

Lecture 15: 11.02.05 Phase changes and phase diagrams of single-component materials

Figure removed for copyright reasons.

Source: Abstract of Wang, Xiaofei, Sandro Scandolo, and Roberto Car. "Carbon Phase Diagram from *Ab Initio* Molecular Dynamics." *Physical Review Letters* 95 (2005): 185701.

Today:

LAST TIME	2
BEHAVIOR OF THE CHEMICAL POTENTIAL/MOLAR FREE ENERGY IN SINGLE-COMPONENT MATERIALS	4
<i>The free energy at phase transitions</i>	4
PHASES AND PHASE DIAGRAMS SINGLE-COMPONENT MATERIALS	6
<i>Phases of single-component materials</i>	6
<i>Phase diagrams of single-component materials</i>	6
<i>The Gibbs Phase Rule</i>	7
<i>Constraints on the shape of phase boundaries (coexistence curves): The Clausius-Clapeyron equation</i>	9
<i>Example single-component phase diagrams</i>	10
<i>Walking along lines of constant temperature or pressure in a single-component phase diagram</i>	12
ICE IX	13
REFERENCES	14

Reading: Engel and Reid Ch. 8.1-8.5

Supplementary Reading: -

Last time

- □ Stable equilibria have requirements set by the second law:

- □ ...these lead to material property requirements:

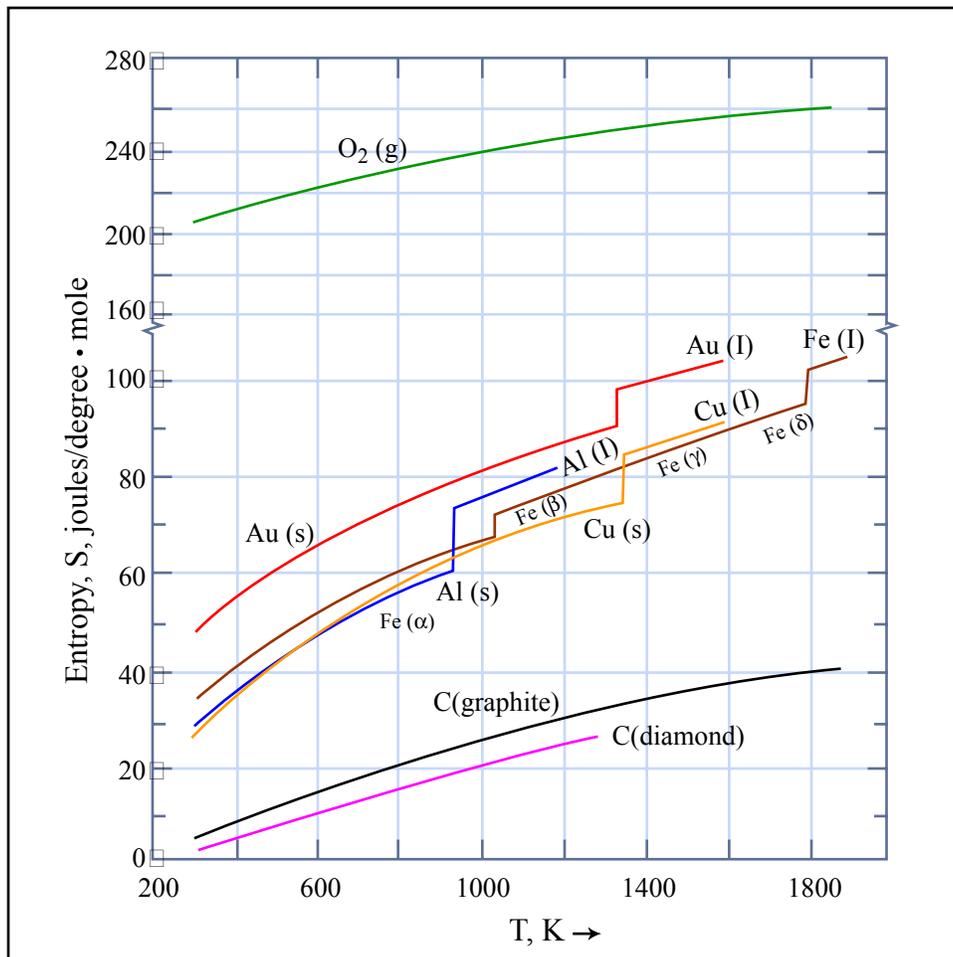
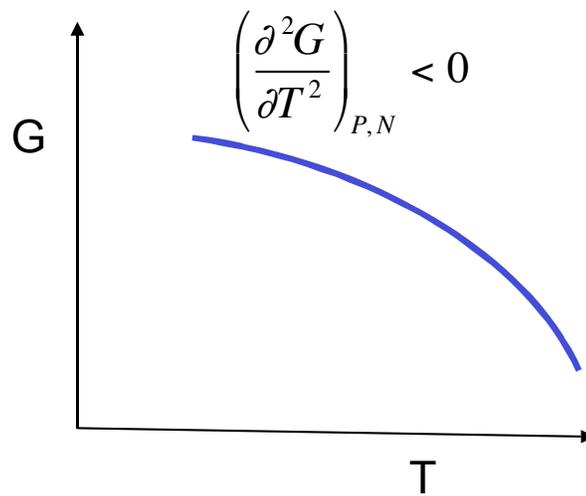


