Citation:

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Physics. — Communication N°. 50 from the Physical Laboratory at Leiden by Dr. H. KAMERLINGH ONNES: "*Standard Gas-manometers.*" (Precision-piezometers with variable volume for gases.)

§ 1. *Purpose.* Further progress in the knowledge of the laws from which we derive the equation of condition for the gaseous and the liquid state, depends for a great deal on accurate determinations with perfectly pure gases and their mixtures in proportions exactly known. In these determinations the principal thing is to measure the pressure and volume of a precisely known quantity of gas at constant temperatures. The standard open manometer [1]) of reduced height formerly described offers us a means of attaining great accuracy in measuring the pressure. In the following pages I intend to describe piezometers in which (at temperatures above the freezing-point of mercury) the volume of a gas, shut off by mercury and compressed to different pressures, in proportion to the volume which it would occupy at 0° and 760 m.m. (the *normal volume*) can also be read with great accuracy. These apparatus enable us to determine the isothermal lines for gases to within $\frac{1}{5000}$, at temperatures (above the limit mentioned) which can be kept sufficiently constant to allow measurements with the standard open manometer of reduced height.

If the piezometer-tubes are filled with a standard gas, of which the equation of condition for ordinary temperatures has been determined by means of the open manometer, or if their indications have been compared immediately with the open manometer indepently from a determination of constants, they can also conversely be used to replace the open manometer when the measurements have to be made in a shorter time than is required for reading the standard open manometer of reduced height at high pressures.

This method has been followed by me in an investigation taken up a long time ago on the isothermal lines of hydrogen (now to be extended of course to the since discovered argon and helium) together with those of different mixtures of gases at low temperatures (for the obtaining and keeping constant of which the cryogenic laboratory was devised [2])).

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[1]) Comm. from the Physical Laboratory at Leiden N°. 44.

[2]) Comm. Phys. Lab. Leiden N°. 14; the means for the accurate measuring of the low temperatures are treated of in Zitt. Versl. 30 Mei and 27 Juni 1896. Comm. Phys. Lab. Leiden N°. 27.

It would be very difficult to keep the temperatures at which those isothermals are to be determined so constant that during the time required for a determination with the open standard manometer no variations can occur which would influence the pressure to be measured more than the errors of adjustment. The best thing to be done seemed to measure the pressure in the piezometers of constant volume filled with gas at a low temperature (a following communication will treat of its construction and use) by means of gas-gauges which have themselves been compared with the open manometer of reduced height, and to construct these closed manometers so that they are not much inferior either in sensibility or reliability to the standard open manometer.

In order to render the indications of the piezometers or manometers as reliable as possible the glass tubes in which the gas is compressed have been taken so wide as appeared to be compatible with a sufficient power of resistance and would not render too difficult the handling. The chance that a perceptible quantity of the gas, albeit in extremely small bubbles, should adhere to the walls when the mercury rises, as well as the influence of a deviating behaviour of the gas-layers at the surface of the glass, becomes less as the tube is wider. Moreover the more regular shape of the meniscus renders the determination of the volume more accurate and diminishes the influence of capillary disturbances on the measurement of the pressure.

The manometer-tubes may be cleaned and refilled without invalidating the determination of constants once made. This is of great importance, also because it enables us to apply a differential method when comparing the isothermals of two gases or mixtures of gases. For if we dispose of two manometers of the kind to be described, we can compress these gases simultaneously under the same pressure, and *interchange* them in the two sets; so the errors which the apparatus might still show, are eliminated for the greater part.

For the rest the closed manometers are so constructed that the normal volume can be very accurately determined not only at the beginning of the measurements made under pressure, but at any time we should want to. In order to do so the manometer-tube filled with gas may be taken from the apparatus, placed in a space of constant temperature, — where the difference between the pressure of the enclosed gas and the atmosphere can be measured, taking into account the capillary depression —, and may be replaced in the apparatus being still as clean as before while the quantity of enclosed gas does not undergo the least change during this operation. The data for the necessary corrections can also be determined with great accuracy.

