Physics. — "*Experimental investigations concerning the miscibility of liquids at pressures up to* 3000 *atmospheres*". By Prof. PH. KOHNSTAMM and Dr. J TIMMERMANS. VAN DER WAALS fund researches N°. 4. (Communicated by Prof. VAN DER WAALS).

(Communicated in the meeting of November 30, 1912).

§ 1. The theoretical researches of the last few years have rendered it possible to give a complete classification of the different types of unmixing which are to be expected. Whether these theoretical expectations are in conformity with reality could be ascertained up to now only for a very limited region, on account of the inaccessibility to experiment of the whole region of pressures higher than two or three hundred atmospheres. The wellknown CAILLETET tubes are namely useless at higher pressures. We have, therefore, been occupied already for a considerable time in devising an apparatus intended for higher pressures, and we have finally succeeded in constructing such an apparatus, with which we have carried out measerements up to 3000 atm., and which can probably also be used up to 4000 or possibly 5000 atm.

The first problem that was to be solved was, of course, to render the phenomena visible. For, to ascertain the critical phenomena of unmixing, and the phenomena of unmixing in general by means of other properties than those which fall within the scope of direct visual observation, seems hardly possible. Our first attempts to effect this visibility by pressing a thick piece of plate glass A (fig. 1) by the aid of a nut B fitting round it, against the steel tube which would then contain the substance to be examined, or strictly speaking against the packing enclosed between C and A, failed entirely. Even the thickest plate glass plates snapped off inexorably, when we tried to screw the nut tight enough to prevent leakage.

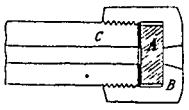

Fig. 1

Led by the figure that AMAGAT gives for the apparatus of his "méthode des regards", with which he has succeeded in carrying out measurements up to 1000 atm., we resolved to arrange the "windows" in such a way that neither on the front nor on the back side unequal pressures should be exerted [1], but that the whole

[1] The "windows" used by AMAGAT have, however, not been constructed according to this principle; they are not cones but cylindres, they bear on the end-plane directed to the observer; AMAGAT uses celluloid packing between steel and glass. We have, however, experienced that to reach the highest pressures, it should carefully be avoided to make the windows bear on their end-plane.

pressure exerted by the liquid inside the tube on the "window", should be borne by the side-walls We therefore gave the window the shape of a truncated cone, the basis turned to the side of the liquid, and the smaller plane parallel to the basis quite free and turned to the observer. The conical wall must be ground as carefully as possible into a steel cylindre with conical opening, which is screwed into the steel tube of observation. Fig. 2, where B is such a steel cylindre, and A the glass cone, will probably make this sufficiently clear. If the cone A is ground with sufficient care, and then fastened in B with a little cement, an absolutely tight closure is obtained in this way; we have never experienced any trouble owing to leakage between glass and steel, nor has any of the glass cones ever burst in consequence of the high pressure, in such a way that the liquid could be pressed through those windows. We did meet, however, with other difficulties. First of all the difficulty of getting pieces of glass from which the required glass cones could be obtained, without too much loss of time. We

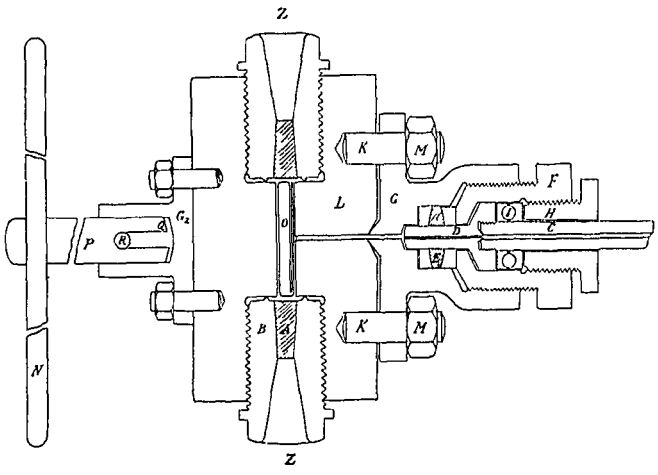

Fig. 2.

first tried to start from thick plates of plate glass (3 cm. thick), but it appeared impracticable to saw or cut off such small pieces (1.5 to 2 cm² area) [1]), that they could serve for further preparation. We then applied to the "Stichtschen Glashandel" at Utrecht, which prepared octogonal rods for us, about 6 cm. long and of a diameter of about 1·5 cm. from the best plate glass. After these rods have been cut off doubly conical (two cones of 3 cm. the bases resting

[1]) When the conus is ready the basis turned to the liquid has a diameter of 12 m.m., the other end-plane a diameter of 10 mm.

against each other), they are cut through in the middle: the planes of section must then be ground once more and polished.

