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T A B L E XIV.

	<i>o</i>	<i>c</i>	<i>o-c</i>
Carbon dioxide	1.00574	1.00570	+ 0.00004
Mixture 0.2	1 00388	1 00413	— 25
» 0.3	1 00352	1.00340	+ 12
Oxygen	1 00064	1.00065	— 1

measured at about 20° C the theoretical normal volume of that quantity of gas (at 0° C).

Physics. — *“Isothermals of mixtures of oxygen and carbon dioxide. III. The determination of isothermals between 60 and 140 atmospheres, and between —15° C and +60° C.”* By W. H. KEESOM. Communication N°. 88 (3rd part) from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of October 31, 1903).

§ 1. During my measurements of the isothermals of mixtures of oxygen and carbon dioxide it appeared desirable to take several precautions and to make some modifications in the usual methods. They will be described here in connection with and in behalf of following papers on the results obtained.

§ 2. *The arrangement.* The manometertube and the experimental tube which beforehand had been cemented into a steel flanged tube (comp. Comm. N°. 70 V, These Proc. IV June 29, '01 p. 107) were placed into steel pressure cylinders. For the shapes of these see also Comm. N°. 43, These Proc. I June 25, 1898, p. 83, fig. 2. The arrangement as drawn there has been modified, viz. the two pressure cylinders into which the aforementioned tubes were placed were entirely filled with mercury. They communicated at their lower ends by means of a steel tube and of a steel T-piece with each other and with a third pressure cylinder. This was filled partly with mercury partly with glycerine. To obtain pressure, glycerine was forced into it by means of a SCHÄFFER-BUDENBERG pump. This arrangement offers the advantage that the tubes filled with gas do not come into contact with the glycerine, and the mercury which is forced into the tubes only slightly with the glycerine. In this way it was very easy to redetermine the normal volume after lifting out the experimental tube from the pressure cylinder, while the mercury menisci in the tubes

kept good during a very long time and no or very little soil was deposited in the tubes.

The pressure cylinders and the connecting tubes had been well cleaned beforehand with benzene, which was removed by heating while air was sucked through. The connections were tightened by leather washers soaked in paraffin. The packing which had to prevent leakage of mercury along the pivot of the high pressure cocks through which the mercury passed which was to be forced into the observation tubes, consisted of rings cut from selected Spanish corks. During the observations the two observation cylinders were disconnected from that where the pressure of the glycerine was transferred to the mercury in order to be independent of leakage that might occur in the pump or in the glycerine lead¹⁾. A perfectly tight fit of this enclosed portion even at the highest pressures was secured.

§ 3. *The measurement of the volumes.* The determination of the normal volume was made in the same way as has been described in Comm. N^o. 70 V. These Proc. IV June 29, 1901, p. 107 and in Comm. N^o. 78, These Proc. VI April 19, 1902, p. 761, especially the same precautions for the constant temperature and pressure were taken.

The normal volume was determined at least twice before and twice after the measurements. It must be recorded, however, that this was not done with the first quantity of carbon dioxide of which the isothermals from 25°.55 C. to 37°.09 C. were investigated, because the experimental tube had broken, while in the case of the manometer we may profitably substitute a direct comparison with a standard manometer, to which comparison I shall refer later.

I found for the normal volume of the hydrogen manometer:

22 Sept. '02:	23.217 cc.
„	23.194 „
„	23.192 „
12 Nov. „	23.220 „

As the first 3 measurements are not made in the bath of constant temperature I have in the calculation of the mean assigned the weight 3 to the last determination and have adopted $V_N = 23.210^5$ cc.

From the following the advantage of a hydrogen manometer may appear²⁾. Most of the determinations with the first mixture (0.1 oxygen in carbon dioxide) were made with an air manometer. During the experiments phenomena occurred which pointed to variations of

¹⁾ Small variations of pressure could then be applied by screwing slightly in or out the pivot of one of the fine high pressure cocks in the enclosed portion.

