

*Citation:*

Quint, N., The determination of isothermals for mixtures of HC1 and C2 H6, in:  
KNAW, Proceedings, 2, 1899-1900, Amsterdam, 1900, pp. 40-52

double walled copper box lined with thick felt, the inner and the outer wall being provided with plate-glass windows in order to enable us to take readings along the whole scale of the tube (comp. Pl. II fig. 4). The space between the two walls was filled with water and the constancy of the temperature was promoted by stirring.

The tube to be calibrated rests on a wooden ring and the lengthening-piece with stopcock, welded on to the upper-reservoir, passes through an india rubber stopper cut in two. The point of the manometer-tube through which the mercury flows is protected from variations of temperature by a copper felt-lined cap fastened to the box by a bayonet-adjustment; this cap can easily be removed (for a short time) whenever we want to let a quantity of mercury flow out from the tube.

The readings for determining the normal volume are made while the manometer-tube is placed in a double-walled box as described above, (comp. Pl. II fig. 5) but in which the windows were only small, as we wanted to read only the position of the mercury in the *U*-tubes and of the thermometer. These readings and that of the standard barometer (the box communicating with the atmosphere by a small tube) yield a perfectly accurate determination of the normal volume, which is of the greatest importance for the investigation of the isothermal lines.

**Physics.** — Prof. VAN DER WAALS presents on behalf of Mr. N. QUINT GZN. a paper on: „*The determination of isothermals for mixtures of HCl and C<sub>2</sub>H<sub>6</sub>.*”

#### *Introduction.*

At the commencement of this investigation there were but few observations made, which might be used for testing Prof. VAN DER WAALS's theory on the behaviour of mixtures of two substances. At that time Mr. KUENEN was the only one who had examined some mixtures and his observations agreed with that theory. In order to add to the material on this subject (to which also Mr. VAN DER LEE, Mr. VERSCHAFFELT, Mr. HARTMAN have since contributed), I have examined mixtures of HCl and C<sub>2</sub>H<sub>6</sub>. The results of the determinations of the isothermals and a short description of the experiments follow; I hope soon to publish some further details and a calculation of volume contraction etc.

*The substances.*

From the theory follows that some mixtures, when being condensed at a certain temperature will show the phenomenon, indicated as retrograde condensation second type. Mr. KUENEN had not been able to observe this phenomenon; therefore it was desirable to select substances, in which at least theoretically, the phenomenon of r. c. II was to be found.

As Mr. KUENEN states in Phys. Soc. (13) 10, 1895, this is the case with some mixtures, if the component that has the higher vapour-pressures, has also the higher critical temperature. We settled therefore on HCl and C<sub>2</sub>H<sub>6</sub>, because each of these substances has also a critical pressure which may be easily attained.

HCl was obtained by adding drops of concentrated sulphurous acid to pure HCl, to which some Fe<sub>2</sub>SO<sub>4</sub> had been added. When the gas obtained in this way, was dried, it was very pure, as appeared from the slight increase of pressure (at 12° about 0,2 atm.), when condensed and from the agreement of the critical data with those found by ANSDELL.

In order to obtain ethane, acetate of sodium was subjected to electrolysis; the gas which was developed, was condensed at a low temperature (about -50°), the vapourphasis was removed, and from the liquid phasis a quantity of gas had been collected. Though this method is the same as had furnished good results to Mr. KUENEN, I have not succeeded in making the gas as pure; this C<sub>2</sub>H<sub>6</sub> presented in being condensed at 21°, an increase of pressure of 1,4 atm. As however the values for the critical data as found by me (crit. temp. 31°,88; crit. pressure 48,94 atm.) did not differ much from those found by Mr. KUENEN for his ethane (crit. temp. 31,95 à 32,2; crit. press. 48,64 à 48,91) and as moreover it is difficult to obtain perfectly pure ethane, as clearly appears from the observations of others (DEWAR, OLSZEWSKY and HAENLEN found resp. for crit. temp. 35°, 34° and 34°,5 and for crit. press. 45,2; 50,2 and 50 atm.) I resolved to continue the observations with the ethane I had obtained.