A second circumstance which gave rise to difficulties, and sometimes does so now, is the becoming opaque of the cones. If such a cone which has become opaque, is removed from the cylindre, it appears that innumerable planes of cleavage have arisen at right angles to the axis of the cone, so that it can be easily broken up with the hand into a great number of plane plates. In consequence of these cracks the at first perfectly transparent cone has become quite opaque. It appears that the cones hardly ever or never become opaque with rising pressure. It is probably the consequence of the compressibility of the steel cylindre. This extends with rising pressure, and so the glass cone is driven deeper and deeper into the cylindre. If then the pressure diminishes, the cone cannot return to its first position and is cracked by the immense pressure of the steel cylindre. In agreement with this is the fact that in experiments at higher temperature the cones become opaque still more frequently than at lower temperatures; the difference of the coefficient of expansion of glass and steel then acts in the same direction. Moreover by means of the brass model used for grinding the glass cones into the cylindre, it could be clearly demonstrated that one of the steel cylindres had widened by use. A cylindre made expressly of specially hard nickel-steel yielded better results in this respect. When this was used, the cones were less liable to crack, though even then it occasionally happened. To protect the window from injury as much as possible it is also desirable to diminish the pressure as carefully as possible, a rapid increase of the pressure, on the other hand, rarely, if ever, gives rise to an accident. Though this cleaving of the cones perpendicular to the axis continues to be a drawback, because the preparation and adjustment of new cones always remains a rather lengthy work, the observations themselves are not disturbed by it, if only the experiments are made as much as possible with rising pressure, and decrease of pressure is effected with the utmost care.

At present the apparatus cannot be used for temperatures much above 70°; the Cailletet cement with which the windows are fastened into the steel cylindres, melts at that temperature, or at least rapidly dissolves in the liquid which is in the pressure tube. First of all this renders the liquid turbid, but moreover it gives rise to leakages and breaking of the windows, which are now directly pressed against the steel. We are now trying to find means to apply the windows also at higher temperatures. As to the limit of pressure, we think we have to fix this for the present at about 5000 atm.

§ 2. A second condition which the apparatus has to fulfil, is this that the mixtures which are to be examined, can be properly stirred during the experiment. Of course there can be no question of an electromagnet stirrer inside the heavy steel vessel. The difficulty seemed the greater as during the experiment, and so also during the stirring the steel vessel, which itself is already very heavy, has to remain connected without leakage with the compression pump and the manometer. We have finally succeeded in finding a construction meeting all demands; it rests on the following consideration. The pivot of a high-pressure cock may be turned round, without giving rise to leakages; we can just as well keep this pivot still, and turn the rest of the apparatus round it. Suppose the inlet tube, which connects the vessel of observation with pump and manometer, at the place of this pivot, and arrange the connection in such a way that the observation vessel can turn round this inlet tube as a pivot, then it must be possible to bring about the most efficient form of stirring viz. turning upside down the whole contents of the vessel of observation.

This idea is realized in the construction represented by fig. 2. C is the inlet tube of the compression pump, it has a diameter of about 15 mm.; the aperture is about 2 mm. wide. A prolongation D[1]) can be screwed on to the tube C, by which a projecting cone is pressed against a conical concavity of C. In this way a steel-to-steel closure is obtained, which is quite tight even at the highest pressures. As is shown in the figure, the piece D pierces with its carefully finished and polished part through the packing E, which is enclosed between two rings, and can be screwed so tightly by means of the gland F in connection with the flange G, that leaking along this packing is prevented, though the pieces G and F with this packing can still turn round DC as pivot. To prevent DC from being pressed outside through the pressure on the end-plane of D, D is kept in its place by a gland H, a ball-bearing adjusted between D and H making it possible to screw H sufficiently tight without making the friction between D and H so considerable that it would hamper the rotation. The flange G is now again pressed against the observation vessel L by means of the bolts K, which pass through it, and which are screwed into the observation vessel L, and the nuts M. In this way the same steel-to-steel closure is applied as between C and D. By means of the handle N the pressure vessel L can, when everything is mounted and put under pressure, be rotated,

[1]) This tube is only 12 mm externally (and has in correspondence with this also a somewhat smaller opening than G) to make the pressure on the ball-bearings as small as possible.

