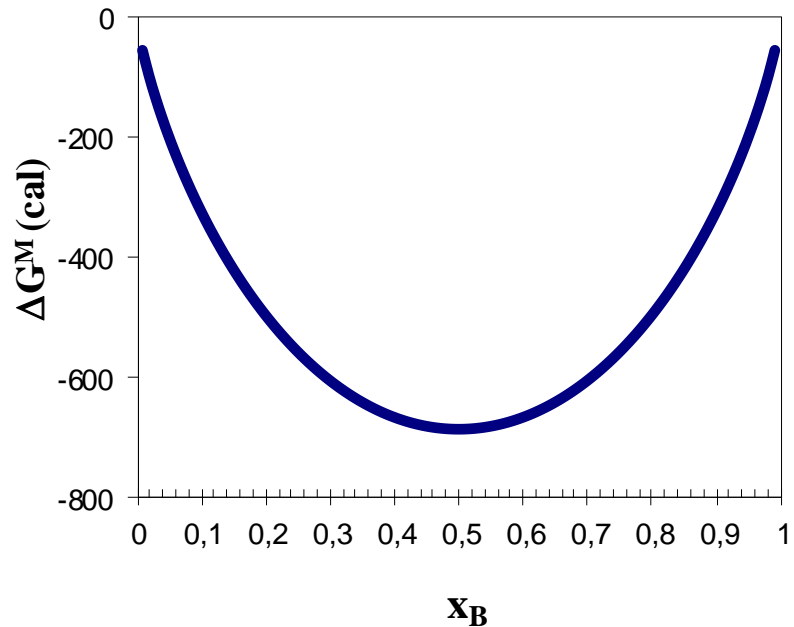




# TERMODINÂMICA DAS SOLUÇÕES

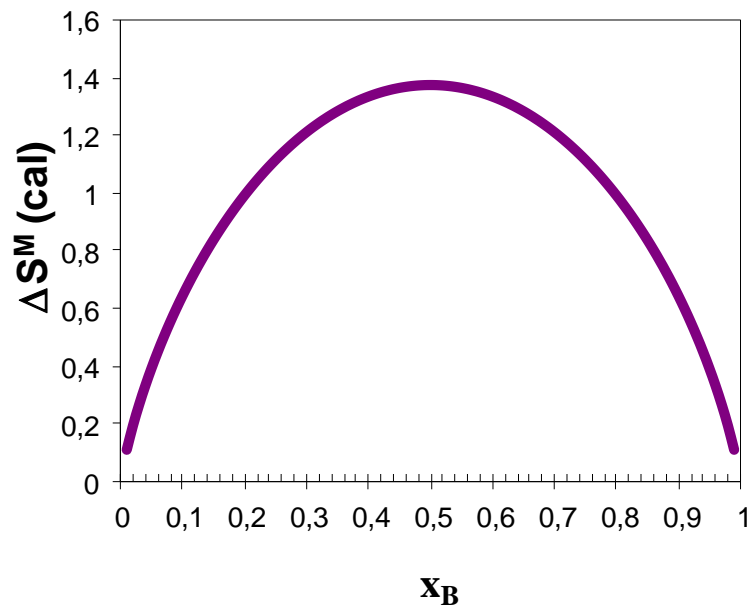
# Solução Ideal

T=500K



$$\Delta S^{M,ideal} = -R. (X_A. \ln X_A. + X_B. \ln X_B)$$

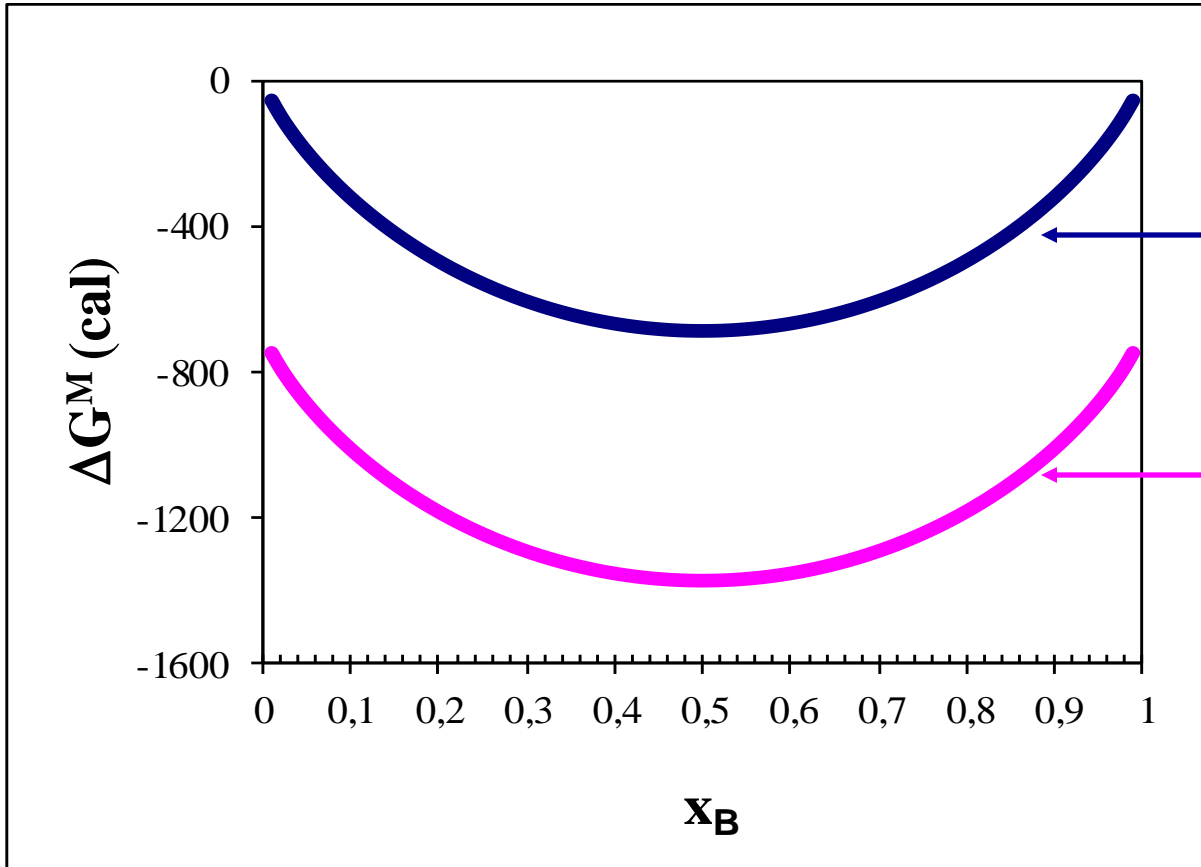
$$\Delta G^{M,ideal} = R. T. (X_A. \ln X_A. + X_B. \ln X_B)$$



