

Citation:

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Chemistry. — “*The shape of the spinodal and plaitpoint curves for binary mixtures of normal substances.*” (Fourth communication: *The longitudinal plait.*) By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

1. In order to facilitate the survey of what has been discussed by me up to now, I shall shortly resume what has been communicated on this subject in four papers in These Proceedings and in two papers in the Arch. Teyler.

a. In the *first* paper in These Proceedings (22 April 1905) the equation:

$$RT = \frac{2}{v^2} [x(1-x)(av - \beta\sqrt{a})^2 + a(v-b)^2] \quad . \quad . \quad (1)$$

was derived for the *spinodal* lines for mixtures of *normal* substances, on the supposition that a and b are independent of v and T , and that $a_{12} = \sqrt{a_1 a_2}$, while

$$(av - \beta\sqrt{a})^3 [(1-2x)v - 3x(1-x)\beta] + \sqrt{a}(v-b)^2 \left[3(ax - \beta\sqrt{a})(av - 2\beta\sqrt{a}) + \frac{a(v-b)(v-3b)}{x(1-x)} \right] = 0 \quad (2)$$

was found for the v, x -projection of the *plaitpoint line*, when $a = \sqrt{a_2} - \sqrt{a_1}$ and $\beta = b_2 - b_1$.

b. In the *second* paper in These Proceedings (27 May 1905) the shape of these lines for different cases was subjected to a closer examination. For the simplification of the calculations $\beta = 0$, i.e. $b_1 = b_2$, was assumed, so that then the proportion θ of the critical temperatures of the two components is equal to the proportion π of the two critical pressures. If we then put $\frac{\sqrt{a_1}}{a} = \varphi$, $\frac{b}{v} = \omega$, $\frac{T}{T_0} = \tau$ (where T_0 is the “third” critical temperature, i. e. the plaitpoint temperature for $v = b$), the two preceding equations become:

$$\tau = 4\omega [x(1-x) + (\varphi + x)^2 (1-\omega)^2] \quad . \quad . \quad . \quad (1a)$$

$$(1-2x) + 3(\varphi + x)(1-\omega)^2 + \frac{(\varphi + x)^3 (1-\omega)^3 (1-3\omega)}{x(1-x)} = 0. \quad (2a)$$

It now appeared that the plaitpoint curve has a *double point*, when $\varphi = 1.43$, i.e. $\theta = \pi = 2.89$. If $\theta > 2.89$, the (abnormal) case of fig. 1 (loc. cit.) presents itself (construed for $\varphi = 1$, $\theta = (1 + \frac{1}{\varphi})^2 = 4$); if on the other hand $\theta < 2.89$, we find the (normal) case of fig. 2 (loc. cit.) (construed for $\varphi = 2$, $\theta = 2\frac{1}{4}$).

At the same time the possibility was pointed out of the appearance of a third case (fig. 3, loc. cit.), in which the branch of the plaitpoint

line running from C_1 to C_2 was *twice* touched by a spinodal line. Here also the branch C_0A is touched by a spinodal line [in the first two cases this took place only once, either (in fig. 1, loc. cit.) on the branch C_1A (A is the point $x=0, v=b$), or (in fig. 2 loc. cit.) on the branch C_0A (C_0 is the before-mentioned third critical point)].

So it appeared that *all* the abnormal cases found by KUENEN may already appear for mixtures of *perfectly normal* substances.

It is certainly of importance for the theory of the critical phenomena that the existence of *two different branches* of the plaitpoint curve has been ascertained, because now numerous phenomena, also in connection with different "critical mixing points" may be easily explained.

c. In the *third* paper in These Proceedings (June 24, 1905)¹⁾ the equation:

$$\Delta = \frac{1}{T_1} \left(\frac{dT}{dx} \right)_0 = \theta \sqrt{\frac{1}{\pi} \left[\theta \sqrt{\frac{1}{\pi} \left(\frac{3}{2} - \frac{1}{2} \sqrt{\frac{1}{\pi}} \right)^2 - 1} \right]} \quad \dots (3)$$

was derived for the *molecular increase* of the lower critical temperature for the *quite general* case $a_2 \leq a_1, b_2 \leq b_1$, which equation is reduced to the very simple expression

$$\Delta = \theta (\theta - 1) \quad \dots \dots \dots (3^a)$$

for the case $\pi = 1$ ($p_2 = p_1$).

This formula was confirmed by some observations of CENTNERSZWER and BÜCHNER.

d. The *fourth* paper appeared in the Archives Teyler of Nov. 1905. Now the restricting supposition $\beta=0$ (see b) was relinquished for the determination of the *double point* of the plaitpoint line, and the quite general case $a_2 \leq a_1, b_2 \leq b_1$ was considered. This gave rise to very intricate calculations, but finally expressions were derived from which for every value of $\theta = \frac{T_2}{T_1}$ the corresponding value of $\pi = \frac{p_2}{p_1}$, and also the values of x and v in the double point can be calculated.

Besides the special case $\theta = \pi$ (see b) also the case $\pi = 1$ was examined, and it was found that then the double point exists for $\theta = 9,90$. This point lies then on the line $v = b$.

¹⁾ The three papers mentioned have together been published in the Arch. Néerl. of Nov. 1905.

e. The *fifth* paper (These Proceedings, Dec. 30, 1905)¹⁾ contained the condition for a *minimum critical (plaitpoint) temperature*, and that for a *maximum vapour pressure* at higher temperatures (i. e. when at lower temperatures the three-phase-pressure is greater than the vapour pressures of the components). For the first condition was found:

$$\theta < \frac{4\pi\sqrt{\pi}}{(3\sqrt{\pi}-1)^2}, \quad \dots \dots \dots (4)$$

for the second:

$$\theta < \frac{\pi}{2\sqrt{\pi}-1}, \quad \dots \dots \dots (5)$$

which conditions, therefore, do not always include each other²⁾.

After this the connodal relations for the three principal types were discussed in connection with what had already been written before by KORTEWEG (Arch. Néerl. 1891) and later by VAN DER WAALS (These Proceedings, March 25, 1905). The successive transformations of main and branch plait were now thrown into relief *in connection with the shape of the plaitpoint line, and its splitting up into two branches as examined by me.*

f. In the *sixth* paper (Arch. Teyler of May 1906) the connodal relations mentioned were first treated somewhat more fully, in which also the p, x -diagrams were given. There it was proved, that the points R_1 , R_2 and R'_2 , where the spinodal lines touch the plaitpoint line, are *cusps* in the p, T -diagram.

Then a graphical representation was plotted of the corresponding values of θ and π for the double point in the plaitpoint line, in connection with the calculations mentioned under d.

Both the graphical representation and the corresponding table are here reproduced. The results are of sufficient importance to justify a short discussion.

