It is further te be seen in this p,x-section, that the two metastable three phase pressure lines for $S_A + G + L$ and for $S_B + L + G$ lie above the stable three phase pressure line for $S_A + S_B + G$, and that the first lies between the two others. At the same time we see that the character of the solubility isotherms does not change, the only modification which is brought about for each of the isotherms compared with the usual case is this that the metastable part is enlarged.

If we now take a temperature which lies still somewhat lower, viz. t_4, we get a p,x-section as represented in fig. 5. All the three phase pressure lines have diverged, and descended, except that for $S_A + S_B + L$, which has strongly ascended. The second point of intersection lies now, in agreement with what the dotted line for the temperature t_4 traced in the P,T-projection shows, far above the point indicating the vapour tension of the supercooled liquid of A. The metastable part of the two solubility isotherms has greatly increased, and with it the region for $S_A + S_B$. With further decrease of temperature the character of the modifications in the p,x-section remains the same, so that it is unnecessary to examine another.

If we had applied the same considerations to the case that the eutectic melting-point curve has a positive course, we should, with the exception of the unstable region, have found but one (lower) point of intersection for the solubility isotherms, for the branches which gave a second (higher) point of intersection in the case under discussion, recede continually from each other.

I have not represented this latter case, as it yields nothing special.

The case treated shows once more, how the examination of the equilibria which are hidden from our eyes, may contribute to widen our insight into those accessible to experiment.

Amsterdam, December 1905.
Anorganic Chemical laboratory of the University.

Chemistry. — *"On the phenomena which occur when the plaitpoint-curve meets the three phase line of a dissociating binary compound".* By Dr. A. SMITS. (Communicated by Prof. H. W. BAKHUIS ROOSEBOOM).

1. In a previous paper [1]) I have already pointed out, that the interesting systems metal-oxygen, metal-hydrogen and metal-nitrogen, to which we may still add many of the systems metal-halogen, and metaloxyde-acidanhydride, belong to the type ether-anthraquinone,

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) Zeitschr. f. physik. chem. **51**, 193 (1905.)

but they are more complicated, because here the components may combine.

Now from a chemical point of view it is of the highest importance to examine also these more complicated phenomena, in order to obtain in this way a general insight into the phenomena of equilibrium for the case that compounds are raised to high temperatures, and placed under such a pressure that critical phenomena are found with saturated solutions. As yet any insight into this was wanting.

By bringing the results of my investigation on ether-anthraquinone in connection with the cases lately discussed by me in a paper: "Contribution to the knowledge of the PX and the PT-lines for the case that two substances enter into a combination which is dissociated in the liquid and the gas phase" [1]), 1 have succeeded in arriving at a clear conception of the above mentioned phenomena.

In all the cases which 1 shall shortly discuss here, I start from the supposition that the compound under consideration is miscible with both components in fluid state in all proportions. On the whole our knowledge as to this is exceedingly slight, nor is there the least certainty on this head for the substances which I shall adduce here as examples.

2. First of all I shall consider the case, that two substances A and B yield a dissociating compound $A_m B_n$, the melting point of which lies above the critical temperature of the substance A. This case is met with in the system $CaO—CO_2$. If now the solubility of the compound $A_m B_n$ in A is still slight at the critical temperature of A, the continuous plaitpoint curve, which starts at the critical point of A (CO_2) and terminates in the critical point of B (CaO) will meet the solubility curve of $A_m B_n$ ($CaCO_3$) in fluid A (CO_2) in two points. That the point p exists has already been demonstrated by Dr. Büchner [2]); in temperature this point lies only slightly above $31°$, the solubility of $CaCO_3$ in fluid CO_2 being still very slight at this temperature.

This case has been represented in Fig. 1. The upper half of this diagram contains the projection of the spacial figure on the PT-plane; the lower half represents the projection of the *two phase regions* [3]) *coexisting with solid substance*, and the plaitpoint curve. The combination of these two projections seems to me the simplest way of

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[1]) These Proc., June 1905, p. 200.

[2]) Thesis for the doctorate, 106. (1905).

[3]) At first I gave the name of *three phase* regions to these regions because, though they indicate only *two* phases, a third coexists with them. It seems, however, better to me to speak of *two phase regions coexisting with solid substance*, which term I shall use henceforth.

representation for a first investigation of these problems. For the sake of clearness I must draw attention to the fact, that in the T-X-projection the lines aE, Ep, qFE' and $E'c$ are the solubility curves, whereas aE_1, E_1p, $qF'E_1'$ and $E_1'c$ represent the vapour lines. In the P-T-projection, however, we get one *three phase line* for each pair of two corresponding lines for the liquid and gas phases coexisting with solid substance. These three phase lines are indicated by $A+L+G$, $A_m B_n +L+G$ and $B+L+G$ in the P-T-projection.

