Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

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Schalkwijk, J.C., Precise Isothermals. V. The isothermal of hydrogen at 20 degrees C. up to 60 atmospheres, in: KNAW, Proceedings, 4, 1901-1902, Amsterdam, 1902, pp. 107-124

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$$x_{1} x_{2} \dots x_{8} x_{9} = \begin{vmatrix} X_{7,8} & X_{7,9} & X_{7,10} \\ X_{7,9} & X_{7,10} & X_{8,10} \\ X_{7,10} & X_{8,10} & X_{9,10} \end{vmatrix} + \begin{vmatrix} X_{8,9} \\ X_{7,10} & X_{9,10} \end{vmatrix}$$

$$y_1 y_2 \cdot \cdot y_8 y_9 = \begin{vmatrix} X_{1,3} & X_{1,6} & X_{1,10} \\ X_{1,6} & X_{1,10} & X_{3,10} \\ X_{1,10} & X_{3,10} & X_{6,10} \end{vmatrix} + \begin{vmatrix} X_{3,6} \\ X_{1,10} & X_{1,10} \\ X_{1,10} & X_{6,10} \end{vmatrix}$$

$$z_{1} z_{2} \ldots z_{8} z_{9} = \begin{vmatrix} X_{1,2} & X_{1,4} & X_{1,7} \\ X_{1,4} & X_{1,7} & X_{2,7} \\ X_{1,7} & X_{2,7} & X_{4,7} \end{vmatrix} + \begin{vmatrix} X_{1,2} & X_{1,7} \\ X_{1,7} & X_{4,7} \end{vmatrix}$$

by which the coordinates of the ninth point are expressed in the coordinates of the 8 other points of intersection.

The obtained results for the products of the corresponding coordinates of the 9 points are forms of the 72nd degree.

Observation: In quite the same way we can determine the eighth point common to three surfaces of the 2nd degree passing through 7 given points. We then obtain for the products of the corresponding coordinates of the 8 points expressions of the 56th degree.

Physics. — J. C. SCHALKWIJK: "Precise Isothermals V. The isothermal of hydrogen at 20°C. up to 60 atmospheres. (Communication N⁰. 70 (3^d continuation) from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES).

§ 1. The small number of observations made with hydrogen, of which the most important are those by REGNAULT (Mém. de l'Ac. XXI) going up to 28 Atm. and those by AMAGAT, of which the published results begin only at 100 atm., together with the small reliability of the values, which can be derived from them for VAN DER WAALS' quantities a and b made me resolve to contribute to the investigation of the isothermal of hydrogen, which has for many years been under consideration in the Physical Laboratory at Leiden (comp. Comm. N^o. 14 by KAMERLINGH ONNES, Proceedings of December 29th '94) and to do this by again experimenting upon this gas at the ordinary temperature.

The apparatus, methods and investigations discussed in the Proceedings of Oct. 29th '98, June 24th '99, Dec. 29th '00, Jan. 26th '01 and May 25th '01 (Comm. N^{os}. 44, 50, 67 and 70) allow us to make such a precise determination of pressure and volume that we can a priori count upon the possibility of determining the values to be ascribed to α and b by observations at pressures up to 60 atm.

The hydrogen has been prepared as described in Comm. No. 27, § 5 (Proceedings of May 30^{th} '96) and No. 60 § 22 (Proceedings of June 30^{th} '00). The four piezometer tubes were simultaneously filled at the apparatus, and were six times entirely exhausted by means of the mercury pump and heat, and then filled again.

§ 2. The normal volume. To calculate each isothermal determined by means of a piezometer it is of the highest importance to know the normal volume. It seems that in most of the measurements of other observers its determination has left much to be desired; but KAMERLINGH ONNES' arrangement of the piezometer tubes allows us, as will be seen from this section, to attain the degree of accuracy desired.

