of the top of the manometertube give an explanation, unless this error were supposed to have been of an amount entirely excluded by the measurements themselves. Naturally it might be questioned, whether the term in v_A^{-3} left out can represent the course of the isothermals in this region with an accuracy corresponding to the accuracy of the observations. The observations in this region are much more accurate than for the rest of the isothermals, the study of which as a whole led to the selection of the polynome in the given form for the purpose of representing the complete net of isothermals. The circumstance, that the deviations in the range below 60 atmospheres show a systematic change, may possibly be a sign, that the development which was chosen is actually not quite sufficient for the present purpose.

In a subsequent paper our observations will be discussed in connection with the further, fairly numerous observational data concerning the equation of state for hydrogen.

Physics. — "*Comparison of a pressure-balance of* SCHÄFFER *and* BUDENBERG *with the open standard-gauge of the Leiden Physical Laboratory between* 20 *and* 100 *atmospheres, as a contribution to the theory of the pressure-balance.*" By Dr. C. A. CROMMELIN and Miss E. I. SMID. (Comm. N°. 146*c* from the Physical Laboratory at Leiden).

(Communicated in the meeting of June 26, 1915).

1. *Introduction. Object of the investigation.* The measurements undertaken to extend the determination of the isothermal of hydrogen at ordinary temperature from 60 to 100 atmospheres, which are described in the preceding communication, afforded a welcome opportunity for carrying out a comparison planned a long time ago of the pressure-balance of SCHÄFFER and BUDENBERG with the open manometer of the Physical Laboratory at Leiden.

In the isothermal-determinations of gases under high pressure undertaken at Amsterdam by Prof. KOHNSTAMM with the apparatus belonging to the VAN DER WAALS-fund the pressure-measurements are based on the indications of a pressure-balance by SCHÄFFER and BUDENBERG, and the unit in which the volume of the gas in the observations under high pressures is expressed is also dependent upon the indications of a pressure-balance of that kind.

In fact this "normal volume" is derived by KOHNSTAMM and WALSTRA [1]) from the volume which corresponds to the pressure given by the pressure-balance according to the isothermal of hydrogen as determined by SCHALKWIJK [2]) at Leiden by means of the open manometer of KAMERLINGH ONNES [3]). In order to reduce the observed pressures and volumes in the investigations by KOHNSTAMM and WALSTRA to real pressures and volumes, which are required for the deduction of the equation of state, an investigation as to the real pressure, corresponding to a definite indication of the pressure-balance, is thus indispensable.

As the open manometer in question allows absolute pressure-measurements up to 120 atmospheres of great accuracy, a calibration of the small pressure-balance, used in the experiments of KOHNSTAMM and WALSTRA, would at any rate yield the normal volume belonging to the measurements at lower pressures.

Independently of the absolute calibration itself of the pressure-balance in the region explored, the comparison of this balance with the open gauge was also of great value for forming an estimate of the accuracy of the determination of the very high pressures. The desirability of such comparison was insisted upon by KOHNSTAMM and WALSTRA not long ago.

Of the theory of the pressure-balance only little is known and even that has not been at all adequately tested by experiment. Worst of all the experiments made so far do not confirm the theory. We are chiefly referring to E. WAGNER's[4]) investigation, whose calculations about an AMAGAT-gauge are also mutatis mutandis applicable to a pressure-balance. WAGNER calculates the force which the cylinder of an AMAGAT-gauge experiences owing to the viscosity of the oil which flows through the narrow interspace between piston and cylinder and finds that this force cannot always be neglected in the practice of accurate measurements. In order to calculate the true pressure from the indications of the gauge a correction has to be applied to the latter, but since in the expression for the force, besides constants of the instrument, only the pressure occurs as a

1) PH. KOHNSTAMM and K. W WALSTRA. These Proceedings 16. p. 754, 822. 1913 and 17 p. 203. 1914 and K W. WALSTRA, Dissertation Amsterdam 1914, where also a description of the pressure balance will be found.

2) J. C. SCHALKWIJK. These Proceedings 3. p. 421, 481 1901. Comm. 67 and Dissertation, Amsterdam. 1902.

