Physics. — *"Isotherms of di-atomic substances and their binary mixtures. XX. The critical curve of oxygen-nitrogen mixtures, the critical phenomena and some isotherms of two mixtures with 50°/₀ and 75°/₀ by volume of oxygen in the neighbourhood of the critical point."* By J. P. KUENEN †, T. VERSCHOYLE and A. TH. VAN URK. Communication N°. 161 from the Physical Laboratory at Leiden. (Dr. KAMERLINGH ONNES, holding his deeply regretted friend in affectionate memory, is glad to perform the honourable task of presenting for the Proceedings a paper by the late Dr. KUENEN which was made almost ready for the press),

§ 1. *Introduction.*

This work is a continuation of that of KUENEN and CLARK [1]), the investigations, however, being carried out in such a way as to allow of the construction of complete isotherms, which involved a slight modification of the apparatus then used. The mixtures on which measurements were made, contained respectively 50 °/₀ and 75 °/₀ by volume of oxygen, and it was found that these gave sufficient data for the construction of the critical curve. This was found to be almost a straight line, while both critical constants proved to be an almost linear function of the composition.

§ 2. *Preparation of the mixtures.*

A simple mixing apparatus was employed, consisting essentially of a measuring-bulb of about a litre capacity, surrounded by a water-jacket and connected with an open manometer tube, in which the gases to be mixed were measured, and of a mixing bulb of some 2 litres capacity. Through 3-way taps the bulbs could be put in connection with each other, the source of gas, the piezometer to be filled, and a vacuum pump, as might be desired. In measuring the relative quantities of the gases to be mixed, the mercury was

[1]) J. P. KUENEN and A. L. CLARK. These Proc. XIX (2) pg. 1088. (Febr. 1917.) Leiden Comm. N°. 150*b*.

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always brought to a mark on the stem below the measuring-bulb, when the pressure-difference was read with a cathetometer, allowing for the height of the barometer, while the temperature of the waterjacket was observed.

The oxygen was prepared from pure potassium permanganate [1]) and the nitrogen from solutions of sodium nitrite and ammonium chloride [1]). In the preparation of nitrogen the air was first driven out by carbon dioxide; to free the nitrogen from the remaining carbon it was frozen out in liquid oxygen boiling under reduced pressure, before being used. The first part of the evaporating nitrogen was pumped off, and the next part used to fill the apparatus; the residue was also removed.

§ 3. *Apparatus.*

a. *Piezometer.*

The usual type of piezometer used in the laboratory at Leiden was employed. The volume of the large reservoir was some 500 cm³. and that of the small reservoir about 1 cm³. The form of the latter differed from that used in Comm. N°. 150b as an other method of stirring was adopted, to avoid the difficulties mentioned there. It consisted of a capillary about 50 cm. long C, with a bore of ± 0.2 mm., and a cylindrical bulb R, about 10 cm. long, which was carefully rounded at the lower end, so that the stirrer r contained within (a short length of iron wire enclosed in a glass tube) could reach the extreme end, thus avoiding any dead space. The bulb R was graduated; and, as its section and the volume of the stirrer were known by previous calibration, it was possible to estimate the volume of any liquid formed in it. The reservoir was calibrated as a whole after its construction had been completely finished.

b. *Manometer.*

Pressures were read on the closed hydrogen manometer M. 60 [2]). For the arrangement of the pressure connections and of the piezometer, reference may be made to Comm. N°. 97a. (Plate I.)

c. *Cryostat.*

The cryostat contained, besides the small reservoir R two platinum resistance thermometers W for reading the temperature, a stirrer B for the cryostat liquid (in this case ethylene), and the usual auxiliary

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[1]) H. KAMERLINGH ONNES, C. DORSMAN and G. HOLST. Proc. XVII (2) pg. 950. (Dec. 1904). Leiden. Comm. N⁰. 145b.

[2]) These Proc. IX p. 754 (Dec. 1906). Leiden Comm. N⁰. 97a.

capillary *H*, a simple helium thermometer[1]) for ascertaining the mean temperature of the portion of the small reservoir capillary within the cryostat, but above the liquid, as well as the necessary tubes for the introduction and removal of the ethylene.

The connections, required for the regulation of the pressure within the cryostat may be seen in Plate I of Comm. N°. 97[a].