*The Method.*

The compressibility of the two substances mentioned and also that of four mixtures (prepared in a mixing-apparatus made completely of glass), was compared with that of dry air, free from carbonic acid, at temperatures which were the same for the two substances and for

4\*

the mixtures. The gas was compressed in a calibrated tube of CAILLETET, on which the mm. were marked, and the thickwalled part of which was placed in a waterbath of about 35 L. After this water had reached the desired temperature, the temperature was kept constant by means of an alternating current, which passed through two tubes filled with a solution of  $\text{NH}_4\text{Cl}$ , which were placed in the bath. Moreover in this bath were found the coil, serving to move the electro-magnetic stirrer in the CAILLETET-tube, and a stirrer, kept in motion by the flow of water.

The temperatures between  $15^\circ$  and  $35^\circ$  were read from a thermometer, which was divided in  $\frac{1}{20}^\circ$ ; the others from thermometers with a division of  $\frac{1}{10}^\circ$ ; now and then the thermometers were tested by means of a normal thermometer, which had been compared with an air thermometer at the Reichsanstalt.

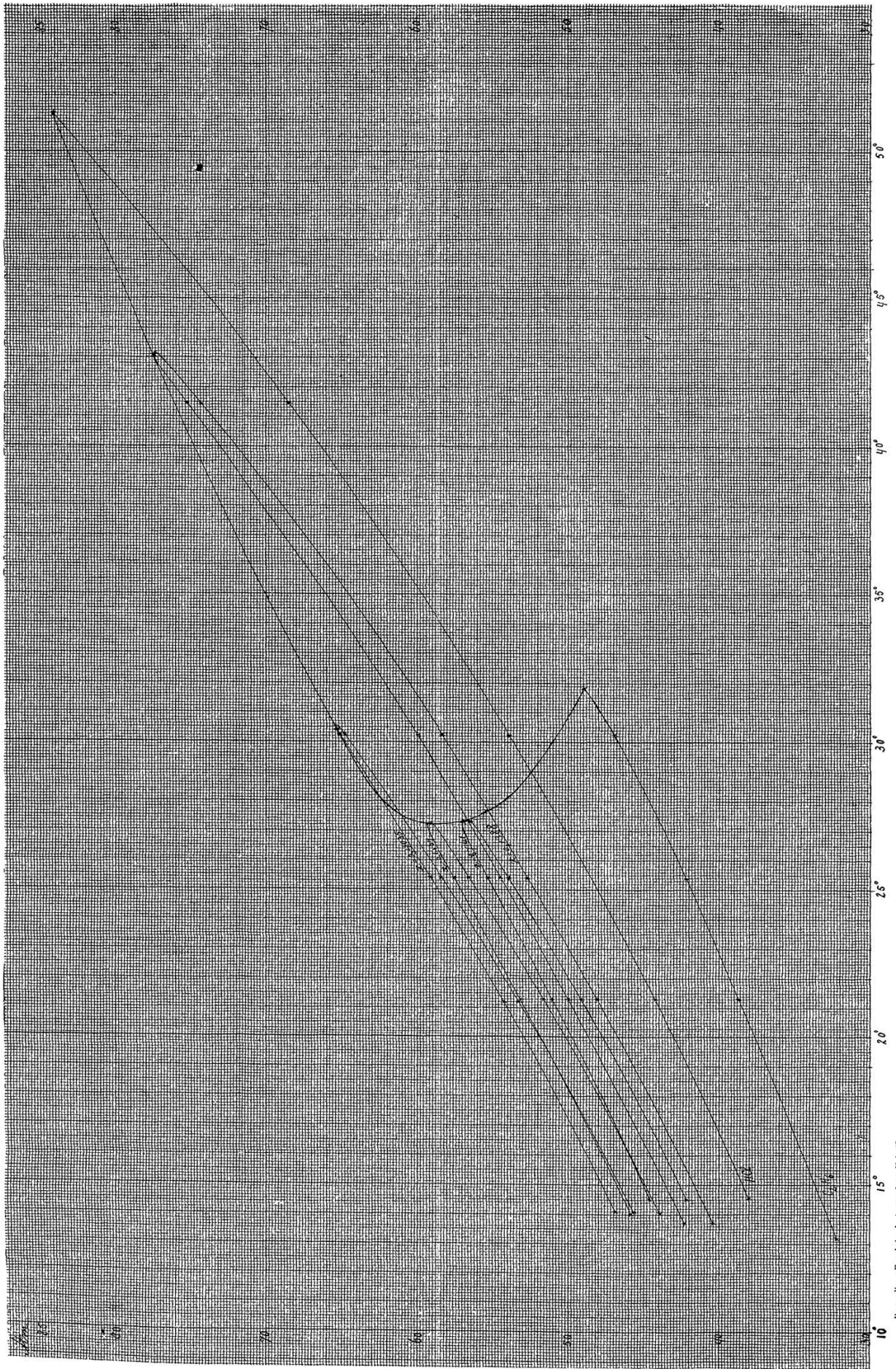
The pressures were calculated by making use of the table which Mr. AMAGAT gives for the compressibility of air in Ann. de Ch. et de Phys. 6<sup>e</sup> série 1898.