Figure by MIT OCW.

- ...ergo, the shape of free energy curves is not arbitrary!

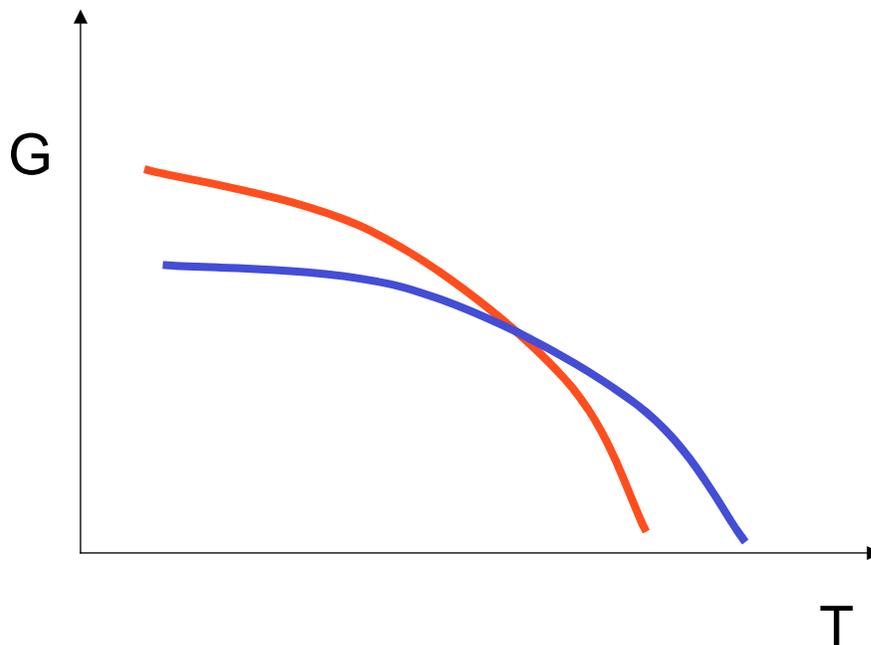


Behavior of the chemical potential/molar free energy in single-component materials

The free energy at phase transitions

• **MAIN IDEA:** Phases of a material are described by unique free energy functions—each phase has its own free energy curve. The stable form of a material is that form with the lowest free energy at any given temperature, and crossing points in free energy curves define the location of phase transitions.

- Earlier in the term, we examined the behavior of the heat capacity and enthalpy as heat was added to single-component materials near a phase transition. We are now ready to address what happens to the free energy at a phase transition? Let's consider the case of a solid that is melting to become a liquid at constant pressure:
 - We can plot the free energy as a function of temperature for the liquid, and for the solid. The free energy curves of each phase are unique- even though both phases are composed of the same atoms in single-component systems, they have unique interactions in the solid and liquid states. Thus the free energy of the liquid has a different temperature dependence than the solid.



- What is going on with the Gibbs free energy at the melting point?

