logram $\times dOdO_1$ or the product of the two cylindres in which points
of velocity were found before impact. The product of the cylindres,
in which points of velocity are found after· impact is equal to the
product of $dOdO_1$ and the area of the rectangle with sides parallel
to the axes $O'd^r$ and $O'd'_1$ described round the parallellogram under
investigation. In this rectangle lie a number of points which have
-no corresponding points in the first rectangle. Only when $m = m_1$
rectangle and paralellogram coincide.

Collisions of opposite kind, now, are such for which the combina-
tions of velocity before impact are represented by points of the
paralellogram in the plane $d'Od'_1$ and after impact by points of the
rectangle in the plane dOd_1.

Physics. — "*Contributions to the knowledge of the ψ-surface of*
van der Waals. XII. *On the gas phase sinking in the liquid
phase for binary mixtures.*" By Prof. II. Kamerlingh Onnes
and Dr. W. H. Keesom. Communication N°. 96^b from the
Physical Laboratory at Leiden.

§ 1. *Introduction.* In what follows we have examined the equi-
librium of the gas phase with the liquid phase for binary systems,
with which the sinking of the gas phase in the liquid phase may
occur.

It lies to hand to treat this problem by the aid of ψ (free
energy)-surfaces for the unity of mass of the mixture (van der Waals,
Continuitat II p. 27) for different temperatures construed on the
coordinates v (volume of the unity of mass of the mixture) and x
(quantity of mass of the second component contained in the unity
of mass of the mixture).

As van der Waals (loc. cit.) has already observed, the laws refer-
ring to the stability and the coexistence of the phases are the same
for these ψ-surfaces as for the more generally used ψ-surfaces for
the molecular quantity. in particular also the coexisting phases are
indicated by the points of contact of the ψ-surface with a plane
which rolls with double contact over the plait in the ψ-surface. In
what follows we have chiefly to consider the projections of the con-
nodal curve and of the connodal tangent-chords on the xv-plane.

More particular cases as the occurrence of minimum or maximum
critical temperature or minimum or maximum pressure of coexistence
we shall leave out of account; we shall further confine ourselves
to the case that retrograde condensation of the first kind occurs.
Moreover we shall restrict ourselves to temperatures, at which the

appearance of the longitudinal plait does not cause any irregularity [1]). The component with the higher critical temperature (T_k) is chosen as first component; its critical temperature is, accordingly, denoted by T_{k_1}. The special case that $T_{k_2} = 0$, is that of a *gas without cohesion* with molecules having a certain extension. The investigation of the ψ-surfaces becomes simpler for this case. For the present it seems probable to us that helium still possesses some degree of cohesion. We will, however, in a following communication compare the case of a gas without cohesion with what the observations yield concerning mixtures with H_e.

§ 2. *Barotropic pressure and barotropic concentration.* We shall call v and x of the gas phase v_g and x_g, of the liquid phase v_l and x_l. At a temperature T a little below T_{k_1}, we shall always have $v_g > v_l$. For then the plait extends only little on the ψ-surface (see fig. 1), the plaitpoint is near the top of the connodal curve, which is turned to $x = 1$, and all the projections of the connodal tangent-chords deviate little in direction from the v-axis, the angle with

the v-axis, $\theta_p = \text{arc tg} \dfrac{x_q - x_l}{v_q - v_l}$, increases regularly if we go from $x = 0$

along the connodal curve to the plaitpoint, but it has but a small value, when $T_{k_1} - T$ is small. Only when we take for T a value a certain amount lower than T_{k_1}, the plait extends sufficiently on the ψ-surface

to allow that $v_g = v_l$ and $\theta = \dfrac{\pi}{2}$.

If at a suitable temperature T we have substances as mentioned at the beginning, as e. g. helium and hydrogen at the boiling-point of hydrogen, we shall find the projection of a connodal tangent-chord denoting the equilibrium considered in the xv projection of the gas-liquid-plait on the ψ-surface for T; to reach it we shall have to ascend from $x = 0$ along the connodal curve up to a certain value of the pressure of coexistence p, before θ, which itself is zero for

$x = 0$, can become $\dfrac{\pi}{2}$. A pressure of coexistence $p = p_b$, under

which $v_g = v_l$ at the temperature T, we call *a barotropic pressure for that temperature*, the corresponding concentrations of liquid and gas phase *the barotropic concentration of the liquid and of the gas phase at that pressure and that temperature*. For when $v_g - v_l$ with increasing pressure of coexistence p passes through zero at $p = p_b$, we find in equilibria with pressures of coexistence above and below the value p_b the phases to have changed positions under the influence of gravity.

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[1]) This will be treated in a following communication.

