

12.1: Phase Stability

We have already encountered the gas, liquid, and solid phases and already discussed some of their properties. These terms are intuitive since these are the three most common states of matter.¹ For this reason, we have previously used the terms without the necessity of formally defining their meaning. However, a formal definition of “phase” is necessary to discuss several concepts in this chapter and the following ones:

Definition: Phase

A region of the system with homogeneous chemical composition and physical state.

Let's now use the total differential of the chemical potential and the definition of molar Gibbs free energy for one component:

$$\begin{aligned} d\mu &= \left(\frac{\partial \mu}{\partial T} \right)_P dT + \left(\frac{\partial \mu}{\partial P} \right)_T dP \\ d\mu &= -SdT + \bar{V}dP, \end{aligned} \quad (12.1.1)$$

to write:

$$\left(\frac{\partial \mu}{\partial T} \right)_P = -S \quad \left(\frac{\partial \mu}{\partial P} \right)_T = \bar{V}. \quad (12.1.2)$$

We can use these definitions to study the dependence of the chemical potential with respect to changes in pressure and temperature. If we plot μ as a function of T using the first coefficient in Equation 12.1.2, we obtain the diagram in Figure 12.1.1. The diagram presents three curves, each corresponding to one of the three most common states of matter – solid, liquid, and gas. As we saw in several previous chapters, the entropy of a phase is almost constant with respect to temperature,² and therefore the three curves are essentially straight, with negative angular coefficients $-S$. This also explains why the solid phase has a basically flat line since, according to the third law, the entropy of a perfect solid is zero and close to zero if the solid is not perfect. The difference between the three lines' angular coefficients is explained by the fact that each of these states has a different value of entropy:

$$\left(\frac{\partial \mu_{\text{solid}}}{\partial T} \right)_P = -S_s \quad \left(\frac{\partial \mu_{\text{liquid}}}{\partial T} \right)_P = -S_l \quad \left(\frac{\partial \mu_{\text{gas}}}{\partial T} \right)_P = -S_g, \quad (12.1.3)$$

and since the entropy of a gas is always bigger than the entropy of a liquid, which in turn, is yet bigger than the entropy of a solid ($S_g \gg S_l > S_s$), we obtain three lines with different angular coefficients that intersect each other. At each temperature, the phase with the lowest chemical potential will be the most stable (see red segments in Figure 12.1.1). At each intersection between two lines, the two phases have the same chemical potential, representing the temperature at which they coexist. This temperature is the temperature at which the phase change happens. Recalling from general chemistry, at the junction between the solid and the liquid lines, the fusion (fus) process occurs, and the corresponding temperature is called the melting point T_m . At the junction between the liquid and the gas lines, the vaporization (vap) process happens, and the corresponding temperature is called the boiling point T_b . Depending on the substance and the pressure at which the process happens, the solid line might intersect the gas line before the liquid line. When that occurs, the liquid phase is never observed, and only the sublimation (subl) process happens at the sublimation point T_{subl} .

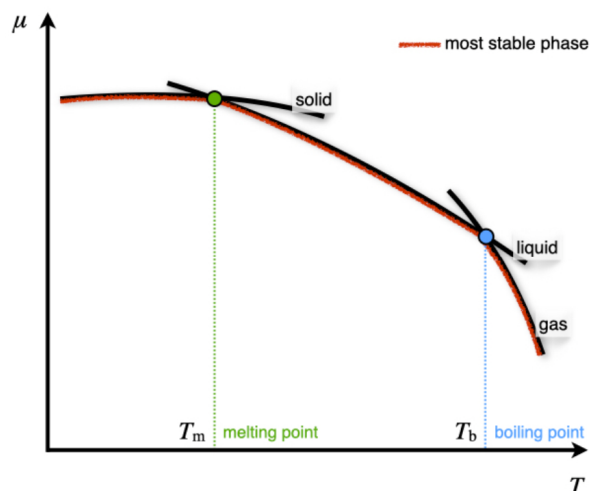


Figure 12.1.1: Dependence of the Chemical Potentials of Solid, Liquid, and Gas Phases on Temperature at Constant Pressure.

