

*Citation:*

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of the cornea very peculiar optic changes show themselves microscopically under low magnification.

From what precedes it appears that in the hardness of physiological objects we should distinguish well between relative and absolute determination of hardness. This is unmistakably connected with the fact that one of the three qualities which are implied in hardness, viz. elasticity, plasticity, and cohesion, comes to the front. Which part each of these qualities has in definite cases and how they are perhaps to be separated in sclerometry, I hope to show later on.

**Chemistry.** — “*On the unary tri-molecular pseudo-ternary system acet-, par-, and met-aldehyde*”. By Prof. A. SMITS and Dr. H. L. DE LÆUW. (Communicated by Prof. A. F. HOLLEMAN). (Communicated in the meeting of June 25, 1910).

During the investigation of the system acetaldehyde-alcohol a great quantity of metaldehyde, which deposited in the shape of needles, was formed in one of the mixtures during the cooling without our being able at the first moment to indicate the reason.

This phenomenon, which recalled to our memory the many contradictory accounts which are to be found in the literature about the behaviour of metaldehyde, induced us to undertake the following investigation on the connection between acet-, par-, and met-aldehyde, in which we were fortunate enough to find a solution, which brings unity in the work of many and makes apparent contradictions conform to a perfect harmony.

In 1872 KÉKULÉ and ZINCKE<sup>1)</sup> found that the formation of metaldehyde from acetaldehyde, just as that of paraldehyde from the same substance, takes place in the presence of certain substances, but that while the formation of paraldehyde takes place at the usual and higher temperatures that of metaldehyde is generally to be observed at lower temperatures. The paper by KÉKULÉ and ZINCKE cited here is distinguished by the great accuracy of the description of the observed phenomena, and contains a passage, whose meaning has been evidently overlooked by others, as it with great clearness points out the direction in which the solution of the problem is to be found.

The passage in question runs as follows:

“Fügt man zu reinem Aldehyd kleine Mengen von Salzsäure-gas, Chlorkohlenoxyd, Schwefliger Säure oder verdünnter Schwefelsäure und kühlt dann sofort, am besten mit einer Kaltmischung ab, so

<sup>1)</sup> Ann. d. Chemie u. Pharm. 162, 125, (1872).

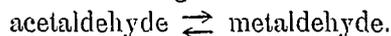
scheiden sich feine lange Nadeln von Metaldehyd ab, die bisweilen die ganze Flüssigkeit wie ein feines Netzwerk durchziehen. Stets wird nur ein kleiner Theil des Aldehyds in Metaldehyd verwandelt und die Menge des letzteren nimmt bei längerem stehen *nicht zu; sie kann sich vielmehr vermindern und der Metaldehyd kann ganz verschwinden, namentlich wenn ein energischer wirkendes Ferment in einigermaßen beträchtlicher Menge zugegen ist und wenn die Temperatur nicht niedrig genug gehalten wird.*

*Neben Metaldehyd entsteht immer Paraldehyd in mehr oder minder grosser Menge."*<sup>1)</sup>

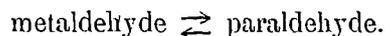
That metaldehyde originates from cooled acetaldehyde in the presence of a katalyser, in which paraldehyde is also always formed, and the statement that this metaldehyde can disappear again when there is enough present of an energetically working katalyser, this result, which has been left unused up to now, joined to the fact stated by TRÖGER<sup>2)</sup>, FRIEDEL<sup>3)</sup>, ORNDORFF and WHITE<sup>4)</sup>, that gradually metaldehyde is converted into paraldehyde and a little acetaldehyde at the usual temperature, and at 120° almost exclusively into acetaldehyde, as KERULÉ and ZINCKE state, all this leads us to suppose that we have to deal here with a pseudo-ternary system, which passes into a unary-trimolecular system in case of internal equilibrium.

This supposition suggested itself, for it was found that metaldehyde can be formed from acetaldehyde at lower temperature, whereas the reversed reaction takes place at higher temperature.

So this points to the following reversible conversion:



In the second place it was found that metaldehyde is converted into paraldehyde. If we assume reversibility also here, we get as second reversible reaction:



It was further known that acetaldehyde is easily convertible into paraldehyde, and also reversely paraldehyde into acetaldehyde.

