Dr. J. P. KUENEN. *On the condensation of a mixture of two gases.*

In a memoir by DUHEM about mixture of two substances recently published[1] in Chapter III[2] the problem of the condensation of a mixture of two gases is discussed. The results obtained by this investigation are laid down by the author in the 16th[3] and 17th[4] figures of his memoir. It is my intention in this paper by using the theory of VAN DER WAALS[5] as far as is needed to complete DUHEM's representation of the phenomena and to correct some mistakes, which have been made by him. Moreover some experimental data will be communicated, which will confirm the theoretical results of this paper.

DUHEM in his investigation uses the thermodynamical potential at constant pressure[1]), which he treats as a function of temperature, pressure and composition. He introduces the potentials for the components in the mixture (GIBBS) and arrives at the well-known conditions of equilibrium between two coëxisting phases[2]):

$$\begin{aligned} F_1(\xi\,\pi\,\tau) - f_1(\chi\,\pi\,\tau) &= 0 \\ F_2(\xi\,\pi\,\tau) - f_2(\chi\,\pi\,\tau) &= 0 \end{aligned} \quad . \quad . \quad . \quad . \quad (1)$$

π denotes the pressure, τ the temperature, the F's the potentials in the liquid phase, the f's those in the vapour, ξ and χ the composition of the liquid and the vapour (i. e. the ratio of the mass of the second to the mass of the first substance), whereas 1 refers to the substance of the higher, 2 to that of the lower critical temperature.

If we imagine ξ to have been eliminated from those two equations and regard π, τ and χ as the coördinates of a point, the equation obtained represents a surface, which DUHEM calls: 'surface de rosée' and which exhibits the conditions of equipoise between the two phases, i. e. the pressure and temperature at which in a mixture (χ) the first small quantity of liquid (rosée) will appear. By projecting the sections of this surface by planes perpendicular to the axis of χ on the plane of $\pi\,\tau$ we obtain the so-called 'lignes de rosée', which give a clear image of the corresponding pressure and temperature at which from a mixture of given composition a liquid phase will begin to condensate. By differentiation of the equations (1) with respect to

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[1]) Travaux et mémoires des facultés de Lille. III Mémoire 13. P. DUHEM, Dissolutions et mélanges. Troisième mémoire 1894.

[2]) l. c. p. 47—75.

[3]) l. c. p. 58.

[4]) l. c. p. 66.

[5]) Archives Néerl. 24. p. 1—56.

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[1]) DUHEM, Le potentiel thermodynamique 1886.

[2]) a. o. l. c. p. 52, formula (9).

ξ, χ, π and τ and elimination of $d\xi$ the following equation is obtained [1]:

$$\left[\frac{\delta F_1}{\delta\pi}+\xi\frac{\delta F_2}{\delta\pi}-\frac{\delta f_1}{\delta\pi}-\xi\frac{\delta f_2}{\delta\pi}\right]\delta\pi+\left[\frac{\delta F_1}{\delta\tau}+\xi\frac{\delta F_2}{\delta\tau}-\frac{\delta f_1}{\delta\tau}-\xi\frac{\delta f_2}{\delta\tau}\right]d\tau=$$

$$=-(\chi-\xi)\frac{\delta f_2}{\delta\chi}d\chi \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and from (2) by means of well known thermodynamical relations [2]:

$$\frac{E}{\tau}\Big[(1+\xi)\,Q-(1+\chi)q+(\xi-\chi)l_2\Big]d\tau+$$

$$+\left\{(1+\xi)\,V-(1+\chi)v+(\chi-\xi)\left[v+(1+\chi)\frac{\delta v}{\delta\chi}\right]\right\}d\pi=$$

$$=-(\chi-\xi)\frac{\delta f_2}{\delta\chi}d\chi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which Q, q and l_2 denote definite quantities of heat, V and v specific volumes of the liquid and the vapour.