²⁾ Comp. Comm. N^o. 50, These Proc. II June 24, 1899, p. 29.

the normal volume of this manometer. The manometer was removed from the pressure cylinder and the normal volume redetermined, and it appeared that from 22.114 cc. (May 9 1901) it had fallen to 22.056 cc. (Aug. 23 '02). After this the manometer has been calibrated for the second time (calibration *B*) ¹⁾ and filled with hydrogen; of each of the isothermals determined some points have been tested by means of the hydrogen manometer. Column *C* of table XV gives the mean relation of the pressure measured with the hydrogen manometer and that measured with the air manometer, where for the normal volume of the latter we have taken the mean between those before and after the experiments. Column *A* gives the date, *B* the temperature relating to the isothermal.

TABLE XV.

A.	B.	C.
20 June '02	17.60	1.0020
20 » »	20.29	1.0017
23 » »	21.99	1.0016 ⁶
24 » »	22.68	1.0023
25 » »	23.29	1.0013
26 » »	25.20	1.0019
mean :		1.0018

From column *C* we cannot derive a regular course in this short period, so that for these isothermals I have multiplied all the pressures measured with the air manometer by the coefficient 1.0018. On June 5, 6 and Aug. 21 points of the border curve have been determined. These could only be brought to harmonize with those determined later with the hydrogen manometer by multiplying the pressures by coefficients which are combined in the following table together with that afore-mentioned. Hence this shows the course of the variation during that period.

If we compare these figures with the values for the normal volume before and after the measurements, it appears that almost the entire variation has taken place during this last period. From May '01 to

¹⁾ Comp. this Comm. I. p. 534.

TABLE XVI.

5/6 June '02	1.00215
20/26 " "	1.0018
21 Aug "	0.9997

June '02 the manometer was but seldom used, and the pressure during that time was low, while the pressure in the months June—Augustus '02 was often and during a long time from 60 to 125 atmospheres. Hence it seems that this variation is much greater at a high than at a low pressure.

A similar variation of an air manometer with the time, probably owing to the absorption of oxygen in the mercury, has also been noted by KUNEN and ROBSON (*Phil. Mag.* Jan. '02 p. 150).

In the mixtures of the molecular proportions 0.1 and 0.2 of oxygen the variations of the normal volume were less than $\frac{1}{1000}$. In those cases we have accepted for the normal volume the mean of the values before and after the measurements.

On the other hand, in a mixture with a molecular proportion of 0.3072, which for some weeks had uninterruptedly been exposed to high pressure, the normal volume of 72.878⁵ cc. before the experiments (15 June '03) had fallen to 70.980 cc. after the experiments (13 Aug.). It being highly probable that the variation of the normal volume involves a considerable variation in composition, the results of the measurements with this mixture which with regard to the end condensation pressures and volumes extended to $-14^{\circ}.7$ C., will not be given here.

This also shows how very important it is that we should be able to determine the normal volume after the measurements¹⁾.

From the observation of the volume occupied by the gas at a temperature of about 20° C. and a pressure of about 1 atmosphere we derived the volume which the gas would occupy at 20° C. and 1 atm. (75.9467 cm. mercury at Leiden, comp. Comm. N^o. 70, *These Proc.* IV June 29, 1901. p. 111). Use was made of the coefficient of pressure variation given in this Comm. II, p. 553, and the law of BOYLE was applied. By multiplication by the values of the coefficients $A_{K_{20}}$ given in table XIV p. 554 under C, we find from this the volume which the gas would have occupied if from an infinitely

¹⁾ Comp. Comm. N^o. 50. *These Proc.* II June 1899, p. 29, and N^o. 70. V. *These Proc.* IV, June 29, 1901, p. 107.

large volume at 20° C. it were reduced to a pressure of 1 atm., and it had followed the laws of the ideal gases. We then find the theoretical normal volume (at 0° C.) by means of the coefficient of pressure variation (= coefficient of dilatation) for the ideal gaseous state. As the calculations of the correction that according to Comm. N^o. 71 (These Proc. IV June 29, 1901, p. 125) must be applied to the coefficient of pressure variation of pure hydrogen in order to find that coefficient for the ideal gaseous state were not finished when I began my calculations, I have adopted for this the value 0.0036625, which in Comm. N^o. 71 was given as a first approximation. The corrections, however, which accordingly must be applied to the results, will certainly lie far below the degree of accuracy which I could attain in my experiments of the isothermals at high pressures.