Now it might naturally be supposed that in this latter reversible conversion metaldehyde always appears as middle-product, but as we have not the slightest reason to suppose this, and the supposition that also the reversible reaction

<sup>1)</sup> The italics are curs. In a still earlier paper by FEHLING [Ann. 27, 319 (1838)] it is also mentioned that metaldehyde disappears again after some time.

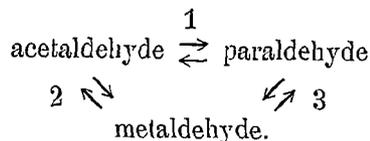
<sup>2)</sup> Rer. 25, 3316 (1892).

<sup>3)</sup> Bull. 9, 384 (1893).

<sup>4)</sup> Americ. Chem. Journ. 16 43 (1894).

acetaldehyde  $\rightleftharpoons$  paraldehyde

exists, leads us to an exceedingly plausible explanation of the different phenomena, we do not hesitate for a moment to insert this latter assumption. In this way we arrive at the existence of a great equilibrium<sup>1)</sup>, which is composed of three others, viz.:



Now it is clear that these three reactions of equilibrium will in general be influenced in a different way by one and the same katalyser which may convey the impression to us as if exclusively or mainly only one reaction takes place.

This is illustrated by an experiment, which we arranged in the same way as KÉKULÉ and ZINCKE's experiments.

If acetaldehyde is cooled in ice, and a very small amount of strong  $\text{H}_2\text{SO}_4$  is added, e. g. 1 mgr., solid metaldehyde is formed when the solution has been shaken for some time, which metaldehyde does not seem to change at the temperature of the room, but which in reality disappears very slowly.

This slow disappearance may be accelerated by the addition of more sulphuric acid.

This points to the fact that for the equilibrium reaction acetaldehyde  $\rightleftharpoons$  metaldehyde  $\text{H}_2\text{SO}_4$  is a much stronger katalyser than for the other two conversions, so that a very small quantity  $\text{H}_2\text{SO}_4$  mainly causes metaldehyde to be formed at 0°.

From the fact that metaldehyde deposits here in solid state follows that the internal equilibrium in the system acetaldehyde—metaldehyde lies in the supersaturate region of metaldehyde.

So if the other two reactions were not at all influenced by this small quantity of  $\text{H}_2\text{SO}_4$ , the whole amount would of course be converted to solid metaldehyde, but this is not the case. Though much less quickly a small quantity of  $\text{H}_2\text{SO}_4$  makes also the other two equilibrium reactions proceed towards their state of equilibrium, this explains the fact that by the side of metaldehyde always paraldehyde is formed, as KÉKULÉ and ZINCKE observed.

It is clear that also with an exceedingly small quantity of sulphuric acid, but then only after a very long time, internal equilibrium will be established; if however, we add more sulphuric acid, every equi-

<sup>1)</sup> BANCROFT, Journ. phys. chem. 5, 182 (1910) arrives at the conclusion, which is erroneous in our opinion, that metaldehyde is always metastable.



very well possible that whereas the inner equilibrium in the pseudo-binary system acetaldehyde-metaldehyde lies in the region that is supersaturate with respect to metaldehyde, the great trimolecular inner equilibrium is unsaturate with respect to metaldehyde.

The adjoined figure 1 holds for constant temperature and pressure, and not to complicate the question needlessly it has been further assumed, that no mixed crystals are formed. If we choose the ordinary temperature, metaldehyde is the only substance which appears in the solid state, and  $pq$  represents the melting-point isotherm of this substance, the points  $a$ ,  $b$ , and  $c$  denoting the inner equilibria in the three pseudo-binary systems.

The point  $b$  lies as follows from TURBABA'S<sup>1)</sup> investigation at about 16 mol. % of acetaldehyde, and 84 mol. % of paraldehyde.

In accordance with the observations the point  $a$  lies in the region which is supersaturate with metaldehyde, and if we take only these two points as quite certain, the following remarks may be made.

Let us suppose that we start from the point  $a$ , and that we add paraldehyde to this supersaturate solution, which is in inner equilibrium. Then if we assume that the inner equilibrium continues to exist, and the paraldehyde is not converted, the concentration would proceed along the straight line  $aP$ , at least if the law of mass-action continued to hold perfectly.

Now we know, that the law of mass-action will certainly not continue to hold perfectly, and that consequently the line  $aP$  will in reality be curved, but this does not affect the essential part of our reasoning, and therefore the line  $aP$  has been taken straight for the take of simplicity.

