Topics

- Solidification with Complete Miscibility
  - Thermodynamic Considerations
Thermodynamic Considerations

The impact of mixing is analyzed by a similar approach as for thermal vacancies in Ch. 1a.

$G$ of the alloy will be obtained based on a linear superposition of the $G$ of the individual elements, $G_A$ and $G_B$, and an excess term $\Delta G^{\text{mix}}$:

$$G = x_A G_A + x_B G_B + \Delta G^{\text{mix}}$$

$\Delta G^{\text{mix}}$ refers to $\Delta H^{\text{mix}}$ and $\Delta S^{\text{mix}}$, when comparing the condition of separated elements A and B and randomly mixed A and B:

$$\Delta G^{\text{mix}} = \Delta H^{\text{mix}} - T \Delta S^{\text{mix}}$$

For so-called ideal solutions, we assume $\Delta H^{\text{mix}} = 0$. 
Thermodynamic Considerations

- The separate crystals have only a single microscopic realization 
  \( \omega^{\text{separat}} = 1 \), hence:
  \[
  S^{\text{separat}} = k_B \ln \omega^{\text{separat}} = 0
  \]

- In the mixed condition, the number of configurations increases:
  \[
  S^{\text{mixed}} = k_B \cdot \ln \frac{N!}{N_A! \cdot N_B!}
  \]

- Applying Stirling’s approximation \( x! \approx x \ln x - x \) for \( x > 751 \) (see Ch. 1a) yields:
  \[
  \Delta S^{\text{mix}} = S^{\text{mixed}} - S^{\text{separat}} = k_B \left( N \ln N - N_A \ln N_A - N_B \ln N_B \right) \\
  = -k_B \left( \frac{N_A}{N} \ln \frac{N_A}{N} + \frac{N_B}{N} \ln \frac{N_B}{N} \right) \\
  \Delta S^{\text{mix}} = -k_B \left( x_A \ln x_A + x_B \ln x_B \right)
  \]
Thermodynamic Considerations

\[ x_A \ln x_A + x_B \ln x_B = x_B \ln x_B + (1 - x_B) \ln(1 - x_B) \]
Ideal Solutions

For the interpretation of $G(T)$ for pure elements, see Chs. 1a & 3a

$$\begin{align*}
G &= x_A G_A + x_B G_B + \Delta G^{\text{mix}} \\
&= x_A G_A + x_B G_B + T k_B (x_A \ln x_A + x_B \ln x_B)
\end{align*}$$
Ideal Solutions

For the interpretation of $G(T)$ for pure elements, see Chs. 1a & 3a

$$ G = x_A G_A + x_B G_B + \Delta G_{\text{mix}} $$

$$ = x_A G_A + x_B G_B + T k_B (x_A \ln x_A + x_B \ln x_B) $$
Ideal Solutions

\[ G = x_A G_A + x_B G_B + \Delta G^\text{mix} = x_A G_A + x_B G_B + T k_B (x_A \ln x_A + x_B \ln x_B) \]
Ideal Solutions

For the interpretation of $G(T)$ for pure elements, see Chs. 1a & 3a

\[
G = x_A G_A + x_B G_B + \Delta G^{\text{mix}} \\
= x_A G_A + x_B G_B + T k_B (x_A \ln x_A + x_B \ln x_B)
\]
Important trends to develop phase diagrams:

- The $G$ curves of liquid phases tend to lower values at a faster rate than the $G$ curves of solid phases with increasing temperature due to the higher $S$ contribution in the liquid.
- The $\Delta S^\text{mix}$ contribution to $G$ becomes more dominant with increasing temperature.
- Thermodynamic equilibrium might be determined by a mixture of individual phases of different composition when their total $G$ is lower than for the homogeneous solution.
For $T < T_{m_A}$, the solid solution of A and B is the stable phase throughout the composition range with the lowest possible $G$. 
For $T = T_{m,A}$, the solid solution of A and B is still stable throughout the composition range with the lowest possible $G$. Only for pure A, liquid and solid are in equilibrium and $G$ is the same for the two.
Phase Diagrams

For $T_m,A < T = T_1 < T_m,B$, the two $G$ curves intersect. There is an intermediate composition range where the co-existence of two phases possess minimal $G$. The composition of the two phase is determined by a common tangent line to the two $G$ curves.
For \( T = T_{m,B} \), the liquid solution of A and B is the stable phase throughout the composition range with the lowest possible \( G \). Only for pure B, liquid and solid are in equilibrium and \( G \) is the same for the two.
Chemical Potential

- The chemical potential of a component \(i\) in a phase \(j\) is obtained by \(G^j(T, p, N_i)\) (see Ch. 1a):
  \[
  \mu^j_i = \frac{\partial G^j}{\partial N_i} \bigg|_{T, p, N_{k \neq i}}
  \]
- For two elements in a single-phase system, this corresponds to:
  \[
  \mu_A = \frac{\partial G(T, p, N_A, N_B)}{\partial N_A} \bigg|_{T, p, N_B}
  \]
- \(G\) can then be constructed in the following way (\(\frac{dN_A}{dN_B} = \frac{x_A}{x_B}\) and \(dx_A = -dx_B\) in order to maintain the total composition):
  \[
  G = \mu_A x_A + \mu_B x_B
  \]
For the two phases obtained by the common tangent, the chemical potential of the species in the two phases is the same:

\[ \mu_A^L = \mu_A^S \]
\[ \mu_B^L = \mu_B^S \]

Hence, there is no change in \( G \) when atoms are transferred from one phase to the other (under maintaining the total composition). That is the essential meaning of chemical equilibrium. Since differences in chemical potential drive diffusion fluxes (in homogeneous solutions, the differences in chemical potential correspond to composition differences), there are no macroscopic fluxes between the phases.

\[ G = \mu_A^L x_A + \mu_B^L x_B = \mu_A^S x_A + \mu_B^S x_B \]
Phase Diagrams

Diagram showing phase transitions in a binary system with compositions $x_B$ and temperatures $T$. The liquidus and solidus lines define the temperature ranges for the liquid ($L$), solid ($S$), and liquid-solid ($L + S$) phases. Key temperatures include $T_{m,B}$, $T_{m,A}$, and the melting point $T_0$.
Phase Diagrams

- There is **complete miscibility within the liquid and the solid**.
- **Alloys need to pass through the two-phase region** between $T_{m,A}$ and $T_{m,B}$ during solidification.
- The individual phases within the two-phase region, need to have the composition indicated by the borders of the single-phase regions (phases are only stable within the stability range and this stability range includes the borders of range!).
- Since the border lines are non-vertical, **there is a need for composition adjustment** between the phases **during solidification** in order to obtain thermodynamic equilibrium in the entire system.
- If this is not possible, thermodynamic equilibrium might only be achieved within the interface of solid and liquid (composition adjustment of phases readily available when being in contact).