# A New Method of the Graphical Representation of a Quarternary System on a Plane Surface*

By Yasuo TANAKA**

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**Introduction** To represent the phase equilibrium of a quartenary system under constant temperature and pressure, a regular tetrahedron or generally a three-dimensional space figure may be employed. When such a model is considered to be placed on a plane which intersects with the three axes at equal angles, it forms, so to speak, a pyramid with three faces. For the representation of the system on a plane surface, the projection of the model on the base of the pyramid has been employed usually. The projection is orthogonal (perpendicular), or clinographical (perspective) from the zenith of the pyramid.(1)(2) However, to express the three coordinates of a space figure on a plane surface, one projection is obviously insufficient, and a numerical table or an additional figure is necessary to supplement it. Moreover, for the representation of these projections, a triangular section-paper must be used and, consequently, the treatment of the figure is rather troublesome.

Since the phase rule of a quarternary system is particularly important to treat sea water systematically*** or to establish the sea-salt industry,(3) a convenient new method of representing the system on a plane surface will be proposed in the present report, and, by the use of this method, the crystallization processes in the system will be solved quite generally.

**New Method Proposed.** The method of the graphical representation proposed here is, as shown in Fig. 1, to project the three-dimensional space model of the system, axes of which intersect each other at right angles, orthogonally on two of the axual planes (i.e., on the surfaces of the pyramid). The two projections correspond to the plan and the elevation of the model. The composition of the system will be expressed, as usual, in terms of the absolute number of equivalents of the solutes per 1000 mols of the solvent.* Fig. 1 is the projection of an ideal system, with three salt components and water, on the axual planes $YOZ$ and $XOZ$. There exist four solid

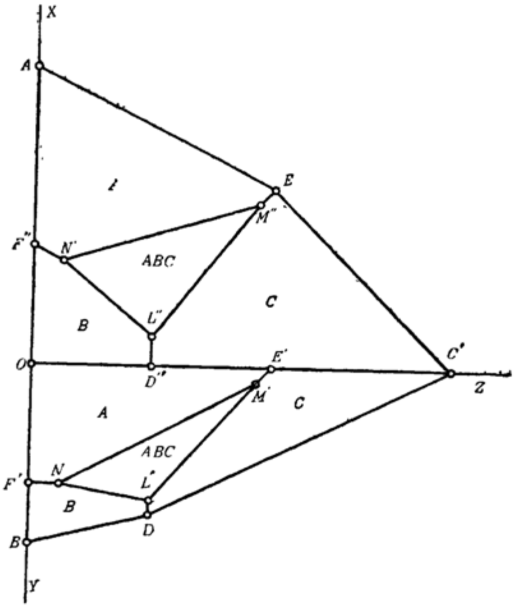

Fig. 1

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** Present address: Himezi University-College of Engineering and Technolygy.

*** A comprehensive review of the literature on the equilibria of the system of sea-salts has been made by D'Ans in (1). While main salt components of sea water are chlorides and sulphates of sodium, potassium and magnesium, owing to the predominance of NaCl, deposition of the other salts takes place always in the coexistence of it; and, under these circumstances, the system can be treated as a quarternary system consisting of three salts or radicals, and water.

(1) J. D'Ans, "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablangerungen," Berlin (1933)

(2) W. C. Blasdale, "Equilibria in Saturated Salt Solutions," New York (1927).

(3) *Cf.*, Y. Tanaka, *J. Japanese Chemistry* (*Kagaku-no-Ryoiki*), 3, 224 (1949)

* For the system of sea-salts, it is convenient to take $K_2^{\cdot\cdot}$, $Mg^{\cdot\cdot}$ and $SO_4^{\cdot\cdot}$ as unite equivalents.

phases **A, B, C** and **ABC** in this example.*

The two projections of the present figure represent the isothermal of the system completely. The three coordinates of a point can be known immediately from the figure; and, as the coordination is rectangular, the drawing and reading of the figure are very easy by the use of common section-paper. As will be shown later, the graphical solution of the crystallization processes can be executed quite conveniently. Only it is advisable to select the planes of projection according to the system or to the object of the study. Reciprocal salt pairs can also be expressed completely by the present figure. Two cations and one anion or the converse are taken as the salt components, a part of the space being left without use.