- We showed earlier in the term that the enthalpy has a discontinuous jump at the melting point- the transformation to the liquid state absorbs thermal energy and 'stores' it in the liquid. The enthalpy of melting ΔH_m is absorbed as the phase fraction of liquid moves from 0 to 1:

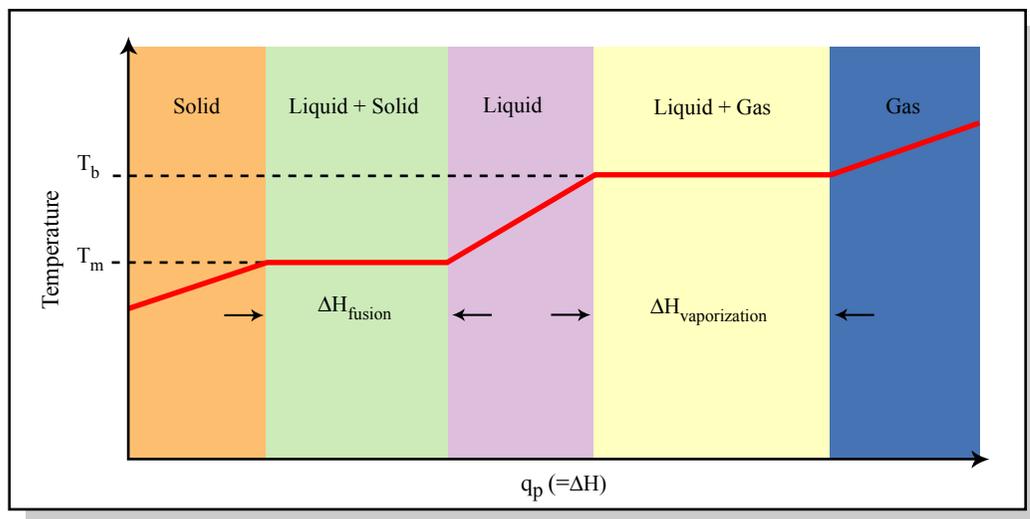
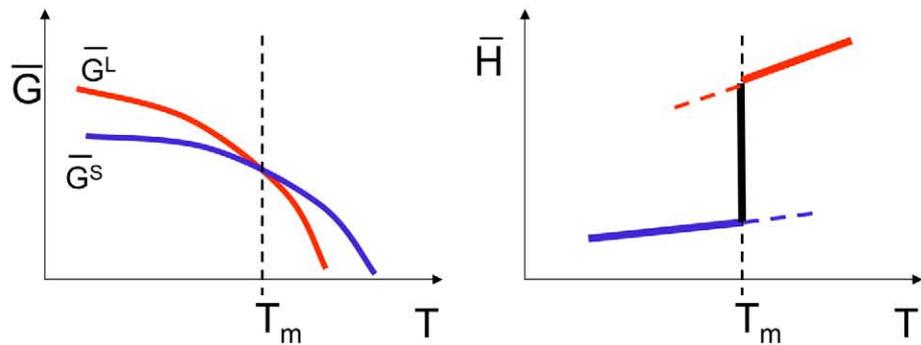
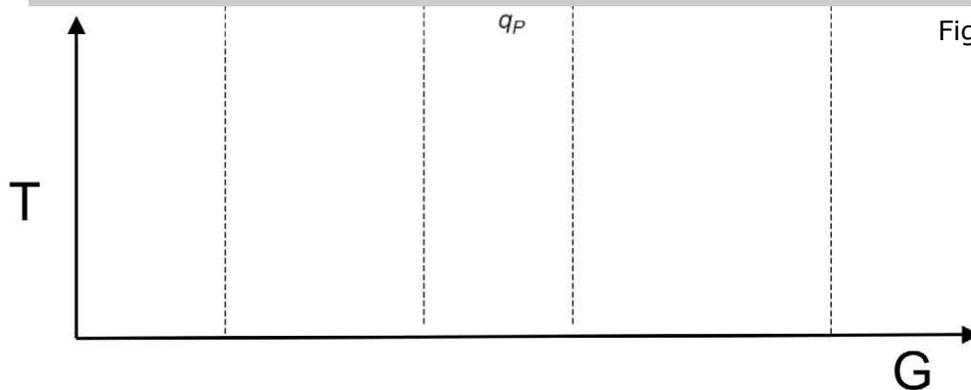


Figure by MIT OCW.



