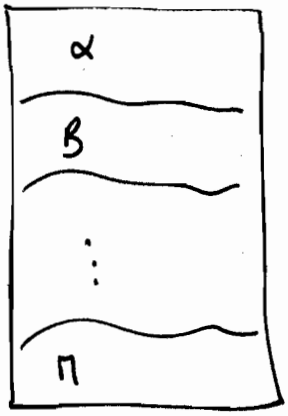
PHASE EQUILIBRIUM + STABILITY (15)

Goal of this Chapter: General Relationships valid for systems at phase coexistence.

Phase Rule



Phases $\alpha, \beta, \ldots \pi$ @ coexistence.

Each phase can be characterized by $n+1$ intensive variables –

Let's chose

$$T, P, x_1, \ldots x_{n-1}$$

n is # of components

total $= (n+1)\times\pi$

For equilibrium,

$$\left.\begin{aligned} T^\alpha &= T^\beta = \cdots = T^\pi \\ P^\alpha &= P^\beta = \cdots = P^\pi \\ \mu_1^\alpha &= \mu_1^\beta = \cdots = \mu_1^\pi \\ &\vdots \\ \mu_n^\alpha &= \mu_n^\beta = \cdots = \mu_n^\pi \end{aligned}\right\} (\pi-1)\times(n+2) \text{ equations}$$

Number of "degrees of freedom" –

$$\text{Variables} - \text{equations} = (n+1)\times\pi - (\pi-1)\times(n+2) =$$

$$= n\pi + \pi - n\pi - 2\pi + n + 2 = \underline{\underline{n - \pi + 2}}$$

<u>Differential Approach</u> (§15.2 - Review Phase Diagrams on your own)

In the book, the relationships below are derived using fugacities. Here, I use chemical potentials. The two approaches are equivalent, since

$$\mu_i = RT \ln \hat{f}_i + \text{a function of } T \text{ only}$$

Consider a binary system with components 1 and 2. Two phases, α and β.

Must have:

$$\left.\begin{aligned} T^\alpha &= T^\beta \\ P^\alpha &= P^\beta \\ \mu_1^\alpha &= \mu_1^\beta \\ \mu_2^\alpha &= \mu_2^\beta \end{aligned}\right\} \text{functions of } T, P \text{ and } x_1^\alpha, x_1^\beta$$

Consider a change in T, P or x_1 <u>while the system remains at equilibrium</u> with phases α and β present.

$$d\mu_1^\alpha = d\mu_1^\beta \Rightarrow$$

$$\left(\frac{\partial \mu_1^\alpha}{\partial T}\right)_{P,x_1^\alpha} dT + \left(\frac{\partial \mu_1^\alpha}{\partial P}\right)_{T,x_1^\alpha} + \left(\frac{\partial \mu_1^\alpha}{\partial x_1^\alpha}\right)_{T,P} dx_1^\alpha =$$

$$= \left(\frac{\partial \mu_1^\beta}{\partial T}\right)_{P,x_1^\beta} dT + \left(\frac{\partial \mu_1^\beta}{\partial P}\right)_{T,x_1^\beta} dP + \left(\frac{\partial \mu_1^\beta}{\partial x_1^\beta}\right)_{T,P} dx_1^\beta .$$

$$\left(\frac{\partial \mu_1^\alpha}{\partial T}\right)_{P,x_1^\alpha} = -\bar{S}_1^\alpha = -\frac{\bar{H}_1^\alpha - \mu_1^\alpha}{T} \qquad \left(\frac{\partial \mu_1^\alpha}{\partial P}\right)_{T,x_1^\alpha} = \bar{V}_1^\alpha$$