Before being placed into the compression apparatus the piezometer tubes were brought into the water bath (represented Comm. N⁰. 50, Pl. 2, fig. 5) between the two brass walls of which water at 20° C. from the thermostate flowed during continual stirring. The inner copper vessel was closed at the upper end by means of an india rubber stopper, through which a thermometer had been passed and also an air tight connecting tube ¹) to the barometer, which tube

¹) This connecting tube could not easily be made at the lower end, as the inner copper vessel was standing loose on three corks, and a long tube reaching from the stopper to the bottom could not be used, as round the steel flanged tube cemented on the glass tube only half a centimeter space was left. (In order to prevent during the experiments the leakage of mercury, the hard red cement of MINDELEJEFF at the lower end was replaced by soft black cement, which moreover was covered at the inside with an india rubber solution). In order to ascertain, that this connecting tube did not interfere with the attainment of equilibrium of pressure, the measurement

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in order to prevent convection currents was bent entirely downwards outside the bath. The standard barometer has been mounted in an other room, and the connecting tube led thither under the floor; it was read by Mr. BOUDIN while I simultaneously made a measurement of the difference in level of the mercury in the U-tube of the piezometer. It is this latter determination which most renders uncertain the measurement of pressure. For the diameter of the U-tube is only about 8 m.m., so that with the greatest height of the meniscus that occurs viz. 1.66 m.m. the depression becomes 0.69 m.m.¹) and a difference in diameter of 0.1 m.m. gives here already a difference of 0.03 m.m., while a difference in height of 0.1 m.m. gives a difference in depression of 0.06 m.m. If moreover we take into account that the height of the mercury in the limbs of the U-tube is read through a water-layer of 6 c.m. thickness, it is obvious that in the measurement mentioned an error may enter, which greatly diminishes the accuracy of the measurement of pressure otherwise to be expected in the normal volume; this may certainly explain the fact that the difference between the largest and the smallest values of the normal volume with tube IV amounts to even $\frac{1}{3,300}$ which under otherwise similar circumstances leads us to expect an accidental difference of 0.22 m.m. in the measurement of pressure. Only from many measurements and repeated mountings — of tube IV 17 were made on 5 different days and every day the apparatus was mounted anew - we can learn the normal volume with sufficient

accuracy, for the mean error then appeared to be $\frac{1}{10.000}$.

The volume occupied by the gas during these measurements was measured in entirely the same way as described in the Proceedings of May 25th '01 (Comm. N^o. 70, 2nd continuation).

for the determination of the normal volume of one of the piezometer tubes was made in four ways: l^{st} . with the connecting tube; 2^{nd} . the connecting tube being disconnected from the waterbath; 3^{rd} . the connecting tube being disconnected from thebaroms ter; 4^{th} . without the connecting tube. These four kinds of observations agreed to within $\frac{1}{2000}$.

¹) In order to judge in how far the depressions occurring in my measurements agree with those given in MENDELEJEFT and GUTKOWSKY's table I have measured directly some depressions for the given width of tube. These gave values which sometimes differed mutually 0.05 m.m., and of which the mean was about 0.03 m m. higher than in the table. To determine the influence of moisture, I lightly breathed into the tube; this greatly diminished the depression, while the height did not perceptibly decrease.

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The temperature within this water bath was not so regular and constant as that of the water in the experiment described in the Proceedings of May 25th '01 (Comm. N^o. 70, 1st continuation) as owing to the much greater height of the water bath, its difference in level with the mixing vessel was much smaller so that the water currents became much weaker. Moreover the piezometer tube was not in the water itself, but in the inner reservoir and it was impossible to stir the air in that enclosed space. To form a judgment of it I give here the temperature readings on April 5th 1900, the temperature of the room being 14° C. The thermometers were suspended against the piezometer tube, N^o. 134 at the higher end near the small reservoir, N^o. 135 in the middle against the steel flanged tube and N^o. 29 at the lower end against the U-tube; the corrections of the thermometers have been applied.

Thing		Calculated			
	No. 134.	No. 135.	No. 29.	temperature.	
4.10	20°.01	20°.07	20°.015	20°.035	
4.25	20°.01	20° 05	20° 00	20°.02	
4 53	19°.99	20°.03	19° 97 ⁵	19°.995	
5.07	19°.98	20°.01	19°.975	19°.98⁵	

Most days were however more favourable as for instance on May 7^{th} 1900.

Time.	2.06	2.21	2.32	2.43	2.55	3.51	4.06	4.19	4.27	4.42	4.51
Mean temp.	20°.02	20°.02	20°.01	20°.01	20°.01	20°.01	20°.02	20°.02	20°.02	20°.03	20°.04

I give here for one of the tubes viz. N⁰. IV, the results of the measurement of the normal volume; the volume is expressed in c.c. and the pressure in c.m. of mercury at Leiden.

