

Citation:

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proportion had fallen to 4,64 H_2O , and for the next three months this proportion varied according to the vapour-tension of the air, between 4,64 and 4,55 H_2O . Unaltered weight, rising or falling were found to agree with the indications of the hygrometer (of KLINKERFUES). Meanwhile a little decline was observable. If the vapour-tension of the air, which in that time varied between 10 and 8 m.m. had fallen to 7 m.m. and had remained stationary for some time, the composition $\pm 4 \text{H}_2\text{O}$ would have been attained. For this amount has been obtained in the Gel I after some months at *that* vapour-tension. That composition would have risen but little if the vapour-tension of the air had become again greater.

That the composition depends on the temperature, that the power of absorption is weakened by heating to higher temperatures, and is destroyed at incandescence, all this I have already communicated before ¹⁾.

Dr. KLOBBIE and I have only succeeded in observing the transition of colloidal ferric oxide to a crystalloidal chemical hydrate in case of monohydrate²⁾, by the influence of water at 15° on the hexagonal crystals of the chemical compound $\text{Fe}_2\text{O}_3 \cdot \text{Na}_2\text{O}$, in which Na_2O is gradually replaced by H_2O without the crystalline structure (form, transparency, power of polarisation) being modified. Nature provides us with the crystalline Monohydrate: Göthit, that can bear heating to $\pm 280^\circ$ without losing water and without passing into the amorphous state ³⁾.

Chemistry. — MR. VAN BEMMELEN presents in the name of MR. B. DE BRUIJN a paper on an investigation held in the Inorganic Chemical Laboratory of the University of Leyden, concerning: „*The equilibrium of systems of three substances, in which two liquids occur*”.

In systems of three components, in which two liquid phases occur, the following cases may be distinguished:

1st. the components A and B form together two liquid phases; equally so the components A and C and B and C.

2nd. the components A and B and A and C form two liquid phases, but the components B and C do not, at least in stable conditions.

¹⁾ Recueil **7**. 111—113. Zeitschr. anorg. Ch. **18**. 24.

²⁾ J. f. pr. Ch. **46** 523—529.

³⁾ J. f. pr. Ch. **46**. 521.

3^d. only the phases A and B form two liquid phases ; A and B or B and C do not do so, at least in stable conditions.

4th. the components in pairs never give two liquid phases at least in a stable condition.

Examples of the first three cases have been investigated by SCHREINEMAKERS ¹⁾; purpose of this investigation was to examine also an example of the last mentioned case. Not until the investigation was nearly finished, did there appear an essay by SNELL on potassiumchloride, acetone and water, by which an example of the fourth case is given ²⁾.

Mr. DE BRUIJN examined the equilibriums in the following systems:

Ammoniumsulphate, ethylalcohol and water.

Potassiumcarbonate, methylalcohol and water.

Potassiumcarbonate, ethylalcohol and water.

Sodiumsulphate, ethylalcohol and water.

Guided by the theory of SCHREINEMAKERS on equilibriums in systems of three components, in which two liquid phases occur, he succeeded in making a sketch of the equilibriums in the systems examined. The composition of the phases is represented in the usual manner by means of a triangle; if the temperature-axis is placed vertically on the plane of the triangle, we get a representation in space.

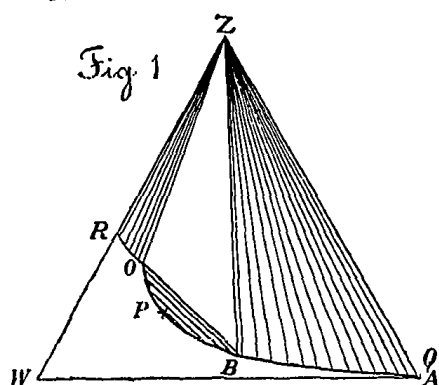
I. *The system: ammoniumsulphate, ethylalcohol and water.*

