Physics. — *"Plaitpoints and corresponding plaits in the neighbourhood of the sides of the ψ-surface of* VAN DER WAALS." By Prof. D. J. KORTEWEG.

(Communicated in the Meeting of December 27, 1902).

FIRST DESCRIPTIVE PART.

1. As in my *"Théorie générale des plis"* [1]) I wish to precede in this paper the demonstrating part by a short summary of the obtained results.

As we know a plaitpoint may occur on the side $x=0$ of the ψ-surface of VAN DER WAALS, [2]) which is represented by the equation:

$$\psi = -MRT \log(v-b_x) - \frac{a_x}{v} + MRT\{x \log x + (1-x) \log(1-x)\} \quad . (1)$$

where:

$$a_x = a_1(1-x)^2 + 2\,{}_1a_2\,x(1-x) + a_2\,x^2 = a_1 + 2({}_1a_2 - a_1)x + (a_1 + a_2 - 2\,{}_1a_2)x^2, \;.\;.\; (2)$$

$$b_x = b_1(1-x)^2 + 2\,{}_1b_2\,x(1-x) + b_2\,x^2 = b_1 + 2({}_1b_2 - b_1)x + (b_1 + b_2 - 2\,{}_1b_2)x^2, \;.\;.\; (3)$$

This occurs only in the case that the temperature T corresponds with the critical T_k of the principal component; but in that case it occurs always. This plaitpoint coincides with the critical point of the principal component for which $v = 3\,b_1$ and which in our figures we shall always represent by the symbol K; the plaitpoint itself will be represented by P.

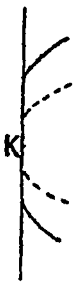
If the temperature varies, the plaitpoint and the corresponding plait can in general behave in two quite different ways. It will namely either, as is indicated by the *first* four cases on fig. I of the plate, on which the (v, x) projections of the sides of the ψ-surface are represented, at increase of temperature leave the v-axis and move to the inner side, therefore entering the surface, and disappear from the surface at decrease of temperature, or it will as in the *last* four cases of that figure, enter the surface at decrease and leave it at increase of temperature.

1) Archives Neérlandaises, T. 24 (1891) p. 295—368: La théorie générale des plis et la surface ψ de VAN DER WAALS dans le cas de symétrie. See there p. 320—368.

2) We take here the equation of the ψ-surface as it has been originally derived by VAN DER WAALS, so without the empiric corrections which seem to be required to make the results agree quantitatively better with the experimental data. So is, for instance, a_x considered to be independent of the temperature, and all the results and formulae mentioned are founded on this supposition. It would not have been difficult to take such empiric corrections into account, as has really been done by VERSCHAFFELT and KEESOM in their papers, to which we shall presently refer; but then the results were of course not so easily surveyed. Therefore I have preferred to leave them out of account, at least for the present.

And this different behaviour of the plaitpoint will necessarily be accompanied by a different behaviour of the connodal and spinodal curves. For they must always cut the v-axis at decrease of temperature, the connodal in the points of contact of the double tangent of the ψ,v-curve of the principal component, the spinodal in its two points of inflection; at increase of temperature above the critical temperature of the principal component, however, they get quite detached from the v-axis. In connection with this they turn in the first four cases of fig. 1 their convex sides, in the last four cases their concave sides towards the side $x=0$ of the ψ-surface as is also indicated in the figure, where the connodal curves are traced, the spinodal curves dotted.

Fig. *a*.



At *decrease* of temperature a figure originates in the *first* four cases as is schematically given here in Fig. *a*. At *increase* of temperature, on the contrary, in the *last* four cases, the spinodal and connodal curves disappear from the surface at the same time with the plaitpoint itself.

Besides to this different behaviour it appeared however desirable, to pay attention to two other circumstances. *First* to the direction of the tangent in the plaitpoint, whether if prolonged towards the side of the large volumes, it inclines to the *inner* side of the ψ-surface, as in cases 1, 2, 5 and 6 of fig. 1, or whether it inclines to the *outer* side, as in the remaining four cases. For on this it will depend which of the two kinds of retrograde condensation will eventually appear [1]). But besides we have to pay attention to the question whether the plaitpoint, entering the ψ-surface, either at decrease or increase of temperature, will move towards the side of the larger volumes as in cases 1, 3, 5 and 7, or whether it will move towards that of the smaller volumes as in the other cases. In connection with this question we may point out here that the line KP in fig 1 of the plate may everywhere be considered as a small chord of the plaitpoint curve of the v,x-diagram and accordingly indicates the initial direction of that curve, which it has when starting from point K.

The three different alternatives, which we have distinguished in this way, give rise to the eight cases represented in fig. 1, and we may now raise the question on what it will depend which of these eight cases will occur at a given principal component with a given

[1]) See on these two kinds of retrograde condensation inter alia, the paper of VAN DER WAALS: "Statique des fluides (Mélanges)": in Tome I of the "Rapports présentés au congrès international de physique, réuni à Paris en 1900", page 606—609.

admixture; of course only in so far as with sufficient approximation the conditions are satisfied on which the derivation of the equation (1) of VAN DER WAALS rests.

2. The answer to this question is given in the graphical representation of fig. 2. It appears, namely, that the case which will occur, is exclusively determined by the quantities $\frac{{}_1a_2}{a_1} = \varkappa$ and $\frac{{}_1b_2}{b_1} = \gamma$, which have already played a prominent part in my above mentioned "*Théorie générale des plis.*"

In accordance with this a $\varkappa$- and a γ-axis are assumed in fig. 2 of the plate and the regions where the points are situated whose $\varkappa$- and γ-values give rise to the appearance of each of these cases, are distinguished by different numbers and colours.

For instance the white region 1 indicates the $\varkappa$- and γ-values for which the plaitpoint enters the ψ-surface at rising temperature, moving from K to the side of the large volumes, while in the well-known way we can derive from its situation on the connodal curve on the right above the critical point of contact R (for which the tangent to the connodal curve runs parallel with the v-axis) that the retrograde condensation will be eventually of the second kind (i. e. with temporary formation of vapour) and also that the temporary vapour phase will have a larger amount of admixture than the permanent denser phase.

In the same way the blue field 5 indicates the $\varkappa$- and the γ-values for which the plaitpoint enters the ψ-surface at decrease of temperature, moving towards the side of the large volumes; whilst the retrograde condensation will be of the first kind and the temporary denser phase will show a smaller proportion of admixture than the permanent vapour phase.

3. When examining this graphical representation we see at once that one of the eight regions which were à priori to be expected, region 8, fails. From this follows that for normal substances the combination of retrograde condensation of the second kind and of a plaitpoint which enters the surface at decreasing temperature and moves towards the side of the small volumes, is not to be expected.

All the other seven regions, however, are represented in the graphical representation.

