Chemistry. — *"On a tetracomponent system with two liquid phases."* By Prof. F. A. H. SCHREINEMAKERS.

(Communicated in the meeting of January 26, 1907).

Although in the systems of three components with two and three liquid phases there may occur many cases which have been predicted by theory, but have not yet been realised by experiment, I have still thought it would be as well to investigate a few systems with four components to have a glance at this as yet quite unknown, region.

I will now describe more fully a few of those systems built up from the substances: water, ethyl alcohol, lithium sulphate and ammonium sulphate.

We may represent the equilibria with the aid of a regular tetrahedron as in Fig. 1; the angular points represent the four components:
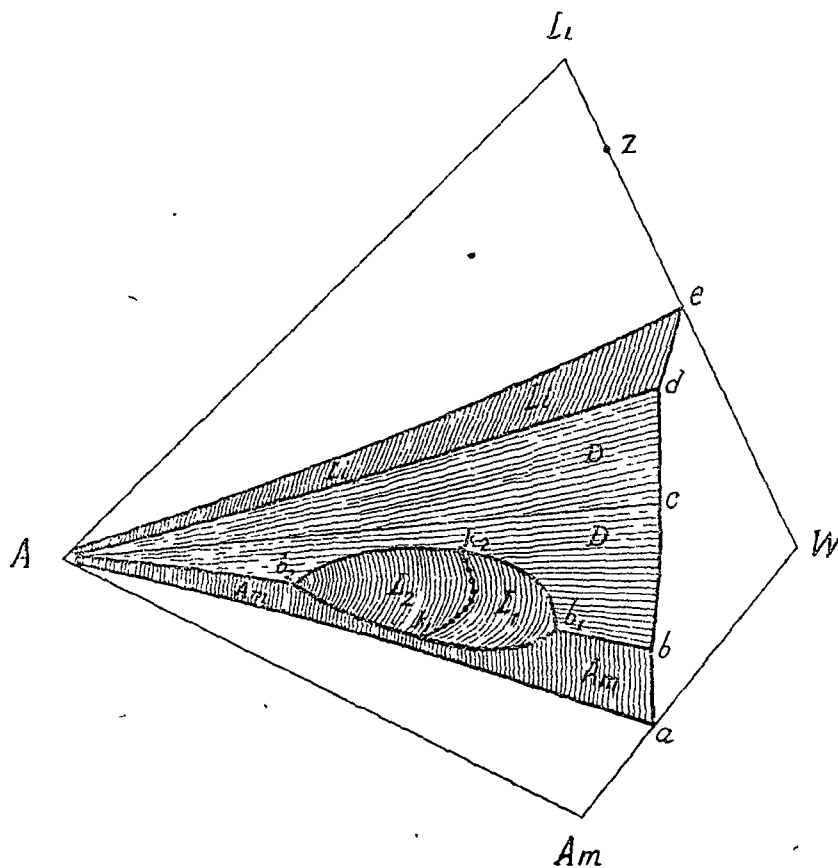

Fig. 1.

W = water, A = alcohol, Li = lithium sulphate, Am = Ammo-

nium sulphate. The side AW being invisible has been left out, also the side $Li\,Am$.

$Li_2SO_4.\,H_2O$ and the double salt $LiNH_4SO_4$ may also occur as solid phases besides Li_2SO_4 and $(NH_4)_2SO_4$. The first is represented by a point Z on the side LiW, the second by a point D, not indicated, on the side $Li\,Am$.

The equilibria occurring at $6°5$ are represented schematically by Fig. 1. The solubilities of the $(NH_4)_2SO_4$ and of the $Li_2SO_4.\,H_2O$ in water are indicated by the points a and e; point c indicates the solubility in water of the double salt and must, therefore, be situated on the line WD (the point D is on the side $Li\,Am$). As Li_2SO_4, $(NH_4)_2SO_4$ and $LiNH_4SO_4$ are practically insoluble in alcohol, their solubility may be represented practically by the point A.

The curve aA is the saturation line of the $(NH_4)_2SO_4$; it indicates the aqueous-alcoholic solutions which are saturated with solid $(NH_4)_2SO_4$.