DC remaining in its fixed position. Thus the two phases in the glass tube O change places, passing through each other and becoming perfectly mixed.

The handle N cannot be directly fastened to the steel observation vessel L. This vessel must namely be surrounded by a thermostat. Quite apart from high or low temperatures, which would make it quite impossible, it would be inconvenient even at the temperature of the room when the handle N was *inside* this thermostat. Therefore the connection of the observation vessel L with N has been effected as follows. The rod P connected with the handle (of which only part has been drawn) passes closely fitting through a stuffing box (not drawn in the figure) in the wall of the thermostat, so that P can still be moved forward and backward and rotated in the thermostat wall. The rod P terminates in a fork Q, which in the position drawn in the figure encloses a pin R, which is rigidly attached to the flange G_2, which like G_1 is again rigidly connected with L by means of bolts and nuts.

So in the position represented in the figure L can be rotated by PN; if P is drawn back in the stuffing box of the wall of the thermostat, P, and together with it the thermostat, gets quite clear of R, G_2, and L.

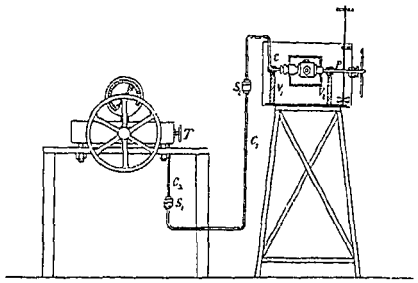

Fig. 3.

The whole arrangement is further elucidated by fig. 3. It exhibits the large SCHAFFER and BUDENBERG hydrostatic press for 6500 atmospheres, belonging to the VAN DER WAALS-fund with the manometer standing on it. The pump is also connected with the large pressure-balance (not drawn) as a control for the manometer. One of us (K.) hopes soon to give a full description of these apparatus in connection with other experiments. The press is in connection with the tube conduit $CC_1\ C_2$, from which it can be shut off if necessary, by means of the high pressure cock T. There are two couplings S_1 and S_2 in this tube conduit, to which we shall presently return. Inside the thermostat C rests on the bearing V_1, which in its turn rests on the bottom of the sheet iron thermostat. This bearing at the same time fixes the tube C, so that the tube is prevented from turning round with the vessel L. A second bearer V_2 supports the rod P, which is already known to us from fig. 2. Fig. 3 also displays the stuffing box in the wall of the thermostat through which P passes. The thermostat is represented in

section, the observation vessel is supposed in a position that the windows B are horizontal (hence turned through 90° compared with fig. 2), the position in which the observations are made. The quadrangle in the figure represents a glass window in the back wall of the thermostat (not to render the figure too indistinct it has been drawn much larger than it is in reality); of course a glass window in the front wall corresponds with it. The thermostat has a capacity of ± 40 L., it is provided with a vigorous stirring-apparatus thermoregulator, and thermometer; it rests on a solid stand of ⌊ shaped bar-iron.

The coupling S_1 is of no importance for the experiments described here; it only serves to make it possible if required to connect the press with other conduits, and if necessary, to clean the tubes. The coupling S_2, on the other hand, is necessary for the filling of the apparatus, as will appear when the filling is described. Fig. 4 gives a section of these couplings.

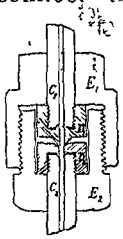

Fig. 4.

At the tops of the tubes C_1 and C_2 two cones D_1 and D_2 have been screwed, which exhibit again two cones fitting into each other at their ends. By means of the glands E_1 and E_2 with hexagon, D_1 and D_2 are pressed against each other, and a steel-to-steel closure is again reached tight even at the highest pressures. It is preferable to take the screws with which D_1 is fastened to C_1 and D_2 to C_2 for such couplings with left-handed thread, that when E_1 and E_2 are tightened, D_1 and D_2 are not unscrewed, but on the contrary, are screwed tighter.