4. Further the point $\varkappa = 1, \gamma = 1$, is remarkable, where no less than six regions meet. This point represents really a very particular

case, namely that in which the molecules of the admixture, both with regard to volume and to attraction, behave towards the molecules of the principal component exactly as if they were identical with these latter molecules.

If at the same time $a_2 = a_1$, $b_2 = b_1$, which is of course not involved in the above suppositions, it is easy to see that at decrease of temperature below the critical temperature the plait would suddenly appear all over the whole breadth of the ψ-surface.

Now it is true that every deviation from these equalities $a_2 = a_1$, $b_2 = b_1$ will prevent such a way of appearance, but it is evident that then the behaviour of plaitpoint and corresponding plait will depend on a_2 and b_2, i.e. the first approximation for which the knowledge of $\varkappa$ and γ is sufficient and which everywhere else suffices to make this behaviour known to us up to a certain distance from the side of the ψ-surface, fails here.

And also already in the *neighbourhood* of the combination of the values $\varkappa = 1, \gamma = 1$, this first approximation will be restricted, to the immediate neighbourhood of the point K and of the critical temperature T_k of the principal component. When we are not in that immediate neighbourhood the influence of a_2 and b_2, — of the former of these quantities specially, — will soon be felt. On the contrary for values of $\varkappa$ or γ sufficiently differing from unity the considerations derived from the first approximation will probably be of force within pretty wide limits, at least in a qualitative sense.

5. Before proceeding to a discussion of the border curves between the different regions, we will shortly point out that we cannot attach an equally great importance to all the parts of the graphical representation. So all points lying left of the γ-axis relate to negative values of ${}_1a_2$, i.e. to the case that the molecules of principal component and admixture should repel each other, which is not likely to occur.

In the same way the negative values of γ, so of ${}_1b_2$, of the points below the $\varkappa$-axis, should be considered as having exclusively mathematical signification. If the relation, ${}_1b_2 = \frac{1}{2}(b_1 + b_2)$, should still be applied also for very unequal values of the b's, then γ would even remain always larger than $\frac{1}{2}$ and so the part below the line $\gamma = \frac{1}{2}$ would lose its physical signification.

6. With regard to the border curves between the different parts, we have first to deal with the parabolic border curve separating the

regions containing blue (blue, green, purple) from the others. It touches the γ-axis in the point $x = 0$, $\gamma = \frac{1}{2}$. Its equation is:

$$(2\gamma - 3x + 1)^2 - 8(\gamma - x) = 0$$

or if we transfer the origin to the point $\gamma = 1$, $x = 1$ and therefore introduce the new variables: $x' = x - 1$; $\gamma' = \gamma - 1$, which brings about a simplification also for the other border curves, we get:

$$(2\gamma' - 3x')^2 - 8(\gamma' - x') = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Then we have everywhere inside that parabola, so in the regions 5, 6, 7:

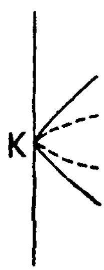
$$(2\gamma' - 3x')^2 - 8(\gamma' - x') < 0$$

and outside it in the regions 1, 2, 3, 4:

$$(2\gamma' - 4x')^2 - 8(\gamma' - x') > 0.$$

In consequence of this it depends on the situation inside or outside the parabola, whether on the corresponding ψ-surface the plaitpoint will enter the surface at *decrease* of temperature or at *increase* of temperature and whether the spinodal curves turn their convex or their concave sides to the side $x = 0$.

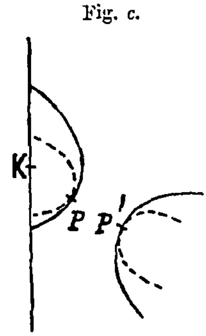
Fig. b.



For points *on* the parabolic border curve the plaitpoint occurring in the point K at the critical temperature of the principal component, is to be considered as an homogeneous double plaitpoint at that moment. The projection on the v, x-surface appears then as is indicated in fig. b.

How the transition to this condition takes place may be made clear by the subjoined fig. c, which represents the same projection for a temperature slightly below that of the critical temperature of the principal component for the case that the x- and γ-values indicate a point, which is still situated in the green region 6, but on the verge of the border curve of the yellow region 2.

Fig. c.



Very near the plaitpoint P we find here already a second plaitpoint P', which at further decrease of temperature soon coincides with P.

If now the point in the green region approaches the border curve of the yellow region, the two points P coincide nearer and nearer to the critical temperature of the principal component and to the point K. *On* the border curve it takes place in the point K itself. *Beyond* the limit, in the yellow region, the plait of P does not develop any more and P' takes the place of P.

7. As second border we get in the graphical representation the straight line:

$$2\gamma'-3\varkappa'=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It separates the regions containing red 3, 4 and 7, — for which $2\gamma'-3\varkappa'<0$, and where the tangent in the plaitpoint, continued in the direction of the large volumes, inclines towards the side $x=0$ — from the others, where it inclines to the inner side of the ψ-surface.

As we saw before, this inclination determines the nature of the retrograde condensation. Not exclusively, however. For in the first four cases of figure 2 the result of the same way of inclination is in this regard exactly the opposite of that in the last four cases; hence the parabolic border curve acts here also as a separating curve; so that retrograde condensation of the first kind (i.e. with temporary formation of the denser phase) occurs in the regions 3, 4, 5 and 6, in the two first with greater proportion of the admixture in the temporary phase, in the two last the reverse, and on the contrary retrograde condensation of the second kind in the regions 1 and 2 (with a larger proportion in the temporary less dense phase) and 7 (with a smaller proportion in that same phase).

8. The third border curve is a cubic curve with the equation:

$$(2\gamma'-3\varkappa')^3-4(4\gamma'-3\varkappa')(2\gamma'-3\varkappa')+16\gamma'=0. \quad . \quad . \quad (6)$$

It consists of two branches, which possess both on one side the common asymptote:

$$2\gamma'-3\varkappa'-2=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and which run at the other side parabolically to infinity.

The right-side branch, whose shape resembles more or less a parabola, touches the curve $\gamma'=0$ in the point $\varkappa'=0, \gamma'=0$ ($\varkappa=1, \gamma=1$).

Between the two branches, so in the regions 2, 4 and 6:

$$(2\gamma'-3\varkappa')^3-4(4\gamma'-3\varkappa')(2\gamma'-3\varkappa')+16\gamma'<0;$$

in all the other regions of course >0.

In the former case the tangent KP to the plaitpoint-curve of the (v, x)-diagram is directed to the side of the small volumes, in the second to that of the large volumes.

If we, however, examine, whether e.g. at *decrease* of temperature the plaitpoint moves towards the large or towards the small volumes, the parabolic border curve acts again as separating curve.

It appears then that the plaitpoint moves towards the large volumes at decrease of temperature in the regions 2, 4, 5 and 7, at increase of temperature in the others.

