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

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

**Today**:

**Reading**:                              Engel and Reid Ch. 8.1-8.5
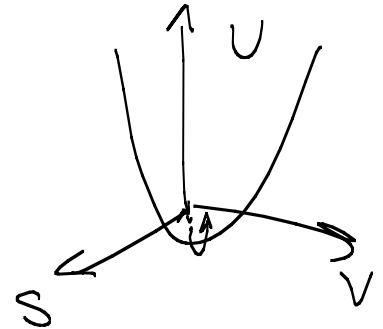
**Supplementary Reading**:        -

## Last time

- Stable equilibria have requirements set by the second law:

FOR CONSTANT S SYSTEM:
(MINIMIZE INTERNAL ENERGY!

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n} \geq 0 \qquad d^2 U \geq 0$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,n} \geq 0$$

- ...these lead to material property requirements:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n} = \frac{T}{C_V} \geq 0 \implies C_p \geq C_V \geq 0$$

$$K_T \geq K_s \geq 0$$

ISOTHERMAL   ISENTROPIC

$K_{\bar{T}} \geq 0$

$\bar{V} \downarrow$ AS $P \uparrow$

$C_p \geq 0$

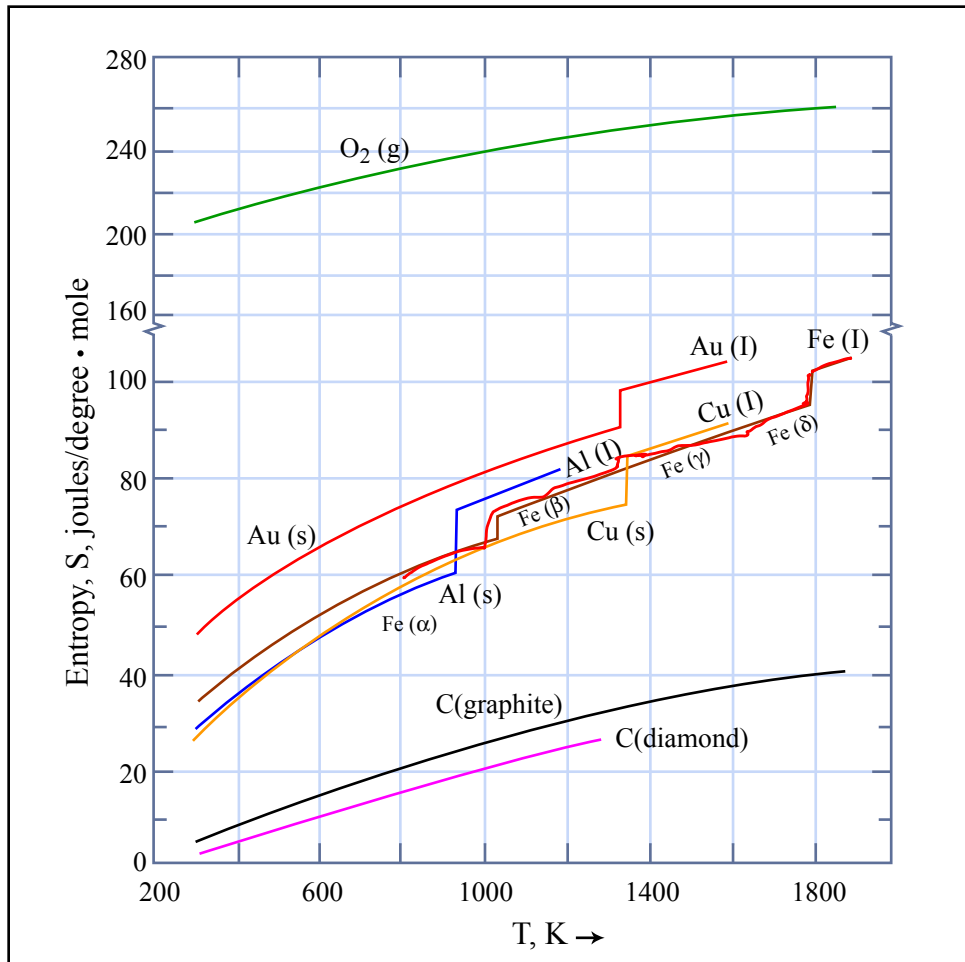$S \uparrow$ AS $T \uparrow$

$\downarrow$ 3rd LAW

$S \geq 0$

$\bar{S} \implies$
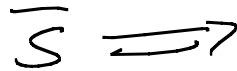


Figure by MIT OCW.

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

$$-\left(\frac{\partial S}{\partial T}\right)_{P,n} = -\frac{C_P}{T} \leq 0$$

$$\frac{C_P \geq 0}{T \geq 0}$$

CURVATURE ?

