[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

A Two Dimensional Representation of Quaternary Phase Systems

BY EDWARD V. SAYRE[1]

The solution of many phase separation problems in quaternary systems has been difficult because no single two dimensional diagram has been presented upon which graphical solutions of these problems may be obtained. Several ingenious methods have been described by which the concentration of all four components of a mixture may be represented in one plane. Some of the ways have been through a special use of polar coördinates,[2] or through the representation of a composition by a vector the length of which is determined by the concentration of one component and the position of which is determined by the concentrations of the other three components.[3,4] Blasdale[5] superimposed a Loewenherz and a Jaenecke projection at an arbitrarily convenient position so that the relations between them determined the solvent concentrations. Ricci and Loucks[6] suggested that an orthogonal projection of a three-dimensional Schreinemakers diagram and a Jaenecke projection may be used together in the same way. These methods of representation, however, do not lend themselves to the graphical solution of other than the most simple phase separation problems.

Most graphical methods of solution are performed with less complicated diagrams, which do not individually describe the systems with respect to all four components. Two or more of such separate diagrams are, therefore, required to arrive at a solution. Typical of such methods are the combined use of a vertical and a horizontal projection of a three dimensional Jaenecke isothermal diagram,[7-9] or the use of projections on two different planes through a solid Schreinemakers type diagram.[6,10]

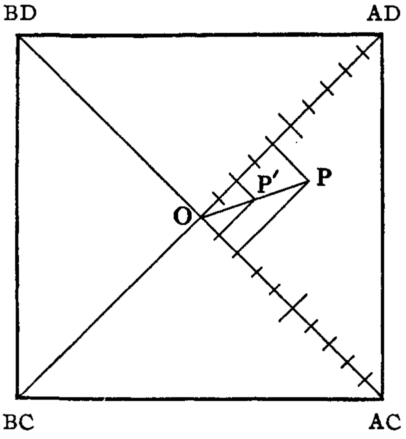

Fig. 1.—Jaenecke plot, P, and Schreinemakers plot, P', for solution of mol fractions 0.2 AD, 0.2 AC, 0.1 BD, and 0.5 solvent.

The diagram described in this paper is the result of a double projection of the equilibrium surfaces of a solid Schreinemakers diagram[10] onto its base. These solid figures are, of course, a tetrahedron for additive systems and a pyramid for reciprocal salt pair systems. One projection is an orthogonal projection of the equilibrium points onto the base. The second figure is obtained by projecting the equilibrium points radially onto the base through lines originating at the solvent apex, *i. e.*, a Jaenecke projection. The two projections are superimposed in such a way that the ratio of the distance of an orthogonally projected point from the center of the diagram to the distance of the corresponding Jaenecke point from the center is exactly equal to the mole fraction of solvent present. Thus the diagram permits the indirect determination of solid phases through Schreinemakers' method of residues,[11] the extrapolation of tie lines. Hence by reverse application of this principle the diagram is well adapted for the graphical solution of problems of precipitation from supersaturated solutions. Also any two corresponding points in the double projections together describe a given mixture unambiguously in all four components.

Construction of the Diagram

The orthogonal projection of a reciprocal salt pair system may be plotted by considering the four half diagonals of the square pyramid base as coördinate axes. As shown in Fig. 1, a point in the diagram quadrant, salt AC—center point O—salt AD, is located by plotting the mole fraction of AC in the total mixture as its abscissa outward along the half diagonal O(AC) and the mole fraction of AD as its ordinate along the half diagonal O(AD). If some of the salt BD, reciprocal to salt AC, is present, the position of the point in the O(AC) direction is plotted equal to mole fraction AC minus mole fraction BD. When the mole

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(1) Present address: Eastman Kodak Company, Rochester, New York.

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(3) W. Lodochinkov, *Ann. inst. anal. phys.-chim.* (*USSR*), **2**, 255 (1924); *Z. anorg. allgem. Chem.*, **151**, 185 (1926); **169**, 177 (1928).

(4) M. Randall and B. Longtin, *J. Phys. Chem.*, **42**, 1157 (1938).