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Date.	Time.	Volume	Pressure 20° C.	Product.	Deviation.
4 April.	4.10	174.265	74.071	12908 0	- 1.2
n 11	4.25	.258	.079	08 8	- 0.4
5 //	4.10	.141	.138	10,6	+ 1.4
	4.25	.128	128	07.8	- 1.4
	4.53	. 121	.142	09.7	+ 0.5
» (f	5.07	. 118	. 151	11.0	+ 1 8
6 <i>r</i>	4.25	.030	. 182	09.8	+ 0.6
• 11	4.39	.027	.174	08.3	- 0.9
// »	4.53	.026	.176	08.5	- 0.7
» <i>II</i>	5,17	.024	.172	07.7	- 1.5
7 .	3.29	.016	. 181	08.6	- 0.6
w 11	3.47	.019	.194	11.2	+ 2.0
11 11	4.02	.019	. 196	11.6	+ 2.4
R 8	4.33	,019	. 182	09.0	- 0.2
9 ,	3.29	.107	.149	09.8	+ 0.6
p "	3.50	.106	.140	08,2	- 1.0
	4.20	. 107	.140	08 3	- 0.9

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The last column headed "Deviation" gives the difference between the mean value and the observed value; from it we calculate the mean error 1.22 which is $\frac{1}{10.000}$ of the value.

In order to derive the normal volume from the value found I assumed that for the reduction of about 74 c.m. to 75,9467 c.m. (the height of the mercury at Leiden for 1 atm. at 45° northern latitude while the constant of gravitation at Leiden is taken as 981.318¹) and at 45° northern latitude as 980.63²)) BOYLE's law was sufficient (the deviation is of the order of $\frac{1}{50.000}$) while I have taken $\alpha = 0.0036613$ for the co-efficient of expansion.

¹⁾ DEFFORGES and BOURGEOIS 1892.

²⁾ Also accepted in GUILLAUME'S "Thermométrie."

1	1	19	2	١
	r	77	<u> </u>	1

Tube.	I A.	11 A.	111.	IV.
Norm Vol.	162.215	126 025	132.135	158.380 _
Mean error.	1 : 13000	1 : 11000	1 : 12000	1 : 10000

In the following table the normal volumes found have been combined and also the relative mean errors have been given -

§ 3. The measurements at higher pressure. After the piezometer tubes have been placed in the compression apparatus and this has been connected with the open manometer, the heights of the mercury in them were read by means of a cathetometer of the Société Génevoise. Both rest on the same common foundation, isolated from the floor, and made by bridging over the firm pillars in the observation room with iron rails and stone slabs.

To insure a constant temperature, the apparatus for the regular current of water at constant temperature was put in motion at 10.30 a. m., and the water bath was constantly stirred, the apparatus was put under pressure at 12.30 p. m. and the measurements began at 2.30 p. m. and were continued uninterruptedly till 5 p. m. without anything being changed in the apparatus; we might then be reasonably certain that the temperature measured with the thermometer agreed with that of the hydrogen and that equilibrium of pressure existed between the open and the closed manometers. For these measurements the height of the barometer must also be known, this was read on an aneroïd, of which the correction had been carefully determined. We took into account that the aneroïd had been placed lower than the mercury in the manometer tube A. (Comm. 44 fig. I).

It will hardly ever be possible to avoid very small leakages in the connecting tubes; in the measurements taken into account they were so small that they could not be discovered by means of soap solution. Hence the corrections which must be applied for the motion of the mercury owing to those leakages are very small; with a view to these corrections however all the readings must be made as symmetrically as possible and the time must be always noted for the mean mercury height both in the open and closed manometers. I will give here one observation (comp. the table of readings in the Proceedings of May 25^{th} '01, Comm. N⁰. 70), of which the calculation will be carried out as an instance.

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Reading on Aug. 25th 1900. Tube III.

