# Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

and bases, where $i =$ nearly 2, this number becomes 650 gr. cal.

So e. g. for KCl, of which the heat of ionisation of 1 gr.mol. $= - 720$ gr. cal. [1]), the total heat of mixing with much $H_2O$, (excluded the change in potential energy) will therefore be not $-720$ gr. cal., but only $- 720 + 650 = - 70$ gr. cal.

So it is seen, that the order of magnitude of the heat to be expected, can be totally modified, and that in general a great mistake would be committed, when we neglected the above calculated 326 $i$ gr. cal. in the calculation of the heat of mixing.

Therefore, with *diluted* solutions of *non-electrolytes* in *associating* solvents, 325 gr. cal. on each gr. mol. of the solved substance must always be subtracted from the absorbed heat determined by experiment, in order to calculate the *pure* (absorbed) heat of mixing, that is to say that heat, which is caused solely by the change in potential energy.

**Physics.** — Prof. BAKHUIS ROOZEBOOM, in the name of Dr. A. SMITS, presents a paper, entitled: "*On the phenomena appearing when in a binary system the plaitpointcurve meets the solubility curve.*" (Third communication). [2])

(Communicated in the Meeting of June 25. 1904).

The previous qualitative examination of the binary system ether-anthraquinone showed that a good survey of the whole could only be obtained by continuing the examination in quantitative direction with the aid of the pump of CAILLETET.

Some difficulties were to be foreseen; the investigation would have to be extended over a range of temperature from $\pm 170°$ to $\pm 300°$, in which the pressure might be expected to reach a pretty considerable amount — and the combination of high temperature and high pressure being exactly the thing against which glass is but seldom proof, it seemed at first that we should meet with great experimental difficulties in the quantitative examination. The experiment however showed that the pressures were not exceedingly high ; it appeared a maximum pressure of 100 atm. would suffice, and this pressure Jena-glass could withstand up to more than $300°$ [3]).

The object of the experiment was to determine the $p$-$x$-sections of the $p$-$x$-$t$-surface at different temperatures, and if possible also the $v$-$x$-sections of the $v$-$x$-$t$-surface. At the same time I should get to the knowledge of some projections already spoken of in the previous paper, viz. the projections of the $p$-$x$-$t$-surface on the $p$-$t$ and the $t$-$x$-plane. I shall briefly state the result here.

In order to have the same succession as was chosen in the preceding communications, the $p$-$t$-projection will be treated first.
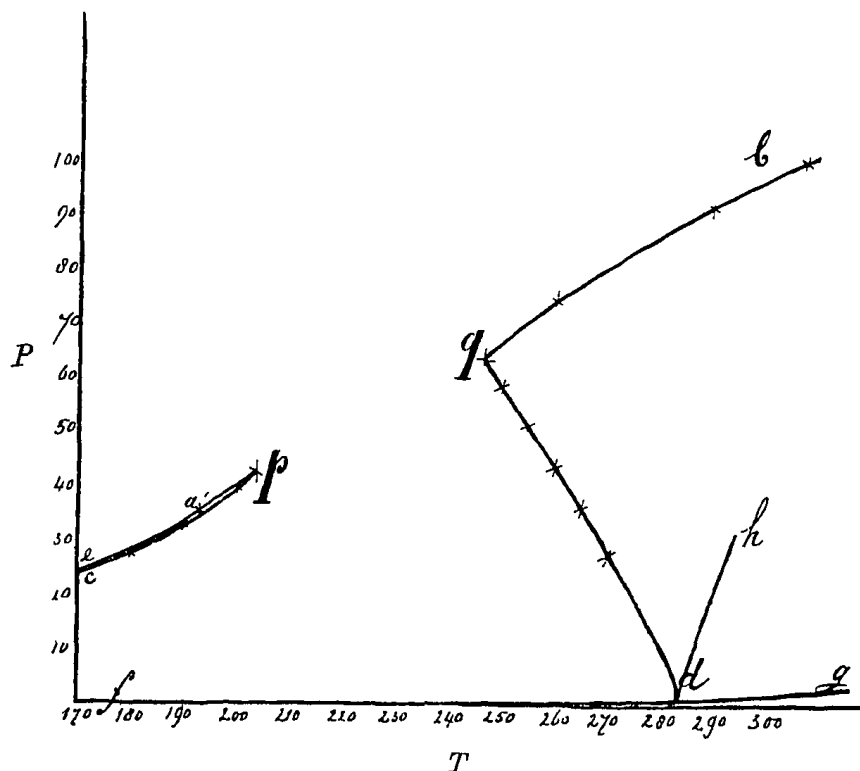


$T$

Fig. 1.

In fig. 1, $ea$ represents the vapour pressure curve of pure ether with the critical point in $a$ (193° and 36 atm.). $cp$ and $qd$ represent the portions of the three phase curve which can be realized. Up to 193° the three phase curve practically coincides with the vapour pressure curve $ea$ of pure ether, in consequence of the very small solubility of anthraquinone in ether. On the curve $ap$ lie the plait-points of the unsaturated solutions of anthraquinone in ether, and $p$ denotes the first plaitpoint of a saturated solution (203° and 43 atm.).

The second plaitpoint of a saturated solution of another concentration lies in $q$ (247° and 64 atm.) and on the curve $qb$ lie the plaitpoints of the second series of unsaturated solutions. Probably this curve, which runs on to the critical point of anthraquinone, has a maximum.

