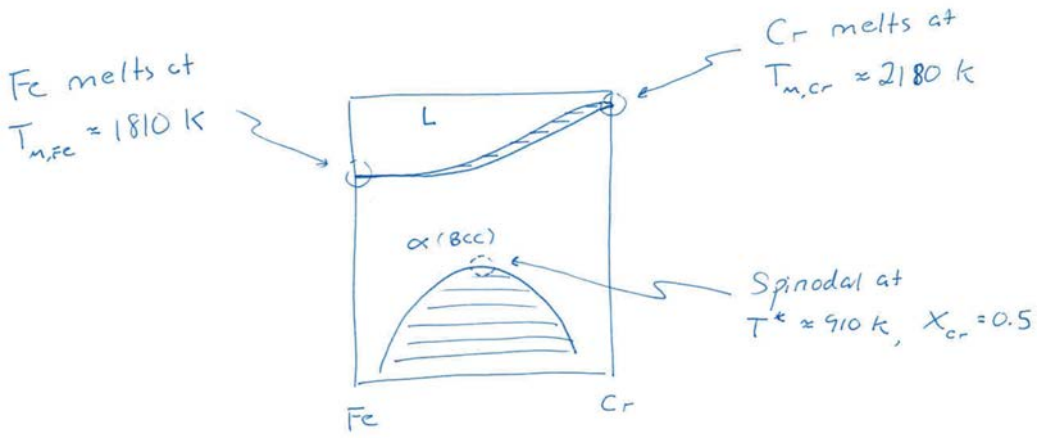
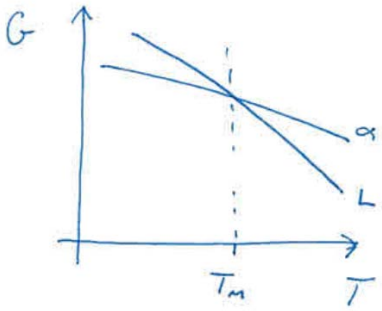
3.020 Lecture 25

Prof. Rafael Jaramillo

1 Modeling the simplified Cr-Fe phase diagram

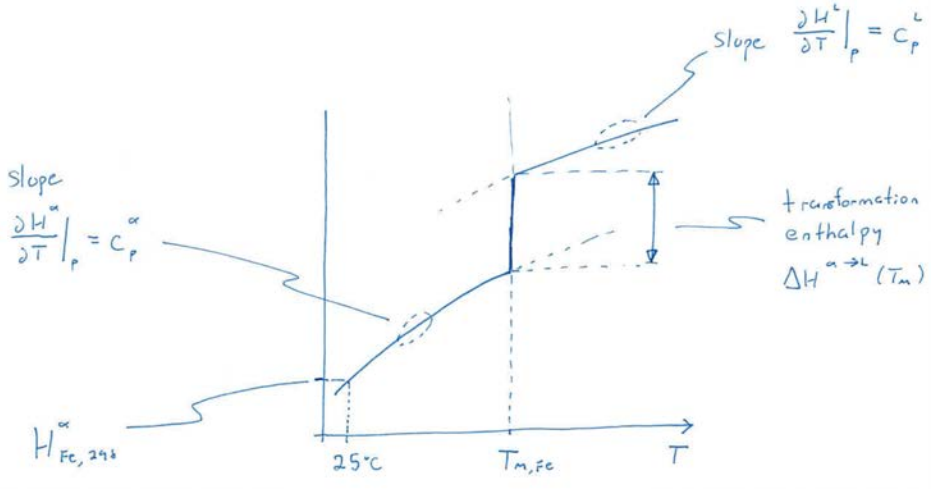


- Start by building model for pure Fe
  - needs to melt at $T_{M,Fe}$
  - G^{α}_{Fe}(T), G^{α}_{L}(T) curves cross at $T_{M,Fe}$
  - $G = H - TS$



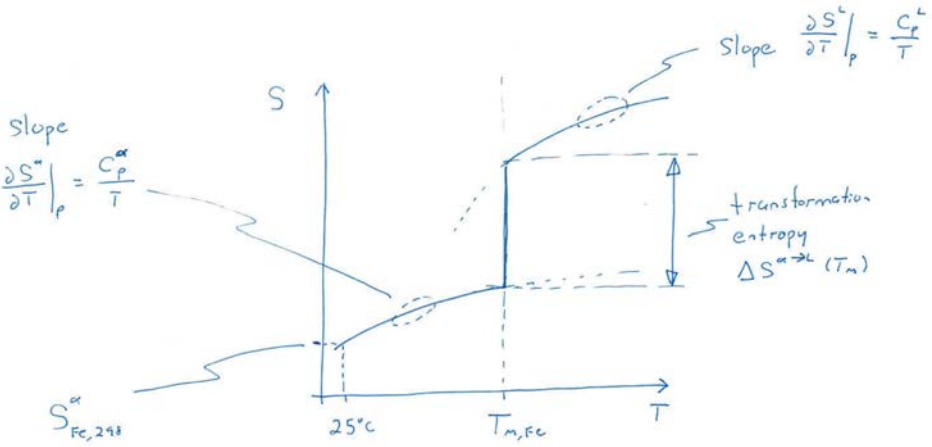
$\Longrightarrow$ model temp dependence of H, S and transformation quantities

$$\Delta H^{\alpha \to L}, \qquad \Delta S^{\alpha \to L} = \Delta H^{\alpha \to L}/T_M$$



enthalpy at standard state 25 ^{o}C and 1 atm:

