and that the value 27.4 represents the true heat of vaporization of hexaphenylethane. The possibility of dissociation being negligible at the lower temperatures but becoming important at higher temperatures is ruled out on account of the straight line obtained by plotting log p against $1/T$. Dissociation would increase the pressure, the partial pressure of the undissociated material being that given by the sublimation pressure of the ethane at that temperature. Hence the curve would be convex toward the temperature axis. Almost complete dissociation of the ethane at all temperatures reported in this work would give a straight line plot but seems very improbable for two reasons. In the first place the total pressure would have to be the sublimation pressure of the ethane plus the pressure of the free radical. If the ethane were practically completely dissociated, this would lead to a total pressure of perhaps 100–1000 times that of the ethane, since the solid ethane would have to be in equilibrium with its vapor. This is not compatible with the observed pressure which is only 1/100 of that of triphenylmethane at about 90°. Furthermore, the slope of the curve would give in this case half the heat of dissociation plus half the heat of sublimation of the ethane. If we were to assume 10 kcal. for dissociation, this would lead to 50 kcal. for sublimation, which seems unreasonably large when compared with the value of 24.1 for triphenylmethane. The fact that hexaphenylethane has twice the molecular weight of triphenylmethane would not lead to doubling the heat of sublimation, as an increase of only 50% is observed in going from triphenylmethane to the peroxide.

If we assume that the dissociation is less than 10% at the lowest temperature, we can calculate that ΔF must be at least $+$ 15 kcal., expressing concentrations in atmospheres. If there is an increase in entropy on dissociation, as seems very probable, the value for ΔH of dissociation in the vapor state may be considerably more than 15 kcal.

Summary

1. The vapor pressures of triphenylmethane, hexaphenylethane and triphenylmethyl peroxide have been measured by means of a quartz fiber gage.

2. The values calculated for the heat of vaporization of these compounds indicate that the C–C bond in hexaphenylethane in the vapor state is weaker than a normal C–C bond. The heat of dissociation, however, is probably greater than that found for hexaphenylethane in solution.

CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 22, 1936

[CONTRIBUTION FROM THE CHEMICAL AND OCEANOGRAPHIC LABORATORIES OF THE UNIVERSITY OF WASHINGTON]

Equilibria in the Saturated Solutions of Salts Occurring in Sea Water. II. The Quaternary System $MgCl_2$–$CaCl_2$–KCl–H_2O at 0°

BY IVER IGELSRUD WITH THOMAS G. THOMPSON

No data on the quaternary system $MgCl_2$–$CaCl_2$–KCl–H_2O occur in the literature. This system is of importance in the study and utilization of the secondary salts in natural deposits originating from sea water. Data at lower temperatures are important to an adequate understanding of the geological processes to which the natural salts and their solutions are subject during cold winter periods.

A survey of the literature on the bounding ternary systems, together with data for their 0° isotherms, has been given in a previous paper.[1] The experimental procedure, the methods of purification of the salts, and the methods of chemical analysis used in the study of the quaternary isotherm were the same as for the ternary systems. Samples of the saturated solutions and solid phases in equilibrium were taken for chemical analysis as described. The time found sufficient for the attainment of equilibrium in the quaternary system was from twelve to fifteen hours as compared with eight to ten hours for the ternary solutions.

The results of the chemical analyses for solutions and residues are given in Table I. The data for the saturated solutions are depicted graphically in Figs. 1, 2 and 3. Figures 4 and 5 illustrate the methods used for the identification of the solid phases.

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[1] Iver Igelsrud and T. G. Thompson, THIS JOURNAL, **58**, 318 (1936).