The line $fd$, which partly coincides with the $T$-axis, is the vapour pressure curve of solid anthraquinone, and $dq$ that of liquid anthraquinone. $dh$ is the meltingpoint-curve, which (as VAN DER WAALS [1]) has proved) marks the direction of the three phase curve near the meltingpoint $d$. These last three curves are drawn here schematically.

The main result represented by this $p$-$t$-figure is this that by the meeting of plaitpointcurve and three phase curve a part of the latter has vanished or rather has become imaginary, and in the examined system that part that contains the maximum.

The plaitpointcurve is metastable between $p$ and $q$ and therefore still to be realized, but this is not the case with the three phase curve. However it appeared to me that at temperatures between $p$ and $q$, with concentrations greater than those of point $q$, three phases could temporarily appear together, if they had originated at a temperature above 247° and if afterwards the system in equilibrium had quickly cooled down to less than 247°. The three phases however were not in equilibrium now, for at a constant temperature a slight change in volume proves to cause a great change in pressure.

The liquid therefore, though in contact with solid anthraquinone, was supersaturated; it was very viscous and passed very slowly, at times not until after an hour, to the stable condition of solid fluid, under secretion of solid anthraquinone.

Fig. 2 gives a number of $p$-$x$-sections for different temperatures, the pressure being given in atmospheres and the concentration in 1 mol. total of the mixture.

We may immediately point out here that all the lines in this figure joining points of equal value, as plaitpoints ($k$), liquids coexisting with vapour and solid anthraquinone ($c$), vapour coexisting with liquid and solid anthraquinone ($e$), are all projections on the $p$-$x$-plane of curves, which occur in the $p$-$x$-$t$-surface [2]).

The branches $c_0\,p$ and $e_0\,p$, which pass into each other continuously, represent the series of liquids and vapours which if we come from a lower temperature, coexist with solid anthraquinone. In $p$, the point of confluence of the two branches, we have *the first* point, where a *saturated* solution reaches its critical condition. This takes place at a concentration 0,015, temperature 203° and pressure 43 atm. If we pass on to higher temperatures a stable solution is impossible over the range of temperature 203°—247°, and instead we

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[1]) These Proc. VI p. 230.

[2]) If the plaitpointcurve has a maximum, it must possess a maximum also in fig. 2. In the $t$-$x$-projection on the contrary no maximum occurs.

get fluid phases coexisting with solid anthraquinone. Above 247° liquids can again exist and the continuous curve $d\,c_7\,c_6\,c_5\,c_4\,c$, $q\,e_3\,e_4\,e_5\,e_6\,e_7$ consisting of two branches then represents the series of liquids and vapours which coexist with solid anthraquinone above 247°. The point of confluence here is $q$, in which therefore for *the second* time a *saturated* solution reaches its critical condition. This occurs with a concentration 0,13, temperature 247° and pressure 64 atm.

The liquid branch $c_0\,p$ of the first loop and the liquid branch $q\,c_5\,d$ of the second loop are what we are accustomed to call two parts of the solubility curve. As however the two liquid branches pass continuously into their vapourbranches, there is no objection to calling the two continuous loops solubility curve.

Branch $c_0\,p$ of the first solubiliy curve and branch $d\,c_5\,q$ of the second show here a particularity. The circumstance that these branches pass continuously into the branches $e_0\,p$ and $d\,c_5\,q$ and that the point of confluence coincides with the highest pressure involves the phenomenon of *retrograde solubility*.

$c_0 p$ points to retrograde solubility in the liquid branch (cf. also fig. 4) and $d\,e_5\,q$ to retrograde solubility in the vapour branch. The extent of these phenomena however surpassed all expectations. It was known that the liquid and the vapour branch of the curve $d\,c_4\,q\,e_4\,d$ from $q$ to a higher temperature have to separate first in order to come together again afterwards, but it was not to be foreseen that the distance would be so large as to make the vapour branch extend to the concentration 0,01. From this particular situation results the very interesting phenomenon that, after we have reached point $p$, with a concentration 0,015 or in other words after the saturated solution has reached its critical condition, at a higher temperature there may again occur three phases. The vapour branch $q\,e_4\,d$ extends namely as already mentioned, to the concentration 0,01, and the concentration of point $p$ is 0,015; therefore we get from point $p$ at a higher temperature into the region on the right of the vapour branch $d\,e_4\,q$, in which three phases may occur. This phenomenon was observed at a temperature nearly 60° above the plaitpoint-temperature of the concentration 0,015 ($p$), that is at 260°. After the formation of the three phases, first the solid and then the liquid might be pressed away by raising the pressure, so that finally only a fluid phase was left.

Fig. 2 shows further the $p$-$x$-sections at temperatures above that of point $q$, beginning at 250°. The $p$-$x$-section corresponding with this temperature is separately drawn in figure 2a. The continuous curve $c_8\,k_8\,e_8$ which represents the coexisting unsaturated liquids and

