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In conclusion one of the few applications of the second kind may be briefly mentioned here.

In my first communication[1]) concerning the system hydrogen sulphide-water I have fully determined the situation of the quadruple point S (hydrate) by the side of two liquids (L_1 and L_2) and gas (G) with the three-phase lines terminating there. If this rule had been known to me already then, I could have directly inferred from the figure of the cited communication that between the three-phase lines $S + L_1 + G$ and $S + L_1 + L_2$ no metastable prolongations occur, that there the coexistences:

$S + L_1$ (angle $< 180°$ between $S + L_1 + G$ and $S + L_1 + L_2$)

$L_1 + G$ „ „ „ $S + L_1 + G$ and $L_1 + L_2 + G$) and

$S + L_2$ „ „ „ $S + L_2 + G$ and $S + L_1 + L_2$)

occur, and that therefore the order of the phases must be GL_1SL_2, if the mentioned coexistences are to take place between phases that are consecutive in concentration. The gas of these phases containing the greatest quantity of hydrogen sulphide, it is clear that the hydrate contains less water than L_2, and that therefore the liquid L_2 lies on the side of the water. From determinations which I carried out later on, and which I have communicated in my second paper[2]) on this system it appears that this conclusion is really valid.

Anorganic Chemical Laboratory of the University.

Amsterdam, September 18, 1912.

Physics. — "*Isotherms of diatomic substances and of their binary mixtures. XII. The compressibility of hydrogen vapour at, and below, the boiling point.*" By H. KAMERLINGH ONNES and W. J. DE HAAS. Communication N°. 127c from the Physical Laboratory at Leiden.

(Communicated in the meetings of May 25 and June 29, 1912).

§ 1. *Introduction.* To the region covered by the investigations which have been made for many years past in the Leiden laboratory upon the equation of state for hydrogen at low temperatures (for the latest paper see Comm. N°. 100a, Proc. Dec. 1907) the present Communication adds the region for hydrogen vapour lying between —252° C. and —258° C. While the lowest reduced temperature

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[1]) These Proc. January. 1911. p. 829.
[2]) These Proc. June. 1911. p. 195.

attained in the measurements of KAMERLINGH ONNES and BRAAK was about $t = 2.2$, in our present investigation we were able to calculate the second virial coefficient B for the further region from $t = 0.7$ to about $t = 0.5$; by this means, since interpolation between $t = 0.7$ and $t = 2.2$ is not a matter of any difficulty, B becomes known over a very extensive region of reduced temperature (from $t = 0.5$ to $t > 12$). The second reduced virial coefficient is therefore known for a single substance over a much more extensive region of temperature than has hitherto ever been the case. This extension was especially to be desired as, in the first place, it allows a better comparison from the point of view of the law of corresponding states of B for hydrogen with its value for various other substances, and this will become of particular importance when the comparison can be extended so as to embrace monatomic substances (a communication by KAMERLINGH ONNES and CROMMELIN will shortly appear dealing with the B for argon at low reduced temperatures). In the second place it allows us to put to the test theoretical deductions concerning B (for instance, the connection between the peculiarities of B with the peculiarities of the specific heats and of viscosity, and also of the dielectric constants and of penetrability by electrons). This is all the more important as B is related to that state which according to REINGANUM can be called the *planetary* gas state in which, in allowing for the influence of collisions between molecules, only two molecules need be considered, as the possibility of the proximity of others may be neglected.

From B, moreover, one can calculate the experimentally determined corrections of the hydrogen thermometer scale to the AVOGADRO-scale, which have hitherto been known only down to $- 217°$ C., down to the lowest temperatures which can be measured with the hydrogen thermometer. (Cf. Comms. Nos. 101b and 102b).