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,n} < 0$$

SLOPE ?

$$\left(\frac{\partial G}{\partial T}\right)_{P,n} = -S \leq 0$$

$$\underline{S \geq 0}$$

G

$\bar{G}^S$

$$\mu_i = \mu_i^\circ + RT\ln a_i$$

$\bar{G}^L$

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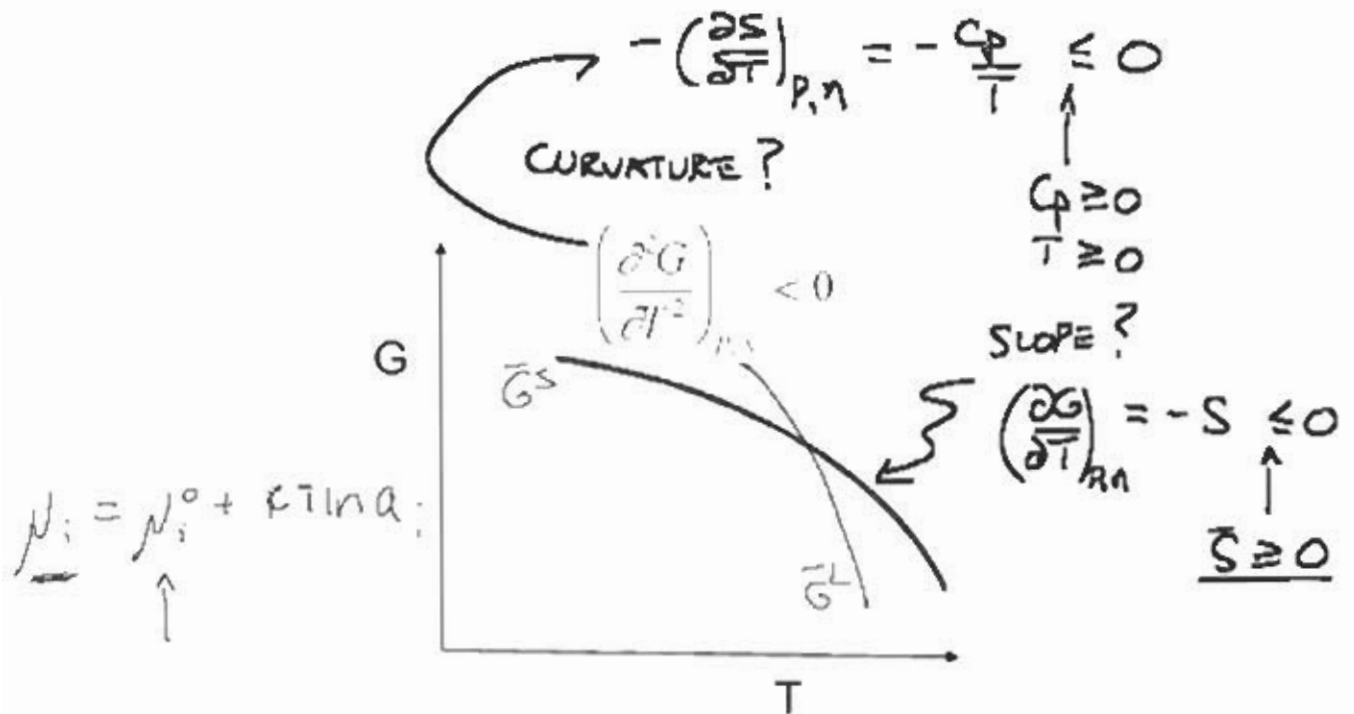
## Behavior of the chemical potential/molar free energy in single-component materials

### 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.

$$\text{CONST } T, P : \text{ SPONTANEOUS PROCESSES : } \Delta \bar{G} < 0$$

PURE
SINGLE
COMPONENT
MATERIAL

$$\bar{G}^L \qquad \Delta \bar{G}_{L \to S} = \bar{G}^S - \bar{G}^L < 0$$

$$\bar{G}^S$$

$$\Delta \bar{G}_{S \to L} < 0$$

SOLID STABLE                    LIQUID STABLE

$$T_1 \qquad T_m \qquad T$$
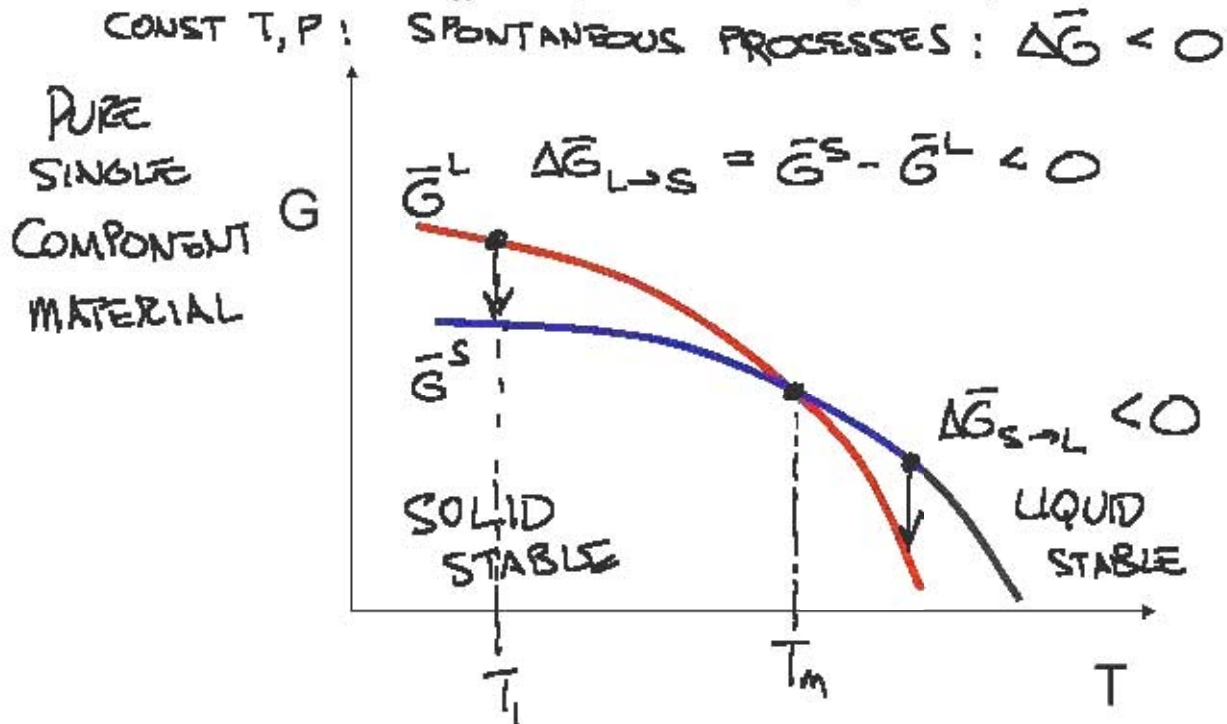
  - What is going on with the Gibbs free energy at the melting point?