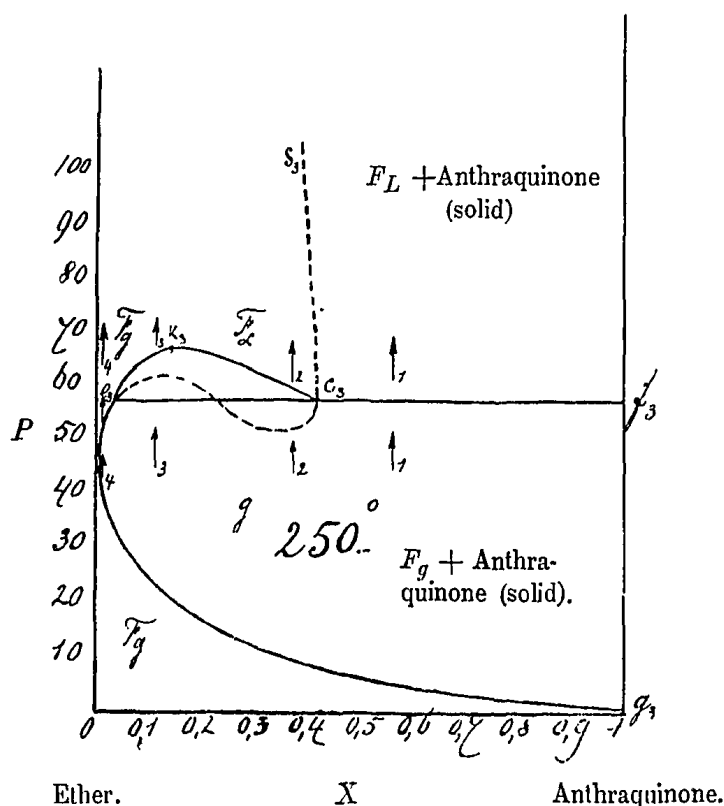vapours, has a peculiar shape and shows that retograde condensation is wanting.



Fig. 2a.

The curve $g_3 e_3$ on the contrary indicates a tolerably strong retrograde solidification. The curve $c_3 s_3$ shows that here the solubility of anthraquinone in ether decreases with increased pressure. The curves $g_3 e_3$ and $c_3 s_3$ are two portions of a continuous curve, of which the partly not realizable intermediate part is schematically represented by a dotted curve. I propose to call this continuous curve henceforth *isotherm of solubility*.

Passing on to a higher temperature, we see that the $p$-$x$-section at 255° is still of the same type as that at 250°. At 260° (fig. 2$b$) however, the situation is already considerably changed; not only the $p$-$x$-loop $c_5 k_5 e_5$ has become much larger, because the points $e_5$ and $c_5$ have become more widely separated and $k_5$ has moved to higher pressure, but also it is clearly visible that the retrograde condensation, which is still wanting here, will have appeared at a slightly higher temperature.

In the part $g_5 e_5$, though in a smaller degree than at 250°, the
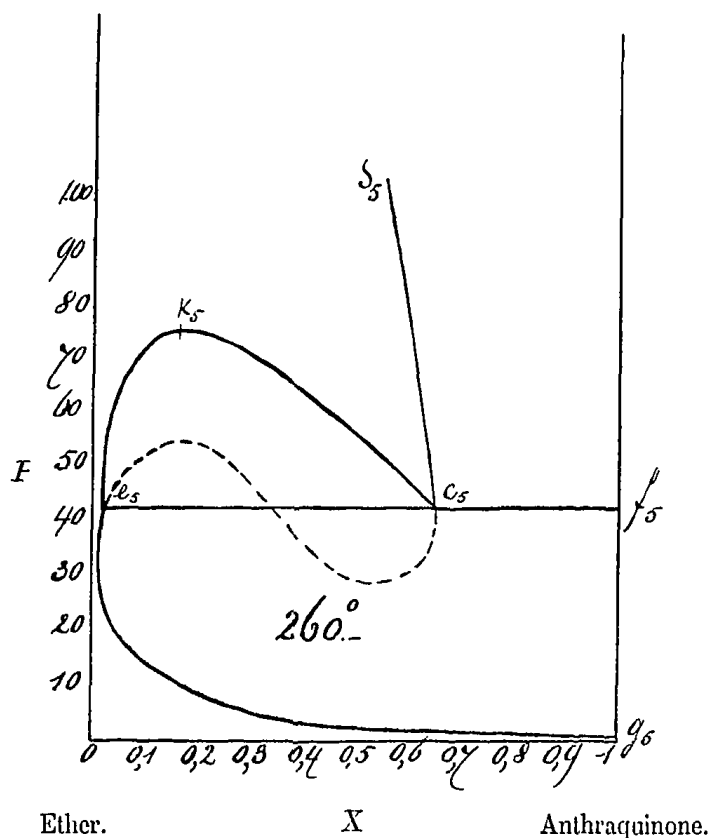
Ether.  X  Anthraquinone.

Fig. 2b.

isotherm of solubility shows still clearly the phenomenon of retrograde solidification.

At a still higher temperature the region of retrograde condensation becomes greater and greater, so that at 270' we get a $p$-$x$-section like that drawn in fig. 2c.

The retrograde condensation is here very strong and undoubtedly ranges over more than 40 atm. A retrograde condensation of such strength, however, could not be observed because the volume of the compression tube was too small; the strongest retrograde condensation observed by me covered a range of pressure from 55 to 39, of 16 atmospheres therefore. The small volume of the tube prevented us from observing whether any retrograde solidification still existed at 270°. As, however, it is not very probable that we still should have retrograde solidification here, it is not represented in the figure.

Above the melting-point of anthraquinone (283°) the retrograde condensation is enormous, so that I could observe it at 290° over a pressure-range of 83 to 40 atmospheres.

