

\_\_\_\_\_Sept. 06 2002: Lecture 2: \_\_\_\_\_

## Course Survey

Last Time

**Course Strucure**

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**Would you buy my batteries?**

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**Energy is Conserved. Energy is Minimized. How can both be true?**

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### Preview of Entire Course

This lecture is an outline of everything I hope to cover in 3.00 this semester. I won't expect the students to follow everything, but I hope it will prove useful as a map of where we are going. I also hope that when the exams roll around that it might be useful to review this lecture.

Think of this lecture as:

- A review for the final exam.
- A preview of the things you learn and how they fit together

Thermodynamics can be categorized into two separate parts:

1. Classical (or continuum) Thermodynamics

## 2. Statistical Thermodynamics or Statistical Mechanics

We will focus on classical thermodynamics in this course as it will prepare you for further studies of phase diagrams, reactions, solution thermodynamics and mostly everything else in materials science. Statistical thermodynamics is useful and we will discuss it from time to time, but the bulk of statistical thermodynamics will be covered in 3.01.

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## 2-1 Continuum Thermodynamics

Continuum thermodynamics substitutes a few average quantities like temperature  $T$ , pressure  $P$ , and internal energy  $U$  that represent the state of a system. These averages reduce the enormous number of variables that one needs to start a discussion of statistical thermodynamics: the positions and momenta of zillions of particles.

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### 2-1.1 State Functions

We use the continuum thermodynamic variables to describe the state of a system, e.g., a *state function*:

$$P = f(N, V, T) \quad (2-1)$$

This simply says that there is a physical relationship between different quantities that one could measure in a system. Some relationships come from the specific properties of a material (*material properties*) and some follow from physical laws that are independent of the material (*the laws of thermodynamics*).

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### 2-1.2 Four Laws

Thermodynamics is a set of four laws (two of which are really more important) that limit the ways the system can change. It is useful to distinguish state functions (that are materials

properties that you would need to measure) for thermodynamic restrictions (which derive from physical laws of nature).

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Question: What is the difference between a physical law and a theorem?

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The power of thermodynamics is that everything—everything—follows from these laws. How it follows from the laws is the hard part.

### 2-1.3 Types of Systems

It is very important to be careful in thermodynamics about the type of system that you are considering: the thermodynamic rules that apply change in very subtle ways depending on whether a system is at constant pressure, absorbs no heat, etc. For instance, to discuss a quantity as simple as the heat capacity, one needs to make very precise specifications about how the physical experiment is actually performed.

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### 2-1.4 Types of Variables

There are two different kinds of continuum thermodynamic variables:

1. Intensive Variables (those that don't depend on the size of the system)
  2. Extensive Variables (those that scale linearly with the size of the system)
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### 2-1.5 Temperature

Defining temperature in thermodynamics is particularly troublesome, even though it seems obvious to all of you about what it is. The Zeroth law is mechanism for defining temperature and it says, “if two objects are in thermal equilibrium with a specified object, then the two objects would be in thermal equilibrium with each other—and in fact they have the same temperature.” That specific object in the previous sentence is a thermometer.

It is very important to learn the difference between temperature, heat capacity and heat. Many people get confused by this. Heat is the work-less transfer of energy from one entity to another. Temperature is that which is equal when heat is no longer conducted between bodies in thermal contact. Heat capacity is how much the temperature changes as you add heat to a body that remains in the same state.

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Note that the sentences in the above paragraph start growing lots of clauses (e.g., "... body that remains in the same state."). This happens in thermodynamics because the exceptions to the rule have to be removed so that the logic can proceed from true statements. Unfortunately, it increases the effort that one must exert in reading (rigorous) thermodynamics books.

## 2-1.6 Phases

A phase is defined a homogeneous form of matter that can be physically distinguished from any other such phase by an identifiable interface. Pedestrian examples are the solid phases, liquid phase, and vapor phase of pure water. Less obvious are the FCC and BCC phases of iron-carbon-nickel-chromium steel or the ferromagnetic and non-ferromagnetic phases of LaSrMnO manganites.

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I'll take this opportunity to quote one of my heros:

We may call such bodies as differ in composition or state, different phases of the matter considered, regarding all bodies which differ only in quantity and form as different examples of the same phase.

.....J. W. GIBBS in Trans. Connecticut Acad. III.

(1875) page 152

## 2-1.7 Thermodynamic Notation

Thermodynamic notation becomes complicated because there are so many things that need to be specified. It is not unusual to see a quantity like  $\mu_i^\alpha$  which means "the chemical potential of the  $i^{\text{th}}$  chemical component in the  $\alpha$  phase in its standard state." You will have to pay attention to sorting out notation—otherwise you will have difficulty understanding how everything fits together.

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The notation for specifying chemical composition becomes necessarily messy, because it can vary from phase to phase. We will spend some time making sure that you understand what is meant by the “concentration of chemical species  $i$  in phase  $\alpha$ :  $c_i^\alpha$ .”

Students often confuse composition with phase fractions. Let’s make sure we understand the distinction.

