H. KAMERLINGH ONNES. On the measurement of very low temperatures. **Part. I.** (30 May 1896).

1. Hydrogen-thermometers for very low temperatures. As the measuring of very low temperatures is becoming more and more important it appears desirable to me to describe the apparatus which during the last few years have been used in the cryogenic laboratory at Leiden. (Compare my Comm. of 29 December 1894)¹).

Under my direction they have been constructed by Mr. H. A. BLOM under-instrumentmaker at the laboratory whose ingenuity has been of great value to me.

As a basis for the determinations of temperature the hydrogen-thermometer at constant volume was chosen.

A gas-thermometer which is to be used for accurate determinations at very low temperatures must fulfil other conditions than ordinary standard-thermometers.

As it is difficult to obtain large quantities of liquid gas, the thermometer vessel must be so small that it can be put entirely into the glasses which are generally used for collecting the liquid gases.

The special precautions which must be taken when working with liquid gases make it very desirable that the apparatus should be easily handled, so that we need not shrink from carrying it from one place to another and that the thermometer-bulb can be placed in the

¹) Communication from the Labor. of Phys. at Leiden, no. 14.

4

vessel of liquid gas and taken out again without difficulty. It is easy to see the reason why. In order to obtain the liquid gas or to keep it, different apparatus are required, which generally are very difficult to move and must also remain available for other experiments. Moreover it is a great advantage to be able to immerse different thermometers successively in the same liquid.

In the following pages two models of hydrogenthermometers will be described, with which very accurate measurements are possible and which fulfil the conditions for very low temperatures. In the one model the smaller volume, in the other the greater accuracy have been specially aimed at. First we shall describe the smaller model and then show in what respect the larger model differs from this. The whole construction of the thermometer and the manner of using it may be seen without further comments from Pl. I, fig. 1 and 2 which represents the comparing of WROBLEWSKI's thermo-element with the hydrogen-thermometer as already mentioned in the Proceedings of 29 Dec. 1894, pag. 179¹) and as will be fully treated in a following communication. The hydrogen-thermometer and thermoelement are immersed in the bath of liquid oxygen, collected in the boilingglass O^{2}) described above. The figure on Pl. I is in some parts semi diagrammetic especially as regards the connections; moreover the

way in which some parts of the apparatus are protected from change of temperature is not represented here, nor are the thermometers on which the temperatures required for correction purposes are read.

2. Description of the small hydrogen-thermometer. The thermometer-part consists of a bulb, a, fig. 1, Pl. II of about 30 cc. blown on to a capillary tube, b, of 0.25 c.m. inner diameter. The capillary has been chosen so narrow because it forms the transition between the parts of the thermometer at a low temperature and those at the temperature of the room; therefore the temperature of the gas at different places in the capillary is rather uncertain.

The little bulb is made of Jena-glass and is tested to a pressure of 2,5 atmospheres above the outside pressure. The volume of the capillary tube is determined with mercury and the volume of the whole bulb with water; the change of volume with pressure is also measured.

The thermometer is connected with the space, where the adjustment at constant volume is made, (the volumenometer part) ¹) by means of a steel capillary tube d: this kind of tube has been used for many years for experimental work at Leiden and may be obtained from P. J. KIPP & SON successor J. W. GILTAY at Delft (comp. Proceed. Amsterdam Dec. 1894, pag. 168: capillary connection of pump body and compression tube). ²) The

¹) CHAPPUIS, Mém. d. Bur. Intern. T. VI, p. 28. WIEBE u. BÖTTCHER, Zeitschrift f. Instr. 1890, p. 17 u. 19.

²) Commun. no. 14 p. 8. A drawing of this is found in MATHIAS l. c., p. 389, fig. 5.

¹) Commun. from the Labor. of Phys. at Leiden no. 14. p. 27.

²) A drawing on a larger scale of the boilingglass is found in the paper of E. MATHIAS: Le laboratoire cryogène de Leyde. Revue Générale des Sciences, 1896 p. 387, fig. 3.

capillary is on the outside covered with oil which is then converted by heating into an adhering varnish and thereby protected from rusting.

The diameter of the capillary is about 0.8 m.m., its length about 180 c.m., its volume therefore nearly 1 c.c. If the temperature of it is determined carefully, a volume of that size is permissible. The connection of the steel capillary to the glass capillary on one side and to the volumenometer-part on the other is made by steel caps c and e, fastened to the steel capillary into which the glass capillary and the volumenometer-tube are cemented. For the precautions taken in fastening the caps to the capillary and in cementing the capillary and the volumenometer-tube into these caps see below (§ 3.)

The lower surface of the steel cap e is provided with a small point f exactly at the centre which has been carefully turned out of the same piece of steel. The adjustment at constant volume is obtained by making the surface of the mercury in the volumenometer touch this point f.