The method of stirring the gaseous and liquid phases within the small reservoir bulb was as follows: round the bulb was fitted a soft iron sheath, which could be moved vertically up and down by means of an electro-magnet *E* above the cryostat, in the same way as the liquid stirrer is worked.[2]) In the lowest position of the sheath *m* (which is of about the same length as the reservoir *R*, and about three times as long as the stirrer), the lower edge was at the level of the bottom of the bulb *R*; in the highest position of *m* its lower edge was raised to fully two thirds of the height of the bulb *R*. In order to be able to obtain a clear view of the whole length of the bulb *R*, two slits were cut out of opposite sides of the sheath *m*, and the latter so arranged that these slits were in line with the clear strips in the silver surfaces of the vacuum-glasses. Round the outer glass a ring electro-magnet *m* was placed with the bottom surfaces slightly above the level of the top of the bulb *R*. By a correct adjustment of the current circulating through this and the weight of the iron sheath *m*, it was possible to raise and lower the latter, which carried the small stirrer *r* with
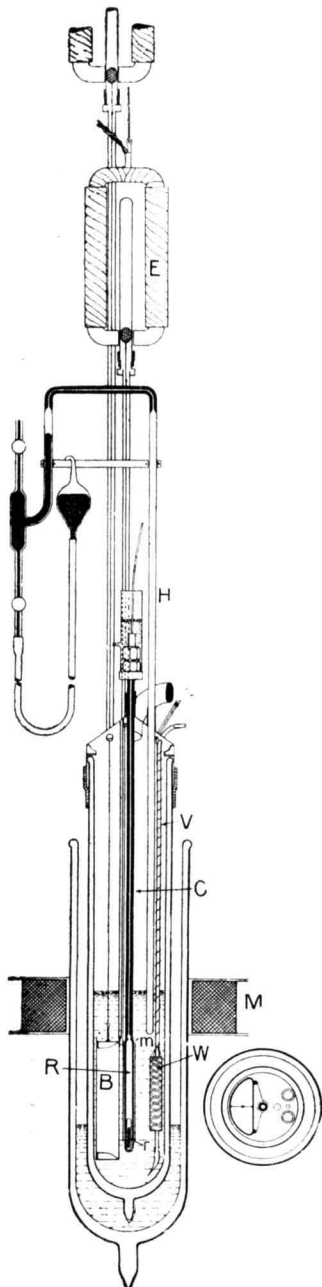

Fig. 1.

[1]) These Proc. IX pg. 754. (Dec. 1906). Leiden Comm. N°. 97*a*.

[2]) These Proc. XX (2) pg. 991 (June 1917). Leiden Comm. No. 152*a* (§ 3).

it, so that the gas and liquid phases in the bulb could be stirred as required. [1])

§ 4. *Observations and precautions.*

Before commencing the work at low temperatures, isotherms were experimentally determined for the two mixtures at 20°, the calculations being carried out on the lines of Comm. N°. 78. The values of the expansion coefficients for the mixtures

$$\alpha = \frac{1}{v_A} \left[\overline{\left(\frac{\partial v_A}{\partial t} \right)_p} \right]_0^{20}$$

required in the calculation of the isotherms were interpolated as linear functions of the composition from the corresponding values of the pure gases, the error involved being negligible. These values were, in the case of oxygen, those found by KAMERLINGH ONNES and HYNDMAN [2]) and, in the case of nitrogen, calculated from isotherms determined at 0° and 20° by one of us, which are not yet published. These normal temperature isotherms were determined with small reservoirs ± 5 cm³ volume. For greater certainty a second series of points were determined for the 75 °/₀ oxygen mixture using the small reservoir of ± 1 cm³ of the piezometer used in the critical zone as a leak occurred during the first series, and consequently only the normal volume determined at the end could be used in the calculations. The agreement of this control is satisfactory. Isotherms were made over a range starting about 5 degrees above the temperature of the critical point of contact, and extending as low as the proportions of the piezometer allowed, i.e., 6 degrees below that temperature for the 50°/₀ mixture, and 2½ degrees for the 75°/₀ mixture. The temperature intervals were in general some 2 degrees, but, in the neighbourhood of the zone, were reduced to ¹/₂₀ degree or less. All observations were made with rising pressure, the importance of which fact is insisted on in Comm. 150*b*; and, after finishing any series, the pressure is completely released, and gas in the piezometer well mixed by successively raising the pressure to 10 atmospheres or so and lowering, before proceeding to a new series. When only one phase was present, the pressure steps were of the order 2—3 atmospheres, but, when two were present, and near the critical zone, they were reduced to a few tenths of an atmosphere and sometimes the raising was accomplished by even

[1]) A. VAN ELDIK. Amsterdam Akad. Versl. Mei—Juni 1897. Leiden Comm. N°. 39.

