J. P. KUENEN. *On the influence of gravitation on the critical phenomena of simple substances and of mixtures.*

I. The fact, that in the neigbourhood of the critical point in consequence of the large compressibility, gravitation must exercice an important influence, has been remarked by GOUY [1]. The influence results in making the density of the substance enclosed in a tube perceptibly different at different levels. As usual the corresponding changes of the pressure and the height are determined by the relation $dp = -\frac{1}{v} g\ dh$, where v denotes the volume and g the acceleration of gravitation; but to a small value of dp near the critical point corresponds a large value of dv. For numerical determination the shape of the isothermals in that neigbourhood should be accurately known. GOUY calculated some values for carbonic acid by aid of SARRAU's formula for that substance; his results are laid down in a table to be found in his paper quoted above.

In the graphic representation with p and v for coördinates, the greater compressibility is expressed by the

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[1] Compt. Rend. 115, p. 720—722.

small slope of the isothermals. The different conditions of a substance present in a vertical column are represented by some subsequent points of an isothermal, which form together a small section of an isothermal. While at some distance from the critical point this section is very short and may be treated as one point for differences of level as may occur in experiments on the critical state, say from 10 to 20 cm., the length of the curve becomes perceptible near the critical point. From GOUY's table one finds that at the critical temperature of carbonic acid near the critical point to a difference of height of 10 cm. corresponds a difference of density of 6 percent: at 20 cm. distance the change of density would amount to about 10 per cent. At a definite temperature and a definite mean volume of the substance, the lenght of the little curve, or what comes to the same the number of the phases, which are in equilibrium above each other in the tube, is only dependent on the height of the column, and this in its turn is connected in a simple manner with the quantity of the substance and the bore of the experimental tube.

Let us suppose the temperature to be lowered towards the critical temperature, the total volume of the substance being kept constant. The mean volume (or density) will remain the same during this process. The lenght of the curve however will increase because the slope of the isothermals decreases and the curve as a whole will shift more or less along the direction of the v-axis, because the distribution of the densities above and below the middle is unsymmetrical. Now three cases may occur: when the temperature reaches the critical temperature the little curve may either be on the left of the critical point 1) or it may be on the right 2), or finally the critical point may fall on the section of the curve itself 3). In the cases A and B the substance will still be homegeneous. Not till after lowering the temperature a little further the curve will reach the so called border-curve also given in the figure with one of its ends. At that moment a very small quantity of a second phase will appear (retardation being excluded): in case A a bubble of vapour will appear in the top of the tube, corresponding to q', in case B a drop of liquid at the lower end of the tube, corresponding to p'' When the temperature goes on being lowered, these small quantities will increase from zero upwards. The conditions of the substance then present in the tube are represented by two sections of the isothermal the one coming on to the border-curve from the vapour-side, the other from the liquid side. From the point in the tube, where the vapour and liquid are in contact, i. e the liquid surface, the phases increase in density downwards and decrease upwards. Gravitation cannot bring any change in the condition of equilibrium and the phases which are in equilibrium with each other at any temperature remain the same. When the temperature reaches some distance below the critical temperature, the lengths of the curves diminish and very soon they may practically be treated as two points, belonging to the border-curve. With a given quantity of substance

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1) (case A, p' q' in fig. 1)

2) (case B, p'' q'')

3) (case C, $p\ r\ q$)

enclosed in a tube above mercury the different cases may of course be realised by taking the volume first a little smaller than the critical volume, afterwards somewhat larger. What will happen however, if the volume is taken very near the critical volume (case C)? At the critical temperature one of the phases, at a certain distance from the ends of the tubes, will have exactly the critical density and pressure. This phase is represented by point r, in which the critical isothermal touches the border-curve. Immediately below the critical temperature in that point of the tube a cloud and then a flat meniscus will appear. The place in the tube, where that will happen, depends on the volume chosen. Consequently: between two limits of volume situated on both sides of the critical volume the distance of which might be calculated from the shape of the critical isothermal and the height of the column, a flat liquid surface will appear at different levels in the tube, the higher the smaller the volume, and, as follows from the consideration of the figure, always exactly at the same temperature, the critical temperature of the substance. In the case of carbonic acid enclosed in a tube of about 10 cm. length, the distance of these limits, between which the liquid surface will appear in the body of the tube, will amount to about 6 percent of the entire volume, as calculated from Gouy's table. The value for this distance resulting from Gouy's experiments ¹) and given by my own ²) is of the same order of magnitude.