In connection with the method of filling another particular of the apparatus deserves being mentioned, which appears from fig. 5. This

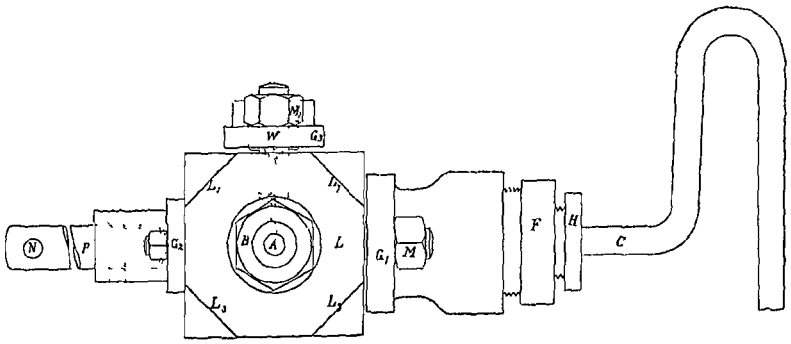

Fig. 5.

figure presents a side view of the observation vessel, a section of which was given in fig. 2, with the parts in connection with it,

on the supposition, however, that the glass windows are again horizontal (not vertical, as in fig. 2, but in the same position as it is represented on a small scale in fig. 3). So A is again the glass window; the other parts too, for so far as they are visible, are denoted by the same letters. It is clear from the figure that besides the main conduit, in which the observation tube O lies, and the branch conduit, which connects this main conduit with DC, there is another branch conduit in the observation vessel L, at right angles to the two first mentioned. This branch conduit is used for the filling; it is then closed by a tight stopper W, which is again provided with a cone, and which is pressed against the vessel L with steel-to-steel closure by means of an oval flange G_3 laid over this cone, with the nuts and bolts belonging to it. This closure is further made clear by fig. 6, where the flange G_3 is represented seen from above, the line ZZ' corresponding with ZZ' of fig. 2. Fig. 6 also shows the general form of the flange plates G. Fig. 5 finally shows the octagon $L_1 \ldots L_8$ of the observation vessel L, which serves to fix the whole piece sufficiently firmly when the steel cylindres B are screwed into it, which cylindres themselves have of course also a hexagon. The closure of B on L takes of course again place steel to steel by means of the raised hardened rim of B, which fig. 2 clearly shows in section.

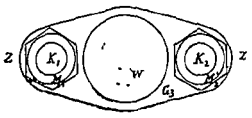

Fig. 6.

We will avail ourselves of this opportunity to express our indebtedness to the instrumentmaker of the VAN DER WAALS-fund, Mr. C. H. STUIVENBERG, for his intelligent assistance in the construction of this apparatus, and particularly in the grinding of the windows.

§ 3. Description of the observations.

When the apparatus described in the preceding paragraphs, is used, care should be taken in the first place that the composition of the examined mixture does not change, and that no impurities can appear, which might have a preponderating influence on the course of the phenomena. This result may be attained by enclosing the mixtures to be examined in a glass tube, closed at the two ends and provided on the side by a capillary (fig. 2, O) as long as possible, which causes the pressure on the liquid inside to be the same as that on the surrounding liquid. This tube has beforehand been filled with a mixture of the required concentration, that of the critical endpoint.

Then the steel tube C is disconnected at S_2, being connected with the observation vessel L at the same time. Now one of the two

windows A with the cylindre B is screwed on, and the glass tube O is placed in the vessel L. After this through the other window opening the vessel L is filled with one of the components, till the liquid begins to flow out at S_2. The tube C is then closed at S_2 by means of a wooden peg, the second window is screwed on, and at last the observation vessel L is quite filled with liquid through the conduit terminating at W (fig. 5). Then W is closed. Beforehand the tube conduit C_2C_1 has been quite filled with mercury, which has been poured in at S_2, to prevent contact of the observation vessel L with the oil from the press. The wooden peg is quickly removed, and the coupling at S_2 is effected. The steel tube C being very narrow, only very little, if any liquid, escapes. Thus the mixture under examination is quite guarded against the influence of contamination, and its concentration changes but exceedingly little on account of the slight compressibility of the investigated liquids, while there can hardly be any question of diffusion through the narrow capillary in the course of the observations. Moreover a slight change in the concentration could not exert an appreciable influence on the results on account of the greatly flattened shape which the liquid-liquid plaits always seem to present.