[2]) These Proc. IV pg. 761. (Maart 1902). Leiden Comm. N°. 78.

smaller steps. As soon as two phases are present, the equilibrium becomes extremely sensitive to the smallest change in pressure or temperature, and therefore the quantities that determine the conditions of equilibrium must be kept as constant as possible. In the critical zone, an alteration of a hundredth of a degree in the temperature will cause the mercury in the stem of the piezometer to rise or fall by millimeters. Although the *end*-points of condensation could be fairly accurately observed, provided the pressure-increases were made with extreme care the tendency of the liquid phase to remain out, despite vigorous stirring, did not allow of accurate observation

Fig. 2.

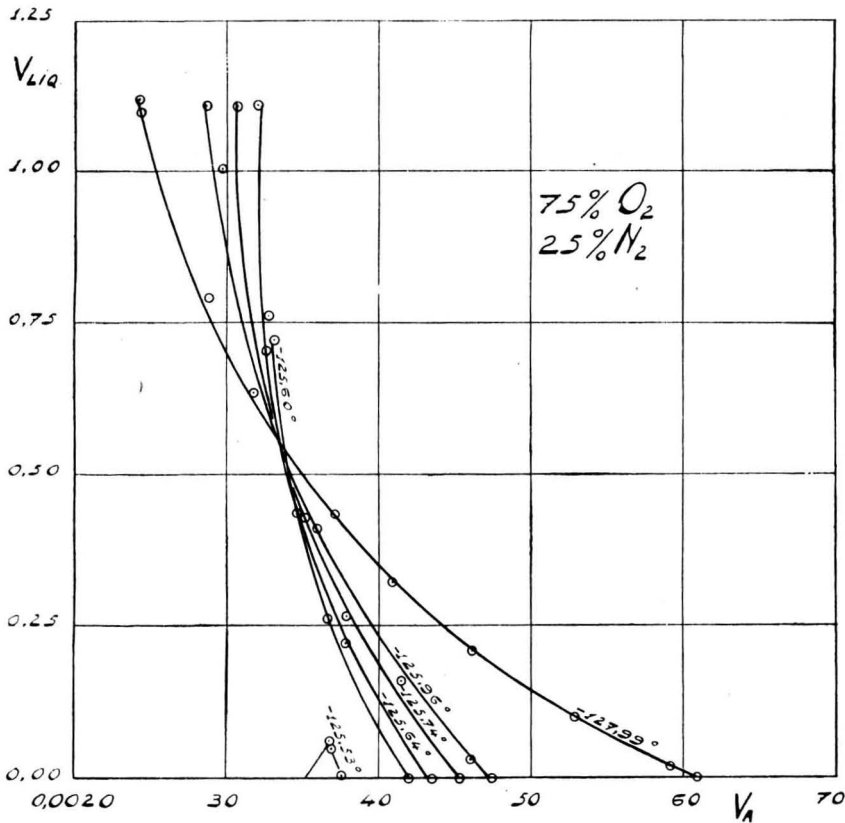of the *beginning*-point. Both points were accordingly graphically taken from the isotherms by finding the intersection of the one-phase and two-phase portions of the latter. Even in this way only very approximate results can be obtained in the critical zone.