If we then start from  $b$ , the concentration will proceed along  $bM$  with addition of metaldehyde on the above conditions.

Now we see that the two lines  $aP$  and  $bM$  intersect in the point  $K$ , and it is now easy to see what this intersection means. In  $K$  we have a liquid in which inner equilibrium prevails, not only between *acet-* and *met-*aldehyd, but also between *acet-* and *par-*aldehyde, from which also follows that there is also equilibrium between *met-* and *par-*aldehyde, and that the line  $cA$  must also pass through this same point  $K$ .

So we see from this derivation that it is possible that while  $a$  lies in the supersaturate region, the great inner equilibrium  $K$  lies in the *unsaturate* region.

Thus KEKULÉ and ZINCKE'S observations have been explained in a rational way.

<sup>1)</sup> Tomsch. Verlag. d. Techn. Hochschule 1901. Aus dem Gebiet der Katalyse

As we may say now with certainty that the great inner equilibrium  $K$  contains dissolved metaldehyde at the ordinary temperature, we may predict with a high degree of probability, that this will still be the case in an appreciable degree at the unary boiling-point, more than  $20^\circ$  higher, which lies at  $41.6^\circ$  according to HOLLMANN<sup>1)</sup>.

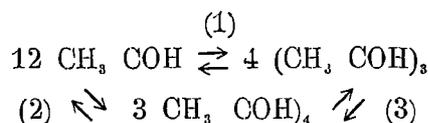
In order to investigate this the boiling liquid was suddenly poured into water of  $18^\circ$  in which the metaldehyde, if it was found in the boiling liquid, would certainly deposit in solid state in consequence of its slight solubility in mixtures rich in water.

In this way a slight but very distinct deposition of metaldehyde takes really place, which proves that HOLLMANN did not deal with a unary bimolecular system, as he thought, but with a unary trimolecular one.

If we ask what will be the change in situation of the point  $K$  when the temperature is raised, the answer is easy to give.

In gaseous state and dissolved in phenol paraldehyde consists of mol.  $(\text{CH}_3\text{COH})_3$ , and metaldehyde dissolved in the same solvent consists of mol.  $(\text{CH}_3\text{COH})_4$ <sup>2)</sup>, so that metaldehyde is the most complicated substance of the three aldehydes.

If we now assume for simplicity that the size of the molecules of the different aldehydes dissolved in each other does not differ from that in the phenol solutions we have this inner equilibrium:



With rise of temperature each of the three unary bimolecular equilibria will shift in the endothermic direction, or in other words the dissociation will increase for these three inner equilibria.

The equilibrium (2) will move more considerably with the temperature than the equilibrium (1), whereas (3) is probably not very susceptible to variations of temperature, at least in comparison with the other equilibria (2) and (1).

So if the temperature rises, the point  $a$  will move to the left, the point  $b$  downward, and the point  $c$  will be slightly moved to the paraldehyde side.

If we now consider that the melting-point isotherm retracts with rise of temperature, it is clear that  $a$  will soon lie in the unsaturate region, and that therefore no katalyser will be able any more to make

<sup>1)</sup> Zeitschr. f. phys. Chem. 43, 157 (1903)..

<sup>2)</sup> W. BURSTJN. Sitzungsberichte *Wien* (1902), 511. HANTZSCH. Ber. 40, 434 (1907).

solid metaldehyde deposit from acetaldehyde, which is in agreement with the fact ascertained by us that  $\text{CaCl}_2$  does not do so any

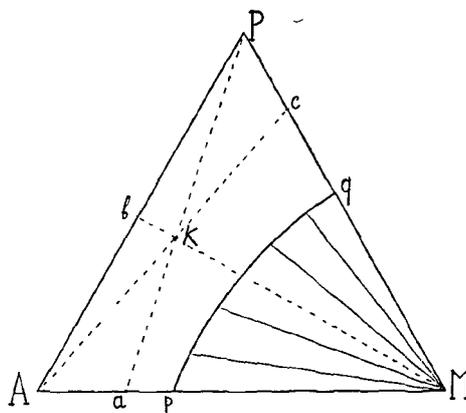


Fig. 2.

more above  $40^\circ$ .

It further follows from all this that the mixture in the state of internal equilibrium becomes richer in acetaldehyde as the temperature rises, as was also found by HOLLMANN.