Above $\pm 8^\circ$ the general form of the isothermals is as given in fig. 1. The isothermal consists namely of three parts: RO, OPB and BQ, meeting in O and B in an angle. RO and BQ indicate all possible solutions, that can be in equilibrium with the solid $(\text{NH}_4)_2\text{SO}_4$. OPB is the connodal line with the plait-point P; it indicates therefore the solutions that coexist; the points O and B are the two liquid phases which are not only in equilibrium with each other, but also with solid $(\text{NH}_4)_2\text{SO}_4$. In case of a change in the temperature the different parts of the isotherm are displaced; at a higher temperature $\angle \text{OZB}$ increases; at a fall in the temperature $\angle \text{OZB}$ diminishes till at $\pm 8^\circ$ the lines OZ and ZB coincide. The points O, B and P coinciding at this temperature, the isothermal consists at this and lower temperatures of only one curve RO and BQ coming in each other's prolongation; there remain therefore only the equilibriums of solid salt with solution. Mr. DE BRUIJN has determined such an isothermal at $6,5^\circ$. Two liquid

¹⁾ Zeitschr. f. phys. Chem. **25** 543 **26** 237 **27** 95 (1898) **23** 417 (1897).

²⁾ Journ. of phys. Chem. **2** 457 (1898).

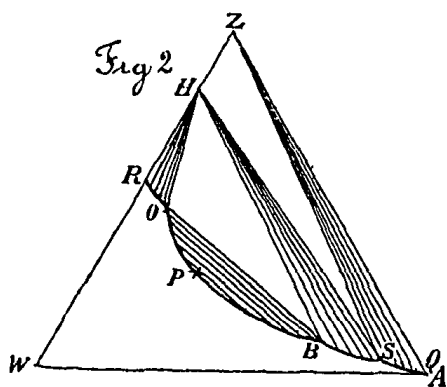
phases are no longer possible in a stable equilibrium. It is true that Mr. DE BRUIJN has noticed them several times, but they disappeared at the appearance of the solid phase.



Mr. DE BRUIJN has also determined several isothermals at higher temperatures, where the isothermals have forms as in fig. 1. As to the connodal lines for the different temperatures, it was proved, that they intersect each other in different manners or cover each other within the limits of the faults of analysis. In order to further investigate this point several sections were determined, in which the proportion of water and alcohol was the same, but the quantity of $(\text{NH}_4)_2\text{SO}_4$ varied. In accordance with the situation of the connodal lines with respect to each other Mr. DE BRUIJN found the following facts. If the proportion of $(\text{NH}_4)_2\text{SO}_4$ is taken for the ordinate and for the abscis the temperature at which two liquid phases become homogeneous or a homogeneous liquid phase is divided into two others, we get, with a greater proportion of alcohol, lines rising with the temperature; with a smaller proportion of alcohol, lines falling with the temperature, between the two, lines showing a maximum, which moves toward a higher temperature with a greater proportion of alcohol. From these different sections follows in accordance with the isothermals given, that it is possible to have solutions of $(\text{NH}_4)_2\text{SO}_4$ in water and alcohol that are homogeneous at a certain temperature, but divide into two layers both in case of a rise and of a fall in the temperature. Mr. DE BRUIJN has made several of these solutions.

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II. The system: Potassiumcarbonate, methylalkohol and water.



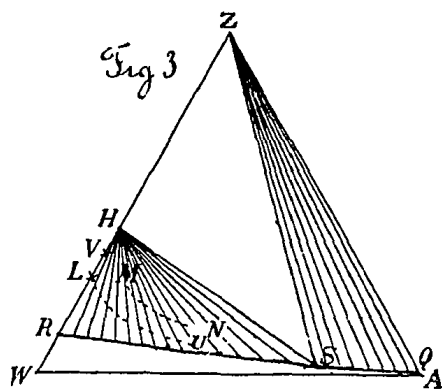
Next to the two liquid phases there appears in this system as a solid phase the hydrate $(\text{K}_2\text{CO}_3)_2(\text{H}_2\text{O})_3$ (at lower temperatures perhaps a still higher hydrate). The isotherm has here the form of fig. 2. RO and BS indicate the solutions that can be in equilibrium with $(\text{K}_2\text{CO}_3)_2(\text{H}_2\text{O})_3$; SQ the solutions in equilibrium with

K_2CO_3 ; OPB is the connodal line with the plait-point P; with each liquid phase of part OP one of PB can be in equilibrium. Mr. DE BRUIJN has determined the situation of the connodal-line OPB at different temperatures. Just as in the preceding system the points O and B approach each other when the temperature is lowered; in the preceding system they met at $\pm 8^\circ$; in this system however no earlier than at $\pm -33^\circ$.

