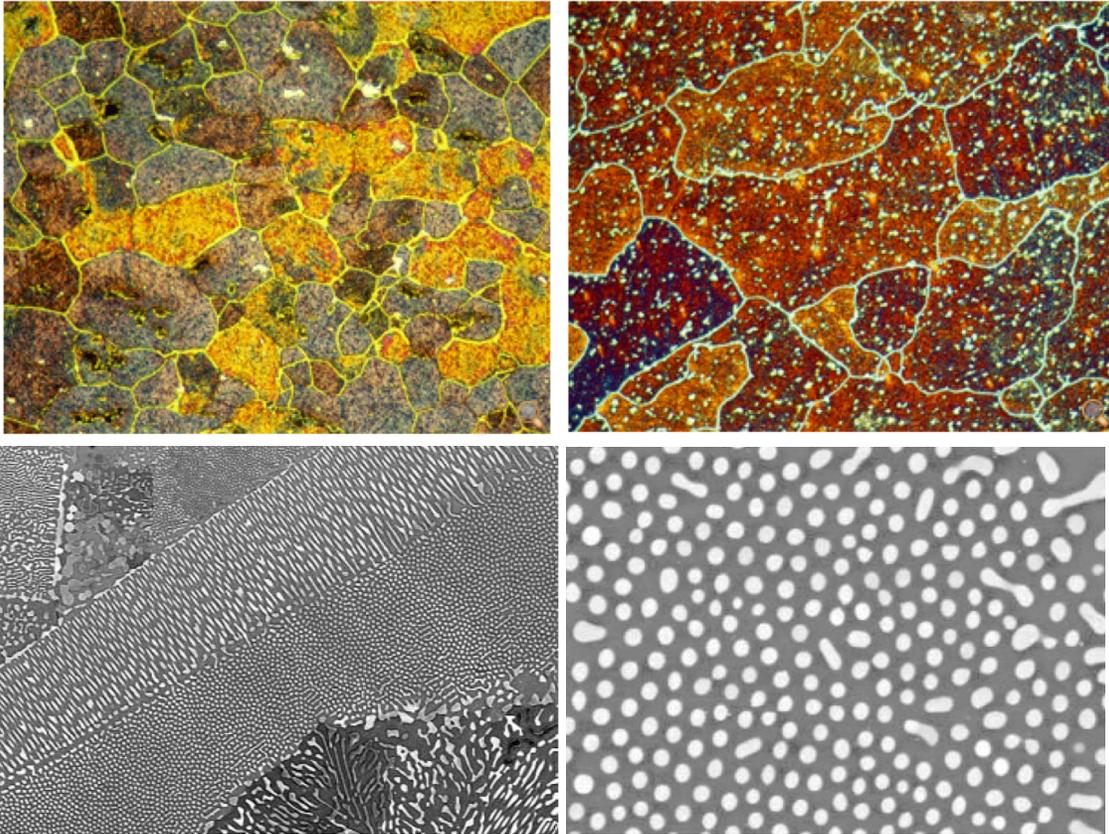


## X. PHASE DIAGRAMS



### 10-1 INTRODUCTION

Take a small sample of almost any material, say a piece of steel, brass or bronze, polish the surface and place it under an optical microscope and you will see crystalline grains of different size shape and composition. For some materials, these grains are apparently randomly distributed, for other there is a clear order to their arrangement. The level of structure revealed through the microscope is referred to as microstructure, because in the past the size of the grains was on the order of micrometers ( $10^{-6}$  meters). However, today with advanced processing techniques, the materials\molecular engineer can produce grains with sizes as small as a few nanometers.

As you may imagine the reason for the interest and control of microstructure is the influence it has on properties. Two materials with exactly the same chemical composition can display very different properties due to their different microstructures.

How does the materials\molecular engineer control and design microstructure? It all starts with an understanding of the phases of matter that can coexist at given temperature and pressure. This information is often presented in the form of a phase diagram and provides the starting point if one wishes to master the art and science of microstructure design.

Before launching directly into phase diagrams we need to define a couple of terms: phase and components.

Phase is a term familiar to you. It goes almost without mentioning that there are three common phases of H<sub>2</sub>O: solid (ice), liquid (water), and gas (steam). More generally, a phase is any region of matter in which physical properties are uniform, e.g., a phase will have the same crystal structure, density, elastic properties, everywhere. For example, ice floating in a glass of water is a two-phase system. The density of the water is everywhere the same in the liquid phase but changes in solid phase. Though we are less familiar with the many solid phases present in the materials around us, they are nonetheless common. Steel is composed of several solid phases, typically iron and another phase called cementite, which is a crystalline arrangement of iron and carbon atoms.

