Tinca vulgaris, Perca fluviatilis. An emptied air-bladder was never filled again after the Rami intestinales Vagi had been cut through on both sides.

Finally I have tried to ascertain if, for some time after the air-bladder has been emptied, an increased absorption of oxygen could be observed. Theoretically there is of course every reason to expect this, and the strong almost asphyxial respiratory movements of the fish after the bladder has been emptied, render it very probable.

The experimental proof is difficult to give. I omit here the technical details relating to the oxygen determinations. On comparing the oxygen consumed by a fish in rest, before the bladder has been emptied and after it, it is found that in the latter case an increase may be observed. It is a remarkable fact, which is difficult to explain, that often immediately after the gas-extraction the oxygen-consumption fell below the average.

Chemistry. — *"On critical end-points and the system ethane-naphtalene"*. By Dr. ADA PRINS. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of Jan. 30, 1915).

After SMITS' investigation of the system ether-anthraquinone [1]) no other binary system has been found which shows in a similar way the critical end-points. It was, therefore, my intention to search for such a case. Should I succeed in finding end-points p and q, which might be easily realized, it would be possible by an appropriate choice of the components to obtain one of the types of ternary systems theoretically developed by SMITS [2]) by combination of two binary ones. As the following shows, I have not been successful in finding a system analogous to ether-anthraquinone; so I had to give up the research of a ternary system.

Obviously either ether or anthraquinone recommended itself as one of the components. As the melting-point of the less volatile component must be above the critical temperature of the more volatile one, and the solubility of the former substance must be slight even at the critical temperature of the latter, and moreover no decomposition may occur, the number of substances suitable for investigation, is not large.

The preliminary experiments, showing whether critical end-points occurred or not, were made in small sealed tubes, which were heated

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[1]) Z. Phys. Chem. 51, page 193.
[2]) Proc. R. Acad. Amsterdam June 1912.'

in an air-bath. If the first critical end-point was observed, the pressure and temperature of p were determined oy the CAILLETET-method and q was also sought for.

The binary systems which 1 examined are the following:

Ether-alizarine.

A preliminary investigation by Smits [1]) had already shown that the three-phase line intersects the plaitpoint line. The meltingpoint of alizarine (290°) is about as high as that of anthraquinone (284.6°) and much above the critical point of ether (T_k 193.9°, P_k 36.1 atm.). I observed the first critical end-point p at 196.4° and 37.5 atm. So the solubility of alizarine in ether proves to be so small, that the critical temperature of ether is only increased by 2.5°. This increment is much smaller than in the case of the ether-anthraquinone system, where p lies at 203° and 43 atm.

For the determination of q a mixture of higher concentration of alizarine was required. The large quantity of alizarine caused however the observation to be extremely difficult; the vapour-phase and the liquid-phase were both dark black-red, so that the meniscus was no more to be distinguished. On this account it could only approximately be established, that q lies about 258°; the system was improper for an exact investigation.

Ether-hexachlorobenzene.

The melting-point of hexachlorobenzene lies at 224°; the difference with the critical temperature of ether being much smaller than in the former case. The solubility appeared to be so great, that the three-phase curve does not meet the plaitpoint line.

Ether-isophtalic acid.

Isophtalic acid having a high melting-point (330°) dissolves so slightly in ether, that the critical line starting from ether is already intersected at 196.1° and 36.8 atm. Since the isophtalic acid is decomposed by heating a long time at high temperatures, q could not be determined.

Hexane-anthraquinone.

This system does not show critical end-points.

As the combination of either ether or anthraquinone with another

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1) Z. Phys. Chem. 51. p. 214.

substance did not give satisfactory results, I resolved to investigate systems one of the components of which is a gas at ordinary temperature.

According to Büchner's research [1]) CO_2 gives critical end-points with several other substances. It was however not closely examined whether these systems belonged to the simple case ether-anthraquinone or to the type diphenylamine-carbonic acid, discovered by Büchner.

