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Lee O Case's "Elements of the Phase Rule", Chapter 2

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I. TWO COMPONENT SYSTEMS

The additional features of two component systems result mainly from the fact that phase concentrations now enter as phase rule variables in addition to pressure and temperature. From the rule for the determination of

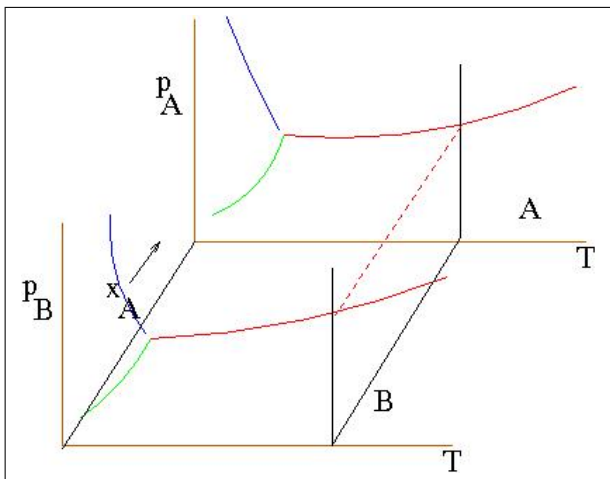


FIG. 1: Schematic construction of 2-component phase diagram from two 1-component phase diagrams, in pseudo three dimensional drawings. One sees the two one-dimensional phase diagrams in the planes at $x_A = 0$ (pure B) and $x_B = 1$ (pure A). Furthermore, one sees the emerging traditional $p-x$ diagram drawn on a plane of constant T (cwd)

phase rule variables it is found that the number of such variables for a two component system will consist in general of $U = P + 2$, since in addition to p and T the composition of each phase present may be expected to vary. Of course only one concentration variable need be counted since if the concentration with respect to either component is known the concentration with respect to the other component is immediately fixed (e.g., for mol fractions,

$$x'_1 + x'_2 = x''_1 + x''_2 = \dots = 1$$

The qualification "in general" was made above in agreement with an earlier remark that practical ends are often served by neglecting very small concentrations; in such

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a case the system may be considered degenerate, to a degree depending upon the number of neglected concentrations. For the non-degenerate cases the phase rule results may be summarized by the following table (assuming both components present in every phase):

P	V = 4-P	U[1]	
1	3	3	(x'_1, p, T)
2	2	4	(x'_1, x''_1, p, T)
3	1	5	$(x'_1, x''_1, x'''_1, p, T)$
4	0	6	$(x'_1, x''_1, x'''_1, x''''_1, p, T)$

Thus as the total number of variables increases with an increase in the number of phases, the number of them which are independent decreases until, if four phases are present, all the variables of the system are fixed. Consequently it is impossible to have more than four phases in equilibrium in a two component system.

A. Two Phase Equilibria

For the simplest case of heterogeneous equilibrium, viz., $p = 2$, the table above shows that $V = 2$, i.e., two independent variables are involved. This means that any one of the variables U (or any other specific property of one of the phases), will be found to depend in a unique and continuous manner upon any two of the remaining variables U . Restricting consideration to the phase rule variables themselves, the following functional relationships may be predicted:

$$\begin{aligned}\varphi_1(x'_1, p, T) &= 0 \\ \varphi_2(x''_1, p, T) &= 0 \\ \varphi_3(x'_1, x''_1, p) &= 0 \\ \varphi_4(x'_1, x''_1, T) &= 0\end{aligned}$$

these representing all possible combinations of three of the four variables. In each function, any two of the variables may be regarded as the independent one. Let p and T be selected as the independent variables; the resulting functions are then φ_1 and φ_2 . The interpretation of these relationships is either

1. that at fixed temperature and pressure the compositions of both phases in equilibrium, x_j and x_k , must have definite values characteristic of the system, or

2. that if p and T be allowed to vary, both x'_1 and x''_1 must vary as continuous functions of p and T in accordance with φ_1 and φ_2 respectively, so long as the two phases in question are coëxistent.

The underlined qualification cannot be too strongly emphasized. Thus, for example, although φ_1 indicates only the dependence of the composition of phase 1 on p and T , it is not valid unless phase 2 be actually present in equilibrium with phase 1, since otherwise x'_1 , p and T are quite independent of one another. (See Table for $P = 1$). Perhaps it would be advisable to indicate the implied restrictions thus: $\varphi_1(x'_1, p, T) = 0$ (phase 2 present): $\varphi_2(x''_1, p, T) = 0$ (phase 1 present), the word “present” as here used being a contraction of “being also present at equilibrium”.

As the simplest means of appreciating these relationships the graphical method suggests itself; the result is a phase rule diagram. Examination of the functions expressed above shows that three dimensions will be required for graphical purposes. Thus φ_1 can be represented by a surface in the three dimensions x'_1 , p and T ; φ_2 can be represented by another surface in the three dimensions x''_1 , p and T . These two three-dimensional figures taken together serve to describe completely the conditions for the coëxistence of the two phases in question. A useful simplification is possible, however, provided the concentrations of both phases are expressed in terms of the same concentration scale, as would of course be the natural choice. In this case, although x'_1 and x''_1 represent different variables the same axis may be used for both. Thus the two characteristic surfaces can be represented on the same figure in the three dimensions p, T, x_1 (since it is now unnecessary to distinguish x'_1 from x''_1). Or in general, for the same pair of components, the composition of any phase expressed on the same scale with x'_1 and x''_1 , can be represented along the same axis. Finally, although it is not a phase rule variable, the total composition of the system, x_1^o may be so represented if desired. Thus, on a single $p - T - x_1$ diagram for a given two-component system, every possible two-phase equilibrium will be represented by a pair of surfaces, one for each phase [2]

II. $p - x$ AND $T - x$ DIAGRAMS

Since the three-dimensional $p - T - x$ figure required for the complete representation of the phase-relations for a two-component system is difficult to construct, the expedient is usually adopted of projecting contours on one of the coördinate planes. Such contours may be produced by planes of constant T, p , or x , the resulting two-dimensional figures being $p - x$, $T - x$ or $p - T$ (not common (cwd)) diagrams. Many examples of these are early met with in the study of physical chemistry in connection with the study of liquid mixtures.

From the phase rule point of view selection of one of these contours corresponds to the assignment of one of

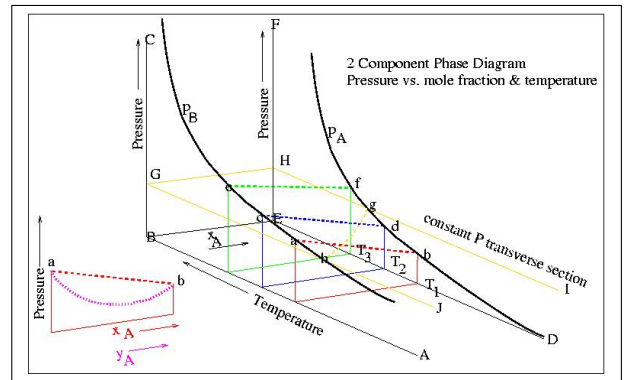


FIG. 2: Schematic construction of 2-component phase diagram from two 1-component phase diagrams, in pseudo three dimensional drawings. Planes of constant T and planes of constant p can be seen which makes it possible to do 2-dimensional plots of $p - x$ and $T - x$ respectively, leading to traditional phase diagrams.

the available degrees of variance. This is a result the surfaces characteristic of two-phase equilibrium become lines on a two-dimensional diagram. Thus at constant p or T , the equations $\varphi_1(x'_1, p, T) = 0$ and $\varphi_2(x''_1, p, T) = 0$ represent curves in the two dimensions T, x_1 - and p, x_1 respectively.

Before proceeding with the general discussion, it may be advisable to refer to an already familiar example of the situation just described. In Figure 3 we see the tra-

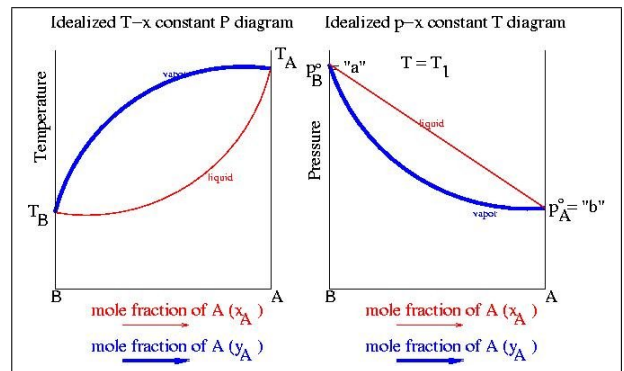


FIG. 3: The two component liquid-vapor diagrams, one at constant T and one at constant p .

ditional 2-dimensional 2-component ($A - B$) liquid \rightleftharpoons vapor phase diagrams. The one on the left is a constant pressure diagram, and the one on the right is a constant temperature one. They reflect different planar cuts in the 3-dimensional T, p, x_A space, where the curves are the intersections of the cutting planes and the surfaces in the 3-dimensional space (cwd).

