

Citation:

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Chemistry. — “*The P, T, X -spacial representation of the system ether-anthraquinone.*” By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

As the type ether-anthraquinone occurs so frequently, and the spacial figure of the substances belonging to this system deviates so greatly from the P, T, X -representation given by BAKHUIS ROOZEBOOM on account of the very different state of the two components at the same temperature, it seemed desirable to me to draw up a spacial representation of the system ether-anthraquinone.

The figures 1, 2, and 3 now give us a view of this P, T, X -spacial representation taken from different sides, and may contribute to facilitate the insight into the peculiarities of this system.

In fig. 1 the plane a, l, f, k, s, h, g represents the p, x -section corresponding with the critical temperature of the component ether, which is thought on the left.

So the point a indicates the critical pressure of pure ether, and the line al the unsaturated liquids containing anthraquinone, which coexist with the vapours on the line ag .

The three-phase-pressure line g, l, s , on which the equilibrium between vapour g , saturated liquid l , and solid anthraquinone s lies, forms the upper boundary of the two-phase equilibrium between solid anthraquinone and vapour, the vapour phases of which lie on the vapour line h, g , and the solid phases coexisting with them on hs .

The line gls is at the same time the lower boundary of the equilibrium between liquid and solid anthraquinone just as of that between liquid and vapour, and lf or the meltingpoint isotherm indicates the liquid phases, and sk the solid phases.

As VAN DER WAALS showed, the lines hg and lf are two branches of one and the same curve, which possesses a partly metastable, partly unstable intermediate portion between g and l . If we wish to have a name for the whole curve, *solubility-isotherm* is convenient.

If we now proceed to higher temperatures, i. e. in a direction normal to the just discussed p, x -section to the left, the principal change is this that the lines la and ga pass continuously into each other, and the liquid-vapour region moves a little to the right as the lines not only get detached from the axis but the vapour and liquid points g and l move also to greater anthraquinone concentrations.

The point where the continuous transition between liquid and vapour takes place lies on the plaitpoint curve $apqb$, which connects the critical point of ether with that of anthraquinone, and running on the liquid-vapour surface connects the points of maximum pressure in the different p, x -sections.

The three-phase region for $G + L + S_B$, which is formed by the successive three-phase-pressure lines gls , runs at first with rise of temperature towards higher pressure, but finally descends again and terminates in the triple point of B .

As fig. 2. shows particularly clearly, the peculiarity of the system ether-anthraquinone consists in this, that the plaitpoint-curve meets the three-phase region in the points p and q .

Fig. 2, namely, gives the photograph of the spacial figure seen in the direction of the x -axis from A towards B .

The line hr is the vapour-pressure line of solid B ; r is the triple point and rb the vapour-pressure line of liquid B terminating in the critical point b .

The lines gp and qr are the projections of the broken three-phase region on the P, T -plane, and between a and p , and q and b are found the two branches of the plaitpoint curve, which is metastable between p and q .

If for the sake of simplicity we confine ourselves for the present only to the point p , it is noteworthy that in this point three remarkable points coincide, viz. the plaitpoint with the vapour point g , and the liquid point l of the three-phase equilibrium $G + L + S_B$.

So in this point p a saturated solution shows the critical phenomenon, and when the mixture contains more B than corresponds with the point p , the said critical phenomenon will occur in the presence of solid B at the temperature of this point.

Exactly the same thing now applies to the second critical end point q .

Above the temperature of the point p solid B can only coexist with a fluid phase, and the peculiarly curved surface $npedqm$ indicates the fluid phases, which can be in equilibrium with solid B at different temperatures and pressures.

The upper part $pedq$ passes continuously into the melting-point surfaces $lfep$ and $qdcr$ (fig. 2), whereas the lower part joins continuously the vapour surfaces $hgpm$ and mqr . It is now still more apparent than before that p and q entirely agree with each other with only this difference that what is observed for p with rise of temperature, takes place for q with fall of temperature. Thus fig. 1 shows that the continuous liquid-vapour surface terminates at p , and begins again at q . It is further worthy of note that the solubility curve of B under the vapour pressure in normal cases runs towards higher concentrations of B at higher temperature.

As, however, a saturated solution becomes identical with the coexisting vapour at p , the solubility line lp , fig. 1, must continuously

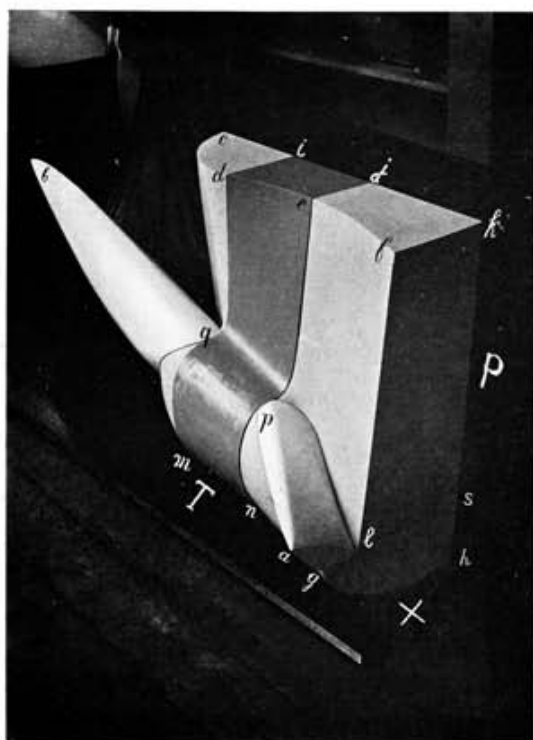


Fig. 1.