As the cap fits accurately in the glass tube g its surface forms a perfectly flat top ') to it and the volume of the volumenometer-part above the mercury-meniscus may be accurately calculated. The volumenometer-tube is made of a perfectly cylindrical tube and is accurately calibrated. Its width is 9 m.m. In choosing this dimension it was taken into account that by measuring the height of the mercury-meniscus the correction for the capillary depression is to be obtained; this correction however leaves an accidental error which becomes smaller as the diameter of the tube is larger. With the dimension chosen this error agrees approximately with the accidental error in the adjustment of the top of the meniscus on the steel point: which latter error would increase with a wider tube. The volumenometer-tube is ¹) connected with the open manometer by an india-rubber tube l, and as usual carries a three-way stopcock. The tube k ends in a fine capillary tube which in the calibration of the volumenometer-tubes serves to run out known quantities of mercury for the computation of which the position of the mercury in the capillary point is taken into account. The manometer-tube is of the same kind and diameter as the volumenometer-tube.

When no observations are made with the thermometer the three-way stopcock remains closed. Above the stopcock is a space *i*, which serves to receive particles of dust or gas-bubbles which might issue from the india-rubber tube. Moreover the volumenometer-tube is provided with a bulb h which in the process of filling the thermometer with hydrogen (comp. § 6) serves to admit so much gas into the apparatus under a little less than the usual pressure that on reducing the volume to its normal value a tension of about 1400 m.m. at 0° is obtained *i*. e. of about 1500 m.m. at 100°, and of about 300 m.m at -200° .

3. Difference in the measurements of the larger pattern. The larger pattern differs from the small one only in having a longer bulb of the same diameter (volume

') JOLLY POGG. Ann. Jubelband.

¹⁾ PERNET according to CHAPPUIS. Mém. Bur. Intern. VI. p. 31.

about 90 c.c. (Pl. II, fig. 2). Like the small one it can be plunged entirely into the boiling-glasses (Proceed. Dec. '94 l. c. § 9. Commun. no. 14. p. 27.)

The volumenometer-tube is taken wider (12 m.m.) and the volumenometer-bulb larger in proportion to the larger volume of the thermometer part.

4. Some precautions and auxiliary apparatus for the construction and use of the thermometers. The glass is cleaned first with boiling concentrated nitric acid, then with 25% alkali solution, finally with distilled water. Further it is dried with a current of air that has passed over caustic soda, sulphuric acid and phosphorus pentoxide, the tube being heated to a high temperature and if possible exhausted by means of a mercury-pump. In order to subject the thermometer part to these operations the bulb is originally provided with a tube (comp. Pl. II, fig. 3a) through which the liquids can be sucked up and the upper part of the capillary is originally lengthened by a wider piece, provided with a ground joint (comp. Pl. II, fig. 3b.) by means of which it can be fastened to the air-pump. After the operations described in this and the preceding paragraph the first tube is sealed off, the second lengthening piece is cut off carefully so as to get a perfectly even crack, which is necessary in order not to leave any additional air-space when the steel cap is cemented on.

The steel capillary is annealed by glowing by means of an electric current furnished by a battery of accumulators; after this air at 100 atmospheres is pressed into it, in order to discover any small leaks, which are often

found in these capillaries, and then dry air is blown through it under high pressure. Finally pure mercury is pressed through and in order to determine the volume it is exhausted and filled with mercury. Both ends of the tube are provided with extremely fine screw threads; after the above described operations the tube is screwed into the two steel caps with marine glue in order to make it tight; after which the capillary is soldered to the upper part of the caps. Another reason why marine glue is used, especially in the cap which is cemented on to the volumenometer tube, is to prevent the mercury from coming in contact with the solder if by accident it should rise in the capillary.

In order to cement the volumenometer tube into its steel cap (comp. Pl. II fig. 4a) the latter is turned upside down, the groove is filled with sealing wax, and into this after being properly heated and covered with a thin layer of sealing wax on the outside the volumenometer part is pressed down with closed stopcock. Care must be taken that air is supplied or sucked out through the steel capillary, so that in consequence the sealing wax may flow out on the outside when the glass piece is being slowly pressed down, while on the inside only a thin line of sealing wax remains round the steel when cooled down. Only when these precautions are taken an air space is obtained which may be accurately calculated. If these precautions were neglected sealing wax might spread over the interior of the glass and would in that way hinder the adjustment of the mercury on the steel point.

In cementing the glass thermometer-capillary into its cap (comp. Pl. II fig. 4b) a thin layer of sealing wax

11

is spread over the glass and also over the inside of the upper rim of the cap.