In order to examine how a barotropic tangent-chord first makes
its appearance on the plait on decrease of T, we point out that with
extension of the plait from T_{k_1} at first $\dfrac{d\theta}{dx}$ remains positive all over
the liquid branch of the connodal curve, so that at first we have to
look for the ·greatest value of θ at the plaitpoint, where we shall
denote its value by θ_{pl}.

When, however, on decrease of T the plait extends over the ψ-
surface, this need not continue to be the case, and we may find
$\dfrac{d\theta}{dx}$ alternately positive and negative. This is immediately seen when
we notice that this must always be the case when the plait extends
all over the ψ-surface.

If with decrease of T the maximum value of θ more and more in-
creases, and T has fallen so low, that the maximum of θ somewhere
in the plait has just ascended to $\dfrac{\pi}{2}$, then at this T the condition for the
barotropic equilibrium $v_q = v_e$ will be satisfied just for the corre-
sponding tangent-chord, and only for this tangent-chord. The *higher
barotropic limiting temperature* is then reached. On further decrease
of temperature the barotropic tangent-chord will then split into two
parallel barotropic tangent-chords, the *higher* and the *lower* tangent-
chord, which at first continue to diverge with further falling tempe-
rature, so that .the higher barotropic tangent-chord may even vanish
from the plait through a *barotropic plaitpoint*, and then, at a lower
temperature, make its appearance again through a barotropic plaitpoint[1]).

At still lower temperature it follows from the broadening of the
plait in the direction of the v-axis, which at sufficiently low tempe-
rature renders the occurrence of a barotropic tangent-chord impossible,
that the maximum of θ falls again, and the barotropic tangent-chords
draw again nearer to each other. At $\theta_{max} = \dfrac{\pi}{2}$ the tangent-chords
coincide again, and the *lower barotropic limiting temperature* is reached.
At lower temperatures $v_g = v_l$ is no longer to be realized, and v_g
is always $> v_l$.

Figs. 2, 3 and 4 represent different cases schematically. In the
spacial diagram of the ψ-surfaces for different temperatures the
barotropic tangent-chords supplemented with the portions of the con-

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[1]) The latter supposes that T_{k_1}/T_{k_2} is not very great; in accepting the contrary
we would come in conflict with the supposition that the longitudinal plait does
not become of influence. Moreover we preliminarily leave out of account the case
that both barotropic tangent-chords follow one another in disappearing or appearing
through a barotropic plaitpoint. [Added in the translation].

nodal curves between the lower and the higher tangent-chords form together a closed surface, which bounds the *barotropic region*.

If on the other hand $\theta_{max} = \theta_{pl}$ remains, till it has reached or exceeded the value $\dfrac{\pi}{2}$, and if not a second maximum value for $\theta > \dfrac{\pi}{2}$ occurs on the plait, a barotropic plaitpoint will occur at the higher barotropic limiting temperature, whereas at lower temperature a *single* barotropic tangent-chord on the plait indicates the equilibrium with $v_q = v_l$. With decreasing temperature this barotropic tangent-chord will at first move along the plait starting from the plaitpoint, but at lower temperatures it will return, and finally (the occurrence of a longitudinal plait being left out of consideration) it will disappear from the plait through a barotropic plaitpoint at the lower barotropic limiting temperature. In this case the barotropic region is bounded on the side towards which the plait extends by barotropic tangent-chords, on the other side by the portions of the connodal curve which are cut off.

It follows from the above that — when the occurrence of barotropic tangent-chords on the ψ-surfaces for a definite pair of substances is attended by the occurrence of barotropic plaitpoints — if $T_b > T_{bpls}$ (*higher baratropic plaitpoint temperature*) or $T_b < T_{bpli}$ *lower barotropic plaitpoint temperature* there always exists at the same time a higher and a lower barotropic tangent-chord ; if $T_{bpls} > T_b > T_{bpli}$ there exists only one barotropic tangent-chord.

The nature of the barotropic phenomenon for He and H_2 may serve for arriving at an estimation of the critical temperature of He. According to the investigation of one of us (K. See Comm. N°. 96 c.) it is probable that the appearance of *a single* barotropic tangent-chord for He—H_2 at the temperature of boiling hydrogen would point to $T_{kHe} <$ about 2°, whereas on the other hand when T_{kHe} is higher, a higher and a lower barotropic tangent-chord is to be expected. Further that, as was already observed in Comm. No. 96 a. (Nov. '06) a barotropic tangent-chord can only appear in the gas-liquid-plait when very unusual relations are satisfied between the properties of the mixed substances, which for the present will most likely only be observed for He and H_2.

Whether it is possible that more than one barotropic region occurs, and whether one or more barotropic tangent-chords can move from the plaitpoint past the critical point of contact, is still to be examined. Also whether it is possible that the lower barotropic limiting temperature descends lower than T_{k_2}, so that fig. 5 might be realised. With regard to these questions too it is only of practical importance to

know in how far the properties of He and H_2 create that possibility.