Substituting expressions for the derivatives:

$$① \left[-\frac{(\bar{H}_1^\alpha - \cancel{\mu_1^\alpha}) - (\bar{H}_1^\beta - \cancel{\mu_1^\beta})}{T} dT + (\bar{V}_1^\alpha - \bar{V}_1^\beta) dP + \right.$$

$$\left. + \left(\frac{\partial \mu_1^\alpha}{\partial x_1^\alpha}\right)_{T,P} dx_1^\alpha - \left(\frac{\partial \mu_1^\beta}{\partial x_1^\beta}\right)_{T,P} dx_1^\beta = \phi \right.$$

Similarly, starting from $d\mu_2^\alpha = d\mu_2^\beta$, we obtain

$$② \left[-\frac{\bar{H}_2^\alpha - \bar{H}_2^\beta}{T} dT + (\bar{V}_2^\alpha - \bar{V}_2^\beta) dP + \left(\frac{\partial \mu_2^\alpha}{\partial x_1^\alpha}\right)_{T,P} dx_1^\alpha - \left(\frac{\partial \mu_2^\beta}{\partial x_1^\beta}\right) dx_1^\beta = \phi \right.$$

In ① and ②, we have dP, dT, dx_1^α and dx_1^β as unknowns. We can eliminate dx_1^α (or dx_1^β) from the Gibbs-Duhem relationship:

$$N_1 d\mu_1 + N_2 d\mu_2 = \phi \Rightarrow x_1 d\mu_1 + x_2 d\mu_2 = \phi \quad \Rightarrow$$

$$\Rightarrow x_1^\alpha \left(\frac{\partial \mu_1^\alpha}{\partial x_1^\alpha}\right)_{T,P} dx_1^\alpha + x_2^\alpha \left(\frac{\partial \mu_2^\alpha}{\partial x_1^\alpha}\right) dx_1^\alpha = \phi \qquad ③$$

$$① \cdot x_1^\alpha + ② \cdot x_2^\alpha \; \underline{\underline{③}} \; - \frac{x_1^\alpha(\bar{H}_1^\alpha - \bar{H}_1^\beta) + x_2^\alpha(\bar{H}_2^\alpha - \bar{H}_2^\beta)}{T} dT +$$

$$+ \left[x_1^\alpha(\bar{V}_1^\alpha - \bar{V}_1^\beta) + x_2^\alpha(\bar{V}_2^\alpha - \bar{V}_2^\beta) \right] dP -$$

$$- \left[\left(x_1^\alpha - x_2^\alpha \frac{x_1^\beta}{x_2^\beta} \right) \left(\frac{\partial \mu_1^\beta}{\partial x_1^\beta} \right)_{T,P} \right] dx_1^\beta = \phi$$

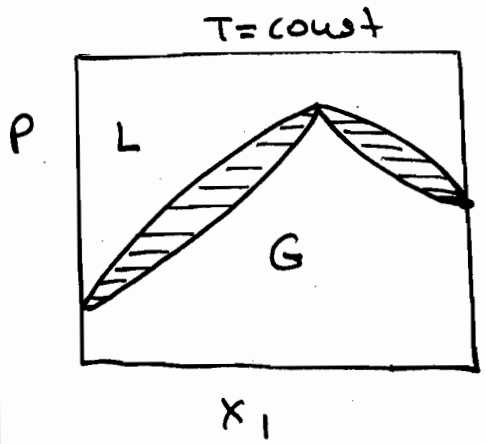
This relationship links dT, dP and dx_1^β at α-β coexistence. In its simplest form, you have seen this as the "Clausius-Clapeyron" Equation for a one-component system.

