## Dr. J. P. KUENEN. *Some experiments about the connections between the two plaits in the surface of* van der Waals *for mixtures.*

As a continuation of my researches about the critical phenomena of mixtures of two substances [1]) some new experiments were made. During my observations of the mixture of $^3/_5$ methyl chloride and $^2/_5$ carbonic acid, occasionally on the fluid, which appears with small volumes, a small quantity of a second fluid phase had become visible, which was separated from the former by an indistinct and gradually (by stirring even immediately) disappearing meniscus. This gave rise to the question, whether it might be possible to acquire such circumstances of temperature and volume, wherein methyl chloride and carbonic acid should show three ocëxisting stable phases. The possibility thereof was not excluded: for Prof. van der Waals in this treatise on the theory of mixtures [2]) laid particular stress on

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[1]) Arch. Néerl. 26. p. 369—390; Zeitschr. Phys. Chem. 11. p. 38—48; Comm. Lab. of Physics. Leiden n°. 4.

[2]) Arch. Néerl. 24. p. 54—56; Zeitschr. Phys. Chem. 5. p. 172—173.

the connection between the situation of the plaitpoint 1) of the gas-fluid plait in the surface on the side of the small volumes and the existence of the second plait, which indicates the not mixing of the substances in the liquid state. In fact this plaitpoint $P_2$ would properly speaking belong to the second plait, which would in this case constitute one whole with the first plait, whereas the plaitpoint of the first plait $P^1$ would but become visible on the binode curve 2), when the temperature had neared the critical temperature of the most volatile component. (conf. the figure in Prof. v. d. Waall's treatise 3), where the form of the spinode curve indicates the approach of a second plaitpoint i. e. of $P^1$). Below that temperature therefore two plaitpoints might be found, that is to say the possibility of three phases for al mixtures the ratio's ($x$) of which are contained within the triangle formed by the three phases. When the temperature sinks below the critical temperature of the above mentioned component and accordingly the plaitpoint $P_1$ falls outside the surface, still a coëxistence of three phases for mixtures within certain limits will remain possible, if only the plaitpoint $P_1$ has not likewise fallen outside the surface or disappeared altogether. In this way we have got the case of two substances, which do not mix in the liquid

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1) Plaitpoint = tacnodal point; cf. Korteweg, Arch. Néerl. 24. p. 57. Wien. Sitz. Ber. 98. IIa, p. 1154; Maxwell, Theory of Heat. p. 205—206.

2) Binode curve = condode curve = node-couple curve cf. Korteweg l.l. c.c.; Maxwell l. c.; v. d. Waals l. c.

3) v. d. Waals l.l. c.c.

state within certain limits of quantity (as ether and water) and will probably do so even less at lower temperatures.

In orde to investigate whether this is the case with methyl chloride and carbonic acid the afore mentioned mixture was accurately observed. The results obtained in my former paper prove that the surface for these two substances has at any rate no two plaitpoints in the neighbourhood of the critical temperature (100° C.—106.5° C.) The mixture was now investigated at lower temperatures nearing the critical temperature of carbonic acid, but here two stable liquid phase were not obtained either. The fact that no three phases were found is no proof at all of the non-existence of the triangle, because it is very probable that by the large quantity of $CH_3Cl$ in the mixture its $\psi$-$v$ plane does not pass through the triangle. But even after a great part of the $CH_3Cl$ had been removed from the mixture nothing like a dividing into two liquids appeared. Besides the non-existence of the triangle is rendered probable by observations at low temperatures down to — 35° C which always showed complete mixing in the liquid state.

So with methyl chloride and carbonic acid the plaitpoint $P_2$ would appear not to exist above — 35° C and the existing plaitpoint (above 31° C) should be considered as actually belonging to the first plait (so as $P_1$), whilst according as the temperature falls towards 31° it moves to the side of the large volumes and at 31° coïncides with the critical point of carbonic acid.

