

3.091 – Introduction to Solid State Chemistry**Lecture Notes No. 10****PHASE EQUILIBRIA AND PHASE DIAGRAMS**

Sources for Further Reading:

1. Campbell, J.A., Why Do Chemical Reactions Occur?, Prentice-Hall, Englewood Cliffs, NJ, 1965. (Paperback)
2. Barrow, G.M., Physical Chemistry, McGraw-Hill, New York, 1973.
3. Hägg, G., General and Inorganic Chemistry, Wiley, 1969.
4. Henish, H., Roy, R., and Cross, L.E., Phase Transitions, Pergamon, 1973.
5. Reisman, A., Phase Equilibria, Academic Press, 1970.

PART A: PHASE EQUILIBRIA AND PHASE DIAGRAMS

Phase diagrams are one of the most important sources of information concerning the behavior of elements, compounds and solutions. They provide us with the knowledge of phase composition and phase stability as a function of temperature (T), pressure (P) and composition (C). Furthermore, they permit us to study and control important processes such as phase separation, solidification, sintering, purification, growth and doping of single crystals for technological and other applications. Although phase diagrams provide information about systems *at equilibrium*, they can also assist in predicting phase relations, compositional changes and structures *in systems not at equilibrium*.

1. GASES, LIQUIDS AND SOLIDS

Any material (elemental or compound) can exist as a gas, a liquid or a solid, depending on the relative magnitude of the attractive interatomic or intermolecular forces vs the disruptive thermal forces. It is thus clear that the stability (existence) of the different

states of aggregation, which are referred to as *phases*, is a function of temperature and pressure (since with increased pressure the atoms, for example of a gas phase, are closer spaced and thus subject to increased interatomic attraction).

In general terms, a “phase” is a homogeneous, physically distinct, mechanically separable portion of a material with a given chemical composition. To illustrate this definition, let us look at a few examples of common multi-phase systems. Ice cubes in water constitute a two-phase system (ice and liquid water), unless we include the vapor above the glass in our system, which would make it a three-phase system. A mixture of oil and water would also be a two-phase system. Just as oil and water represent two distinct liquid phases, two regions of a solid with distinctly different composition or structure separated by boundaries represent two solid phases.

If we look at a one-component system, such as liquid water, we recognize that because of the energy distribution of the water molecules, some water molecules will always possess sufficient energy to overcome the attractive forces on the surface of H₂O and enter into the *gas phase*. If thermal energy is continuously supplied to a liquid in an open container, the supply of high energy molecules (which leave the liquid phase) is replenished and the temperature remains constant – otherwise the loss of high energy molecules will lower the temperature of the system. The total quantity of heat necessary to completely “vaporize” one mole of a liquid at its boiling point is called its *molar heat of vaporization*, designated by ΔH_V . Similarly, the heat required to completely melt one mole of a solid (the heat required to break the bonds established in the solid phase) is called the (*latent*) *heat of fusion* (ΔH_V).

Visualize a liquid in a sealed container with some space above the liquid surface. Again, some of the most energetic liquid molecules will leave the liquid phase and form a “gas phase” above the liquid. Since gas molecules will thus accumulate in the gas phase (at a constant temperature), it is inevitable that as a result of collisions in the gas

phase some molecules will re-enter the liquid phase and a situation will be established whereby the rate of evaporation will equal the rate of condensation – i.e., a dynamic equilibrium between the liquid and gas phase will exist. The established pressure in the gas phase is referred to as the *equilibrium vapor pressure*, which is normally significantly less for solids than for liquids.

For obvious reasons it is desirable to know for any given material the conditions (P, T) under which the solid state, the liquid state and the gaseous state are stable, as well as the conditions under which the solid and liquid phases may coexist. These conditions are graphically presented in *equilibrium phase diagrams*, which can be experimentally determined.

2. THE ONE-COMPONENT PHASE DIAGRAM

Figure 1 illustrates the temperatures and pressures at which water can exist as a solid, liquid or vapor. The curves represent the points at which two of the phases coexist in equilibrium. At the point T_t vapor, liquid and solid coexist in equilibrium. In the fields of the diagram (phase fields) only one phase exists. Although a diagram of this kind delineates the boundaries of the phase fields, it does not indicate the quantity of any phase present.

It is of interest to consider the slope of the liquid/solid phase line of the H_2O phase diagram. It can readily be seen that if ice – say at $-2^\circ C$ – is subjected to high pressures, it will transform to liquid H_2O . (An ice skater will skate not on ice, but on water.) This particular pressure sensitivity (reflected in the slope of the solid/liquid phase line) is characteristic for materials which have a higher coordination number in the liquid than in the solid phase (H_2O , Bi, Si, Ge). Metals, for example have an opposite slope of the solid/liquid phase line, and the liquid phase will condense under pressure to a solid phase.

