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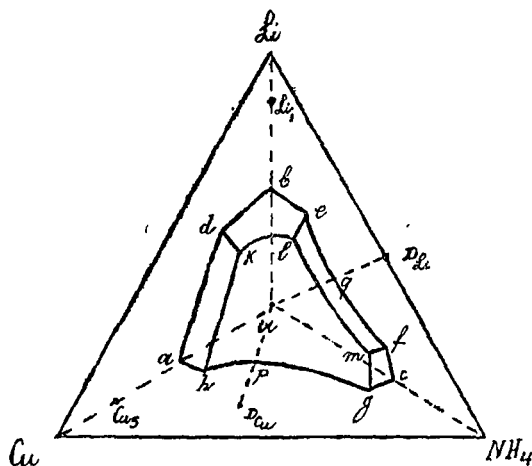
the virial of the resulting mean molecular attraction need only be taken into account. It is true that the molecules exercise on each other still other forces besides this mean attraction, but these forces yield a virial zero. The forces normal to the radius vector, namely form together a couple, and the virial of a couple is zero. For the same reason the directing couples working on the molecules need not be taken into account. And from the forces working in the direction of the radius vector we need only take into account the average value, for attracting and repulsing forces which equally often occur between different pairs of molecules, cancel each other.

In calculating the virial, the influence of the molecular attraction on the distribution in space of the molecules must of course still be taken into account.

Chemistry. — "*Equilibria in quaternary systems.*" By Prof. Dr. F. A. H. SCHREINEMAKERS.

In the system: Copper sulphate, ammonium sulphate, lithium sulphate and water two more solid compounds occur at 30° in addition to the three sulphates namely, $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4$, $6 \text{H}_2\text{O}$ and $\text{Li}_2 \text{SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4$.

We will again represent the equilibria in the wellknown manner with the aid of a tetrahedron but now choose quite a different projection than that used in the previous communication; we will in fact project all saturation lines and surfaces perpendicularly on one of the side planes of the tetrahedron.



A projection of this kind is represented in the figure; the points

Cu, Li, NH₄ and W indicate the four components Cu SO₄, Li₂ SO₄, (NH₄)₂ SO₄ and water; the triangle Cu Li NH₄ is the side plane on which all is projected. The dotted lines Cu W, Li W and NH₄ W are the projections of the rising sides of the tetrahedron and it is obvious that the point W must lie in the centre of the triangle.

The question is now what connection exists between the position of a point in the tetrahedron and its projection on the triangle Cu Li NH₄.

Let us take a phase with the composition: Cu proportions of Cu SO₄, Li proportions of Li₂ SO₄, N proportions of (NH₄)₂ SO₄ and W proportions of water. The projection of this point on the triangle Cu Li NH₄ may then be taken as indicating a phase which only contains the three components Cu SO₄, Li₂ SO₄ and (NH₄)₂ SO₄.

Let us call these proportions Cu', Li' and N'. It is now easily demonstrated that

$$\text{Cu}' = \text{Cu} + \frac{\text{W}}{3} \quad \text{Li}' = \text{Li} + \frac{\text{W}}{3} \quad \text{N}' = \text{N} + \frac{\text{W}}{3}$$

so that if the composition of a phase is known its projection may be readily represented in a drawing.

The double salt Li₂ SO₄. (NH₄)₂ SO₄ is represented in the figure by D_{Li}; it is obvious that it must be situated on the line Li NH₄ as it consists merely of the components Li₂ SO₄ and (NH₄)₂ SO₄. The double salt Cu SO₄. (NH₄)₂ SO₄. 6 H₂ O which contains three components must lie on the side plane W Cu NH₄ and is represented by D_{Cu}.

Both copper and lithium sulphate occur as hydrates, namely Cu SO₄. 5 H₂ O and Li₂ SO₄. H₂ O; they are represented in the figure by Cu₅ and Li₁; of course Cu₅ must lie on the side Cu W and Li on Li W.

Let us first consider the three ternary equilibria.

1. *Copper sulphate—ammonium sulphate—water.* The equilibria occurring in this system at 30° have been determined by Miss W. C. DE BAAT; the results of this investigation are represented by the saturation lines *ah*, *hpg*, and *gc*; *ah* indicates the solutions saturated with Cu SO₄. 5 H₂ O; *gc* is the saturation line of solid (NH₄)₂ SO₄ and *hpg* represents the solutions saturated with Cu SO₄. (NH₄)₂ SO₄. 6 H₂ O. As the line W D_{Cu} intersects the saturation line *hpg*, the double salt is soluble in water without decomposition; its solubility is represented by *p*.

2. *Lithium sulphate—ammonium sulphate—water.* The equilibria occurring in this system at 30° are represented by the saturation lines *be*, *eqf* and *fc*; the first is the saturation line of Li₂ SO₄. H₂ O;

the second that of the double salt $\text{Li}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$, the last that of $(\text{NH}_4)_2\text{SO}_4$. As the line W D_{Li} intersects the saturation line of the double salt it is soluble in water without decomposition.

As regards the branch be I stated that this indicates solutions which are in equilibrium with $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$; this is not quite correct for lithium sulphate, although only to the extent of a few %, gives mixed crystals with ammonium sulphate.

3. *Lithium sulphate—copper sulphate—water.* Whereas in the two previous ternary systems a double salt occurs, this is not the case in this system at 30° ; the isotherm therefore only consists of two branches; ad is the saturation line of $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$ and bd that of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

These two branches have been determined by Mr. KOOPAL.