$$\Delta G^M = \Delta H^M - T\Delta S^M$$

**Solução**  
**Não-Ideal: Desvio Negativo**  
 $\gamma=0,5$

**T=500K**

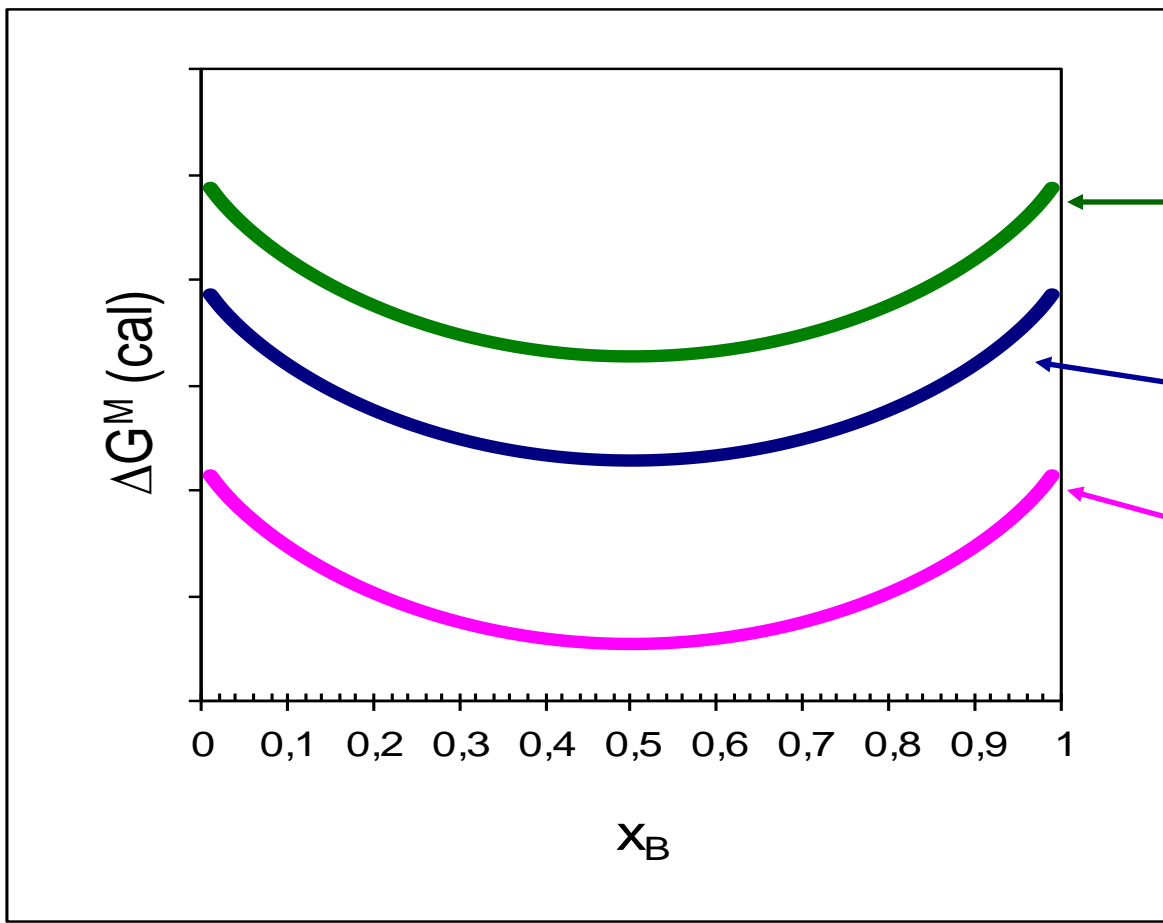


Ideal

Desvio  
Negativo

$$\Delta G^M = \Delta H^M - T\Delta S^M$$

**Solução**  
**Não-Ideal: Desvio Positivo**  
 $\gamma=1,5$



**T=500K**

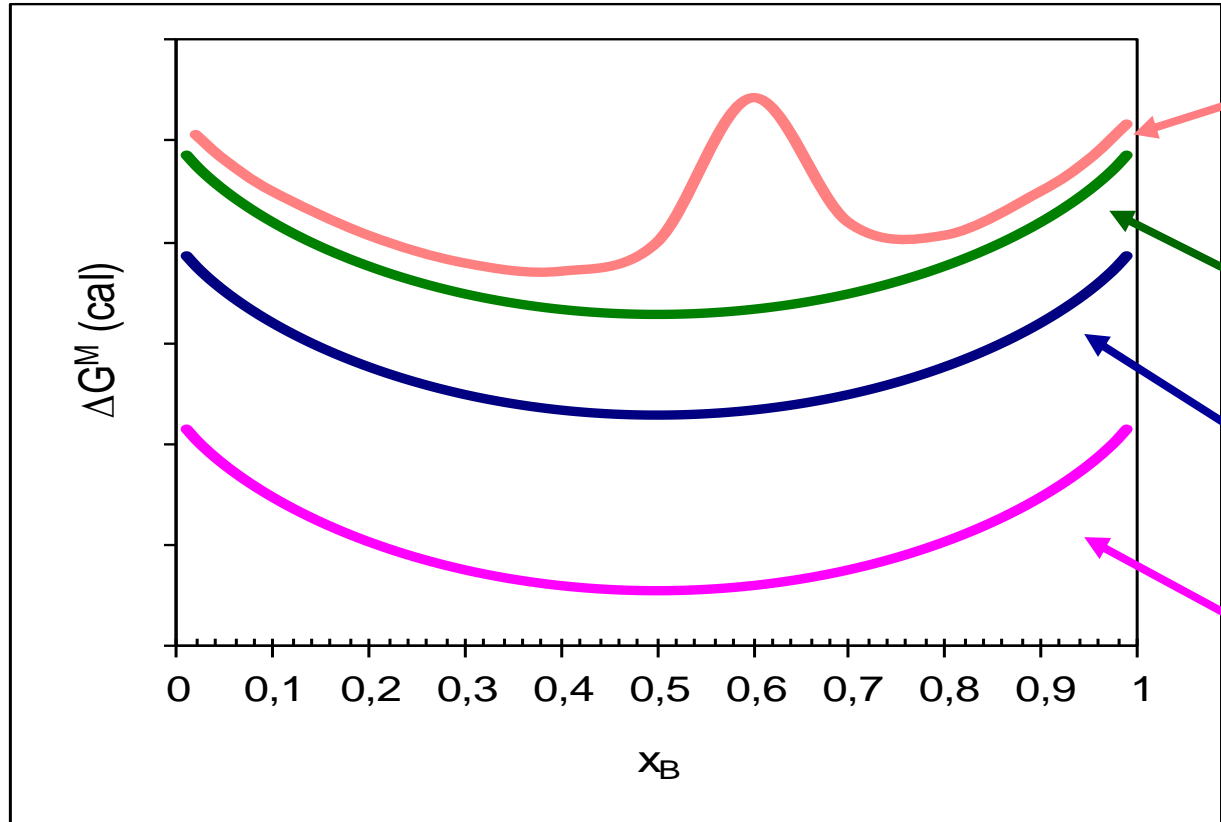