(5) Blasdale, "Equilibria in Saturated Salt Solutions," Chemical Catalog Co. (Reinhold Publishing Corp.), New York, N. Y., 1927, p. 123.

(6) Ricci and Loucks, *J. Chem. Ed.*, **15**, 329 (1938).

(7) Jaenecke, *Z. anorg. Chem.*, **51**, 132 (1908); **71**, 1 (1911).

(8) H. Buraus, *J. Phys. Chem.*, **45**, 968 (1941).

(9) Findlay and Campbell, "The Phase Rule and Its Applications," 8th edition, Longmans, Green and Co., London, 1938, Chap. XVII.

(10) Schreinemakers, *Z. physik. Chem.*, **69**, 557 (1909).

(11) Schreinemakers, *ibid.*, **11**, 81 (1893); **59**, 641 (1907).

fraction of total salts in the particular mixture plotted is increased by the simple removal of solvent, the mole fraction of each individual salt is increased in the same proportion. In this case, the representing point is extended outward along a straight line originating at the center O, where the mole fraction of total salt is zero. In the full three dimensional diagram, contained in a regular tetrahedral pyramid as illustrated in Fig. 2, the locus of these points representing change of solvent concentration alone is a radial line from the apex terminating on the base. A diagram can be thus radially projected through the Schreinemakers construction of a phase system onto the pyramid base, where total mole fraction of salts equals one. This projection can be plotted in the manner described above by substituting as coördinates the mole fractions of the individual salts in the total dry salts in place of mole fractions in the total salt–aqueous mixture. This figure is the two dimensional Jaenecke diagram of the phase system, and is identical with the figure obtained by the more conventional procedure of plotting mole fractions of ions as coördinates. If the number of moles of a given salt in a mixture is X, the total number of moles of salt Y and the number of moles of solvent Z, then the coördinate of the given salt in the orthogonal projection is $X/(Y+Z)$, and the coördinate in the Jaenecke projection is X/Y. The ratio of the orthogonal coördinate to the Jaenecke coördinate, $X/(Y+Z)/X/Y$, is then equal to the mole fraction of total salts, $Y/(Y+Z)$. Therefore, the ratio of the distance of the orthogonal point from the center origin to the distance of the Jaenecke point from the center is also equal to the mole fraction of total salts. And, since the Jaenecke point alone unambiguously specifies the molar ratios of the salts, the two points together completely define a given mixture. Any finite number of equilibrium data points may be so plotted, and thus a description of an isothermal four-component reciprocal salt pair system may be obtained in a plane.

Figure 3 presents the 25° isothermal diagram of the sodium nitrate–potassium chloride–water system, which is of importance in the manufacture of conversion saltpeter. For simplicity, all equilibrium surfaces have been considered planes and their intersections, therefore, straight lines. This assumption need not be made, since any finite number of data points describing the equilibrium surfaces may be plotted and contour lines drawn between them to represent the true equilibrium surfaces and lines within the accuracy of the available data. Primed figures will designate the orthogonally projected diagram; the unprimed ones the Jaenecke diagram. The data for this system were taken from Findlay and Campbell.[9] Point P completely describes the mixture 0.50 KNO_3, 0.40 $NaNO_3$, 0.10 KCl, 0.00 H_2O. If water is added to the mixture until its mole fraction is 0.8 (0.10 KNO_3, 0.08 $NaNO_3$, 0.02 KCl, 0.80 H_2O) points P and P′ are necessary to describe it. If the mole fraction of water is then halved (0.30 KNO_3, 0.24 $NaNO_3$, 0.06 KCl, 0.40 H_2O) points P and P″ will describe the solution. It is apparent that the distance PP″ is half the distance PP′. Henceforth, points in the Jaenecke diagram will be called base points, and those in the orthogonal diagram called projected points. They will always be designated by unprimed and primed letters, respectively.