This brings us to components. A component is a chemically independent constituent of a system. Our ice water system from above is a one component system, as only the amount of H<sub>2</sub>O can be varied independently. Note that hydrogen and oxygen are not components, as they cannot be varied independently. If you alter the number of oxygen atoms in a glass of water, the number of hydrogen atoms will change accordingly. The simplest steels are two component systems with iron and carbon as the two components.

## 10-2 PHASE DIAGRAMS IN SINGLE COMPONENT SYSTEMS

Suppose that only pressure and temperature are considered in determining the equilibrium state of water. (This is a close approximation to reality in solids and liquids; other variables have a much smaller effect.) It is possible now to diagram the *equilibrium* phase constitution of water at all combinations of  $P$  and  $T$ , which have been observed. Such a compilation of observations is called a *P-T Phase Diagram*, which is exemplified

in Figure 1.

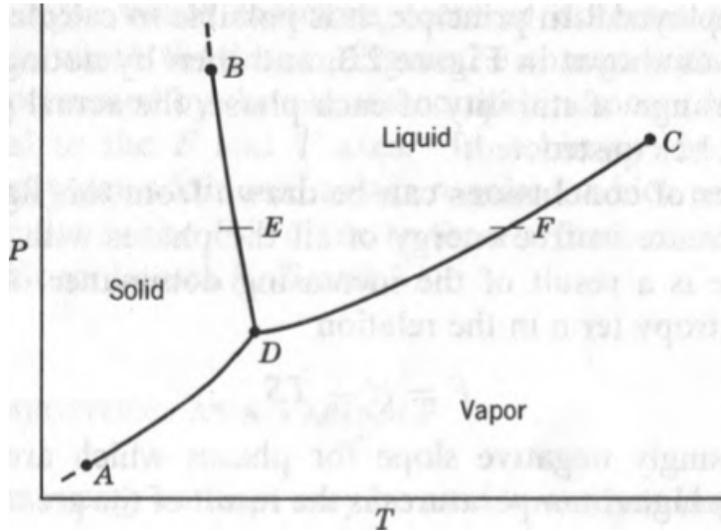


Fig 10-1 P-T Phase diagram for H<sub>2</sub>O

To use such a diagram, we locate points in  $P$ - $T$  space by specifying values for the two variables. If such a point lies in the area labeled “liquid,” that would be the state (and phase) in which H<sub>2</sub>O exists. If the point is on the line (e.g.,  $DC$ ), two phases would exist in *equilibrium*. If the specified temperature and pressure are the coordinates of point  $D$ , all three phases coexist in equilibrium with one another. Point  $D$  is called the *triplepoint*. It is located, for H<sub>2</sub>O, at 0.0098°C and at a pressure of 4.58 mm of mercury. Notice that the three-phase equilibrium is *invariant*; that is, it exists at only one point. For two phases to exist at equilibrium (as is the case along the lines  $AD$ ,  $DC$ , and  $DB$ ), if either  $P$  or  $T$  is varied, the other must assume a specific value. Therefore, in a one-component system, a two-phase equilibrium is *univariant*. If only one phase is to remain present, any combination of  $P$  and  $T$  that lies in the *phase field* of interest (i.e., in the solid, liquid, or vapor region) may be selected. This is a *bivariant equilibrium*. These rules apply to the  $P$ - $T$  diagram of any one-component system. Two more familiar points are also shown in Figure 1.  $E$  represents liquid-solid equilibrium at one atmosphere pressure and 0°C, and  $F$  represents liquid-vapor equilibrium at one atmosphere pressure and 100°C.

A diagram such as Figure 1 may be used to describe the phase or phases present at a given set of  $P$  and  $T$  conditions. It may also be used to indicate at what point phase changes would occur when one quantity is varied and the other held constant. The slopes, directions, and intersections of the various lines in Figure 1 can be related to the thermodynamic properties of  $H_2O$ .

Since the study of materials is usually limited to the consideration of condensed systems (liquid and solid), it is important to consider the thermodynamic description of *allotropic transformations*, which are phase changes occurring in a single state of aggregation. These occur in many systems, such as  $SiO_2$ ,  $Al_2O_3$ , Sn, Ti, Zr, and Fe. The allotropic transformations of iron are the most thoroughly understood of all and are of great practical importance, since they cause the wide property variations that may be produced by the heat treatment of steel.

