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**Chemistry.** — “*On Milk-Sugar*”. I. By Prof. A. SMITS and J. GILLIS. (Communicated by Prof. S. HOOGWERFF).

(Communicated in the meeting of June 30, 1917).

### 1. *Introduction.*

When in 1880 SCHMOEGER <sup>1)</sup> and ERDMANN <sup>2)</sup> began their investigations about milk sugar, besides the hydrate, an anhydride was known, which was obtained by heating the hydrate in a drying stove at 125°. Later on this anhydride, in contradistinction to another anhydrous modification, was called the  $\alpha$ -form. This other anhydrous modification, the  $\beta$ -form, was obtained by SCHMOEGER and ERDMANN by evaporation of a saturate solution of milk sugar at the boiling temperature ( $\pm 108^\circ$ ).

That this was another anhydrous modification than the  $\alpha$ -form followed from this that while the  $\alpha$ -modification is very hygroscopic, gives a clear *generation of heat* when brought into water, and yields a solution, the optic rotatory power of which *decreases* with the time, the  $\beta$ -modification on the contrary is not hygroscopic, dissolves under *heat-absorption* and yields a solution, the rotation of which *decreases* with the time.

HUDSON <sup>3)</sup> was the first to consider the problem offered by the milksugar, from a physico-chemical point of view. He demonstrated that whatever form of the milk-sugar is dissolved in water, the final condition is always the same, and represents an equilibrium.

HUDSON showed further that the muta-rotation has the same course as a mono-molecular reaction; he determined on one side  $k_1 + k_2$ , on the other side  $k_2$ , and thus found  $k_1$  indirectly; in this way he got  $K' = \frac{k_1}{k_2} = 1,6$  for the constant of equilibrium at  $11^\circ, 2$ .

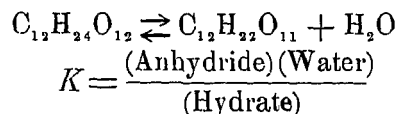
HUDSON started from the supposition that the hydrate possessed a high rotation, and the  $\beta$ -anhydride a low rotation, and he was of opinion therefore that the said equilibrium was to be represented by the equation:

<sup>1)</sup> Berichte 13 1915 (1880).

<sup>2)</sup> Berichte 18 2180.

<sup>3)</sup> Zeitschr. Phys.-Chem. 44 487 (1903).

or



or

$$K' = \frac{(\text{Anhydride})}{(\text{Hydrate})}$$

Through the slow setting in of the internal equilibrium in solution milk-sugar hydrate presents the remarkable phenomenon that the initial solubility is much smaller than the final solubility.

As, when the total concentration is not too great, it may be assumed as certain that the concentration of the hydrate in the solution in equilibrium with the solid hydrate, remains permanently the same, the constant of equilibrium will follow from the determination of initial and final solubilities, for then:

$$\frac{\text{final solubility} - \text{initial solubility}}{\text{initial solubility}} = \frac{(\text{Anhydride})}{(\text{Hydrate})} = K'.$$

In this way was found  $K' = 1.44$  at  $15^\circ$ <sup>1)</sup>, hence a value which is considerably smaller than that found from the reaction velocities, from which it therefore follows that the total concentration for this determination of  $K'$  was already too great.

From initial and final rotation of hydrate and  $\beta$ -anhydride also the constant  $K'$  can be determined.

HUDSON found  $[\alpha]_{20}^D = 86^\circ,0$  as initial rotation for the hydrate, and  $[\alpha]_{20}^D = 35^\circ,4$  for the  $\beta$ -anhydride. On the other hand the value  $55^\circ,3$  had already been fixed for the final rotation by SCHMOEGER.

From this follows for  $20^\circ$ <sup>2)</sup>:

$$K' = \frac{86,0 - 55,3}{55,3 - 35,4} = 1.54$$

a value which lies between the two others.

In consequence of the slow setting in of the internal equilibrium in the solution it was possible to determine the initial solution heats of the different modifications, and likewise the heats of the transformation of the hydrate and of the  $\alpha$ -anhydride in the  $\beta$ -anhydride in dissolved state.

In this HUDSON and F. C. BROWN<sup>3)</sup> succeeded according to a method of H. T. BROWN and PICKERING<sup>4)</sup>.