Lastly care has been taken that the mercury in the apparatus does not come into contact with anything but carefully cleaned glass or iron and cork or solidified cement. Accordingly the menisci in the manometer-tubes remain perfect. All this entitles us to call the apparatus described in the following pages when used as gasmanometer, a standard manometer.

§ 2. *General arrangement.* The apparatus now used in the Leiden Laboratory is designed for measurements with 4 piezometers ranging from 4 to 64 atmospheres. In the construction of the apparatus, I have successively been ably assisted by Dr. LEBRET and especially by Mr. SCHALKWIJK, both assistants and Messrs. CURVERS and FLIM, instrumentmakers, to all of whom I render thanks. It contains, when used for measurements of pressure, and as represented in Plate I, four closed manometers placed in a row, on each of which a definite range of pressure is read, viz. 4—8, 8—16, 16—32, 32—64 atm.; each following manometer has a small range of pressure in common with the preceding, through which proper continuity and mutual testing are obtained. The piezometer-tubes are placed in compression-cylinders, each of which can be connected separately with the apparatus in which the pressure is to be measured, while all can be connected mutually.

The whole apparatus is mounted usually in a definite place. The pressure is transferred from the apparatus, in which we want to measure it, to the manometer through a narrow tube filled with compressed gas. This method offers many advantages in a research laboratory like that at Leiden.

The choice of the stages of pressure agrees with the division into pieces for 4 atmospheres of the standard open manometer which ranges as far as 60 atm., and with which the closed manometer is used as an auxiliary apparatus in order to attain a pressure higher than 60 atm., in the way described in Comm. n⁰. 44.

As the closed manometer for the next stage made after the same principle is not yet ready (it requires a compression tube with a thicker wall and greater volume than those existing) we use for pressures above 64 atm. closed manometers of simpler construction [1].

The mutual testing of the various closed manometers will be described when the observations made with the apparatus are com-

[1] Comp. VERSCHAFFELT, Thesis for the doctorate. Leiden 1899.

municated, together with the measurements made in order to test the accuracy of the standard open manometer of reduced height by dividing it into two parts, which are equilibrated with each other or simultaneously with one or two closed manometers.

§ 3. *The piezometer- or manometertubes.* These are made of Jena normal glass and recall in so far as the general form is concerned the type used by CAILLETET (comp. fig. 3 and 4). On to the upper end of the stem a wider reservoir has been blown of about the same volume as the divided stem in order that on each manometer the range of the pressures extends only so far that the highest pressure at which an adjustment in that tube can be made is twice the lowest. In this way we ensure the sensibility to be about the same at the different parts of the graduated scale.

The diameters of the reading-tubes (comp. fig. 3 and 4) are for the four manometer-tubes 8, 6, 4 and 3 mm. respectively. The diameters of the upper reservoirs and the thickness of the reading tubes and of the upper reservoirs have been chosen so as to be in accordance with these (comp. fig. 6).

A very accurate determination of the volume of the enclosed gas when compressed is rendered possible by fixing a very fine capillary tube of known volume (diameter about 0.3 mm.) on to the upper reservoir just as with AMAGATS's piezometer (e_3 comp. fig. 6).

After sealing off we can, by measuring the length of that part of the capillary tube that has remained unchanged and by estimating the volume of the conical part formed by the sealing off, compute its whole volume from a definite mark. The error thus remaining may be entirely neglected.

A wider capillary e' (fig. 7) carrying a small cock has formerly been welded on to the capillary tube at the place where it will be sealed off. By means of this cock we can connect the tube with the vacuum pump, suck up liquids in the manometer-tube, supply dry air, etc.; moreover it is useful in calibrating.

The tube, dried and ready to be filled is sealed off at the place where the wider capillary tube has been welded on to the narrow one. If the tube has afterwards to be cleaned again, which can not but imperfectly be done without opening it and sucking liquid through, or if the tube has to be calibrated anew, the fine point is filed off and at that place a new tube resembling the one sealed off is joined on. In this way we lose in each operation only a few mm. of the capillary tube e and we can use the same manometer for numerous sets of measurements before it is necessary to weld on a new capillary to the upper part of the reservoirs. If this happens to be the case we can no longer calculate the new volume of the reservoir from the old one by means of an insignificant and perfectly sure correction, which is possible as long as we preserve the same capillary tube.

