Physics. — Dr. KAMERLINGH ONNES and H. H. FRANCIS HYNDMAN:
„*Isothermals of diatomic gases and their binary mixtures. I. Piezometers of variable volume for low temperatures.*"
(Communications from the Physical Laboratory at the University of Leiden. No. 69.)

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§ 1. On theoretical grounds, for accurate measurements on the isothermals of pure gases and their binary mixtures, we should have preferred to use monatomic gases alone since results obtained from them would certainly be the most important.

Unfortunately of the three monatomic gases available for this kind of work i. e. He, A, Hg, the two first are costly and the latter has a critical temperature so high that the research would offer great experimental difficulties.

From these we naturally turn to the next group, that of the diatomic gases. Very complete researches on these gases have been made at temperatures above 0° C. and with pressures up to 3000 At. especially by AMAGAT. At low temperatures however no data exist with the exception of two pioneer researches by v. WROBLEWSKI [1]) on Hydrogen down to — 180° C. and by WITKOWSKI [2]) on air down to — 145° C.

The series of experiments which we now consider has been before alluded to in Comm. No. 14 p. 4, 1894 and Comm. No. 50 p 4, 1899 and has been kept in view in the arrangement of the cryogenic laboratory with its auxiliary apparatus as well as for the standard manometers. (Comms. 44 and 50.)

In order to obtain the required data two methods present themselves. In the first a constant volume is filled at a constant measurable temperature and pressure by compressed gas which is afterwards expanded so that its volume can be obtained under normal conditions. This method has been used by REGNAULT, V. WROBLEWSKI and WITKOWSKI and where the purity of the gas is not of the greatest importance and especially at high temperatures it is excellent, but to arrive at high precision piezometers of a relatively considerable volume are necessary. Since the piezometer must be refilled for every measurement, somewhat considerable quantities of compressed gas are required for a series of measurements. For determinations in the neighbourhood of the critical point however

[1]) Wien Sitz. Ber. 1888.
[2]) Bull. Int. Acad. Cracovie Mai 1891.

it is absolutely necessary to employ only gas of the greatest purity to obtain any definite results. A method which requires large volumes of such gas is necessarily both troublesome and costly, so that we have been obliged to introduce some modifications and additions. Of these the most important is a compression cylinder in which the gas after expansion to normal volume can be collected and compressed again into the piezometer, without any loss of purity. However even with this modification a considerable volume of compressed gas is required to fill the piezometer and the necessary connecting tubes. In subsequent communications we will consider the application of this modified method for measurements in the critical region and of a higher accuracy than we are concerned with below.

In the second method, which we are employing for the present investigation because of its relative simplicity, we use a piezometer of variable volume in which a quantity of gas that has once been measured under normal conditions is employed for a series of determinations. In principle this method is an adaptation of the one described in Comm. N° 50 with which SCHALKWIJK has determined the isothermal of Hydrogen at 20° C.

The results of these measurements which will soon be published show that the method is capable of great accuracy under these advantageous circumstances, but we have been unable to maintain this high standard in modifying it for low temperatures. A consideration of the various difficulties to be surmounted in the apparatus we shall describe and the unavoidable errors belonging thereto, show that an accuracy of $\frac{1}{1000}$ is not of easy attainment and that very special apparatus, again of large volume, would be required to reach a higher degree.

This accuracy is not sufficient to determine the deviations of the hydrogen isotherms from the law of corresponding states relatively to other gases, for it follows from the available data that unless constant temperatures of below 200° C or very high pressures are employed determinations to this accuracy will not teach us much on the most important questions.

However with the other gases of this group and especially for a review of the relations between Oxygen and Nitrogen and their mixtures this accuracy may be considered to be sufficient.

§ 2. *General arrangement.* The apparatus which is in use for these measurements has been designed to allow of the determination

of volume in a room where the liquid gases to produce the low temperature baths can be most readily obtained, and of the pressure in the room containing the precision piezometers and standard manometer. The pressure has thus to be transferred for a distance of some 25 meters by a tube filled with compressed air. The general arrangement of the apparatus is shown diagrammatically in Plate I where the manometer (cf. § 5), is not drawn. The steel cylinder A is connected to the reservoir C and the level tube C_3 (cf. § 3) by steel tubes of 2 mm. bore provided for manipulation with steel cocks C_5 and C_6 of the type given in Comm. N° 46 fig. 10. Dry air under pressure is admitted at the brass cock C_7 its approximate pressure being read by the operating metal manometer M while its actual pressure is determined by the gas manometer (cf. § 5) connected at C_8. The cock C_9 is for emergency and for reducing the pressure and C_{10}, C_{11} for manipulation.