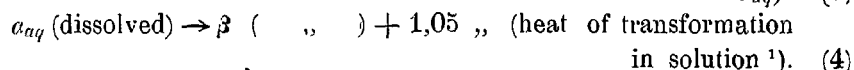
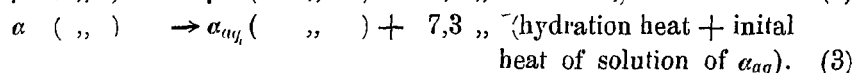
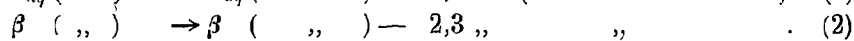
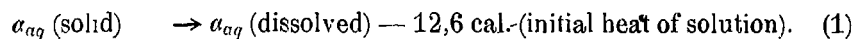
<sup>1)</sup> J. Amer. Chem. Soc. 26 1074 (1904).

<sup>2)</sup> J. Amer. Chem. Soc. 30 1781 (1908).

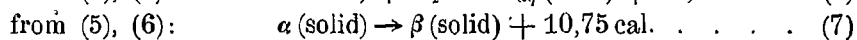
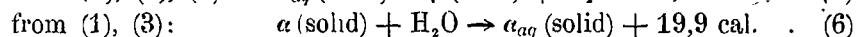
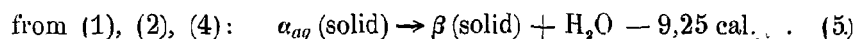
<sup>3)</sup> J. Amer. Chem. Soc. 30 960 (1908).

<sup>4)</sup> Chem. Soc. 71, 782 (1897).

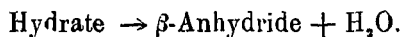
The following results refer to 1 gram of anhydrous milk sugar and to the temperature of 20°.



From these data the following calculation can be made:



In these determinations HUDSON found also that the difference between initial and final heat of solution, both starting from  $\alpha$ -anhydride and from hydrate, had exactly the same value, from which, therefore, follows that  $\alpha$ -anhydride in contact with water *hydrates immediately*, and that then the following slow conversion takes place:



We also come to the same conclusion when we consider that  $\alpha$ -anhydride and hydrate show the same initial rotation.

HUDSON has also determined the temperature where the transformation of hydrate to  $\beta$ -anhydride takes place, i.e. he determined the temperature at which the coexistence  $S_H + S_\beta + L$  occurs.

From the final solubility of the hydrate between 0° and 89° and from two final solubilities (0° and 100°) of the  $\beta$ -anhydride followed 92° as transformation temperature.<sup>1)</sup>

He further determined this point from the intersection of the three-phase lines of  $S_H + L + G$  and  $S_H + S_\beta + G$ , and then the temperature of the quadruple point  $S_H + S_\beta + L + G$  was found at 94°.

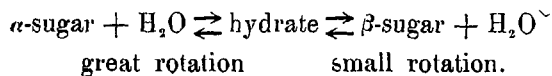
Attempts to determine the transformation point thermically and dilatometrically proved unavailing, because of the exceedingly small velocity of conversion.

On the ground of these data HUDSON in 1910 drew up a general theory of muta-rotation<sup>2)</sup>, which for all sugars can be given schematically as follows:

<sup>1)</sup> In this the situation of the equilibrium at 20° has been taken into account.

<sup>2)</sup> J. Amer. Chem. Soc. **30** 1775 (1908).

<sup>3)</sup> J. Amer. Chem. Soc. **33** 893 (1910).



The equilibrium 1 sets in with great velocity, whereas equilibrium 2 does so slowly, so that the mutarotation lies in the second equilibrium process.

## 2. *Experimental part.*

*a. Inquiry into the stability of the occurring solid phases; determination of the transformation point Hydrate— $\beta$ -anhydride + solution.*

This was the state of affairs when we began our examination of the milksugar, which examination was very attractive, because here a very slow establishment of the internal equilibrium was found, which opened the possibility to get to know something about the relation between the pseudo-system and the setting in of the internal equilibrium.

In the first place we had to examine what was the stability of the solid phases, hydrate,  $\beta$ -anhydride, and  $\alpha$ -anhydride in the system water-milksugar. It appears clearly from the method of preparation and the investigation of HUDSON that the hydrate is stable below  $93^\circ$ ; accordingly both the  $\beta$ -anhydride and the  $\alpha$ -anhydride always yielded the hydrate below  $93^\circ$  in contact with water.

It further appeared again both from the method of preparation and from HUDSON's investigation that above  $93^\circ$ ,  $\beta$ -anhydride is the stable solid phase; accordingly the hydrate gave the  $\beta$ -anhydride above this temperature in contact with the saturate solution, and the  $\alpha$ -anhydride always gave the  $\beta$ -modification under these circumstances.