- If we plot the Gibbs free energy vs. the heat absorbed by the material (remember, the heat absorbed $dq = dH$ at constant pressure), we get the lower diagram. During the transformation, the free energy of the solid and liquid are equal and constant.

Phases and phase diagrams single-component materials

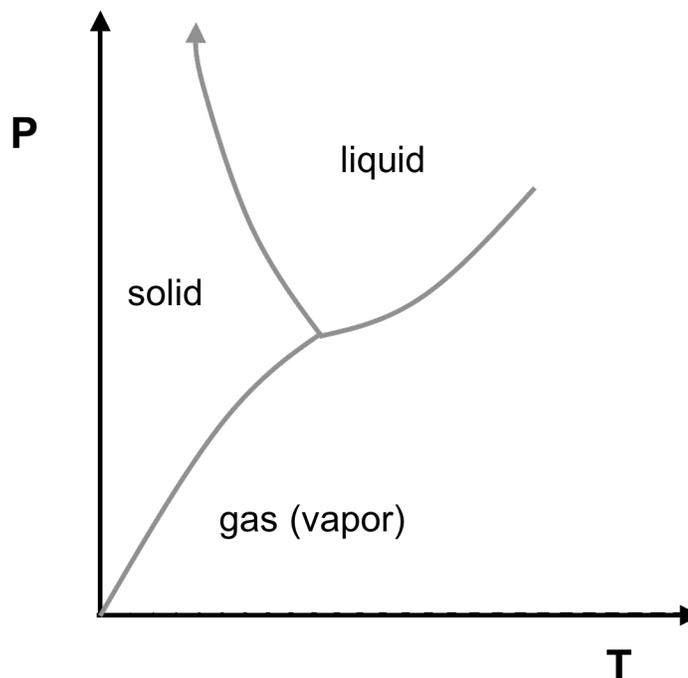
- **MAIN IDEA:** Single-component phase diagrams map out in P-T, P-V, or P-V-T space the identities of the stable equilibrium form or forms of a material as a function of the environmental conditions.

Phases of single-component materials

- Day-to-day experience tells us that many materials exist in multiple forms as a function of the environmental conditions- particularly temperature. Solids melt, liquids boil, and solids can sublime directly to vapor. Materials may also exhibit different crystalline forms in the solid state, depending on the conditions of temperature and pressure. Such structural variants (that have the same composition in single-component materials) are known as **polymorphs** or **allotropes** (an allotrope typically refers to different structural forms of pure elements). Many compounds have 4 or 5 different stable crystal structures, depending on the temperature.

Phase diagrams of single-component materials

- Phase diagrams are maps of the phases present in a system *at equilibrium* as a function of 2 or more thermodynamic variables. They are extremely useful as practical indicators of the equilibrium phase behavior of even complex systems.



- Phase diagrams obey the laws of thermodynamics! Thus there are constraints on the structure of phase diagrams. To understand these constraints and discuss single-component phase diagrams further, we will first introduce the *Gibbs phase rule*.

The Gibbs Phase Rule

- **MAIN IDEA:** The Gibbs phase rule determines how many phases can be in equilibrium simultaneously, and whether those phases are stable along a field, line, or point in the phase diagram.

- The condition for equilibrium at constant temperature and pressure for closed systems is given by a set of equations for the chemical potentials of each component:

(Eqn 2)

$$\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \dots = \mu_1^P$$

$$\mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \dots = \mu_2^P$$

...

$$\mu_C^\alpha = \mu_C^\beta = \mu_C^\gamma = \dots = \mu_C^P$$

- Since each = sign in the above set provides one independent equation, we have in total $C(P-1)$ equations.
- In addition to the chemical potential criteria, we have an additional set of relationships between the variables of the system at equilibrium, via the Gibbs-Duhem equation. Recall Gibbs-Duhem is:

- ...which can be written for each of the P phases present in a system. Thus in total we have $C(P-1) + P$ equations.

- **Degrees of freedom:**

- This last equation is called the Gibbs phase rule. This is a very useful equation, as it specifies the number of phases that can co-exist for a given condition of a system.