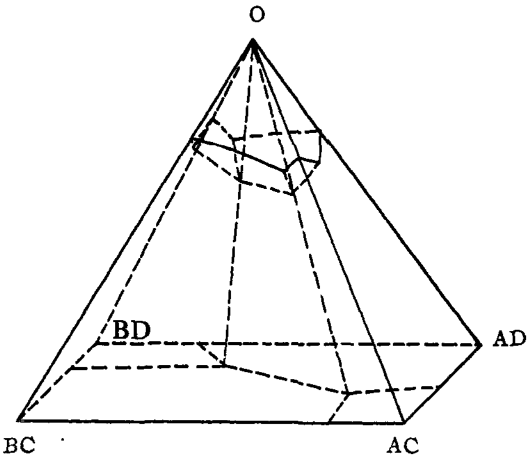

Fig. 2.—Three-dimensional Schreinemakers diagram showing Jaenecke projection on its base.

It is apparent that a solution is not uniquely defined if its base point lies at the center position O. The occurrence of a solution at this position, however, in general simplifies the solution of phase change problems by other methods. The properties of a system in this condition will be discussed later.

Solution of Phase Change Problems

When one determines in what planes a point pair might move through a pyramidal Schreinemakers diagram, the most apparent restriction is that they be planes containing both the base point and the projected point. Therefore, they are planes through the line connecting the base point to the water apex. Considering the point pair P and P′ in Fig. 3, since the position of the base point is in the potassium nitrate section, we know that if any solid phase crystallizes out it will be potassium nitrate. The plane of operation of this phase separation must, therefore, include the base corner point KNO_3. The projection of this plane, determined by points KNO_3, O, and P, is shown in Fig. 3, where it is drawn completely through the figure to point R, its intersection with the base line connecting the $NaNO_3$ and NaCl corners. Then R′, the projection of point R in the orthogonal diagram, is readily determined by the intersection of lines OR and ($NaNO_3$′)B′. Similarly, Q′, the intersection of the plane with the equilibrium line F′A′, is determined by the intersection of F′A′ with the line OQ, where Q is the intersection of the base lines FA and (KNO_3)R.