When the filling is finished, the thermostat is put in its place. An intense metal wire incandescent lamp of 300 candles is placed behind the window in the back wall. In this way, the mixture, particularly the place of the meniscus, can be very clearly observed.

We have confined ourselves in this investigation to plaitpoint observations, as criterion the same phenomenon was taken as was also used by one of us ($T.$) in his observations in Cailletet tubes [1]: while the pressure is kept constant, the temperature is slowly made to oscillate round the plaitpoint temperature, the liquid being continuously stirred. The temperatures are recorded at which the turbidity resp. the transparency sets in, and the mean of all the observations is taken as plaitpoint temperature. Proceeding in this way temperatures of turbidity are always obtained which diverge only some hundredths of degrees when the experiment is repeated. It may also be assumed that the temperature of the mixture follows that of the thermostat very closely, for also the mean of the temperatures of turbidity deviates but a few hundredths of degrees from the mean of the temperatures at which transparency sets in in general. This circumstance proves at the same time that equilibrium is properly secured by the constant stirring of the liquid. This was further confirmed when a glass ball was placed in the glass tube

[1] These Proc. XIII p. 507.

O. This would have to make the mixing still more thorough, if possible but it did not cause the slightest change of the plaitpoint temperature.

The critical phenomenon preserves its characteristic peculiarities and the same intensity up to the highest pressures that we have examined, which bears further witness to the fact that the plaitpoint concentration changes only very little, so that it remains the same all over the extensive range of pressure and temperature considered here. In this it is absolutely required to keep the pressure perfectly constant during the measurements, as otherwise the VAN DER LEE effect [1]) would disturb the observations. It is fortunately, however, easy to distinguish whether the cloudiness which appears in the liquid, is the consequence of the slow cooling of the thermostat or of an abrupt cooling which takes place in the examined liquid itself owing to an expansion by decrease of pressure. In the former case, namely, the cloudiness begins on the ontside. and proceeds towards the centre, whereas in the latter case it arises in the centre, and spreads from there in all directions. The sensitivity of the VAN DER LEE effect in these circumstances shows that the equilibrium of pressure between the manometer and the liquid itself sets in almost immediately. A last proof for the accuracy of the measurements in the new apparatus is afforded by the comparison of the results obtained in this way at low pressure with those obtained in Cailletet tubes.

Some values will give an idea of the attainable accuracy.

a. The plaitpoint temperature remains constant, also after the mixture (nitrobenzene + petroleum) under investigation has been in the apparatus for two days, under pressures up to more than 500 atm. As a mean of ten measurements 13.°95 ± 0.°06 was found.

b. The plaitpoint temperature remains constant when the experiment is repeated with different fillings.

Water + triethylamine, critical end-point	18.°35 and 18.°36
The same system in a Cailletet tube yields	18.°33

c. The increase of the plaitpoint temperature per atmosphere is the same for different fillings, and also for determinations in a Cailletet tube. As an example we take the system cyclohexane + aniline.

$\frac{dt}{dp}$ between 1 and 200 k.g. per cm.^{2} yields	+ 0.0067
in a Cailletet tube was found.	+ 0.0066

[1]) These Proceedings, XIII p. 517.

$\frac{dt}{dp}$ between 1 and 1000 k.g. per cm.^{2} yields

for the first filling	+ 0.0078
for the second filling	+ 0.0079

The temperature determinations were made with thermometers compared with standard ones tested at the Reichsanstalt; the manometrical determinations were controlled with the large pressure balance [1]) of the VAN DER WAALS fund; the observations are accurate to about 10 k.g. and 0.°05.

