

Citation:

Leeuw, H.L. de & A. Smits, On the system acetaldehyde-alcohol, in:
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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).

PERRIN¹⁾ 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 COLLES²⁾ 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.

¹⁾ Journ. chem. soc. **51**, 826 (1887).

²⁾ Journ. chem. soc. **87**, 1434 (1905).

” ” ” **89**, 1249 (1906).

To decide this mixtures of aldehyde and alcohol were placed in glass tubes, which were then fused together.

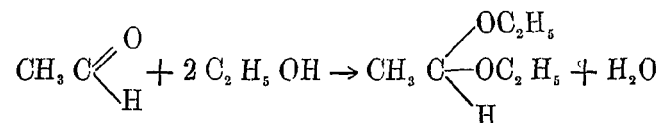
After the lapse of different times these tubes were opened, and anhydrous copper sulphate was added.

The result was that mixtures which had been preserved at the ordinary temperature for *a year*, do not assume a blue colour with CuSO_4 , even after a quarter of an hour's contact, the same result being obtained with mixtures which had not been kept for a year at the ordinary temperature, but had been heated to 100° for some hours.

In this way it was proved that no water had split off, and that when a compound is formed when aldehyde and alcohol are mixed, this must be no acetale, but an addition product, an aldehyde-alcoholate.

In the above-mentioned experiments another remarkable phenomenon was found, which is worth mentioning here.

It appeared namely that when aldehyde-alcohol mixtures are left in contact with CuSO_4 for a *long* time, a blue colour does really appear, and that this is to be ascribed to the fact that CuSO_4 is a katalyser for the formation of acetale according to the equation:



To show this clearly a mixture of 1 mol. of aldehyde and 2 mol. of alcohol was placed with CuSO_4 in a glass tube, which was then fused together.

After a few days the tube was opened, the liquid filtered off from the copper sulphate, which had become *blue*, and then the liquid was distilled by fractions during which process a great quantity of *acetale* could be isolated. In this way a very convenient method of preparing acetale was found at the same time.

As the strong contraction which occurs when aldehyde and alcohol are mixed, led us to suspect, that the determination of the specific weight might give some indication about the existence of a compound, the systematical investigation was opened with these determinations.

The difficulty we met with here, was this, that just as PERKIN had found for aldehyde and water, the spec. weight was *not* constant for some time after the mixing, as the contraction continues for a long time.

To ascertain how long after the mixing the spec. weight yields

reliable results, it was examined by means of a very sensible dilatometer, when the volume of a mixture had become constant, for which we found at 18° one day after the mixing.

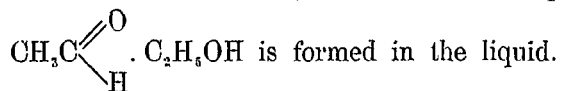
So before the specific weight could be determined, every mixture was placed in a glass tube which was fused at the end, in a thermostat of 18° for more than a day.

The result of the determinations carried out in this way, was as follows:

mol. % of aldehyde	spec. weight 18°/4°
100	0.7834
84.28	0.8277
75.08	0.8474
66.86	0.8601
53.86	0.8715
50.32	0.8719
44.56	0.8709
36.50	0.8627
29.70	0.8501
18.48	0.8296
13.02	0.8200
0	0.7907

If we represent this result graphically, we get the following diagram (p. 332).

So this curve of the specific weights exhibits a very distinct maximum at 50 mol. %, which makes it probable that the compound



We see further from this curve that a determination of the spec. weight can make the concentration of the mixture known to us with fairly great accuracy, if we namely know what component is present in excess. Only in the neighbourhood of 50% this method becomes too inaccurate, on account of the level shape of the curve at that place.

