The	follow ng	values were found:	
		Obs.	Calc.
	CH ₃ Cl	143.0	143.0
	$\frac{3}{4}$ C H ₃ Cl	123.0	117.8
	$\frac{1}{2}$ C H ₃ Cl	97.1	90.9
	$\frac{1}{4}$ C H ₃ Cl	65.4	62.0
	$\frac{1}{9}$ C H ₃ Cl	46.0	45.1
	$C O_2$	31.0	31.0

At last from the equations some Tables were calculated for the deviations from DALTON's law and for the increase of pressure by mixing at constant volume. Dr. J. P. KUENEN. On retrograde condensation and the critical phenomena of mixtures of two substances.

In my dissertation "Measurements concerning the surface of VAN DER WAALS for mixtures of carbonic acid and methyl chloride. Leiden 1892"¹) I discussed a case, which occurs pretty often with mixtures of two substances, namely that by compression during the condensation, i. e. in those conditions, in which two phases are in equilibrium, the surface between the two phases gradually becomes flatter and at length disappears entirely. This is the well-known phenomenon, which was successively observed by CAILLETET ²), VAN DER WAALS ³), ANDREWS ⁴) and others and also during my investigations under certain circumstances. I succeeded by aid of VAN DER WAALS's theory in discovering the probable cause of it and to open the prospect of an early experimental confirmation. The following

²). Compt. Rend. 90, p. 210.

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³) The continuity of the liquid and gaseous states. Phys. Memoirs etc. I 3, p. 472.

⁴) Phil. Trans. 178, p. 53.

¹⁾ cf. the above communication.

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may serve to recall these facts and to complete them.

Examining how, according to the theory, the condensation must take place, and ascribing to the first plait ') the peculiar form, which it must probably have for temperatures between the critical temperatures of the two ingredients ²), I concluded, that at a given temperature we can arrange the mixtures in three groups according to the nature of the condensation: for the first group, consisting of those mixtures, which contain the largest quantity of the substance of the lower critical temperature, a separation in two coëxisting phases is impossible. For a second group the condensation has the ordinary aspect, that is to say, the relative quantity of the denser phase regularly increases with decreasing volume, till the other phase has disappeared; these mixtures contain the largest quantity of the substance possessing the highest critical temperature. Between these groups there is a third, for which the relative quantity of the denser phase at first increases by compression, attains a maximum and then again diminishes and disappears: with expansion the same phenomena but in opposite order are to be observed. This kind of condensation I proposed to call "retrograde condensation". The limits, within which this group of mixtures in contained, may be easily indicated: one limit is formed by a mixture, in which the proportion of the ingredients

is that of the plaitpoint, the other limit by a mixture, whose plane parallel to the ψ , υ plane touches the connode curve. From this we may derive, how on the other hand for one given mixture the nature of the condensation must alter with the temperature. Above a definite temperature, the critical temperature or rather the temperature of the critical point of contact, separation is impossible; beneath another lower temperature, which I call the *plaitpoint-temperature* of the mixture, the condensation is normal; between these we must find retrograde condensation. If we consider the difference in density and proportion of the coëxisting phases we find, that this difference will be very slight at the end of the condensation close to the plaitpoint-temperature, both above and beneath it and that, according as the temperature diverges from it, this difference will increase. So the very small quantity of liquid, which is formed close by the critical temperature may show a considerable difference from the vapour-phase: a flat surface is not to be expected there. The well-known property of the critical temperature of simple substances, that above it no two phases can coëxist, here belongs to the temperature of the critical point of contact and in this respect the critical point of contact is to be compared with the critical point of simple substances. In the plaitpoint however we meet with the property of the coëxisting of two identical phases ¹). Consequently with mixtures

¹) The phenomena described here are modified a little by the influence of gravitation, as in the case of simple substances was first pointed out by Gouy (Compt. Rend. 115, p. 720.

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¹) For the names used here compare: Communications etc. n⁰. 7, p. 4.

²) vid. VAN DER WAALS l. c. The case of other possible cases is discussed in my paper Arch. Néerl. l. c., Zeitschr. Phys. Ch. l. c.

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the properties of the critical point are so to say divided over two points, the plaitpoint and the critical point ^of contact.

The observations were partly in contradiction with all this; especially retrograde condensation had never been observed: instead of it the flattening and disappearing of the liquid surface. As the cause of this deviation from theory I suggested the influence of retardation, which with mixtures may already modify the phenomena in the gaseous state and shows itself clearer still, when two phases are present. This retardation, the result of slow diffusion, is not to be mistaken for the thermodynamical retardation, which may delay for a time the appearing of the first small quantity of a new phase ¹).