The glass capillary is then heated carefully and slowly (5 minutes) pushed into the cap; care being taken that the air can escape from the steel capillary. In this way we get a perfect connection without any air space being left except the top of the tube itself. In order to acquire the necessary skill in this operation, it is first tried several times on a trial piece which is then coupled to a cylinder with liquid carbonic acid in order to see whether a good fit is obtained.

The india-rubber tube is treated with pure mercury for a long time before using it and while hot is cemented on to the tubes with sealing-wax. The manometer-tube and india-rubbertube are filled with mercury, which has been distilled in vacuo in a mercury distiller into which only mercury is put which is free from admixture with other metals.

The volumenometer- and manometer-tubes are fastened in a very light but carefully worked stand by means of clips which have a very true motion. They are adjustable with a micrometer. This expensive stand is generally only used for the thermometer with which the observations are made. Thermometers temporarily out of use are clamped in ordinary stands by means of ordinary clips. The manometer- and the volumenometertubes when taken out of the clipstands can be held in one hand and the thermometer proper in the other hand and in that way the thermometer may without difficulty be transferred into the apparatus where the temperature is to be observed, the volumenometer part being fixed in the stand which is placed near these apparatus. Also if the apparatus is fastened in the above described stand, we can easily remove the whole by holding the stand in one hand and the thermometertube in the other.

It has proved a great advantage that the thermometer with which we can reach the accuracy of a standard instrument is so easy to handle. This is owing especially to the steel capillary being used.

In order to bring the thermometer into apparatus which have to be usually closed and must often be subjected to exhaustion it is provided with a stopper as represented in Pl. II, fig. 5.

The copper ring c may be slid over the bulb. In the ring, supported by the rim e, a copper plate is placed consisting of two parts which serves as a bottom, the cylindrical part is filled with a cork cut in two and finally in the conical part an india-rubber stopper cut in two is put and made tight with dissolved indiarubber. The cylindrical part of the ring is fastened to the mouth-piece of the apparatus, in which the temperature is to be measured, by means of india-rubber rings, cement and tightening strips of brass.

5, Apparatus for the preparation of pure hydrogen-gas. For measurements at very low temperatures it is of great importance that the thermometer should be filled with absolutely pure hydrogen gas. For this purpose the gas is prepared electrolytically and following COOKE and RICHARDS '), who have made ample researches about

1) Proceed. Amer. Acad. 1887-88.

the preparation of hydrogen for determinations of atomic weights, I have chosen diluted hydrochloric acid as the electrolyte. Plate I, fig. 3, shows the apparatus used for this method. The figure is again diagrammetical: e.g. the glass tubes which act as a glass spring and connect together the generating apparatus, the mercuryair-pump and the apparatus which is to be filled have been left out.

The voltameter V, (comp. Pl. I, fig. 3) consists of a glass vessel a (comp. Pl. II, fig. 6) with an ebonite cover b, containing a bell jar c, with a stopcock d. In this jar c, hangs a piece of platinum foil e, from a properly insulated wire which serves as one of the electrodes; the hydrogen generated at the electrode collects in c. The neck of the jar is fastened in the same indiarubber stopper g, as the wire through which the current is led off. The bottom of the vessel is covered with a layer of zinc-amalgam, h, obtained by dissolving chemically pure zinc in chemically pure mercury. The current is supplied by a bundle of twisted platinum wire soldered to a copper wire, and together of a section sufficient to carry the current. The juncture is protected by a surrounding tube l, sealed on to the lower end k of the platinum by means of enamel. The electrode (the upper part of which is covered in the way described) is fixed into the apparatus by means of a second tube m, which is cemented in the cover and reaches below the surface of the amalgam. In this tube the electrode is fastened airtight by means of india-rubber.

Only few gas-bubbles are formed on the surface of the amalgam. But in order to prevent even these from finding their way into the jar which receives the hydrogen, a glass dish n floats on the amalgam the upper edge of which reaches above the bottom of the jar. The dish is prevented from rising by three rods of enamel p, sealed together, and hooked over the edge of the dish and resting against the bottom rim of the jar. The india-rubber stopper in the neck of the jar, the neck of the jar itself, and the india-rubber stopper which carries the jar, are joined airtight to each other and to the ebonite cover by means of dissolved indiarubber. For drawing off and running in the electrolytic liquid two tubes q and r, the former being provided with a cock s, are cemented into the cover.

The cover is made airtight by means of a washer u and tightening rods t, which press it down on to the ground rim of the vessel.

The hydrogen passes through the stopcock at the top of the bell jar into two wash-bottles (comp. Pl. I, fig. 3aand b) filled with a chemically pure 25% alkali-solution. The first of these a, is really a sloping tube which contains glass beads in order to divide the slowly rising hydrogen bubbles; the second is a Woulf's bottle, filled also with glass beads and alkali-solution. After the gas had passed through the wash-tube alone a trace of chlorine could still be detected in it by means of silver nitrate. The solution is brought into the alkali-apparatus and if necessary renewed by the aid of the taps d, c and k and the tap-bottles.

