

# Lecture\_14

November 7, 2022

## 1 The Chemical Potential and Phase transitions

At the end of the last lecture, we defined the chemical potential as

$$\mu_i = -T_i \left( \frac{\partial S_i}{\partial N_i} \right)_{V_i, U_i}.$$

such that for a single component which has two phases that are in equilibrium gives that

$$\mu_1 = \mu_2.$$

So what does this do to the fundamental thermodynamic relation? Consider again

$$dS = \left( \frac{\partial S}{\partial U} \right)_{V,N} dU + \left( \frac{\partial S}{\partial V} \right)_{U,N} dV + \left( \frac{\partial S}{\partial N} \right)_{V,U} dN.$$

Using our known substitutions, we get

$$dS = \frac{1}{T} dU + \frac{1}{T} P dV - \frac{1}{T} \mu dN.$$

Tidying up gives

$$dU = T dS - P dV + \mu dN.$$

From this, we can express  $\mu$  in terms of  $U$  as

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{S,V}$$

which is not altogether useful, as both  $S$  and  $V$  are hard to keep constant. Modifyign either the Helmholtz free energy or the Gibbs free energy to account for this change to the fundamental thermodynamic relation thus gives

$$dF = -P dV - S dT + \mu dN. \tag{1}$$

$$dG = V dP - S dT + \mu dN. \tag{2}$$

$$\tag{3}$$

which leads to

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{V,T} \tag{4}$$

$$\mu = \left( \frac{\partial G}{\partial N} \right)_{P,T} \tag{5}$$

In the case we are considering of single component system (remember, this is us saying that we only have one type of molecule in the system, like a system containing just water molecules), then the Gibbs free energy depends on  $N$ , the particle number, such that

$$G(T, P, N) = N G(T, P, 1) = N g(T, P)$$

where

$$g(T, P) = \frac{G(T, P, N)}{N}$$

is the Gibbs free energy per particle. From above, this then means that we can write the chemical potential for a single component, homogenous system as

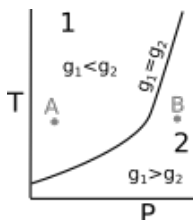
$$\mu = g(T, P).$$

Finally, this means that for a two state, single component system, where each state is homogenous, we require that

$$g_1(T, P) = g_2(T, P)$$

This condition defines a curve in the  $(P, T)$  plane. For any combination of temperature and pressure which lie on the curve, the phases are in equilibrium, while for any points that lie off of the curve, they are not.

A simple example of this is shown below. In this, 1 and 2 define the regions in which  $g_1 < g_2$  and  $g_2 < g_1$  respectively.



If  $N_1$  and  $N_2$  are the number of molecules in phases 1 and 2 respectively, then the Gibbs free energy of the system is

$$G = N_1 g_1(T, P) + N_2 g_2(T, P)$$

For a system at a pressure and temperature given by point A in the figure above,  $g_1 < g_2$ , and so the Gibbs free energy is minimised if all of the substance is in phase 1. Similar logic applies to point B, where  $G$  is a minimum if all of the substance is in phase 2. Thus, the curve divides the  $(P, T)$  plane into regions where one or other phase represents the stable equilibrium state.

It is only along the curve that the phases can coexist in equilibrium - as such, this curve is called a **phase equilibrium curve**. This curve has a different name depending on which 2 phases are being discussed:

- If the two phases are liquid and vapour, it's a vapour pressure curve.
- If the two phases are liquid and solid, it's a melting curve.
- If the two phases are vapour and solid, it's a sublimation curve.

Let's now briefly consider what happens for a 3 phase system. The equilibrium condition for such a system is given by

$$g_1(T, P) = g_2(T, P) = g_3(T, P)$$

Rather than just describing a curve, this condition describes the intersection of two curves, with the intersection point known as the triple point. A simple curve is plotted below as an example, but I recommend looking up the curve for water to get an idea of the full complexity of such a graph. The triple point of water occurs at a temperature and pressure of (611.567 Pa, 273.16 K).

## **2 The Clausius Clapyeron equation**

So how do we utilise this information?