

Thermodynamics

7/17/04

CIDER/ITP Summer School

Mineral Physics Program

Fundamentals of mineralogy, petrology, phase equilibria

- Lecture 1. Composition and Structure of Earth's Interior (Lars)
- Lecture 2. Mineralogy and Crystal Chemistry (Abby)
- Lecture 3. Introduction to Thermodynamics (Lars)

Fundamentals of physical properties of earth materials

- Lecture 4. Elasticity and Equations of State (Abby)
- Lecture 5. Lattice dynamics and Statistical Mechanics (Lars)
- Lecture 6. Transport Properties (Abby)

Frontiers

- Lecture 7. Electronic Structure and Ab Initio Theory (Lars)
- Lecture 8. Experimental Methods and Challenges (Abby)
- Lecture 9. Building a Terrestrial Planet (Lars/Abby)

Tutorials

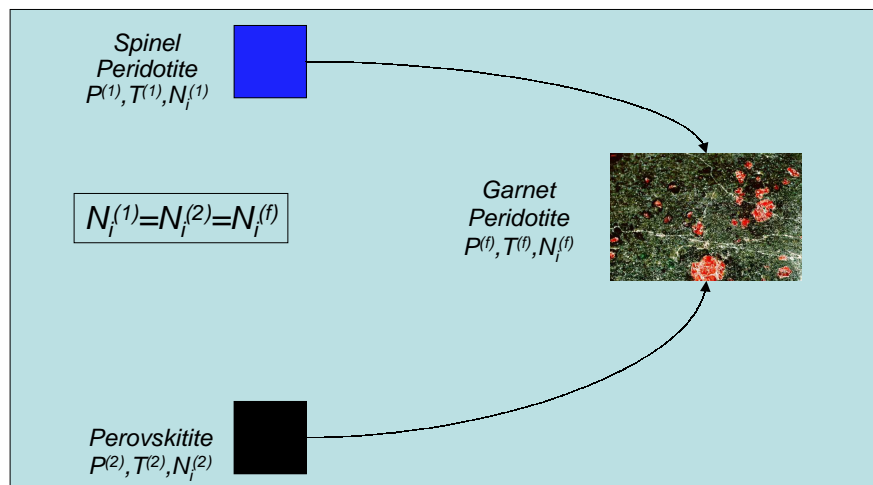
- Constructing Earth Models (Lars)
- Constructing and Interpreting Phase Diagrams (Abby)
- Interpreting Lateral Heterogeneity (Abby)
- First principles theory (Lars)

Scope of Thermodynamics

- Applicable to any system
- Only to a certain set of states, called equilibrium states
- Only to certain properties of those states: macroscopic
- No specific, quantitative predictions, instead, limits and relationships

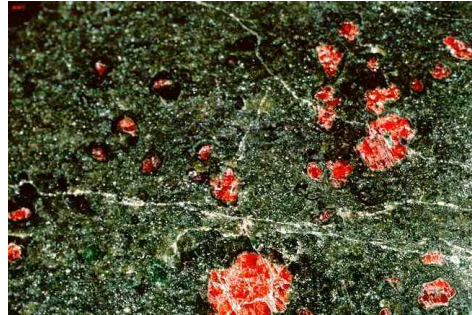


Equilibrium



Macroscopic Properties

- Volume (Density)
- Entropy
- Energy
- Proportions of Phases
- Composition of Phases
- ...
- Not
 - Crystal size
 - Crystal shape
 - Details of arrangement

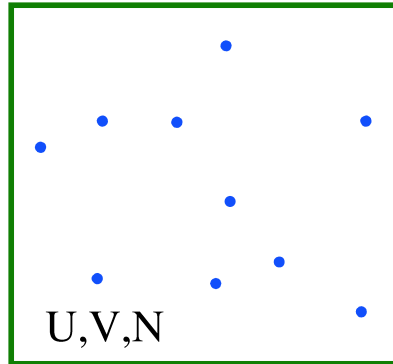


Thermodynamic Variables

- Second Order
 - Heat capacity $C_p = T \left(\frac{\partial S}{\partial T} \right)_{P, N_i}$
 - Thermal expansivity $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P, N_i}$
 - Bulk modulus $K_S = -V \left(\frac{\partial P}{\partial V} \right)_{S, N_i}$
 - Grüneisen parameter $\gamma = -\frac{V}{T} \left(\frac{\partial T}{\partial V} \right)_{S, N_i}$
- First Order
 - V: Volume,
 - S: Entropy
 - N_i : Amount of components
 - P: Pressure
 - T: Temperature
 - μ_i : Chemical Potential