$$\text{AT } T = T_m : \quad \Delta \bar{H}_{S \to L} = \Delta \bar{H}_m$$

AT $T_m$,
SOLID AND LIQUID ARE
IN EQUILIBRIUM

$$\Delta \bar{S}_{S \to L} = \frac{q}{T_m} = \frac{\Delta \bar{H}_{S \to L}}{T_m} = \frac{\Delta \bar{H}_m}{T_m}$$

$$\Delta \bar{G}_{S \to L} = \Delta \bar{H}_{S \to L} - T_m \Delta \bar{S}_{S \to L} = \Delta \bar{H}_m - T_m \frac{\Delta \bar{H}_m}{T_m} = 0$$

- 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 $\Delta H_m$ is absorbed as the phase fraction of liquid moves from 0 to 1:
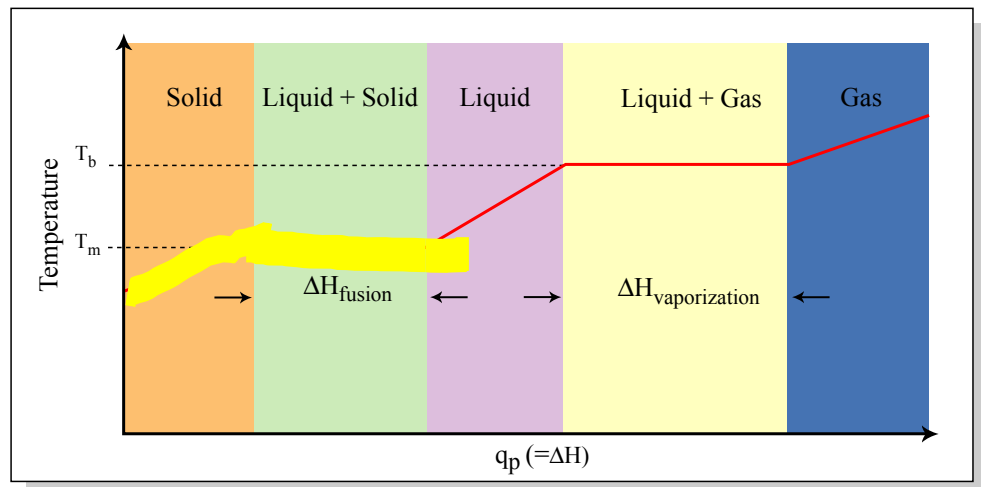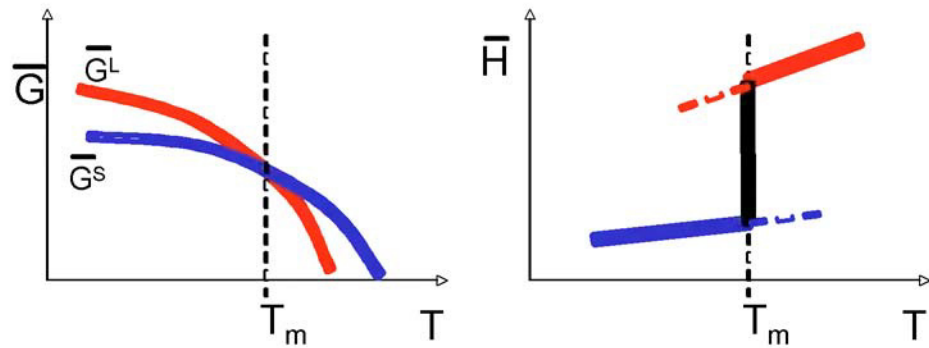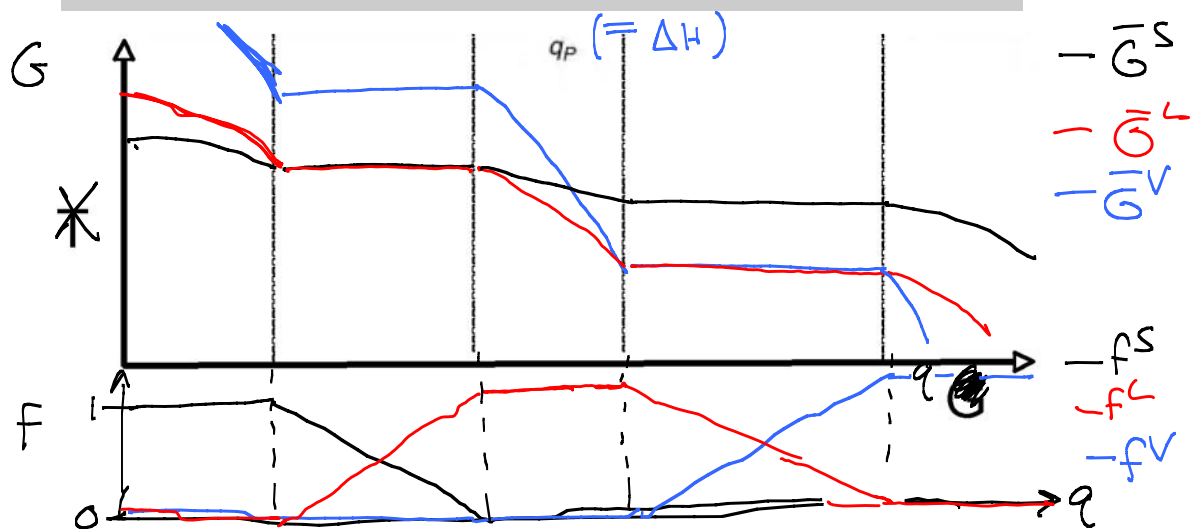