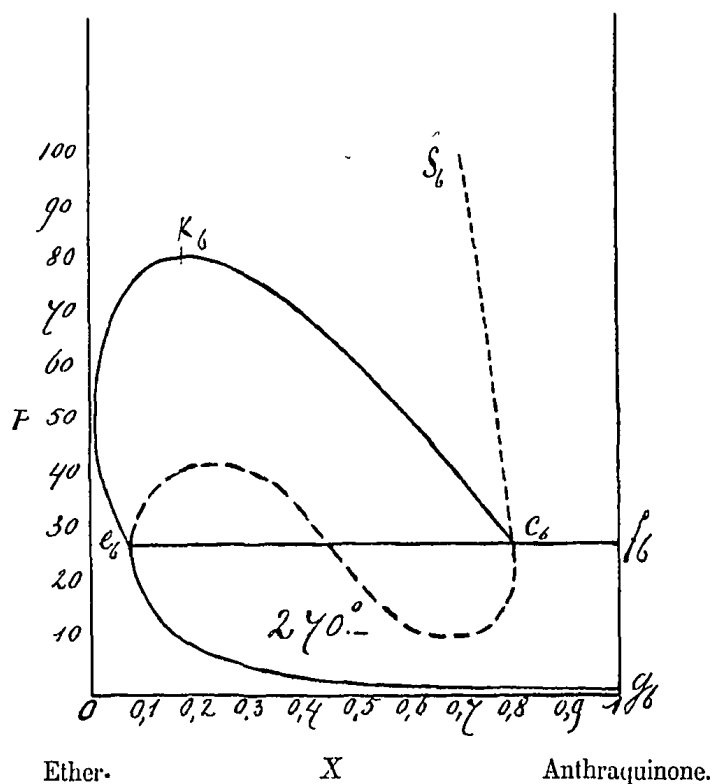Further I mention that most of the $p$-$x$-sections are crossed in

Ether.                    X                    Anthraquinone.

Fig. 2c.

different ways. In fig. 2a the regions passed are marked with arrows.

1 indicates the transition from the region for $F_q$ + solid anthraquinone into the region for $F_L$ + solid antraquinone, the three phases appearing intermedially. $F_q$ denotes here a fluid phase which in ordinary circumstances, that is to say below the critical temperature of ether, would be called gas-phase; and $F_L$ denotes a fluid phase which in ordinary circumstances would be styled liquid phase. It is evident that the difference between $F_q$ and $F_L$ exists solely in their foregoing history.

2 marks the transition from the region $F_q$ + anthraquinone into the region $F_L$, the three phases appearing intermedially.

3 indicates essentially the same as 2, but yet the phenomenon is somewhat different, because now we do not in the end pass the liquid branch, as in 2, but the vapour-branch; this is marked by the sign $F_q$ over the branch $e_3 k_s$.

4 is a very remarkable transition, as here we pass directly from the region for $F_q$ + solid anthraquinone into the region for $F_q$.

As to the lack of retrograde condensation at temperatures between 247° and ± 260° and its appearance at higher temperatures, I want

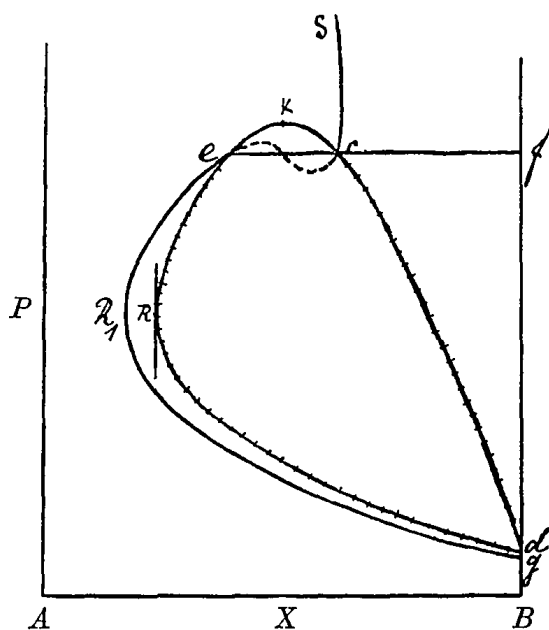to say a few words about it in connection with the appearance of retrograde solidification.



Fig. 3.

If in fig. 3 the $p$-$x$-loop $dckeR$ represents the liquids and vapours which may coexist at a given temperature, but of which a series of liquids and vapours are not to be realized in a stable state because of the appearance of the threephase pressure curve [1]), then several cases are possible. If the threephase pressure curve, as drawn in fig. 4 lies above the critical point of contact $R$, then no retrograde condensation will occur, notwithstanding its possibility is strongly pronounced in the character of the $p$-$x$-loop, because the part giving rise to the retrograde condensation lies in the metastable region. Now this occurs in the system ether-anthraquinone from 247° to 260°.

The dotted vapour and liquid curves below the threephase-pressure curve $ecf$ are metastable; the stable state here is solid $B$ by the side of a fluid phase, and now the question was raised: "how is this part of the isotherm of solubility situated?" Evidently this stable curve must lie left of the metastable curve $dRe$ or in other words towards smaller $B$-concentrations. This conclusion is of great importance for us, for from it follows that, *if the threephase-pressure-curve lies above the critical point of contact of the vapour curve coexisting with liquid and for that reason the retrograde condensation falls in the metastable region, retrograde solidification must occur instead of retrograde condensation*, and this retrograde solidification must be *stronger* than the retrograde condensation would have been. If the threephase-pressurecurve passes exactly through the critical point of contact, retrograde solidification is no longer necessary.

Resuming, we conclude that, given the case that the plaitpoint-

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[1]) I propose to give this name to the curve that in a $p$-$x$ section denotes the pressure at which the three phases coexist. This curve refers therefore to one temperature, whilst the *threephasecurve* embraces a series of temperatures.

curve meets the solubility curve, it is possible to prove in a very simple way the necessity of the appearance of retrograde solidification in $p$ and $q$.

