3.020 Lecture 19

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1 The simple regular solution model (refresher)

generic form of a regular solution model

$$\begin{aligned}\Delta G_{mix} &= \Delta H_{mix} - T\Delta S_{mix,ideal} \\ &= a_0 X_1 X_2 + RT\sum_i X_i \ln X_i\end{aligned}$$

a_0 parameterizes enthalpy of mixing :

- $a_0 > 0$: endothermic
- $a_0 < 0$: exothermic

Bonds made and broken.

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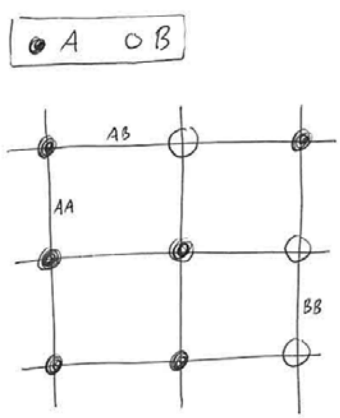
2 The quasi-chemical model

- Molecules/atoms on a lattice



bond	internal energy
AA	e_{AA}
AB	e_{AB}
BB	e_{BB}
beyond nearest-neighbor	$\emptyset$

- add up the total internal energy

$$U' = N_{AA}e_{AA} + N_{AB}e_{AB} + N_{BB}e_{BB}$$

$$N_{TOT} = \frac{1}{2}Mz$$

N_{ij} = # of bonds of type ij; M = total # of sites; Z = coordination #

- conservation of mass

$$zMX_A = 2N_{AA} + N_{AA}$$

$$zMX_B = 2N_{BB} + N_{AB}$$

- solve for $\Delta U_{mix'}$

$$\begin{aligned}\Delta U'_{mix} &= U' - X_A \underbrace{(\frac{1}{2}Mze_{AA})}_{\textbf{pure A}} - X_B \underbrace{(\frac{1}{2}Mze_{BB})}_{\textbf{pure B}} \\ &= N_{AB}(e_{AB} - \frac{1}{2}(e_{AA} + e_{BB}))\end{aligned}$$

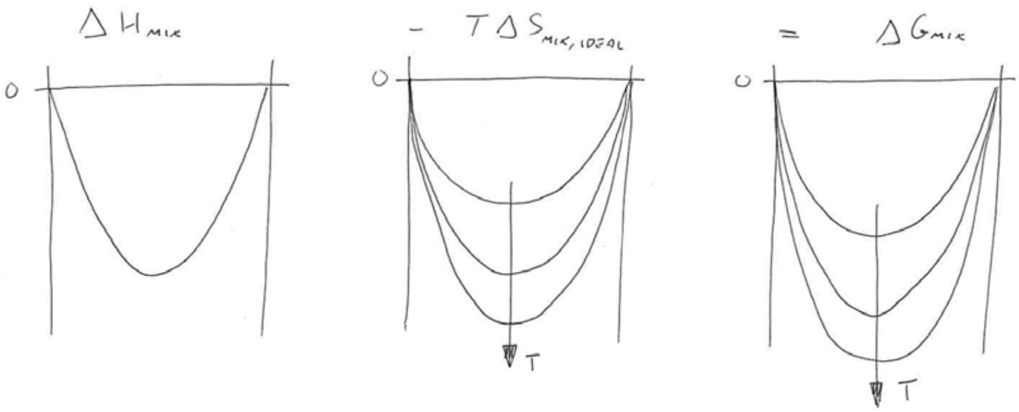
- in general, N_{AB} depends on alloy <u>structure</u>
- if alloy is random - as it should be if entropy of mixing is ideal - then we have :

$$\begin{aligned}P_{nab}(AB) &= X_A X_B + X_B X_A \\ &= 2X_A X_B \\ N_{AB} &= \frac{1}{2}Mz \times P_{nab}(AB) \\ &= MzX_A X_B\end{aligned}$$

