Physics. — "*Isothermals of mixtures of oxygen and carbon dioxide. I. The calibration of manometer and piezometer tubes*". By W. H. KEESOM. Communication N° 88 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of September 26, 1903).

§ 1. With a view to the investigations of isothermals, critical and condensation phenomena, of which I hope to give the results in a following paper, I have carefully calibrated a manometer and a piezometer tube. The results of these calibrations have been reduced according to a method to which Prof. KAMERLINGH ONNES has drawn my attention. According to that method the bore of the tube is represented by some terms of a series of FOURIER, the coefficients of which are derived from the observations. Thus we start from a continuous representation of that bore in opposition to the discontinuous variations which we must adopt when we derive mean bores from the length of the mercury column at different places, and regard them as bores at the middle of the column. From the following may be judged what can be reached by means of this method. [1])

§ 2. The manometertube was constructed after the model described in Comm. N° 50 of the Phys. Lab. at Leiden, [2]) differing herein that with a view to the higher pressures a ring was blown on to the part b_3 [3]), thus preventing the tube from moving along the cement in consequence of which the thinwalled part a_3 would be pressed against the steel of the flanged tube, while the tube h_3 is bent parallel to the length of the tube with the same purpose and in the manner as has been described in Comm. N° 69 (These Proc. III March 30, 1901, p. 625). The stem (c_3 of fig. 4 Comm. N° 50), graduated in mm., had a length of 50 cm., the innerbore was 0.83 mm., the outer bore 6 mm., the capacity of the reservoir a_3 was about 25 cc., the widened part d_3 above had an inner bore of 2.6 mm., an outer bore of 9 mm. and had been taken so long that the manometer, filled with hydrogen, could indicate pressures from about 60 to about 190 atmospheres. The upper cylindrical part of the experimental tube for the investigation of the

1) In consideration of the circumstance that with these tubes observations have been made which will form the subject of following papers, we shall give already here for the sake of simplicity some data on stem calibration, together with some remarks on the way in which the further data about these tubes are obtained.

2) These Proc. II June 24, 1899, p. 29.

3) See plate I, fig. 4 of that Comm.

mixtures was originally long 50 cm. and divided in mm.'s, had an inner bore of about 2.6 mm., an outer bore of about 7 mm.

The relation of the bores of the graduated parts of the manometer tube and the experimental tube at different places was determined by repeatedly moving a mercury column of about 10 cm. length over 5 cm. and then measuring its length. To effect this the manometer tube was placed in a horizontal position and the places of the ends of the mercury column were read with an eye-glass. We avoided parallax by taking care that the nearest graduation on the glass should be seen to cover its image on the mercury. For the wider experimental tube this method could not be used owing to the change of form of the mercury meniscus at the ends of the column in consequence of gravitation. Therefore the experimental tube was provided with a glass cock to which a narrow glass capillary had been connected. From this the air escaped only slowly under the excess of pressure of 10 cm. mercury. Then the tube was placed vertically after a mercury column of the length mentioned had been admitted. The latter could each time easily be moved over 5 cm. and the position of the ends read.

Then a longer mercury column was admitted into the tube in order to derive the mean bore from its weight. The bore of the above mentioned tube under the great reservoir (f_3), and also the volume of the reservoir were then determined by weighing the mercury.

§ 3. As an instance of the process of the calibrations and the

TABLE I.

M	L	Δ
6.90	11.40	+0 11
9.96[5]	11 33	+0.04
14.98[5]	11.31	+0.02
19 89	11.30	+0.01
24 76	11 30	+0.01
30.08[5]	11.31	+0.02
35.02[5]	11.25	−0.04
39.90	11.20	−0.09
44.22	11.18	−0.11
mean: 11.29		

calculations the data about the manometer will be given. The graduated tube has been calibrated twice, in 1901 (*A*) and in 1902 (*B*). I shall give here the data and the calculations concerning calibration *B*. Calibration *A* has been made in entirely the same way; the results of it will be given at the end of this paper and compared with those of *B*. Table I shows the results of the calibrations with the mercury column; column *M* contains the means, *L* the length of the mercury thread, Δ the difference from the mean length. The temperature could be considered as having remained constant.

