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Chemistry. — *"On the course of the PT-lines for constant concentration in the system ether-anthraquinone."* By Prof. A. SMITS and J. P. TREUB. (Communicated by Prof. J. D. VAN DER WAALS).

Already in 1903 [1] VAN DER WAALS indicated by means of PT-sections for constant concentrations how in the neighbourhood of the critical end-points p and q the meeting of the lines for *solid-fluid*, and *liquid-vapour* would have to take place.

Theory, however, was in this respect far in advance of experiment, so that a perfectly unexpected peculiarity found afterwards by one of us (S.), in consequence of which the said lines must partly have another position with respect to each other than VAN DER WAALS had supposed, could not be taken into account in these considerations, and for this reason it was very desirable to investigate this point more closely experimentally.

The just-mentioned peculiarity consists in this that for some mixtures lying on the ether-side of the critical end-point p, far above the critical temperature, which was of course observed here for unsaturate solutions, three-phase equilibrium $(S+L+G)$ appeared again.

This behaviour points to the fact that the line *solid-fluid* for a concentration on the left of the first critical end-point does not meet the border-line *liquid-vapour twice,* as VAN DER WAALS supposed, but *four times,* so that the PT-figure for this concentration becomes about as indicated in fig. 2, which is of course preceded by contact on the right, as drawn in fig. 1, which contact of course takes place for the vapour most rich in ether of the second part of the three-phase region.

Since in the case that the critical phenomenon is observed for an unsaturate solution, the plaitpoint K lies between the liquid point L and the vapour point G, we see that the peculiar phenomenon discussed here is in connection with the enormously large difference which must exist for this system between the plaitpoint temperature and the maximum temperature.

As one of us (S.) has set forth in his first communication [2] on the $(PT)_x$-lines for *solid-fluid* by means of the formula:

$$T\left(\frac{dp}{dT_{sf}}\right)_x = \frac{\dfrac{\partial^2\psi}{\partial v^2} w_s}{\dfrac{\partial^2\psi}{\partial v^2} v_{sf}}$$

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[1] These Proc. Oct. 1903, p. 230; Nov. 1903, p. 357.

[2] These Proc. May 1906, p. 9.

these lines possess two horizontal and two vertical tangents in normal cases, and with regard to fig. 1 we may now observe that as we have assumed to be near the concentration of a critical end-point, v_{sf} is positive not only on the connodal line, but also far outside it, so that the liquid branch starting from L and the vapour branch starting from G possess vertical tangents in the stable region.

If we now go to greater concentrations of anthraquinone, the border curve moves more to the right with respect to the line solid-fluid, i.e. towards higher temperature. Moreover both curves move upwards, so towards higher pressure, but the left-side branch of the line *solid-fluid* moves quickest in this respect, so that the left-hand meeting changes into contact at a certain concentration, after which this contact is quite broken off.

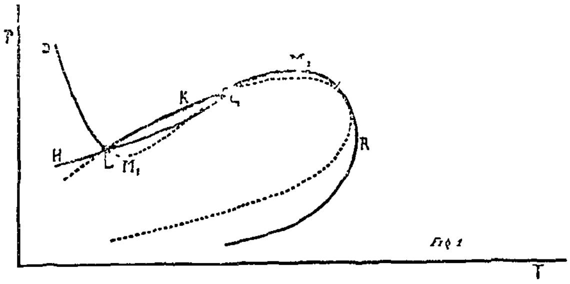

Fig 1

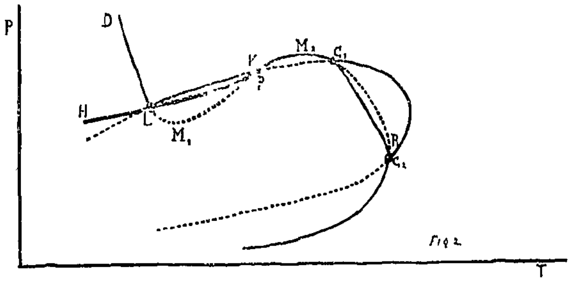

Fig 2

Before this takes place, however, the discussed critical end-point appears, for the plaitpoint moves to the right, and when this at last has coincided with the point G, the end-point of the first three-phase pressure line (Fig. 1), this implies that the liquid- and vapour phase coexisting with solid anthraquinone, have become identical.

This case, which is indicated by fig. 2, presents also this peculiarity that the three-phase line HLK and the line for solid-fluid $DLM_1G_1G_2$ touch in K, for as VAN DER WAALS proved:

$$T\frac{dp}{dT_{SLG}} = T\left(\frac{dT}{dp_{sf}}\right)_x$$

holds for this point.

For greater concentrations of anthraquinone the plaitpoint lies on the metastable branch of the border curve, so that not a single critical phenomenon is to be observed in stable state.