Figure by MIT OCW.



- o   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 sublimate 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.
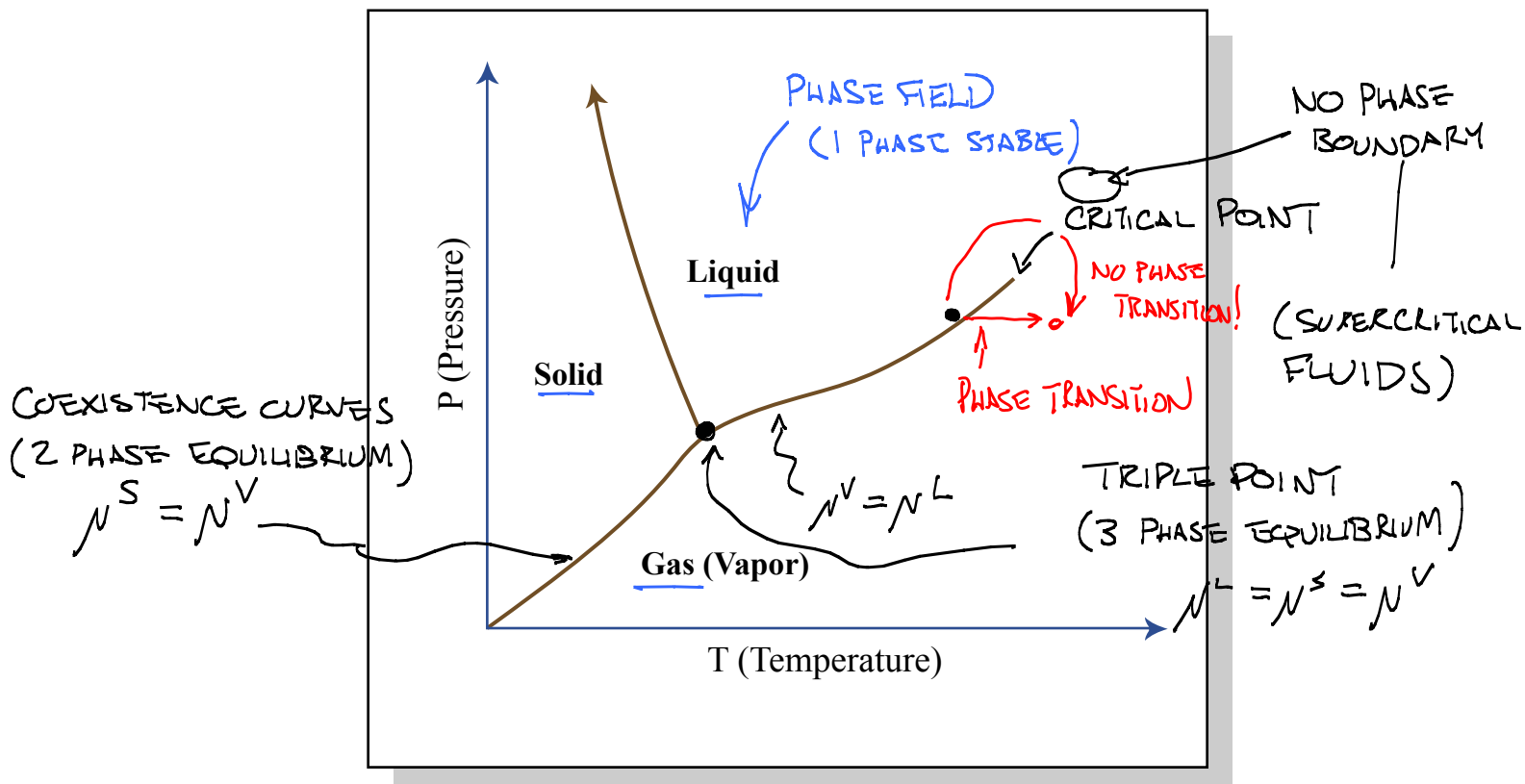


Figure by MIT OCW.

- 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:

$C = $ # COMPONENTS  $P = $ # PHASES  WHAT ARE REQUIREMENTS FOR EQUILIBRIUM?