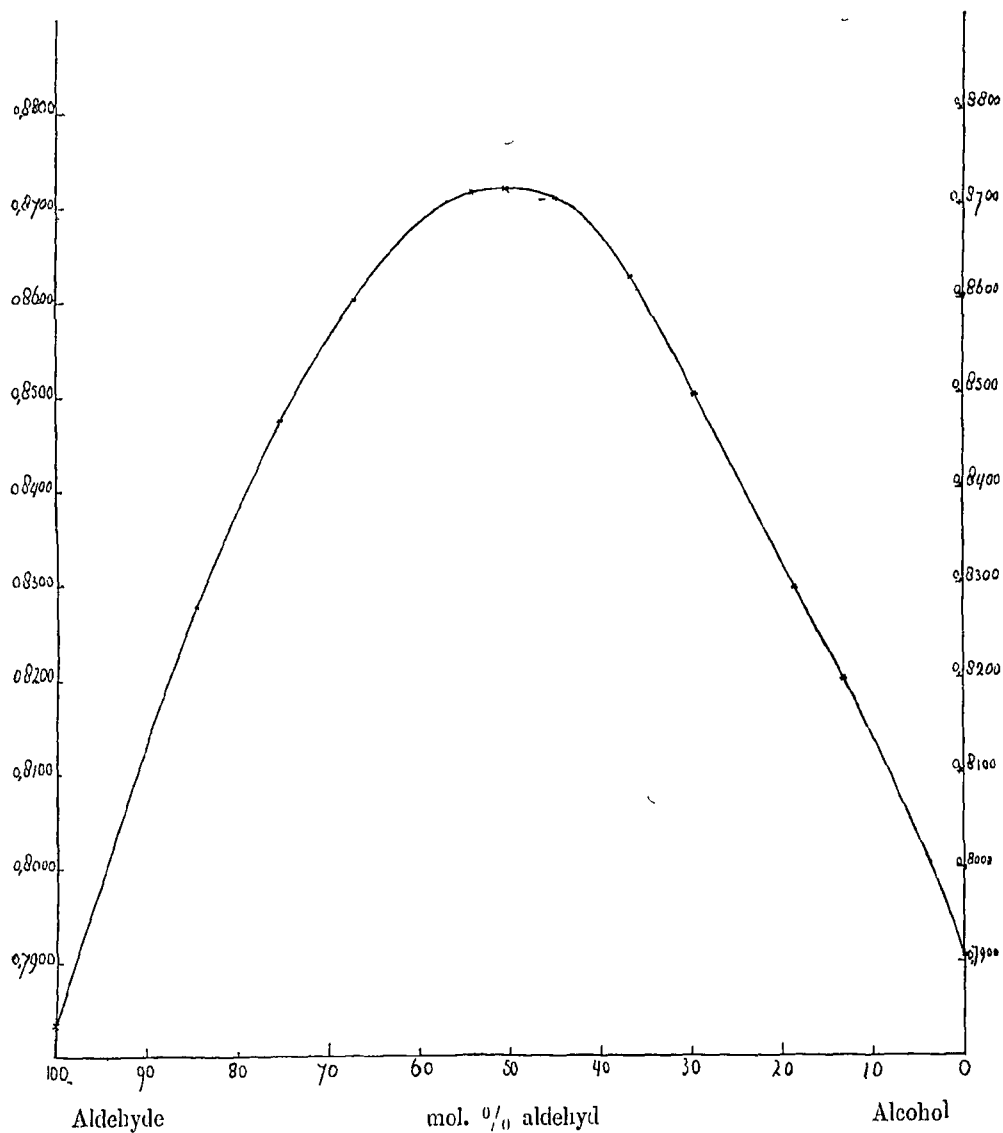


Fig. 1.

After having obtained some indications in this way, we proceeded to the determination of the boiling-points of different mixtures, and the concentration of the coexisting phases at different pressures.