III. *The system: Potassiumcarbonate, ethylalkohol and water.*

The isotherm has here the same form as in the preceding system. The composition of the two liquid phases in equilibrium with the hydrate was determined at temperatures of -18° to 75° . The proportion of salt rises with the temperature, that of alcohol changes less than the amount of the faults of analysis. That a change in the composition of the two liquid phases does however decidedly take place when the temperature is changed may be deduced from the observation, that such homogeneous solutions divide into two liquid phases at a change in the temperature. Different pairs of conjugated points were determined on the connodal line at 17° and at 35° . The connodal lines for different temperatures intersect here too. Sections, as in the case of ammoniumsulphate are not determined here; from a single observation made by SNELL it may be deduced that these sections will not show a maximum here but a minimum.

A great difference in the conduct of methyl- and ethylalcohol is shown by what follows. At 17° the upper layer contains in equilibrium with the solid phase 91,5 pCt. ethylalcohol and 0,06 pCt. K_2CO_3 ; the lower-layer 0,2 pCt. ethylalcohol and 55,2 pCt. K_2CO_3 . The ethylalcohol and the potassiumcarbonate form therefore each of them, with part of the water, a liquid in which the other component hardly occurs. In the system K_2CO_3 , CH_3OH and H_2O the upper layer contains however at the same temperature 69,6 pCt. methylalcohol and 6,25 pCt. K_2CO_3 . the lower layer 5,7 pCt. methylalcohol and 48,4 pCt. K_2CO_3 . Another great difference in the conduct of methyl- and ethylalcohol in these systems is the following. In the system with ethylalcohol the temperature has hardly any influence on the position of the points O and B; the proportion of water and alcohol remaining in two liquid phases, that are in equilibrium with the solid hydrate of K_2CO_3 , nearly unaltered from -18° to $+75^\circ$. In the system with methylalcohol the temperature has on the other hand a great influence on the proportion of water and methylalcohol, the latter being more miscible in presence of the solid salt than water and ethylalcohol.

IV. *The system sodium sulfate, ethylalcohol and water.*

In this system Mr. DE BRUIJN investigated besides the stable equilibria also some less stable ones. Fig. 3 indicates the general form of the isothermals below $32^{\circ}5$; the drawn curves RS and SQ show the stable equilibria, the dotted curves LU and MN the less stable ones. RS indicates the solutions that can be in equilibrium with solid $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; SQ the solutions in equilibrium with Na_2SO_4 . S is the solution in equilibrium with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and Na_2SO_4 . At a rise in the temperature the point S moves to the left and upwards and at $32^{\circ}5$ joins R in V, this point indicating the composition of the aqueous solution that can be in equilibrium with solid $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and Na_2SO_4 . When the temperature rises, the line RS therefore dwindles, while SQ is prolonged; at $32^{\circ}5$ RS disappears and only SQ is left, while S falls on the line WZ. Mr. DE BRUIJN has determined these isothermals for different temperatures experimentally.

Besides the stable equilibria mentioned above viz. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{solution}$ and $\text{Na}_2\text{SO}_4 + \text{solution}$ Mr. DE BRUIJN also determined the less stable system $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O} + \text{solution}$. The solutions in equilibrium with the hydrate $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ are represented by line LU (fig. 3). The latter being situated entirely above the curve RS, the solutions pass into a solution of RS, if the less stable condition ceases to exist.

If it was possible for two liquid phases in stable condition to appear in the systems of equilibrium mentioned above, this is no longer the case here. But on the other hand it is easy to get these systems, if care is only taken that neither Na_2SO_4 nor $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, nor $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ can come in contact with the two liquid phases. Consequently Mr. DE BRUIJN has succeeded in determining the connodal lines for different temperatures; care being however taken to prevent the liquid phases to come in contact with the air. If the latter happened or if only a particle of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was introduced, the crystallisation of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ followed at once, and the two layers passed into one. That this must necessarily be the case is shown by fig. 3, the connodal line MN, determined by Mr. DE BRUIJN being situated not only above RS, but even above LU.