When we have arrived at that concentration for which contact takes place on the left, we have the case that at a certain temperature, with compression of the three-phase system ($S+L+G$), the solid substance and the vapour disappear simultaneously, while this was the case at two different temperatures with smaller concentrations.

It is of importance to point out here that this contact does not take place in the point where $w_{sf}=0$, but where this quantity has a positive value. (See the communications on retrogressive melting point lines [1]).

If we take a greater concentration of anthraquinone, the line for *solid-fluid* has got detached from the border line on the left, and as we now proceed to still greater anthraquinone concentrations, the plaitpoint K approaches the point G_1, and finally coincides with it.

If this takes place, the second critical end-point q has been reached, which case is indicated by fig. 3.

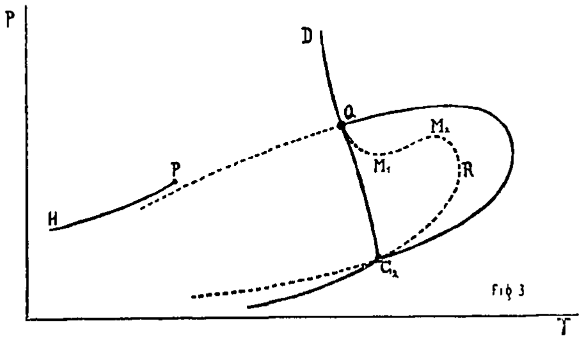

Fig 3

If now with our concentration we pass the point q, the plaitpoint K will lie on the right of the line for *solid-fluid,* and again critical phenomena are observed for unsaturate solutions.

The following figure 4 shows what the investigation of the system ether-anthraquinone has yielded on this point.

In this fig. 4 we see the two parts of the three-phase line and further the PT-sections of the surfaces *solid-fluid* for different constant values of x, (mol. $^0/_0$ anthraquinone), while for some very slight anthraquinone concentrations also the section of the *liquid-vapour* surface is indicated, which however is rather indistinct in consequence of its being so small.

If we begin with the PT-sections corresponding to the very slight

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[1] These Proc. p. 170 and p. 189.

anthraquinone concentrations of 0.1 and 0.2 mol. $^0/_0$, it is noteworthy that, whereas the point where the border line for liquid-vapour possesses a vertical tangent, so where $v_{lq} = 0$, still lies in the stable region, the line for solid-fluid under the three-phase line already shows a maximum pressure and a maximum temperature in the stable region, from which follows that we find here a *double retrograde* phenomenon.

At the same temperature retrograde condensation and retrograde solidification may namely be successively observed with increase or decrease of volume, (See fig. 3 of the communication "On retrogressive vapour lines" in the Proceedings of this Meeting p. 180).

At the concentration 0.3 mol. $^0/_0$ the retrograde condensation has just disappeared, but the retrograde solidification under the three-phase line continues to exist. This phenomenon of retrograde solidification must also exist above the three-phase line, but the point where the upmost branch of the line *solid-fluid* possesses a vertical tangent lies at such high pressures that up to now no retrograde solidification has been found above the three-phase line.

If we now consider the $(PT)_x$ section corresponding to the concentration 0.9 mol. $^0/_0$, i. e. the concentration of the first critical end-point, we notice that the line for *solid-fluid* passes for the second time through the border line with this concentration, and that in such a way that the upper section takes place at about **46** atmospheres, from which follows that the same phenomenon must be found already for smaller anthraquinone concentrations, as was found indeed.

A consequence of this second meeting is this that the righthand branch of the line for solid-fluid no longer runs on uninterruptedly, but is stopped by the three-phase line, where it becomes metastable resp. unstable, as was already shown schematically in fig. 2, after which it appears again in the stable region at lower pressure.

For the concentration 1.3 *mol.* $^0/_0$ the first branch of the three-phase line is still cut, and the line for solid-fluid just shows still a pressure maximum in the stable region, but it is so faint, that we may be justified in saying that this is the greatest anthraquinone concentration, at which this pressure-maximum still occurs in the stable region.

So up to this moment the meeting of the solid-fluid line with the three-phase lines has taken place in the points where w_{sf} is neg., but for greater concentrations this is changed.

If we now consider the concentration 1.9 *mol.* $^0/_0$, we observe that he line for *solid-fluid* has already got detached from the first branch of the three-phase line, so that now the *pressure-minimum* has got into the stable region; the *pressure-maximum*, on the other hand, has disappeared, and now the meeting with the three-phase line takes place in a point where w_{sf} is positive, from which follows that w_{sf} has passed through zero on the three-phase line; and if we now consider that this holds for an anthraquinone concentration which is smaller than that corresponding to the second critical end-point q, it follows from this that the reversal of sign of w_{sf} takes place on the vapour-branch of the second three-phase region.