TABLE I

THE QUATERNARY SYSTEM $MgCl_2$–$CaCl_2$–KCl–H_2O AT 0°

Point or line	Solution weight, %			Residue weight, %			Solution mol., %			Solid phases
	$MgCl_2$	$CaCl_2$	KCl	$MgCl_2$	$CaCl_2$	KCl	$MgCl_2$	$CaCl_2$	K_2Cl_2	
E	...	37.27	1.96	...	...	...	...	9.02	0.35	$CaCl_2 \cdot 6H_2O$ + KCl
EI	1.33	35.53	1.93	...	...	...	0.37	8.55	.35	$CaCl_2 \cdot 6H_2O$ + KCl
	1.64	35.10	1.91	1.57	36.56	5.73	0.46	8.43	.34	$CaCl_3 \cdot 6H_2O$ + KCl
	2.53	34.62	1.88	...	...	...	.71	8.35	.34	$CaCl_2 \cdot 6H_2O$ + KCl
	2.62	34.21	1.86	...	...	...	.73	8.22	.33	$CaCl_2 \cdot 6H_2O$ + KCl
	2.68	34.70	1.86	...	...	...	.76	8.39	.34	$CaCl_2 \cdot 6H_2O$ + KCl
	2.98	33.84	1.82	...	...	...	.83	8.12	.33	$CaCl_2 \cdot 6H_2O$ + KCl
I	3.27	33.52	1.85	...	...	...	.92	8.04	.33	$CaCl_2 \cdot 6H_2O$ + KCl + carnallite
	3.34	33.26	1.85	...	...	...	.93	7.96	.33	$CaCl_2 \cdot 6H_2O$ + KCl + carnallite
	3.30	33.40	1.92	8.96	25.55	16.15	.92	8.01	.34	$CaCl_2 \cdot 6H_2O$ + KCl + carnallite
Mean	(3.30	33.39	1.87)				(.92	8.01	.33)	
IF	6.55	27.66	2.02	12.20	18.43	18.66	1.78	6.44	.35	KCl + carnallite
	10.37	21.13	2.10	14.56	12.89	21.91	2.72	4.76	.35	KCl + carnallite
	14.19	16.05	2.13	16.24	10.33	22.30	3.67	3.56	.35	KCl + carnallite
	15.32	14.55	2.15	...	...	...	3.94	3.21	.35	KCl + carnallite
	19.17	9.33	2.15	...	...	...	4.85	2.03	.35	KCl + carnallite
	20.54	7.65	2.15	21.36	4.74	19.85	5.18	1.65	.35	KCl + carnallite
F	26.78	...	2.13	...	...	...	6.63	..	.34	KCl + carnallite
IH	3.68	32.99	1.88	5.18	32.25	10.49	1.03	7.91	.34	$CaCl_2 \cdot 6H_2O$ + carnallite
	8.13	28.75	0.59	...	...	...	2.24	6.78	.105	$CaCl_2 \cdot 6H_2O$ + carnallite
	11.77	25.33	.32	...	...	...	3.23	5.96	.055	$CaCl_2 \cdot 6H_2O$ + carnallite
	23.77	13.99	.031	20.14	20.18	5.27	6.52	3.29	.0055	$CaCl_2 \cdot 6H_2O$ + carnallite
H	23.95	14.08	.032	23.21	17.46	4.50	6.59	3.32	.0055	$CaCl_2 \cdot 6H_2O$ + carnallite + $MgCl_2 \cdot 6H_2O$
	23.91	13.99	.027	21.78	19.24	3.30	6.57	3.30	.0047	$CaCl_2 \cdot 6H_2O$ + carnallite + $MgCl_2 \cdot 6H_2O$
	24.05	14.05	.050	...	...	...	6.62	3.32	.0089	$CaCl_2 \cdot 6H_2O$ + carnallite + $MgCl_2 \cdot 6H_2O$
Mean	(23.97	14.04	.036)				(6.59	3.31	.0064)	
HG	29.30	6.96	.021	...	...	...	7.88	1.61	.0036	$MgCl_2 \cdot 6H_2O$ + carnallite
	29.29	6.79	.036	...	...	...	7.86	1.56	.0061	$MgCl_2 \cdot 6H_2O$ + carnallite
G	34.68	...	.024	...	...	...	9.13	..	.0040	$MgCl_2 \cdot 6H_2O$ + carnallite
HD	23.88	14.01	.019	21.21	20.45	0.001	6.56	3.30	.0034	$MgCl_2 \cdot 6H_2O$ + $CaCl_2.6H_2O$
D	23.94	14.00	...	...	...	...	6.58	3.30	....	$MgCl_2 \cdot 6H_2O$ + $CaCl_2.6H_2O$

