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Lee O Case's "Elements of the Phase Rule", Chapter 3

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I. SYNOPSIS

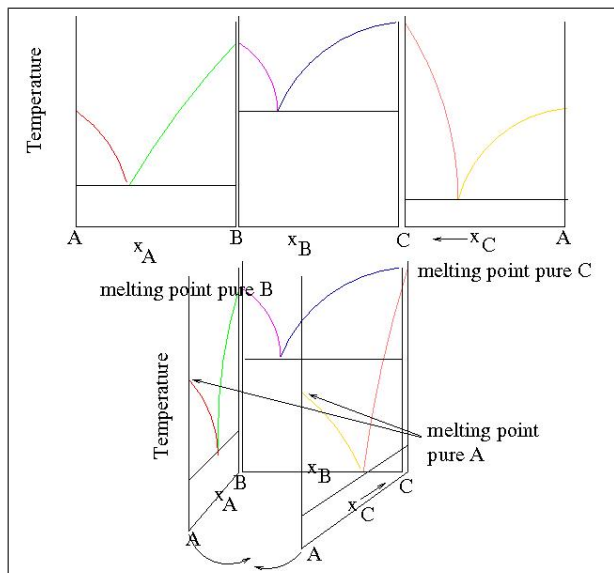


FIG. 1: Stitching three 2-component eutectic $T-x$ diagrams into one 3-component phase diagram. Slices at constant T make the normal triangular diagram we're used to (cwd).

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Three component systems require plotting p , T , x_A and x_B simultaneously ($x_C = 1 - x_A - x_B$). Clearly, this is impossible to do on a two dimensional piece of paper, and stratagems have been invented to allow representations of slices of the full dimensional functionality which can be placed on a two-dimensional page. This chapter discusses three-component systems and their representations (cwd).

II. THREE COMPONENT SYSTEMS

With the addition of another component it is clear that each phase will involve a second concentration variable, so that in case all three components may exist at appreciable concentrations in every phase the phase rule analysis furnishes:

P	$V = 5 - P$	$U = 2P + 2$	$V_c = V - 1$	$U_C = 2P + 1$
1	4	4 (x'_1, x'_2, p, T)	3	3(omit p)
2	3	6 ($x'_1, x''_1, x'_2, x''_2, p, T$)	2	5(omit p)
3	2	8 ($x'_1, x''_1, x'''_1, x'_2, x''_2, x'''_2, p, T$)	1	7(omit p)
4	1	10 do. (x''''_1, x''''_2, p, T)	0	9(omit p)
5	0	12 do. ($x''''''_1, x''''''_2, p, T$)		

As always, V represents the number of independent variables so that the conditions for the simplest case of heterogeneous equilibrium ($P = 2$) are represented by a set of functions involving four variables. For this simplest case, the number of possible choices which may be exercised in the selection of these functions is $\frac{6!}{4!2!} = 15$. However, the very natural choice corresponding to that discussed under two component systems is:

$$\varphi_1(x'_1, x'_2, p, t) = 0; \varphi_2(x''_1, x''_2, p, t) = 0$$

Evidently it is impossible to represent such relations directly in available space, although for condensed systems

(p constant) three dimensions are adequate. While limitations of space will make it necessary to restrict discussion to condensed systems, two points should be made in this connection:

1. A $p-T$ curve for a three component system implies the coexistence of four phases; this means for example that in order that a solution shall have a vapor pressure which is a definite function of the temperature only, it must be saturated with respect to two solid salts.

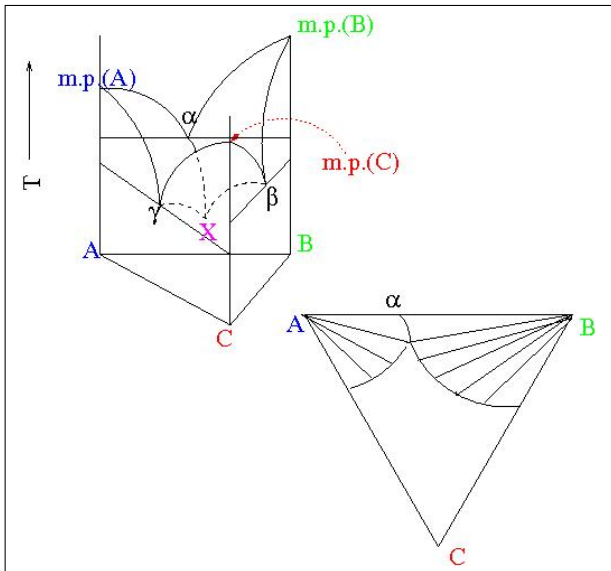


FIG. 2: For a system with three separate eutectics, located at α , β and γ , the triple eutectic is depicted at a temperature below each of the individual eutectic temperatures. A temperature for the “cut” has been chosen such that we are below the melting points of pure A and B. The temperature is also below the eutectic temperature of the A-B system.

2. The three dimensional figure $T - x_1 - x_2$ adequate for the complete representation of condensed systems may be regarded as the contour cut from the four-dimensional $p - T - x_1 - x_2$ figure by a plane of constant pressure.

Just as in the case of two component systems, the expedient of making a single axis serve for several phase concentrations makes it possible to show all the phase relations for a condensed system on one diagram. With the natural choice of the same concentration scale throughout, the total and phase compositions for component 1 are shown along one axis, those for component 2 along a second axis while the third axis is employed for the temperature. (Figure 4).

III. ISOTHERMAL DIAGRAMS

Again, just as for the two component $p - T - x$ diagram, practical ends are often served by employing the two-dimensional contours corresponding to constant values of one of the variables. The most important one of these in this case is the isotherm. The result is a two dimensional figure in which each axis represents the composition with respect to one of the three components. Again any one of the ordinary concentration scales may be, and actually are, employed, the choice depending upon the particular system and the range of the variables it is desired to show. Thus the x_1 and x_2 axes might be graduated in grams or mols of components A and B respectively

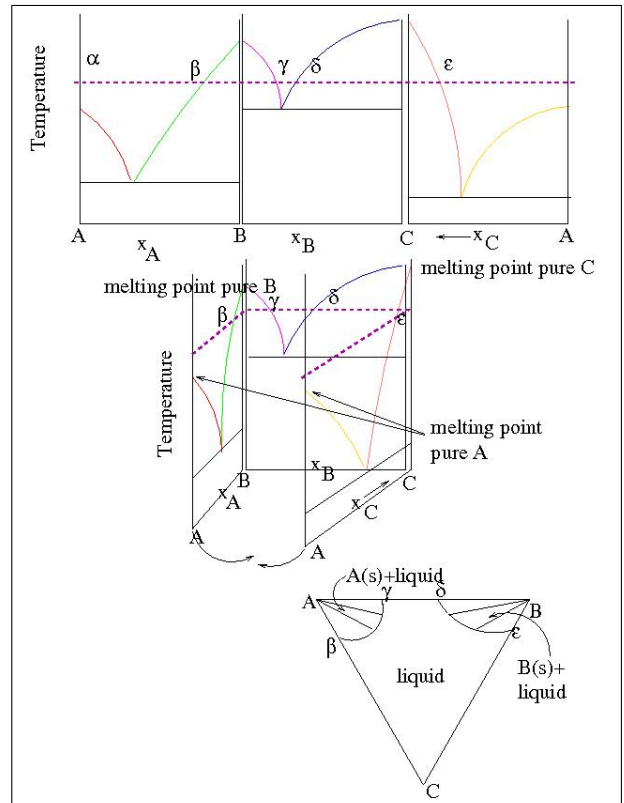


FIG. 3: The familiar triangular plot where their vertices correspond to pure A , B , and C respectively, and the two curves correspond to the intersection of a constant temperature cut of the original stitched together “three dimensional” T, x_A, x_B, x_C diagram. α represents the intersection of the $A - C$ eutectic curve with the constant temperature line. Other “greek” indicators show corresponding intersections in other parts of the pure 2-component phase diagrams contributing to each edge of the triangular plot.

per 1000 grams of component C . A very common concentration scale for salt and water systems is the number of mols or equivalents of each salt per 1000 mols of water; the former, of course, differs from the molal concentration only by the factor 18. Phase rule diagrams employing such concentration scales, in which the basis chosen is a fixed amount of one component, have the disadvantage that it is inconvenient or impossible to represent on them the concentrations of all the phases, since for example the concentration of either of the other pure components in these terms, is infinite. If, however, it is desired to show only the compositions of a set of solutions saturated with respect to different pure compounds (different salt hydrates, for example) one of these choices may be advantageous.