Solid and liquid iron are normally handled at near-atmospheric pressure. At this pressure condensed-phase equilibria are relatively insensitive to small pressure variations. Accordingly, the phase diagram for pure iron may be drawn on a temperature coordinate only, as in Figure 2.

We know that the free energy of the crystallographic form stable within a particular temperature range must be less than that of any other form. From the experimental observation of phases present, and the temperatures at which they are present, and from a calculation of heat capacities and enthalpy changes accompanying various phase changes, the free energy of each of the allotropic forms of iron can be expressed as a function of temperature as shown Figure 3. The phase with the lowest free energy over a particular temperature range will be the observed form of the iron.

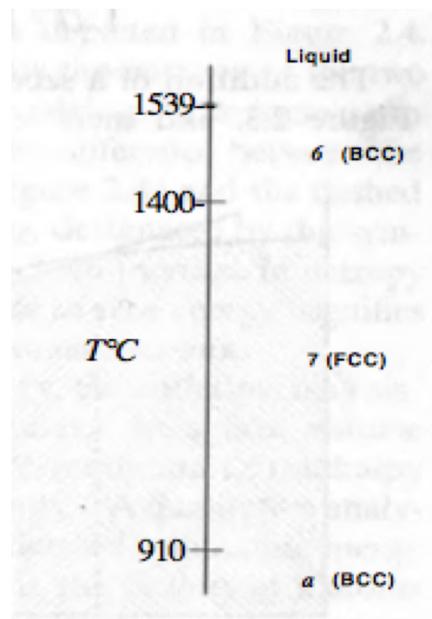


Fig. 10-2: Phase diagram of pure iron at one atm pressure

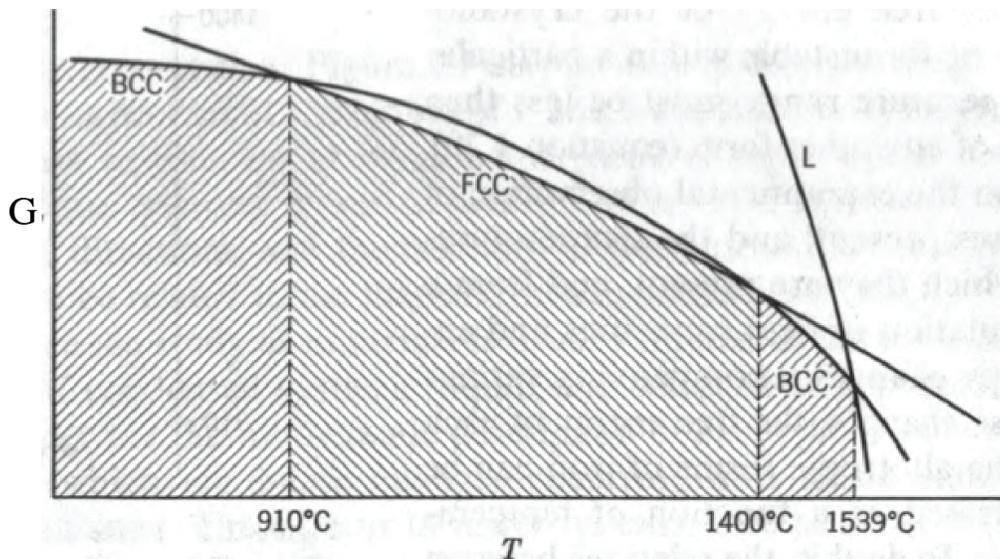


Fig. 10-3: Free energy ( $G$ ) versus temperature ( $T$ ) for the various allotropic forms of iron

The general decrease in free energy of all the phases with increasing temperature is a result of the increasing dominance of the temperature-entropy term in the relation  $G = H - TS$

### 10-3 COMPOSITION AS A VARIABLE

Now let's include composition as a variable, then the free energy will depend on temperature pressure and composition. We begin with the two-component systems. The mixing of two miscible components into a single, homogeneous solution is in all cases an irreversible process. Once they are mixed, complete unmixing is impossible unless we have the aid of Maxwell's Demon. Consequently, mixing always increases the entropy of the universe and also of the system, and we would expect such an increase to be largest near the 50-50 composition, as depicted in Figure 4.