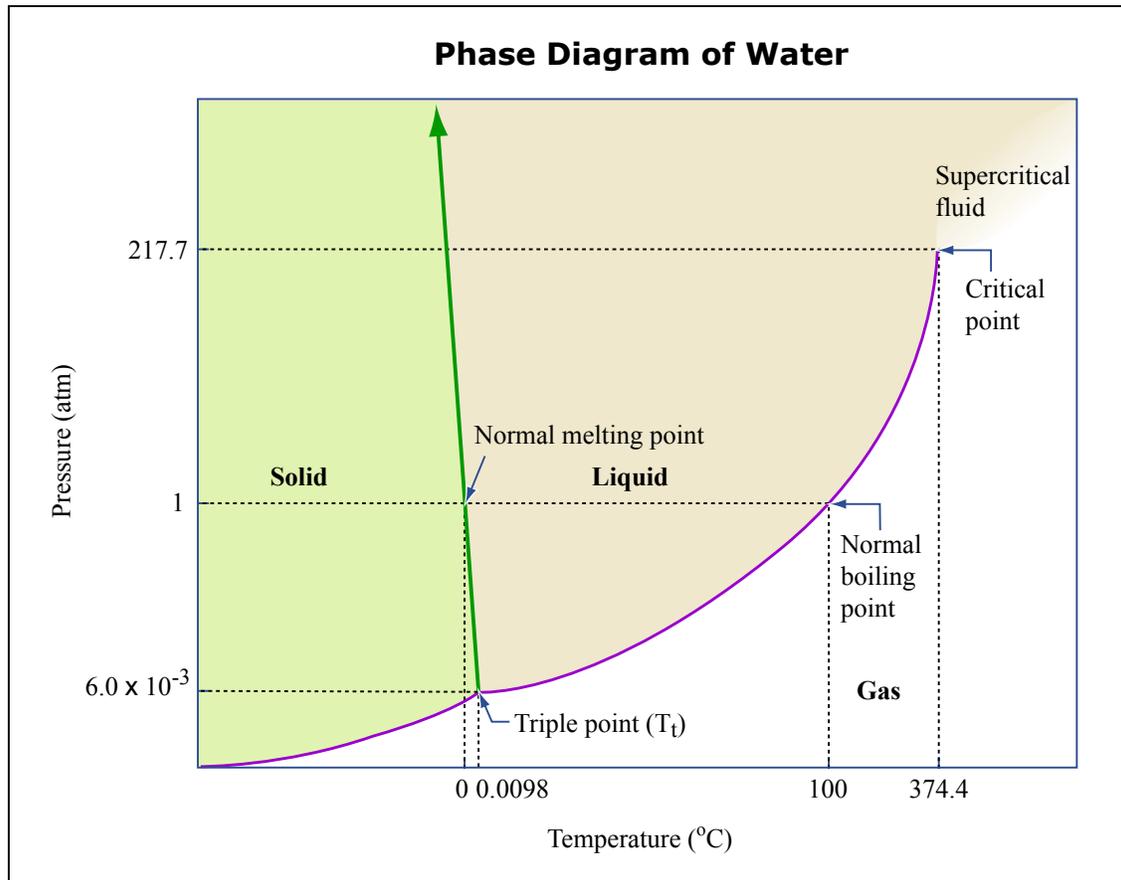


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Fig. 1 Pressure/Temperature Diagram for Water. (Not drawn to scale.)

3. PHASE RULE AND EQUILIBRIUM

The phase rule, also known as the Gibbs phase rule, relates the number of components and the number of degrees of freedom in a system at equilibrium by the formula

$$F = C - P + 2 \quad [1]$$

where F equals the number of degrees of freedom or the number of independent variables, C equals the number of components in a system in equilibrium and P equals the number of phases. The digit 2 stands for the two variables, temperature and pressure.

The number of degrees of freedom of a system is the number of variables that may be changed independently without causing the appearance of a new phase or disappearance of an existing phase. The number of chemical constituents that must be specified in order to describe the composition of each phase present. For example, in the reaction involving the decomposition of calcium carbonate on heating, there are three phases – two solid phases and one gaseous phase.



There are also three different chemical constituents, but the number of components is only two because any two constituents completely define the system in equilibrium. Any third constituent may be determined if the concentration of the other two is known. Substituting into the phase rule (eq. [1]) we can see that the system is univariant, since $F = C - P + 2 = 2 - 3 + 2 = 1$. Therefore only one variable, either temperature or pressure, can be changed independently. (The number of components is not always easy to determine at first glance, and it may require careful examination of the physical conditions of the system at equilibrium.)

The phase rule applies to dynamic and reversible processes where a system is heterogeneous and in equilibrium and where the only external variables are temperature, pressure and concentration. For one-component systems the maximum number of variables to be considered is two – pressure and temperature. Such systems can easily be represented graphically by ordinary rectangular coordinates. For two-component (or binary) systems the maximum number of variables is three – pressure, temperature and concentration. Only one concentration is required to define the composition since the second component is found by subtracting from unity. A graphical representation of such a system requires a three-dimensional diagram. This, however, is not well suited to illustration and consequently separate two-coordinate diagrams, such as pressure vs temperature, pressure vs composition and temperature

vs composition, are mostly used. Solid/liquid systems are usually investigated at constant pressure, and thus only two variables need to be considered – the vapor pressure for such systems can be neglected. This is called a condensed system and finds considerable application in studying phase equilibria in various engineering materials. A condensed system will be represented by the following modified phase rule equation:

$$F = C - P + 1 \quad [3]$$

where all symbols are the same as before, but (because of a constant pressure) the digit 2 is replaced by the digit 1, which stands for temperature as variable. The graphical representation of a solid/liquid binary system can be simplified by representing it on ordinary rectangular coordinates: temperature vs concentration or composition.