The first meeting of a solubility curve with the plaitpoint curve takes place in p and the second in q. According to VAN DER WAALS' theory a continuous transition from the solubility curve into the coexisting vapour curve takes place in these two points. If we take once more the system CO_2—CaO as an example, p indicates the critical point of the saturated solution of $CaCO_3$ in fluid carbonic acid, and q the critical point of another solution saturated with $CaCO_3$ with a much larger concentration of $CaCO_3$.

Between these points p and q a fluid phase may occur alone or by the side of solid $A_m B_n (CaCO_3)$, and in the neighbourhood of these points the phenomenon of retrograde solidification must present itself. I will further emphatically point out here, that it is assumed, as is easily seen in the T-X-projection, that near the melting point the difference of the volatility of the components is not so large as to prevent the occurrence of a vapour of the composition of the compound. The point F', where the composition of the vapour is the same as that of the compound, is the *maximum-sublimation point* and the point F, where the concentration of the liquid is the same as that of the compound, is the *minimum melting point*, or the melting point under the three phase pressure [1]. What I did not yet show in my previous paper is this that two lines start from the points F and F', which pass continuously into each other at K. These lines form the continuous bounding curve of the two sheets of the PTX-surface for the composition of the compound. The continuous bounding curve touches the plaitpoint curve in K, so that K denotes the critical point of the dissociating compound. That this point K does not constitute a special point of the continuous plaitpoint curve is due to the fact that when the compound is assumed to dissociate, the critical point of the liquid compound does not essentially differ from that of the liquids with other compositions.

In fig. $1a$ the projection of the two phase regions coexisting with solid substance is represented, and also that of the plaitpoint curve

[1]) These Proc., June 1905, p. 200.

on the p-x-plane: further the solubility isotherms corresponding with the temperatures of the points p and q are indicated, from which the phenomenon of retrograde solidification appears clearly.

3. In the case discussed the situation of the points p and q depends on different properties of the compound and its components. In special cases it will, therefore, depend on this, on what part of the three phase line of the compound the point q lies. Undoubtedly there will be many cases where this point falls below the melting point. Probably this case will occur the sooner the more the volatility of the two components differs. In this paper, however, I continue to assume, that a vapour- of the composition of the compound may exist.

In this different cases may present themselves, which each call for a separate discussion. So highly remarkable phenomena make e. g. their appearance, when the plaitpoint curve cuts the three phase line of the compound between the melting point and the maximum sublimation point. I shall, however, discuss this case and some others in another paper, and restrict myself now to the phenomena, which occur, when the point of intersection q, as has been drawn in Fig. 2, lies not only below the melting point of the compound, but also below the maximum sublimation point. *Also in this case the possibility is excluded that the compound melts, and the only way in which the solid compound can vanish, is by evaporation.*

The line for solid $A_m B_n + G$, which would touch the three phase line $A_m B_n + L + G$ in the maximum sublimation point, if this point existed, runs on uninterruptedly to infinity, at least when no further complications appear.

The T-X-projection occurring in fig. 2 may contribute te elucidate some points. As is to be seen there, the two phase region $E'_1 qE'$ coexisting with the solid compound, does not possess any liquid or vapour of the composition of the compound, which is in harmony with the supposition, that the points F and F' are wanting.

In fig. 2a I have traced the projection of the two phase regions coexisting with solid substance, and of the plaitpoint curve on the p-x-plane. Further there are some solubility isotherms in this diagram, which require a few words of explanation,

The curve $fGecf''$ denotes the solubility isotherm for a temperature somewhat below that of the point q. If we now consider the temperature of the point q, we get a solubility isotherm which touches in q, and which has two more points of inflection, as is indicated by the curve f, G, q, gf''. At a higher temperature we get a solubility isotherm, which does not touch any more, and from which the two points of inflection may disappear.

4. In the third place I will point out what I have already demonstrated in a previous publication [1]), that when the tension of a compound is smaller at its melting point than that of the components, a three phase curve may occur with a very peculiar shape, viz with one minimum and two maxima.

Let us now consider the case that the melting point of this compound lies above the critical temperatures of the components, then the very peculiar phenomenon may present itself, that what occurred once in the system ether and anthraquinone, is here to be realized twice, and that the solubility curve which runs from one eutectic point to the other, meets the plaitpoint curve *four times*, which appears in the PT-projection fig. 3 as a four times repeated intersection of the three phase curve A_mB_n+L+G and the continuous plaitpoint curve $bKLd$ in the points p, q, q' and p'.