3) H. KAMERLINGH ONNES. These Proceedings 1. p. 213. 1898. Comm. 44.

4) E WAGNER, Dissertation. Munchen, 1904 and Ann. d. Phys. (4) 15 p. 906, 1904. Comp. also G. KLEIN, Dissertation Techn. Hochsch. Berlin, 1909.

factor, the correction can be made to the sectional area on which the pressure acts; the area thus corrected, the "functional" area, is therefore according to WAGNER's theoretical deductions a constant for the instrument and naturally differs a little from the real area. WAGNER determined the functional area of his AMAGAT-gauge by means of experiments at low pressure, he also measured the real area and found the two exactly equal! This result is in contradiction with the theory, and, assuming WAGNER's experiments to be trustworthy, this would indicate, that the theory is not so simple and that there are possibly other factors which might influence the functional area, in which case it might very well happen that the functional area would turn out to be dependent on the pressure.

Before this matter can be cleared up, i.e. before a revised theory of the pressure-balance can be tested by experiment, it will be necessary to study the instrument as fully as possible from an experimental point of view, i.e. to compare its indications over as wide a range of pressures as possible with those of a standard-manometer and on the other hand to make very accurate measurements of the dimensions of its various parts. On the basis of these data it will then perhaps be possible to build up a more exact theory.

If it appeared that the functional area in accordance with WAGNER's theory were independent of the pressure over the whole range of comparison, one would be justified in extrapolating beyond the region, where the comparison with the open gauge is possible (i.e. above 120 atmospheres), and thus in calculating the actual pressure at 250 atmospheres from the indication of the balance with the same functional area as was found say at 100 atmospheres; the large pressure-balance of the VAN DER WAALS-fund which has a range from 250 to 5000 atmospheres could then be compared with the small balance at 250 atmospheres and in this manner the pressures on the isothermals of hydrogen measured by KOHNSTAMM and WALSTRA with both instruments could be corrected using the functional area thus determined.

So far we have not gone beyond 100 atmospheres with the comparison, as it was made in connection with the determination of the isothermal of 20° C. dealt with in the preceding communication. The range from 60 to 100 atmospheres gave sufficient data for the purposes of the investigation: they show the desirability of a further systematic investigation of various questions in connection with the theory of the pressure-balance; but this investigation can be carried out, independently of the apparatus in the possession of the laboratory. We resolved to defer the continuation of the measurements, which become more an more difficult as the pressure rises, until the above investigation should have been carried out.

2. *Experimental method.* A simultaneous reading of the open gauge and the pressure-balance turned out to be practically impossible. In fact in the pressure-balance the pressure in the oil-passages is only constant, while the piston with its weights is turning freely, and this motion does not continue longer than a few minutes at the utmost; when the rotation has come to a stop and the piston is again set in motion by hand, there are always, however carefully the operation is conducted, small vertical forces exerted on the piston which are propagated in the tubes as pressure-impulses and disturb the pressure-equilibrium. On the other hand the various readings on the open gauge require much more time than the two or three minutes which the pressure-balance, while left to itself, allows; in fact, when all the tubes are at the proper pressure, a complete reading carried out by two cooperating observers requires about three quarters of an hour.

A simultaneous reading of pressure-balance and open gauge being therefore attented with practically unsurmountable difficulties, we resolved to carry out the comparison through the intermediary of the two closed hydrogen-manometers of the Leiden-Laboratory M_{60} and M_{120}, the former of which has a range from 20 to 60 atmospheres, the latter from 60 to 120. We already will mention here, that this procedure did not impair the accuracy aimed at in any respect, as will moreover appear from the discussion in the next section.

The accompanying plate shows the open manometer *O. M.*, the two closed manometers M_{60} and M_{120} and the pressure-balance *D. B.* with its oil-forcing pump *O. P.* besides the connections and stopcocks by which the various apparatus are joined up together. The construction and method of working of the various gauges having been repeatedly described and represented need not be gone into on this occasion [1]).