The critical phenomena were well observed, both as regards the typical opalescence at and near the plait-point, and the process of
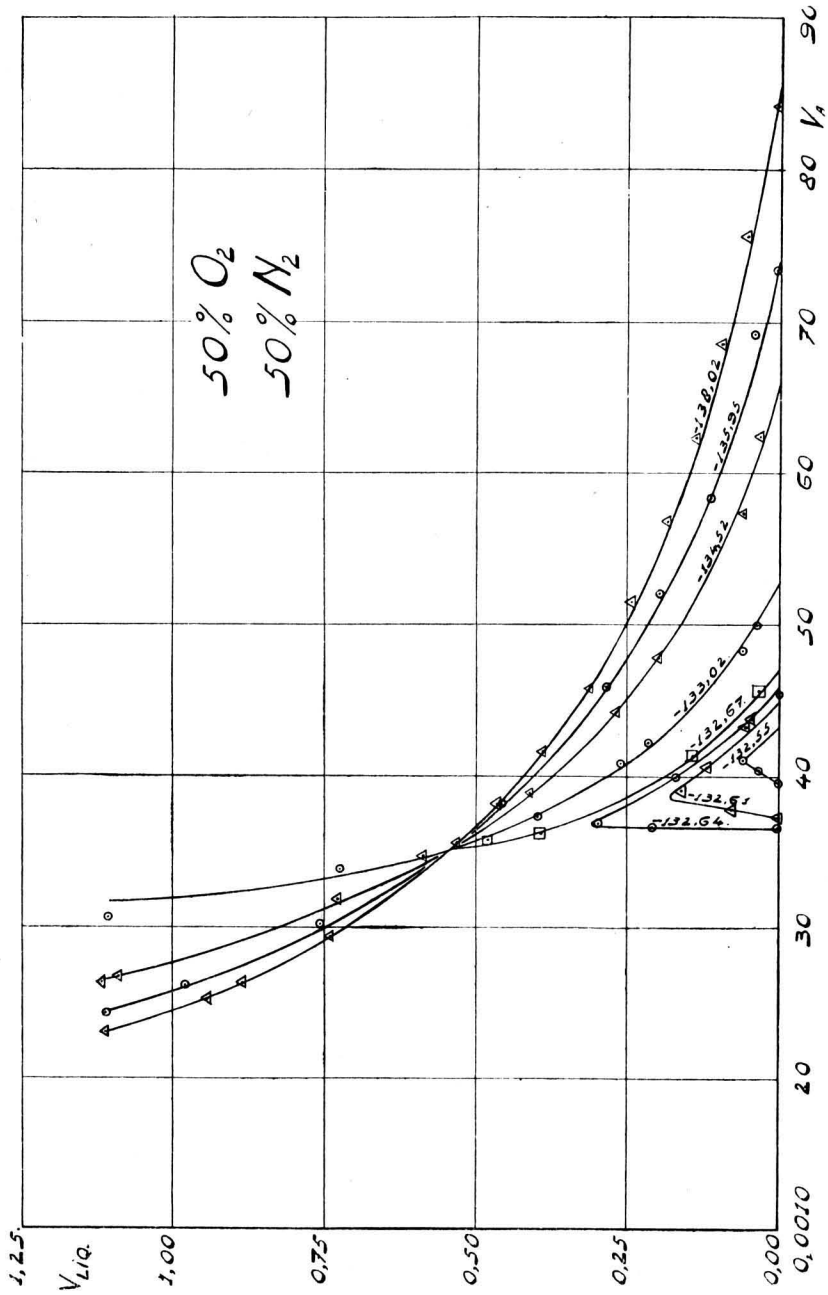
Fig. 3.

retrograde condensation, although the latter was limited to a range of 0.13 degree at most.

As an illustration of the perfection to which the regulation of pressure and temperature has been brought in the Leiden Laboratory, the 50 % mixture was maintained under the plait-point conditions for over an hour, the blue opalescence being continually there, while an indefinite meniscus alternately appeared and disappeared in the middle of the bulb on stirring. From the results a p, v_A graph for each mixture is constructed, and the points of beginning and end condensation determined as previously stated : the border curve is drawn through these. It was found that the two-phase line during the period of observation is to all intents and purposes a straight line, although, in the case of the 50 % mixture, the first points determined after condensation lie below this line on every isotherm. This can hardly be explained by any delay in the appearance of the liquid phase (which would give the reverse effect), and the deviation is far greater than any error of observation.

The accuracy of the pressure determination is at least 1 in 5000[1]); that of the temperature reading within 0.02 of a degree, while the probable observation error of the volumes is not greater than 1 in 2000 when one phase was present, and 1 in 200 when two phases were present — apart from a possible constant calibration error of 1 in 500. To eliminate the last error it would have been necessary to measure a few points of the isotherm of 20 ° C. of hydrogen with this piezometer, and to compare the results with the accurate isotherm of SCHALKWYK. But as such accuracy was of little importance in our case, this was not done.

The results for the two mixtures are given below with :

p = pressure in atmospheres.

v_A = volume, expressed in the normal volume.

V_L = volume of liquid, expressed in volume of the small reservoir.

θ = temperature on the provisional intern. Kelvin scale, reduced by 273.09.

The condensation points, as found from the p,v_A graphs, are plotted on a p,t $(t = \theta)$ graph; the results of KUENEN and CLARK being included on the same graph. (Fig. 4). The vapour pressures of pure oxygen[2]) and nitrogen[3]) are also plotted, and the critical

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[1]) C. A. CROMMELIN and Mej. E. J. SMID. These Proc. XVIII (1) pg. 472. Leiden. Comm. Leiden. N⁰. 146c.