4. H vs T PHASE DIAGRAM

With the aid of a suitable calorimeter and energy reservoir, it is possible to measure the heat required to melt and evaporate a pure substance like ice. The experimental data obtainable for a mole of ice is shown schematically in fig. 2. As heat is added to the solid, the temperature rises along line “a” until the temperature of fusion (T_f) is reached. The amount of heat absorbed per mole during melting is represented by the length of line “b”, or ΔH_f . The amount of heat absorbed per mole during evaporation at the boiling point is represented by line “d”. The reciprocal of the slope of line “a”, (dH/dT), is the heat required to change the temperature of one mole of substance (at constant pressure) by 1°C . (dH/dT) is the molar *heat capacity* of a material, referred to as “ C_p ”. As the reciprocal of line “a” is C_p (solid), the reciprocals of lines “c” and “e” are C_p (liquid) and C_p (vapor) respectively.

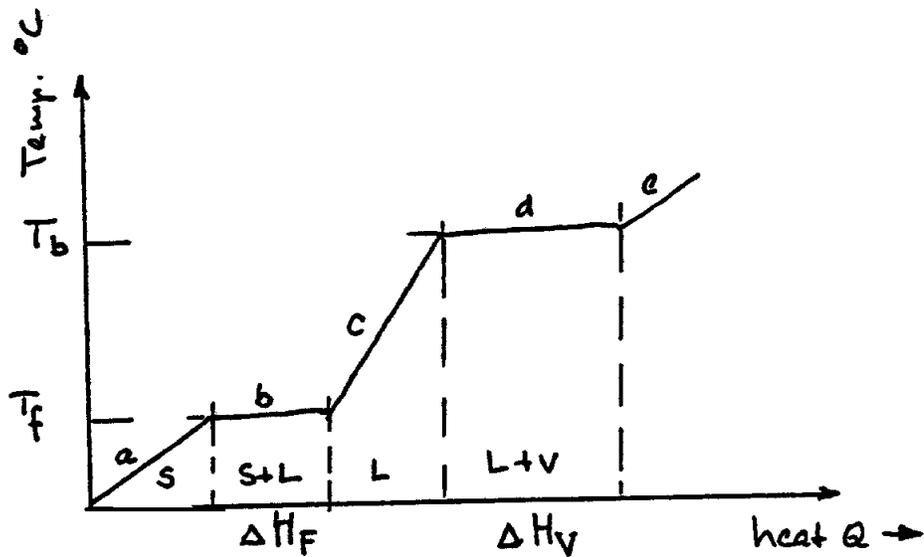


Fig. 2 H vs T Diagram for Pure H₂O. (Not to scale.)

From a thermodynamic standpoint, it is important to realize that fig. 2 illustrates the energy changes that occur in the system during heating. Actual quantitative measurements show that 5.98 kJ of heat are absorbed at the melting point (latent heat of fusion) and 40.5 kJ per mole (latent heat of evaporation) at the boiling point. The latent heats of fusion and evaporation are unique characteristics of all pure substances. Substances like Fe, Co, Ti and others, which are allotropic (exhibit different structures at different temperatures), also exhibit latent heats of transformation as they change from one solid state crystal modification to another.

5. ENERGY CHANGES

When heat is added from the surroundings to a material system (as described above), the energy of the system changes. Likewise, if work is done on the surroundings by the material system, its energy changes. The difference in energy (ΔE) that the system

experiences must be the difference between the heat absorbed (Q) by the system and the work (W) done on the surroundings. The energy change may therefore be written as:

$$\Delta E = Q - W \quad [4]$$

If heat is liberated by the system, the sign of Q is negative and work done is positive. Q and W depend on the direction of change, but ΔE does not. The above relation is one way of representing the **First Law of Thermodynamics** which states that the energy of a system and its surroundings is always conserved while a change in energy of the system takes place. The energy change, ΔE , for a process is independent of the path taken in going from the initial to the final state.

In the laboratory most reactions and phase changes are studied at constant pressure. The work is then done solely by the pressure (P), acting through the volume change, ΔV .

$$W = P\Delta V \quad \text{and} \quad \Delta P = 0 \quad [5]$$

Hence:

$$Q = \Delta E + P\Delta V \quad [6]$$

Since the heat content of a system, or the *enthalpy* H , is *defined by*:

$$H = E + PV \quad [7]$$

$$\Delta H = \Delta E + P\Delta V \quad [8]$$

so that:

$$\Delta H = Q - W + P\Delta V \quad [9]$$

or

$$\Delta H = Q \quad [10]$$

Reactions in which ΔH is negative are called *exothermic* since they liberate heat, whereas *endothermic* reactions absorb heat. Fusion is an endothermic process, but the reverse reaction, crystallization, is an exothermic one.

6. ENTROPY AND FREE ENERGY

When a gas condenses to form a liquid and a liquid freezes to form a crystalline solid, the degree of internal order increases. Likewise, atomic vibrations decrease to zero when a perfect crystal is cooled to 0°K. Since the term *entropy*, designated by S, is considered a measure of the degree of disorder of a system, a perfect crystal at 0°K has zero entropy.

