Chemistry. — "*On critical end-points in ternary systems*". By
Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

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

In a previous paper [1] some remarks were made about the ternary
system which is obtained when a third substance is added to ether
and anthraquinone, which does not yield critical end-points p and q
either with ether or anthraquinone, and is miscible with the other
two components in all proportions in the liquid state.

It was then pointed out that with addition of this third substance
the two critical end-points p and q at first continue to exist, but
that at last with greater quantities of the third substance they dis-
appear in consequence of the fact that the points p and q mentioned
approach each other more and more, and at last coincide.

It was demonstrated on the same occasion that interesting pheno-
mena must precede this coinciding, which was another incitement
to investigate experimentally the case under consideration.

This investigation though not quite completed is far enough advanced
to be fit for publication and in order to set forth clearly what has
been found, some theoretical considerations must be premised.

At the beginning of the investigation the surprising phenomenon
occurred that with increase of volume the three phase equilibrium
$S + L + G$ could form from a mixture which was at a temperature
a few degrees *above* the critical temperature.

This phenomenon seemed so surprising to me that I thought at
first that it was to be ascribed to impurities, but it soon appeared
to be essential. It is very significant that the V,x-diagram, which
also solved so many questions in the system ether-anthraquinone,
showed the true connection of the equilibria in the clearest way
here too, and indicated the necessity of the above surprising pheno-
menon with great clearness.

This has again proved the advantage of this way of representation,
and this is the reason why the figures discussed here will be derived
from the V,x-diagram for the ternary system.

The adjoined figure holds for the system alcohol-ether anthraquinone,
and for a temperature lying between that of the two critical end-
points p and q of the system ether-anthraquinone, so between 203°
and 247°, e. g. 230°.

In the front plane of the trilateral prism the V,X-figure of alcohol-
anthraquinone has been drawn. The critical point of alcohol lies at
243°.1; so pure alcohol is still below its critical temperature in this

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[1] These Proc. Sept. 1909, p. 182

figure, and this is the reason why the liquid point d and the vapour point a still lie comparatively far apart.

The field $abde$ is the region for the coexistence of unsaturate liquid and vapour, and the points e and b indicate the liquid and the vapour, which are in equilibrium with solid anthraquinone, lying in f. So the triangle ebf is the three-phase triangle, which is bounded on the right by the region for solid anthraquinone $+$ fluid, which latter phases lie on the line bc, which is one of the stable branches of the continuous solubility isotherm $cbeh$, of which the second branch eh indicates the liquids coexisting with solid anthraquinone.

In the plane for alcohol-ether the drawing is exceedingly simple for, as 230° lies far above the critical temperature of ether, liquid curve and vapour curve have continuously flowed together, and so we have got a continuous binodal curve with a plaitpoint in K.

On the plane for ether-anthraquinone the V,X-figure is equally simple; there we have the continuous solubility isotherm ch_2, which is stable over its full length. Further we see in this plane the line gK_2P, which indicates the metastable continuous binodal curve, which may be realised if the solid substance did not appear, so if the critical phenomenon, as has been found already, is to be realised for a supersaturate solution.

If we now start from the three-phase equilibrium $S + L + G$ in the system alcohol-anthraquinone, and gradually add more ether, the quantity of anthraquinone always exceeding that of ether, the points b and c will move in the space, because the liquids and vapours which now coexist with solid anthraquinone, will contain also ether, and the vapour of course more than the liquid.

Hence the three coexisting phases no longer lie in the same plane for a constant proportion alcohol-ether; such a section can contain only two of the three coexisting phases, $S + L$ or $S + G$, or in other words on each section lie two pair of coexisting phases, but to $S + L$ belongs a vapour, which contains more ether than L, and to $S + G$ belongs a liquid, which contains more alcohol than G.

Thus the three points $f l_1 g_1$ form a three-phase triangle, and it is evident that g_1 lies farther back in the figure, consequently it contains more ether than l_1, and the same thing is to be observed for the succeeding three-phase triangles.

Now it is clear that this ternary liquid and vapour line cannot proceed to the plane for ether-anthraquinone, for in this plane no stable liquids can exist at the temperature under consideration.

So we see that before this time the lines mentioned will have to merge continuously into each other, and so that the critical pheno-

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menon will appear for a saturate solution at the moment of this continuous transition, just as this can be the case in the system ether-anthraquinone.