Desvio Positivo

Ideal

Desvio Negativo

$$\Delta G^M = \Delta H^M - T\Delta S^M$$

# Solução Não-Ideal: Desvio Positivo



Desvio fortemente Positivo

Desvio Positivo

Ideal

Desvio Negativo

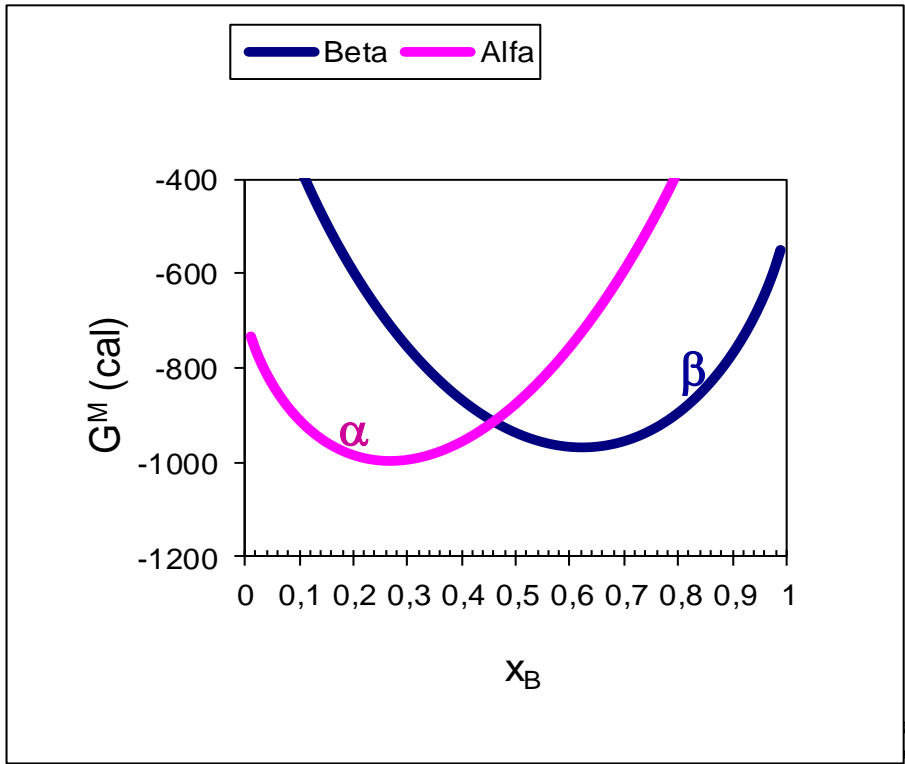
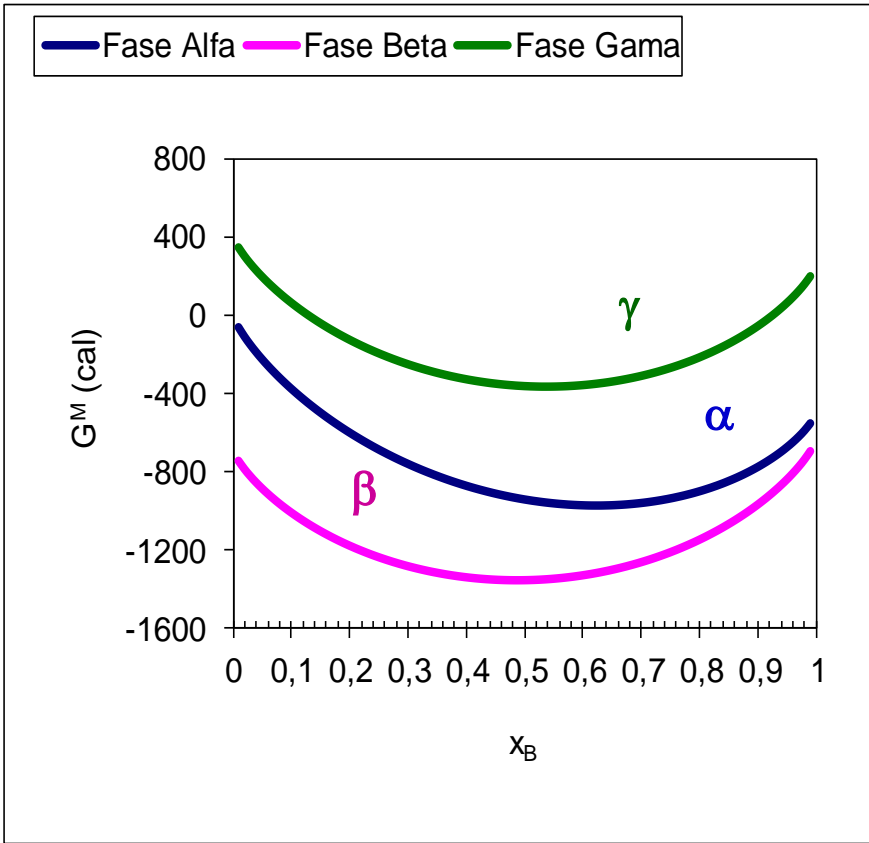
O mesmo raciocínio pode ser feito para os valores de  $G^{M, fase}$