9. The following table gives the characteristics for the different regions.

Region			
1	$(2\gamma'-3\varkappa')^2-8(\gamma'-\varkappa')>0$;	$2\gamma'-3\varkappa'>0$;	$(2\gamma'-3\varkappa')^3-4(4\gamma'-3\varkappa')(2\gamma'-3\varkappa')+16\gamma'>0$
2	„ >0;	„ >0;	„ <0
3	„ >0;	„ <0;	„ >0
4	„ >0;	„ <0;	„ <0
5	„ <0;	„ >0;	„ >0
6	„ <0;	„ <0;	„ <0
7	„ <0;	„ <0;	„ >0

where:

$$\varkappa' = \varkappa - 1 = \frac{{}_1a_2 - a_1}{a_1};\ \gamma' = \gamma - 1 = \frac{{}_1b_2 - b_1}{b_1}. \quad . \quad . \quad . \quad (8)$$

A similar tabular survey of the physical properties of the regions seems superfluous, as these properties may be immediately read from the illustrations of fig. 1 of the unfolding plate.

10. It seems not devoid of interest to know how the breadths of the regions change with regard to each other, when continually increasing values of γ' are considered. An inquiry into this shows at once that the blue region 5, measured along a line parallel to the $\varkappa$-axis, has a limiting value for the breadth of $\frac{2}{3}$. All the other regions mentioned, however, continue to increase indefinitely, and do this proportional with $\sqrt{\gamma'}$ and in such a way that the yellow and the red region get gradually the same breadth and in the same way the green and the purple one, but that the breadth of the two first mentioned regions will amount to 0,732 of that of the two last mentioned.

If we also take the white region (reckoned e. g. from the γ-axis) into consideration then we find its breadth at first approximation to be proportional with γ', so that it exceeds in the long run the other mentioned; the orange region keeps of course an infinite breadth.

The limiting values of the ratios may therefore be represented as follows:

$$\frac{white}{\infty} = \frac{yellow}{0{,}732} = \frac{green}{1} = \frac{blue}{0} = \frac{purple}{1} = \frac{red}{0{,}732} = \frac{orange}{\infty} \quad . \quad . \quad . \quad (9)$$

We may see that if we keep $\varkappa$ constant and make γ to increase we always reach the white region, while reversively increase of $\varkappa$ with constant γ leads finally to the orange region. Strong attraction between the molecules of the admixture and those of the principal component promotes therefore in the long run the relations of case 4, large volume of the molecules of the admixture promotes those of case 1.

11. We may conclude this descriptive part with mentioning some formulae which we have obtained in the course of our investigation, and which will be derived in the second part. We do not, however, give them as new, as they must essentially agree with similar equations obtained by KEESOM[1]) and VERSCHAFFELT[2]), if the simplifying hypotheses are introduced on which the original equation of the ψ-surface, used by us, rests. Nor does the way in which they are derived, in which the method of the systematic development into series is followed, differ considerably from that of VERSCHAFFELT.

In these formulae we have restricted the number of notations as much as possible. They only hold at approximation in the neighbourhood of point K and of the critical temperature T_k of the principal component.

We shall first give expressions for the radii of curvature $R'_{sp.}$ and $R'_{conn.}$ of the projections on the (v,x)-surface of the spinodal and connodal curves in the plaitpoint; from which appears that the radius of curvature of the connodal curve in the neighbourhood of the point K is at first approximation three times as great as that of the spinodal.

$$R'_{sp.} = \frac{3}{2}\, b_1{}^2\, [(2\gamma' - 3\varkappa')^2 - 8(\gamma' - \varkappa')] \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$R'_{conn.} = \frac{9}{2}\, b_1{}^2\, [(2\gamma' - 3\varkappa')^2 - 8(\gamma' - \varkappa')] = 3R'_{sp.} \quad . \quad . \quad (11)$$

These radii of curvature are here considered as being positive when both curves turn their convex sides to the v-axis as in the cases 1—4 of fig. 1 and negative in the cases 5—7.

We may shortly point out here that the corresponding radii of curvature on the ψ-surface itself, on account of the strong inclination of the tangential plane in the neighbourhood of the v-axis, are quite different and much smaller, though the relation 1 : 3, of course

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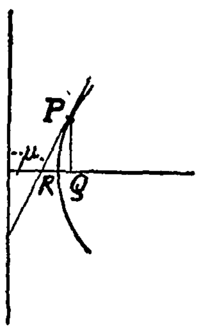
1) W. H. KEESOM. "Contributions to the knowledge of VAN DER WAALS's ψ-surface. V. The dependence of the plaitpoint constants on the composition in binary mixtures with small proportions of one of the components". Proc. Royal Acad. IV. p. 293—307. Leiden, Comm. phys. Lab. N⁰. 75.

2) J. E. VERSCHAFFELT. "Contributions to the knowledge of VAN DER WAALS, ψ-surface. VII. The equation of state and the ψ-surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components". Proc. Royal Acad. V, p. 321—350, Leiden, Comm. Phys. Lab. N⁰. 81.

continues to exist. They even become *zero* when the plaitpoint coincides with the critical point K, so that both curves have then a cusp.

12. The knowledge of the radius of curvature $R_{conn.}$ is of importance specially because it may be used in connection with the formula:

Fig. *d.*



$$tg\,\mu = \mu = \frac{1}{4b_1}(2\gamma'-3\varkappa')x_P, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

through which we know the small angle which the tangent of the plaitpoint forms with the v-axis, to calculate in a very simple way the differences in density and volume between the phases of the plaitpoint P and the critical point of contact R at first approximation [1]).

According to fig. *d* we have, within the indicated limit of accuracy:

$$v_P - v_R = PQ = PR = \mu R'_{conn.} = \frac{9b_1}{8}(2\gamma'-3\varkappa')\,[(2\gamma'-3\varkappa')^2 - 8(\gamma'-\varkappa')]\,x_P \, .. \; (13)$$

$$x_P - x_R = RQ = \frac{1}{2}\mu^2 R'_{conn.} = \frac{9}{64}(2\gamma'-3\varkappa')^2[(2\gamma'-3\varkappa')^2 - 8(\gamma'-\varkappa')]\,x^2_P \, . \; (14)$$

13. We proceed now to give the formulae relating to the plaitpoints phase at a temperature T, which does not differ much from the critical temperature T_k of the principal component.