The dashed line in Figure 4 represents the entropy of the two components, at all compositions, before mixing. The increase in entropy due to mixing is then simply the difference between the ordinate of the total entropy curve in Figure 4 and the dashed line. This quantity, the *entropy of mixing*, designated by the symbol  $S$ , is represented in Figure 4. Such an increase in entropy or, equivalently a decrease in free energy, signifies a tendency on the part of the two components to mix.

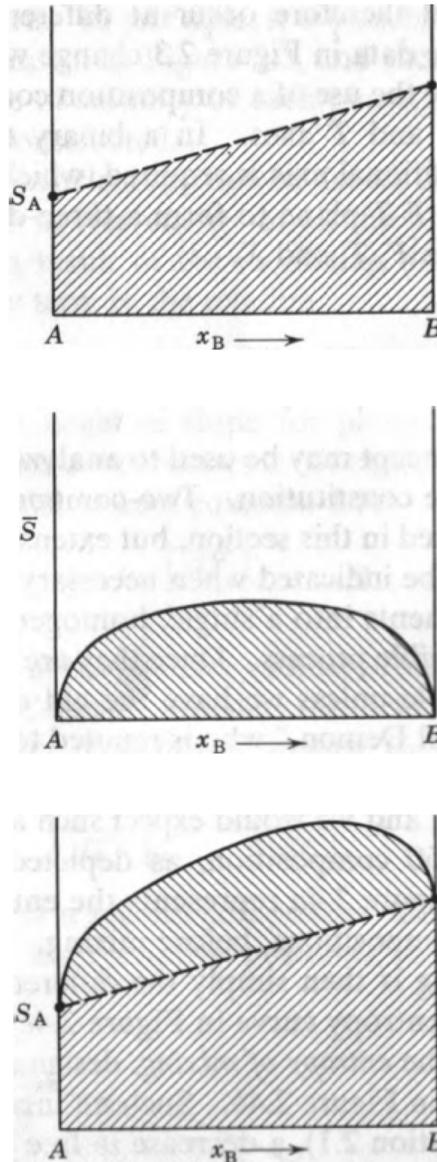


Fig. 10-4: (top) Total entropy before mixing; (middle) entropy increase due to mixing; {bottom} total entropy of mixture

The other contribution to the free energy, the enthalpy, may signify either mixing or unmixing tendencies. In solids, volume changes are relatively small and, therefore, enthalpy may be approximated by considering bond energies. If A atoms prefer to be in the vicinity of B atoms rather than other A atoms, and B atoms behave in a like manner, the enthalpy will be lowered by mixing. This is true because bond energies are negative for stable bonds. Consequently, in Figure 5a, where the dashed lines are the total enthalpy before mixing, the enthalpy after mixing lies below the dashed one at all compositions.

The maximum enthalpy decrease is expected to lie near the 50-50 composition, because a maximum number of “A-B bonds” would be formed there, if the mixture is truly homogeneous. This situation is depicted in Figure 5a, and is sometimes referred to as a *negative deviation from ideality*. The ideal case is the middle diagram, Figure 5b. Here bond energies equal for A-A, B-B, and A-B combinations, and no enthalpy change occurs on mixing. A *positive deviation* is shown in Figure 5c. Such a situation occurs if A and B atoms prefer the company of their own kind. The average bond energy after mixing is less negative and therefore enthalpy is raised by mixing. These considerations are, of course, oversimplified. Lattice strains due to atomic size differences have not been considered. The actual energetics of such solutions are more complicated than single-atom bonding and many solid solutions are not completely homogeneous at equilibrium. Figure 5 is, nevertheless, qualitatively correct in almost all cases.