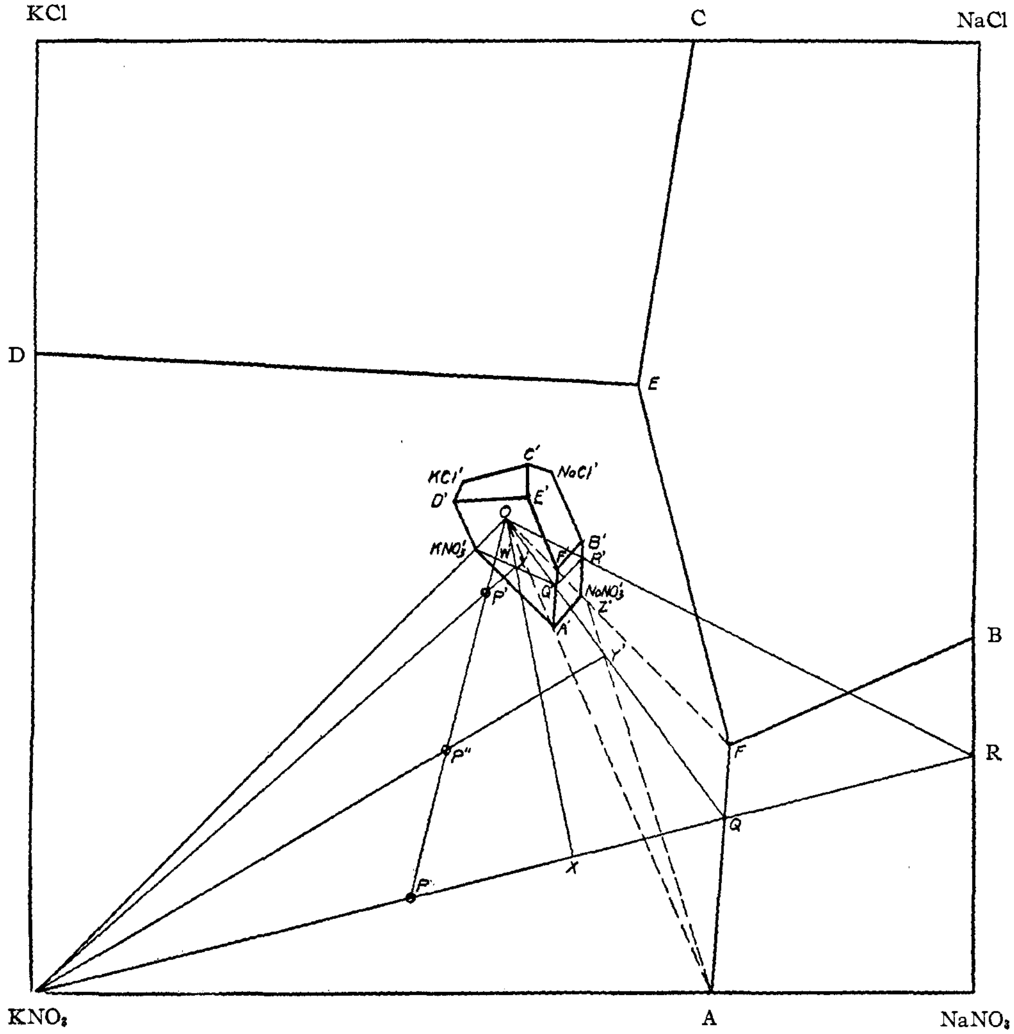

Fig. 3.—Isothermal diagram at 25° of system sodium nitrate, potassium chloride, water, with constructions determining precipitation from supersaturated solutions PP′ and PP″.

The lines $(KNO_3')Q'$ and $Q'R'$ then are the vertical projections of the intersection of plane $(KNO_3)RO$ with the equilibrium surfaces of the phase diagram. The intersection of line OP with line $(KNO_3')Q'$ then is the projection of the point at which OP pierces the equilibrium surface $(KNO_3')A'F'E'D'$. If the projected point along OP is closer to the origin O than this intersection, W′, the mixture represented is an unsaturated solution of salt mixture P; if the projected point is at W′, the solution is saturated with these salts; and if the projected point is below W′, as is P′, solid potassium nitrate will crystallize out.

Since all points along the base line $(KNO_3)R$ express a constant ratio of NaCl to $NaNO_3$, all points in the $(KNO_3)RO$ plane obviously must do likewise. (It has already been shown that a line in this plane originating at the water apex O represents mixtures of constant salt ratios differing only in their water contents.) Similarly, a line in this plane originating at base point KNO_3 fixes a constant ratio of water to mixture R, and motion along such a line correctly describes the addition or removal of pure potassium nitrate to the system. As one crystallizes potassium nitrate from the supersaturated solution of pair PP′, the projected point P′ moves along the line $(KNO_3)P'$ until it reaches the equilibrium surface at X′, the intersection of the operating line with $(KNO_3')Q'$. The base point will at the same time move along $(KNO_3)P$ until it reaches X, the point of intersection with a straight line through O and X′. Evaporation of water from the equilibrium mixture XX′ would move the projected point along the line segment X′Q′ while the base point would move to corresponding positions along XQ.

When potassium nitrate is separated from the supersaturated solution PP″, the base point reaches an equilibrium line on the Jaenecke diagram, *i. e.*, point Q on line AF, before the corresponding projected point Y′ has reached an equilibrium position on the orthogonal diagram. This indicates that solution PP″ was supersaturated with respect to more than one salt. The crystallization path that such a solution would follow may be decided unambiguously by asking what would occur if water were added to it until the solution was in equilibrium, then this extra water evaporated away, the solution being allowed to follow an equilibrium course. In this particular problem this path would first involve the conversion of PP″ to PW′. Evaporation of water from PW′ would result in precipitation of potassium nitrate until composition QQ′ was reached. At this point a salt mixture of composition A would start crystallizing out, and the saturated solution proceed down path Q′F′. One may theoretically stop this process at any point, however, and remove the remaining added water in a non-equilibrium manner, leaving a supersaturated solution. If one did this upon reaching QQ′, the resulting supersaturated solution would be QY′, exactly the same point at which one arrives by the direct path P″Y′. Since the system is conservative, the simple direct path is as good for calculation as the one detouring over the equilibrium surface.

