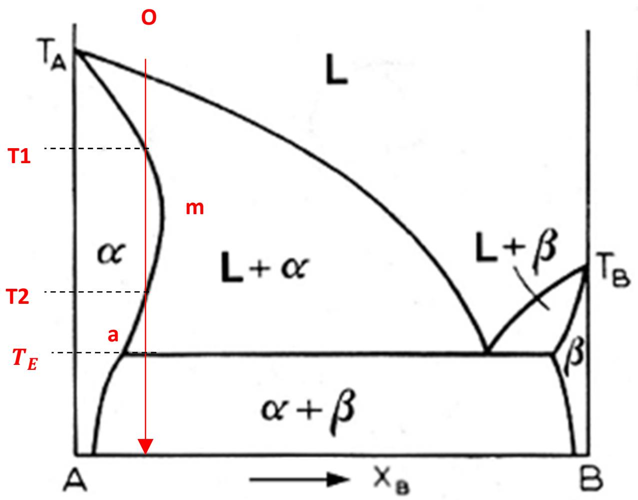
H5_ Explain retrograde solidus curves



- **Summary**

In 1908, van Laar predicted the form of solidus curve as shown in the figure based on the idea that the solid solution region increases in width from the melting point to the eutectic horizontal.
These curves exhibit **a maximum solubility of the solute at a temperature between the melting point of the solvent and eutectic point** (an invariant reaction isothermal).

Retrograde solidus curves are associated with **high** $\Delta\overline{H}_B^S$.

In most general alloy systems, the value of $\Delta\overline{H}_B^S$ is relatively small.

A high value of $\Delta\overline{H}_B^S$ is associate with a significant difference in atomic radii for A and B, which can lead a high strain energy contribution to the heat of solutions. Moreover, the difference in atomic radii leads to very low solubilities of the solute in the solvent.
Another definition of retrograde solidus curve is dX/dT=0 at a temperature T, where $T_E < T < T_A$.

- **Thermodynamic stand point**

Thurmond and Struthers have analyzed this curve from a thermodynamic strand point. They assume an ideal behavior for the liquid solution and regular behavior for solid solution.
For a dilute solid solution the partial molar free energy of the solute
$\overline{G}_B^S = (G_B^{\cdot})^S + RT\ln\gamma_B^S X_B^S$ so, $\overline{G}_B^S - (G_B^{\cdot})^S = \Delta\overline{H}_B^S - T\overline{S}_B^S$
Then, $RT\ln\gamma_B^S + RT\ln X_B^S = \Delta\overline{H}_B^S - T\overline{S}_B^S$
$\Delta\overline{H}_B^S$ is independent of composition and temperature,
$\overline{S}_B^S = -R\ln X_B^S$ and $\Delta\overline{H}_B^S = RT\ln\gamma_B^S$
So the first equation can be written by $\overline{G}_B^S = (G_B^{\cdot})^S + RT\ln X_B^S + \Delta\overline{H}_B^S$
Turning to liquid $\Delta\overline{H}_B^l$=0 $\overline{G}_B^l = (G_B^{\cdot})^l + RT\ln X_B^l$
Then, $(G_B^{\cdot})^S + RT\ln X_B^S + \Delta\overline{H}_B^S = \overline{G}_B^l = (G_B^{\cdot})^l + RT\ln X_B^l$
And $(G_B^{\cdot})^S - (G_B^{\cdot})^l = \Delta H_B - T\Delta S_B$ can replace

$$\ln\frac{X_B^S}{X_B^l} = \frac{\Delta H_B - \Delta\overline{H}_B^S}{RT} - \frac{\Delta S_B}{R}$$

$$\ln X_A^S - \ln X_A^l = \frac{\Delta H_A}{R}\left(\frac{1}{T} - \frac{1}{T_A}\right)$$

$$\ln(1 - X_B^l) = \frac{\Delta H_A}{R}\left(\frac{1}{T_A} - \frac{1}{T}\right)$$

Generally $\Delta\overline{H}_B^S$ is very small, but the greater value the retrograde soluble tendency like written above.

- **Partial remelting**

The phenomenon of partial remelting occurs during solidification of alloys whose composition between a and m. Consideration of alloy O shows that it is completely solid at T1 and remains so until it again crosses the solidus curve at T2. At T2 it partially remelts, the amount of liquid formed increasing until the eutectic horizontal is reached. At T_E the small quantity of liquid undergoes the eutectic reaction and the alloy once more becomes completely solid.

Alloy phase equilibria, A. Prince (1966)