The washers at the numerous joints are all of prepared leather and require much trouble and attention before they are quite tight, though this is now satisfactorily attained.

§ 3. *The Piezometer.* Although the principle of the method employed is the same as that described in Comm. N°. 50 many modifications are necessary to adapt it for measurements at temperatures below the freezing point of mercury. The simplest would be to separate the bath and graduated tube by a long fine glass capillary bent twice at right angles so that the bulb could be immersed in the low temperature bath while the graduated tube remained at an ordinary constant temperature. Such a rigid connection would give much difficulty in manipulation and would be liable to fracture with apparatus of the weight and dimensions here used, so that a more flexible arrangement is necessary.

The one first tried, which combines the accuracy of the above with the required flexibility, is shown diagrammatically in fig. 1, plate II where d_1 is the graduated tube at the end of the large reservoir (Cf. *b.* fig. 2), d_2 a steel capillary, d_3 another graduated tube, d_4 the glass capillary and d_5 the bulb. After many trials however and even after measurements had been made, we had to abandon this arrangement owing to the impossibilily of cleaning the steel capillary so thoroughly that it should not spoil the mercury meniscus after this had passed through it.

The arrangement finally adopted is that shown in Plate II, fig. 2. The dimensions of the present apparatus were controlled by the size of the steel apparatus available (designed for 500 At). The steel

cylinder A Plate I has a length of about one meter and a capacity of about one liter. The glass tube b_3 was chosen as large as possible and has a capacity of about 600 cc. This with its graduations b_4 is connected to the various piezometer bulbs and is of the same type as the piezometer for the highest pressure described in Comm. N°. 50, the internal diameter of b_4 being about 3 mm. The graduations were only made on 20 cm. in order to keep the apparatus within manageable dimensions. The tube b_4 terminates in a capillary tube b_5 of sufficient internal diameter to admit a steel capillary.

The various piezometers, which are all of the same type as that shown in fig. 2 f and fig. 3, are of dimensions corresponding to the various temperatures to be employed so that the pressure which will cause the mercury to appear at the middle of the graduations of the tube b_4 shall be within the prescribed region. The stems f_2 are fine glass capillaries some 70 cm. long to enable them to project above the cryostate Comm. N°. 51, and with internal volumes of about 50 mm.^{3} in order that the temperature correction may be reduced to a small order without at the same time offering too great a retardation to complete equalisation of pressure. At the end of the capillary stem f_2 of the piezometer fig. 4 a small cavity f_3 is made to receive the end of the steel capillary. This cavity must be large enough to avoid any chance contact between the glass and steel and yet not large enough to introduce uncertainties in the volume. It was found most satisfactory to open out the capillary tube in the blow pipe to a diameter and depth of some 1.5 mm. and then to bore the first mm. cylindrical at the lathe. The upper surfaces of both b and f are ground off at right angles to produce a more constant and perfect joint.

The connecting steel capillary g fig. 2 must be long enough to allow of the manipulation of the piezometer without incurring the danger of bending the capillary sharply at any point, a proceeding which usually results in a leak. Under some circumstances a capillary of 40 cm. length could be used, but for the majority of the measurements it was found most convenient to employ one of 130 cm. The capillary is furnished at its ends with screw-connections g_1, g_2 (see fig. 2) to enable it to be fastened securely to b and f.

The various parts can now be readily removed for cleaning, filling etc. while the arrangement is such that it allows the parts to be replaced without producing any appreciable change in the volume up to the graduations on the tube.

The steel tube f_4 with hexagonal portion f_5 and thread f_6 is made about $\frac{1}{10}$ mm. larger than f_2 and is fastened to it by red sealing wax.

Between the steel flanged tube g_4 and the glass f_2 fig. 4 a washer g_5 of prepared leather is introduced; as however leather gives somewhat under compression it has been found necessary to employ washers which have been subjected for some time to considerable pressure. When the requisite precautions are taken, a joint is obtained which is perfectly tight at 60 Æ and which only requires screwing up one half turn (about 7 mm.) during a long period under this pressure, thus insuring a practically constant volume.