Here however we must at once point out that, as will be discussed presently, retrograde solidification also occurs between $p\,q$. The fact that theory requires this, can only be proved mathematically [1]).

Returning to fig. 2, we must still state that the curve $q\,b$ uniting the plaitpoints of the different $p$-$x$-loops, is very steep and, as far as it has been observed, parallel to the first part of the plaitpointcurve $a\,p$. This course however will probably change towards a higher temperature, for if the plaitpointcurve possesses a maximum, which is probably the case, then the projection of the plaitpointcurve on the $p$-$x$-plane must also show a maximum.
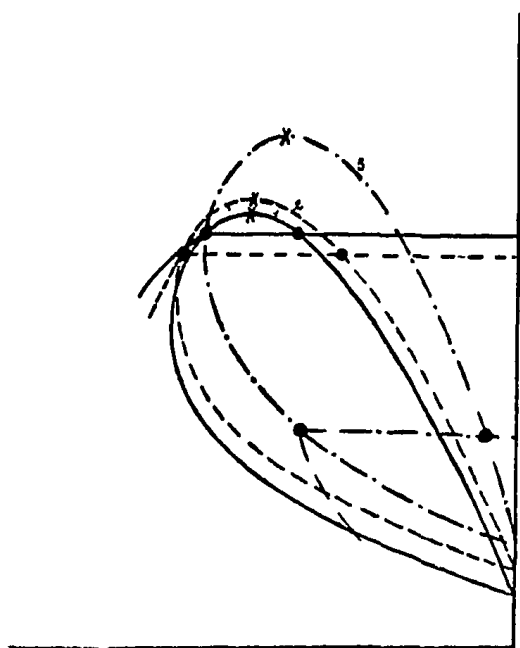


Fig. 4a.

The $p$-$x$-sections below the temperature 203° are not drawn in fig. 2, as the scale is too small to render the particulars conspicuous. Therefore this part of fig. 2 is separately reproduced on a larger scale in fig. 4.

In accordance with the preceding we see that, though at 200° no retrograde condensation occurs, instead of it there appears retrograde solidification. Soon however the situation changes here, for already at 196° retrograde condensation could be observed.

What was observed when going from point $q$ to a higher temperature, is naturally also found in point $p$, but here towards a lower temperature. This is illustrated by figures 4a and 4b; fig. 4a applies to temperatures above point $q$ and fig. 4b applies to temperatures below point $p$. In both figures three $p$-$x$-sections are represented schematically, the sections 1 and 2 differ but slightly in temperature, and 3 applies to a temperature considerably different from that with which 2 corresponds.

In fig. 4a section 1 applies to the lowest and 3 to the highest of

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[1]) VAN DER WAALS, l. c.

the observed temperatures; in fig. 4*b* the reverse is seen, but all the same it is seen that in the two figures the same things are to be met with in the succession of sections 1, 2 and 3. The three
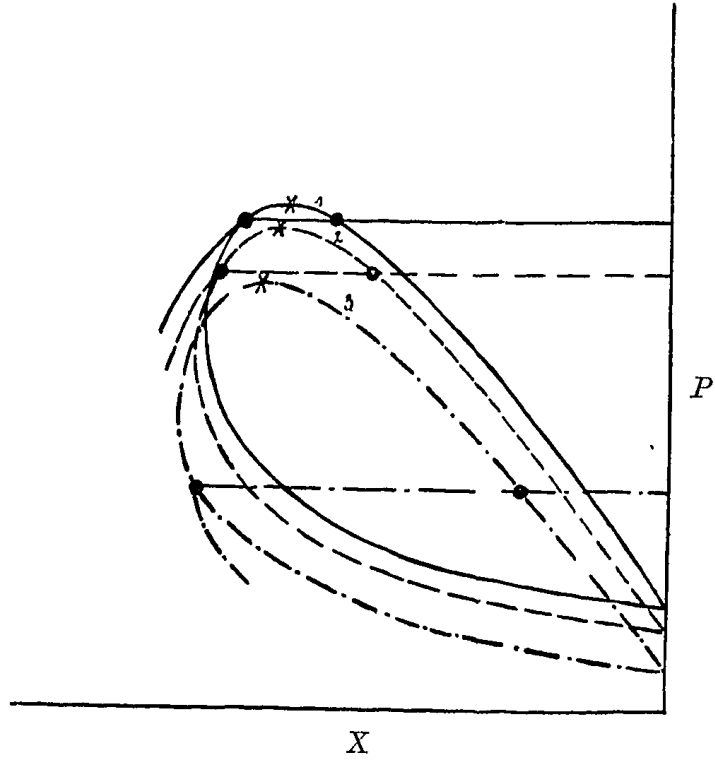


*X*

Fig. 4*b*.

pressure curve lies highest in 1 and lowest in 3. In 1 and 2 we do not find any retrograde condensation, but retrograde solidification, and in 3 we find retrograde condensation only. In fig. 4*a* however the plaitpointpressure increases in the order 1, 2, 3, and decreases in fig. 4*b*, but this is due to the fact that in the first case the order 1, 2, 3 means towards higher temperatures, and in the second towards lower.
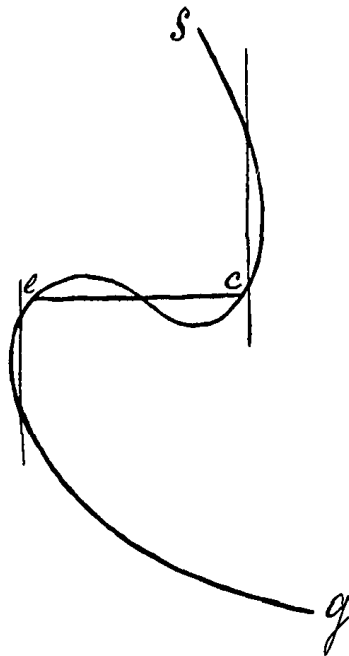
Concerning the course of the isotherms of solubility above the three phase pressure curve, VAN DER WAALS has shown the probability of a course as given in fig. 5, from which results that the branch *c s* also shows retrograde solidification. This case, in which



Fig. 5.