The product of the absolute temperature, T, and the change in entropy, ΔS , is called the *entropy factor*, $T\Delta S$. This product has the same units (Joules/mole) as the change in enthalpy, ΔH , of a system. At constant pressure, P, the two energy changes are related to one another by the Gibbs free energy relation:

$$\Delta F = \Delta H - T\Delta S \quad [11]$$

where

$$F = H - TS \quad [12]$$

The natural tendency exhibited by all materials systems is to change from one of higher to one of lower free energy. Materials systems also tend to assume a state of greater disorder whereby the entropy factor $T\Delta S$ is increased. The free energy change, ΔF , expresses the balance between the two opposing tendencies, the change in heat content (ΔH) and the change in the entropy factor ($T\Delta S$).

If a system at constant pressure is in an equilibrium state, such as ice and water at 0°C, for example, at atmospheric pressure it cannot reach a lower energy state. At equilibrium in the ice-water system, the opposing tendencies, ΔH and $T\Delta S$, equal one another so that $\Delta F = 0$. At the fusion temperature, T_F :

$$\Delta S_F = \frac{\Delta H_F}{T_F} \quad [13]$$

Similarly, at the boiling point:

$$\Delta S_V = \frac{\Delta H_V}{T_V} \quad [14]$$

Thus melting or evaporation only proceed if energy is supplied to the system from the surroundings.

The entropy of a pure substance at constant pressure increases with temperature according to the expression:

$$\Delta S = \frac{C_p \Delta T}{T} \quad (\text{since: } \Delta H = C_p \Delta T) \quad [15]$$

where C_p is the heat capacity at constant pressure, ΔC_p , ΔH , T and ΔT are all measurable quantities from which ΔS and ΔF can be calculated.

7. F vs T

Any system can change spontaneously if the accompanying free energy change is negative. This may be shown graphically by making use of F vs T curves such as those shown in fig. 3.

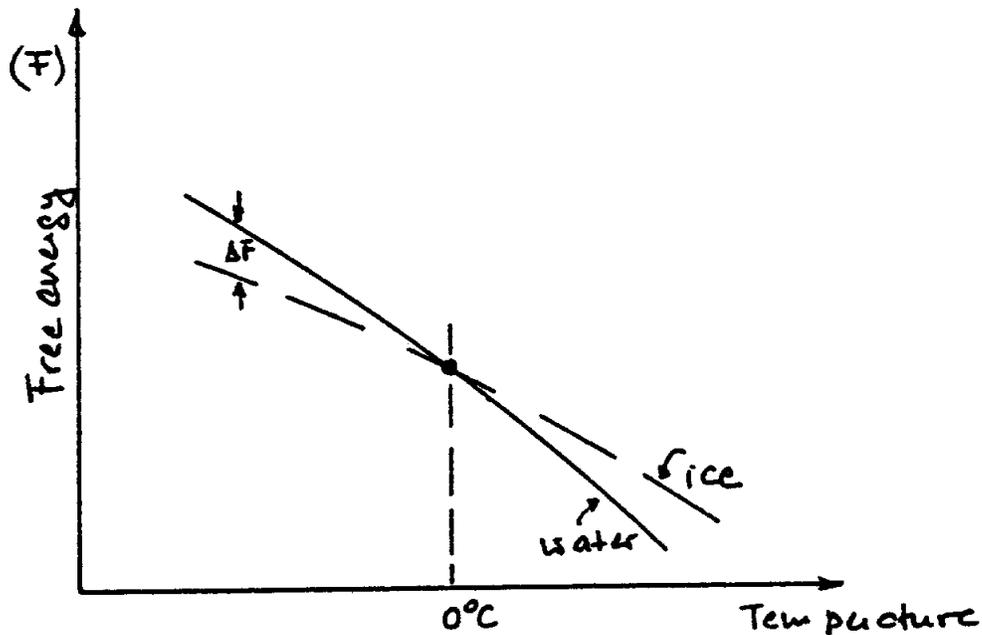


Fig. 3 Free energy is a function of temperature for ice and water.

The general decrease in free energy of all the phases with increasing temperature is the result of the increasing dominance of the temperature-entropy term. The increasingly negative slope for phases which are stable at increasingly higher temperatures is the result of the greater entropy of these phases.

PART B: PHASE DIAGRAMS (TWO-COMPONENT SYSTEMS)

1. SOLID SOLUTIONS

A solution can be defined as a homogeneous mixture in which the atoms or molecules of one substance are dispersed at random into another substance. If this definition is applied to solids, we have a *solid solution*. The term “solid solution” is used just as “liquid solution” is used because the solute and solvent atoms (applying the term solvent to the element in excess) are arranged at random. The properties and composition of a solid solution are, however, uniform as long as it is not examined at the atomic or molecular level.

