data, we have to write everywhere, hx and $h'y$, instead of x and y, whence

$$\varepsilon^{-1} = \frac{n!m!}{2^{n+m}} \frac{\pi}{hh'}.$$

The scale factors h and h' can then be determined by putting

$$A_{2.0} \text{ en } A_{0.2} = 0$$

and the two unmixed means of the second order can be disposed of for the determination of these constants:

$$\mu_2(x) = \frac{1}{2h^2} \text{ en } \mu_2(y) = \frac{1}{2h'^2}$$

If, further, we make the axes rotate about the origin so that they coincide with the principal axes of inertia, then also $A_{1.1}$ has to be put equal to zero and the corresponding mean

$$\mu_2(x, y)$$

enables us to calculate the direction of the principal axes.

The series (30) then becomes:

$$u = e^{-x^2-y^2}[A_0 + A_{3.0}U_3 + A_{2.1}U_2V_1 + A_{1.2}U_1V_2 + A_{0.3}V_3 + \\ + A_{4.0}U_4 + A_{3.1}U_3V_1 + A_{2.2}U_2V_2 + A_{1.3}U_1V_3 + \\ + A_{0.4}V_4 + \text{enz.}$$

where all terms except the first represent the deviations from the normal exponential law, the terms of odd degree being a measure of the different kinds of skewness, the terms of even degree of the different kinds of symmetrical deviations.

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

Let us first take the system with the components: *water*, *ethyl alcohol*, *methyl alcohol* and *ammonium nitrate*; we then have at the ordinary temperature one solid substance and three solvents which are miscible in all proportions so that the resulting equilibria are very simple. The equilibria occurring in this system at 30° have been investigated and are represented in the usual manner in Fig. 1; the angular points W, M, A and Z of the tetrahedron indicate the components: water, methyl alcohol, ethyl alcohol and the salt: ammonium nitrate.

The curve *wa* situated on the side plane WAZ represents the solutions consisting of water and ethyl alcohol and saturated with solid salt; the curve *wm* represents the solutions of water and

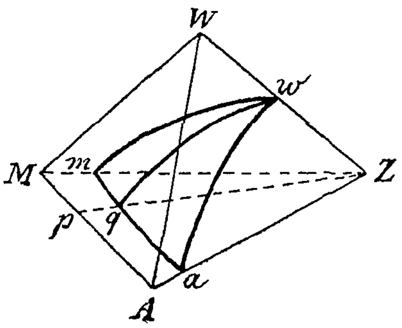

Fig. 1.

methyl alcohol mixtures saturated with solid salt, whilst *ma* indicates the solutions of mixtures of ethyl alcohol and methyl alcohol, also saturated with solid salt.

The quaternary equilibria, namely the solutions of mixtures of water, methyl alcohol and ethyl alcohol saturated with solid salt are represented by the surface *wma* which we may call the saturation surface of the solid salt *Z*.

If we introduce through one of the sides for instance through *WZ* a plane such as the plane *WZp* all points of that plane then represent phases containing the components *A* and *M* in the same proportion. This plane intersects the saturation surface along the curve *wq*; this, therefore, indicates solutions saturated with solid salt in which the relation between methyl alcohol and ethyl alcohol is constant.

The points of such a curve are easy to obtain; the two alcohols are first added together so as to yield a mixture represented by *p* for instance; on adding varying quantities of water we obtain the points of the line *pW* and on saturating these solutions with the salt the points of the curve *qw* are indicated.

In this manner different sections of the saturation surface with planes passing through the side *WZ* have been obtained.

In the system, water, methyl alcohol, ethyl alcohol and potassium nitrate perfectly analogous equilibria occur; the saturation surface for 30° in this system has been determined by Miss C. DE BAAT.

In the system: *water, ethyl alcohol, ammonium nitrate* and *silver nitrate* the relations are somewhat less simple, for at 30° we have two solid components and one double salt: $AgNO_3 . NH_4NO_3$; the equilibria occurring at 30° are represented in Fig. 2. Whereas Fig. 1 is a perspective representation of the tetrahedron, Fig. 2 is a projection on a plane parallel to two sides crossing each other, in this case the sides: WA and AgN, so that in the projection, these stand perpendicular to each other and divide each other in two.