Plate I

Fig. 2.

A SMITS "On the phenomena appearing when in a binary system the plaitpointcurve
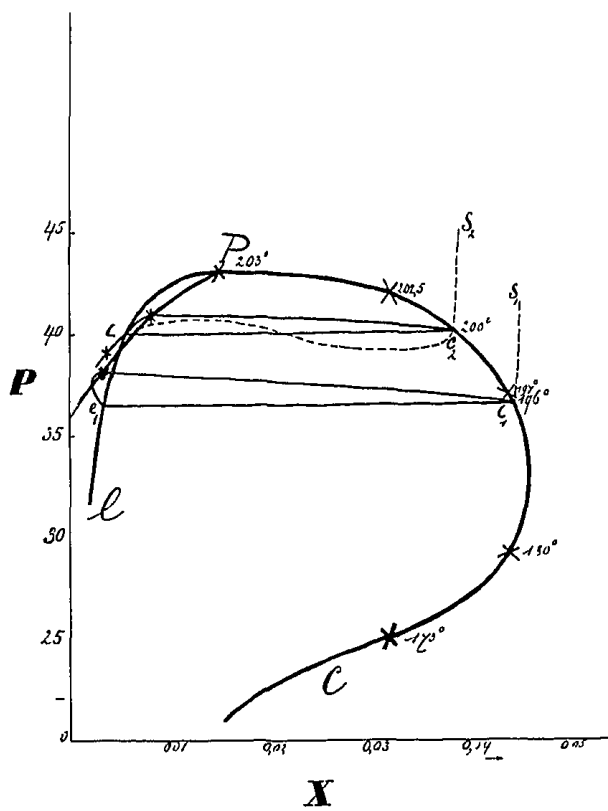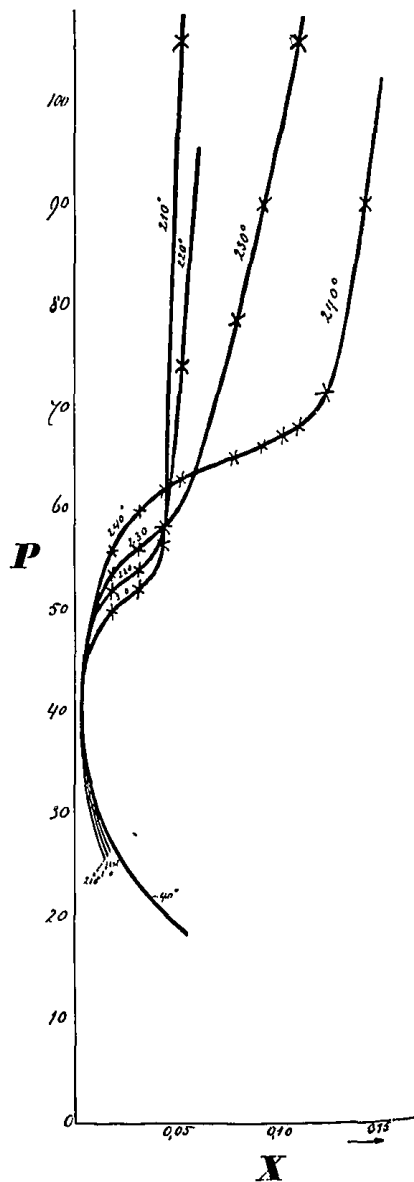meets the solubility curve"
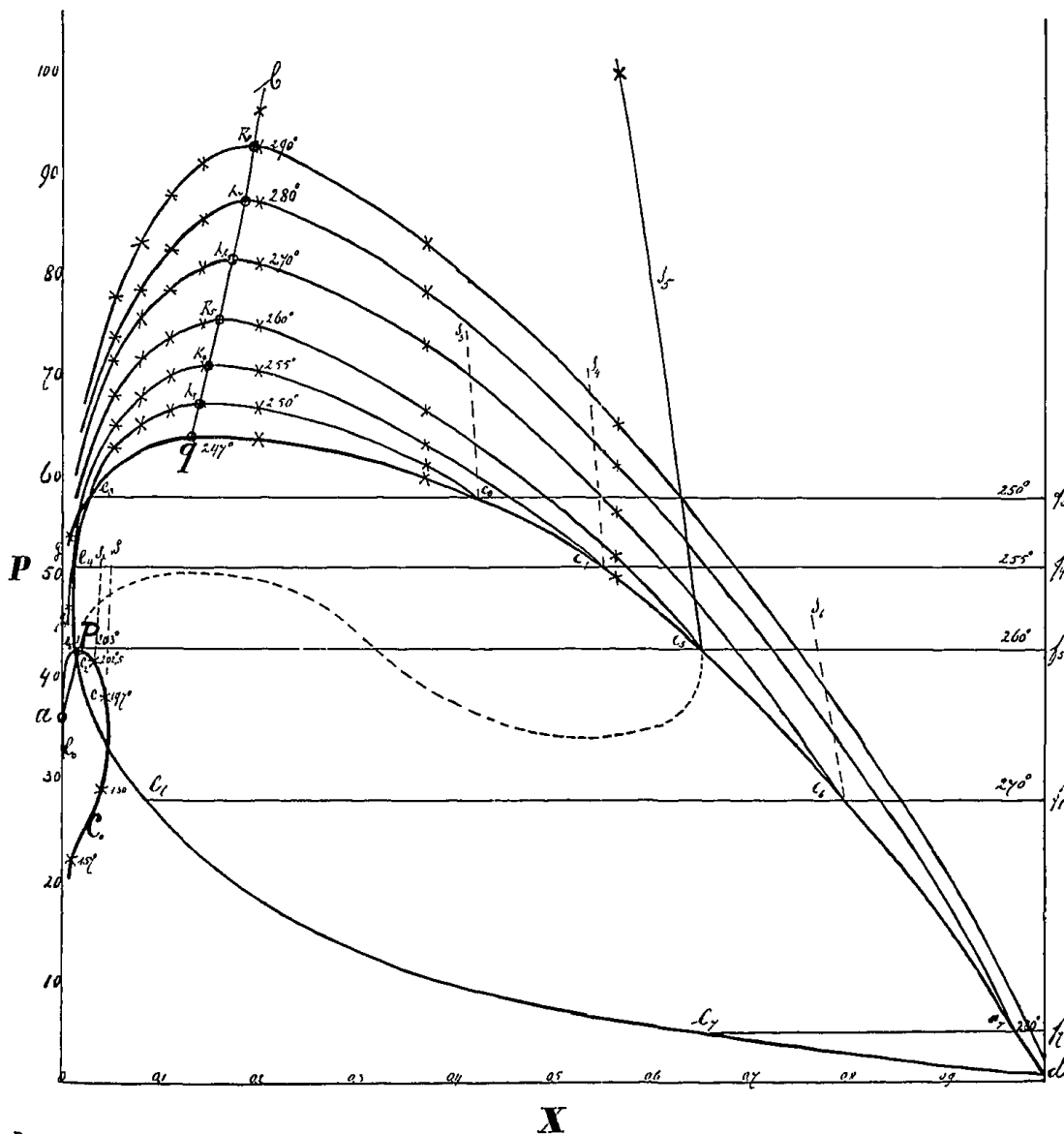
*Fig. 6.*