Solid solutions in alloy systems may be of two kinds: substitutional and interstitial. A substitutional solid solution results when the solute atoms take up the positions of the solvent metal in the crystal lattice. Solid solubility is governed by the comparative size of the atoms of the two elements, their structure and the difference in electronegativity. If the atomic radii of a solvent and solute differ by more than 15% of the radius of the solvent, the range of solubility is very small. When the atomic radii of two elements are equal or differ by less than 15% in size and when they have the same number of valency electrons, substitution of one kind of atom for another may occur with no distortion or negligible distortion of the crystal lattice, resulting in a series of homogeneous solid solutions. For an unlimited solubility in the solid state, the radii of the two elements must not differ by more than 8% and both the solute and the solvent elements must have the same crystal structure.

In addition to the atomic size factor, the solid solution is also greatly affected by the electronegativity of elements and by the relative valency factor. The greater the difference between electronegativities, the greater is the tendency to form compounds and the smaller is the solid solubility. Regarding valency effect, a metal of lower valency is more likely to dissolve a metal of higher valency. Solubility usually increases with increasing temperature and decreases with decreasing temperature. This causes precipitation within a homogeneous solid solution phase, resulting in hardening effect of an alloy. When ionic solids are considered, the valency of ions is a very important factor.

2. CONSTRUCTION OF EQUILIBRIUM PHASE DIAGRAMS OF TWO-COMPONENT SYSTEMS

To construct an equilibrium phase diagram of a binary system, it is a necessary and sufficient condition that the boundaries of one-phase regions be known. In other words, the equilibrium diagram is a plot of solubility relations between components of the system. It shows the number and composition of phases present in any system under equilibrium conditions at any given temperature. Construction of the diagram is often based on solubility limits determined by thermal analysis – i.e., using cooling curves. Changes in volume, electrical conductivity, crystal structure and dimensions can also be used in constructing phase diagrams.

The solubility of two-component (or binary) systems can range from essential insolubility to complete solubility in both liquid and solid states, as mentioned above. Water and oil, for example, are substantially insoluble in each other while water and

alcohol are completely intersoluble. Let us visualize an experiment on the water-ether system in which a series of mixtures of water and ether in various proportions is placed in test tubes. After shaking the test tubes vigorously and allowing the mixtures to settle, we find present in them only one phase of a few percent of ether in water or water in ether, whereas for fairly large percentages of either one in the other there are two phases. These two phases separate into layers, the upper layer being ether saturated with water and the lower layers being water saturated with ether. After sufficiently increasing the temperature, we find, regardless of the proportions of ether and water, that the two phases become one. If we plot solubility limit with temperature as ordinate and composition as abscissa, we have an isobaric [constant pressure (atmospheric in this case)] phase diagram, as shown in fig. 4. This system exhibits a *solubility gap*.

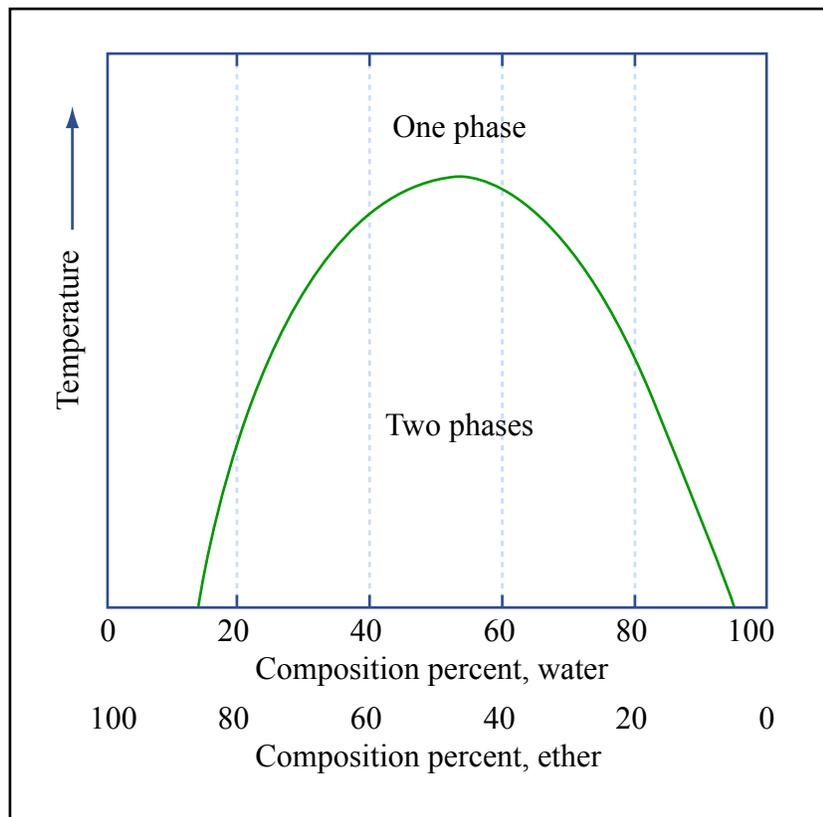


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Fig. 4 Schematic representation of the solubilities of ether and water in each other.