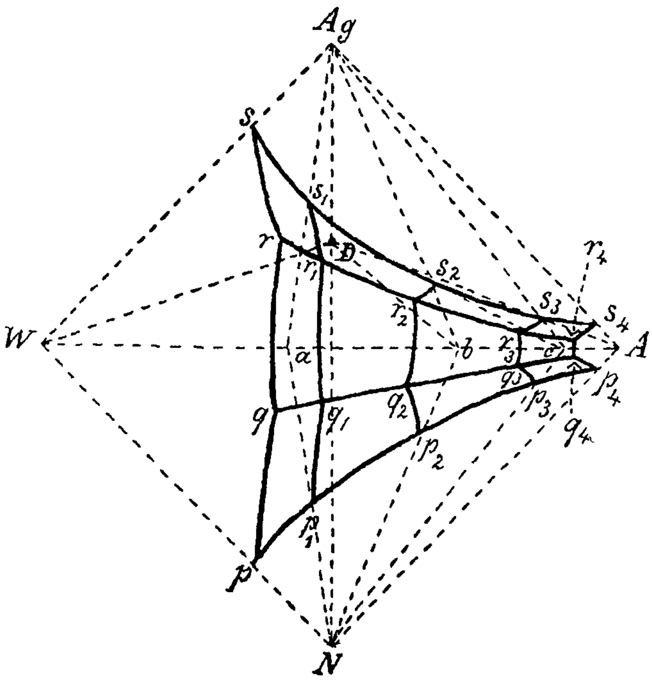

Fig. 2.

The angular points W, A, Ag and N indicate the components water, ethyl alcohol, silver nitrate and ammonium nitrate. The projection of an arbitary point within the tetrahedron on the projection plane is easily indicated. If we take the line WA as X-axis and the line NAg as Y-axis of a co-ordinate system and if we take as positive directions those towards A and Ag we find:

$$X = \frac{A-W}{2} \qquad Y = \frac{Ag-N}{2}$$

when A, W, Ag and N represent the quantities of alcohol, water, silver nitrate and ammonium nitrate indicated by the said point within the tetrahedron.

In this manner Fig. 2 has been deduced and it is readily noticed that the equilibria are represented by three surfaces, namely $s s_4 r_4 r$, $r r_4 q_4 q$ and $q q_4 p_4 p$. The first surface is the saturation surface of silver nitrate, the second that of the double salt and the third that of the ammonium nitrate.

The double salt is represented in the figure by the point D which, of course, must be situated on the line $Ag\,N$. If the compositions of the phases were expressed in mol. $^0/_0$ D would fall in the origin of the co-ordinate system; this is however, not the case as the compositions are expressed in percentages by weight. The curve $s\,s_1\,s_2\,s_3\,s_4$, situated on the side surface $W\,Ag\,A$ is the saturation line of silver nitrate in water-alcohol mixtures; the solubility of this salt in water (point s) gradually becomes less on addition of alcohol; the solubility in absolute alcohol is represented by s_4.

The saturation line of ammonium nitrate in water-alcohol mixtures is represented by $p\,p_1\,p_2\,p_3\,p_4$. It will be noticed that the solubility of ammonium nitrate in water is much lessened by alcohol. The equilibria in the ternary system water, silver nitrate and ammonium nitrate are represented by the three saturation lines sr, rq and qp, situated on the side surface $W\,Ag\,N$; sr indicates the solutions saturated with silver nitrate, qp those saturated with ammonium nitrate and rq those saturated with the double salt. On drawing the line WD this will be seen to intersect the saturation line rq of the double salt; this is therefore soluble in water without decomposition.

In order to study the equilibria in the quaternary system I operated as follows. Instead of water, I took a water-alcohol mixture containing 41,8 $^0/_0$ of alcohol and in this determined the saturation lines or the silver nitrate, ammonium nitrate and the double salt. As the solutions all contained water and alcohol in constant proportion they must lie in a plane passing through the side $Ag\,N$ of the prism and intersecting WA in a point a indicating a 41,8 $^0/_0$ alcohol. In this manner I found the three saturation lines s_1r_1, r_1q_1 and q_1p_1 which therefore are all situated in the surface $a\,Ag\,N$: if the line aD is drawn it will be noticed that this branch intersects r_1q_1 showing that the double salt is also soluble without decomposition in dilute alcohol.