We can, namely, characterize all possible pairs of substances by the values of θ and π , and finally it will only depend on these values, which of the three main types will appear. To understand this better, it is of importance to examine for what combination (π, θ) one type passes into another. As to the transition of type I to II (III), it is exactly those combinations for which the plaitpoint line has a double point. In fig. 1 (see the plate) every point of the

¹⁾ Inserted in the Arch. Néerl. of May 1906.

²⁾ These results were afterwards confirmed by VERSCHAFFELT (These Proceedings March 31, 1906; cf. also the footnote on p. 749 of the English translation).

plane denotes a combination (θ, π) , to which every time a certain pair of substances will answer.

$\theta = \frac{T_2}{T_1}$	$\pi = \frac{p_2}{p_1}$	α	v/b
1,00	7,50 en 0,13	0,96 en 0,040	2,57 en 2,57
1,19	7,21 » 0,13	0,94 » 0,036	2,49 » 2,60
1,71	6,26 » 0,13	0,84 » 0,025	2,26 » 2,68
1,88	5,76 » 0,13	0,78 » 0,021	2,18 » 2,71
2,04	5,42 » 0,12	0,72 » 0,018	2,11 » 2,74
2,22	4,94 » 0,12	0,63 » 0,014	2,02 » 2,79
2,89	2,89 » 0,12	0,24 » 0,003	1,73 » 2,87
9,90	1,00 » 0,11	0,01 » 0,001	1,00 » 2,95
∞	— » 0,11	— » 0,000	— » 3,00

In the said figure the line $C'APB$ denotes the corresponding values of θ and π from $\theta = 0$ to $\theta = 9,9$. For C' $\theta = 0$, $\pi = 9$, for A $\theta = 1$, $\pi = 7,5$; with $\theta = 2,22$ corresponds $\pi = 4,94$. (Case $\pi = \theta^2$ or $\alpha_2 = \alpha_1$); for P $\pi = \theta = 2,89$ (Case $\pi = \theta$ or $b_2 = b_1$); for B $\theta = 9,9$, $\pi = 1$. For values of $\theta > 9,9$ the double point would lie on the side of the line $v = b$, where $v < b$. It appears from the figs. 23, 24 and 25 of the said paper, that then the line BD ($\pi = 1$) forms the line of demarcation between type I and II (III). For starting from a point, where $\pi < 1$ (however little) and θ is comparatively low, where therefore we are undoubtedly in region II (III), we see clearly that we cannot leave this region, when with this value of π that of θ is made to increase. For we can never pass to type I, when not for realizable values of v (so $< b$) a double point is reached, and now a simple consideration (see the paper cited) teaches, that for $\pi < 1$ a double point would always answer to a value of $v < b$.

Now it is clear that $\theta = 0$, $\pi = 9$ is the same as $\theta = \infty$, $\pi = 1/9$; that $\theta = \pi = 2,89$ is identical with $\theta = \pi = 1/2,89 = 0,35$; etc., etc. (the two components have simply been interchanged), so that the line CA' will correspond with the line $C'A$, while $A'B'$ corresponds with AB . If we now consider only values of θ which are > 1 , if in other words we always assume $T_2 > T_1$, we may say that the

region of the normal type II (III) is practically bounded by the lines ABD , AA' and $A'C$. On the right of ABD we have the abnormal type I ($C_2H_6 + CH_3OH$, ether $+ H_2O$); on the left of $A'C$ we have also the type I. But whereas in the first region of I the branches of the plaitpoint line are C_2C_0 and C_1A , they are C_1C_0 and C_2B (see figs. 23—25 loc. cit.) in the second region. It is namely easy to show, (loc. cit.), that for $\pi > 1$ the branches of the plaitpoint line are either C_1C_2 and C_0A (type II and III), or C_1A and C_0C_2 (type I), while for $\pi < 1$ these branches are C_1C_2 and C_0B (type II and III) or C_2B and C_0C_1 (type I). The line $\pi = 1$ divides therefore the region of type II (III) into two portions, where we shall resp. find the shape of the plaitpoint line branches mentioned (viz. for $\theta > 1$). But in practice it will most likely never happen, that with $\theta > 1$ a value of π corresponds which is much smaller than 1, for a higher critical pressure goes generally together with a higher critical temperature. We may therefore say that with a given value of π the abnormal type I is found when θ is *comparatively large* [larger than the double point (of the plaitpoint line) value of θ], whereas the normal type II (or III) appears when θ is *comparatively small* (smaller than the said double point value).

It is now of the greatest importance to examine, when type II passes into III, where the plaitpoint line C_1C_2 is twice touched by a spinodal line (in R_1 and R_2'). This investigation forms the conclusion of the last paper in the Arch. Teyler.

The calculations get, however, so exceedingly intricate, that they proved practically unfeasible for the general case $a_2 \gtrless a_1$, $b_2 \gtrless b_1$.

Only the special cases $\beta = 0$ ($b_2 = b_1$ or $\pi = \theta$) and $\pi = 1$ admitted of calculation, though even then the latter was still pretty complicated.

Then it appeared, that for $\beta = 0$ the region of type III is exactly $= 0$, that it simultaneously appears and disappears in the double point P , where $\pi = \theta = 2,89$. But in the case $\pi = 1$ the region lies between $\theta = 4,44$ and $\theta = 9,9$ (the double point). This is therefore QB in fig. 1; i. e. for values of $\theta > 1$ and $< 4,44$ we find type II (see fig. 2^a); for $\theta = 4,44$ (in Q) the plaitpoint line gets a point of inflection (see fig. 2^b), whereas from $\theta = 4,44$ to $\theta = 9,9$ we meet with type III (fig. 2^c) with two points R_1 and R_2' , where the spinodal lines touches the plaitpoint line. This type disappears in the double point P , where $\theta = 9,9$ and R_2 and R_2' coincide in P (fig. 2^d), and passes for values of $\theta > 9,9$ into type I (fig. 2^e). We point out, that the figs. 2^a—2^e represent an intermediate case (i. e. between $\pi = \theta$ and $\pi = 1$, see fig. 1), for in the case of

$\pi = 1$ the branch AR_2C_0 would coincide with AB ($v = b$). Therefore the special value 4,44 has been replaced by θ_q (the value of θ in Q) and the value 9,9 by θ_p (the value of θ in P).

Of the curve which separates type II from type III we know as yet only the points P and Q (see fig. 1) and the further course of this line is still quite unknown, for which reason we have denoted it by a dotted line.

In any case the investigations, described in the Arch. Teyler have proved, that this very abnormal type III is possible for mixtures of normal substances. If the critical pressures of the two components are the same ($\pi = 1$), then we meet with this type when θ lies between 4,4 and 9,9. The critical temperatures must therefore lie far apart, but not so far (see fig. 1) as would be necessary for the appearance of type I.