The Quaternary Isotherm.—The quaternary isotherm requires a three-dimensional coördinate system for a complete representation of the compositions of the saturated solutions. It is schematically so represented in the conventional regular tetrahedron in Fig. 1. The usefulness of this figure is impaired because it is impossible to represent a three-dimensional figure on a flat sheet of paper in a manner so that quantitative measurements may be made upon it. It is necessary, therefore, to resort to projections. The most simple method of projection of the tetrahedral figure is that suggested by Schreinemakers.[2] One of the vertices, the H_2O vertex, is made the origin of a coördinate system. The three edges radiating from this vertex and making angles of 60° with one another, are the magnesium, calcium and potassium chloride axes. The three planes determined by the three pairs of axes are the coördinate planes of the system. In the coördinate planes are represented the ternary equilibria in the usual manner. Projections of the quaternary equilibria upon the coördinate planes are made parallel to the axes. For example, a quaternary point representing 30% $MgCl_2$, 15% $CaCl_2$, 2% KCl, and (100 − 30 − 15 − 2)% H_2O projected parallel to the $CaCl_2$-axis appears on the $MgCl_2$–H_2O–KCl plane at 30% $MgCl_2$ and 2% KCl; projected parallel to the $MgCl_2$-axis, it appears on the $CaCl_2$–H_2O–KCl plane at 15% $CaCl_2$ and 2% KCl. Two of the three possible projections are sufficient to determine the point completely.

Figures 2 and 3 present, in this way, the complete data for the saturated solutions of the quaternary isotherm. The space figure has been projected upon the two planes $MgCl_2$–H_2O–KCl and $CaCl_2$–H_2O–KCl. Because some of the saturation surfaces, notably that of $MgCl_2 \cdot 6H_2O$, are small it was necessary for the sake of clearness to make the scale on the KCl-axis three times as great as on the other two axes.

The most striking feature of this system is the smallness of the area representing solutions satu-

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(2) F. A. H. Schreinemakers, *Z. physik. Chem.*, **59**, 641 (1907).

rated for $MgCl_2 \cdot 6H_2O$. The same characteristic of magnesium chloride solutions is noted in the quaternary system that was found in the ternary system, namely, that carnallite is almost wholly insoluble in solutions saturated for $MgCl_2 \cdot 6H_2O$. Calcium chloride solutions dissolve, relatively, more carnallite.

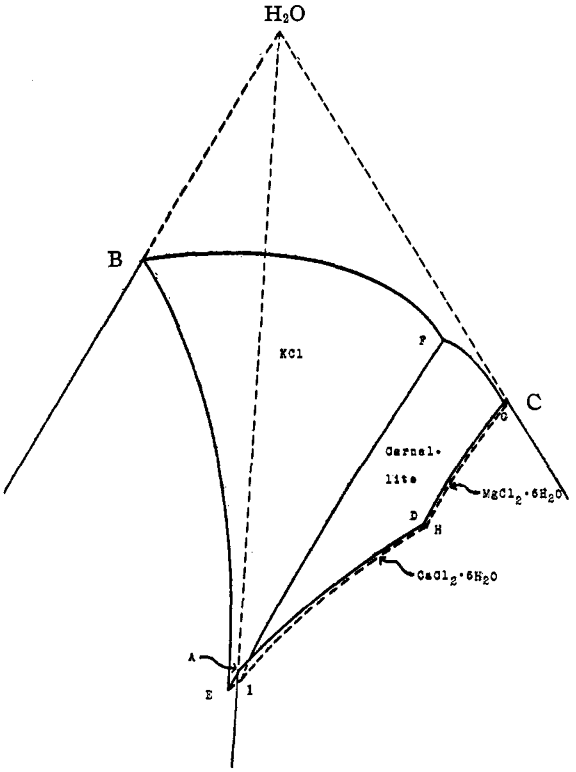

Fig. 1.—The system $MgCl_2$–$CaCl_2$–KCl–H_2O at 0°. Only the upper portion of the tetrahedron is shown.

The saturation surface for $CaCl_2 \cdot 6H_2O$ is also small but not so small as that for $MgCl_2 \cdot 6H_2O$. The chief reason for the larger area is undoubtedly the fact that calcium and potassium chlorides, at this temperature, form no hydrated double salt similar to carnallite. Menge,[3] working with the fused salts, obtained an anhydrous calcium carnallite, $CaCl_2$–KCl, which melted at 754° and formed eutectics at 641 and 597°.

