Physics. — *"The equilibrium between a solid body and a fluid phase, especially in the neighbourhood of the critical state."* By Prof. J. D. van der Waals.

After the publication of the experiments of Dr. A. Smits in the proceedings of the September meeting, communicated by Prof. Bakhuis Roozeboom, I had a discussion with the latter chiefly on the question if and in what way the liquid equilibriums and the gas equilibriums which may exist by the side of a solid phase, must be thought to be connected by a theoretic curve at given temperature, in consequence of the continuity between liquid and gas. It is in agreement with the wish of Prof. Bakhuis Roozeboom, that I communicate the following observations.

Let us imagine the ψ-surface of a binary mixture, anthraquinone and ether, in which we will call ether the second substance, at a temperature slightly above T_k for ether. Then there is a liquid-vapour plait, closed on the side for ether.

Let us add the ψ-curve or the ψ-surface for the solid state, the ψ-curve when the solid state has an invariable concentration. If only pure anthraquinone should be possible in the solid state, this ψ-curve would lie in the surface for which $x = 0$. For the sake of perspicuity we shall start from this hypothesis in our first description. Then we find the phases which coexist with the solid anthraquinone, by rolling a plane over the ψ-surface and the conjugate ψ-curve.

On account of the slight compressibility of the solid body, we can describe a cone, unless the pressure be excessively high. This surface enables us to find the coexisting phases; its vertex lies viz. in the point $x = 0$, $v = v_s$ and $\psi = \psi_s$, if v_s represents the molecular volume of the solid anthraquinone and ψ_s the value of the free energy, both at the temperature considered. The curve of contact of this cone and the ψ-surface represents then the coexisting phases. For shortness' sake we will use for it the name of contact-curve, though it is properly speaking also a connodal curve on the ψ-surface of the binary mixture having its second or conjugate branch on the ψ-surface of the solid state.

Now we can have three cases for the course of this contact-curve. 1st. It may remain wholly outside the liquid-vapour-plait, and will form then a perfectly continuous curve. 2nd. It may pass through that plait, in which case one part of this curve will represent gas phases and another liquid phases, which two parts will be connected by a third part lying between the two branches of the connodal

curve and representing metastable and unstable phases. 3ᵈ. It may touch as intermediate case the connodal curve of the transverse plait in a point which will be the plaitpoint, as will appear presently.

As to the course of the liquid part of the contact-curve we may at once conclude, though this will be shown afterwards in a more striking way, that two cases may occur. From the point on the connodal curve where it enters the liquid part of the ψ-surface with increasing pressure, the curve will namely move more and more towards decreasing values of x, and finally terminate at $x = 0$ — or it can move towards increasing values of x.

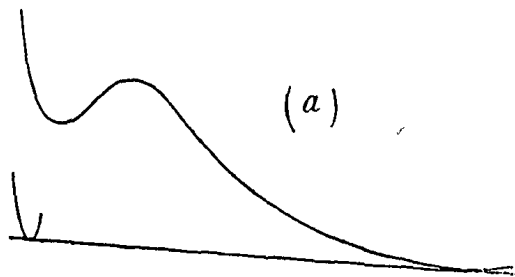If we trace the ψ-curve for $x = 0$, and add a portion of the

fig. 1 (a)

ψ-curve for the solid body to the figure, then if this portion has position (a), so if the volume of the solid body is smaller than that of the liquid, only one bi-tangent can be drawn, and this will represent a coexisting gas phase. If on the other hand the added portion of the ψ-curve for the solid phase has position (b),
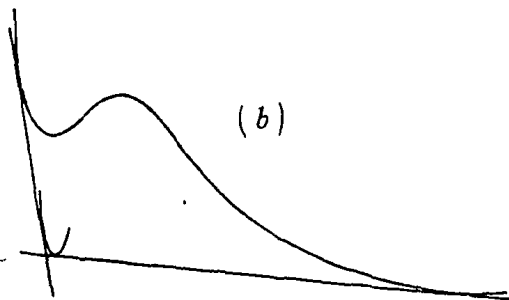

fig. 1 (b)

so if the volume of the solid phase is larger than that of the liquid, two bi-tangents may be drawn. At low pressure, a coexisting gas phase will exist, and at high pressure a coexisting liquid. In the latter case the liquid part of the contact-curve will move towards points for which x decreases when the pressure increases.