### *The Results.*

It appeared already in the observation of the first mixture, that I, no more than Mr. KUENEN, should succeed in observing the retrograde condensation 2<sup>nd</sup> type. For the critical temperature of the point of tangency and of the plaitpointcurve were so near each other, that I could scarcely state a difference between these temperatures. Moreover, also in these mixtures the phenomenon of a maximum pressure and a minimum critical temperature appeared, which made the region, where r. c. II was possible, still more limited. (See KUENEN, experiments on mixtures of  $\text{N}_2\text{O}$  and  $\text{C}_2\text{H}_6$  etc. Zeitschr. für phys. Chem. XXIV, 4, 1897).

This maximum pressure occurs when  $x = 0.44$  and this minimum critical temperature when  $x = 0.62$  (ethane is considered as the solved substance,  $\text{N}_2\text{O}$  as the solving substance), as appears from the graphical representation, in which the course of the plaitpointcurve, of the curves of the vapour pressure of the simple substances and the border-curves of the mixtures are indicated. This diagram, drawn up according to the initial and final points of condensation, occurring in the tables, is founded on the following tables.

N. QUINT Gen., Flakpointcurve and border-curves for mixtures of HCl and C<sub>2</sub>H<sub>4</sub>.



HCl		C <sub>2</sub> H <sub>6</sub>		Mixture I. $x = 0,1388$				
$t$	$p_a$	$t$	$p_a$	$t$	$p_a$	$p_b$		
14,55	38,03	13,2	32,21	13,7	40,42	42,33		
21,3	44,25	21,3	38,75	21,3	48,11	49,97		
30,23	53,82	25,4	42,19	25,4	52,74	54,48		
41,45	68,47	30,23	46,92	30,23	58,36	59,93		
51,3	84,13	31,88	48,94	41,45	74,37	75,26		
				43,1	77,51			
Mixture II. $x = 0,4035$			Mixture III. $x = 0,6167$			Mixture IV. $x = 0,7141$		
$t$	$p_a$	$p_b$	$t$	$p_a$	$p_b$	$t$	$p_a$	$p_b$
14,1	45,72	46,94	14	43,96	45,83	14,5	42,18	44,60
21,2	53,36	54,25	21,3	51,64	53,18	21,3	49,08	51,10
25,4	58,42	59,19	25,4	56,55	57,57	25,4	53,87	55,25
30,23	64,80	65,11	27,25	59,15		27,33	56,49	56,92
30,43		65,30	27,25	59,30		27,37	56,81	
30,53	65,42							

The results of the determinations of the isothermals are represented in the tables from A to F. The following remarks may be added:

The values represent the observations, so that the corrections, which might be drawn from the graphical representation, have not been applied.