Similarly, therefore, one may assume upon reaching QY′ the supersaturated solution will separate only salt of composition A. The diagram points may be assumed then to move in the new plane OFA, which is determined by line OQ and base point A (see Fig. 3). The orthogonal projection of the intersection of this plane with the equilibrium surface is obviously A′F′. Again in this case the base point, moving inward along the extended line AQ, reaches a new position of equilibrium, the quintuple base point F, before its projected point, moving inward along line AY′, intersects the equilibrium surface. It is, of course, completely fortuitous that FF′ lies along the diagonal KCl–$NaNO_3$.

The new supersaturated solution FZ′ will crystallize out the triple component mixture of composition F. The position of the base point, F, may be assumed not to change during this process, while the projected point will move inward along line OF until it reaches the equilibrium position F′. Following the usual proportional balance the ratio of number of moles of solid crystallized out to number of moles of saturated solution remaining is given by the ratio of F′Z′ to Z′F.

An interesting special problem arises when the precipitating salt is hydrated. One would have then separate projected and base points representing the solid salt. In the problem of describing the separation of this salt from its supersaturated solution, the course of the projected point of the solution would be along the straight line originally connecting it to the projected point of the solid, while the course of the base point would be along the straight line connecting it to the base point of the solid.

In the solution to the problems presented above, two simplifying assumptions were made. One of them was that the equilibrium surfaces were planes and their intersections straight lines. This assumption may be easily avoided and in no way affects the fundamentals of the method presented above. For example, in Fig. 3 one might have plotted a number of experimental points of the surface A′(KNO_3′)D′E′F′ and drawn contour lines between these experimental points both in the orthogonal and Jaenecke projections. Then the intersections of line (KNO_3)Q with the contour lines on the base would determine the intersections of plane (KNO_3)OQ with the corresponding orthogonally projected contour lines. Hence the path of crystallization, (KNO_3′)Q′, would have been determined in its true curved form.

The second simplifying assumption was that the proportion of two salts precipitating along a line of two-fold saturation is constant. This is the same as assuming that, for example, Jaenecke line AF in Fig. 3 is straight. This assumption is fundamental to the procedure of solutions described, for without it one would have to move by trial and error in the curved surface OAF. The assumption is a very good approximation, however, since the degree to which line AF would vary from straightness would be no greater than the degree to which the activity coefficients of potassium nitrate and sodium nitrate would change at different rates along the path A′F′.

Limitations of the Method.—It is apparent that occasionally one would operate in a plane vertically intersecting a three dimensional Schreinemakers diagram. The projection of such a plane in the two dimensional diagram would be a straight line, on which it would be impossible to perform many of the geometric constructions described above. However, because all motion in this case is restricted to a straight line in the diagram, it is usually apparent where at least one of the composition points will come to rest, as it was in the case of motion along the line OF in Fig. 3. Phase separations from the special type of solution described above for which the base point lies directly beneath the center origin will always take place in such vertically placed planes. Therefore, if the original concentration is known, it is usually easy to calculate changes from it with the help of the diagram even though it is impossible to plot the original concentration in an unambiguous manner.

If the phase system is one of very insoluble salts, the orthogonal projection will be inconveniently close in toward the origin, and an extremely large diagram might be required for exact construction. This difficulty can be avoided by enlarging the center portion of the diagram containing all of the orthogonal projection into a second diagram. The intersection of lines in the normal diagram with the periphery of the center section in it chosen for enlargement, together with the equilibrium points concerned, give sufficient information for transfering lines from the normal to the enlarged partial diagram and vice versa.

Application to other Four-Component Systems.—The methods described above can be applied to systems composed of water and three salts with a common ion if the following method of plotting is followed. The figure appears in an equilateral triangular graph with vertices A, B and C and point of intersection of perpendiculars from these vertices to their opposite bases, O. Then a point is determined by plotting the mole fractions of salts A and B as coördinates along the axes OA and OB originating at the center O. The point is then moved parallel to the third axis OC, a distance equal to mole fraction of salt C.

Acknowledgment.—The author wishes to thank Professor J. J. Beaver for his constructive criticism of this paper.