The solubility of potassium chloride in solutions saturated for $CaCl_2 \cdot 6H_2O$ is but slightly less than in solutions saturated for carnallite. In going from F to I along the KCl–carnallite curve, the solubility drops only about 0.3%. The effect of the addition of calcium chloride to carnallite solutions on this curve is, however, quite marked. In proceeding along FI the magnesium chloride in solution is exchanged for calcium chloride and precipitates as carnallite. As shown by the data in Table I, the magnesium chloride content is decreased from 26.7% at F to 3.3% at I by successive additions of calcium chloride. When the magnesium chloride content of the solution falls below 3.3% or the calcium chloride content rises above 33.4%, carnallite cannot exist as a solid phase and KCl and $CaCl_2 \cdot 6H_2O$ become the only two possible solid phases.

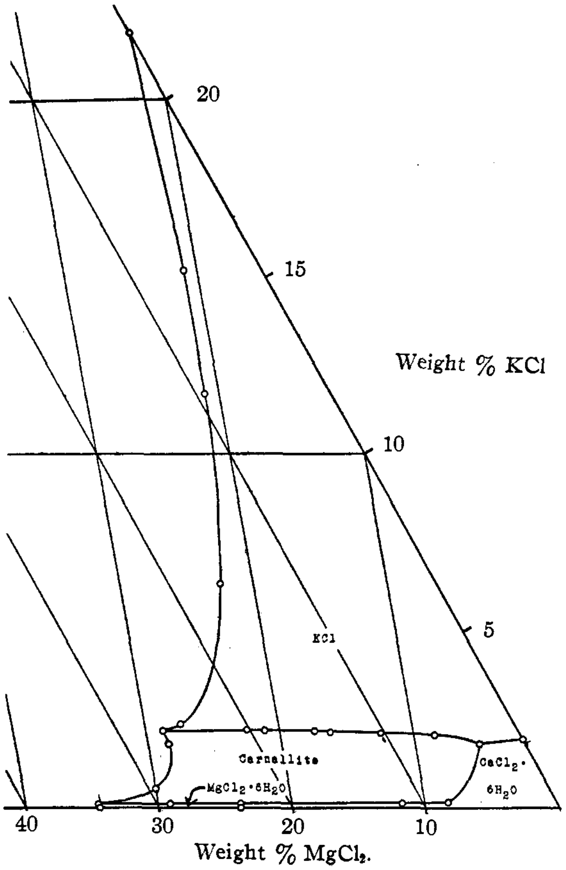

Fig. 2.—The quaternary isotherm projected upon the plane $MgCl_2$–H_2O–KCl.

In discussing the system $MgCl_2$–KCl–H_2O,[1] it was remarked that all solutions saturated for carnallite were incongruently saturated. The same may be said of all saturated carnallite solutions in the quaternary system. The ratio of potassium chloride to magnesium chloride, by weight, in carnallite is the ratio of their molecular weights, 74.56/95.23 = 0.783. All points on the curve FI which borders on the carnallite saturation surface, have lower ratios than this. The point I thus represents an incongruently saturated solution in equilibrium, in the presence of an ex-

(3) O. Menge, *Z. anorg. Chem.*, **72**, 162 (1911).

cess of solid potassium chloride, with the three solid phases $CaCl_2 \cdot 6H_2O$, KCl and carnallite. The point H, on the other hand, represents a congruently saturated solution in equilibrium with $CaCl_2 \cdot 6H_2O$, carnallite and $MgCl_2 \cdot 6H_2O$. The composition of the solution at I is 3.30% $MgCl_2$, 33.39% $CaCl_2$ and 1.87% KCl; the composition of that at H is 23.97% $MgCl_2$, 14.04% $CaCl_2$ and 0.035% KCl.