After what has been said on the calibrations¹⁾, the measurement of the normal volume and the reduction to the theoretical normal volume I can confine myself to a short note on the measurement of the volumes. The top and the base of the mercury were read with an eye-glass, parallax was avoided in the way described before (Comp. this Comm, I p. 533). In this manner 0.1 mm. could be read. We assumed that the mercury meniscus in the graduated stem of the experimental tube has the form of a spherical segment, hence by multiplication of the bore by half the height the volume may be found with a sufficient degree of accuracy, our method of reading considered. When the mixtures split into two phases, the position of the liquid meniscus was also read. Corrections were applied for the expansion of glass due to heat and to the inner pressure.

§ 4. *The measurement of the pressures.* The pressures were measured with a hydrogen manometer, ranging from 62 to 196 atmospheres²⁾.

In the first part of this Comm. (p. 532 ff.) I have discussed the calibration, in § 3 of this paper the determination of the normal volume. We need only add that the hydrogen was prepared as described in Comm. N^o. 27 Zittingsversl. V, Mei 1896 p. 42.

From the means of the values of V_A and V_B of the table from which table VII forms an extract and from the normal volume

¹⁾ Comp. this Comm. I, p. 532.

²⁾ It appeared that the manipulations of the stems of the manometer and the piezometer tubes in the blow-pipe, as for instance the sealing of the top of the latter, had to be made with special care and the tube had to be cooled very carefully and slowly, else tensions will rise in the glass and consequently when high pressure is applied (in these experiments 140 atm. was reached, the manometer has stood 195 atms. several times) the tube will burst.

given in § 3, while the volume of the narrow capillary above between the mark and the place where it is sealed was accounted for, a table was derived. This new table gives for each division Q the density d_A of the hydrogen when the mercury reaches that division at a temperature of 20° C., expressed in terms of the normal density (0° C., 1 atm. 45° N.L.) as unity. For the values of Q between 25 and 50 the table increases by 0.5; hence also for the higher values of the pressure (as far as $Q = 40$) the error made by interpolating linearly is less than 1 atm.

To derive from these densities the corresponding pressures we must know the isothermal of hydrogen at 20° C. Measurements of this have been made by SCHALKWIJK; they do not, however, exceed the density 54. An extrapolation from these observations for the densities wanted is not allowed with a view to the mean error of his determination of the C of the series of KAMERLINGH ONNES (cf. SCHALKWIJK's Thesis for the doctorate, p. 115). Observations at higher densities have been made by AMAGAT (from 100 to 3000 atms.) The isothermal for hydrogen at 20° C. derived from AMAGAT's data:

$$pv_{A_{20}} = 1.07252 + 0.0007194 d_A + 0.000000672 d_A^2$$

(cf. SCHALKWIJK's Thesis for the doctorate p. 121) does not agree, however, with that from SCHALKWIJK's observations. From these for instance, follows at $d_A = 55$: $pv_{A_{20}} = 1.11194$ (cf. l. c. p. 124), hence $\mu = 61.157$, whereas from the isothermal given by AMAGAT we derive at $\mu = 61.157$: $d_A = 54.897$. SCHALKWIJK's observations have been made very carefully especially his determination of the normal volume (see Comm. N^o. 70, V, These Proc. IV June 29, 1901, p. 107). If with this we compare the way in which AMAGAT has determined his normal volume (Ann. de Chimie et de Physique, t. 39, 1893, p. 83) it seems not entirely without reason if, while waiting for more accurate determinations of the isothermals of hydrogen at higher densities, we make those of AMAGAT agree with those of SCHALKWIJK by multiplying all the volumes of the former by the factor $\frac{54.897}{55}$

So we obtain:

$$pv_{A_{20}} = 1.0705 + 0.000717 d_A + 0.00000067 d_A^2.$$

To test this we compare the value of $pv_{A_{20}}$ at $d_A = 1$, viz.: 1.0712 resulting from it, with the value of $pv_{A_{20}}$ which follows from the value of the coefficient of expansion according to CHAPPUIS: $\alpha_v = 0.0036606$ ¹⁾, viz.: 1.0732. The difference is $\frac{1}{500}$, so that the

¹⁾ See SCHALKWIJK, Thesis for the doctorate p. 116.

ation found, which deviates from AMAGAT's observations at higher densities $\frac{1}{500}$, does not deviate from the observations at smaller densities by more than $\frac{1}{500}$.