The aqueous-alcoholic solutions saturated with Li_2SO_4 and $Li_2SO.H_2O$ are represented by the curve eA which, however, must show a discontinuity in the immediate vicinity of the point A, for the curve consists of two branches, of which the one to the right indicates the solutions saturated with $Li_2SO_4.\,H_2O$ and the one to the left those saturated with anhydrous Li_2SO_4.

The equilibria in the ternary system: water, lithium sulphate and ammonium sulphate are represented by the curves ab, bcd and de, which are situated in the side plane of the tetrahedron. ab is the saturation line of the ammonium sulphate, bcd that of the double salt $LiNH_4SO_4$, de that of $Li_2SO_4.\,H_2O$. In my opinion, however, this latter is not quite correct, for, according to several analyses, Lithium sulphate seems to mix with the ammonium sulphate, although only to the extent of a few per cent, so that branch de indicates solutions saturated with mixed crystals. As, however, I have not accurately investigated this mixing, I will continue to speak in future of lithium sulphate monohydrate $Li_2SO_4.\,H_2O$.

Let us now look at the equilibria in the quaternary system. The surface Am or $Aabb_1k_1b_3A$ represents solutions saturated with solid ammonium sulphate; surface D or $Ab_2k_2b_1bcdA$ represents the solutions saturated with $LiNH_4SO_4$; the curve Ac of this surface has as pecial significance, because it indicates the solubility of $LiNH_4SO_4$ in aqueous-alcoholic mixtures. The points of the surface D facing the curve Ac represent solutions which, in relation to the double salt, contain an excess of $(NH_4)_2SO_4$; the points behind this line show solutions containing an excess of Li_2SO_4.

The curve Ac must therefore, be situated in the plane passing through AW and the point D of the side $Li\,Am$. The surface Li or Ade indicates the liquid saturated with Li_2SO_4 or $Li_2SO_4H_2O$, or with the above mentioned mixed crystals; it must, therefore, consist of different parts which however, are not further indicated in the figure. At the temperature mentioned here (6°5) systems of two liquid phases may occur also; in the figure these are represented by the surface L_1L_2 or $b_1K_1b_2K_2$ which we may call the binodal surface; this binodal surface is divided by the line K_1K_2 into two parts L_1 and L_2 in such a manner that each point of L_1 is conjugated with a point of L_2. Two conjugated points indicate two solutions in equilibrium with each other: with each solution of the surface L_1 a definite solution of the surface L_2 may be in equilibrium.

Instead of a critical point, such as occurs with ternary mixtures at a constant temperature and pressure, a critical line is formed here, represented by K_1K_2. Each point of this line represents, therefore, a solution which is formed because in the system of two liquid phases $L_1 + L_2$ the two liquid phases become identical. Let us now look at the sections of the different surfaces: Ad then represents the solutions saturated with $LiNH_4SO_4$ as well as with $Li_2SO_4H_2O$; Ab_2 and b_1b indicate the liquids saturated with $LiNH_4SO_4$ and $(NH_4)_2SO_4$.

The intersection of the binodal surface with the surface Am namely, the curve $b_1K_1b_2$ indicates the system: $L_1 + L_2 + (NH_4)_2SO_4$ namely, two liquid phases saturated with solid ammonium sulphate. With each point of the curve b_1K_1 a point of b_2K_1 is conjugated. Each liquid of b_1K_1 may, therefore, be in equilibrium with a definite liquid of b_2K_1 while both are saturated with solid $(NH_4)_2SO_4$.

The intersection of the binodal surface with the surface D, namely, the curve $b_1k_2b_2$ represents the solutions of the system $L_1 + L_2 + Li$ NH_4SO_4. With each liquid of b_1k_2 another one of b_2k_2 may, therefore, be in equilibrium while both are saturated with solid $Li\,NH_4SO_4$.

The points of intersection b_1 and b_2 of these two curves give the system: $L_1 + L_2 + (NH_4)_2SO_4 + Li\,NH_4SO_4$, namely two liquids both saturated with ammonium sulphate and lithium ammonium sulphate which may be in equilibrium with each other.