Time.		3 52								
Barometer.		75.97								
	 			Open	Mano	neter.				
Thermometer Reading Corrected.	19°.6 19°.47	19° ² .35 19°.22	t ₃ 19° 25 19°.07	t4 19°.55 19°.45	t ₅ 19° 32 19° .24	t_6	t ,	t _s		T ₁ =19°.31
Manom.tube above l. to r.	A 276.53	BI 5.02	B _{II} 6.27	В п 1.97	B _{1V} 0.77	By 3,32	Bvi 2.11	Bvii 2.06	Bviii 2.27	$\Sigma_1^1 = 300.32$
Time.					4.00					
below r. to l.	28.26	5,83	6.03	4.15	3.61	10.15	7.38	8.28	7.90	$\Sigma_{2}^{1} = 81.59$
				ŀ	lezome	ter.				
Thermometer Corrected.	19°.88⁵ 19°.78⁵									
Time.		4.07								
top men. in tube level - // // mark 50.9 top men. in meas- uring glass. level in meas.gl.	Catho	Cathetom. reading 60 853 Reading of level 0.7 Temperature. 19°.1 60.787 1.85 " 60.832 1.5 " 31.422 3.0 " 31.284 3.15 "								
Time.					4.11*					
Barometer.					75 985					
				Open	Manor	ieter.				
Thermometer Reading Corrected.	19°.5 19°.47	t <u>a</u> 19°.35 19°.22	19°.3 19°.12	t ₄ 19°.53 19°.43	19°.28 19° 20	t _e	t ₇	t _s		T ₂ = 19°31
Manom tube below 1. to r.	A 28.27	B1 5.86	B11 6.04	B111 4.21	BIV 3.70	By 10.25	By1 7.57	Bv11 8.43	By111 8.10	$\Sigma_{g}^{2} = 82.43$
'Time,	4.19									
above r. to l.	276.52	5.00	6.18	1.89	0.66	3.19	1.91	1.89	2.16	$\Sigma_1^9 = 299.40$

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For the way in which we derive from this the pressure at 4 p.m and 4.19 p.m. I refer back to the Proceedings of May 25^{th} '01 (Comm. N⁰. 70 § 4); only the barometer height must be added to this, and it must be taken into account that the aneroïd was on the same height as the zero of the measuring rod suspended between the limbs of tube A. The correction for the compression of the mercury was applied to pressures above 32 atm. (Comp. Proceedings of May 25^{th} '01, Comm. N⁰. 70 § 2. G.).

To obtain the pressure at 4.7 p.m. I assumed that the pressure varied proportionally with the time.

The pressure now measured is that of the lower reservoir of the last manometer tube in use; the mercury height in this agreed always within a few centimeters with the height in the level-glass of the piezometers. The correction for the hydrostatical pressure in the gas, which transfers the pressure, may then be neglected.

In measuring the excess of pressure, caused by the difference in mercury level in the piezometer tube and in the level-glass, we must bear in mind that the temperatures of those columns are generally different. However the error is sure to remain within the limits of observation if we assume that the mercury in the steel flanged tube 10 c.m. below the water bath has reached the temper-

Time.	Corrected merc. height open manom.	Barom. at level of mercury.	Reading level glass.	Corr. for depress.	Tempera- ture.	Corr. for temp.	Corr. height levelgl.
2.40	2639.47						
2.48		75.91	31,418 .	0.110	19°.3	- 0,098	32.23
3.005	2638.36						
3.09		75.92	31.418	0.110	19°.3	- 0 098	32.24
3.205	2636.63						
3.28		75.93	31.427	0.115	19°.2	- 0.098	32.19
3.40	[•] 2635.09						
3.48		75.94	31 . 429	0.114	19°.1	- 0.097	32.21
4.00	2633.59					•	
4.07		75.95	31.426	0.107	19°.1	- 0.097	32.22
4.19	2631.83						
4.265		75.96	31.423	0.114	19°.	- 0.097	32.21
4.385	2630.50						

August 25th TABLE I.

ature of the room; this height co-incided with the zero of the cathetometer scale.

The preceding table gives the mercury heights to be summed for the measurements on Aug. 25th 1900. (Comp. p. 000).