Application of the phase rule

- Let's return to our model single-component phase diagram above, and apply the phase rule to it. Consider first a single-phase region:

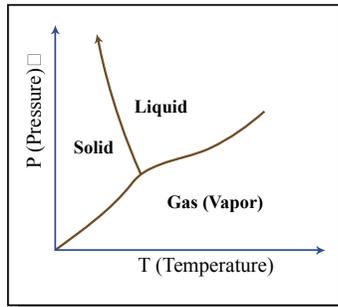


Figure by MIT OCW.

- There are two degrees of freedom in a single-phase region of a single-component system- thus 2 parameters of the system can vary and that single phase will remain in equilibrium. This is shown in the diagram by the range of T and P values that remain in the solid phase, for example.
- What about the boundaries between two phases? If two phases are in equilibrium at the boundary, then we have:

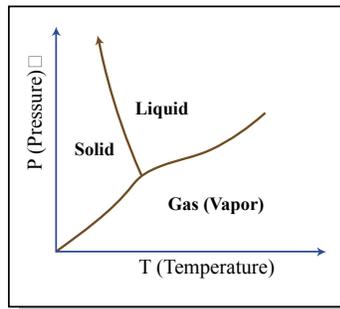


Figure by MIT OCW.

- Thus only one variable can vary independently along the coexistence curve- the other variable must be coupled to it. Mathematically, for a P - T diagram:
- Lastly, let's consider the vertex of the solid-liquid, liquid-gas, and solid-gas coexistence curves:

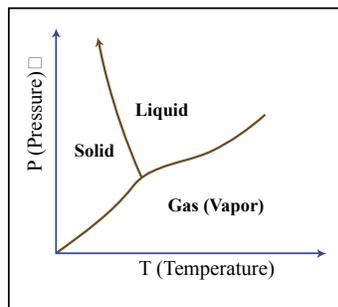


Figure by MIT OCW.

- There is one unique value of pressure and temperature, the **triple point**, that can allow the 3 phases to co-exist; any change in the variables of the system causes the equilibrium to shift to one between only 1 or 2 phases.

Constraints on the shape of phase boundaries (coexistence curves): The Clausius-Clapeyron equation

- □ Just as the relationship between thermodynamic variables dictates the shape of free energy curves, equilibrium relationships have something to say about the shape of coexistence curves on a phase diagram. An important relationship known as the **Clausius-Clapeyron equation** provides a link between the conditions for 2-phase equilibrium and the slope of the 2-phase line on the P vs. T diagram:
 - □ For 2 phases in equilibrium (let's use the example of solid and liquid in equilibrium at the melting temperature):