The uncertainty in the adjustment of a cryostat bath to an accurate definite temperature and in the measurement of that temperature is much greater than that with which a temperature, once steadied, can be maintained constant. Since, now, uncertainty in the determination of the temperature is of great influence upon the values of B obtained from the observed pv_A, it was decided to proceed with isothermal measurements so as to be as independent as possible of thermometrical measurements. A further advantage of constancy of temperature in the comparison of values of pv_A at different pressures lies in the circumstance that the possible difference between the temperature of the gas in the piezometer and that of the thermometer in the bath is constant throughout. The advantages of isothermal measure-
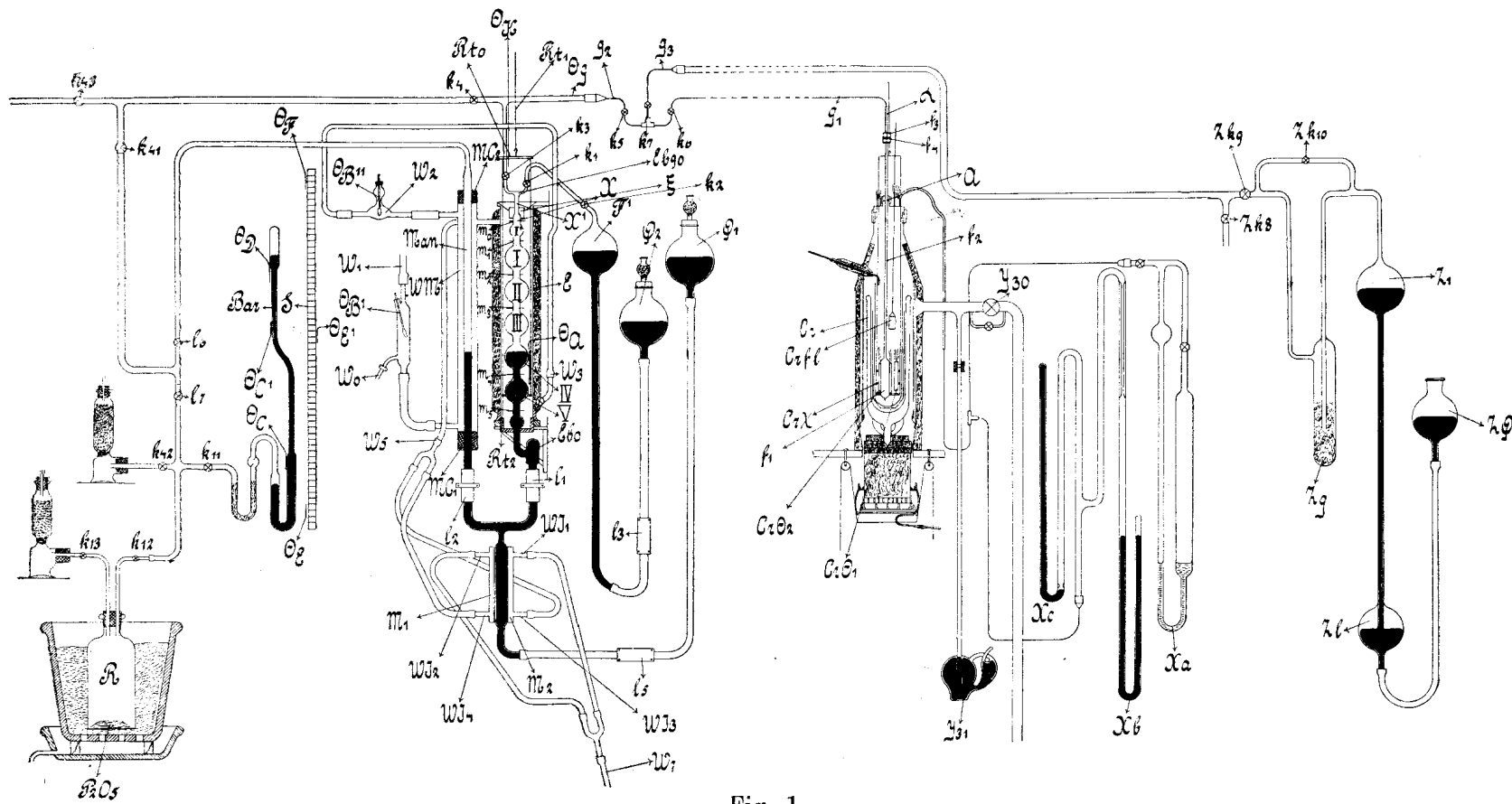
Fig. 1.

ments would have been far greater for us had we not frequently been obliged to aim at obtaining the same reading of the resistance thermometer instead of at the maintenance of a definite temperature.