From the corrected mercury position in the open manometer reduced at the time of the observation augmented by the height of the barometer at the level of mercury and the corrected position of the level glass, the corrected height in the piezometer tube must be subtracted and to this we must apply the correction for the compression of the mercury; the pressure then found is that of the hydrogen at the temperature measured; in order to reduce this pressure to 20° C. I have assumed 0.003663 for the co-efficient of expansion of hydrogen, while the influence of the pressure on that co-efficient could be left out of consideration owing to the small deviation of the temperatures measured from 20° C.

The pressure now measured is the one immediately above the mercury and hence the mean pressure of the hydrogen is lower. The greatest difference (when the mercury is at the lower end of the stem) however remains when p is the mean pressure in atm. below 0.000004 p atm., which therefore may be neglected in comparison with p atm.

Time.	Reading of piezom.	Corr. for depr.	Temp. of H.	Corr. for temp.	Corrected reading.	Corr. compr.	Pressure.	Pressure of H at 200	Pressure at 20° in atm. 45° NL.
2.40									[
2.48	60.907	0.115	19.785	0.193	60.829	0.00	2685.55	2687.52	35.387
3.005		}							
3.09	60.897	0.127	19,785	0.193	60.831	0.00	2684.15	2686.12	35.368
3,20⁵									
3.28	60.881	0.117	19.785	-0.193	60.805	0.00	2682 63	2684.60	35.348
3,40				} .					
3.48	60.868	0.123	19.78°	-0.193	60.798	0.00	2681.06	2683.03	35.327
4.00									
4.07	60.850	0.125	19.785	-0.193	60.782	0.00	2679.55	2681.52	35.307
4.19									
4.265	60.825	0.126	19.78	-0 193	60.758	0.00	2677.96	2679.93	35.286
4.385				} .					

And hence we obtain for the pressure the following calculation: August 25th TABLE II. (116)

I have purposely given this series of observations as it appears from the foregoing table that there must have been a leakage on that day, which could however not be detected by means of soap solution; the observations on other days show a much smaller decrease of pressure; as for instance on July 11th when the pressure at 2.44 p. m. amounted to 36.898 atm. and at 4.35 p. m. to 36.871 atm. And yet it will appear that the decrease of pressure mentioned has had no disturbing influence on the equilibrium, since the product of volume and pressure, bearing in mind the degree of accuracy attained, may be considered as sufficiently constant.

For the measurement of the volume I refer back to the Proceedings of May 25th 1901 "The calibration of piezometer-tubes". The following table has been calculated in the way described there.

		Mark Sectio	on ation fo	n alastia d	-	50.9 0.1264			
Time.	level men. under mark.	Height of men 1)	Mean height men.	Reduced length	Mean section	Volume	Corrected Volume	Specific- volume.	
2.40 2.48 3.00 ⁵ 3.09	-0.024	0.057	0 029	32 213 32 227	0.12690	4 0878	4.0887	0.030944	
3.20 ⁵ 3.28 3.40	0 008	0.001	0.030	32.244	*	4.0918	4.0927	0.030973	
3.48 4.00 4.07	0.026 0.046	0.061 0.062	0.032 0 032	32 260 32.280	"	4.0938 4 0963	4 0947 4.0972	0.030989 0 031008	
4 19 4.26 ⁵ 4.38 ⁵	0.064	0.063	0.033	32.297	N	4 0985	4.0994	0.031024	

August 25th. TABLE III.

¹) In Comm. N⁰. 67 § 7 I neglected to draw attention to the scale of reciprocals devised by Boys to facilitate the drawing of curves by their curvature.

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The correction for the thermal expansion of glass may be neglected on account of the small deviation of the temperature from 20° C.

For the calculation of the product of the specific volume and the pressure in atmospheres at 45° northern latitude the following table is obtained.

Time	Pressure Atm. 45° NL.	Specific volume	P × V.
2.40			
2.48 3.00^{5}	35.386	0.030944	1.09498
3.09	35,368	0.030958	1.09492
3.20 ⁵ 3.28	35.346	0.030973	1,0948 ³
3.40	07 00m	0.020000	4 00/76
3.48 4.00	35.321	0.030989	1,0947°
4.07	35.307	0.031008	1.09482
4.19 4.26 ⁵	35.286	0.031024	1.09473
4.385			
Mean	- 35.337	0.030983	1.09484

August 25th TABLE IV

§ 4. Results. In the manner described above I have calculated every time the mean value for one pressure i.e. from 4-8 atm. for every atmosphere, from 8-16 for every 2 atm., from 16-32 for every 4 atm. and from 32-64 atm. for every 8 atm. The values of PV for 4-8 atm. are not given here because when the apparatus was taken to pieces it appeared that the reservoir of tube IA had burst, so that the determination of the normal volume was valueless.