Connections of the type described in Comm. N°. 60, fig. 5, appeared not to allow of sufficient accuracy in the determination of the volume, when the joints were made to stand the pressure in our experiments. Moreover in that case the connection of different piezometer-bulbs to the same graduated tube presents much greater difficulties.

At the lower end of the U tube b_2 fig. 2 of which the leg connected to b_3 is calibrated, the short capillary tube b, carrying a ground joint has been made parallel to the whole length and not bent at an angle as in fig. 4 Comm. No. 50.

The connection with the gas apparatus is made by the short tube h carrying two ground joints h_1 h_3 and a cock h_2. By means of this the tube b containing the requisite mercury can be easily and quickly brought into a nearly horizontal position, when it is necessary to fill it with gas, and the joints closed by rotating tube h. When the tube is filled h_2 is shut b and h removed together, brought into a vertical position and the cock again opened; the mercury then runs quietly into place and tube h can be removed. By this contrivance the troublesome process of turning about the tap h, described in Comm. No. 50 § 1, is no longer necessary.

§ 4. *The compression cylinders, reservoirs and connections.* Like the apparatus described in Comm. N°. 50, the compression cylinder is filled with pure mercury only to which the pressure is transferred also by mercury from the reservoir where it is produced by means of compressed air. Owing to the large volume of mercury required for the tube b the reservoir C must have a capacity of nearly a liter, the level of the mercury in it being indicated by the level tube C_3. A scale C_4 is attached to this tube and the position of the mercury is read by the eye. The distance between the zeros of this scale and that on b_4 is determined by the cathetometer.

The steel head b_6 must be put onto the glass tube b_4 with the precautions mentioned in Comm. N°. 50 especially as the clearance is only some 2 mm. at the bottom of the tube b. On to this head

b_6 is screwed a water bath b_7 b_8 through which flows a constant upward stream of water of constant temperature. [1])

The steel nut a_3 Plate I and fig. 6, Plate II is divided into two portions connected by screws to enable it to be applied more conveniently. At every joint of this apparatus there is a prepared leather washer between two flat steel surfaces provided with concentric depressions and a central tube. In consequence of the two large washers at a_2 and c_2 being in contact with mercury it has been possible to entirely eliminate leakage at the pressures employed.

§ 5. *The manometer.* The glass portion of this apparatus, made especially for this research, differs little from those employed by VERSCHAFFELT and HARTMAN and could be replaced if necessary by one reading to higher pressures used by the former. The cylinders, reservoir and level tube are identical in construction with those described above for the piezometer only of smaller dimensions. These were so chosen that pressures from 20 to 70 Æ could be read with an accuracy of $\frac{1}{2000}$. Such an accuracy is however only actually obtained by careful preliminary calibrations to determine the volumes of the bulb etc. and the inequalities of the stem, combined with comparisons with the standard manometer at many points over the entire scale.

No attempt was made to determine the normal volume (cf. Comm. N°. 44 note 1) as several measurements of the pressure at the zero of the scale by the standard manometer give an accuracy to this point of some $\frac{1}{200}$ Æ. The capillary depression in the manometer capillary is 7 mm. when the height of the meniscus is 0.1 mm. and in the level tube about 1.5 mm. with a meniscus of 1 mm. The difference must be considered, but is small enough to allow us to assume a constant value the small differences from this being considered as accidental errors.

If we assume that 0.2 mm. can be read with certainty by the eye, and this is probably an underestimate if a mirror is employed, the reading error in the middle of the scale is some $\frac{1}{125}$Æ, though it is not probable that the comparisons and calibrations can be quite trusted to this high degree.

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[1]) The constancy of the temperatures will be discussed in a later communication.

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Plate I.

