1. Phase Equilibria

- Will first focus on two phases: $\alpha$-phase and $\beta$-phase
  (e.g. vapor and liquid)

Recall:

“a phase is a region of space throughout which all physical properties of a material are essentially uniform”

Remarks:

a) Physical properties include density, opacity, viscosity… including energy content
b) Could be aggregated (one region for each phase) or dispersed (e.g. wet steam)

- Three criteria for equilibrium:

  Assuming no additional boundaries between phases, i.e. no insulation, no membranes,

  o **Thermal criteria**: $T_\alpha = T_\beta$ (equal temperature)

    $\Rightarrow$ if there are temperature differences between phases then heat will flow from hot to cold until thermal equilibrium is obtained

  o **Mechanical criteria**: $P_\alpha = P_\beta$ (equal pressure)

    $\Rightarrow$ if there are pressure differences between phases then the region (volume) with high “total phase pressure” will expand against the region with low “total phase pressure” until both phases exert equal forces, thus mechanical equilibrium is obtained
- **Chemical criteria:** $\mu_i^\alpha = \mu_i^\beta$ (equal chemical potential for each substance $i$)

where

$$
\mu_i^\alpha = \left[ \frac{\partial G}{\partial n_i} \right]_{T,P,n_{j\neq i}}^\alpha
$$

= Partial molar Gibbs energy of the $i^{th}$ substance in $\alpha$-phase (development to come later)

**Special case:** if phase has a single component, $\mu_i^\alpha = g_i$ (molar Gibbs energy of substance $i$)

→ details to be discussed next:

a) Equilibrium criteria for two phase, single component
b) Properties of mixing in one phase → partial molar properties
c) Equilibrium criteria for two phases, multiple components

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2. Systems involving one specie and two phases

- Consider a closed system at constant $T$ and $P$ (with possibly more than one phase) before equilibrium sets in, i.e. the differential will be the path towards equilibrium,

$$
dU = dQ_{in} - dW_{by}
$$

including irreversibilities,

$$
dU \leq TdS - PdV
$$

Using the condition that $T$ and $P$ are constant,

$$
[dU - d(TS) + d(PV)]_{T,P} \leq 0
$$

$$
d(U + PV - TS)_{T,P} \leq 0
$$

$$
(dG)_{T,P} \leq 0
$$

a) For two phases at fixed constant $T$ and $P \rightarrow g^\alpha$ and $g^\beta$ will be fixed and constant
b) Since the system is closed, any decrease of moles in $\alpha$-phase is the increase of moles in $\beta$-phase, i.e. $dn^\alpha = -dn^\beta$
Thus, with $G = n^\alpha g^\alpha + n^\beta g^\beta$,
\[
(dG)_{T,P} = g^\alpha dn^\alpha + g^\beta dn^\beta = (g^\alpha - g^\beta)dn^\alpha \\
\leq 0
\]

→ if $g^\alpha > g^\beta$ then ( ), and if $g^\alpha < g^\beta$ then ( )

Thus, for equilibrium (no more transfer of moles from either phases), we need:

- **The Clapeyron equation, Clausius-Clapeyron and Antoine Equations**

  **Main Interest**: when two phases coexist for a single component, either $T$ or $P$ need to be specified. How does $P$ change as $T$ changes (or vice versa) ?

  ○ At equilibrium, $g^\alpha = g^\beta$. If we move to a different $T$ by an amount $dT$,

    \[
    \frac{dP}{dT} = \frac{\left(h^\beta - h^\alpha\right)}{T(v^\beta - v^\alpha)} \quad \text{Clapeyron Equation}
    \]

    (the difference $s^\beta - s^\alpha$ occurs at constant $T$ and $P$, thus $(h^\beta - h^\alpha) = T(s^\beta - s^\alpha)$)
- Special case: $\alpha$ is liquid phase, while $\beta$ is vapor phase

Additional assumptions:

i. $\Delta h_{vap} = (h^\beta - h^\alpha)$ is constant

ii. $v^{vap} \gg v^{liq}$ so $v^{vap} - v^{liq} \approx v^{vap}$

iii. $v^{vap}$ behaves as an ideal gas $\Rightarrow v^{vap} = RT/P$

$$\frac{dP}{dT} = \frac{\Delta h_{vap}P}{RT^2}$$
$$\frac{dP}{P} = \frac{\Delta h_{vap}}{RT^2} \cdot dT$$

$$\ln \left( \frac{P_{2 \text{sat}}}{P_{1 \text{sat}}} \right) = \frac{\Delta h_{vap}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

This is the “Clausius-Clapeyron Equation”

Empirical fit based on the Clausius-Clapeyron equation $\Rightarrow$ Antoine Equation

$$\ln(P_{\text{sat}}) = A - \frac{B}{T + C}$$