By aid of this equation and a few hypothesis Duhem derives the form and relative position of the 'lignes de rosée', as they must be situated between the two curves, which hold good for the pure substances, i. e. between the two vapourpressure-curves; and he adds, what he calls the 'ligne critique', i. e. locus of the points at which the corresponding liquid and vapour-phases become identical. In the way sketched out here the figures 16 and 17 of his memoir have been obtained. His conclusions briefly come to this: for two groups of mixtures, which are contiguous to the pure substances, the process of condensation *must* be

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[1] l. c. p. 53 formula (10).

[2] l. c. p. 54 formula (13).

normal at all temperatures up to the critical temperature: for an intermediate group of mixtures however not contiguous to the pure substances the *possibility* of retrograde condensation exists.

According to Duhem [1] the principal lines of this theory were drawn by him as early as 1888 [2] in his memoir on the condensation of Cailletet's mixture of carbonic acid and air. Though not intending to refute this rather vague assertion, I cannot but point out that 1⁰ as Duhem himself states, in 1888 the 'ligne critique' was not yet taken into consideration by him; 2⁰ the particular form of the 'ligne de rosée' was introduced as an hypothesis, however the phenomenon of retrograde condensation was not predicted from it [3]) and 3⁰ entirely in accordance with that,

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[1] l. c. passim, a. o. p. 71: "En 1888 nous avons proposé...." and "en résumé, dès ce moment, nous avons esquissé les principaux traits de la théorie que l'on vient de lire; nous avions seulement omis de considérer la ligne critique du mélange."

[2] P. Duhem. Journ. de Phys. 2 VII p. 158 1888.

[3] When Duhem writes (l. c. 1888 p. 166): "à ce moment le liquide disparaît pour ne plus reparaître sous aucune pression" it appears from the accordance with Cailletet's experiments, which he observes, that he has not in view the disappearing of the liquid phase by a gradual diminishing of the quantity of it, but by the flattening and disappearing of the liquid-surface, though as appears from his recent memoir a logical application of the theory, which he had started, might have led him to draw the conclusion, that Cailletet's experiments give a false image of the condensation-phenomena. Cf. the abstract of Duhem's memoir of 1888 in Beibl. 13. p. 156 by M. P.

the results obtained at that time were regarded by him as an explanation of Cailletet's experiment ("Nous n'avons pas besoin de faire ressortir l'accord, que ces conséquences présentent avec les faits, que M. Cailletet a observés" [1]), whereas now he writes: "or ces conclusions ne sont pas conformes aux observations de M. Cailletet etc." [2]). Therefore I think that my priority with respect to the prediction as to the experimental confirmation of retrograde condensation cannot be questioned [3]). Moreover its complete explanation and in general of the critical phenomena of mixtures, which has been derived by me from van der Waals's theory, is not included in Duhem's theory, because in it the composition, density and quantities of the coëxisting phases do not come to light properly. Therefore, when Duhem writes [4]): "la théorie donnée par M. van der Waals et par M. Kuenen concorde entièrement avec celle, que nous venons de développer" we should read it this, that Duhem's results regarding the condensation of gaseous mixtures, as far as they are right, are contained in the more complete theory of van der Waals. It will appear however, that the graphical method, introduced here by Duhem, with π and τ as the axes of coördination, exhibits the phenomena very clearly and even gives occasion to the prediction of new facts, which would not have been directly derived from van der Waals's surface so easily.

Comparing however Duhem's conclusions, briefly stated above, with what may be drawn from the thermodynamical surface of van der Waals, we find a striking difference. The result of van der Waals's theory, taken generally, regarding the problem now before us comes to the existence of the so-called first plait, the plaitpoint of which appears on the possible part of the surface as soon as the temperature comes between the two critical temperatures of the pure substances. As this plaitpoint can only coïncide with the point, which I have called the critical point of contact, in a special case at one definite temperature and in general must deviate to either of the two sides of the plait, to the liquid-side as a rule, the condensation *must* be retrograde between two definite temperatures for *all* mixtures possible between the two substances and not, as Duhem has it, for a system of mixtures between certain limits only. The figures 16 and 17 are therefore incorrect. In order to obtain the correct representation of the phenomena we shall follow the way taken by Duhem and, if needed, make use of the general result of the complete theory as it has been formulated above: in this manner the difference with Duhem will come to light in due time.