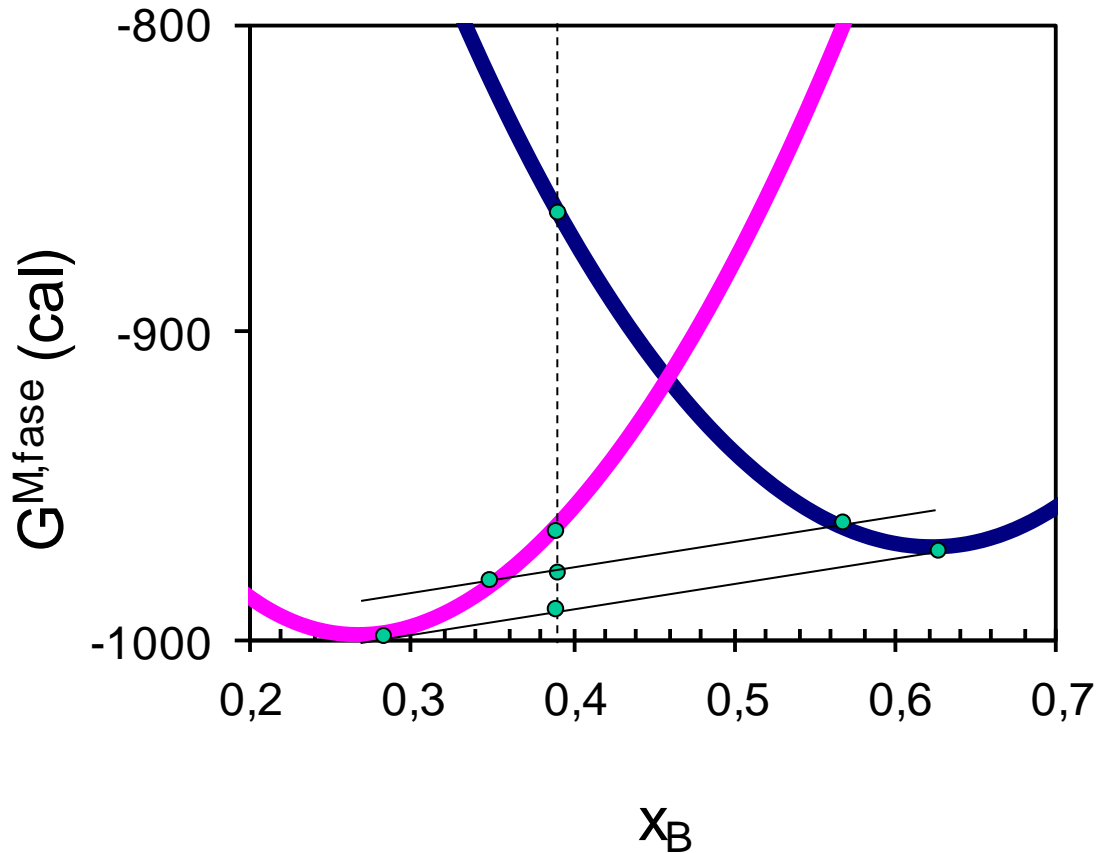
Isto é, para a *energia livre de Gibbs* das **fases** presentes no sistema.

$$\text{IDEAL} - G^{fase} = X_A \cdot G_A^0 + X_B \cdot G_B^0 + R \cdot T \cdot (X_A \cdot \ln X_A + X_B \cdot \ln X_B)$$