To give a survey of the whole system with all its peculiarities a spacial figure has been constructed in an equilateral prism, on each of the side-planes of which the  $T, X$ -projection of the three-phase regions of one of the pseudo-binary systems has been given (fig. 3).  $A$  represents acetaldehyde,  $P$  paraldehyde, and  $M$  metaldehyde.

In agreement with what was predicted already before by one of us it was found that none of these pseudo-binary systems possesses a eutectic point, which has been taken into account in the diagram.

On the plane  $APT$  the  $T, X$ -projection of the three-phase regions in the system acetaldehyde-paraldehyde has been indicated.

$a_0$  is the triple-point of acetaldehyde situated at  $-123^\circ 3$ .

The temperature of the four-phase equilibrium vapour + liquid + solid acetaldehyde + solid paraldehyde, which is denoted by the letters  $h, c, d, e$ , in the figure was found to lie at about  $-123^\circ$ . As is known, 4 three-phase regions intersect on this line  $hcd$ .

If we denote the mixed crystals which chiefly consist of acetaldehyde by  $S_A$ , those which chiefly contain paraldehyde by  $S_P$ , and the mixed crystals of metaldehyde by  $S_M$ , we can easily indicate the intersecting three-phase regions.

Thus we have in the first place the three-phase region of  $S_A + L + G$  indicated by the lines  $ad$ ,  $ac$ , and  $ah$ . In the second place the three-phase region of  $S_P + S_A + G$  indicated by  $ge$ ,  $fd$ ,

and  $h'h$ . In the third place the three-phase region for  $S_P + L + G$ , which is indicated here by  $eb_0$ ,  $cb_0$ , and  $hb_0$ , in which  $b_0$  is the triple-point of paraldehyde, lying at  $12,55^\circ$ . In the fourth place the three-phase region for  $S_A + S_P + L$ , but this has been omitted in the figure.

On each of the three side-planes of the trilateral prism such a figure is found, of which in each case the three most important points have been determined, viz.: the triple points of the components, and the four-phase temperatures. Thus the temperature of the equilibrium between  $S_M + S_A + L + G$ , indicated in the figure by the letters  $e_1, d_1, c_1, h_1$ , was found to be  $-122,8^\circ$ . The temperature for the four-phase equilibrium between  $S_M + S_P + L + G$ , which in the figure is to be found on the line  $e_2, d_2, c_2, h_2$  was found to be  $12^\circ,9$ .

So it appears from this that the four-phase temperatures in the three pseudo-binary systems lie only little higher than the temperature of the triple-point of the component with the lowest melting-point, from which follows that the  $TX$ -projections will show a very one-sided situation.

In the figure this one-sidedness has not been made too pronounced, because this would have impaired the clearness of the figure.

The attempts to determine the triple point of metaldehyde had failed up to now in consequence of the conversion of metaldehyde into paraldehyde and acetaldehyde. Now this point has been determined by us by the method of Сохн<sup>1)</sup>, which consists in this that a substance is placed in a thin-walled capillary melted together at the bottom, after which it is examined at what temperature of a bath the contents of the capillary when immersed in this bath, show melting after a few seconds (here 2).

As the triple-point-pressure of metaldehyde lies above 1 atmosphere, the capillaries had, of course, to be fused together, in which the vapour volume was always chosen as small as possible.

The result was that under its vapour pressure metaldehyde melts at  $246^\circ,2$ , whereas BAKHUIS ROOSEBOOM<sup>2)</sup> gives  $184^\circ$  and HOLLMAN  $167^\circ$ .

The spacial figure has been made clearer by sections.

Above the triple point of paraldehyde  $b_0 = 12,55^\circ$  this section is exceedingly simple.

If we take the section  $U_1, V_1, W_1$  as an example, we see there a continuous melting-point isotherm  $L_1L_2$ , a continuous vapour line  $G_1G_2$ , and a continuous mixed crystal line  $S_1S_2$ .

If, however, we get below the triple point of paraldehyde, the

<sup>1)</sup> Journ. Phys. chem. 2, 364 (1898).

<sup>2)</sup> Heterogene Gleichgewichte.

sections get more intricate, specially on account of the discontinuity in the mixed crystal series of paraldehyde-metaldehyde. In consequence of this we get two melting-point isotherms, three vapour-lines, and four mixed crystal lines in the section  $U, V, W$ .

