PHASE EQUILIBRIUM DIAGRAMS FOR MULTICOMPONENT SYSTEMS

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THE diagrammatic representation of phase equilibrium systems has receded into the background in recent years, owing, to a certain extent, to the greater interest in dynamic systems at the expense of systems in equilibrium. Also, with many of the problems met in practice, particularly in industrial fields, the number of components seldom can be restricted to the two or three which form the limit of experience for most graduates. Very often, when a more complex system is met, every endeavor is made to avoid detailed study, the difficulties of which are accentuated by methods described in textbooks (or omitted) for diagrammatic representation of results. The classic researches covering such complex systems as the salts of the Stassfurt salt beds have generally been described in terms of space models, which are always difficult to use quantitatively and to retain as a mental picture for comparative purposes. There have been numerous attempts to simplify this problem by the use of projections. But here again it requires an appreciable mental effort to relate these projections to the space model and obtain a real understanding of their meaning.

The purpose of this paper is to draw attention to the work of Jänecke (1) published during the earlier part of this century, which contains very useful ideas for the quantitative delineation of multicomponent systems. He put forward several methods of projection, but in the words of Purdon and Slater (2) "his presentation was not good and did not receive the merit it deserved, and in fact some fifteen years later (in 1921) Le Chatelier (3) put forward as new ideas, some of the ideas which Jänecke had introduced." While the author believes that Purdon and Slater in their book have rendered commendable service in bringing Jänecke's ideas before their readers, it is felt that even these authors have not done full justice to Jänecke. Rivett (4) also dismisses the Jänecke suggestions rather summarily, indicating preference for the more conventional pyramidal models. The author is of the opinion that the publication of Blasdale (5) provided a more easily understood account of Jänecke's schemes, and that extension of these can greatly facilitate the quantitative treatment of multicomponent phase equilibrium systems. The application of the Jänecke principle has found some favor for reciprocal salt-pair systems, and Findlay (6) has included this among other methods of treating four-component systems of this type. Ricci (7) has also drawn attention to Jänecke projections and very usefully discusses their applications with interesting examples. In the author's opinion, he likewise leaves the impression that their application is limited to the field of the reciprocal salt-pair type of system. In this paper it is submitted that there is a wider field to which this principle could be applied with advantage.

THREE-COMPONENT SYSTEMS

The more conventional method of delineating equilibrium conditions for three-component systems uses triangular coordinates with the sum of the three components equal to unity or some appropriate multiple such as 100. While this convention is frequently advantageous, the author feels that we have become too closely wedded to the idea and that more flexibility in methods of delineation is warranted for the wide range of conditions that is met in practice. It is considered that the use of rectangular coordinates for this purpose could be availed of more widely and the particular advantages of such a system of plotting employed in special cases. If rectangular coordinates are used, then the sum of two components is taken as unity and the third component identified as so much per unit sum of the other two. Jänecke (1), adopting this procedure, treated the solvent as the third component and represented it with a vertical axis, and 100 parts of dissolved solutes were represented along the horizontal base line of unit length. Objection was raised to this method of representation on the ground that pure solvent would be represented only at infinite distance from the horizontal axis. This objection was met by expressing solvent concentrations in terms of $100m/(100 + m)$ rather than by m, where m is the water associated with one part of solute mixture. Although this device yields a diagram which correctly expresses the relations of the different phases to each other, it gives a distorted picture of the actual concentrations concerned. The special cases for which the author believes this method of representation has definite advantages are those in which one component has a very low solubility, or in the case of alloy diagrams where it is desired to exaggerate the scale for one component to illustrate conditions in a small part of the conventional triangular diagram.

In Figure 1 an example is given in which sucrose and $CaSO_4$ are the solutes and water the solvent. The solubilities of $CaSO_4$ in sucrose are those determined by Stolle (8) in 1900, which serve to illustrate the point that the solute of low solubility—$CaSO_4$ in this case—may be represented on the vertical axis with advantage. Referring to Figure 1, for example, solution of composition represented by point E would, on evapora-