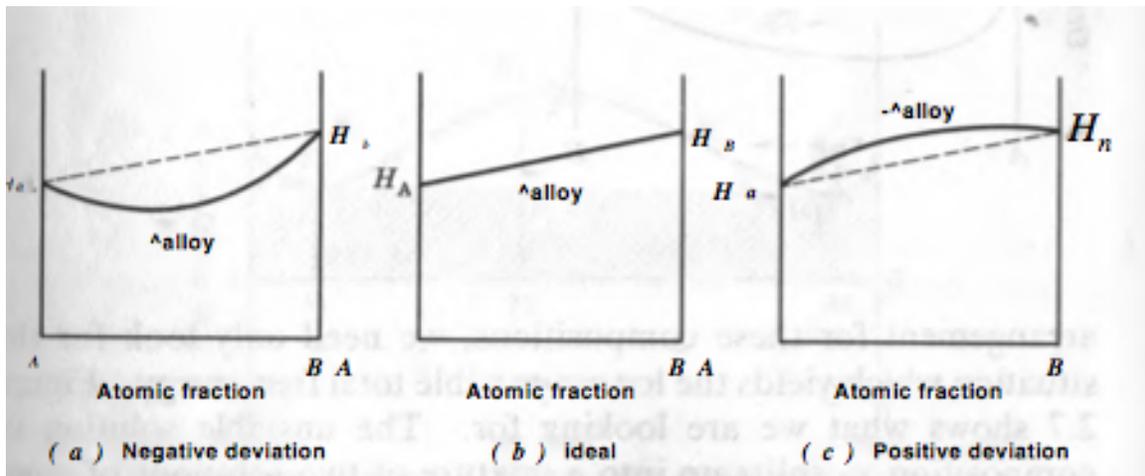


Fig. 10-5: Enthalpy composition diagram

We may now obtain the free energy of a typical solution by multiplying the ordinate of Figure 4c by the temperature and subtracting this quantity from the enthalpy. Figures 6 a, b, and c cover the three cases described in Figure 5. For negative deviations and ideal solutions, we see immediately that mixing decreases the free energy and conclude that such solutions are stable. The positive deviation is more interesting. At higher temperatures, the entropy term would dominate the free energy change on mixing, and the solution would always be stable. At lower temperatures

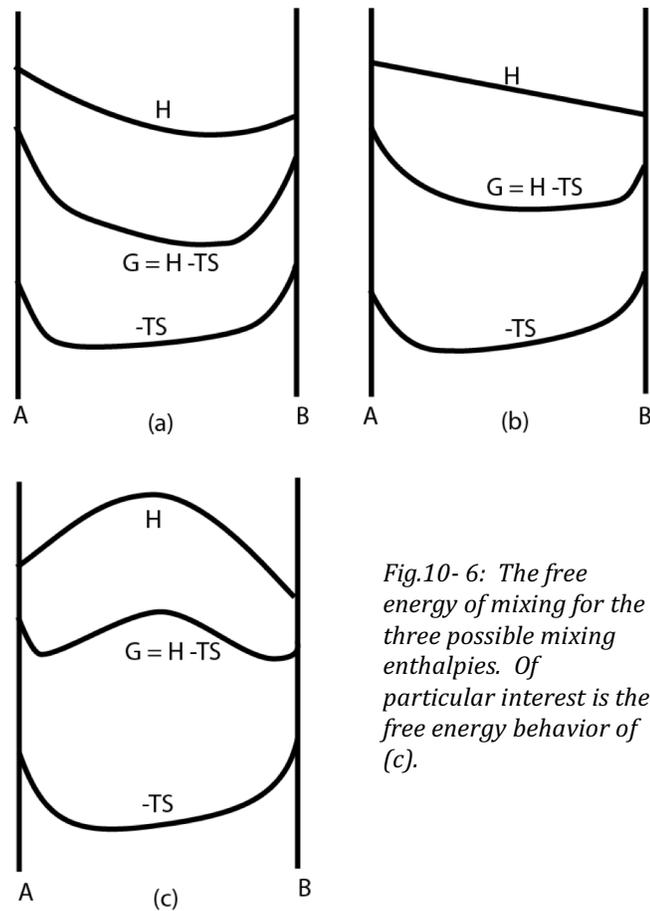


Fig.10- 6: The free energy of mixing for the three possible mixing enthalpies. Of particular interest is the free energy behavior of (c).

(Figure 6c), the positive contribution from the enthalpy shows up. The free energy of mixing for solutions with intermediate compositions (i.e., near the middle of Figure 6c) may be positive, signifying that such solutions are unstable. To find the stable arrangement for these compositions, we need only look for the situation that yields the lowest possible total free energy. Figure 7 shows what we are looking for. The unstable solution of composition  $x_3$  splits up into a mixture of two solutions of compositions  $x_1$  and  $x_2$  respectively. The free energy of the mixture lies on the dashed line, for all total compositions between  $x_1$  and  $x_2$ . Since the free energy of the mixture is less than that of the single solution over this entire composition range, we conclude that, for all total compositions between  $x_1$  and  $x_2$ , a mixture of two solutions of those two compositions is the most stable state. Note that this is so even for compositions where the free energy of mixing is negative.