So if K is this ternary critical end-point, the liquid point l and the vapour point g coincide there and the spacial solubility isotherm touches the three-phase coexistence curve bK_1l exactly in K_1.

Before we proceed it is necessary to mention what are the principal modifications which the figure undergoes, when the temperature is varied.

These modifications are obvious; for it is clear that at the temperatures of the critical end-points p and q the three-phase coexistence curve bK_1l will just touch the plane for ether-anthraquinone namely in the critical end-points p and q.

Between these temperatures no contact with the plane for ether-anthraquinone can occur, because then a stable solution cannot occur in this system.
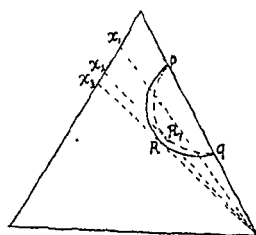
So it is to be expected in the simplest case that the ternary plaitpoint curve pRq in projection on the concentration triangle has a course as is indicated in the adjoined drawing, and from which it is to be seen at the same time that the concentration R is the last at which a critical end point still occurs.

Fig. 2.

So it is clear from what precedes that the three-phase coexistence curve bK_1l between the two critical end-temperatures beginning at p will first recede into the space, and approach the ether-anthraquinone plane again afterwards, and finally touch it again at q for the second time.

It follows from this that it is easy to derive from the v-x-spacial representation what will have to be observed when a mixture of alcohol and ether x_1 with an excess of anthraquinone is studied at different temperatures, for the phenomena must on the whole agree with those which would be met with if at constant temperature we first made the alcohol-ether mixture richer in alcohol, and then poorer in alcohol, till the original concentration was reached again. In this case, however, we get exactly to the same point, whereas this is not the case with change of temperature.

So we shall begin with projecting a plane through the axis of anthraquinone and the liquid point l_1; we then get the following section, it being noteworthy, however, that now l_1, f, and g are no coexisting phases now.
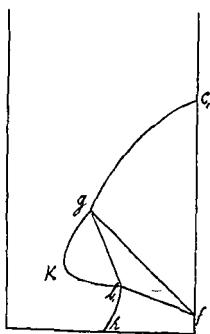
Fig. 3.

l_1 without vapour, can indeed be in equilibrium with f, and also g, when there is no liquid present, but the three phases cannot be in equilibrium together, because there belongs a vapour phase to the liquid l, which contains more ether than g.

Nor do the coexisting liquid and vapour phases lie on the line l_1Kg, for they contain different quantities of the three components, and can therefore, never lie in the same section.

The lines gc_1 and l_1h represent vapour and liquid phases which can coexist with solid anthraquinone.

If in accordance with this v-x-section we project the corresponding p-x-figure, we get this.

The point g corresponding with a liquid which contains less ether than l_1, the three-phase pressure in g is smaller than in l_1, and this is the reason that we now get a p-x-figure with a three-phase region $l_1S_1g_1S$, and the boundary between this region and that for $G + L$ is formed by the line g_1l_1.
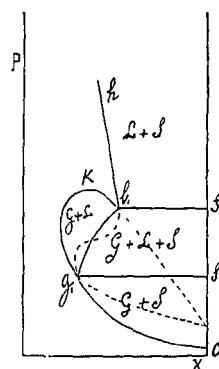
As to the continuous curve l_1Kg_1, no more

Fig. 4.

than in the v-x-figure do coexisting liquid and vapour phases lie on this line here, so that we must regard it as a mere line of demarcation.

The lines hl_1 and g_1c_1 are also boundary lines, but there lie phases on these lines which can coexist with solid anthaquinone [1]).

If we now project a plane through the axis for anthraquinone and the liquid point l_5, then the p-x-figure corresponding with this v-x-section is as indicated in fig. 5.

The region for $G + L$ has become smaller and the points l_1 and g have risen.

Fig. 5.

If we now think a plane projected through the axis of anthraquinone and the critical endpoint K_1, the p, x figure corresponding with this v-x-section has the following shape (fig. 6).

We see that the plaitpoint K has coincided with the point l

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[1]) The continuity is indicated schematically in all the figures.

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and so that the critical phenomenon is observed for a solution saturate with solid anthraquinone.

