KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING of Saturday February 27, 1909.

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CONTENTS.

Chemistry. — "*The system: Copper sulphate, Copper chloride, Ammonium sulphate, Ammonium chloride and Water at* 30°". By Prof. F. A. H. SCHREINEMAKERS.

(Communicated in the Meeting of January 30, 1909).

Although the above mentioned five substances take part in the construction of this system only four need be considered as components, as between the four salts exists the relation;

$$CuSO_4 + 2NH_4Cl = (NH_4)_2SO_4 + CuCl_2.$$

The system constructed from the four salts only ought, therefore, to be looked upon as a ternary one; we will now see first of all how we may represent such a system.

Let us take the four substances: AB, AC, BD and CD between which may take place the double decomposition:

$$AB + CD = AC + BD$$

If we represent the substances AB, AC and BD by the angles of a rectangular isoxeles triangle the rectangular side of which has the length 1 [fig. 1] substance CD is represented by the point CD so situated that the four points representing the four substances form the angles of a tetragon. What will now be the composition of a

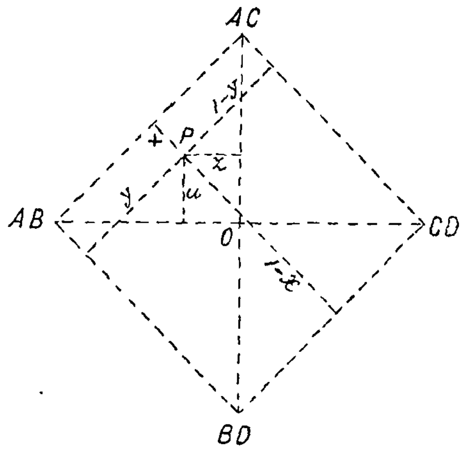

Fig. 1.

phase represented by point p? This may be represented in various manners according to the nature of the three substances in which it has to be expressed.

1. We take as components AB, AC and BD.

The point p then represents x Mol. BD, y Mol. AC and, therefore, $1 - x - y$ Mol. AB.

2. We take as components AB, AC and CD; p then represents: $1 - y$ Mol. AB, x Mol. CD and, therefore $y - x$ Mol. AC.

3. We take as components AC, CD and BD; the point p then lies outside the triangle having these substances as angles; it then represents $1 - y$ Mol. BD, $1 - x$ Mol. AC and, therefore, $x + y - 1$ Mol. CD; $x + y - 1$ is negative in this case.

4. If we take as components AB, BD CD p again lies outside the observed triangle; it then represents y Mol. CD, $1-x$ Mol. AB and, therefore, $x-y$ Mol. BD which latter quantity is negative.

We may, therefore, assume in four ways that the phase p is constructed of three of the four snbstances; it is obvious that each of the four assumptions leads to the same composition. This may be explained also in the following manner.

If, for instance, we calculate the quantity A of this phase in the four ways described we always get the same result: According to 1 the phase contains y Mol. AC and $1-x-y$ Mol. AB, therefore $1-x$ Mol. A; the same is found according to 2, 3 and 4.

We also find in each of the four cases that that phase contains $1-y$ Mol. B, y Mol. C and x Mol. D.

If we draw from p the perpendicular lines z and u these are also significant. For we find:

$$z = \frac{1}{2}(1-x-y)\sqrt{2} \quad \text{and} \quad u = \frac{1}{2}(y-x)\sqrt{2}.$$

For the composition of the phase p we may write according to 1.

x Mol. BD, y Mol. AC and $1-x-y$ Mol. AB.

As, however, between the four substances exists the relation

$$AB + CD = AC + BD$$

we may express the composition also in the four substances, for instance:

$x-n$ Mol. BD, $y-n$ Mol. AC, $1-x-y+n$ Mol. AB and n Mol. CD.

From this it follows that $1-x-y$ represents the number of Mols. AB minus the number of Mols. CD, while $y-x$ represents the number of Mols. AC minus the number of Mol. BD, Therefore:

$$z = \frac{1}{2}(\text{Mol. } AB - \text{Mol. } CD)\sqrt{2} \quad , \quad u = \frac{1}{2}(\text{Mol. } AC - \text{Mol. } BD)\sqrt{2}.$$

The half diagonal of the square is now $\frac{1}{2}\sqrt{2}$; if, however, the half diagonal is taken as 1 we have:

$$z = \text{Mol. } AB - \text{Mol. } CD \quad \text{and} \quad u = \text{Mol. } AC - \text{Mol. } BD.$$

The composition of the phase represented by point p may, therefore, be deduced in two ways.

1. From the situation of p in regard to one of the four triangles whose angles represent the solid substances. The length of the sides of the square is then called 1. We then obtain the composition expressed in those three substances which form the angles of the observed triangle.

2. From the situation of p in regard to the two diagonals of the square. The length of the half diagonals is then taken as 1.

If we now add a fourth component, this may be placed on an axis in the point O perpendicularly to the plane of the square; if

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on this we take a piece $OW = 1$, point W then represents the fourth component W. The different phases occurring in the system will then be represented by the points within the prism $W . AB . AC . CD . BD$.