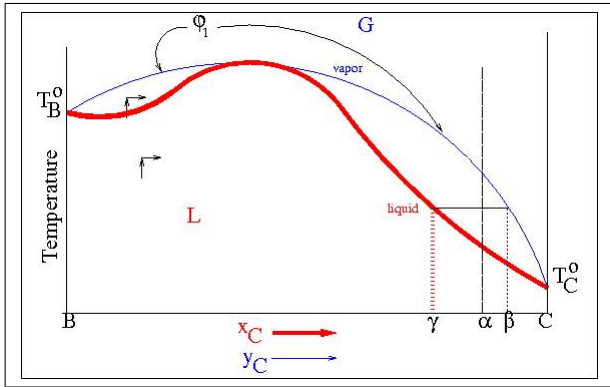


FIG. 4: The two component liquid-vapor azeotrope diagram at constant p , i.e., $T - x$ diagram.

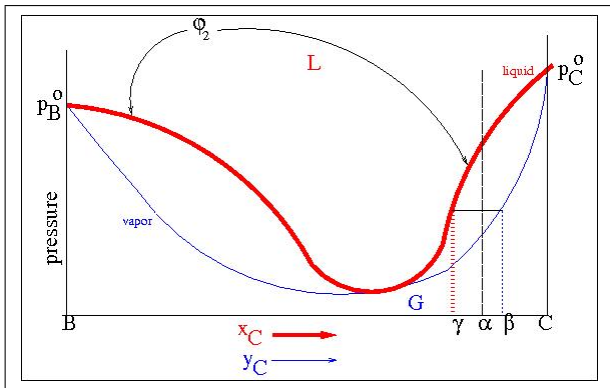


FIG. 5: The two component liquid-vapor azeotrope diagram at constant T , i.e., $p - x$ diagram.

III. SOME AZEOTROPIC MIXTURE DIAGRAMS

In Figures 4 and 5 are shown the characteristic $T - x$ and $p - x$ diagrams for a pair of volatile liquids soluble in all proportions and including a mixture of maximum boiling point.

In Figure 6 we see the “construction” of an azeotropic diagram using two juxtaposed “2-component” phase diagrams, one consisting of A and azeotrope, and the other consisting of azeotrope and C (we forsook B in this construct) (c wd).

A. Theoretical Plates and $x-y$ diagrams

The separation of liquid mixtures (and solid solutions, by the way) can be accomplished by removing the vapor in equilibrium with a given liquid mixture, cooling it until it condenses, then re-heating it until it establishes a new equilibrium with new vapor, whereupon, one repeats the procedure, separating the new vapor, cooling and condensing it, and so on and so on until the concen-

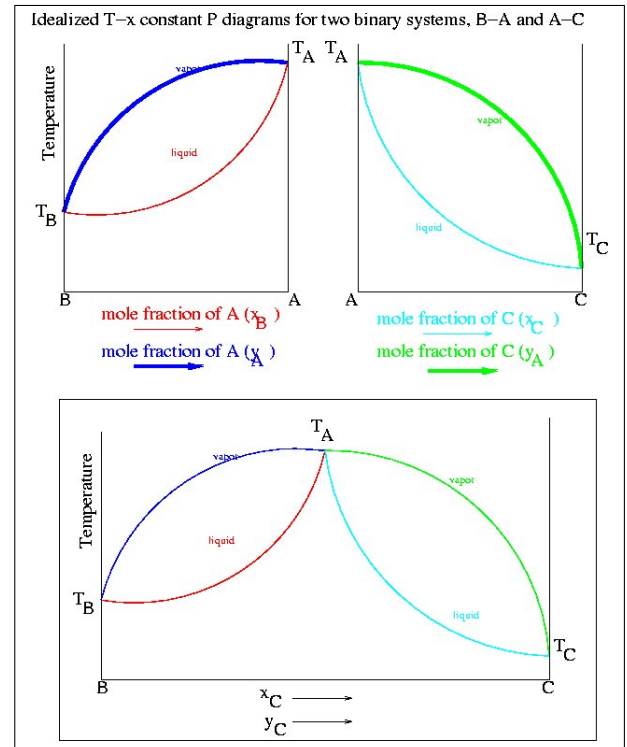


FIG. 6: Juxtaposing two two-component diagrams, A and azeotrope with azeotrope and B , one generates the standard azeotropic diagram.

tration of one component has risen (or lowered) to the desired purity level. Figure 7 shows how this procedure is pictured using a traditional $T - x$ diagram (constant

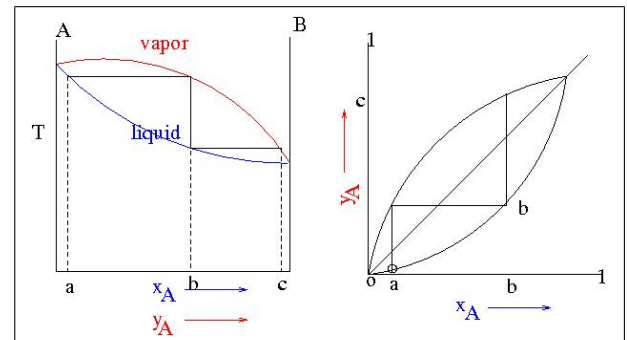


FIG. 7: Distillation of a simple constant pressure mixture, using theoretical plates to relate the liquid and vapor in equilibrium with that liquid (ready to be made the liquid of the next theoretical plate). Also shown in the equivalent $x - y$ diagram.

pressure distillation, which is the most common) and a $x - y$ diagram showing the same construct for theoretical plates. This material is covered in all elementary physical chemistry texts.

B. Return to main manuscript

In application to these figures, the functions φ_1 and φ_2 taken to refer respectively to the vapor (G) and liquid (L) curves, the former representing the compositions of the saturated vapors as functions of T or of p , the latter the compositions of the liquids which can exist in equilibrium with vapors. The existence of the two separate curves on the same figure is seen to be the natural result of the fact that the abscissa x_1 may represent x'_1 in case the vapor curve is referred to, or x''_1 if reference is made to the liquid curve. The two curves naturally touch at their extremities since if one component is absent, $C = 1$ and $V = 1 + 2 - 2 = 1$, which is used up by specification of either T or p [3]. Moreover at the maximum or minimum $C = 1$ since the requirement $x'_1 = x''_1$ furnishes a relation E among the phase rule variables. Elsewhere the liquid and vapor lines are separate, serving to bound an area on the diagram within which the liquid and vapor are coëxistent.

At this point in the discussion, an apparent paradox should be resolved. In an area on one of these diagrams there are apparently two degrees of variance available ($V = 2 + 2 - 1 = 3$, of which one degree has been used up in the selection of constant p or T .) Above or below the liquid-vapor region this is certainly true since the composition of a single phase can, of course, be varied as well as T (or p) at constant p (or T). (See arrows in Fig, 3 in region L.) But in the same way it appears that in the area included between the liquid and vapor lines p (or T) can be varied and at the same time a change in composition can be produced, for example, by addition of component 1. Closer study of this situation, however, shows that in the latter case addition of component 1 cannot change the phase compositions but only the total composition and the total composition, as pointed out many times before, is not a phase rule variable. In other words, at constant p (or T) there can be no phase having a composition included between the liquid and vapor lines. The compositions of the phases into which such a mixture breaks up are located at the intersection of a line of constant T (or p) with the liquid and vapor lines. Thus although such areas are commonly designated L-G on phase rule diagrams it must be kept clearly in mind that the phase compositions are found on the boundaries of the area and not within it.

C. A side trip down distillation lane (cwd)

Two-component liquid \rightleftharpoons vapor equilibrium is used to introduce distillation processes, which is of great interest to chemical engineers and chromatographers (as well as chemists who actually do distillation). This review of binary distillation is therefore dedicated to those practical people.