(Eqn 2)

C ROWS OF EQNS

$$\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \ldots = \mu_1^P$$
$$\mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \ldots = \mu_2^P$$
$$\ldots$$
$$\mu_C^\alpha = \mu_C^\beta = \mu_C^\gamma = \ldots = \mu_C^P \leftarrow P-1 \text{ INDEPENDENT EQNS}$$

$\left. \begin{array}{c} \\ \\ \end{array} \right\} C(P-1)$ EQUATIONS

- 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:

$\mu_A^\alpha = \mu_A^\beta$  $C = 2$  
$\mu_B^\alpha = \mu_B^\beta$  $P = 2$

$dG = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$

$dG = VdP - SdT + \sum_i \mu_i dn_i$

GIBBS-DUHEM EQN:

$0 = VdP - SdT - \sum_i^C n_i d\mu_i$

$+ P$ EQNS $\leftarrow$ $\boxed{0 = V^\alpha dP - S^\alpha dT - \sum_{i=1}^{C} n_i^\alpha d\mu_i^\alpha}$ FOR EACH PHASE

- ...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:** D.O.F $= D$

HOW MANY VARIABLES CAN CHANGE WHILE MAINTAINING A GIVEN EQUILIBRIUM?

$D = (\text{\# VARIABLES}) - (\text{\# EQUATIONS}) \Rightarrow$

$= (CP + 2) - (C(P-1) + P)$

$N_i^j$  $T, P$

GIBBS PHASE RULE

$\boxed{D + P = C + 2}$

# PHASES   # COMPONENTS

- 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:
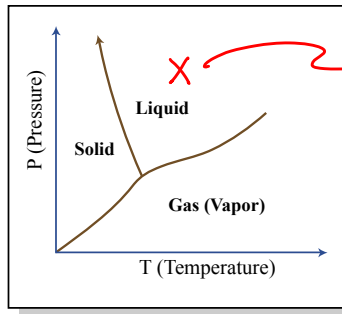


Figure by MIT OCW.

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$C = 1 \quad P = 1$

$D + P = C + 2$

$D + 1 = 1 + 2$

$\boxed{D = 2} \quad \therefore \text{TWO VARIABLES CAN CHANGE...}$

  o 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.

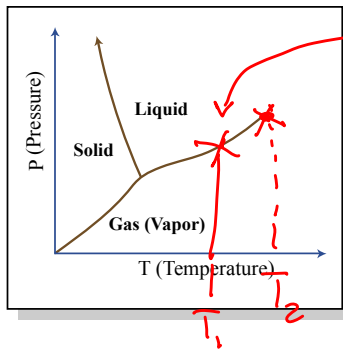- What about the boundaries between two phases? If two phases are in equilibrium at the boundary, then we have:



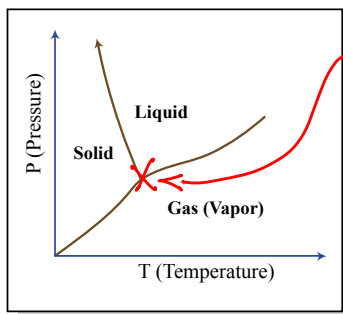Figure by MIT OCW.

$C = 1 \quad P = 2$

$D + 2 = 1 + 2$

$D = 1 \longrightarrow \text{ONLY 1 VARIABLE CAN INDEPENDENTLY VARY}$

  o 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:

$$\therefore \frac{dP}{dT} = f(T, P) \qquad dP = dT(f(T, P))$$

FOR SOME $\Delta T$, $\Delta P$ WILL BE PREDETERMINED

- Lastly, let's consider the vertex of the solid-liquid, liquid-gas, and solid-gas coexistence curves:



Figure by MIT OCW.

$D + P = C + 2$

$D + 3 = 1 + 2$

$D = 0$

NO FREEDOM TO ALTER T, P FROM T.P.

  o 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.
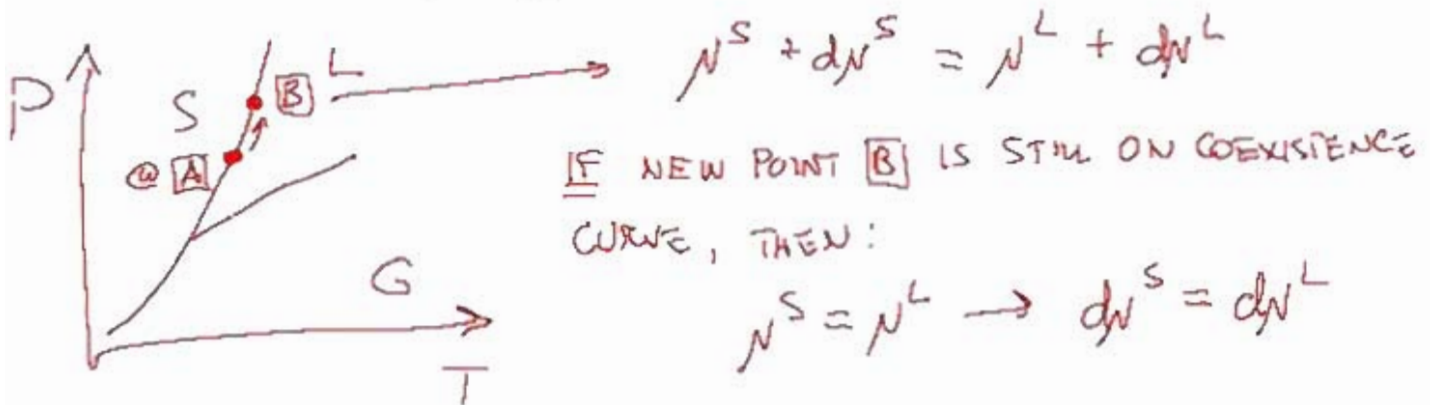
**Lecture 15 – Single-component phase diagrams and phase transitions**
**11/2/05**

