Phase Transformation of Materials

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NRL of Charged Nanoparticles

1.2 Single Component Systems
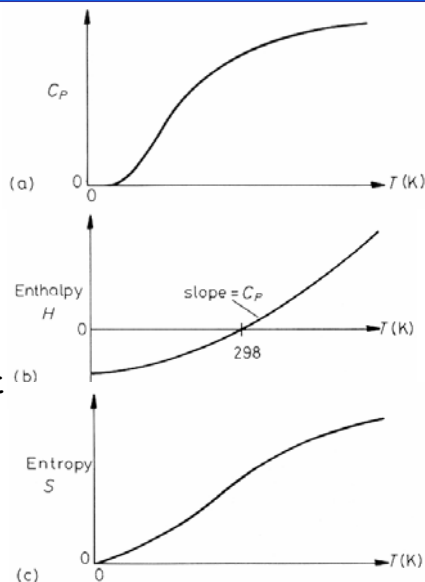
Draw the plots of C_p vs. T, H vs. T and S vs. T.

How is C_p related with H and S?

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

H = ?

$$H = \int_{298}^{T} C_P \, dT$$

H = 0 at 298K for a pure element in its most stable state.

S = ?

$$S = \int_{0}^{T} \frac{C_P}{T} \, dT$$

(a) C_P vs. T (K)

(b) Enthalpy H, slope = C_P, 298, T (K)

(c) Entropy S vs. T (K)

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1.2.1 Gibbs Free Energy as a Function of Temperature

Plot the curves of G vs. T.

What is the slope in the plot of G vs. T?
$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$G = H - TS \qquad H = \int_{298}^{T} C_P \, dT \qquad S = \int_{0}^{T} \frac{C_P}{T} \, dT$$

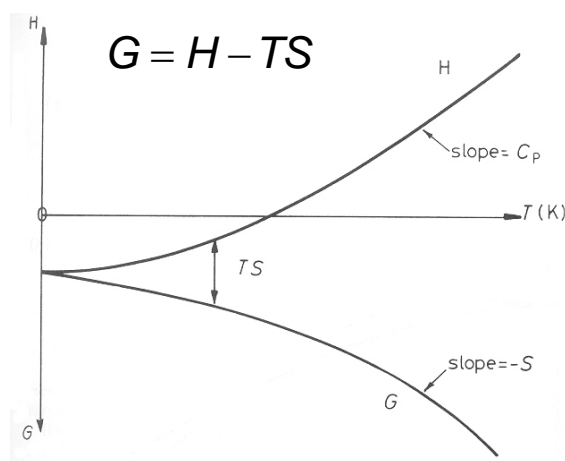$$G = \int_{298}^{T} C_P \, dT - T \int_{0}^{T} \frac{C_P}{T} \, dT$$

At which temperature G is equal to H?

1.2.1 Gibbs Free Energy as a Function of Temperature

Compare the plots of H vs.T and G vs. T.

dG = ?

$$G = H - TS$$

$$dG = -SdT + VdP$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

G decreases with increasing T with a slope of –S.

1.2.1 Gibbs Free Energy as a Function of Temperature

Which is larger, H^L or H^S?

$H^L > H^S$ at all temp.

Which is larger, S^L or S^S?

$S^L > S^S$ at all temp.

$\rightarrow$ Gibbs free energy of the liquid decreases more rapidly with increasing temperature than that of the solid.

Which is larger, G^L or G^S at low T?

$G^L > G^S$ (at low Temp) and $G^S > G^L$ (at high Temp)

What is a relation between G^L and G^S at T_m?

For temperature up to T_m, solid is stable and above T_m, liquid is stable.

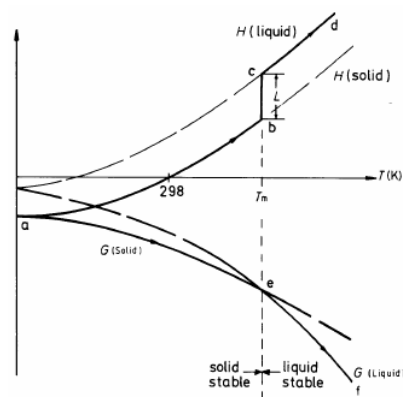**Draw Fig. 1.4.**

<u>At T_m both phases exist in equilibrium.</u> $G^l = G^S$

What is a relation between H^L and H^S at T_m?

$L = H^L - H^S$

L: Latent heat of melting at T_m

Fig. 1.4 Variation of enthalpy (H) and free energy (G) with temperature for the solid and liquid phases of a pure metal. L is the latent heat of melting, T_m the equilibrium melting temperature.
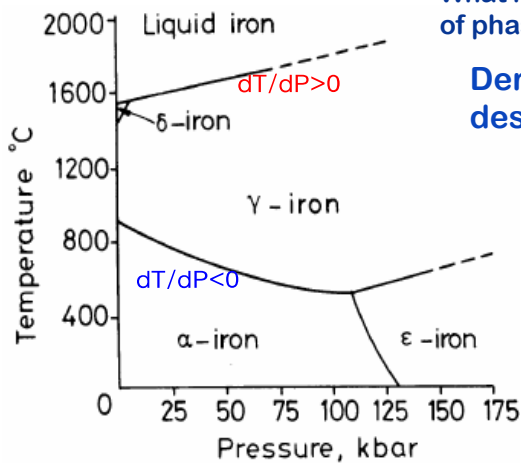
1.2.2 Pressure Effects

What is the thermodynamic meaning of phase boundaries?