The graduated stem *c* is made from a carefully selected perfectly straight and almost cylindrical tube. The graduation extends from 0 to 50 cm., continued on either side over some cm. in order to make sure that the diameter of the tube in the neighbourhood of 0 and 50 does not show any particular change. It did not seem desirable to make the graduation extend over more than 50 cm. as it is necessary to keep the whole length at a constant temperature. The divisions are at distances of 1 mm. and the readings are taken by means of a kathetometer.

It is of great importance that the whole tube should be perfectly vertical. Therefore care is taken that the stem and the cylinders of the manometer-tubes are well centred, and that the tube is truly centred in the steel tube with flange *O* (fig. 3. Pl. I) the whole apparatus being placed vertical by means of the plummet (compare also § 5).

The reading tube is connected with the lower reservoir *a* by means of a wider tube, *b* fig. 3. By means of this wider part the manometer-tube is cemented[1]) in the flange *O*, which for this purpose must be made so that it can be pushed over the upper reservoir. The outer diameter and the thickness of the wider part are taken a little larger than those of the upper reservoir, and the bore of the flange belonging to it so much larger that between the glass and the flange space remains for a thin layer of cement (about 0.5 mm.).

The lower cylinder *a* is thin, as in the manometers of the type used by CAILLETET and AMAGAT. At its lower end however the manometer-tube terminates differently; it is provided with a *U*-shaped tube placed under the lower reservoir, of which the branch *f* connected with the reservoir is graduated. The purpose of this tube is to enable us to determine accurately the normal volume or to test it (as has been mentioned in § 1) at any time we should wish. Before we proceed to the filling with gas we, in the manner in-

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[1]) In some cases, when for instance we should want to heat the piezometer-tube, it may be desirable not to cement the piezometer but to enclose it in the flange by packing. But as we have principally in view its use as gasmanometer we need not dwell on this particular.

dicated by CAILLETET, introduce in the lower reservoir, held in a sloping position, a quantity of mercury sufficient to fill this U-tube. After the manometer has been filled with gas in the said position, we cause the mercury to enter the U-tube by turning the manometer into the vertical position. Then by reading the position of the surface of the mercury in the divided and calibrated branch f, after the manometer-tube is detached from the filling apparatus, we can determine the volume of the enclosed gas, while the difference in level with the other branch g indicates the excess of pressure, above the pressure indicated by the barometer. And this determination can be made with great accuracy because we could allow the diameter of both the branches of the small manometer to be 8 mm., so that the correction for the capillary depression can be determined with sufficient accuracy from the form of the menisci.

The length of the U-tube warrants that the gas remains shut off even when changes of temperature and atmospheric pressure occur.

The peculiar position of the U-tube with regard to the manometer-tube leaves room under the lower reservoir for the tube h, which acts a very important part in different operations, viz. the exhausting with the mercury-pump, the filling with pure gas and the shutting off of a definite quantity of gas. This tube h is bent downwards slantingly and backwards and carries at the end a ground tap which fits in a ground cap, welded on to the glass conduit of the mercury-pump and the gas-generating apparatus (Comm. N°. 27 p. 15).

After the piezometer-tube is cleaned and dried, the capillary end at the top of its upper reservoir has been sealed off, and the wider part of its stem has been cemented in the flange, it can be successively exhausted and filled with gas by means of this tube h. Then by revolving the piezometer-tube round the axis of the joint we can admit the mercury from the lower reservoir into the U-tube and so shut off the gas perfectly sure, after which the tube may be separated from the gas-generating apparatus. It needs no comment that the operation described must be done with great care in order to prevent that the tube h breaks off, as the manometer is already burdened with the heavy flange.

In order to facilitate any repairs to be made in the U-tube, its branches are connected by a narrower tube that can easily be straightened in the flame and after the repair is finished can be bent again into the original form without any damage to the calibrated tube.