3. COOLING CURVES

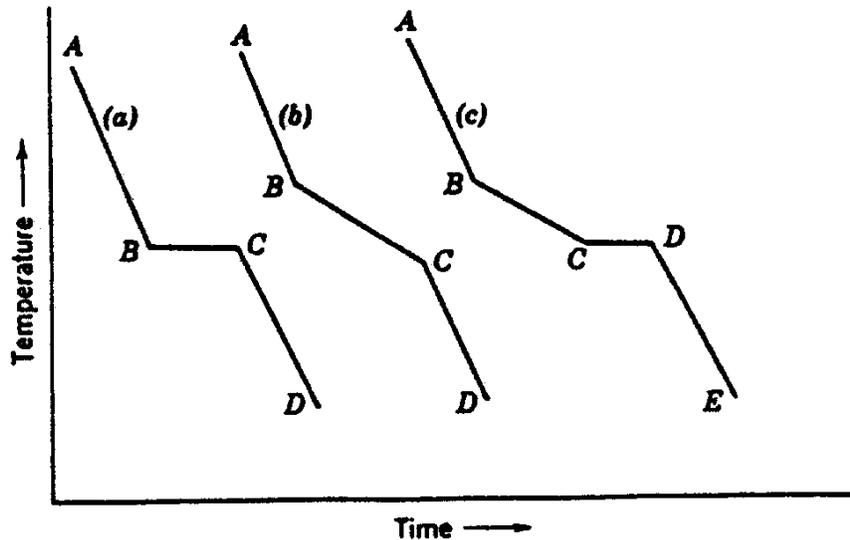


Fig. 5 Cooling curves: (a) pure compound; (b) binary solid solution; (c) binary eutectic system.

Source: Jastrzebski, Z. *The Nature and Properties of Engineering Materials*. 2nd edition. New York, NY: John Wiley & Sons, 1976. Courtesy of John Wiley & Sons. Used with permission.

4. SOLID SOLUTION EQUILIBRIUM DIAGRAMS

Read in Jastrzebski: First two paragraphs and Figure 3-4 in Chapter 3-8, "Solid Solutions Equilibrium Diagrams," pp. 91-92.

Read in Smith, C. O. *The Science of Engineering Materials*. 3rd ed. Englewood Cliffs, NJ: Prentice-Hall, 1986. ISBN: 9780137948840. Last two paragraphs and Figure 7-8 in Chapter 7-3-1, "Construction of a Simple Equilibrium Diagram," pp. 247-248.

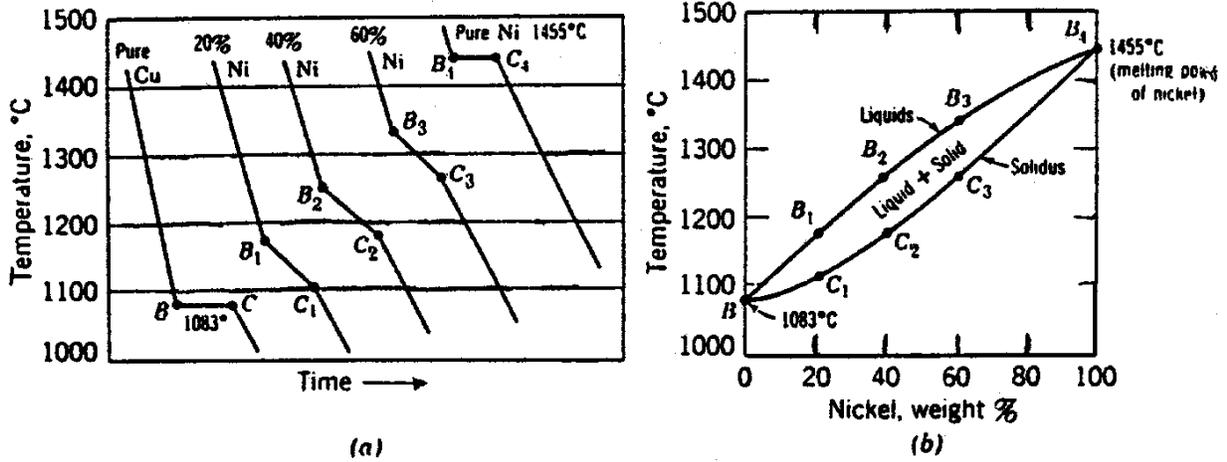


Fig. 6 Plotting equilibrium diagrams from cooling curves for Cu-Ni solid solution alloys. (a) Cooling curves; (b) equilibrium diagram.

Source: Jastrzebski, Z. *The Nature and Properties of Engineering Materials*. 2nd edition. New York, NY: John Wiley & Sons, 1976. Courtesy of John Wiley & Sons. Used with permission.