TABLE II.

Ends of the mercury column:

1st position:	3.79^3	49.98^5		temp.	20.7
2d »	30.35 in the graduated stem,...		9.25 mm. above the division of the thin capillary e_3;	»	20.65
3d »	2.80	49.00		»	20.6

Weight of the mercury (in vacuo): 3.3777 gr.

Calculation:

Let s be the bore of the tube at an arbitrary place, indicated by the coordinate x (from 0 to 50). We may put:

$$s = s_n + d$$

where s_n is a particular, normal, bore.

The volume between the 2 divisions p and q will be:

$$V_p^q = \int_p^q s\, dx = \int_p^q (s_n + d)\, dx = s_n (q - p) + \int_p^q d \quad dx \quad . \quad . \quad (1)$$

The length of the mercury column:

$$q - p = m + \Delta$$

if $m =$ the mean length (comp. table I). If V_k represents the volume of the mercury column then:

$$V_k = s_n\, m + s_n\, \Delta + \int_p^q d \,.\, dx.$$

We may choose s_n so that:

$$m\, s_n = V_k,$$

then:

$$\Delta = -\frac{1}{s_n}\int_p^q d \,.\, dx = -\int_p^q d' \,.\, dx$$

if $d' = \frac{d}{s_n}$. If we knew the form of the function d', we might derive a number of equations from table I to determine the coefficients occurring there. Although the form of that function is unknown, yet d' for x between 0 and l must be representable by a series of FOURIER. It may now be asked whether it is possible within the limits of the accuracy given by the observations, to represent d' by some terms of a series of FOURIER. Therefore I have put:

$$d' = a'_1 \cos\frac{\pi x}{l} + a'_2 \cos\frac{2\pi x}{l} + a'_3 \cos\frac{3\pi x}{l},$$

where l is the length of the tube.

The term a'_0 is omitted, because, in connection with the circumstance that Δ represents the difference between the length of the mercury column and the mean length, we could expect beforehand that it would become small.

For $-\Delta = \int_p^q d' \, . \, dx$ we then find, if we bear in mind that $q - p = m + \Delta$, where Δ may be put small:

$$\left.\begin{aligned} -\Delta = a'_1 & \left\{\frac{2l}{\pi} \sin\frac{\pi}{2l} m + \Delta \cos\frac{\pi}{2l} m\right\} \cos\frac{\pi}{l}\frac{q+p}{2} \\ + a'_2 & \left\{\frac{l}{\pi} \sin\frac{\pi}{l} m + \Delta \cos\frac{\pi}{l} m\right\} \cos\frac{2\pi}{l}\frac{q+p}{2} \\ + a'_3 & \left\{\frac{2l}{3\pi} \sin\frac{3\pi}{2l} m + \Delta \cos\frac{3\pi}{2l} m\right\} \cos\frac{3\pi}{l}\frac{q+p}{2}. \end{aligned}\right\} \quad . \quad . \quad . \quad (2)$$

For the case under consideration $l = 50$, $m = 11.29$, so that if as in table I we put: $\frac{q+p}{2} = M$:

$$\left.\begin{aligned} -\Delta = a'_1 & \left\{11.05 + 0.94\,\Delta\right\} \cos\frac{\pi}{l} M \\ + a'_2 & \left\{10.37 + 0.76\,\Delta\right\} \cos\frac{2\pi}{l} M \\ + a'_3 & \left\{9.28 + 0.48\,\Delta\right\} \cos\frac{3\pi}{l} M. \end{aligned}\right\} \quad . \quad . \quad . \quad (3)$$

The data of table I now lead to the equations combined in table III: first I have derived from table I the values of L for $M = 10$, 15 etc., as this offers some advantage in the calculations (the value L with $M = 6.90$ is kept, as it did not seem advisable to me to extrapolate as far as $M = 5$).

