$$(\frac{\partial\mu_1}{\partial P})_T dP + (\frac{\partial\mu_1}{\partial T})_P dT = (\frac{\partial\mu_2}{\partial P})_T dP + (\frac{\partial\mu_2}{\partial T})_P dT$$

or

$$(\frac{\partial\mu_2}{\partial P} - \frac{\partial\mu_1}{\partial P})_T dP = -(\frac{\partial\mu_2}{\partial T} - (\frac{\partial\mu_1}{\partial T})_P dT$$

or

$$\frac{dP}{dT} = -\frac{(\frac{\partial\mu_2}{\partial T} - (\frac{\partial\mu_1}{\partial T})_P}{(\frac{\partial\mu_2}{\partial P} - \frac{\partial\mu_1}{\partial P})_T} \quad (2)$$

and from Maxwell's relations

$$(\frac{\partial\mu}{\partial T})_{P,N} = -(\frac{\partial S}{\partial N})_{P,T}$$

and

$$(\frac{\partial\mu}{\partial P})_{T,N} = (\frac{\partial V}{\partial N})_{P,T} \quad (3)$$

Putting this value in Eq. (2), we get

$$\frac{dP}{dT} = -\frac{(\frac{\partial S}{\partial N_2} - (\frac{\partial S}{\partial N_1})}{(\frac{\partial V}{\partial N_2} - \frac{\partial V}{\partial N_1})}. \quad (4)$$

Where all the derivatives are at constant P and T. For given P and T, S and V are linear function of the N_i. Then Eq.(4) is written as

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad (5)$$

Where ΔS and ΔV are, respectively, the change in entropy and volume for a given number of particles. Integrating Eq.(5) gives the coexistence curve, i.e. the relation between P and T which must hold if the two phases are in equilibrium.

The energy which must be supplied to change one K-mole (N particles) from phase 1 to phase 2 at constant pressure and temperature (i.e. the enthalpy change ΔH) is the K-mole latent heat L. At constant pressure, $dH = TdS$, so that $L = TdS$ and Eq.(5) can be written as

$$\frac{dP}{dT} = \frac{L_{vap.}}{T\ \Delta V_m}. \quad (6)$$

Where ΔV_m is the change in volume per K-mole. This relation, which gives the slope of the coexistence curve, is called Clausius-Clapeyron equation. Since L is positive by definition, the sign of ΔV_m determine the sign of the slope. The same reasoning applied to the solid-liquid and solid – vapour phases gives the corresponding Clausius-Clapeyron relations.