The following results were obtained:

(333)

Pressure 699 m.m. Hg

temp.	concentration liquid	concentration vapour
20.1	100 mol % aldehyde	—
25.3	81.2 " " "	—
29.6	69.7 " " "	—
34.7	57.8 " " "	—
40.1	48.2 " " "	95.8 mol.% aldehyde
48.8	34.6 " " "	85.2 " " "
57.7	20.5 " " "	69.2 " " "
65.3	10.8 " " "	51.1 " " "
76.1	0 " " "	—

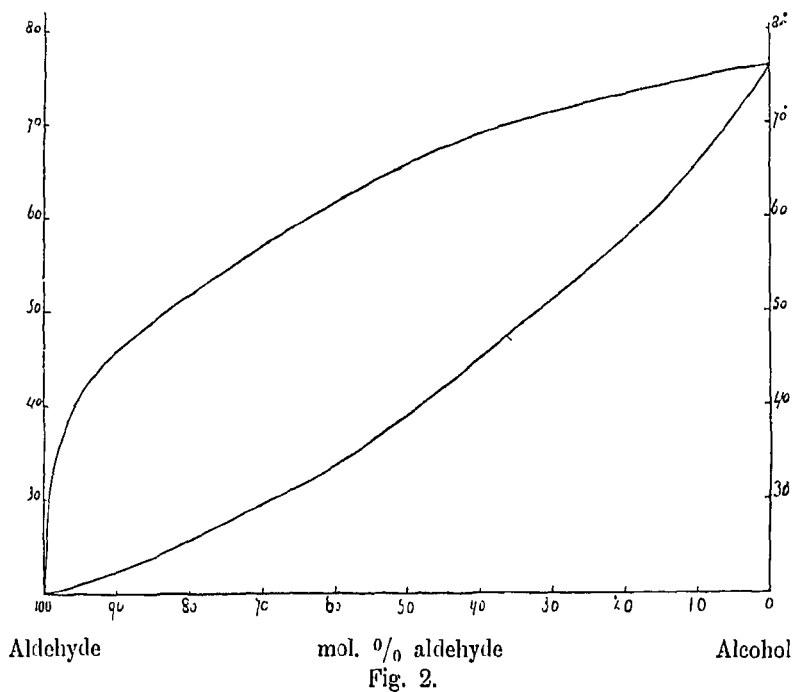
Pressure 398 m.m. Hg.

temp.	concentration liquid	concentration vapour.
5.08	100 mol. % aldehyde	—
11.0	81.2 " " "	—
15.9	69.7 " " "	—
21.9	57.8 " " "	—
29.2	51.5 " " "	95.5 mol.% aldehyde
30.4	46.5 " " "	—
32.3	42.3 " " "	—
37.2	34.6 " " "	91.7 " " "
44.2	24.7 " " "	—
45.4	22.6 " " "	67.1 " " "
51.8	13.6 " " "	—
53.2	11.4 " " "	44.5 " " "
62.8	0	—

(334)

Pressure 97 m.m. Hg.

temp.	concentration liquid	concentration vapour.
- 23.09	100 mol. % aldehyde	—
- 15. 7	66.4 " " "	—
- 7	33.8 " " "	—
- 1. 8	51.6 " " "	—
+ 3. 6	46.5 " " "	—
5. 4	—	94.8 mol. % aldehyde
7. 8	40.9 " " "	—
8. 5	—	91.0 " " "
11. 1	36.9 " " "	—
15. 9	31.6 " " "	79.5 " " "
21. 2	24.8 " " "	—
22. 3	—	67.8 " " "
23. 3	20.3 " " "	65.3 " " "
25. 1	15.5 " " "	—
27. 8	10.2 " " "	—
29. 7	—	38.8 " " "
29. 9	—	34.3 " " "
30. 1	6.9 " " "	24.1 " " "
31. 4	—	20.9 " " "
34. 3	0. " " "	—



If we represent these results in diagrams, we get figs. 2, 3, and 4.