Before proceeding, however, to the discussion of this section, we will point out, that of the four coexisting phases  $S_M, S_P, L, G$ , which are denoted by the points  $e_2, d_2, c_2, h_2$ , four lines proceed into space. The first two are mixed crystal lines, the third is a melting-point line, or rather a eutectic line under the vapour pressure, and the fourth is a vapour line.

Four such lines also start from the points  $e, d, c, h$  and  $e_1, d_1, c_1, h_1$ .

At the ternary eutectic temperature, to which the base corresponds, the solid lines, the eutectic lines, and the vapour lines which belong together meet, and so we get the coexistence of five phases, three solid ones  $S_A + S_P + S_M$ , a liquid one  $L_e$ , and a vapour one  $G_e$ .

If we now return to the section  $UVW$  we may remark that the line  $S_{m_2}S_m$  indicates the metaldehyde mixed crystals which coexist on one side with the paraldehyde mixed crystals  $S_{p_2}S_p$ , and on the other side with the gases  $G'_2G_2$ .

The line  $S_{p_1}S_P$  indicates the paraldehyde mixed crystals, which coexist with the liquids  $LR$ , and the gases  $GG_2$ , and the line  $S_{m_1}S_m$  indicates the metaldehyde mixed crystals which coexist with the liquids  $L_3R$  and the gases  $G_3G_2$ .

It follows from this that at this temperature four phases can coexist, viz.:  $S_m + S_P + R + G_2$ , i. e. mixed crystals which consist chiefly of metaldehyde, mixed crystals which contain chiefly paraldehyde, a saturated solution, and a gas coexisting with these phases.

These four phases lie in the angles of a quadrangle, which is composed of *four* three phase triangles.

If we now assume that the temperature of this section agrees with the unary melting-point, we are certain that the liquid in which internal equilibrium prevails, will have to lie on one of the liquid lines  $LR$  and  $L_3R$ .

HOLLMANN, who thought he had to deal with a pseudo-binary system, found that the liquid which behaved as a unary one deposited solid paraldehyde at  $6^\circ.75$ . If we now correct this result by means of the newly-acquired knowledge, we arrive at the following result.

If the temperature of a liquid, which is in inner equilibrium, decreases, and we assume that this liquid is in equilibrium with its vapour, which is then, of course, also in inner equilibrium, the liquid will move with decrease of temperature along the line  $L_0, L'_0, L''_0$ , and the coexisting vapour along the line  $G_0, G'_0, G''_0$ .

If we have now descended to the unary melting temperature, the liquid line has reached the melting plane of the paraldehyde mixed crystals in  $L_1$ , and the vapour the vapour plane coexisting with it in  $G_1$ , at which moment solid substance deposits, which is a mixed crystal phase  $S_1$ , which is also in inner equilibrium, as one of us showed already before.

This unary three-phase equilibrium can only exist at one temperature and pressure, so that below this temperature we get two-phase equilibria between solid phases and vapour phases both in internal equilibrium.

The solid phases move along the line  $S_1S_2$  and the vapour phases along  $G_1G_2$ .

A representation which is in closer agreement with the investigations which have been made up to now, is obtained when the  $T, X$ -sections for constant pressure, e g. for one atmosphere, are indicated on the sides of the prism.

If we do this, we get the  $T, X$ -section for the pseudo-binary system acetaldehyde-paraldehyde on the  $APT$ -plane, as it was determined by HOLLMANN, only with this difference, that the eutectic point has disappeared (fig. 4).

This  $T, X$ -section is indicated by the melting-point figure  $a, c, b, e, g, d, f$ , and by the boiling-point lines  $kl$ . The temperatures of the most important points are indicated in the figure, so that this section does not require any further elucidation.

We get a more complicated figure on the plane for paraldehyde-metaldehyde, the  $PMT$ -plane, because metaldehyde sublimates under the pressure of 1 atm. In consequence of the conversion of metaldehyde into acetaldehyde and paraldehyde it is impossible to determine how high this sublimation point is, for the method followed for the determination of the triple-point cannot be applied here.

The only thing that can be said about it at present is this that this sublimation point probably lies little under the triple-point temperature, as the triple-point pressure probably does not lie much above 1 atmosphere.