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I have tried to express the values found by a formula, and for this I have chosen the following expression:

$$PV = \alpha + \beta d + \gamma d^2, 1$$

where d = 1/V stands for the density of the gas with regard to that at 0° C. and 1 Atm. at 45° northern latitude. By means of the method of least squares I have calculated α , β and γ from 16 mean values derived from 107 measurements, where the equation which is obtained when V = 1 is taken to be absolutely correct and where the weight 1 is given to all measurements, while it was taken into account that the normal volume had been determined by means of REGNAULT's coefficient of expansion $\alpha = 0.0036613$, which does not agree with CHAPPUIS' coefficient of tension $\beta = 0.0036626$. If the latter is taken to be correct, we obtain the following table, for which the mean errors have been derived by means of the weights from the mean errors of the observations to be given subsequently.

	Value.	Weight	Mean error.
a	1.072,58	6,909.	0.000,003
β	0.000,6675	6,914.	0.000,003
y	0.000,000,98	10,421,200.	0.000,000,08

The following table gives the densities measured at different dates, the product PV corrected for the correct coefficient of expansion and its deviation from the values calculated from α , β and γ .

⁾ As appears from a development in series borrowed from AMAGAT's results, the term with d^3 would be 0, while the term with d^4 has little influence below 60 atm.

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• **	Date		Time	Tubo	Density	PVV	Deviation	
			1406.	Denerty.				
23	April	1901	3.48	lIA.	6.2403	1.07673	0.00005	
»	ຶ	»	4.00	»	6.2399′	79	+ 01	
D	»	»	4.10	»	99	71	07	
»	»	»	4.22	ຶ	91	79	+ 01	
»	Ø	»	4.34	»	87	72	<u> </u>	
		On an	average.		6.2394	1.07675	-0.0000 ³	
15	Aug.	1900	2.53	IIA	8.2352	1 C776 ⁸	- 47	
»	»	»	3.035	D	45	78	- 37	
»	»	»	3.16	»	52	6 ⁸	47	
»	»	»	3.26	D	45	78	- 37	
»	»	»	3.36	»	38	8 ⁸		
))	»	D	3.47	»	25	98	— 1 ¹	
»	»	۵	3.57	»	25	9 ⁸	- 17	
28	»	»	3.25	»	447	88	- 27	
»	»	»	3.35	»	47	8 ⁸	- 27	
))	»	»	3.45	»	33	80 ^s	- 07	
»	»	»	3.55	D	33	08	- 07	
»	»	ÿ	4 05	»	27	6 ⁸	- 07	
D	D	»	4.16	»	20	18	+ 0 ³	
»	D	»	4.26	»	20	18	+ 0 ³	
»	»	»	4.35	»	13	18	+ 0,	
		On an	average.	<u> </u>	8.2385	1.07795	0 0002 ³	
16	Aug.	1900	2.57	IIA	10.5775	1.07978	+ 03	
»	»	»	3.09	۵	64	8 ⁸	+ 1 ⁸	
D	»	»	3.20	»	64	78	+ 03	
»	»	»	3.30	»	64	78	+ 0 ³	
D	»	»	3.44	ه	64	78	+ 03	
D	»	»	3.55	»	64	78	+ 03	
		On an	average.		10.5766	1.07980	+0.0000 ^s	
						•	8*	