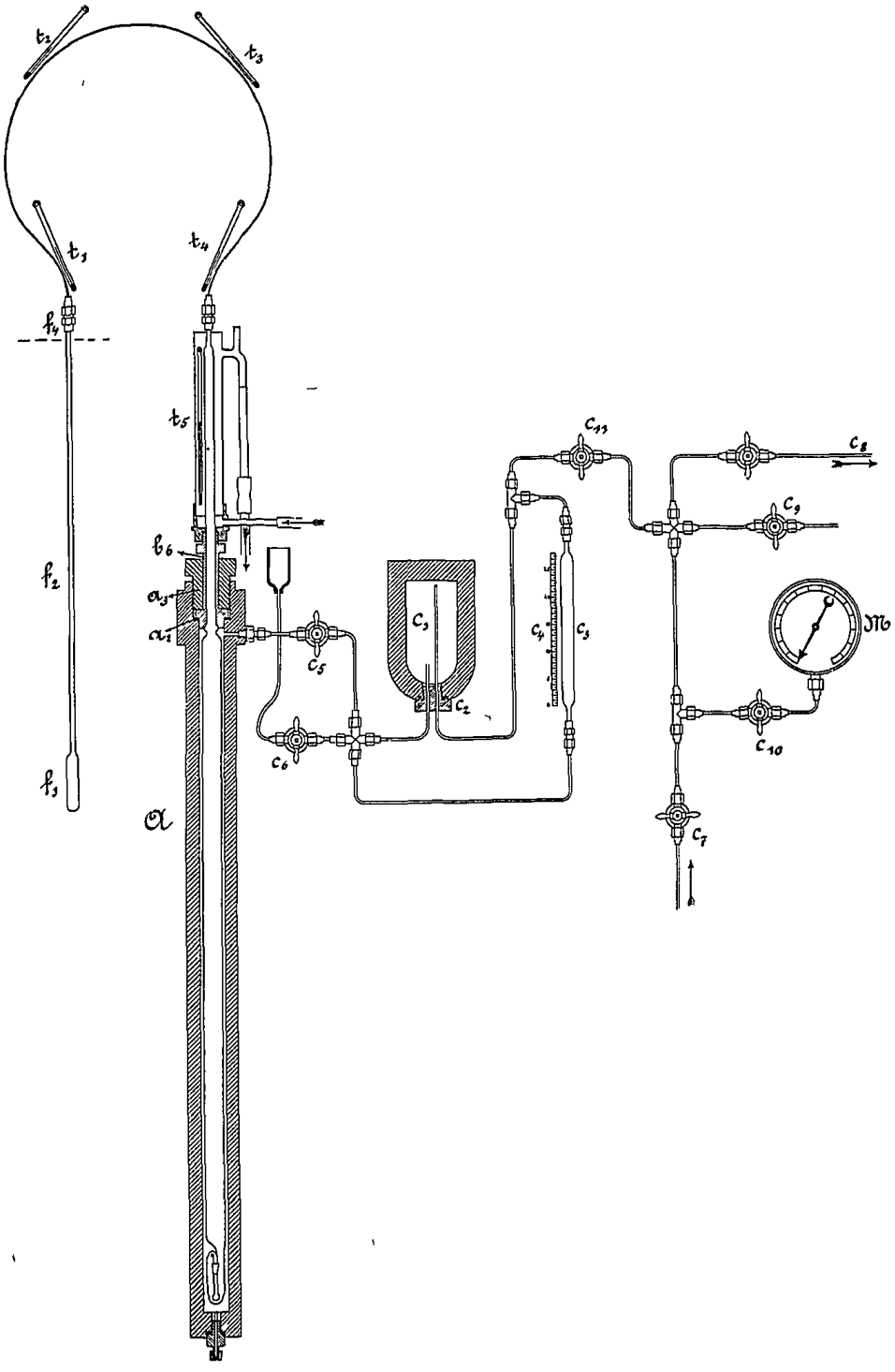

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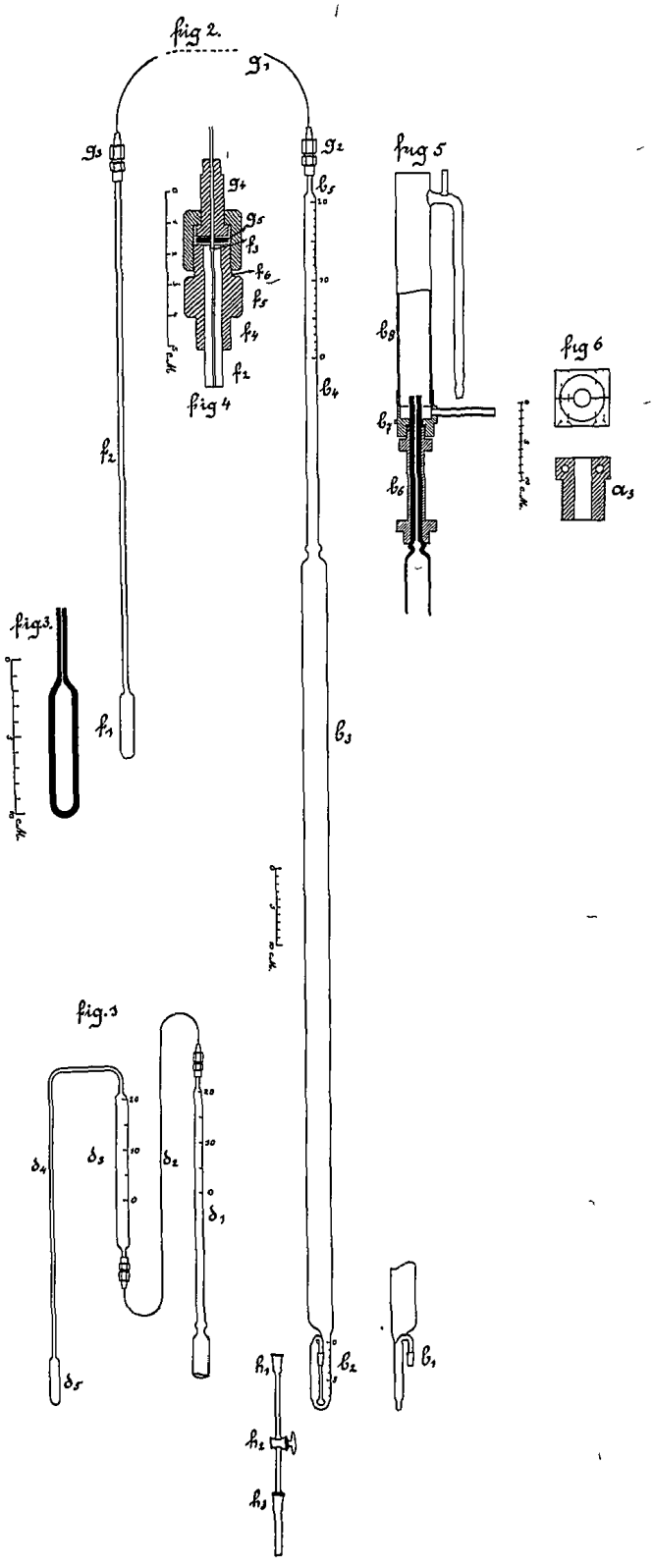
Plate II.



The manometer is filled with pure dry hydrogen and is read at temperatures between 15° and 20° C.

In a further communication more details will be given with the measurements, it is sufficient to mention here that the higher pressures deduced from the lowest pressure and determined directly agree very satisfactorily, which we believe is an advance on former apparatus.

§ 6. *Errors belonging to the construction.* In conclusion we may consider the accuracy which we may reasonably expect from such apparatus as that described in § 3.

The volumes of the various portions have been determined to less than

2 mm.^{3} in the piezometer bulbs, 1 mm.^{3} in the piezometer stem, 1 mm.^{3} on the total volume of v_4 (6.0 cc) and certainly less than 3 mm.^{3} from point to point.

The principal cause of error will undoubtedly be the steel capillary with its connections for among many measurements a difference of 1 mm.^{3} was found in the longest capillary with a volume of about 1 cc., we will however assume the error 3 mm.^{3} as reckoned in Comm. 60 § 20.

The cathetometer used to observe the meniscus reads with care to $\frac{1}{50}$ mm. so that an error of $\frac{1}{25}$ mm. may occur in reading the position of the meniscus in v_4 corresponding to a volume of 1.2 mm^3.

The volume of a meniscus of the average height of 1 mm. in a tube of 30 mm.^{2} cross section Ω 10· mm.^{3} with an error at a maximum of 5 %[1]) = 0.5 mm^3.

Hence the total error in the position of the meniscus may be evaluated at $1.2 + 0.5 = 1.7$ mm.^{3} The most unfavorable case gives for the total error $2 + 1 + 3 + 3 + 2 = 11$ mm.^{3} and if we put the probable error 5 mm.^{3}, it appears that the arrangement of the apparatus allows us to reach an accuracy of $\frac{1}{1000}$ with piezometer bulbs larger than 5 cc.

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[1]) SCHALKWIJK, Comm. No. 67.