

Citation:

Büchner, E.H. & Prins, A., Vapour pressures in the system: carbon disulphide-methylalcohol, in: KNAW, Proceedings, 19 II, 1917, Amsterdam, 1917, pp. 1232-1242

4. From the preceding developments there is seen to be every reason for the expectation, that the development of the solution in powers of the excentricity of Titan, supposing the free libration of θ to be zero, will meet with no difficulties. This conclusion is at variance with NEWCOMB's opinion in his paper: "On the motion of Hyperion. A new case in Celestial Mechanics". There he reaches the conclusion, that the development in powers of e' is not possible. The incorrect performance of this development by NEWCOMB is the reason of this difference of opinion; he omits the terms in the differential equation, which arise from the part of the perturbative function that does not contain e' ; thus he gets a divisor of the order of m'' instead of one of the order of m' . In this respect the theory of Hyperion appears to present no difficulty.

In my dissertation I hope to extend the preceding developments by taking into account the amplitude of the free libration, as well as by giving more accurate results as regards the number of decimals.

Chemistry. — "*Vapour pressures in the system: carbon disulphide-methylalcohol*". By Dr. E. H. BÜCHNER and Dr. ADA PRINS. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of March 31, 1917).

With regard to the vapour of partially miscible liquids, we find in many textbooks the following consideration for the case that the composition of the vapour lies between that of the liquid phases. When, on altering the temperature, the concentrations of the two liquids tend to the same value and, finally, become identical in a critical solution point, the vapour also, it is argued, must have the same composition at that temperature. It is then, however, tacitly assumed that the vapour, which lies at any low temperature between the liquids L_1 and L_2 , remains between them at all other temperatures. This is, however, not at all the case, as KUENEN¹⁾ already showed some years ago with the help of VAN DER WAAALS' theory. In an analytical way he proved, on the contrary, that at the critical point the vapour must have a different composition.

Also from general considerations it is easily seen that a vapour lying within the region of the two liquids must pass without, before the critical point is reached. If it did not, there would exist a point where three phases had the same composition. Now, it is already

¹⁾ These Proc. 6, Oct. 1903.

a particularity, when two phases of a binary system have the same concentration; this only occurs, when the components satisfy definite conditions. To allow of a third phase having also the same composition, still more special conditions, hardly ever to be expected, must be fulfilled. Although this does not prove the absolute impossibility of such a point, we see at once that it is highly improbable, and in any case that it cannot occur in general.

Until now, no single example has been experimentally investigated; it seemed, therefore, important to prove with some system the exactness of the above considerations. We chose the system carbon disulphide-methylalcohol.

The principal thing is to show that in the t, x -diagram the curve indicating the concentration of the vapour, runs as is drawn in figure 1. This gives the change of composition, which the three

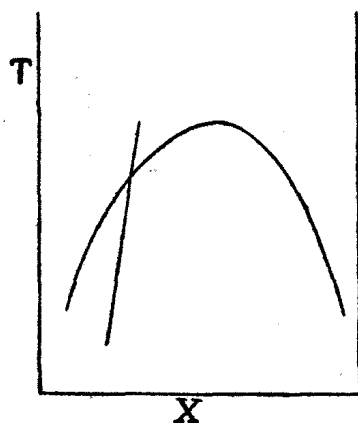


Fig. 1.

phases — permanently remaining in equilibrium — undergo by rise of temperature, or, as we may also express it, the t, x -projection of the triple curve. At low temperatures, the order of the phases is L_1GL_2 ; G and L_1 become equal at a certain temperature after which the order is GL_1L_2 ; at this peculiar temperature, the G -curve cuts the L_1 -curve.