The following term in the series of KAMERLINGH ONNES would be

If we derive a value of D_1 from the data given in Comm. N^o. 71, see Proc. IV June 29, 1901, p. 132, for hydrogen at 0°C., 15°.4C., 25 C. and 200°.25 C., we find that this term for $d_A = 150$ would yield in $p v_{A_{20}} : 0.0009$, so that if we omit this term at the best pressures an error of less than $\frac{1}{1000}$ is made. As there exists

already some uncertainty about the exact shape of the isothermal, we have omitted this term.

The values $p v_{A_{20}}$ calculated thus for the different values of d_A of the table mentioned at the beginning of this section, have been added to this table together with the values for p derived from them¹⁾

When the isothermal of hydrogen at the densities occurring here can be known more accurately, the pressures given here will require correction for which the afore mentioned table may be useful.

The temperature of the manometer differed at most a few tenths of a degree from 20° C. The temperature coefficients for hydrogen at 20° C. are found from the value of A_{A_0} (given in Comm. N^o. 71) in the series of KAMERLINGH ONNES and AMAGAT's values of B_A and C_A (given in SCHALKWIJK's Thesis for the doctorate, p. 120), for the temperatures 0° C., 15°.4 C. and 47°.3 C., observing the reduction mentioned to obtain the agreement with SCHALKWIJK's isothermal.

TABLE XVII.

p	$\left(\frac{\partial p}{\partial T}\right)_v$	p	$\left(\frac{\partial p}{\partial T}\right)_v$	p	$\left(\frac{\partial p}{\partial T}\right)_v$
200	0.714	150	0.531	100	0.349
190	0.677	140	0.494	90	0.314
180	0.640	130	0.458	80	0.279
170	0.603	120	0.422	70	0.243
160	0.567	110	0.385	60	0.208

¹⁾ This table has been given in my thesis for the doctorate.

Column $\left(\frac{\partial p}{\partial T}\right)_v$ of table XVII gives the temperature coefficients thus found for the different pressures p .

Also a correction was applied for the difference in level of the mercury columns in the manometer and the experimental tube, for the expansion of the volume of the manometer tube caused by the inner pressure, and for the difference in capillary depression in the two tubes. For the latter a separate experiment has been made to determine the depression in a tube of the same inner bore as the manometer tube. This correction was 0.01 atmosphere.

The manometer was read in the same way as the piezometer (see p. 558). The level of the mercury in the manometer tube and the temperature of this were read before and after the reading of the meniscus and the temperature of the experimental tube. The temperature of the manometer could be read to within 0°.05.

After the isothermal determinations the hydrogen manometer was compared with the standard manometers (Comm. N°. 50, Proc. June 1899) which have been very accurately compared with the open manometer by SCHALKWIJK (Comm. N°. 67, Proc. Dec. 1900 and Jan. 1901, Comm. N°. 70, Proc. May and June 1901). To render this possible the hydrogen manometer had been constructed so that the lowest pressure which could be read on it could still be measured with the standard manometer IV¹⁾. Table XVIII gives under the heading A the pressure as measured with the hydrogen manometer used by me, under the heading B the same pressure measured with the standard manometer.

TABLE XVIII.

A	B
64.04	64.040
64.02	64.024

Obviously the agreement is quite satisfactory. This comparison comes in the place of the determination of the normal volume after the measurements, and also of more determinations of the normal bore of the graduated stem. (Comp. p. 540). As there mentioned mean percentage difference 0.19 % is principally due to the difference

¹⁾ For the way in which this comparison has been made comp. VERSCHAFFELT. Thesis for the doctorate p. 17.

between the two determinations of the normal bore, this comparison highly improves the accuracy of the manometer.