They are:

$$x_P = \frac{4}{(2\gamma'-3\varkappa')^2 - 8(\gamma'-\varkappa')} \cdot \frac{T-T_k}{T_k} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$v_P - 3b_1 = \frac{3}{8}b_1\,\{(2\gamma'-3\varkappa')^3 - 4(4\gamma'-3\varkappa')(2\gamma'-3\varkappa') + 16\gamma'\}\,x_P \; . \; (16)$$

$$\frac{p_P - p_k}{p_k} = \{(2\gamma'-3\varkappa')^2 - 4\gamma' + 2\varkappa'\}\,x_P \quad . \quad . \quad . \quad . \quad (17)$$

By means of (15) we may transform (13) and (14), so that they become:

$$v_P - v_R = \frac{9b_1}{2}(2\gamma'-3\varkappa')\frac{T-T_k}{T_k} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and

$$x_P - x_R = \frac{9}{16}(2\gamma'-3\varkappa')^2 x_P \frac{T-T_k}{T_k} \quad . \quad . \quad . \quad . \quad (19)$$

[1]) A similar method is given by KEESOM at the conclusion of the before-mentioned paper of VERSCHAFFELT.

to which we add:

$$\frac{p_P - p_R}{p_k} = -\frac{1}{4b_1}(2\gamma'-3\varkappa')^2(v_P - v_R)\,x_P = -\frac{9}{8}(2\gamma'-3\varkappa')^3\frac{T-T_k}{T_k}\,x_P \quad (20)$$

14. We shall conclude with giving some formulae relating to coexisting phases, where the index *one* refers to the liquid-, the index *two* to the gas phase. Where the index fails, we may arbitrarily take the value for the one or for the other coexisting phase; either because it is indifferent at the degree of approximation used, or because the formula will equally hold for either state.

$$v_1 = 3b_1 - 3b_1\sqrt{-4\frac{T-T_k}{T_k} + [(2\gamma'-3\varkappa')^2 - 8(\gamma'-\varkappa')]x} \quad . \quad (21)$$

$$v_2 = 3b_1 + 3b_1\sqrt{-4\frac{T-T_k}{T_k} + [(2\gamma'-3\varkappa')^2 - 8(\gamma'-\varkappa')]x} \quad . \quad (22)$$

$$\frac{p-p_k}{p_k} = 4\frac{T-T_k}{T_k} + 2\,(2\gamma'-3\varkappa')\,x \quad . \; . \; . \; . \quad (23)$$

$$x_2 - x_1 = \frac{1}{4b_1}(2\gamma'-3\varkappa')(v_2 - v_1)\,x \quad . \; . \; . \; . \; . \; . \; . \quad (24)$$

$$\frac{1}{2}(v_2+v_1) - 3b_1 = -\frac{54}{5}b_1\frac{T-T_k}{T_k} + 3b_1\left\{\frac{7}{5}[2\gamma'-3\varkappa')^2 - 8(\gamma'-\varkappa')] +\right.$$

$$\left. + \frac{1}{8}[(2\gamma'-3\varkappa')^3 - 24\,(\gamma'-\varkappa')(2\gamma'-3\varkappa') + 16\,(3\gamma'-2\varkappa')]\right\}x \quad . \; . \; . \quad (25)$$

in which formula (23) holds also for non-coexisting phases.

SECOND DEMONSTRATING PART.

Transformation of the ψ-surface and preliminary development into series.

15. We begin with a transformation of the ψ-surface by introducing the following variables:

$$v' = \frac{v-3b_1}{3b_1}; \quad t' = \frac{T-T_k}{T_k}; \quad \psi' = \frac{\psi}{MRT_k}; \quad . \; . \; . \quad (26)$$

which means that we henceforth measure the volume v' from the critical volume and with that volume as unit, the temperature in the same way with regard to the critical temperature $T_k = \dfrac{8a_1}{27b_1MR}$ and the free energy ψ' with MRT_k as unit.

If we moreover put:

$$\frac{{}_1a_2-a_1}{a_1}=\varkappa' ; \quad \frac{{}_1b_2-b_1}{b_1}=\gamma' ; \quad \frac{a_2-a_1}{a_1}=\lambda' ; \quad \frac{b_2-b_1}{b_1}=\delta' ; \quad . \quad (27)$$

we find easily from (1), (2) and (3) for the equation of the new surface: [1]):

$$\psi' = -(1+t') \log 3b_1 (b_x'+v') - \frac{a_x'}{1+v'} + (1+t')\{x \log x + (1-x) \log (1-x)\}, \quad (28)$$

where

$$a_x' = \frac{9}{8} + \frac{9}{4}\varkappa' x - \frac{9}{8}(2\varkappa'-\lambda') x^2 \quad . \quad . \quad . \quad . \quad . \quad (29)$$

$$b_x' = \frac{2}{3} - \frac{2}{3}\gamma' x + \frac{1}{3}(2\gamma'-\delta') x^2 , \quad . \quad . \quad . \quad . \quad . \quad (30)$$

further:

$$p = -\frac{\partial \psi}{\partial v} = -\frac{MRT_k}{3b_1} \cdot \frac{\partial \psi'}{\partial v'} = -\frac{8}{3} p_k \frac{\partial \psi'}{\partial v'} \quad . \quad . \quad . \quad . \quad (31)$$

16. For investigations in the neighbourhood of the sides it is desirable to develop the expression for ψ' so far as possible according to the powers of x. We write therefore:

$$\psi' = (1+t')\, x \log x + \chi_0 + \chi_1 x + \chi_2 x^2 + \ldots \quad . \quad . \quad (32)$$

where in finite form [2])

$$\chi_0 = -(1+t') \log b_1 (2+3v') - \frac{9}{8(1+v')} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

$$\chi_1 = (1+t')\left(\frac{2\gamma'}{2+3v'}-1\right) - \frac{9\varkappa'}{4(1+v')} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

$$\chi_2 = (1+t')\left[\frac{2\gamma'^2}{(2+3v')^2} - \frac{2\gamma'-\delta'}{2+3v'} + \frac{1}{2}\right] + \frac{9(2\varkappa'-\lambda')}{8(1+v')} \quad . \quad . \quad . \quad (35)$$

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[1]) If we wanted to consider a_x as function of the temperature, the simplest way of doing this would be by writing the second term of the second member: $\frac{a'_x(1+\varepsilon_1 t' + \varepsilon_2 t'^2 + \ldots)}{1+v'}$. The formula $T_k = \frac{8\,a_1}{27\,b_1\,MR}$ would continue to hold unmodified for the critical temperature of the principal component, provided we take for a_1 the value it has at that critical temperature. With CLAUSIUS' hypothesis that a_x is inversely proportionate to T, we should get $\varepsilon_1=-1$; $\varepsilon_2=+1$. Also (29) continues to hold and the modifications in the developments into series and in the formulae derived from them would be easy to apply.