It appears from the PT and TX-projections that for all possible concentrations a range of temperature may be pointed out, within which the solid compound can only coexist with a fluid phase. When, however, which is conceivable, the portions cut out of the three phase line have no range of temperature in common, the temperature regions for solid $+$ fluid, lie above each other, and so we have no symmetrical phenomena for any temperature on both sides of the line for A_mB_n in the PT-projection.

The systems hydrogen-water and oxygen-water belong to the type ether-anthraquinone when the components are miscible in all proportions. Each of these systems will then yield a point p and a point q. Supposing, which is, however, highly improbable, that by the application of a catalyser we could bring about equilibrium between oxygen, hydrogen and water vapour at any temperature, we should get a continuous three phase line for ice $+$ L $+$ G as is indicated in fig. 3, and also one continuous plaitpoint curve. The equilibrium with water, however, lying theoretically almost quite on the side of water at lower temperatures, we should commit a practically unappreciable error, when we tried to realize at these lower temperatures the diagram drawn here by starting in one case from ice, resp. water $+$ hydrogen, and in another case from ice, resp. water $+$ oxygen.

This example, however, is not suitable for illustration of the assumed case, because for this purpose we require a compound which appreciably dissociates at its melting point. I have only mentioned the system H_2—O_2 to show how remarkable this system is.

It is very probable that systems are to be found, with which the

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[1]) loc cit.

supposed case may be realized without excessive experimental difficulties. This may succeed with NH_3—HCl. A system for which fig. 3 holds, presents also this particularity, that we have here a P, T, X-surface of two sheets with a *minimum curve* bounded on the upper side by a continuous plaitpoint curve, which, in consequence of the great difference between the critical temperatures of the compound and the components might possibly have the shape described here.

Prof. VAN DER WAALS was so kind as to draw my attention to the particularities of the P, T, X-surface of two sheets, which may be derived directly from those of a surface with a maximum curve, by simply reversing everything. The minimum curve, i. e. the locus of all points for which the concentration of liquid and vapour are the same, forms here the lower boundary of the projection of the P, T, X-surface of two sheets on the P, T-plane. This curve is represented in fig. 3 by the dotted line LL', which touches the plaitpoint curve at L, and the continuous three phase line at N. This point N, lying between the minimum M in the three phase line and the maximum sublimation point F', as I have shown in a paper forwarded to the Zeitschr. f. phys. Chem. towards the end of September, is a point where the concentration of the vapour is equal to that of the liquid, and is therefore at the same line a point of the minimum curve, which becomes metastable on the left of N. The peculiar feature in the P, T, X-surface of two sheets drawn here manifests itself, when the bounding curves are traced for different concentrations.

It appears then, that if we come from the side of B, the concentration of the point L is the first, at which the bounding curve presents some particularity. At this concentration we get, viz., two bounding curves, which starting from Q and S, terminate at L in a so-called cusp, as is here once more separately represented.

With a concentration somewhat richer in A we get now two bounding curves which pass continuously into each other. The continuous transition takes place where the bounding curve touches the plaitpoint curve. Further this continuous bounding curve shows, this particularity that the two branches touch each other near the critical

Fig. 1.

Fig. 1a.

Fig. 2.

Fig. 2a.

Fig. 3.

Fig. 3a.

point, and form in this way a loop, as is separately represented below.

The point of tangency m lies on the minimum curve.

r With concentrations still richer in A, the character of the bounding curves remains the same, only the point m shifts along the minimum curve towards N, so that, when we choose the concentration corresponding with the point N, the bounding curve gets this shape, where the vapour branch as well as the liquid branch touches the three phase line at N.

If we now pass on to greater concentration of A, we get again bounding curves of the usual form, for the point of tangency m lies now in the metastable region. If the critical point of the bounding curve, coincides with the maximum temperature of the plaitpoint curve then m lies at the absolute zero point. Leaving further particularities undiscussed, I will only just point out that the minimum curve, beyond the point N towards lower temperatures, lies below the three phase line, which is necessary, because the supersaturate solution has a smaller vapour tension than a saturate one and it is wanted for the realisation of the metastable branch of the minimum curve that the solid substance does not make its appearance.

Now as to the T-X-projection on fig. 3 we may still remark, that in accordance with the foregoing remark the liquid line $qF''Nq'$ cuts the vapour line $qF Nq'$ in N at a temperature and pressure lying somewhat below that of the maximum sublimation point F', but slightly above that of the minimum point M of the three phase line. In N vapour and liquid are therefore of the same concentration, but this is not the case at the minimum M.

In fig. 3a the projection is represented of the two phase regions coexisting with solid substance on the p,x-plane, which diagram does not call for further elucidation.

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Anorganic-Chemical-laboratory of the University.

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