Derive the equation describing the P-T diagram.

$$dG^\alpha = -S^\alpha dT + V_m^\alpha dP$$
$$dG^\beta = -S^\beta dT + V_m^\beta dP$$

In equilibrium, $G^\alpha = G^\beta$

$$\rightarrow dG^\alpha = dG^\beta$$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T_{eq}\Delta V}$$

Clausis-Clapeyron Eq.

Fig. 1.5 Effect of pressure on the equilibrium phase diagram for pure iron.

dT/dP>0

dT/dP<0

1.2.3 The Driving Force for Solidification

Liquid was supercooled to T below T_m. What is a driving force for this phase transformation (solidification)?

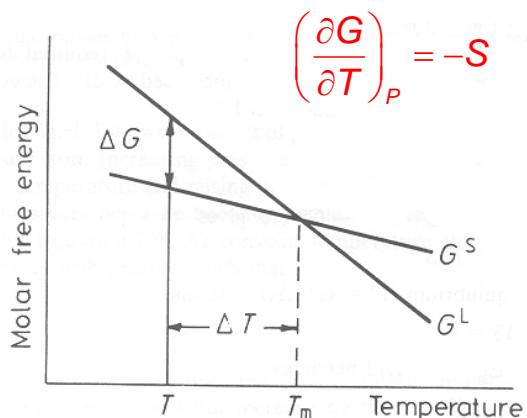→ Decrease in Gibbs Free Energy ($\Delta G^{L \rightarrow S}$) between Initial and Final States

$\Delta G^{L \rightarrow S}$ = ?

(1) $\Delta H^{L \rightarrow S}$, $\Delta S^{L \rightarrow S}$

(2) T_m, ΔT, L

How is the slope determined in G-T diagram?

Plot the dependence of Molar Gibbs free energy on T for Liquid and Solid.

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

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1.2.3 The Driving Force for Solidification

$G^L = H^L - TS^L$

$G^S = H^S - TS^S$

At T, $\quad \Delta G^{L \to S} = \Delta H^{L \to S} - T\Delta S^{L \to S}$

We know T, ΔT and L
but do not know $\Delta H^{L \to S}$, $\Delta S^{L \to S}$.
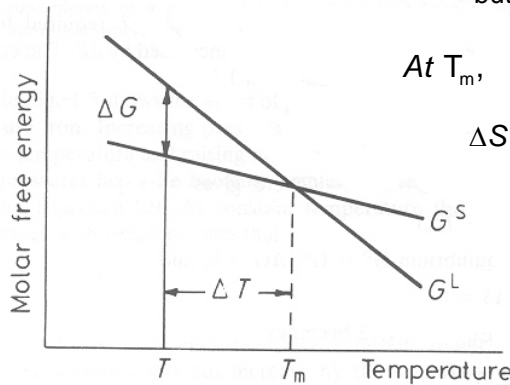
At T_m, $\quad \Delta G^{L \to S} = \Delta H^{L \to S} - T\Delta S^{L \to S} = 0$

$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m} : Entropy\ of\ Fusion$$

**If ΔH and ΔS do not vary
with temperature,
$\to$ if ΔT is small**

$$\Delta G \cong L - T\frac{L}{T_m} \qquad \Delta G \cong \frac{L\Delta T}{T_m}$$

1.3 Binary Solution: Gibbs free energy

Variables ?
$\to$ **composition, temperature, and pressure**
$\to$ **composition and temperature at constant pressure**

**It is assumed that A and B have the same crystal
structures in their pure states and can be mixed in any
proportion to make a solid solution with the same
crystal structure.**

**The molar Gibbs free energies for pure A and B are
given as G_A and G_B, respectively.**

**How can you derive the expression of the molar Gibbs
free energy for binary solution?**

Problems that will be asked in the next class

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1.3 Binary Solution: Gibbs free energy

$$G = X_A G_A + X_B G_B + \Delta G_{mix}$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

ΔH_{mix} : Heat of Solution i.e. heat absorbed or evolved during step 2
ΔS_{mix} : difference in entropy between the mixed and unmixed state

If the bond energy of A-A, B-B and A-B is the same, what would be ΔH_{mix}?

Derive the expression of ΔS_{mix} for ideal mixing.

Compare ΔG_{mix} for ideal solution between high and low T.

What is the meaning and the usage of chemical potential (μ_A)?

Derive μ_A and μ_B for the ideal solution of a binary mixture.

Draw the graphical relationship between the molar
free energy curve and chemical potentials
for an ideal solution.

	Bond energy	Number of bond
A-A	ε_{AA}	P_{AA}
B-B	ε_{BB}	P_{BB}
A-B	ε_{AB}	P_{AB}

What is the Internal energy of the solution?

What is ΔH_{mix} of the solution?

What would be ΔG_{mix} of this solution if mixing is ideal?

What is the meaning and the usage of activity (a)?

What are Henry's law and Roult's law
and their meaning?