*Fig. 4.*

the whole isotherm of solubility points to a double retrograde solidi-
fication, has not been ascertained as yet. What has been found, is
that below 240° the upper part of the isotherm of solubility runs
toward the right, which points to an increase of solubility of anthra-
quinone in the fluid phase with increase of pressure [1]), whereas
above 250° a reversed course was found. Between 240° and 250° a
change of direction seems to have taken place, and in this range it
might be possible to ascertain the course foretold by VAN DER WAALS.
As however the small range of temperature 240°—250° corresponds
with a great difference in concentration, the point when the change
of direction takes place is not easily ascertained.

The results obtained at temperatures between 203° and 247° are
represented in fig. 6. Here the isotherms of solubility for the fluid
phases at 210°, 220°, 230° and 240° are drawn. All these isotherms
show, as predicted by VAN DER WAALS [2]), the phenomenon of retro-
grade solidification, and the nearer we get to point $q$, in other words
the nearer to 247°, the larger the region of this retrograde solidification.



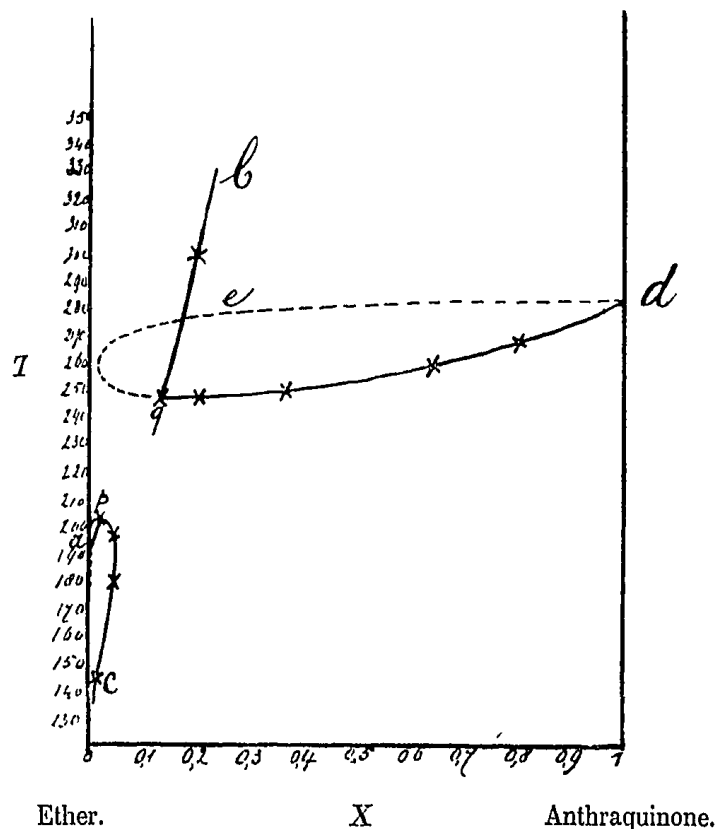| Ether. | X | Anthraquinone. |

Fig. 7.