[2]) H. KAMERLINGH ONNES, C. DORSMAN and G. HOLST, l. c.

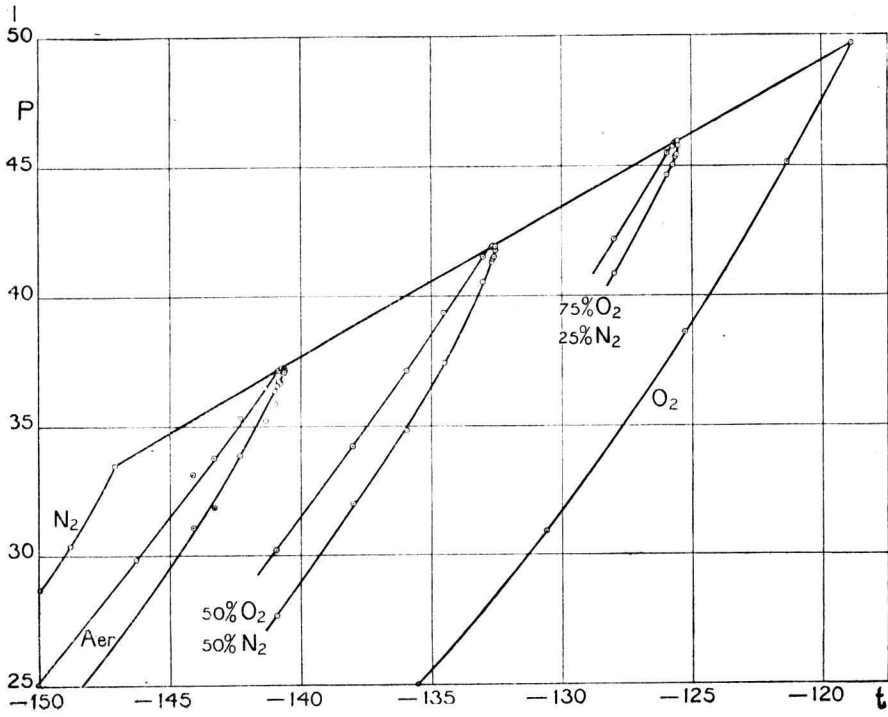[3]) C. A. CROMMELIN. These Proc. XVII (2) 959 (Dec. 1914.) Leiden Comm. N⁰. 145d.

Fig. 4.
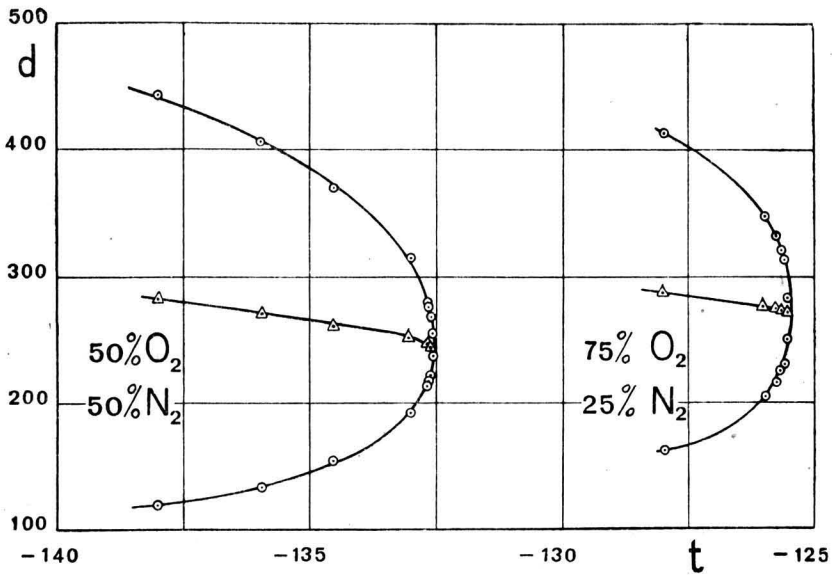
Fig. 5.

curve drawn tangential to the various border curves, touching those in the plait points.

By plotting V_L the volume of the liquid against v_A a series of curves are obtained which clearly show the process of retrograde condensation in the case of the 50% mixture [1]).