Partial quantities are other variables that the treatment of an intensive variable like pressure as a linear combination of all the present chemical species—as in the case of partial pressures.

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## 2-1.8 The First Law

The first law says that heat and work have the same effect of increasing the internal energy of body—and the internal energy is a state function. Heat and work have the same units and they are ways of transferring energy from one entity to another. It may seem obvious to you, but it was not obvious 200 years ago that heat and work could be converted from one to another.

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## 2-1.9 Types of Work

There are many different ways that energy can be stored in a body by doing work on it: elastically by straining it, electrostatically by charging it, polarizing it in an electric field  $\vec{E}$ , magnetizing it in a magnetic field  $\vec{H}$ , chemically by changing its composition with a chemical potential  $\mu$ . Each example is a different type of work—they all have the form that the (differential) work performed is the change in some extensive variable of the system multiplied by an intensive variable.

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Students often get confused about where to put minus signs in equations dealing with work, heat and changes in energy. This confusion can usually be removed by forming a physical picture of what is actually happening in the system and using common sense.<sup>1</sup>

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<sup>1</sup>I know it is true because I have seen it and have done it myself—but students are reluctant to use common

## 2-1.10 Reversible Work

Some work always gets wasted as heat. In other words, all of the work that is done on a body cannot get stored as internal energy—some of it leaks out as heat. The amount of wasted work is minimized when a process is carried out reversibly. A reversible process happens very slowly and the system is always in equilibrium (i.e., the intensive variables are uniform) during a reversible process.

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This idea of a minimum of something is very useful because it allows the definition of new thermodynamic variables associated with the limiting (minimizing) case. This is an abstraction—like the notion of limits in calculus—which seems confusing at first, but becomes natural with familiarity.

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## 2-1.11 Entropy

Because there is a limiting process that minimizes something (in this case the wasted heat), we can define a new state variable based on this limiting idealization. This lets us define a new and very important state function called the entropy  $S$ .  $S$  is necessarily extensive thermodynamic quantities.

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Entropy also has quite a different looking definition in statistical thermodynamics—it says that entropy is proportional to the logarithm of the number of states accessible at the systems energy. Because the number of states of two systems together is the product of the number of each system taken individually and because entropy, being an extensive function, must go like the sum of the individual system entropies, entropy must go like a log.

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sense. I wish I knew why it is true.

### 2-1.12 Enthalpy

It is useful to imagine a system that changes at constant pressure. In this case, the change in energy as a body is heated is not exactly the internal energy, but a new state function called enthalpy  $H$ .  $H$  represents the available thermal energy at constant pressure. It is the first new derived state function we will learn about after entropy.

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### 2-1.13 The Second Law

The second law states that entropy is a state function and—if added up for all parts of system—never decreases. This turns out to be incredibly useful, since if we want to find the condition that a system stops changing (i.e., when it is in equilibrium) then the entropy of the entire system is as large as possible.

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It is also difficult to apply because it forces us to consider *everything* that may be affected by a process and not the little bit of material in which we may be interested.

There are many different ways to state the second law and they all sound quite different from each other. This fact is not terribly enlightening, but showing that all the differing statements are consistent is terribly enlightening.

### 2-1.14 The Gibbs Free Energy and Helmholtz Free Energy

The entropy gives a maximal principle, but for the entire universe. It would be useful to find other functions that have similar extremal properties but for a subsystem of the universe. For example, one doesn't usually state that ice will freeze at a particular temperature and pressure because the entropy of the ice plus the freezer plus the wires that run to the power station plus the power station, etc, have a total sum entropy that increases. Rather, it is decidedly more useful to have some other quantity that applies to the water/ice itself as a function of temperature and pressure of its environment.

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The quintessential concept in the application of the laws of thermodynamics is how to derive that useful quantity from the second law. Their derivation depend on what aspects of the material can vary—in other words, a precise description of the experiment that would be

performed on the material in which you are interested. The two most famous such quantities are the Gibbs Free Energy and Helmholtz Free energies.

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The entropy allows us to define two new extensive thermodynamic variables: the Helmholtz free energy,  $F$ , is the maximum amount of work a system can do at constant volume and temperature; the Gibbs free energy  $G$  is the maximum amount of work a system can do at constant pressure and temperature.  $G$  is a minimum for a closed system at equilibrium with a fixed temperature and pressure.

Why define all these different functions—can't we just have one? No, because in practice, systems have different constraints imposed on them, and to understand them we need to find the physical principles that describe their behavior.

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### 2-1.15 Phase Changes

When a body changes phase (e.g., melts, freezes, evaporates, changes crystal structure), its enthalpy increases or decreases depending on whether heat is absorbed or given off at constant pressure. When the body changes phase at the equilibrium temperature, the entropy of the universe should not change therefore  $G \equiv H - TS$  does not change. Therefore the Gibbs free energy per mole of two phases in equilibrium are equal. Such equalities are very useful.