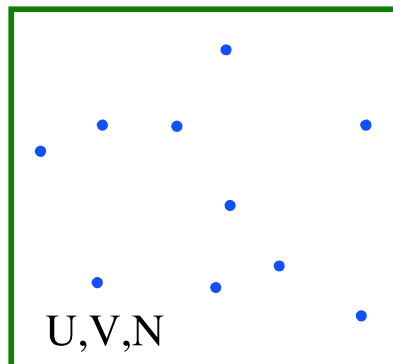
Foundations 1

- What defines the equilibrium state of our system?
 - Three quantities
 - N_i (Composition)
 - V (Geometry)
 - U (“thermal effects”)
- Ideal Gas
 - Energy is all kinetic so
 - $U = \sum_i m_i v_i^2$
 Ω ways to redistribute KE among particles while leaving U unchanged



Foundations 2

- Entropy
 - $S = R \ln \Omega$
 - $S = S(U, V, N_i)$
- Relationship to U
 - As U decreases, S decreases
 - S monotonic, continuous, differentiable: invertible
- $U = U(S, V, N_i)$
- *Fundamental Thermodynamic Relation*



Properties of Internal Energy, U

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, N_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N_i} dV + \left(\frac{\partial U}{\partial N_j}\right)_{V, S, N_{i \neq j}} dN_j$$

define

$$T = \left(\frac{\partial U}{\partial S}\right)_{V, N_i}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S, N_i}$$

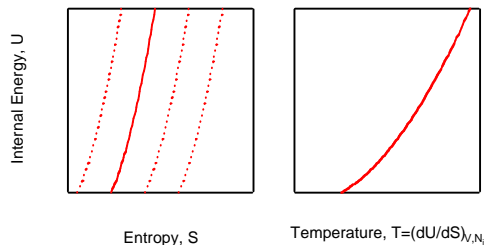
$$\mu_j = \left(\frac{\partial U}{\partial N_j}\right)_{V, S, N_{i \neq j}}$$

then

$$dU = TdS - PdV + \mu_j dN_j \quad \bullet \text{ Complete First Law}$$

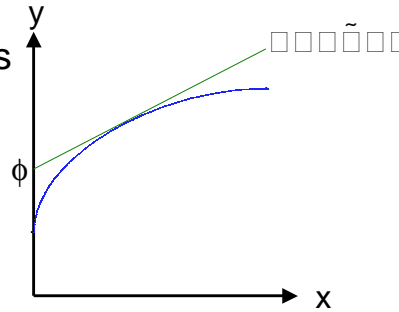
Fundamental Relation

- $U = U(S, V, N_i)$
- Complete information of all properties of all equilibrium states
- S, V, N_i are natural variables of U
- $U = U(T, V, N_i)$ not fundamental



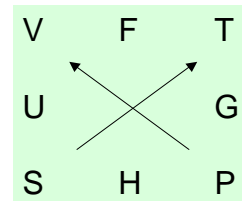
Legendre Transformations

- Two equivalent representations
 - $y=f(x)$
 - $\phi=y-px$
 - i.e. $\phi=g(p)$
- Identify
 - $y \rightarrow U$, $x \rightarrow V, S$, $p \rightarrow P, T$, $\phi \rightarrow G$
- $G = U - dU/dV V - dU/dS S$ or
- $G(P, T, N_i) = U(V, S, N_i) + PV - TS$
- $G(P, T, N_i)$ is also fundamental!