*It followed, therefore, from this that the  $\alpha$ -form is metastable not only below  $93^\circ$ , but also above it.*

The question is now whether there exists a transition point between the  $\alpha$  and  $\beta$ -modification at higher temperatures. For this purpose the final solubility was first determined from  $93^\circ$  to  $200^\circ$ , both starting from the  $\beta$ - and from the  $\alpha$ -modification.

The result was that the  $\alpha$ -form was always first visibly converted into the  $\beta$ -form, and that the found points lay without exception on the solubility curve of the  $\beta$ -modification.

These determinations could now be made to fit in with HUDSON's results about the hydrate, as the  $T_x$ -figures 1 and 2 express.

From the graphical representation in fig. 3, in which  $\log x$  is represented as function of  $\frac{1}{T} \cdot 10^3$ , follows the temperature  $93^\circ,5$  for

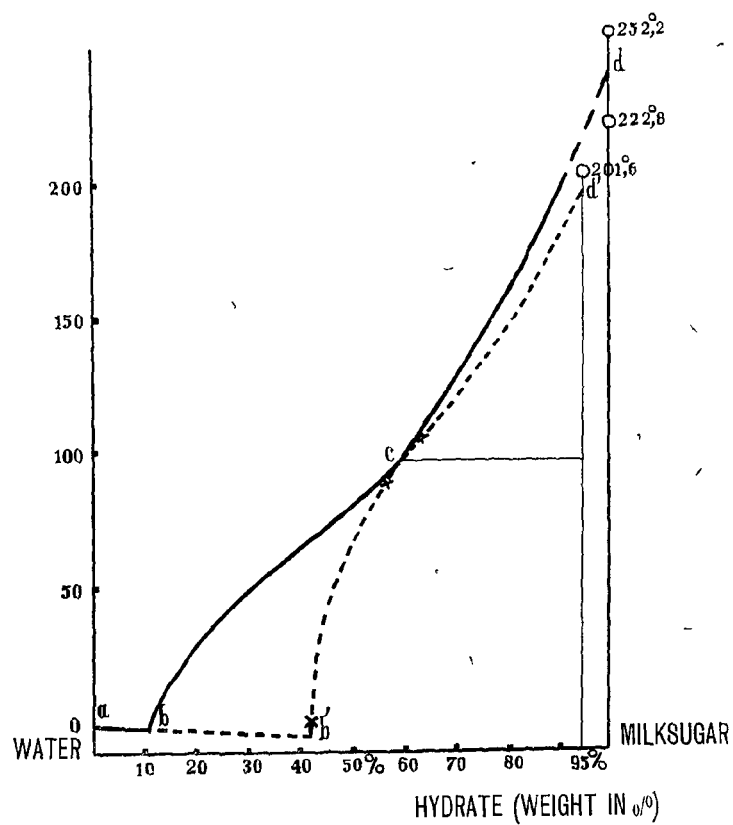


Fig. 1

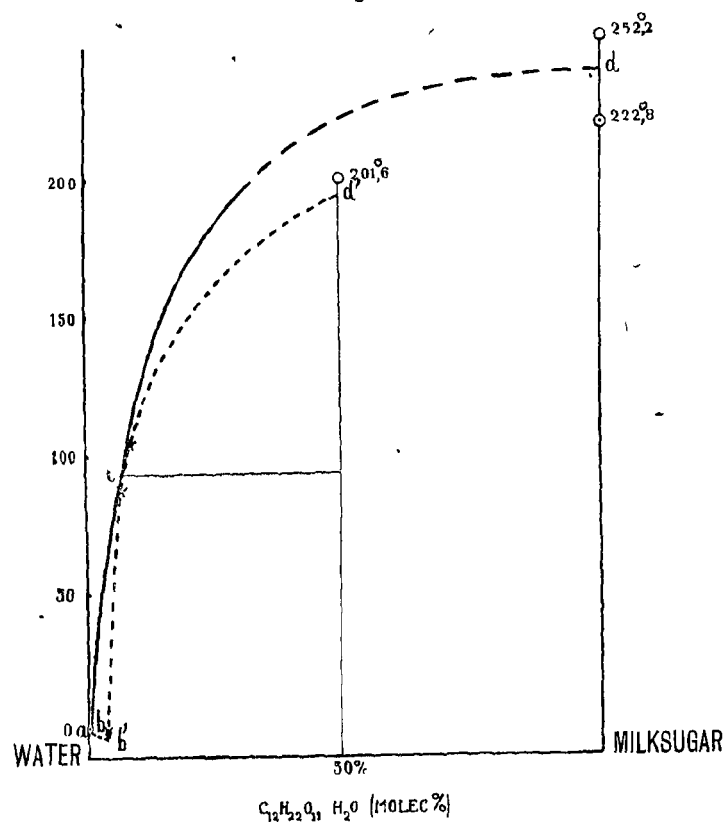


Fig. 2.

the temperature of the three-phase equilibrium hydrate +  $\beta$ -anhydride + solution.