The particularities which present themselves here for a ternary system, are now very evident, for we see that at the temperature of this critical end-point no region has disappeared as yet, and so that no continuity exists as yet between the region for $L + S$ and $G + S$, which is the case in a binary system at the corresponding critical end-temperature.

If we now proceed to still greater concentrations of ether, the point l moves downwards along

Fig. 6.
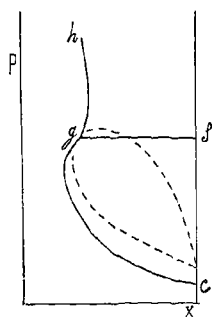
the vapour branch, g upwards, and if we now project a plane which, passing through the axis of anthraquinone just touches the three-phase coexistence line bK_1e, the points l and g, which past K_1 may be most appropriately called two different fluid phases, and at first differ very much in density, have coincided. For this case we get then the p, x diagram, which has been drawn in fig. 7.

Fig. 7.

In the point g, where the curve for solid-fluid just touches the p-x-loop, a three-phase equilibrium is possible for the last time.

If we now take a section, which corresponds with still more ether, equilibrium in stable state is possible only between fluid phases and solid anthraquinone, as the p-x-loop for liquid-vapour has no longer any point in common with the curve for solid-fluid, as fig. 8 shows.

If we now pass to greater contents of alcohol, in which the just-discussed sections, but in reversed order, are obtained, this succession gives us an *idea* of what we get when a liquid mixture x (see Fig. 2) with an excess of anthraquinone is studied for a series of temperatures, if we also

Fig. 8.

take into account what will generally be the influence of the temperature on the concentration and the pressure.

If we now indicate these sections in a perspective spacial representation, we get figure 9, from which follows that the curve which connects the liquid points or the *maximum three-phase points* l and
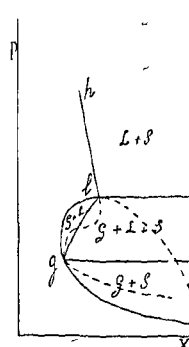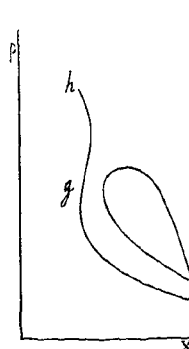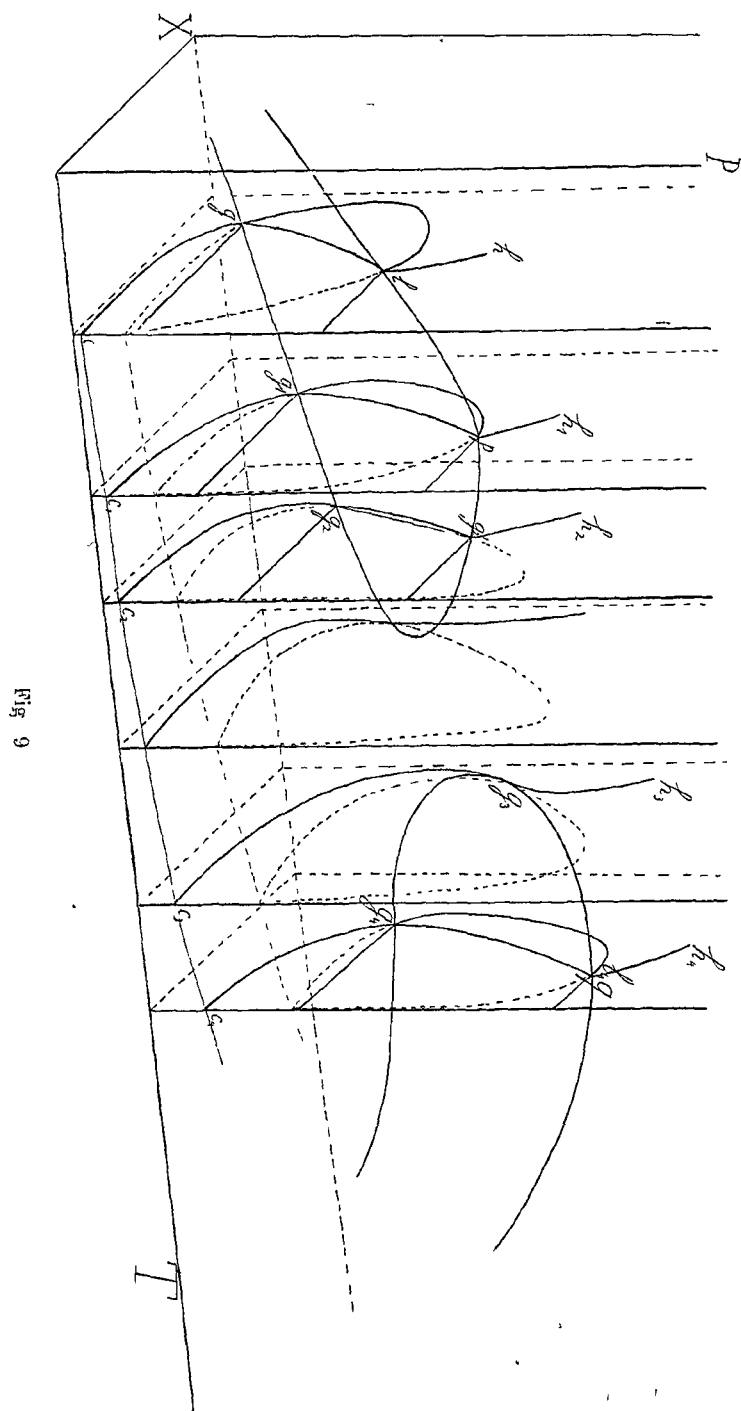
Fig 9

