For the complexes of *two* phases, the relative proportions may also be read off in the figure; for those of *three* or *four* phases it would be necessary to also know the relation of the volumes.

The figure also makes it possible to ascertain what changes a mixture will undergo, when the temperature, pressure[1]) or concentration are changed.

Chemistry. — "*Equilibria of phases in the system acetaldehyde +
paraldehyde with and without molecular transformation*". By
Prof. H. W. Bakhuis Roozeboom.

(Communicated in the meeting of September 27, 1902).

The character of the equilibria of phases is exclusively determined by the number of independently variable constituents — components — of which the system is built up.

Sometimes this is equal to the number of the different kinds of molecules. It may also be smaller, if there are among the molecules those which may pass into each other as in the case of associating, ionizing or isomeric substances. If these molecular changes proceed more rapidly than the equilibria of the phases, they exercise no influence on them.

Although water, for example, is a mixture of at least two kinds of molecules, its freezing point is quite as sharply defined as that of a single substance.
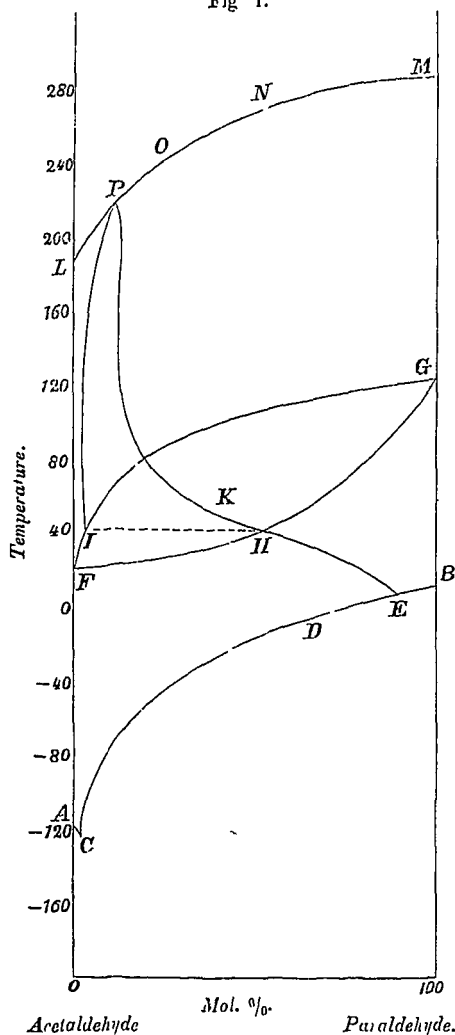
If however, the velocity of the molecular change is small, the system on being treated rapidly will behave like one with more components than it shows if treated more slowly. The effect of this on the phenomena of solidification has already been mentioned by Bancroft in 1898 and by myself in 1899. So far, however, no suitable example has been found which would enable us to consider

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[1]) It demonstrates, for instance, in a simple manner that on compressing vapour mixtures with a sufficient amount of A, the component B first deposits in the solid state in increasing quantity but then again completely disappears at a certain pressure to make room for a liquid phase.

This phenomenon has recently been observed by Kuenen (Phil. Mag. July 1902) with solid CO_2 mixed with C_2H_6

It must always show itself with the component which in the liquid mixtures is the least volatile: in this case B. When however, the liquid-surface has a maximum pressure as in the instance cited by Kuenen, the phenomenon will be noticed with both components. If the surface has a minimum pressure it can only occur with one of the two.

Fig 1.

the whole of the equilibria of phases from that point of view.

Such a system has now been investigated in my laboratory by Dr. HOLLMANN of Dorpat. It is the system acetaldehyde+paraldehyde, which has the further advantage of not undergoing molecular transformation except in the presence of a catalyzer and so behaves like a system with two components, whilst it undergoes transformation rapidly enough on addition of a trace of sulphuric acid to appear as a system with only one component. It becomes possible, thus, for the first time to obtain a general insight into the position which equilibria with apparently one component occupy among the systems with two components.

The chief results of the research are the following.

First of all the solidification phenomena of mixtures of acetaldehyde and paraldehyde were investigated. As is well known, paraldehyde in a pure state melts at 12°.55 (point B). This melting point is lowered by addition of acetaldehyde along to the curve $BEDC$, which continues until the liquid consists almost entirely of acetaldehyde.