The isothermal of 25°,4 for HCl and that of 52°,5 for mixtures II are not given, as the former was most likely not reliable, and as the latter could not be determined, because the CAILLETET-tube was broken.

When the substance was divided into heterogeneous phases, the vapour-volumes then present were also repeatedly measured; they are, however, less accurate than the total volumes on account of the uncertainty of the correction, which is to be made for the meniscus. All volumes are expressed in the theoretical normal volume (i. e. the volume at 0° and 1 atm. multiplied with  $(1 + a)(1 - b)$ ) as unity; moreover the volumes, at which for the first time liquid is to be observed, are underlined, and those at which the vapour phasis disappears, are doubly underlined.

The pressures are expressed in atmospheres, the error will seldom exceed  $\frac{1}{1000}$ , at least for the lower pressures.

A. Hydrochloric acid.  $V_0 = 54,348 \text{ cm}^3$ .

Temp.	Tot. Vol 0,0	Vapour Vol 0,0	Pressure.	Temp.	Tot. Vol 0,0	Pressure.
14°,55	<u>1890</u>		38,03	30°,23	2170	39,08
	1738	1717	38,09	(contin)	2112	39,81
	1615	1584	38,09		2077	40,29
	0902	0796	38,09		2041	40,74
	0420	0258	38,14		1990	41,36
	0190		38,21		1930	42,16
	<u>0189</u>		38,25		1820	43,84
21°,30	2157		37,18		1733	45,20
	2149		37,25		1628	46,85
	2122		37,58		1505	48,94
	2105		37,81		1402	50,75
	2086		38,01		<u>1230?</u>	53,82
	2065		38,23		0219	53,95
	2043		38,46		<u>0207</u>	54,10
	2023		38,69	41°,45	2347	39,32
	1897		40,24		2200	41,14
	1885		40,38		2069	43,05
	1804		41,45		1951	44,78
	1792		41,64		1840	46,64
	1780		41,81		1712	48,88
	1710		42,74		1531	51,17
	1686		43,07		1431	54,64
	1615		44.		1261	58,47
	44,16		1603		1148	61,20
44,25		<u>1566</u>	1027		64,18	
44,47		<u>0194</u>	0913		66,96	
30°,23	2318		37,44		<u>0830</u>	68,47
	2269		37,96		<u>0239</u>	68,63
	2220		38,50			

( 45 )

Temp.	Tot Vol 0,0	Pressure.	Temp.	Tot. Vol. 0,0	Pressure.
51°3 crit. point	0414	84,13	52°5	1986	47,05
			(contin)	1807	50,34
52°5	2706	37,22		1638	53,72
	2546	39,08		1450	58,28
	2358	41,45		1260	63,42
	2168	44,14		1075	68,88

B. Ethane.  $V_0 = 54,491 \text{ cM}^3$ .

Temp.	Tot Vol. 0,0	Vapour Vol. 0,0	Pressure	Temp.	Tot. Vol 0,0	Vapour Vol. 0,0	Pressure.
13°2	1968		32,21	25°4	1822		37,02
	1818	1781	32,29		1599		39,19
	1599	1521	32,36		1414		40,88
	1321	1178	32,48		1265		42,10
	1032	0822	32,72		1255		42,19
	0725	0443	33,05		0880	0696	42,56
	0434	0072	33,53		0665	0362	42,89
	0387		33,71		0477	0067	43,29
	<u>0368</u>		33,89		<u>0430</u>		43,54
21°3	1876		35,26	30°23	1785		38,86
	1785		36,05		1599		40,86
	1692		36,91		1414		42,88
	1599		37,70		1228		44,88
	1506		38,38		1042		46,39
	1488		38,59		0949		46,90
	1479		38,66		<u>0940</u>		46,92
	1469		38,72		0930		46,94
	<u>1464</u>		38,75		<u>0498</u>		47,76
	0526	0173	39,76				
	<u>0404</u>		40,13				