The 20% hydrochloric acid, which serves as electrolytic liquid is previously boiled in a flask as was also

done by COOKE and RICHARDS '). During this operation as well as during the cooling a current of hydrogen is led through. For this hydrogen was used from a pressure cylinder supplied by JOHN ORCHARD, which might have been washed beforehand in hydrochloric acid and caustic potash. According to the rules of the Leiden laboratory, while the boiling is going on, the cylinder f, containing the compressed gas is not brought into the room where the flame is burning.

In the same way the air is previously expelled from the alkali with hydrogen from the cylinder and the whole apparatus before and after the introduction of the solutions is also filled with hydrogen. When the solutions are put into a and V there is only very little space left which is filled with almost pure gas. The generation of electrolytic hydrogen is now set in motion and the hydrogen is not used until the whole space has been once more swept out with it: in the meantime it escapes through the safety-tube.

While thus the air is expelled from a and V by a constant gas-current, the same object is reached with the drying battery by repeated exhaustion by means of the mercury-air-pump. The partition between the two parts of the apparatus one only of which has to be exhausted is formed by the regulating-cock R, of the kind that are used at Leiden in operations with compressed gases ²).

¹) l. c. pag. 167.

²) Compare Stoel. Measurements on the influence of the

The drying battery consists in the first place of a double or safety drying tube g^{-1} with strong sulphuric acid ²). In a tube of that kind the reversal of the air current has no other effect than that of carrying the liquid from the one half into the other; it cannot flow back into the rest of the apparatus. For exhausting purposes this drying tube is provided with a connecting tube carrying a cock h, which is shut when we want gas to pass through the liquid but is opened during exhaustion. When the apparatus is exhausted the fine regulating cock R must be opened with the utmost care in order to let the first gas-bubbles pass through the sulphuric acid. The gas afterwards goes through two drying towers i, i, filled with chemically pure phosphoruspentoxide spread on glass-wool.

As preparation of pure hydrogen has been repeatedly necessary for some years, the generating- and washingapparatus are permanently mounted together on a board fastened on the table by means of clamps, the connection with the mercury-air-pump L and the apparatus which has to be filled Th, being obtained by means of springs

temperature on the inner friction of liquids between the boilingpoint and the critical state. Diss. Leiden, 1891, p. 12.

Матных l. c. pg. 383. fig. 1, nº. 8.

¹) Comp. DE VRIES. Measurements on the influence of temperature on the capillary elevation of ether. Diss. Leiden, 1893, Pl. I.

²) An action of the gas obtained by electrolysis on the sulphuric acid as noticed by CHAPPUIS (Mém. Bur. Intern. VI p. 105), who filled his apparatus with hydrogen, obtained by electrolysis of orthophosphoric acid was neither detected by COOKE (in his determinations) nor by me.

16

of glass tubes which are joined to these by ground joints, and are sealed together, when connected to the apparatus, with the hand blow-pipe.

6. Filling the thermometer. In order to fill the thermometer with the pure gas, the volumenometer part is provided with a thickwalled side-tube, originally ending in a ground joint (comp. Pl. II, fig. 7), which forms the connection with the mercury-air-pump and the apparatus furnishing the gas.

After mercury from the manometer and india-rubbertubes has flown out for some time through the threeway stopcock of the volumenometer part, and a layer of about 1 c.m. has been let in above the cock, it is shut. The thermometer- and the volumenometer part on the one hand and the drying battery of the hydrogenapparatus on the other are now exhausted to a few thousandths of a m.m. by means of the mercury-airpump through the tube mentioned above; when everything is found to be absolutely tight, the current is closed, and is regulated by means of a resistance to a strength of 2 or 3 Ampères; the regulating cock is then opened so wide that the same quantity of gas as is generated in the apparatus flows into the drying battery; the progress of the filling process is followed on the manometer. Special care must be taken not to open the regulating cock too far, in order to prevent liquid from flowing over into the washbottle at a Pl. I, fig. 3. The operation of exhausting and filling, which takes about 2 hours each time, is repeated several times. After the lats exhaustion so much mercury is admitted in the volumenometer part that the space i is not only shut off but becomes completely filled with mercury when the gas is admitted. The side tube is then sealed off and the mercury in the volumenometer part is pressed up.