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For a contact-curve which passes through the plait of the ψ-surface, the property holds of course good that the pressure is the same for the two points, in which it meets the connodal curve of the transverse plait. If namely a bi-tangent plane is made to roll simultaneously over the ψ-curve (or the ψ-surface) of the solid substance, and over the gas part of the ψ-surface of the binary mixture, then if this tangent plane meets a point of the binodal curve of the transverse plait, this tangent plane will also touch the ψ-surface in a point of the other branch of the binodal curve, and this point will represent a liquid phase. Three phases are then in equilibrium. The pressure that then prevails, is therefore the three-phase-pressure at given temperature. If the temperature should be such that the contact-curve no longer passes through the plait, then no three-phase pressure exists any longer for that value of T. For the intermediate case the solid body is in equilibrium with two phases, which have become equal and the two points of the connodal curve which the contact-curve has in common with it, have coincided in the plaitpoint.

Particulars as to the course of the contact curve are found from the differential equation of p, when x and T varies. If we represent the concentration and the molecular volume of the solid body by x_s and v_s and that of the coexisting phase, whether it be a gas phase or a liquid phase, by x_f and v_f; this equation may be brought under the following form, which is perfectly analogous to that which holds for the coexisting phases of a binary mixture :

$$v_{sf}\, dp = (x_s - x_f)\left(\frac{d^2\zeta}{dx_f^2}\right)_{pT} dx_f + \frac{W_{sf}}{T}\, dT$$

For the signification of v_{sf} and W_{sf} I refer to Cont. II, p. 107 etc. If T is kept constant, we have for the course of p the differential equation :

$$v_{sf}\frac{dp}{dx_f} = (x_s - x_f)\left(\frac{d^2\zeta}{dx_f^2}\right)_{pT}$$

As long as the contact-curve does not pass through the plait, $\dfrac{d^2\zeta}{dx^2_f}$ is always positive.

If in the solid state only the pure first substance (in the case under consideration anthraquinone) should occur, then $x_s = 0$.

But the same differential equation holds also, if x_s should be variable. For the case of anthraquinone and ether the value of x in the gas phase is higher than that of the liquid phase for coexisting liquid and gas phases, or $x_2 > x_1$. It is therefore to be expected,

that the value of x_s in the solid state will a fortiori be smaller than that of the phase coexisting with it, whether the latter is a gas or a liquid phase. We do not wish to state positively that there are no exceptions to this rule. But for the case ether and anthraquinone we may safely assume that $x_s - x_f$ is negative.

Now it remains only to know the sign of v_{sf}, to be able to derive the sign of $\dfrac{dp}{dx_f}$.

The expression v_{sf} stands in the place of $(v_s - v_f) - (x_s - x_f)\left(\dfrac{dV_f}{dx_f}\right)_{pT}$ and represents the decrease of volume per molecular quantity when an infinitely small quantity of the solid phase passes into the coexisting phase at constant pressure and constant temperature. If this coexisting phase should be a vapour phase, this decrease of volume is undoubtedly negative. But this quantity may also be positive, and if we make the series of pressures include all kinds of values, so if we make the pressure ascend from very low values up to very high ones, there is undoubtedly at least once reversal of sign, and for the case that the contact-curve under high pressure moves towards increasing values of x there is even twice reversal of sign.

To demonstrate this, we inquire first into the geometrical meaning of v_{sf}. Let the point P be the representation of the solid phase, with v_s and x_s as coordinates — and the point Q the representation of the coexisting fluid phase with v_f and x_f as coordinates. Let us draw through Q the isobar and let us determine the point P', in which the tangent to this isobar of Q cuts the line which has been drawn through P parallel to the volume-axis, then $-v_{sf} = PP'$. If the point P' lies on the positive side of P, then v_{sf} is negative. For the special case that the tangent to the isobar of Q passes through P, $v_{sf} = 0$. In the same way v_{sf} would be positive, if P' should lie on the negative side of P.