The systems *naphtalene-carbonic acid* and *diphenyl-carbonic acid*, which I studied, showed both the first critical end-point. The fact. that in both systems the three-phase curve starting from the triple point of the solid substance had a steep rise (fig. 1), led to the conclusion, that the systems were analogous to the system diphenylamine-carbonic acid.
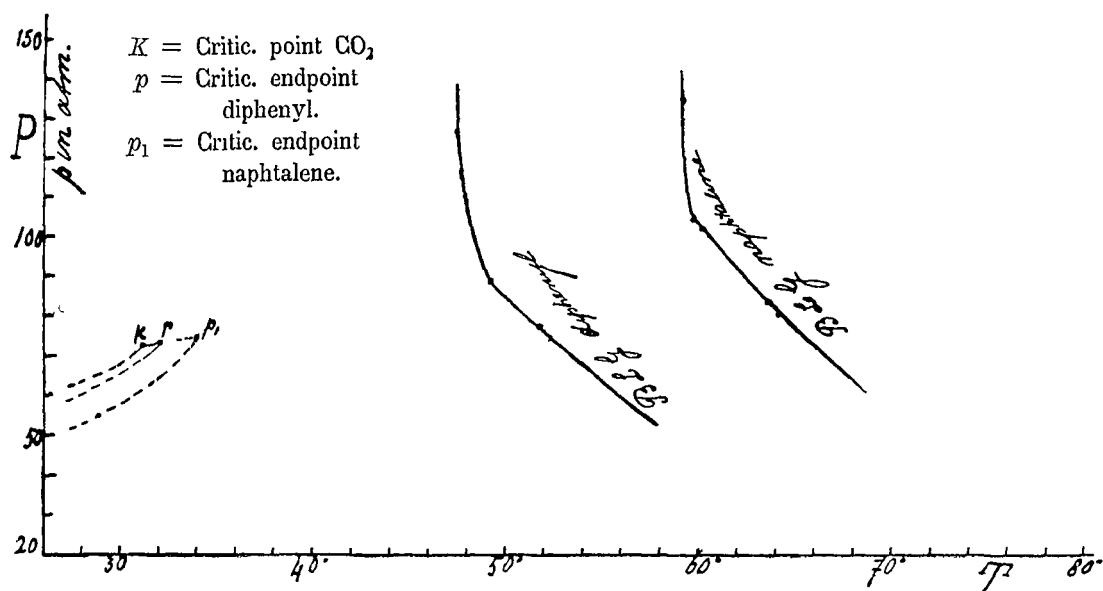

K = Critic. point CO_2
p = Critic. endpoint diphenyl.
p_1 = Critic. endpoint naphtalene.

Fig. 1.

This made me suppose that other systems with carbonic acid would also show a steep three-phase curve and accordingly q at a high pressure or no q at all. So I resolved to try systems with ethane.

Ethane-naphtalene.

Preliminary experiments showed also this system to have the above _ mentioned property. Because it had proved very difficult to find another example of the type ether-anthraquinone and as moreover the phenomena suggested that in this system points might be realized which had not yet been observed, I still commenced a closer study.

[1]) Thesis for the doctorate, Amsterdam 1905.

The type, to which this system belongs has been theoretically developed by BUCHNER[1]) in his study on systems with limited miscibility, in which together with the equilibrium of fluid phases a solid phase occurs. It has in common with the system ether-anthraquinone, that the melting-point of the less volatile component *B* lies above the critical point of the more volatile *A* and that the solubility of solid *B* in liquid *A* is small. The three-phase curve, on which solid *B* coexists with its solution in liquid *A* and with a vapour-phase, intersects the critical curve starting from the critical point $L = G$ of the first component, giving rise to the first critical end-point *p*. As however the component *B* has not only in the solid state a small solubility in liquid *A*, but also molten *B* is only partially miscible with *A*, the second critical end-point may arise in a way different from that in the system ether-anthraquinone.

From the triple point of *B* a second three-phase curve starts, giving the equilibrium of solid *B* with the solution of *A* in liquid *B* and with a vapour phase. As the melting-point of *B* lies above the critical point of *A* the vapour of this three-phase line at high pressures will have densities corresponding to a liquid; therefore the line will rise steeply. The point of intersection of this curve and the critical line $L_1 = G$ or $L_2 = L_1$ is the second critical end-point. Here two liquid phases
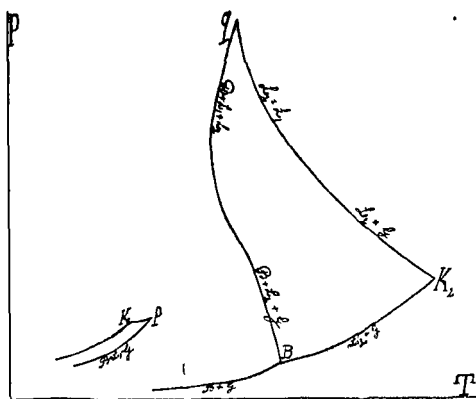

Fig. 2

become identical in presence of a solid phase. Figure 2 represents the *P-T* projection of the space figure of this case. BÜCHNER has found the first experimental instance of this type in the system diphenylamine-carbonic acid. The critical end-point *q* could not be determined because the critical pressure was not attainable or did not exist.