7. The zero. For the determination of the zero planings of ¹) pure ice are used. Pl. II, fig. 8 shows the apparatus for planing the ice²). The block of ice is slid to and fro along the fixed plane; the fine shavings of ice fall into a vessel under the knife and when soaked with distilled water form a grainy mass of icy particles covered with a thin layer of water. In this condition they do not treeze together and even after hours the mass is as powdery as in the beginning. The knife a is of iron and has a steel edge; by adjusting it by means of adjusting screws, b the planings become coarser or finer. If the ice planings are very fine there is no objection to placing the hydrogen thermometer, although it is fragile, into the ice, which for this purpose is put into a large flower-pot. At some distance from the thermometer the ice may even be pressed tightly together if done carefully. The melted ice flows off through several holes into an earthen-ware plate from which it flows off again through a small tube on a level with the bottom of the flower-pot.

It is intended to cover the top of the plane with two plates of marble-glass in order to protect the ice even better from becoming dirty.

¹) PERNET, Meteorol. Zeitschr. 1879, p. 131. ²) GUILLAUME, Mém. Bur. Intern. T. V. p. 41.

Part. II. (27 June '96).

8. Boiling point. For heating the hydrogen thermometer in steam, the copper boiling point apparatus represented in Pl. III, fig. 1 is used. The section of the vessel a, which



contains the water is so large that the walls above the water cannot be heated above the boiling point by ascending currents of hot air. The steam therefore cannot become superheated. (For the same purpose a similar apparatus of smaller size (Pl. I, fig. 2) was provided with an asbestos ring below which the

water surface is not allowed to fall. As the outlet of the steam is on one side the steam might be too much in that direction, to prevent which the annular space above the outlet is fitted (comp. fig. 1) with a perforated ring, the holes being closer together the further away they are from the side of the outlet). The apparatus is carefully cleaned and only distilled water is used in order that the water may always boil from a pure metal-surface. The cover of the double jacket b is convex so that water which condenses on the cover flows off to the exterior jacket. Moreover the upper part of the apparatus is covered with felt and the part of the stem which projects above the cork in the cover, is tightly packed in fine sheepswool, so that the space above the cover is heated to near the boiling point. In this manner the flowing down of drops along the stem is prevented and the thermometer remains enveloped in the thin water-layer which condenses on it in the beginning and gradually assumes the temperature of the steam. From the thermometer a funnel-shaped glass-screen, c, is suspended which protects the thermometer from splashed drops. A floater, d, indicates the position of the surface of the liquid, which does not fall more than 3 cm. per hour when boiling at the greatest rate. The velocity of the steam in the outlet of the jacket is at least 40 cm. Under these circumstances cold air currents cannot flow back into the apparatus. The velocity of the steam in the inner space is from 3 to 10 cm.

At this rate of boiling the excess of pressure inside is also nearly constant and without fluctuations, (the diameter of the outlet is 2,5 cm.) and may be measured by means of a water-manometer, which is in communication with the inner space, in which the thermometer is suspended. Following PERNET, JAEGER and GUMLICH, ¹) the one level of this water-manometer is heated to 100° and exposed alternately to the pressure of the steam and to that of the atmosphere, the other level being maintained constant and always at ordinary temperature and at the pressure of the atmosphere. The excess of pressure of the steam however never exceeds 1 m.m. of water pressure, corresponding to about $\frac{1}{300}$ th of a degree in the boiling point, if the outlet is not narrowed on purpose, which would occasion fluctuations of pressure.

In the operation represented in Pl. III, fig. 1 of the calibration of a thermoelement for low temperatures, the determination of the slight differences, that may yet occur in the pressure of the steam with a given

¹) PERNET, Bureau Intern. I. B. 16. 1881.

PERNET, JAEGER und GUMLICH, Zeitschr. f. Instr. XV, p. 124, 1895.

velocity of boiling, may as a rule be omitted and it will be more than sufficient to use for this end a value determined once for all. For in comparison with the disturbances and uncertainties, which are as yet not to be avoided in determining low temperatures, the above deviation may be neglected.

In order to carry off the steam, without giving rise to differences of pressure or fluctuations, Mr. BLOM has constructed the apparatus represented Pl. III, fig. 1 and on a larger scale Pl. III, fig. 3. In this apparatus the steam which flows in from the top is condensed by fine jets of water, which issue from holes in the tube, b. This tube may revolve round the supply-tube of the condensing water, or axis and when lifted up by the water pressure it rests against a glass plate with a sharp point in the direction of the axis. A fine hole having been made in the side at each end, the tube is set in motion as a reactionwheel as soon as the supplycock is opened. With an apparatus of this kind which may easily be placed anywhere, the steam is sufficiently condensed. If there is no objection to employ a wide tube leading to a draught chimney in the manner indicated by BUNSEN¹), this method is simpler.

The values for the coefficient of expansion of hydrogen, deduced from the measurements at the boiling point and the zero point, will be treated of in a following communication.