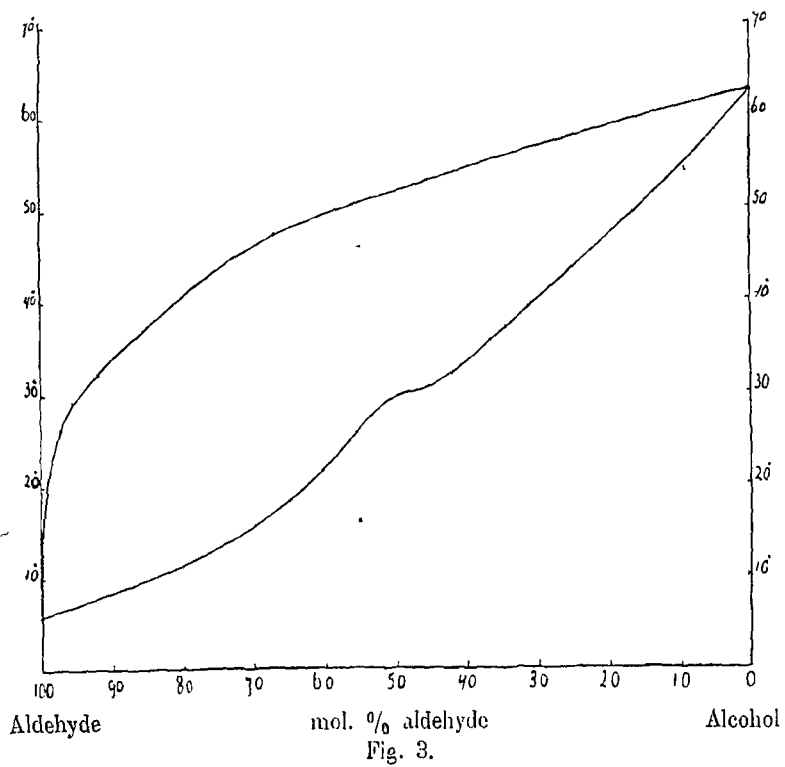


Fig. 3.

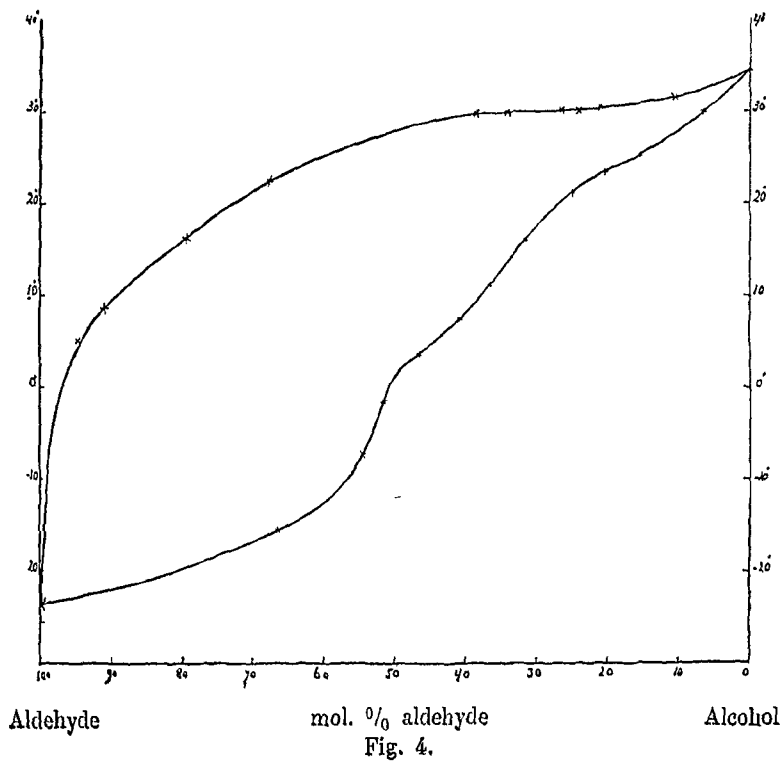


Fig. 4.

Fig. 2, which represents the T, X -section of the liquid-vapour surface corresponding to the pressure of 699 mm. Hg., does not present any particularity; the liquid and the vapour curve lie very far apart, which is a consequence of the pretty large difference in vapour tension between aldehyde and alcohol.