The investigation was carried out at three temperatures, approximately — 252°.6 C., — 255°.5 C. and — 257°.3 C. A lower temperature than — 257°.3 was not desirable as the smallest pressure to be measured at this temperature had already sunk as low as 5 cm. and further progress in this direction would have necessitated another apparatus.

For each isotherm the densities were so chosen that the ratio of the extreme densities was about two to one in each case. By this means it was brought about that in the solution of B_A from the two equations

$$pv_{A_1} = A_A + B_A d_{A_1} + C_A d_{A_1}{}^2$$
$$pv_{A_2} = A_A + B_A d_{A_2} + C_A d_{A_2}{}^2$$

the coefficient of B_A was approximately 1. In this solution C_A was taken as a correction term from the equation of state VII. H_2.3 (formula (16) Comm. N°. 109a).

Finally, for practical reasons, it was necessary to remain as far as possible away from the region of condensation, as a sudden fluctuation of the temperature could quite well occasion condensation to take place upon the walls of the piezometer, and particularly of the capillary, and this, in view of the excessively slow liberation of liquid and vapour from the glass, would render the measurements valueless.

The measurements were made with a piezometer immersed in a bath of liquid hydrogen and connected through a capillary with the volumenometer studied in detail in Comm. N°. 127a (See Fig. 1, p. 407). The piezometer was first evacuated and a quantity of gas measured in the volumenometer; the valve between the two was then opened. Pressure equilibrium was then allowed to establish itself at the desired value, and then the pressure and the quantity of gas remaining in the volumenometer were determined.

§ 2. *Arrangement of experiments. Auxiliary apparatus.*

The experimental arrangements are shown in fig. 1, p. 407 [1]). One portion of the apparatus had already been utilised in the investigation of the diameter for oxygen, and is described in Comm. N°. 117, Proc. Febr. 1911. The left hand part of fig. 1, p. 407 is an impro-

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[1]) In the drawing some details of no importance are incorrectly represented, viz: the ice ought to cover the bottle R, the air-trap Zl is in reality much smaller, the safety-tube Y_3 is of course not wholly filled with mercury.

ved copy of the left hand part of Pl. 1 of that Communication, to which we may in the first place refer. The improved diagram embraces the modifications which were introduced later, and which are described in Comm. No. 121a. Identical parts are indicated by the same letters in fig. 1 and in Comms. Nos. 117 and 121a, parts which have undergone modification are distinguished by accents, while parts which are new or are now lettered for the first time have new letters attached to them. We may refer to W. J. DE HAAS's thesis for further details concerning the water circulation, W, which, supplied from the thermostat, keeps constant and uniform the temperature of the volumenometer and of the manometer.

The volumenometer is connected to the auxiliary reservoir F' through the taps k_1 and k_2. This allows one to add gas to the measured quantity contained in the volumenometer, or to temporarily abstract a measured quantity from the volumenometer. This was essential in our experiments as the volume of the piezometer, in which the gas density was sometimes practically 20 times as great as that in the volumenometer, was 110 c.c. and that of the volumenometer was not more than 1250 c.c. Hence, if, for instance, the volume is adjusted to the smallest volume in the volumenometer (the neck m_0 in the figure) at a pressure of one atmosphere, then even when the volumenometer is completely filled (to the neck m_5 in the figure) the second equilibrium pressure of half an atmosphere, which, according to § 1, is desirable in this case, is not yet attained. The admission of gas from the volumenometer to F' and vice versa can be of use in another way, viz. in the transition to another temperature and in the adjustment of pressure equilibrium. In the course of our experiments, however, we have not been able to make such free use of the auxiliary reservoir as we should have liked. The volumenometer can be evacuated through the valves k_3, k_4, k_{43}; and it can be connected to the barometer and to the constant pressure reservoir, R, (Comm. No. 60, Pl. VI) through $k_3, k_4, k_{41}, l_7, k_{11}, k_{12}$. When the volumenometer adjustments and the value of the pressure permit of it, the valve l_7 may be closed and the pressure then determined from the manometer M alone, the space above which is then evacuated through l_8. We may refer to Comm. No. 121a by W. J. DE HAAS for further details concerning the pressure measurement.