$$\text{REAL} - G^{fase} = X_A \cdot G_A^0 + X_B \cdot G_B^0 + R \cdot T \cdot (X_A \cdot \ln a_A + X_B \cdot \ln a_B)$$

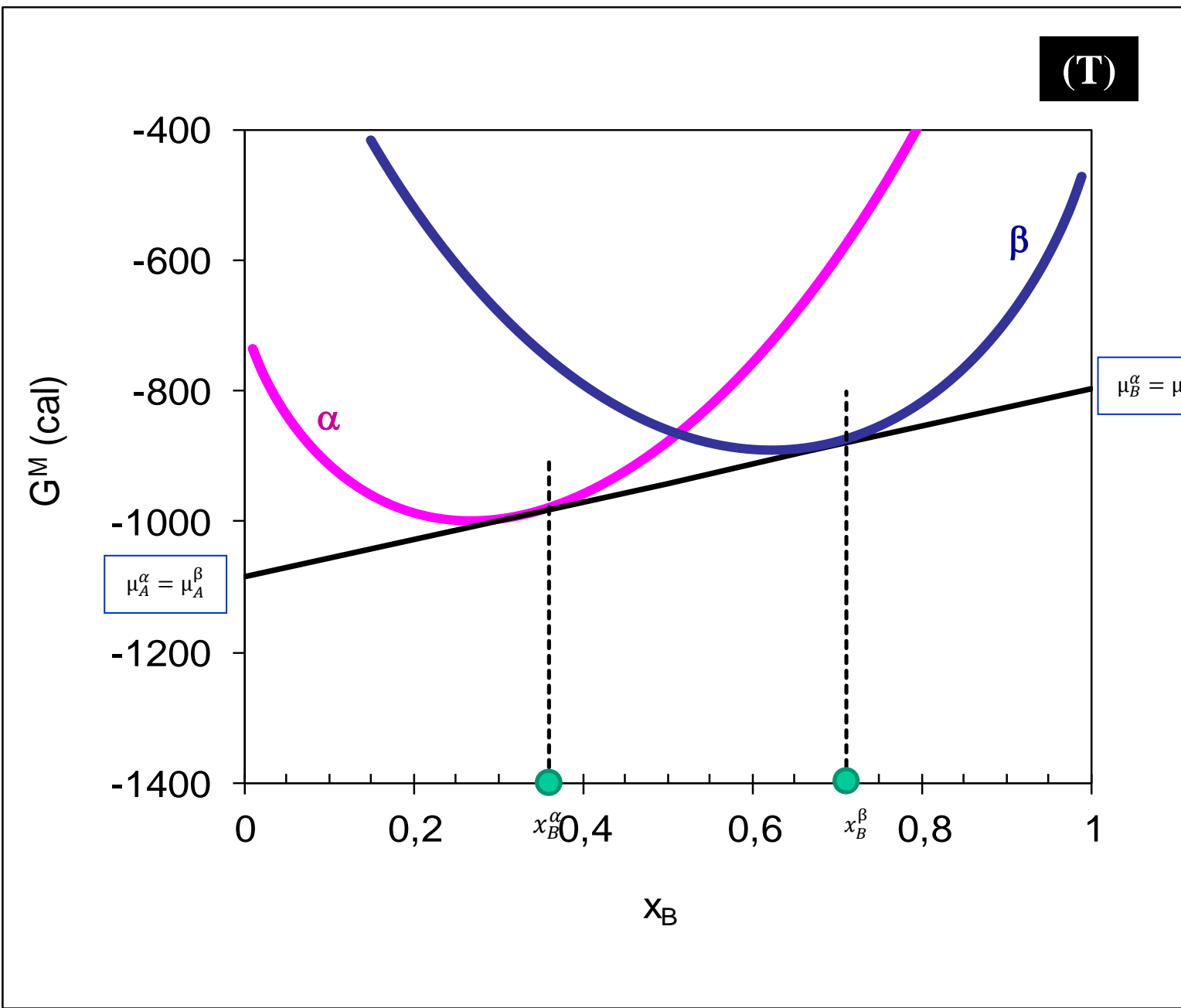
$$\text{REGULAR} - G^{fase} = X_A \cdot G_A^0 + X_B \cdot G_B^0 + \Omega \cdot X_A \cdot X_B + R \cdot T \cdot (X_A \cdot \ln X_A + X_B \cdot \ln X_B)$$