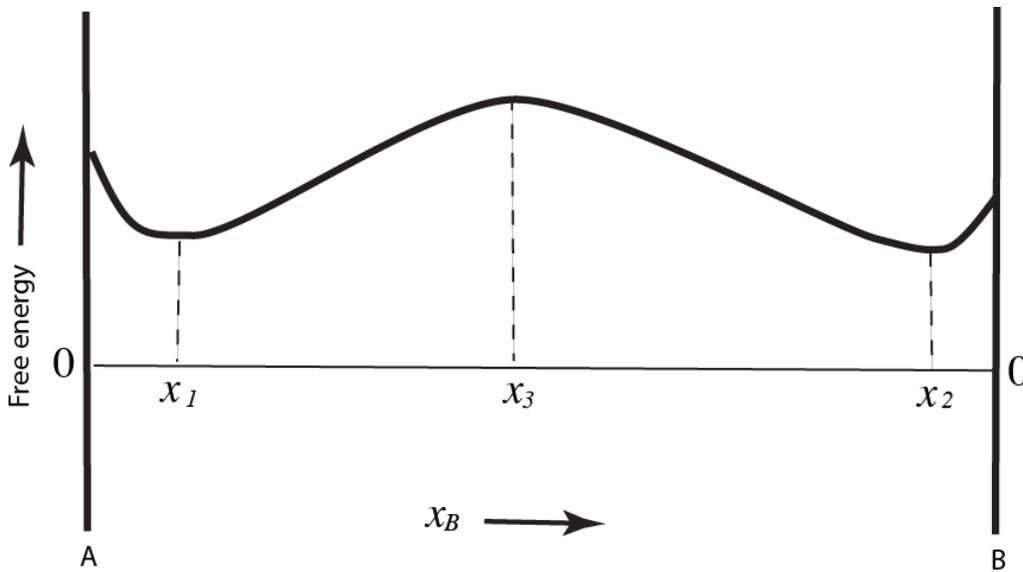


Fig. 10-7: Free energy diagram for binary alloy showing separation into two solid solutions

The procedure for finding stable phase equilibria may also be applied in binary systems where a number of alternate phases are formed. Consider Figure 2.8. The stable states for all compositions are described by the lowest possible “envelope” of free energy curves and tangent lines. In Figure 8,  $\gamma$  and liquid are unstable at all compositions,  $\alpha$  is stable for A-rich mixtures, and  $\beta$  for B-rich mixtures. At overall compositions between the points of tangency with the dashed line, mixtures of  $\alpha$  and  $\beta$  are stable. The  $\alpha$

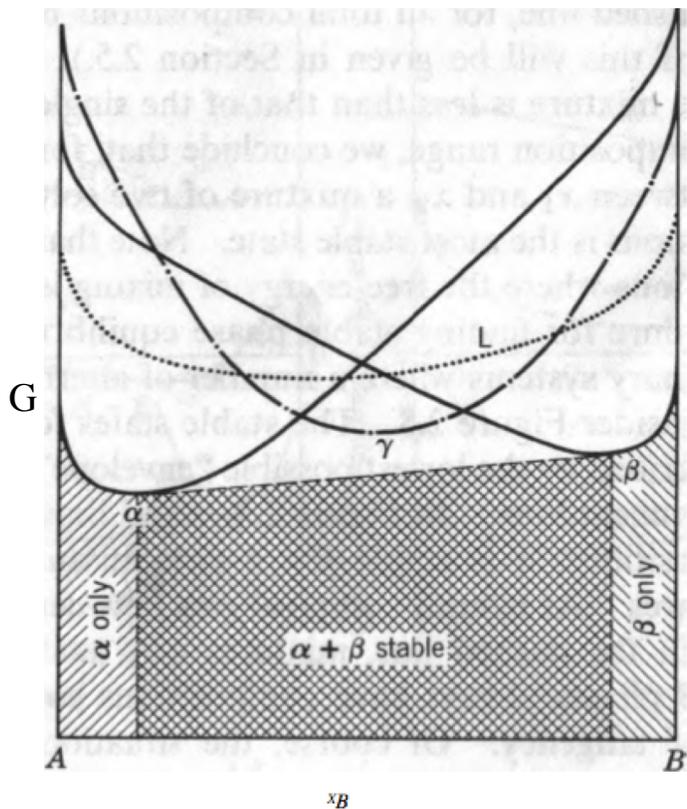


Fig. 10 - 8: Binary system showing two stable solid phases.

and  $\beta$  phases always have compositions corresponding to the points of tangency. Of course, the situation changes with changing temperature. If the temperature is high enough, the free energy-composition curve for the liquid will lie below all other curves and tangent lines, signifying stability of the liquid phase at all compositions. If the relative positions of the free energy composition curves for a binary system are known for a series of temperatures, the stable phases or mixtures of phases may be deduced immediately for each temperature. As you did in lab these data may then be plotted in temperature-composition space; the result a *phase diagram*, which maps out the regions of stability for each phase and phase mixture.