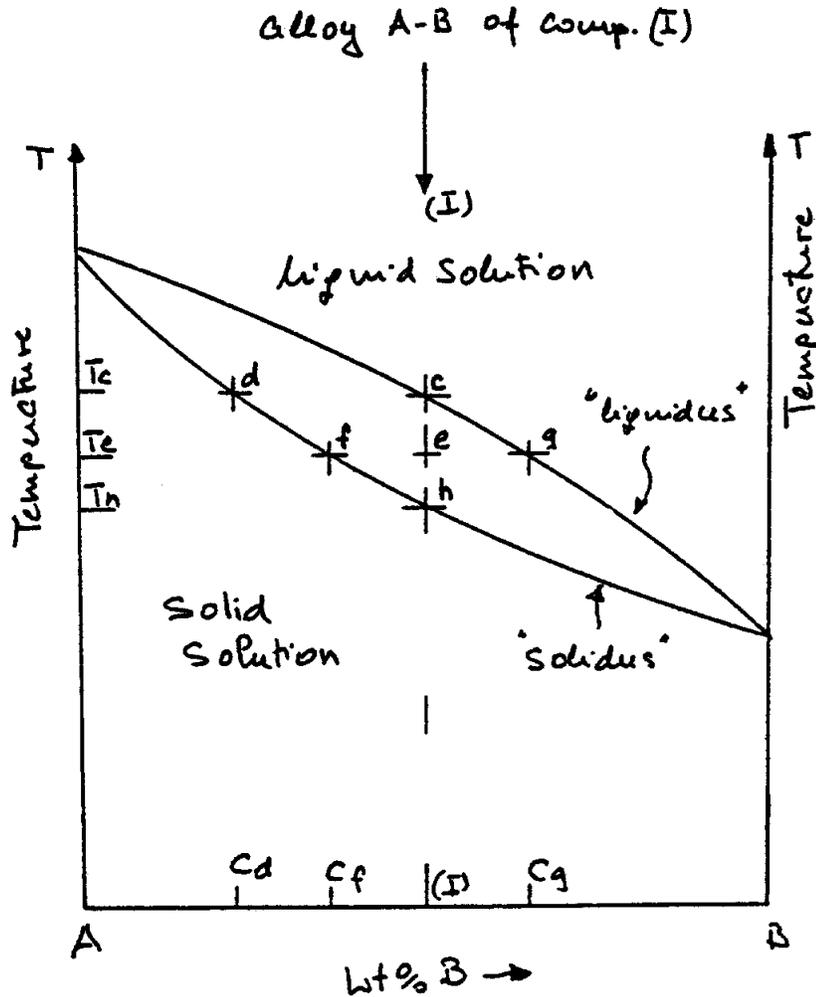


Fig. 7

5. INTERPRETATION OF PHASE DIAGRAMS

From the above discussion we can draw two useful conclusions which are the only rules necessary for interpreting equilibrium diagrams of binary systems.

Rule 1 - Phase composition: To determine the composition of phases which are stable at a given temperature we draw a horizontal line at the given temperature. The projections (upon the abscissa) of the intersections of the isothermal line with the liquidus and the solidus give the compositions of the liquid and solid, respectively, which coexist in equilibrium at that temperature. For example, draw a horizontal temperature line through temperature T_e in fig. 7. The T_e line intersects the solidus at f and the liquidus at g, indicating solid composition of f% of B and (100-f)% of A. The liquid composition at this temperature is g% of B and (100-g)% of A. This line in a two-phase region is known as a *tie line* because it connects or “ties” together lines of one-fold saturation – i.e., the solid is saturated with respect to B and the liquid is saturated with respect to A.

Rule 2 - The Lever Rule: To determine the relative amounts of the two phases, erect an ordinate at a point on the composition scale which gives the total or overall composition of the alloy. The intersection of this composition vertical and a given isothermal line is the fulcrum of a simple lever system. The relative lengths of the lever arms multiplied by the amounts of the phase present must balance. As an illustration, consider alloy I in fig. 7. The composition vertical is erected at alloy I with a composition of e% of B and (100-e)% of A. This composition vertical intersects the temperature horizontal (T_e) at point e. The length of the line “f-e-g” indicates the total amount of the two phases present. The length of line “e-g” indicates the amount of

solid. In other words:

$$\frac{eg}{fg} \times 100 = \% \text{ of solid present}$$

$$\frac{fg}{fg} \times 100 = \% \text{ of liquid present}$$

These two rules give both the *composition* and the *relative quantity* of each phase present in a two-phase region in any binary system in equilibrium regardless of physical form of the two phases. The two rules apply only to two-phase regions.

6. ISOMORPHOUS SYSTEMS

An isomorphous system is one in which there is complete intersolubility between the two components in the vapor, liquid and solid phases, as shown in fig. 9. The Cu-Ni system is both a classical and a practical example since the monels, which enjoy extensive commercial use, are Cu-Ni alloys. Many practical materials systems are isomorphous.

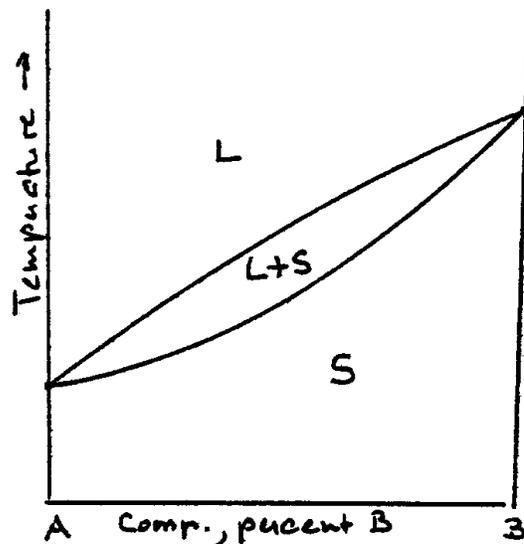


Fig. 9 Schematic phase diagram for a binary system, A-B, showing complete intersolubility (isomorphism) in all phases.