tion, change in composition along line EF in a direction away from the origin or point representing pure water. At point F, crystallization of $CaSO_4 \cdot 2H_2O$ will commence, and composition of liquid phase will change along the line FB. At point B sucrose will also crystallize, and a mixture of sucrose plus 640 p. p. m. of $CaSO_4$ as the dihydrate will continue to crystallize until evaporation is complete. Only solutions with a
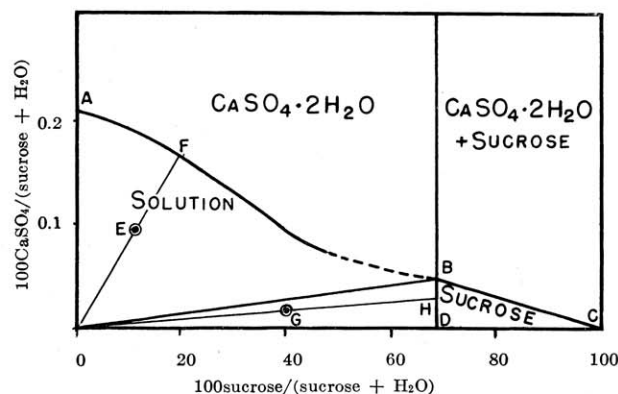

Figure 1. The System $CaSO_4$–Sucrose–H_2O

composition lying below the line OB will allow any sucrose free from $CaSO_4 \cdot 2H_2O$ to crystallize. For example, a solution with composition represented by point G would, on evaporation, change composition along line GH. At point H sucrose free from $CaSO_4$ would crystallize and continue to do so with the composition of the liquid phase changing from H to B when $CaSO_4 \cdot 2H_2O$ begins to crystallize. This diagram gives an indication of the difficulty of obtaining pure sucrose by crystallization if a second solute of low solubility is present. If it is desired to obtain useful
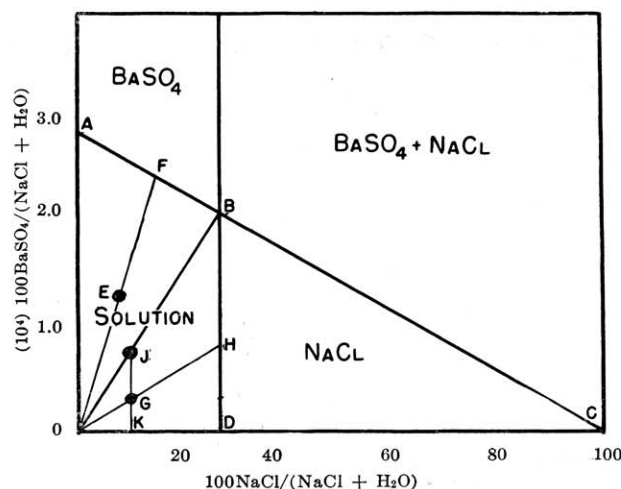

Figure 2. The System $BaSO_4$–$NaCl$–H_2O

proportions of pure sucrose it is necessary to remove the solute of low solubility by some means other than crystallization, e. g., adsorption, and this of course is standard industrial practice in sugar refineries all over the world.

While this influence of low-solubility impurities may be fairly well known to many people as a matter of fact, the phase equilibrium relationships are not so often recognized as having such a bearing on the purification of chemicals. For example, in a sodium chloride solution from which sulfate has been removed by precipitation as $BaSO_4$ it is impossible to crystallize pure sodium chloride free from $BaSO_4$. The reason for this may be clearly illustrated in a phase-equilibrium diagram using vertical and horizontal coordinates in the manner just described, with $BaSO_4$ represented on the vertical axis; this is illustrated in Figure 2. The composition of any solution prepared in this manner will lie somewhere along AB, as it will be saturated with $BaSO_4$, and $BaSO_4$ will crystallize on evaporation, with composition of the liquid phase moving along to B, at which stage $NaCl$ will begin to crystallize but will do so with approximately 80 p. p. m. of $BaSO_4$. If the initial solution is treated for removal of $BaSO_4$ by an adsorption process, enough must be removed to bring the composition of the liquid phase into the area OBD if any crystalline $NaCl$ free from $BaSO_4$ is to be obtained. For example, if the purified solution composition may be represented by point G, then the proportion of $NaCl$ which may be crystallized free from $BaSO_4$ will be represented by JG/JK. On evaporation, the composition of the solution will move along GH, when pure $NaCl$ will commence to crystallize upon evaporation, the composition of the solution changing along JB until the "impure" $NaCl$ begins to crystallize. Any point in the area OAB will give free $BaSO_4$ after sufficient evaporation. For example, the solution of composition represented by point E will change in composition until it reaches F, at which stage $BaSO_4$ will crystallize and the composition of the liquid phase will change along line FB, and when it reaches B then $NaCl$ with 80 p. p. m. of $BaSO_4$ will crystallize.

