Physics. — „*The influence of pressure on the critical temperature of complete mixture*". By Mr. N. J. van der Lee. (Communicated by Prof. J. D. van der Waals.)

In 1886 (Wied. Ann. Bd. 28) Mr. Alexejew published investigations, undertaken to find out the influence of temperature on the mutual solubility of two liquids which are but partly soluble in each other. A temperature proved to exist, above which mixture in all proportions takes place (critical temperature of complete mixture). The existence of this temperature had been already supposed before. In 1880 (Verh. Kon. Ak.), Prof. van der Waals had pointed out, that the pressure too, must play a part in this phenomenon, and he had found that in a mixture of ether and water, the meniscus, parting the two phases, becomes flatter by higher pressure. Though this might be considered as a proof that the two phases approached each other as far as composition is concerned, complete mixture is not attained. Mr. Alexejew seems to have been induced through this treatise, to examine also the influence of pressure for the mixtures investigated by him, but with a negative result. (I have not been able to consult the description of these last experiments. I know them only from citations). By the theory of the surface ψ (J. D. van der Waals: „Théorie moléculaire d'une substance composée de deux matières différentes. Arch. Néerl. T. 24 or Versl. Kon. Ak. 23 Febr. 1889) the influence of the pressure on the mutual solubility was also examined. In 1894 Mr. J. de Kowalsky published the description of his investigations (C. R. T. CXIX p. 512) concerning this theory. No influence of the pressure was found — not even by very high pressures — except for a triple mixture of aethylalcohol, isobutylalcohol and water. A pressure of 900 atm. made the liquid homogeneous at a temperature of about 3° below the temperature of complete mixture. Of late Mr. Klobbie (Zeitschr. f. phys. Chem. 24. 617. 1897) has found a perceptible influence of the pressure for mixtures of ether and water by a pressure of 100 atmospheres, without, however, determining its degree.

The purpose of the experiments which will be described here, was, to find something about the influence of the pressure on the mixture of liquids.

Of all the mixtures examined by Mr. Alexejew the pair water and phenol seemed best fitted for these investigations. The critical temperature of complete mixture is about 67°. The phenol used was from Merck & Co. and was tested beforehand by determining the fusing-point. It was preserved in the dark in sealed glass tubes,

each containing about the quantity necessary for one experiment. The proportion of the mixtures was regulated by putting together quantities of a given weight of the two substances. As the determinations were made for mixtures whose temperature of complete mixture was near the critical, the liquids were divided into two phases at the temperature of the room. Therefore the mixture was well shaken, so that an emulsion was obtained. A certain quantity of this was quickly poured into a capillar funnel, with which the liquid was brought into the observation-tube. This tube consisted of a straight tube of thick glass with about 3 m.M. inside diameter. It was fused together at one end, widened in one place just as the CAILLETET-tubes are, and cemented in a brass mounting. After a sufficient quantity of the mixture was poured into this tube, the stirring-contrivance was applied to the liquid, consisting of a magnetised needle, round which a closely fitting glass capillar was slided, which was then fused together on both ends and provided with glass balls to prevent its sticking to the glass walls. To bring this bar in motion an electro-magnetic stir-apparatus was used, like the one described by A. VAN ELDIK (Versl. Kon. Ak. 1897). After the stir-apparatus had been put in, the air-bubbles were removed as much as possible, and then the mercury was put in the tube. For this a not too great quantity was first carefully put in at the top of the tube. If care was taken that the mercury had but very little velocity, it kept sticking high in the tube, in consequence of the capillarity. After that it was easy to make it glide along a capillar down to a few cM. above the surface of the mixture. Now mercury could be poured in by means of a capillar-funnel, in which air-bubbles could be avoided. At last the whole mercury fibre could be lowered, till the lower end reached the surface of the mixture. After the tube had been completely filled with mercury, it could be turned upside down and placed in a steel vessel, which was in connection with the forcing-pump. Within this steel vessel a glass vessel filled with mercury, was placed in such a way, that the lower end of the glass tube was below the surface of the mercury. The space was further filled with glycerine, and the glass vessel closed with a brass nut. To have it hermetically closed, rubber rings are used.