A small complication arose in connection with the transmission

[1]) Open manometer: H. KAMERLINGH ONNES. These Proceedings I. p. 213. 1898. Comm. 44, and J. C SCHALKWIJK Dissertation, Amsterdam 1902. H. KAMERLINGH ONNES, C. DORSMAN and G. HOLST These Proc. Supra Comm. 146a. Manometer M_{60}: H. KAMERLINGH ONNES and H. H. F. HYNDMAN, These Proceedings 4. p. 761. 1902, Comm. 78. § 17, H. KAMERLINGH ONNES and C. BRAAK. These Proceedings 9. p. 754. 1906. Comm. 97a, § 3. Manometer M_{120}: These Proceedings Supra. Comm. 146a, 146b. Pressure-balance: PH. KOHNSTAMM and K. W. WALSTRA l.l. c.c.

of the pressure from the oil-passages of the pressure-balance to the tubes of the Leiden-manometers, in which compressed air is always used for transmitting the pressure. This transmission was at first carried out by means of the steel tube D_1 with its level-gauge P_3. The level of the oil in it could be easily kept up at the desired height by the aid of the oil-pump $O. P.$ When this arrangement had been in use for some time, it appeared that small changes of pressure in the oil of the pressure-balance, produced by the addition of small weights on the piston, were but very slowly and gradually transmitted to the manometers M_{60} and M_{120}; it was therefore desirable to transmit the pressure in the oil of the pressure-balance to the mercury of the closed gauges by means of tubes exclusively filled with liquid, eliminating all air connections. This arrangement could be easily applied to M_{120} by screwing a steel tube with a level-gauge P_1 to the tap K_{23} (the object proper of which is to fill the manometer with mercury, when being mounted). Beyond this gauge P_1 a second gauge P_2 was mounted and the latter was in connection with the oil-passages. Between the mercury in the lower half of P_1 and the oil in the upper half of P_2 the pressure was transmitted by means of glycerine.

Our procedure was to bring up the pressure at first in the usual manner with compressed air; if the stop-cock K_{20} was then opened and K_{27} and K_{28} closed, the pressure-transmission exclusively by means of liquids was realized. The pressure was further raised by means of the oil-pump. This arrangement completely answered our expectations: pressure-changes of $\frac{1}{10000}$ in the oil of the pressure-balance were now instantaneously indicated on M_{120}.

3. *Accuracy.* An opinion as to the accuracy which may be expected may be formed by giving some data respecting the absolute and relative accuracy of the indications of the various instruments.

The open manometer, when free of leakages and with a room-temperature which is carefully kept constant, gives with certainty an accuracy (absolute) of 0.01 %.

The manometer M_{60}, if the reading is certain to 0.1 mm. — which is undoubtedly to be attained — guarantees

at 20 atmospheres an accuracy of 0.008 %
„ 60 „ „ „ „ 0.020 %

For the manometer M_{120} the following figures hold:

at 65 atmospheres an accuracy of 0.007 %
„ 100 „ „ „ „ 0.016 %

The accuracy given for the two closed manometers is not only a relative one, but for a large number of points an absolute one as well, seeing that both instruments have been directly compared with the open manometer at those points. As to the pressure-balance, neither with respect to the absolute nor to the relative accuracy was anything known with certainty at the beginning of our investigation. It had only been found, that the sensitivity of adjustment in the neighbourhood of a definite pressure is very high and certainly amounts to 0.02 °/₀ or even 0.01 °/₀. As an instance, the pressuretransmission through liquids being used, and the pressure-balance being loaded with 65 kilogrammes, the addition of 10 grammes to that load could be observed on M_{120} with absolute certainty. The data regarding the accuracy of the pressure-balance which we have now obtained by our investigation will be given further down, when the results are discussed.