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### 2-1.16 Molar Entropies

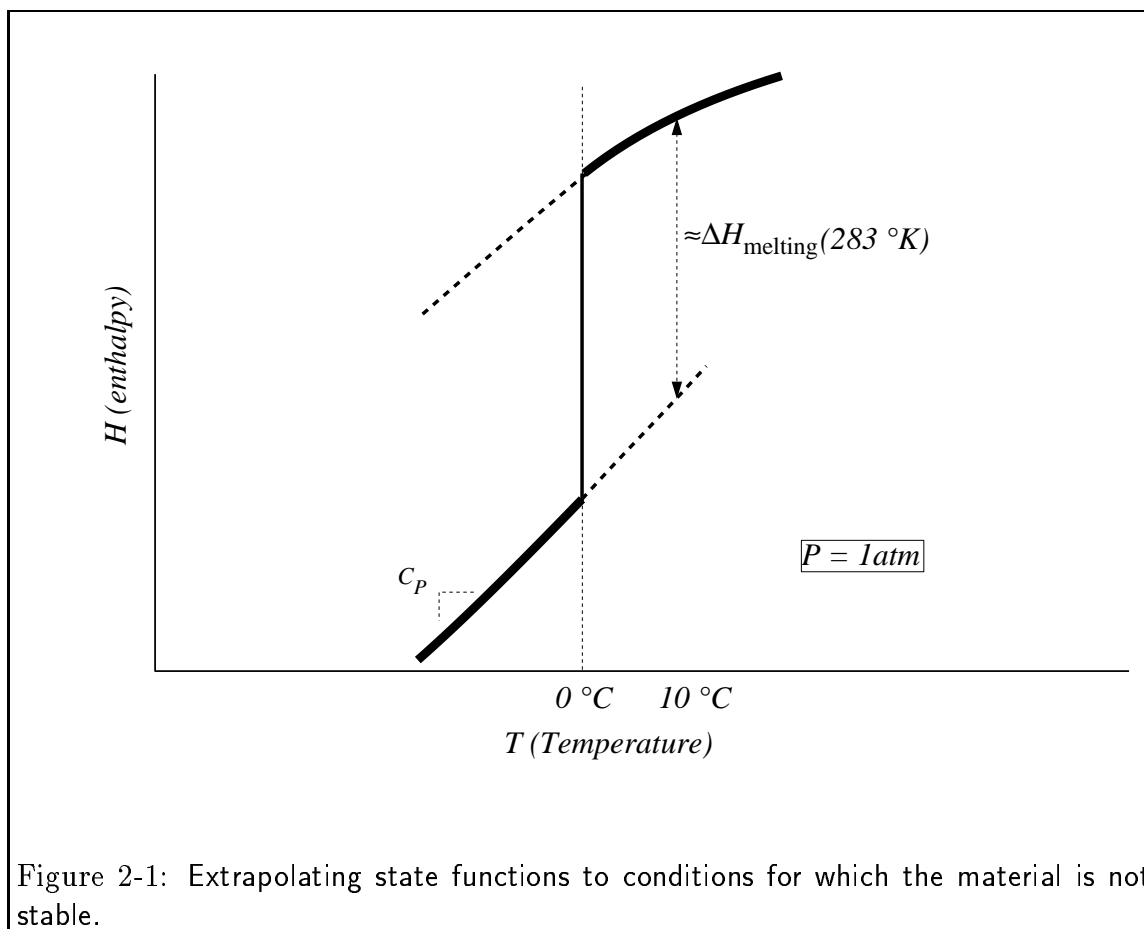
The molar entropies of dense objects tends to be smaller than not dense objects so  $G = H - TS$  tends to favor not-dense objects (gases) at high temperatures. The molar entropies of complex crystals are generally larger than simple ones. Molar entropies of ordered systems like crystals generally are generally smaller than those with no long-range order like fluids. Apparently, entropy has something to do with the number of different ways a system can be rearranged and still have the same energy.

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### 2-1.17 Extrapolation to Non-Stable States

We can calculate the enthalpies, entropies for substances at conditions that they are not stable by extrapolating data. This is a useful trick as it allows us to make predictions about non-equilibrium changes in a system.



### 2-1.18 Minimum Principles

The principle that  $S$  is a maximum at constant energy allows us to prove the obvious, that  $T$  and  $P$  are uniform in systems that are in thermal and mechanical contact. This idea is not terribly useful until we consider two systems in mechanical and thermal contact, one so large that it hardly changes at all and the other being the system we are interested in studying. To see if our little system is in equilibrium, we consider all of its internal degrees of freedom. It turns out that if the internal degrees of freedom are the chemical compositions of all the phases in our little system, then what must be minimized is the sum of the partial Gibbs free energies each weighted by the amount of substance present.

### 2-1.19 Gibbs Free Energy is Minimized at constant Pressure and Temperature

The Gibbs free energy is partitioned into a potential for each chemical species  $i$ ,  $\mu_i$  and the number of moles of  $i$ ,  $N_i$ . Then, the Gibbs free energy,  $G = \sum_{i=1}^C \mu_i N_i$  must be a minimum. Knowing that it is a minimum means its derivative is zero—and this gives us a bunch of useful equations that apply to states of equilibrium. The fact that it is a minimum also means that its second derivative is positive definite—this implies restrictions on the properties of stable materials (such as the bulk modulus and the heat capacity must be positive).

