

3.C. Classification of Phase Transitions

The fundamental equation (2.61) written in terms of the Gibbs energy is [see (2.107)]

$$G(T, Y, \{n_j\}) = \sum_{j=1}^l \mu_j n_j = \sum_{j=1}^l \mu_j' N_j \quad (3.7)$$

where l is the number of molecular species present.

In the presence of phase transitions, several phases of the substance may coexist so that

$$G = \sum_{\alpha=1}^r G^\alpha(T^\alpha, Y^\alpha, \{n_j^\alpha\}) \quad (3.7a)$$

where r is the number of coexisting phases. As explained in §3.B, the equilibrium conditions are

$$T^\alpha = T \quad Y^\alpha = Y \quad \mu_j^\alpha = \mu_j \quad \forall \alpha \text{ and } j \quad (3.7b)$$

Since matter transfer is always much slower than energy or heat transfer, we can assume thermal and mechanical equilibria everywhere even though matter is still in flux between regions of different phases. Thus, the system point is restricted to the subspace Γ_{TY} spanned by $(T, Y, \{n_j^\alpha\})$. Now, the extensive variables (S^α, X^α) conjugate to (T, Y) are given by

$$S^\alpha = -\left(\frac{\partial G^\alpha}{\partial T}\right)_{Y, \{n_j^\beta\}} \quad X^\alpha = -\left(\frac{\partial G^\alpha}{\partial Y}\right)_{T, \{n_j^\beta\}} \quad (3.7c)$$

Since S^α & X^α must be well defined everywhere in Γ_{TY} except at the boundaries between different phases, G itself must be at least continuous everywhere in Γ_{TY} . However, there is no restriction on its derivatives, e.g., S^α, X^α and their derivatives.

Ehrenfest defined the **order of a phase transition** as the order of the lowest derivative of G that has a discontinuity at the transition point. Thus, transitions between the gas, liquid and solid phases of a substance are mostly 1st order since they usually involve a discontinuous change in density or volume. However, transition at the gas-liquid critical point is 2nd order with no abrupt density or volume change involved. Ferromagnetic transitions are also 2nd order since the magnetic susceptibility is discontinuous.

After the discovery of the power law divergence at the critical point in critical phenomena, the Ehrenfest scheme fell into disuse owing to its inability to account for the former.

The modern classification scheme consists of only 2 categories.

- a) **1st order phase transitions** that involve a latent heat and discontinuous change in an order parameter.
- b) **2nd order, or continuous, phase transitions** that involve no latent heat but a continuous change in an order parameter.

Consider the PVT system as an example. For a 1st order transition, there are discontinuities in the 1st derivatives of $G(T, P)$. Thus, at the transition point where

$$T^I = T^{II} = T_c \quad \text{and} \quad P^I = P^{II} = P_c \quad (3.9a)$$

we have

$$(G^I - G^{II})_{T=T_c, P=P_c} = 0 \quad \rightarrow \quad \Delta G_c = G_c^I - G_c^{II} = 0 \quad (3.9b)$$

$$\left[\left(\frac{\partial G}{\partial P} \right)'_T - \left(\frac{\partial G}{\partial P} \right)''_T \right]_{T=T_c, P=P_c} \neq 0 \quad \rightarrow \quad \Delta V_c = V_c' - V_c'' \neq 0 \quad (3.9)$$

$$\left[- \left(\frac{\partial G}{\partial T} \right)'_P + \left(\frac{\partial G}{\partial T} \right)''_P \right]_{T=T_c, P=P_c} \neq 0 \quad \rightarrow \quad \Delta S_c = S_c' - S_c'' \neq 0 \quad (3.10)$$

On the other hand, there is a discontinuity in the enthalpy,

$$\Delta H_c = H_c' - H_c'' = T_c \Delta S_c \neq 0 \quad (3.11)$$

which is called the **latent heat** of the transition. The adjective “latent” denotes the fact that heat is required to be absorbed or released without causing any change in T to facilitate the phase transition.

For a continuous phase transition, the 1st derivatives are continuous

$$\Delta V_c = 0 \quad \& \quad \Delta S_c = 0$$

so that there is no latent heat. Discontinuities in the higher derivatives of G are optional.