The pressure could be kept constant with this instrument for a considerable time and could be read by a metal-manometer, a new one specially used for these experiments. This manometer had been tested, before it was received by us. As the influence of the pressure proved to be very slight, little differences of pressure were not paid

attention to, and it was not necessary to use a more accurate instrument. This slight influence, which had been expected beforehand from the theory and in connection with the experiments before-mentioned, made it necessary to make the observations near the temperature of complete mixture. Here the difficulty presented itself, that the heat which would be developed by compression, might be the cause that the temperature, which had first been below the temperature of complete mixture, would rise above it. In this case mixture would not be the direct consequence of the pressure. There-fore it was of great importance to make an arrangement by means of which it would be possible to keep the temperature round the glass-tube constant for a considerable time: for in this way it would be possible to remove the disturbing influence mentioned before. The attempts to get a suitable thermostat, led to the following arrangement agreeing in many respects with the one described by W. WATSON (Phil. Mag. Vol. 44 July 1897): a glass cylinder, 30 cM. high and with a diameter of 5,5 cM., is closed on both ends with caoutchouc stoppers. These stoppers are pierced in the middle, so that a glass cylinder of the same height as the former and with a diameter of 2,6 cM., can be placed concentrically with the other.

The annular cylindric vessel obtained in this way, is placed so as to have its axis vertical. Two holes made in the higher stopper, give an opportunity of adjusting two glass tubes. One of these is closed with a tap and serves to bring the liquid into the vessel. The other is (the glass tubes being in close contact) connected by means of a rubber tube with another glass tube placed vertically, which leads through a cooling-apparatus, and is bent horizontally just above it. It leads further to a T shaped piece to which are fastened 1°. an open manometer 2°. another T shaped piece. One arm of the latter T shaped piece has a rubber tube with a squeezer. This squeezer is so constructed that by means of a screw the admission of air can be nicely regulated or entirely stopped. The other arm leads to two large closed bottles, having together about 40 L. contents, and from there to a rubber tube (with a squeezer), which brings about the connection with a waterairpump. In this way the vessel is connected with a large space, in which the pressure can be lowered. The regulating of this pressure, read by means of the open manometer, can be easily done by the two squeezers mentioned. Then a small quantity of mercury is first brought into the vessel, enough to cover the bottom, and to preserve the caoutchouc in this way, and on it a quantity of aethyl-alcohol, which can be made to boil under various pressures. The

heat required was furnished by an alternating current, easily obtained by the installation of Electra which is found in the laboratory. This current is led through a spiral, wound round the inner cylinder of the boiling-vessel, the ends of which have been sealed through the glass of the outer cylinder. A necessary condition for the remaining constant of the temperature proved to be that the spiral remained entirely merged in the liquid.

The glass forcing-tube containing the mixture was then placed nearly in the axis of the inner cylinder with a thermometer and the tube of the electro-magnetic stir-apparatus near it. The space was then closed with wads on both sides. The thermometer was quite inside that part of the inner-cylinder, where the temperature had proved to be the same throughout. Therefore correction for the sticking out of the mercury was not necessary. Within the same space the mixture which was to be examined and the tin tube were placed.

The mixture was now brought to about the temperature of complete mixture, which took about an hour. Then the temperature was made to rise a little under continual stirring; after a moment's rest it was made to rise again etc., till the cloudiness (the proof of the presence of two phases), had quite disappeared. Then the temperature was read. After that the temperature at which the cloudiness reappeared was determined in the same way by cooling the mixture. By repeating these observations a few times, the temperature of complete mixture could be very accurately determined. (The thermometer was verified at the Reichsanstalt). In the same way the temperature of complete mixture by greater pressure was determined. The results of these observations follow:

$22\,^0/_0$ $x = 0.05$

pressure:	norm.	30	60	90	120	150	180 atm.
temp. of compl. mixt.:	66.7	66.7	66.9	67	67.1	67.2	67.3

$34\,^0/_0$ $x = 0.09$

pressure:	norm.	30	60	90	105	130 atm.
temp. of compl. mixt.:	67.6	67.6	67.8	67.8	68	68.1

$38\,^0/_0$ $x = 0.11$

pressure:	norm.	60	90 atm,
temp. of compl. mixt.:	67.3	67.5	67.7

47 °/₀ $x = 0.15$

pressure:	norm.	60	90	120 atm.
temp. of compl. mixt.:	64.8	65.1	65.3	65.3

49 °/₀ $x = 0.16$

pressure:	norm.	30	60	90	120	150	180 atm.
temp. of compl. mixt.:	65	65	65.1	65.2	65.3	65.5	65.6

55 °/₀ $x = 0.18$

pressure:	norm.	30	60	90 atm.
temp. of compl. mixt.:	61.2	61.2	61.3	61.3

(The percentage of phenol has been given here. In the theory of the surface ψ we suppose that the quantity of one of the liquids is $M_1 (1-x)$ and of the other $M_2 x$, in which M_1 and M_2 represent the molecular weights. Here $M_2 = C_6 H_5 OH$.)