The thermodynamical equilibrium in the experimental tube was reached by means of an electromagnetic stirring apparatus; to secure the equilibrium of pressure between the experimental tube and the manometer I waited 5 minutes after each adjustment before reading. Of each isothermal two series of observations were usually made, one beginning with the lowest and ending with the highest pressure, the other in reversed order. Only rarely the results of these two differed as much as $\frac{1}{500}$. To judge of this see table XIX, which relates to the isothermal for 22°.68 C. of a mixture of 0.1047 oxygen in carbon dioxide. Here v represents the volume, p , and p_f the corresponding pressures in the two series, with a constantly rising and a constantly falling pressure respectively, Δp the difference, v_{liq} , and v_{liqf} the volumes of the liquid also in the two series, Δv_{liq} the difference between them.

The agreement of the pressures is satisfactory, that of the volumes of the liquid leaves to be desired. Although this is partly explained by the circumstance that the volume of the liquid cannot be read so accurately because the form of the meniscus is not so sharply determined as is the case with mercury, and parallax could not so easily be avoided as with the mercury menisci, it yet appears that, if we desire to investigate this subject more fully, more care should be taken to procure equilibrium by stirring and waiting.

§ 5. *The constancy and the measurement of the temperatures.* The manometer was surrounded by a jacket with flowing water kept at constant temperature by a thermostat, as described by SCHALKWIJK (Comm. N°. 70, Proc. May '01) with the modification in the thermoregulator described in Comm. N°. 78 (Proc. April 1902 p. 762).

In the same way the experimental tube was kept at constant temperature by means of a second thermostat. This differed from the former in the following respects:

The connection between the heating bath and the mixing bath, the mixing bath and the connection between the mixing bath and the observation bath have been insulated more carefully by means of wool, paper and felt; this was necessary because greater differences of temperature with the surrounding atmosphere occur here.

To the glass portion of the thermoregulator a side-tube with a cock is sealed on, which facilitates the admission of a quantity of mercury from a mercury reservoir, which by means of an india rubber tube is connected with that side-tube, into the thermoregulator

TABLE XIX.

v	l_r	pf	Δp	$u_{g r}$	$v_{lq. f}$	Δv_{lq}
0.012159	58.66	58.60	+0.06			
11384	60.88	60.92	-0.04			
10605	63.27	63.31	-0.04			
0.009826	65.74 ^s	65.77 ^s	-0.03			
9047	68.26	68.31	-0.05			
8269	70.90	70.94	-0.04			
7489 ^s	73.47	73.51	-0.04			
6712 ^s	76.07	76.11	-0.04			
5908 ^s	78.72 ^s			<i>b.c.</i> difference in saturation volume:		
5917 ^s		78.75 ^s	-0.03	<i>b.c.</i> -0.000009		
5546	79.95 ^s	79.98 ^s	-0.03	0.000217	0.000180	+0.000037
5157	81.26 ^s	81.39 ^s	-0.13	397	403	- 6
4768	82.88 ^s	82.89 ^s	-0.01	612	583	+ 29
4379	84.70 ^s	84.76 ^s	-0.06	746	672	+ 47
4309		85.05			591	
4278	85.22			625		
4258		85.35			288	
4243		85.40			95	
4219	85.54			125		
4215 ^s	85.54			<i>e.c.</i> difference in saturation volume:		
4220 ^s		85.52	+0.02	<i>e.c.</i> -0.000005		
3991 ^s	87.10 ^s	86.95 ^s	+0.15			
3604	90.24	90.22	+0.02			
3049	99.29 ^s	99.08 ^s	+0.21			
2752	112.63	112.71	-0.08			
2612	124.64	124.36	+0.28			

and hence the adjustment for different temperatures¹⁾. The narrow part of the glass tube where the supply of gas is regulated, has

¹⁾ A similar arrangement has been described by FRIEDLÄNDER, Zeitschrift für physikalische Chemie, Bd. 38 p. 401, 1901.

been graduated in mm. over a length of 4 cm., which facilitates a finer adjustment by moving up and down the supply tube.