We shall once more emphatically point out that the *numeric* results of our investigation will naturally be modified, when b is not assumed to be independent of v and T , or when one of the two components should be associating substances. This will cause the types III and I to make their appearance *earlier* than has been derived above (i. e. with lower values of θ with for the rest equal values of π), but that *qualitatively* everything will remain unchanged. This appears already from the fact that the substitution of the quite general assumption

$b_1 \lesseqgtr b_2$ for the simplified assumption $b_1 = b_2$ (in the first paper in the Arch. Teyler) has made no change is the existence of a double point in the plaitpoint line with certain corresponding values of θ and π , and that also the calculations for the limits of type III (in the second paper in the Arch. Teyler) may be carried out for the quite general case $b_1 \lesseqgtr b_2$. So the phenomena remain qualitatively

the same for very different pairs of values of b_1 and b_2 , and will therefore not change *essentially* either, when one definite pair of values, holding e. g. for the critical circumstances of one of the components, is subjected to changes, whether by association, or by other causes, when v or T change — no more as e. g. the critical phenomena for a simple substance will *essentially* change when b is no longer constant, but is supposed to be dependent of v and T , or when that substance forms complex molecules.

The longitudinal Plait.

2. In former papers it has been demonstrated that in the neighbourhood of C_0 a minimum plaitpoint temperature makes its appearance

both with type I in the line C_0C_2 and with type II in the line C_0A , and that therefore with decrease of temperature a *separate plait* begins to detach itself starting from C_0 at a definite temperature T_0 (the plaitpoint temperature in C_0), which plait will merge into the main plait (or its branch plait) later on in an homogeneous double point. The consequence of this is, that with type I e. g. at lower temperatures the main plait will always be *open* towards the side of the small volumes, so that increase of pressure will never cause the two split phases to coincide.

Let us however specially consider the case of type II. Here the usual course, inter alia described in the last cited paper in the Proceedings of Dec. 30, 1905, is this. At a certain temperature, passing from higher to lower temperatures, a spinodal curve touches the branch of the plaitpoint line AC_0 in R_2 . In the well-known way a closed connodal curve begins to form within the connodal line proper, which closed curve gets outside the original connodal curve at lower temperatures, and gives rise to a new (branch) plait, and at the same time to a three phase equilibrium (figs. 3^a and 3^b). In many cases this branch plait has already appeared before the plait which starts from C_0 , begins to develop at somewhat lower temperature. Later on the two branches coincide (at the minimum temperature in D), and then form again a continued branch plait (fig. 3^c).¹⁾

Now for the special case $b_2 = b_1$ the point D lies always very near C_0 (see the paper in these Proceedings referred to under b . in § 1). If then e. g. $T_2/T_1 = 2^{1/4}$, then $T_m/T_0 = 0,96$, when T_m represents the temperature in the minimum at D . The real longitudinal plait round C_0 exists then only at very high pressures (fig. 3^b), while the open plait of fig. 3^c can hardly be called a longitudinal plait, but is much sooner to be considered as the branch plait of the transverse plait which has joined the original longitudinal plait. Increase of pressure makes here always the two coexisting liquid phases approach each other, unless with very high pressures, when these phases diverge again.

The calculation proves that in the quite general case $b_1 \lesseqgtr b_2$ the point D may get much nearer in the neighbourhood of R_2 , and also that the temperature in the plaitpoint C_0 may be comparatively high, so that in opposition to what has been represented in fig. 3^a the longitudinal plait has already long existed round C_0 before a three phase equilibrium has formed at M (fig. 4^a and 4^b). The meeting

¹⁾ In this and some other figures the spinodal curves seem to touch in the homogeneous double point D , instead of to intersect, as they should.

of this longitudinal plait, which has then already greatly extended, with the branch plait takes place much more in the neighbourhood of the line 1, 2 of the three phase triangle, so that after the meeting the plait assumes the shape drawn in fig. 4^c, which makes it for the greater part retain its proper character of longitudinal plait. So at first increase of pressure makes the phases approach each other (this portion may be exceedingly small, but as a rule it will exist); then further increase of pressure makes the phases 1 and 2 again diverge, till x_1 and x_2 approach to limiting values at $p = \infty$, without the longitudinal plait ever closing again — as was formerly considered possible [cf. inter alia VAN DER WAALS, Cont. II, p. 190 (1900)]. For in consequence of the minimum at D the longitudinal plait always encloses the point C_0 . Only at temperatures higher than T_0 , at which the longitudinal plait does not yet exist, there can be question of homogeneity till the highest pressures. But then the plaitpoint P belongs to the *branch plait* of the *transverse plait*, and *not* to the longitudinal plait. This is indicated among others by fig. 3^a, *after* the closed connodal curve in M has broken through the connodal curve proper of the transverse plait; or by fig. 3^b, *before* a longitudinal plait has developed round C_0 .

Of course we may also meet with the case, that the plait round C_0 coincides with the branch plait at the moment that the latter with its plaitpoint just leaves the transverse plait, as shown in fig. 5^a, but this involves necessarily a *relation* between θ and π , and is therefore always a *very special case*. Then the branch plait happens to leave the transverse plait exactly in the minimum at D . After the meeting the plait shows the shape as traced in fig. 5^b. Now increase of pressure causes the two phases 1 and 2 to diverge *from the beginning*.

But the longitudinal plait round C_0 may also meet the connodal line of the transverse plait, *before* the closed connodal line has got outside the transverse plait (fig. 6^a). Then the three phase equilibrium does not develop, as in fig. 4^a, at the transverse plait (from which a branch plait issues), but at the *longitudinal plait* round C_0 . The latter penetrates then further into the transverse plait, till it meets the isolated closed connodal curve in D (fig. 6^b), after which the confluence with it takes place in the unrealizable region (fig. 6^c).

This plait is then the *longitudinal plait proper*, of which there is generally question with mixtures of substances which are not miscible in all proportions. But we should bear in mind that just as well the above treated case of fig. 4 may present itself, with that of fig. 5 as transition case.

The calculation teaches that the transition case presents itself when the proportion θ of the critical temperatures of the two components is in the neighbourhood of 1, and the proportion π of the critical pressures is at the same time pretty large.

A clear representation of these different relations is also given by the two p, T -diagrams of fig. 7 and fig. 7^a. (The temperature of C_0 is there assumed to be lower than that of R_2 , but it may just as well be higher). The plaitpoints p' on the part R_2A below the cusp are the unrealizable plaitpoints (see also figs. 3—6), the plaitpoints p on the part R_2M before M also (then the isolated closed connodal curve has not yet got outside the main plait); the plaitpoints P beyond M are all realizable.

So after the above we arrive at the conclusion that in all cases in which a distinct longitudinal plait appears of the shape as in figs. 4^c or 6^c (so when the minimum D lies near R_2), the critical mixing point M of the three phases need not always lie on the longitudinal plait (see fig. 4^a), and also that the longitudinal plait with its plaitpoint P will not always coincide with the transverse plait itself, but it can also coincide with the branch plait of the transverse plait, so that at that moment no three phase equilibrium, i. e. no vapour phase is found (see fig. 4^c). The two liquid phases 1 and 2, however, coincide in this case.

