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Physics. — “*Investigation of the equilibrium liquid—vapour of the system argon—nitrogen*”. By G. HOLST and L. HAMBURGER.
(Communicated by Professor H. KAMERLINGH ONNES.)

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SUMMARY: I *Introduction*. II. *Preparation and analysis of the gases*. 1. Preparation. 2. Test of purity. 3. Methods of analysis. III. *Temperature measurement*. IV *Determination of the end-points of condensation*. 1. Apparatus. 2 Vapourpressures of oxygen, nitrogen and argon. 3. Mixtures. V. *Determination of the points of beginning condensation*. 1. Apparatus. 2. Measurements. 3. Equation of state of the mixtures. VI. *Tx- and px-diagrams*. VII. *Resumé*.

I. *Introduction.*

Owing to the development in recent years of the incandescent-lamp industry the problem of the technical preparation of argon has come to the front. For this purpose it was natural that beside chemical methods the cryogenic method should draw the attention. As it is a simple matter to obtain mixtures of argon and nitrogen by chemically removing the oxygen from oxygen-nitrogen mixtures which are rich in argon, an investigation became desirable of the behaviour of argon-nitrogen mixtures at low temperature with a view to collecting useful data for a possible argon-nitrogen rectification. This investigation has been carried out by us and we have determined the composition of the liquid and vapour phase as a function of temperature and pressure in the corresponding range of temperatures.

II. *Preparation and analysis of the gases.*

1. *Preparation.*

The preparation of the gases was in general carried out in glass apparatus which had been previously exhausted with a mercury pump and liquid air to a pressure of 0.0003 to 0.001 mm. and subsequently washed out with pure gas. For the calibration of our thermometer the vapour-pressure of pure oxygen was used.

a. *Oxygen.*

This gas we prepared from recrystallised, dry potassium permanganate; the first portion of the gas evolved was drawn away and the rest of the oxygen formed was condensed; the middle fraction of the condensed gas was used.

b. *Nitrogen.*

This gas we prepared from ammonium sulphate, potassium chromate and sodium nitrite; in the purification special attention

was given to the removal of nitric oxide (glowing copper); for further details we refer to a paper which will appear elsewhere.

In this case, as well as in that of oxygen, the purity of the gas was proved *inter alia* by the equality of the vapour-pressures obtained at the beginning and at the end of condensation.

c. *Argon.*

For this gas we could start from the strongly argonous gas-mixtures which the firm of LINDE has recently brought into the market. The final purification was effected by means of HEMPEL's mixture¹⁾ in a manner similar to that given by CROMMELIN²⁾. The only modification which we applied in our apparatus consisted in each tube containing chemical substances which might develop impurities, such as water-vapour etc., or conversely might react with them, being flanked at each end by cooling tubes immersed in liquid oxygen. Care was taken, moreover, that during the complete circulation-process the gas should be at a higher pressure than the atmosphere throughout the whole apparatus.

Again in this case the final product was found to satisfy the test of equal pressures at the beginning and the end of condensation.

d. *The mixtures.*

The mixtures were prepared by adding nitrogen to LINDE's argon-nitrogen mixtures after these had been freed from oxygen by means of glowing copper. The nitrogen had been obtained from air by liberation from oxygen. We gladly acknowledge our indebtedness to Mr. H. FILIPPO JZN. for his kind collaboration in this part of our work. In a few cases use was made of the method of diminishing the percentage of nitrogen of LINDE's mixtures (down to about 5%) by means of a fraction-apparatus constructed by Mr. FILIPPO.

2. *Test of purity.*

The gases and mixtures were tested for the following impurities or, if necessary, simultaneously freed from them.

a. *Water-vapour and carbon dioxide* were removed from the gases which were kept above water, freed from air by boiling, by passing them previously to the measurements through a couple of cooling tubes immersed in liquid oxygen.

b. *Hydrocarbons.* It was found that these were not present: a thin spiral wire of tungsten which was made to glow in the gas mixture was found not to change in resistance³⁾.

¹⁾ W. M. HEMPEL. *Gasanal. Methoden*, 3rd edition p. 151.

²⁾ C. A. CROMMELIN. *Dissert.* Leiden 1910.

³⁾ Comp. L. HAMBURGER, *Chem. Weekbl.* 12, (1915) 62.

c. *Oxygen* was completely removed with yellow phosphorus.

d. *Carbon monoxide*. The gas was tested for this by means of I_2O_5 ¹⁾: it was found not to contain more than $\frac{1}{50}$ %.

e. *Hydrogen*. In testing for this gas we used the method given by PHILLIPS²⁾. The gas contained less than 0.01 % of hydrogen. We may add, that the gases were always condensed before they were used in the measurements and that the liquefied gases were then made to boil under reduced pressure; the vapour that was drawn off must have contained the last traces of hydrogen present and the small admixture of neon must also have been for the greater part removed in this way.

Finally we may give the following data as providing a measure of the purity of the gases.

A. *Oxygen*. The gas was analysed by means of copper (immersed in an ammoniacal solution of ammonium carbonate), later on with sodium hydrosulphite. It was found to contain more than 99.9 % of oxygen.

B. *Nitrogen*. Observations were made with nitrogen, obtained from air by removal of oxygen, which corresponded completely to those made with chemically prepared nitrogen, taking into account the percentage of argon in air nitrogen.

This correspondence, with such widely different methods of preparation, may give us additional confidence that our gases were satisfactorily free from impurities.

C. *Argon*. This substance was tested for absence of nitrogen indirectly by means of the determination of the pressure at the beginning and the end of condensation, but also more directly by means of glow-discharges in potassium vapour (comp. 3) in which no diminution of volume could be detected. (Comp. also the determination of specific gravity § 3c).

3. *Methods of analysis*. It follows from the above that the only gas besides argon which could be present in the mixtures which were intended for the measurements was nitrogen. This fact made it possible to determine the percentage of nitrogen by means of a baroscope. It appeared, however, that the sensitivity of the available balance was not so high as we should have wished, in consequence of which these determinations, at least in the most unfavourable

¹⁾ Comp. DENNIS, Gas analysis (1913) p. 231 and 235.