If it is desired to cover the entire range of composition on the diagram, the basis chosen must be the total amount of the system or phase in question. This is, of course, the characteristic of the scales: weight-, mol-, or volume-fraction or -per cent. With the choice of one of

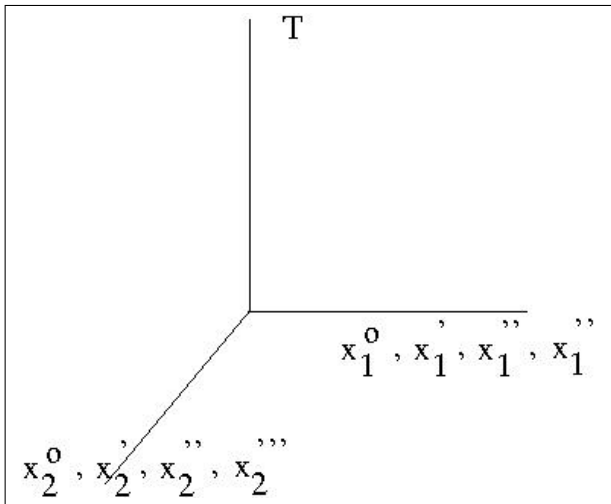


FIG. 4: Three component phase diagram. With four variables, p, T, x_1 and x_2 , one usually fixed the pressure (reducing the dimensionality to three; remember that x_3 is determined by the other two mole (or mass) fractions).

these scales all total or phase compositions possible at a given temperature can be represented on a diagram on which the axes are graduated in terms of the fraction or per cent of any two of the three components. While it might seem most natural to use the rectangular system for these axes, an important advantage is found to result if the axes are drawn at an angle to one another of 60° rather than 90° . This advantage derives from the property of the equilateral triangle that the sum of the perpendicular distances of a point from the three sides is equal to the altitude. If then the altitude of an equilateral triangle be taken to represent 100%, the percentages of the three components in a ternary system may be measured along the perpendicular distances to the sides of the triangle. Thus, in Figure 5, each vertex represents 100% of one of the components. A point on the base line represents a mixture of the two components A and B . A line drawn parallel to the base line at, say, 0.3 of the distance to the vertex represents all possible mixtures containing 30% of component C . A line drawn parallel to the side AC at 20 of the distance to the B -vertex represents all possible mixtures in which the percentage of B is 20. The point at which these lines intersect accordingly represents a mixture containing 30% C and 20% B , and therefore 50% A .

It must not be supposed that the use of the equilateral triangle makes possible the representation of three independent variables in two dimensions; it merely permits the selection of any particular pair as the independent ones at any time after the diagram is constructed. It may be of interest to point out that the analogous property in one dimension, of which use has already been made, is simply that the sum of the distances of a point on a straight line from the extremities of the line is equal

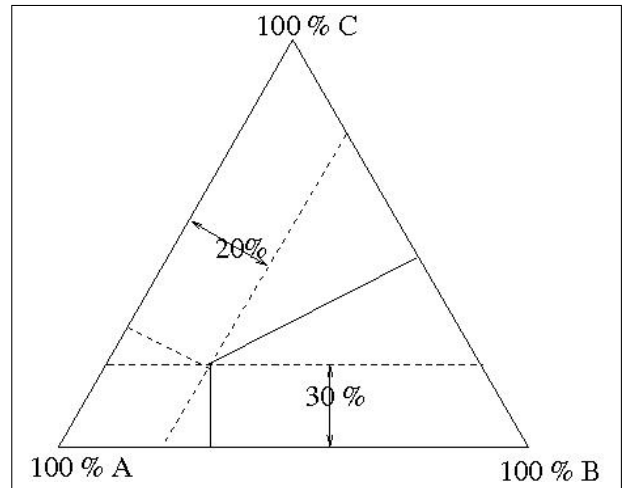


FIG. 5: After fixing the pressure and temperature, we can create a stylized triangular plot in which a point in the interior of the bounding triangle represents the %'s of each component

to the length of the line, and that the corresponding property can be stated in three dimensions for the regular tetrahedron.

Application of the phase rule to an isotherm for a three component condensed system furnishes the following results for the general case in which each component is present in every phase (the use of p and T as subscripts signifying constancy of pressure and temperature):

P	$V_{p,T} = 3 - P$	$U_{p,T} = 2P$
1	2	2 (x'_1, x'_2)
2	1	4 (x'_1, x''_1, x'_2, x''_2)
3	0	6 ($x'_1, x''_1, x'''_1, x'_2, x''_2, x'''_2$)

For any of the coordinate systems discussed above, in which axis is measured (x'_1, x''_1, \dots) etc., and along the other (x'_2, x''_2, \dots), etc., the phase rule requires for the simplest case of heterogeneous equilibrium ($P = 2$):

$$\begin{aligned} f_1(x'_1, x'_2) = 0 & \text{ phase II present} \\ f_2(x''_1, x''_2) = 0 & \text{ phase I present} \end{aligned} \quad (3.1)$$

This means that for each phase of a pair in equilibrium a curve can be constructed showing the dependence of the concentration of that phase with respect to one component upon its concentration with respect to a second component.

For the sake of concrete illustration, a case of equilibrium between two liquid phases will be briefly examined, the system chosen being that formed from phenol, water and acetone. At ordinary pressures, the two component system water-phenol may exist in two liquid phases as shown by the temperature-composition diagram in the upper half of Figure 6. The phase rule shows that in this region, at constant pressure and temperature, the composition of each layer is fixed ($V_c = 2 + 1 - 2 = 1; V_{p,T} = 0$).

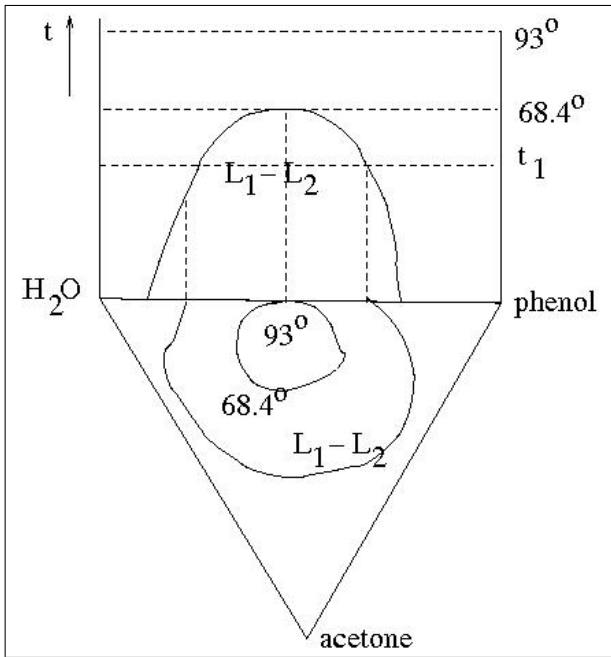


FIG. 6: From the two component phenol-water system, addition of acetone allows the immiscible mixture layers to remain so in the ternary system. What was a “paraboloidish 2-D hump” of immiscibility becomes a “3-D hill”. Contours at 68.4 and 93° C show how the maximum is being approached at temperatures higher than 93° C, which is higher than the maximum in the water-phenol immiscibility area. cwd

The isotherm for the two component condensed system therefore consists of a straight line on which are marked off the points representing the compositions of the mutually saturated liquid layers. But this line may be made the base line for the three component system resulting when acetone is also present, e.g., the triangular diagram shown in the lower half of Figure 6. In the presence of the added component the composition of each liquid layer is represented by a line instead of a point, the general equations for the two lines being given by Equation 3.1 in which phase $I = L_1$, phase $II = L_2$. For this particular system the two curves become continuous at a so-called “critical point”, K , before either one happens to intersect another solubility curve.