Fig. 3, the T, X -section at the pressure of 398 mm. Hg. shows a constriction at about 50 mol. %, which as is known, points to a compound, whose existence was already suspected on the ground of the density determinations. The vapour which coexists with the liquid of 50 mol. % is much richer in aldehyde, contains, namely, about 95 mol. % of aldehyde, as a proof that the compound is already greatly dissociated at $29^{\circ}.2$.

This is in perfect accordance with the fact that the boiling-point line at the pressure of 699 mm. Hg. does not show anything of a compound.

The most interesting is fig. 4, in which the T, X -section has been drawn which corresponds to the pressure of 97 mm. Hg., for this figure not only points to the existence of a compound of 1 mol. of aldehyde to 1 mol. of alcohol, but also to a second compound of 1 mol. of aldehyde and 2 or 3 mol. of alcohol, because in its neighbourhood the liquid line also shows a constriction, which is, indeed faint, but without doubt essential.

This second compound, whose existence is made probable in this way, must be still more greatly dissociated than the first, which is in accordance with the fact that the boiling-point line of 398 mm. Hg. does not exhibit anything that would point to its existence.

The third method which was followed to get to know the character of the system aldehyde-alcohol was the *calorimetric* one.

As was said before when aldehyde and alcohol are mixed, first absorption of heat occurs, and then generation of heat.

Now it is clear that the heat-effect of the first period is not to be accurately determined from the fall of the temperature, as the exothermic reaction also goes on during this time, the endothermic process, however, at first predominating.

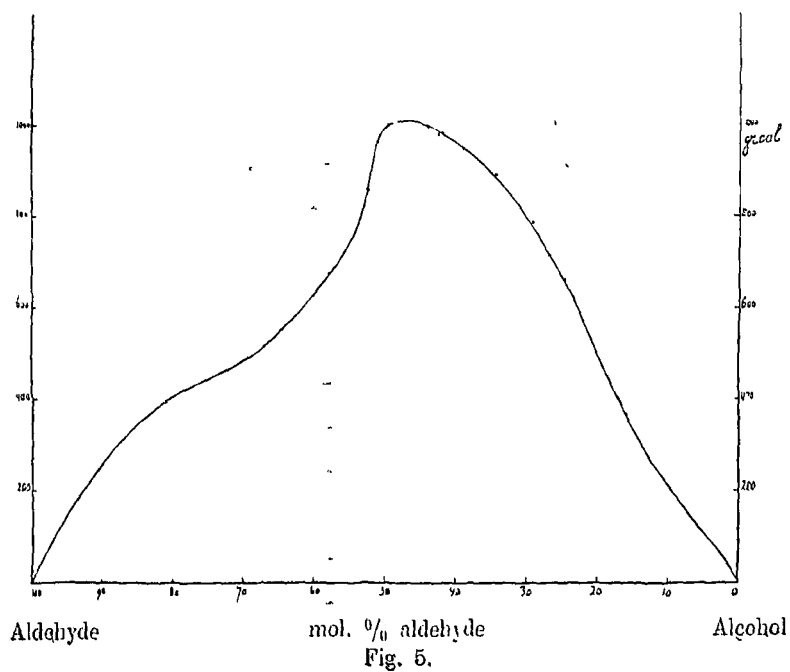
Besides, this fall of the temperature is very greatly dependent on the completeness of the mixing, which is certainly not reached with equal rapidity in the different experiments. So this is the reason that oscillating values are obtained for the negative heat of mixing, and that calculations could be based only on the rise of temperature.

The heats of reaction calculated from this rise of temperature are represented in the following table.