This is the cause of another particularity, which may also be considered as a characteristic of these systems. The

p, x -diagram must have the form of fig. 2 at low temperatures — when the order is L_1GL_2 —, and that of fig. 3 at higher ones, as is easily seen graphically. The transition between these is formed

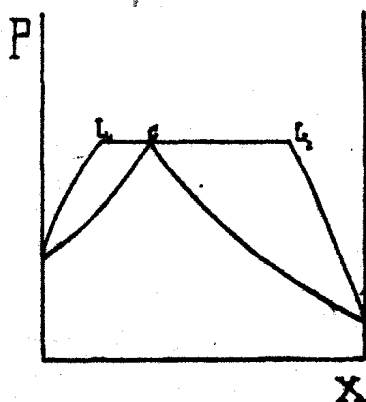


Fig. 2.

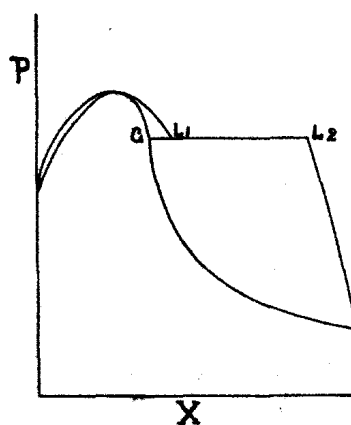


Fig. 3.

by a peculiar figure, in which G and L_1 coincide exactly at the triple pressure, where also the maximum-point (at which the liquid and vapour curves touch each other) is situated. We tried to study both figures in the system chosen.

In the first place, we investigated the p, x -diagrams at several temperatures. With a tensimeter the vapour pressures of different

TABLE 1.

CS ₂		CH ₃ OH		Triple curve	
t	p	t	p	t	p
21.4°	307 mm	33.4°	188 mm	0°	154 mm
24.3	344	36.2	210	8.6	227
25.0	357	42.3	280	9.6	239
26.5	376	45.3	319	10.1	245
28.9	414	48.0	370	12.8	272
29.5	420	50.8	410	13.0	280
32.4	467	53.5	463	14.8	303
33.3	480	56.1	529	13.8	313
36.0	530	58.6	590	18.3	345
37.2	550	60.0	627	19.6	372
38.3	573	64.6	760	20.8	389
40.4	616			21.4	403
43.2	676			22.0	410
43.6	685			26.0	484
44.8	715			26.3	491
46.5	761			28.2	523
				29.0	550
				29.4	556
				31.0	588
				33.6	654
				34.1	668
				34.5	679
				36.4	725
				36.6	734

mixtures were determined at a set of temperatures. So long as there are three phases together, we find of course always the triple pressure; as soon, however, as one of the liquids has disappeared, we leave the triple curve, and every mixture will exhibit its own pres-