The points k_1 and k_2 have a special significance; both are critical liquids which, however, are distinguished from the other critical liquids of the critical curve k_1k_2 in that they are also saturated with a solid substance: k_1 is saturated with ammonium sulphate and k_2 with lithium ammonium sulphate.

If the temperature is raised the heterogeneous sphere is extended;

at about ± 8° the point k_1 arrives on the side $AWAm$, so that above this temperature a separation of water-alcohol-ammonium sulphate may occur in the ternary system.

I have further closely investigated at 30° the equilibria occurring in this quaternary system; the results are represented by the schematic figure 2.

The saturation surface Am which at 6°.5 still consists of a coherent whole, now consists (experimentally) of two parts separated from each other: this is because the binodal surface L_1L_2 now terminates on the side plane $AWAm$ in the curve $a_1k_1a_2$.
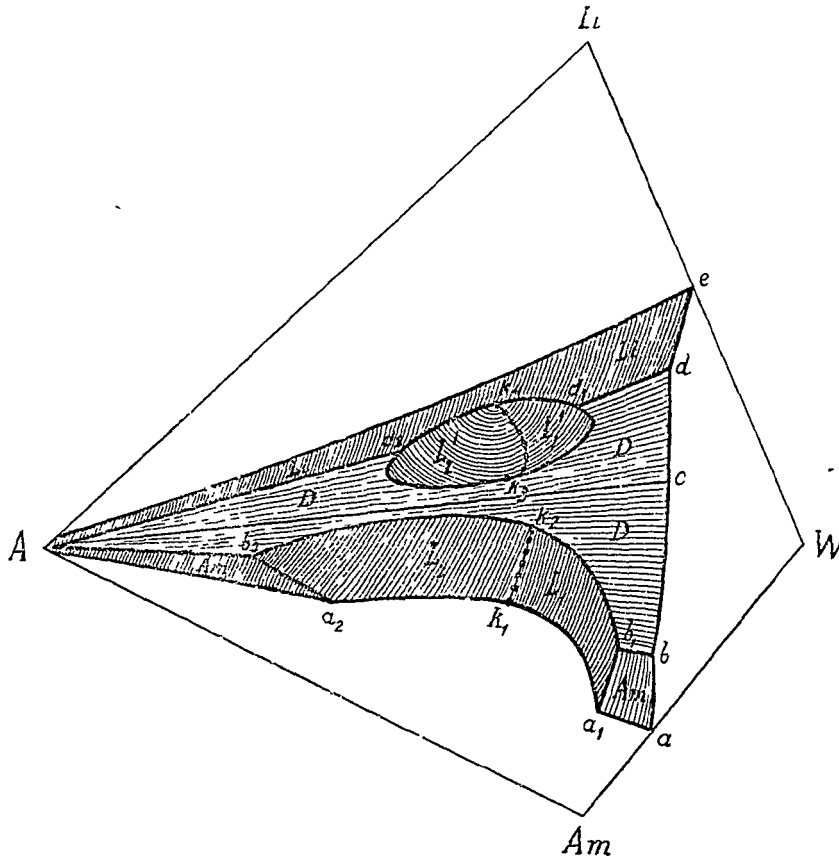

Fig. 2.

Of the critical line k_1k_2 the terminal point k_1 represents a ternary critical liquid; all other liquids of this line are quaternary critical ones, of which k_2 is saturated with solid lithium ammonium sulphate.

The phenomenon of the existence of a second heterogeneous region at this temperature was quite unexpected; it is represented in the figure by the binodal surface $L_1^1L_2^1$ or $d_1k_4d_2k_3$ with the critical line k_3k_4. I have not further investigated at what temperature this is formed; it is sure to be present at about 18°.