The traditional way of dealing with the vapor pressures

over liquid mixtures starts with Raoult's Law,

$$p_A = x_A p_A^o$$

and

$$p_B = x_B p_B^o = (1 - x_A) p_B^o$$

where the superscript indicates purity, i.e., the vapor pressures of pure A and B separately. The total pressure over a solution made up at a given mole fraction (of say A) would be

$$p_{total} = p_A + p_B = x_A p_A^o + (1 - x_A) p_B^o$$

written as a function of x_B . In the vapor phase

$$p_A = y_A p_{total}$$

with an equivalent expression for B . We then have

$$y_A = \frac{x_A p_A^o}{x_A p_A^o + (1 - x_A) p_B^o}$$

which shows us a relationship between the mole fraction in the liquid, and the mole fraction in the vapor which is in equilibrium with that liquid. This leads to the idea of plotting both x and y of A (or B) as the abscissa, with pressures (or temperatures) as the ordinate. This double usage causes unending confusion for many students .

IV. RETURN TO MAIN DOCUMENT

Again as in the case of one component systems it must be borne in mind that the p -coordinate must represent the pressure of the system and not for example of the system plus air. Thus, in the discussion of ordinary distillation problems, these diagrams are strictly applicable only when the boiling point has been reached (when the vapor pressure does in fact become equal to the external pressure.)

Since the phase rule is concerned with the number of phases present in a system and not with their nature. It is clear that for any possible pair of coëxistent phases in a two-component system the same general behavior is to be expected as for coëxistent liquid and vapor phases. That is, any two-phase equilibrium will be represented on a $p - x$ or $T - x$ diagram by an area, bounded laterally by two curves, each indicating the composition of one of the mutually saturated phases, the compositions included between the curves representing the range of total compositions which can result in the two-phase equilibrium in question. With respect to two-phase equilibria the phase rule itself can go no further than this. The quantitative features of individual systems must be determined by experiment, supplemented in some cases by other theoretical principles of physical chemistry such for example as the Mass Action Law. The specific differences to be noted among different examples of two phase equilibria within this general restriction imposed by the phase rule may be classified as follows:

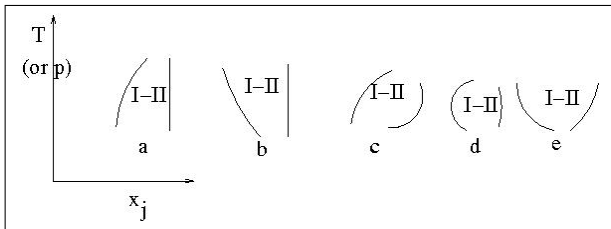


FIG. 8: The various ways in which a two-phase region can be bounded. As noted in the text, often, vertical lines are not perfectly vertical, indicating a solubility of the compound whose composition is given by the “vertical” line, with the other phase involved.

1. As to the magnitudes and signs of the slopes of the two bounding curves, i.e., whether large or small, of like or unlike sign. A special degenerate case of a slope very large in absolute magnitude occurs if a saturated phase is a pure component or a pure compound, in which instance the corresponding boundary curve is vertical, (Figures 8 (a) and (b)). Kinetic theory considerations appear to deny this possibility except as a appearance of this feature on actual diagrams being merely an indication that analytical determinations have not yet been carried out with sufficient accuracy to detect the departure from verticality of the curve in question. Except for these degenerate cases the saturated phases are to be identified as saturated solutions, of which the physical state may be gaseous (saturated vapors), liquid or solid. Concerning the signs of the slopes of the boundary curves it will be sufficient to note that while in general one would expect that the slopes might have either the same or opposite signs, nature apparently imposes certain limitations which may perhaps be best learned by experience.

For example, in the case of liquid-vapor equilibria, the slopes of both curves have the same sign (Figure 8 c) for two mutually saturated liquids the slopes are of opposite sign (Figures 8 d and e), while in the case of solid-solid equilibria both types of behavior are noted .

2. As to the physical states of the mutually saturated phases, designating the gaseous phase by G ; liquid phases by L_1, L_2 , solid phases by S_1, S_2 , the possible types of two-phase equilibria in two-component systems are as follows: $G-L, G-S, L_1-L_2, L-S, S_1-S_2$. If the degenerate case referred to in the previous paragraph be allowed to enter as a means of practical distinction between solid phases of essentially invariable composition, designated by K_1, K_2 , and solid phases of variable composition (i.e., solid solutions), designated by α, β , the classification becomes: $G-L, G-K, G-\alpha, L_1-L_2, L-K, L-\alpha, K_1-K_2, \alpha-K, \alpha-\beta$.

3. As to the range of temperature or pressure over which the equilibrium in question extends. The limit of the existence of a given two-phase area on a phase rule diagram is in general imposed by one of the following:

- degeneration of the system from one of two components to one of one component, as at one of the vertical boundaries of the diagram;
- the occurrence of a so-called “critical point”, at which the position and properties of the two phases become identical; or
- by the occurrence of three-phase equilibria, the conditions for which will be considered in a later section.

A. Condensed Systems

Although as indicated above the phase rule itself indicates no reasons for differences in behavior of systems depending upon physical states of the phases in equilibrium, practical considerations make possible a very considerable simplification of treatment of those equilibria which involve liquid and solid phases only. The reason for this can be found in the fact that pressure has very little effect on such equilibria, in contrast with the very considerable effect of pressure upon equilibria involving the vapor phase. As a result the $T-x$ diagram for equilibria a given system at all ordinary values of the pressure, or in particular regardless of whether the system is under its own vapor pressure only or under the constant pressure of the atmosphere. Since the latter condition is so much easier to establish in practice it is commonly used for the investigation of phase equilibria involving only solid and liquid phases. The resulting systems are called “condensed systems” for the reason that the presence of the vapor phase is neglected. Although as pointed out earlier the imposition of the external pressure by means of the atmosphere will prevent the formation of the vapor of the system, the result is the same for solid and liquid equilibria as if the pressure were imposed, for example, by a solid piston in which case the vapor phase would actually be absent (provided, of course, that the vapor pressure of the system be less than atmospheric pressure.)

In adapting the phase rule to the treatment of condensed systems several different points of view might be adopted. Perhaps the simplest is to restate the phase rule. Since in the derivation of the phase rule, the figure “2” entered due to the assumption that both temperature and pressure were phase rule variables, it will be necessary to count only temperature as an external variable for condensed systems. As a result the variance for the condensed system, V_c , will be less by one, $V_c = V - 1$ or $V_c = C + 1 - P$. In counting the number of phases in the system, then, the vapor phase is neglected.

The simplification resulting by treating solid-liquid systems as condensed systems is considerable. Instead of having to deal with a three-dimensional phase diagram, or with the three projections of its contours on the coordinate planes, we are concerned only with two-dimensional figures as was the case for one-component systems. The characteristic diagram is now a $T - x$ diagram, however, instead of a $p - T$ diagram.

B. Three-Phase Equilibria in Two -Component Condensed Systems

Since if three phases are in equilibrium with one another, each phase considered by itself must be separately in equilibrium with each of the others, it is evident that there is a close connection between three-phase and two-phase equilibrium. Consequently it is simplest to introduce this topic by extension of the principles already discussed for two-phase equilibrium. For this purpose, let the phases without distinction as to their physical states, be designated by I, II, III, IV, and let (their compositions with respect to component A be designated $x'_A, x''_A, x'''_A, x''''_A$. Suppose now that the two two-phase equilibria I-II and I-III are possible in the same range of temperature, as shown in Figure 9. According to the principles previously outlined the functions which describe these situations may be realized as follows: For the equilibrium I-II:

$$f_1(x'_A, T) = 0; II \text{ present}$$

$$f_2(x''_A, T) = 0; I \text{ present}$$

For the equilibrium I-III:

$$f_3(x'''_A, T) = 0; III \text{ present}$$

$$f_4(x''''_A, T) = 0; I \text{ present}$$

These functions are obtained from the corresponding functions φ_1 and φ_2 of page 1 by imposing the restriction of constant pressure, required for condensed systems. Examination of these functions shows that two of them, f_1 and f_3 , involve the the same variables, x'_A and T , the two equations differing, however, in the restrictions under which each applies, namely, f_1 describes the dependence upon temperature of the composition of phase I when it is saturated with respect to phase II, while f_3 describes the dependence upon temperature of the composition of phase I when saturated with phase III.