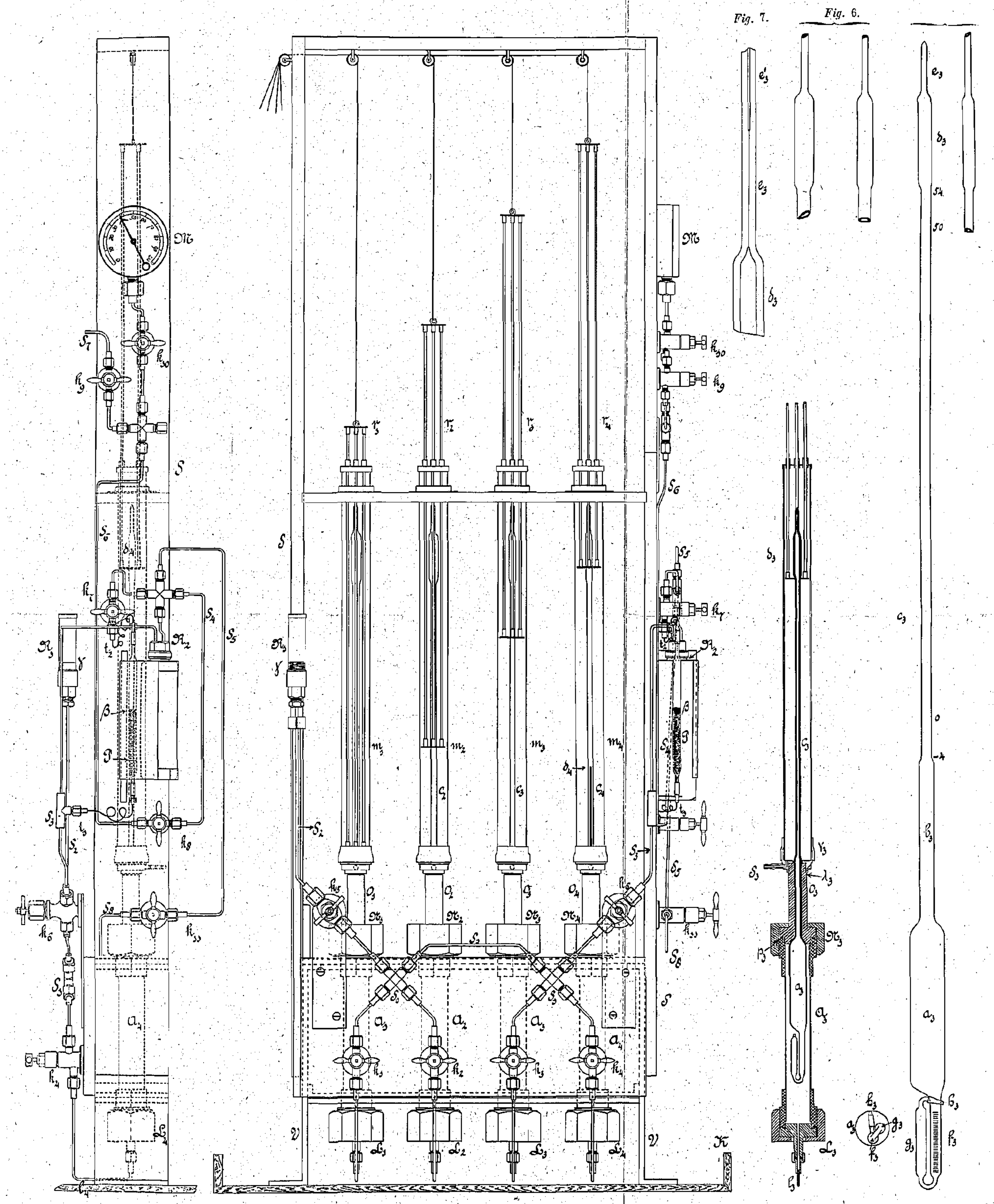

Fig. 2. Fig. 1. Fig. 3. Fig. 5. Fig. 4. Fig. 6. Fig. 7.

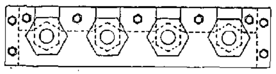

Fig. 1.