the line on which the vapour points g or the *minimum three-phase points* lie, are two curves which continuously merge into each other at the maximum three-phase temperature, so past the first ternary critical end-point p.

Above the maximum three-phase temperature we find for a series of temperatures only fluid phases or equilibrium between fluid phases and solid anthraquinone, till at a certain temperature, which we may now call a minimum three-phase temperature, the just-mentioned phenomena repeat themselves, but now in reversed order.

It is now easy to derive from this spacial figure what will be observed when mixtures of ether and alcohol of the concentration x_1 (Fig. 2) are examined with varying quantities of anthraquinone at different temperatures.

If we now assume that the anthraquinone-concentration is not sufficient to reach the ternary first critical end-point, the $(PT)_x$-section which we study, will lie beyond p, and have the following shape (fig. 10).

If the concentration of the anthraquinone just suffices to realize the critical end-point, the $(PT)_x$-section is that of fig. 11 from which follows that the plaitpoint K and the minimum-three-phase point g
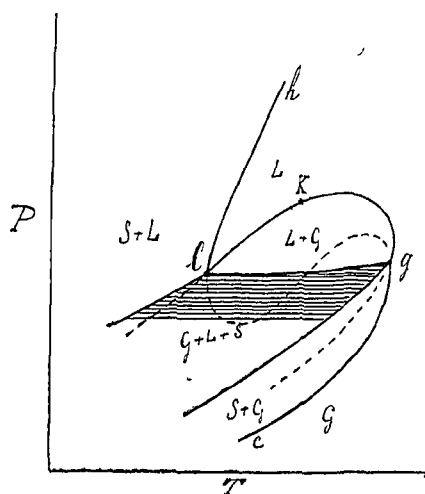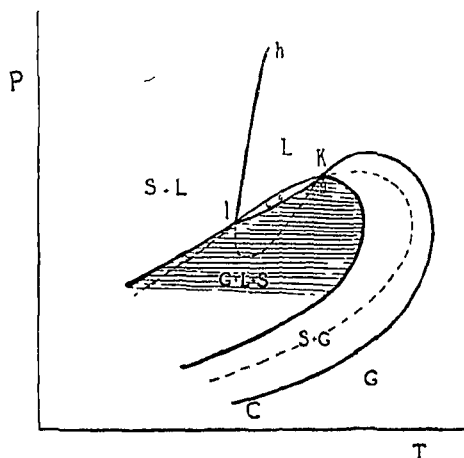

Fig. 10.   Fig. 11.

have coincided, and that a liquid saturate with solid anthraquinone shows the critical phenomenon.

In the mean time we see that the three-phase equilibrium $S + L + G$ can occur with increase of volume above the critical temperature.