In order to know the sign of v_{sf}, the course of the curves of equal pressure must therefore be known. In my "Ternary systems" I (These proceedings Febr. 22ᵈ 1902, p. 453) I have represented for the analogous case of a binary system, for which the second component has the lowest T_k, the course of the isobars by the line $BEDD'E'B'$ in Fig. 2. I have added another isobar to the reproduction of this figure — and I have represented the solid phase by the point P_s. The added isobar passes through the plaitpoint. This isobar has an inflection point somewhat to the right of the plaitpoint. Each of these lines of equal pressure having an inflection point, there is a locus for these points, which I have left out in the
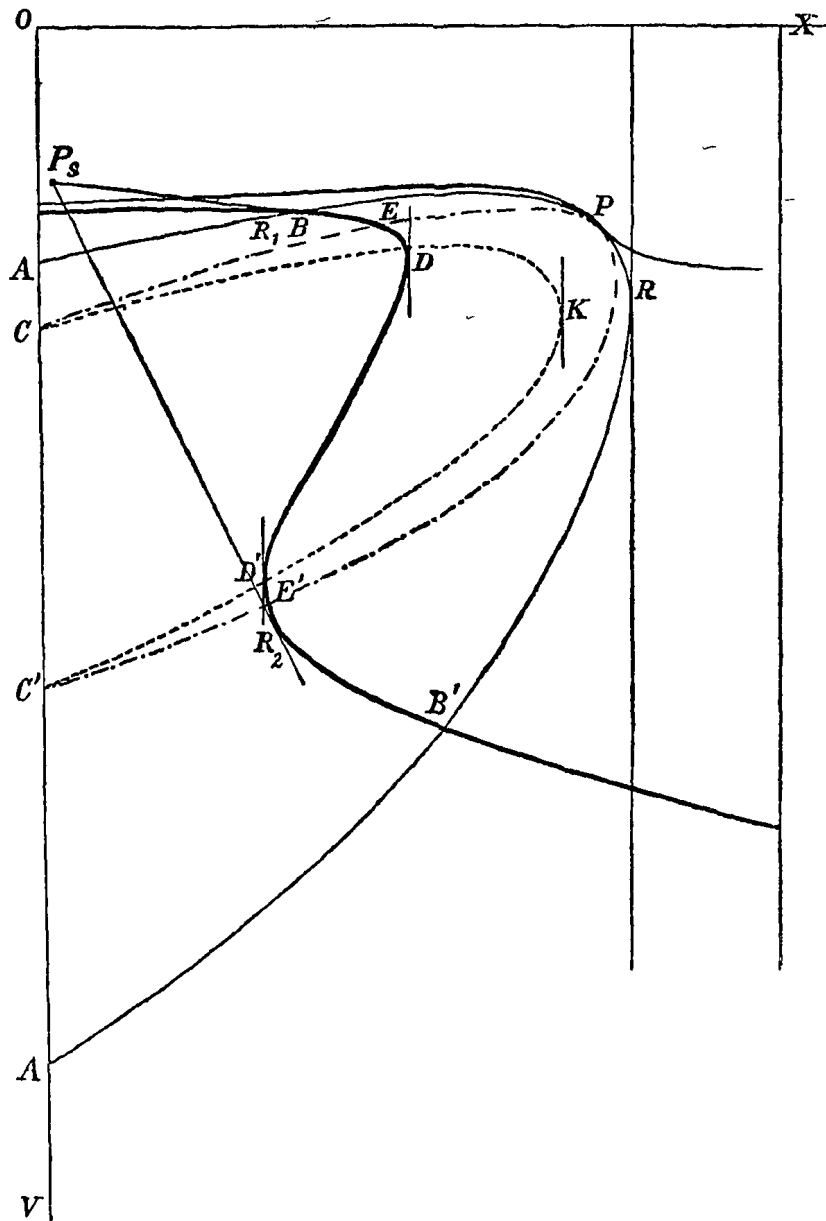
fig. 2.

figure. It extends all over the width of the figure. Always when P_s lies on the side of the small volumes of an isobar, two tangents may be drawn to such a line from P_s. These tangents touch the isobar at points, lying on either side of the inflection point; and for these points of contact $v_{sf} = 0$ Another isobar will furnish two other points of contact, if we leave the point P_s unchanged. We have therefore for every point P_s a locus, consisting of two branches, for which $v_{sf} = 0$. If the point P_s lay at greater volume, i. e, on

the other side of the isobars, it would no longer be possible to draw two tangents, and the locus for which, with regard to P_s, the value of v_{sf} is 0, would have but one branch.

Now, however, the point P_s is variable, first because the volume of the solid body depends on the pressure, and secondly when the concentration should change. This enhances of course the difficulty, if we wished to determine this locus. But this will not detract from the thesis that for the contact-curve, when it ascends from low pressure to high pressure, twice v_{sf} is 0, when the solid body has a smaller volume than it would have in fluid form at the same temperature and under the same pressure — and that only once v_{sf} is 0 in the opposite case. When P_s is variable, the locus for which $v_{sf} = 0$, is construed by drawing from every special position of P_s the tangents to the isobar of the pressure of P_s, and by joining the points of contact obtained in this way.

If the contact-curve does not pass through the plait, the value of v_{sf} is negative for the points outside the two branches of the locus $v_{sf} = 0$, and positive for the points inside.