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This isotherm of 210° has the steepest course; with increase of temperature the course becomes at first less steep, but at 240° a steeper course seems to reappear, which is probably connected with the change of direction which appears above 240°.

The projection of the solubility curve and the plaitpoint curve on the $t$-$x$-plane is represented in fig. 7, where the dotted curves represent the vapourbranches. The projections of the two parts $ap$ and $qb$ of the plaitpointcurve are almost straight lines. If we examine the course of the line $qb$, in order to see at what temperature this line will meet the line for pure anthraquinone, we shall find $\pm$ 800°.

Lastly we find in fig. 8 the course of the molecular volumina of



Ether.                                                           X                                                   Anthraquinone.
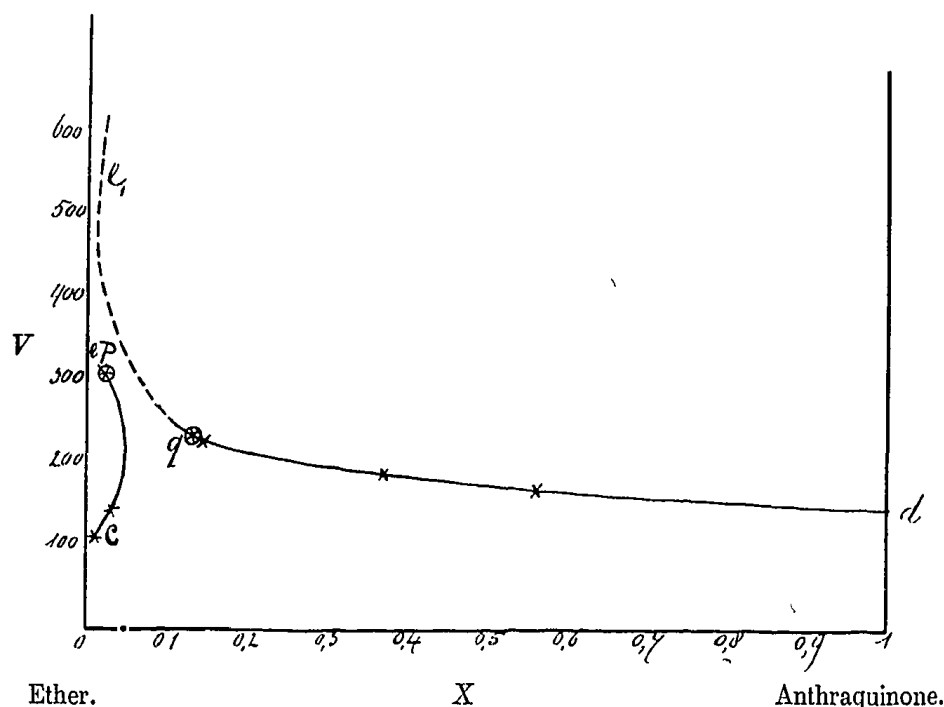
Fig. 8.

the saturated solutions. Here too we have two continuous branches, each of them consisting of a liquid and a vapour branch. $dq$ and $cp$ are the liquid branches and $qe_1$ and $pe$ are the vapour branches. $p$ and $q$ denote the molecular volumina of the two critical saturated solutions. The dotted vapourcurve $qe$ runs on to the concentration 0.015, so that from this figure also directly follows that at higher temperatures and larger volumina three phases may again be obtained with the concentration with which point $p$ may be realized. Here too the curves $cp$ and $qe$ indicate clearly the phenomenon of retrograde solubility.

So the investigation described here has furnished proof positive of the general points of view which were prominent in the qualitative

investigation, and of which the theory of VAN DER WAALS could give a closer description.

The peculiarity of the examined system, which lies in the fact that the vapour pressure of the one substance (ether) far exceeds that of the other (anthraquinone), caused some wholly unexpected phenomena, and made it on the other hand possible to realize retrograde solidification on a much larger scale than had been thought possible till now.

*Laboratory for Anorganic Chemistry of the University.*

*Amsterdam,* June 1904.

**Chemistry.** — *"The preparation of silicon and its chloride."* By Prof. A. F. HOLLEMAN.

(Communicated in the meeting of June 24, 1904).

The numerous proposals which have been made for the preparation of the element silicon in both the amorphous and crystallised form prove that a simple method has not as yet been found. W. HEMPEL and VON HAASY [1]) have published in 1899 an additional process consisting in the decomposition of silicon fluoride with sodium. They melt this metal in small portions at a time in an iron apparatus and then pass over the mass a current of silicon fluoride, which is then very readily decomposed. The brown porous mass, which has been brought to a faint red heat is allowed to cool for two or three hours in the current of silicon fluoride. An attempt to convert it into silicon chloride by heating the mass without previous purification in a current of chlorine was unsuccessful. It was impossible to remove the $NaFl$ and $Na_2SiFl_6$ by boiling with water; so in order to obtain pure silicon it was necessary to fuse the mass with sodium and aluminium. The latter dissolves the silicon which is then left insoluble on treating the regulus with dilute hydrochloric acid.

Mr. H. J. SLIJPER who has repeated these experiments in my laboratory showed (1) that by a small modification of the process the crude product may be purified to such an extent by boiling with water that it may be used for preparing silicon chloride; (2) the reason why the crude product on being treated with chlorine does not yield silicon chloride.

1. It is known that sodium fluoride readily absorbs $SiFl_4$ and

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[1]) Zeitschr. f. anorg. Ch. **23**, 32.

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