### 2-1.20 Chemical Reaction Equilibria

One immediate consequence of Gibbs free energy being minimized is that we can calculate the equilibrium concentrations in a chemical reaction from the molar change in Gibbs free energy of the reaction. The resulting equation is a fraction containing chemical activities raised to stoichiometric powers is equal to an equilibrium constant that can be calculated from  $\Delta \overline{G}^{RX}$ .

This minimization leads directly to what may be a familiar formula for the equilibrium concentrations in a chemical reaction, i.e.,

$$\begin{aligned}
 p\text{P} + q\text{Q} &\rightleftharpoons r\text{R} + m\text{M} \\
 \frac{P_{\text{R}}^r P_{\text{M}}^m}{P_{\text{P}}^p P_{\text{Q}}^q} &= e^{-\left(\frac{\Delta \overline{G}_{rxn}}{RT}\right)} = K_{eq}(T) \\
 \frac{X_{\text{R}}^r X_{\text{M}}^m}{X_{\text{P}}^p X_{\text{Q}}^q} &= P_{\text{total}}^{p+q-r-s} K_{eq}(T)
 \end{aligned} \tag{2-2}$$

### 2-1.21 Mathematical Thermodynamics

There are some mathematical consequences of our friends,  $U$ ,  $S$ ,  $H$ ,  $F$ , and  $G$ , being state functions. They are the Maxwell relations. It is useful to know they exist because it allows you

to form relations between different quantities that are not intuitive at all. They are good fodder from questions on exams in other thermodynamics courses. I'd like you to understand where they come from and be able to manipulate them in the calm quiet atmosphere of your home, but I won't put questions about them on exams. What's the point? I would feel perfectly comfortable asking you questions about *why* they are important or *where* the Maxwell relations come from. There are also some implications that follow from the maths that imply how you should draw free energy curves—for some reason, materials scientists are amused by this fact.

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We will have to go through some exercises about how to do mathematical manipulations in thermodynamics. I happen to like this kind of thing. You are expected to have seen them so I will teach them to you and give you some homework exercises.

### 2-1.22 Le Chatelier's Principle

Le Chatelier's principle says that a system will respond to mitigate the effect of an implied stimulus. Another way of stating this is that perturbing a system will excite internal degrees of freedom that respond to the stimulus—you push on ice, it transforms to a lower volume liquid phase; you increase the pressure in a chemical reaction, it produces more of the reactants that take up less space.

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### 2-1.23 Gibbs-Duhem Equation and its Consequences

You might have noticed that we have defined the Gibbs free energy in two different ways above, once by subtracting off combinations of  $S$ ,  $H$ , and  $T$  and once as a sum of chemical potentials and amounts of species. The fact that they are equal gives a new useful relation called the "Gibbs-Duhem Relation." The Gibbs-Duhem relation allows us to calculate relationships between quantities as a system remains in equilibrium. One example is the Clausius-Clapeyron equation that relates equilibrium changes in pressure to changes in temperature as a function of material parameters. These relationships restrict the degrees of freedom in a system at equilibrium. These restrictions make up the famous "Gibbs Phase Rule"  $P + f = C + 2$ . The Gibbs phase rule tells you how many things you can change and still have equilibrium and it depends on the number of chemical components and the number of existing phases. You will all know Gibbs phase rule by the end of the class—I hope I can also teach you what it means.

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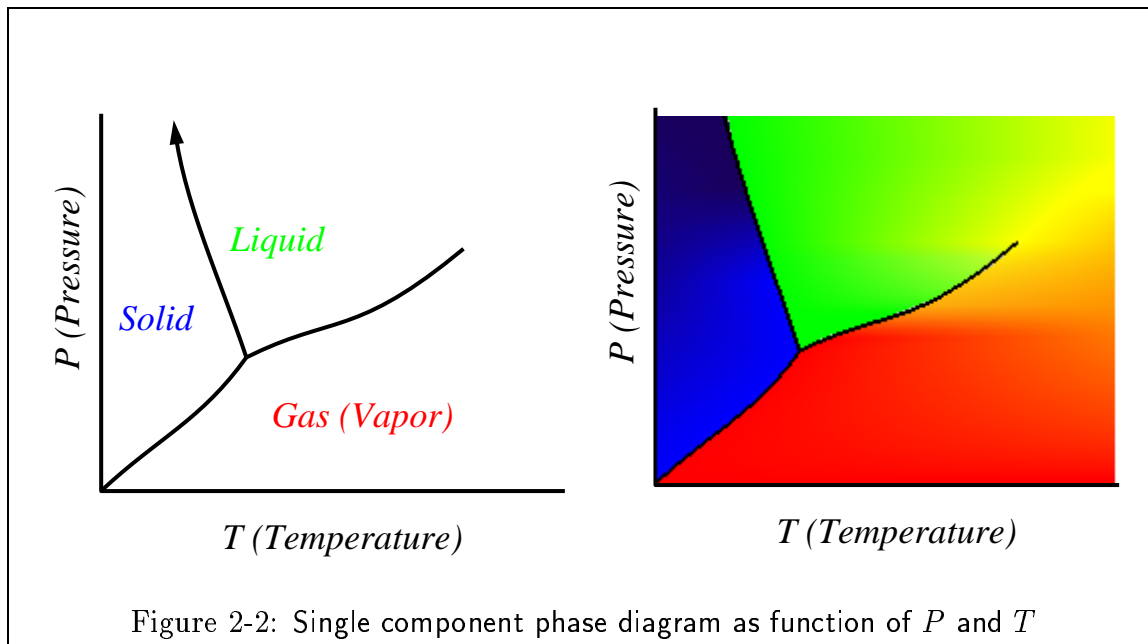
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## 2-1.24 The Relation between Gibb's Free Energy and Equilibrium Phase Diagrams