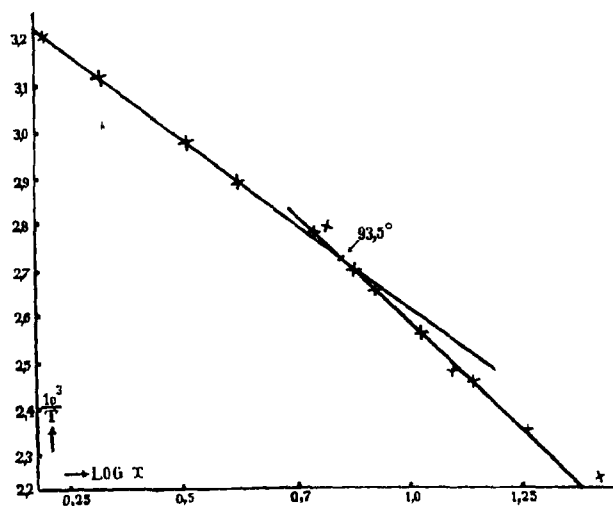


Fig. 3.

The  $\alpha$ -modification appeared, therefore, to be metastable below  $200^\circ$ , and now it was the question how it is at the higher temperatures. The solubility lines could not be pursued towards higher temperatures, because the milk sugar decomposes during the time necessary for a determination.

The only thing that offered a chance of success was the determination of the melting point in exceedingly thin capillary tubes, according to the method of Soch.

This investigation gave a perfectly convincing result, for the  $\alpha$ -modification<sup>10</sup> melted in 2 seconds in a bath of  $222^\circ,8$ , while the  $\beta$ -modification melted in the same time in a bath of  $252^\circ,2$ . Hence the  $\beta$ -modification melted  $29.4^\circ$  higher than the  $\alpha$ -form, which shows that the  $\alpha$ -modification is metastable up to its melting-point.

On this occasion also the melting-point of the hydrate was determined according to Soch's method, for which was found  $201^\circ,6$ . It may serve as a proof for a very small velocity of transformation in the solid substance, when as here, the melting-point of a hydrate is to be realised more than  $100^\circ$  above the already discussed dehydration point.

*b. The hydrate is a hydrate of the  $\alpha$ -modification.*

All this did not solve the problem offered by the milk sugar, however, by any means, for another highly remarkable peculiarity

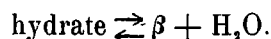
presented itself for the hydrate, a peculiarity which as far as we know, has never yet been observed for another hydrate, though it is probable that it will occur in more cases.

We found, namely, that the hydrate when heated at 125° in dry condition, always yields the  $\alpha$ -modification, whereas in presence of the saturate solution the hydrate at the same temperature always passes into the  $\beta$ -modification.

To study this interesting phenomenon more closely the hydrate was brought in contact with a vessel of strong sulphuric acid of ordinary temperature at temperatures between 0.5° and 200° in vacuum. It appeared in all these experiments that the hydrate was *exclusively* converted to the  $\alpha$ -anhydride, and this happened both below and above 93°.5.

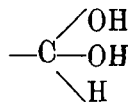
This result enables us, as we shall see presently, to consider the milk sugar problem from another point of view, which will make it possible to account for all the phenomena observed up to now in the system water-milk sugar in a simple way.

HUDSON already assumed the transformation:

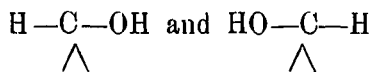


In this the expectation that the hydrate is a hydrate of the  $\beta$ -modification is of course implied.

Now HUDSON assumes further that the water in the hydrate is bound in this way



from which would follow that the hydrate might just as well be called a hydrate of the  $\alpha$ -modification as a hydrate of the  $\beta$ -modification, because the stereochemical difference in the final carbon atom, which he assumed for the  $\beta$ - and  $\beta$ -modifications<sup>1)</sup>, viz.



has perfectly disappeared in the structure formula for the hydrate.

If this were so the hydrate would be neither  $\alpha$ - nor  $\beta$ -hydrate and then it could absolutely not be understood why the dry hydrate always gives  $\alpha$ -anhydride, also above 93°, whereas the damp hydrate passes into  $\beta$ -anhydride above 93°.