A peculiarity of the last mixture is that all the lines in this graph go through the point $V_L =$ half the volume of the small reservoir, which means that the corresponding line of constant division of volume is a line of constant v_A, therefore in the p,v_A diagram it runs parallel to the p-axis [2]).

If a d_A, t graph is drawn, a diameter is obtained which is rectilinear (as for a pure substance), but which is strongly curved towards the temperature axis at the extreme end, though in this zone, the position of the point as found must be necessarily rather qualitative than quantitative.

The plait-point constants were found to be:

	50% O_2 Mixture. (series XIV. 4.)	75% O_2 Mixture. (series IX. 5.)	
p	41.90	45.89	(observed)
v_A	0.00358	0.00336	(from p,v_A graph)
θ	—132°.66	—125°.60	(observed)

The critical point of contact constants were found to be:

	(series IX. 4.)	(series X. 3).	
p	41.90	45.86	(from p,v_A graph)
v_A	0.00404	0.00375	(from d_A,t graph)
θ	—132°.53	—125°.53	(observed)

For the critical point of contact temperature it was found that, at 0.01 of a degree above it no condensation was, of course, observed, and at 0.01 below there was a momentary, but very evident condensation.

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[1]) J. E. VERSCHAFFELT. These Proc. I. pg. 288 (Dec. 1898.) Leiden Comm. N⁰. 45.

[2]) Leiden Comm. Suppl. N⁰. 23, p. 51. Enc. Math. Wiss. V 10.

Results for the mixture 50 % O_2—50 % N_2.

Isotherm of 20° C.

Point.	p	d_A	pv_A	Point.	p	d_A	pv_A
1	34.24	32.39	1.0573	7	52.34	49.82	1.0507
2	37.55	35.56	1.0561	8	46.25	43.91	1.0533
3	41.39	39.25	1.0548	9	41.12	38.99	1.0546
4	46.41	44.07	1.0531	10	37.28	35.28	1.0567
5	51.88	49.37	1.0508	11	34.03	32.17	1.0579
6	51.85	49.35	1.0507				
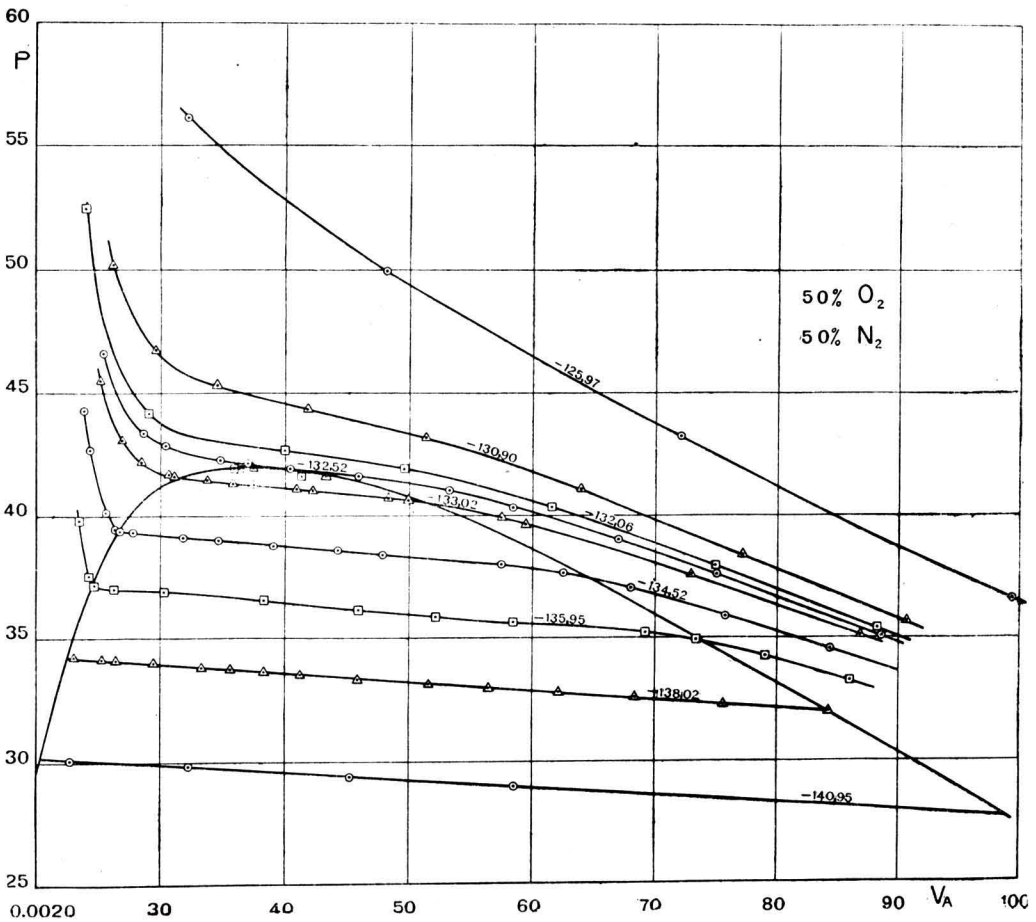
Fig. 6.