Suppose now that at constant temperature acetone is continuously added to a mixture of phenol and water existing in two liquid layers. The path of the total composition will move along a straight line from the point on the base representing the initial mixture of phenol and water toward the acetone vertex opposite (easily verified by similar triangles based upon the fact that the ratio of phenol to water must remain unchanged during such a process). So long as two liquid layers are present during this operation, the phase compositions must be located on the two lines bounding the $L_1 - L_2$ area. When the path of the total composition crosses one of the boundary lines one of the layers disappears. The application of

this principle to the determination of the phase diagram is obvious, see Figure refchapter3fig19.

Similar relations, of course, hold for other temperatures and for other total compositions. With respect to the former factor, it is interesting to note that for this particular system at temperatures above 68°C (the critical solution temperature for the phenol-water system) a two phase area, continues to exist on the three component diagram up to 93°C, the boundary in this region becoming a continuous closed curve. With respect to the total composition it may be noted that, owing to the unusual form of the boundary curves, it is possible at all temperatures below 93°C to select homogeneous mixtures of phenol and water which on continued addition of acetone first form two layers and later become homogeneous again.

The diagram as discussed so far does not express all the information that might be desired. It is true that if the concentration of one component in one of the coexisting liquid phases is known, the concentration of the other components in the same phase can be immediately read from the diagram. However, the concentrations of the components in the other phase in equilibrium with the first can not be so determined. In other words, although it is known that the compositions of all coexisting phases are located somewhere on the boundary curve, it cannot be told which are corresponding phases. This, however, is a limitation characteristic of the choice of coordinates and not of the phase rule itself. For, if the tabulation of the phase rule results for two-phase systems be again referred to, it will be noted that in addition to the two relations already employed there are also available:

$$\begin{aligned} f_3(x'_1, x''_1) &= 0; \\ f_4(x'_2, x''_2) &= 0; \\ f_5(x'_1, x''_2) &= 0; \\ f_6(x''_2, x'_1) &= 0; \end{aligned} \quad (3.2)$$

of which the first pair serve to relate the concentrations of the same component in different phases. Thus for example a new diagram of which the axes are x'_1 and x''_1 would give just the information which was found lacking ten: to the previous diagram. Although this new type of diagram is sometimes very useful, it is possible to represent the same information, somewhat less specifically, on the diagram already constructed. This is achieved, by the use of so-called “tie-lines”-straight lines linking the compositions of the phases in equilibrium with one another. (Figure 7).

When the tie lines have been located on the diagram it becomes possible, knowing the concentration of one to in one phase, to read off not only the the concentrations of the other components in that phase but also (by T interpolation if necessary) the concentrations of all the components in the other phase as well.

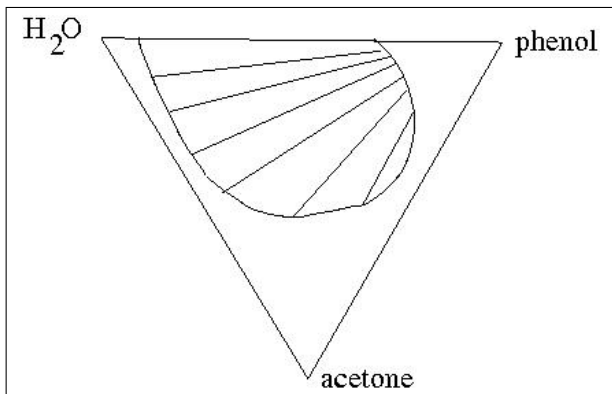


FIG. 7: Two layer liquid equilibria changed by adding a third component. Immiscible liquids of water and phenol remain immiscible if acetone is added to keep the two layers intact. The tie lines are experimental data points reflecting the compositions of the two layers.

IV. RELATIVE AMOUNTS OF PHASES

It may readily be proved that a tie-line is the-locus of the total compositions of all mixtures which separate into the phases joined by the tie-line. An infinite number of mixtures may there-fore be prepared all of which possess the same phase compositions but differ only in the amounts of the phases. If reference now be made to the derivation of the rule for the relative amounts of two phases present in a two component system, it will be found that the restrictions there made are necessary and sufficient for the present case also. Thus the same rule is applicable for the determination of the relative weights of two phases present in a system of three components as for one of two components (in fact regardless of the number of components). To restate the rule: The amounts of the phases are in inverse ratio to the segments of the tie-lines cut off by the total composition.

If application of this rule for the relative amounts of the phases be now made to the process previously discussed, viz., continuous addition of acetone to an initial mixture of phenol and water, it will be noted that in general, as the amount of one phase increases, that of the other decreases until it finally disappears.

Whether L_1 or L_2 disappears first depends upon the initial composition; there is one initial mixture, however, for which the path of the total composition passes through the critical solution point and for which therefore the rule shows that the two phases are present in nearly equal amounts at the instant of passage into the one phase area. The reason for the name "critical solution point" is probably evident from the analogy of this behavior to that of a pure substance at its critical point.

V. OTHER FEATURES OF ISOTHERMAL DIAGRAMS

In the example cited above only one-phase and two-phase equilibria were noted, the two solubility curves happening to become continuous. If, instead, one of the solubility curves happens to intersect another for the same phase, three-phase equilibrium occurs, indicated by a set of three points on the diagram, each being located at the intersection of two solubility lines. The close analogy of this situation with that for the $T - x$ diagram for a two component system is worth, noting. The analogy, however, fails of completeness in one respect: While for the two component system uniformity of temperature requires that the three phase-points be ranged along a straight line, no corresponding limitation exists on the $x_1 - x_2$ diagram for a three component system. Consequently in the latter case the three phase-points define instead a triangular area which includes all those total compositions which can give rise to the three-phase equilibrium in question; these three-phase triangles therefore constitute a new feature in this type of diagram.

The only other point deserving of special mention in this connection is the degeneration of the diagram which occurs when one or more of the saturating phases are regarded as pure components or pure compounds. In this event, which is very common in actual diagrams, the corresponding solubility lines degenerate to points representing the compositions of the components or compounds?

The analysis of a diagram in accordance with the above principles involves labeling the various one- two- and three-phase areas with symbols indicating the physical nature of the phases concerned. The literal use of tie-lines to join those phases which are in equilibrium with one another probably constitutes the best method of ensuring correctness in this operation.

VI. TEMPERATURE-COMPOSITION DIAGRAMS

While limitations of space prevent the detailed discussion of the many interesting cases that may arise in three component systems, the power of the phase rule in organizing and interpreting the diverse examples that exist in nature should by now be apparent. In order to permit some discussion of one technically important application, the examination of other possible cases must be limited to a brief mention of the general characteristics of the $T - x - \ell(\text{iquid})$ diagram for three component condensed systems.