In connection with the question here investigated it seemed that great importance was to be attached to an observation of Wroblewski[1]) with a mixture of $^5/_6$ carbonic acid and $^1/_6$ air (the same mixture, which was olso investigated by Cailletet[2])); at compression and subsequent expansion at 0° C he observed two liquid and one gaseous phase[3]). If this observation were correct, the surface for these two substances would contain the above mentioned triangle at 0° C (at this temperature air may be considered as a simple substance). The same mixture was now investigated by me with the aid of my electro-magnetic stirring-apparatus[4]) and produced in the first place entire confirmation of previous results about the critical plenomena of mixtures in general. For the critical temperature I obtained 19° C, for the plait-point-temperature 15°6 C, between both *retrograde condensation.* Cailletet found at first[5]) 20° C as the critical temperature, afterwards[6]) there still was condensation at 25° C. The reason of these considerable differences between the two numbers is to be found in the phenomena of retardation, the influence of which was discussed in my treatise already cited[7]).

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[1]) a. o. Wied Ann. 26. p. 134—135.

[2]) Compt. Rend. 90. p. 210.

[3]) Wroblewski observed the same phenomenon with liquid air.

[4]) Arch. Néerl. 26. p. 372; Zeitschr. Phys. Chem. 11 l. c.; Comm. etc. n° 4.

[5]) Compt. Rend. 90. p. 210.

[6]) Jamin, Compt. Rend. 96. p. 1451.

[7]) Arch. Néerl. 26. p. 371. sqq; Zeitschr. Phys. Chemie 11. p. 40. sqq.

The efforts in consequence of Wroblewski's investigation to obtain the three phases near 0° C were in vain however; though very often a second, even a third meniscus was formed, it soon appeared that these states were transient and disappeared by stirring. This proves that the triangle does not exist at the chosen temperatures.

In order to find a case at last, in which the fluid-plait might be expected and would make its influence felt even between the critical temperatures, a treatise of Dewar[1]) was referred to, who compressed carbonic acid in the presence of several substances. One case, in which Dewar states that liquid carbonic acid was clearly visible on the other fluid was that of carbon disulphide: no particulars are given about the quantity used. I began by repeating this experiment. In a tube filled with pure carbonic acid a thin layer of $CS_2$ was brought. By a treatment with mercury and distillation the $CS_2$ had been purified to a colourless fluid of an agreeable smell, which did not attack the mercury at all. When the mixture was compressed the second layer of liquid showed itself on the $CS_2$: at low temperatures especially the phenomenon was very clear; as soon however as the small piece of iron, within the tube, was moved, it became evident, that equilibrium did not exist, and the substances mixed completely; in fact in the vicinity of the meniscus mixing-phenomena were to be observed from the be-

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[1]) Proc. R. S. of L. 30. p. 538.

ginning. THILORIER [1]), as I found out afterwards, already states in opposition to DEWAR that $CO_2$ and $CS_2$ are miscible in all proportions.

The investigations into the connection between the two plaits are now being carried on with carbonic acid and water.

The results communicated here show clearly, how great the influence of retardation may be and of how great a significance careful stirring is for those experiments.

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[1]) Ann. Ch. et Phys. 60. p. 430.

## Dr. L. H. SIERTSEMA. *The dispersion of the magnetic rotation in oxygen.*

The dispersion of the magnetic rotation follows in most substances pretty much the same law that governs the natural rotation, viz. that the rotation varies inversily as the square of the wave-length. The strongly magnetic substances form an exception to this law. In solutions of iron-salts and a few others the dispersion is, according to BECQUEREL [1]), much greater, the rotation varies inversely as the fourth power of the wave-length. In iron, nickel and cobalt the rotation, according to KUNDT [2]) and LOBACH [3]), increases with the wave-length. Also with the phenomenon of KERR, which is closely connected with the foregoing, KUNDT [2]), RIGHI [4]), DU BOIS [5]) and ZEEMAN [6]) found anomalous

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[1]) H. BECQUEREL, C. R. 83. p. 125 (1876); Ann. de Ch. et de Ph. (5) 12. p. 68 (1877).

[2]) KUNDT, Wied. Ann. 23. p. 228 (1884).

[3]) LOBACH, Wied. Ann. 39. p. 347 (1890).

[4]) RIGHI, Ann. de Ch. et de Ph. (6) 9. p. 136 (1886).

[5]) DU BOIS, Wied. Ann. 39. p. 25 (1890).

[6]) ZEEMAN, Dissertatie Leiden (1893); Verslag Kon. Akad. v. Wetensch. Amsterdam Oct. 1892 en Febr. 1893.