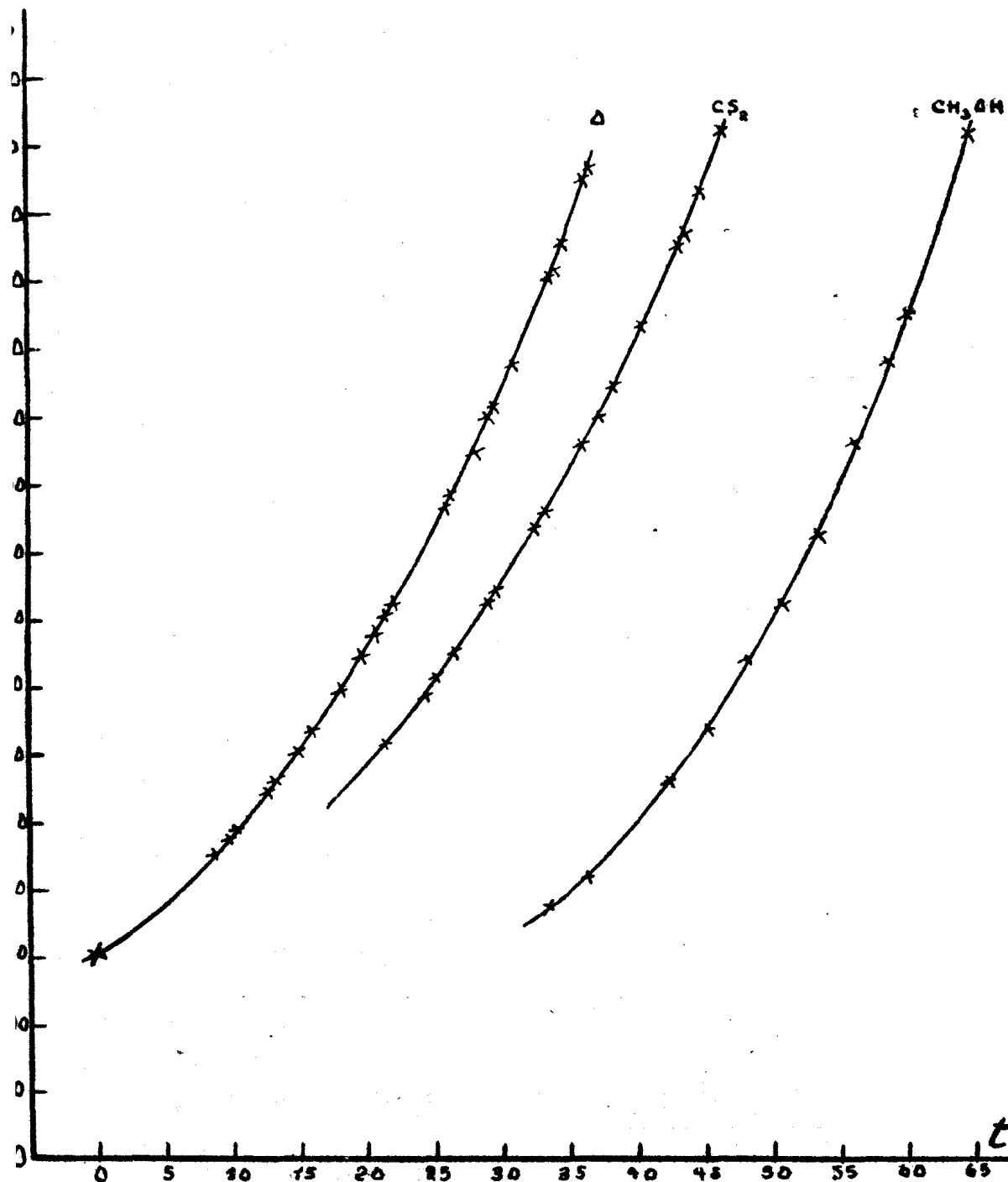


Fig. 4.

sure. On the p, t -curves thus found, we interpolated the pressures at definite temperatures and construed from these the p, x -curves. The tensimetric method has the great advantage, that the mixtures come into contact with no other substance than mercury, the appa-

TABLE 2. Concentration in mol.proc. methylalcohol.

4.66%		11.72%		19.43%		26.4%		30.66%		52.9%		72.17%		90.3%	
t	p	t	p	t	p	t	p	t	p	t	p	t	p	t	p
17.8°	339 mm	34.4°	669 mm	39.9°	828 mm	40.2°	841 mm	39.8°	826 mm	37.7°	759 mm	17.2°	333 mm	0°	128 mm
21.0	388	38.2	767	43.2	936	41.0	865	41.2	877	38.6	792	22.6	416	14.3	240
23.1	422	41.5	874	46.8	1072	43.4	944	42.5	915	38.8	799	27.4	507	18.6	289
23.9	438	41.9	883	50.0	1193	45.8	1031	44.0	966	40.0	835	32.8	626	19.0	291
28.8	536	46.1	1033			48.3	1128	46.0	1037	42.0	896	39.2	790	19.4	296
34.8	672	50.2	1190			49.6	1178	46.8	1073	43.2	943	44.9	975	27.2	405
38.1	767							47.4	1090	43.6	954	45.1	979	27.8	416
44.4	959							47.9	1106	45.0	1001	50.0	1168	34.0	526
48.2	1092							49.6	1179	47.0	1075			39.2	639
50.4	1176									50.0	1196			45.4	798
52.4	1259													51.3	976
														54.6	1097
														58.3	1238

ratus being sealed as soon as it is filled. Much preliminary work showed us the importance hereof; rubber stoppers are attacked by carbon disulphide, corks cannot be used, because the methylalcohol absorbs water from them; when using ground stoppers or taps, one experiences difficulties with the lubricants.