The binodal surface $L_1 L_2$ intersects the saturation surfaces Am and D; we have, therefore, one series of two liquid phases, saturated with solid $(NH_4)_2SO_4$, and one series saturated with solid $LiNH_4SO_4$. The binodal surface $L_1{}^1 L_2{}^1$ intersects the two saturation surfaces D and Li. We have, therefore, one series of two liquid phases saturated with $LiNH_4SO_4$ (curve $k_3 d_1$ and $k_3 d_2$), and one series saturated with $Li_2SO_4 . H_2O$ (curve $k_4 d_1$ and $k_4 d_2$). By d_1 and d_2 are represented two liquid phases which are in equilibrium with each other and saturated with $LiNH_4SO_4$ and $Li_2SO_4 . H_2O$. Of the series of the critical liquids represented by the curve $k_3 k_4$, k_3 is saturated with $LiNH_4SO_4$ and k_4 with $Li_2SO_4 . H_2O$.

The curve Ac which indicates the liquids saturated with $LiNH_4SO_4$ without any excess of either of the components runs between the two heterogeneous regions. From this it follows that this double salt at 30° cannot give two liquid phases with water-alcohol mixtures.

We, therefore, have at 30° the following equilibria in the quaternary system.

<center>liquids saturated with</center>

1. $(NH_4)_2SO_4$,   represented by the surface Am
2. $LiNH_4SO_2$,   „   „ „ „ D
3. $Li_2SO_4 H_2O$,   „   „ „ „ Li
4. $(NH_4)_2SO_4$ and $LiNH_4SO_4$ „   „ the curves: bb_1 and $b_2 A$
5. $Li_2SO_4 H_2O$ and $LiNH_4SO_4$ „   „ „ „ dd_1 and $d_2 A$

<center>system of two liquid phases :</center>

6. in itself represented by the surface $L_1 L_2$
7. „ „ „ „ „ „ $L_1{}' L_2{}'$
8. saturated with $(NH_4)_2SO_4$, represented by the curves $a_1 b_1$ and $a_2 b_2$
9. „ „ $LiNH_4SO_4$, „ „ „ „ $b_1 K_2$ and $b_2 K_2$
10. „ „ $LiNH_4SO_4$, „ „ „ „ $d_1 K_3$ and $d_2 K_3$
11. „ „ $Li_2SO_4 H_2O$, „ „ „ „ $d_1 K_4$ and $d_2 K_4$

<center>two liquid phases saturated with :</center>

12. $(NH_4)_2SO_4$ and $LiNH_4SO_4$, represented by the points b_1 and b_2
13. $Li_2SO_4 H_2O$ and $LiNH_4SO_4$, „ „ „ „ d_1 and d_2

<center>critical liquids :</center>

14. one series represented by the curve $K_1 K_2$
15. „ „ „ „ „ „ $K_3 K_4$
16. one critical liq. saturated with $LiNH_4SO_4$, represented by the point K_2
17. „ „ „ „ „ $LiNH_4SO_4$, „ „ „ „ K_3
18. „ „ „ „ „ $Li_2SO_4 H_2O$, „ „ „ „ K_4

On raising the temperature over 30' the two heterogeneous regions gradually approach each other and finally unite; at what temperature this happens has not been determined, but from the experiments it is shown that this is already the case below 40'; I have also not been able to determine whether this point of confluence is situated in front or behind the curve Ac, or perhaps accidentally on the same.