[2]) In this form they may be used for investigations concerning the conditions at the side of the ψ-surface at temperatures greatly differing from the critical temperature of the principal component, as are made by KEESOM: Contributions to the knowledge of the ψ-surface of VAN DER WAALS. VI. The increase of pressure at condensation of a substance with small admixtures. Proc. Royal Acad. IV, p. 659—668; Leiden, Comm. phys. Lab. N⁰. 79.

or, after development into series with respect to the powers of v':

$$\chi_0 = -(1+t')\log 2b_1 - \frac{9}{8} - \left(\frac{3}{8}+\frac{3}{2}t'\right)v' + \frac{9}{8}t'v'^2 - \frac{9}{8}t'v'^3 +$$

$$+ \frac{9}{64}(1+9t')v'^4 - \frac{63}{160}v'^5 + \dots \qquad (36)$$

$$\chi_1 = (1+t')(\gamma'-1) - \frac{9}{4}\varkappa' - \frac{3}{4}\Big[(2\gamma'-3\varkappa')+2\gamma't'\Big]v' +$$

$$+ \frac{9}{4}\Big[(\gamma'-\varkappa')+\gamma't'\Big]v'^2 - \frac{9}{8}(3\gamma'-2\varkappa')v'^3 + \dots \qquad (37)$$

$$\chi_2 = \frac{1}{2}(1+t')[(1-\gamma')^2+\delta'] + \frac{9}{8}(2\varkappa'-\lambda') - \frac{3}{8}(4\gamma'^2-4\gamma'+2\delta'+6\varkappa'-3\lambda')v' + \dots \qquad (38)$$

for which last expression we write:

$$\chi_2 = \sigma_0 + \sigma_1 t' + \sigma_2 v' + \dots \qquad (39)$$

Determination of the plaitpoint and classification of the different possible cases.

17. For calculating the coordinates v'_P and x_P of the plaitpoint we have the following relations: [1])

$$m\frac{\partial^2\psi'}{\partial x^2} + \frac{\partial^2\psi'}{\partial v'\,\partial x} = 0 \qquad (40)$$

$$m\frac{\partial^2\psi'}{\partial v'\,\partial x'} + \frac{\partial^2\psi'}{\partial v'^2} = 0 \qquad (41)$$

$$m^3\frac{\partial^3\psi'}{\partial x^3} + 3m^2\frac{\partial^3\psi'}{\partial v'\,\partial x^2} + 3m\frac{\partial^3\psi'}{\partial v'^2\,\partial x} + \frac{\partial^3\psi'}{\partial v^3} = 0 \qquad (42)$$

where m represents [2]) the tangent of the angle formed by the (v', x)-projection of the common tangent of spinodal and connodal curve in the plaitpoint with the v'-axis.

If by means of (32), (36) and (37) we introduce in these equations everywhere the values of the differential quotients at first approximation, in which, as appears, m, x_P and v'_P may be treated as small quantities of the same order, we find:

$$\frac{m}{x_P} - \frac{3}{4}(2\gamma'-3\varkappa') = 0 \qquad (43)$$

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[1]) D. J. KORTEWEG. Ueber Faltenpunkte. Wiener Sitzungsberichte, Bd. 98, Abt. II, (1889), p. 1171.

[2]) See l. c. p. 1163.

$$-\frac{3}{4}(2\,\gamma'-3\,\varkappa')\,m+\frac{9}{4}t'+\frac{9}{2}(\gamma'-\varkappa')\,x_P=0 \quad . \quad . \quad . \quad (44)$$

$$-\frac{m^3}{x^2_P}+\frac{27}{2}(\gamma'-\varkappa')\,m-\frac{27}{4}t'+\frac{27}{8}v'_P-\frac{27}{4}(3\,\gamma'-2\,\varkappa')\,x_P=0, \quad (45)$$

from which it is easy to deduce:

$$m=\frac{3}{4}(2\,\gamma'-3\,\varkappa')\,x_P\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

$$x_P=\frac{4}{(2\,\gamma'-3\,\varkappa')^2-8(\gamma'-\varkappa')}\,t'\,, \quad . \quad . \quad . \quad . \quad (47)$$

$$v'_P=\frac{1}{8}\,[(2\gamma'-3\varkappa')^3-4(4\gamma'-3\varkappa')\,(2\gamma'-3\varkappa')+16\gamma']x_P\,, \quad . \quad (48)$$

The formulae (12), (15) and (16) of the first descriptive part of this paper may be derived from these formulae by means of the reverse transformation into the original ψ-surface with the aid of the formulae (26). Applying equation (31) we may also derive formula (17). In the course of this we get first at formula (23), which is given at the end of the descriptive part as serving also for the calculation for coexisting phases. The last statement might be objected to, because for those phases not v' but v'^2 is a quantity of the same order as x and t'; but this objection loses its force when we observe that in $\frac{\partial \psi'}{\partial v'}$ no term occurs with v'^2 alone.

18. From these formulae (46), (47) and (48) follows now immediately the classification of the plaitpoints according to the eight cases and all the particularities of the corresponding graphical representation, as described in § 2—9. It is only necessary to say a few words about the construction of the cubic border curve.

$$(2\,\gamma'-3\varkappa')^3-4\,(4\,\gamma'-3\varkappa')\,(2\,\gamma'-3\varkappa')+16\,\gamma'=0\,. \quad . \quad . \quad (49)$$

A closer examination of this equation shows, namely, that the curve possesses a double point, i.e. the point at infinity of the straight line $2\,\gamma'-3\,\varkappa'=0$. A simple parameter representation is therefore possible and it is really obtained by putting

$$2\,\gamma'-3\,\varkappa'=s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

from which follows:

$$s^3-4\,s\,(s+2\gamma')+16\,\gamma'=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

hence:

$$\gamma'=\frac{s^2(s-4)}{8\,(s-2)}\quad ; \quad \varkappa'=\frac{s^3-8\,s^2+8s}{12\,(s-2)} \quad . \quad . \quad . \quad . \quad (52)$$

The points of the left-side branch are then given by the values of s, between $+\infty$ and 2, those of the right-side branch by the others.

For $s=2$ we get the two infinite branches belonging to the asymptote:

$$2\gamma' - 3x' = 2 \quad \ldots \ldots \ldots \quad (53)$$

19. Nor do we meet with any difficulties in the calculation of the breadth-relations of the regions for very large values of γ' mentioned in § 10.