The equality of the molar Gibbs free energy can be graphically depicted in phase diagrams. It is very important for you to understand how the Gibbs free energy is related to phase diagrams. This is very very important.

Here is a single component phase diagram:



A phase diagram is a map that tells you what phases will be stable at what conditions. You *must* understand and be able to explain how these diagrams follow from plots of free energy curves—this involves using intersections of the free energy curves and the common tangent construction.

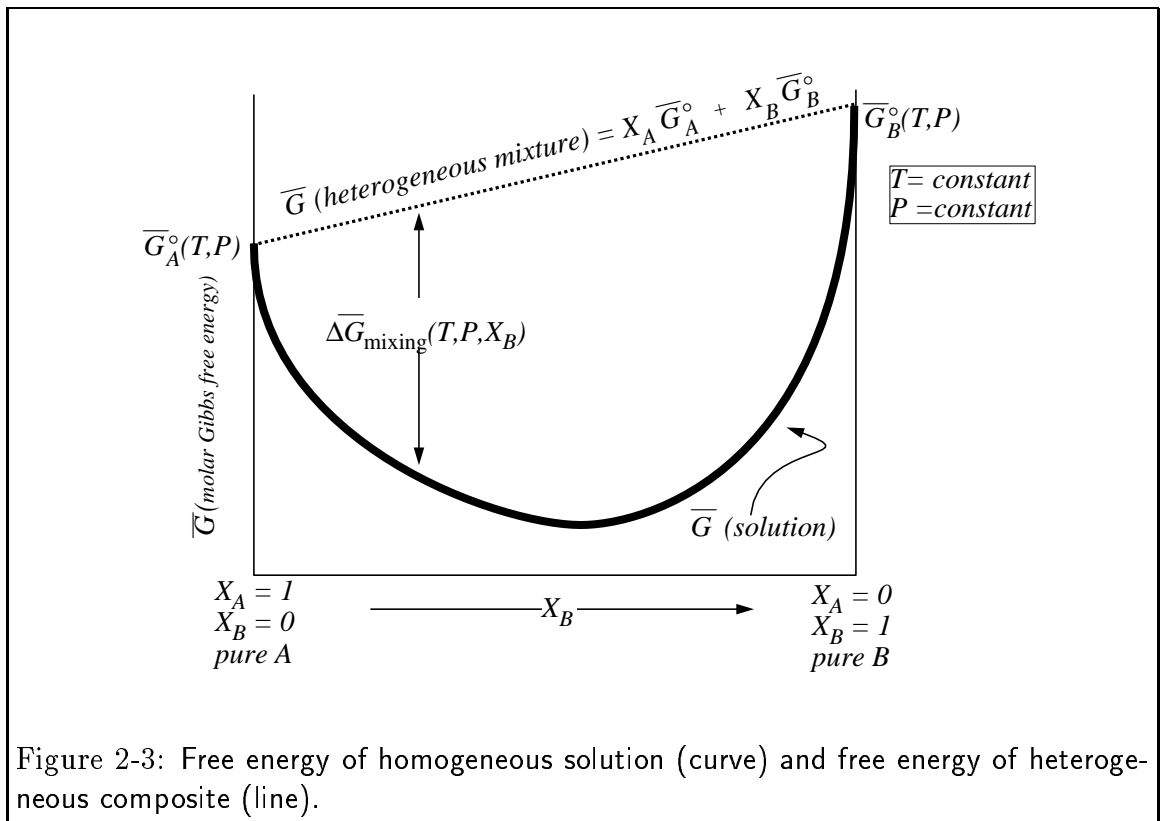
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## 2-1.25 Gibb's Free Energy of Solution