The condition for three-phase equilibrium is now seen to be that f_1 and f_3 be simultaneously satisfied, leading to the result [4]:

$$x'_A = \text{const}; T = \text{const}; \text{both II and III present}$$

On the phase rule diagram of Figure 9 these fixed values of x'_A and T obviously represent the coordinates of

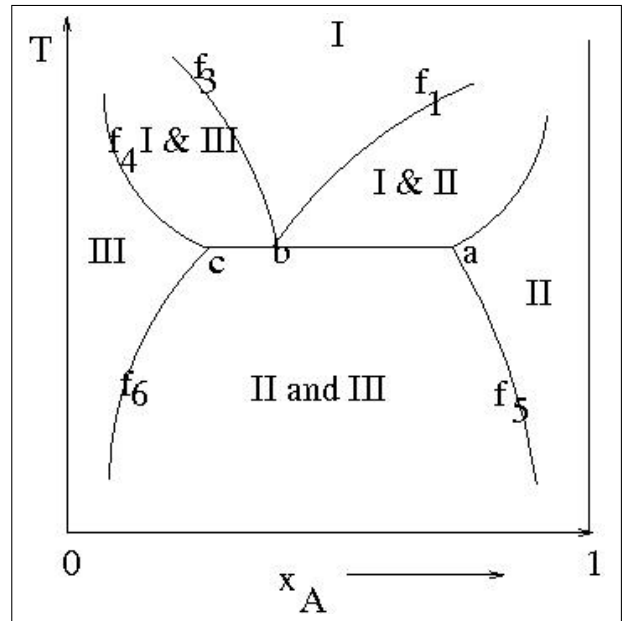


FIG. 9: A simple eutectic, with limited solubility of each component, i.e., pure component can not be obtained by crystallization from any mixture in this system.

the point of intersection, "a", of the curves representing f_1 , and f_3 . But more than this is involved. The condition of constant temperature resulting from the intersection of the curves of, f_1 and f_3 , when applied to the functions f_2 and f_4 shows that x''_A and x''''_A must also have definite values. Hence the existence of equilibrium among the three phases requires that the four quantities T, x'_A, x''_A, x''''_A all have definite values fixed by nature for the system considered. This result is, of course, that predicted formally by application of the phase rule, since for $P = 3, V_c = 2 + l - 3 = 0$. The consequences for the diagram of Figure 9, however, need to be more carefully examined. These are that since T is the common coordinate for all four curves, the condition of three-phase equilibrium must be represented by three points ranged along a horizontal line, point "a" (x'_A, T) representing the condition of phase I, point "b" (x''_A, T) that of phase II, point "c" (x'''_A, T) that of phase III. Removal of phase III allows the remaining two points to describe the two curves of f_1 and f_2 ; removal of II permits the generation of curves f_2 and f_4 . Suppose now that phase I be removed; what will be the consequence for the diagram? Obviously, since the new two-phase equilibrium II-III is now involved, the result must be a new two-phase area bounded by two new curves representing these mutually saturated phases and described by the new functions:

$$f_5(x''_A, T) = 0; III \text{ present, and } f_6(x'''_A, T) = 0; II \text{ present}$$

Although these new curves in Figure 9 may be regarded as generated by the movement of the points "b" and "c", there is, of course, no reason why they should be prolongations of, or otherwise simply related to, the corre-

sponding curves in the region above, since although the variables are the same the restrictions are different.

The occurrence on the diagram of the two new regions designated II and III respectively may be briefly noted. Like the area marked I, these surely represent regions of unsaturation in which temperature and phase composition may be independently varied. ($V_c = 2 + 1 - 1 = 2$). Depending upon the extent of these regions, or otherwise stated, upon the extent of the mutual solubility of II and III, diagrams of superficially very different characteristics may result. The limiting cases are those represented in Figure 10 showing complete solubility (phases II and

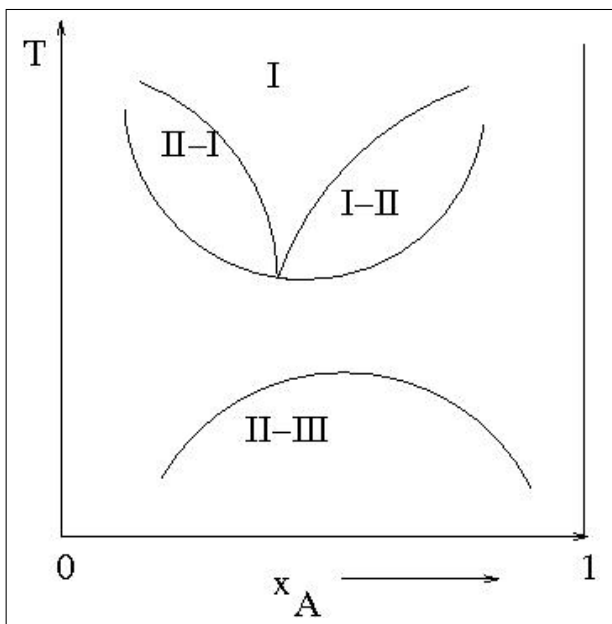


FIG. 10: A precursor of Figure 9 in which a limited solubility (top part) and an immiscibility (bottom part) are going to collide if the pressure is properly chosen.

III becoming in this case identical and the three-phase equilibrium disappearing) and in Figure 11, illustrating the degenerate case of zero mutual solubility between II and III.

C. Eutectic Type Diagrams

Special designations are commonly applied to certain situations of the type of Figures 9 and 11. If the intermediate phase I is liquid, the diagram is described as of “eutectic” type; if phase I is solid, the word “eutectoid” is employed, phases II and III in both cases being solid. The “eutectic” itself (or the “eutectoid” as the case may be) is the solid mixture (not phase) of the two phases of compositions corresponding to “b” and “c”, which separates from the “eutectic solution” or “eutectoid solution” of composition “a”. The “eutectic (or eutectoid) temperature” is that of the horizontal line through the points “a”, “b”, and “c”. Lack of precision in the use of these

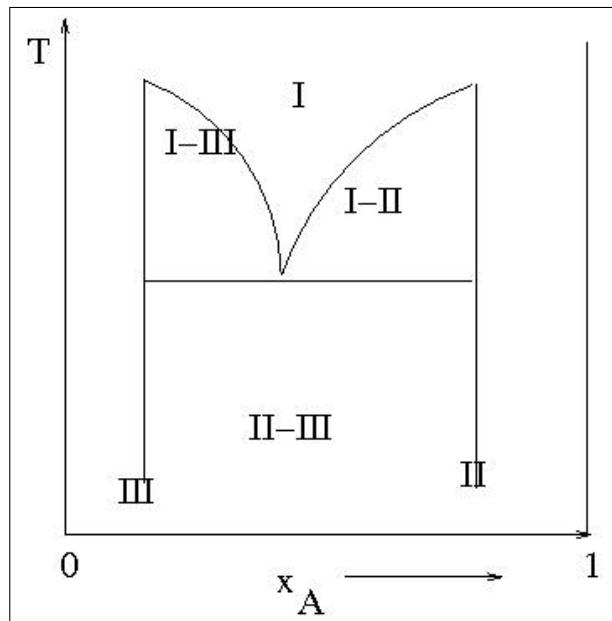


FIG. 11: An old fashioned perfect eutectic mixture. Sometimes, a vertical dotted line is extended from the “eutectic compound” down, separating the solid part into two regions, one corresponding to $III(s)$ and $eu(s)$ while the other corresponds to $II(s)$ and $eu(s)$; the solid mixture would appear slightly different, hence the distinction, but from the point of the phase rule, this is irrelevant.

terms often leads’ to misconceptions. Thus the common statement that “three phases are present at a eutectic point”, has meaning only if the word “point” as here used is identified with “temperature”, since as emphasized above, the eutectic situation involves not one point but three points on the diagram.

D. Peritectic Type Diagrams

Returning now to the discussion by means of which the topic of three-phase equilibrium was introduced, it will be recalled that the condition used was the recurrence of two two-phase equilibria involving a single phase in common. Three-phase equilibrium was then shown to be the result of the intersection of the two curves f_1 and f_3 relating to the common phase. The actual-features of the diagram of Figure 9 proceeded from the assumption that two of the three two-phase areas occur above the other below the three-phase temperature. It is however, equally likely that this distribution might be reversed, In such a case the diagram of Figure 12 may result, in which the designations are the same as those of Figure 9. Although systems of the types illustrated in Figures 11 and 12 are completely indistinguishable from the standpoint of the phase rule itself, so that the discussion previously given will apply equally to both figures, they show characteristic inferences in their reaction to changes in con-

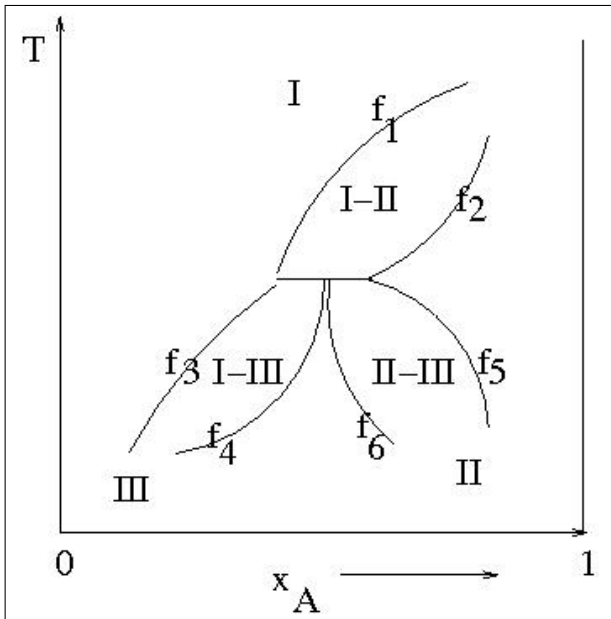


FIG. 12: A typical peritectic phase diagram

ditions which will merit further study in a later section. By way of differentiation from the phase previous type, certain examples of Figure 12 are given special designations. Thus, phases II and III being solid, the system is of “peritectic” type if phase I is liquid, “peritectoid” if phase I is solid.