For the cubic curve, we may put:

$$3x' = 2\gamma' + k\sqrt{\gamma'} \quad \ldots \ldots \ldots \quad (54)$$

through which its equation passes into:

$$(-k^3 + 8k)\sqrt{\gamma'} + 16 - 4k^2 = 0 \quad \ldots \ldots \quad (55)$$

from which appears that for very large values of γ' we find $-2\sqrt{2}$, 0 and $+2\sqrt{2}$ for k. We get therefore for the leftside branch of the cubic curve approximately:

$$x' = \frac{2}{3}\gamma' - \frac{2}{3}\sqrt{2}\,.\sqrt{\gamma'} \quad \ldots \ldots \ldots \quad (56)$$

and for that on the right-side:

$$x' = \frac{2}{3}\gamma' + \frac{2}{3}\sqrt{2}\,.\sqrt{\gamma'} \quad \ldots \ldots \ldots \quad (57)$$

while of course the middle branch with asymptote corresponds with $k=0$. For this branch we have:

$$x' = \frac{2}{3}\gamma' - \frac{2}{3} \quad \ldots \ldots \ldots \quad (58)$$

In a similar way we find for the parabolic border curve:

$$x' = \frac{2}{3}\gamma' \pm \frac{2}{9}\sqrt{6}\,.\sqrt{\gamma'} \quad \ldots \ldots \ldots \quad (59)$$

Taking this into consideration we may equate the breadth of the yellow region at infinity to $\frac{2}{9}(3-\sqrt{3})\sqrt{2}\,.\sqrt{\gamma'}$, that of the green one to $\frac{2}{9}\sqrt{6}\,.\sqrt{\gamma'}$, that of the blue one to $\frac{2}{3}$, that of the purple one again to $\frac{2}{9}\sqrt{6}\,.\sqrt{\gamma'}$ and that of the red one to $\frac{2}{9}(3-\sqrt{3})\sqrt{2}\,.\sqrt{\gamma'}$ from which the relations of equation (9) easily follow, while $\sqrt{3}-1 = 0.732$.

The spinodal curve.

20. The equation of the spinodal curve is found by elimination of m from (40) and (41). We must, however, take into account, when writing these two equations, that v' along the spinodal curve must be considered to be of the order $\sqrt{x}$, so that the terms with v'^2 must also be taken into consideration.

We get then:

$$\frac{m}{x_{sp.}} - \frac{3}{4}(2\gamma'-3\varkappa') = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

and

$$-\frac{3}{4}(2\gamma'-3\varkappa')\, m + \frac{9}{4}t' + \frac{27}{16}v'^2_{sp.} + \frac{9}{2}(\gamma'-\varkappa')\, x_{sp.} = 0 \quad . \quad (61)$$

from which follows for the equation of the spinodal curve:

$$v'^2_{sp.} - \frac{1}{3}\left[(2\gamma'-3\varkappa')^2 - 8(\gamma'-\varkappa')\right] x_{sp.} + \frac{4}{3}t' = 0 \quad . \quad . \quad (62)$$

This is, however, its equation on the ψ'-surface. In order to know it on the original ψ-surface, we must transform it with the aid of (26) into

$$(v_{sp.} - 3b_1)^2 - 3b_1^2\left[(2\gamma' - 3\varkappa')^2 - 8(\gamma' - \varkappa')\right] x_{sp.} + 12b_1^2 t' = 0. \quad . \quad (63)$$

For that of the circle:

$$(v-3b_1)^2 + (x-R-\delta)^2 = R^2, \quad (\delta \text{ small})$$

we may write with the same approximation:

$$(v-3b_1)^2 - 2Rx + 2R\delta = 0,$$

from which we may immediately derive the expression (10) for the radius of curvature of the (v, x) projection of the spinodal curve.

The two first connodal relations. Equation of the connodal curve.

21. We shall now take $P_1(x_1, v'_1)$ and $P_2(x_2, v'_2)$, for which $v'_2 > v'_1$, as denoting two corresponding connodes.

We put then:

$$v'_1 = v'' - \eta; \quad v'_2 = v'' + \eta; \quad x_1 = x'' - \xi\eta; \quad x_2 = x'' + \xi\eta; \quad . \quad (64)$$

hence:

$$v'' = \frac{1}{2}(v'_1+v'_2); \quad \eta = \frac{1}{2}(v'_2-v'_1); \quad x'' = \frac{1}{2}(x_1+x_2); \quad \xi = \frac{x_2-x_1}{v'_2-v'_1}; \quad (65)$$

where therefore (x'', v'') indicates a point halfway between the two connodes and ξ denotes the tangent of the angle which the projection on the (v', x)-surface of the join of the connodes forms with the v'-axis.

It is then easy to anticipate, and it is confirmed by the calculations, that all these quantities v'', x'' and ξ with the exception of η, are of the same order with each other and with t'; on the contrary not η but η^2 is of this same order.

22. Taking this into consideration the *first* connodal relation:

$$\frac{\partial \psi'_2}{\partial x_2} = \frac{\partial \psi'_1}{\partial x_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

yields at first approximation:

$$log\,(x''+\xi\eta) - \frac{3}{4}(2\gamma'-3\varkappa')(v''+\eta) = log\,(x''-\xi\eta) - \frac{3}{4}(2\gamma'-3\varkappa')(v''-\eta) \quad . \quad (67)$$

or also, subtracting on either side $log\ x''$:

$$log\left(1+\frac{\xi\eta}{x''}\right) - \frac{3}{2}(2\gamma'-3\varkappa')\,\eta = log\left(1-\frac{\xi\eta}{x''}\right) \quad . \quad . \quad (68)$$

or, as $\frac{\xi\eta}{x''}$ is a small quantity of the order of η, we get after development into series and division by η:

$$\xi = \frac{3}{4}(2\gamma'-3\varkappa')\,x'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (69)$$

in which we shortly point out that this formula passes into formula (46) in the plaitpoint, and further that it leads immediately to formula (24) of the descriptive part.

In the same way the *second* [1]) connodal relation:

$$\frac{\partial \psi'_2}{\partial v_2} = \frac{\partial \psi'_1}{\partial v_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (70)$$

yields at approximation:

$$-\frac{3}{8} - \frac{3}{2}t' + \frac{9}{4}t'(v''+\eta) + \frac{9}{16}(v''+\eta)^3 - \frac{3}{4}(2\gamma'-3\varkappa')(x''+\xi\eta) +$$

$$+\frac{9}{2}(\gamma'-\varkappa')(v''+\eta)\,x'' = -\frac{3}{8} - \frac{3}{2}t' + \frac{9}{4}t'(v''-\eta) + \frac{9}{16}(v''-\eta)^3 -$$

$$-\frac{3}{4}(2\gamma'-3\varkappa')(x''-\xi\eta) + \frac{9}{2}(\gamma'-\varkappa')(v''-\eta'')\,x'', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (71)$$

or, after reduction and division by η:

1) We must here have recourse to the terms of the order $t'^{\frac{3}{2}}$ or η^3, as all those of lower order cancel each other. For the sake of clearness we have kept $(v''+\eta)$ and also $(v''-\eta)$ together, though it is evident, that we may write e.g. for $(v''+\eta)^3$ at once η^3 on account of the difference in order of v'' and η.

$$\frac{9}{2} t' + \frac{9}{8} \eta^2 - \frac{3}{2} (2\gamma'-3\varkappa') \xi + 9 (\gamma'-\varkappa') x''=0, \quad . \quad . \quad (72)$$

from which follows in connection with (69):

$$\eta^2 - [(2\gamma'-3\varkappa')^2 - 8 (\gamma'-\varkappa')] x'' + 4 t' = 0. \quad . \quad . \quad . \quad (73)$$

23. This formula yields at once the radius of curvature of the (v, x)-projection of the connodal curve. We need only observe that according to definition:

$$v'_{conn.} = v'' \pm \eta ; \quad x_{conn.} = x'' \pm \xi\eta ; \quad . \quad . \quad . \quad . \quad (74)$$

so at first approximation:

$$\eta = \pm v'_{conn.} = \pm \frac{v_{conn.} - 3b_1}{3b_1} ; \quad x'' \mp x_{conn.} . \quad . \quad . \quad . \quad (75)$$

Substitution of these last relations in (73) now yields immediately the equation of the connodal curve and in exactly the same way as for the spinodal curve we find from it the value of the radius of curvature R_{conn} given in formula (11). A further explanation of the way in which the knowledge of this value leads to the formulae (13) and and (14) need not be given here, nor need we explain the derivation of the formulae (18) and (19), (21) and (22).