It is possible to point out a little clearer, why retardation may have such a great influence under the given circumstances, and thereby render the explanation more accurate. We may best express the influence of retardation by saying, that with increasing pressure the two phases are compressed separately and that then by interchange at the surface and by diffusion equilibrium will be slowly occasioned. In the case, we are referring to, a particularity shows itself, namely that both the phases, when compressed, remain in stable

¹) cf. BLÜMCKE, Wied. Ann. 36, p. 916.

equilibrium, because the corresponding points of the connode curve are both situated at the liquid side of the plait, and therefore pass into the stable part of the surface. As the phases are not in equilibrium with each other, probably a continuous transition between them will be formed, which reveals itself in the disappearing of the surface observed. Of course this reasoning holds good for temperatures lying not too far beneath the plaitpoint-temperature as well as for temperatures ranging between it and the critical temperature. The disappearing of the surface with insufficient mixing may therefore not only take the place of retrograde but also of normal condensation. The fact, that, if one of the two points is situated at the vapourside of the plait, this point with compression must enter the semi-stable or even the unstable part of the surface and so immediately give rise to a new separation and an increase of the liquid phase, must be considered as the reason, why retardation causes less marked abnormalities there. It is also to be borne in mind, that here the difference between the phases becomes greater as a rule.

Some days ago I have succeeded, by aid of my stirring-apparatus mentioned before, entirely to confirm the theoretical predictions and the explanation of the ordinary phenomena. With the utmost care a new mixture was, prepared: the process was conducted in such a manner, that the possibility of decomposition of the methyl chloride during the closing of the tube by the blow-pipe was excluded. Moreover the apparatus was made of glass and copper only, so that probably

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cf. Communications etc. n^o. 8, p. 10). The flattening and disappearing of the surface will not be possible exactly at the plaitpoint-temperature only, but also at temperatures a little above and beneath it, the limits of which will depend a. o. upon the length of the tube employed.

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the gases were very pure. The proportion of the carbonic acid in the mixture amounted to 0.41.

If, during the condensation, I did not stir and only waited some time before the readings were taken, between varying limits of temperature, depending upon the time of waiting, (circa 100° C-107° C) the separating surface could be effaced by pressure. The movement of the piece of iron within the tube changed the phenomenon entirely, as the theory had predicted. Beneath 102° C the condensation was normal. At 102.5° C and 103° C the observations were dubious; at 103.5° C retrograde condensation was already discernible, though very indistinct still. The difficulty of the observations in this neigbourhood is caused by the nearly complete similarity of the phases. A small change of temperature may cause considerable deviations and a too sudden change of pressure, which often occurred with my regulator of pressure, was sufficient to make the line of demarcation disappear at once against my intention. In these cases I succeeded far better in producing the opposite phenomenon, which occurs with expansion. Though exact numbers were not to be obtained at 103.5° C, the existence of the retrograde condensation at that temperature was not doubtful ¹). At 104° C the phenomenon could be followed entirely, also at 105° C and 106° C. The critical temperature was fixed at 106.5°. The difference between the phases close to 106.5° C was very marked: the focal lines, which are to be observed in a glass tube, had a different breadth

') 103° C = plaitpoint-temperature.

in the two phases and the surface was much more curved than at lower temperatures, entirely in accordance with theory. The following numbers were obtained at 105° C; the volumes are expressed in an arbitrary unit, the pressures in atmosferes.

Vol.	Vol. of the	liquid.	Pressure.
117.9	• 0		73.3
99.6	3.9		77.2
81.2	· 8.2		81.8
81.0	8.6		81.8
78.6	7.6		82.4
77.3	. 4.3		83.1
75.3	4.7		83.3
75.4	2.8		83.5
74.3	2.5		83.8
74.0	0		83.8

We may call the succession of volumes and pressures pretty regular, considering the great difficulties of the observations.

The limits, between which retrograde condensation takes place, are much narrower than those of the ordinary phenomenon (disappearing of the liquid surface). This agrees with what was pointed out before, viz. that the limits become wider by the influence of retardation.

The results of former experimenters especially of ANDREWS, who describes his experiments most accura-

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tely, are also quite in accordance with the explanation laid down here. That an investigator like ANDREWS has not seen the true state of affairs is due to his want of a theory, without which the critical phenomena of mixtures would not have been disentangled easily.

COMMUNICATIONS

FROM THE

LABORATORY OF PHYSICS

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. II. KAMERLINGH ONNES.

Nº. 5.

Dr. P. ZEEMAN. Measurements on KERR'S phenomenon in the case of reflexion from the polar surface of a magnet made of iron, cobalt and nickel.

Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akademie te Amsterdam van **25 Juni 1892,** p. 19; published in extenso Archives Néerlandaises, T. 27. p. 252, 1893.

Dr. P. ZEEMAN. Measurements on KERR'S phenomenon in the case of reflexion from the polar surface of a magnet made of cobalt at different angles of incidence.

Translated from the same 29 October 1892, p. 58; published in extenso with subsequent investigations in the Archives Néerlandaises referred to above.

Dr. P. ZEEMAN. On a subjective phenomenon in the eye, Translated from the same 25 Februari 1893, p. 155.

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