The substances used in these experiments, were identical in preparation and properties with those used by one of us (T.) on a former occasion [2]); only the decane (di-isoamyl) and the tri-ethylamine have been used here for the first time. These two substances have been purified by fractional distillation (the tri-ethylamine over sodium), they presented the following physical constants: Freezing point: Decane — 52°,5 Triethylamine —114,75; boilingpoint 160°,05 ± 0.10 resp. 89°5 ± 0°02; d 0°/4° 0.73852 resp. 0.74585 ± 7.

It may finally be mentioned that all the observations have been made by one of us (T.).

§ 4. Results obtained:

TABLE I.

Hexane + nitrobenzene

Press. in kg. [3]) per cm.^{2}	Plaitpointtemp.	$\frac{dt}{dp}$ per kg.
1	20°.81 ± 0°.03	
		— 0°.0164
100	19. 17 ± 0. 04	
		— 0. 0127
250	17. 27 ± 0. 10	
		— 0. 0083
425	15. 82 ± 0. 05	
		— 0. 0051
625	14. 80 ± 0. 05	
		— 0. 0031
825	14. 18 ± 0. 03	

For a comparison we give the results obtained with a Cailletettube:

[1]) See above p. 1025.

[2]) These Proc. l. c.

[3]) All the pressures and temperatures have been corrected to the standard thermometer and the pressure balance.

TABLE II.

p	T Press. apparat.	T Cailletettube	Difference
1	20°.81	20°.96	+ 0°.15
100	19. 17	19. 23	+ 0. 06
250	17. 27	17. 29	+ 0. 02

The nitrobenzene solidifies (quadruple point)

at — 1°,5 under ordinary pressure

at + 13°,8 under a pressure of 825 kg. per cm² ± 25.

$$\frac{dt}{dp} = + 0°,018.$$

TAMMANN found + 0°,022 for pure nitrobenzene.

TABLE III.

Decane (di-isoamyl) + Nitrobenzene

p	T	$\frac{dt}{dp}$
1	28°.37 ± 0°.04	
100	27. 69 ± 0. 05	— 0°.0068
250	27. 06 ± 0. 04	— 0. .0042
425	26. 63 ± 0. 07	— 0. 00245
625	26. 44 ± 0. 05	- 0. 0010
825	26. 52 ± 0. 04	+ 0. 0004
1025	26. 67 ± 0. 03	+ 0. 00075
1225	26. 97 ± 0. 07	+ 0. 0015
1425	27. 31 ± 0. 05	+ 0. 0017

The nitrobenzene melts:

at + 1°,5 under a pressure of 1 kg. per cm².

at + 28° under a pressure of 1300 kg. per cm².

$$\frac{\partial t}{\partial p} = + 0°,020.$$

TABLE IV.

American petroleum [1]) + Nitrobenzene

p	T	$\frac{dt}{dp}$
1	13°.95 ± 0°.06	
100	14. 22 ± 0. 07	+ 0°.0018
325	14. 51 ± 0. 09	+ 0. 0017
525	15. 11 ± 0. 04	+ 0. 0030
725	15. 70 ± 0. 03	+ 0. 0030
925	16. 35 ± 0. 05	+ 0. 0033

The nitrobenzene solidifies at 925 kg. per cm² and 16°.

TABLE V.

Cyclohexane + Aniline

p	T	$\frac{dt}{dp}$
1st filling [2])		
1	30°.26 ± 0°.07	
200	31. 60 ± 0. 06	+ 0. 0067
400	33. 20 ± 0. 07	+ 0. 0080
700	35. 52 ± 0. 10	+ 0. 0077
1000	38. 04 ± 0. 10	+ 0. 0084
2nd filling		
1	31°.03 ± 0°.04	
500	34. 77 ± 0. 09	+ 0°.0075
1000	38. 95 ± 0. 08	+ 0. 00835
1100	39. 79 ± 0. 08	+ 0. 0084

For a comparison we give the following results obtained with a Cailletet tube:

critical end-point 31°,02 instead of 31°,03,

[1]) By way of comparison with the preceding binary systems we have also carried out a few observations with this mixture.

[2]) With this first filling the critical concentration was not quite reached; there was a little too much aniline, and it was clearly to be seen how the cyclohexane was dissolved in it.

$\frac{dt}{dp}$ between 1 and 200 atm. 0°,0066 instead of 0°,0067.

The cyclohexane solidifies at 42°,5 under 1200 atm. at —1°.1 under 1 atm. $\frac{dt}{dp} = +\ 0°.036$.