4. *The calculations.* The reduction of the indications of the open manometer is very simple in principle; the various corrections, however, require some care, if an accuracy of 0.01 °/₀ is to be guaranteed. These corrections have all been fully discussed by SCHALKWIJK in his Dissertation, so that we may confine ourselves to a few remarks. The correction for the weight of the columns of compressed air, which transmit the pressure from each tube to the next, becomes considerable at the higher pressures. Instead of air hydrogen might be used[1]), which would yield a double advantage: in the first place the correction thereby becomes ten times smaller and secondly the isothermal for hydrogen at 20° is at present very accurately known up to 100 atmospheres[2]), so that the correction can be calculated with great accuracy. It is true, that this method requires very pure hydrogen being available, in order to be certain of the specific gravity, but at the present time hydrogen prepared in the cryogenic laboratory by distillation is so absolutely pure, that an influence on the specific gravity of traces of admixed air, which is relatively large, need not be feared. We have ascertained, however, that for pressures up to 100 atmospheres it is not yet necessary

[1]) This method was recommended by H. KAMERLINGH ONNES in 1898; comp. These Proceedings 1, p 213, 1898, Comm. N°. 44.

[2]) J. C SCHALKWIJK, These Proceedings 3, p. 421, 481, 1901. Comm. N°. 67. These Proceedings 4, p. 23, 29, 35 1901. Comm. N°. 70, Dissertation, Amsterdam, 1902 H. KAMERLINGH ONNES, C. A CROMMELIN and Miss. E. I. SMID, These Proceedings supra Comm. N°. 146b. For the temperature correction compare the empirical equation of state of H. KAMERLINGH ONNES in the paper by J P. DALTON. These Proceedings 11, p. 863, 1909. Comm. N°. 109a.

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to introduce this complication and we have therefore preferred to calculate the corrections for air.

For this purpose AMAGAT's [1]) isothermals are available which have been represented in different ways by equations by BRINKMAN [2]) and by KAMERLINGH ONNES [3]): from these equations tables of correction were drawn up. The corrections calculated by the two methods agree to 0.5 mm. even at 100 atmospheres. As will appear further down the results prove, that in this manner the correction is approximated with sufficient accuracy.

The correction for the compression of the mercury remains small, it is true, even at 100 atmospheres, but still comes into account. For this correction we have also calculated a table, based on the compressibility of 0.00000392 according to AMAGAT.

There was no need for a correction for the flow of the mercury through the tubes, fully discussed by SCHALKWIJK, as the mercury did not move at all. Thanks to the steel connecting tubes being *soldered* to the glass tubes, to the fibre-washers and to all the couplings being immersed in oil [4]) we succeeded in obtaining the open manometer completely free of leakages even at 100 atmospheres, while at the same time the room-temperature was kept constant so successfully (owing to steam-heating, improved illumination by metal-wire lamps, which give very little heat etc.) that even with the very lengthy readings at the higher pressures there was hardly any sign of flow in the tubes.

The corrections for capillary depression have not been applied. A discussion showed, that the algebraic sum of these corrections would have no influence on the accuracy aimed at, especially if by tapping the tubes care was taken to obtain well-shaped convex menisci [5]). As a matter of fact the correction would have been very difficult, seeing that with the illumination used the height of the menisci could not be determined with the telescopes which served for reading the mercury-surfaces.

The further corrections do not require any special mention. The method of reducing the indications of the manometers M_{60} and M_{120} do not call for any remarks either. As regards the load on the

[1]) E. H. AMAGAT, Ann de chim. et de phys. (6) 29, Juni and Augustus 1893.

[2]) C. H. BRINKMAN, Dissertation, Amsterdam, 1904.

[3]) Zie J. P. DALTON, These Proceedings 11, p. 874, 1909 § 2 Comm N°. 109c

[4]) The oil-vessels in question are not shown in the somewhat diagrammatic figure. For some of the improvements mentioned here compare H. KAMERLINGH ONNES, These Proceedings 8, p. 75, 1905, Comm. N°. 94*b*.

[5]) Here again the results prove the reasoning to have been correct.

pressure-balance, it has to be kept in mind, that it consists of the total weight of piston and imposed weights, with the addition of the atmospheric pressure multiplied by the functional section.

The pressure of the atmosphere at Leiden is taken as equivalent to 75,9488 cms. mercury, one atmosphere being equal to 1,0336 kilogrammes.

5. *Measurements and results.* As explained in § 2 the measurements consisted in (1) a comparison of M_{60} and M_{120} with the open manometer, (2) a comparison of the pressure-balance with M_{60} and M_{120}.