## 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):

$$@ \boxed{A} : \mu^s = \mu^l$$

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

$$\mu^s + d\mu^s = \mu^l + d\mu^l$$

IF NEW POINT $\boxed{B}$ IS STILL ON COEXISTENCE

CURVE, THEN:

$$\mu^s = \mu^l \longrightarrow d\mu^s = d\mu^l$$



GIBBS-DUHEM EQN!

$$0 = VdP - SdT - nd\mu$$

FOR SOLID:

$$0 = V^s dP - S^s dT - n^s d\mu^s$$

DIVIDE BY $n^s$:

$$0 = \bar{V}^s dP - \bar{S}^s dT - d\mu^s$$

FOR LIQUID:

$$0 = \bar{V}^l dP - \bar{S}^l dT - d\mu^l$$

$$\bar{V}^s dP - \bar{S}^s dT = \bar{V}^l dP - \bar{S}^l dT$$

$$\downarrow$$

$$\left( \bar{S}^l - \bar{S}^s \right) dT = \left( \bar{V}^l - \bar{V}^s \right) dP$$

$$\underbrace{\qquad}_{\Delta \bar{S}_{s \to L}} \qquad \underbrace{\qquad}_{\Delta \bar{V}_{s \to V}}$$

$$\Delta \bar{S}_m \qquad\qquad \Delta \bar{V}_m$$

CLAUSIUS-CLAPEYRON EQUATION

$$\boxed{\frac{\Delta \bar{H}_m}{T_m \Delta \bar{V}_m} = \frac{\Delta \bar{S}_m}{\Delta \bar{V}_m} = \left. \frac{dP}{dT} \right|_{\substack{COEXISTENCE \\ CURVE}}}$$

- 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.
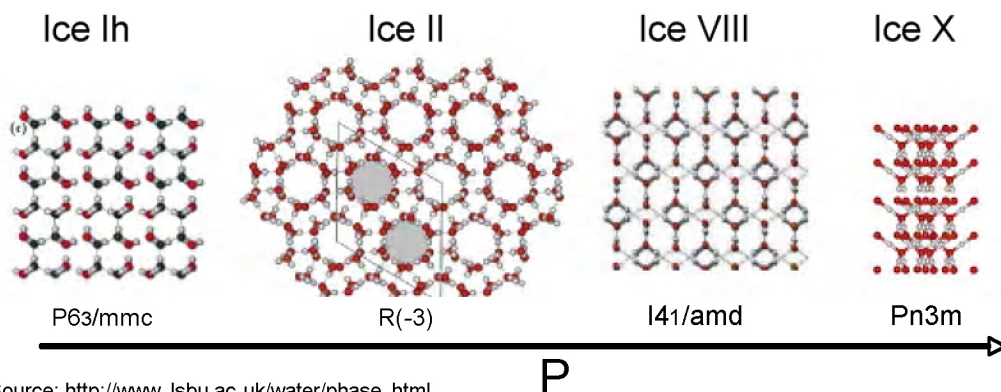
- The phase diagram of water:



Source: http://www. lsbu.ac.uk/water/phase.html
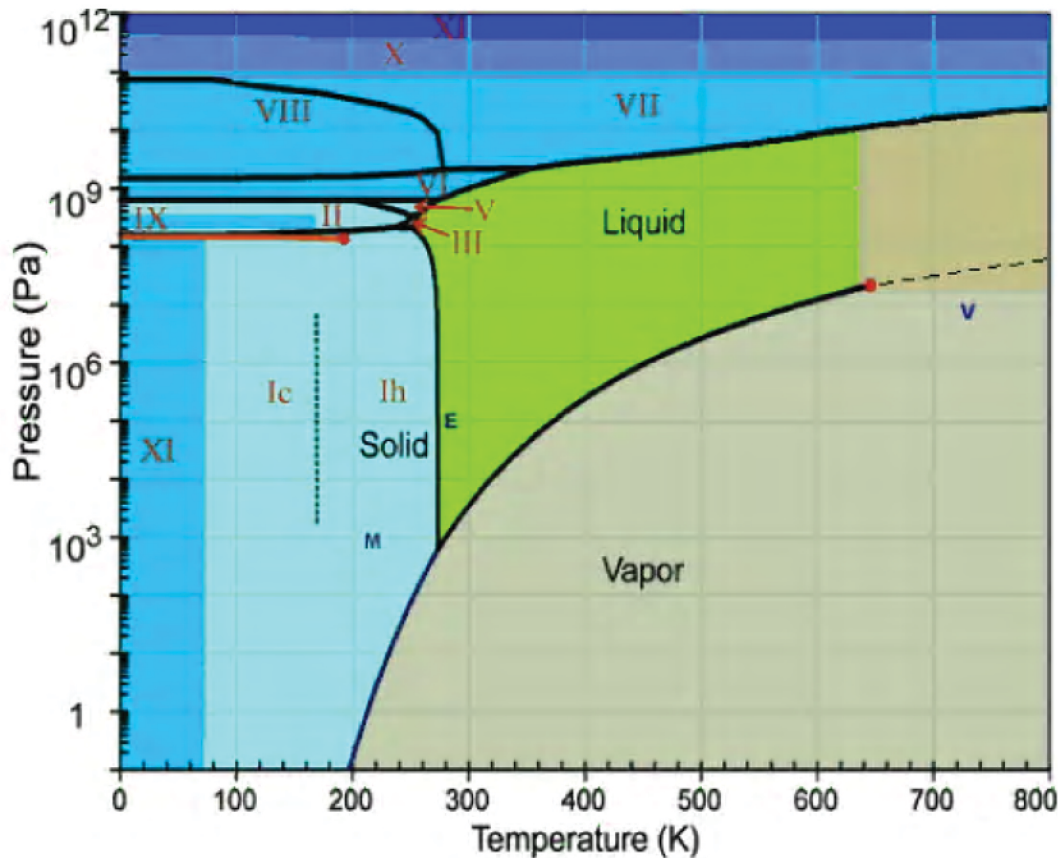
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- Water transitions through increasingly dense crystal structures as pressure is increased:



| Ice Ih | Ice II | Ice VIII | Ice X |
|---|---|---|---|
| P6₃/mmc | R(-3) | I4₁/amd | Pn3m |

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

Courtesy of London South Bank University.  Used with permission.

CARBON PHASE DIAGRAM

Temperature vs. pressure phase diagram for carbon:  A diamond is not forever.

Figure by MIT OCW.
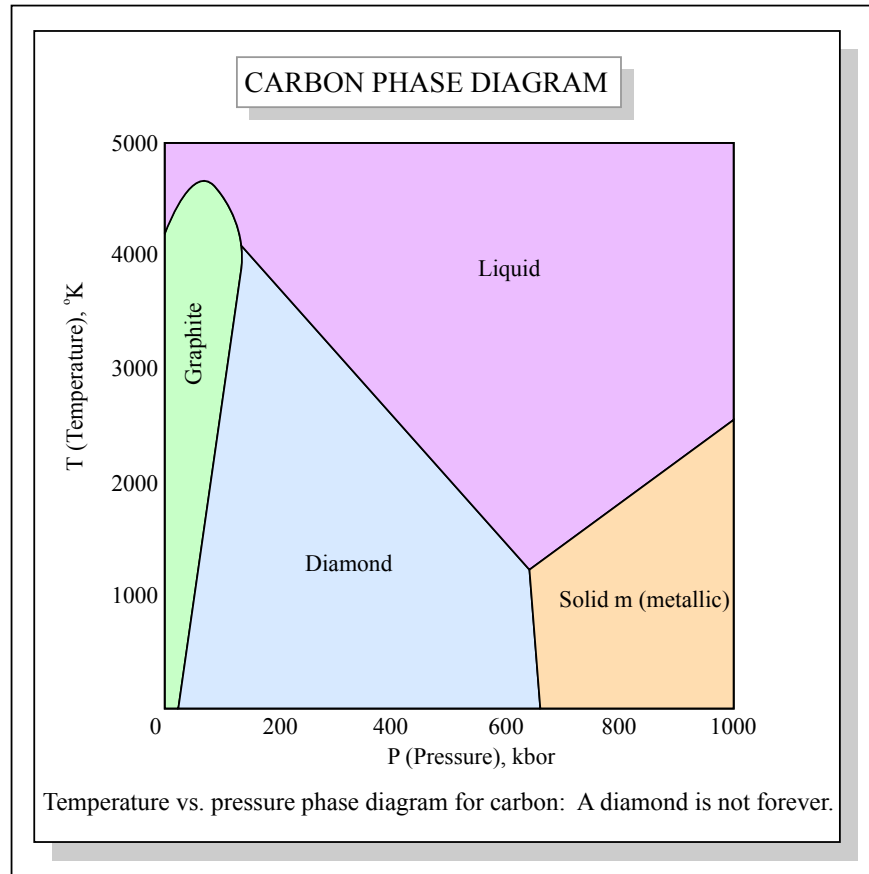


IRON PHASE DIAGRAM
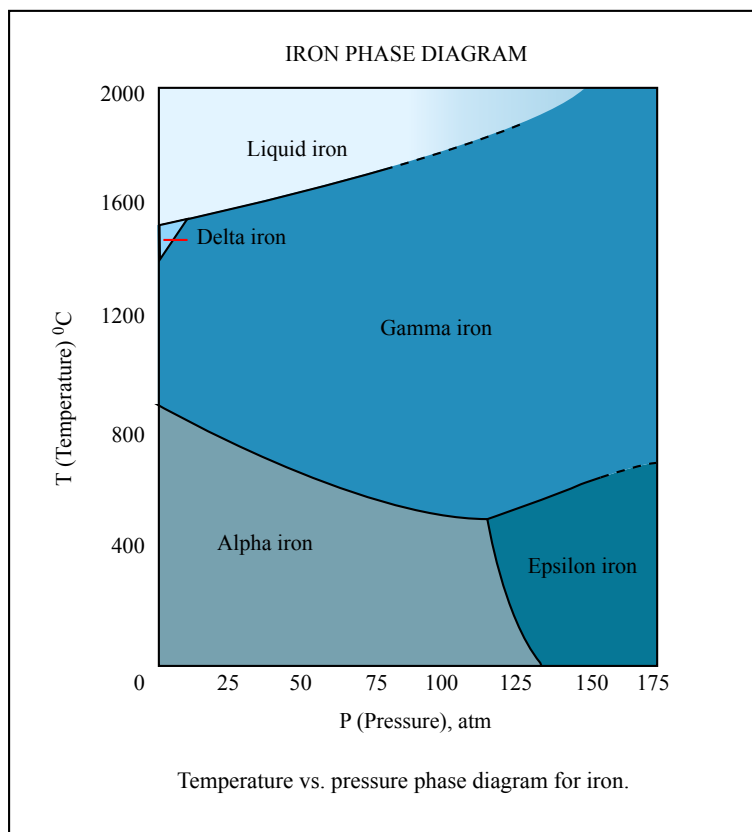
Temperature vs. pressure phase diagram for iron.