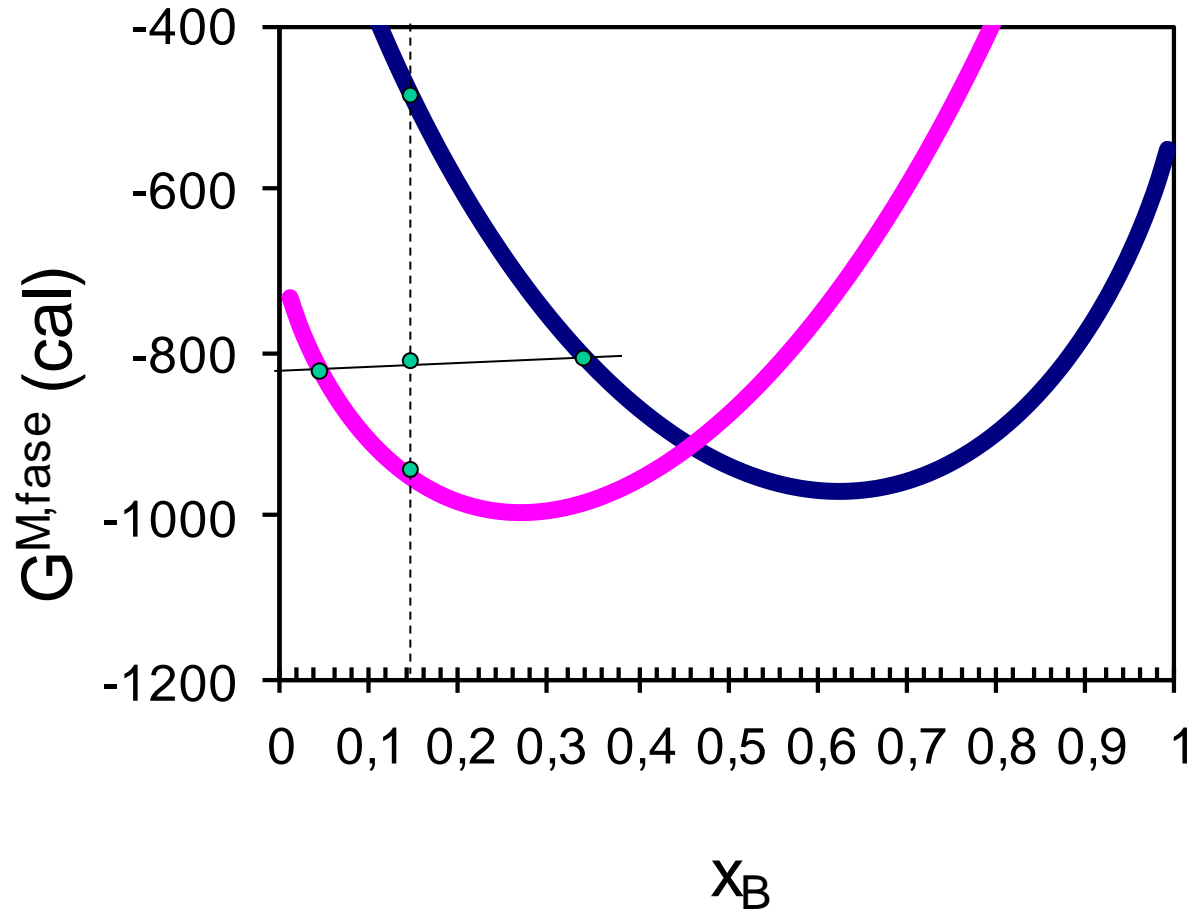




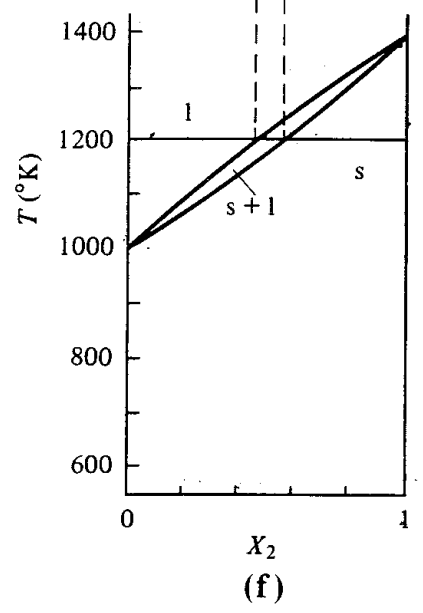
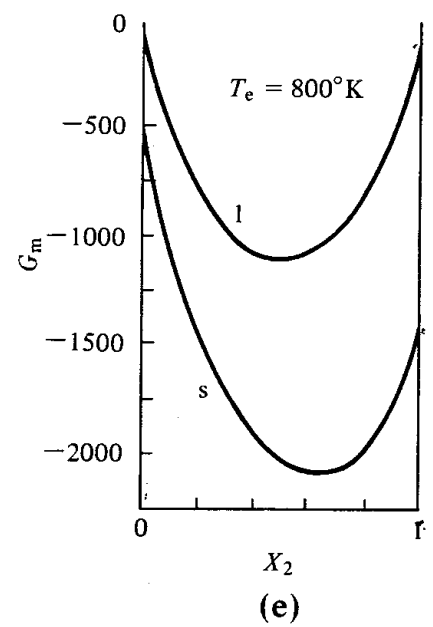
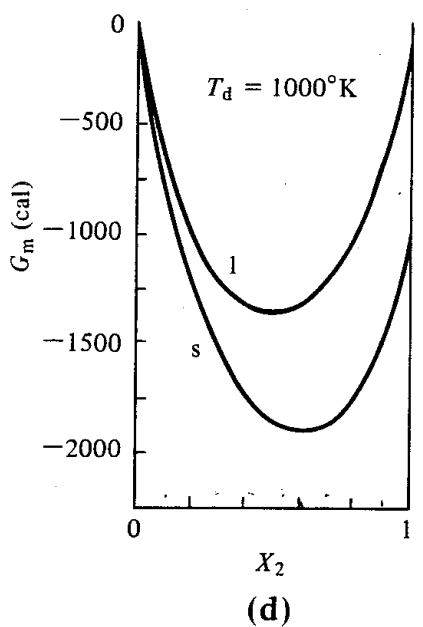
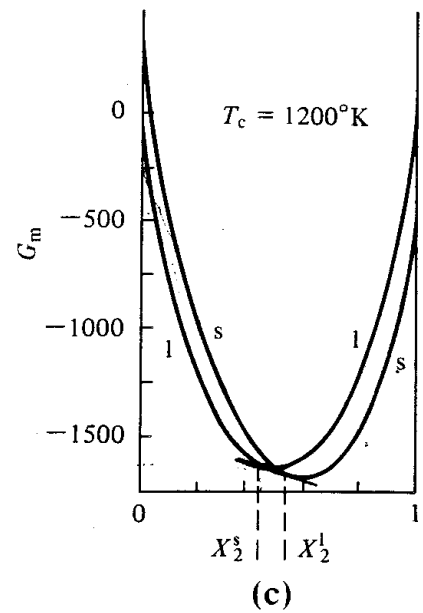