We will first discuss the *measurements between* 20 *and* 60 *atmospheres carried out by means of* M_{60}.

Before undertaking the comparison of M_{60} with the pressure-balance we made sure by means of a comparison of M_{60} with the open manometer (fully described in the preceding communication), that the indications of the closed manometer still deserve the confidence which had always been given them in recent years. As shown in that communication the result of this comparison was, that since the last comparison [1]) a few years ago the closed manometer had not undergone any change.

The comparison of M_{60} with the pressure-balance was carried out as follows. The pressure having been adjusted at a chosen value, the pressure-balance was set in rotation and we waited, until the mercury-surface in M_{60} did not change any more. The pressure was in this case transmitted from air to oil and as the pressure-impulses which are due to the setting and keeping in motion of the pressure-balance are only very tardily propagated to M_{60}, it appeared possible to turn the pressure-balance without any modification of the position of the mercury-column being noticeable. A reading was taken, when the mercury-surface had been constant for a considerable time.

Table I gives the results of two series of measurements. For the measurements of June 22 the pressure-balance was once more carefully centred, as we thought that the adjustment had not been quite perfect.

The observations marked with an asterisk were calculated by means of SCHALKWIJK's isothermal and in these observations the manometer has thus not merely been used as an indicator. The concordance between the two kinds of observations appeared, however, to be so excellent, that it was considered unnecessary to establish

[1]) These Proceedings supra, Comm N⁰. 146*b*, § 3.

the pressure by direct measurement with the open manometer for the points in question.

We now proceed to the *measurements from* 60 *to* 100 *atmospheres carried out by means of* M_{120}.

In this case we could not check the readings by means of the isothermal and the calibration, as the comparison of a few years ago [1]) did not appear to have fully given the desired accuracy; this was the reason, why it was repeated together with the present

TABLE I. Comparison pressure-balance with M_{60}. [2])

Date	N⁰	Weights on pressure-balance in kilogrammes	Pressure according to M_{60} in kilogrammes per cm², diminished by atm. pressure	Reciprocal functional section in cm⁻².	Functional section in cm².
6 Febr. 1915	I	21.650	21.729	1.0036	0.9964
	IX*	25.650	25.744	36	64
	II*	31.410	31.520	35	65
	VIII*	36 000	36.121	33	67
	III	41 760	41.895	32	68
	VII*	46 050	46.188	30	70
	IV*	50.130	50 269	28	72
	VI*	55.710	55.848	25	75
	V	61.300	61 445	24	76
22 June 1915	VIII*	25.000	25.089	1.0035	0.9965
	I*	30.000	30.086	28	72
	VII*	35.000	35 092	26	74
	II	40.000	40.114	28	72
	VI*	45.000	45.098	22	78
	III*	50.000	50.120	24	76
	V*	55.000	55.112	20	80
	IV	60.000	60.112	19	81

determinations and replaced by a new calibration [3]). In this region we have therefore made the comparison at a larger number of

1) These Proceedings Supra Comm. 146*a*

2) The arrangement of the tables is somewhat different from that in the original Dutch publication.

3) These Proceedings Supra Comm 146*b*.