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¹) Gouy, Compt. Rend. 116, p. 1289.

²) Kuenen, Communic. etc. n⁰. 8, p. 11—12.

From the above follows immediately what will be observed by reversing the process, i. e. by heating the substance at different constant volumes. If the volume is smaller than a definite volume v_1, the liquid will increase regularly and at a temperature mose or less below the critical temperature fill up the whole tube. If the volume is greater than a larger volume v_2, the liquid will decrease during the heating and evaporate entirely. Between v_1 and v_2 however the liquid surface will rise or fall, but at last become flat and disappear, at a definite temperature independent of which volume between the limits v_1 and v_2 has been chosen. That temperature is the critical temperature and no other.

This result was mentioned by me on a former occasion ¹) without further explanation. It justifies completely 'the method of the meniscus' for determining critical temperatures. The same may be said about the method as it was originally described by Andrews in which, instead of change of temperature at constant volume, was used change of volume at constant temperature, although the first for reasons of practice seems to me to be preferable; with pure substances the method is bound to give correct values for the critical temperature and differences from the results of other methods find their explanation in impurities or in many cases in the uncertainty of the rival methods. The method of the densities (Mathias) ²) which serves very well for determining the critical volume, when the critical tem-

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¹) Kuenen, Communic, etc. n⁰, 8 p. 10.

²) Cailletet et Mathias, Compt. Rend. 102 p. 1202, 104 p. 1563.

perature is already known, is not to be recommended for the critical temperature itself as some extrapolation is always wanted, even when it is applied with the ~~a~~most care [1]). Whichever method is used, it will always be very desirable to stir the substance, because impurities, which are never entirely absent, produce retardation and also differences of density [2]).

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It may also be observed, that the method in question makes it possible to measure the critical pressure and also, with a near approximation, the critical volume of the substance. In taking the volume equal to the volume at which the meniscus appears and disappears in the middle of the column the mistake is only very small. Sometimes the critical volume has been taken equal to the volume at which the liquid at the moment of the disappearing of the meniscus filled the tube entirely: this erroneous procedure leads to great mistakes.

II. In deriving the influence of gravitation on the critical phenomena of mixtures of two substances, I shall make use of the ψ-surface of VAN DER WAALS [3]). I shall only consider the case of one plait, the vapour-liquid plait, existing on the surface. On page 35 of his treatise he treats of the action of exterior forces on the mixture. The results obtained by him have therefore simply to be applied here. The ψ-surface may be described either for a constant weight of the mixture

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[1]) AMAGAT. Compt. Rend. 114 p. 1093—98.

[2]) KUENEN. Commun. etc. n°. 11.

[3]) VAN DER WAALS. Archives Néerl. 24, p. 1—56, Zeitschrift für Phys. Chemie 5, p. 133—173.