Thermodynamic Square

- Thermodynamic Potentials
 - F = Helmholtz free energy
 - G = Gibbs free energy
 - H = Enthalpy
 - U = Internal energy
- Surrounded by natural variables
- First derivatives
- Second derivatives (Maxwell Relations)

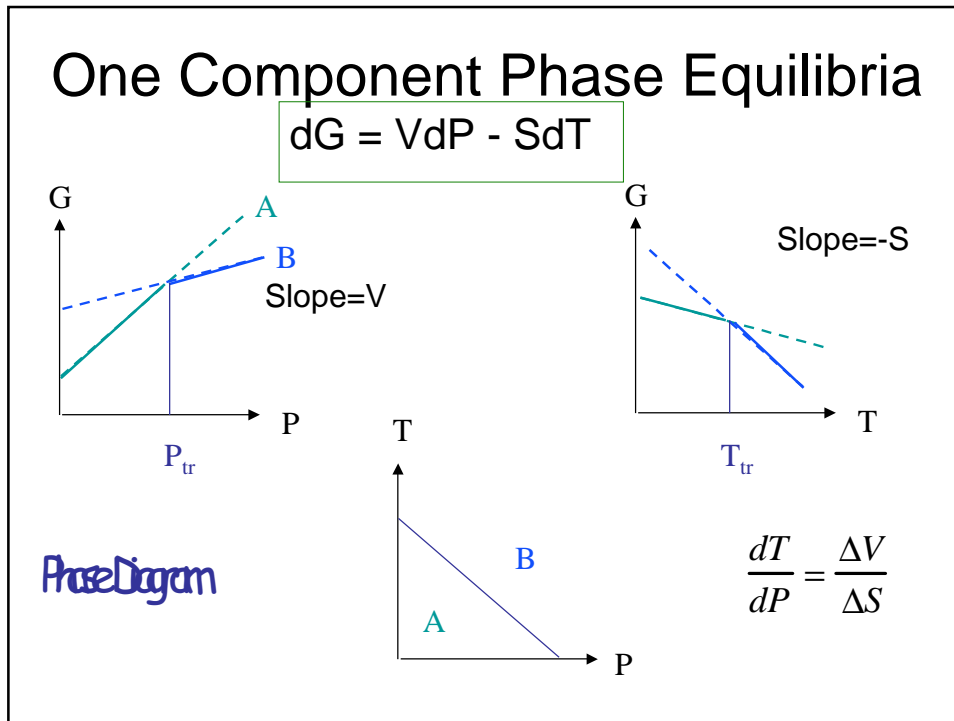


Summary of Properties

| | | | |
|--|------|---|--|
| | 1 | $\left(\frac{\partial}{\partial P}\right)_T$ | $\left(\frac{\partial}{\partial T}\right)_P$ |
| 1 | G | V | $-S$ |
| $\left(\frac{\partial}{\partial P}\right)_T$ | V | $-\frac{V}{K_T}$ | $V\alpha$ |
| $\left(\frac{\partial}{\partial T}\right)_P$ | $-S$ | $-\left(\frac{\partial S}{\partial P}\right)_T$ | $-\frac{C_P}{T}$ |

Phase Equilibria

- How does G change in a spontaneous process at constant P/T?
 - L1: $dU = dQ - PdV$
 - L2: $dQ \leq TdS$
 - $dG = dU + PdV + vdP - TdS - SdT$
 - Substitute L1, take constant P,T
 - $dG = dQ - TdS$
 - This is always less than zero by L2.
- G is lowered by any spontaneous process
- State with the lowest G is stable

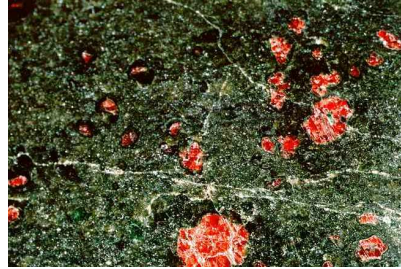


Two Component Phase Equilibria

- Phase: Homogeneous in chemical composition and physical state
- Component: Chemically independent constituent
- Example: $(\text{Mg,Fe})_2\text{SiO}_4$
- Phases: olivine, wadsleyite, ringwoodite, ...
- Components: $\text{Mg}_2\text{SiO}_4, \text{Fe}_2\text{SiO}_4$
- Why not Mg, Fe, Si, O?