If we then proceed to the concentration 2.6 *mol.* $^0/_0$, we see that the line for *solid-fluid* has mainly the same shape as that of the concentration 1,9 *mol.* $^0/_0$, but it has moved pretty much upwards and to the right, the *pressure-maximum* having become less deep.

For the following concentration of 3,6 *mol.* $^0/_0$ the latter takes place in a far greater degree, and for 4,2 *mol.* $^0/_0$ the minimum is only just present, and for 5,7 *mol.* $^0/_0$ it has quite disappeared. So we see from this that the meeting with the three-phase line for this concentration takes place in a point where w_{sf} is negative, so that we come to the conclusion that the quantity w_{sf} has passed through zero for the second time, and as the concentration of the second critical end-point has not been reached as yet, it follows from this that all this takes place on the vapour branch of the second part of the three-phase region.

That this is a necessity is at once to be seen when we consider that the line for solid-liquid possesses horizontal tangents in two points, so two places where $w_{sf} = 0$, which will lie inside the connodal line for systems without critical end-points, but which here have got outside it for a series of concentrations lying between p and q.

Now we know that for the concentration of the second critical end-point q:

$$T\frac{dp}{dT_{SLG}} = T\left(\frac{dp}{dT_{sf}}\right)_x = \frac{w_{sf}}{v_{sf}},$$

and $T\dfrac{dp}{dT_{SLG}}$ being negative for the system ether-anthraquinone, w_{sf} will also be negative in the point q.

We know further that this point q must lie on the upper branch of the line solid-liquid, from which follows that before we have reached the second critical end-point, first the maximum, and then the minimum will have entered the metastable resp. unstable region, in consequence of which w_{sf} must twice pass through zero on the vapour branch of the border line.

We may also express this as follows: the locus for $w_{sf} = 0$ gets outside the connodal line only on the vapour side.

If the plaitpoint curve had only cut a portion out of the ascending part of the three-phase line, w_{sf} would still have been positive in q, and the locus $w_{sf} = 0$ would run quite round the connodal line near the plait.

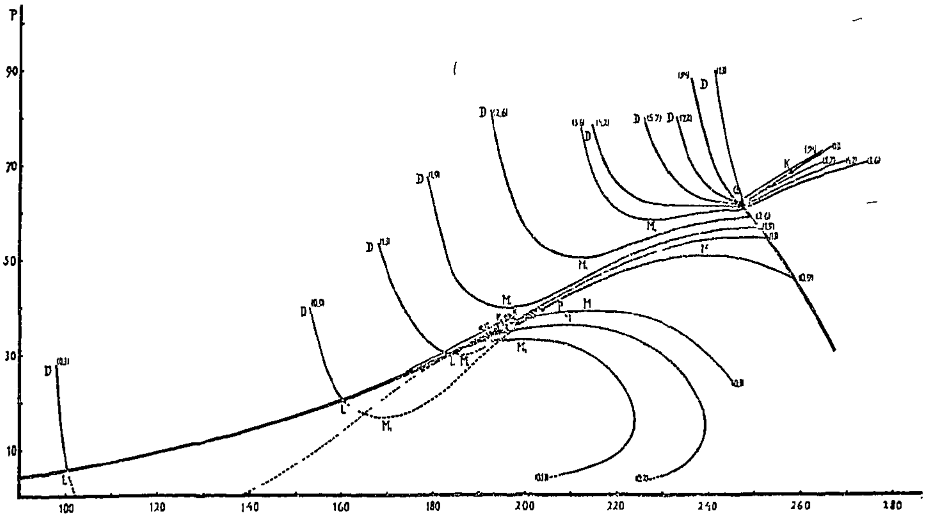

Fig. 4.

If we return to fig. 4, we see that when we exceed the concentration 5,7 *mol.* %, the line for *solid-fluid* sinks more and more into the metastable and unstable region so that the portion remaining in the stable region becomes steeper and steeper, and when at last the concentration of the second critical end-point has been reached the *three-phase* line and the line for *solid-fluid* touch each other in the point q. As is to be seen from the figure, this concentration lies between 9,4 and 13 mol. %.

When the concentration of anthraquinone becomes still greater, the upper branch of the line for solid-fluid will even have to change its direction entirely, for this branch must possess a point where the tangent is vertical, and this point must move to smaller pressures for greater anthraquinone concentrations, till at last it will enter the metastable region, at which moment the liquid branch of the line solid-fluid runs to the right from the beginning.

Before this moment has been reached, and so when the point where $v_{sf} = 0$ still lies in the stable region, the phenomenon of *retrograde solidification above the threephase line,* must make its appearance, which has not been found as yet, and will soon be the subject of an investigation.

Amsterdam, June 1911. *Anorg. Chem. Lab. of the University.*