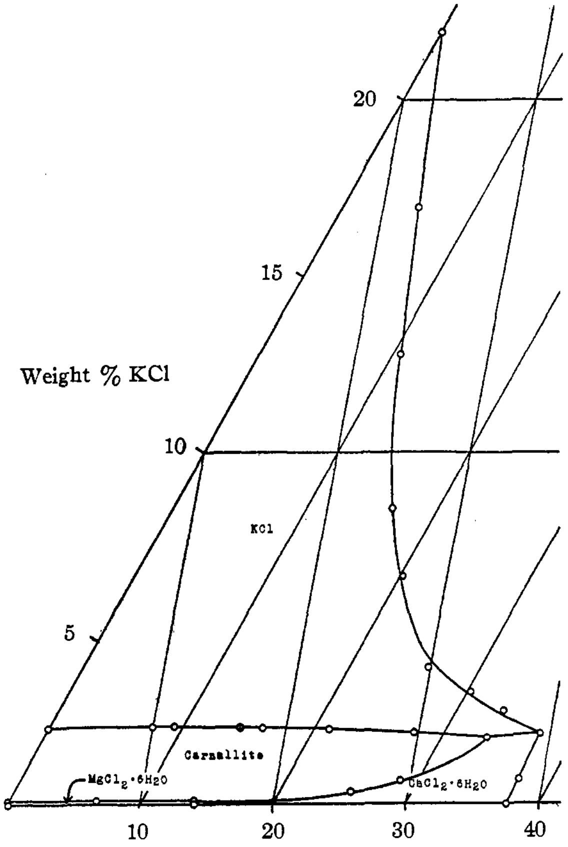

Fig. 3.—The quaternary isotherm projected upon the plane $CaCl_2$–H_2O–KCl.

A point of interest in connection with this isotherm is the water content of some of the solutions. At the monovariant point of the 0° isotherm of the system $CaCl_2$–KCl–H_2O, the percentage of water was 60.77.[1] At I, it is 61.44 and at H, 61.95. From the motion observed along the curves, on successive additions of the fourth component, during the experimental work, the point H appeared to be the isothermal drying-up point of the solutions. This anomaly disappears when the percentages are computed on a molecular basis. The molecular percentages of water are 90.63, 90.74 and 90.09, respectively. The difference between the values for the first two points, 0.11%, is of no significance since it lies within the experimental error of the analytical determinations.

The Quaternary Solid Phases.—The Schreinemakers residue method, since originally published in 1893, has been widely used for the identification of unknown phases in ternary systems. This method was later extended by the discoverer[2] to quaternary systems, but this extension has received no notice in the more common treatises on phase rule methods. It was used in the present investigation and, since it is a valuable tool, its application is described somewhat in detail.

In applying it to a quaternary system, it need only be remembered that where the single solid phase occurs along a saturation curve in the ternary system, it occurs on a saturation surface in the quaternary system. If the compositions of two or more saturated solutions of this surface and the compositions of the corresponding residue samples are determined, conjugation lines are obtained which intersect at the point representing the composition of the unknown phase. The method may be used also to show the simultaneous presence of two or more solid phases in contact with a saturated solution. This is of great convenience in experimental work because it furnishes an absolute check on the phases present and eliminates much uncertainty when working with complicated systems.

In the three component system $CaCl_2$–KCl–H_2O, Fig. 4, for example, a series of conjugation lines, EE′, EE″ and EE‴, determined by the residue method, radiate from the point E which represents saturation for the two salts $CaCl_2 \cdot 6H_2O$ and KCl. The points on any one of these lines represent mixtures of the saturated solution with various amounts of the two coexisting solid phases. Each of these lines, since it lies in the same plane, intersects the line joining the points corresponding to the compositions of the two salts $CaCl_2 \cdot 6H_2O$ and KCl and thus shows the presence of both of these solid phases. Now consider this system and its relation to the four-component system. If a small amount of magnesium chloride be added to the solution, the resultant solution has a composition represented by a point on the quaternary line EI. But the solid phases are still KCl and $CaCl_2 \cdot 6H_2O$. If the composition of the residue sample is represented by the point a′, the conjugation line aa′ must intersect the line KCl–$CaCl_2 \cdot 6H_2O$ in the point a″.

If enough magnesium chloride is added so that the composition of the solution becomes that at the point I, a third solid phase, carnallite, separates. Because carnallite contains magnesium chloride, the composition of the mixture of solid phases can now no longer have a value lying on the line KCl–$CaCl_2 \cdot 6H_2O$. While the composition of a mixture of three substances cannot be represented on a straight line, it can be represented in a triangle each of whose vertices corresponds to 100% of one of the substances. In the present case, the triangle KCl–carnallite–$CaCl_2 \cdot 6H_2O$ is the one required. The appearance of carnallite shifts the foot of the conjugation line to I'' for a residue sample whose composition corresponds to I' and to K' for one whose composition corresponds to K.

In order to show the simultaneous presence of two or more solid phases in a four-component system, it is thus only necessary to find the point of intersection of a given conjugate line with the plane determined by the three phases concerned. If the intersection falls in the interior of the triangle determined by the three solid phases, it shows that all three are present; if it falls on the edge of the triangle, that is, on a line joining the points representing the compositions of two solid phases, it shows that the two phases determining this line are present and that the third phase is absent.