Although the discussion of this section has been restricted to condensed systems, it is obvious that the same principles apply completely to systems containing the gas phase, provided the pressure on the system is constant. The only important difference in general behavior is that the location on the diagram of those curves relating to equilibria involving the gas phase will be greatly affected by the value selected for the constant pressure.

E. $p - T - x$ Diagrams

If the restriction of constant pressure is removed, complete representation of the equilibrium relations requires three dimensions. While one seldom cares to take the trouble to construct a solid figure for the purpose, one may sometimes wish to show it in projection. It is therefore worth while to see how the phase rule may assist in the visualization of the important features of such a figure. For the most common, the $p - T - x$ figure, the results in brief are as follows: (these are easily verified by reference to the table appearing at the beginning of this section):

1. Two-phase equilibrium is represented by a pair of surfaces ($V = 2$), one for each phase, bounding a solid region which includes those total compositions which can result in the two-phase equilibrium in

question.

2. Three-phase equilibrium is represented by a set of three lines ($V = 1$), one for each phase. It will be recalled from analytic geometry that a line in three dimensions is located by the intersection of two surfaces each perpendicular to one of the coordinate planes. But among the relations predicted by the phase rule for three-phase equilibrium, there occur (for example for phase I of the set of three):

$$p = f_1(T); p = f_2(x'_1); T = f_3(x'_1): \text{ II and III present}$$

Each of these functions may be taken to represent either

- (a) a curve in two dimensions or
- (b) a surface perpendicular to one of the coordinate planes in three dimensions. In the $p - T - x$ diagram therefore the space curves for three-phase equilibrium are expressed in terms of their projections upon the coordinate planes. It is worthy of note that due to the requirement of uniform pressure and temperature the space curves for all three phases must furnish the same projection on the $p - T$ plane.
- (c) Four-phase equilibrium is represented by a set of four points ($V = 0$), one for each phase. From each such point there must radiate three space curves, each describing the conditions for equilibrium of the selected phase with a possible pair of the other phases. Again uniformity of pressure and temperature requires that these four points be ranged along a straight line perpendicular to the $p - T$ plane.

V. COMPLEX DIAGRAMS

It has been shown that two-phase equilibrium is represented in a $p - x$ or $T - x$ diagram by a pair of solubility curves, in a $p - T - x$ diagram by a pair of solubility surfaces. If by an accident of nature the solubility curve or surface for a single phase in equilibrium with a second intersects the solubility curve or surface for that same phase in equilibrium with a third phase, then the conditions for three-phase equilibrium are satisfied; moreover with the three-phase equilibrium there must be associated three sets of two-phase equilibria. The apparent complexities of actual phase diagrams result simply from repetition of such situations in different regions of the phase variables for the same system. An attempt to classify and describe all the possible types of diagrams that might occur on the basis of the physical states of the phases and the individual characteristics of the associated two-phase equilibria, would be merely academic [5]. If, however the underlying principles are once understood, any actual diagram can readily be analyzed by reducing it to elements of the general types described above. The

analysis consists merely in labeling the various regions of the diagram with symbols indicating the physical nature of the phases concerned. Recommended designations are: G for the gas phase, L_1, L_2 for liquid phases, α, β, γ for solid solutions; pure components or pure compounds in the solid state are designated by their chemical formulae.

The mere labeling of phase rule diagrams does not, of course, complete the application of the phase rule. While this represents a necessary first step, it is of much more practical importance to be able to interpret the diagram as a means of predicting how the system will react to changes in conditions. For condensed systems this requires the discussion of the effect of

1. changes in temperature and
2. changes in the relative amounts of the components.

These will now be considered.

VI. EFFECT OF TEMPERATURE CHANGE IN TWO -COMPONENT CONDENSED SYSTEMS

A. Cooling Curves

Reviewing the results for the variance for two component condensed systems, it is noted that for $P = 1, 2$ or 3 , $V = 2, 1$ or 0 respectively. With respect to these simple results, the characteristics of cooling curves will be examined for such systems. A cooling curve is, of course, merely a graph of simultaneous readings of temperature and time taken while heat is being continuously removed from the system, e.g., by radiation or conduction to its environment. The discussion will first relate to the case that the heat is removed so slowly that equilibrium is practically attained at all times.

1. Theoretical Cooling Curves

Suppose that the two components are mixed in a definite ratio and raised to a sufficiently high temperature so that the mixture consists of a single liquid phase (I). Since for $P = 1, V_c = 2$, it is obviously possible thus to assign both the temperature and the composition of the phase (which in this case must be the same as the total composition). If heat be now removed at a uniform rate, the phase (of arbitrarily fixed composition) will assume a succession of different temperatures (See Figure 13).

Suppose now that a temperature T_1 is reached at which a second phase makes its appearance. Since now $V_c = 1$, it might at first sight appear that since the composition was fixed in making up the original mixture no variance is left and the temperature must remain constant. Note carefully, however, that the fixed composition referred to was the total composition and that this is necessarily the same as a phase composition only if the system is existing in a single phase. It is still possible therefore to

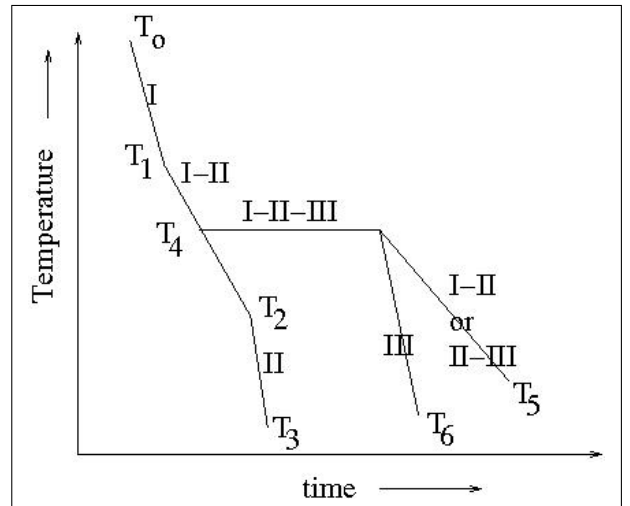


FIG. 13: A typical set of cooling curves, showing “breaks” and “halts”, etc..

exercise the variance of I by continued removal of heat resulting in a new succession of lower temperatures. In what way then does the new situation differ from the previous one? The answer is furnished, by the Le Chatelier principle. According to this principle the formation of the new phase (II) from the original phase (I) must be accompanied by the evolution of heat, since it is in this way that the system must react in order to oppose the effect of removal of heat by the surroundings. As result a so-called “break” occurs in the cooling curve at the temperature at which the new phase II begins to form; below this temperature the rate of decrease of temperature with time will be less than before (always assuming equilibrium and a uniform rate of heat removal), and must so continue as long as the new phase continues to separate. At each temperature in the series during this process the phase compositions must be fixed, since the available variance is used up by the specification of temperature. The phase compositions must actually describe the two curves: $f_1(x'_A, T) = 0$; $f_2(x''_A, T) = 0$. Neither phase therefore can have the same composition as the entire system; we can in fact infer that one phase composition must be greater, the other less than the total composition, since it is clearly impossible to find any ratio in which two phases of different composition can be mixed so as to give the total composition a value other than intermediate between the two phase compositions. With further cooling there are two possibilities:

1. the system again becomes one of one phase or
 2. a third phase also appears.
1. If the system reverts to one phase, it must in general be by the completion of the process by which the new phase II formed at the expense of the original phase I. Since the cooling rate was retarded, by this process, the rate will increase again when the

process is completed, e.g., at the temperature T_2 in Figure 13; the remaining curve in the direction $T_2 - T_3$ represents merely the cooling of phase II

- It may happen, however, that before the phase change I-II is completed, a third, phase III makes its appearance, say at the temperature T_4 in Figure 13. Since with three phases present, the variance V_c is zero, the Phase Rule now requires that the temperature must remain constant in, spite of the continued removal of heat from the system, producing a so-called “halt” on the temperature-time curve. This means that the process by which III now forms in the presence of the other two phases must not only liberate heat in accordance with Le Chateliers principle, but must do so at a rate which just compensates for the removal of heat by the surroundings. In maintaining the constancy of temperature, of course, the relative amounts of the phases present must change since it is only by such phase reactions that the required latent heat can become available.