For this purpose, suppose that the equilateral triangular diagram has been selected as the basis for the concentration relations. (This is, of course, only a matter of convenience.) If it is now desired to indicate also the influence of temperature, it is only necessary to erect the temperature-axis at right angles to the $x_1 - x_2$ plane. The resulting figure is an equilateral triangular prism. It

will now be evident that each of the faces of such a prism constitutes the phase rule diagram for one of the possible two component condensed systems which results by omission of one of the three components. Just as in turn each of the vertical boundaries for one of the two component systems represents the phase rule diagram for a one component condensed system. Accordingly any of the many possible two component diagrams may be found associated in sets of three to form possible three component diagrams.

Now just as a point representing the conditions for coexistence of two phases in a one component condensed system becomes a line with the addition of a second component, so this line generates a surface on addition of a third component. Similarly points representing the conditions for three-phase equilibrium in the two component condensed system become lines on the addition of the third component. Finally points on a ternary diagram result from the intersection of a pair of lines each of which indicates the conditions for equilibrium of a certain phase with two others.

Thus on such a diagram any two-phase equilibrium is indicated by two surfaces, these bounding a solid region which comprises those total compositions which result in the two phases. Any three-phase equilibrium will be represented by three lines, one for each phase. Finally, any four-phase equilibrium will be represented by a set of four points, which, owing to the requirement of uniform temperature, must all lie in the same horizontal plane?

While actual diagrams for three component systems may appear to differ greatly in characteristics, these are only minor modifications of the general principles outlined above, which in turn represent only logical extensions of the principles discussed in more detailed fashion for two component systems. In the same way, the reaction of a ternary system to changes in its temperature or to additions of one of its components can be analyzed in the light of the phase rule just as readily as for two component systems. While lack of space will prevent such an analysis here, there is one type of variation in conditions to which a system may be subjected which has important characteristic features for systems of three components and which is of sufficient practical significance to merit separate consideration at this point. The variation in conditions referred to is the isothermal removal of one component and the practical application is to the problem of separation of salt constituents from naturally occurring brines by evaporation of the solvent.

VII. SALT CRYSTALLIZATION

Some of the features of systems consisting of water and two salt components will now be considered.

At first thought it might seem that any pair of salts would form a three component system with water. In general, however, this is not the case. Owing to dissociation even a simple salt produces two kinds of ions so that

in addition to electroneutrality the further restriction is necessary that the salts possess an ion in common in order that the system be one of three components only. Examples are: Ca^{++} , Sr^{++} , Cl^- , H_2O ; Na^+ , K^+ , SO_4^{--} , H_2O ; Na^+ , CO_3^{--} , HCO_3^- , H_2O .

Suppose, therefore, that a system composed of H_2O plus two salts, A and B , possessing an ion in common be selected for study and that with reference to this system the problem of separating these salts from their solutions be examined. The discussion will be related to a rectangular diagram in which the concentrations are expressed in equivalents of each salt per 1000 mols of H_2O , a scale very frequently used for this type of system in which the solid phases are usually limited to pure components or pure compounds.

According to the phase rule, solutions saturated with respect to a single salt will be represented by lines on such a diagram ($V_{p,T} = 3 - 2 = 1$), $f_1(x'_1, x'_2) = 0$. Points, produced by the intersection of two such lines, represent solutions saturated with respect to two salts ($V_{p,T} = 3 - 3 = 0$). Such a diagram is shown in Figure 8 an isotherm at an hypothetical temperature T_1 . It is

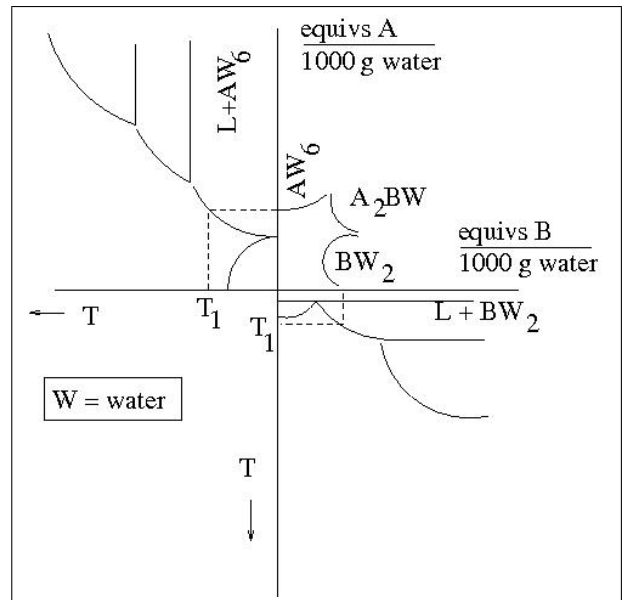


FIG. 8: Saturated solutions in relation to each other (a diagrammatic mystery:-)

instructive to relate the three component diagram to the two component $T - x$ diagrams as has been done in the figure. In addition to the solubility curve for the single salts, another solubility curve for a supposed double salt has been shown also, these being very common in salt systems. (Any or all of these salts may be hydrated.) As has been done in the figure, it is customary to label each line with the formula of the salt constituting the saturating phase, but it must be kept clearly in mind that the phases actually shown on the diagram are all liquid; if it were desired for example to actually locate the solid

phase AW_6 on this diagram it would be represented by a point $(100/6) = 167$ units up on the vertical axis (the equivalent weight of A being assumed equal to its molecular weight); the anhydrous salt A would be located at infinity. Although it is to be expected that the solubility lines will be curved, it frequently happens that the only data available are the coordinates of the points such a case the only recourse is to connect with straight lines points having a saturating salt in common.

With respect to the diagram constructed, the effect of isothermal evaporation of water from an unsaturated brine will be discussed. Such a brine will be represented by a point within the area included between the solubility lines and the axes. On evaporation of water the brine composition will move along a straight line away from the origin, since so long as the brine remains unsaturated. The ratio of the salt components in the solution must remain constant. Eventually the brine will become saturated, this result being indicated on the diagram by the intersection of the radius vector through the brine composition with one of the solubility lines. The composition of the solution and hence the amount of water evaporated up to this point could be easily determined if desired either by graphical or analytical means.

On continued removal of water the now saturated solution must precipitate the saturating salt, the solution composition being constrained to follow the appropriate solubility curve until a point is reached at which the solution is saturated with respect to two salts.

The first question which arises is as to the direction in which the saturated brine composition will move along the solubility curve.

A. beginning of inserted pages

Instead of using the horizontal or isothermal sections of the $T - x_A - x_B$ figure, one may study the phase relations in a ternary system by means of the vertical sections. Each of these methods has its advantages. Thus isothermal diagrams are obviously better suited to the organization of an experimental program involving analysis of the phases (either by chemical or physical means) and to the representation of the data so obtained. On the other hand vertical sections are more useful if thermal analysis by means of cooling curves is to be employed since the resulting data can be plotted directly on such a diagram. The method is of course precisely that used for two-component systems mixtures of various total compositions are made up and their cooling curves analyzed for "breaks" and "halts". (Note that a "halt" in the case denotes 4-phase instead of 3-phase equilibrium) It is most convenient to select for study total compositions ranged in a systematic manner along various plane sections of the solid figure, the most common used involving either

1. constant total composition with respect to one component (a section parallel to a T-x face) or

2. constant total composition ratio for two of the components (a section thru a vertical edge of the figure.).

