher entropy than the solid.

Water → ice
Peridotite → basaltic melt + olivine rich residue (partial melting)
Liquid iron alloy ↔ Solid nearly pure iron plus liquid enriched in impurities.
Liquid water with “impurities” (dissolved salt, ammonia) ↔ Solid nearly pure water ice + liquid enriched in impurities.

The next example is an important one for cores in terrestrial planets. It shows how sulfur lowers the freezing point of iron (i.e., S in the liquid iron is favorable but S does not go into solid iron. This entropy effect favoring the liquid drives the melting point down.)

![Phase Diagram](image)

**Figure 6.6**

It is important to understand how to “read” a phase diagram like this. For example, suppose you had a hot liquid Fe-S alloy that has lower sulfur content than the eutectic composition (which is ~30% sulfur by mass at low pressure). Now cool that alloy down. It will reach and cross the liquidus curve (the curve that joins the pure melting point of iron to the eutectic in this diagram). At that point, the liquid is unstable with respect to forming almost pure solid iron. But it only has to form a small amount of iron to shift the sulfur abundance in the liquid back to the liquidus curve value. So as you cool still further you will make a liquid that follows the liquidus curve and a coexisting solid that is pure iron. The masses of each are dictated by the total amount of sulfur and iron you started with: These are conserved quantities. Finally you will reach the eutectic, which is
also the solidus, i.e., the temperature below which no liquid can exist. At that point, further cooling will lead to the formation of FeS solid and some additional Fe solid. This is all reversible. Suppose I start with a solid mixture of Fe and FeS at less than the solidus (i.e., eutectic) temperature. I heat it up to the eutectic. At that point some finite fraction of this solid mixture will melt completely to form an alloy of eutectic composition. As always, the amount of remaining coexisting solid is determined by mass balance. If my starting composition was less sulfur–rich than the eutectic then the solid will be pure Fe. As I heat still further, the remaining solid will progressively melt until I reach the liquidus, at which point it is all liquid.

Here is an illustration of the same principle, but for the H$_2$O-NH$_3$ system (which has a very similar type of phase diagram). The diagram is shown only approximately.

Figure 6.7

Suppose a liquid at composition $x_1$ is cooled, starting at $T>T_1$. The total number of molecules is $N$ (say), so $x_1 N$ are NH$_3$ and $(1-x_1) N$ are H$_2$O. At $T=T_1$ it will start to freeze out pure water ice; the remaining liquid will follow the phase boundary down to $T=173$K and $x=x_e$. At that point, all of the ammonia is still in the liquid. Therefore,

$$x_e N_{\text{liq}} = x_1 N$$
$$\quad (1-x_e) N_{\text{liq}} = (1-x_1) N + N_{\text{sol}}$$

where $N_{\text{liq}}, N_{\text{sol}}$ are the number of molecules in the liquid and solid phases respectively. Thus, $N_{\text{sol}}/N = 1-x_1/x_e$. Further cooling produces complete freezing. Likewise, if we heat up an initially completely solid ice mixture of composition $x_1$ then upon reaching ~173K, $x_1/x_e$ of the molecules enter the liquid phase. This means that a liquid will exist at 173K even if the amount of ammonia is small. This has very important implications for the behavior of water-ammonia ice satellites. In a similar way, you only need to reach the eutectic temperature of Fe-S to have a liquid outer core in Mercury (say) even if Mercury has very little sulfur. This is important because the eutectic temperature is way below the melting point of pure Fe. (it has been suggested that Mercury reached the eutectic and produced an FeS snow. This is controversial.)
6.5 *An important Multicomponent Example: Immiscibility*

If there are two materials of very different chemical (e.g. electronic) character, they don’t like to mix. Water and oil is a common everyday example. In planets, there are two very important examples:

- Silicates + metallic iron phase separate
- Hydrogen + helium phase separate

The former explains the mantle-core structure of terrestrial planets. The latter probably explains atmospheric helium depletion and part of the luminosity for Jupiter and Saturn.

**Figure 6.8**

In this example, you can imagine a cosmic mixture of H and He cooling until it crosses the phase boundary. Once it does so, it will cause helium raindrops to form at the correct co-existing composition on the other side of the phase-separation curve.

Another possibly important example is water+hydrogen, which may phase-separate in Uranus and Neptune to allow formation of a deep water ocean in these bodies.

6.6 *Appendix: The Gibbs Phase Rule*

This rule is simply a statement about the number of degrees of freedom that a system possesses. It is best understood by examples.
Consider first a single component system. By “single component” we mean that there is only one kind of atom or molecule possible. Thermodynamic equilibrium then states that if we have two phases I and II then the Gibbs energies are equal.

\[ G_I(P,T) = G_{II}(P,T) \]

But these are a function of two variables, P and T, so this defines a line in P,T space.