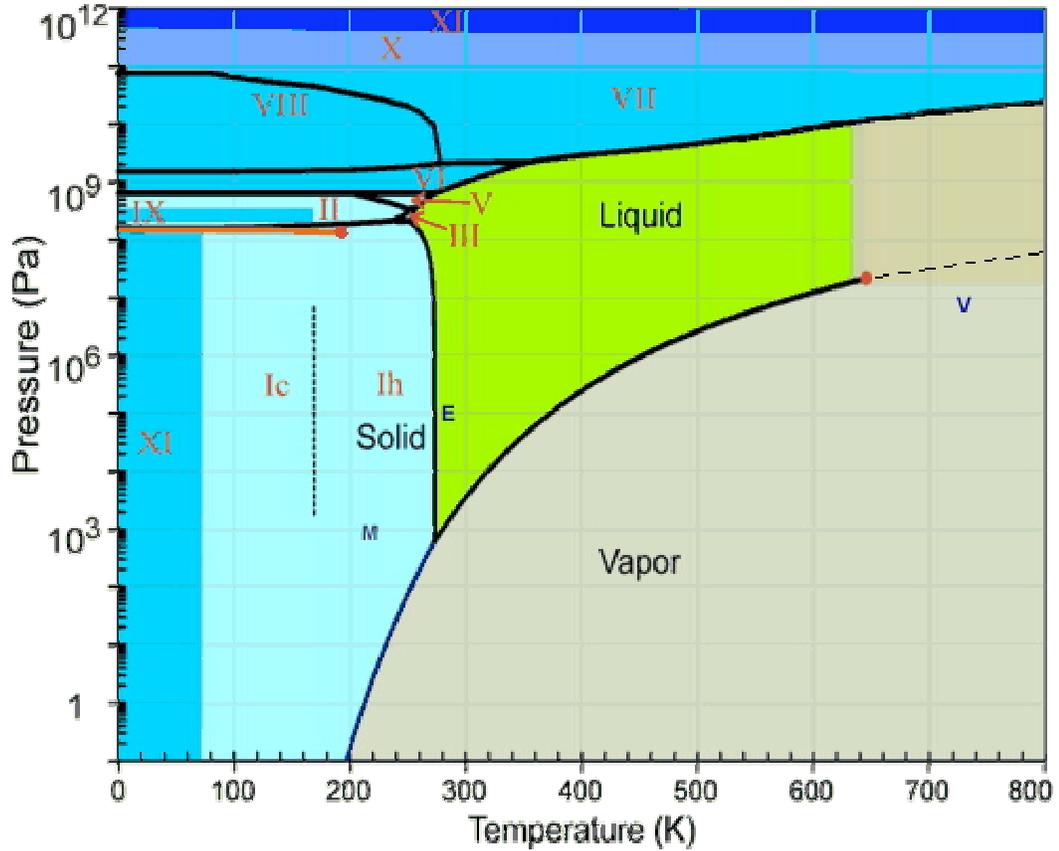
$$\mu^S = \mu^L$$

- To find a nearby condition of T and P where the two phases are still in equilibrium, we must have:(2)

- The Clausius-Clapeyron equation dictates the slope of the two-phase co-existence curve for single-component materials. We already know that the enthalpy change on melting is typically positive, therefore the sign of the change in volume on melting will usually dictate whether the slope of P vs. T is positive or negative.

Example single-component phase diagrams

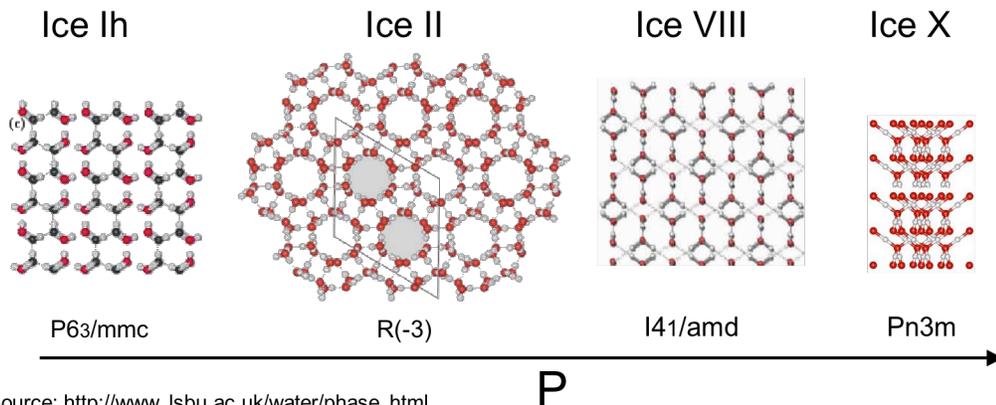
- The phase diagram of water:



Source: <http://www.lsbu.ac.uk/water/phase.html>

Courtesy of London South Bank University. Used with permission.

- Water transitions through increasingly dense crystal structures as pressure is increased:



Source: <http://www.lsbu.ac.uk/water/phase.html>

Courtesy of London South Bank University. Used with permission.

