3.020 Lecture 9

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1 Heat Capacity: Key to the (thermo) Kingdom

- $G = H - TS$
- equilibrium at fixed T & P is a balance between H and S

Q: How to calculate H and S for a given phase at a given (T, P) ?

1.1 Calculating $H(T)$ at fixed P

$$\begin{aligned} H &= U + PV \\ dH &= dU + PdV + VdP \quad \longleftarrow \textbf{chain rule} \\ &= TdS - PdV + PdV + VdP \quad \longleftarrow \textbf{combined statement} \\ &= TdS + VdP \end{aligned}$$

$$dH\Big|_P = TdS = \delta Q_{rev} = C_P dT$$

$$H(T_2, P) = H(T, P) + \int_{T_1}^{T_2} dH = H(T, P) + \int_{T_1}^{T_2} dT C_P(T)$$

need $C_P(T)$

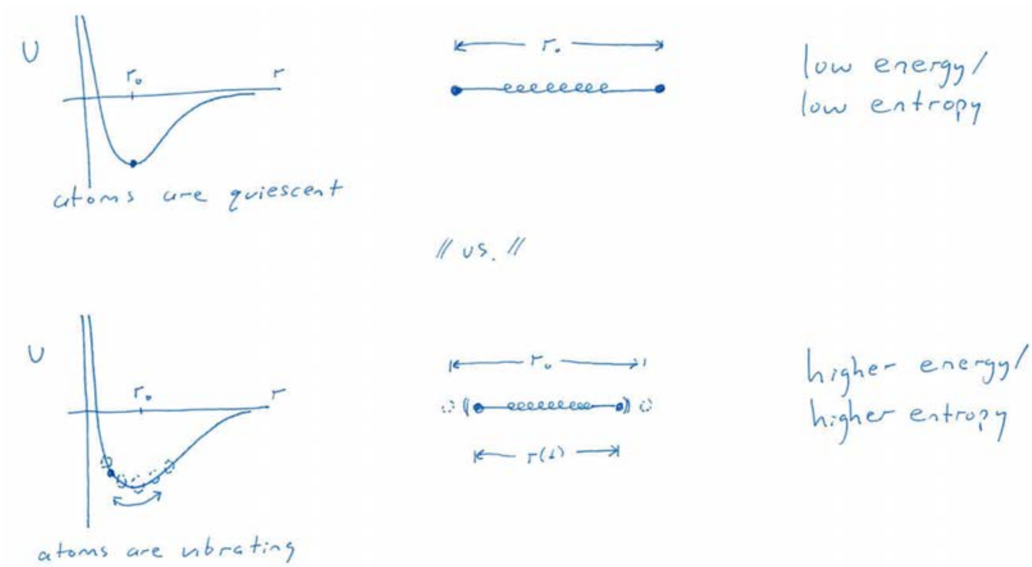
1.2 Calculating $S(T)$ at fixed P

$$\begin{aligned} dS &= \frac{C_P}{T} dT - V\alpha dP \quad \longleftarrow \textbf{DeHoff table 4.5} \\ dS\Big|_P &= \frac{C_P}{T} dT \\ S(T_2, P) &= S(T_1, P) + \int_{T_1}^{T_2} dS = S(T_1, P) + \int_{T_1}^{T_2} dT \frac{C_P(T)}{T} \end{aligned}$$

need $C_P(T)$

Q: What is $C_P(T)$ for real materials ?

- Consider bonds as atoms on springs



- Models for $C_P(T)$ that consider vibrations of atoms in crystals = phonons
  - Einstein: all vibrations have fixed frequency
  - Debye: range of vibration frequencies available
    (will solve these models later in the class, using stat. mech.)

slides: 1. Einstein & Debye models; 2. Heat capacity of cobalt

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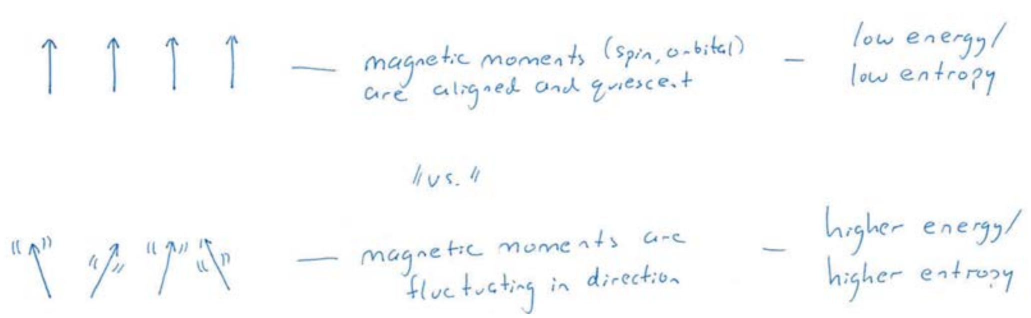
- Heat capacity includes all "defrees of freedom" within a system
  e.g. molecular rotation, electronic states, magnetism, etc ...

ways of partitioning energy

- Consider ferromagnet such as cobalt



slide: $C_P(T)$ of cobalt, again

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2 Phase transformations

- Consider $S \leftrightarrow L$ transformation in Si
- Enthalpy change $\Delta H^{S \to L}(T_m) = 50.2 kJ/mol$
  change at the equilibrium melting temp $T_m = 1685K (1412^o C)$
  Q. What is enthalpy change $\Delta H^{S \to L}$ for $T < T_M$?
  - For S phase: $H^s(T) = H^s(T_M) + \int_{T_M}^{T} dT' C_P^S(T')$
  - For L phase: $H^L(T) = H^L(T_M) + \int_{T_M}^{T} dT' C_P^L(T')$

$$\Delta H^{S \to L}(T) = \Delta H^{S \to L}(T_M) + \int_{T_M}^{T} dT' (C_P^L - C_P^S)$$

$(C_P^L - C_P^S) = \Delta C_P^{S \to L}(T) \quad \longrightarrow$ **heat capacity difference**

slides: Si thermo data

- Use thermo data
  - from NIST, $C_P = A + Bt + Ct^2 + Dt^3 + E/t^2$,

empirical

$$t = \frac{T}{1000K}$$

	A (J/k·mol)	B (J/k·mol)	C	...
S	22.82	3.90	(—)	(—)
L	27.20	(—)	(—)	(—)

by inspection, choose to ignore these terms

$$\Delta C_P^{S\to L}(T) = (A^L - A^S) + (\underbrace{B^L}_{0} - B^S)t + \ldots$$
$$= (A^L - A^S) + (-B^S)\frac{T}{1000K}$$
$$\Delta H^{S\to L}(T) = \Delta H^{S\to L}(T_M) + (A^L - A^S)(T - T_M) - (\frac{B^S}{1000K})\frac{1}{2}(T^2 - T_M^2)$$

Very important quantity for controlling Si solidification, critical process for making computer chips & solar cells

slide: ΔH plotted