At first thought it might seem that a vertical section thru the $T - x_A - x_B$ figure would have the appearance of a $T - x$ diagram for a 2-component system. While certain similarities do in fact exist, differences occur which are at least equally characteristic and significant. The fundamental reason for the new features is that while an isotherm or isobaric section corresponds in general to a limitation of the variance of the system, a section at constant total composition does. This circumstance has two important results:

1. the maximum number of coexisting phases is the same in the vertical section as in the solid figure;
2. although when the diagram is properly labeled the nature of the coexisting phases can be read from it, their compositions in general lie outside the section.

In order to understand the characteristics of the vertical sections, it will be necessary to review briefly the properties of the solid figure. Since this involves a certain amount of visualization the best approach will be to summarize the properties of the now familiar Isothermal sections. These are as follows:

Any arbitrary horizontal section is marked off by means of lines into a number of areas, each comprising all those total compositions which can result in the phase equilibrium characteristic of the area.

I. For one-phase equilibrium the total composition is necessarily also the phase composition, which can be freely varied within the area. The boundaries of such an area are either

1. external boundaries of the diagram or
2. lines representing the phase in question when saturated with respect to other single phases.

The boundaries of type (2) for a single one-phase area are in general curved, independent of one another and not limited in number by theoretical considerations.

II. For 2-phase equilibrium the phase compositions can be varied only along two boundary curves each representing the composition of one of the mutually saturated phases. (The curves in I (2) above.) In special cases these boundary curves may

1. become continuous with one another (the critical phenomenon) or
2. may degenerate to a point (the corresponding phase being a pure compound or a pure component).

Otherwise additional boundaries not exceeding two in number may be provided by

1. external boundaries of the diagram or

2. limiting tie-lines, each linking those representatives of the pair in question which are capable of coexistence with an additional phase.

Boundaries of the latter type are necessarily straight lines.

III. For 3-phase equilibrium, the phase compositions are necessarily fixed, each being represented by a characteristic point. The boundaries of such an area are three in number and consist of straight lines joining the 3 points [the lines of II (2) above]. That the total compositions which can result in a given 3-phase equilibrium must necessarily be included within a triangular area will be evident when it is considered that all possible mixtures of 2 phases of fixed compositions must lie along a straight line connecting the 2 phase-points and the section to any such mixture of a 3rd phase (of necessarily fixed composition) must be represented on the diagram by movement of the total composition toward the 3rd phase-point as a limit. It is clear that any or all of these 3-phase-area boundaries may coincide with an external boundary of the figure.

If now temperature be admitted as a variable, each feature of the isothermal section acquires an additional degree of variance. Thus each type of boundary curve of the isothermal section generates a surface, the only restriction upon the nature of these being that those of type II (2) above are obviously ruled surfaces, i.e., they are generated by the movement of straight lines.

With the added degree of variance a new possibility is presented that of 4-phase equilibrium. Although the phase rule immediately predicts that any 4-phase equilibrium, will be represented by a set of 4 points in a common temp. plane, the distribution of these points merits brief further consideration. There are in fact two possibilities to this distribution; (1) One pt. may lie within the triangle formed by the other 3 (Figure 9 (left)) or (2) the 4 points may define a quadrilateral (Figure 9 right). If

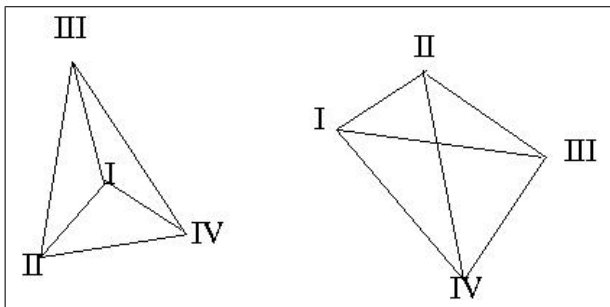


FIG. 9: Four phases in a 3 component system.

now all the points are interconnected with tie-lines it is noted that in each case a set of 4 overlapping triangles is formed, each of which involves a different association of the 4 phases into a set of three. These sets of 3-phase triangles in fact represent the various 3-phase equilibria into which the 4-phase equilibrium must pass on alter-

ation of temperature (It may be considered that this occurs by splitting of the figures along the interior tie-lines) Inspection of the figures shows that the two different distributions of points lead to different distributions of the 3-phase equilibria about the 4-phase temperature, the distribution of Figure 9(left) resulting either in (1) three 3-phase equilibria above and one below the 4-phase temp. or (2) one above and 3 below, while the distribution of Figure 9(right) involves two 3-phase equilibria above and two below the 4-phase temp, (the latter distribution was involved in Prob No. 37.).

As a result of the situations described, there will in general appear in the interior of the solid figure three types of surfaces; (1) surfaces representing single phases which are in equilibrium with another phase, (2) ruled surfaces representing mixtures of two phases which are in equilibrium with a 3rd phase, (3) horizontal plane surfaces characteristic of 4-phase equilibria.

All the characteristic features of the solid $T - x_A - x_B$ figure have now been described. Passage of a vertical plane through this figure will obviously cut its surfaces in a new series of lines each having the significance of the corresponding surface. From the nature of the figure it is evident that horizontal lines in such a section will result only from intersection with a 4-phase plane (except for the accidental cutting of a ruled surface in one of its rectilinear elements).

Since it is difficult to carry in mind the meaning of each of the curves appearing in a vertical section, it is convenient to designate each one as explicitly as possible, i.e., to show not only the phase or phases represented by the curve, but also in parenthesis the other phase or phases involved in the equilibrium. Thus, for example, L(x) designates a liquid which is saturated with a solid solution; L(B) represents a mixture of the mutually saturated phases L and which is in equilibrium with another phase, etc. For reasons noted above in the case of Figure 9(left) and Figure 9(right) the horizontal lines cut from a 4-phase plane are capable of alternative designations.

Once the characteristic curves in the vertical section have been designated as outlined above, the significance of their points of intersection and of the areas which they bound becomes evident. Thus for example a point of intersection of two curves must represent a phase or phases common to the two intersecting curves.

A final point to be noted in connection with the Interpretation of these sections is that any internal feature of the diagram which persists to an external 2-component boundary does so with decrease of variance but without change of designation.

VIII. END OF INSERTED EXTRA PAGES

The answer is furnished, by a consideration of the effect on the ratio of the components due to separation of the saturating salt relative to the ratio of the components in the initial saturated brine.

For the sake of numerical illustration, reference is made to the system shown in Figure 10, in which it is assumed that the salts A and B of the type of CaCl_2 , such that the equivalent weight is one half the molecular weight. Let $s = \text{mols } A_2BW$ separated. Then by separation of A_2BW the ratio of the salt components in solution becomes:

$$\frac{y}{x} = \frac{8 - 2x2s}{12 - 2s} = \frac{4 - 2s}{6 - s}$$

Evidently the ratio y/x decreases, resulting in movement of the point representing the brine composition in the direction of the arrow.