The case drawn in figs. 5^a and 5^b remains of course an exception, and the conditions for its occurrence may be calculated (see above). But this calculation, as well as that which in general indicates the situation of the points R_2 , D and M , will be published elsewhere (in the Arch. Teyler). It is, however, self-evident that the above general considerations are by no means dependent on these special calculations.

It is perhaps not superfluous to call attention to the fact that the concentration x_3 of the vapour phase is neither in fig. 4^a, nor in fig. 5^a or 6^a, the same as the concentration of the two coinciding liquid phases $x_{1,2}$, as VAN DER LEE wrongly believes to have shown in his Thesis for the doctorate (1898), [see p. 66—69, 73—74 and Thesis III; also VAN DER WAALS, Cont. II, p. 181 (1900)]. Now we know namely, that when x_3 lies between x_1 and x_2 at lower temperatures, this need not continue to be so till x_1 and x_2 have coincided. The latter would be quite accidental; in general one of the maxima, e. g. in the p, x -line, which lie in the unstable region between x_1 and x_2 , will get outside the plait before x_1 and x_2 have coincided. Cf. the figs. 12^a to 12^f in my Paper in These Proceedings of March 25 1905 and § 8 p. 669—670, and also the footnote on p. 665.

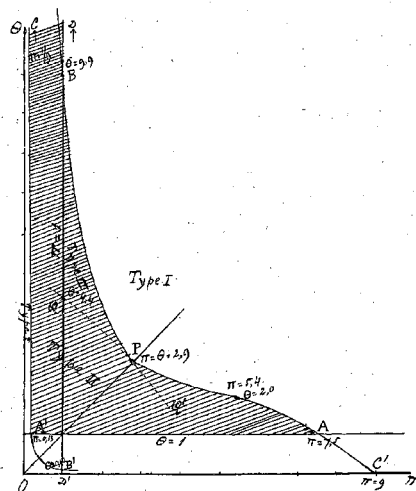


Fig. 1.

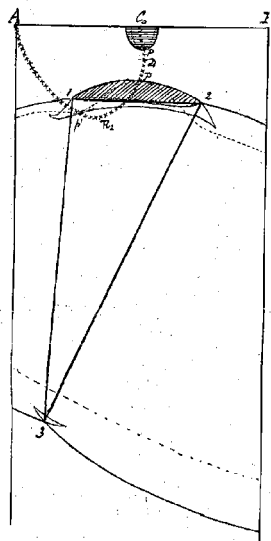


Fig. 3a.

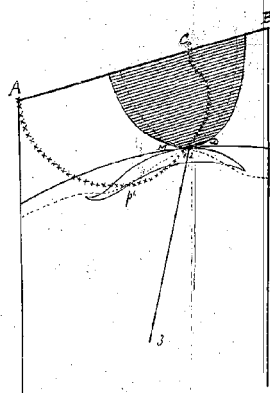


Fig. 5a.

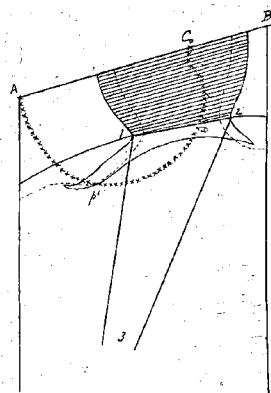


Fig. 5b.

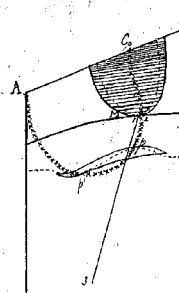


Fig. 6a.

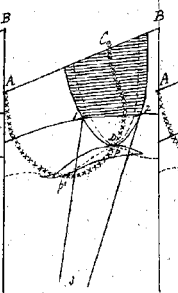


Fig. 6b.

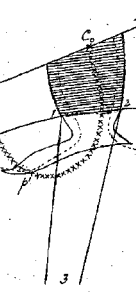


Fig. 6c.

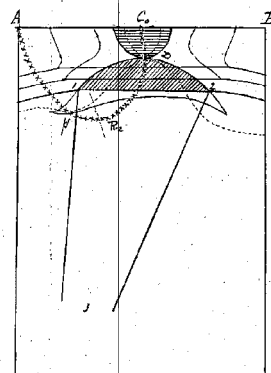


Fig. 3c.

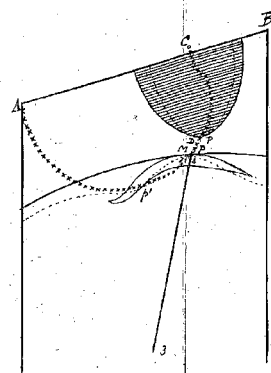


Fig. 4a.

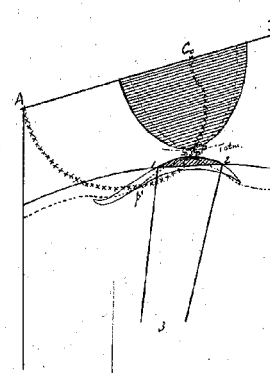


Fig. 4b.

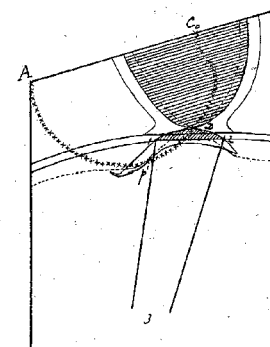


Fig. 4c.

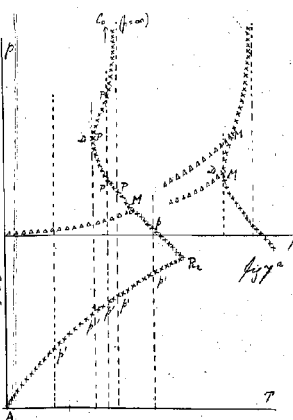


Fig. 7.

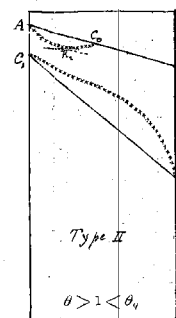


Fig. 2a.

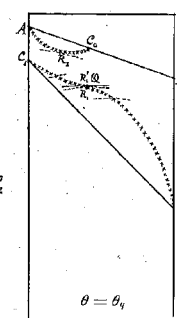


Fig. 2b.

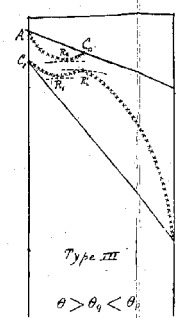


Fig. 2c.

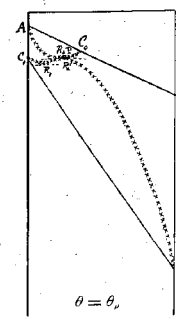


Fig. 2d.