As in the system now investigated the relation

$$Cu\,SO_4 + 2\,NH_4\,Cl = (NH_4)_2\,SO_4 + Cu\,Cl_2$$

takes place between the four salts we will, in the case of ammonium chloride, take the double molecule $(NH_4\,Cl)_2$ and not the single one. If we proceed along the circumference of the square in a constant direction the angles represent successively the components: $CuSO_4$, $CuCl_2$, $(NH_4Cl)_2$ and $(NH_4)_2SO_4$ the water will then be indicated by point W in space.

We may now project the different points in space on an arbitrary plane; for this we choose a projection on the square and then obtain something like what is represented in Fig. 2. As the drawing would become too large the diagonals have only been drawn as far as necessary; the sides and angles of the square have been omitted.

We will now consider first the different ternary systems.

1. The system: water, $CuSO_4$, $(NH_4)_2SO_4$.

In this system investigated by Miss W. C. DE BAAT three solid substances occur at 30° in equilibrium with the liquid, namely, $(NH_4)_2SO_4$, $Cu\,SO_4 . 5\,H_2O$ and $Cu\,SO_4 . (NH_4)_2\,SO_4 . 6\,H_2O$.

The isotherm therefore consists of three saturation lines, namely:

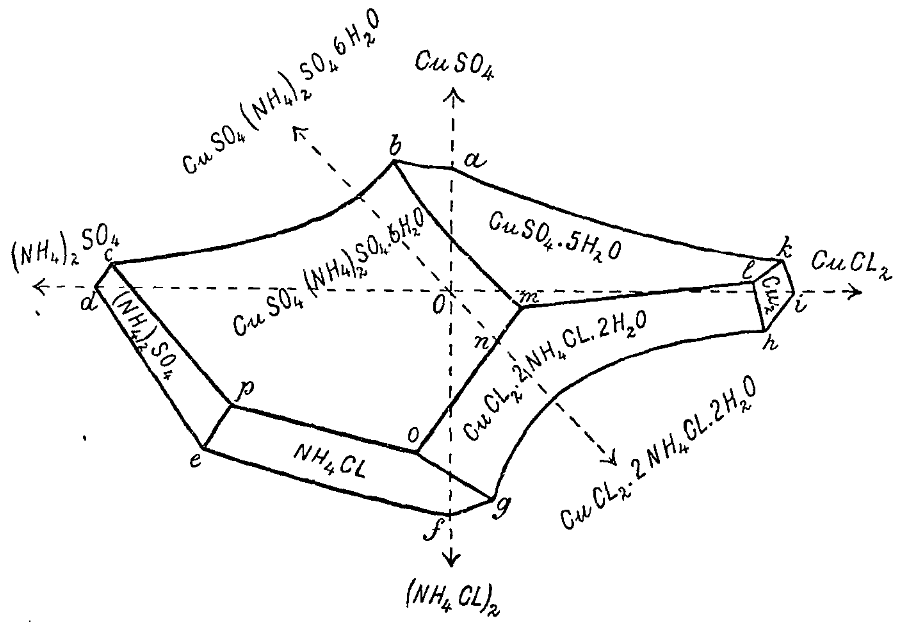

Fig. 2.

dc the saturation line of the $(NH_4)_2\,SO_4$

cb „ „ „ „ „ $Cu\,SO_4 \,.\, (NH_4)_2\,SO_4 \,.\, 6\,H_2O$

ba „ „ „ „ „ $Cu\,SO_4 \,.\, 5\,H_2O$.

If we unite the point O with the point representing the double salt $CuSO_4 \,.\, (NH_4)_2SO_4 \,.\, 6\,H_2O$ we intersect the saturation line of double salt the latter being, therefore, soluble in water without decomposition.

2. The system: water, $Cu\,SO_4$, $Cu\,Cl_2$.

Only two solid substances namely $CuSO_4 \,.\, 5H_2O$ and $CuCl_2 \,.\, 2\,H_2O$ occur in this system as solid phases by the side of liquid; point *k* is the solution saturated with both salts, *ki* is the saturation line of the $CuCl_2 \,.\, 2\,H_2O$, *ka* that of the $CuSO_4 \,.\, 5\,H_2O$.

3. The system: water, $CuCl_2$, NH_4Cl.

The isotherm of 30° has already been determined by Dr. P. Meerburg. As solid substances occur, by the side of liquid, $CuCl_2 \,.\, 2\,H_2O$, NH_4Cl and $CuCl_2 \,.\, 2\,NH_4Cl \,.\, 2\,H_2O$. The saturation line of the $CuCl_2 \,.\, 2\,H_2O$ is represented by *ih*, that of the $CuCl_2 \,.\, 2\,NH_4Cl \,.\, 2\,H_2O$ by *hg*, and that of the NH_4Cl by *fg*. The line uniting point *O* with the point representing the double salt intersects the saturation line of the double salt the latter being, therefore, soluble in water without decomposition.