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or for a constant number of molecules. In the case before us the first method is preferable as regards simplicity. In fact VAN DER WAALS proves that in that case for phases being in equilibrium under the influence of gravitation $\left(\frac{\delta\psi}{\delta x}\right)_v$ [1]) has a constant value, while in the other case that quantity still depends on the height h and only: $\left(\frac{\delta\psi}{\delta x}\right)_v$ ⌉ $(M_2-M_1)gh$ ($M=$ molecular weight) is a constant. We shall therefore use the first method. In order to show by means of the surface, what phases will be present in a vertical column, we imagine curves to be drawn on the surface, for which $\left(\frac{\delta\psi}{\delta x}\right)_v$ has a constant value. I shall call these curves 'gravitation-curves'. The phases in question form together a section of a gravitation-curve. (For simple substances the gravitation-curve coincides with the isothermal). A second condition makes it possible to determine which points of a gravitation-curve correspond to definite heights of the column. This condition is simply $dp = -\frac{g}{v}\,dh$, and is in itself clear apart from its thermodynamical derivation. If not only the gravitation-curves but also the isopiestics $\left\{p = -\left(\frac{\delta\psi}{\delta v}\right)_x = \text{constant}\right\}$, the determination of which is entirely analogous to that of the gr.-curves, are drawn on the surface these two sets of curves make it possible to derive the phases present in the tube

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[1]) $x =$ composition. The v added to the differential coëfficient expresses that v is kept constant during the differentation.

completely. For our purpose it is sufficient to consider the course of the curves in the critical region. We obtain this soonest, if we use the relation between *dp* on the one and *dx (*or *dv)* on the other side along the gravitation-curve. This relation is given by a formula on page 37 of VAN DER WAALS's treatise, viz:

$$\left\{\frac{\partial^2 \psi}{\partial x^2} - \frac{\left(\dfrac{\partial^2 \psi}{\partial x\, \partial v}\right)^2}{\dfrac{\partial^2 \psi}{\partial v^2}}\right\} d\,x = -\left(\frac{\partial v}{\partial x}\right)_p d\,p \quad . \; . \quad (1)$$

or also by aid of well known relations:

$$\left\{\frac{\partial^2 \psi}{\partial^2 x}\,\frac{\partial^2 \psi}{\partial v^2} - \left(\frac{\partial^2 \psi}{\partial x\, \partial v}\right)^2\right\} d\,x = -\left(\frac{\partial p}{\partial x}\right)_v d\,p \quad . \quad (2)$$

Let:

$$\frac{\partial^2 \psi}{\partial x^2}\,\frac{\partial^2 \psi}{\partial v^2} - \left(\frac{\partial^2 \psi}{\partial x\, \partial v}\right)^2 = A \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

this A is the expression that with $\frac{\partial^2 \psi}{\partial v^2}$ and $\frac{\partial^2 \psi}{\partial x^2}$ determines the stability. In all the points of the connodal curve $A > o$ except in the plaitpoint, that being a point of the spinodal curve at the same time: there $A = o$. If we substitute that in (1) or (2), as in the plaitpoint we have in general $\left(\frac{\partial v}{\partial x}\right)_p$ or $\left(\frac{\partial p}{\partial x}\right)_v \gtrless o$, we find

$$\frac{d\,p}{d\,x} = o \qquad \text{or} \qquad \frac{d\,x}{d\,p} = \infty \,.$$

This result has no other meaning than that in the plaitpoint an element of the isopiëstic coïncides with an element of the gravitation-curve. As the isopiëstic touches the connodal-curve in the plaitpoint the gravitation-curve will do the same. In fig. 2 is represented the case of the plaitpoint lying to the side of the small volumes. The pressure in the plaitpoint in that case is a maximum-pressure and

$$\left(\frac{\partial v}{\partial x}\right)_p > o \qquad \text{or} \qquad \left(\frac{\partial p}{\partial x}\right)_v > o$$

not only in the plaitpoint but also close by it. As at the same time $A > o$, $d\,x$ and $d\,p$ according to (1) and (2) have the opposite sign and the two curves isopiëstic and gravitation-curve will intersect in the manner shown in fig. 2. Two curves which intersect and touch each other in the same point have a mutual contact of the 2nd order. Hence it follows that in the v, x projection not only $\frac{d\,v}{d\,x}$ is equal for both curves in P but also $\frac{d^2\, v}{d\,x^2}$. The curves have the same radius of curvature.