( 46 )

Temp.	Tot. Vol. 0,0	Pressure.	Temp	Tot. Vol. 0,0	Pressure.
31°,38	0759	48,26	41°,45	1210	50,48
31°,63	<u>0759</u>	48,79	(contin.)	1191	50,73
31°,63	<u>0563</u>	49,06		1172	51,05
31°,83	0669	48,95			
31°,86	0697	48,93	52°,5	1786	45,45
31°,88	0688	48,94		1767	45,64
crit.point.				1749	45,87
33°,73	0473	54,41		1730	46,14
41°,45	1785	42,13		1711	46,50
	1767	42,34		1526	49,73
	1748	42,63		1507	50,02
	1730	42,83		1489	50,26
	1711	43,10		1470	50,68
	1526	45,74		1228	55,47
	1507	45,99		1210	55,81
	1489	46,23		1191	56,11
	1470	46,52		1173	56,65
	1228	50,12			

C. Mixture I.  $V_0 = 54,989 \text{ cm}^3$ . $x = 0,1388$ .

Temp.	Tot. Vol 0,0	Vapour Vol. 0,0	Pressure	Temp.	Tot. Vol. 0,0	Vapour Vol 0,0	Pressure.
13°,7	2019		37,20	13°,7	1110	1031	40,96
	1957		37,86	(contin)	0868	0759	41,21
	1897		38,54		0617	0465	41,51
	1840		39,22		0348	0015	41,90
	1783		39,91		0217		42,13
	<u>1725</u>		40,41		<u>0213</u>		42,33
	1704		40,42				
	1548	1529	40,60	21°,3	2132		37,84
	1367	1324	40,72		2020		39,20
					1897		40,74

( 47 )

Temp	Tot. Vol. 0,0	Vapour Vol. 0,0	Pressure.	Temp	Tot. Vol. 0,0	Vapour Vol 0,0	Pressure.
21°,3	1783		42,27	30°,32	<u>1032</u>		58,36
(contin.)	1655		44,11	(contin )	0808	0742	58,78
	1548		45,66		0479	0312	59,38
	1428		47,48		<u>0250</u>		59,93
	<u>1382</u>		48,11	41°,45	2559		37,10
	1061		48,48		2406		38,79
	0760	0642	48,86		2221		41,20
	0450	0274	49,52		2031		43,88
	<u>0227</u>		49,97		1854		46,71
					1675		50,07
25°,4	2270		37,19		1511		53,36
	2145		38,63		1316		57,81
	2020		40,27		1136		62,25
	1893		41,94		0953		67,09
	1773		43,65		0853		69,93
	1655		45,43		<u>0613</u>		74,37
	1540		47,29		0515		74,72
	1419		49,34		0425		74,95
	1300		51,41		<u>0313</u>		75,26
	<u>1212</u>		52,74	43°,1	0420		77,51
	0961	0907	53,10	pl. p. t.			
	0643	0515	53,57	52°,5	2735		37,15
	0408	0216	53,96		2690		37,62
	<u>0236</u>		54,48		2531		39,48
					2342		41,96
30°,23	2369		37,10		2146		44,78
	2232		38,71		1959		47,92
	2045		40,98		1769		51,63
	1863		43,54		1585		55,55
	1707		45,99		1406		60,11
	1569		48,34		1234		65,06
	1404		51,35		1049		71,03
	1257		54,25		0878		77,04
	1255		54,28				

