Announcements

Reading: p. 92-95

Homework 1 due today

Thermodynamics: Why?

- Description of what we observe through macroscopic, measurable quantities
- Qualitative and quantitative understanding of crystallization and melting

"It must be admitted, I think, that the laws of thermodynamics have a different feel from most of the other laws of physics. There is something more palpably verbal about them- they smell more of their human origin. The guiding motif is strange to most of physics: namely, a capitalizing of the universal failure of human beings to construct perpetual motion machines…"

-P.W. Bridgman, experimental thermodynamicist

Laws of Thermodynamics, or… things you can’t do

First Law: the total energy is conserved.

Can’t make a device that continuously outputs energy as work without the need for any energy input

Second Law: the total entropy increases.

Can’t make a device that continuously converts all energy taken in as heat into work, or

All heat engines require a temperature difference to operate

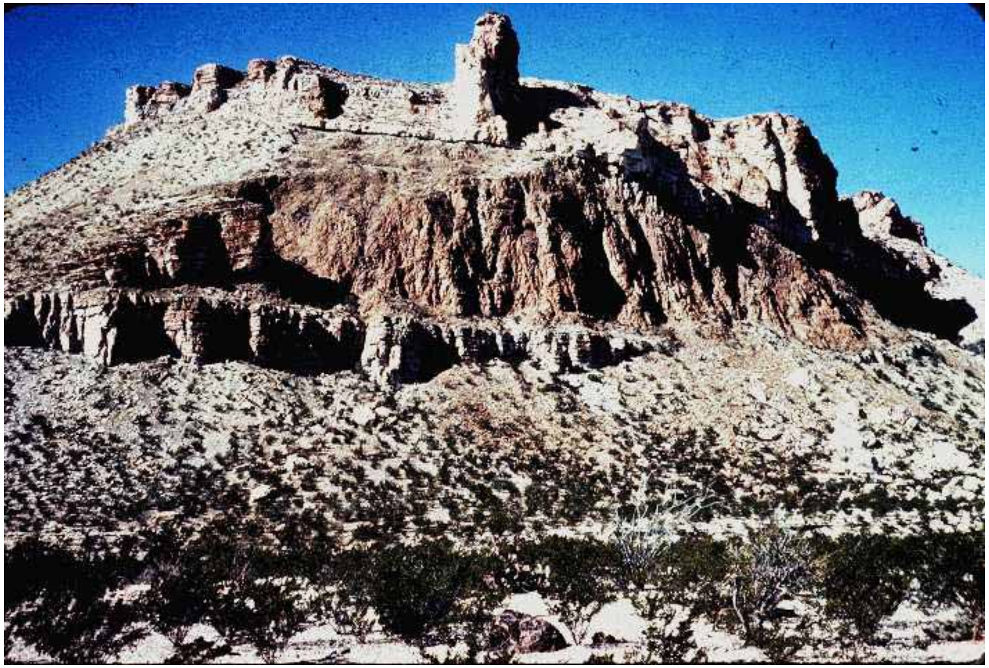
Third Law: the absolute temperature remains above zero degrees.

Can’t make a freezer that reduces the temperature of any macroscopic system to absolute zero.

Thermodynamics: definitions

- A system:

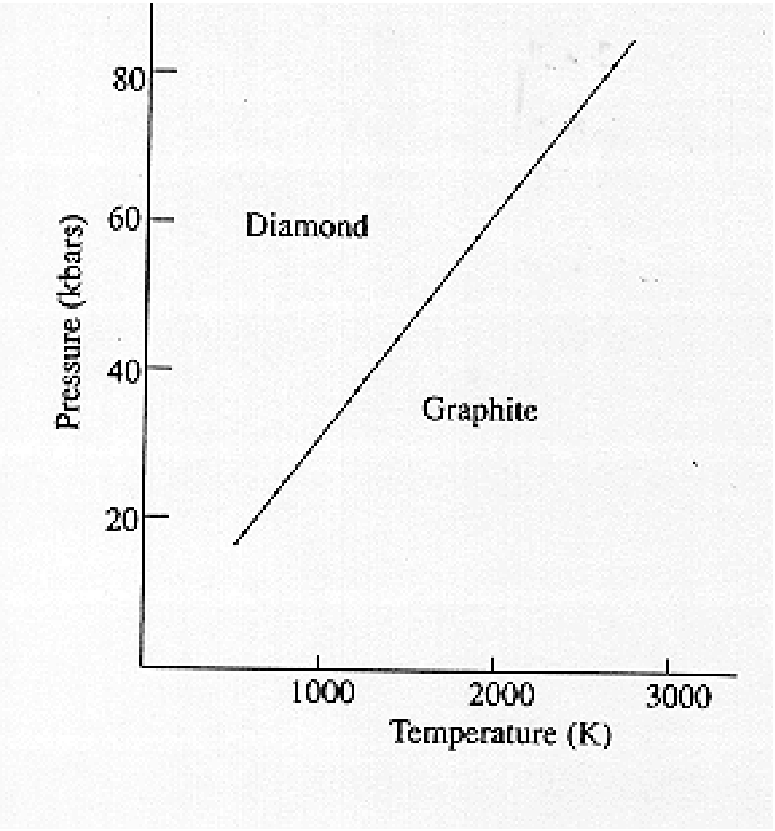
  Some portion of the universe that you wish to study