7. INCOMPLETE SOLUBILITY

Read in Smith, C. O. *The Science of Engineering Materials*. 3rd ed. Englewood Cliffs, NJ: Prentice-Hall, 1986. ISBN: 9780137948840.
Chapter 7-3-5, "Incomplete Solubility," pp. 252-253.

8. EUTECTIC SYSTEMS

Read in Smith: Chapter 7-3-6, "Eutectic," pp. 253-256.

9. EQUILIBRIUM DIAGRAMS WITH INTERMEDIATE COMPOUNDS

Read in Jastrzebski, Z. D. *The Nature and Properties of Engineering Materials*. 2nd ed. New York, NY: John Wiley & Sons, 1976. ISBN: 9780471440895.
Chapter 3-11, "Equilibrium Diagrams with Intermediate Compounds," pp. 102-103.

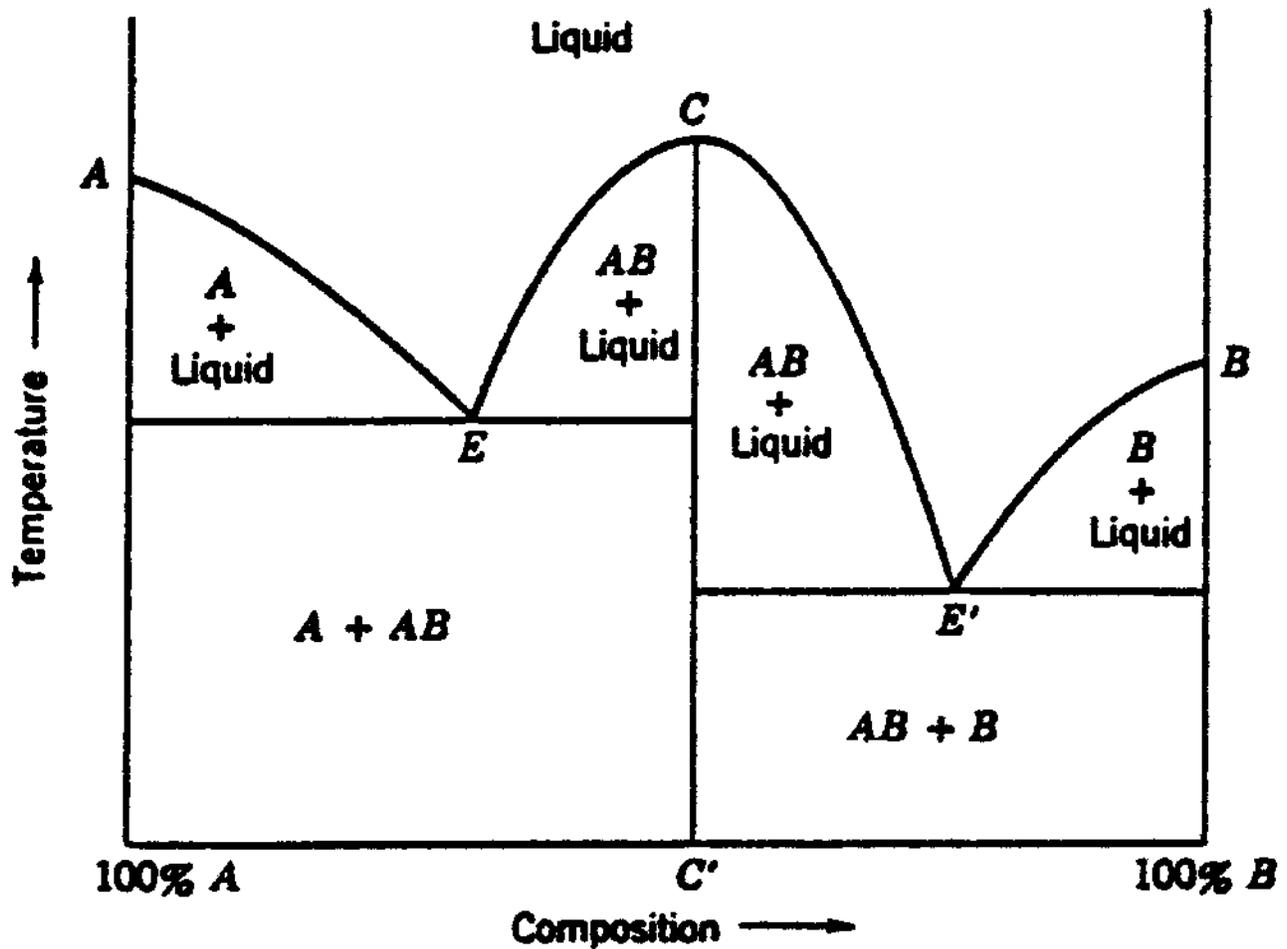


Fig. 15 Binary system showing an intermediate compound. C is the melting point (maximum) of the compound AB having the composition C'. E is the eutectic of solid A and solid AB. E' is the eutectic of solid AB and solid B.

Source: Jastrzebski, Z. *The Nature and Properties of Engineering Materials*. 2nd edition. New York, NY: John Wiley & Sons, 1976. Courtesy of John Wiley & Sons. Used with permission.

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