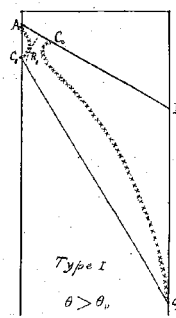


Fig. 2e.

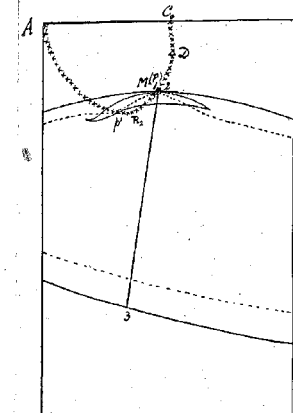


Fig. 3a.

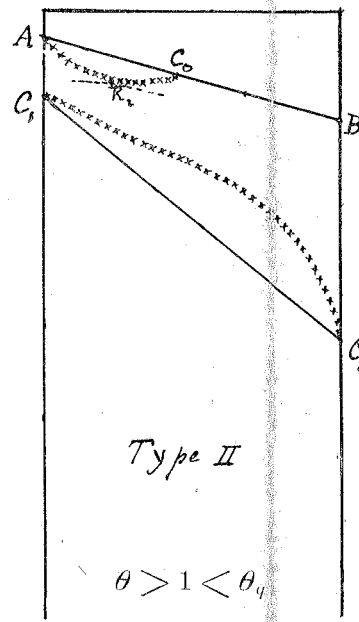


Fig. 2a.

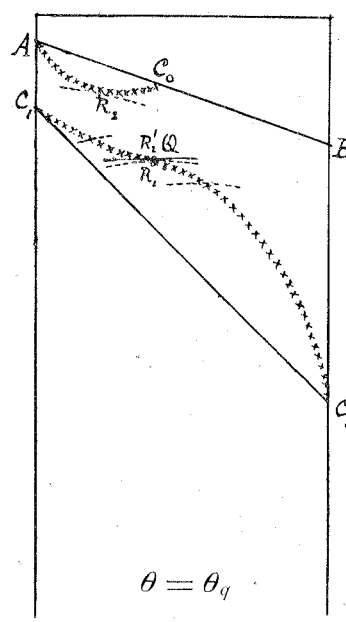


Fig. 2b.

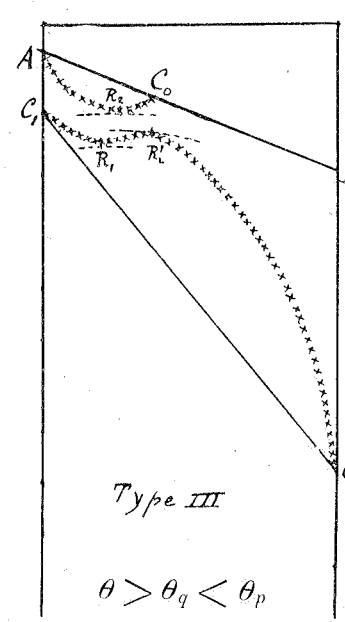


Fig. 2c.

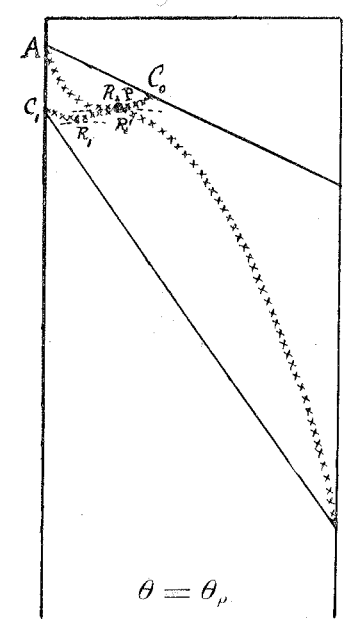


Fig. 2d.

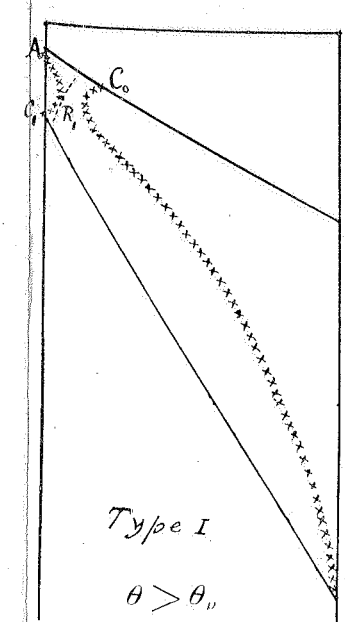


Fig. 2e.

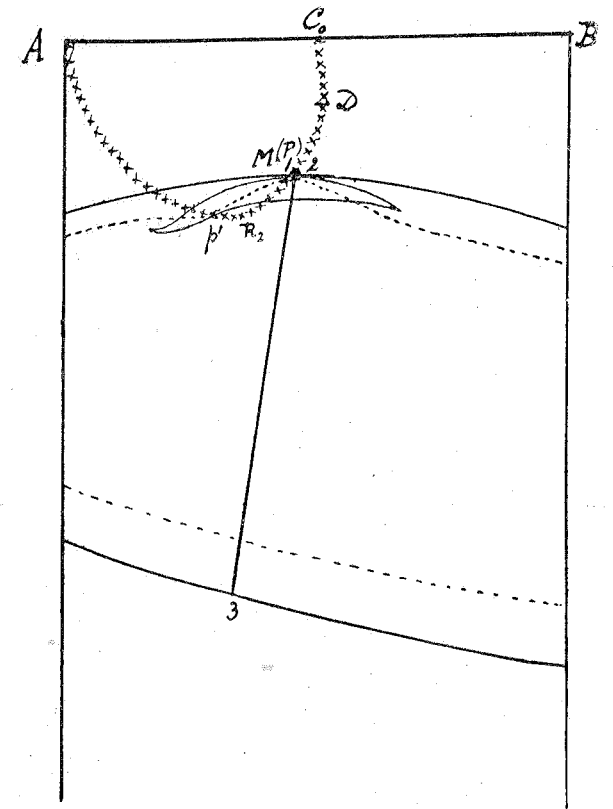


Fig. 3a.

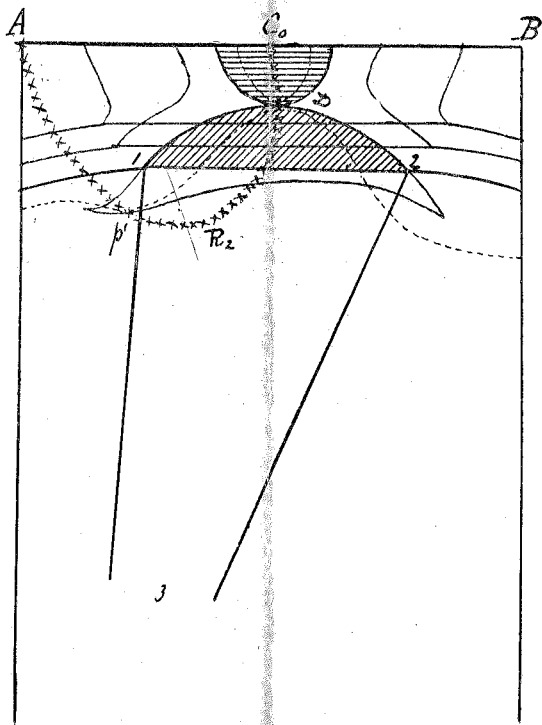


Fig. 3c.