The  $T, X$ -section of this system is indicated by  $b, c_2, n_2, l, m_2, o, p_2, e_2, g_2, d_2, f_2$ . We determined the temperature of the three-phase equilibrium  $S_M + L + G$ , indicated by the line  $p_2, n_2, m_2$ , at about  $124^\circ$ , when we worked very quickly, from which it therefore follows that the boiling solution which coexists with aldehyde mixed crystals, contains comparatively little metaldehyde.

On the front plane, the plane for acetaldehyde-metaldehyde, we have the  $T, X$ -section for this system, indicated by  $a, c_1, n_1, k, m_1$ ,

$o, p_1, e_1, g_1, d_1, f_1$ , which section, in its nature closely agrees with that for paraldehyde-metaldehyde.

We found the three-phase equilibrium  $S_M + L + G'$ , or in other words the boiling-point of the solution which is in equilibrium with metaldehyde-mixed crystals, at  $21^\circ.0$ , so only  $0^\circ.2$  higher than the boiling-point of acetaldehyde, from which follows that the solubility of this solid phase in acetaldehyde is exceedingly slight at  $21^\circ$ .

With regard to the most important parts of the spacial figure, they are elucidated by sections here too, which will not require any further explanation in connection with what precedes.

The only thing that calls for explanation is the situation of the unary system in the trimolecular, pseudo-ternary system.

HOLLMANN found  $41^\circ.6$  for the boiling-point of the unary system, and now we shall assume that the section  $U, V, W_1$  holds exactly for this temperature.

This section is perfectly analogous to the section  $U, V, W$ , which holds for a higher temperature.

In the section  $U, V, W_1$ , however, the points of the three-phase triangle have shifted so considerably towards the front-plane, that this triangle could no longer be indicated clearly, which, however, is of minor importance here.

What we want to draw attention to in this section is the coexisting phases which are in inner equilibrium, so the boiling liquid phase  $L_1$ , and the vapour phase  $G_1$ .

HOLLMANN thought that this liquid consists of 53.4 mol. % of paraldehyde, and 46.6 mol. % of acetaldehyde, but our investigations have taught that this liquid also contains metaldehyde, though this quantity is very small; the same remark holds of course for the vapour phase  $G_1$ .

If we now examine what we find at temperatures above and below the boiling-temperature in the unary system, we see at once that only vapour can exist above this temperature, and so that only vapour phases in inner equilibrium are possible; these vapour phases are indicated in the spacial figure by the line  $G_1, G_0$ , the direction of which shows that these phases get richer in acetaldehyde with rise of temperature. Below the boiling-temperature of the unary system only liquids in inner equilibrium are possible, so that a liquid line runs from  $L$ , towards lower temperature, till the melting point plane of paraldehyde is reached in  $L_2$  at the temperature of  $6^\circ.75$ .

At this temperature the mixed crystal phase  $S_2$  deposits, and from there another line runs again towards lower temperatures, viz.  $S_2, S_1$ , which curve denotes the inner equilibria in the solid phases.



So it has appeared from what precedes that the observed phenomena are in perfect harmony with the conception that the three considered aldehydes really form a unary, trimolecular, pseudo-ternary system, the connections of which have been examined theoretically here for the first time.

Anorg. Chem. Laboratory of the University.

*Amsterdam*, June 17, 1910.

**Chemistry.** — “*On the system acetaldehyde-alcohol*”. By Prof. A. SMITS and Dr. H. L. DE LEEUW. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of June 25, 1910).

PERRIN<sup>1)</sup> was the first who observed that there exists a close analogy between the behaviour of the system aldehyde-water, and aldehyde-alcohol.

He found for both systems that when the two liquids are mixed, first an absorption of heat appears, and then generation of heat.

PERRIN naturally ascribed the absorption of heat to the physical process, the mixing, and the subsequent generation of heat to a purely chemical reaction, the formation of a compound.

Also Miss HOMFRAY and COLLES<sup>2)</sup> found indications by different ways for the existence of different compounds in the system aldehyde-water, so that a systematical investigation of the system *aldehyde-alcohol* promised to yield a positive result.

An important question, which had first to be answered was this: when compounds are formed, are these compounds addition products or are they bodies which form from these substances with separation of water.

It is clear that this is an important question, because the system can be considered as binary in the case of the existence of addition products, whereas in the other case the system is much more complicated viz. quaternary.

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<sup>1)</sup> Journ. chem. soc. **51**, 826 (1887).

<sup>2)</sup> Journ. chem. soc. **87**, 1434 (1905).

” ” ” **89**, 1249 (1906).