The effects of pressure on this diagram can be studied using the second coefficient in Equation 12.1.2. For the majority of substances, $\bar{V}_g \gg \bar{V}_l > \bar{V}_s$, hence the curves will shift to lower values when the pressure is reduced, as in Figure 12.1.2. Notice also that since $\bar{V}_l \approx \bar{V}_s$, the shifts for both the solid and liquid lines is much smaller than the shift for the gas line. These shifts also translate to different values of the junctions, which means the phase changes will occur at different temperatures. Therefore both the melting point and the boiling point in general increase when pressure is increased (and vice versa). Notice how the change for the melting point is always much smaller than the change for the boiling point. Water is a noticeable exception to these trend because $\bar{V}_{\text{H}_2\text{O},l} < \bar{V}_{\text{ice}}$. This explains the experimental observation that increasing the pressure on ice causes the ice to melt³

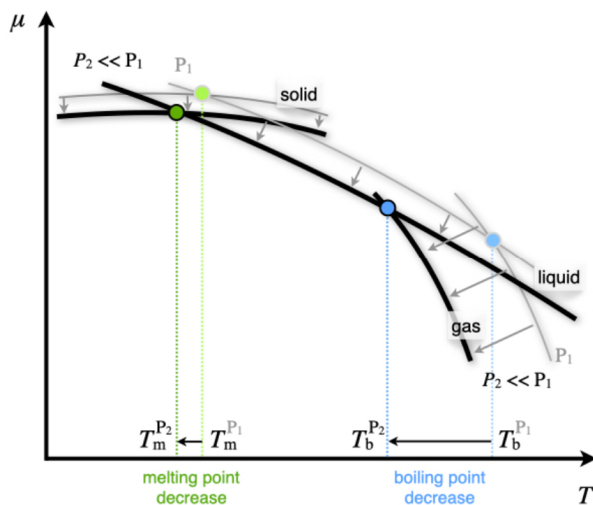


Figure 12.1.2: Effect of Pressure on the Chemical Potential Diagram.

Considering the intersections between two lines, two phases are in equilibrium with each other at each of these points. Therefore their chemical potentials must be equal:

For two or more phases to be in equilibrium, their chemical potential must be equal:

$$\mu_\alpha = \mu_\beta. \quad (12.1.4)$$

If we now change either the temperature or the pressure, the location of the intersection will be shifted (see again Figure 12.1.2 and the discussion above). For infinitesimal changes in variables, the new location will be:

$$\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta, \quad (12.1.5)$$

which using Equation 12.1.4, simply becomes:

$$d\mu_\alpha = d\mu_\beta. \quad (12.1.6)$$

Replacing the differential with the definition of chemical potential in Equation 12.1.1, we obtain:

$$\begin{aligned} -S_\alpha dT + \bar{V}_\alpha dP &= -S_\beta dT + \bar{V}_\beta dP \\ \underbrace{(S_\beta - S_\alpha)}_{\Delta S} dT &= \underbrace{(\bar{V}_\beta - \bar{V}_\alpha)}_{\Delta \bar{V}} dP, \end{aligned} \quad (12.1.7)$$

which can be rearranged into:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta \bar{V}}. \quad (12.1.8)$$

This equation is known as the **Clapeyron equation**, and it is the mathematical relation at the basis of the pressure-temperature phase diagrams. Plotting the results of Equation 12.1.8 on a PT phase diagram for common substances results in three lines representing the equilibrium between two different phases. These diagrams are useful to study the relationship between the phases of a substance.

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1. Other states of matter—such as plasma—are possible, but they are not usually observed at the values of temperature and pressure that classical thermodynamics is usually applied to. Discussion of these extreme cases is beyond the scope of this textbook.
 2. Think, for example, at the integral $\int SdT$, for which we can assume S independent of temperature to obtain $S\Delta T$. In practice, the entropy increases slightly with the temperature. Therefore the curves in Figure 12.1.1 are slightly concave downwards (remember that they are obtained from values of $-S$, so if S increase with T , the curves bend downwards.)
 3. Despite the effect being minimal, it is one of the contributing causes to the fact that we can skate on ice, but we can't on stone. If we increase our pressure on ice by reducing our footprints' surface area using thin skates, ice will slightly melt under our own weight, creating a thin liquid film on which we can skate because of the reduced friction.
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