In the preparation of the diagram no allowance has been made for possible conditions of supersaturation, or for the possible influence of one salt on the solubility of the other. It is also recognized that this system is really that of a reciprocal salt pair in which four different solid phases might be expected from the various possible combinations of the ions. However, for the purpose of examining the conditions for preparing a pure crystalline $NaCl$ free from sulfate, the diagram as illustrated is considered to show the requirements with the maximum of clarity.

In both Figures 1 and 2 it is recognized that pure material represented by the vertical axis would be at an infinite distance from the horizontal axis. This, however, is considered to be a minor deficiency compared with the advantages in use of this system for purposes such as those just described.

In the case of alloy systems the great difficulties experienced in obtaining metals of really high degrees of purity may be illustrated in similar types of diagrams, where the element of low concentration is represented on the vertical axis. Similarly, in silicate systems or other systems in which solid solutions are prominent,

coordinates of this nature may be used with advantage to draw attention to specific conditions occurring where one compound is present in small concentration.

FOUR-COMPONENT SYSTEMS

Blasdale (5) has described clearly the Jänecke method of representing four-component systems in which the percentages of three solutes are referred to the sides of an equilateral triangle and the solvent associated with 100 parts of solute to perpendiculars to the plane of the triangle. The author has found this system to be very useful in practice and relatively easily comprehended, particularly if pictured as a projection of the surface of a vertical prism on the base. Perhaps this is more easily understood than the picture given by Purdon and Slater (2), who describe the Jänecke projection as assuming that a shadow is cast from a point of light situated at the apex of a pyramid.

The projection of the surface of the vertical prism on its base gives a triangle with contour lines representing changes in solvent quantities. Similar criticism may be made of these diagrams as for those with three components where solvent is the vertical axis and pure solvent is at infinite distance from the horizontal axis. For the four-component system represented by a vertical triangular prism with solvent as the vertical axis, pure solvent would be at infinite distance from the triangular base. The contour system of marking solvent concentrations is, however, very convenient, and most of the usual calculations for a three-component system may be carried out with this type of diagram. In Figure 3 is reproduced the diagram for the system BaCl₂–CuCl₂–KCl–H₂O prepared and published by Blasdale (5) from results obtained by Schreinemakers and de Baat (9). The author (10) is at present preparing diagrams for the publication of results obtained by him for four-component systems of sugars, inorganic salts, and water. This method of representation has proved particularly helpful in the preparation of preliminary diagrams from which synthetic solutions are prepared, and useful indications given of the conditions likely to be obtained in the final system.

Four-component alloy or silicate systems may be represented by triangular diagrams with the concentration of the fourth component shown as contours and represented as a concentration per unit of the sum of the other three components. Where such systems are complex it is necessary to use discretion as to which of the components is represented as the fourth component. It may even be necessary to use two or even more diagrams to illustrate a system completely, but such would be the case even with projections from space models such as the tetrahedron. The author considers that the contour system may be comprehended more easily and may be more amenable to quantitative treatment.

Where solutions are being dealt with there may well be cases in which one of the solutes could, with advantage, be taken as the fourth component. This would more likely be the case where one of the solutes has a

very low solubility, as was true of the three-component systems just described.

It is also possible, and sometimes both convenient and desirable, to employ rectangular coordinates similar to the example of Figures 1 and 2. However, in a four-component system two components would be represented on the vertical axis with the quantitative relationship indicated as so much per unit sum of the first two components. The fourth component would then be represented by contour lines on the diagram and quantitatively referred to as so much per unit sum of the first two components.