If we now take a mixture with still more anthraquinone, the points l and g, the latter of which is now also a maximum three-

phase point draw nearer and nearer to each other, and they finally coincide, the maximum and minimum three-phase-curves merging continuously into each other, and giving rise in this way to the following $(PT)_x$-section (fig. 12).
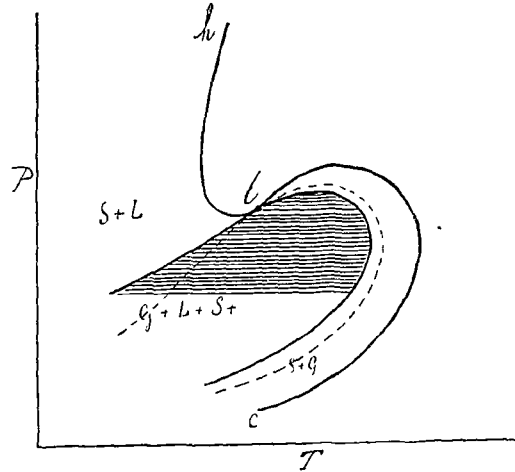

Fig 12.

For a still greater quantity of anthraquinone the continuous three phase line of demarcation and the line for solid fluid get detached.

For a certain content of anthraquinone the second three phase region will now be reached. At this moment, i. e. with this content of anthraquinone a $(PT)_x$-diagram will be found as is shown in Fig. 13, consisting only of a continuous curve of solid-fluid touching the metastable loop liquid-vapour.
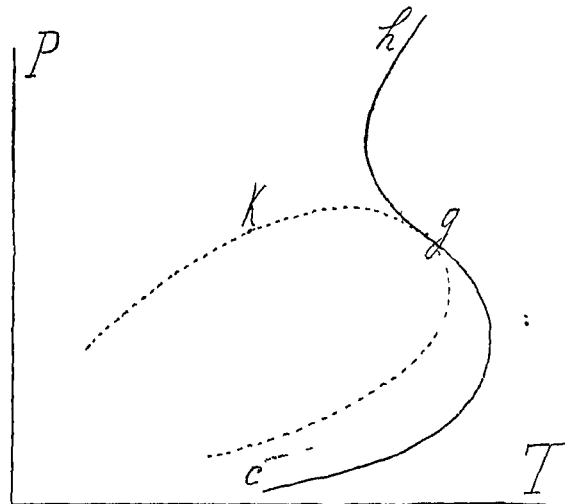
Fig. 13.

If we then choose a concentration which still contains too little anthraquinone to realise the second critical end-point, we get Fig. 14, of which it is noteworthy that the plaitpoint K still lies in the metastable region.

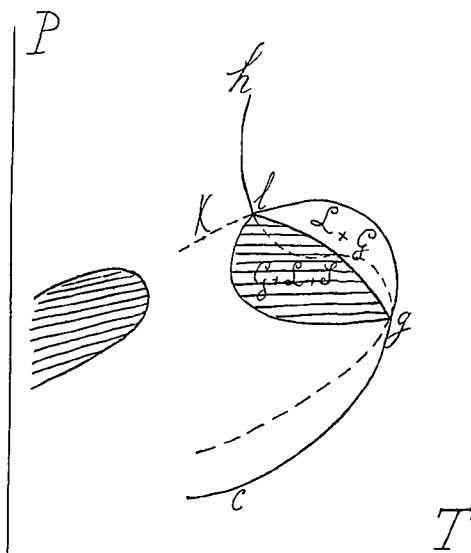
Fig. 14.