§ 3. *Barotropic phenomena at the compression of a mixture of definite concentration.* What will take place in this case is easy to be derived from the foregoing survey of the different equilibria which are possible at a same temperature. For the further discussion we have to trace the *isomignic* line, the line of equal concentration ($x =$ const.) for this mixture, and to examine the section with the connodal curve, the successive chords, and finally again with the connodal curve.

In the description of the barotropic phenomena we shall confine ourselves to the more complicated case, that at the T considered both a higher and a lower barotropic tangent-chord occur, after which it will be easy to survey the phenomena when only one barotropic tangent-chord appears.

To distinguish the different cases we must divide the liquid branch of the connodal curve at T into an *infra-* ($x = 0$ to $x = x_{lb_i T}$, *lower barotropic concentration of the liquid phase at T*), *inter-* ($x_{lb_i T}$ to $x_{lb_s T}$) and *supra-* ($x = x_{lb_s T}$ to $x = x_{pl}$)-*barotropic* part, and the gasbranch into the three corresponding pieces falling within and on either side of the region between the two barotropic tangent-chords (the lower $b_i T$ and the higher $b_s T$) at that temperature.

Whether the phenomena of retrograde condensation attend those of the barotropic change of phase or not depends on this: whether both barotropic concentrations of the gas phases fall below the plait-point concentration or not.

Let us restrict ourselves in this description to the case that this complication does not present itself or let us only consider mixtures for which $x < x_{pl}$. On compression the first liquid accumulates in the lower part of the tube for $x < x_{gb_i T}$ and for $x_R > x > x_{gb_s T}$, and in the higher part for $x_{gb_s T} > x > x_{gb_i T}$. On further compression, when $x_{gb_i T} > x_{lb_s T}$, change of phase will take place *once* for mixtures of the concentration x, so that $x_{gb_s T} > x > x_{gb_i T}$ or $x_{lb_s T} > x > x_{lb_i T}$; it will take place *twice* for mixtures of the concentration x, so that $x_{gb_i T} > x > x_{lb_s T}$. So the last remains of the gasphase will vanish above for $x < x_{lb_i T}$ and for $x_{pl} > x > x_{lb_s T}$, and below for $x_{lb_s T} > x > x_{lb_i T}$. If it is possible that over a certain range of temperature the barotropic tangent-chords get so far apart that $x_{lb_s T} > x_{gb_i T}$, change of phase will again take place *once* for these temperatures for mixtures of the concentration x, so that $x_{gb_s T} > x > x_{lb_s T}$ or $x_{gb_i T} > x > x_{lb_i T}$.

This description will, of course, only be applicable to He and H_2 when the suppositions mentioned prove to be satisfied.

§ 4. *Disturbances by capillary action.* As is always tacitly assumed in the application of the ψ-surface when the reverse is not expressly stated, the curvature of the surfaces of separation of the phases is put zero in the foregoing discussion. If the curvature may not be neglected, e. g. at the compression of a mixture in a narrow tube, then, when the barotropic pressure is exceeded, the phase which has thus become heavier, will only sink through the lighter phase under it, when the equilibrium has become labile taking the capillary energy of the surface of separation into account. For this it is required that θ_p has become larger than $\frac{\pi}{2}$ to an amount of $\Delta\theta_{cap}$, which will depend on the capillary energy of the surface of separation and the diameter of the tube in which the experiment is made. Thus capillarity causes a retardation of the appearance of the barotropic phenomenon: both with increase and with decrease of pressure the barotropic tangent-chord must be exceeded by increase or decrease of pressure to a certain amount, before the two phases interchange positions. In this way the difference of pressure mentioned in Comm. N°. 96*ⁿ*, (Nov. 1906, p. 460) between the sinking of the gas phase chiefly consisting of helium and its rising again at expansion (49 and 32 atms.) is e. g. to be explained by the aid of the following suppositions which are admissible for a first estimation.

1. that at — 253° and 32, resp. 49 atms. He is in corresponding state with H_2 at 150° and 160, resp. 245 atm., in agreement with the assumptions $M_{He}v_{kHe} = \frac{1}{4}M_{H}v_{kH}$ according to the ratio of the molecular refractive powers, $T_{kHe} = 1°.5$ (according to OLSZEWSKI $< 1°.7$); if the gas phase consisted only of He (molec. weight 4), the density at the temperature and pressures mentioned would be 0.062, resp. 0.081, and if moreover the liquid phase had the same density with the two pressures, $\Delta\theta_{cap}$ would have to correspond to a difference of density of $\pm$ 0.01; owing to the fact that the two last mentioned suppositions are not satisfied, the difference of density will be smaller;

2. that the capillary energy of the surface of separation between the phases coexisting at the above temperature and pressures is not many times smaller (or greater) than that of liquid hydrogen at that temperature in equilibrium with its saturated vapour, and that the latter may be derived from that of nitrogen [1]) by the aid of the principle of corresponding states. The gas bubble will then in a tube like that in which the experiment described in Comm. N°. 96*a* was made (int. diam. 8 mm.) only sink through the liquid or rise again, when

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[1]) BALY and DONNAN, Trans. Chem. Soc. 81 (1902) p. 907.