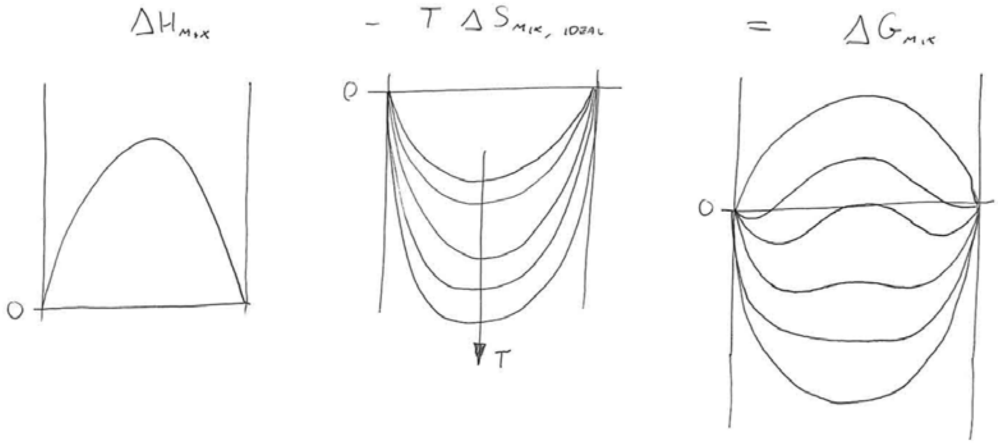
- gathering terms we have

$$\begin{aligned}||\Delta U_{mix} &= a_0 X_A X_B, \quad a_0 = Mz(e_{AB} - \frac{1}{2}(e_{AA} + e_{BB}))|| \\ &= \Delta H_{mix} - P\Delta V_{mix} \\ &\approx \Delta H_{mix} \quad \textbf{for solid solutions}\end{aligned}$$

- Plotting the simple regular model
  case $a_0 < 0$, exothermic mixing



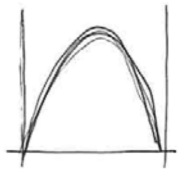
case $a_0 > 0$, endothermic mixing



3 Curvature at ΔG_{mix} and stability of solutions

- For sinmple regular model with $a_0 > 0$, curvature changes with temp.

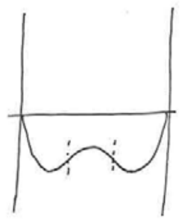
- Low temp



$\frac{d^2 \Delta G_{mix}}{d X_2^2} < 0$ everywhere

no inflection points

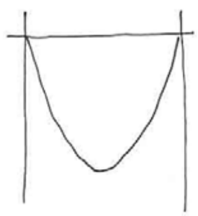
- Medium temp



$\frac{d^2 \Delta G_{mix}}{d X_2^2}$ changes sign

two inflection points

- High temp

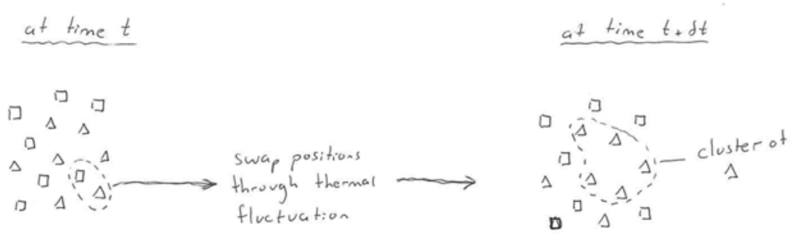


$\frac{d^2 \Delta G_{mix}}{d X_2^2} > 0$ everywhere

no inflection points

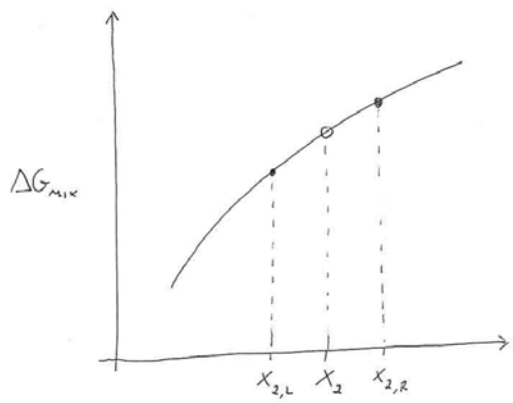
- Consider spontaneous, microscopic composition fluctuations

eg. $X_\square = X_\Delta = 0.5$



Q. Will this Δ-rich cluster spontaneously dissolve or grow ?
Follow the free energy.

- calculate free energy change of spontaneous composition fluctions



- system initially uniformly mixed at X_2
- spontaneous fluctuation into regions with composition $X_{2,L}$, $X_{2,R}$
- phase fractions f_L, f_R determined by lever rule
  - for $X_{2,R} - X_2 = X_2 - X_{2,L} = dX$, it's simply $F_L = f_R = \frac{1}{2}$
- calculate differential change in ΔG_{mix}

$$d\Delta G_{mix} = \underbrace{f_L \cdot \Delta G_{mix}(X_{2,L}) + f_R \cdot \Delta G_{mix}(X_{2,R})}_{\textbf{after fluctuation}} - \underbrace{\Delta G_{mix}(X_2)}_{\textbf{before fluctuation}}$$

- can show that $\frac{d^2\Delta G_{mix}}{dX_2^2} < 0$ leads to spontaneously unmixing a.k.a. spinodal decomposition
- stable mixtures for $\frac{d^2\Delta G_{mix}}{dX_2^2} > 0$