

Crust to Core workshop: An introduction to Perple_X

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Part 1: A very brief introduction

American Oxford Dictionary

Thermodynamics: the branch of physical science that deals with the relations between heat and other forms of energy (such as mechanical, electrical, or chemical energy), and, by extension, of the relationships and interconvertibility of all forms of energy.

An introduction to (or some revision on) thermodynamics

American Oxford Dictionary

The **first law of thermodynamics** states the equivalence of heat and work and reaffirms the principle of conservation of energy. The **second law** states that heat does not of itself pass from a cooler to a hotter body. Another, equivalent, formulation of the second law is that the entropy of a closed system can only increase. The **third law** (also called Nernst's heat theorem) states that it is impossible to reduce the temperature of a system to absolute zero in a finite number of operations.

An introduction to (or some revision on) thermodynamics: Some definitions

- A **system** is some part of the universe that you want to study and understand
- The **surroundings** are everything else in the universe that is not in our system
- The **system** can be *open* or *closed* to (*isolated from*) the surroundings in terms of both matter and energy

All Changes in a system are associated with the **transfer of energy**

Natural systems tend toward states of minimum energy

**An introduction to (or some revision on) thermodynamics:
Some definitions**

- In our case, a **system** is likely to be a mineral or a rock
- In this case, it is comprised of chemical **components** that describe chemical variability in that mineral or a rock
- Typical **components** might be FeO, MgO and SiO₂ used to describe olivine
- A **phase** is any mechanically separable and chemically homogenous portion of the system, e.g. a melt, a fluid, or a mineral in a rock
- A **reaction** is anything that changes the nature of the phases within a system

**An introduction to (or some revision on) thermodynamics:
Some definitions**

- Thermodynamics is primarily concerned with macroscopic energies of microscopic processes that we might or might not fully understand.
- It is convenient to group all of the variables required into two classes:

Intensive variables are independent of the amount of material present:

e.g. Pressure (P) & Temperature (T)

Extensive variables are dependent on the amount of material present:

e.g. Volume (V) & Entropy (S)

An introduction to (or some revision on) thermodynamics

First Law of thermodynamics:

The increase in the internal energy (U) of a thermodynamic system is equal to the amount of heat energy (Q) added to the system plus the work (W) done on the system by the surroundings.

$$0 = dQ + dW - dU$$

$$W(\text{J}) = N \cdot m = P \cdot V \quad (P = \text{force/area [N/m}^2\text{] and } V = \text{m}^3)$$

$$dU = dQ + PdV$$

An introduction to (or some revision on) thermodynamics

Second Law of thermodynamics:

This introduces the notion of entropy (S) which relates change in temperature (T) with the heat energy (Q) added to the system:

$$dS \geq \frac{dQ}{T}$$

Which can be substituted into the first law:

$$dU \leq TdS - PdV$$

An introduction to (or some revision on) thermodynamics

$dU \leq TdS - PdV$ tells us about the energetics of a system without chemical change (i.e. a homogenous phase with no compositional change during the process).

To describe energetic changes coming from mass transfer we use the concept of chemical potential (Gibbs, 1876)

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i} \right)_{S, V, \text{ other components}}$$

Summing the energies associated with all components in the system and adding to our combined laws equation yields

$$dU = TdS - PdV + \sum_{i=1}^k \mu_i dn_i$$

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$$dU = TdS - PdV + \sum_{i=1}^k \mu_i dn_i$$

Is the fundamental equation that we will use to quantify internal energy. This can be transformed to give various combinations of S , V , T and P as the independent variables.

$$\text{Gibbs free energy: } dG = -SdT + VdP + \sum_{i=1}^k \mu_i dn_i$$

Gibbs free energy will be of most interest to us, since P and T are the most obvious choices of independent variables for geologic application

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$$\text{Gibbs free energy: } dG = -SdT + VdP + \sum_{i=1}^k \mu_i dn_i$$

$$\left(\frac{\partial G}{\partial T} \right)_{P, n_i} = -S$$

Change in G with respect to *temperature* = *entropy*

$$\left(\frac{\partial G}{\partial P} \right)_{T, n_i} = V$$

Change in G with respect to *pressure* = *volume*

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} \text{ (Clausius-Clapeyron)}$$

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$$\text{Gibbs free energy: } dG = -SdT + VdP + \sum_{i=1}^k \mu_i dn_i$$

Ignoring (for a while) heat capacity, thermal expansion and isothermal compression...

- If a chemically closed system has two possible states (configurations of phases), the one with the lowest absolute G at any PT should be more stable.
- If both have the same absolute G (the ΔG of moving from one state to the other = 0), they have the same relative stability and a reaction between them is stable.

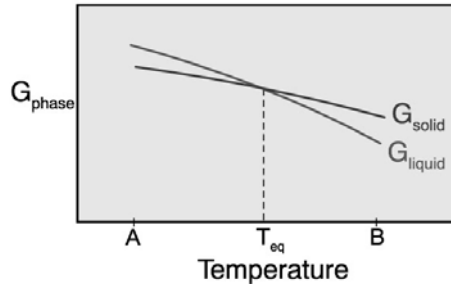
An introduction to (or some revision on) thermodynamics

$$\left(\frac{\partial G}{\partial T}\right)_{P, n_i} = -S, \text{ so } S_{\text{liquid}} > S_{\text{solid}}$$

A: Solid more stable than liquid (low T)
 B: Liquid more stable than solid (high T)

Equilibrium at T_{eq}
 $G_{\text{Liq}} = G_{\text{sol}}$

Melting reaction occurs at T_{eq}



Relationship between Gibbs free energy and temperature for the solid and liquid forms of a substance at constant pressure. After Winter (2001) An Introduction to Igneous and Metamorphic Petrology, Prentice Hall.

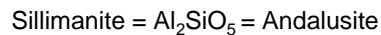
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Two fundamentally different approaches are commonly-used:

1. Find the lowest absolute G to predict the most stable configuration of phases:
 e.g. Perple_X (Connolly)
2. Find the reactions between phases by finding where G is equal between configurations ($\Delta G = 0$):
 e.g. THERMOCALC (Holland & Powell)

Both approaches are very simple for chemically simple systems, for example...

An introduction to (or some revision on) thermodynamics



$$-TS_{\text{Sillimanite}} + PV_{\text{Sillimanite}} = -TS_{\text{Andalusite}} + PV_{\text{Andalusite}}$$

If we know the entropy and volume of sillimanite and andalusite (which are PT dependent), we can easily calculate the PT line along which they both occur...



Useful resources:

- Frank Spear's book (*Metamorphic Phase Equilibria and Pressure-Temperature-Time Paths*) is good for the thermodynamic laws and their derivation (especially chapter 6).
- So are chapters 1-4 of Jamie Connolly's ETH course notes (http://www.perplex.ethz.ch/thermo_course)