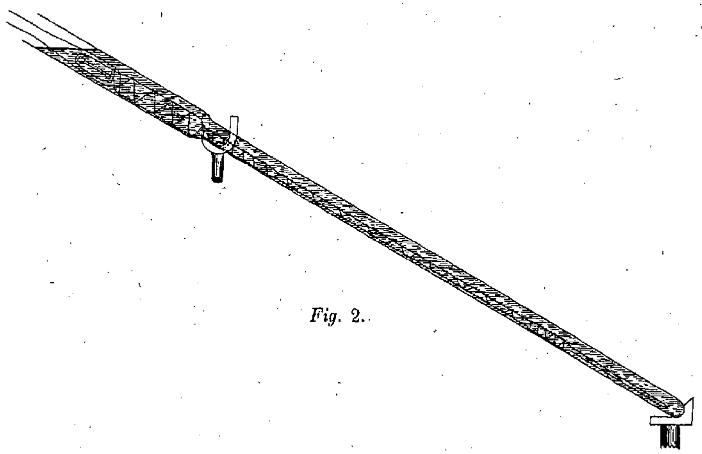

Fig. 2.

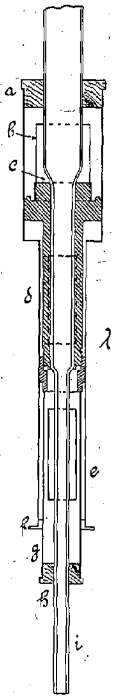

Fig. 3.

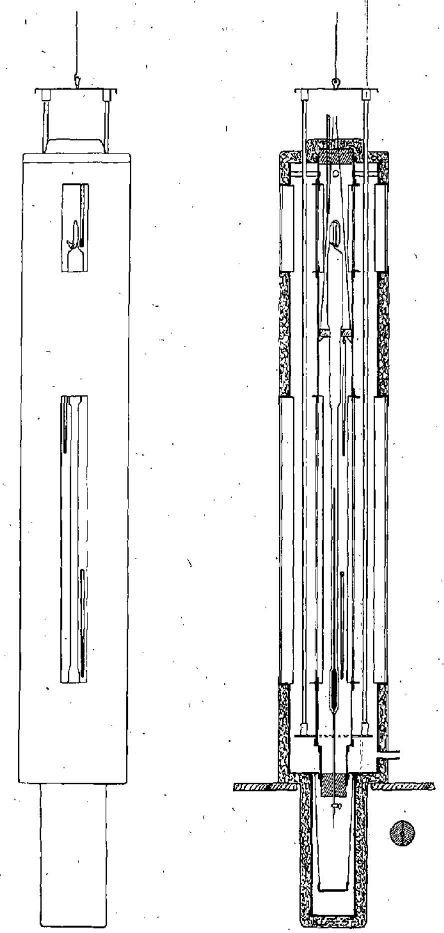

Fig. 4.

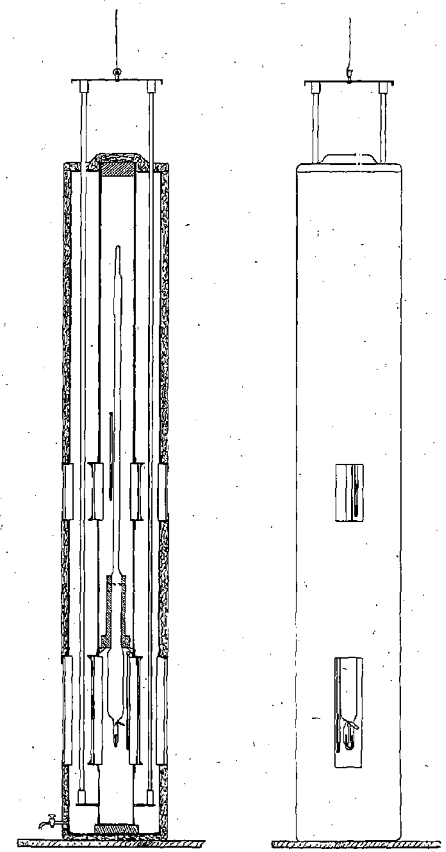

Fig. 5.