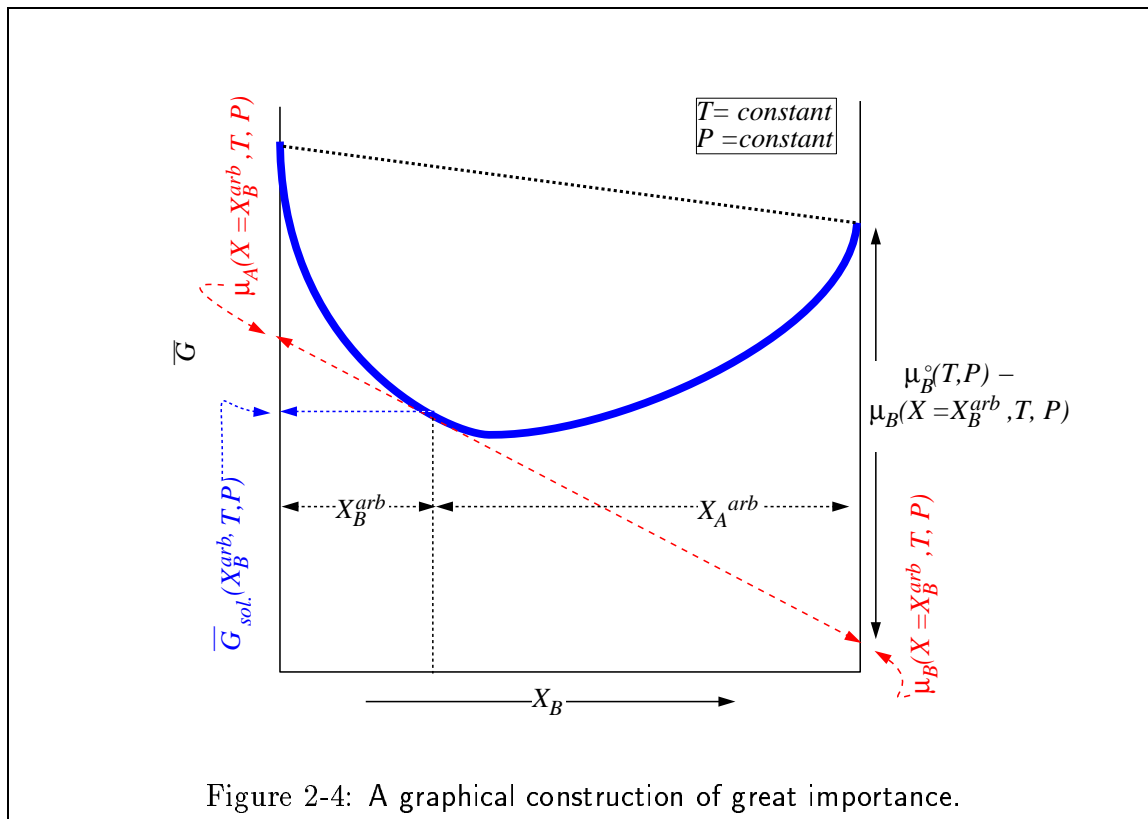
The free energy of a homogeneous solution is very different from a heterogeneous composite.



The reduction in free energy at a fixed composition drives systems into solution.

## 2-1.26 Binary Phase Diagrams

There is a graphical construction that allows you to determine the chemical potentials of chemical species in solution:



This construction and the equality of chemical potentials results in the common tangent construction between several phases of heterogeneous solution in a binary alloy:

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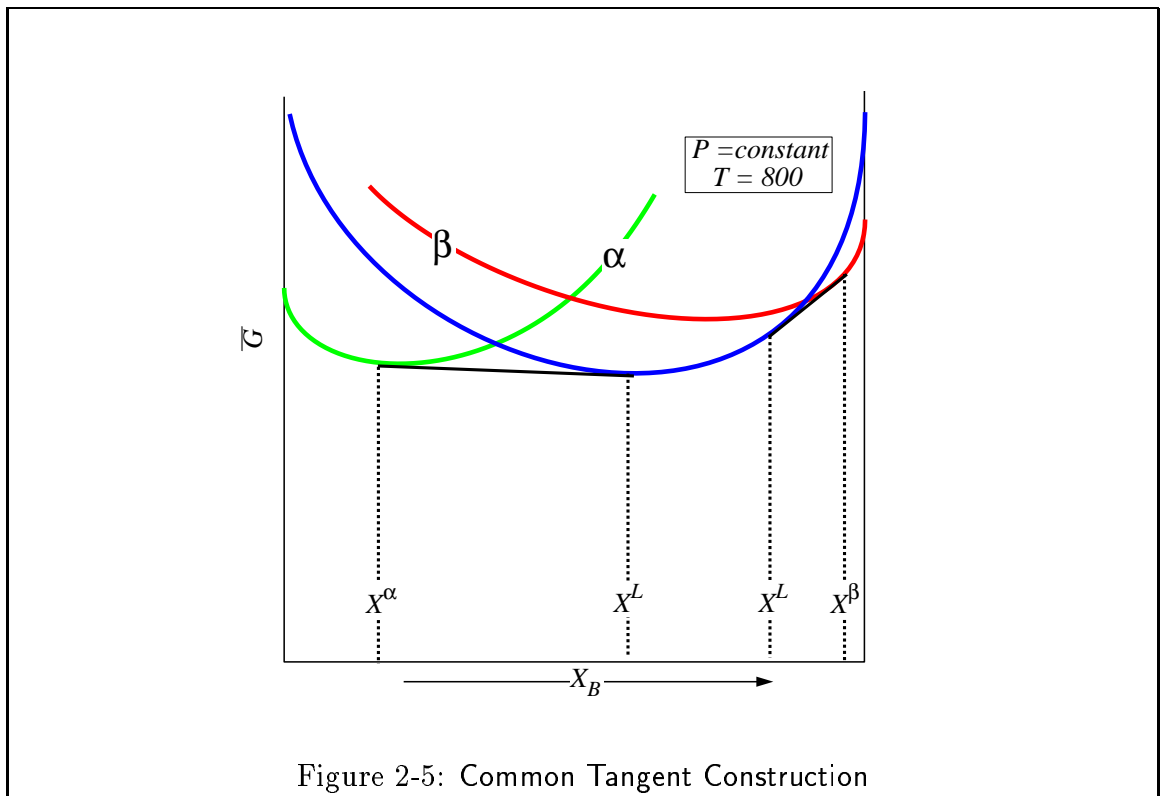