To ascertain when pressure equilibrium has been attained we applied the method already described in Comm. No. 127a; the pressure in the volumenometer was under constant observation, and from the curve expressing the pressure as a function of the time, we deduced, during the observations, the time at which the pressure difference

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originally existing between the volumenometer and the piezometer had sunk to a value that was insignificant. The reliability of this method is shown by the calculations published by W. J. DE HAAS in Comm. No. 127a. For assistance rendered in the application of this method and for further help given in the course of this research we should like to express our indebtedness to Mrs. DE HAAS-LORENTZ.

Readings were taken with a very fine Société Genevoise cathetometer with three telescopes [1]), each with a micrometer eyepiece and level. A scale with very accurate subdivisions (Comm. N°. 60) was used for the readings with the micrometer eyepieces.

Communication between the volumenometer and the piezometer (see the right hand portion of the diagram) was obtained through the tap k_3, the glass T-piece (closed on the other side by k_4) over which a connecting tube is cemented, a copper capillary g_2 (to give a certain elasticity to the connections), the steel taps k_5, k_6, a steel capillary g_1 and a glass capillary f_2. The steel taps k_5, k_6, k_7, were provided with selected cork packing and were kept for about half an hour at a pressure of 50 atm. They closed perfectly. Connections between steel and glass capillaries were also made with the greatest care. This connection was made by means of a brass screw soldered to the glass capillary, the capillary being very slightly rounded and projecting about $1/4$ mm. beyond the screw; this joint sustained a high vacuum for a long time. The rounded end of the glass capillary was covered with a packing ring made of fibrous plate, and could be screwed with force into the brass nut soldered to the steel capillary.

The diagram does not show the wool with which all the principal parts of the apparatus were wrapped. The barometer was wrapped with the greatest care in wool, and was, moreover, surrounded by a double layer of paper so as to eliminate all convection currents.

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[1]) Compare the similar adjustments of Comm. No. 95e, Table I.

The difference between the levels of the top and the edge of the meniscus and between the top of the meniscus in one of the necks and the central line on a screen (Cf. Comm No. 84, Pl. II, Proc. March 1903) can be obtained with sufficient accuracy and more quickly from the catethometer scale than with the standard scale and level and the micrometer eyepiece. In the majority of cases it is sufficient and much simpler still to estimate these differences of level from the standard scale without focussing the micrometer upon the divisions of the standard scale at all. For an error of 10% in the determination of the height of the meniscus leads to an error of 1% in the capillary depression; and an error of 1 mm. in the estimation of the height of a line on the screen induces an error of only 16 or 17 mm³. in the volume, which makes a difference of only 1 in 60,000 in the volume of gas usually employed.

Neither are the numerous thermometers shown in the diagram which were suspended along the whole apparatus.

Finally, the connections Zk_9, Zk_{10} lead to the hydrogen reservoir Z_1. To this reservoir is attached a side tube with a valve, Zk_8, through which the whole apparatus can be filled with hydrogen; it is also provided with a purifying chamber Zq, through which the gas passes on its way to the measuring apparatus and consisting of a tube filled with glass wool surrounded by a DEWAR flask containing liquid air. After the measurements the gas can be collected in Z_1 through Zk_9, Zk_{10}.

We may refer to Comms. Nos. 83, 94c, 94d, 94e, and 121a for descriptions of the thermostat, the water circulation and the cryogenic bath and auxiliary apparatus.

§ 3. *The hydrogen.* The apparatus was filled with distilled hydrogen by means of the arrangement described in Comm. N°. 94e, § 2; the tap Zk_9 (see fig. 1) was utilised for the repeated evacuations and washings with hydrogen.

§ 4. *The temperatures.* The thermostat supplied the water circulation, W, with water at very uniform temperature. (See Comm. N°. 121a).

Stirring was continuous during the measurements. A thermometer divided into 20-ths of a degree and calibrated by the Reichsanstalt was attached to the stirrer of the volumenometer, the mean temperature being thus obtained. The influence was studied beforehand of fluctuations in the room temperature upon that of the water in the jacket surrounding the volumenometer, and it was found sufficient to keep it constant to within one deg. Cent. This was always done. (For further details see dissertation by W. J. DE HAAS). Every determination of the volumenometer temperature can then be regarded as certain to within $0°.02$ C.