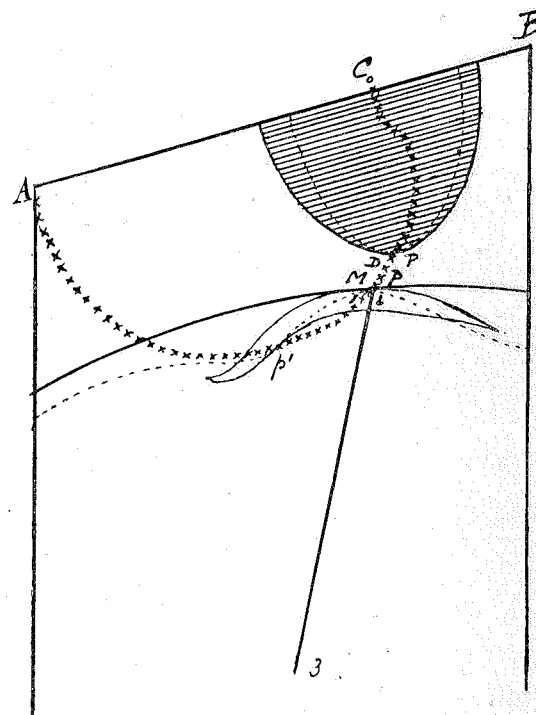


Fig. 4a.

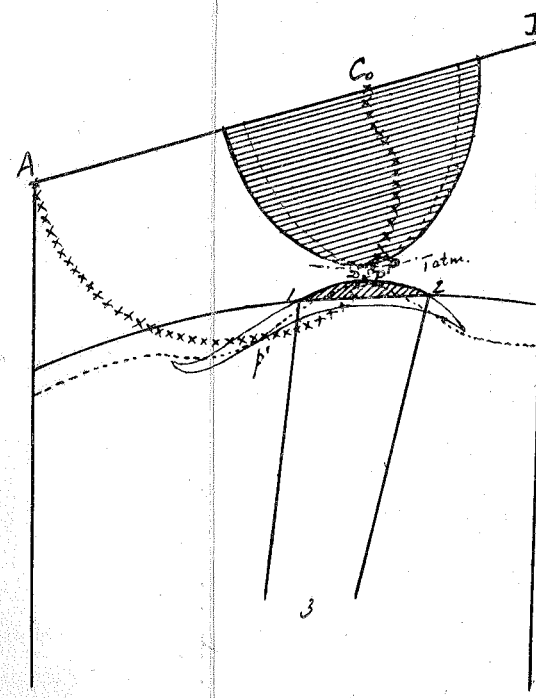


Fig. 4b.

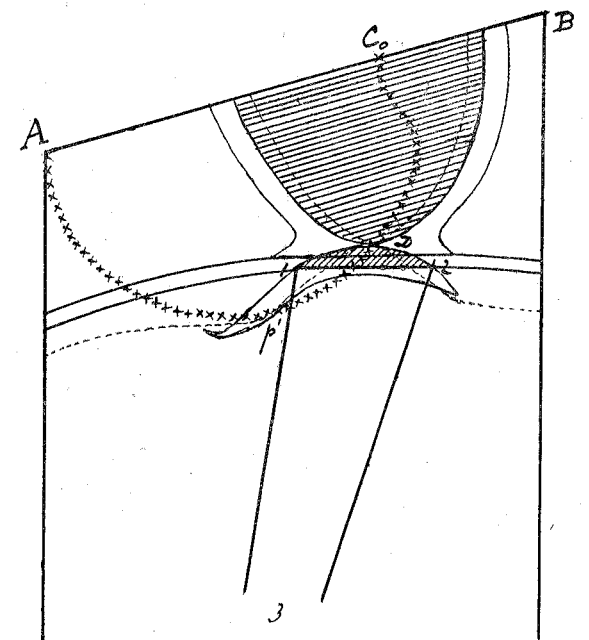


Fig. 1.

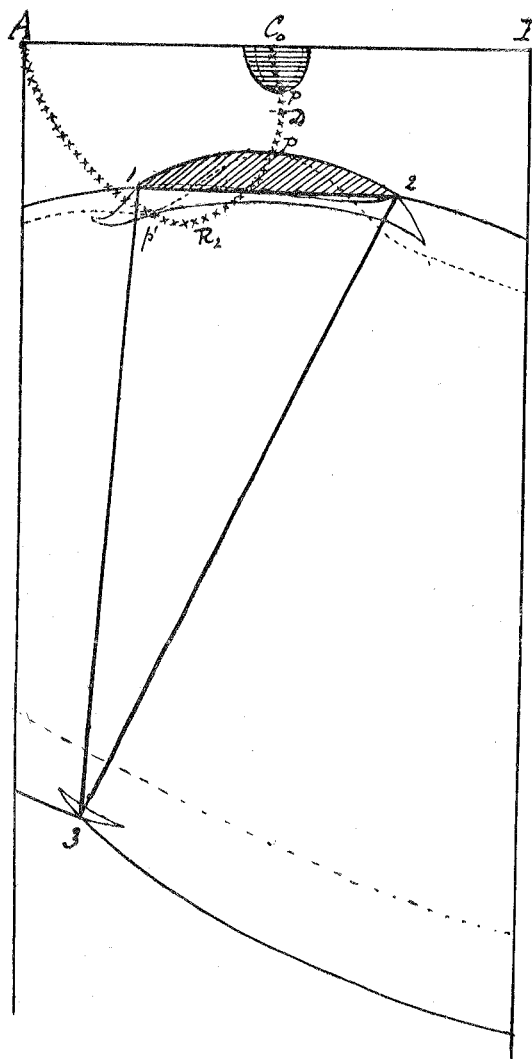


Fig. 3b.

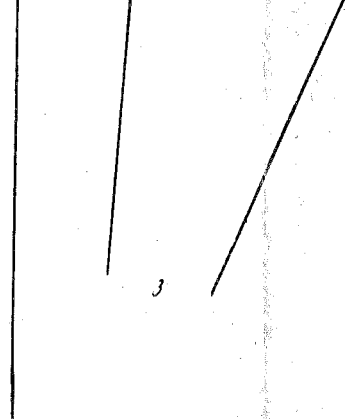


Fig. 3c.