Phase Rule

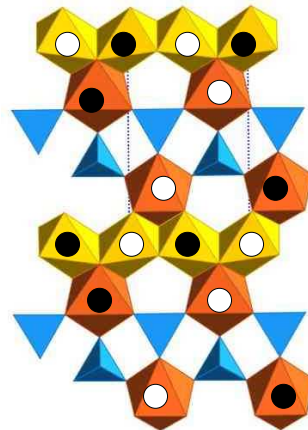
- p phases, c components
- Equilibrium: uniformity of intensive variables across coexisting phases:
- $P^{(a)}, T^{(a)}, \mu_i^{(a)}$
- Equations
 - $2(p-1) + c(p-1)$
- Unknowns
 - $2p + p(c-1)$
- Degrees of Freedom
 - $f = c - p + 2$



$c \approx 5, p \approx 4$
 $f \approx 3$

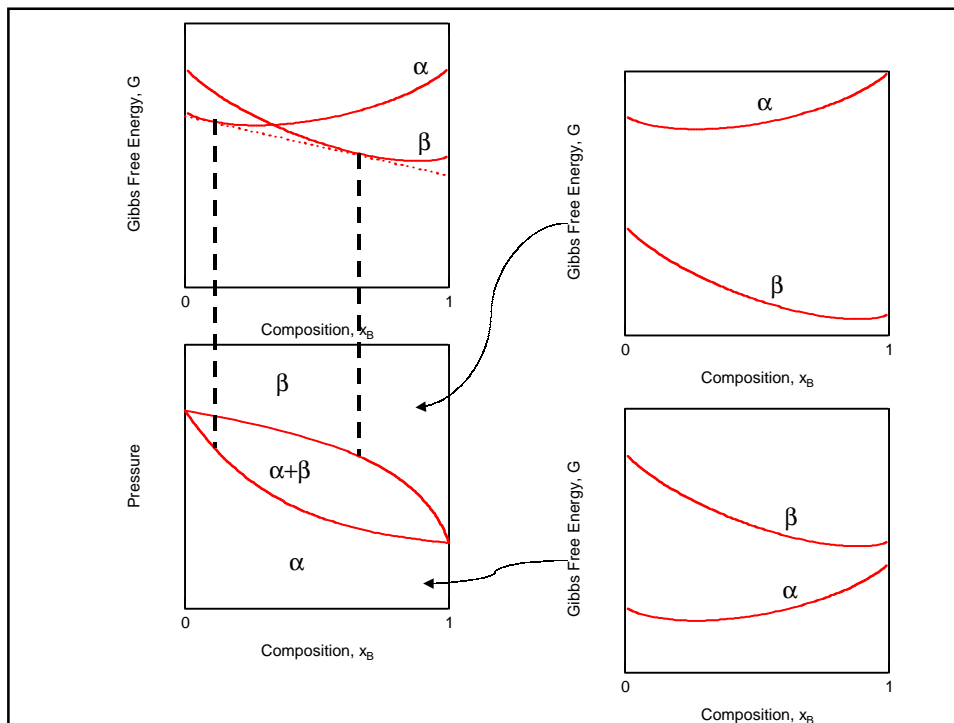
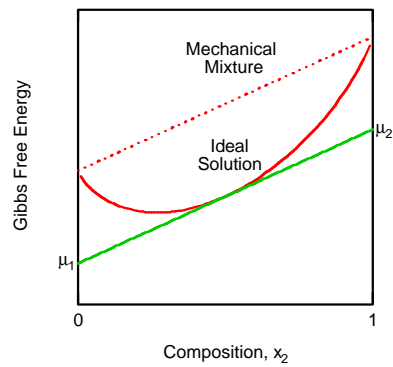
Properties of ideal solution 1

- N_1 type 1 atoms, N_2 type 2 atoms, N total atoms
- $x_1 = N_1/N, x_2 = N_2/N$
- Volume, Internal energy: linear
 - $V = x_1 V_1 + x_2 V_2$
- Entropy: non-linear
 - $S = x_1 S_1 + x_2 S_2 - R(x_1 \ln x_1 + x_2 \ln x_2)$
- $S_{conf} = R \ln \Omega$
 Ω is number of possible of arrangements.