We must, therefore, certainly reject this supposition; the hydrate must be a hydrate of  $\alpha$  and  $\beta$ -anhydride, and now all the experi-

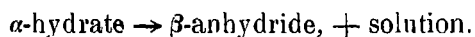
<sup>1)</sup> J. Amer. Chem. Soc. 31 66 (1909).



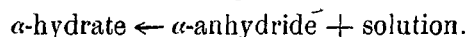
ments made by us, in which it was found that the hydrate in dry condition gives the  $\alpha$ -anhydride at all the temperatures examined point to this *that the milk sugar hydrate is the hydrate of the  $\alpha$ -modification.*

*c. The hydrate presents a transition-dehydration point.*

This conclusion throws another light on the problem: the transformation point of  $93^{\circ}.5$  is no ordinary transformation point, for in this point takes place the conversion



If we had to do here with an ordinary transformation point, the conversion would be the following:



*For milksugar, however, the dehydration is accompanied with a transition of the  $\alpha$ -modification into the  $\beta$ -form, so that here a phenomenon is met with, which as far as we know, has never been observed as yet. To express this particular behaviour also in the denomination of the transformation point we shall call this point henceforth the transformation-dehydration point, resp. transition-hydration point.*

*d. The system water-milksugar must be considered as pseudo-ternary. Derivation of the isotherm-diagram.*

This remarkable result must be expressed in our way of representation of the system considered here.

As the occurrence of the said transition-dehydration point shows with the greatest clearness that we must consider the system water-milksugar as pseudo-ternary, we have begun collecting data for the representation of the solubility-isotherms of the system  $\text{H}_2\text{O} + \alpha\text{-milk-sugar} + \beta\text{-milk-sugar}$  at a temperature below  $93^{\circ}.5$ .

In fig. 4 the points *a* and *b* indicate the initial-solubility of the hydrate  $\alpha_{aq}$  and of the  $\beta$ -anhydride determined by HUDSON<sup>1)</sup> at the temperature of  $0^{\circ}$ . The three-phase-equilibrium  $\alpha_{aq} + \beta + h$  was not determined, and was found by us by starting from these three phases, and by squirting off the liquid through a filter after 1 hour's vigorous stirring. The total concentration of this liquid was determined by evaporation and weighing, i.e. the total quantity of milksugar. In this way we find, therefore, on what line drawn parallel to the line  $\alpha\beta$ , the point *D* lies. In order to be able to indicate the place of the point *D* on this line, a second quantity was pressed through a filter, and then through a bent tube provided with a refrigerator, through which water flowed of the same temperature as that of the

<sup>1)</sup> J. Amer. Chem. Soc. 30 1767 (1908).

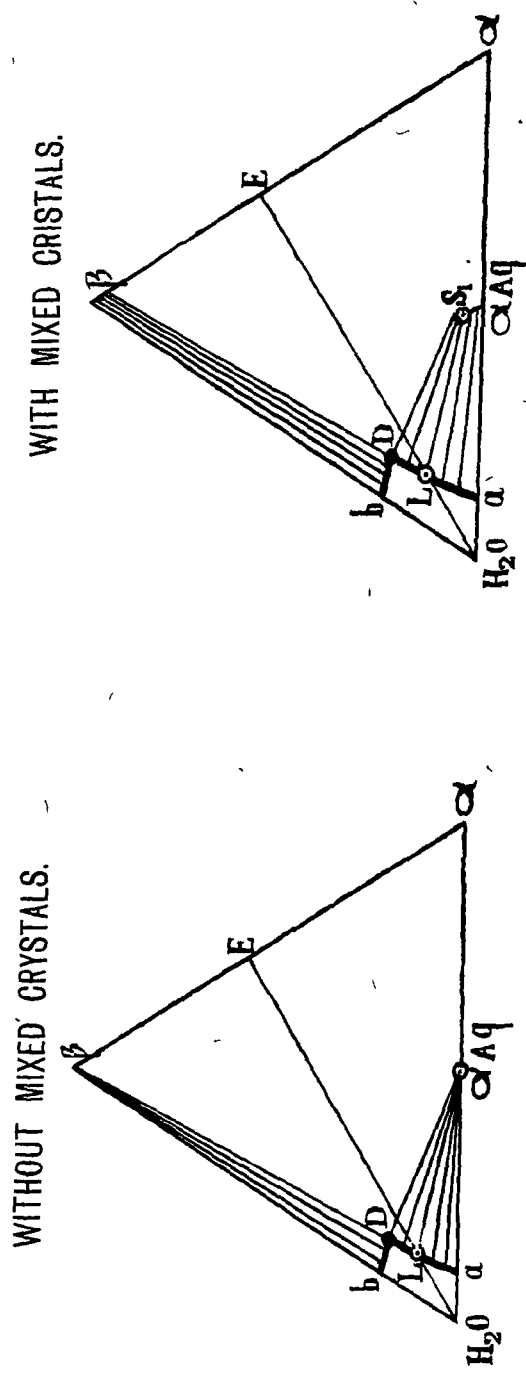


Fig. 4.