The proof of this proposition may also be given thus. In corresponding points of the connodal curve not only $\left(\frac{\partial \psi}{\partial v}\right)_x$ but also $\left(\frac{\partial \psi}{\partial x}\right)_v$ have the same value. The first can be expressed by saying that the pressure is the same in the two points. In approachting the plaitpoint the two corresponding points approach each other and at last coïncide, in the plaitpoint. From this we conclude at once that the isopiëstic in P has an element in common with the connodal curve, i. e. touches the connodal curve. Exactly the same reasoning holds good for the curve along which $\left(\frac{\delta \psi}{\delta x}\right)_v$ is a constant; i. e. the gravitation-curve also touches the connodal curve in P. Therefore the two curves touch each other and as they have to intersect at the same time the mutual contact will be of the second order: accordingly $\frac{d^2 v}{d x^2}$ equal for both.

We need therefore only determine $\frac{d^2 v}{d x^2}$ for one of the two curves in order to know the same quantity for the other. We shall calculate here $\left(\frac{d^2 v}{d x^2}\right)_p$, i. e. for the pressure-curve [1]).

From $d p = \left(\frac{\delta p}{\delta x}\right)_v \; d x + \left(\frac{\delta p}{\delta v}\right)_x \; d v$ follows:

$$\left(\frac{\delta v}{\delta x p}\right) = - \frac{\frac{\delta^2 \psi}{\delta x \delta v}}{\frac{\delta \psi^2}{\delta v^2}}$$

As moreover for any function ϕ

$$\left(\frac{\delta \phi}{\delta x}\right)_p = \left(\frac{\delta \phi}{\delta x}\right)_v + \left(\frac{\delta \phi}{\delta v}\right)_x \left(\frac{\delta v}{\delta x}\right)_p$$

one finds:

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[1]) The idea of considering the sign of $\left(\frac{d^2 v}{dx^2}\right)_p$ in the plaitpoint I took from a letter from Prof. VAN DER WAALS, written on occasion of my paper communicated to the Physical Society of London. May 24th.

$$\left(\frac{\delta^2 v}{\delta x^2}\right)_p =$$

$$= \frac{- \left(\frac{\delta^2 \psi}{\delta v^2}\right)^2 \frac{\delta^3 \psi}{\delta x^2 \delta v} + 2 \frac{\delta^2 \psi}{\delta x \delta v} \frac{\delta^3 \psi}{\delta x \delta v^2} \frac{\delta^2 \psi}{\delta v^2} - \left(\frac{\delta^2 \psi}{\delta x \delta v}\right)^2 \frac{\delta^3 \psi}{\delta v^3}}{\left(\frac{\delta^2 \psi}{\delta v^2}\right)^3}$$

Into this expression we now introduce the quantity A as defined by (3). This leads to:

$$\left(\frac{\delta^2 v}{\delta x_2}\right)_p = - \frac{\left(\frac{\delta A}{\delta v}\right)_x}{\left(\frac{\delta^2 \psi}{\delta v^2}\right)^2} + \frac{\frac{\delta^3 \psi}{\delta v^3}}{\left(\frac{\delta^2 \psi}{\delta v^2}\right)} A.$$

This expression is generally true. It may be used to determine the course of the p-curves in the v, x projection. In P, where we want to know the value at present, $A = o$, while $\frac{\delta A}{\delta v} > o$ because a point shifting from P in the direction of the positive v-axis enters the unstable region. Hence in the plaitpoint:

$$\left(\frac{\delta^2 v}{\delta x^2}\right)_p = - \frac{\left(\frac{\delta A}{\delta v}\right)_x}{\left(\frac{\delta^2 \psi}{\delta v^2}\right)^2} > o.$$

i. e. the curvature of both isopiëstic and gravitation-curve is turned to the same side as that of connodal curve.

A similar reasoning may be used to determine the relative situation of the curves in case the plaitpoint should lie towards the side of the large volumes of the plait. In that case $\left(\frac{\delta_2 \upsilon}{\delta x^2}\right)_p < o$ because $\frac{\delta A}{\delta \upsilon} > o$ and it appears that again the curvature has the same sign as that of the connodal curve in the plaitpoint.