§ 4. *The compression-cylinders and stopcocks.* (Pl. I, fig. 1, 2, 3.) The manometer-tubes filled with gas and closed by the mercury in the *U*-tubes are introduced into the compression-cylinders A previously filled to the rim with mercury. In order to prevent the air from getting into the *U*-tube, care is taken that the mercury is flowing out of the tube (by heating the manometer reservoir) at the moment that its opening is immersed below the mercury surface in the compression-cylinders. When the compression-cylinder is closed by the flange in which the manometer is cemented, the mercury pushed up by that part of the flange which fits in the compression-cylinder, drives the air out. The superfluous mercury escapes until by firmly screwing on the nut *N* we obtain a tight fit on the washer *p*. Then the reservoir of the manometer-tube is contained in a space wholly and exclusively filled with mercury.

By means of this contrivance we can take the manometer-tube from the apparatus without its coming in contact with any liquid but mercury, and avoid the great number of difficulties which always arise when we transfer, as usualy is done, the pressure by another fluid on the mercury in the compression-cylinder.

It is desirable that we should have at hand a greater number of manometer-tubes with flanges in order that we may successively place several piezometers previously prepared into the compression-cylinders. The 4 compression-cylinders of the apparatus on Pl. I consist of well-drawn iron tubes, carrying taps welded on at both ends[1]). They are mounted together on a stand *V*, in the notches of which they fit in with the parts of the two taps that are filed sexangularly; they are shut up by a counter plate, in which likewise notches have been filed. These notches together with those in the stand hold the sexangular taps, as clearly shown in fig. 1 Pl. II.

Thus it is easy to place into and to take out of the apparatus each of the compression-cylinders separately, while the tubes with the stand form a whole and are kept as it were in a large wrench, which can be held firmly so as not to meet with the difficulty, which else so often occurs, whenever we want to screw the nut of a compression-cylinder tightly by means of a wrench with a long lever.

The whole stand is placed in a wooden receptacle for the mercury that might flow out.

The compression-cylinders can be opened on both sides. In

[1]) The boring of a bar is very expensive and it is difficult to get smaller pieces of tubing with walls sufficiently thick to be provided with screw-thread and a sexangular tap.

cleaning the inner surface we therefore do not meet with the difficulty, which generally is occasioned by the bottom part. At their lower ends the compression cylinders are closed by nuts L, similar to those at the upper ends; through these they are coupled to steel tubes l_1, l_2, l_3, l_4 bent rectangularly, terminating in the stopcocks k_1, k_2, k_3, k_4 [1]) which serve to couple each manometer (sometimes two) to the pressure-conduit or to disconnect them according as to whether or no the pressure to be measured is within the range of the manometer.

These stopcocks are below the upper rim of the compression cylinders so as to allow us to fill without difficulty the compression-cylinder and the tube entirely with mercury; as they are provided with cork stuffing the mercury cannot become dirty by streaming along, in or out.

The pressure is transferred on to the mercury in the compression-cylinders by means of mercury in the tubes s_1. The stopcocks of the different compression tubes are mounted on a board, screwed on to the stand V (see Pl. I fig. 1 and 2) together with a system of supply-tubes. These supply-tubes filled entirely with mercury connect the compression-cylinders with:

1⁰. a mercury-reservoir R_1, serving to supply mercury and to guarantee that, when the apparatus is not watched there still remains in case of change of temperature and atmospheric pressure a sufficient excess of pressure in the apparatus even if the stopcocks were open. This reservoir is always closed by the iron stopcock k_5 when determinations of pressure are being made.

2⁰. the principal tube s_3 through which the pressure is transferred on to the mercury in the tubes, and which may be closed by an iron stopcock k_6 [2]).

The tubes s_1 are entirely filled with mercury by exhausting them and then admitting mercury from R_1; the stopcocks, like the other ones are provided with cork stuffing.

Through the supply-tube s_3, immersed in the mercury down to the bottom of the reservoir R_2 we supply from the mercury in R_2 as much as is required to compress the gas in the manometer tubes. The pressure to be measured is transferred on to the mercury in the reservoir by means of compressed gas. In order to apply the

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[1]) The construction of steelwork of this kind is described in Comm. N⁰. 27 and 44.