4. The system: water, $(NH_4)_2SO_4$, NH_4Cl.

In this system only $(NH_4)_2SO_4$ and NH_4Cl occur as solid substances; the saturation line of the first salt is represented by *de*, that of the second by *ef*; *e* represents the solution saturated with both salts.

After this short review of the four ternary systems we can now discuss the quaternary system.

At 30° the following substances can occur as solid phases in coexistence with liquid:

$CuSO_4 \,.\, 5\,H_2O$, $CuCl_2 \,.\, 2\,H_2O$, $(NH_4)_2SO$, NH_4Cl, $CuSO_4 \,.\, (NH_4)_2SO_4 \,.\, 6\,H_2O$ and $CuCl_2 \,.\, 2\,NH_4Cl \,.\, 2\,H_2O$.

As the solutions, which in a quaternary system are saturated with solid matter are represented by a surface, there must be six saturation surfaces; their projections are indicated in the figure, namely:

abmlk is the saturation plane of the $CuSO_4 \,.\, 5H_2O$

iklh „ „ „ „ „ „ $CuCl_2 \,.\, 2H_2O$

fgope „ „ „ „ „ „ NH_4Cl

dcpe „ „ „ „ „ „ $(NH_4)_2SO_4$

hlmog „ „ „ „ „ „ $CuCl_2 \,.\, 2NH_4Cl \,.\, 2H_2O$

bmopc „ „ „ „ „ „ $CuSO_4 \,.\, (NH_4)_2SO_4 \,.\, 6H_2O$

In order to facilitate the survey, I have indicated on each of the saturation surfaces the solid substances with which the solutions are saturated; *for the sake of brevity* Cu_2 *stands for* $CuCl_2 . 2H_2O$.

The lines in which the surfaces intersect each other two by two represent the solutions saturated with two solid substances. They are the following:

ep, the saturation line of $(NH_4)_2SO_4 + NH_4Cl$
cp, „ „ „ „ $(NH_4)_2SO_4 + CuSO_4 . (NH_4)_2SO_4 . 6H_2O$
bm, „ „ „ „ $CuSO_4 . 5H_2O + CuSO_4 . (NH_4)_2SO_4 . 6H_2O$
lk, „ „ „ „ $CuSO_4 . 5H_2O + CuCl_2 . 2H_2O$
lh, „ „ „ „ $CuCl_2 . 2H_2O + CuCl_2 . 2NH_4Cl . 2H_2O$
og, „ „ „ „ $NH_4Cl + CuCl_2 . 2NH_4Cl . 2H_2O$
mo, „ „ „ „ $CuSO_4 . (NH_4)_2SO_4 . 6H_2O +$
$+ CuCl_2 . 2NH_4Cl . 2H_2O$
po, „ „ „ „ $CuSO_4 . (NH_4)_2SO_4 . 6H_2O + NH_4Cl$
lm „ „ „ „ $CuSO_4 . 5H_2O + CuCl_2 . 2NH_4Cl . 2H_2O$

The *points* in which the *saturation lines* meet three by three are the saturation points; they represent the solutions saturated with three solid substances. We have;

p, saturated with $CuSO_4 . (NH_4)_2SO_4 . 6H_2O + (NH_4)_2SO_4 + NH_4Cl$
o, „ „ $CuSO_4 . (NH_4)_2SO_4 . 6H_2O + CuCl_2 . 2NH_4Cl . 2H_2O +$
$+ NH_4Cl$
m, „ „ $CuSO_4 . (NH_4)_2SO_4 . 6H_2O + CuCl_2 . 2NH_4Cl . 2H_2O +$
$+ CuSO_4 . 5H_2O$
l, „ „ $CuCl_2 . 2NH_4Cl . 2H_2O + CuSO_4 . 5H_2O +$
$+ CuCl_2 . 2H_2O$

We can now see plainly from the figure the solid substances by the side of which a defined solid substance can exist in saturated solution. We notice that $CuSO_4 . (NH_4)_2SO_4 . 6H_2O$ can exist in coexistence with $(NH_4)_2SO_4$, NH_4Cl, $CuSO_4 . 5H_2O$ and $CuCl_2 . 2NH_4Cl . 2H_2O$ but not together with $CuCl_2 . 2H_2O$; $CuSO_4 . 5H_2O$ can exist by the side of $CuCl_2 . 2H_2O$, $CuCl_2 . 2NH_4Cl . 2H_2O$ and $CuSO_4 . (NH_4)_2SO_4 . 6H_2O$ but not together with $(NH_4)_2SO_4$ or NH_4Cl. It further appears that both double salts behave in regard to each other and to water as single substances; at 30° we may have a series of solutions saturated with $CuSO_4 . (NH_4)_2SO_4 . 6H_2O$, a series saturated with $CuCl_2 . 2NH_4Cl . 2H_2O$ and one solution saturated with both at the same time; the latter is represented by point *n*.

Many other conclusions may be drawn from the figure, but this I must leave to the reader.