TABLE VI.

Water + tri-ethylamine

p	T	$\frac{dt}{dp}$
First series 5	18°.36 ± 0°.06	
200	22.37 ± 0.06	+ 0°.0206
600	29.53 ± 0.06	+ 0.0179
1000	about 34.5	about + 0.0125
Sec. series 5	18.35 ± 0.05	+ 0.0182
600	29.19 ± 0.11	+ 0.0127
1000	34.26 ± 0.13	+ 0.0103
1500	39.40 ± 0.20	+ 0.0080
2000	43.45 ± 0.15	

In neither of the series was the critical concentration perfectly reached; hence the discrepancy, which is, however, small, between the results. The critical opalescence was, however, clearly to be perceived. In both cases the experiments had to be broken off on account of the appearance of a leak in the piston of the hydrostatic press.

For a comparison we give the following results obtained in a Cailletet tube, which have not yet been published until now:

Plaitpoint for 5 kg. per cm²: 18°,31 instead of 18°,36 and 18°,38.

$\frac{dt}{dp}$ between 1 and 200 kg. per cm²: 0°,0201 instead of 0°,0206.

Above this pressure the plaitpoint temperature increases greatly; at a pressure of 1100 kg. per cm² the mixture remains homogeneous at every temperature, at least no turbidity sets in up to at least 85°, but a decrease of 10 atm. in the pressure suffices to bring us back to the heterogeneous region. When the temperature rises still higher, we seem to reach the maximum pressure of the plaitpoint line, where the branch which comes from the lower critical end-

TABLE VII.

Water + methylethylketone

p	T	$\frac{dt}{dp}$
225	+ 0°.7	
250	+ 3.1 ± 0.1	+ 0°.096
300	+ 7.8 ± 0.2	+ 0.094
350	+ 12.1 ± 0.1	+ 0.086
400	+ 16.05 ± 0.1	+ 0.079
450	+ 19.75 ± 0.15	+ 0.074
500	+ 23.2 ± 0.1	+ 0.069
600	+ 30.2 ± 0.1	+ 0.070
700	+ 37.3 ± 0.1	+ 0.071
800	+ 44.1 ± 0.3	+ 0.068
900	+ 51.3 ± 0.3	+ 0.072
1000	+ 61.6 ± 0.3	+ 0.103
1050	+ 66.9 ± 0.3	+ 0.106

point joins that proceeding from the upper end-point. For though e.g. at 80° the mixture, homogeneous under a pressure of 1100 kg. per cm². becomes turbid when the pressure falls to 1085 kg. per cm². the pressure must be lowered to 1075 kg. at 86°.5 to reach the heterogeneous region. Moreover a mixture homegeneous at 86°5 and 1075 kg. unmixes no longer on *heating*, as it did before, but on *cooling*; on further cooling, if the same pressure is retained, finally the homogeneous region is again reached.

In the last-mentioned system the observations were less accurate than with the others, because the critical opalescence is almost entirely wanting, and the indices of refraction of the two phases are nearly the same; we think, however, that we are justified in accepting the above results with certainty, at least as far as the general course is concerned, because also another filling, with a somewhat different concentration, gave analogous results. Here too the highest pressure for which there was still question of unmixing is about 1100 kg. per cm²; the plaitpoint then was at about 80°; above this temperature the windows became opaque.

§ 5. Summary of the results.

The preceding determinations sufficiently prove the efficiency of

the given method. The material of observation recorded in the tables gives rise to the following remarks.

1. The systems formed by nitrobenzene with a hydrocarbon are not simple cases of retreat as we thought at first [1]; on the contrary they represent cases in which the plait is split up, and belong to case II*b*, in reference to which we had to state in 1909 that we had not found an example of it for normal substances, and about whose possibility for abnormal substances we then ventured to pronounce an opinion only with the greatest reservation [2].

This conclusion appears with perfect certainty for the system nitrobenzene + decane; the critical end-point (meeting of three-phase line and plaitpoint line) lies here on a branch of the plaitpoint line with negative $\frac{dt}{dp}$; if the plaitpoint line is pursued further, $\frac{dt}{dp}$ becomes zero, and then positive. Accordingly the plaitpoint line passes through a minimum, and this minimum is experimentally realisable: the branchplait exhibits a point where the closed portion gets detached, a homogeneous double plaitpoint, and this lies in the absolutely stable region. The question proposed p. 409 of the Lehrbuch der Thermodynamik [3] has, therefore, been answered in the affirmative by experiment.