D. Mixture II.  $V_0 = 55,887 \text{ cM}^3$ . $x = 0,4035$ .

Temp	Tot Vol. 0,0	Vapour Vol. 0,0	Pressure.	Temp.	Tot Vol. 0,0	Vapour Vol 0,0	Pressure.
14°,1	2116		36,29	25°,4	0511	0288	58,72
	1918		38,51	(contin.)	<u>0332</u>		59,19
	1745		40,63	30°,23	2414		36,52
	1573		42,84		2235		38,56
	1398		45,11		2059		40,83
	<u>1345</u>		45,72		1867		43,50
	0949	0847	45,86		1698		46,21
	0609	0404	46,10		1528		49,20
	<u>0282</u>		46,94		1341		52,80
					1162		56,46
			0865			62,20	
			<u>0610</u>			64,80	
21°,2	2241		36,55	0528	0378	64,99	
	2056		38,67	0465	0178	65,10	
	1867		41,03	<u>0417</u>		65,11	
	1697		43,41	30°,43	<u>0439</u>		65,30
	1523		45,98	30°,53 plattp.	0471		65,42
	1340		48,95	30°,58	0488		65,45
	1161		51,79	41°,45	2537		37,29
	<u>1045</u>		53,36	2355		39,46	
	0839	0607	53,57	2173		41,83	
	0489	0254	53,76	1976		44,75	
<u>0306</u>		54,25	1799		47,70		
25°,4	2294		36,83	1641		50,80	
	2098		39,16	1461		54,60	
	1914		41,60	1292		58,58	
	1754		43,87	1105		63,49	
	1583		46,59	0872		70,24	
	1401		49,73	0582		78,02	
	1208		53,18				
	1039		56,18				
	<u>0877</u>		58,42				
	0732	0647	58,48				

E. Mixture III.  $V_0 = 54,207 \text{ cM}^3$ .

$$x = 0,6167.$$

Temp.	Tot. Vol. 0,0	Vapour Vol 0,0	Pressure	Temp.	Tot. Vol. 0,0	Vapour Vol 0,0	Pressure.	
14°	2015		36,53	25°,4 (contin.)	1778		42,50	
	1854		38,28		1550		45,83	
	1651		40,61		1306		49,65	
	1490		42,56		1122		52,66	
	<u>1355</u>		43,96		0926		55,39	
	1177	1121	44,17		<u>0799</u>		56,55	
	0969	0850	44,43		0662	0517	56,87	
	0775	0588	44,70		0520	0216	57,17	
	0531	0266	45,13		<u>0416</u>		57,57	
	<u>0327</u>		45,83		0361		64,38	
	0317		54,33		27°,25	2271		36,79
	0305		66,94			2152		38,16
	21°,3	2160				36,69	1928	
1974			38,81	1734			43,61	
1786			41,18	1554			46,40	
1612			43,53	1336			49,97	
1422			46,18	1119			53,65	
1243			48,73	0893			57,14	
<u>1015</u>			51,64	0772			58,35	
0857		0768	51,92	0714			58,68	
0662		0459	52,27	0684		58,88		
0484		0184	52,75	0666		58,91		
<u>0365</u>		53,18	0629		59,10			
0337		63,01	<u>0612</u>		59,15			
0326		69,15	0583	0525	59,19			
25°,4	2245		36,72	0562	0460	59,23		
	2 34		39,14	0546	0296	59,28		
				pl. p.	0 40	0296?	59,30	

Temp.	Tot. Vol. 0,0	Pressure.	Temp.	Tot. Vol. 0,0	Pressure.
27° <sub>25</sub>	0498	59,34	41° <sub>45</sub>	2113	41,85
(contin )	0469	59,54	(contin,)	1920	44,70
	0439	60,06		1740	47,67
	0406	61,56		1553	51,26
	0384	63,98		1372	54,99
	0366	67,80		1192	59,26
27° <sub>30</sub>	0587	59,21		1185	59,40
	0564	59,25		1045	62,97
				0814	69,11
				0579	76,07
				0469	81,32
30° <sub>23</sub>	2337	36,73			
	2188	38,42			
	2174	38,60			
	1984	40,96	52° <sub>5</sub>	2665	37,20
	1795	43,63		2445	39,80
	1618	46,35		2195	43,18
	1432	49,60		2006	46,07
	1256	52,70		1830	49,13
	1057	56,41		1817	49,42
	0796	60,57		1624	53,38
	0493	63,64		1391	58,90
	0365	74,91		1192	64,42
				1017	70,19
41° <sub>45</sub>	2518	36,89		0854	76,19
	2285	39,63			