For temperatures higher than 35° the water streamed successively through two heating baths, each provided with a thermoregulator; the first brought the water to 35° C., the second to the desired temperature. To avoid exchange of heat with the surrounding atmosphere the last bath was coated with asbestos, except where it came into contact with the flames.

One thermoregulator had been constructed for higher temperatures, filled with xylene and goes as far as + 90° C., the other for lower temperatures was filled with benzole, of which the coefficient of expansion was determined at 0.0011 and goes from -40 to + 40° C.

For temperatures below that of the water supply, the water streamed between the overflow and the heating bath through a zinc vessel insulated with felt, where small pieces of ice were continually brought in.

By leading the water back to the overflow after it has flown through the observation jacket by means of a membrane pump¹⁾ through tubes enclosed in wool, we could make measurements to about 1°.9 C. For the experiments with the mixture 0.3, mentioned in § 3, we used the current of solution of calciumchloride at constant temperature, described in Comm. N°. 87, Zittingsversl. Deel XII Juni 1903 (see Pl. II of that Comm., which shows the whole arrangement with the thermostat and the observation bath).

For temperatures above 30°, and also for temperatures as much again below the temperature of the room, it appeared necessary to replace the observation bath, which first consisted of a simple glass tube, by a vacuum jacket²⁾. After this the difference in temperature at 34° C. over a height of 33 cm. without stirring amounted to 0°.02 C. Moreover we have always stirred before each observation. The water was insulated from the copper piece with which the jacket was fastened to the steel flanged tube of the experimental tube by a layer of sulphur. This prevented the cement from softening.

In order to prevent variations of temperature of the gas compressed in the experimental tube owing to conduction of heat along the mercury column to the mercury in the compression tubes, we took care that in the observations, where the mercury meniscus was lowest the mercury column still stood over a length of 40 cms. in the jacket.

¹⁾ Comp. DE HAAS, Thesis for the doctorate fig. I.

²⁾ Comp. Comm. N°. 85, Versl. Deel XII Juni 1903, p. 214. The case acting, as a spring was placed as low as possible to leave room for the coil which moves the electro-magnetic stirrer.

The temperature of the experimental tube was read with an eye-glass to within $0^{\circ}.01$ on an "Einschlussthermometer", divided into $0^{\circ}.1$, with a scale on milkglass. From time to time this was compared at different temperatures with a similar thermometer tested at the Reichsanstalt with the air thermometer, while the variation of the zero of the latter in the mean time was accounted for and also the temporary depression of the zero, which, after the thermometer had for a long time been heated at 48° C., amounted to $0^{\circ}.02^{\circ}$ C.

6. *Reduction of the observations.* In cases where, in contrast to the determination of the plaitpoint and the point of contact of the mixtures and the critical point of carbon dioxide, the greatest possible constancy of the temperature was not absolutely necessary, the temperature during the determination of an isothermal which lasted on an average from 3 to 4 hours was allowed to vary a few hundredths of a degree. For the reduction to one temperature, temperature coefficients for the different volumes were derived from the observations.

In the two series, one at an always increasing, the other at an always decreasing pressure, pressures were measured, corresponding to different volumes, which in the two series differed but little. Pressures were derived from them for the same volume and then the mean was found. When it appeared that these pressures agreed sufficiently (comp. § 4) we have afterwards simply taken for two corresponding points the mean of the volume and the pressure.

Physics. — "*Isothermals of mixtures of oxygen and carbon dioxide. IV. Isothermals of pure carbon dioxide between 25° C. and 60° C. and between 60 and 140 atmospheres.*" By W. H. KESOM. Communication N^o. 88 (4th part) from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES.

§ 1. *Reason for the investigation of carbon dioxide.* Although the isothermals of carbon dioxide have been extensively investigated by AMAGAT, I have yet determined a number of isothermals together with its critical point. I was led to it by the following considerations:

1st. it was desirable that I should be able to judge of the purity of the carbon dioxide which I used for the preparation of the mixtures, and it seems that this judgment may best be derived from the increase of the vapour pressure with condensation at a stationary temperature¹⁾;

¹⁾ Comp. Comm. N^o. 79. Proc. April 1902.