Summary

A two-dimensional, quaternary phase diagram is presented in which compositions are described in all four constituents and in which graphical solutions to general phase separation problems may be made. The diagram is constructed by superimposing an orthogonal projection of a three dimensional Schreinemakers diagram upon a Jaenecke projection in such a way that the method of wet residues may be applied.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XLIV. Conductance of Some Long Chain Salts in Ethylene Chloride, Pyridine and Nitrobenzene at 25°[1]

BY HAROLD L. PICKERING[2] AND CHARLES A. KRAUS

I. Introduction

Weaver[3] has measured the conductance of several long chain salts in ethylene chloride and nitrobenzene. In these solvents the salts behaved like normal electrolytes. It seemed worth while, therefore, to measure the conductance of a larger number of long chain salts. It was of particular interest to determine the limiting conductance of long chain ions and to find how the conductance of such ions depends on the number of carbon atoms that they contain, on the one hand, and their arrangement about the central nitrogen atom, on the other.

To this end, the conductance of a number of long chain salts was measured in ethylene chloride, pyridine and nitrobenzene. In addition, the conductance of several ordinary quaternary ammonium salts was determined in order to fill gaps in the list of ion conductances.

II. Experimental

1. **Salts.**—These were prepared according to conventional methods. It is important to use only well purified starting materials. Nitrates and picrates were prepared by metathesis of iodides with silver salts in methanol or ethanol. The following salts were prepared: (1) *n*-octadecylpyridonium nitrate (m. p., 79–80°), (2) di-*n*-octadecyldimethylammonium picrate (m. p., 75.5–76.2°), (3) di-*n*-octadecyldi-*n*-butylammonium picrate (m. p. 50.5–51.5°), (4) *n*-octadecyltri-*n*-butylammonium nitrate (m. p., 90.5–91.5°), (5) *n*-octadecyltri-*n*-butylammonium picrate (m. p., 42–43°), (6) *n*-octadecyltrimethylammonium iodide (m. p., 237–238.5°), (7) *n*-octadecyltrimethylammonium picrate (m. p., 134–135°), (8) *n*-propylpyridonium picrate (61–62°), (9) tetra-*n*-butylammonium picrate (m. p., 73.5–74.5°), (10) tetra-*n*-propylammonium picrate (m. p., 115–116°). Earlier preparations of tetra-*n*-butylammonium triphenylborofluoride (11) and formate (12) were measured after several recrystallizations.

The salts were recrystallized as follows: (1) hexane plus few drops of ethanol, (2) hot absolute ethanol, (3), (5) methanol plus few drops of ethanol, (4) dioxane–water followed by hexane–ethanol, (6), (7) absolute ethanol, (8) 99% ethanol, (9), (10), (12) 95% ethanol, (11) ethanol plus 10% hexane.

2. **Solvents.**—Solvents were prepared as described in earlier papers.[4] Solvent resistances were measured with a special parallel arm bridge permitting of precise measurements up to 10^7 ohms.

3. **Apparatus and Procedure.**—These were the same as those described in earlier papers of this series.[4]

III. Results

In Table I are given equivalent conductances at different concentrations (expressed in moles per liter of solution) for several salts in ethylene chloride. Similar data are given for solutions in pyridine in Table II and for solutions in nitrobenzene in Table III. All measurements were carried out at 25 ± 0.01°. In computations, the following values were employed for physical constants.

	Density	Viscosity	Diel. const.
Ethylene chloride	1.2455	0.00787	10.23
Pyridine	0.97792	.008824	12.01
Nitrobenzene	1.1986	.01811	34.5

IV. Discussion

1. **Ethylene Chloride and Pyridine.**—The data of Table I for ethylene chloride and those of Table III, for pyridine, have been analyzed

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[1] This paper is based on a portion of a thesis presented by Harold L. Pickering in partial fulfilment o f the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, August, 1947.

[2] National Research Council Fellow, Brown University, 1946–1947. Present address: Research Laboratory, Stanolind Oil and Gas Company, Tulsa, Oklahoma.

[3] Weaver and Kraus, THIS JOURNAL, **70**, 1707 (1948).

[4] (a) Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **33**, 594 (1936), ethylene chloride; (b) Witschonke and Kraus, THIS JOURNAL, **65**, 2472 (1947), nitrobenzene; (c) Carignan and Kraus, *ibid.*, **71**, 2983 (1949), pyridine.