- set to 0 for elements, by convention
- if pure component is a compound (e.g. SiO_2), then use $\Delta H^o_{form,298}$



entropy at standard state (S^o_{298})

- data needed for model of pure Fe

$C_P^\alpha(T)$, $C_P^L(T)$: each can be modeled as a polynominal
$\Delta H^{\alpha \to L}(T_m)$, $\Delta S^{\alpha \to L}(T_m)$, T_m : a triple, two are independent

standard state	S^0_{298}, $\Delta H^0_{form,298} = 0$
heat capacity	$C^\alpha_P(T)$, $C^L_P(T)$
transformation	$\Delta H^{\alpha\to L}(T_m)$, $\Delta S^{\alpha\to L}(T_m)$, T_m

$$
\begin{aligned}
C^\alpha_P(T) &= a^\alpha + b^\alpha T + C^\alpha/T^2 \\
C^\alpha_L(T) &= a^L + b^L T + C^L/T^2 \\
\Delta S^{\alpha\to L}(T_m) &= \Delta H^{\alpha\to L}(T_m)/T_M
\end{aligned}
$$

- temp-dependence of H

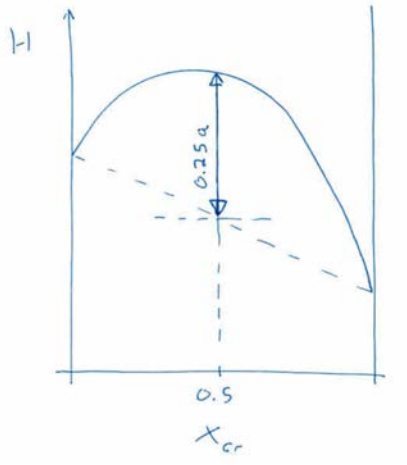
$$
\begin{aligned}
H &= p_1 T^2 + p_2 T + p_3 \qquad \text{polynomial coefficients} \\
\frac{\partial H}{\partial T} &= 2p_1 T + p_2 \qquad \text{as in Matlab} \\
&= a + bT \qquad \text{heat capacity model}
\end{aligned}
$$

- Build model for pure Cr, as above
- Build solution models
  - start with the spinodal phase α (BCC)
  - model as simple regular $\longrightarrow$ only 1 adjustable parameter

$$
\begin{aligned}
\Delta H_{mix} &= aX_1X_2 = aX_{Fe}X_{Cr} \\
H &= H^o_{Fe}X_{Fe} + H^o_{Cr}X_{Cr} + aX_{Fe}X_{Cr}
\end{aligned}
$$

- estimate a_0 by eye by recording values at $X_{Cr} = 0.5$

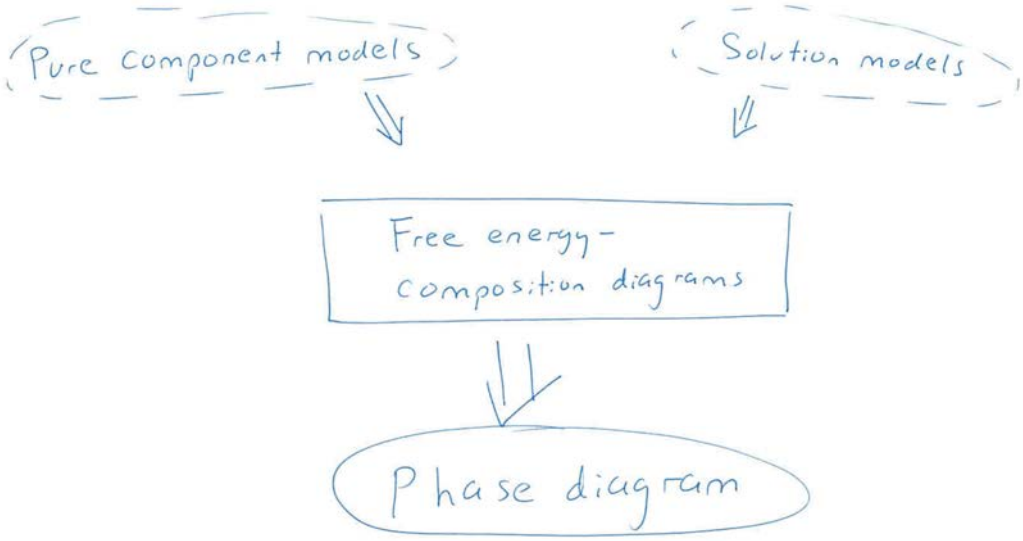
- $H^o_{Fe} \approx 25,750\ J/mol$
- $H^o_{Cr} \approx 19,450\ J/mol$
- $H(X_{Cr} = 0.5) \approx 29,000\ J/mol$
- $a^{BCC} \approx 28,000 J/mol$



- alternatively could export data and fit
- likewise build model fro liquid phase

- At each temp, draw free energy-composition diagram and identify common tangents (if only)

$$G^{\alpha} = X_{Cr}\mu^{o,\alpha}_{Cr} + X_{Fe}\mu^{o,\alpha}_{Fe} + \Delta G^{\alpha}_{mix}$$
$$G^{L} = \underbrace{X_{Cr}\mu^{o,L}_{Cr} + X_{Fe}\mu^{o,L}_{Fe}}_{\substack{\textbf{pure component models,} \\ \textbf{will contain reference} \\ \textbf{state changes}}} + \underbrace{\Delta G^{L}_{mix}}_{\textbf{Solution models}}$$



3.020 Thermodynamics of Materials

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