It is easy to generalize this result, noting that the direction will be the same for all brines in which the ratio

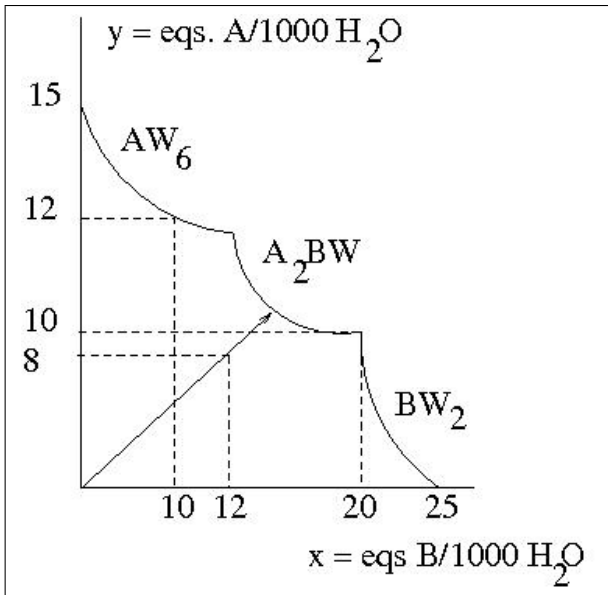


FIG. 10: Another unique diagram concerning the various salts and salt hydrates :-).

of A to B is less than this ratio for the separating salt. It is worth noting in this connection that if the separating salt is one of the components (hydrated or not) the brine composition must always move toward the interior of the diagram. For example, suppose that the solubility line intersected is that for the BW_2 . Then if $t = \text{mols } BW_2$ separated, $\frac{y}{x} = \frac{8}{12-2t}$ or the ratio must increase for all positive values of t .

The second question of interest is: How much of the pure saturating salt can be obtained by continued evaporation? Evidently the limit is reached when the brine has just become saturated with a second salt also, since if evaporation is continued further both salts will be present. The answer can be obtained in quantitative form by substitution for y/x of its value at the saturation point for A_2BW and BW_2 . Thus,

$$\frac{y}{x} = \frac{8 - 2x2s}{12 - 2s} = \frac{10}{20}$$

whence $4 - 2s = 3 - \frac{s}{2}$ or $s = 2/3$.

A third question is: How much water must be evaporated in order to attain the result just noted? If $h = \text{mols water evaporated}$, then

$$\frac{8 - 4(2/3)}{1000 - h - (2/3)} = \frac{10}{1000}$$

whence $h = 466$.

It may be noted that all the results so far obtained represent solutions of the "material balances" for the three components:

$y = \frac{w}{1000}y_o + 2.2s$	where $x, y = \text{original brine composition}$ $x_o, y_o = \text{composition of brine saturated with both salts.}$
$x = \frac{w}{1000}x_o + 2s$	$s = \text{mols } A_2BW \text{ separated}$ $h = \text{moles water evaporated,}$
$1000 = w + s + h$	$w = \text{moles water still in solution}$

The question might finally be raised: What will occur if evaporation be continued after the solution has become saturated with the second salt? The phase rule readily supplies the answer. Since three phases are now present at constant pressure and temperature, $V_{p,T} = 3 - 3 = 0$.

This means that the solution phase (in this case the only one of potentially variable composition) must maintain constant composition so long as all three phases remain. Consequently as the new salt separates, some mechanism must be provided to compensate for the

change in solution composition which this would occasion. In some cases this mechanism will consist in continued separation of the original salt; in other cases it will involve the re-solution of the original salt. Which of these mechanism is required for a given system will depend upon the ratios of the salt

components in the three phases at equilibrium. If the ratio of the salt components in the solution is intermediate between those for the two solid phase, the original salt will continue to separate with the new one; if, on the

other hand, the ratio of the salt components is greater than, or less than, those for both salts, then as the new salt separates the original salt must go back into solution. A general illustration will make clearer why it is that this mechanism satisfies the phase rule requirement. Suppose that a point (x_o, y_o) has been reached on the diagram at which the solution is saturated with respect to the two salt A_mB_n and A_uB_v (either or both might be hydrated), the latter being the new salt which begins to separate at this point. If $(m/n) > (y_o/x_o) > (u/v)$, then both salts separate together since separation of A_uB_v , which tends to increase the ratio of A to B in solution, can be compensated by-the separation of some positive quantity of which tends to decrease the ratio of A to B. If, on the other hand $(m/n) > (u/v) > (y_o/x_o)$, separation of either salt tends to decrease the ratio of A to B in solution; separation of A_uB_v can therefore be compensated only by solution of A_mB_n .

Suppose now that for the system In question the phase rule requirement at the three-phase point is met by resolution of the salt A_mB_n originally separated. What is the final result of this process? There are again two possibilities:

1. The liquid may disappear first, leaving a mixture of the two solid salts,
2. All the A_mB_n may return to solution before the last liquid disappears, leaving a solution saturated

only with respect to A_uB_v .

In the second case then, continued, evaporation separates more A_uB_v with gradual change in the solution composition until another three-phase point is reached.

Complete analogy may be drawn between the cases just discussed and the behavior of two component systems earlier examined. Reference may be made to Figures 11 and 12, the first for a two component, the second for a three component system. On the latter diagram radius vectors have been drawn indicating the ratios of the salt components in the solid salts (the actual compositions of which would be located at infinity in the directions indicated.). On either diagram, systems of type "b" will result ultimately in mixtures of the two solid salts, while systems of type "a", after preliminary separation of A_mB_n will later consist of liquid and A_xB_y

(the final result depending upon other features of the diagram). An intermediate possibility of course, exists for systems of initial composition equal to that of A_uB_v , which must ultimately consist of the pure single salt A_uB_v produced by simultaneous disappearance of the liquid- and A_mB_n - phases.

IX. FOUR COMPONENT SYSTEMS

P	V = 6-P	U = 3P + 2	V _c = 5 - P	U _c = 3P + 1	V _{p,T} = 4 - P	U _{p,T} = 3P
1	5	5	4	4	3	3
2	4	8	3	7	2	6
3	3	11	2	10	1	9
4	2	14	1	13	0	12
5	1	17	0	16	-	-
6	0	20	-	-	-	-

(As usual the values given for the number of variables are based upon assumption that each component is present in every phase. For the simplest case of heterogeneous equilibrium (P=2), five variables are involved (one dependent, four independent. While this increase In the number of variables to be dealt with involves nothing new or difficult of comprehension in the way of fundamental principles, it does entail vastly Increased labor in the determination of experimental data as well as additional ingenuity in graphical representation. As a result, reasonably complete data have been determined for relatively few systems. At the same time, many new methods of graphical treatment have been proposed, each of which may be particularly adapted to a certain type of system. Limitations of space will make it necessary here to restrict discussion to a single type of system and method

of representation. The type selected is chosen both for its technical importance and its relation to the three component type last discussed.

Inspection of the table above shows that all three physical dimensions are required for the construction of an isotherm for a condensed four component system ($P = 2, V_{p,T} = 2$). For complete representation even of the condensed system, therefore, it is necessary to construct a number of isotherms, each consisting of a three-dimensional figure, and each of which may be regarded as a contour cut from a four-dimensional figure by a plane of constant temperature. Following the usual choice of coördinates, each such Isotherm would involve three concentration axes, one for each of three of the four components. Again any convenient choice may be made for the concentration scales. For a system composed of water

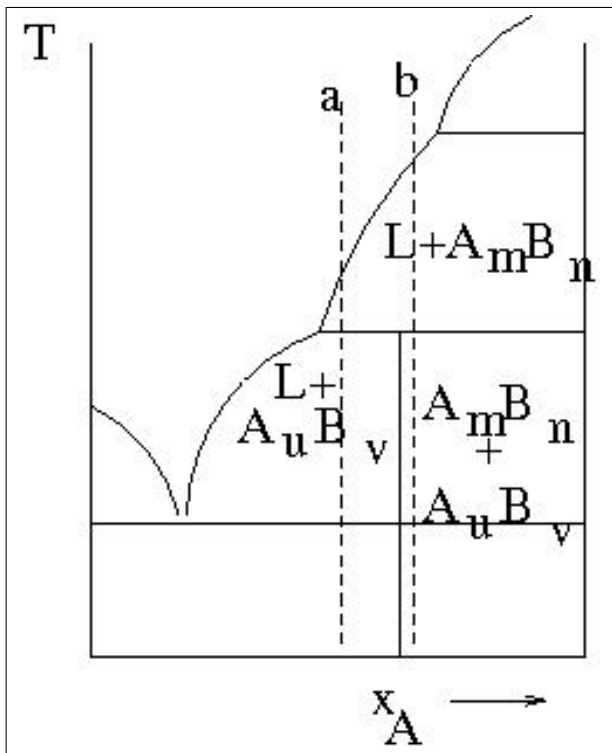


FIG. 11: A eutectic coupled with a peritectic. The r.h.s. is neither A nor B , but a compound, $A_m B_n$, i.e., the phase diagram continues to the right.