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Date.		Time.	Tube.	Density.	$P \times V.$	Deviation.		
17	Aug.	1900	3.04	IIA	12.8353	1.08138	+ 08	
ຶ	»	' »	3.18	»	20	5 ⁸	+ 2 ⁸	
»	>	»	3.32	»	287	6 ⁸	+ 3°	
»	Ŋ	»	3.45	»	71	6 ⁸	+ 3 ⁸	
»	»	»	3.58	»	54	5°	- -	
»	»	»	4.14	α	22	5 ⁸	+ 2 ⁸	
		On an	average.		12.8285	1.08158	+0.0002 ⁸	
21	Aug.	1900	3.45	111	13.0097	1.08147	+ 04	
»	2	»	4,00	»	78	51	+ 08	
»	»	»	4.14	»	60	58	+ 15	
»	»	»	4.27	»	42	60	+ 17 -	
ס	»	»	4.41	»	25	6 ⁸	+ 2;	
»	»	»	4.57	»	07	70	+ 27	
27	D	»	2.44	»	70	20	2 ⁸	
»	»	D	2.56	、»	66	18	25	
D	»	»	3.08	»	66	17	26	
»	»	»	3.22	»	49	2º	- 14	
»	»	»	3.36	»	39	22	21	
»	»	»	3,48	×	37	10	- 38	
		On an	average.		13.0053	1.08139	0.00004	
18	Aug.	1900	2.45	II A	15.2835	1.08298	- 03	
»	Ŋ	Ŋ	3.00	»	788	308	+ 07	
»	»	»	3.21	x	88	29 ⁸	— 0 ³	
»	ນ	»	3.35	»	65	3 0 ⁸	+ 07	
»	»	»	3.49	»	18	28	+ 27	
»	»	»	4.04	»	695	38	+ 37	
»	»	»	4.19	»	48	58	+ 57	
		On an	average.	·	15.2748	1.08319	+0.0001 ⁸	

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(Sectored as	the second se								
	Date.		Time.	Tube.	Density.	$P \times V.$	Dev	iation.	
22	Aug.	1900	3.25	111	16.6803	1.08382	-	17	
»	»	»	3.37) »	775 86		-	13	
»	»	»	3.49	»	56	87		19	
»	D	»	4.00	»	39	8 ³	_	1 ⁶	
»	»	»	4.11	D	31	72	_	27	
»	»	»	4.24	»	692	75	-	2⁴	
		On an	average.	l	16.6750	1.08381	-0	0 001 ⁸	
23	Aug.	1900	3.57	III	21.2988	1.08760	+	35	
»	»	»	4.03	»	52	70	+	45	
»	»	»	4.26	»	15	66	+	4 ¹	
»	»	»	4.41	»	866	75	+	50	
	On an average.				21.2930	1.08768	-+0.	+0.0004 ³	
24	Aug.	1900	3.00	111	25.408	1.09087	+	6 ⁹	
»	»	»	3.21	»	398	50	+	32	
»	»	»	3.39	»	92	12	_	05	
»	ຶ	۵	3.56	»	87	8991		26	
»	»	Ņ	4 12	»	80	94		2^2	
»	»	»	4.29	»	75	91	_	25	
		On an	average.		25.390	1.09021	+0.	00004	
28	June	1900	4.56	1V	26.524	1.09120	+	22	
29	»	r	4.05	ø	624	14	+	0 ⁹	
»	»	ø	4.51	Ŋ	04	30	+	26	
30	»	»	2.46	»	777	01		15	
»	»	»	3.17	x	66	30	+	14	
×	D	»	3.54	»	50	<u>4</u> 1	+	27	
×	»	¢	4.28	»	37	34	+	21	
5	July	x	4.11	»	86	1 ⁹	+	0°	
»	v	»	4.42	»	71	24	÷	08	
	On an average.				26.704	1 .0912 ³	+0.0	00013	

ø

	Date.		Time	Tube.	Density.	$P \times V.$	Deviation.
7	July	1900.	2.29	IV	29.956	1.09317	2º
»	»	»	2.47	»	41	30	15
»	»	»	3.09	×	37	06	— 3 ⁸
»	»	»	3.24	, »	35	0,	35
מ	»	D	3.44	D	20	18	2;
»	»	ð	3.59	×	04	17	25
D	»	v	4.16	»	887	19	
>	»	D	4.34	»	73	14	
		On an	average.		29.919	1.09316	0.00027
25	Aug.	1900	2.48	111	32.316	1.0949	- 23
»	»	•	3.09	»	01	90	- 28
»	»	»	'3,28	»	286	81	36
ø	D	»	3.48	p	70	74	- 42
»	D	¢	4.07	»	50	81	34
»	v	»	4.26	»	53	71	- 42
		On an	average. 32.276 1.09482 -		0.00034		
11	July	190 0	2.44	IV	33.656	1.09629	+ 12
n	»	»	3.10	»	46	48	+ 3²
ນ	»	»	3.30	×	47	47	+ 3 ¹
»	»	מ	3.52	»	44	22	+ 0°
»	, л	x	4.13	»	37	33	+ 17
»	D	מ	4.35	»	34	23	+ 0 ³
		On an	average.		33.644	1.09634	+0.00018
12	July	1900	2.43	1V	40.254	1.10083	- 23
»	α	»	3.05	»	11	98	04
»	»	»	3.28	»	167	93	07
»	D	»	3.51	≫	23	91	05
		On an	average.		40.189	1.10091	-0.0001