batn. Directly after it had left this tube, the solution was received in ice, to fix the equilibrium in the homogeneous liquid. By deter-

mination of the initial and the final rotation the ratio  $\frac{\alpha}{\beta}$  was found.<sup>1)</sup>

In the determination of the final rotation use was made of the positive catalytic influence of a drop of a solution of ammoniac.

It is clear that when the ratio  $\frac{\alpha}{\beta}$  is given, it is not stated that the molecules of the two modifications  $\alpha$  and  $\beta$  really occur in perfectly unhydrated condition in the solution; it only expresses what the ratio is between the concentration of  $\alpha$  and  $\beta$ , leaving it quite an open question in how far these molecules are hydrated.

Thus also the point  $D$  was determined, which is the point of intersection of the isotherms of the  $\alpha_{aq}$  and of the  $\beta$ -modification.

It has already been ascertained by Hudson whether the situation of the equilibrium between  $\alpha$  and  $\beta$  in solutions of different total concentration shifts with the concentration. The result was that the equilibrium  $\alpha \rightleftharpoons \beta$  does not change on dilution of the solution, as was indeed to be expected in dilute solutions, as we have there to do with isomers. We can, therefore, represent these equilibria in our triangle by a straight line<sup>2</sup> starting from the point  $H_2O$ .

As it had appeared that  $\alpha_{aq}$  below  $93^{\circ},5$  is the stable solid phase in the system water-milksugar, it was certain that the said line for the homogeneous equilibrium would have to intersect the isotherms of  $\alpha_{aq}$ .

This point of intersection is now determined by shaking  $\alpha_{aq}$  with water for 2 or 3 days at  $0^{\circ}$  with the aqueous solution. On analysis of this solution in the same way as this had been done with the liquid  $D$  the point  $L$  was found lying on the isotherm of  $\alpha_{aq}$ . Hence the phases  $\alpha_{aq}$  and  $L$  and the homogeneous equilibrium line  $H_2O-E$  denote the binary equilibrium system water-milksugar at the existing temperature.

Now it is clear that the observations must show that at  $93^{\circ},5$  the equilibrium line  $H_2O-E$  must pass through the three-phase point  $D$  as Fig. 5 expresses, so that then  $\alpha_{aq} + \beta \pm L$  can coexist in the binary equilibrium system.

<sup>1)</sup> The ratio between initial rotation  $r_0$  and final rotation  $r_{\infty}$  was determined at  $0^{\circ}$  for hydrate and  $\beta$ -anhydride mixtures of different concentration. The graphical representation of this gave a straight line, which enabled us, not only to determine the ratio  $\frac{\beta}{\alpha}$  from  $\frac{r_0}{r_{\infty}}$ , but also to find the accurate value of the equi-

librium-constant  $K'$  at  $0$ , because  $K' = \frac{\beta}{\alpha}$ , when  $\frac{r_0}{r_{\infty}} = 1$ .

$K' = 1,65$  was found.

Above this temperature the equilibrium line  $H_2O-E$  must intersect the isotherm for  $\beta$ -anhydride, which is represented in fig. 6.

