3.020 Lecture 22

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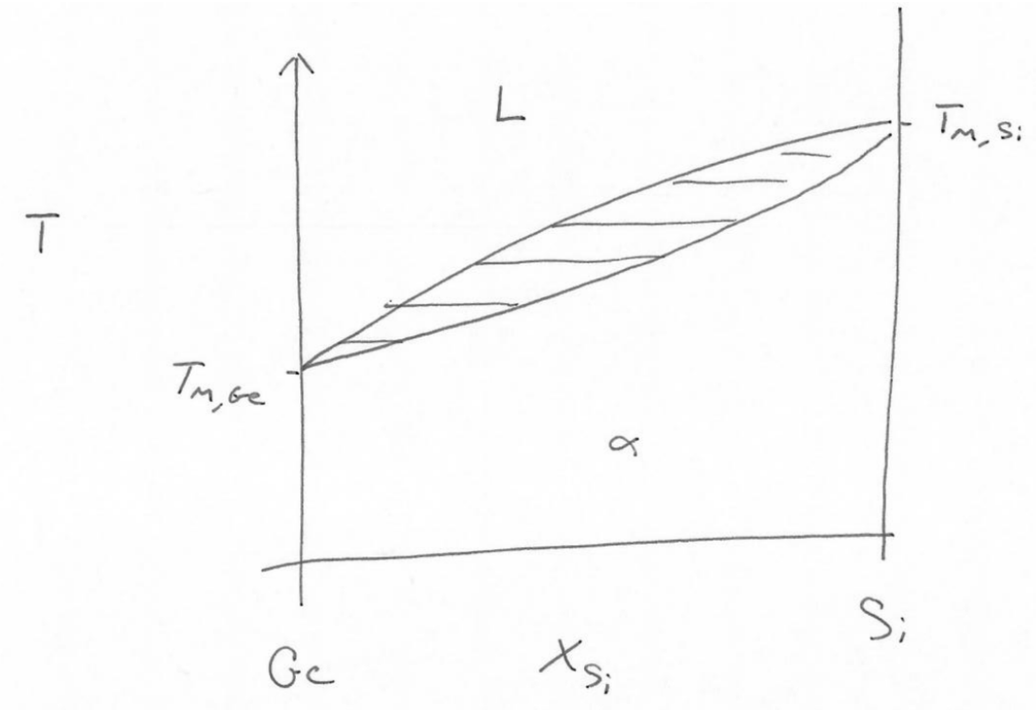
1 Thermodynamics of binary phase diagrams

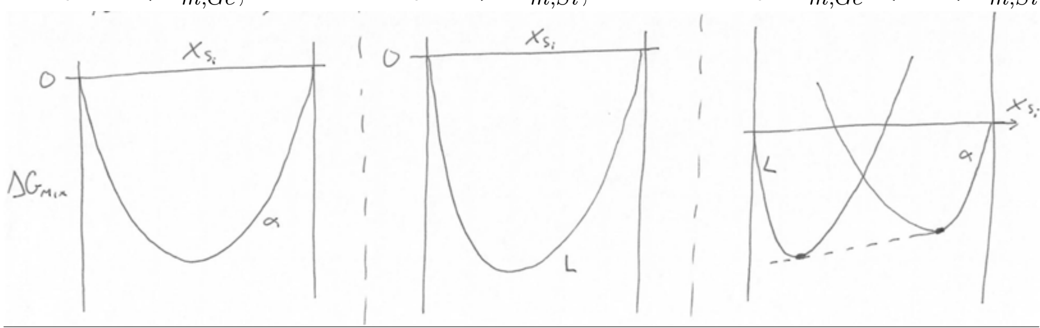
- Thus far :
  - notation - bookeeping, partial molar properties
  - solution modeling, ideal and simple regular models
  - spinodal systems: spontaneous unmixing when both pure components are in same structure

only need one solu. model in free energy-composition diagram

- More generally, pure components may be in different structures e.g. Si-Ge system for $T_{m,Ge} < T < T_{m,Si}$