Figure 2-5: Common Tangent Construction

Which allows the construction of binary phase diagrams, for example:

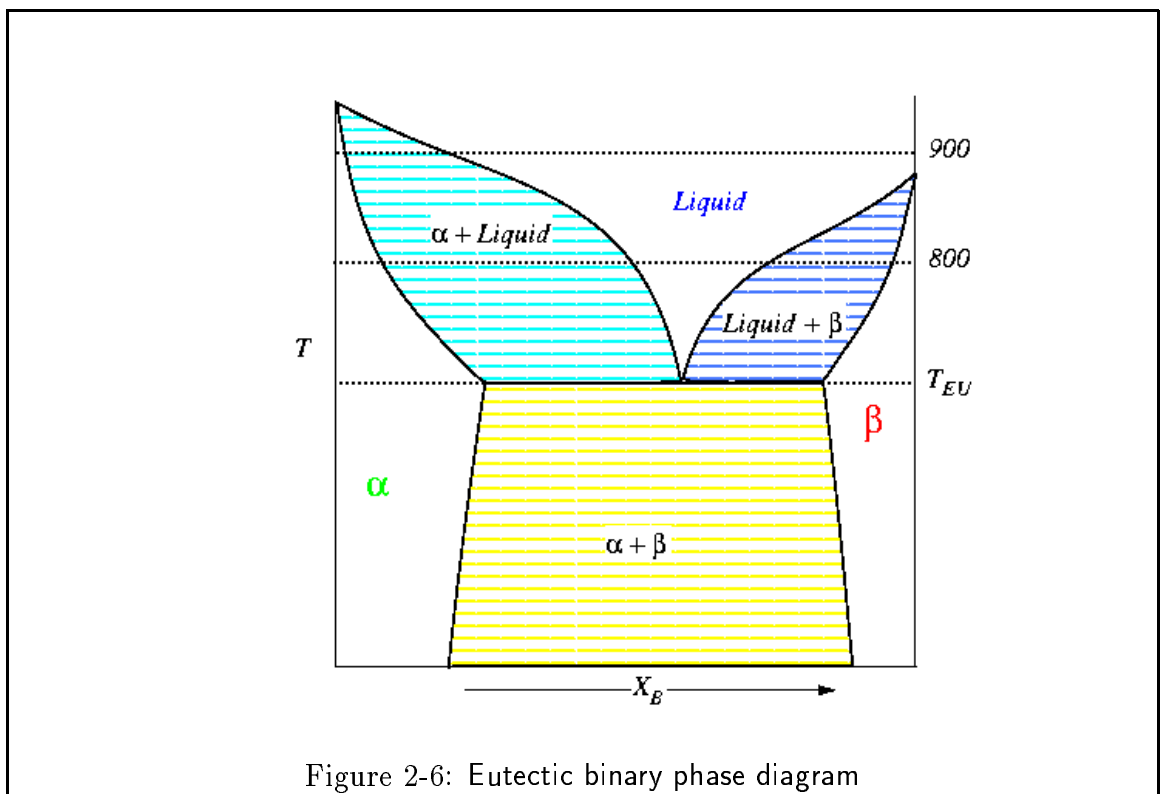


Figure 2-6: Eutectic binary phase diagram

The two phase regions are composed of the limiting compositions on either side of the two-phase region on the phase diagram; the *lever rule* allows us to determine the fractions of each phase.

There are four main types of binary phase diagrams: Eutectic-type, Peritectic-type, Spinodal, and Lens. You should be able to draw these without too much effort.

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### 2-1.27 Phase Diagrams with more than Two Independent Components

For systems with more than two components, the phase diagrams become more complicated. Ternary phase diagrams are drawn in triangles at constant pressure and temperature. There are constructions that are similar to the lever rule.

### 2-1.28 Ideal Solutions

To construct a phase diagram for a material, one needs the Gibbs free energy as a function of composition of the solution. There are various standard models for solutions that provide approximations to the Gibbs free energy.