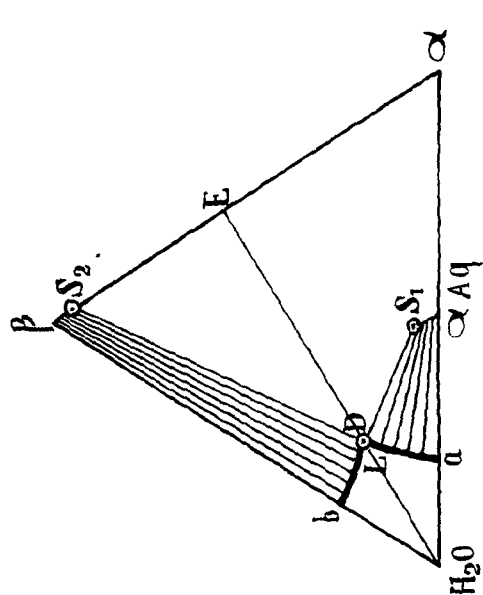


Fig. 5

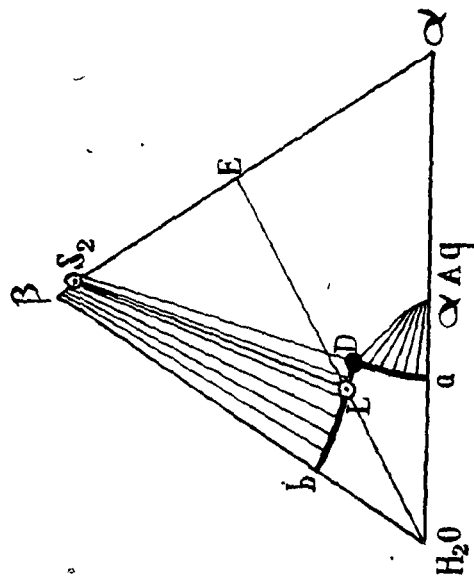


Fig. 6

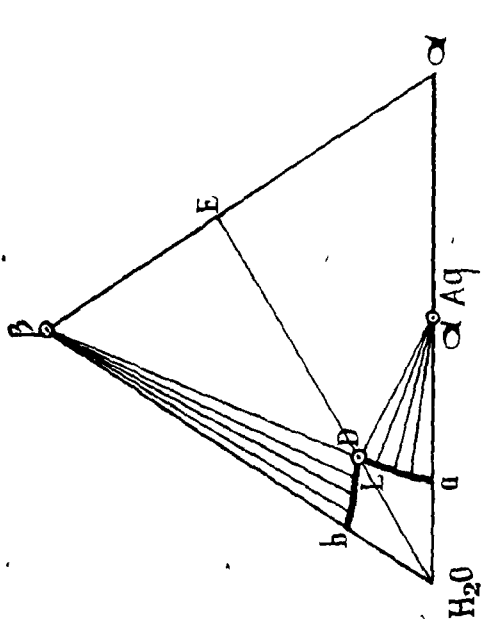


Fig. 5

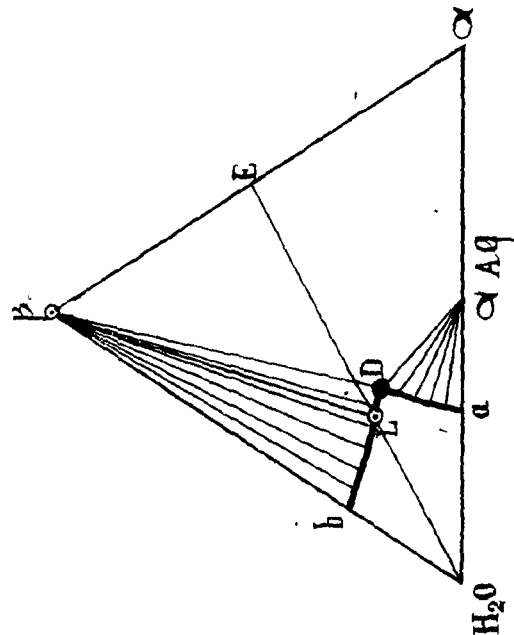


Fig. 6

*a. Experimental confirmation of the validity of the pseudo ternary views.*

To show that this is actually the case, it was examined how the situation of the points  $D$  and  $L$  changes with increase of temperature. The shifting of  $L$  with the temperature was easy to examine, and we have therefore different observations at our disposal, which, as the figures 7 and 8 show, prove that the equilibrium  $\alpha \rightleftharpoons \beta$  shifts a little to the  $\alpha$ -side on increase of temperature.