F. Mixture IV.  $V_0 = 54,305 \text{ cm}^3$ .

$$x = 0,7141.$$

Temp.	Tot. Vol. 0,0	Vapour Vol. 0,0	Pressure.	Temp	Tot Vol. 0,0	Vapour Vol. 0,0	Pressure
14°,5	1895		37,13	25°,4	1426		46,54
	1735		38,81	(contin.)	1237		49,35
	1598		40,31		1052		51,84
	1451		41,92		<u>0853</u>		53,87
	1448		41,96		0709	0574	54,26
	<u>1422</u>		42,18		0586	0310	54,72
	1153	1072	42,64		<u>0434</u>		55,25
	0882	0710	43,15				
	0611	0347	43,77	27°,33	<u>0530</u>		56,92
	0606	0339	43,78	27°,34	<u>0677</u>		56,49
21°,3	<u>0347</u>		44,60	27°,35	0811		55,69
	2066		37,15	27°,37 pl p.	0576	0271?	56,84
	1905		38,85	27°,39	0664		56,62
	1709		41,26		0645		56,68
	1539		43,43		0621		56,75
	1357		45,81		0590		56,87
	<u>1079</u>		49,08	27°,40	0617		56,83
	0838	0705	49,62				
	0582	0300	50,44	30°,23	2266		37,03
	<u>0385</u>		51,10		2095		38,90
25°,4	2142		37,24		1913		41,20
	1974		39,17		1714		43,96
	1774		41,69		1542		46,56
	1589		44,20		1361		49,51

Temp.	Tot. Vol. 0,0	Pressure	Temp	Tot. Vol. 0,0	Pressure.
30°,23	1182	52,51	41°,45	1179	58,10
(contin.)	0993	55,61	(contin.)	0993	62,47
	0797	58,24		0800	67,27
	0560	60,48		0571	73,93
	0399	68,04			
			52°,5	2613	37,40
41°,45	2445	37,29		2428	39,59
	2285	39,12		2168	43,03
	2100	41,48		1921	46,90
	1910	44,18		1662	51,70
	1727	47,04		1187	63,13
	1545	50,42		0936	71,12
	1362	54,08		0758	77,77

Physics. — “*The elementary theory of the ZEEMAN-effect. Reply to an objection of POINCARÉ.*” By Prof. H. A. LORENTZ.

§ 1. In a recent article in *L'Éclairage Électrique*<sup>1)</sup> POINCARÉ comes to the conclusion that the well known theory of ZEEMAN's phenomenon, according to which every luminous particle contains either a single movable ion, or a certain number of such ions whose vibrations are mutually independent, can account for the doublet which is seen along the lines of force, but is unable to explain the triplet which one observes in a direction perpendicular to these lines. This result is obtained by treating, not the emission but the absorption in the magnetic field, and it is curious that the same mode of reasoning has led VOIGT<sup>2)</sup> to formulae implying the existence of the triplet. I believe this discrepancy to be due to POINCARÉ's erroneously omitting the term

<sup>1)</sup> POINCARÉ, La théorie de LORENTZ et le phénomène de ZEEMAN, *Éclairage Électrique*, T. 19, p. 5, 1899.

<sup>2)</sup> VOIGT, Ueber den Zusammenhang zwischen dem ZEEMAN'schen und dem FARADAY'schen Phänomen, *Göttinger Nachrichten*, 1898, Heft 4, p. 1.