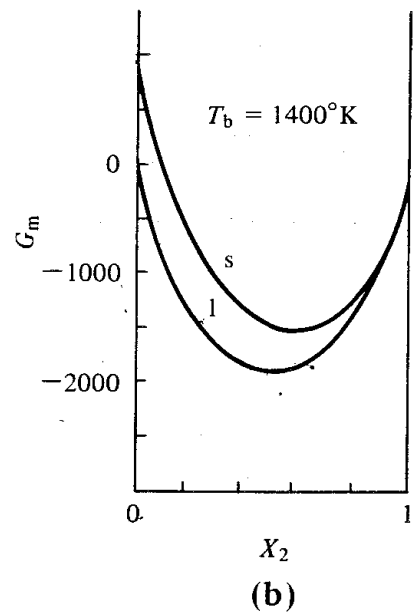
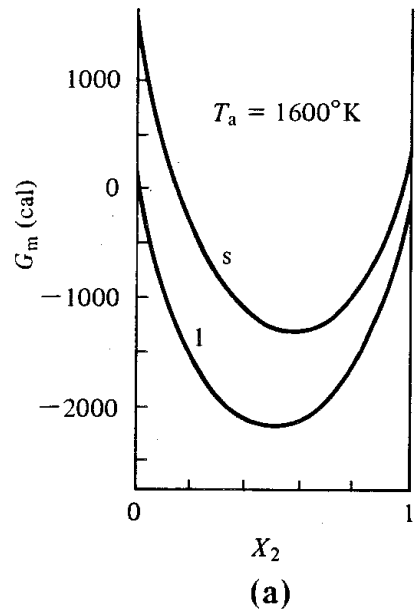
1.  $\alpha$  seria mais estável
2. MM  $\alpha+\beta$  é mais estável
3. MM  $\alpha+\beta$  com os mesmos  $\mu$