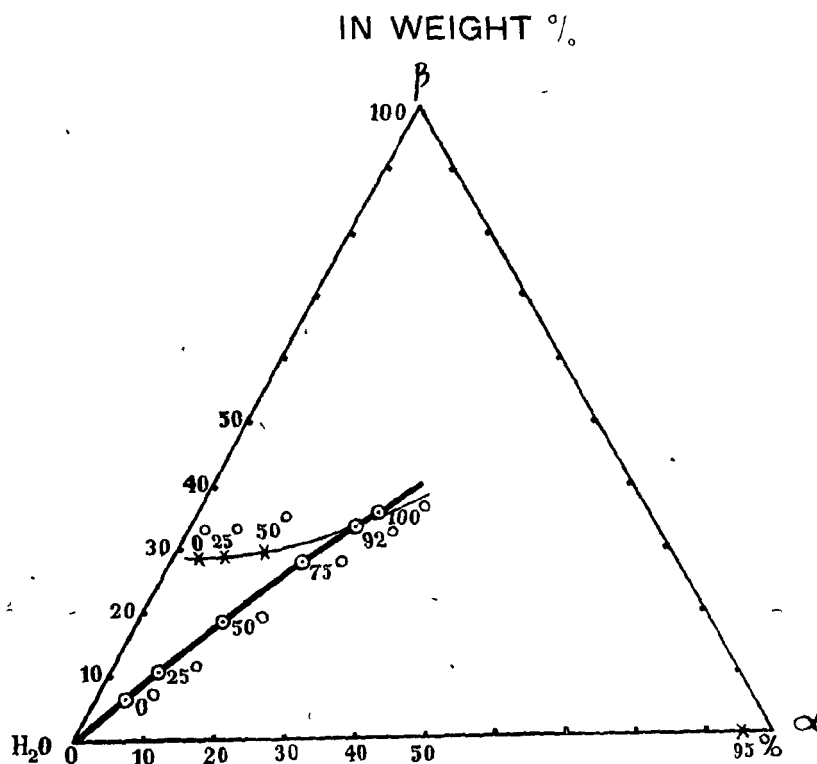


Fig. 7.

It follows already from this that also the point  $D$  will have to shift towards the  $\alpha$ -side, and to a much greater extent too.

The determination of the shifting of the point  $D$  with the temperature does not present any difficulties at temperatures below  $50^\circ$ , as the velocity of transformation of  $\beta$ -anhydride into  $\alpha_{aq}$  takes place slowly, so that we can take care, e. g. by continually adding  $\beta$ -anhydride, that there is always  $\beta$ -anhydride present by the side of the  $\alpha_{aq}$ .

At higher temperatures this velocity of transformation increases,

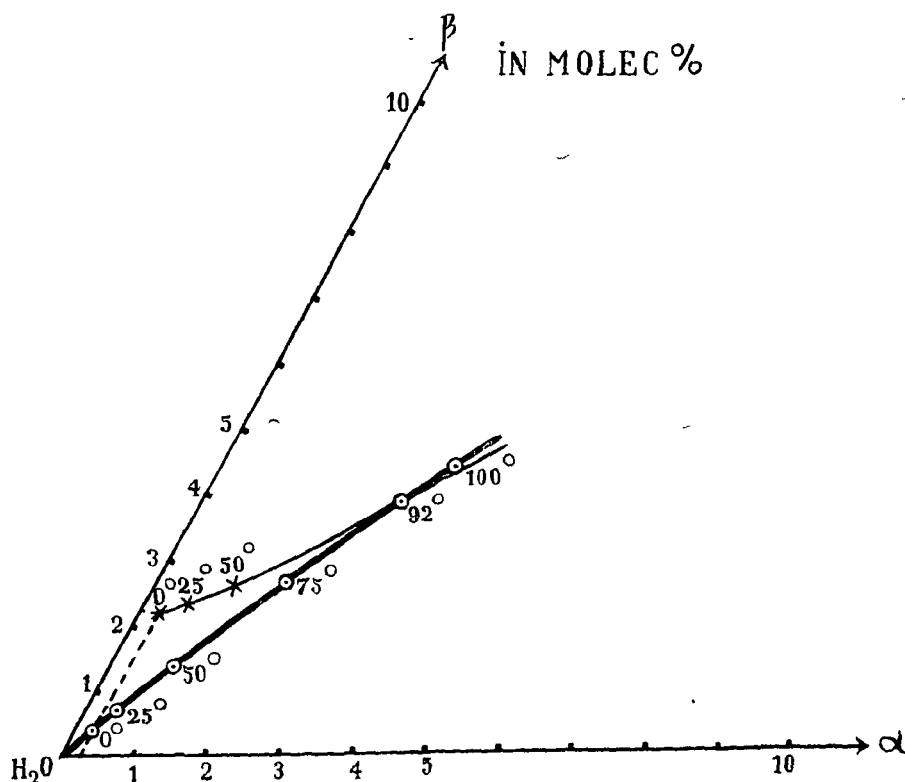


Fig. 8.

however, greatly, and on account of this 50° was the highest temperature at which a reliable observation could still be made.

As, however, appears from the figures 7 and 8, the points *D* shift exactly as had been predicted, and the line traced through the points *D* points with perfect certainty to an intersection at  $\pm 93^\circ$ , so that a complete confirmation of the supposition made has been obtained in this way.

We are therefore justified in saying that above  $93^\circ,5$  the diagram of isotherms with the binary system of equilibrium lying in it will be as was represented in fig. 6. *(To be continued).*

Amsterdam, July 1917. *Laboratory for General and Anorg.  
Chemistry of the University.*