As regards the second surface described for a constant number of molecules mentioned before, the conditions belonging to it may be decuded from those for the first surface by means of the substitutions.

$$\psi = \frac{\psi'}{M_1\ (1-x') + M_2\ x'} \qquad \upsilon = \frac{\upsilon'}{M_1\ (1-x') + M_2\ x'}$$

$$x = \frac{M_2\ x'}{M_1\ (1-x') + M_2\ x'}$$

where the dashes denote the quantities belonging to the 2nd surface. They can also be derived independently. It has already been stated that the formulas become less simple. Instead of (1) one obtains ¹):

$$\left\{ \frac{\delta^2 \psi'}{\delta x^2} - \frac{\left(\dfrac{\delta^2 \psi'}{\delta x'\ \delta \upsilon'}\right)^2}{\dfrac{\delta^2 \psi'}{\delta \upsilon^2}} \right\} d\ x' = - \left\{ \left(\frac{\delta \upsilon'}{\delta x'}\right)_p + \right.$$

$$\left. + \frac{(M_1 - M_2)\ \upsilon'}{M_1\ (1-x') + M_2\ x'} \right\} d\,p$$

The sign of the second side in this case cannot be fixed in general. Excluding the special case in which the coëfficients become zero the conclusion with respect

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¹) Van der Waals l. c. p. 42 by putting $P_1 = P_2 = gh$.

to the plaitpoint remains the same. If $M_1 > M_2$ as in the case of CO_2 and $CH_3\ Cl$ ¹) the coëfficient is still positive: but this need not be so. With very large volumes, where $\left(\frac{\delta \upsilon'}{\delta x'}\right)_p$ is about zero, the sign depends entirely upon $M_1 - M_2$, but near the plaitpoint such is not the case. In every special case one will have to determine the sign of the second side. However all that cannot affect the general conclusion about the plaitpoint, which forms the basis of the whole argument.

The conclusion in question is sufficient to derive the critical phenomena of a mixture under the influence of gravitation. The most natural way to describe the phenomena is to consider what will happen during continuous change of volume at the temperatures that come into account. In the case represented in fig. 2 if we do not take into account the influence of gravitation we obtain the following result ²): between two definite temperatures, different for every mixture, the temperature of the critical point of contact T_R and the plaitpoint temperature T_P ($T_R > T_P$), with increase of volume, the point representing the condition of the mixture will pass through the connodal curve between the points P and R. In those cases so called retrogade condensation of the first kind (r. c. I.) takes place, i. e. a liquid appears the quantity of which increases regularly from zero up to a certain point and then decreases and at last disappears. Below T_P the condensation is

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¹) Communications etc. n⁰. 4.

²) Communications etc. n⁰. 4, p. 8.

normal, i. e. the liquid surface appears right at the top of the tube and the quantity decreases down to zero, all this with slow increase of volume. Exactly at the plaitpoin-ttemperature the point on the surface passes through the plaitpoint and in that case only a flat liquid surface will appear somewhere in the body of the tube, which falls on further increase of volume and in the meantime becomes more and more distinct, until the liquid is evaporated.

We shall now take into account gravitation. The condition of the mixture is now no longer represented by one point but by a small section of a gravitation-curve, the length of which as with a simple substance is connected with the height of the column. The values of v and x in the different points of the tube are situated on both sides of the mean value of these quantities for the whole mixture. The mean value of x of course does not change with change of volume. If the course of the gravitation-curves, some of which have been drawn in fig. 2 [1], is considered, three cases will be seen to be possible. If the temperature is somewhat below T_P the little curve will with its left end, corresponding to the top of the tube, reach the connodal curve on the right of P. At the top of the tube therefore a liquid surface will appear and the liquid will decrease continually (case A). It may also happen that the temperature is so much above T_P, that the curve-