The substances used were carefully purified. The purest commercial carbon disulphide was shaken with mercury, left for some time on quick-lime and distilled off. Finally it was distilled once more, all these operations being performed at red light. It was kept continually in the dark. The boiling point was 46.4° at 760 mm.; it did not stick to the condenser and had hardly any, in any case only a not disagreeable ethereal odour.

The methylalcohol, also the purest commercial product, was treated with iodine and natron, boiled afterwards with quick-lime, left for some time on sodium and distilled off. At last it was fractionated, and the fraction, which distilled between 64.5° and 64.6° (760 mm.) was separately received. It was absolutely free from water, as was proved by the well-known reaction with anhydric coppersulphate. The salt itself remained perfectly white, while part of it dissolved slowly with a light-green colour.

In table 1 (p. 1234) and fig. 4 (p. 1235) the results as to the components themselves and the triple curve are given. The points of the latter are determined with different mixtures; they all fit very well into the curve.

The measurements, relating to different mixtures above their solution point are joined in table 2. It appears that the pressures of most mixtures are nearly equal, and that the pressure curves run so closely to each other that we had to refrain from joining them in one figure. Instead thereof, we have construed for a number of temperatures the p,x -diagrams, by interpolating on the different curves the pressure values corresponding to those temperatures.

The result showed it to be impossible to realize in this system the transition sought for. Until just below the critical point, which we found at 37.4° , the p,x -curve retains the shape of fig. 2, in which the triple pressure is the highest (fig. 5, (p. 1238) that is given as an example for 35°). The form is very remarkable: the liquid branches change almost imperceptibly into the horizontal line, as is already known indeed for other systems with partial miscibility; a maximum however is not to be observed.

The curves for temperatures above the critical point might happen to give some decisive answer to the question.

If there had been a distinct transition from the curve of fig. 2

into that of fig. 3, we should have found above the critical point a curve with a maximum and an inflexion point. The curves however appeared to run very flat (fig. 6); it was therefore impossible to ascertain, where the maximum lies, while the inflexion point has already disappeared immediately above the critical point. ¹⁾

It still remained to investigate, if a satisfactory result might be obtained by determinations of the vapour concentrations. We heated therefore a two layer system to boiling, distilled off a part of the vapour and determined the solution point of the distillate in order to find the concentration thereof.

First of all, we wanted the determination of the whole solubility curve, which we carried out by the well-known synthetic method in sealed tubes. Our results (table 3 and fig. 7) differ from those obtained formerly by ROTHMUND; our critical point lies 2.5° lower.

Doubtless this difference is to be explained by difference in purity of the substances; in the first place we think of traces of water. ²⁾