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[1]) loc. cit.

In the system ethane-naphtalene I succeeded not only in finding the point *p*, but also *q*.

The ethane was prepared by electrolyzing sodiumacetate. The anode gas was purified by bromine water and a strong solution of potassium hydroxide, dried over sodalime and condensed in a receiver , by liquid air. Subsequently it was again dried over phosphorus pentoxide and separated from the more volatile part by fractionating by the use of liquid air. The disappearance of the discharge in a GEISLER tube attached to the apparatus served as criterion of purity. I determined the critical point from three fractions of the so purified ethane. The following well agreeing values were found:

	T_k		P_k	
1st fraction	31.8°		48.23 atm.	
2nd fraction	32.3°	mean 32 32°	48.09 atm.	mean 48.13 atm.
3rd fraction	32.35°		48.18 atm.	

The further investigations were made with the second and third fraction.

The naphtalene was purified by sublimation; the melting-point was 80.8°.

The apparatus represented in fig. 3 was used for the preparation of the mixtures.

A is the storing-vessel with purified ethane. *B* is calibrated. In *C* ethane may be condensed by liquid air, whereas *D* is filled with cocoanut charcoal to absorb the last traces of air after the evacuation of the apparatus. The Cailletet tube *E* was connected with the rest of the apparatus by rubber tubing protected by mercury. A weighed' quantity of naphtalene and an electromagnetic stirrer were placed beforehand in the Cailletet tube and fused on to the top by carefully heating. After exhausting the whole apparatus, the naphtalene being cooled by solid carbonic acid and alcohol, ethane of definite pressure, to be read on the manometer *G*, was pressed over into the Cailletet tube by the aid of air-free mercury contained in the vessel *F*; in this way the required quantity of gas was mixed with the naphtalene. The tube was then placed in the pressure cylinder filled with pure mercury freed from air by boiling. The tube was heated and the pressure regulated in the same way as
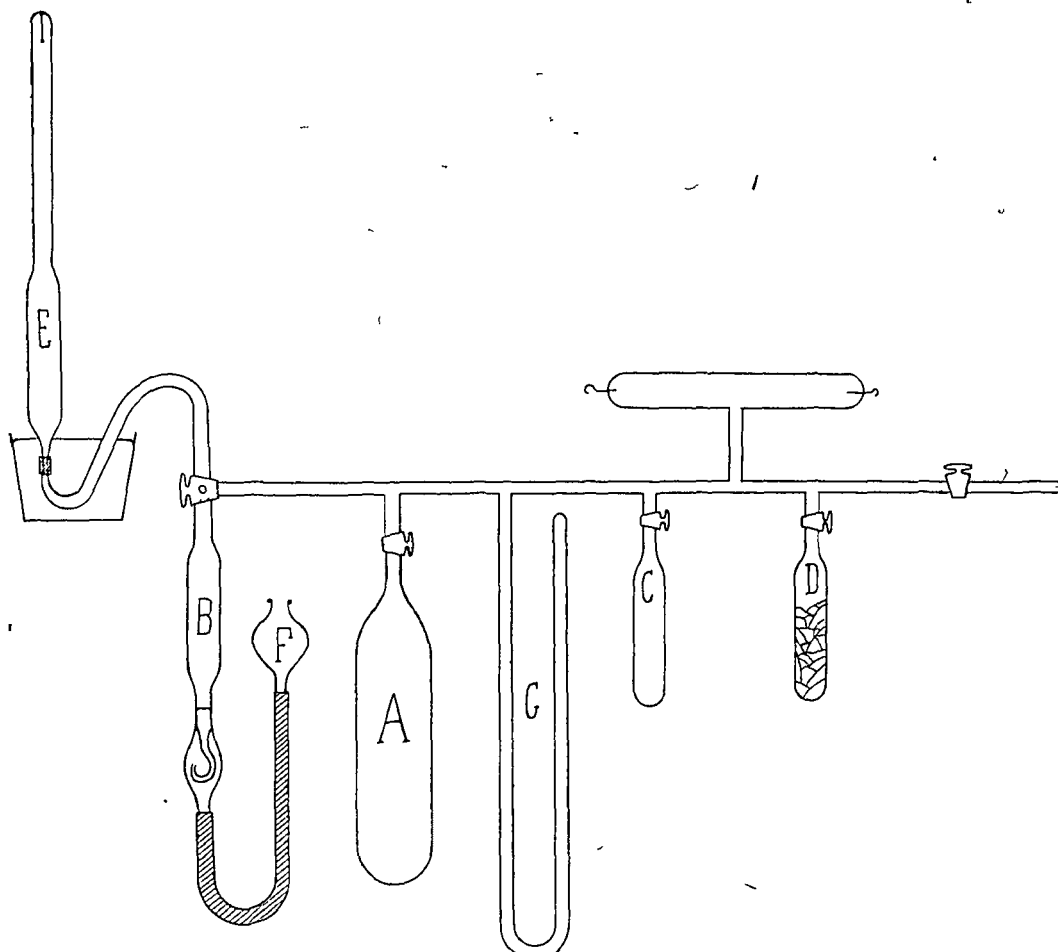
Fig. 3