²⁾ Am. Chem. J. 16 259 (1894).

case, are not more accurate than to about 0.2%. Fortunately we were able to carry out the analysis more accurately by a chemical method, which enabled us to attain an accuracy of 0.1%.¹⁾ We shall begin by a description of the latter method.

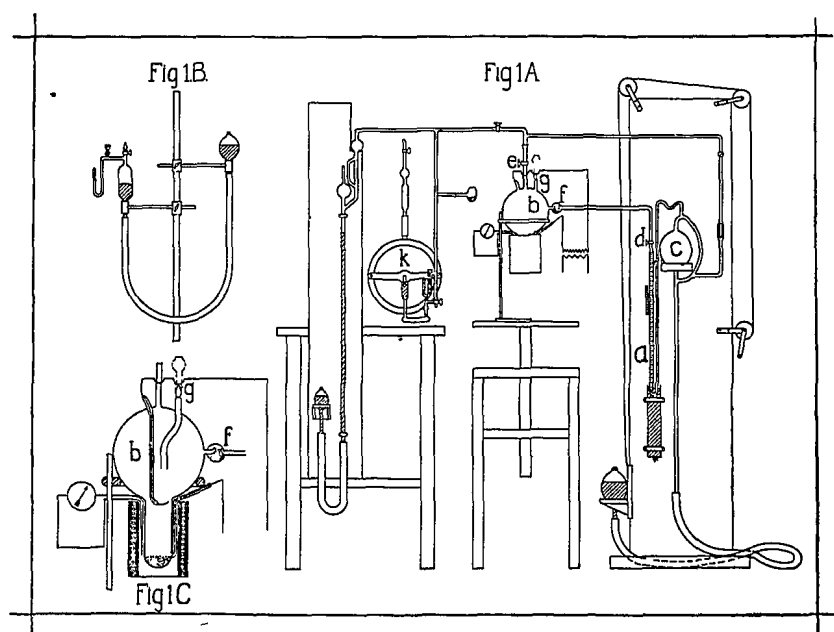
A. *Determination of the percentage of nitrogen in Ar—N mixtures by means of glow discharges in potassium vapour.*

It has been long known²⁾, that in electric discharges through gases such as nitrogen, hydrogen etc. a chemical reaction may occur, especially between the material of the cathode and the rarified gas.

MEY³⁾ pointed out, that this provided a means of liberating rare gases from admixtures. This method was further developed by GEHLHOF⁴⁾, who succeeded by means of glow discharges through potassium vapour in preparing spectroscopically pure rare gases comparatively rapidly — although not in large quantities.

In order to adopt this method to a quantitative analysis of Ar—N mixtures the following apparatus was constructed by us.

A definite quantity of the gas-sample which is collected above



¹⁾ The readings might have been further refined by the use of a cathetometer. but we did not adopt this method, as an accuracy of 0,1% was sufficient for our purpose.

²⁾ Comp. G. SALET, Pogg. Ann. (158) 332, 1876. L. ZEHNDER, Wied. Ann. (52) 56, 1894.

³⁾ MEY, Ann d. Phys 11 127 (1903). GEHLHOFF and ROTTGARDT, Verh. d. D. phys. Ges. 12 411 (1910).

⁴⁾ GEHLHOFF, Verh. D. phys. Ges. 13 271 (1911).

mercury (fig. 1B) was drawn into the burette *a* (fig. 1A). Previously the absorption-apparatus *b* and the TÖPLER-pump *c* had been exhausted by means of the mercury pump *k*; tap *e* was then closed and by opening *d* the gas was transferred from the burette into *b* by means of the mercury column in *C*. On the bottom of the absorption-apparatus (fig. 1C) is the potassium, which is now heated to 200°C. by means of a small electric furnace. An induction-coil is used to send a glow-discharge through the evolved potassium-vapour.

After a few hours — the time required depends on the percentage of nitrogen in the mixture — the unabsorbed portion is transferred back to the burette by means of the TÖPLER-pump.

In using the method the question arises, whether the potassium which may be deposited from the vapour on the cooler parts of the absorption-vessel¹⁾ may possibly absorb argon at its large, freshly formed surface. It is well known, that sublimated metals may absorb at their finely divided surface even the rare gases. Fortunately argon often does not show the phenomenon²⁾. It appeared, moreover, that in our case an absorption of this nature was improbable, from the fact that, after the nitrogen had been absorbed, there was always a residue of gas left which did not show any further contraction however long it remained exposed to the glow-discharge. In the mean time the potassium goes on evaporating and depositing on the colder surfaces, so that the metallic surface is constantly being renewed. If an appreciable absorption of argon took place, it would have been impossible to obtain a constant final volume. It may finally be noted, that a sample of the pure argon which we had prepared did not show any contraction in the absorption-apparatus.

We have also tried to utilize for the purpose of analysis the method of binding nitrogen recommended by STARK³⁾ (electric discharge through mercury vapour). It was found, however, that for a sufficient rate of absorption we had to work at much lower pressures — even when the electrodes were placed opposite each other in the middle of the vessel. With potassium on the other hand every gas-mixture, however high the percentage of nitrogen might be, could be made to react with the metallic vapour at relatively high pressures.⁴⁾

1) As well as the compound which is formed.

2) TRAVERS. Proc. Roy. Soc 60 449. Comp. also KOHLSCHUTTER, Jahrb. Radioakt. 9 402. (1912).

3) Phys. Zeitschr. 1913 p. 497.

4) It is very probable that the reaction is in general started by the splitting of

B. Determination of the percentage of nitrogen by means of a baroscope.

For this purpose use was made of the difference in the upward pressure produced by the gas-mixture on a glass body (volume about 300 c.m.³) which was suspended from one arm of a balance as compared to an open glass vessel of an equal outer surface on the other arm.