If in this connection the closely related system nitrobenzene-hexane is considered, it appears that it is only owing to an accessory circumstance that the homogeneous double plaitpoint cannot be realized. For here too $\frac{dt}{dp}$ is negative in the critical end-point, but this negative value becomes smaller and smaller; but just before it has become zero, further investigation is prevented by the appearance of the solid phase. So the plaitpoint line becomes metastable by its meeting with the threephase line solid + two liquid phases; we have again a critical end-point, but now the critical point of two " saturated solutions".

The system petroleum + nitrobenzene — if we may compare it for a moment in this connection with a binary system — no more belongs to type II*b*, but to type II*a*. In the critical end-point $\frac{dt}{dp}$ is here positive, the plaitpoint line is intersected by the three-phrase line above the homogeneous double plaitpoint; hence the latter falls

[1]) These Proc. XII p. 243 and table at p. 239.

[2]) loc. cit. p. 243.

[3]) VAN DER WAALS KOHNSTAMM, Vol. II. Leipzig, Barth. 1912.

in the metastable region inside the transverse plait, and for this reason cannot be realized experimentally.

So we have now realized the succession which we supposed possible in our first communication [1]) for the systems propane + methylalcohol, isobutane + methylalcohol, pentane [2]) + methylalcohol, but about which we could then only pronounce a guarded opinion in the absence of further experimental material to prove the point. We now hope before long to be able to ascertain also for the system propane + methylalcohol whether it really belongs to case II*b*, or to case I.

2. In the second place we have been able for the first time to fully demonstrate a case of type I, with its two critical end-points F and G, and its maximum pressure E [3]). The system water-methylethylketone furnishes an example of this even though we cannot quite reach the lower end-point in consequence of the appearance of the solid phase. So we have a system here for which simply by change of pressure one passes from a partially miscible system to a system with complete miscibility. So such a case, to find which many attempts have been made, appears really to occur. In how far other systems will belong to this, and if particularly the systems classed up to now in case I will appear to belong to II*b*, or possibly to a case I*a* with a plait-point line which has a line parallel to the p-axis as asymptote will have to be revealed by further experiment. In the same way further experiment will have to show whether systems may be found belonging to type II*b*, in which the maximum temperature I and the maximum pressure E can be reached.

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[1]) Loc. cit p. 243.

[2]) We avail ourselves of this opportunity to rectify a few inaccuracies in former tables. In the table annexed to p. 239 loc. cit, for methylalcohol + isopentane read: normal pentane. Idem in table VI, These Proc. XIII, p. 877. In the last table erroneously a L (lower mixing-point) is added to the system ethane + methylalcohol; this should be omitted, just as it is not found in the table of our first paper. Finally the said table VI shows an L? for the system ether and water. As the note of interrogation denotes, we think this lower mixing-point by no means proved. With our new apparatus we have already carried out a few experiments with the system water + ether; they all show that on increase of pressure and decrease of temperature the two phases will approach each other more and more; they point, indeed, in the direction of a lower mixing-point, but we have not succeeded as yet in definitely ascertaining whether or no this will be realisable on account of the appearance of the different ice modifications. We hope we shall be able to return to this subject later on.

We owe the different corrections mentioned in this note to Prof. KUENEN's great kindness, who drew our attention to the mistakes made.

[3]) Fig. 1 l c.

Summarizing we may state:

1. That we have given an experimental method to determine plaitpoints, and other phenomena which must be made directly visible, at high pressures to an amount of more than 3000 atm.

2. That we have demonstrated that the course of the theoretically predicted plaitpoint lines is in concordance with reality in the systems under investigation, albeit that the more intricate case of the splitting-up of a plait occurs more frequently, the less intricate case of simple retreat more rarely than was supposed.

Meteorology. — "*On the interdiurnal change of the air-temperature.*" By Dr. J. P. VAN DER STOK.

(This communication will not be published in these Proceedings).

(April 24, 1913).