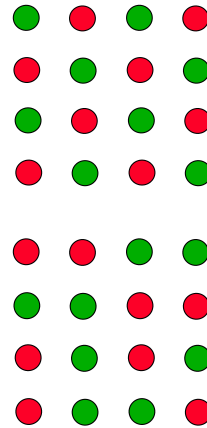
Properties of Ideal Solution 2

- Gibbs free energy
 - $G = x_1 G_1 + x_2 G_2 + RT(x_1 \ln x_1 + x_2 \ln x_2)$
- Re-arrange
 - $G = x_1(G_1 + RT \ln x_1) + x_2(G_2 + RT \ln x_2)$
- $G = x_1 \mu_1 + x_2 \mu_2$
 $\mu_i = G_i + RT \ln x_i$



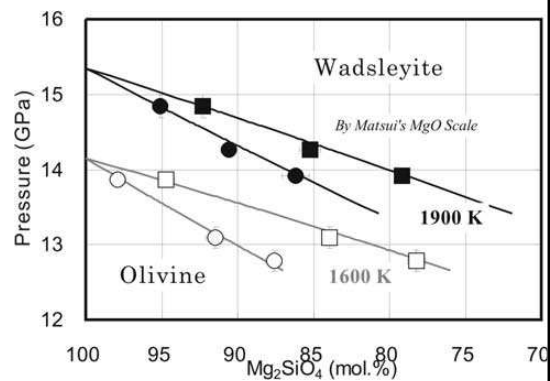
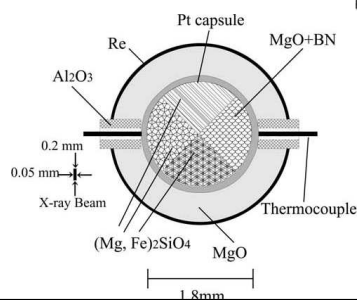
Non-ideal solutions

- Internal Energy a non-linear function of composition
 - Compare A-B bond energy to average of A-A, B-B
 - Tendency towards dispersal, clustering.
- Exsolution
 - cpx-opx, Mg-pv, Ca-pv
- Formally:
 - $\mu_i = G_i + RT \ln a_i$
 - a_i is the activity and may differ from the mole fraction



Example: Phase Equilibria

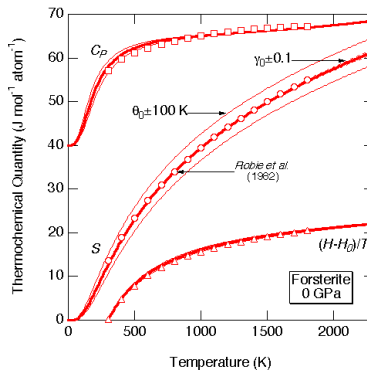
- Mg_2SiO_4 - Fe_2SiO_4 System
- Olivine to wadsleyite phase transformation



Katsura et al. (2004) GRL

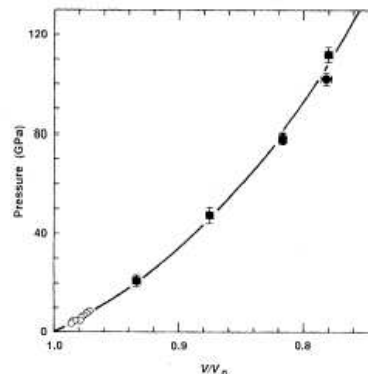
Example: Thermochemistry

- Increase temperature slightly, measure heat evolved
- $C_P = (dH/dT)_P$
- Calculate S, H by integration
- $(dT/dP)_{eq} = \Delta V / \Delta S$



Example: Equation of State

- Volume: x-ray diffraction
- Pressure: Ruby Fluorescence
- $(dG/dP)_T = V(P, T)$
- More useful theoretically:
- $-(dF/dV)_T = P(V, T)$



Knittle and Jeanloz (1987) Science

Road Map

- Equation of State
- Elasticity
 - $V \rightarrow \epsilon_{ij}$
 - $P \rightarrow \sigma_{ij}$
- Statistical Mechanics
 - Microscopic to Macroscopic
- Irreversible Thermodynamics
 - States vs. Rates