In a similar manner I determined the saturation line in water-alcohol mixtures containing 71,23 and 91,3 $^0/_0$ of alcohol; I always found three branches in the figure; they are represented by s_2r_2, r_2q_2 and q_2p_2 and by s_3r_3, r_3q_3 and q_3p_3.

As the line bD intersects the saturation line q_2r_2, the double salt is soluble without decomposition in 71,23 $^0/_0$ alcohol; with the line cD it is different; this no longer intersects the saturation line q_3r_3 of the double salt but only that of the silver nitrate r_3s_3 showing this is decomposed by 91,3 $^0/_0$ alcohol with separation of silver nitrate.

As the solubility of the components in absolute alcohol amounts to a few percent only, I have not investigated the ternary system alcohol — silver nitrate — ammonium nitrate but there is hardly any doubt that the solubility lines will give something as represented by $s_4\, r_4\, q_4\, p_4$ and the double salt is bound to be decomposed by absolute alcohol with separation of silver nitrate.

From the preceding it is obvious that the following equilibria occur in the quaternary system:

L + $Ag\,NO_3$	of which L is represented by the surface: $s\,r\,r_4\,s_4$
L + $NH_4\,NO_3$	" " " " " " " " $q\,p\,p_4\,q_4$
L + $Ag\,NH_4\,(NO_3)_2$	" " " " " " " " $r\,q\,q_4\,r_4$
L + $Ag\,NO_3$ + $Ag\,NH_4\,(NO_3)_2$	" " " " " " " curve: $r\,r_4$
L + $NH_4\,NO_3$ + $Ag\,NH_4\,(NO_3)_2$	" " " " " " " " $q\,q_4$

On looking at these equilibria several questions arise one of which I will mention. If, for instance we know that in the ternary system water, silver nitrate, ammonium nitrate, of which both salts are anhydrous, an anhydrous double salt occurs at 30° we may ask ourselves what equilibria will occur if the water is substituted by another solvent such as aqueous or absolute alcohol.

It is impracticable to answer this question in its entirety; if, however, we argue that no solid phases are formed which crystallise with the new solvent it becomes a fairly easy one. As a rule we can demonstrate that the same three saturation lines will occur also in the new solvent so that a solution saturated with the two components or solutions saturated with another double salt cannot be formed.

Therefore, although the same double salt must appear in both solvents, its behaviour in regard to the two pure solvents, may however, be quite different and various cases may occur; it may, for instance be soluble in both solvents without decomposition or it may be that, as in the case mentioned, it is soluble in the one solvent without and in the other with decomposition; or it may dissolve in both solvents with decomposition. In the latter event we may meet with two more cases; it may be that the same component is deposited from both solvents or it may be that one of the components is deposited from the one and the other from the other solvent.

Similar equilibria occur also at 30° in the systems:

water — alcohol — silver nitrate — potassium nitrate

and water — alcohol — benzoic acid — ammonium bezoate.

In the first system occurs a double salt of silver nitrate and potassium nitrate; in the latter, which is being investigated by Dr. H. Filippo, a combination of benzoic acid and ammonium benzoate is formed.

In the system: water, alcohol, ammonium sulphate and manganese sulphate quite different equilibria occur. The results of this investigation for 50° are represented in fig. 3; this is again the projection of the tetrahedron on a plane parallel to the sides *WA* and *MnN*. The angular points *W*, *A*, *N* and *Mn* indicate the components: water, alcohol, ammonium sulphate and manganese sulphate.