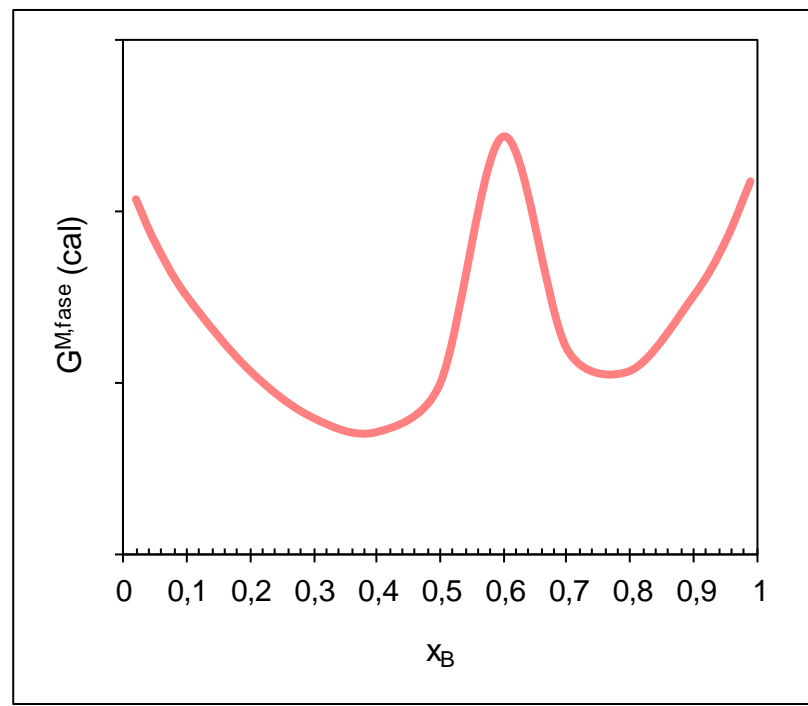






1.  $\alpha$  seria mais estável
2. MM  $\alpha+\beta$  é menos estável que  $\alpha$





# Para casa

Considerando que os sistemas isomorfos são sistemas ideais, calcular os diagramas de equilíbrio de fases. Comparar com os diagramas experimentais e discutir diferenças (ver material de cálculo no moodle):

1. Cu-Ni
2. FeO-MnO
3. Si-Ge
4. NiO-MgO
5. Ag-Au
6. Nb-Ta
7.  $\text{Al}_2\text{O}_3$ - $\text{Cr}_2\text{O}_3$
8. CaO-MnO
9. Ti-Ta
10. Ta-W

# CONSTRUÇÃO GRÁFICA DE DIAGRAMAS DE EQUILÍBRIO

- A precisão gráfica da tangente nas curvas de energia livre das fases é baixa – pode ser obtida analiticamente

- Sistemas Ideais

- para as fases sólida e líquida: isomorfo

- $\mu_i^{\text{sólido}} = \mu_i^{\text{líquido}}$

- $\mu_i^{\text{fase}} = \mu_i^{\text{o,fase}} + R.T. \ln a_i^{\text{fase}}$

- Para a reação  $\langle i \rangle = \{i\}$

- $\ln \left( \frac{a_i^{\text{líquido}}}{a_i^{\text{sólido}}} \right) = - \frac{\Delta \mu_i^{\text{o,fusão}}}{R.T}$

# CONSTRUÇÃO GRÁFICA DE DIAGRAMAS DE EQUILÍBRIO

$$- \Delta\mu_i^{o, fusão} = \mu_i^{o, líquido} - \mu_i^{o, sólido} = \Delta H_{f,i}^o - T \cdot \Delta S_{f,i}^o$$

$$- \Delta\mu_i^{o, fusão} = \Delta H_{f,i}^o \cdot \left(1 - \frac{T}{T_{f,i}}\right)$$

$$- \ln \left( \frac{a_i^{líquido}}{a_i^{sólido}} \right) = - \frac{\Delta H_{f,i}^o}{R} \cdot \left( \frac{1}{T} - \frac{1}{T_{f,i}} \right)$$

– Como para as soluções ideais  $a_i = X_i$

$$X_i^{líquido} = X_i^{sólido} \cdot \exp \left[ - \frac{\Delta H_{f,i}^o}{R} \cdot \left( \frac{1}{T} - \frac{1}{T_{f,i}} \right) \right]$$

# CONSTRUÇÃO GRÁFICA DE DIAGRAMAS DE EQUILÍBRIO

Mas, para um sistema binário A-B

$$\bullet X_A^{fase} + X_B^{fase} = 1$$

$$X_A^{sólido} \cdot \exp\left[-\frac{\Delta H_{f,A}^0}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{f,A}}\right)\right] + X_B^{sólido} \cdot \exp\left[-\frac{\Delta H_{f,B}^0}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{f,B}}\right)\right] = 1$$

e

$$X_A^{líquido} \cdot \exp\left[\frac{\Delta H_{f,A}^0}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{f,A}}\right)\right] + X_B^{líquido} \cdot \exp\left[\frac{\Delta H_{f,B}^0}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{f,B}}\right)\right] = 1$$