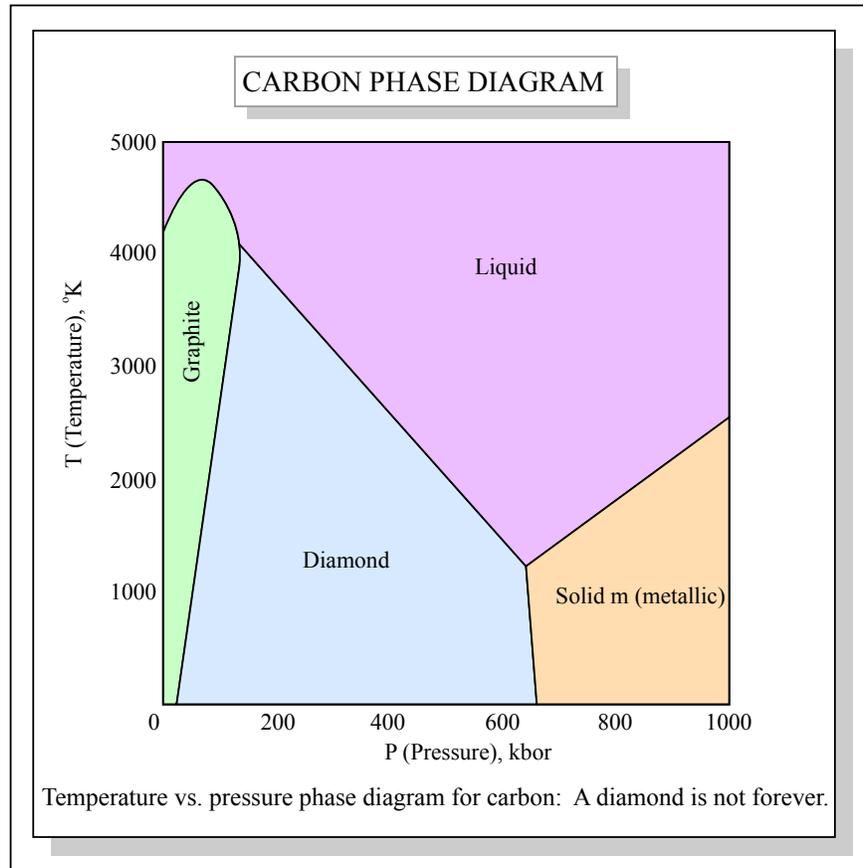


Figure by MIT OCW.

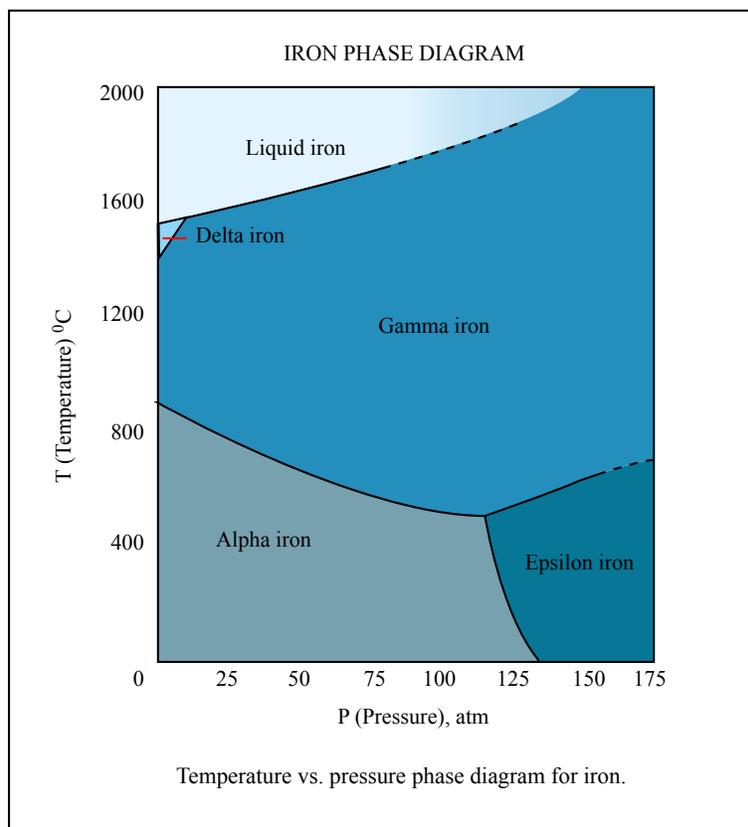


Figure by MIT OCW.