The apparatus was arranged in such a manner, that by the turning of a properly shutting glass tap the arresting arrangement of the balance could also be put into action in a high vacuum. The pressures were read by means of a cathetometer.

The following data¹⁾ were used for the baroscope-determinations: density of *air*, free from water-vapour and carbon dioxide, 45° N.L., sea-level, 0° and 76 cm.

	0.0012928
<i>nitrogen</i> (RAYLEIGH and LEDUC)	12514
<i>argon</i> (WATSON)	17809

C. Results.

The following table (p. 878) (column 1—6) gives a survey of different determinations by methods A and B.

In deducing the mean (column 6) we have attributed a double weight to the determinations by method A.

When the mean of the results by method A is compared with those by method B, a systematic deviation will be seen to exist which increases with the percentage of argon in the mixture. As the baroscope had been previously calibrated with other gases (carbon dioxide, nitrogen, air) with satisfactory results, we were led to conjecture that the atomic weight of argon, respectively its specific

the nitrogen molecules by the electric discharge, the atoms which are formed combining with the potassium. STRUTT, (Proc. Royal Soc. Serie A 85 219 and subsequent volumes) found that the re-combination of the N-atoms to molecules (which do not react with the potassium) is much accelerated by an increase of the pressure. This was the main ground, on which we chose the dimensions of the absorption-vessel large as compared with those of the burette. (The low pressure also facilitates the production of the discharge). The fact explains in particular, why the time of absorption in our analyses increases with the percentage of nitrogen in the mixtures. It is also known (STRUTT l. c. comp. also KOENIG Zeitschr. f. Electroch. 1915. 1 June), that metallic vapours accelerate the molisation of nitrogen atoms. (An afterglow on interrupting the discharge was therefore entirely absent in our apparatus). It is of course possible that mercury has this property to a higher degree than potassium, although a different affinity of mercury towards N may also play a part here; this might be one reason for the stronger reaction of the potassium vapour

¹⁾ LANDOLT-BÖRNSTEIN Phys. Chem. Tabellen. 4th ed.

gravity, as at present assumed, was probably not entirely accurate, and we made preparations for an accurate determination. A preliminary measurement gave the normal density as 0.001783⁴.

Number of the gas-mixture.	Method A % N.			Method B % N.	Assumed value.	Method B. modified value.	Final value.
	1st determination.	2nd determination.	3rd determination.				
I.	82.6	82.6	—	82.5	82.6	82.6	82.6
II.	65.2	65.3	65.4	65.0 ⁵	65.2 ⁵	65.2	65.3
III.	31.4	31.6	—	31.3	31.4 ⁵	31.6 ⁵	31.5
IV.	9.9	9.9	—	9.7 ⁶	9.9	10.2 ⁵	10.0
V.	74.2	74.0	—	73.7	74.0	73.8 ⁵	74.0 ⁵
VI.	52.9	52.8	—	52.4	52.7 ⁵	52.7	52.8
VII.	24.4	24.2 ⁵	—	23.8	24.2	24.2	24.3
Pure argon. }	0.0	—	—	—0.5	0.—	0.0	0.0
1.	2.	3.	4.	5.	6.	7.	8.

The account of our investigation had already been written, when a paper appeared by H. SCHULTZE¹⁾ in which the specific gravity of argon is given as 0,00178376. When we use this value, we obtain the results given in columns 7 and 8 of the above table. The mean difference between the determinations with the baroscope and those by method A is now only 0.04%, in other words there is no sign now of a systematic deviation between the two methods. This result proves on the one hand the reliability of method A and may on the other hand be taken to confirm SCHULTZE'S result. We hope soon to be able to publish the results of a more accurate direct determination.

III. *The temperature measurement.*

The measurements were made in a bath of liquid oxygen. In the construction of the cryostat as well as of many other parts of our apparatus we could avail ourselves of the experience gained in the cryogenic Laboratory at Leiden, where one of us had the advantage of working for several years under the guidance of

¹⁾ Ann. d. Physik 48 (1915) p. 269. Heft 2 published 14 Oct. '15.

Professor H. KAMERLINGH ONNES. The temperatures were measured with the aid of a platinum resistance-thermometer. The wire was about 0,1 mm. in diameter and was wound bifilarly on a small tube of Marquardt-material on which a double spiral groove had been cut. At the ends of the tube stouter platinum wires were autogenically sealed on; to these wires the four copper leads were soldered. Before using the thermometer it had been treated thermally by a tenfold immersion in liquid air, each time followed by glowing at about 700°. By that means a constant zero-point was obtained. On three different days the resistance w_0 was found equal to 18.4695 Ω , 18.4697 Ω and 18.4695 Ω respectively; it was measured with a differential galvanometer by KOHLRAUSCH's method.

The calibration of the thermometer took place by using the vapour-pressures of oxygen as determined by KAMERLINGH ONNES and BRAAK, ¹⁾ in the apparatus in which the end-points of the condensation were determined. If p represents the vapour-pressure in mms., the relation between T and p in the range 83,5° and 90° abs. is: ²⁾

$$T = \frac{369,83}{6,98460 - \log. p}.$$

The ratio $\frac{w}{w_0}$ was determined at the same time.

For the Leiden standard platinum thermometer Pt' , the ratio $\frac{w}{w_0}$ as a function of the temperature in the range of temperatures in question is accurately known. It is therefore possible to calculate the value of the constant α in the linear relation which according to NERNST holds for different thermometers:

$$\Delta \left(\frac{w}{w_0} \right) = \alpha \left(1 - \frac{w}{w_0} \right).$$

With $\alpha = 0,00121$ our thermometer could be reduced to Pt' and this constant was therefore used in calculating the temperatures.

To test the apparatus which served for the determination of the points of beginning condensation for its utility, the boiling point of oxygen was also determined in it. The pressure was 762.4 mm. According to the vapour-pressure formula this corresponds to a temperature of 90°.15; the ratio $\frac{w}{w_0}$ gave 90°.16, which agrees very closely. As α was comparatively small for our thermometer ³⁾ and,

¹⁾ H. KAMERLINGH ONNES en BRAAK. Comm. Leiden No. 107a.