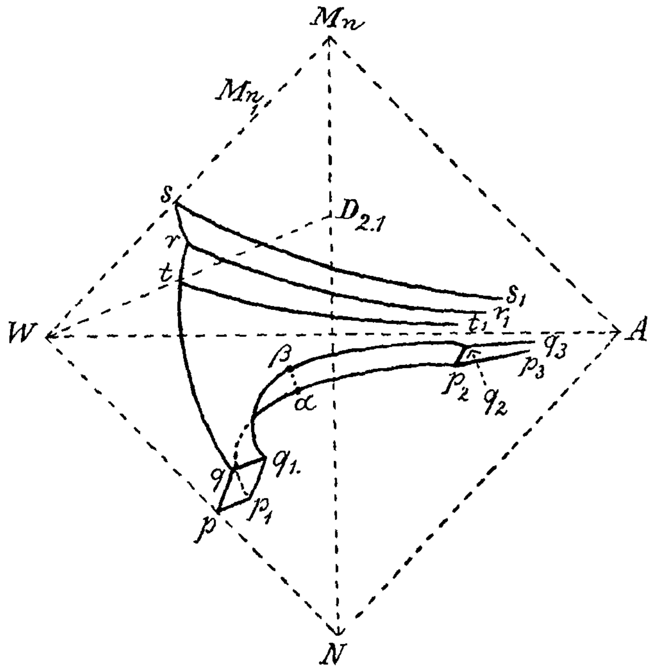

Fig. 3.

In this system an anhydrous compound $(Mn\,SO_4)_2\,(NH_4)_2\,SO_4$ occurs at 50° which is represented in the figure by the point D_2. The $Mn\,SO_4$ gives at that temperature the compound $Mn\,SO_4 . H_2O$, represented by the point Mn_1.

On the side plane *MnWN* we find the equilibria in the ternary system water, manganese sulphate, ammonium sulphate. Three saturation lines are found: *sr* is that of the $Mn\,SO_4 . H_2O$, *rtq* that of the double salt D_2, and *qp* that of the $Mn\,SO_4$. As the line WD_2, intersects the saturation line of the double salt in *t* this is soluble in water without decomposition; *t* represents this saturated solution.

The isotherm ss_1 which indicates the equilibria in the ternary system water, alcohol, manganese sulphate consists of two saturation lines of which only one ss_1 has been determined. This indicates the solution saturated with $Mn\,SO_4 . H_2O$; to this should join a saturation line with the anhydrous $Mn\,SO_4$ as solid phase which however, has not been determined.

The equilibria occurring in the ternary system: water, alcohol, ammonium sulphate are represented in the plane WAN by the isotherm $pp_1ap_2p_3$; this consists of the saturation lines pp_1 and p_2p_3 of the ammonium sulphate and of the branch p_1ap_2 of a binodal line with the critical liquid a. The points p_1 and p_2 therefore represent two ternary conjugated liquids saturated with ammonium sulphate.

The quaternary equilibria are represented by four surfaces:

srr_1s_1 is the saturation surface of the $Mn\,SO_4 . H_2O$

$rtqq_1\beta q_2q_3r_1$ is the saturation surface of the $D_{2.1}$

qpp_1q_1 and $q_2p_2p_3q_3$ are the saturation surface of the ammonium sulphate

$p_1ap_2q_2\beta q_1$ is the binodal surface.

The latter surface is divided in two parts by the critical line $a\beta$; with each point of the one part, a point of the other is conjugated; a similarly conjugated pair of points represents a pair of quaternarly conjugated liquid phases. The binodal surface, therefore, represents the equilibria liquid + liquid. The sections of the four saturation surfaces give three saturation lines.

rr_1 represents the solutions saturated with $Mn\,SO_4 . H_2O + D_{2.1}$

qq_1 and q_2q_3 represent ,, ,, ,, ,, $(NH_4)_2\,SO_4 + D_{2.1}$

$q_1\beta q_2$ represents the conjugated liquid pairs saturated with ammonium sulphate. The point β is the critical solution saturated with ammonium sulphate.

If a plane is brought through the side WA and the point $D_{2.1}$ this intersects as far as has been determined the saturation surface of $D_{2.1}$ in the curve tt_1; the double salt is therefore not only soluble in water but also in dilute alcohol without decomposition.

At 25° quite different equilibria occur in this system; on the side plane $W\,Mn\,A$ a new area of immiscibility is developed. At the same time the double salt $D_{2.1} = (Mn\,SO_4)_2\,(NH)_4)_2\,SO_4$ disappears in order to make room for the double salt $Mn\,SO_4 . (NH_4)_2\,SO_4 . 6H_2O$. The resulting equilibria much resemble those mentioned previously which occur at 30° in the system: water, alcohol, ammonium sulphate and lithium sulphate.

I will therefore not discuss these equilibria any further.