FIVE-COMPONENT SYSTEMS

The contour system of delineation may also be used for five-component systems. In the case of solutions with four solutes, one of these solutes may be selected as a component to be illustrated with a second set of contours and concentrations referred to as so much per unit sum of the other three solutes, which are themselves
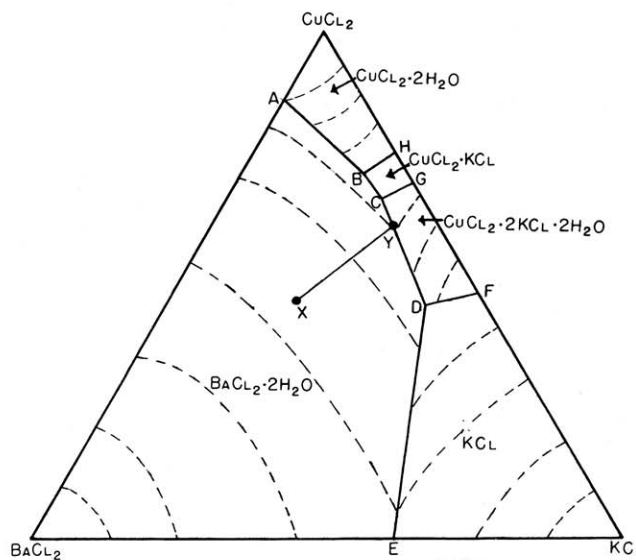

Figure 3. The System BaCl₂–CuCl₂–KCl–H₂O

represented at the corners of an equilateral triangle. Two or more diagrams will be necessary to represent conditions adequately. The author is at present working on a system which will be expressed in a diagram of this nature.

MORE COMPLEX SYSTEMS

The contour system may be extended to even more complex systems by the exercise of a certain amount of ingenuity and use of multiple diagrams, and such a method is considered to be more useful than space models and projections, which are difficult to visualize.

Reciprocal salt pairs in which six solid phases may appear offer a problem of a special nature, but may be treated by the contour system with triangular basic coordinates and a multiple set of contour lines. However, this about reaches the limit of complexity which may be represented with any reasonable degree of

satisfaction. Systems in which there are three bases and three acid radicals offer the possibilities of nine individual solids aside from the possibility of double-salt formations, and are extremely difficult to represent graphically by whatever system may be adopted. Fortunately, with most of these very complex systems it is seldom necessary to work out the full diagram, as interest may be concentrated over relatively small concentration ranges. The original paper of Jänecke (1) is well worth while studying before dealing with complex problems of this nature, as he has some useful diagrams of complex salt systems.

TEMPERATURE AND PRESSURE CONSIDERATIONS

Blasdale (5) draws attention to what he considers a more important use of Jänecke's scheme in representing the effect of temperature upon a system. He illustrates the effect of temperature on the system Na_2SO_4–$MgSO_4$–H_2O between $-10°C.$ and $+100°C.$, in which the relative proportions of Na_2SO_4 and $MgSO_4$ are represented along a horizontal axis and temperature on the vertical axis of rectangular coordinates. He advocates the use of a table to identify water concentrations in different parts of the diagram. The author considers this type of diagram very useful for representing the effect of temperature on a three-component system of this nature, but feels that the water concentration could be shown with advantage on the same

diagram with the use of a contour system of representation, thus eliminating the necessity for using a chart as an additional aid to interpretation.

If pressure variation is important to the system there is no reason why this could not be represented on the vertical axis in a diagram of this nature, instead of temperature, as Jänecke himself has done. The simultaneous representation of changes in both temperature and pressure on the same diagram for a three-component system does, however, present some difficulties, even if triangular coordinates are used.

LITERATURE CITED

(1) JÄNECKE, E., Z. anorg. Chem., **51,** 132 (1906).
(2) PURDON, F. F., AND V. W. SLATER, "Aqueous Solution and the Phase Diagram," Edward Arnold and Co., London, **1946,** p. 93.
(3) LE CHATELIER, H., Compt. rend., **172,** 345 (1921).
(4) RIVETT, A. C. D., "The Phase Rule," Clarendon Press, Oxford, **1923,** p. 171.
(5) BLASDALE, W. C., "Equilibria in Saturated Salt Solutions," The Chemical Catalog Co., Inc., New York, **1926,** pp. 77, 126.
(6) FINDLAY, ALEXANDER, "The Phase Rule," 8th ed., Dover Publications, New York, **1938,** p. 293, et al.
(7) RICCI, J. E., "The Phase Rule," D. Van Nostrand Co., Inc., New York, **1951,** p. 439, et al.
(8) STOLLE, F., Z. Ver. deut. Zücker-Ind., **50,** 331 (1900).
(9) SCHREINEMAKERS, F. H. H., AND DE BAAT, Proc. Acad. Sci. Amsterdam, **17,** 782 (1914).
(10) KELLY, F. H. C., unpublished data.