was already used before in this laboratory.[1] Fig. 4 shows the *PT*-projection of the space figure, whilst table I gives a survey of the observations.

The three-phase line *BSQ*, on which solid naphtalene coexists with a solution of ethane in liquid naphtalene and vapour, was determined by slowly heating at a definite pressure till the mass began to fuse. As the equilibria established themselves extraordinarily slowly, the experiments required much time, and it was very difficult to fix the moment that the liquid appeared and increased.

The second critical end-point *q* could not directly be observed. It was almost impossible to determine the point, where two phases became identical in the presence of the third, because the temperature varies only extremely slightly at considerable changes of

[1] SCHEFFER, Proc. Royal Acad. Amsterdam 1912.

TABLE I.

T	P atm.	
32.32	48.13	Critical point ethane.
37 40	51.73	Critical point unsaturated solution
39.40	**52.89**	p
		Curve BSQ
62.1	47.81	$S_B L_2 G$ of $S_B L_2 L_1$
58.4	59.28	„ „
56.3	97 07	„ „
55.7	85.96	„ „
55.5	78.17	„ „
55.1	70.43	„ „
		End-condensation line EF, mixture 25 à 26 mol. % napht.
71.4	133.89	$L + G \rightarrow L$
69.3	132.11	„
67.4	130.45	„
65.4	128.68	„
63.5	127.07	„
62.1	125.79	„
59 9	123.76	„
55.7	120.56	„ (metastable)
		End-condensation line GH, mixture 24.75 mol. % napht.
66.0	130.26	$L + G \rightarrow L$
62.2	127.57	„
61.05	126.59	„
59.9	125.75	„
57.5	124 06	„
56.5	123 06	„ (metastable)
55.05	122.57	„ „
52.4	122.27	„ „
59.9	126.64	Point max. pressure mixture ± 24 % napht.
55.5	123.81	Point upperbranch PT-loop same mixture.
57.4	**124.8**	q

Fig. 4.

the pressure and moreover the appearing and disappearing of the solid is much liable to retardation.

To determine the point q still as exactly as possible I used the method described below, which offers values, deviating only slightly from the real ones. The following figures will illustrate it.

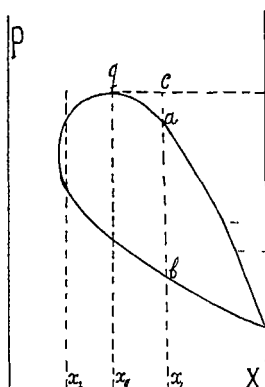Fig. 5 gives the P-X projection of the three-phase line. When we
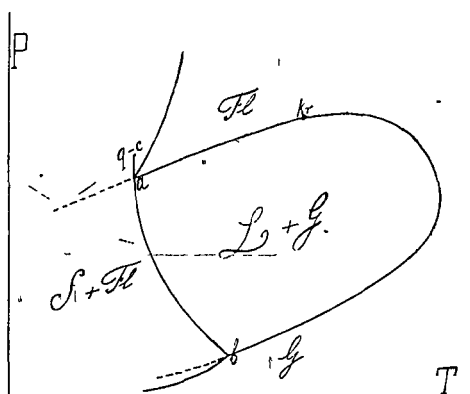

Fig. 5.