Duhem, as we saw it, draws the curves, which refer to the beginning of the condensation (lignes de rosée). It seems natural to add the curves giving the relation between π and τ at the end of the condensation of a

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[1]) P. Duhem 1888. p. 167.

[2]) P. Duhem 1894. p. 74.

[3]) Communications etc. n°. 4. Archives Néerland. 26. p. 374 sqq.

[4]) l. c. 1894 p. 73.

definite mixture. The pertaining formulas are analogous to the formulas (2) and (3). From the same equations of equilibrium (1) by differentiation and elimination this time of $d\chi$ we get two other formulas, in which only L_2 is a new quantity with a meaning analogous to that of l_2 [1]), whereas for clearness' sake accents have been put to the other letters.

$$\left[\frac{\delta F_1}{\delta \pi}+\chi'\frac{\delta F_2}{\delta \pi}-\frac{\delta f_1}{\delta \pi}-\chi'\frac{\delta f_2}{\delta \pi}\right]d\pi+$$

$$+\left[\frac{\delta F_1}{\delta \pi}+\chi'\frac{\delta F_2}{\delta \tau}-\frac{\delta f_1}{\delta \tau}-\chi'\frac{\delta f_2}{\delta \tau}\right]\delta\tau=-(\chi'-\xi')\frac{\delta F_2}{\delta \xi}d\xi \;.\;.\; (4)$$

from which:

$$\frac{E}{\tau}\left[(1+\xi')\,Q'-(1+\chi')\,q'+(\chi'-\xi')\,L_2\right]d\tau+$$

$$+\left\{(1+\xi')\,V'-(1+\chi')v'+(\chi'-\xi')\left[V'+(1+\xi')\frac{\delta V'}{\delta \xi'}\right]\right\}d\pi=$$

$$=-(\chi'-\xi')\frac{\delta F_2}{\delta \xi}d\xi. \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\; (5)$$

The direction of the two lines is obtained by putting in (3) and (5) $d\chi=o$ and $d\xi\ o=$ respectively. Of the two formulas obtained in this manner the first occurs in DUHEM's memoir [2]):

$$\left(\frac{d\pi}{d\tau}\right)_v=-\frac{E}{\tau}\,\frac{(1+\xi)\,Q-(1+\chi)\,q+(\chi-\xi)l_2}{(1+\xi)\,V-(1+\chi)\,v+(\chi-\xi)\left\{v+(1+\chi)\frac{\delta v}{\delta \chi}\right\}}\;(6)$$

$$\left(\frac{d\pi}{d\tau}\right)_l=-\frac{E}{\tau}\,\frac{(1+\xi')Q'-(1+\chi')q'+(\chi'-\xi')L_2}{(1+\xi')V'-(1+\chi')v'+(\chi'-\xi')\left\{V'+(1+\xi')\frac{\delta V'}{\delta \xi'}\right\}}\;(7)$$

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[1]) DUHEM l. c. 1894, p. 6–8.

[2]) DUHEM l. c. 1894 p. 56 formula (16).

It should be observed, that (6) and (7) only relate to the same mixture, if we take $\chi=\xi'$, i. e. if the vapour-phase of DUHEM's curve has the same composition as te liquid-phase of our curve.

With rise of temperature the two curves will approach each other and at last meet in a point corresponding to the plaitpoint of VAN DER WAALS's surface. In the plaitpoint the phases have equal composition and equal density. In order to introduce this condition, we devide the numerator and denominator by $\chi-\xi$ and $\chi'-\xi'$ and by some transformations we find:

$$\left(\frac{d\pi}{d\tau}\right)_v=-\frac{E}{\tau}\,\frac{-q-(1+\xi)\frac{q-Q}{\chi-\xi}+l_2}{-(1+\xi)\frac{v-V}{\chi-\xi}+(1+\chi)\frac{\delta v}{\delta \chi}} \;.\;.\;.\; (8)$$

$$\left(\frac{d\pi}{d\tau}\right)_l=-\frac{E}{\tau}\,\frac{-Q'-(1+\chi')\frac{q'-Q'}{\chi'-\xi'}+L_2}{-(1+\chi')\frac{v'-V'}{\chi'-\xi'}+(1+\xi')\frac{\delta V'}{\delta \xi'}} \;.\;.\;.\; (9)$$

