

## 5.3: Phase Transitions

If we have a single constituent, for thermodynamic equilibrium, we should have equality of  $T$ ,  $p$  and  $\mu$  for different subparts of the system. If we have different phases of the system, such as gas, liquid, or solid, in equilibrium, we have

$$\begin{aligned} T_1 &= T_2 = T_3 = \dots = T \\ p_1 &= p_2 = p_3 = \dots = p \\ \mu_1 &= \mu_2 = \mu_3 = \dots \end{aligned} \quad (5.3.1)$$

where the subscripts refer to various phases.

We will consider the equilibrium of the two phases in more detail. In this case, we have

$$\mu_1(p, T) = \mu_2(p, T) \quad (5.3.2)$$

If equilibrium is also obtained for a state defined by  $(p + dp, T + dT)$ , then we have

$$\mu_1(p + dp, T + dT) = \mu_2(p + dp, T + dT) \quad (5.3.3)$$

These two equations yield

$$\Delta\mu_1 = \Delta\mu_2, \quad \Delta\mu = \mu(p + dp, T + dT) - \mu(p, T) \quad (5.3.4)$$

This equation will tell us how  $p$  should change when  $T$  is altered (or vice versa) so as to preserve equilibrium. Expanding to first order in the variations, we find

$$-s_1 dT + v_1 dp = -s_2 dT + v_2 dp \quad (5.3.5)$$

where we have used

$$\frac{\partial\mu}{\partial T} = -\frac{S}{N} \equiv s, \quad \frac{\partial\mu}{\partial p} = \frac{V}{N} \equiv v \quad (5.3.6)$$

Equation 5.3.5 reduces to

$$\frac{dp}{dT} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{L}{T(v_1 - v_2)} \quad (5.3.7)$$

where  $L = T(s_1 - s_2)$  is the latent heat of the transition. This equation is known as the Clausius-Clapeyron equation. It can be used to study the variation of saturated vapor pressure with temperature (or, conversely, the variation of boiling point with pressure). As an example, consider the variation of boiling point with pressure, when a liquid boils to form gaseous vapor. In this case, we can take  $v_1 = v_g \gg v_2 = v_l$ . Further, if we assume, for the sake of the argument, that the gaseous phase obeys the ideal gas law,  $v_g = \frac{kT}{p}$ , then the Clausius-Clapeyron Equation 5.3.7 becomes

$$\frac{dp}{dT} \approx p \frac{L}{kT^2} \quad (5.3.8)$$

Integrating this from one value of  $T$  to another,

$$\log\left(\frac{p}{p_0}\right) = \frac{L}{k} \left(\frac{1}{T_0} - \frac{1}{T}\right) \quad (5.3.9)$$

Thus for  $p > p_0$ ,  $T$  must be larger than  $T_0$ ; this explains the increase of boiling point with pressure.

If  $\frac{\partial\mu}{\partial T}$  and  $\frac{\partial\mu}{\partial p}$  are continuous at the transition,  $s_1 = s_2$  and  $v_1 = v_2$ . In this case, we have to expand  $\mu$  to second order in the variations. Such a transition is called a second order phase transition. In general, if the first  $(n - 1)$  derivatives of  $\mu$  are continuous, and the  $n$ -th derivatives are discontinuous at the transition, the transition is said to be of the  $n$ -th order. Clausius-Clapeyron equation, as we have written it, applies to the first order phase transitions. These have a latent heat of transition.

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