Figure by MIT OCW.

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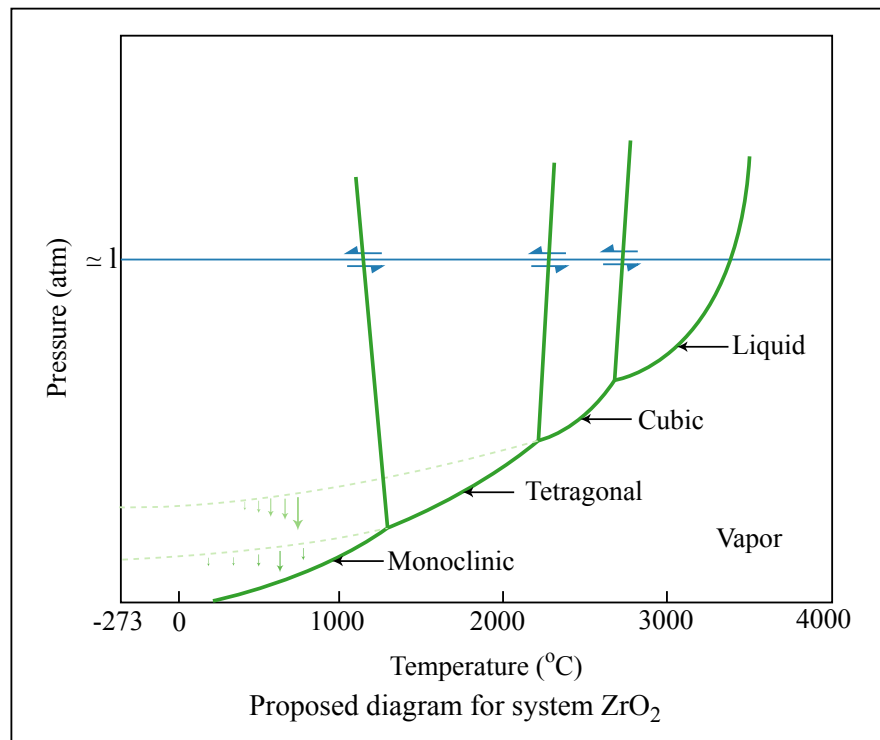Figure by MIT OCW.

(Bergeron and Risbud(3))

## 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:
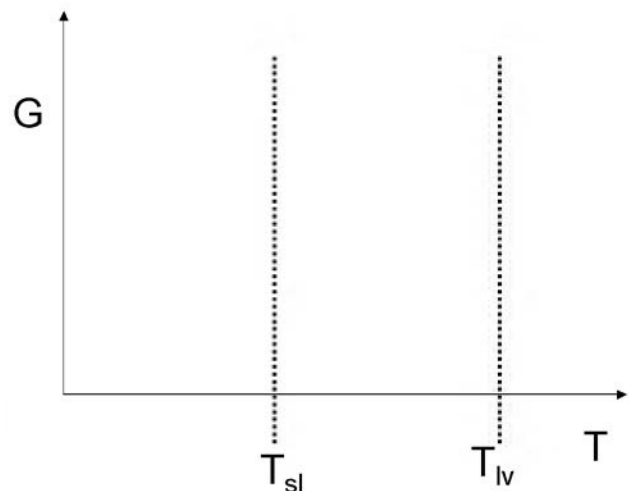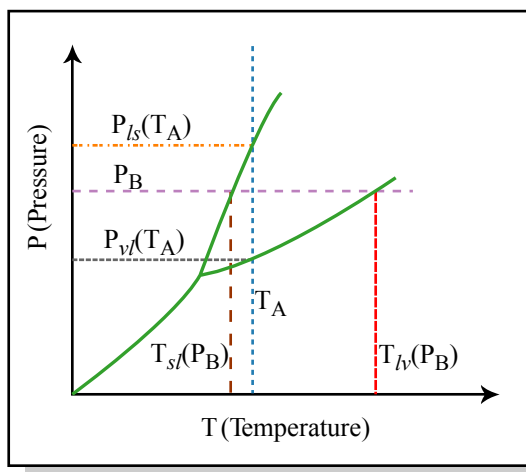


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## ICE IX

H.G. Wells          Irving Langmuir          Kurt Vonnegut

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http://www.encyclopedie-enligne.com/i/ir/irving_langmuir.html
http://www.harvardsquarelibrary.org/stafford/rs_vonnegut.htm

## 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.