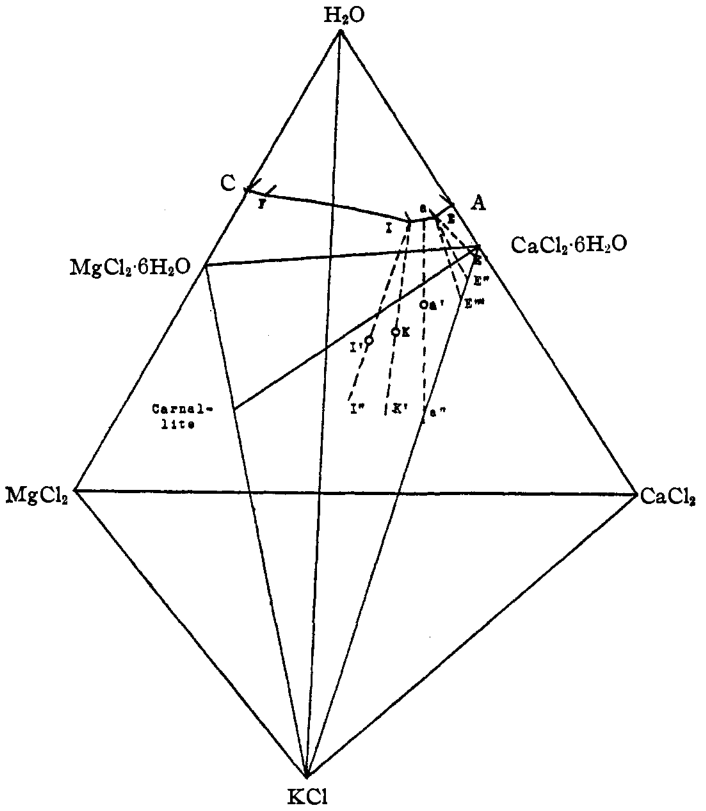

Fig. 4.—Diagram illustrating the method for determining the simultaneous presence of two and of three solid phases.

The intersection of a conjugation line with a plane may be found either analytically or graphically. The analytical problem is equivalent to finding the point of intersection of three planes, two of which pass through the conjugation line. This is done by solving the equations of the three planes simultaneously for the coördinates, or percentages of the three salts, at the point of intersection. The analytical method has, as far as is known to the authors, never been described in the chemical literature.

The analytical process will be illustrated by finding the point of intersection of the plane KCl–carnallite–$CaCl_2 \cdot 6H_2O$ with the conjugation line from the point I in Fig. 4. The necessary data are taken from Table I. The saturated solution contains 1.92% KCl, 33.40% $CaCl_2$ and 3.30% $MgCl_2$ and the residue sample 16.15% KCl, 25.55% $CaCl_2$ and 8.96% $MgCl_2$. These values furnish two points. Since three points determine a plane, two more are needed, one for each of the two planes through the conjugation line. The points representing pure KCl and pure $CaCl_2 \cdot 6H_2O$ are convenient. The amounts of the three salts in KCl are 100% KCl, 0% $CaCl_2$ and 0% $MgCl_2$ and in $CaCl_2 \cdot 6H_2O$ are 0% KCl, 50.64% $CaCl_2$ and 0% $MgCl_2$. The equation of the plane through the conjugation line and the KCl corner of the tetrahedron, in determinant form, is then

$$\begin{vmatrix} x & y & z & 1 \\ 100 & 0 & 0 & 1 \\ 1.92 & 33.40 & 3.30 & 1 \\ 16.15 & 25.55 & 8.96 & 1 \end{vmatrix} = 0$$

where x = % KCl, y = % $CaCl_2$ and z = % $MgCl_2$. Upon expanding this determinant, there is obtained the equivalent equation

$$x + 2.801y + 1.371z - 100 = 0.$$

The equation of the plane through the conjugation line and the point representing $CaCl_2 \cdot 6H_2O$, obtained in a similar manner, is

$$x - 0.5036y - 3.213z + 25.50 = 0.$$

That through the points representing all three solid phases is

$$x + 1.975y + 2.135z - 100 = 0.$$

Solving the three equations simultaneously there are obtained as the coördinates of the point of intersection, I″

$$x = 35.0\%\ \mathrm{KCl}$$
$$y = 15.2\%\ \mathrm{CaCl_2}$$
$$z = 16.4\%\ \mathrm{MgCl_2}$$

The projections of the point I″ have been plotted in Fig. 5 as e and e′. It lies well within the triangle determined by the three solid phases.