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Ideal solutions are the simplest case, they are a direct analogue of an ideal gas mixture. All solutions take on ideal behavior when they are dilute, this is called Raoult's law for the solvent and Henry's law for the solute.

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### 2-1.29 Regular Solutions

Better models of the free energy of solution come from consideration of the interactions between atoms in the system. The most simple version is called the regular solution model—it averages the interactions between like and unlike atoms to calculate the enthalpy and uses the ideal solution to calculate the entropy. Regular solution models can predict “unmixing” and this results in a spinodal phase diagram.

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### 2-1.30 Types of Transformations

The local curvature of the Gibbs free energy of solution with respect to composition determines whether an unstable composition will achieve stability by small widely-spaced composition fluctuations or large isolated fluctuations in composition. The later is an important process called nucleation.

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For the case of nucleation of very small nucleating particles, one needs to consider the extra energy associated with a surface of the particles. This extra energy has to be overcome by a decrease in the Gibbs free energy of the entire particle. This leads to the possibility of under-cooling and the prediction of minimum size of a particle (a nucleus) that can grow.

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### 2-1.31 Chemical Reactions involving Pure Condensed Phases

When considering chemical reactions of involving pure condensed phases, we can calculate equilibrium concentrations by considering the chemical potentials in the vapor that is equilibrium with the system. This leads to an important approximation that one can set the activities of the pure condensed reactants and products to one—in other words, they don't appear in the equilibrium constant. This allows us to make quantitative predictions on the reduction and oxidation of materials in terms of the partial pressure of oxygen.

The data for free energies of reaction for oxidation of metals is conveniently represented in an Ellingham diagram.

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### 2-1.32 Electrochemistry

When reacting components are charged or involve electron transfer, additional terms must be added to the chemical potential to represent the extra energy of a charged species in an electrostatic potential. The sum of the chemical potential and the electrostatic potential defines the “electrochemical potential.” At equilibrium, the electrochemical potentials are equal between phases. The electrochemical potential yields the Nernst equation. The Nernst equation is exactly the same as an equilibrium constant equation, except with the energy of charged species being added in.

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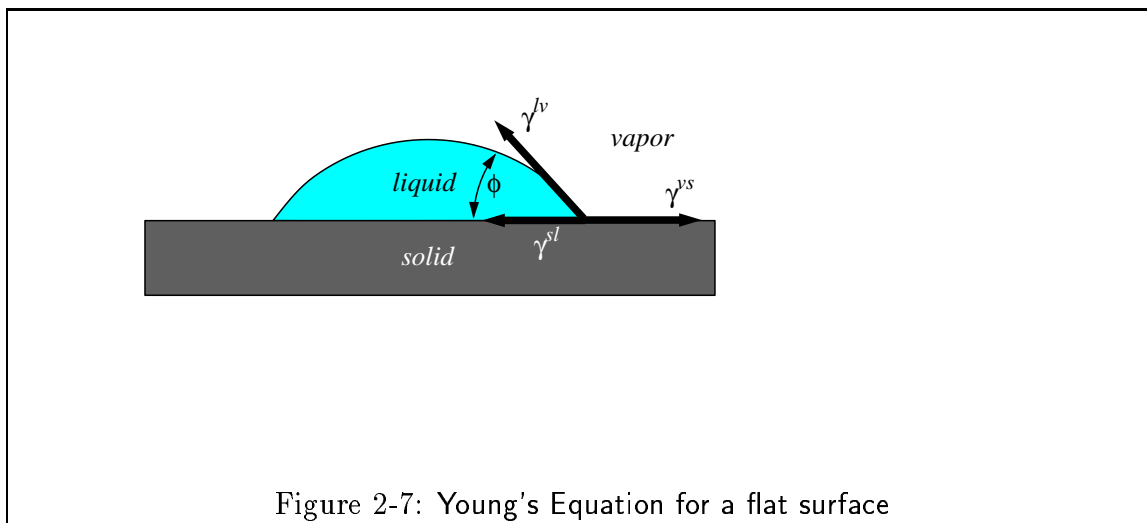
### 2-1.33 Interfacial Thermodynamics

A material can store energy at interfaces. The energy contribution is the surface tension multiplied by the area of interface. Surface tension can result in the pressure of two phase being different if the interface between them is curved. The chemical potential at an interface is increased if it is curved, this is the Gibbs-Thompson effect. Material can segregate preferentially to interfaces if it decreases the surface tension. This follows from the Gibbs-Duhem equation for surfaces and the result is called the Gibbs Adsorption equation.

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Surface tensions act a force balances and specify the contact angle between two phases:



Considerations of the geometry of such surfaces has important implications on the sizes of nuclei and therefore on the entire topic of phase transformations.

### 2-1.34 Defect Equilibria

Chemical equilibria between species on a lattice with a fixed number of sites is known as defect chemistry. Defects in ionic lattices are charged; Kroger-Vink notation is introduced to distinguish the various types of defects and their associated charges.

The results also apply to the equilibrium concentration of charged carriers in a semiconductor.