The temperature of the cryostat was regulated in the usual way; great care was devoted to keeping it constant by Mr. G. HOLST, whom we wish to thank for his assistance. It would take up too much space here to give all the curves of this temperature regulation, but as an example we may state that in the determination of the isotherm at $-255°.5$ C., made on the 24th of June, and on the 8th and 14th of July, 1911, the values of the differences at five points from the first determination were

0.005, 0.012, 0.010, 0.000 degrees Centigrade.

This corresponds to an uncertainty of 0.00004 in the value of pv_A.

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The temperature of the bath was furnished by the determinations themselves. See § 6.

§ 5. *Calibration, Constants and calculation of corrections.*

a. Pressures.

The corrections, and in particular the optical corrections, for the apparatus have already been discussed in part in Comm. N°. 121a.

The pressures were always reduced to the normal atmosphere of 45° N. For this the value of the Leiden atmosphere, 75.9463[1]), was used. The following corrections were applied to the pressures:

1. A temperature correction for the inequality between the temperatures of the mercury in the manometer and in the volumenometer (Comm. N°. 121a).

2. A correction for the standard meter which is 999.91 mm. at 0° C. (Comm. N°. 70).

3. An optical correction for the refraction of light by the glass windows (Comm. N°. 121a) and by the manometer tube.

4. A correction for the capillary depression. These corrections were tabulated for various widths of tube, being obtained from Kelvin's graphical construction and from Lohnstein's[2]) formula.

5. A correction for Knudsen's transpiration pressure[3]).

6. A correction, where necessary, for the pressure of the air column between the lower barometer meniscus and the manometer meniscus.

7. A correction for the aerostatical difference between the pressure in the volumenometer and that in the piezometer was neglected.

A discussion of the degree of accuracy attained in the determination of the pressure has already been given in Comm. N°. 121a.

b. Volumes.

Reference may be made to Comm. N°. 121a for the calibration of the volumenometer.

The volumes as measured were always corrected at their calibration temperature. This correction was always very small.

A correction for the compression of the glass vessels was applied by means of the formula

$$\frac{dV}{V} = {}^3/_2 \frac{(1-\mu)(p_i - p_e)}{E}\frac{1}{d} R$$

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[1]) This value has been calculated with the number for the gravity at Leiden used in Comm. N°. 60, Sept. 1900, p. 304, and $g_{norm} = 981.625$ according to Suppl. N°. 23, "Einheiten" a. (Note added in the translation).

[2]) F. Lohnstein. Ann. der Physik (4) 33 (1910), n°. 2.

[3]) M. Knudsen. Ann. der Physik (4) 31 (1910), n°. 8.

in which $E = 6500$ K.G./mm^2., $\mu = \frac{1}{4}$, $R = 3.9$ cm., $d = 0.5$ mm. (See Comm. N^0. 88).

In the calculation of the volumes, the volumes of the mercury menisci were taken from the table given by Scheel and Heuse [1]).

As regards the accuracy of the volumes measured we may remark that a variation of one degree in the temperature causes a change of only 1 in 40000 in the volume. The correction for the compression gives $\dfrac{1.3}{10000}$ for $\dfrac{dV}{V}$ at the lowest pressure measured (5 cm.). If this correction is applied, the remaining uncertainty is certainly less than $\frac{1}{10000}$.

As regards the volume of the mercury menisci as, for instance, in the case of $2R = 14.8$ mm. where the volume is 179.4 mm^3· for a meniscus height of 1.6 mm., and 192.2 mm^3. for a height of 1.7 mm., the error for heights lying between these two values is certainly not so great as 10 mm^3. This is certainly negligible in a volume which would, at ordinary temperature, be at least 1200 cm^3. seeing that the volume of the piezometer is 110 cm^3. and contains gas of density from 12 to 20 times the normal. The same may be said of the uncertainty in the volume of the dead space. Such portions of this as were not separately calibrated with mercury (steel and glass capillary, see dissertation de Haas' were volumenometrically calibrated. The total dead space was about 10 cm^3. An error of 1 $^0/_0$ in the calibration or of 3 degrees in the temperature causes an uncertainty of 100 mm^3. This is only 1 in 12000 of the 1200 cm^3. just mentioned. The volume calibration, however, was much more accurate, while, as was stated above, the room temperature was kept constant to within a degree.