For a slightly greater content of anthraquinone the critical end-point can just be reached, and the $(PT)_x$-section has the following shape, l and K having coincided.
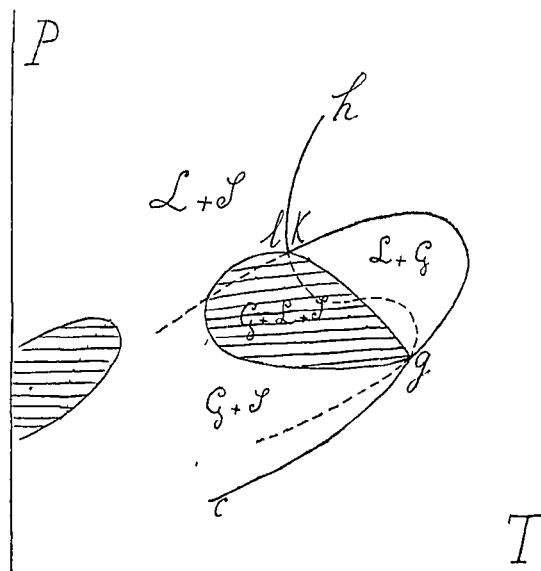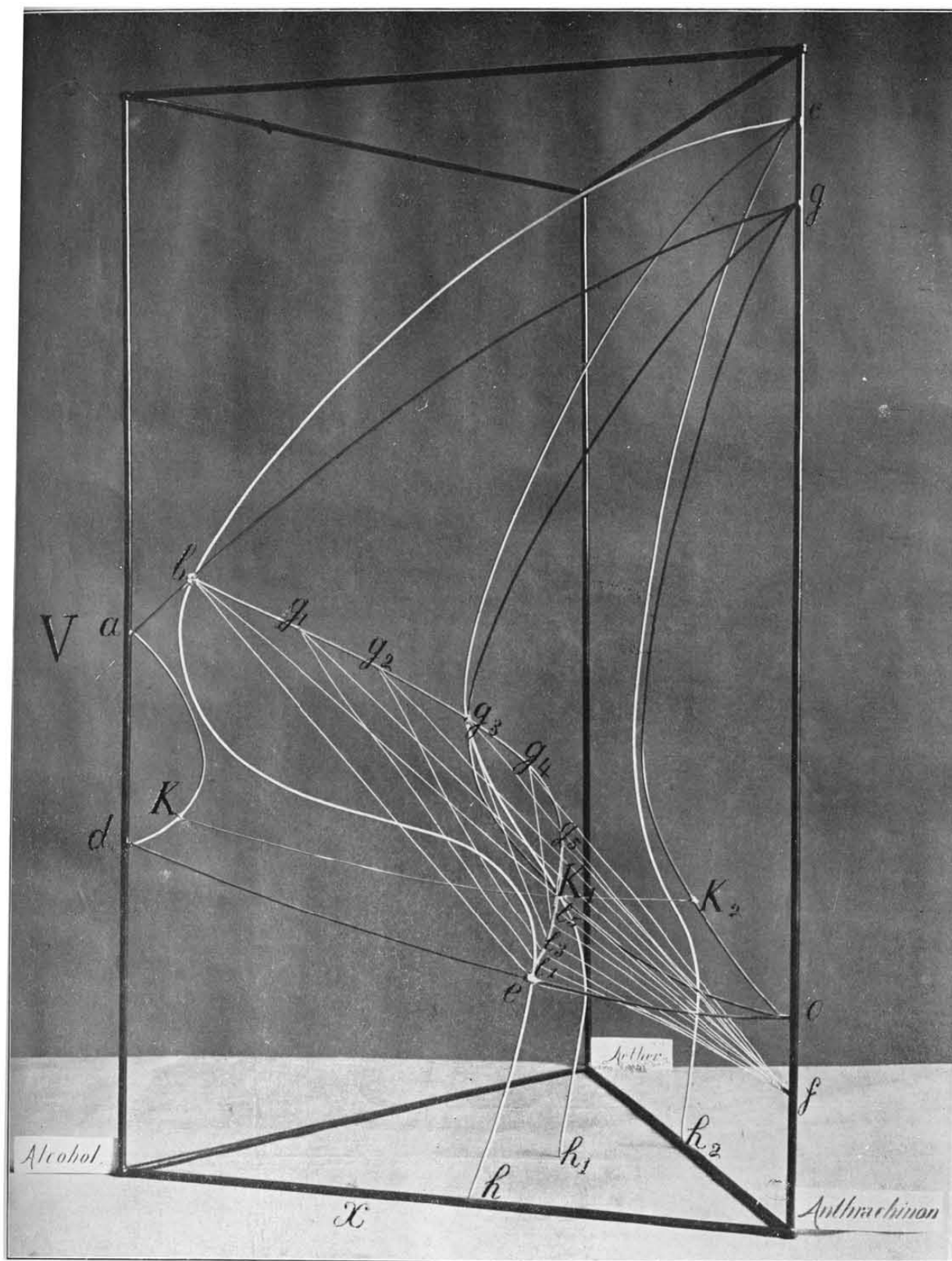

Fig. 15.