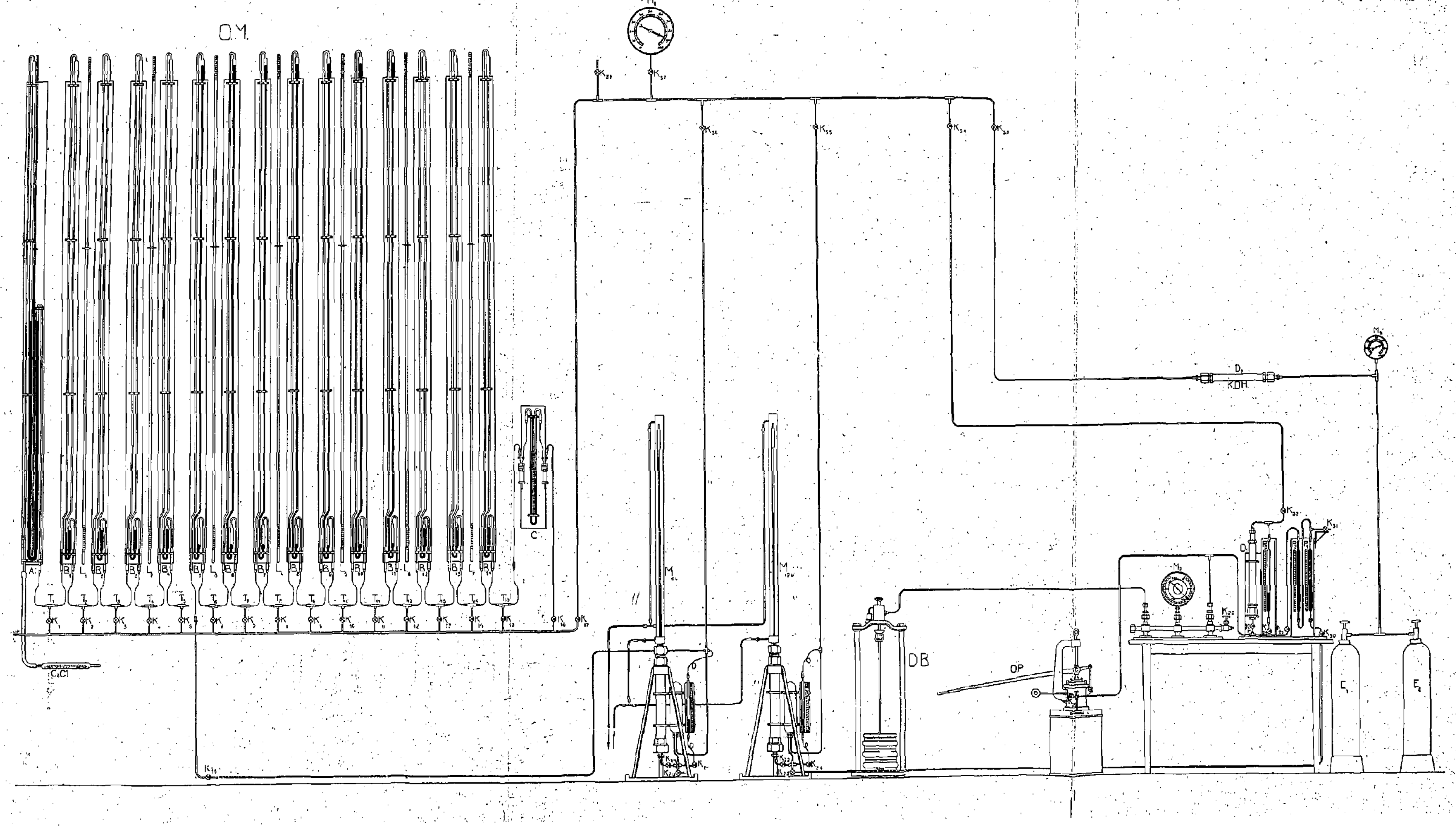
TABLE II. Comparison pressure-balance with M_{120}.

Date	N⁰.	Weights on pressure-balance in kilogrammes	Pressure according to M_{120} in kilogr per cm^2, diminished by atm. pressure	Reciprocal functional section in cm^{-2}.	Functional section in cm^2.
27 March 1915	I	67.000	67.143	1.0021	0.9979
	II	71.050	71.210	22	78
	III	75.000	75.147	19	81
	IV	79.650	79.865	27	73
	V	83.500	83.729	27	73
	VI	87.550	87.795	28	72
	VII	91.050	91.291	26	74
	VIII	95.550	95.790	25	75
	IX	99.500	99 815	31	69
	X	103.500	103.884	37	63
29 March 1915	X	67.200	67.329	1.0019	0.9981
	IX	71.100	71.236	19	81
	VIII	75.100	75.248	19	81
	VII	79.600	79.776	22	78
	VI	83.050	83.329	33	67
	V	87.550	87 745	22	78
	IV	91.050	91.292	26	74
	III	95.450	95.694	25	75
	II	99.350	99.667	32	68
	I	103.350	103 686	32	68
24 June 1915	II	75.000	75.187	1 0025	0.9975
	VII	80 000	80.216	27	73
	III	85.000	85.234	27	73
	VIII	90.000	90.271	30	70
	IV	95.000	95.298	31	69
	IX	100 000	100.362	36	64

TABLE II continued. Comparison pressure-balance with M_{120}.