If however the contact-curve passes through the plait, the value of v_{sf} is more complicated. In the figure the two tangents have been drawn to the isobar $BEDD'E'B'$, P_s being supposed to be in the position that corresponds to the pressure of this line. In this case too the value of v_{sf} is negative for the points lying outside the two points of contact. For the points between the points of contact we cannot assume v_{sf} to be positive, however. This holds only till the points D and D' are reached. Between D and D', v_{sf} is again negative, and the transition from positive to negative takes place in the points D and D' through infinitely great.

In the same way the value of $\left(\dfrac{d^2\zeta}{dx_f^2}\right)_{pT}$ is complicated for the points of a contact-curve, passing through the plait. I have stated this already in "Ternary systems" I, Proceedings February 22nd 1902 footnote p. 456. For the points between the connodal and the spinodal curve this quantity is still positive ; for the points between the spinodal and the curve for which $\dfrac{\partial^2\psi}{\partial v^2}$ is 0, it is negative ; whereas for the points inside this last curve it is again positive. This last transition from negative to positive takes place through infinitely great.

Let us write the equation for the determination of $\dfrac{dp}{dx_f}$ in the following form :

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$$\frac{\partial^2\psi}{\partial v_f^2}\, v_{sf}\, \frac{dp}{dx_f} = (x_s - x_f)\, \frac{\partial^2\psi}{\partial v_f^2}\, \frac{\partial^2\zeta}{\partial x_f^2}$$

or

$$\frac{\partial^2\psi}{\partial v_f^2}\, v_{sf}\, \frac{dp}{dx_f} = (x_s - x_f)\, \left\{ \frac{\partial^2\psi}{\partial x_f^2}\, \frac{\partial^2\psi}{\partial v_f^2} - \left(\frac{\partial^2\psi}{\partial x_f \partial v_f}\right)^2 \right\}.$$

In this way we simplify the discussion. The factor of $x_s - x_f$ never becomes infinitely great in this case. This factor is then positive outside the spinodal curve and negative inside it. On the spinodal curve itself it is zero. As $x_s - x_f$ is always negative in the case of anthraquinone and ether, the second member of the last equation is negative outside the spinodal curve and positive inside it. From this last equation follows: 1st that if we follow the contact-curve throughout its course, there exists a maximum and a minimum value for the pressure for the points lying inside the plait, that is when the spinodal curve is passed. 2nd that when $v_{sf} = 0$, the value of $\frac{dp}{dx}$ is either twice or only once infinitely great. In the points where $\frac{d^2\psi}{dv_f^2} = 0$,

$\frac{dp}{dx_f}$ has the value of $\left(\frac{\partial p}{\partial x_f}\right)_v$, as follows from the equation given if we put there $\frac{\partial^2\psi}{\partial v_f^2} = 0$, but which also follows directly from :

$$dp = \frac{\partial p}{\partial x_f}\, dx_f + \frac{\partial p}{\partial v_f}\, dv_f,$$

putting $\frac{\partial p}{\partial v_f} = 0$.

For contact-curves which pass through the plait not far from the plaitpoint, it appears clearly from the figure, that the points for which $\frac{dp}{dx}$ is infinitely great, lie outside those for which $\frac{dp}{dx_f} = 0$. That is to say, that the locus for which $v_{sf} = 0$, lies outside the spinodal curve. In the neighbourhood of the top of the plait they lie even outside the connodal curve. Also for the isobar $BEDD'E'B'$ I have drawn them in the figure given in such a way that the points of contact of tangents from P_s lie outside the spinodal curve. I have not yet been able to decide whether there are any exceptions. In the following figure (3) I have represented the relation between p and x_f for a contact-curve, assuming that the points of contact lie as I have drawn them in fig. 2, and as they are sure to lie, when we are in the neighbourhood of the plaitpoint. The gas phases which are in equilibrium with the solid body lie below B.
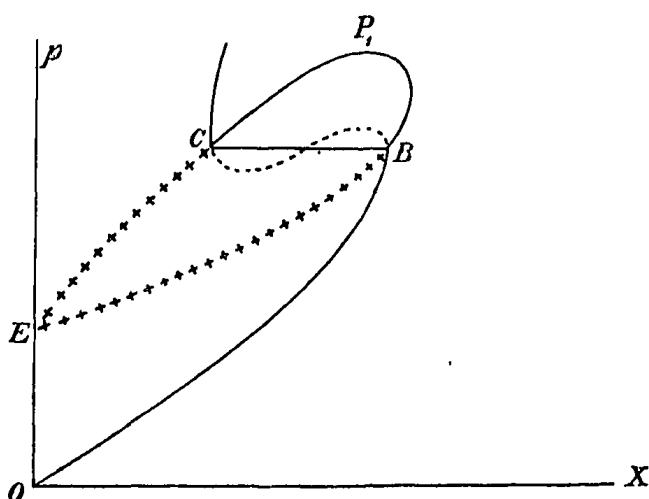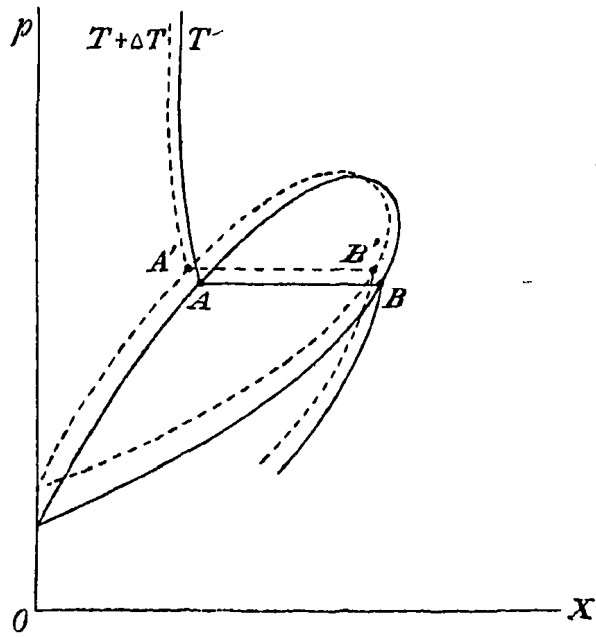