²⁾ G. HOLST. Comm. Leiden No. 148a.

³⁾ H. SCHIMANK, (Ann. d. Phys (45) 706, 1914), gives 0.1–0.2° as the uncertainty for $\alpha = 0.03$.

p_{mm}	T	$\left(\frac{W}{W_0}\right)$	$\left(\frac{W}{W_0}\right)Pt'_1$	α
758.1	90 10	0.25258	0.25166	0.00123
757.6	90 09	0.25251	0.25162	0.00119
593.2	87 82	0.24273	0.24184	0.00118
751.2	90 01	0.25220	0.25127	0.00124
Mean . . . 0.00121				

as our platinum was obtained from HERAËUS like that of Pt'_1 , it is very probable that the temperatures as given by us are correct to about 0.02° .

IV. Determination of the end-points of condensation.

1. *The apparatus.* The end-points of condensation were measured by means of a vapour-pressure apparatus provided with a stirrer, as used by KUENEN. The small vessel was placed in a cryostat which contained, beside the resistance-thermometer, a small pump which provided a thorough circulation in the oxygen-bath. The temperature was regulated by an adjustment of the pressure in the cryostat. The constancy of the temperature during the measurements was about 0.01° .

2 Vapour-pressures of oxygen, nitrogen and argon.

Beside the measurements which served as a calibration of our thermometer we determined the vapour-pressure of oxygen at two other temperatures.

T	p	T calc. from vapour pressure formula
83.49	357.7	83.47
78.42	184.3	78.37

Whereas at $83^\circ.5$ the temperature as measured agrees with that calculated from the vapour-pressure to within 0.02° , there is a difference of 0.05° at 78° . It will therefore be advisable as a precaution not to use the formula for T as a function of $\log p$ for purposes of extrapolation.

For nitrogen we found ·

TABLE 4.	
T	p
80.88	1138.0
78 50	878.1
72.10	396.6
69.29	264.6

For argon ·

TABLE 5.	
T	p
89.95	1001.0
87 78	801 7
87.76	802.2
84.02	533.9
83.84	522.6
83.78	518.7
83.71	514.1
83.62	509 2

and hence for the triple point $T = 83^{\circ},81$ $p = 521,4$ m m.

We shall compare these figures with some recent ones of other observers

For oxygen the measurements by HENNING¹⁾ and by v SIEMENS²⁾ may be used.

For all these measurements we have drawn $\log. p = f\left(\frac{1}{T}\right)$ The

¹⁾ F. HENNING Ann. d. Phys. (43) 282, 1914.

²⁾ H v. SIEMENS. Ann. d. Phys. (42) 882, 1913. Comp. also G. HOLST. Comm. Leiden N^o. 148a

greatest differences with HENNING are about 0.02° , v. SIEMENS's measurements differing a little more at the lower temperatures, not more than 0.06° however.

For nitrogen we can also compare our measurements with those by v. SIEMENS; here again the difference is very small at the higher pressures and increases as the temperature falls.

At the higher temperatures our measurements agree but moderately with those of CROMMELIN¹⁾, even if we discard his lowest point which he himself considers less accurate.

The values which we obtain for the vapour-pressures of pure nitrogen by extrapolating the measurements with the argon-nitrogen mixtures are in good agreement with our direct observations.

Argon has also been investigated by CROMMELIN²⁾ in the same temperature-range. His results correspond very well to ours.

There is only a small difference as regards the triple point. As we made a number of observations in the immediate neighbourhood of this point (fig. 2) and as our points fall very accurately on the curve drawn through the other points determined by CROMMELIN, we think it probable that the triple point as determined by us is to be preferred. The differences are for the rest of the order of magnitude of the errors of observation.

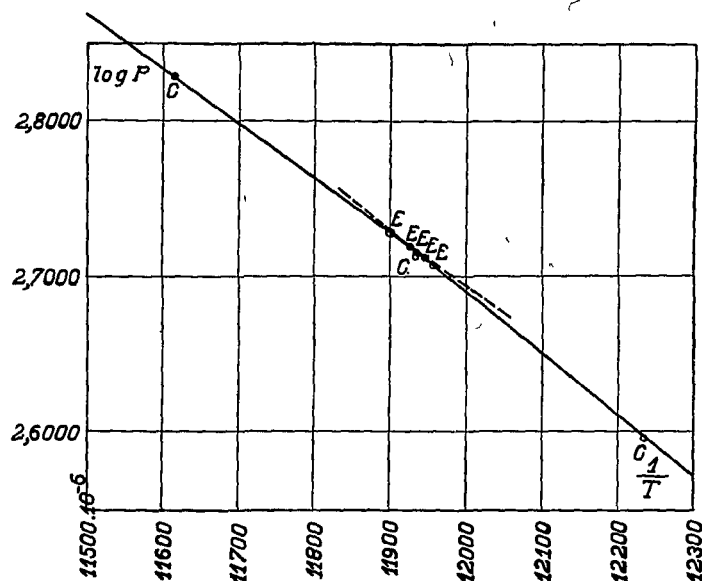


Fig. 2

1) C. A. CROMMELIN. Comm. Leiden N^o. 145d.

2) C. A. CROMMELIN. Comm. Leiden N^o. 138b.

3. *Mixtures.*

For five mixtures the pressure at the end of the condensation was measured at three different temperatures. Not more than $\frac{1}{2}\%$ of the gas was uncondensed.

The composition of the mixtures was given above.