TABLE III.			TABLE III*b*.
-0.11	$=$	$10.13\,a'_1 + 6.76\,a'_2 + 2.49\,a'_3$	$+5.14\,b'_6$
-0.04	$=$	$8.97\,a'_1 + 3.07\,a'_2 - 2.74\,a'_3$	$+0.00\,b'_6$
-0.02	$=$	$6.51\,a'_1 - 3.07\,a'_2 - 8.83\,a'_3$	$-6.24\,b'_6$
-0.01	$=$	$3.26\,a'_1 - 8.40\,a'_2 - 7.51\,a'_3$	$+0.00\,b'_6$
-0.01	$=$	$0.00\,a'_1 - 10.38\,a'_2 + 0.00\,a'_3$	$+6.24\,b'_6$
-0.02	$=$	$-3.19\,a'_1 - 8.41\,a'_2 + 7.52\,a'_3$	$+0.00\,b'_6$
$+0.04$	$=$	$-6.47\,a'_1 - 3.05\,a'_2 + 8.81\,a'_3$	$-6.25\,b'_6$
$+0.09$	$=$	$-8.88\,a'_1 + 3.04\,a'_2 + 2.73\,a'_3$	$+0.00\,b'_6$
$+0.11^5$	$=$	$-10.42\,a'_1 + 8.33\,a'_2 - 5.42\,a'_3$	$+6.26\,b'_6$

By means of the method of least squares [1]), we find the normal equations combined in table IV.

TABLE IV.	TABLE IV*b*.
$475.8\,a'_1 - 17.92\,a'_2 - 130.65\,a'_3 + 3.8284 = 0$	$-13.31\,b'_6$
$-17.92\,a'_1 + 401.4\,a'_2 - 28.31\,a'_3 - 0.6606 = 0$	$-60.33\,b'_6$
$-130.65\,a'_1 - 28.31\,a'_2 + 319.0\,a'_3 + 0.0882 = 0$	$-21.02\,b'_6$

$$-13.31\,a'_1 - 60.33\,a'_2 - 21.02\,a'_3 + 182.6\,b'_6 + 0.0331 = 0$$

These equations yield:

$$\left.\begin{aligned} a'_1 &= -0.00908\ , \\ a'_2 &= 0.000964, \\ a'_3 &= -0.00391\ . \end{aligned}\right\} \qquad (4)$$

By means of the equation (3) we can now calculate the values of Δ for the different values of M in order to judge whether they agree sufficiently with the values given by the experiment. Then in the second number we may assign to Δ the values of table I, and so use the coefficients given in table III, as these terms have little influence on the result. It now appeared that it was advantageous

1) Although each of the equations (3) contains 2 quantities deduced from observation, I have not applied here the method described in Supplement N⁰ 4 to the Communications from the Phys. Lab. of Leiden, These Proc. V Sept. 27, 1902 p. 236 on the reduction of equations of observations containing more than one measured quantity, because M in comparison with Δ may be supposed to be accurately known.

to add a fourth term to the equation (3), viz. one that contained the factor $sin \frac{5\pi}{l} M$. Independent of this, I had arrived at the same conclusion in the calculation of the calibration A. Therefore I put:

$$d' = a'_1 \cos \frac{\pi x}{l} + a'_2 \cos \frac{2\pi x}{l} + a'_3 \cos \frac{3\pi x}{l} + b'_5 \sin \frac{5\pi x}{l}, \quad . \quad . \quad (5)$$

so that we had to add to the second member of (2):

$$+ b'_5 \left\{ \frac{2l}{5\pi} \sin \frac{5\pi}{2l} m + \Delta \cos \frac{5\pi}{2l} m \right\} \sin \frac{5\pi}{l} \frac{p+q}{2} \quad . \quad . \quad . \quad (2b)$$

and to the second member of (3):

$$+ b'_5 \left\{ 6.24 - 0.20 \Delta \right\} \sin \frac{5\pi}{l} M. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3b)$$

To the equations of table III we had to add the terms combined in table III*b*, to those of table IV to the first members the terms given in table IV*b*, and also the fourth equation given there. These equations gave:

$$\left. \begin{aligned} a'_1 &= -\ 0.00915 \\ a'_2 &= \ \ \ \ 0.000796 \\ a'_3 &= -\ 0.00402 \\ b'_5 &= -\ 0.001048 \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

By means of these we have derived from the equation (3) with the supplementary term (3*b*) the values for Δ for the different values of M. The results are given in table V under the heading Δ_c, while column Δ_o shows the observed values, and the last column contains

TABLE V.