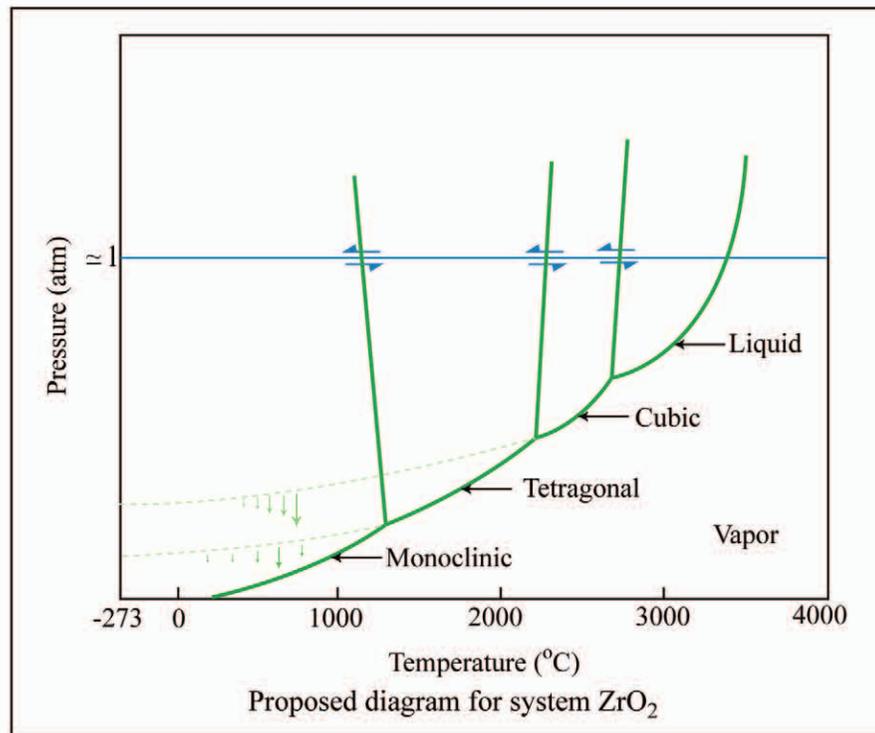


Figure by MIT OCW.

Walking along lines of constant temperature or pressure in a single-component phase diagram

- Consider now how the free energy varies as we move along a line of a single-component phase diagram at constant pressure or constant temperature:

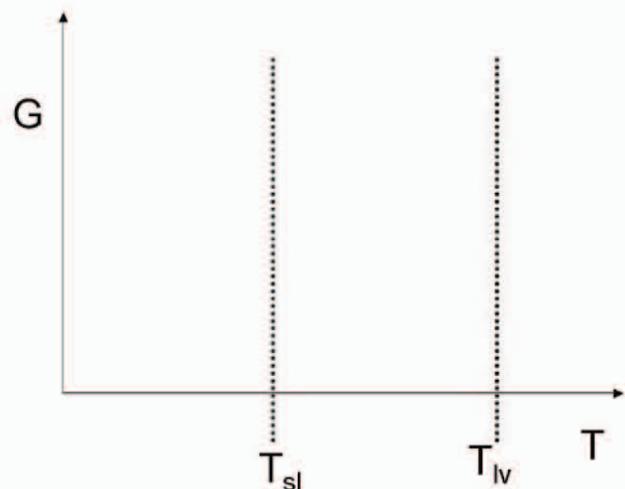
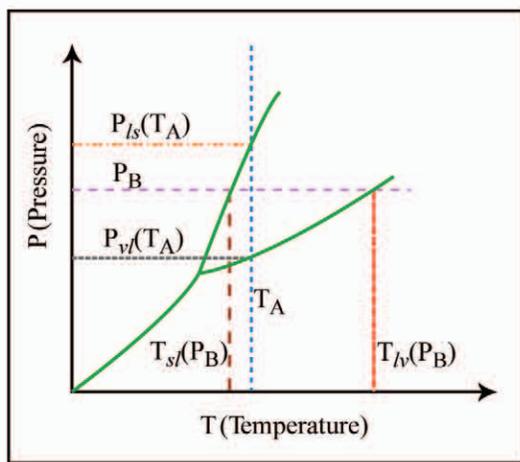


Figure by MIT OCW.

ICE IX

Photographs removed for copyright reasons.

References

1. □ Gaskell, D. R. 1981. *Introduction to Metallurgical Thermodynamics*. Hemisphere, New York.
2. □ Denbigh, K. 1997. *The Principles of Chemical Equilibrium*. Cambridge University Press, New York.
3. □ Bergeron, C. G., and S. H. Risbud. 1984. *Introduction to Phase Equilibria in Ceramics*. American Ceramic Society, Westerville, OH.