With the aid of the apparatus of Prof. KAMERLINGH ONNES[1] the melting point of acetaldehyde was determined at $-118°.45$ (A). The melting point line of acetaldehyde does not extend further than $-119°.9$ (C) where it meets that of the paraldehyde. C is therefore a eutectic point,

	Melting point.	% Paraldehyde.
B	+ 12°.55	100
E	+ 6 .8	88.1
D	− 4 .0	67.6
C	− 119 .9	1.4
A	− 118 .45	0

[1] LADENBURG gave − 120°.

The boiling points of the mixtures were next determined at a pressure of 1 atmosphere and the composition of the vapour of these boiling mixtures was also determined by means of a special apparatus. The former form the line FHG, the latter the line FIG of which the following points are the most important:

F 20°.7 boiling point of acetaldehyde

I 41 .7 vapour   2.5 $^0/_0$ paraldehyde

H 41 .7 liquid   53.5 „   „

G 123 .7 boiling point of paraldehyde.

On account of the great difference in volatility of the two components the liquid- and vapour lines are situated far from each other. The vapour of a boiling mixture is much richer in acetaldehyde than the liquid, for which reason the two are readily separated by fractionation.

In the third place the critical temperatures of the components and of a few mixtures were determined. (Only that of acetaldehyde had been previously found by Prof. van der Waals to be 184°).

Result:

Critical temp.		$^0/_0$ Paraldehyde.
L	188°	0
P	221°	11.0
O	241°	22.0
N	270°	50.0
M	286°	100.0

These are the relations when there is no transformation of acetaldehyde into paraldehyde, or the reverse.

If, however, a trace of a catalyzer is added, acids in particular, the two molecules can be converted into each other, till the condition of equilibrium corresponding to p and t has been reached [1]).

It appeared that by these means the boiling point of *all* mixtures came in a very short time to 41°.7 and as this point according to the line FHG is situated at 53.5 $^0/_0$ of paraldehyde, it represents the relation of equilibrium in the liquid condition at that temperature and 1 atm. pressure. As the corresponding vapour according to point I of the vapour line FIG only contains 2.5 $^0/_0$ of paraldehyde a rational explanation has thus been found of the long-known fact

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[1]) A little meta aldehyde is also formed but the quantity remaining in solution is so very trifling that its influence on the system considered may be utterly neglected. It must still be ascertained what place meta-aldehyde occupies in regard to the two forms at high temperatures.

that on distilling paraldehyde with a little sulphuric acid, nearly pure acetaldehyde is collected.

At temperatures below 41°.7, the equilibrium appeared to be displaced along the line HE, which at 6°.8 and 88.1 % of paraldehyde meets the melting point line of paraldehyde.

The consequence is that, from whatever mixture we may start, paraldehyde will always crystallise out on adding a trace of sulphuric acid and cooling to 6°.8 and as the transformation of acetaldehyde into paraldehyde proceeds very rapidly even at this temperature, the whole mixture becomes at last a solid mass of paraldehyde. This even proved to be the case when pure acetaldehyde was taken as starting point. On the other hand paraldehyde in the presence of a trace of a catalyzer does not melt at 12°.5 but at 6°.5 owing to partial conversion into acetaldehyde.

We have no knowledge of the equilibrium in the vapour at these low temperatures but something can be said regarding higher temperatures.

The lines FHG and FIG have regard to 1 atm. pressure. Similar lines might however, be determined for a higher pressure and in that manner the displacement of the points H and I with the pressure would be determined. Finally, we should thus arrive at the critical line LM and here the compositions of the vapour and liquid, which indicate the relation of equilibrium, must become the same. It appeared from a series of determinations that the point P at 221° and 11% of paraldehyde is this very point.

At these high temperatures, the equilibrium is also reached after some time without a catalyzer.

It appears from the position of P that the line which gives the composition of the liquid when equilibrium is attained slopes in the beginning very rapidly, with rising temperature, towards the acetaldehyde side of the figure (portion EHK)[1]) but afterwards much less rapidly.

The line of equilibrium of the vapour certainly does retrograde, for at 41° the vapour still contains 2.5% of paraldehyde, at 100° less, and at 221° again 11%. In this case the influence of the pressure prevails obviously. As paraldehyde is a triple polymer, the influence of the pressure is very marked.