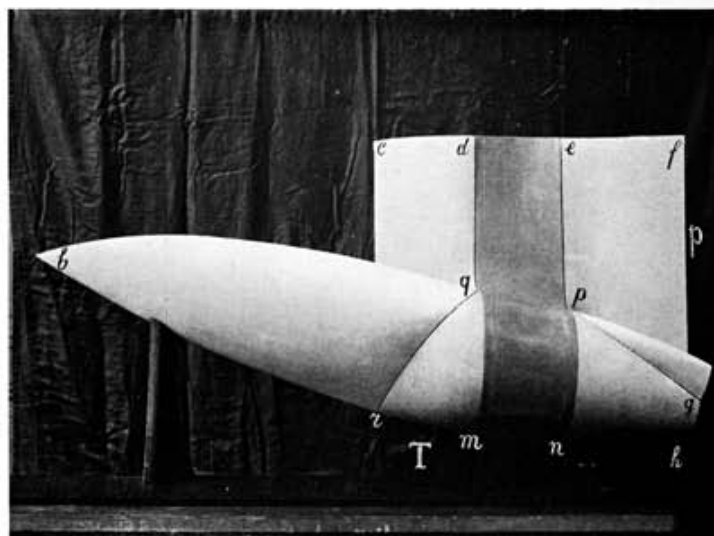
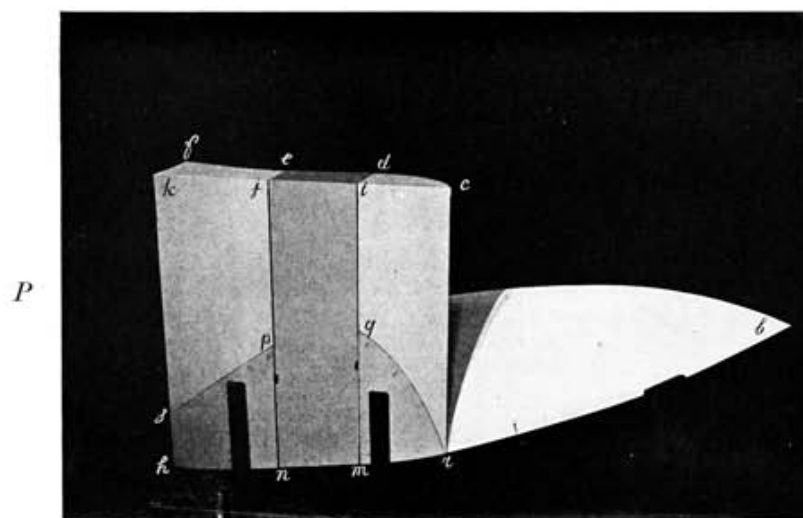


Fig. 2.



T

Fig. 3.

pass into the vapour line gp in p , and in consequence of this the solubility line will have to bend to the left, which gives rise to the phenomenon of retrograde solubility.

As is evident from fig. 1 we get the retrograde phenomenon at q on the vapour line for the same reason.

Another remarkable phenomenon which fig. 1 also reveals, is that of retrograde condensation and of retrograde solidification.

It is clear that if starting from the point a we roll a vertical tangent plane along the spacial figure in the direction of the axis of temperature, this plane touches the vapour sheet of the continuous liquid-vapour surface first for some time, but a change has come before the temperature of the point p is reached. The before mentioned vapour sheet is no longer touched, and contact now takes place with the vapour sheet of solid B . The change takes place at the moment that the two vapour surfaces are touched, which reveals a *double retrograde phenomenon*.

This behaviour now proves that we have first only the phenomenon of retrograde condensation, which at a certain temperature is succeeded by the phenomenon of retrograde condensation and solidification, and afterwards only by the phenomenon of retrograde solidification.

What has been discussed here holds also for the neighbourhood of q , but here the phenomenon takes place in reversed order. Starting from q we get first retrograde solidification and then retrograde condensation with rise of temperature.

The phenomenon of retrograde solidification continues to exist between p and q (this was found for ether-anthraquinone, but it has proved not necessary theoretically), and this is the reason why the surface for the equilibrium between solid B and fluid has such a peculiar shape.

Now it is to be seen in fig. 1 that at the temperature of p the solubility isotherm has a somewhat different shape from that of q ; this is in perfect harmony with the experiment. It has viz. appeared that the part of line pe running to the right is much larger than that of line qd , and in consequence of this the melting-point line will have a shape as indicated by the line $cdef$, which is a melting-point line with two vertical tangents at a pressure higher than that corresponding with the highest three-phase pressure¹⁾.

In conclusion I may call attention to fig. 3, which shows the backside of fig. 2, or rather the spacial figure on the B -side seen slightly from above, so that the melting-point line $cdef$ is clearly visible.

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¹⁾ This question will be examined in detail.