M	Δ_c	Δ_o	$\Delta_c - \Delta_o$
6 90	+ 0 103	+ 0.11	— 0 007
10	+ 0 069	+ 0 04	+ 0 029
15	+ 0 020	+ 0.02	0.000
20	+ 0 006	+ 0 01	— 0 004
25	+ 0 015	+ 0 01	+ 0 005
30	+ 0 007	+ 0 02	— 0 013
35	— 0.028	— 0 04	+ 0 012
40	— 0 073	— 0.09	+ 0 017
45	— 0 117	— 0.115	— 0.002

the differences. From this we derive for the probable error: 0.009, which with regard to the accuracy is permissible, so that the equation (5) with the coefficients (6) well represents our observations.

From equation (1) follows for the volume between the divisions 0 and Q:

$$V_0^Q = s_n \left\{ Q + \int_0^Q d' \, . \, dx \right\} = s_n \, Q' ,$$

where $Q' = Q + q$ and

$$q = \int_0^Q d' . dx = \frac{l}{\pi} \left[a'_1 \sin \pi \frac{Q}{l} + \frac{a'_2}{2} \sin 2\pi \frac{Q}{l} + \frac{a'_3}{3} \sin 3\pi \frac{Q}{l} + \frac{2b'_5}{5} \sin^2 \frac{5\pi}{2} \frac{Q}{l} \right].$$

Table VI gives for the values for Q from 0 to 50 the values computed in this way for Q', the reduced readings. By means of this table we may inter alia judge of the irregularity of the tube.

TABLE VI.

Q	Q'	Q	Q'	Q	Q'
0	0 000	17	16 878	34	33 864
1	0 987^5	18	17 878	35	34.866
2	1.975	19	18 878	36	35 869
3	2.962	20	19 878	37	36 872^5
4	3.950	21	20 877	38	37 877
5	4 938	22	21 877	39	38 882
6	5 927	23	22 875^5	40	39 888
7	6 917	24	23 874	41	40 895
8	7.908	25	24 872	42	41 903
9	8 900	26	25 870^5	43	42 911
10	9 893	27	26 868	44	43.920^5
11	10 888	28	27.867	45	44.931
12	11.884	29	28 865	46	45 942
13	12.881	30	29 864	47	46.954
14	13.879	31	30 863	48	47.966
15	14 878	32	31.863	49	48 980
16	15 878	33	32 863	50	49 993

The data of table II enable us now to determine the normal bore s_n. By means of table VI we find for the reduced length of the mercury column at 20°.6 C. the values :

$$\begin{array}{rl} & 46.232 \text{ cm.} \\ & 46.215 \text{ cm.} \\ \hline \text{mean:} & 46.223^5 \text{ cm.} \end{array}$$

Hence at 20° C.: $s_n = 0.0053948$ cm².

From the data of table II we may also derive the volume of the widened part d_3 (fig. 4 of Comm. N° 50). The bore of the capillary e_3 was measured with a microscope by comparison with a fine graduation on glass by means of a micrometer eyepiece. The bore is : 0.000301 cm². We then find for the volume of the part d_3 between the division 50 on the graduated stem and the mark on the capillary at 20° C.: 0.14239 cc.

Using the value found for s_n, we may derive from table VI the volumes V_0^Q between the division 0 and the division Q, and then, using the volume found for the widened upper part, the volumes from division Q to the mark on the narrow capillary.

The calibration A has been made and reduced in entirely the same way. The results of either are combined in a table which indicates the volume for each centimeter division Q from 0 to 50. Table VII is an extract from that table.

TABLE VII.