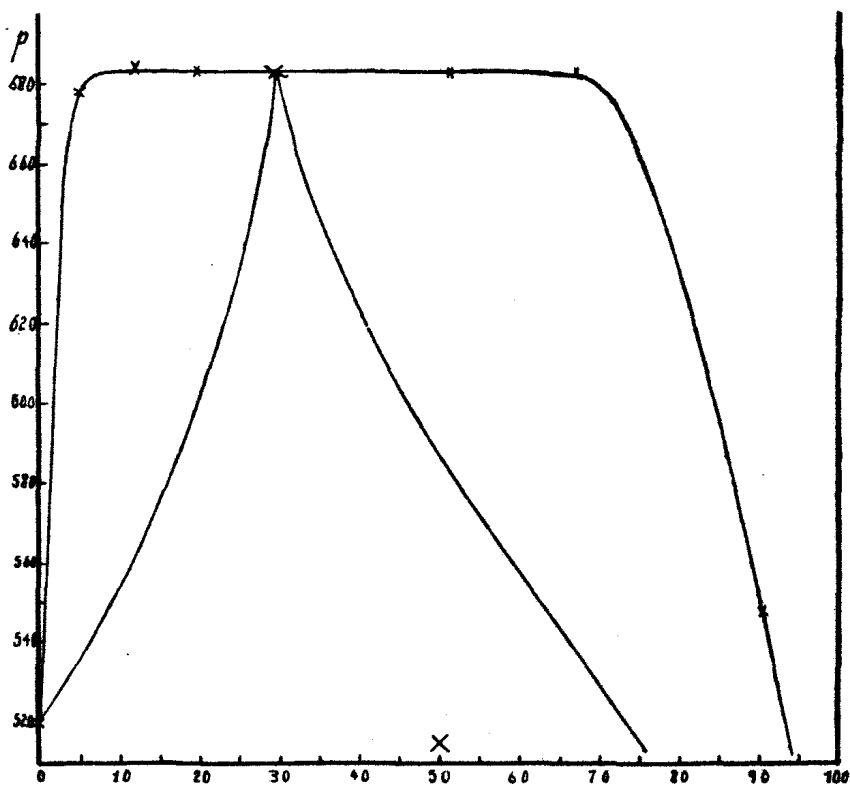


Fig. 5.

¹⁾ Cf. the system phenol-water investigated by SCHREINEMAKERS, Z. f. phys. Ch 35, 459, 1900.

²⁾ We found experimentally, that the solution point is increased 0.7° by addition of 1 ‰ water.