Now consider a two-component system. We must now introduce a mole fraction variable, call it x. In the water-ammonia system, for example, it could be the mole fraction of ammonia (call it “species 1”, say). Equilibrium now dictates two equations:

\[ \mu_{I,1}(P,T,x_1) = \mu_{II,1}(P,T,x_2) \]
\[ \mu_{I,2}(P,T,x_1) = \mu_{II,2}(P,T,x_2) \]

where \( \mu_{I,1} \) is the specific Gibbs energy (otherwise known as chemical potential) of species 1 in phase I and it is of course a function of not just P and T but also the amount \( x_1 \) of that species in that phase. Likewise \( \mu_{I,2} \) is the chemical potential of species 2 in phase I, etc. And there is no requirement that \( x_2 \) (the amount of species 1 in phase II) is the same as \( x_1 \) (the amount of species 1 in phase I). So we have two equations in four unknowns: P,T,x_1 and x_2. This means that the solution is not (in general) a line in T,P space. For example, if we keep T fixed, then the solution in P,x space must a pair of lines that describe the two compositions (of phase I and phase II) that can coexist. The amount of each phase will of course be determined by the overall composition (mean x) of the starting material. So if we specify mean composition, then there will be a unique solution to the above two equations at each P,T (within a limited range of P and T) that tells me what mass of each phase I will have.

**Ch. 6 Problems**

6.1) It is often useful to construct non-dimensionalized phase diagrams, for example a diagram in which the vertical axis is \( \log T \) and the horizontal axis is \( \log P \). (Use of logs automatically nondimensionalizes anything because increments in log of a variable correspond to ratios of that variable to some arbitrary reference value). From the Clausius–Clapeyron equation, show quantitatively that most high-pressure solid-to-solid phase transitions have steep slopes on such a diagram whereas melting boundaries usually have shallow slopes. Here’s the relevant information: volume changes associated with major crystallographic changes are often ~10%, whereas melting often involves only ~2-4% changes. Entropy changes upon melting are large, of order \( k_B \) per atom but are typically only a few tenths of this for solid-to-solid transitions (since these do not involve major disorder).

*Solution: \( \frac{d\ln T}{d\ln P} = \frac{P \Delta V}{T \Delta S} \). But \((PV)(\Delta V/V) \sim (few \ eV) \cdot 0.1 \sim 0.5 \ eV \) at high P (e.g. if P= 1 megabar =10^{12} \ cgs and V =10^{-23} \ cm^3 then PV=10^{-11} \ erg \sim 6 \ eV). However, \( T \Delta S \sim 0.3 \ k_B T \sim 0.1 \ eV \) if T~6000K. So the slope on this log-log diagram is then \sim -5. However, in melting, the \( P \Delta V \) term is smaller by a factor of ~three and the \( T \Delta S \) term is larger by a factor of*
~three and then the slope of the phase boundary on a log–log plot might only be ~0.5. Of course, this is not a universal truth, merely a common observation.

6.2) Liquids are often more compressible than their coexisting solids. However, the solid can undergo substantial first order phase transitions. The entropy difference between liquid and solid is always dominated by the entropy of disorder and does not change much with pressure or with the identity of the solid phase. Use this information to explain the shape of the phase diagram below. (This shape is commonly observed near a solid-solid-liquid triple point. It doesn’t always lead to an actual negative melting curve slope.. the important point is the curvature of the melting curves.)

6.3) In fig 6.5 there is a steeper melting curve for water above a certain pressure (~35GPa). The solid phase above this pressure is referred to as superionic water because the oxygen nuclei form a lattice while the protons are free to roam. Explain why this would be a high entropy state. Hence explain why this leads (via the Clausius–Clapeyron relation) to a steep melting curve.

6.4) Here is a simple model for the Gibbs energy of a two component system, labeled as species 1 and species 2 (so \(N_1\) is the number of atoms of species 1, etc.)

\[
G = N_1G_1 + N_2G_2 + \frac{N_1N_2\Delta G}{N_1 + N_2} + kBT\left[\frac{N_1\ln\left(\frac{N_1}{N_1 + N_2}\right)}{N_1} + \frac{N_2\ln\left(\frac{N_2}{N_1 + N_2}\right)}{N_2}\right]
\]

This has simple interpretation: The \(\Delta G\) term represents the interaction of the two species assuming they encounter each other randomly in proportion to their abundances. And the \(kT\) term comes from the ideal entropy of mixing (a term that by itself always favors mixing in accordance with the second law). [Note: This model can be found in textbooks, but you are expected to do it without looking for it in a textbook.]

(a) Show that if \(\Delta G\) is positive, this model exhibits phase separation (i.e., coexistence of two immiscible phases) provided the temperature is sufficiently low. Hint: Think about the shape of the Gibbs energy curve as a function of composition.

(b) What is the critical temperature of this system (the \(T\) above which the two constituents can mix in all proportions)? Sketch the phase diagram.
(c) Neon is depleted by a factor of ten in the atmosphere of Jupiter, relative to cosmic abundance. Given that this arises from insolubility of neon in metallic hydrogen at a place where the temperature is \(~6000\text{K}\) \((k_B T = 0.5 \text{ eV})\), what is the required value of \(\Delta G\) in electron volts? [Assume cosmic abundance of neon as given earlier in the text. Assume hydrogen in the form of “atoms”, not molecules. Ignore helium, etc. This is not the preferred explanation for the neon depletion, because it requires an unacceptably large \(\Delta G\), but it is nonetheless an interesting exercise. The atmosphere will exhibit any depletion that occurs deep down because of convective mixing.]