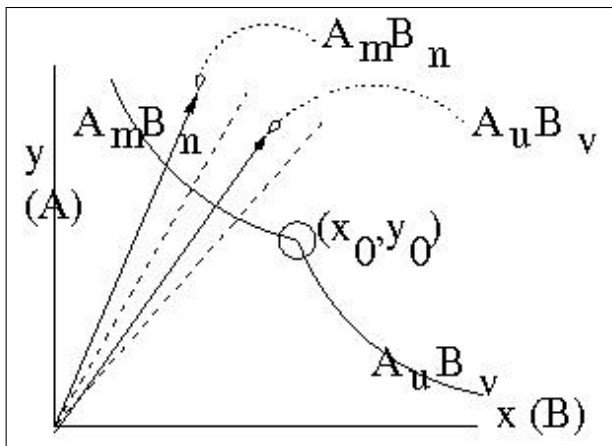


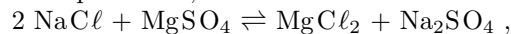
FIG. 12: Yet another mysterious diagram:-

plus three salt components, an obvious choice would be three rectangular axes, each, graduated in equivalents of one of the salts per 1000 mole of water. The isometric projection of this figure is in fact commonly employed for systems of water plus three salts having an ion in common, such for example as the system: H_2O , $CaCl_2$, $SrCl_2$, $BaCl_2$.

The type of system just mentioned possesses no features which are not readily interpreted by extension of

the principles already discussed for the corresponding case of water plus two salt components. For water plus three salt components, an important type does occur, however, which, particularly with reference to the graphical treatment, possesses interesting features. This type, involving what are known as “reciprocal salt pairs”, will be briefly discussed.

A system of the type referred to results from water plus two salts which do not possess a common ion, e.g., $NaCl$, $MgSO_4$. Owing to ionization of the salts this system, as pointed out earlier, consists not of three but of four components. Even if the ions are not considered, the equilibrium, must be satisfied:



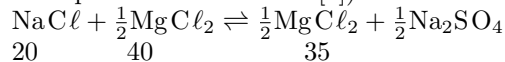
so that, of the four salts possible, any three constitute the salt components, which with water give rise to a four component system ($E = 1$, $C = 5 - 1 = 4$)

The method which is most satisfactory for the graphical treatment of such a system will now be described. While at the outset this method may appear arbitrary and unnecessary, its merits can be made clear later. The three coördinates chosen (all in terms of equivalents per 1000 mole of water) are:

1. the concentration of salt component I;
2. the concentration excess of salt component II over salt component III;
3. the total concentration of all three salt components.

Further, in order to gain the advantage of two-dimensional representation, the resulting solid figure is shown by means of its horizontal and vertical projections. One more feature is involved: Each of the four principal directions in the horizontal projection is labelled with the formula for one of the four salts, salts, having common ions being given adjacent positions. Such a diagram is illustrated in Figure 13. It should be clear that this is not a device for the representation of four independent variables in two dimensions but is merely a method of facilitating the selection of any three salts as the salt components during or after the construction of the diagram.

The process of locating a point on the diagram will now be illustrated.. Assume the following values (in equivalents per 1000 mols water [1]):



Since, of the salts for which the concentrations are given, the pair $NaCl$, $MgSO_4$ appear along opposite directions of the same axis, it will be convenient to select $MgCl_2$ as salt component I in the list of coördinates given above. The coördinate of the horizontal projection of the point

$$y = \left(\frac{1}{2}MgCl_2 \right) = 35$$

$$x = (NaCl) - \left(\frac{1}{2}MgSO_4 \right) = 20 - 40 = -20$$

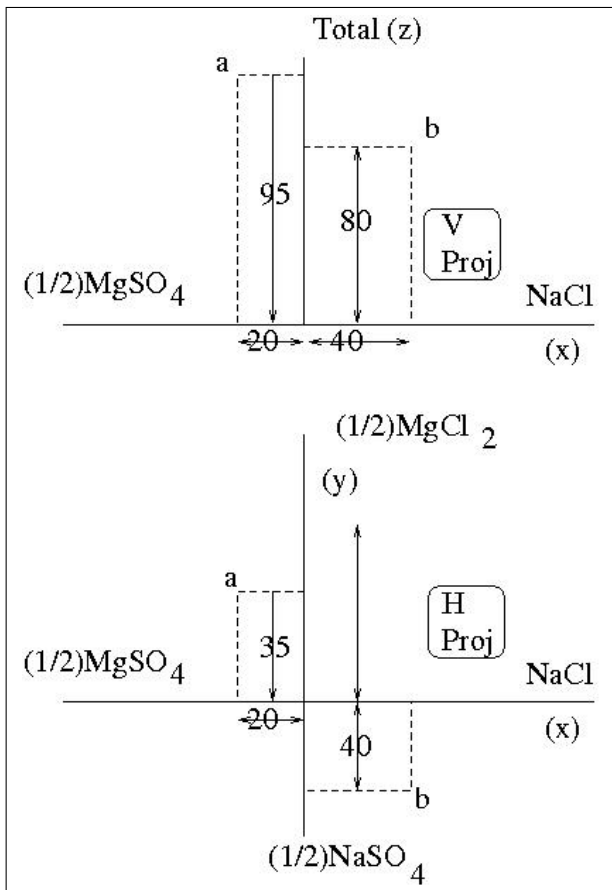


FIG. 13: The last mysterious figure demanding a close reading of the text!

In the vertical projection (a'), the coordinates will be:

$$x = -20; z = (\text{NaCl}) + \left(\frac{1}{2}\text{MgSO}_4\right) + \left(\frac{1}{2}\text{MgCl}_2\right) = 20 + 40 + 35 = 95.$$

It should be noted that the selection of NaCl , MgSO_4 and MgCl_2 as the salt components was quite arbitrary; any set of three might have been chosen. For example, suppose that MgSO_4 , MgCl_2 , Na_2SO_4 are preferred. The concentrations of these salts which would lead to the same system (by virtue of the equilibrium relation, since by definition the salts react equivalent for equivalent) are

NaCl	$+$	$\frac{1}{2}\text{MgCl}_2$	\rightleftharpoons	$\frac{1}{2}\text{MgSO}_4$	$+$	$\frac{1}{2}\text{Na}_2\text{SO}_4$
20-20		40-20		35+20		0+20
0		20		55		20

It is readily seen that the use of these coordinates leads to the same location for the point:
 $x = -\left(\frac{1}{2}\text{MgCl}_2\right) = -20$;
 $y = \left(\frac{1}{2}\text{MgCl}_2\right) - \left(\frac{1}{2}\text{Na}_2\text{SO}_4\right) = 55 - 20 = 35$;
 $z = \left(\frac{1}{2}\text{MgSO}_4\right) + \left(\frac{1}{2}\text{MgCl}_2\right) + \left(\frac{1}{2}\text{Na}_2\text{SO}_4\right)$

It has thus been shown that the method described.

provides a means of locating uniquely any system composed of the four salts chosen plus water. The reverse operation of determining the salt concentration from the coordinates of a point on the diagram should perhaps be illustrated. For the point (b, b') in Figure 13:

- $x = (\text{NaCl}) = 40$
- $y = \left(\frac{1}{2}\text{MgCl}_2\right) - \left(\frac{1}{2}\text{Na}_2\text{SO}_4\right) = -30$
- $z = (\text{NaCl}) + \left(\frac{1}{2}\text{MgCl}_2\right) + \left(\frac{1}{2}\text{Na}_2\text{SO}_4\right) = 80$
whence
 $(\text{NaCl}) = 40$; $\left(\frac{1}{2}\text{Na}_2\text{SO}_4\right) = 35$; $\left(\frac{1}{2}\text{MgCl}_2\right) = 5$.