Fig. 6.

consider a mixture of the composition x_1, which contains more naphtalene than is necessary for realizing q, we see that the PT projection of this mixture must be as is drawn in fig. 6, in which the points a, b, and $c(= q)$ correspond with the homonymous in fig. 5. This section gives the part of the three-phase line between b and $c'(= q)$. If a direct determination had been possible, q might have been found with this mixture. Although I failed to find q, I could study in this section the line of end-condensations, and the point of intersection a of this curve with the three-phase line (see table 1 and fig. 4).

This point a will slightly differ from q, when x_1 lies near x_q. From the distance of $kr(L = G)$ from a we can judge whether this is actually the case, because in the PT section $x_q kr$ and a coincide. The smaller the distance the nearer we are to q. It is however possible that the composition along the critical line varies only slightly with the temperature, so that in a mixture the composition of which differs slightly from $x_q kr$ is nevertheless far from a. This proved to be actually the case on studying a second mixture. If the concentration of this mixture had been exactly that of q, then the PT projection of fig. 7 would have been found. Here the point q lies just on the line of the end-condensations. By studying the upper branch of the loop-line LG, on which the meniscus dis-

appears at the bottom and determining graphically the point of intersection with the three-phase line, q might be found.
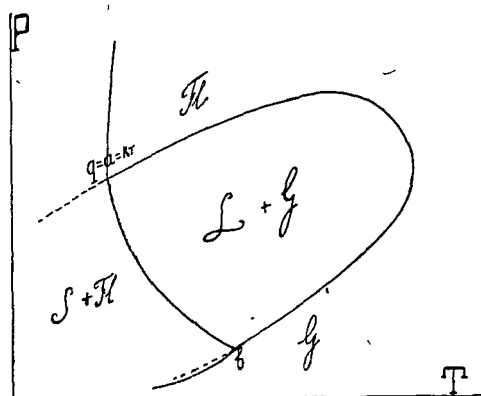

Fig. 7.

Fig. 8 gives the P-T projection for a mixture x_2, which has a concentration smaller than x_q. The point kr has entered the meta-stable region, so that the upper limit of the L-G region here also
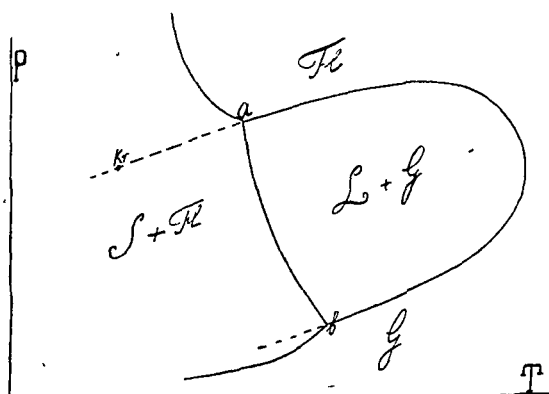

Fig. 8.

is indicated by the disappearance of the meniscus at the bottom. Here the point kr can only be realized, when the solid phase does not appear. The stable part of the L-G loop must offer everywhere retrograde phenomena. If the composition on the critical line varies only slightly when the temperature rises, the point kr in fig. 8 also will move rapidly from a to lower temperatures, when x_2 differs slightly from x_q. The point q is never to be realized with a mixture $x_2 < x_q$, though here as well a will deviate slightly from q when the difference between x_2 and x_q is small.
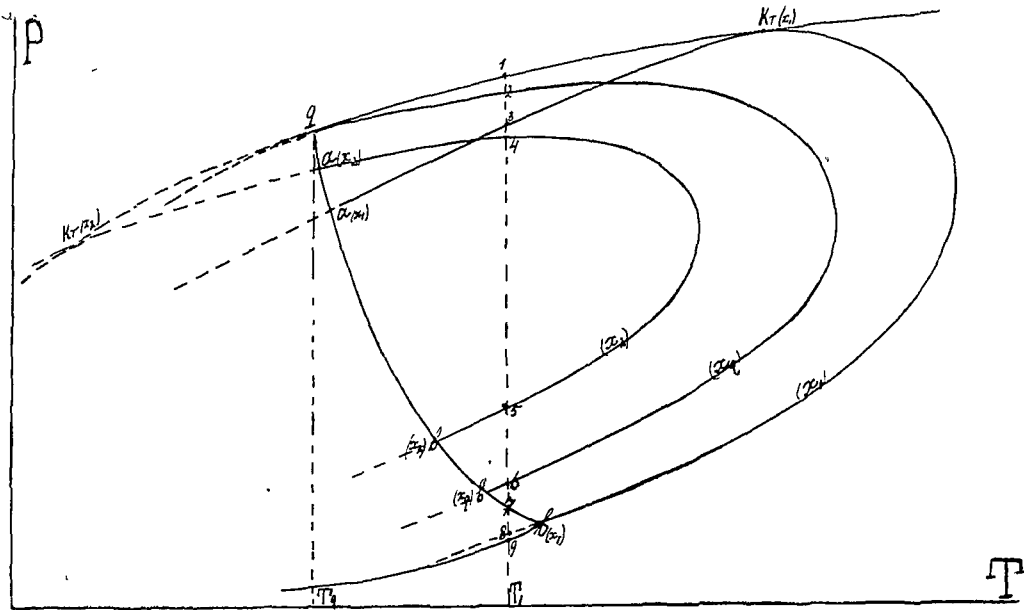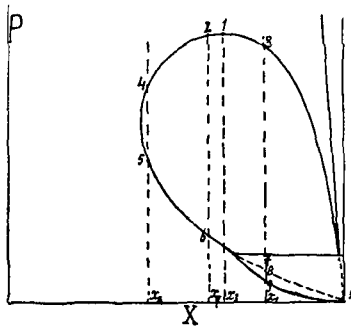
Fig. 9.