Isotherms at low temperature.

Point	p	v_A	V_L	θ	Point	p	v_A	V_L	θ
I. 1	37.12	0.01080		$-120°.76$	IV. 1	35.41	0.00882		$-132°.06$
2	44.81	00793		8	2	37.95	749		6
3	54.30	533		6	3	40.33	615		6
					4	41.91	495		7
II. 1	36.57	0.00994		$-125°.97$	5	42.67	398		6
2	43.23	721		7	6	44.17	290		6
3	49.95	481		8	7	52.44	239		6
4	56.13	322		7					
					IX. 1	35.08	0.00886		$-132°.51$
III. 1	35.65	0.00907		$-130°.90$	2	37.57	751		1
2	38.38	771		0	XV. 1	39.03	670		2
3	41.03	639		89	IX. 3	40.34	584		1
4	43.16	513		91	XV. 2	41.02	532		2
5	44.35	418		0	3	41.60	458		2
6	45.26	345		0	IX. 4	41.90	404		3
7	46.73	295		0	5	42.13	369		0
8	50.18	261		0	XV. 4	42.25	347		2
					5	42.78	303		2
					IX. 6	43.38	285		1
					XV. 6	46.60	253		2

Point	p	v_A	V_L	δ	Point	$p.$	v_A	V_L	δ
X. 1	41.84	0.00410	0.051	−132°.56	VI. 4	41.69	0.00306	1.000	−132°.00
2	41.89	403	029	5	V. 6	42.16	284		3
3	41.93	395	000	5	XVI. 6	43.13	268		1
					7	45.78	251		2
XII. 1	41.60	0.00436	0.042	−132°.61					
XI 1	41.62	433	046	0	XVII. 1	34.52	0.00843		−134°.50
XII. 2	41.77	406	107	0	2	35.89	757		2
XI. 2	41.85	392	138	1	3	37.03	680		1
XII. 3	41.92	379	068	0	4	37.60	624	0.030	1
XI. 3	41.95	372	000	1	5	37.98	574	054	3
XII. 4	41.97	373	000	0	6	38.41	478	177	2
					7	38.58	442	240	2
XIII. 1	41.46	0.00455	0.000	−132°.64	8	38.80	390	369	2
2	41.75	399	151	4	9	39.01	346	524	2
3	41.89	369	268	4	10	39.14	318	653	1
4	41.91	366	186	4	11	39.33	277	916	2
5	41.91	366	000	4	12	39.40	267	978	3
					13	39.46	263	1.000	2
XIV. 1	41.40	0.00455	0.026	−132°.67	14	40.15	256		1
2	41.61	413	123	7	15	42.64	242		2
3	41.89	362	350	7	16	44.25	237		2
4	41.90	358	430	6					
					XVIII. 1	33.21	0.00860		−135°.98
V. 1	35.12	0.00867		−133°.01	VII. 1	34.32	790		1
2	37.58	728		1	XVIII. 2	34.85	733	0.002	8
3	39.67	594		3	VII. 2	35.21	692	037	1
XVI. 1	39.92	574		3	3	35.66	584	101	3
VI. 1	40.62	499	0.031	2	XVIII. 3	35.82	521	175	7
XVI. 2	40.65	527		2	4	36.14	459	255	7
V. 4	40.73	482	54	1	VII. 4	36.60	382	408	1
VI. 2	41.03	421	192	0	XVIII. 5	36.90	302	677	7
XVI. 3	41.08	408	235	2	6	37.09	262	877	6
VI. 3	41.29	373	356	−132 .99	VII. 5	37.19	246	990	2
V. 5	41.34	358	472	−133°.03	6	37.56	242	1.000	2
XVI. 4	41.46	336	648	2	XVIII. 7	39.77	234		7
5	41.62	310		2					