The results are contained in Table 6:

TABLE 6.			
Mixture I. 82.6 % N.		Mixture III. 31.5% N.	
<i>T</i>	<i>p_{mm}</i>	<i>T</i>	<i>p</i>
82.63	1218.1	86.55	1162.3
78.53	781.5	83.47	852.2
74.02	451.0	78.46	487.8
Mixture II. 65.3 % N.		Mixture IV. 10.0% N.	
<i>T</i>	<i>p</i>	<i>T</i>	<i>p</i>
83.49	1175.9	89.86	1198.6
78.53	686.5	87.69	972.0
74.53	424.2	83.53	631.2
Mixture VIII (atmospheric nitrogen 99.—% N. (baroscope)).			
<i>T</i>		<i>p</i>	
81.06		1151.6	
78.43 ^s		863.5	
71.29 ^s		350.9	

When $\log. p$ was drawn as a function of $\frac{1}{T}$ for argon, nitrogen and the mixtures, a set of straight lines was obtained which converge at higher temperatures. The values of p and T which will be used later on for the construction of the px - and Tx -diagrams were taken from this graphic representation.

V. *Determination of the points of beginning condensation.*

1. *Apparatus.*

The apparatus used for this purpose was arranged in the manner of a constant volume gas-thermometer. Its vessel had a volume of about 142 cc. and was provided at the lower end with a small appendix 8 mms. long in which the liquid gas collected. In order to make sure that equilibrium was attained the liquid could be stirred by means of a small steel ball, which on closing a current was drawn up in the field of a small electro-magnet with pole-pieces cut at 45°. In calculating the changes of volume of the vessel the coefficient of expansion was taken as 0.0000212, the mean of the results obtained by TRAVERS, SENTER and JAQUEROD¹⁾ and by KAMERLINGH ONNES and HEUSE²⁾ for Thuringen-glass between 0° and -190°.

The measurement was conducted as follows: a measured quantity of gas was transferred to the vessel and the pressure read at a definite temperature; a second quantity of gas was then measured and transferred to the vessel, and the pressure was read again, etc. etc. until condensation set in. The vapour-pressure was then measured at increasing densities of the vapour.

For a convenient measurement of the quantities of gas which were added, the manometer-tube on the vessel-side was provided with a scale-division and had been accurately calibrated. For the reading of the pressures a cathetometer was sometimes used, sometimes a vertical comparator with steel measuring-rod. In the latter case the accuracy is smaller, but not smaller than about 0,1 mm.

2. *The measurements.*

For each mixture at three different temperatures $\frac{pv}{760}$ was now determined as a function of the pressure, where p is the pressure of the mixture in mms. and v the volume of the gas in the vessel, divided by the theoretical normal volume of the same quantity.³⁾ The point, where this curve shows a discontinuity, is the point of beginning condensation in question.

For each quantity of gas which was added the normal volume was each time calculated; this volume was diminished by the quantity contained in the dead space and the capillary in order to obtain the quantity of gas in the vessel.

¹⁾ TRAVERS, SENTER and JAQUEROD. Phil. Trans. A 200. p. 138.

²⁾ H. KAMERLINGH ONNES and W. HEUSE. Comm. Leiden No. 85.

³⁾ H. KAMERLINGH ONNES and W. H. KEESOM. Enc. d. Math. Wiss. Comm. Leiden Suppl. 23.

TABLE 7.							
Mixture V. 74.05 % N.							
T = 83.°54		RT = 0.3059 ^s		T = 78.°62		RT = 0.2879	
$v = \frac{v_r}{v_{thn}}$	p	$\frac{pv}{760}$	$-\frac{pv}{760} + RT$	$v = \frac{v_r}{v_{thn}}$	p	$\frac{pv}{760}$	$-\frac{pv}{760} + RT$
0.4424	513.5	0.2991	0.0068 ^s	0.6956	308.9	0.2829	0.0050
3541	637.7	2973	0.0083 ^s	0.4421	482.1	0.2806 ^s	0.0072 ^s
2853	786.4	2954	0.0105 ^s	0.3540 ^s	597.4	0.2785	
2423	920.4	2937	0.0122 ^s	0.3540 ^s	597.1	0.2783 ^s	
2117	1044.9	2913	0.0146 ^s	0.2849	630.4	0.2365	
1854	1079.8	2635	—	0.2849 ^s	629.2	0.2360	
1854	1079.0	2633	—	0.2419	650.9	0.2073	
1773	1088.9	2542	—				
1682 ^s	1099.1	2435	—				
Mixture V. 74.05 % N.				Mixture VI. 52.8 % N.			
T = 73.°78		RT = 0.2702		T = 85.°93		RT = 0.3147	
0.8861	228.6	0.2667	0.0035	1.3663	169.7	0.3123	0.0024
6954	290.0	2655	0.0047	0.6310	373.0	0.3099	0.0048
5657	327.8	2443	—	0.2316	989.0	0.3016	0.0131
4413 ^s	349.3 ^s	2031	—	0.2144	1053.9	0.2974 ^s	—
3530	363.2	1688	—	0.2078	1061.6	0.2905	—
				0.2004	1065.3	0.2811	—
Mixture VI. 52.8 % N.							
T = 80° .89		RT = 0.2962 ^s		T = 76° .22 ^s		RT = 0.2791	
1.3979	159.8	0.2941	0.0021 ^s	1.3964	150.6	0.2769	0.0022
0.9459 ^s	235.5	0.2933	0.0029 ^s	0.9439	221.7	0.2755	0.0036
0.7125	311.5	0.2923	0.0039 ^s	0.7122 ^s	293.0	0.2748	0.0043
0.4697	468.4	0.2897	0.0065 ^s	0.6303	330.2	0.2741	0.0050
0.4047	541.8	0.2887	0.0075 ^s	0.5628 ^s	340.5	0.2523 ^s	—
0.3742 ^s	584.1	0.2878	0.0084 ^s	0.4690	357.5	0.2208	—
0.3465	606.6	0.2767 ^s	—	0.4038 ^s	379.8	0.1966	—
0.3069	624.0	0.2521 ^s	—				
0.2807 ^s	636.0	0.2351	—				