This point will be examined in greater detail later.

When, due to the continued removal of heat, one or two of the phases disappears it again becomes possible to lower the temperature of the system—in the first case, in the direction T_5 (loss of I or II), and in the second case, in the direction T_6 (loss of both I and II).

Obviously processes of which the ones described are typical may occur in any sequence and, in any number along the cooling curves for a particular system. The interpretation of such curves, however, merely involves repeated application of the same principles

In concluding this discussion of theoretical cooling curves, it should perhaps be pointed out that, even, for a constant rate of removal of heat, the inclined portions of the cooling curves would not in general, be straight lines and that, for example, there is no necessity that the line $T_0 - T_1$ be parallel to the line $T_2 - T_3$ (if so, the heat capacity of phase II would be equal to that of phase I). Finally, it may be noted that the sharpness of the break at T_1 depends upon the magnitude of the latent heat of the transformation I→II.

2. Actual Cooling Curves

Some of the features which distinguish actual from theoretical cooling curves should now be mentioned. The effect of variations in the rate of heat removal is perhaps sufficiently obvious, and may be dismissed with the remark that while a uniform rate may be approximated, it is usually easier in practice to employ a somewhat uniformly varying rate, such as would be obtained by melting the sample and allowing it to cool (with or without lagging) in surroundings of uniform temperature. The

more important differences result from the impossibility of ensuring equilibrium conditions at every temperature. This is particularly the case when a temperature is reached at which a new phase should appear – at a “halt” or a “break” in the curve. If equilibrium were instantaneously established, at such a temperature it would require the separation of an infinitesimal amount of the new phase. Invariably, however, a finite degree of supersaturation must be established, before the system becomes

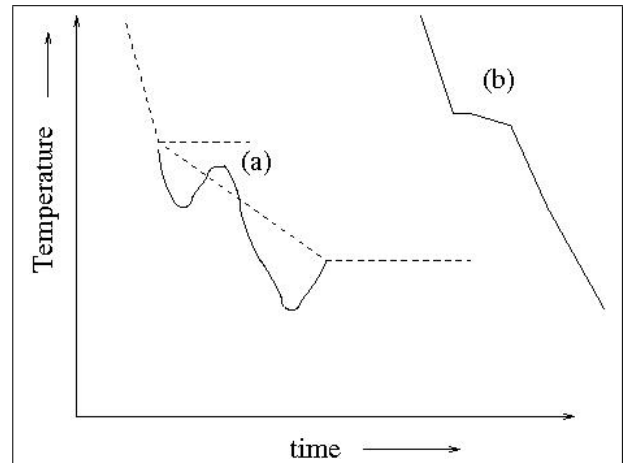


FIG. 14: Supercooling results in metastability of phases (out of synch with what’s required by true equilibrium thermodynamics).

sufficiently unstable to revert to its equilibrium condition; the resulting fall in temperature below the equilibrium value is known as “supercooling”. When the stable phase does begin to form (it may be necessary to introduce a small crystal of the stable phase in order to start the process the system rapidly approximates the equilibrium condition by the separation of a finite amount of the new phase and the consequent rapid liberation of sufficient latent heat to cause a rise in the temperature to the equilibrium value; thereafter the temperature again falls as the new phase continues to separate. Where a break would be expected the cooling curve therefore shows a maximum, Figure 11 (a), which sometimes may even resemble a brief halt, Figure 11 (b); in such a case the minimum on the curve is always lower than the temperature of the expected break and more so the greater the degree of supercooling; the reason for this, of course, is that the separation of a finite amount of the new phase produces an appreciable change in the composition of the original phase and that the temperature of the phase change corresponding to this new concentration is necessarily lower than for the original composition.

If, however, supercooling below a three-phase temperature occurs the temperature must revert to the true equilibrium value on relief of the unstable condition since the composition of the phase as well as their equilibrium temperature is fixed by the phase rule.

It is evident that the experimental determination of

cooling curves for different total compositions of the system represents a valuable method for the determination of phase diagrams. Unfortunately it is not always possible to use this method. As the heat effects accompanying phase changes become smaller and smaller and as the rate at which the system adjusts itself to its successive equilibrium states becomes less and less the experimental difficulties of detecting the temperatures at which phase changes should occur become more and more serious and may frequently prove insurmountable. Other factors being the same, the first difficulty – that due to the magnitudes of the heat effects – tends to be more serious the less the differences in the chemical and physical nature of the components or of the phases involved. The second difficulty – that due to the rate of phase changes – is apt to be greatest in the solid state, although occasionally – as in most mineral systems – even liquids may show such pronounced supercooling that cooling curves cannot be employed. In conclusion it may be pointed out that most of the foregoing discussion – certainly all that relating to theoretical cooling curve – can be readily adapted to the reverse process of determining heating curves.

B. Relative Amounts of Phases

In the discussion of cooling curves consideration has so far been given only to the variations of temperature with time. It has been indicated, however, that in adjusting itself to phase rule requirements a change in the relative weights of the phases present has to occur, since it is only by liberation of latent heats of transition that “breaks” or “halts” can be produced. It is now proposed to make this discussion quantitative, The following notation is employed:

W', W'', W''' = weights of phases I, II, III.

W_A^o, W_B^o = total weights of components A and B,

$W^o = W' + W'' + W'''$ = total weight of system,

$= W_A^o + W_B^o$

f'_A, f''_A, f'''_A = weight fraction of component A in phases I, II, and III respectively.

f_A^o = weight fraction of component A in entire system.

Along any single cooling curve, the quantities W_A^o, W_B^o, W^o, f_A^o must, of course, remain constant.

Case I. Two phases present.

($W''' = 0$). A “material balance” for the component A at any temperature along the cooling curve in such a region gives:

$$W_A^o = f'_A W' + f''_A W'' = f_A^o (W^o) = f_A^o (W' + W'')$$

From the second and fourth members

$$\frac{W'}{W''} = \frac{f''_A - f_A^o}{f_A^o - f'_A}$$

or

$$\frac{W'}{W' + W''} - \frac{W'}{W^o} = \frac{f''_A - f_A^o}{f_A^o - f'_A} \quad (6.1)$$

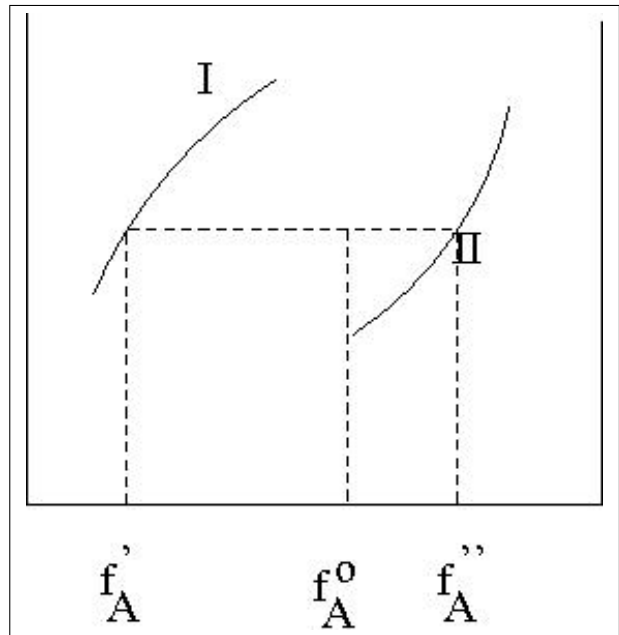


FIG. 15: Two phases, connected by a tie line, so that as the relative amounts of each phase changes, the total composition changes or *vice versa*.