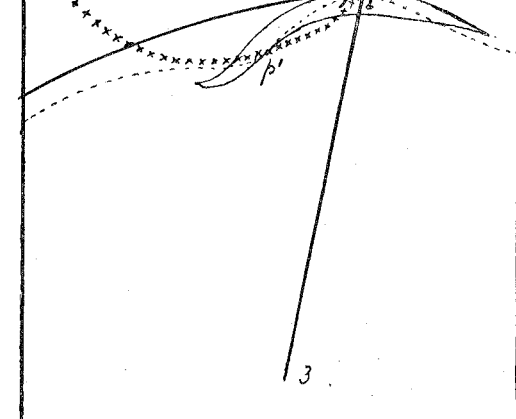


Fig. 4a.

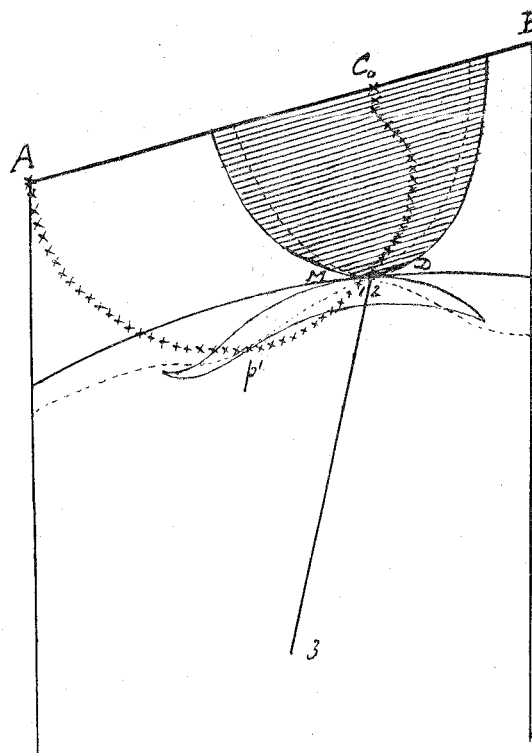


Fig. 5a.

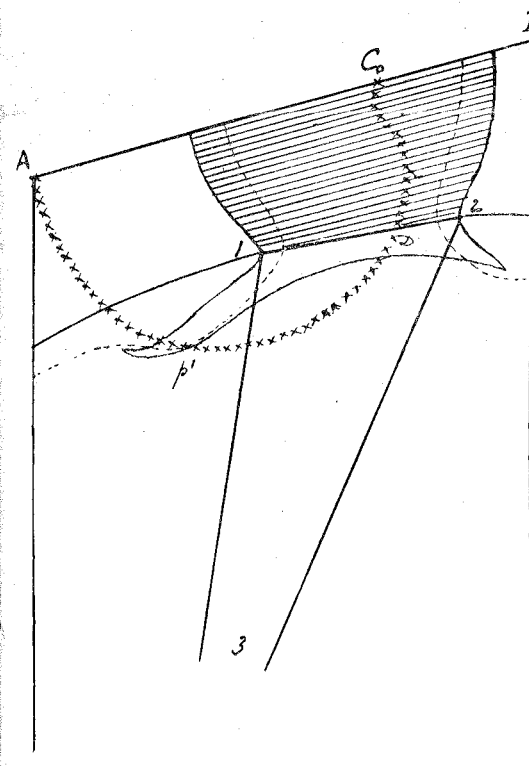


Fig. 5b.