[2]) These stopcocks did not require the same great care as bestowed on the steel stopcocks of the single manometers (which must be perfectly reliable) as not all manometer-tubes may be exposed to the highest pressure.

correction resulting from the difference in level between the surface on which the pressure to be measured is applied, β, and the top of the meniscus of the mercury in one of the manometer-tubes δ_4, it is necessary to know the level of the mercury in the reservoir R_2. This is indicated by the gauge-glass P, beside the reservoir R_2. It consists of a thick-walled tube, drawn out on both ends and provided with steel caps and steel capillary tubes t_1, t_2, as described in Comm. n°. 44, which form at the higher and lower ends the connection with the mercury-reservoir R_2 (or what comes to the same with the siphon tube s_3). The stopcock k_7 serves to close the gauge-glass when the reservoir has been exhausted and we want to let mercury flow into it through the tube s_3.

The correction just mentioned for the vertical distance between the level of the mercury in the reservoir (as indicated by the gauge-glass) and the meniscus in the manometer where the reading is taken, which in the case of many manometrical measurements could but very roughly be applied, is accurately determined here with a kathetometer.

A divided scale on which we can immediately transfer the readings is placed at the side of the gauge-glass. With the aid of the kathetometer we compare the level of the graduations with the level of the graduations on the manometer-tubes to be read. This is done before and after they have been provided with the waterjackets m_1, m_2, m_3 and m_4. To protect the observer the gauge-glass is provided at the back and on the sides with iron plates and in front with a thick plate-glass.

On a board near R_2 stopcocks and tubings are fastened which are represented in Pl. I fig. 1 and 2 require no separate description. By means of these we can:

1°. close (by means of k_9) the conduit s_7 through which the pressure is transferred [1]) by means of compressed gas;

2°. read the pressure (k_8 being shut) transferred through this conduit, on an auxiliary manometer M, before the compressed gas is allowed to transfer the pressure into the measuring apparatus, in order to get to know, which manometer is to be connected;

3°. make and break arbitrarily the connection with the auxiliary manometer, whenever this seems desirable, while making the measurements of pressure;

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[1]) As for instance a tube which forms a connection with an apparatus like that ot Dr. SIERTSEMA's Comm. N°. 49, or a tube, which connects the manometers with the piezometer for gases compressed at low temparatures, mounted in another room.

4⁰. exhaust the conduits (through k_9 and k_{11} before the connecting of s_7 and s_8) and to fill the reservoir R_2 with mercury through k_6 and k_5);

5⁰. To connect the apparatus with the standard open manometer (through k_{11}).

When the apparatus is used as a manometer the bottoms of the waterjackets on to which the glass waterjackets are fastened with india-rubber, are screwed on to the flanges O at λ (seefig. 3). The temperature is kept constant by means of circulating water [1]) and of the stirring rods r_1, r_2, r_3, r_4, while thermometers (not represented in the figure) enable to read the temperature at differents heights. The stirring rods are suspended from the stand S_1, which is constructed so that it can easily be removed.

§ 5. *Some remarks on cleaning, cementing and filling.* The cleaning of the tubes is of great importance. Only when this is done with the greatest care, it is possible that the menisci remain perfect. As for the precautions to ensure this, I refer to Comm. N⁰. 27. Attention must be drawn however to the fact that, without particular precautions it would be impossible to clean the tubes by boiling for instance with nitric acid. In the first place different parts of the walls are very thick; moreover they are very long and terminate on one end in a comparatively narrow tube, on the other end in an extremely narrow capillary tube, which almost closes them. The difficulty arising from this, was removed by placing the tubes, as shown in Pl. II fig. 2, in expressely made boiling-tubes of ordinary size in which the cleansing-liquid is poured also filling the manometer-tube (being not entirely shut on both sides), and is heated until the liquid begins to boil within the manometer-tube.

Round the manometer-tube a platinum wire is slung, which prevents contact between manometer-tube and boiling-tube, and serves to take the manometer-tube out of the boiling-tube.

In cementing the manometer-tubes in the flanges, we must take care that the axes of the two coincide. Therefore it seemed desirable to make special moulds in which the tube and the flange are fastened. (Compare fig. 3 Pl. II).