- The surroundings:

  The adjacent part of the universe outside the system

Thermodynamics: definitions



Include examples!

A Component: chemical constituent: CaO, Ca, $CaSiO_3$

A Phase: a mechanically separable portion of a system

- Mineral
- Liquid
- Vapor

More thermodynamic ideas

a Reaction: some change in the nature or types of phases in a system

reactions are written in the form:

reactants = products

Changes in a system are associated with the transfer of energy

Natural systems tend toward states of minimum energy

Energy States of a System

- Unstable: falling or rolling
- Stable: at rest in lowest energy state
- Metastable: in low-energy perch
- Diamonds at the Earth's surface?

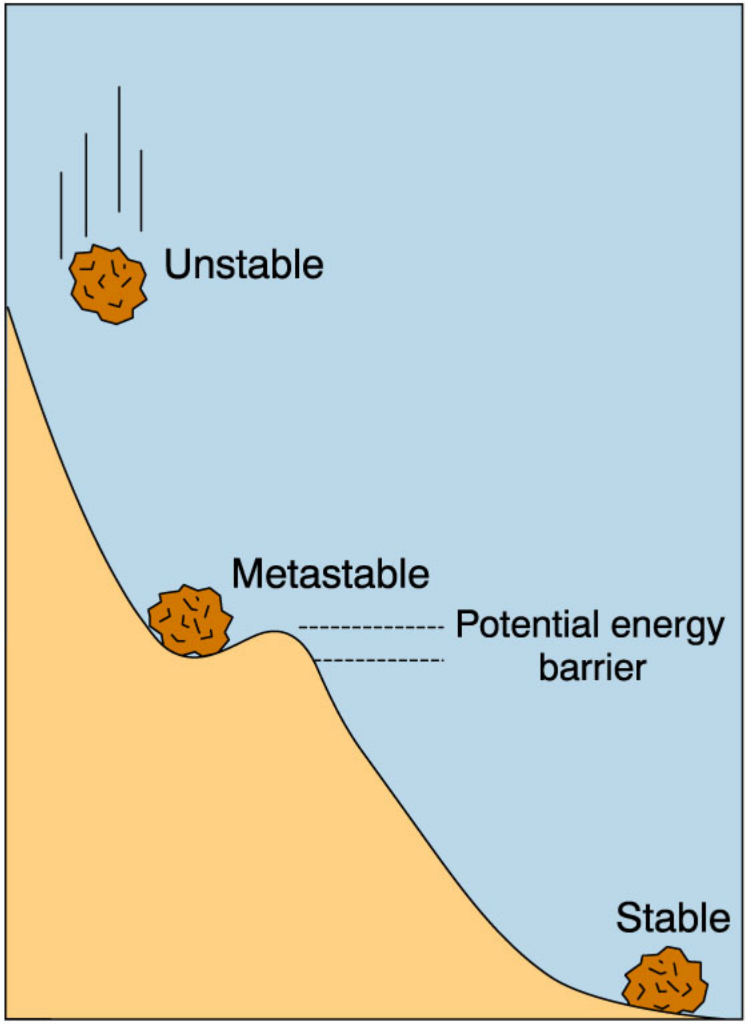


Figure 5-1. Stability states. Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

Gibbs Free Energy

Gibbs free energy is a measure of chemical energy

All chemical systems tend naturally toward states of minimum Gibbs free energy

$$G = H - TS$$

Where:

G = Gibbs Free Energy

H = Enthalpy (heat content)

T = Temperature in Kelvins

S = Entropy (can think of as randomness)

Gibbs Free Energy

The change in some property, such as G for a reaction of the type:

$$2\,A + 3\,B = C + 4\,D$$

$$\Delta G = \Sigma\,(n\,G)_{products} - \Sigma(n\,G)_{reactants}$$

$$= G_C + 4G_D - 2G_A - 3G_B$$

- Is negative when products are more stable than reactants
- Is positive when the other way around

A note about variables

Intensive variables: value doesn't change with quantity of material

T, P, X (composition)

Extensive variables: value changes with quantity of material

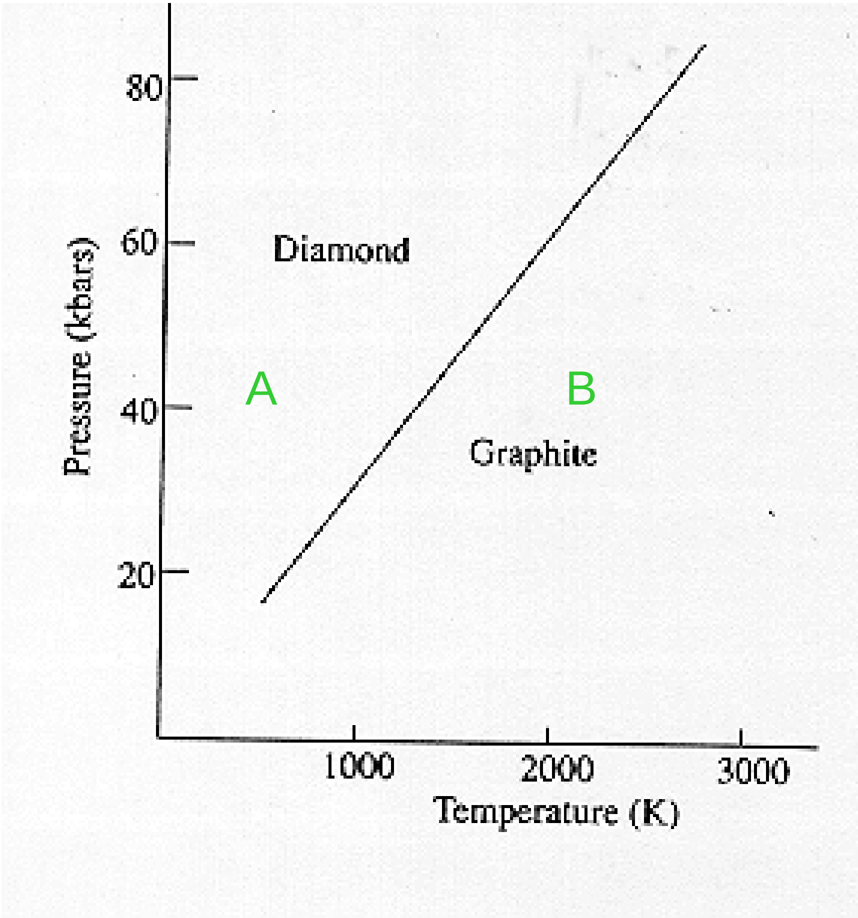
G, H, S

Turn extensive into intensive by making molar values:

$\bar{G}$, $\bar{H}$, $\bar{S}$

Molar values have a bar on top!

Gibbs Free Energy



Does diamond or graphite have the lowest G at point A?

What about at point B?

The phase assemblage with the lowest G under a specific set of conditions is the most stable

The Phase Rule

$$F = C - P + 2$$

In isobaric or isothermal systems, this = 1 instead of 2!

F = # degrees of freedom

The number of intensive parameters that must be specified "dialed" in order to completely determine the system

P = # of phases

phases are mechanically separable constituents

C = minimum # of components

(chemical constituents that must be specified in order to define all phases)

2 = 2 intensive parameters

Usually T, P, or x(composition) for geologists

System must be in equilibrium!!!

One-component systems

- Our old friends the SiO_2 polymorphs

Summary of important points

The laws of thermodynamics have never been broken

- Definitions
- Natural systems tend to states of minimum energy
- Phase with lowest G (under set conditions) is most stable
- Phase rule allows us to determine F (degrees of freedom) of a system