Date	N°.	Weights on pressure balance in kilogrammes	Pressure according to M_{120} in kilogr. per cm^2. diminished by atm. press.	Reciprocal functional section in cm^{-2}.	Fu s i
23 April 1915	I	67.000	67.174	1.0026	(
	II	71 000	71.212	29	
	III	75.000	75.217	29	
	IV	79.000	79.239	30	
	V	83.000	83 268	32	
	VI	87.000	87 263	30	
	VII	91.000	91.294	32	
	VIII	95.000	95 338	35	
	IX	99.000	99.383	38	
	X	103.000	103.406	39	
24 April 1915	X	67.000	67.174	1.0026	(
	IX	71.000	71.180	26	
	VIII	75.000	75.229	30	
	VII	79.000	79.259	32	
	VI	83.000	83 272	32	
	V	87.000	87 278	32	
	IV	91.000	91.313	34	
	III	95.000	95.328	34	
	II	99.000	99 395	39	
	I	103 000	103 423	41	
18 June 1915	III	70 000	70 185	1.0026	0
	IV	80.000	80 263	32	
	V	90.000	90.295	32	
	VI	100.000	100.390	39	
18 June 1915	X	70.000	70.181	1.0025	0
	IX	80 000	80.256	32	
	VIII	90 000	90.301	33	
	VII	100.000	100.360	36	
19 June 1915	III	70.000	70.179	1.0025	0
	IV	80.000	80.247	30	
	V	90.000	90.286	31	
	VI	100.000	100.375	37	

C. A. CROMMELIN and Miss E. I. SMID: "Comparison of a pressure-balance of Schäffer and Budenberg with the open standard-gauge of the Leiden Physical Laboratory between 20 and 100 atmospheres, as a contribution to the theory of the pressure-balance of S. and B".



points. After the completion of the investigation described in the preceding communication the various points could be each separately checked by a comparison with the isothermal deduced from the points combined. If the manometer had been filled with a different gas or an arbitrary mixture of gases, it would have served its purpose as an intermediary between pressure-balance and open manometer equally well.

Table II contains the results of the comparison of the pressure-balance with M_{120}, extending over the range from 60 to 100 atmospheres. The measurements of March 27 and 29 and June 24 were made with the air-liquid transmission of pressure, as had been those with M_{60}, whereas in those of April 23 and 24 and June 18 and 19 use was made of the liquid system mercury-glycerine-oil which was arranged later on as described in one of the preceding sections.

6. *Discussion.* The results of all the measurements as contained in the above tables lead to the following conclusions:

1. The functional section is not independent of the pressure, but as the pressure rises above 20 atmospheres it increases, goes through a greatest value at about 70 atmospheres and then diminishes with greater rapidity as far as the comparison reached. The greatest deviation is 0.0020.

2. When the determinations were repeated, the same value was not always found for the functional section, the greatest deviation being about 0.0005 in this case.

3. The functional section differs from the geometrical section as given by SCHÄFFER and BUDENBERG (1 cm^2) by about 0.0030.

4. The sensitivity of the pressure-balance $\frac{1}{10000}$ thus far exceeds its accuracy. If the latter is to be raised to the value of the sensibility, the theory of the instrument will have to be developed and means will have to be found to obtain constant results within the limits of the sensibility. Probably in order to attain this accuracy a pressure-balance will always directly or indirectly have to be compared with an open manometer.

5. Pressures which have been measured with a SCHÄFFER and BUDENBERG pressure-balance which has not been calibrated cannot at present be estimated at a higher accuracy than about $\frac{1}{400}$, provided that the error in the area of the piston is not larger than 0,1 $^0/_0$.

In conclusion we wish to thank Professor KAMERLINGH ONNES and Professor KOHNSTAMM for their sustained interest in our work.