The points of intersection, with their proper planes, of the remaining conjugation lines, for which analytical values are given in Table I, were obtained by similar procedures.

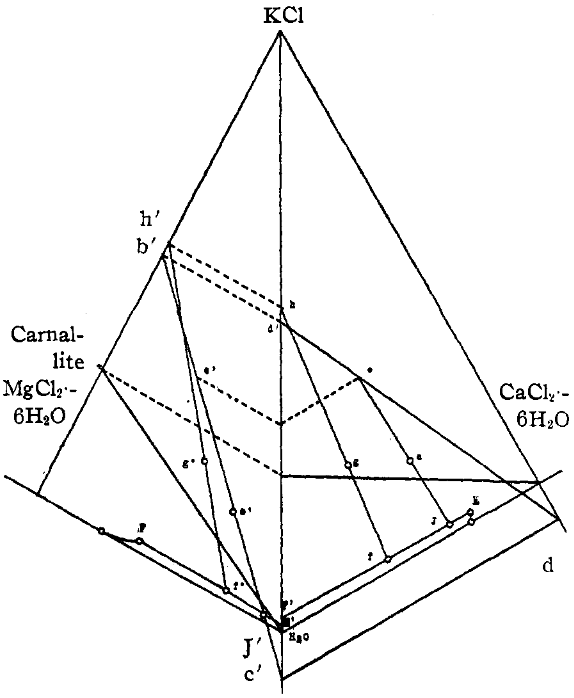

Fig. 5.—Method for determining the solid phases by projection of the conjugation lines upon the sides of the tetrahedron.

It usually involves less labor to obtain the points of intersection graphically as done by Schreinemakers. The points determined by chemical analysis are projected upon two sides of the tetrahedron taken as coördinate planes. The projections of the conjugation line for each solution and residue are drawn through the proper points and intersection with the plane determined by the three solid phases found by the methods of ordinary descriptive geometry.

The graphical method is illustrated to scale in Fig. 5 for the point I and for the line FI of Fig. 4. At I the solid phases are supposed to be KCl, carnallite and $CaCl_2 \cdot 6H_2O$ and on FI, carnallite and KCl. If the data used in illustrating the analytical method are plotted, the two projections of the point I are J and J′ and of the point corresponding to the composition of the residue, a and a′. The two projections of the conjugation line are thus Ja and J′a′. The line J′a′ is extended to meet the line KCl-carnallite in b′ and its projection in the KCl-axis in c′. From b′, the line b′d′ is drawn parallel to the $MgCl_2$-axis and from c′, the line c′d parallel to the $CaCl_2$-axis. If now d is joined to d′, the line dd′ cuts the line Ja in one projection, e, of the point of intersection sought. The other projection is found as indicated in Fig. 5 at e′. Since e and e′ lie well within the respective projections of the triangle KCl–carnallite–$CaCl_2 \cdot 6H_2O$, it is shown that all three of these phases are in contact with the solution at I. It is to be noted that the point found graphically coincides with the point previously found analytically.

The intersection for a conjugation line originating on the line FI, along which two solid phases exist, is obtained even more simply. On FI the composition of a solution was 10.37% $MgCl_2$, 21.13% $CaCl_2$ and 2.10% KCl and of the corresponding residue sample 14.56% $MgCl_2$, 12.89% $CaCl_2$ and 21.91% KCl. The projections of the point for the solution are f and f′ and for the residue g and g′. The projections of the conjugation line are the lines fg and f′g′. The line f′g′ is extended to meet the line carnallite–KCl in h′ and the line fg to meet its projection in the KCl-axis in h. But h is the projection in the KCl-axis of the point h′. This is readily seen because the line hh′ lies parallel to the $MgCl_2$-axis. The conjugation line thus meets the line KCl–carnallite and shows the presence of both of these solid phases and absence of the third phase $CaCl_2 \cdot 6H_2O$.

The application of the Schreinemakers method of residues to other systems whose phases, in addition to the vapor phase, are all liquids, all solids, or combinations of liquids and solids, differs only in the details of application. It may further be extended, although it never has been, to systems containing metathetical elements. A quaternary isotherm of this type is commonly represented in a regular pyramid with a square base. If the diagonal planes of this pyramid are made the projection planes, the foregoing methods are readily applied.