The quaternary equilibria at 30° are represented by surfaces, lines and points.

The surface $ahkd$ is the saturation surface of $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$; it therefore indicates the quaternary solutions which are saturated with $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$.

The surface $dkleb$ is the saturation surface of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

The surface $cfmg$ is the saturation surface of $(\text{NH}_4)_2\text{SO}_4$.

The three surfaces observed are the saturation surfaces of the components or of their hydrates; in addition we also have the saturation surfaces of the double salts; that of $\text{Li}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ is represented by $elmfq$; that of $\text{Cu SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$ by $hklmgph$.

The saturation lines are formed by the intersection of the saturation surfaces taken two by two; they consequently represent solutions saturated with two solid substances.

We now see at once that solutions represented by the points of the lines:

hk	are saturated with	$\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$	and	D_{Cu}
dk	„	„	„	$\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
kl	„	„	„	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and D_{Cu}
le	„	„	„	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and D_{Li}
lm	„	„	„	D_{Li} and D_{Cu}
mf	„	„	„	D_{Li} and $(\text{NH}_4)_2\text{SO}_4$
mg	„	„	„	D_{Cu} and $(\text{NH}_4)_2\text{SO}_4$

The quaternary saturation lines may be distinguished into external lines and middle lines; the external lines such as kh , kd , le , mf and mg each terminate in a point of a side plane, therefore in a ternary solution; the middle lines such as kl and lm are situated quite within the tetrahedron.

In each of the saturation points three saturation surfaces and therefore also three saturation lines meet each other; such a point therefore represents a solution saturated with three solid substances.

From this it follows that the solution represented:

by k is saturated with $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$, $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$ and D_{Cu}

„ l „ „ „ D_{Li} , $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$ and D_{Cu}

„ m „ „ „ D_{Li} , $(\text{NH}_4)_2 \text{SO}_4$ and D_{Cu} .

This shows that each of these solutions is saturated with $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$.

With the aid of this figure we may readily draw some conclusions. Let us therefore observe the external lines, for instance dk . The point d represents a ternary solution saturated at 30° with $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$ and $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$. To this solution we add $(\text{NH}_4)_2 \text{SO}_4$; the solution will now alter its composition until at last a third solid phase appears. What is this phase? $(\text{NH}_4)_2 \text{SO}_4$ forms a double salt with copper as well as with lithium sulphate and the question now arises which of these two will appear first. The experiment shows that $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$ is formed. If we start from the ternary solution h which is saturated at 30° with $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$ and $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$ and if $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$ is added the solution undergoes the changes represented by points of the line hk until finally the third solid phase occurs in k in this case $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$.

If we start from the ternary solution f saturated at 30° with $(\text{NH}_4)_2 \text{SO}_4$ and $\text{Li}_2 \text{SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4$ and if we add $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$ and represent the solution by m $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$ is formed as the third solid phase; if we start from the ternary solution g which is saturated with $(\text{NH}_4)_2 \text{SO}_4$ and $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$ and add $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{Li}_2 \text{SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4$ will form in m as the third phase.

If we start from the ternary solution e which is saturated with $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Li}_2 \text{SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4$ and add $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$ the solution traverses the branch el ; in l however a new solid phase is formed, namely, $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$.

Suppose a plane is passed through the points W , Cu and D_{Li} of the tetrahedron; the points of this plane represent solutions with a constant proportion of the components $\text{Li}_2 \text{SO}_4$ and $(\text{NH}_4)_2 \text{SO}_4$; this ratio is the same as that in which they occur in the double salt. This plane intersects the saturation surface $leqfm$ of this double salt, so that this is not only soluble without decomposition in water but also in solutions of copper sulphate of a definite concentration.

In order to find the composition of the solid phases which can be in equilibrium with definite solutions I have acted in the same manner as I did previously with ternary systems; I have applied the "residue-method".

If the solution is in equilibrium with one solid substance the conjugation line solution-residue must pass through the point indicating this solid substance; if it is in equilibrium with two solid substances the conjugation line solution-residue intersects the communication line of the two solid substances and if it is in equilibrium with three solid substances it intersects the triangle which has those three solid substances as its angular points.

These constructions are much facilitated by taking a rectangular tetrahedron instead of an equilateral one and projecting the whole on two of the side planes.

Astronomy. — "*The investigation of the weights in equations according to the principle of the least squares*". By J. WEEDER. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN).

When results of measurement deduced from different modes of measuring or originating from different observers are equated mutually, it is generally advisable to test the weights assigned to these results, before equating, with the apparent errors produced by the equation in order to be able to judge whether it is necessary to correct them and to distinguish in what direction correction is obtained. Let the material of observation break up according to its origin into groups and let out of the apparent errors of each group separately the mean error of the unity of weight be deduced, then it is a necessity for the differences of those values to be small, at least they may not overstep the limits which can be fixed taking into account the numbers of apparent errors in each group.

Already at the outset of such investigations the problem thus appears how the mean error of the unity of weight can be calculated, if one wishes to use but a part of the apparent errors.

When equating determinations of errors of division of the Leyden meridian circle I have applied the following formula:

$$\mu = \sqrt{\frac{\sum gf^2}{n-k}}$$

Here

μ = the mean error of unity of weight,
 g = the weight of a result of observation,