Now, when χ and ξ, and χ' and ξ' approach each other, all quantities in (8) and (9), the four fractions included, will remain finite. Moreover we have;

$$\xi=\chi=\xi'=\chi',\ q=Q=q'=Q',\ v=V=v'=V',$$
$$l_2=L_2,\ \frac{\delta v}{\delta \chi}=\frac{\delta V'}{\delta \xi'},$$

and as the point has the properties of a plaitpoint the differential coëfficients, to which the four fractions:

$$\frac{q-Q}{\chi-\xi},\ \frac{v-V}{\chi-\xi}\quad\text{and}\quad\frac{q'-Q'}{\chi'-\xi'},\ \frac{v'-V'}{\chi'-\xi'}$$

approach, will become identical two by two. The expressions (8) and (9) therefore become equal in the plaitpoint, i. e. the curves meet in such a manner, that the tangents coïncide. A set of two of those curves belonging together we shall call a *border-curve*. The meeting point corresponds with the plaitpoint and is situated on the 'ligne critique' which therefore we prefer to call '*plaitpoint-curve*'. In order to find the direction of the plaitpoint-curve in a given point, we must make use of the conditions fulfilled by a plaitpoint. These are $\chi = \xi$, $V = v$ to begin with. Besides putting $d\tau = 0$ for instance in (3) we find the relation between $d\pi$ and $d\chi$ on the connodal curve of the plait In the plaitpoint we have $\frac{d\pi}{d\chi} = 0$. Introducing this condition we find as the conditions of a plaitpoint: $\frac{df_2}{d\chi} = 0$ and in the same manner from (5) $\frac{dF_2}{d\xi} = 0$ (and consequently $\frac{df_1}{d\chi} = 0$, $\frac{dF_1}{d\xi} = 0$). These conditions added to the other $\chi = \xi$, $V = v$ and $\chi' = \xi'$, $V' = v'$, we can now again introduce into the complete equations (3) and (5): by doing so we get the relation between $d\pi$ and $d\tau$ for the plaitpoint-curve; $\frac{d\pi}{d\tau}$ is found to agree entirely with the same quantity for the border-curve in the plaitpont, and so we arrive at the conclusion, that the border-curves touch the plaitpoint-curve, i. e. that the plaitpoint-curve is the envelop of the border-curves.

We come to the same conclusion by the following reasoning using the properties of the plait. We consider a definite mixture with its plaitpoint-temperature. With rise of temperature towards the plaitpoint-temperature of the mixture the change of pressure of the mixture can be regarded as consisting of two parts: one part is due to the fact that the composition belonging to the plaitpoint approaches the composition of the mixture; the second part is the change of the pressure in the plaitpoint itself. As the temperature approaches the plaitpoint-temperature of the mixture, the first part of the change approaches to zero and becomes zero at last, because $\frac{d\pi}{d\chi} = 0$ along the connodal curve in the plaitpoint. Only the second part, the change of the plaitpoint-pressure itself, remains. Hence $\frac{d\pi}{d\tau}$ for the mixture in the plaitpoint is equal to the same quantity along the plaitpoint-curve *q. e. d.* [1]).

Instead of the figures 16 and 17 of Duhem's memoir we obtain a figure like figure 1. The curves are for the greater part experimental. The figure represents the case of mixtures of carbonic acid and methyl chloride. The vapourpressure curve for CH_3Cl is drawn according to my own experimental data [2]), the one for CO_2 according to Amagat's results [3]): they end in the two critical points C_1 and C_2. The border-

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[1]) A meeting of the 'ligne critique' and the 'ligne de rosée' at a definite angle, as is the case in Duhem's figures, is therefore impossible.

[2]) Arch. Néerl. 26, p. 392—395.