Summary

1. The isotherm for the quaternary system $MgCl_2$–$CaCl_2$–KCl–H_2O has been determined at 0°.

2. The solid phases occurring in the quaternary isotherm are KCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$ and the double-salt hydrate carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$.

3. The isotherm at 0° is characterized by the extreme insolubility of potassium chloride and of carnallite in solutions saturated for magnesium chloride. This was noted previously[1] in studying the 0° isotherm of the system $MgCl_2$–KCl–H_2O. Both potassium chloride and carnallite are more soluble, within a restricted concentration range, in magnesium chloride solutions containing calcium chloride. Carnallite, however, cannot exist at 0° in contact with solutions containing less than 3.3% magnesium chloride or more than 33.4% calcium chloride.

4. All quaternary solutions saturated for carnallite are incongruently saturated.

5. Schreinemakers' method of residues was used for identification of the solid phases in this isotherm.

6. A method is suggested for extending the method of residues to quaternary systems containing metathetical components.

SEATTLE, WASHINGTON RECEIVED APRIL 23, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Solubility of Cupric Oxide in Alkali and the Second Dissociation Constant of Cupric Acid. The Analysis of Very Small Amounts of Copper

BY LEON A. MCDOWELL AND HERRICK L. JOHNSTON

The blue solutions produced when either cupric oxide or cupric hydroxide is treated with alkali have been objects of investigation[1–3] for more than a century. They were thought by some investigators[2] to be colloidal but have been shown, more recently, to represent true cases of chemical solution.[3] The most decisive work in support of this conclusion is that of Müller,[3] who obtained reproducible values of solubility and determined solubility curves, both for the oxide and for the hydroxide, between five normal and about twenty normal sodium hydroxide concentrations. At about fifteen normal alkali maxima were obtained in the solubility curves and at concentrations above these maxima the stable solid phase consisted of dark blue crystals whose analysis corresponded to the formula Na_2CuO_2. Aldridge and Applebey[4] have identified similar copper salts of the alkaline earths.

Müller observed that the solubility of the hydroxide exceeds that of the oxide several fold, which represents a case of metastable equilibrium since the hydroxide solubility diminishes with time and, simultaneously, the solid phase is converted to what appears to be a solid solution of hydroxide with oxide. The oxide solubility does not change with time. An apparently permanent difference between the solubility of the oxide and that attained, after several days, by the hydroxide is not explained.

The present investigation, at lower alkalinities than those employed by Müller, was carried out to obtain additional information on the nature of the copper-bearing ions present in solution and to determine dissociation constants of cupric acid.

Experimental

The method employed was similar to that followed by Johnston, Cuta and Garrett[5] in a similar study with silver oxide, and the solubility apparatus and general manipulations were the same.

Cupric oxide was prepared by dropping 0.06 *N* solutions of copper sulfate and of potassium hydroxide, simultaneously, into an initial 500 cc. of boiling conductivity water in a Pyrex reaction vessel. The entire process including subsequent washings (15 to 20 in number) was carried out in an atmosphere of nitrogen. The wash water gave no test for sulfate ion (barium chloride test) after seven or eight washings and the final product gave no test for sulfate when dissolved in nitric acid and the solution diluted.

Potassium hydroxide at concentrations below 1 *N* was prepared from pure amalgams in the manner described by Johnston, Cuta and Garrett. Potassium and sodium hydroxides at concentrations above 1 *N* were prepared from solutions of the reagent quality hydroxides by the addition

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(1) Proust, *J. Phys.*, **59**, 395 (1804); Low, *Z. anal. Chem.*, **9**, 463 (1870); Donath, *ibid.*, **40**, 137 (1901).

(2) Fischer, *Z. anorg. Chem.*, **40**, 39 (1904); Chatterji and Dhar, *Chem. News.*, **121**, 253 (1920).

(3) (a) Creighton, THIS JOURNAL, **45**, 1237 (1923); (b) Melbye, *Vetenskapsakad, Nobelinst*, **4**, No. 8 (1922); (c) E. Müller, *Z. physik. Chem.*, **105**, 73 (1923).

(4) Aldridge and Applebey, *J. Chem. Soc.*, **121**, 238 (1922).

(5) H. L. Johnston, F. Cuta and A. B. Garrett, THIS JOURNAL, **55**, 2311 (1933).