These comments are also all applicable to the determinations of Comm. N^0. 121a.

The accuracy attained in the calibration of the piezometer was greater than 1 in 10000 (cf. dissertation de Haas). The volume was corrected for the temperature of the cryostat by means of the formula

$$v_t = v_0\left[1 + \left\{ k_1 \frac{t}{100} + k_2 \left(\frac{t}{100}\right)^2 \right\} 10^{-6}\right]$$

in which

$$k_1 = 2343$$
$$k_2 = 272$$

(See Comm. N^0. 95b, § 1). The error arising from this method can only be very small.

Temperature corrections for the gas in the glass capillary were

[1]) K. Scheel and W. Heuse. Ann. d. Phys. (4) 33 (1910), n^0. 2

applied in the manner published in Comm. N°. 97a § 8. For this, the temperature distribution along the stem was taken from Comm. N°. 95c. That this temperature distribution is approximately correct was apparent, moreover, from the time it took pressure equilibrium to be established. Cf. Comm. N°. 127a.

Collecting all these, we may regard the volumes occupied by the cooled gas as certain to within 1 in 10000. Allowing for what we have already stated regarding the pressure, but not taking temperature uncertainty into account, we may expect an accuracy of 0,00002 in the pv_A's, or, at the highest pressure to within one fivethousandth, and at the lowest pressure, to within $^1/_{2500}$ th of the value of pv_A.

§ 6. *Calculation and Results.* The quantities of gas were always expressed in terms of the normal volume. For this purpose equation I of Comm. N°. 127a was used:

$$pv_{A200c} = 1.07258 + 0.000667\, d_{A200c}.$$

Using, where necessary, an approximate temperature as a correction factor for the piezometer, the measurements yielded values of d_A, the density of the gas in the piezometer under the observed pressure. The temperature of the gas in the piezometer for each series was obtained from the pv_A itself for that particular series. For that purpose values of C_A in

$$pv_A = A_A + B_A d_A + C_A d_A{}^2$$

were used in the calculation which were obtained for each (at first approximate) temperature from the special reduced equation of state for hydrogen VII . H$_2$. 3 given in Comm. N°. 109a equation (16) which was deduced from the observations of KAMERLINGH ONNES and BRAAK and adjusted to a temperature of — 217° C. A_A and B_A then follow from our observations and also pv_A at the same temperature for the density of the gas in the hydrogen thermometer of 1100 mm. zero pressure. From this with

$$(pv_A)_{ts} = (pv_A)_0 (1 - 0.0036627\, t_s)$$

we finally obtain the temperature on our hydrogen thermometer of 1100 mm. zero pressure.

The temperatures obtained in this way yield a calibration on the hydrogen scale of the resistance thermometer whose readings serve as a guide to the regulation of the temperature of the bath. This resistance thermometer was also calibrated with the hydrogen thermometer independently. The two calibrations are not quite in agreement. A subsequent paper by KAMERLINGH ONNES and HOLST will return to the question of this difference.

We obtained (where t_s is the temperature on our hydrogen thermometer of zero pressure 1100 mm.):

TABLE I. H_2. Values of pv_A.						
Series	N⁰.	t_s	p	d_A	pv_A	O—C
I. 23 and 29 June 1911	1	} —252°.63	0.34786	4.7568	0.073129	
	2		0.60358	8.4597	0.071348	
II. 24 June 8 and 14 July 1911	1	} —255°.46	0.10964	1.6918	0.064216	
	2		0.20672	3.2560	0.063469	0.000031
	3		0.27759	4.4133	0.062898	0.000012
	4		0.31318	5.0026	0.062603	0.000008
	5		0.31294	4.9992	0.062598	
III. 14 and 18 July 1911	1	} —257°.26	0.06698	1.1582	0.507834	
	2		0.13153	2.3031	0.057104	