T A B L E 7. (Continued).							
Mixture VII. 24.3% N.							
T = 90.11		RT = 0.3300		T = 85.36		RT = 0.3126 ⁵	
$v = \frac{v_r}{v_{thn}}$	p	$\left(\frac{pv}{760}\right)$	$-\frac{pv}{760} + RT$	$v = \frac{v_r}{v_{thn}}$	p	$\left(\frac{pv}{760}\right)$	$-\frac{pv}{760} + RT$
4.0803	61.1	0.3280	0.0020	4.079	57.7	0.3101	0.0025 ⁵
0.5666	434.7	0.3243	0.0057	2.073	114.0	0.3110	0.016 ⁵
0.3170	766.0	0.3197	0.0103	1.0943	215.3	0.3102	0.024 ⁵
0.2959	819.6	0.3191	0.0109	0.4327	534.3	0.3044 ⁵	0.0082
0.2011	1186.7	0.3142	0.0158	0.3437	669.3	0.3029	0.0097 ⁵
0.1928	1228.4	0.3118	—	0.3174	722.8	0.3021	0.0105 ⁵
0.1882	1232.7	0.3054	—	0.3108	737.6	0.3018	0.0108 ⁵
0.1795	1236.7	0.2923	—	0.3048	752.5	0.3018	0.0108 ⁵
				0.2956	756.2	0.2954	—
				0.2867	758.6	0.2864	—
				0.2743	762.5	0.2754	—
T = 80.53		RT = 0.2950		T = 80.53		RT = 0.2950	
4.078	54.6	0.2931	0.0019	0.5961 ⁵	368.0	0.2888	0.0062
2.072	107.6	0.2935	0.0015	0.4923	429.5	0.2785	—
1.094 ²	202.9	0.2923	0.0027	0.4444	438.7	0.2567	—
0.8446	261.5	0.2908	0.0042	0.4324	439.3	0.2502	—
0.5961 ⁵	368.0	0.2888	0.0062	0.4212	439.4 ⁵	0.2437	—

The first column of the above table 7 contains the volume of the vessel v_r , divided by the theoretical normal volume v_{thn} of the quantity of gas which it contains.

For argon we assumed $\frac{v_n}{v_{thn}} = 0,9992$ ¹⁾

„ nitrogen „ „ „ = 0,9996 ²⁾

for the mixtures intermediate values were taken.

¹⁾ H. KAMERLINGH ONNES and C. A. CROMMELIN, Comm. Leiden 118b.

²⁾ Recueil des constantes p. 189.

The second column gives the pressures in mm mercury, all reduced to the same temperature, the third column gives $\frac{pv}{760}$ and the last $\left(\frac{pv}{760}\right) - RT$ for the gaseous state

In fig. 3 $\frac{pv}{760}$ is drawn as a function of p for each of the mixtures for the purpose of determining the pressure at which the condensation begins.

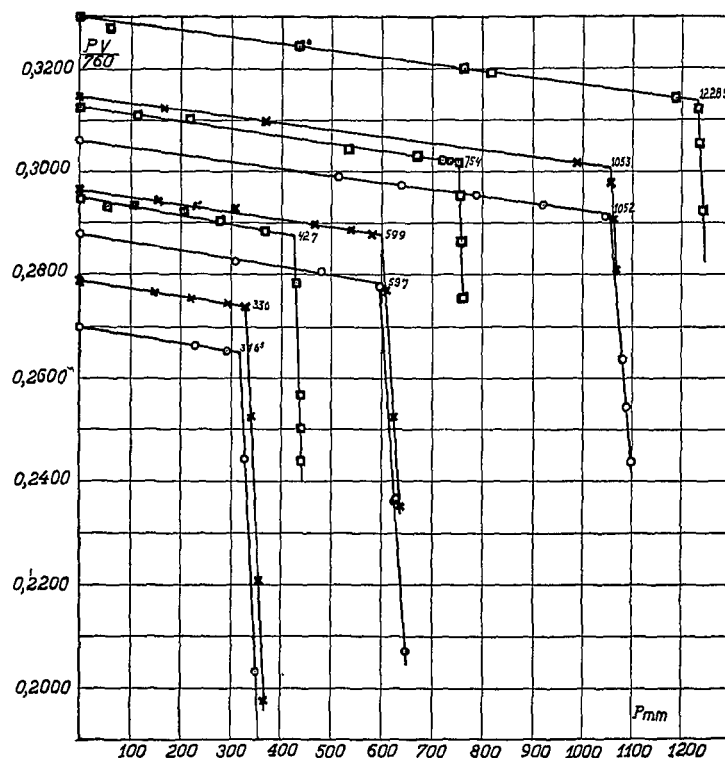


Fig 3

Table 8 contains these pressures and the corresponding temperatures; it also gives the volumes of the saturated vapour expressed in the theoretical normal volume as unit.

When $\log. p$ was represented as a function of $f\left(\frac{1}{T}\right)$, a set of straight lines was obtained, in this case also. As before, the values which served for the construction of the final diagrams were derived from these curves.

It may be mentioned, that with the last mixture of 24.3% N at a temperature very little below $80^{\circ}.50$ the solid began to separate out.

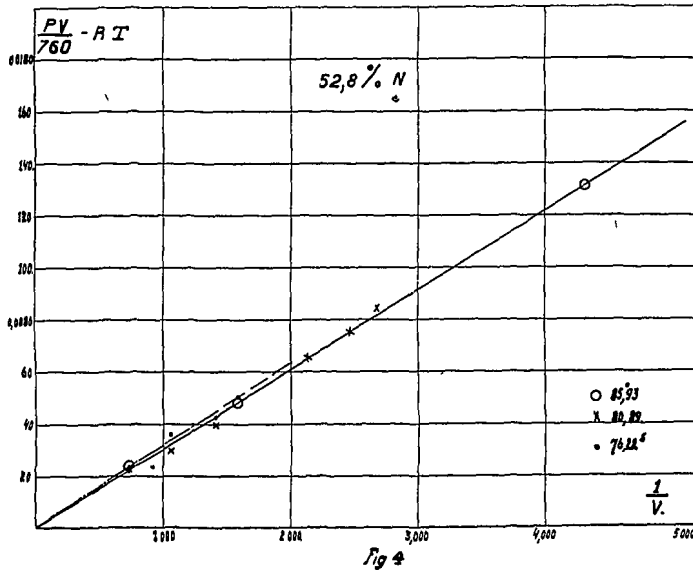
TABLE 8.