**Mathematical Solution of the Crystallization Processes** Such cases as only a single solid phase is concerned are not yet completely discussed in the four-component system consisting of three salts and water, while the deposition of two or three solid phases at the same time has already been treated extensively. Therefore, before treating the crystallization processes graphically, general solution of the above problem will be made.

An isothermal process, in which the compositon of the solution changes according to the water content of the system due to the concentration or the dilution and, at the same time, according to the elimination or the addition of a certain solid phase, may represent the case quite generally. The deposition of a solid phase by the isothermal evaporation of a solution corresponds to this case, and the polythermal changes can also be treated by this procedure.

A unit amount of a mixture, $x_p$, $y_p$ and $z_p$ mols of the salt component A, B and C, respectively, per 1000mols of $H_2O$, which is not necessarily in equilibrium and in which solid phases may be included, is taken as a starting substance. The point corresponding to this composition will be mentioned as $P$. It is considered that the system undergoes the above-mentioned process and reaches an equilibrium at a certain point, $Q$. The solid phase concerned will be taken as $A_hB_iC_j \cdot mH_2O$, and let the composition of the solution at $Q$ be $x$, $y$ and $z$ mols of the components per 1000 mols of $H_2O$. Then,

$$x_p = hn + wx,\ y_p = in + wy \text{ and } z_p = jn + wz \quad \ldots\ldots\ldots (1)$$

where $1000\,w$ is the water content in mol of the solution of $Q$, and $n$ is the amount of the compound substracted from the system in mol up to that time.* Since, in the present process, the composition of the solution may be altered from the point $P$ along this plane, the plane will be mentioned as the composition plane.

Now, when the solid phase exists at $Q$, as the system is considered to be in equilibrium, $Q$ should lie at the same time on the saturation surface of the compound. Therefore, $Q$ is to lie on the intersecting line between the composition plane and the saturation surface, and, if they do not cross each other practically, the compound does not appear as a solid phase. This line is the crystallization path from $P$ with regard to the solid phase in question.

Generally, the saturation surface of a compound is by no means plane. However, when it is assumed as such, a point on this plane can be expressed as

$$x/a + y/b + z/c = 1 \quad \ldots\ldots\ldots (2)$$

where $a$, $b$ and $c$ are the length of the three axes $OX$, $OY$ and $OZ$ at which they intersect with the saturation plane.** Then the crystallization path in question can be obtained from (1) and (2) as a straight line. Thus the path has been determined mathematically quite in general. When a third condition is defined, special points on the path can also be determined.

**Application of the New Method on the Graphical Solution** Now, the above mentioned process will be followed graphically by using the present figure. At first, the intersection of a plane saturation surface (or generally a plane) with the plane of projection will be considered. The trace of the saturation surface of the compound **ABC** in Fig. 1, $LMN$, on the plane $XOZ$ will be taken for illustration. As shown in Fig. 2, let the line $MN$ cross with $XOZ$ at $t$, and $t'$ be its projection on $YOZ$. Then, since $t'$ should lie on $OZ$, the point can be found from the figure at once, and consequently, $t$ is easily obtainable. The same is for $w'$ and $w$, and the trace can be represented by the line $tw$. Similarly, $LMN$ intersects with $YOZ$ on $uv$, and accordingly, the intersecting points of this plane with the axes $OX$, $OY$ and $OZ$ ($a$, $b$ and $c$) are determined immediately.

The determination of the trace of a composition plane on the axual planes is more simple. For example, the trace of this plane on $XOZ$ is expressed, from (1), as

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* The figure has been chosen so that all the saturation surfaces are plane.

* According to the concentration or the dilution, $w<1$ or $>1$; and since $n>0$ by the elimination, $n<0$ by the addition. As $h$, $i$ and $j$ are simple intergers and frequently some of them become 0, the equations are simplified for practical instances.