These observations prove, that increase of pressure causes the temperature to rise. Considered in connection with the theory of the surface ψ, they show that the longitudinal plait (second plait) has a plait-point on the side of the greater volumes and that at that plait-point it turns its hollow side towards the x-axis. As moreover, it is possible to prove in general theoretically, that rise of temperature makes the plait move in such a way that the projection of the connodal line on the XV plane falls within that of a preceding connodal line, it follows from this, that the longitudinal plaits (second plaits) will be moved to the side of the x-axis if the temperature rises. At a certain temperature the two connodal lines will intersect. Then we have three co-existing phases. When the temperature rises, the two points of intersection approach each other, in other words, the phases begin to resemble each other more and more. At last the two curves touch; there is only one liquid phase left, co-existing with the gas-phase. This temperature is called the temperature of complete mixture. This, however, is but one of the many critical temperatures of complete mixture, for at a higher temperature it is possible, by increasing the pressure, to get two liquid phases, which can become perfectly equal in composition and molecular volume. In this case also, there is a critical temperature. So the critical temperature rises through increase of pressure in the mixture examined.

If once more the case that two connodal lines intersect is examined, it is easily seen, that the two intersection-points are nodes of the longitudinal plait (second plait). When the temperature rises they approach each other, and when the curves touch, the point of contact may be considered as two nodes having fallen together. From this follows, that when two connodal curves touch, the point of contact is a plait-point of the longitudinal plait (second plait). The spinodal curve of the longitudinal plait will therefore also touch the spinodal curve of the transverse plait (first plait). A consequence of this is, that the differential coefficient $\dfrac{dp}{dx_1}$ (see T. M. p. 15) must be 0 in this case which points to a maximum or minimum of the line $p = f_1(x_1)$, that is the curve, which represents the relation between the composition and the pressure of the saturated vapour of the mixture.

To test this conclusion experimentally, some pressures of vapour were measured according to the method denoted by LEHFELDT (Phil. Mag. July 1898), the results follow:

4.8% T.	$x = 0.01$ P. in m.M.	10.1% T.	$x = 0.02$ P. in m.M.	18,9% T.	$x = 0.04$ P. in m.M.
72.4	263	77.2	321	72.2	260
73.9	280	77 3	323	72.3	262
74.9	291	77.5	325	72.9	269
75.1	294	81.9	388	73.7	277
76.1	306	85	438	75.5	299
77.4	323			75.7	301
78.5	338			76.5	312
79.9	357			77.7	328
81.6	382			77.9	331
83	403			78.9	344
83.8	416			79.6	353
85.4	443			80.5	367
86.6	464			81.6	384
87	471			83	405
				84.4	428

33.6% T.	$x = 0.09$ P. in m.M.		50.9% T.	$x = 0.17$ P. in m.M.
71.2	251		71.2	251
72.2	261		71.4	253
73.1	272		72.4	264
74.1	284		73.7	277
74.4	288		74.6	289
75.5	300		76	306
76.7	315		77.2	321
76.9	318		78.3	337
77	319		79.3	351
77.7	328		81.3	378
78.7	343		81.8	386
79.4	352		82.8	401
79.9	360		83.8	417
80.9	375		85.6	448
81.6	385		86.6	462
82.6	400		86.7	468
84.2	426		86.8	470
85	440			
77.2% T.	**$x = 0.39$ P. in m.M.**		**84.% T**	**$x = 0.5$ P in m.M.**
73.3	253		75.9	212
73.5	254		76.3	215
74.5	262		77.5	229
75.7	276		77.9	234
76.5	282		79.7	253
77.7	296		81.6	274
78.9	311		82.8	287
79.3	315		85.8	323
80.6	330		89	381
81	336		89.1	382
81.6	344		89.4	389
83.2	367			
84.4	387			
86.2	419			
86.4	422			
87.6	444			

From these figures the following values were found by interpolation for the curves $p = f_1 (x_1)$. (The pressures for pure water are taken from the tables of LANDOLT. A slight correction ought to be made in the figures mentioned, which is, however of no influence on the general course of the pressure curves).

%	x	75°	77°	79°	81°	83°	85°
0	0	289	314	340	369	400	433
5	0 01	293	318	344	373	403	436
10	0.02	294	319	345	374	405	438
19	0.04	294	319	345	374	405	438
34	0.09	294	319	346	375	406	440
51	0.17	294	319	345	374	404	438
77	0.39	268	289	310	336	364	397
84	0.5	201	223	245	267	290	311

Though its exact place cannot be determined from these figures, yet it appears that there is a maximum, which corresponds nearly with value 34 pCt. ($x = 0,1$), so nearly with the composition by the critical temperature of complete mixture of three phases.

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