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Date.			Time. Tube.		Density.	$P \times V.$	Deviation.	
13	July	1900	4.34	17	47.218	1.10634	+	03
»	»	ď	4 59	»	165	56	+	2 ^s
On an average.				,	47.192	1.10645	-+-0 .0	0015
14	July	1900	3.01	1V	54,127	1.11179	+	1 ⁸
»	D	D	3.26	»	069	68	+	12
ง	»	ຶ	3 56	Ð	3.987	60	+	1º
»	D	»	4 22	»	23	· 4 ⁸	+	03
»	»	»	4.53	»	836	. 1º		1 ⁹
		On au	average.	i	53.988	1.1115	- 0.0	0003

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The agreement is satisfactory; it may be judged from the following table:

	Number of obser- vations.	Number of positive deviations.	Number of negative deviations.	Sum of the positive deviations.	Sum of the negative deviations.	Mean error in 1 measurement.
Tube II A	39	22	17	0.00342	0.00328	0.00024
» III	34	12	22	0.00368	0.00534	0.00032
» IV	34	20	14	0.00309	0.00288	0.00020
Total	107	54	58	0.01019	0.01150	0.0002\$

The fourth tube gives the best agreement. With the value found for the mean error in one measurement, to which I had given the weight 1, I have also calculated the mean errors in the table for the values of α , β and γ .

§ 5. We might calculate values of VAN DER WAALS' a and b from the values of α , β and γ , supposing that his original equation of state would hold for the same temperature within the limits of pressure mentioned. It is obvious that then the values of a and b must be corrected, because the terms with higher powers than the second power of density were neglected. If we want to calculate these corrections of a and b by means of the method of least squares,

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we meet with the difficulty that the terms containing the second powers of those corrections cannot be neglected in comparison with the terms containing the first power, because although each of these are much larger, they yet partially neutralize each other. A calculation in which the terms mentioned were kept, did not give a good result. Therefore by means of the value of δ , derived by approximation from α , β and γ , viz. b = 0.0009, I have calculated the correction term, which VAN DER WAALS' formula requires in addition to the terms used, viz. $RT'b^3 d^3 (1-bd)$, subtracted this value from PV and have equalized the derived value to $\alpha' + \beta'd + \gamma'd^2$, from which is found:

$$lpha' = 1.07258, \ eta' = 0.000670, \ \gamma' = 0.00000088.$$

By putting:

$$\alpha' = RT,$$

$$\beta' = RTb - a,$$

$$\gamma' = RTb^{2},$$

we find:

 $a = 0.00030, \quad m_a = 0.00004^2, \\ b = 0.00091, \quad m_b = 0.00004,$

Finally let us compare our results with those of REGNAULT and AMAGAT. The values determined by me are indicated in the figure by circles, those found by REGNAULT by squares; in this I have supposed that at the lowest pressure REGNAULT's result and mine were the same; after this the other points have been drawn.

From a development in series, calculated from AMAGAT's observations at 0°, 15°.4 and 47.°3 C., we find by means of interpolation:

$$PV_{20^\circ} = 1.07252 + \frac{0.000719}{V} + \frac{0.00000067}{V^2}$$

If we substitute V = 0.01129, AMAGAT's greatest volume at 15°.5 C. we find $PV_{20^\circ} = 1.1414$ ($PV_{15^\circ 5} = 1.1290$), while from the values of α , β and γ we obtain $PV_{20^\circ} = 1.1394$ and from the original equation of VAN DER WAALS with the given values of α and $b: PV_{20^\circ} = 1.1401$.