Figure 9 depicts the development of a eutectic phase diagram from a series of free energy-composition diagrams. At each temperature, the appropriate tangents are drawn to the free energy curves. The points of tangency mark the constant compositions of the two phases in the two-phase (mixture) region, and the boundaries between two-phase and single-phase regions. At  $T_2$  three curves possess a common tangent. Here, the so-called *eutectic reaction*, occurs. The three-phase equilibrium occurs only at  $T_2$ , between phases having compositions corresponding to the points of tangency with the free energy curves. For other temperatures, the liquid free energy curve shifts, and the common tangent disappears. Because three-phase equilibria exist only for fixed temperatures and phase compositions in binary systems they are called *invariant*.

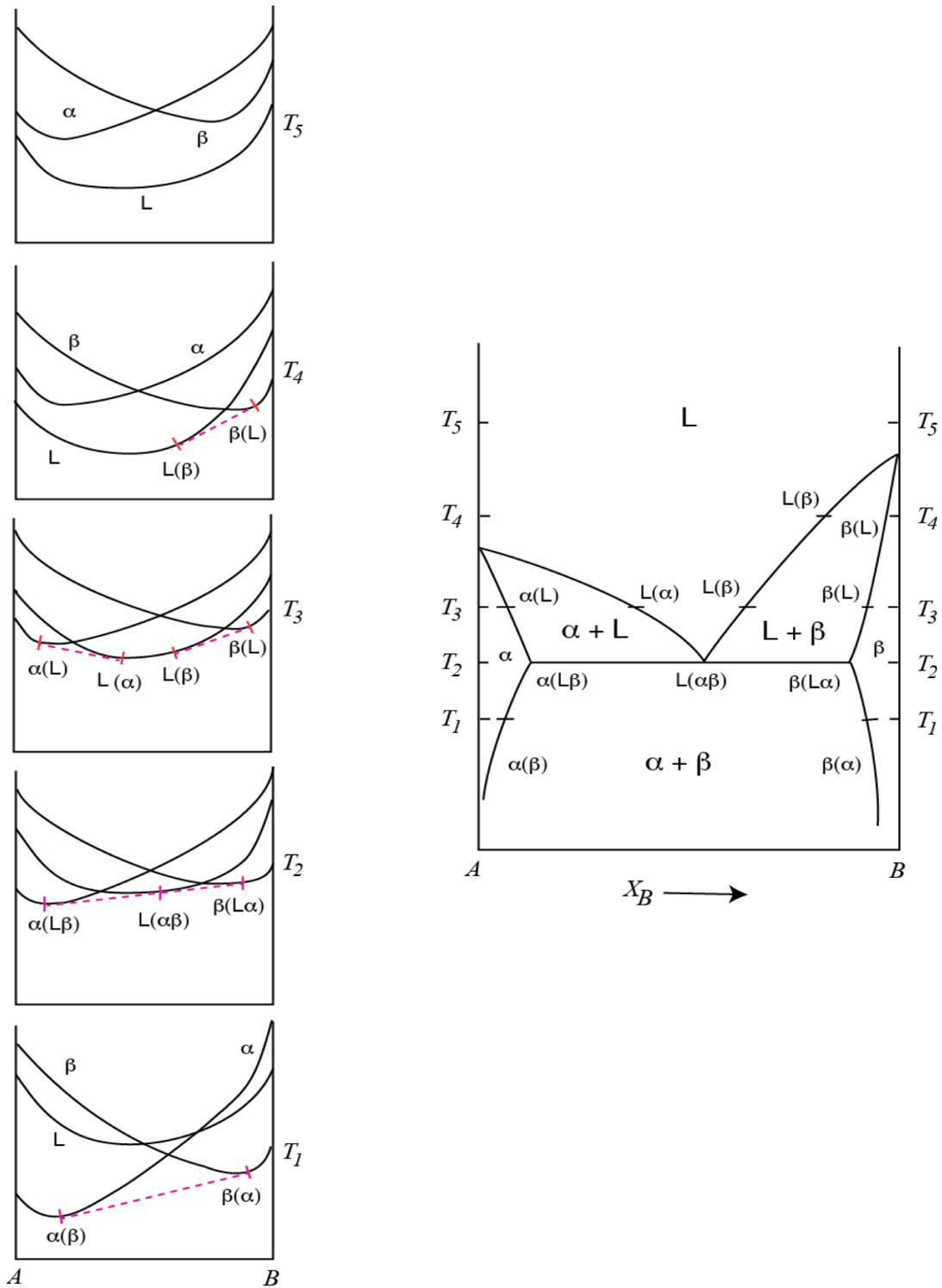


Fig. 10-9: Construction of a eutectic T-X diagram from a number of G-X diagrams

The eutectic diagram is technologically important and helps to illustrate the underlying principles that give rise to phase equilibria in two component systems, but it is just one of many possible phase diagrams. Figure 10 show the iron rich end of Fe-C phase diagram, which we will consider in the next section.

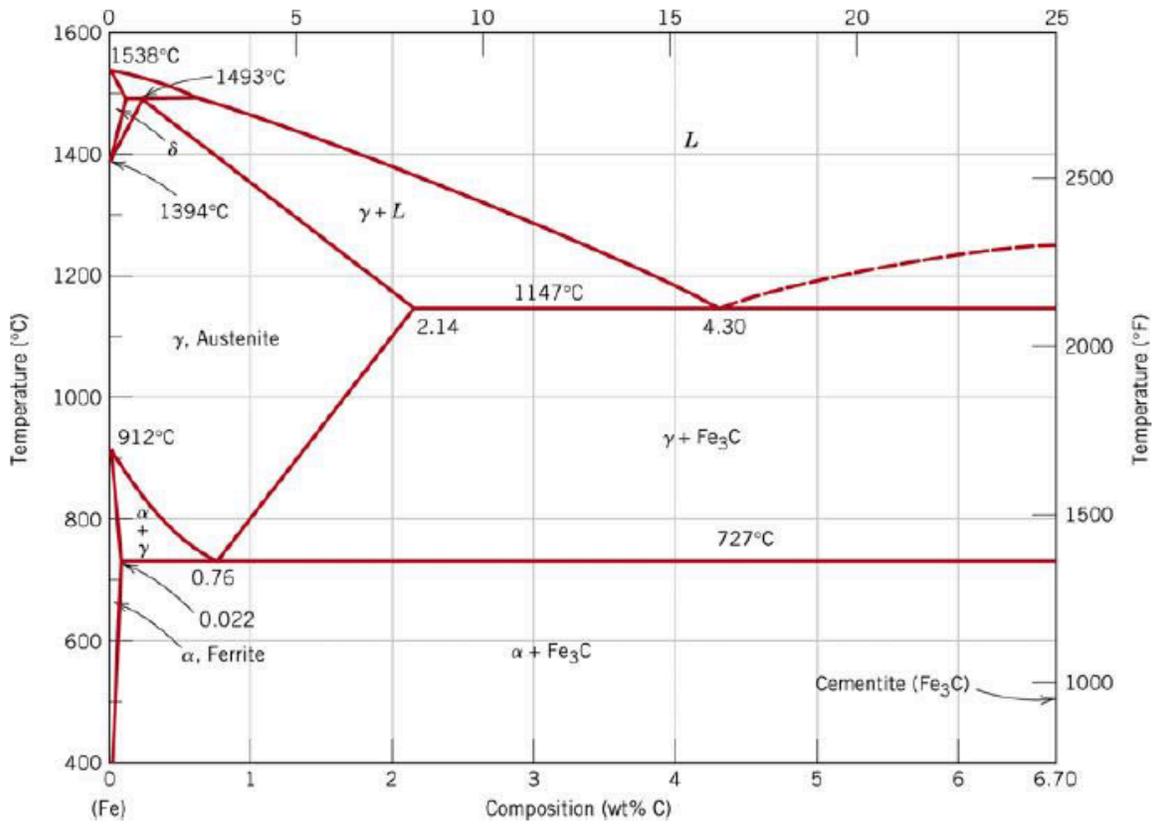


Fig.10 -10: The iron-carbon phase diagram