Q	V_A	V_B	% diff.
0	0.41161	0 41209	0 11
5	0.38487	0.38545	0.15
10	0 35800	0.35872	0.20
15	0 33125	0 33183	0 17
20	0.30441	0 30485	0 14
25	0 27731	0 27791	0 22
30	0.25028	0.25098	0.28
35	0.22357	0.22400	0.19
40	0.19673	0.19690⁵	0.09
45	0.16938	0 16970	0.19
50	0 14189	0.14239	0 35

Column V_A contains the volumes from the mark on the narrow capillary to the division Q at 20° C., as resulting from the calibration A, V_B as resulting from the calibration B. The last column shows the percentage differences. The mean percentage difference between V_A and V_B in the complete table amounts to 0.19 %, for the part from 0 to 41 inclusive, which only was used in the following observations: 0.17 %. For our purpose this agreement is sufficient. From the fact that $V_B - V_A$ is always positive it follows that the accuracy might be improved by more determinations of s_n and of the volume in the widened upper part. I hope to revert again to this subject in a following paper.

§ 4. To determine the capacity of the reservoir a_3 with b_3 (see fig. 4 l.c.) and also the bore of the part f_3, the manometertube, which at the end e_3 was provided with a cock with a fine point, was exhausted by the mercury vacuumpump and then filled with mercury in a reversed position until the mercury stood above at f_3 (in the drawing below). A quantity of mercury was drawn off twice and weighed so that we could determine the bore of f_3 at different places. The level of the mercury in the tube was read by means of a cathetometer. Then so much mercury was drawn off that the mercury still stood in the graduated stem c_3, and this was weighed. This served to determine the capacity of $a_3 + b_3$. The following results were obtained· the portion f_3 is divided into millimeters, the centimeterdivisions are marked from 0 to 6, 0 being nearest to a_3. It appeared that the bore could not be put constant; I have put:

$$s = s_0 \left\{ 1 + ax \right\},$$

and found:

$$a = 0.0058 \quad , \quad s_0 = 0.3564 \text{ (cm}^2\text{)},$$

so that

$$V_0{}^Q = 0.3564 \left\{ 1 + 0.0029\, Q \right\} Q.$$

Table VIII (p. 541) contains the volumes from the division 0 to the division Q at 20° C.

For the calculation of the volumes of the menisci I have used SCHALKWIJK's table occurring in Comm. N°. 67 [1]). For the volume between the division 0 on f_3 and the division 0 on c_3 I found at 20° C. : 25.021 cc.

In the calibration of an experimental tube it will in general be

[1]) These Proc. III Jan. 27, 1901, p. 488.

TABLE VIII.

Q	$V_0 \varrho$
1	0 3574
2	0 7169
3	1 0785
4	1 4421
5	1 8078
6	2 1756

necessary to take into account an electromagnetic stirrer, consisting of a soft iron rod in glass. In my case it consisted of a cylindrical portion with two bulbs at either end. The bores were measured with a micrometer screw, the length with a pair of sliding compasses. Each time when the experimental tube had to be refilled with a new quantity of gas, it had to be opened at the top in order to be cleaned. Because the stirrer had to be brought in, it was not possible to seal on a thin capillary as had been done for the manometer tube. Nor could the stirrer be placed into it beforehand, as this would be a hindrance in the cleaning and especially in the calibration with mercury. The volume of the top portion was determined each time after the measurements by cutting off so much from the top that on that piece one division at least was well visible (the upper divisions over a length of about 5 mm. were lost in the sealing). The fracture was ground flat, the piece after being cleaned and dried was entirely filled with mercury and the superfluous mercury was removed by sliding a properly cleaned flat piece of glass over the ground off end. The mercury was weighed, the position of the ground end was observed with regard to the divisions of the tube with a cathetometer and from this the volume of the top portion was derived.

Physics. — "*Isothermals of mixtures of oxygen and carbon dioxide. II. The preparation of the mixtures and the compressibility at small densities.*" By W. H. KEESOM. Communication N°. 88, continued, from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of September 26, 1903).

§ 1. In this paper I shall describe the preparation of the mixtures of accurately known composition in the mixing apparatus