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[1] These curves may be continued within the plait and the parts contained between the connodal-curve are those which will play a part in the theory of capillarity of a mixture.

section reaches the connodal-curve with its right end between P and R. In that case liquid appears down at the lower end of the tube: the liquid increases, reaches a maximum value, then decreases and disappears (case B). Within a region of definite extent, situated on both sides of T_P, a different thing happens. The gravitation-curve comes into contact with the connodal-curve, the two curves touching each other always exactly in P (case C) [1]. At the point in the tube corresponding to the point of contact (the height of which depends on the temperature at which the change of volume takes place) occur the plaitpoint-pressure, volume and composition. At that point therefore with gradual increase of volume a cloud and afterwards a flat liquid surface will appear. At a certain distance above T_P (the plaitpoint temperature of the homogeneous mixture) the motion of the meniscus will still preserve the character of retrograde condensation I, but at temperatures very near T_P the appearing meniscus will not rise perceptibly, but move downwards from the beginning after its appearance. Hence the region in which retrograde condensation exist will be somewhat smaller than without gravitation. It must not be overlooked that the temperature T_R will also appear a little

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[1] An accurate contemplation of the figure will make clear that these three cases are the only ones possible. In that lies the point of the whole reasoning. It will never happen that the curvesection reaches the connodal-curve between P and R with its left end, which corresponds to the top of the tube. This would lead into extraordinary difficulties.

higher, because the curve-section will reach the connodal curve even if its mean point lies a little beyond the plait. But this rise of $T_{\mathfrak{R}}$ is probable less than the rise of the lower limit of r. c. I, because the influence of gravitation is bound to be greatest near P.

On reversing the process, i. e. in compressing the mixture at constant temperature, the following phenomena appear. Below a definite temperature: normal condensation; next above that a range of temperatures at which the liquid surface disappears during compression before the whole of the mixture is liquid; next a region, in which the meniscus before disappearing begins to fall more or less and at last a region in which the liquid evaporates entirely [1]. This last one is really the only one in which the typical critical phenomenon of mixtures, viz. retrograde condensation, is manifested completely.

This result may explain the difficulty which the determination of the plaitpoint temperature gave me in my experiments on CO_2 and CH_3 Cl [2].

Entirely analogous phenomena will be the consequence of gravitation in the other case, when the plaitpoint lies on the other side of the critical point of contact. I shall not go into this at length. In this case also gravitation will reduce the region in which retrograde condensation (here r. c. II [3]) comes clearly to

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[1] This result was briefly mentioned by me some time ago. Communications etc. No. 4, p. 9 note.

[2] Kuenen, Communications etc. No. 4, p. 12.

[3] „ „ „ „ 13, p. 15.

light. In an experimental investigation which I have carried out lately, originally undertaken with a view to realise the case of r. c. II, the results of which have been communicated by me to the Physical Society of London in its meeting of May 24th, gravitation must have largely contributed in concealing the phenomenon, the possibility of which however could be proved. A circumstance which in the case of mixtures encumbers the observation of the phenomena is, that stirring, though desirable for eliminating retardation, on the other hand disturbs the gravitation-equilibrium and therofore is of little use. With simple substances this drawback of course does not exist.

For insertion in Volume II, N⁰. **13—24.**

Erratum Communication N⁰. 18.

In part of the copies of this Communication the formula on p. 9 line 9 from the top has been printed incorrectly. Read:

$$h^1 = (h + 0{,}029)\,\frac{\dfrac{2d}{(r_3 - r_2)^2}}{\dfrac{1}{r_1} - \dfrac{2d}{(r_3 - r_2)^2}}$$

Erratum Communication N⁰. 20.

In part of the copies of this Communication on the title-page in the title: for plantinum read platinum.

Fig. 2.