** According to the orientation of the plane, $a$, $b$ and $c$ may have negative values.

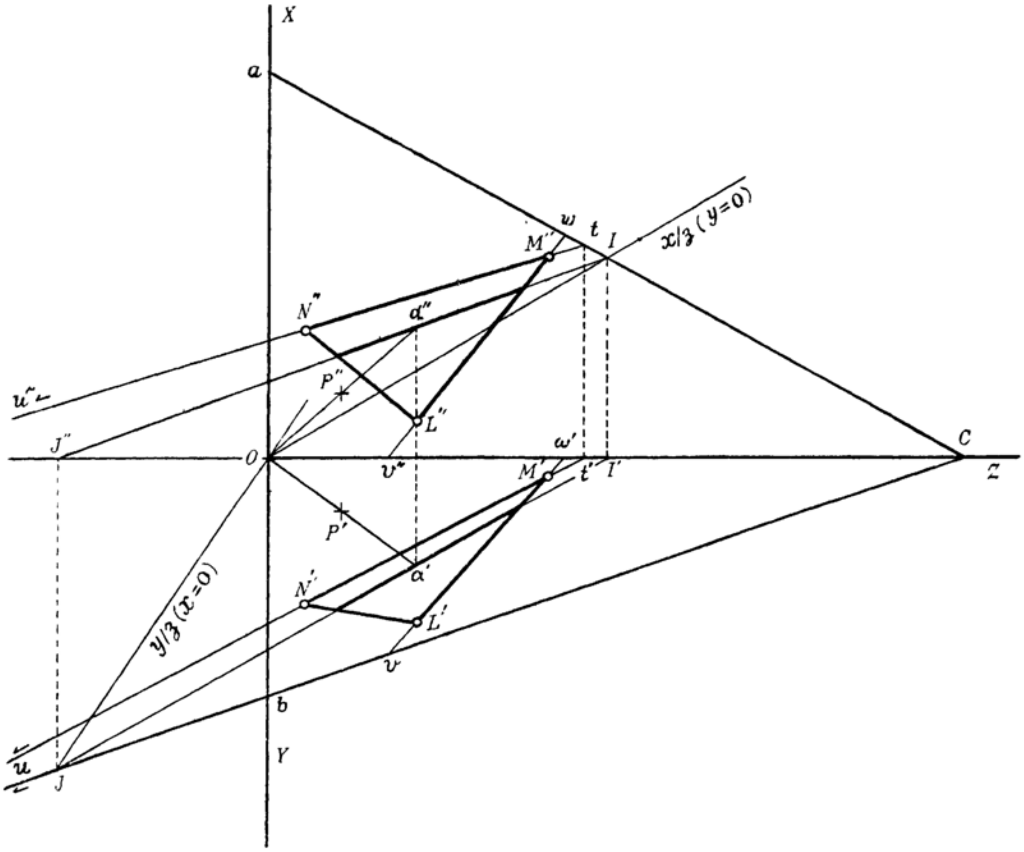

Fig. 2.

$$x/z=(jx_p-hz_p)/(iz_p-jy_p),$$

because $y=0$ on this plane. For the compound **ABC**, as $h=i=j=1$, it becomes

$$x/z=(x_p-y_p)/(z_p-y_p).$$

The line is shown in Fig. 2, and it crosses with $ac$ at $I$, and similarly the trace on $YOZ$ crosses with $bc$ at $J$. Then, $IJ$ represents the intersecting line between the saturation plane and the composition plane; it is the crystallization path. In the figure, the path is shown as its projections, $IJ''$ and $I'J$.

Curved saturation surfaces may be treated by assuming that a limited part of them is plane. Special points on the path can also be obtained easily, and the behavior of crystallization on the boundary of the saturation surface has, as already mentioned, been discussed extensively. The present method may particularly be suitable for the treatment of these instances.* The details will be published elsewhere.

## Summary

A new method of representing the phase equilibrium of a quarternary system under a constant temperature and pressure on a plane surface has been proposed. The method is to project the three-dimensional space model of the system, axes of which intersect each other at right angles, orthogonally on two of the axual planes. The two projections can represent the complete state of the system, and the treatment of the figure is quite simple and convenient.

The crystallization processes in such a quarternary system have been solved mathematically quite in general, and the application of the present method of graphical representation on the solution of the processes has been illustrated.

*The Central Laboratory, Dairen*

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* For instance, on concentrating the solution with the composition at $P$, **A** begins to deposit at $\alpha$ in Fig. 2.