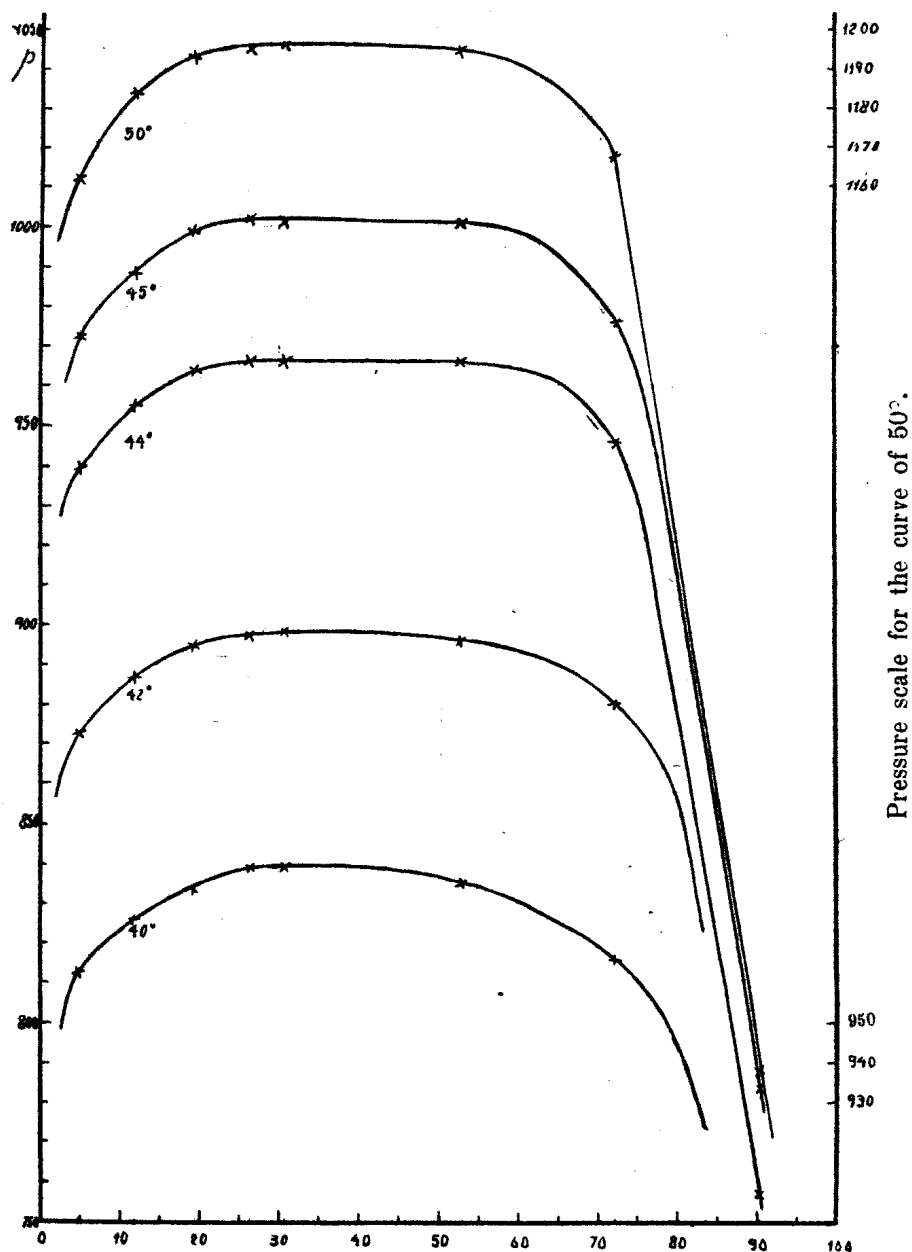


Fig. 6.

We too found in our first experiments critical points of 40° or even higher. It is sufficiently known that small impurities have an enormous influence, especially on the critical point; they may cause it to rise, for instance, 100 times as fast as the boiling point. This is the reason why the triple curve is not nearly so sensitive to impurities and why our former determinations with substances, which showed the critical point 39.5° , as well as the more recent ones fit perfectly into one line.

TABLE 3.

Conc. in mol.proc.	<i>t</i> solution point
8.1	21.8
14.1	30.8
21.2	35.9
24.4	37.4
29.4	37.1
34.6	37.2
42.4	37.4
50.8	35.3
52.9	34.7
61.0	28.7
72.8	11.2
81.0	-15

} The critical point is situated between these two concentrations.

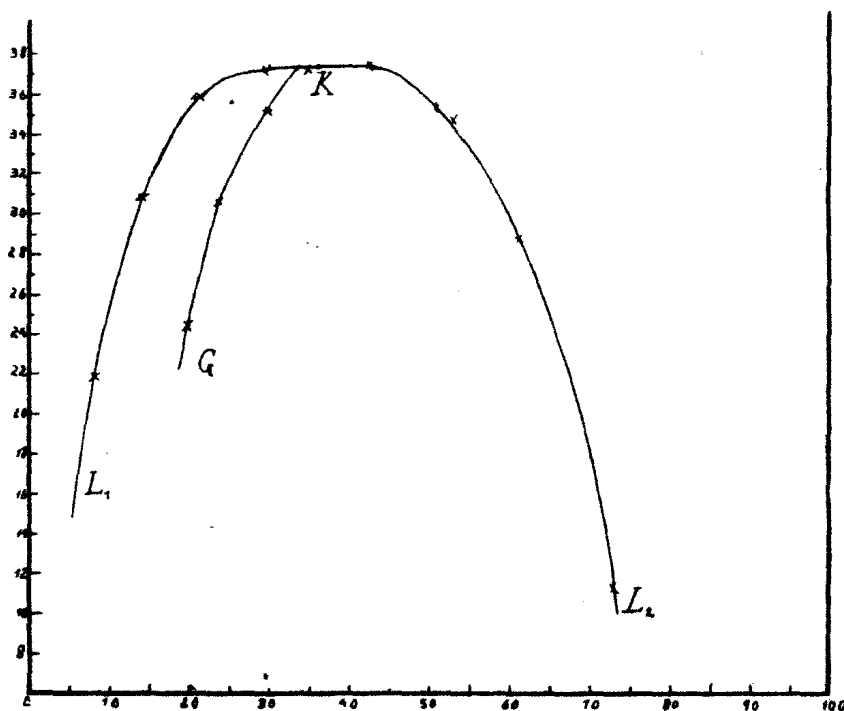


Fig. 7.