In words, the first expression states that the weights of the phases are in the inverse ratio of the segments cut off by the total composition on the horizontal line joining the phase compositions, (See Figure 15). In each two-phase area traversed by the line of total composition this rule can be applied to determine the variation in the weights of the phases present at equilibrium. It is seen at once that the separation of a new phase along a theoretical cooling curve is an essentially continuous process, initiated at the crossing of the upper phase boundary by the separation of an infinitesimal amount of the new phase and proceeding by infinitesimal increments as the temperature falls. It can also be seen more clearly from this point of view why it is that after supercooling the temperature tends to rise rapidly on formation of the new phase, since in this case the separation of a finite amount of the new phase is necessary to restore equilibrium. It is again worth while to distinguish two special cases:

Case Ia. The total composition line completely traverses the two-phase area (See Figure 15). In this case application of the rule shows that at the lower phase boundary the last infinitesimal amount of phase I disappears, completing the process I→II.

Case Ib. The total composition line crosses a three-phase temperature line, (Figure 16). In this case, application of the rule shows that the continuous process is not yet completed at the three-phase temperature but that at this temperature a discontinuity occurs with respect to the weights of the phases, resulting (for the example shown) in the final complete disappearance of the remaining phase I at constant temperature. The rule derived

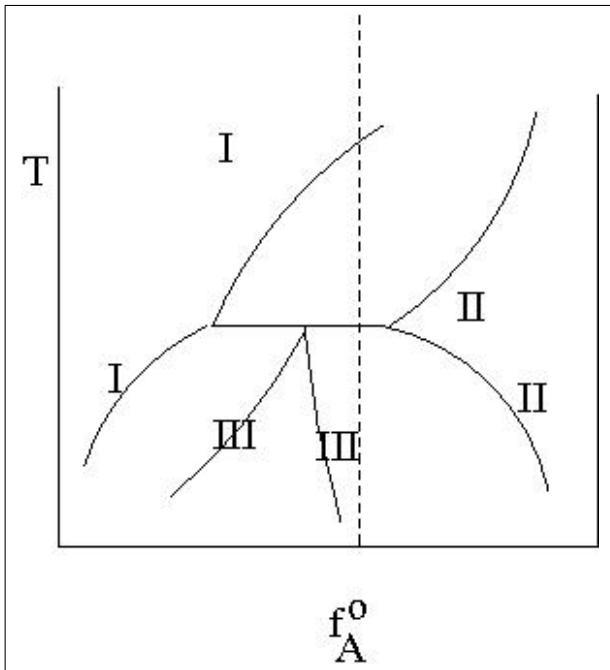


FIG. 16: Peritectic phase diagram, where above the three phase line is the *III*, while on the horizontal line we have $I \rightleftharpoons II \rightleftharpoons III$

above therefore cannot be applied at this temperature, although it is still completely valid at temperatures infinitesimally above and below it. The process involving the three phases accordingly requires separate treatment.

Case II. Three phases present. For any change in the weights of the phases present, a material balance for the component *A* requires (since $W_A^o = f'_A W' + f''_A W'' + f'''_A W'''$):

$$dW_A^o = 0 = f_A dW' + f''_A dW'' + f'''_A dW''' + df_A W' + df''_A W'' + df'''_A W'''$$

But for the condensed system existing in three phases, the phase rule requires not only $dT = 0$ but $df'_A = df''_A = df'''_A = 0$, whence

$$0 = f'_A dW' + f''_A dW'' + f'''_A dW'''$$

Also for a constant total weight of the system:

$$dW^o = 0 = dW' + dW'' + dW'''$$

Multiplying the last equation successively by f_A , f'_A and f'''_A and subtracting from the preceding equation gives:

$$\begin{aligned} (f''_A - f'_A) dW'' + (f'''_A - f'_A) dW''' &= 0 \\ (f'_A - f'''_A) dW' + (f'''_A - f'_A) dW''' &= 0 \\ (f'_A - f'''_A) dW' + (f''_A - f'''_A) dW'' &= 0 \end{aligned}$$

or

$$\frac{dW''}{dW'''} = \frac{f'''_A - f'_A}{f'_A - f'''_A}$$

and

$$\frac{dW'}{dW'''} = \frac{f''_A - f'''_A}{f'_A - f'''_A}$$

Inspection of these expressions shows:

1. the amount of the phase of intermediate composition changes in the opposite sense to the amounts of the phases of extreme composition, ergo, if $f'''_A > f'_A$, then

$$\frac{dW''}{dW'''} < 0; \frac{dW'}{dW'''} < 0$$

The same result follows if the signs of the inequalities are reversed.

2. The rate at which the weight of any phase changes with respect to the weight of another is a constant depending only upon the (fixed) compositions of the phases present at the three-phase temperature and entirely independent of the total composition of the system.

The first conclusion above may perhaps be put in more usable form by application to the two characteristic general types of three-phase equilibria to which attention has previously been called. Let the compositions of the three

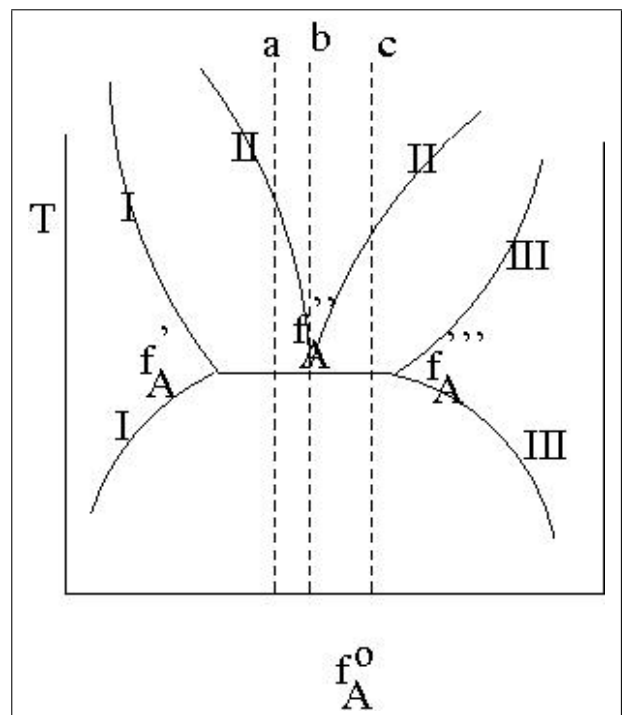


FIG. 17: What happens in cooling a melt due to undergo a peritectic reaction. Paths “a”, “b”, and “c” cool differently, and the cooling curve for “b” actually looks like the cooling of a pure compound.

phases I, II, III, capable of coexistence be in the order

$$f'_A < f''_A < f'''_A$$

1. If at the three phase temperature, Phase I (or III) starts to form, it must be at the expense of phase II and accompanied by the formation of III (or I) in a definite ratio, (a, b, c, Figure 17.)
2. If at the three-phase temperature, phase II starts to form (Figure 18), it must be at the expense of both I and III which are consumed in a definite ratio. Depending then upon the relative amounts of phases I and III which were present just as the three-phase temperature was reached, the system resulting when the process is completed will consist of I and II (e, Figure 18), or II only (e, Figure 18), or II and III (f, Figure 18). As a matter of fact both

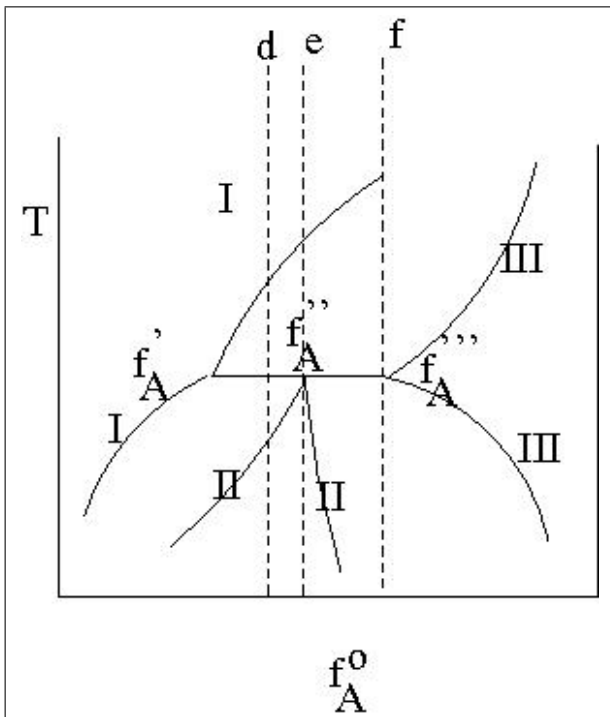


FIG. 18: Colling a peritectic mixture at various overall compositions.

situations arise on the same diagram if addition as well as removal of heat is allowed, since it will be noted that Figure 18 represents essentially the inversion of Figure 17.