If we finally take a concentration of anthraquinone, which is slightly greater than that which corresponds with the second critical end-point, the corresponding $(PT)_x$-section is represented in Fig. 16.
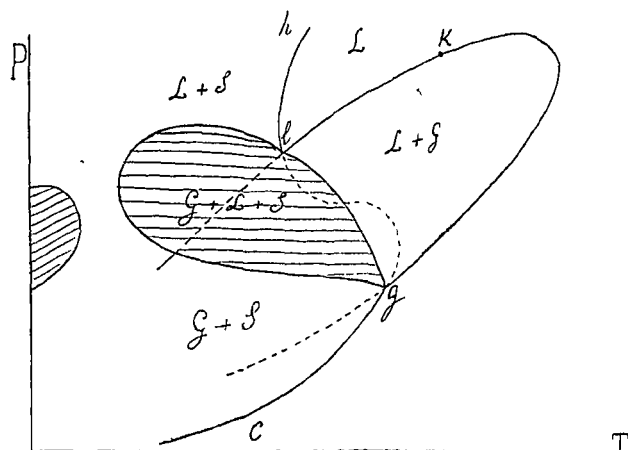

Fig. 16

For a mixture of alcohol-ether with more alcohol, we shall be able to realise two critical endpoints, as appears from fig. 2, till the alcohol-ether concentration has become x_2, for if we join this point x_2 with the point which represents anthraquinone, this joining line just touches the line pR_1q, and this is the line on which the points lie of the maximum three-phase temperature, so that we should get a contact of the three-phase regions for this alcohol-ether concentration, which, however, changes into intersection, as fig. 17 shows.
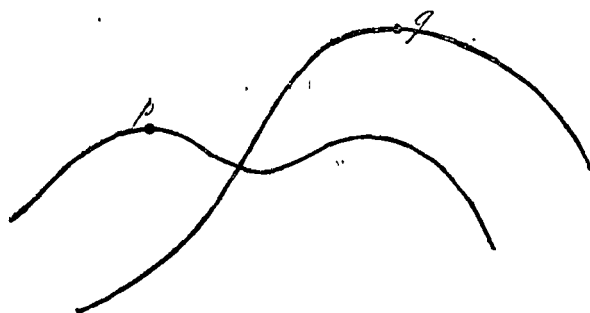

Fig. 17.

If we have a mixture alcohol-ether, lying between x_2 and x_3 communication has been brought about between the two three-phase regions, as Fig. 18 shows.
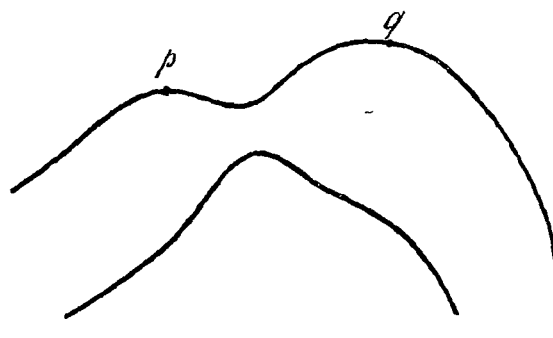
Fig. 18

And p_1 and p_2 coincide for the alcohol-ether concentration x_3, and all the peculiarities have disappeared except this one that there still exists one saturate solution which shows the critical phenomenon (Fig 19), but this too disappears, when we take a mixture with still more alcohol.
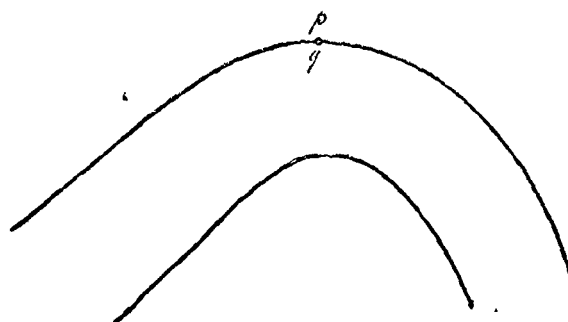

Fig. 19.

In how far this theory has already been corroborated by the experiment, will appear from the communication of Dr. ADA PRINS, who has not studied the system *alcohol-ether-anthraquinone*, but the system *naphthalene-ether-anthraquinone*.

Amsterdam, June 24.   *Anorg. Chem. Laboratory*
                                         of the University.