(-337)

Composition of the mixture, obtained by mixing, in mol. % of aldehyde.	Mol. heat of reaction in gr. Cal.
81.10	— 396.2
67.17	— 516.2
64.78	— 554.5
58.12	— 675.3
54.70	— 737.1
52.85	— 859.9
51.14	— 962.8
49.73	— 1000.8
44.22	— 998.2
42.44	— 980.6
42.11	— 987.2
39.06	— 949.5
34.22	— 897.4
30.59	— 781.2
29.10	— 788.5
27.09	— 711.8
24.75	— 657.0
16.21	— 385.5

If we reproduce this result graphically (Fig. 5), we get a curve which shows a maximum for the concentration of 50 mol. %, and



further presents this peculiarity that the course on the lefthand side of the maximum is very different from that on the right.

The curve lies higher on the alcohol side than on the aldehyde side, which proves that special heat-effects are active on the alcohol side, which may find an explanation in the formation of a second compound which is richer in alcohol.

To obtain perfect certainty we proceeded to the determination of the melting-point line, which investigation required much liquid air, for which the arrangement was not yet ready at the beginning of our experiments.

Though we really met with the anticipated obstacles, the difficult crystallisation of the liquids, yet we succeeded in determining the most important parts of the melting-point line, producing in this way the most striking proof for the existence of *two* compounds in the discussed system.

Concentration in mol. % aldehyde.	Final melting-point.
100	— 123.3
90.31	— 125.4
83.90	— 127.6
80.19	not to be determined very viscous mass probably below -132°
77.34	— 126.0
74.45	— 126.05
66.01	— 124.3
59.70	— 123.5
50.73	— 122.3
44.53	— 125.3
39.50	— 128.05
34.33	— 123.2
29.25	— 126.8
25.06	— 132.2
17.32	— 130.6
9.78	— 120.6
0	— 114.

The investigation, which was carried out with a very sensible resistance thermometer, made by Messrs. DE LEEUW and ZERNIKE, yielded the results given in the table on p. 338.

These results enable us to draw also the T, X -section of the P, T, X -spacial figure corresponding to the pressure of 1 atmosphere in so far as the equilibria with solid phases are concerned or in other words the melting-point lines.

From the course of these melting-point lines (fig. 6), in which

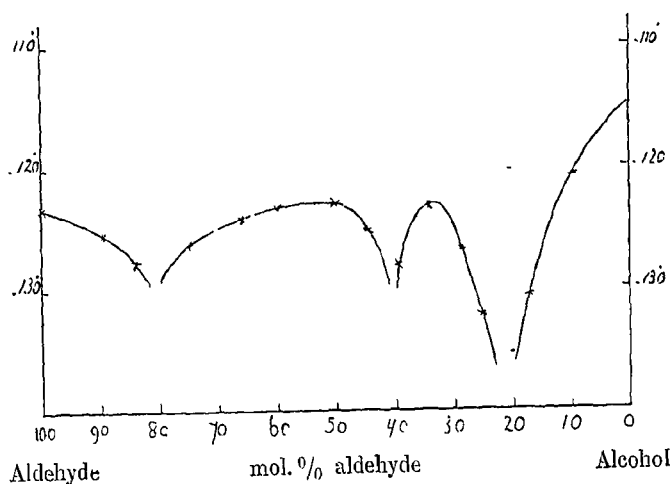


Fig. 6.

two maxima occur, one at 50 % and one at 33 % aldehyde, follows with sufficient certainty the existence of the two compounds $\text{CH}_3\text{COH.C}_2\text{H}_5\text{OH}$ and $\text{CH}_3\text{COH.2C}_2\text{H}_5\text{OH}$, which are considerably dissociated even at the low melting-point temperatures -122° and -123° .

Amsterdam, June 18. *Anorg. Chem. Lab. of the University.*

Chemistry. — “On the system chlorine-sulphur dioxide”. By Prof. A. SMITS and W. J. DE MOOY. (Communicated by Prof. A. F. HOLLMAN).

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

In our search for a clear example of the influence of light on heterogeneous equilibria we have fixed upon the above-mentioned system, of which it was already known that the conversions $\text{SO}_2 + \text{Cl}_2 \rightleftharpoons \text{SO}_2\text{Cl}_2$ do not take place in the dark and in the absence of a katalyser, while light or a katalyser as camphor, animal