Point	p	v_A	V_L	ϑ
XIX. 1	32.02	0.00842	0.000	$-138°.02$
2	32.31	755	048	2
3	32.57	684	082	2
4	32.78	621	123	2
5	32.98	564	165	2
6	33.16	514	219	1
7	33.37	457	279	2
8	33.54	415	349	2
9	33.65	382	414	2
10	33 75	355	480	2
11	33.84	331	540	2
12	33.99	293	663	1
13	34.11	263	792	1
14	34.16	253	843	1
15	34.24	230	1.000	2
VIII. 1	27.69		0.000	$-140°.95$
2	28.99	0.00585	186	5
3	29.41	452	316	5
4	29.85	322	544	4
5	30.09	227	901	6

Results for the mixture 75 % O_2,—25 % N.

Isotherm of 20° C.

Point	p	d_A	pv_A	Point	p	d_A	pv_A
I. 1	51.68	49.49	1.0441	II. 1	36.91	35.08	1.0521
2	45.18	43.15	1.0471	2	42.90	40.89	1.0492
3	40.12	38.20	1.0503	3	48.79	46.63	1.0464
4	35.91	34.14	1.0520	4	56.40	54.08	1.0429
5	32.69	31.01	1.0542				
6	28.89	27.34	1.0564				

Isotherms at low temperature.

Point	p	v_A	V_L	θ	Point	p	v_A	V_L	θ
I. 1	33.93	0.01206		$-119°.95$	II. 7	50.16	0.00426		$-122°.47$
7	35.00	1151		7	8	52.05	327		6
2	37.20	1045		5	9	54.15	280		6
3	39.31	0956		5	10	56.41	260		6
8	39.55	944		6					
4	42.27	835		5	III. 1	32.71	0.01159		$-125°.00$
5	45.54	715		4	2	35.59	1006		0
9	45.88	704		6	3	38.40	0869		4.99
6	48.66	608		4	4	41.19	737		5.01
10	50.64	540		7	5	44.28	587		1
11	53.36	443		8	6	46.04	467		1
12	55.97	355		6	7	46.83	359		1
13	59.13	294		7	8	47.51	293		1
					9	48.73	265		1
II. 1	33.29	0.01183		$-122°.47$	10	50.60	248		2
2	35.82	1055		6					
3	38.60	0926		6					
4	41.72	793		6					
5	45.00	661		7					
6	48.02	535		6					

Point	p	v_A	V_L	δ	Point	p	v_A	V_L	δ
VI. 1	32.68	0.01149		—125°.42	VII. 6	45.65	0.00326	0.631	—125°.73
2	35.97	9973		3	7	45.70	307	1.000	4
3	39.30	813		2	8	46.19	277		3
4	42.54	657		2	IV. 1	32.53	0.01143		—125°.96
5	44.89	520		1	2	35.93	0959		6
6	45.67	440		2	3	39.41	789		8
7	45.93	382		2	4	42.37	641		7
8	46.14	346		3	5	43.68	561		7
9	46.59	294		2	6	44.67	474	0.000	7
10	47.95	261		2	7	44.75	460	025	6
X. 1	45.89	0.00369	0.041	—125°.53	8	44.91	415	142	6
2	45.90	345	53	3	9	45.15	361	368	6
3	45.86	375	000	3	10	45.43	297	901	6
IX. 1	45.49	0.00419	0.000	—125°.60	11	45.51	287	1.000	6
2	45.72	366	236	0	12	46.11	267		6
3	45.81	347	394	0	13	48.83	248		6
4	45.85	333	648	59	V. 1	32.74	0.01076		—127°.99
5	45.89	336	1.000	60	2	35.41	0926		8.00
VIII. 1	44.89	0.00394		—125°.64	3	38.10	785		0
2	45.36	433	0.000	4	4	40.19	663		0
3	45.46	408	78	4	5	40.89	609	0.000	7.99
4	45.59	378	199	3	6	40.95	592	020	9
5	45.75	343	455	4	7	41.14	529	090	9
6	45.80	328	682	4	8	41.38	462	186	9
7	45.83	321	1.000	5	9	41.55	409	289	9
VII. 1	44.43	0.00523		—125°.75	10	41.70	371	389	8.00
2	45.09	453		5	11	41.88	318	569	0
3	45.12	448	0.000	4	12	42.04	288	709	7.98
4	45.38	378	239	6	13	42.19	244	994	9
5	45.50	354	384	4	14	42.28	242	1.000	9
					15	43.17	236		8.00