Fig. 10.

The combination of the fig. 6, 7, and 8 gives fig. 9. When we draw the P-X section for T_1 we obtain fig. 10, where the points corresponding with those in fig. 9 are denoted by the same numbers.

The point of maximum pressure lies on the critical curve. The composition of 1 will deviate a little from x_q when T_1 lies slightly higher than T_q, and this is still more exactly the case when the composition of the critical line varies little with variation of the temperature. To find the composition of 1 experimentally we must start from a mixture x_1, which contains more solid substance than is required for q. With this mixture we determine at T_1 the point of end-condensation 3. Then after cooling some of the solid substance is pushed under the mercury meniscus, whereby the composition of the mixture is changed a little to the left in fig. 10. Again with the composition so obtained e.g. x_2 we determine the upper limit of the loop LG at T_1. When we isolate successively different quantities of the solid, points of the line, 3, 1, 2 and 4 in the P-X section may be found. Evidently the maximum pressure, point 1, corresponds to the mixture x_3. If therefore the maximum pressure is realized, we have the mixture x_3, deviating a little from x_q, at least if T_1 deviates slightly from T_q.

So when with this mixture the upper limit of the P-T loop is determined, the intersection of this curve with the three-phase line will give approximately. the point q.

The first mixture, that I studied, corresponds to x_1 in fig. 5. Determining the upper limit of the P-T loop, I saw the meniscus always disappear in the top of the tube, so that kr must lie at a temperature higher than 71.4°. (see fig. 6, fig. 2 line EF and table I). The composition of this mixture was between 25 and 26 mol. °/₀ naphthalene. As I did not succeed in observing q directly with this mixture, although I sometimes saw a fluid phase in contact with solid, I resolved to proceed along the previously described way.

The second mixture contained 24.75 mol. °/₀ naphtalene; it might therefore lie on the left or on the right of q, or it might happen to have exactly the composition of x_q itself.

On determining the P-T loop the meniscus also here always disappeared in the top of the tube, indicating, that the mixture contained more naphtalene than x_q (see table 1 and fig. 2 line GH). Three points could be found on the metastable part of the curve. The pressure of the point at 52.4° and 122.27 atm. is high, which can be explained by assuming that perhaps some solid has got under the mercury.

With this mixture the composition of point 1 from fig. 10 was experimentally sought. From the intersection of the two end-condensation lines with the three-phase curve I might conclude, that q lay at about 57°. I chose 59.9° as temperature of the experiment, also 2.9° higher than the assumed T_q. The above mentioned method gave at 59.9° a pressure maximum of 126.64 atm.

With this mixture, showing kr at 59.9° and 126.64 atm. another point of the PT loop was determined at a temperature lower than kr. The meniscus disappeared a little below the middle of the tube at 55.5° and 123.81 atm. (metastable point). The intersection of the curve, which joins those two points, with the three-phase curve offers a value for q, which is very near the true one. This shows the second critical end-point to lie at 57.4° and 124.8 atm. and the composition to be between 20 and 25 mol. °/₀.

Finally I wish to express my thanks to Dr. F. E. C. Scheffer for his help and advice.