Fig. 4

the branches AA' and BB' have met, and so there is a minimum value for the value of x_A.

To the second case applies fig. 5. Then the curve AB will move to the right with decreasing temperature. With decreasing value of T the branches $A'A$ and BB' will approach each other; and this
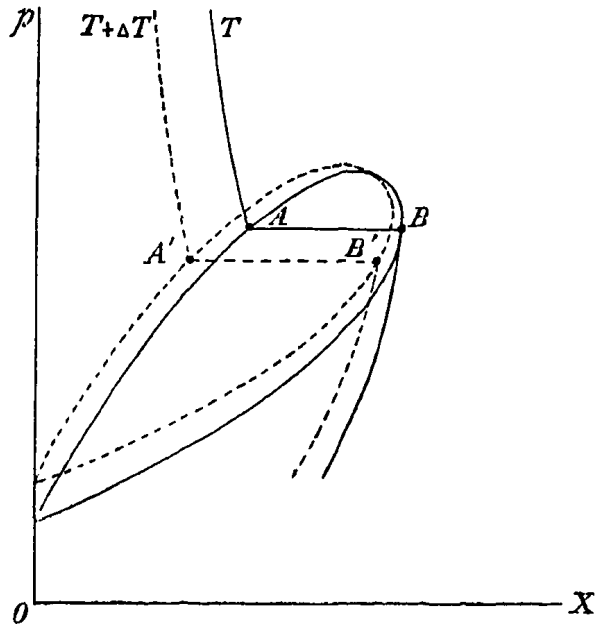

Fig. 5.

leads to the conclusion that there will be a maximum value of x_B. In fig. 6 the value of x for the two fluid phases of the three-phase-
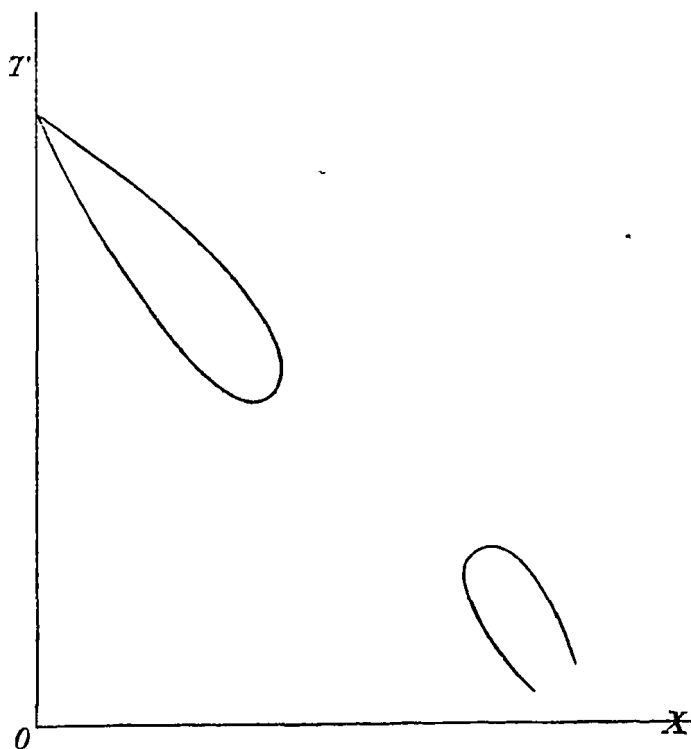
Fig. 6.

pressure as function of T is graphically represented. The highest temperature (the triple point of anthraquinone) applies to $x = 0$. The lowest point of the part of the x, T figure lying on the left is one plaitpoint and the highest point of the part of the x, T figure lying on the right is the second plaitpoint.