[3]) Journ. de Phys. (3) 1. p. 288.

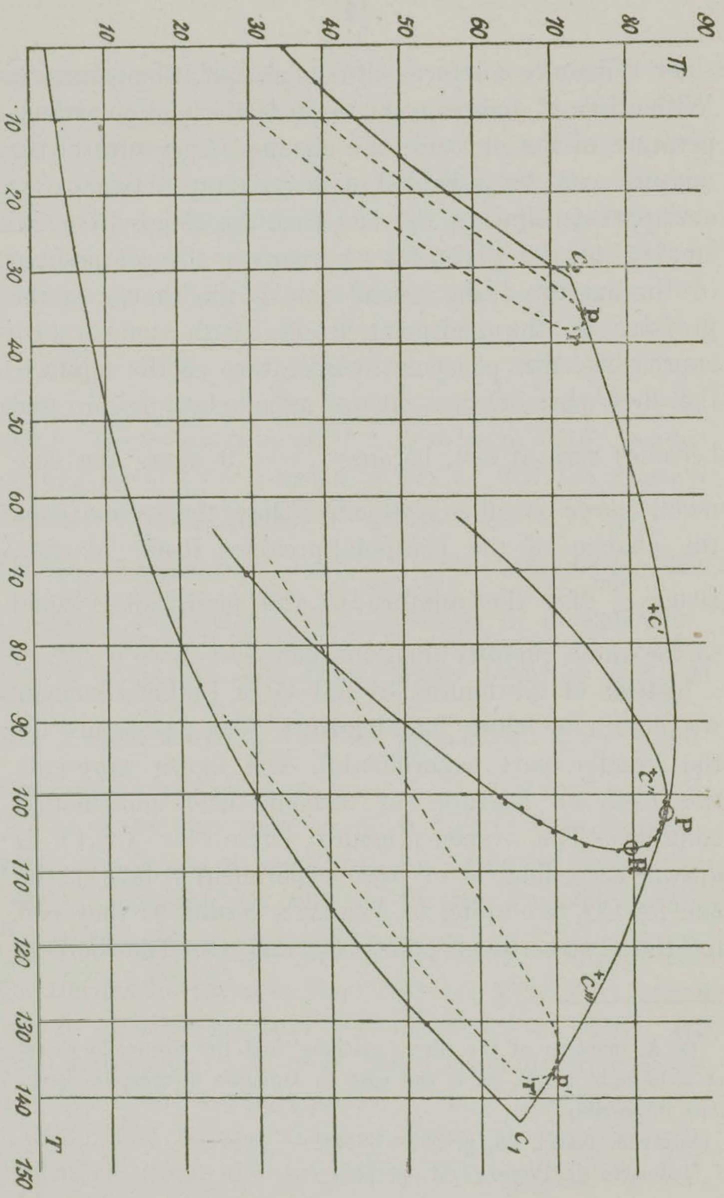

Fig 1.

curve drawn in the figure holds good for a mixture of $^2/_5$ CO_2 and $^3/_5$ CH_3Cl, which I experimented on in 1892. A part of my results was published before on occasion of my first paper regarding retrograde condensation and the critical phenomena of mixtures [1]). Though only few, these observations, now that I have represented them graphically on occasion of the publication of Duhem's memoir, appear to be quite sufficient to show the form of the border-curve with great approximation: it entirely agrees with what was to be expected from the above theory.

Temp.	Press. at the beginning.	Press. at the end.
70	28.8	64.9
100	63.1	—
100.6	63.3	84.4
101.5	65.7	84.7
103.0	67.9	84.0
104.0	69.7	83.8
105.0 [2])	72.2	83.2
106.1	74.0	82.1
106.7	78.6	80.2

From these numbers we derive as probable values for the temperature and pressure of the critical point of contact 106.8 and 79.5 (point R).

The plaitpoint-curve has been drawn in such a

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[1]) Communications etc. n⁰. 4. p. 13.