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[1]) I shall not dwell on this circulation. When the piezometers are used at temperatures much differing from that of the room we must surround them with liquid- or vapour-jackets (or liquid-jackets enclosed in vapour-jackets).

On to the part λ of the flange provided with a screw-thread, we screw a brass tube in which two openings *e* have been cut, and in which the stem of the manometer-tube may be fastened by means of the wooden stopper *h* cut in two. Over the wider lower-part of the flange, we slide the tube consisting of a narrow and a wide piece in which openings have been cut at *b*, *d* and also at *e*, and which fits at λ round the former tube. By means of a tight ring at *f* the two tubes are kept in a coaxial position. In the wide end of the second tube the lower cylinder of the manometer-tube may be fastened at *a* by means of a wooden stopper likewise cut in two.

The cementing is done in the following way: the manometer-tube is heated to a little above the melting-point of the cement, a thin layer of which is spread on the tube. In the meantime the steel piece with the brass tube screwed on to it is heated also to about the same temperature. Then the manometer-tube (in the reversed position of fig. 3) is slid into the steel piece, over this the second tube is slid and then the halves of the wooden stopper are put in their places. In this way the manometer-tube is truly centred and the space between manometer-tube and flange is entirely filled up with cement. Through the openings we may pour in additional cement. After this is solidified we turn the apparatus upside down (position of fig. 3) so that the glass-reservoir rests on the collar *c* of cement oozed out.

The superfluous cement is washed away with benzine.

For the filling with pure hydrogen I refer to Comm. N°. 27; for the revolving of the manometer-tube round the axis of the tube *h*, in order to shut off the gas by means of mercury admitted beforehand into the reservoir, I refer to § 3 of this paper.

§ 6. *Calibration, determination of the volume of the tube and measurements of the normal volume of the enclosed gas.* In order to calibrate the graduated tubes and to determine the volumes of the reservoirs, we weld a wider tube with a glass stopcock on to the capillary tube where the manometer-tube is to be sealed off. On the other side of the stopcock, this wider tube terminates in a fine point.

After being cleaned and dried the manometer-tube is entirely filled with mercury. The calibration and gauging is done by weighing the mercury which we let flow out. I will not dwell on these operations and the corrections they require as they can better be treated of when the observations made are communicated, but here I will only mention that in these operations much time was saved and the degree of accuracy was greatly increased by placing the tube in a

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double walled copper box lined with thick felt, the inner and the outer wall being provided with plate-glass windows in order to enable us to take readings along the whole scale of the tube (comp. Pl. II fig. 4). The space between the two walls was filled with water and the constancy of the temperature was promoted by stirring.

The tube to be calibrated rests on a wooden ring and the lengthening-piece with stopcock, welded on to the upper-reservoir, passes through an india rubber stopper cut in two. The point of the manometer-tube through which the mercury flows is protected from variations of temperature by a copper felt-lined cap fastened to the box by a bayonet-adjustment; this cap can easily be removed (for a short time) whenever we want to let a quantity of mercury flow out from the tube.

The readings for determining the normal volume are made while the manometer-tube is placed in a double-walled box as described above, (comp. Pl. II fig. 5) but in which the windows were only small, as we wanted to read only the position of the mercury in the *U*-tubes and of the thermometer. These readings and that of the standard barometer (the box communicating with the atmosphere by a small tube) yield a perfectly accurate determination of the normal volume, which is of the greatest importance for the investigation of the isothermal lines.

Physics. — Prof. VAN DER WAALS presents on behalf of Mr. N. QUINT GZN. a paper on: „*The determination of isothermals for mixtures of* HCl *and* C_2H_6."

Introduction.

At the commencement of this investigation there were but few observations made, which might be used for testing Prof. VAN DER WAALS's theory on the behaviour of mixtures of two substances. At that time Mr. KUENEN was the only one who had examined some mixtures and his observations agreed with that theory. In order to add to the material on this subject (to which also Mr. VAN DER LEE, Mr. VERSCHAFFELT, Mr. HARTMAN have since contributed), I have examined mixtures of HCl and C_2H_6. The results of the determinations of the isothermals and a short description of the experiments follow; I hope soon to publish some further details and a calculation of volume contraction etc.