If we represented the relation between p and x for the fluid phases of the three-phase-equilibrium, we should also get two separate parts. It is easy to see that for smaller values of x an ascending closed branch is obtained, not unlike the closed p,x curve for a binary mixture at constant temperature — and that for higher values of x, a similar but descending curve is found.

The p, T projection for the three-phase-pressure, so of the curve according to which the two p, x, T surfaces intersect, consists of two separate curves, that for the higher temperatures being a descending curve, terminating in the p and T of the triple point of anthraquinone. The part for the lower temperatures is an ascending curve, beginning in the triple point of ether, if namely, we assume

perfect mixture also for the solid state. The two p, x T surfaces meant in the preceding statement, are that for the coexistence of the two fluid phases with each other and that for the solid state and the fluid phases.

I shall proceed to give a few mathematical observations, which may serve to gain a better understanding of the whole phenomenon, and which are also required for the proof of some properties, which have been given above.

First the assumed deformation in the shape of the p, x curve (solid and fluid phase) for increase of temperature.

From the equation :

$$V_{sf}\, dp = (x_s - x_f)\left(\frac{\partial^2 \zeta}{dx_f^2}\right)_{pT} dx_f + \frac{W_{sf}}{T}\, dT$$

follows that for constant x_f the equation holds:

$$T\left(\frac{dp}{dT}\right)_{xf} = \frac{W_{sf}}{V_{sf}} = \frac{\dfrac{\partial^2 \psi}{\partial V_f^2}\, W_{sf}}{\dfrac{\partial^2 \psi}{\partial V_f^2}\, V_{sf}}.$$

W_{sf} being negative, the numerator of this expression is negative outside the curve for which $\frac{\partial^2 \psi}{\partial v^2} = 0$, and positive inside this curve.

The numerator is the same quantity as has been discussed before (p. 235). From this follows that for constant x_f the curve p,T has a tangent normal to the T-axis in two points, and between them two points, in which a maximum and a minimum value of p occurs — just as was the case with the p, x curve at constant temperature. One curve might be substituted for the other, but still, there is a difference. The p, x curve has its maximum and minimum coinciding in the plaitpoint. The p, T curve has it, when it runs through the point for which $\frac{\partial^2 \psi}{\partial v^2}$ has two coinciding values equal to zero; so in the point which would be the critical point, when the binary mixture behaved as a simple substance. [1]) The consequence of this is, that if we trace the two p,T curves, (that for liquid and vapour and that for solid and fluid), these two curves intersect in the plaitpoint for the value of x of a plaitpoint, and that they do not touch as is the case with the p,x curves. Only for another value of x (the maximum

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[1]) It has appeared to me that the course of the p,T curve requires further elucidation. I intend therefore to soon add some remarks on this subject to this communication.

and minimum discussed above) the two p, T curves touch. This point of contact yields of course an element for the three-phase-pressure.

The differential equation for the section of the two p, T, x surfaces, is found from the two relations which hold both at the same time:

$$v_{21} \, dp = (x_2 - x_1) \left(\frac{\partial^2 \zeta}{\partial x_1^2} \right) dx_1 + \frac{w_{21}}{T} \, dT$$

and

$$v_{s1} \, dp = (x_s - x_1) \left(\frac{\partial^2 \zeta}{\partial x_1^2} \right) dx_1 + \frac{w_{s1}}{T} \, dT.$$

We find then:

$$\frac{dp}{(x_s - x_1) w_{21} - (x_2 - x_1) w_{s1}} = \frac{\left(\frac{\partial^2 \zeta}{\partial x_1^2} \right)_{pT} dx_1}{v_{s1} w_{21} - v_{21} w_{s1}} = \frac{\frac{dT}{T}}{(x_s - x_1) v_{21} - (x_2 - x_1) v_{s1}}$$

We shall shortly mention some obvious consequences. (1) If $\left(\frac{\partial^2 \zeta}{\partial x_1^2} \right)_{pT} = 0$, the p, x and the T, x figure show a minimum or a maximum. So they exist for a plaitpoint. (2). For a maximum or minimum of x, $\frac{w_{21}}{v_{21}}$ must be $\frac{w_{s1}}{v_{21}}$.

