McLean(麦克林)晶界偏析公式
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构成晶界的原子总数 N^{gb}.

偏析在晶界处的溶质原子数目 n^{gb}

晶粒内部原子总数 N^{α}，其中溶质原子数为 n^{α}.

1个溶质原子的晶界偏析能 ΔE_x^{gb}.

溶质原子分布服从 Maxwell-Boltzman 分布

由 n^{gb} 个 x 原子偏析于晶界所造成的自由能变化.

$$\Delta G \approx -\Delta \varepsilon_x^{gb} n^{gb} - T k_B \ln\left[\frac{N^{gb}!}{n^{gb}!(N^{gb}-n^{gb})!}\cdot\frac{N^{\alpha}!}{n^{\alpha}!(N^{\alpha}-n^{\alpha})!}\right]$$

公式: $\ln N! \approx N\ln N - N$

$$\ln[\text{第一项}] = \underbrace{n^{gb}\ln N^{gb}}_{\text{添加}} - n^{gb}\ln n^{gb} \underbrace{-n^{gb}\ln N^{g}}_{\text{添加}} + N^{gb}\ln N^{gb} - (N^{gb}-n^{gb})\ln(N^{gb}-n^{gb})$$

$$= n^{gb}\ln\frac{N^{gb}}{n^{gb}} + (N^{gb}-n^{gb})\ln N^{gb} - (N^{gb}-n^{gb})\ln(N^{gb}-n^{gb})$$

$$= -\left[n^{gb}\ln\frac{n^{gb}}{N^{gb}} + (N^{gb}-n^{gb})\ln\frac{N^{gb}-n^{gb}}{N^{gb}}\right]$$

$\ln[\ ] =$ 第一项 + ($gb \to \alpha$)

$n^{\alpha} + n^{gb}$ (x原子) 为一定值时.

$$0 = \frac{\partial \Delta G}{\partial n^{gb}} - \frac{\partial \Delta G}{\partial n^{\alpha}}$$

$$\approx -\Delta\varepsilon^{gb} + k_B T\left[\left(\ln\frac{n^{gb}}{N^{gb}} + \quad N^{gb} \quad + \ln\frac{N^{gb}-n^{gb}}{N^{gb}} + -N^{gb}\right) - (\quad)\right]$$

$$= -\Delta\varepsilon^{gb} + k_B T \ln\left[\frac{n^{gb}}{N^{gb}-n^{gb}} \Big/ \frac{n^{\alpha}}{N^{\alpha}-n^{\alpha}}\right]$$

$\because X^{gb} = \dfrac{n^{gb}}{N^{gb}}$, $X^{\alpha} = \dfrac{n^{\alpha}}{N^{\alpha}}$

$$\therefore \frac{X^{gb}}{1-X^{gb}} \approx \frac{X^{\alpha}}{1-X^{\alpha}}\exp\left(\frac{\Delta E_x^{gb}}{k_B T}\right)$$

$$1 - X^{\alpha} \approx 1$$

$$\therefore \frac{X^{gb}}{1-X^{gb}} \approx X^{\alpha}\exp\left(\frac{\Delta E_x^{gb}}{k_B T}\right)$$

$$X^{gb} \approx \frac{X^{\alpha}\exp\left(\frac{\Delta E_x^{gb}}{k_B T}\right)}{1 + X^{\alpha}(\quad)}$$