But the derivation of formula (20) will detain us for a moment; we require, namely, for it a more accurate expression for p than that given in formula (23). If we therefore develop (31) as far as needful for the purpose, we find [1]):

$$p = -\frac{8}{3} p_k \left(-\frac{3}{8} - \frac{3}{2} t' + \frac{9}{4} t' v' - \frac{3}{4} (2\gamma'-3\varkappa') x + \frac{9}{2} (\gamma'-\varkappa') v' x \right), (76)$$

or:

$$\frac{p - p_k}{p_k} = 4 t' - 6 t' v' + 2 (2\gamma'-3\varkappa') x - 12 (\gamma'-\varkappa') v' x \, . \, . \quad (77)$$

thence:

$$\frac{p_P - p_R}{p_k} = -6 t' (v'_P - v'_R) + 2 (2\gamma'-3\varkappa') (x_P - x_R) - 12 (\gamma'-\varkappa') (v'_P - v'_R) x_P, (78)$$

for, with regard to the last term, the difference of x_P and x_R is slight compared to that between v'_P and v'_R.

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1) It might appear as if $\frac{9}{16} v'^3$ ought also to be inserted in the following expression, but it is easy to see that this term leads to a small quantity of higher order than those that will occur in the final result.

It is now easy to find:

$$x_P - x_R = \frac{1}{2} m (v'_P - v'_R) = \frac{3}{8} (2\gamma' - 3\varkappa') x_p (v'_P - v'_R), \quad . \quad (79)$$

either by paying attention to the fact that we have in Fig. *d*, § 12 (see the first descriptive part), if applied to the (v', x)-diagram, with a sufficient degree of approximation:

$$RQ = PQ \,.\, tg\, RPQ = PQ \,.\, tg \frac{1}{2} \mu = \frac{1}{2} \,.\, PQ \,.\, tg\, \mu = \frac{1}{2} \,.\, PQ \,.\, m,$$

or by application of the formulae (13) and (14), observing that $v_P - v_R = 3\, b_1 (v'_P - v'_R)$.

This yields by substitution in (78):

$$\frac{p_P - p_R}{p_k} = \left(-6t' + \frac{3}{4} (2\gamma' - 3\varkappa')^2 x_P - 12 (\gamma' - \varkappa') x_P \right) (v'_P - v'_R), \, (80)$$

or finally substituting for t' its value from (47)

$$\frac{p_P - p_R}{p_k} = -\frac{3}{4} (2\gamma' - 3\varkappa')^2 x_P (v'_P - v'_R) = -\frac{1}{4 b_1} (2\gamma' - 3\varkappa')^2 x_P (v_P - v_R), \, (81)$$

from which we immediately derive formula (20), applying (18).

The third connodal relation.

24. We have now obtained the principal formulae. For the sake of completeness, however, we shall treat here also the third connodal relation, the more so as this leads to a new determination of the formulae (47) and (48), which puts the former to the test.

This third relation reads:

$$\psi'_2 - x_2 \frac{\partial \psi'_2}{\partial x_2} - v'_2 \frac{\partial \psi'_2}{\partial v'_2} = \psi'_1 - x_1 \frac{\partial \psi'_1}{\partial x_1} - v'_1 \frac{\partial \psi'_1}{\partial v'_1} . \quad . \quad (82)$$

We first transform $\psi' - x \frac{\partial \psi'}{\partial x} - v' \frac{\partial \psi'}{\partial v'}$, with the aid of (32). It proves to be necessary to keep all terms up to the order $t^{\frac{5}{2}}$ or η^5. So we find:

$$\psi' - \frac{\partial \psi'}{\partial x} - v' \frac{\partial \psi'}{\partial v'} = -(1+t') x + \chi_0 - v' \frac{\partial \chi_0}{\partial v'} - v' x \frac{\partial \chi_1}{\partial v'} - \left(\chi_2 + v' \frac{\partial \chi_2}{\partial v'} \right) x^2 . \quad . \quad (83)$$

From this follows:

$$\psi'_2 - x_2 \frac{\partial \psi'_2}{\partial x_2} - v'_2 \frac{\partial \psi'_2}{\partial v'_2} = -(1+t')(x'' + \xi\eta) - (1+t') \log 2b_1 - \frac{9}{8} - \frac{9}{8} t' (\eta^2 + 2v''\eta) +$$

$$+ \frac{9}{4} t'\eta^3 - \frac{27}{64} (\eta^4 + 4v''\eta^3) + \frac{63}{40} \eta^5 + \frac{3}{4} [(2\gamma' - 3\varkappa') + 2\gamma' t'] (\eta + v'') (x'' + \xi\eta) -$$

$$- \frac{9}{2} (\gamma' - \varkappa') (\eta^2 + 2v''\eta) (x'' + \xi\eta) + \frac{27}{8} (3\gamma' - 2\varkappa') \eta^3 x'' - \sigma_0 (x''^2 + 2x''\xi\eta) - 2\sigma_2 \eta x''^2 . (84)$$

If we equate this to the corresponding expression for

$$\psi'_1 - x_1 \frac{\partial \psi'_1}{\partial x_1} - v'_1 \frac{\partial \psi_1}{\partial v'_1},$$

which is obtained by changing η into $-\eta$, we get, dividing by η:

$$-2\xi - 2t'\xi - \frac{9}{2} t'v'' + \frac{9}{2} t'\eta^2 - \frac{27}{8} v''\eta^2 + \frac{63}{20}\eta^4 + \frac{3}{2}(2\gamma' - 3\varkappa')x'' + 3\gamma't'x'' +$$

$$+ \frac{3}{2}(2\gamma' - 3\varkappa')v''\xi - 9(\gamma' - \varkappa')\xi\eta^2 - 18(\gamma' - \varkappa')v''x'' +$$

$$+ \frac{27}{4}(3\gamma' - 2\varkappa')\eta^2 x'' - 4\sigma_0 x''\xi - 4\sigma_2 x''^2 = 0. \quad \ldots \ldots \quad (85)$$

At first approximation this yields:

$$\xi = \frac{3}{4}(2\gamma' - 3\varkappa')x''.$$

This relation is, however, identical with the relation (69) which is derived from the first connodal relation. So we cannot draw any further conclusion from equation (85) without bringing it into connection with the first connodal relation; but for this it is required to introduce a further approximation for the latter.