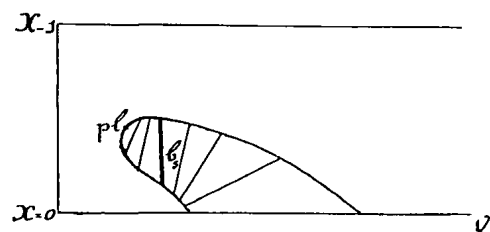Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. "Contribution to the knowledge of the ψ-surface of van der Waals. XII. On the gasphase sinking in the liquid phase for binary mixtures."
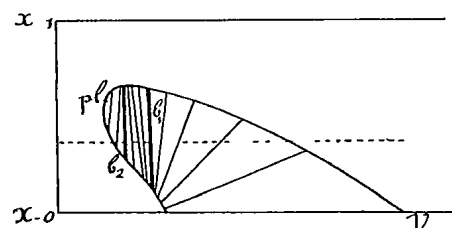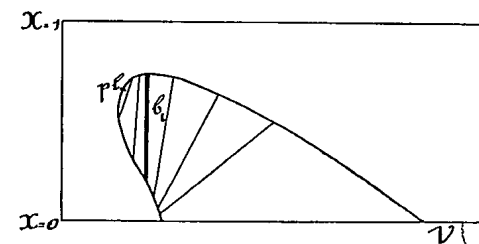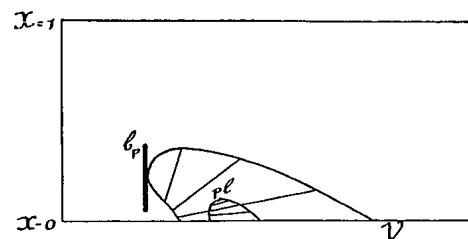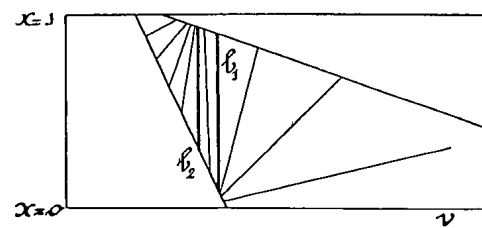

Fig. 2.

Fig. 3.

Fig 4.

Fig. 1.

Fig. 5.

the difference of the radii of curvature of the tops of the bounding menisci exceeds that between 3 and 5 mm.

At those temperatures for which $\theta_{max} < \dfrac{\pi}{2} + \Delta\,\theta_{cap}$, the phenomenon of the phase which is uppermost at low pressure, sinking and rising again does not make its appearance in consequence of gravity alone. If this condition is satisfied for mixtures of a definite pair of substances for every temperature between the lower and the higher barotropic limiting temperature, the phenomenon could only be realised for these mixtures by the aid of a suitable stirrer.

§ 5. *Remarks on further experiments with helium and hydrogen.*

a. In the experiments mentioned in Comm. N°. 96[a] the gas phase proved to remain below on compression to the highest pressure which the apparatus will allow. When we repeat these experiments at a higher temperature (which may e. g. be obtained by boiling the hydrogen of the bath under higher pressure[1])) it is to be expected that the barotropic pressure will first rise, as in the beginning starting from — 253° the gas phase will continue to expand more strongly than the liquid phase. At higher temperature the liquid phase begins to expand more strongly than the gas phase, but the mutual solubility plays already such an important rôle then that a definite expectation cannot be expressed, unless this, that on account of the retreating of the plait and the impossibility of the barotropic tangent-chord to reach the side of the hydrogen, the higher barotropic limiting temperature may be pretty soon reached. Also in connection with the estimation, which may be made from this concerning T_{kHe}, it will be of importance to investigate whether with a suitable concentration and at a suitable higher temperature we may observe *the liquid phase sinking after it had first risen.* That the phenomena at higher temperature, if the glass tube used should prove strong enough to bear the pressure, should be prevented by capillary action, is not probable, as capillarity together with the differences of density decreases at higher temperature; moreover in spite of capillarity the phenomena might be realised by the aid of a suitable stirrer.

b. With decrease of temperature the limit is soon reached at which we meet with the solid phase. The question rises whether then the phenomenon: the *solid phase, (the solid hydrogen) floating on the gas phase (chiefly the as yet still gaslike helium),* might not be realised.

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[1]) Or by using the vapour from boiling hydrogen in a separate vessel [added in the translation].