I have closely investigated the equilibria occurring at 50° and represented the same by figure 3; any further explanation is super-
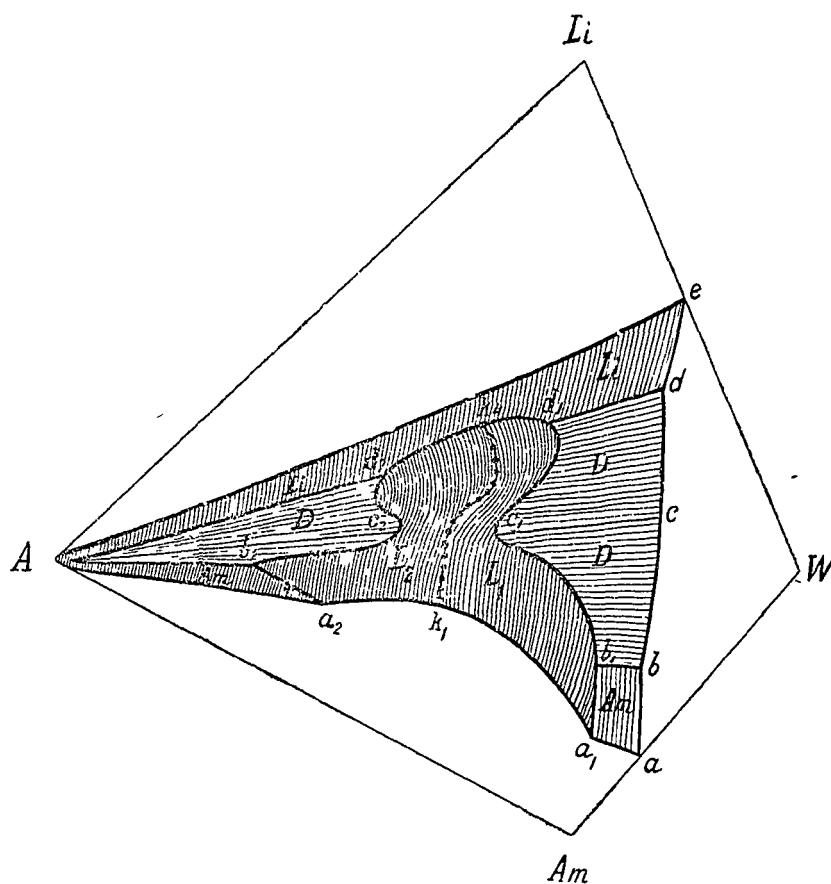

Fig. 3.

fluous. I must, however, say something as to the points c_1 and c_2, namely the intersecting points of the curve Ac with the saturating curve of the two liquid phases $b_1 d_1$ and $b_2 d_2$. At first sight we might think that these two liquids may be in equilibrium with each other. That possibility, of course, exists. Suppose we take a water-alcohol mixture of such composition that two liquid phases occur on saturating with $LiNH_4SO_4$. Both liquids will now contain Li_2SO_4

and $(NH_4)_2SO_4$ and it is evident that two cases may occur. It may be that the two liquids contain the two components in the same proportion as they occur in the double salt; it is then as if the double salt dissolves in both liquids without decomposition. If this is the case the liquids c_1 and c_2 will be in equilibrium with each other.

The second possibility is that one of the liquids has in regard to the double salt an excess of Li_2SO_4 and the other, therefore, an excess of $(NH_4)_2SO_4$; in this case, c_1 and c_2 cannot be in equilibrium with each other. The experiment now shows such to be the case. When I saturated a water-alcohol mixture with $LiNH_4SO_4$ at $50°$, the alcoholic layer contained a small excess of Li_2SO_4 and the aqueous layer a small excess of $(NH_4)_2SO_4$. From this it follows that the conjugation line does not coincide with the surface $DA\,W$ but intersects it; the part to the right of the line must be situated in front of the plane and the left part behind it. The alcoholic solution c_2 of the double salt cannot, therefore, be in equilibrium with the aqueous solution c_1 of this double salt, but may be so with a solution containing an excess of $(NH_4)_2SO_4$.

Chemistry. "*On catalytic reactions connected with the transformation of yellow phosphorus into the red modification.*" By Dr. J. Böeseken. (Communicated by Prof. A. F. Holleman).

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I.

From the researches of Hittorf (Pogg. Ann. 126 pag. 193) Lemoine (Ann. Ch. Ph. [4] 24. 129) Troost and Hautefeuille (Ann. Ch. Ph. [5] 2 pag. 153), R. Schenck (B. Ch. G. 1902 p. 351 and 1903 p. 970) and the treatises of Naumann (B. Ch. G. 187 2p. 646), Schaum (Lieb. Ann. 1898. 300 p. 221), Wegscheider and Kaufler (Cent. Blatt 1901 I p. 1035) and Roozeboom (Das heterogene Gleichgewicht I p. 171 and 177) it appears highly probable that red phosphorus is a polymer of the yellow variety, which polymerism is, however, restricted exclusively to the liquid and the solid conditions: the vapour (below $1000°$) always consists of the monomer P_4.

From the above considerations it moreover follows that the yellow phosphorus is metastable at all temperatures below the melting point of the red phosphorus ($630°$); it may, therefore, be expected that it will endeavour to pass into the red variety below $630°$.