Second approximation of the first connodal relation.

25. From the first connodal relation in connection with the equation

$$\frac{\partial \psi'}{\partial x} = 1 + t' + (1 + t')\,log\,x + \chi_1 + 2\chi_2 x + \ldots \quad \ldots \quad (86)$$

the following relation may easily be derived, if we take into account the terms up to the order t'^2 or η^3:

$$(1+t')\,log\,\frac{1 + \frac{\xi\eta}{x''}}{1 - \frac{\xi\eta}{x''}} - \frac{3}{2}(2\gamma' - 3\varkappa')\eta - 3\gamma'\eta t' + 9(\gamma' - \varkappa')v''\eta - \frac{9}{4}(3\gamma' - 2\varkappa')\eta^3 +$$

$$+ 4\sigma_0\xi\eta + 4\sigma_2\eta x'' = 0 \quad \ldots \ldots \ldots \ldots \quad (87)$$

Within the same order of approximation we have however:

$$log\,\frac{1 + \frac{\xi\eta}{x''}}{1 - \frac{\xi\eta}{x''}} = \frac{2\xi\eta}{x''} + \frac{2\xi^3\eta^3}{3x''^3}.$$

In the second term of the second member of this equation, however, we may safely make use of the first approximation furnished by equation (69). Taking this into account (87) passes after multiplication with x'' and division by η into.

$$2\xi + 2\xi t' + \frac{9}{32}(2\gamma'-3\varkappa')^3\eta^2 x'' - \frac{3}{2}(2\gamma'-3\varkappa')x'' - 3\gamma' x'' t' + 9(\gamma'-\varkappa')v''x'' -$$

$$-\frac{9}{4}(3\gamma'-2\varkappa')\eta^2 x'' + 4\sigma_0 \xi x'' + 4\sigma_2 x''^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

Further reduction of the third connodal relation.
Derivation of equation (25) *of the first descriptive part.*

26. By addition of (85) and (88) we find: [1])

$$-\frac{9}{2}t'v'' + \frac{9}{2}t'\eta^2 - \frac{27}{8}v''\eta^2 + \frac{63}{20}\eta^4 - 9(\gamma'-\varkappa')\xi\eta^2 - 9(\gamma'-\varkappa')v''x'' +$$

$$+\frac{3}{2}(2\gamma'-3\varkappa')v''\xi + \frac{9}{32}[(2\gamma'-3\varkappa')^3 + 16(3\gamma'-2\varkappa')]\eta^2 x'' = 0. \quad . \quad . \quad (89)$$

When we add to this relation (72), which is deduced from the second connodal relation, after having multiplied it with v'', we can divide by η^2 and we get:

$$\frac{9}{2}t' - \frac{9}{4}v'' + \frac{63}{20}\eta^2 - 9(\gamma'-\varkappa')\xi + \frac{9}{32}[(2\gamma'-3\varkappa')^3 + 16(3\gamma'-2\varkappa')]x'' = 0 \quad . \quad (90)$$

Making use of (69) we may solve the quantity v'' from this equation:

$$v'' = 2t' + \frac{7}{5}\eta^2 + \frac{1}{8}[(2\gamma'-3\varkappa')^3 - 24(2\gamma'-3\varkappa')(\gamma'-\varkappa') + 16(3\gamma'-2\varkappa')]x'', \quad (91)$$

or finally with the aid of (73):

$$v'' = -\frac{18}{5}t' + \left\{\frac{7}{5}[(2\gamma'-3\varkappa')^2 - 8(\gamma'-\varkappa')] + \right.$$

$$\left. + \frac{1}{8}[(2\gamma'-3\varkappa')^3 - 24(2\gamma'-3\varkappa')(\gamma'-\varkappa') + 16(3\gamma'-2\varkappa')]\right\}x'' . \quad (92)$$

from which equation (25) follows immediately with the aid of (65) and (26).

In this way we have found the starting-point of the curve in the (v, x)-diagram described by the point halfway between the points which represent coexisting phases. The tangent in that starting point also is now known.

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[1]) Remarkable is the disappearance of the terms derived from $l_2 x^2$, which makes also γ' and δ', i. e. $\frac{a_2}{a_1}$ and $\frac{b_2}{b_1}$ disappear from the result. We have tested the truth of this in different ways.

A new determination of the plaitpoint, independent of the preceding one.

27. It is now easy to obtain such a determination with the aid of (73) and (91). For in the plaitpoint we have:

$$\eta = 0 \quad ; \quad x'' = x_P \quad ; \quad v'' = v'_P .$$

From (73) follows immediately (47); from (91):

$$v'_P = 2t' + \frac{1}{8}\left[(2\gamma'-3x')^3 - 24\,(2\gamma'-3x')\,(\gamma'-x') + 16\,(3\gamma'-2x')\right]x_P ; \quad . \quad (93)$$

from which in connection with (47) we find again (48).

Physics. — "*Some remarkable phenomena, concerning the electric circuit in electrolytes*". By Mr. A. H. Sirks. (Communicated by Prof. H. A. Lorentz).

On etching of metal-alloys by means of the electric current, as communicated in the proceedings of the meeting of September 27, 1902, I met with a great difficulty. In some cases the hydrogen developed at the kathode was very troublesome, namely when, instead of escaping immediately it divided itself in small bubbles through the liquid and stuck to the object to be etched used as anode. This obstacle was overcome by surrounding the kathode with fine brass-gauze, so that the gasbubbles were compelled to escape directly in this case. The gauze was hung up apart, consequently there was no contact, whatever, with one of the electrodes. The etching being finished, copper proved to have been precipitated on the wires of the gauze, which deposit was almost conform to the shape of the electrodes.

This was still more visible at a second etching-experiment with the same copper-alloy: a small cup was placed under the anode, which partly hung in it. Again on the gauze a copper-deposit was perceptible, which showed at the lower side a distinctly designed horizontal margin, nearly as high as the brim of the cup.

It was to be expected, that copper should precipitate on the gauze, placed between the electrodes, as the whole apparatus can be considered as two voltameters, connected in series[1]). But, why is by this electrolysis not the whole side of the gauze, facing the anode, coppered, as is the case with the kathode by any ordinary electrolysis?

To answer this question the experiments were altered somewhat.

[1]) The anode and the side of the gauze facing it, are the electrodes of one, the other side of it and the kathode, those of the other voltameter.