Mixture V. 74.05 % N				Mixture VI. 52.8 % N		
T	p	$\frac{vp}{760}$	v	T	p	$\frac{vp}{760}$
83.54	1052	0.2918 ⁵	0.2107	85.93	1053	0.3007 ⁵
78.62	597	0.2787 ⁵	0.355	80.89	599	0.2879 ⁵
73.78	316 ⁵	0.2652	0.638	76.22 ⁵	330	0.2741 ⁵

Mixture VII. 24.3 % N			
T	p	$\frac{vp}{760}$	v
90.11	1228.5	0.3138	0.1942
85.36	754	0.3017 ⁵	0.304
80.53	427	0.2878 ⁵	0.512

3. Equation of state of the mixtures.

Fig. (3) shows on inspection that $\frac{pv}{760}$ is a linear function of $\frac{1}{v}$; preferable, however, to choose $\frac{1}{v}$ as the independent variable in the equation of state for the mixtures under investigation in the



in question can then be represented in the form

$$pv = RT \left(1 + \frac{B}{v} \right)^{-1}.$$

In fig. 4 $pv - RT$ is represented as a function of $\frac{1}{v}$ for mixture VI.

We have computed the values of B in this equation and have obtained the following results

TABLE 9.			
Mixture V. 74.05 % N.		Mixture VI. 52.8 % N.	
T	B	T	B
83.54	- 0.0100	85.93	- 0.0096
78.62	- 0.0113	80.89	- 0.0103
73.78	- 0.0118	76.22	- 0.0108
Mixture VII. 24.3 % N.			
T		B	
90.11		- 0.0100	
85.36		- 0.0107	
80.53		- 0.0122	

Unfortunately so far determinations of B -values for argon at these low temperatures have not been published²⁾. For nitrogen measurements by BESTELMEYER and VALENTINER³⁾ are available.

These measurements give $B = -0.0116$ at $T = 81.4$ in good agreement with our results as regards the order of magnitude.

The equation of state finally enables us to calculate the volume of the saturated vapour. This calculation we are, however, obliged to defer. Table 8 gives the volumes of the saturated vapour for the points which were experimentally determined.

¹⁾ Comp. H. KAMERLINGH ONNES and W. H. KESOM. Enc. d. Math. Wiss. Comm. Leiden Suppl. 23.

²⁾ We understand that the measurements of B for argon undertaken by KAMERLINGH ONNES and CROMMELIN in the Leiden Laboratory will not be completed for a considerable time.

³⁾ A. BESTELMEYER and S. VALENTINER. Ann. d. Phys. (15) 61, 1904.

VI. *Tx- and px-diagrams.*

The data found above enable us to derive temperature-composition as well as pressure-composition diagrams. The values which we obtained are arranged in Table 10 on page 891; by means of these a few *Tx*-curves were drawn (fig. 5) and the *px*-diagram for $T = 85^{\circ}.11$ (fig. 6¹⁾).

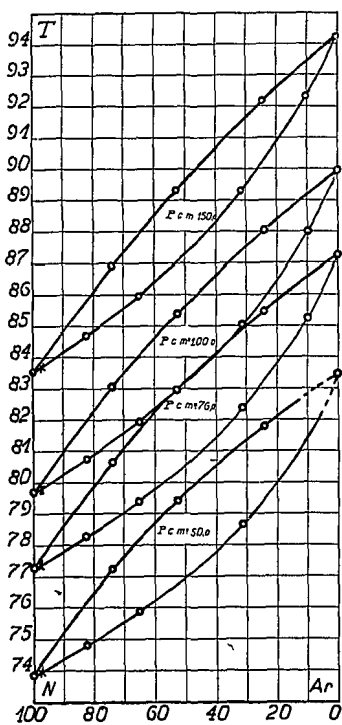


Fig 5.

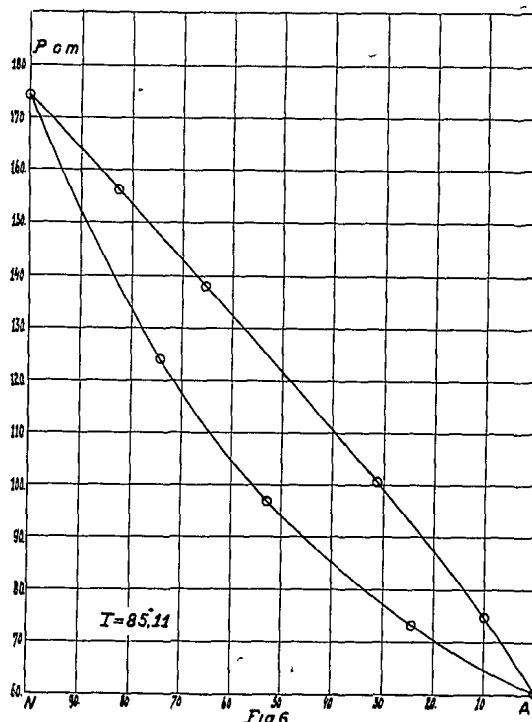


Fig 6

It will be seen, that the difference in composition between the liquid- and vapour-phases is a little smaller on the nitrogen- than on the argon-side. A glance at the figure further shows, that in the preparation by means of fractionation of argon from mixtures containing only a few hundredths of argon no great advantage can be gained from raising the pressure, although the advantages of a better exchange of cold at the higher pressures must not be lost sight of, where a technical method is concerned.

The change of the composition of the gas-phase with that of the liquid-phase satisfies the relation²⁾:

¹⁾ The *Tx* curves for $p = 50$ have been dotted on the argon-side, as the solid makes its appearance here.

²⁾ LEHFELDT, Phil. Mag. (5) 40 397 (1895).

$$\log r' = a + b \log r$$

where r' represents the ratio of the components in the liquid and r the same quantity in the vapour.