9. Thermoelement, German silver-copper. With this element the first measurements of low temperatures were

made by WROBLEWSKI. I have chosen it as being at the time the most suitable, partly also because, taking into account that the resistance of German silver varies little with the temperature. In the observations made at Leiden a method has been followed, closely resembling that of WROBLEWSKI. We had occasion to investigate in this way what difficulties may have presented themselves in his determinations. It appeared that different sources of error may endanger the accuracy of the measurements and that special precautions are necessary to make a long series of temperature readings with the same thermoelement.

CHASSAGNY and ABRAHAM¹) in their investigation on accurate determinations of temperatures between 0° and 100° by means of a thermoelement have arrived at experiences and precautions which are in different respects similar to ours. The research described in the following pages was undertaken quite independently of theirs with a view to measurements of low temperatures in the cryogenic laboratory. In former investigations on this subject these precautions have never been specially considered nor is attention drawn to them by DEWAR and FLEMING in their investigation on the thermo-electric forces of metallic combinations at very low tempe ratures.

First of all we shall consider the construction of two similar thermoelements which were to be used for accurate temperature determination, the one as observation element, the other as comparison element. The commercial covered galvanoplastic copper wire has as a rule a sufficiently homogeneous structure to be used without further precautions as part of a thermoelement. If a

') Ann. de Ch. ct de Phys. 6 Sér. t. 27, 355, 1892.

¹) Wied. Ann. XXXI p. 6. 1887.

galvanometer is closed by a wire of this kind and the wire is heated with a BUNSEN flame at a sufficient distance from the galvanometer, it is not probable that one shall find a greater deviation than corresponds to a fraction of a microvolt. Not so with commercial German silver (even the best kinds) especially not if it has been strongly bent. Differences which give disturbances of some microvolts when part of the wire is heated to 130° are very common; in heating with a BUNSEN flame they become so capricious that one would be inclined to reject the wire altogether. When annealed with a BUNSEN flame the wire generally did not yet prove fit for use. Nor was this the case after it had been shut up in an asbestos box, put on a blacksmith's fire and afterwards cooled slowly. The German silver wires (1 m.m. section) which were used by me for the construction of thermoelements, were therefore carefully drawn straight, annealed with the aid of a battery of accumulators (28 Volt, 20 Amp.) 1) and cooled carefully by slowly diminishing the current. Both ends of the German silver wire are then connected with the galvanometer by means of copper conductors and avoiding sharp curves. The wire is immersed by parts in an oilbath heated to 130°, or stretched through a T tube, into which steam is led sideways which flows towards the two ends, by which the wire enters and leaves. In those parts of the wire which were near the connecting-screws supplying the current during the annealing, considerable irregularities are left. But apart from this, no greater

¹) Also NoLL, Wied. Ann. 53, p. 583 has annealed his wires in this manner.

differences than some tenth parts of a microvolt should remain. It the wire after repeated annealing and if possible after yet more careful cooling does not fulfil this condition, it is totally unfit for use.

If one succeeds in finding a piece of sufficient length, where the electromotive force by the aforesaid heating rises nowhere above $\frac{1}{2}$ microvolt, and which does not show any appreciable potential difference (less than 0,05 microvolt) at the therminals over a length of 50 to 60 cm., this piece is cut off the wire, and both terminals serve as the legs of the thermoelement. If there is some difference the worst terminal is chosen as the zero-leg, i. e. that which will be placed in ice. Along this part of the wire the differences of temperature will as a rule be much smaller than along the part which is used as measuring needle.

Further we must prevent the wire from being bent into sharp curves. The wire is to that end (see Pl. III fig. 5) enclosed in a thick-walled india-rubber tube C, through which it can be drawn, by soldering it to a thin auxiliary wire, which is worked through the rubber tube by means of a small ball. This rubber tube serves at the same time to isolate the German silver wire completely and to dry the element.

10. The protecting of thermoelements. Thermoelements consisting of bare wires, which are plunged into the bath, the temperature of which one wishes to determine, have the great advantage of indicating the temperature almost immediately. To be able to use those bare elements in each special case it is necessary to make sure beforehand that they can be plunged into the liquid gas, without any danger for chemical action or without generation of chemical potential differences.

As moreover bare wires cannot be brought into ice or steam (because of this action) the calibration of the element must be performed by plunging the element into suitable liquid baths (petroleum at 0°, oil at 100°) which are brought to the required temperature by ice or steam.

A bath of that kind is represented in fig. 1 and 2 Pl. III. The edges, g, which project from the steam or ice, must be protected as much as possible from exchange of heat with the air and by filling up with wool and closing with a non-conducting lid; air currents above the liquid must be prevented. Stirring appears to be indispensable, and there remain small differences of temperature which have to be determined separately. In calibrating the element by comparing with the hydrogen thermometer it is preferable to immerse the thermoelement and the fragile hydrogen-thermometer together in the one liquid bath, in that case, in order to protect the latter, a cylinder f is placed in the bath and the stirrer r (wooden rod through glass tube) is moved up and down in the exterior space.