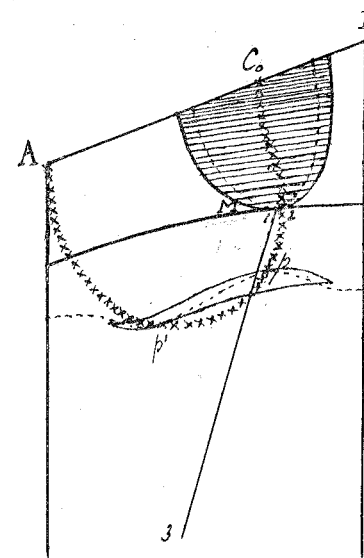
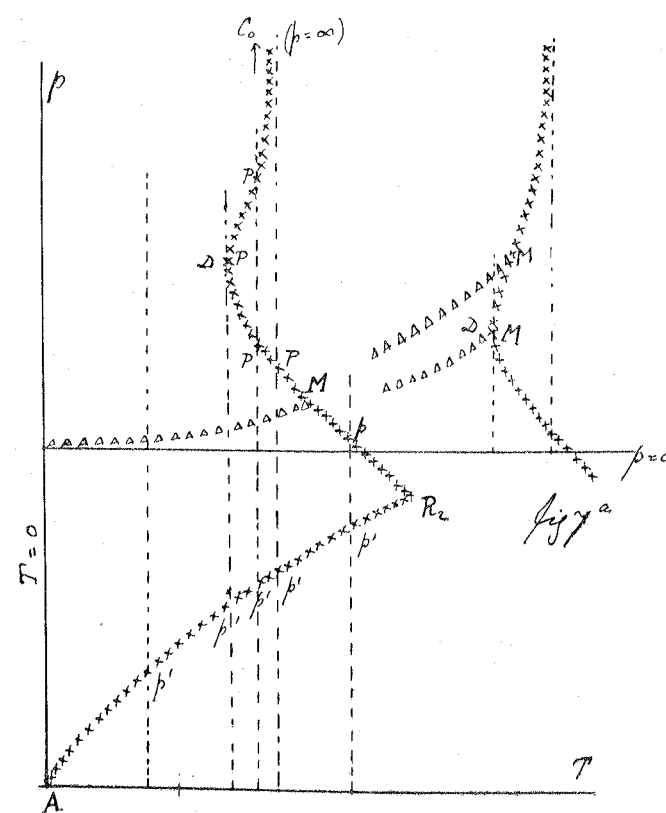
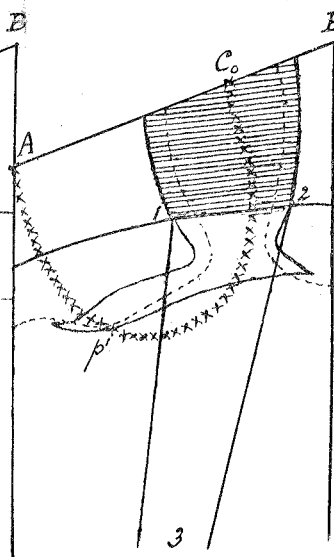
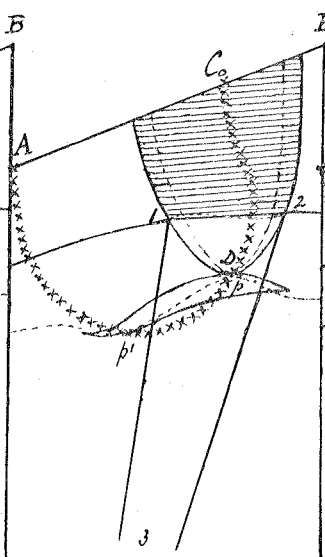
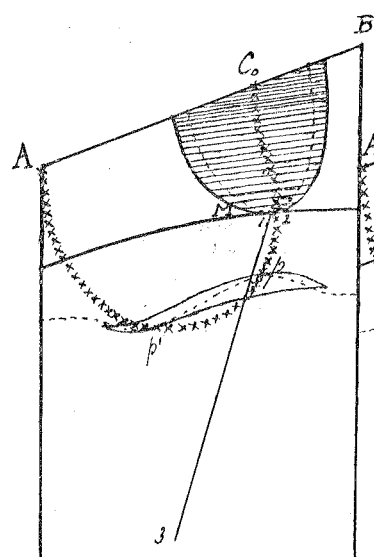
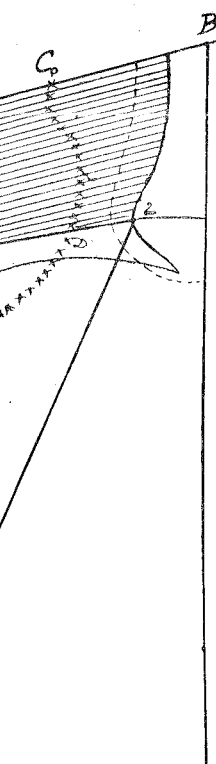
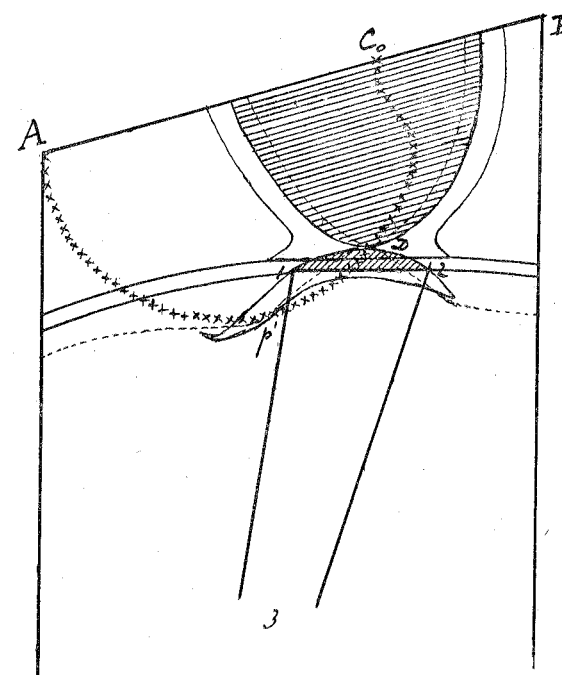
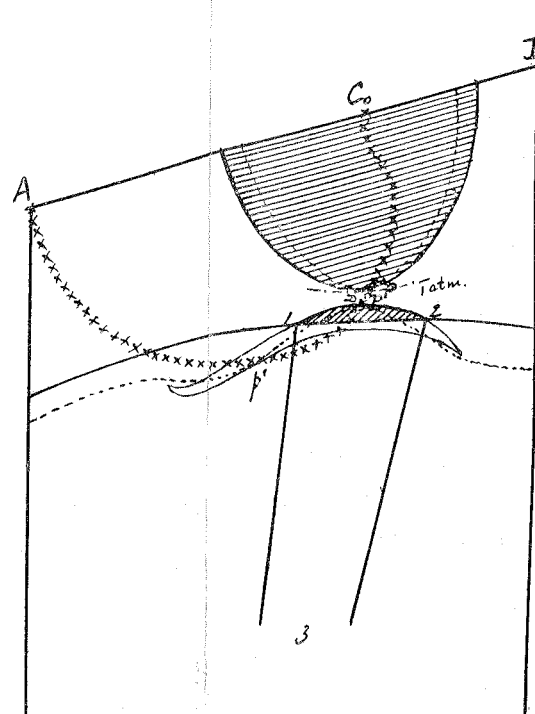
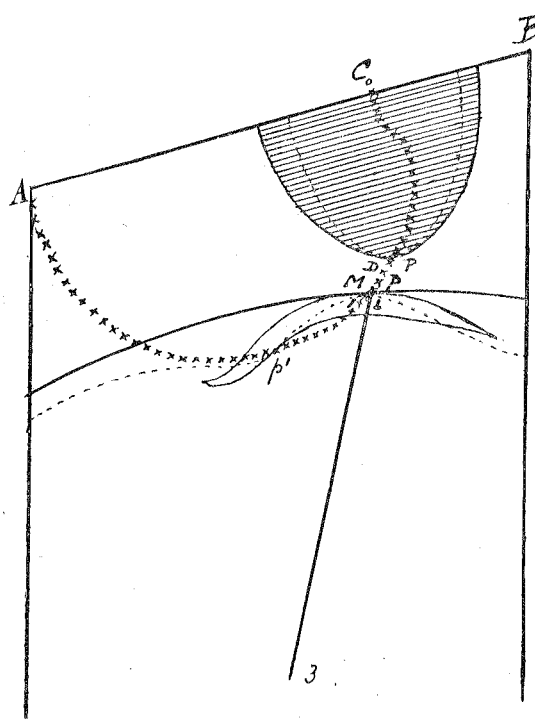


Fig. 6a.



Already in a previous paper (These Proceedings June 27 1903) I had elaborately demonstrated this, and somewhat later (These Proceedings 31 Oct. 1903) KUENEN arrived at the same opinion independently of me.¹⁾ And in 1900 SCHREINEMAKERS (Z. f. Ph. Ch. **35**, p. 462—470) had experimentally demonstrated that one maximum leaves the longitudinal plait for exactly the same mixture (phenol and water), for which VAN DER LEE thought he could theoretically prove, that $x_3 = x_{1,2}$.²⁾

Finally I shall just point out that in the peculiar shape of the p, T -diagram of the plaitpoint line (fig. 7) in the neighbourhood of the point D , and in the fact that the two critical moments represented by figs. 4^a and 4^c (as D and M in general do *not* coincide) do *not* coincide, the clue may be found for the explanation of a highly puzzling and as yet unexplained phenomenon, which has been observed as well by GUTHRIE as by ROTHMUND [Z. f. Ph. Ch. **26**, p. 446 (1898)]³⁾ in their experiments, viz. the appearance and disappearance of a distinct cloudiness when the mixture is heated above the "critical temperature of mixing", which cloudiness often continued to exist up to 10° above this temperature.

¹⁾ C. f. also KUENEN: Theorie der Verdampfung und Verflüssigung von Gemischen. Leipzig 1906, p. 170, note

²⁾ For the rest the assumption $x_3 = x_{1,2}$ at the point M leads, as the calculations teach, not only to strange, but to highly absurd conclusions.

³⁾ C. f. also FRIEDLÄNDER, Ueber merkwürdige Erscheinungen in der Umgebung des kritischen Punktes. Z. f. Ph. Ch. **38**, p. 385 (1901).

(October 25, 1906).