While no specific advantage has yet been indicated for this choice of coordinates, it has been demonstrated that the method will serve for the description of the equilibrium relations for this type of system. In principle the use of such a set of derived coordinates is no different from the practice of showing $p - T$ relations in terms of the derived coordinates $\log p$ and l/T .

In the light of the phase rule the characteristics of the diagram will now be predicted. Since for $P = 2$, $V_{p,T} = 2$, a solution saturated with respect to a single salt will be represented by a surface, shown by its two projections on the diagram. The saturating salt may, of course, be a single salt, a double salt, or, rarely, a triple salt, and any or all of those may be hydrated; occasionally, in case the single salts are isomorphous, the saturating phase may even be a solid solution. By intersection of two such surfaces, lines result which represent the conditions for saturation of a solution with the two salts characteristic of the intersecting surfaces (in agreement with the phase rule, since for $P = 3$, $V_{p,T} = 1$, the distinguishing characteristic of a line). Finally, by intersection of two such lines, points result. Since for $V_{p,T} = 0$, $P = 4$, only three solid phases can be present, or one solid phase must be common to the two pairs; in other words, a four-phase point (a solution which is saturated with three solids) must result by intersection of three solubility surfaces, and from such a point must radiate not merely two, but three lines each indicating the conditions for saturation with respect to one of the three possible solid pairs. It may be mentioned that although the surfaces will not be expected to be planes, nor the lines straight, lack of concrete information may require that such simplifying assumptions be made. For example, a line representing solutions saturated with respect to two salts ($V_{p,T} = 4 - 3 = 1$) must connect two points ($V_{p,T} = 4 - 1 = 0$) having these two salts in common; if no information is known concerning the trend of this line, it is approximated by a straight line connecting the two points.

The advantage of the peculiar choice of coordinates adopted may now be indicated. The surfaces and lines of the four component diagram may be regarded, from a familiar point of view, as generated by the movement respectively of lines and points appearing in diagrams for three component systems. For such a system as the one under discussion, the corresponding three component systems are those formed from water plus the possible

combinations of two salts having a common ion. But a glance at Figure 13 will show that in the horizontal projection each quadrant represents the three component diagram usually employed, for such a system. (Compare Figure 10). Thus the solubility lines forming the external boundaries in Figure 13 represent the various possible three component systems which can be formed by proper combination of the four salts plus water. On addition to any of these systems of another one of the salts the four component system results, the consequences for the diagram being the inward movement of the lines and points to produce the characteristic features discussed above for the four component system.

As in the case of the three component salt-water systems, the most important practical application of these diagrams is to the problem of crystallization, i.e., in the determination of the yields of salts which can be separated from natural or artificial brines. While it would be impossible in the limited space available to discuss this problem in detail, a few suggestions may be offered. as to the modifications introduced into the problem by the presence of an additional salt component. For such a system, an unsaturated solution will be represented by a point in space, lying below the saturation surfaces for the various single salts. On isothermal evaporation of water from such a solution, the locus the solution composition must be the prolongation of the radius vector through the original point, since removal of water must increase the concentrations of all components while maintaining their ratios unchanged. Eventually this will result in saturation with (in general) some single salt, indicated on the diagram by the piercing of the saturation surface for this salt by the prolonged radius vector. Thereafter the point representing the solution composition is constrained to move in the saturating surface. The limit of this process in turn is reached. when saturation with respect to a second salt is attained, as indicated on the diagram by intersection of the path of the solution composition with one of the solubility lines characteristic of two-fold saturation. Following along such a line, the point representing the solution composition will eventually reach a four-phase point, indicating the composition of a solution saturated with three salts. Here the brine composition must remain so long as the four phases are present, the only allowable alterations in the system consisting of changes in the relative amounts of the phases. In complete analogy with the corresponding situations for systems of two and, three components the consequences of continued evaporation at this point will in general be either: (1) the solution may disappear first, leaving a mixture of the three solids or (2) one of the salts may disappear by resolution leaving a solution saturated with two salts only, with reversion to a situation of an earlier type.

As for systems containing smaller numbers of components, the calculation of the amounts of the various phases present at any stage in the evaporation process is accomplished by means of "material balances" for com-

ponents. As a single illustration may be cited the conditions which must be satisfied for the limiting yield of a mixture of two solid salts from an initially unsaturated brine:

Let a, b, c = concentrations of components in original unsaturated brine,

a_o, b_o, c_o = concentration of components in solution saturated with three salts,

s = moles of salt $A_m B_n W_q$ separated,

t = moles of salt $A_u B_v$ separated,

h = moles of water evaporated,

w = moles of water remaining in solution.

(Here, m, n, u, v represent equivalents per mol of the components in the salts named.)

Then for an initial amount of brine which contained 1000 mols of water

$$a = \frac{w}{1000} a_o + ms + ut$$

$$b = \frac{w}{1000} b_o + ns + vt$$

$$c = \frac{w}{1000} c_o$$

$$1000 = w + h + qs$$

These four equations serve for the determination of the unknown s, t, w , and h .

In an attempt to obtain a numerical solution for such a problem as the one expressed algebraically above, the questions naturally suggest themselves:

1. Which of the various four-phase points on the diagram can actually be reached by evaporation of the given brine, i.e., what values should be selected from the data for a_o, b_o, c_o ?
2. This question being answered, which of the three salts constituting the saturating phases at the four-phase point will actually separate in reaching this point.

Now while it is possible, on the basis of the ratios of the components in the various phases, to work out criteria which permit answers to these questions in advance, it is generally preferable from a practical point of view to depend upon trial and error. That is, answers to the two questions posed above are assumed and the resulting equations solved; obvious tests for the correctness of the assumptions made are furnished by a consideration of the magnitudes and signs of the values obtained for the quantities s, t, w , and h .

X. CONCLUSION

It cannot be claimed that the treatment of the phase rule here given is in any sense exhaustive. Indeed only a

few actual illustrations have been presented and, even for these, relatively few aspects have been examined. Rather, major attention has been devoted throughout to the development of a point of view, with emphasis on general, instead of special principles. With this point of view, no special difficulty should be encountered in the study of particular examples; without it, the vast literature of heterogeneous equilibrium is characterized by a bewildering diversity.

XI. EPILOGUE

The time has come to retire. I've checked each of these scanned documents thoroughly, and corrected all errors

that I can find. However, I should note that I found the second half of the text as boring this time as I found it last time while a student. There is something incredibly tedious here, and forgive me if I'm unmotivated to check every technical jot and tittle (is that the word?) for errors. Maybe, in a few years, I'll return to this and see if I can modernize it, but any interest level is so low that I tend to think that there will be no interest elsewhere.

The L^AT_EX document resides on Goggle Docs, so future alterations are possible if readers feel a need.

Goodbye.

Carl David; May, 2009

[1] We no longer teach equivalent weights!!!