As a rule however it will be necessary to insulate the wires of the thermoelement completely from the bath. This cannot be avoided even if one wishes to plunge the measuring needle immediately into steam or ice, or if the wires or the junctures run the risk of being attacked in the long run, either by the liquid gas or by the moisture of the atmosphere which condenses on the cooled element, when it is removed from the apparatus. Nor can it be avoided where in using bare wires chemical potential differences may arise which will endanger the accuracy of the observations even in shunt-circuits of considerable resistance, because they are so much larger than the thermoelectric potential differences.

Finally by enclosing the thermoelement in a separate covering one prevents the wires from being exposed to sudden great cooling, sometimes in one place, sometimes in another, which might have some influence on it. A priori it is not to be taken for impossible, that such irregular sudden coolings may influence the thermoelement, which is prevented by the envelope.

For these reasons it seemed desirable in the measurements hitherto performed to use protected elements.

If the wires of the thermoelement are protected special attention has to be paid to the heat, which is carried away from the juncture by the conduction of the wires. In precise determinations it must be negligible in comparison with the heat-supply from the bath in which the thermoelement is immersed. To increase the heat-supply the contact of both wires is soldered into a small block of copper a.

In several respects it is desirable to keep the resistance of the element small and it is therefore not allowed to diminish the conduction by taking the newsilver wire very thin: it has to go straight to the juncture in order to avoid sharp bents. Wire of 1 mm. section caused no difficulties.

The German silver wire is insulated by a glass tube b, (Pl. III, fig. 4) which is put into the india-rubber tube c; 50 c.m. of the copper wire of 1/2 m.m. diameter covered with silk is wound spirally round this tube ¹). If the spiral was omitted a variation of temperature of the juncture could be detected in some cases. The glass tube b_2 insulates the whole element, with the exception of the small copper block a, from the bath into which it is plunged. In previous constructions an attempt was made to replace the glass tube by a very thin-walled brass tube, which was insulated from the apparatus, containing the bath. Such a tube would have had the advantage of being able to be soldered to the copper block and therefore tightly connected to it. But the temperature of the juncture proved then to be no longer certain to $\frac{1}{50}$ degree, even when the thermometer was plunged very deeply into the bath.

It is very difficult to join copper and glass, especially if the joint has to resist steam and stand exhaustion. If the joint is not absolutely tight, moisture may penetrate into the element during the calibrating in steam and there cause disturbing potential differences. India-rubber tube tirmly tied round the glass is not sufficient. Ordinary cements melt at 100° or are difficult to remove. It is intended to try if a juncture of glass and metal according to CAILLETET's method can resist the considerable and repeated variations of temperature which the thermoelement undergoes; also a stuffing-box with screw-fastening on a glass ring might be tried.

But provisionally I have resorted to cementing with

¹) The mutual insulation of the turns of the spiral might be obtained by sealing a spiral of thin glass thread round the glass tube. sulphur, because it is not necessary to heat the element above 100° . On the copper block a small piece of tinned tubing is slid; tubing, block and contact place are soldered together, the copper block being heated with a pointed flame and resin serving as melting agent. The groove g between copper and glass is filled with melted sulphur and care is taken that the sulphur in the interior does not come in contact with the copper wire, which would soon be dissolved.

If such a tube cemented with sulphur has been heated in steam several times, as is often necessary for testing purposes, the sulphur is gradually pulverized. To prevent this interaction the joint is protected by a piece of vulcanized india-rubber which is renewed from time to time. When the copper tubing was used untinned, it was attacked by the sulphur especially at 100°. It is still to be proved whether tinning (or blackening) prevents this action sufficiently. But there is no difficulty in replacing the copper tubing or even the copper block and glass cover by a new one The element itself need not undergo any change thereby.

When the glass covers are fastened to both the legs, A and B, fig. 5, of the thermoelement, they are connected hermetically by an india-rubber tube and rubber-cement to the rubber tube which covers the newsilver wire. The copper wires K are allowed to remain free. The element is thereby enclosed in a completely closed space, communicating with the atmosphere by the tubes s_a , s_b only. By means of these tubes, dry air is sucked through this space under proper heating, entering by the first tube s_a , passing by the juncture c_a , through

the interior insulating tube into the tube C and further through the tube of the juncture c_b to the side-tube s_b . After the operation the side-tubes are sealed off.

The envelopes of the thermoneedles being of glass, one can always easily make sure between the experiments that no moisture has found its way into the apparatus. If this should be the case it can be removed by means of the side-tubes.