[2]) l. c. we gave 73.3 and 83.8: the calculation had been only preliminary then.

manner that it touches the border-curve of the mixture $^2/_5$ CO_2 in its plaitpoint P. We may not expect the critical points of the other mixtures [1]) indicated as C′, C″, C‴ to lie on the plaitpoint-curve. For these points were determined before I had made clear the difference between the plaitpoint-temperature and the temperature of the critical point of contact. Hence exactness wass impossible and the only thing, we may say, is that the points as they were fixed must lie somewhere between the two real critical points p and r, rather nearer to r: the plaitpoint-curve is drawn in such a manner that its position with relation to C′, C″ and C‴ is in accordance with that supposition. Two dotted curves have been added to the figure not having an experimental basis; they serve to show the slowly narrowing of the border-curves and the transition into the vapourpressure-curves.

An extensive interpretation of the figure seems hardly necessary. All the border-curves will be seen to have a vertical tangent: consequently all the mixtures must show retrograde condensation between the two critical points p and r. The line drawn through all the points r terminates in the two critical points C_1 and C_2, in contrast to the same line in Duhem's figures, which ends in two points Y_1 Y_2 situated on the plaitpoint-curve. It is evident, how it can be, that without any discontinuity mixtures differing only a little from the pure substances immediately show retrograde condensation and a vertical tangent in contrast to the curves for the pure substances themselves.

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[1]) Archives Néerl. p. 398, 401, 403.

It should be observed that only in an exceptional case the plaitpointpressure is a maximums-pressure at the same time: whether the maximum occurs on the liquid branch of the border-curve or on the vapour-branch depends upon the fact whether the curve rises or falls in the point under consideration. Both cases occur in the figure.

The intersection of two border-curves gives the pressure and temperature at which the mixtures, to which the curves belong, may coëxist.

Some time ago [1]) the possibility of a second kind of retrograde condensation was pointed out by me, in which compression would occasion the appearance and subsequent disappearance of a vapour-phase, instead of a liquid-phase. In this case the plaitpoint on van der Waals's surface must lie towards the vapour-side of the critical point of contact. Transferring this into the graphical representation used here we get, that the plaitpoint will lie beneath the critical point of contact and this point consequently on the liquid-branch of the border-curve. Taking into account the connection between border-curve and plaintpoint-curve we find that this will be the case, if the vapourpressure-curve belonging to C_1 lies above that for C_2 and also for a part of the mixtures, if the plaitpoint-curve has a vertical tangent, or, which comes to the same, if the

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[1]) Archives Néerl. p. 26. p. 388.

critical point of contact of a part of the mixtures lies outside the critical temperatures of the two substances

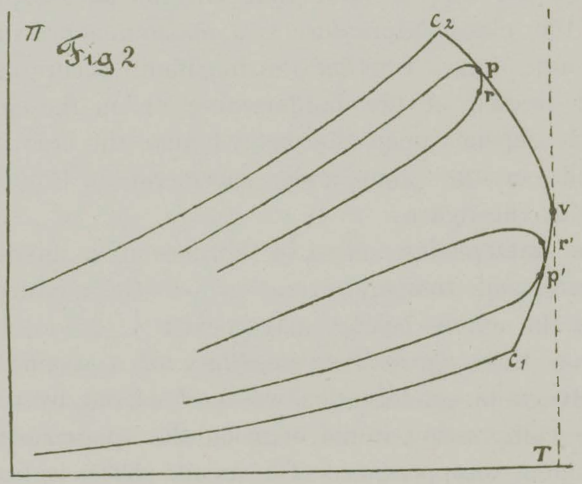

Figure 2 shows, what the situation of the curves might be, if the critical temperatures of a part of the mixtures are higher than those of the pure substances. In one of the border-curves p lies above r; the other has a plaitpoint p', which lies beneath v, at which point the plaitpoint-curve has a vertical tangent: p' therefore falls beneath the critical point of contact r and between the two corresponding temperatures retrograde condensation of the second kind must exist. Experiments will have to decide, whether this case may occur.

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COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 14.

Dr. H. KAMERLINGH ONNES on the cryogenic laboratory at Leiden and on the production of very low temperatures.

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