Now :

$$w_{21} = p v_{21} + \varepsilon_2 - \varepsilon_1 - (x_2 - x_1) \left(\frac{\partial \varepsilon_1}{\partial x_1} \right)_{pT}$$

and :

$$w_{s1} = p v_{s1} + \varepsilon_s - \varepsilon_1 - (x_s - x_1) \left(\frac{\partial \varepsilon_1}{\partial x_1} \right)$$

(See Cont. II p. 110). From this we derive :

$$\frac{\frac{\varepsilon_2 - \varepsilon_1}{x_2 - x_1} - \left(\frac{\partial \varepsilon_1}{\partial x_1} \right)_{pT}}{\frac{v_2 - v_1}{x_2 - x_1} - \left(\frac{\partial v}{\partial x_1} \right)_{pT}} = \frac{\frac{\varepsilon_s - \varepsilon_1}{x_s - x_1} - \left(\frac{\partial \varepsilon_1}{\partial x_1} \right)_{pT}}{\frac{v_s - v_1}{x_s - x_1} - \left(\frac{\partial x}{\partial x_1} \right)_{pT}} = \frac{\frac{\varepsilon_2 - \varepsilon_1}{x_2 - x_1} - \frac{\varepsilon_s - \varepsilon_1}{x_s - x_1}}{\frac{v_2 - v_1}{x_2 - x_1} - \frac{v_s - v_1}{x_s - x_1}}$$

This leads to $\left(\frac{dp_{21}}{dT} \right)_x = \left(\frac{dp_{s1}}{dT} \right)_x = \frac{dp_{12s}}{dT}$; or in words, the direction of the $(p, T)_x$ curve for liquid and vapour, and that of the $(p, T)_x$ curve for solid and fluid state are the same in the point of maximum and minimum value of x and the same as that of the p, T curve for the three-phase-pressure. The p, T curve of the three-phase-pressure descending with the temperature in the case of minimum x and vice versa, we conclude concerning the point of contact that in the first case it lies between critical point of contact and maximum pressure of the liquid vapour curve, in the second case on the vapour branch of the curve.

If we suppose that the two critical phases with which the solid body can coexist, and which differ considerably in concentration for anthraquinone and ether, approach each other, the two separate parts of the T, x figure and also that of the p, x figure and that of the p, T figure will approach each other. At the point of contact the two parts of the T, x figure, and that of the p, x figure will intersect at an acute angle. If we continue this modification further, the two upper branches of these figures have joined, forming one continuous curve; in the same way the two lower branches. Then the p, T curve shows a maximum. The existence of this maximum three-phase-pressure has already been demonstrated and discussed by me on the occasion of former investigations by prof. BAKHUIS ROOZEBOOM [1]. We find again the result obtained before, now under the following form:

$$\frac{p(v_2-v_1)+\varepsilon_2-\varepsilon_1}{x_2-x_1} = \frac{p(v_s-v_1)+\varepsilon_s-\varepsilon_1}{x_s-x_1} = \frac{p(v_s-v_2)+\varepsilon_s-\varepsilon_2}{x_s-x_2};$$

which means, that if we write for that special point of the three-phase-pressure :

$$T\frac{dp}{dT}=\frac{\Delta w}{\Delta v},$$

the value of Δw would be 0.

If we now examine the course of the x, T curve for the three-phase-pressure more closely, making use of the formula on p. 241, or what comes to the same thing according to the formula of Verslag 1897, Deel 5, p. 491, it appears, that other complications may occur; and that it is not perfectly accurate to say that the p, T curve on the side of the anthraquinone is an ascending curve, till the triple point of this substance has been reached. Then we can also account for the asymmetric behaviour of the p, T curve. It ascends from the triple point of ether and descends on the other side.

In this consideration we shall denote by x_d, x_l and x_s the concentration of the vapour, of the liquid and of the solid body. In the same way we shall use ε_d, ε_l and ε_s ; then we get for a very small quantity of the admixture :

$$T\frac{dp}{dT}=\frac{\begin{vmatrix}1 & x_d & \varepsilon_d + pv_d \\ 1 & x_l & \varepsilon_l + pv_l \\ 1 & x_s & \varepsilon_s + pv_s\end{vmatrix}}{\begin{vmatrix}1 & x_d & v_d \\ 1 & x_l & v_l \\ 1 & x_s & v_s\end{vmatrix}} = \frac{\lambda(x_d-x_s)-(x_l-x_s)(r+\lambda)}{(x_d-x_s)(v_l-v_s)-(x_l-x_s)(v_d-v_s)} \text{ [2]}$$

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[1] Verslag Kon. Akad. Amsterdam, 1885, 3e reeks, Deel I, pag. 380.