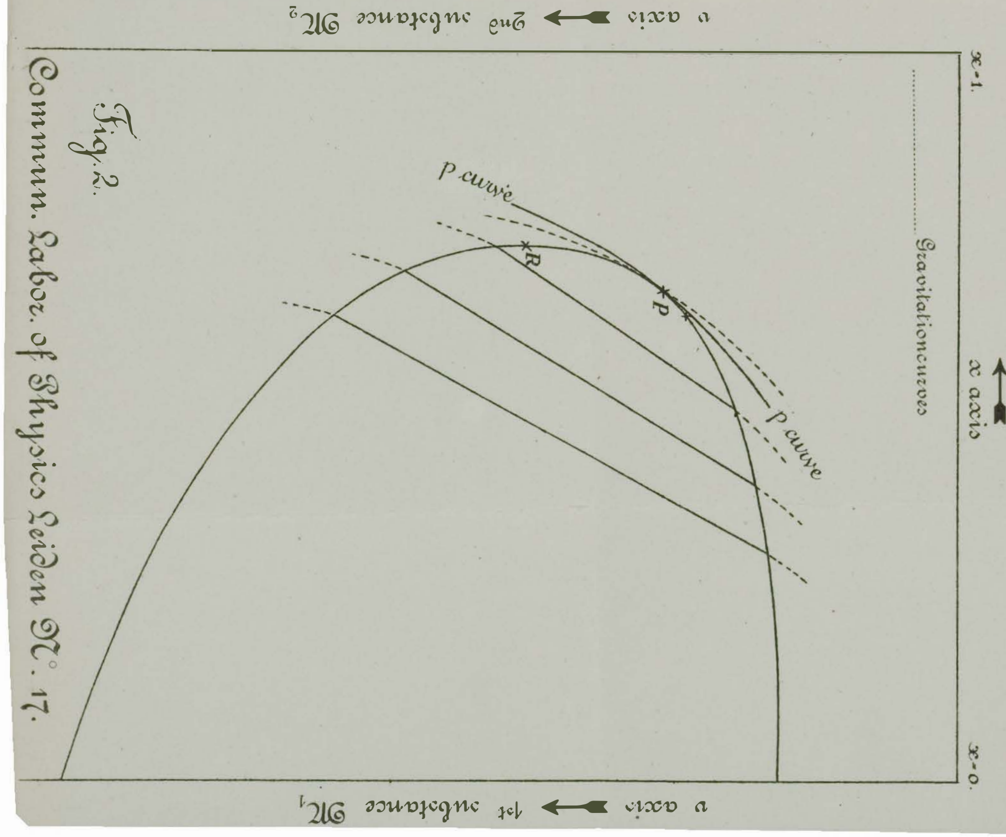
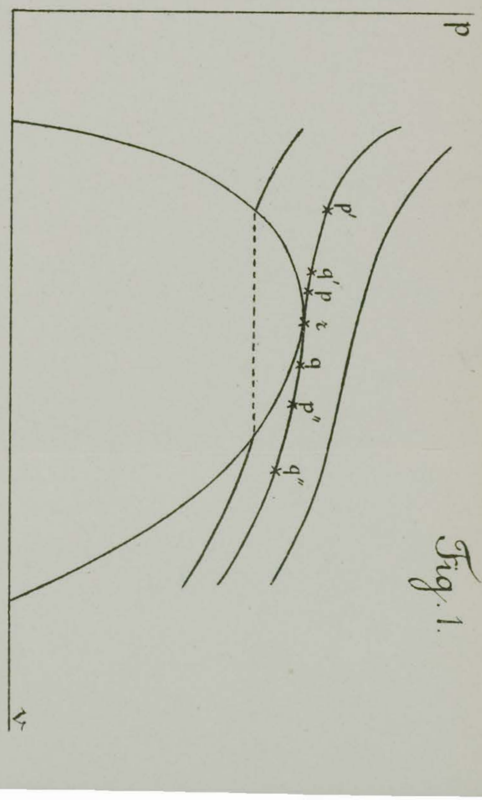


Fig. 1.



Commun. Labor. of Physics Leiden N°. 17.