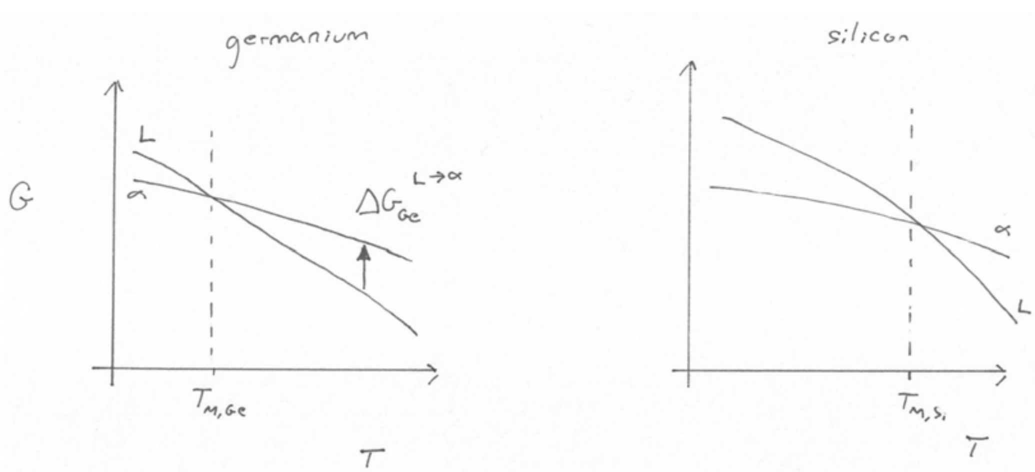
for $T < T_{m,Ge}$, for $T > T_{m,Si}$, for $T_{m,Ge} < T < T_{m,Si}$



- Consider the process of making on α-phase Si-Ge solid solution at temperature $T_{m,Ge} < T < T_{m,Si}$

1. Convert the Ge from L to α phase
2. Mix solid Ge and Si in the α phase

- Temperature-dependence of free energy of pure components



- Accounting for $\Delta G_k^{\alpha\to\beta} = \Delta H_k^{\alpha\to\beta}(T) - T\Delta S_k^{\alpha\to\beta}(T)$
  both terms may be temp-dependent
  - At equilibrium transition temp $T^{\alpha\to\beta}$, $\Delta G_k^{\alpha\to\beta} = 0$
  - If $\Delta C_P^{\alpha\to\beta} \approx 0$, then $\Delta H_k^{\alpha\to\beta}$ and $\Delta S_k^{\alpha\to\beta}$ are approximately temperature-independent, and the expression for the temp-dependence of $\Delta G_k^{\alpha\to\beta}$ simplifies:

this is a reference state change

this is described by solution modeling

from unary phase diagrams

$$\Delta G_k^{\alpha\to\beta}(T) \approx \Delta S_k^{\alpha\to\beta} \times (T^{\alpha\to\beta} - T)$$

- linear in T
- need data: transition temp $T^{\alpha\to\beta}$ and $\Delta S_K^{\alpha\to\beta}$

- Solving 2-phase coexistence condition for $T_{m,Ge} < T < T_{m,Si}$

1.

$$\mu_{Si}^{\alpha} = \mu_{Si}^{L} \qquad \Longrightarrow \qquad \mu_{Si}^{0} + \Delta\mu_{Si,mix}^{\alpha} = \mu_{Si}^{0} + \Delta\mu_{Si}^{\alpha\to L} + \Delta\mu_{Si,mix}^{L}$$

- μ_{Si}^{0} : reference state of Si, which is α-phase
- $\Delta\mu_{Si,mix}^{\alpha}$: solution model for α-phase, PMP of mixing
- $\Delta\mu_{Si}^{\alpha\to L}$: reference state change
- $\Delta\mu_{Si,mix}^{L}$: solution model for L phase, PMP of mixing

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2.

$$\mu_{Ge}^{\alpha} = \mu_{Ge}^{L} \qquad \Longrightarrow \qquad \mu_{Ge}^{0} + \Delta\mu_{Ge}^{L\to\alpha} + \Delta\mu_{Ge,mix}^{\alpha} = \mu_{Ge}^{0} + \Delta\mu_{Ge,mix}^{L}$$

- μ_{Ge}^{0} : reference state of Ge, which is L-phase
- $\Delta\mu_{Ge}^{L\to\alpha}$: reference state change
- $\Delta\mu_{Ge,mix}^{\alpha}$: solution model for α-phase, PMP of mixing
- $\Delta\mu_{Ge,mix}^{L}$: solution model for L phase, PMP of mixing

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- If both solutions behave ideally and if $\Delta C_P^{\alpha\to L} \approx 0$ for both Si and Ge, then coexistence condition and phase diagram can be solved explicitly, $\longrightarrow$ see DeHoff sec. 10.2.1, Fig. 10.22
- In all other cases we use computers $\longrightarrow$ CALPHAD