The second series was represented by

$$pv_A = 0,065043 — 0,00489\, d_A + C_A d_A^3$$

deduced from Nos. 1 and 5, with C_A as before, and the column O—C gives the differences between observation and calculation. These differences are smaller than those corresponding to the observed temperature fluctuations of the bath (see § 4), which is in agreement with the assumption that it is the mean temperature of the bath which must be taken as the temperature of the gas in the piezo-meter. This series also supports the use of the assumed C_A. Series I and III, lacking the controls possessed by series II in itself, are less reliable. Various circumstances have obliged us to postpone our

TABLE II. H_2. Individual virial coefficients B_A for hydrogen vapour	
t_s	B_{At}
— 252°.63	0.000481
— 255°.46	0.000489
— 257°.26	0.000638

experiments for some time to come, so that for the temperatures of series I and III we have not been able to give such extensive series of measurements as in series II.

From Table I we finally obtain Table II (see p. 415)

§ 7. *Smoothed values of the virial coefficients, and corrections of the international hydrogen thermometer to the absolute scale.*

These corrections are to be determined from the virial coefficients B_A by the method employed by KAMERLINGH ONNES and BRAAK in Comm. N°. 101b. For this, however, it is desirable to use smoothed values. This was tried by plotting log B as a function of log T. Taking account of the accuracy of the various measurements there seemed to be much to recommend the smoothing given in Table III (in which the temperatures $\theta = T - 273.09$ are given in KELVIN degrees, Table IV having been used for the calculation).

TABLE III.	
H_2. Smoothed virial coefficients B_A for hydrogen vapour.	
θ	B_{AT}
— 252°.47	— 0.00047
— 255°.32	— 0.00049
— 257°.10	— 0.00055

In Table IV these values of B_{AT} have been used to supplement by data for — 252° C., — 255° C. and — 257° C. the list given in Comm. N°. 101b of experimental corrections $\Delta t_i = \theta - t_i$ of the international hydrogen thermometer to the absolute scale.

TABLE IV.	
Corrections of the international hydrogen thermometer to the absolute scale.	
t_i	$\angle t_i$ in degrees K.
— 252°.59 C.	+ 0.118
— 255°.45	+ 0.125
— 257°.24	+ 0.144

Physics. — *"On the second virial coefficient for di-atomic gases".* By Dr. **W. H. Keesom**. Supplement N°. 25 to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. Kamerlingh Onnes).

§ 1. *Introduction. Synopsis of the more important results.* In Supplements N°. 24*a* (§ 1) and *b* (§ 6), in which the second virial coefficient was deduced from different particular assumptions concerning the structure and action of the molecule, a comparison was contemplated between the results then obtained and such experimental data as are at present available. The present paper will discuss some results obtained by carrying out such a comparison in the case of di-atomic gases. The importance of such a comparison, as well as of a comparison of the second virial coefficients for various gases, especially for di- and mon-atomic gases, from the point of view of the law of corresponding states, was emphasized in Comm. N°. 127*c*, § 1 (these Proceedings p. 405). That such a comparison can now be made with any fruitful result is due to the extensive series of accurate isotherm determinations made by Kamerlingh Onnes and his collaborators, Braak, Crommelin, and W. J. de Haas.

In the present investigation a beginning is made with the di-atomic gases, especially with hydrogen, for these reasons : In the first place the most immediately indicated simplified hypothesis that can be made concerning the genesis of molecular attraction and can give any hope of agreement with experimental results [1]) is that first introduced by Reinganum, which represents it as originating in the mutual electrostatic action of doublets of constant moment immovably attached to the molecules at their centres; this, together with the assumption that the molecules collide as if they were rigid spheres of central symmetry, leads to a value of the specific heat which agrees most closely with that of the di-atomic gases dissociating with difficulty at ordinary temperature; for these gases a law of dependence of B upon the temperature quite definite, and therefore ready to be tested, was deduced in Suppl. N°. 24*b* § 6 from the above assumptions. In the second place, values of B for hydrogen are known over a much more extensive temperature range than for any other gas with the

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[1]) See M. Reinganum, Ann. d. Phys. (4) 38 (1912), p. 649 for the rejection of the explanation of molecular attraction by gravitation, or (at least of the total molecular attraction, cf. p. 429 note 2) by the magnetic action of series of magnetons assumed to be present in the molecules of paramagnetic and ferromagnetic substances.