The reason for the behavior of the system shown in Figure 18 can now be explained more precisely in terms of the quantitative relations worked out for the cases of two and three-phase equilibria: For any total composition between f'_A and f'''_A , phases I and III must have adjusted their compositions to f'_A and f'''_A just as the three-phase temperature is reached; this is accomplished by the separation of an amount of phase III which depends upon the total composition and which can be calculated from Equation 6.1. If the total composition happened to be equal to f''_A , then just as the three-phase temperature is

reached,

$$\frac{W'}{W'''} = \frac{f'''_A - f''_A}{f''_A - f'_A}$$

In this case the relative rate at which these two phases disappear at the three-phase temperature, $\frac{dW'}{dW''}$, is just equal to the ratio in which they were present when that temperature was reached; consequently both disappear together, leaving only phase II. If instead the total composition is greater or less than f''_A then a relative excess of III or I respectively is present over that required to maintain the compositions at the fixed values of f'_A , f''_A , f'''_A : this excess is then still present when the other phase has disappeared.

C. Changes in Relative Amounts of Components

As pointed out previously any one-phase area in a $T-x$ diagram is a region of unsaturation; any two-phase area is a region of mutual saturation. In general one-phase and two-phase areas will be expected to alternate across the diagram at constant temperature, although degenerate cases are frequently noted in which one or more expected areas of either type are apparently missing; this merely means that its limits are so narrow that they either do not show on the scale of the diagram or have not yet been determined.

Although it would be readily possible to develop a new set of quantitative relations to describe the changes in the amounts of the phases resulting when increasing amounts of one component are added to a fixed amount of a phase, there is little gain in precision to be derived thereby over the use of the relations just developed. It will be sufficient for the purpose to discuss one hypothetical case. (Figure 19) Suppose that component A be continuously added to a fixed amount of component B at a temperature above the melting point of B . A at first dissolves increasing the concentration of the solution, (and, of course, the weight of it as well) until when the concentration of the solution reaches the value f'_A , it becomes saturated with respect to the solid solution α . Continued addition of A will cause the formation of increasing amounts of the phase α for each value of the total composition the ratio of the weights $\frac{W_\alpha}{W_L}$ can be determined by application of eq.0 (10), and is readily shown to vary from 0 to ∞ as the total composition changes from f'_A to f''_A . The mechanism by which the system makes the required adjustment in this case is by the destruction of the liquid phase since α must contain some of component B which can be derived only from the liquid phase. This process is completed when the total composition reaches f''_A . On further addition of A , the solid solution, which has previously been saturated with respect to liquid, becomes unsaturated and remains so as the total composition proceeds to f_A . As the degree of unsaturation with respect to L increases the degree of unsaturation with respect to the compound K_1

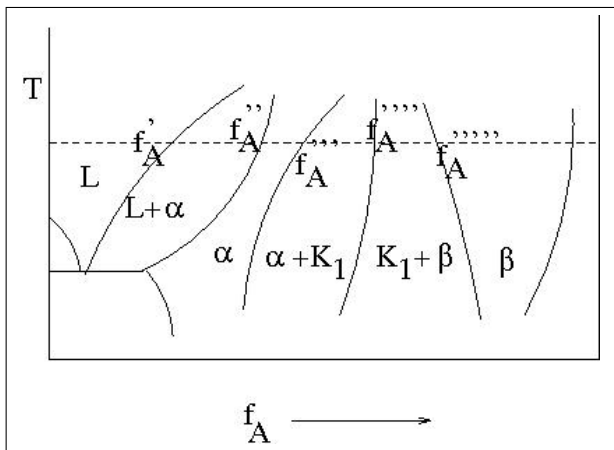


FIG. 19: A modestly difficult phase diagram showing various solid solutions

decreases until at f_A''' the solution is saturated or this new phase; K_1 then forms at the expense of α until it alone is present at The same analysis can be pursued through any number of areas, In each case involving a two-phase area within the diagram, the increase in the relative weight of the phase of higher composition due to addition of the component A proceeds by simultaneous increase in the weight of the phase of higher concentration and decrease in the weight of the phase of lower concentration.

Suppose now that instead of adding component A to a phase in the region of composition f_A'' to f_A''' (unsaturated α), we add the compound K_1 . At f_A''' the solution is saturated with respect to the added phase and will maintain that composition in the presence of any amount of it whatever. In this case therefore continued addition of the saturating phase causes the total composition to approach that of K_1 only as a limit and without decreasing the weight of the saturated phase α .

Obviously a second method of tracing phase rule diagrams is here implied, viz., instead of tracing cooling curves for various fixed compositions, the variations in the phase compositions may be noted as the total composition is changed for various fixed temperatures? The direct method of effecting this, of course, is to separate and analyze the phases, and represents the normal procedure for example in determining the solubility curves for solids in liquids. If, however, both phases are solid, it is obviously impracticable to try to separate them for chemical analysis. In this case some physical means of analysis will frequently be found satisfactory. The principle involved is simple since all the physical properties of the phases are functions of the Phase Rule variables and since the total composition of the system at a fixed temperature regulates either

1. the phase composition if only one phase is present or
2. the nature and relative amounts of the phases if

two phases are present, it will generally be found that the rate of change with total composition of any physical property, while varying continuously within a given area, will suffer discontinuities at the boundaries of that area.

Almost any physical property may be tried subject to the obvious practical criterion that the experimental method available for its measurement be sufficiently sensitive to detect the discontinuities in the rate curve for the system in question. Hardness, refractive index, electrical conductivity, magnetic permeability, lattice constants as determined by X-ray analysis, ease of reaction to etching agents and abrasives as noted under the microscope may be mentioned among the properties which have found application in this connection.

In case it is desired to locate the area boundaries for solid systems at elevated temperatures, advantage may be taken of the slowness with which equilibrium is established in such systems— the characteristic which constitutes a serious disadvantage in the use of cooling curves. The system may be maintained at the desired temperature until equilibrium has been established and then rapidly cooled (“quenched”) to room temperature where the physical property is measured.

D. Intermetallic Compounds and Solid Solution

A few words should be said concerning the nature of the so-called “compounds” which appear on the phase diagrams of alloy systems. Although in case one of the components is a non-metal or one of the intermediate elements which may function either as a metal or as a non-metal some of the compounds may correspond with the ordinary valences of the components, in general this is not the case and the only obvious qualification, these substances possess entitling them to the name “chemical compounds” is the fact that the atomic ratios of their constituents are expressible in terms of small integers. Where X-ray analysis has been made, however, evidence of their claim to individual entity is often shown in the possession of a definite crystal structure usually represented by a more complicated unit cell than those of the components. On the whole one of the most satisfactory classifications of these compounds which can be made is on the basis of the atomic volumes of the components (determined by the atomic weights and densities of the elements); this classification demonstrates that the chief reason for the existence of the simple atomic ratios characteristic of the compounds of a given pair of components is the possibility of close packing of the atoms at these ratios; the determining factor is therefore geometrical rather than chemical. However, in many cases the valence electrons carried by the component atoms apparently also contribute to the stability of the structure as evidenced by certain existing generalizations as to the ratio of valence electrons to atoms in the compound.

Solid solutions are mainly of two types "interstitial" and "substitution". In the first, the solute enters the interstices or spaces within the lattice of the solvent; it is therefore necessary for the formation of solid solutions of this type that the solute atoms be small as is the case for example with carbon and hydrogen. In the substitution type of solid solution, the solute atoms replace the solvent atoms at random points on the lattice of the latter.

In the substitution type of solid solution, the solute atoms replace the solvent atoms at random points on the lattice of the latter. In case complete series of solid so-

lutions are formed it will always be found that the components crystallize in the as the lattice pattern; as the substitution or solution progresses therefore, the lattice constants change continuously from those of one to those of the other component. When several solvents and solutes are the intermetallic compounds. Indeed some of these compounds never exist as such at total compositions greater or less than their own but instead form solid solutions with both components or with neighboring compounds.

[1] Assuming both components present in every phase

[2] As previously indicated, any concentration scale may be selected for x , since conversion from one scale to another is always allowable. If, however, it is desired to represent the entire composition range from one pure component to the other, the choice will be made among the scales mol-, weight-, or volume-fraction or -per cent. For these scales, of course, the composition of the system or of the phases composing it with respect to both components can be indicated, the two components being measured in opposite direction along the x-axis, since the sum of the concentrations on these scales is always one or one hundred. (The

error must not be made of assuming that this represents a method of representing two independent variables in one dimension.)

[3] Actually, since the composition of the azeotrope depends on the pressure (or temperature) it is not really a component, and this argument is not quite perfect (c wd).

[4] When not saturated with respect to either phase II or phase III, phase I may be represented by any point in the area designated I, such a point being described by the then unrelated coordinates x'_A, T .

[5] well really!!!!