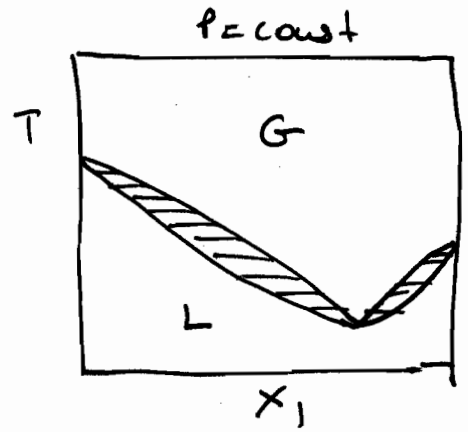
For example:

$$\left(\frac{dP}{dT}\right)_{x_1^\beta,\,[\alpha-\beta\ \text{coex}]} = \frac{x_1^\alpha\left(\bar{H}_1^\alpha-\bar{H}_1^\beta\right)+x_2^\alpha\left(\bar{H}_2^\alpha-\bar{H}_2^\beta\right)}{T\left[x_1^\alpha\left(\bar{V}_1^\alpha-\bar{V}_1^\beta\right)+x_2^\alpha\left(\bar{V}_2^\alpha-\bar{V}_2^\beta\right)\right]} \quad (1)$$

$$\left(\frac{\partial P}{\partial x_1^\beta}\right)_{T,\,[\alpha-\beta\ \text{coex}]} = \frac{\left(x_1^\alpha - x_2^\alpha\dfrac{x_1^\beta}{x_2^\beta}\right)\left(\dfrac{\partial \mu_1^\beta}{\partial x_1^\beta}\right)}{x_1^\alpha\left(\bar{V}_1^\alpha-\bar{V}_1^\beta\right)+x_2^\alpha\left(\bar{V}_2^\alpha-\bar{V}_2^\beta\right)} \quad (2)$$

<u>Exercise</u>: Prove that fig. 15.1 is wrong!





For an azeotrope, $x_1^\alpha = x_1^\beta \Rightarrow x_2^\alpha = x_2^\beta$

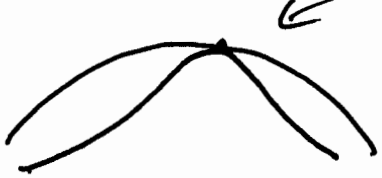
From (2) above,

$$\left(\frac{dP}{\partial x_1^\beta}\right)_{T,\,[\alpha-\beta],\ \text{azeotrope}} = \phi = \left(\frac{\partial P}{\partial x_1^\alpha}\right)_{T,\ \text{azeotr.},\ [\alpha-\beta]}$$

Similarly,

$$\left(\frac{\partial T}{\partial x_1^\alpha}\right)_{T,\,[\alpha-\beta\ \text{coex}]\ \text{azeotr.}} = \phi = \left(\frac{\partial T}{\partial x_1^\beta}\right)_{T,\,[\text{azeotr.}]}$$

Correct figure:



<u>zero</u> slope for both curves at maximum.

Simplification for 1-component systems

Equation ① on the previous page is simplified for one-component systems:

$$\left(\frac{dP}{dT}\right)_{\alpha-B\ coex} = \frac{H^{\alpha}-H^{B}}{T\left(V^{\alpha}-V^{B}\right)} = \frac{\Delta H^{\alpha B}}{T\Delta V^{\alpha B}}$$

In the case α = vapor B = liquid, further simplifications are possible. $\Delta V^{\alpha B} = V^{vapor} - V^{liquid} \simeq$

$$V^{vapor} \simeq \frac{RT}{P} \Rightarrow \left(\frac{dP}{dT}\right)_{VL} = \frac{P\,\Delta H^{vap}}{RT^2} \Rightarrow$$

$$\left.\frac{d(\ln P)}{d(1/T)} = -\frac{\Delta H^{vap}}{R}\right\} \text{ Clausius-Clapeyron}$$

For solid-liquid equilibria, $\left(\frac{dP}{dT}\right)_{S-L} = \frac{\Delta H^{melt}}{T\Delta V^{melt}}$

$H^{LIQ} - H^{SOLID} > 0 \Rightarrow \left(\frac{\partial P}{\partial T}\right)_{S-L} > 0$ if $V^{LIQ} > V^{solid}$

$\left(\frac{\partial P}{\partial T}\right) < 0$ if $V^{LIQ} < V^{solid}$ (e.g. for water)