We used for the boiling experiments an apparatus, constructed some time ago by Prof. SMITH. At first, we had boiled the liquids

by electric heating by means of a platinum wire in the liquid. It appeared, however, that in this case decomposition occurred, as was immediately proved by an abnormally high solution point of the distillate. Prof. SMITH then directed our attention to the apparatus represented in fig. 8. To the flat bottom of a glass tube 20 cm long and having a diameter of 2 cm a little, narrow tube *A*, 2 cm long, is sealed, which is wrapped with a sheet of asbestos paper, round which nickelin wire is wound. By an electric current the liquid in this short tube is then so strongly heated, that it brings the whole mass very quickly to boiling. Nevertheless, when making experiments under lower pressures, it was desirable to throw in some little capillary tubes, as the substances are very highly liable to superheating. The whole apparatus was packed with cottonwool in an asbestos mantle. It is provided with a ground stopper, from which a thermometer (Anschütz) is hanging, and with two side tubes: *B*, leading to a reflux condenser, and *C*, which — enveloped by nickelin wire and sufficiently heated during the experiment — leads the vapour to the receiver.

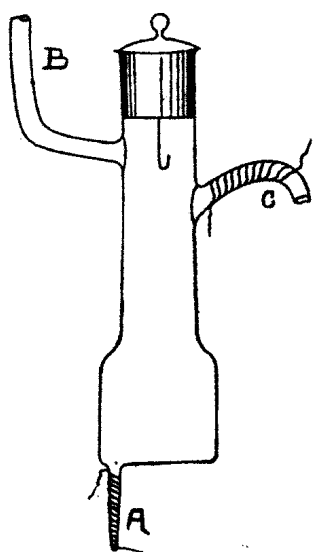


Fig. 8.

This consisted of a wide glass tube cooled by carbon dioxide and alcohol, in which one or two small tubes, provided with a constriction, were placed, which might contain about 1 c.c. of liquid. When the moment of receiving the distillate has arrived, the wide tube is turned in such a way that one of the narrow tubes comes to stand under the end of *C*. When it is sufficiently filled, the experiment is finished, and the tube is sealed.

By a determination of the solution point, we knew at the observed boiling temperature the concentration of the vapour, while the composition of the liquids was found from the solubility curve. We made this experiment at three different pressures with the results given in table 4 and drawn in fig. 7.

TABLE 4.

p	t	x_G
444 mm	24.4°	19%
600	31.5	24
688	35.2	30

Whereas the two first determinations were easily made, we met in the third with a serious difficulty, which made us refrain from further experiments above 35°.2. The solution point of the last distillate lies namely at 37°.2, so on the almost horizontal part of the solubility curve. Thereby, the determination of the concentration in this manner becomes inexact, which would become still worse at the higher temperatures. We have checked it for this distillate by adding a weighed quantity of carbon disulphide, altering thereby the composition and the solution point so as to bring them on to a part of the solubility curve, which is more easily determined. No important difference was found.

The experiments carried out show, however, clearly, that this system does not afford a plain proof of the theory. Although we see that the vapour line after extrapolation cuts the solubility curve at 32 molproc., whilst the critical point lies at 36%, the temperatures of the intersection point and the critical point cannot be distinguished. The course of the curves being so unfavourable for our purpose, we decided to take no more experiments with this system. Our result is remarkable in this point: although the theory proves, that the vapour branch does not leave the region of limited miscibility in the critical point, the opinion previously expressed that this had to be the case, is not very far from the truth.

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Experimental Psychology. “— *Intercomparison of some results obtained in the Investigation of Memory by the Natural and the Experimental Learning-Method*”. By Dr. F. ROELS. (Communicated by Prof. C. WINKLER).

(Communicated in the meeting of March 31, 1917.)

In the investigation of memory psychologists have always had recourse to learning-experiments, with the purpose to ascertain, under definite experimental conditions, the retentive capacity of the memory with regard to the material impressed upon it. Whatever method was employed (the learning-, or the saving- or the hitting-, or the helping-method) the imprinting occurred invariably in the same way. The material to be learned, by preference meaningless, was presented to the observer at a certain rate of succession, and more or less frequently, according to the object in view. Psychologists did not always take into account the learning-method peculiar to every