TABLE 10. $T-x$ -diagrams.					
	x % N.	$T_p = 50.0$ c.m.	$T_p = 76.0$ c.m.	$T_p = 100.0$ c.m.	$T_p = 150.0$ c.m.
End of cond.	0.0	83.45	87.26	89.93	94.18
	10.0	81.42	85.25	87.98	92.32
	31.5	78.65	82.40	85.05 ^s	89.29
	65.3	75.86	79.41	81.95	85.97
	82.6	74.82	78.30	80.76	84.70
	100.0	73.87	77.28	79.71	83.57
Beginn. of cond.	24.3	81.79	85.46	88.04	92.15
	52.8	79.41	82.97	85.40	89.33
	74.05 ^s	77.21 ^s	80.66	83.08	86.93
End of cond.	99.—	73.94	77.35	79.78	83.64

$p-x$ diagram for $T = 58^{\circ}11$		
	x %	p. c.m.
End of cond.	0.0	60.28
	10.0	74.75
	31.5	100.5
	65.3	137.9
	82.6	156.2
	100.0	174.3
Beginn. of cond.	24.3	73.18
	52.8	96.78
	74.05 ^s	124.2

TABLE 11.							
$p = 50.0$ cm.				$p = 76.0$ cm.			
$a = -0.545$		$b = 1.08$		$a = -0.496$		$b = 1.06$	
T	r'	$r_{\text{calc.}}$	r_{found}	T	r'	$r_{\text{calc.}}$	r_{found}
76.00	1.74	5.36	5.37	80.00	1.34	3.87	3.85
78.00	0.605	2.01	2.01	82.00	0.534	1.64	1.65
80.00	0.247	0.879	0.869	84.00	0.227	0.725	0.718
82.00	0.0695	0.269	0.270	86.00	0.0593	0.205	0.206
$p = 100.0$ cm.				$p = 150.0$ cm.			
$a = -0.451^s$		$b = 1.04$		$a = -0.396^s$		$b = 1.03^s$	
82.00	1.825	4.82	4.81	86.00	1.85	4.32	4.32
84.00	0.706 ^s	1.94	1.93	88.00	0.750	1.83	1.84
86.00	0.305 ^s	0.869	0.872 ^s	90.00	0.346	0.866	0.866
88.00	0.108 ^s	0.323	0.324 ^s	92.00	0.134	0.348	0.348
$T = 85^{\circ}.11$							
$a = -0.466$		$b = 1.11$					
p cm.	r'	$r_{\text{calc.}}$	r_{found}				
80.0	0.164	0.516	0.513				
100.0	0.446	1.27	1.26 ^s				
120.0	0.942	2.49	2.49				
140.0	2.067 ^s	5.06	5.06				

As appears from the above Table 11, the values of a and b in the several Tx -diagrams change with the pressure. In each diagram taken separately the agreement between the calculated and found values is very good.

The result that the liquid-curve in the px -diagram (especially on

the nitrogen side) is only very faintly curved ¹⁾ had been found before in a series of unpublished preliminary determinations and may be looked upon as an indirect confirmation of our observations respecting the vapour-pressures of nitrogen (IV. 2).

The *px*-diagrams shows that especially on the nitrogen-side, the values of the composition of the liquid and vapour phases do not differ much from each other. This would lead to the expectation that the fractionation, especially of the mixtures with little argon, will not be a very easy matter.

When the change with pressure of the composition of the phases is taken into consideration, it follows that the differences in composition increase with diminishing pressure, so that a comparison of the *T-x* diagram for argon-nitrogen at 76.0 cms with BALY'S diagram ²⁾ for the fractionation of air puts the problem of the fractionation of the mixtures in question in a less unfavourable light. At the same time it follows from our results, that the use of mixtures with little argon will give considerable difficulty.

VII. *Resumé.*

1. A method was worked out enabling us to determine the composition of argon-nitrogen mixtures with an accuracy of 0,1 % or, if need be, higher.

2. A systematic difference was found between the results of the determinations with the baroscope and the method referred to under 1, which led us to the conclusion, independently of SCHULTZE'S work (l.c.), that the atomic weight of argon hitherto assumed might not be quite exact. As this systematic difference disappears when SCHULTZE'S value is adopted, the latter is thereby rendered highly probable. A preliminary direct determination gave a value in good agreement with SCHULTZE'S result.

3. New measurements of vapour-pressures for oxygen, argon and nitrogen are published and critically compared with those of previous observers. The triple point of argon was determined with greater accuracy.

4. The end-points of condensation of the argon-nitrogen mixtures were determined with an accuracy corresponding to 0.02° in the temperature.

¹⁾ Pointing to a simple behaviour of argon towards nitrogen.

²⁾ Phil. Mag. 49 (1900) p. 517.

5. At the points of beginning condensation the accuracy is about the same. The saturated vapour-volumes are given.

6. The observations with the mixtures are compared with the equation of state in the form $\frac{pv}{760} = RT \left(1 + \frac{B}{v} \right)$. The accuracy in $\frac{pv}{760}$ was found to be about 0,1 %.

7. Within the range of temperatures investigated $\log p$ for the mixtures can be represented as a linear function of $\frac{1}{T}$, both for the points of beginning condensation and for the end-points.

8. The p - v - and T - v -diagrams are established. As regards the composition of the gas-phase (r) and the liquid-phase (r') they were found to satisfy the relation $\log r' = a + b \log r$.

9. Conclusions were drawn from the shape of the curves in the diagrams in connection with a possible fractional distillation of argon-nitrogen mixtures.

We are glad to be able here to express our sincere thanks to Mr. G. L. F. PHILIPS for the unstinted support afforded to us by which this investigation was made possible.

We also wish to record our cordial thanks to Messrs. W. KOOPMA and J. SCHARP DE VISSER for their zealous assistance in carrying out the measurements and calculations.

*Physical and Chemical Laboratory of the Philips
Eindhoven. Incandescent-lamp works Ltd.*