If we make a representation in space of the whole figure, like the one mentioned in the previous communication, it will be noticed that the equilibria where the possibility of the mutual transformation of acetaldehyde and paraldehyde is admitted, are lines on the surface

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[1]) The point K has been determined by TURBABA at 50°.5 and 39.4%.

which represents the case that the two components are not subject to transformation.

For this another new representation may be given which considers the matter from a more general point of view.

Taking p, t and x as coordinates, a surface may be constructed which shall represent the equilibrium between the two kinds of molecules in a homogeneous phase, vapour or liquid.
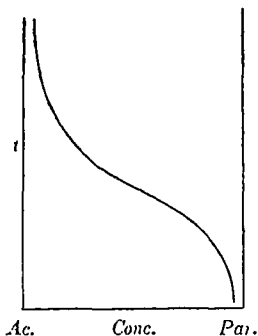

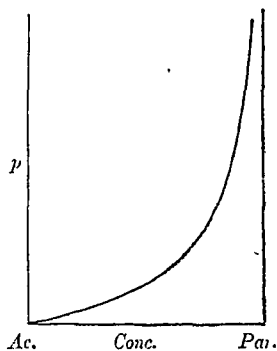|		
Ac.	Conc.	Pan.
Fig. 2.		

Ac.	Conc.	Pan.
Fig. 3.		

The general form of such a surface of equilibrium for the system acet-paraldehyde may be readily deduced from analogy with other known equilibria in the gaseous condition, if one considers that paraldehyde requires heat to pass into acetaldehyde and may be reobtained from the same by compression.

The general course of the equilibrium line at a constant pressure is indicated in fig. 2, that at constant temperature in fig. 3. If we now imagine that on the different points of the t, x-line in a horizontal plane, p, x-lines are erected in vertical planes, we obtain a p, t, x surface of a very peculiar shape which gives the equilibrium relation between acetaldehyde and paraldehyde for every temperature and pressure.

The course may be theoretically calculated for the vapour if the pressure is not too large. With greater pressures and for the liquid state this becomes a difficult matter but the general course remains fairly certain. We might therefore, imagine this equilibrium surface first of all at temperatures higher than those of the critical curve LM. Here, the surface would for some time extend itself undisturbed both vertically and horizontally. At lower temperatures, the surface, on account of its form, must necessarily meet first of all the surface for liquid-vapour; according to the investigation this takes place in the point P. From here to lower temperatures, the

equilibrium surface which was at first continuous will become discontinuous and break up into an equilibrium surface for the vapour state and another for the liquid state.

The lines of intersection of these two surfaces with the surface of two sheets are the lines PI and $PKHE$ in fig. 1. To these must, of course, also be added lines of intersection with the other gas- and liquid surfaces, which have been mentioned in the previous communication.

In this manner, it appears that special equilibria, which occur when transformation between the two components is possible, may be always considered to originate from the intersection of the general space figure for the equilibria of phases with the surface of equilibrium for the molecular equilibria in each phase.

Chemistry. — *"On the action of sulphur on toluene and xylene."* By L. Aronstein and A. S. van Nierop. (Communicated by Prof. J. M. van Bemmelen).

(Communicated in the meeting of September 27, 1902.)

The researches on the molecular weight of sulphur according to the boiling point method of L. Aronstein and S. H. Meihuizen [1] showed that this molecular weight was found to agree with the formula S_8 and this in liquids the boiling point of which varied from 45° to 214°. But when toluene and xylene were used as solvents for sulphur the determination of the molecular weight had given values which corresponded with those calculated from formulae ranging between S_7 and S_8. It was then suspected that this difference might be due to chemical causes. In the following lines we will communicate the results of our efforts to trace those causes.

Action of sulphur on toluene. It had already been noticed that on boiling a solution of sulphur in xylene hydrogen sulphide was given off which was shown by means of lead acetate. A similar evolution of hydrogen sulphide was not noticed on boiling sulphur with toluene. As the chemical action of sulphur on toluene at the usually observed boiling point could probably not amount to much, a preliminary experiment was made by heating a solution of sulphur in toluene in sealed tubes at 250°—300° so as to accelerate the action until on

[1] Proc. Kon. Akad. Wetensch. 1898. First section VI, 3.