[2] The more accurate value of the numerator of the last fraction is :

$$(x_d-x_l)\{\lambda_A(1-x_s)+\lambda_B x_s\}-(x_l-x_s)\{r_A(1-x_d)+r_B x_d\}$$

In this we have, however, disregarded the heat of rarefaction.

We denote then the latent heat of liquefaction by λ and the heat of evaporation by r.

Let the principal component be anthraquinone at its triple point. If we add a very small quantity of ether, x_s and x_l and x_d will be small but $x_d > x_l > x_s$. We may even assume by approximation for this case, that no ether passes into the solid phase; hardly any will be found in the liquid, but most of it in the vapour. So $x_s = 0$ and $\dfrac{x_d}{x_l}$ is very great. For the limiting case which may be supposed, in which x_l would be zero, we have:

$$T \frac{dp}{dT} = \frac{\lambda}{v_l - v_s}$$

The initial direction of the p,T curve is that of the melting curve, and when $v_l > v_s$, this curve begins as an ascending curve with increasing temperature. But as soon as after further addition of ether the value of $\dfrac{v_l - x_s}{x_d - x_s}$ has become equal to $\dfrac{v_l - v_s}{v_d - v_s}$, in which still a very small value of x_l is supposed, the numerator of the expression for $T\dfrac{dp}{dT}$ is infinitely large and on further addition the sign of the numerator is reversed and the p,T curve is no longer ascending, but descending with increase of T.

Now let ether be the principal component. In this case we have to distinguish two different cases. 1st. Ether and anthraquinone are in solid state miscible in all proportions; then the solid substance which we must think present, is *solid ether* and we start from the triple point of ether. 2nd. For all equilibriums anthraquinone remains unmixed with ether. Then the temperature must be thought slightly above the triple point of ether.

In the first case, if at the triple point of ether a little of the so much less volatile substance, anthraquinone is added, it is to be expected neither in the vapour, nor in the solid body, but only in the liquid; then we find:

$$T \frac{dp}{dT} = \frac{r + \lambda}{v_d - v_s}.$$

So an increase of p with T, as occurs in the case of equilibrium between vapour and solid, in concordance with the rule, that if two phases of a mixture in which more phases are present, are of the same concentration, the equilibrium conforms to these two phases.

In the second case, in which we think ether present in liquid and vapour state at slightly higher temperature than that of the

triple point, added anthraquinone in solid condition will not pass into the vapour state. Then $x_s = 1$ and $x_d = 0$. We get:

$$T \frac{dp}{dT} = \frac{r - x_l \,(r + \lambda)}{v_d - v_l - x_l(v_d - v_s)}$$

The quantity λ is now the latent heat of liquefaction of anthraquinone.

For vanishing value of x_l we find increase of p with T, as is found in case of equilibrium between liquid and vapour. In neither of these cases the numerator can become equal to zero when a small quantity of the second substance is added to the principal substance.

But I shall not enter into more particulars, nor discuss the treatment of special circumstances. If they are brought to light by the experiment, they can necessarily be derived from the above formulae. Nor shall I discuss the v, x, T curves, which would lead to greater digressions. For this discussion we should have to make use of two equations, of which that for the coexistence of liquid and vapour occurs in Cont. II, p. 104. For the v,x projection of the three-phase-equilibrium we get for anthraquinone and ether two separate branches, lying outside the limits of the maximum and the minimum value of x mentioned above. When these two values of x coincide, these branches meet, intersecting at an acute angle; at further modification the two v,x curves, viz. those for liquid and vapour, will yield a highest and a lowest value for the volume; at any case the v,x curve for the vapour phase. As appeared in an oral communication, Dr. SMITS had already arrived at this result.

I shall conclude with pointing out, that cases of *retrograde solidification* must repeatedly occur, both when the temperature is kept constant with change of pressure and when the pressure is kept constant with change of temperature.

Chemistry. — *"The possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances."* By J. J. VAN LAAR. (2nd communication). (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. My investigations concerning the possible forms of the melting-point-curve for binary mixtures of isomorphous substances, communicated in the Proceedings of the meeting of the 27th of June 1903, have, apart from the different theoretical considerations, led to the following practical 'results.