In order to bring the themoneedle into the apparatus in which the temperature is to be determined it is provided with a stopper as represented Pl. II, fig. 5, and if necessary the copper block a and the joint with the glass are protected in the way required by each special bath.

11. The testing of thermoelements. When completed the thermoelement is submitted to the ordinary test, that no current arises, when both junctures are at the same temperature. For this purpose it is connected to the galvanometer (§ 13) by suitable "current-make and break's" and "current-reverser" (see § 12) and as is usual, put into ice with both junctures.

In general this single test in considered sufficient. However in this test the temperature of the contactplaces differs only little from the surrounding temperature and defects might be overlooked which become considerable at greater differences of temperature. For this reason an obvious improvement consists in putting the two contacts into steam also and immersing them to different depths in order to see if by the method followed one has actually succeeded in avoiding the defects, which can be detected by this experiment. To this end the two needles of the thermoelement are put into two identical boiling apparatus as described in § 8.

When a needle of the thermoelement is heated above the surrounding temperature and the little block turned downwards a convection current of more or less importance will begin to flow in this needle. By observations with a third boiling-apparatus, in which the needle is placed with the block turned upwards we may ascertain whether possibly such a convection current can lower the temperature of the juncture somewhat.

Pl. III fig. 6 shows this steamcap. It can be drawn out to different lengths and the steam is supplied from a separate boiler through a tube wrapped up in wool. The whole steamcap is covered with felt. The water condensed in the interior space flows off by a capillary tube c, in the bottom. This capillary is closed by the drop hanging from it. The remarks made in § 8 with respect to the temperature of the steam are also applicable here. Moreover as an additional test the contacts are interchanged in both the boiling apparatus.

The thermoelement is finally subjected to a third test by plunging both contacts in a mixture of solid carbonic acid and alcohol, which to this end is poured into a DEWAR-vacuum-glass. After having been subjected to these tests the thermoelement is calibrated by comparing it with the hydrogen thermometer at different temperatures. Plate I represents the comparison in liquid oxygen, Pl. III, fig. 1 and 2 show the thermoelement together with the hydrogen thermometer immersed in steam and ice.

12. "Current-make and break's", commutators and "current-reserver's" with contact surfaces of mercury. In making measurements of the small thermoelectric potential differences it is necessary to avoid with the utmost care disturbing potential differences at the contacts in the apparatus, which serve for making or breaking the current. The method that presents itself at first is to use commutators of pure copper. In that case only small thermoelectric forces are possible as the circuit including the galvanometer wire usually consists of pure copper. But if the copper commutators are not made with the greatest care and packed in cotton-wool these disturbances are not to be neglected.

If the contact is made by causing mercury to flow together, potential differences at the place of contact are excluded. But the use of these contacts is necessarily accompanied with the introduction into the circuit of the considerable potential differences mercury-copper. These are bound to give rise to disturbing forces, if the contacts are not kept exactly at the same temperature. It is just the same difficulty as that caused by resistance-boxes wound with German silver wire. If the terminals of the separate resistances are not exactly at the same temperature disturbances must arise, which may influence the results especially in zero methods.

If on the other hand we succeed in keeping the fixed contacts of circuit and commutators at temperatures sufficiently near ') (as is also the case in resistance-boxes) these mercury-commutators have the great advantage

1) CHASSAGNY and ABRAHAM l. c. p. 361.

31

that with pure mercury one is perfectly sure of the contact, and that by a suitable construction of the apparatus the flowing together may be obtained by a slight motion of the hand as with a POGGENDORF-switch, while on the other hand it is well known that perfect contacts with plug-commutators are very difficult to obtain. When using an aperiodic galvanometer and a mercury-commutator the observer seated before the reading-telescope may take one reading immediately after the other.

For a long time therefore I have tried to make use of contacts obtained by causing mercury to flow together. At first I constructed very simple apparatus for this purpose, the principle of which may be seen from Pl. IV, fig. 1 and 2. By lifting the weight q the mercury in the tube b fig. 1 rises and causes contact between c_3 and c_2 ; by putting an additional weight the mercury rises in a and causes contact between c_2 and c_1 . Similarly in the apparatus fig. 2, a rise of the mercury in the tubes a and b causes contact between c_1 and c_3 , c_2 and c_4 , by a rise in the tubes d and c contact is obtained between c_1 and c_2 , c_3 and c_4 . The motion of the mercury is controlled by the strap f (a piece of the belt of a lathe) Several difficulties, however, remained in the use of these apparatus, viz. uncertainty of adjustment, splashing of mercury, necessity of cleaning the apparatus from time to time, difficulties of properly protecting the contacts against changes of temperature.

These difficulties were removed by constructing completely closed glass apparatus. Plate IV, fig. 3 and 4, and Plate V represent the very handy patterns invented by the technical attendant of the laboratory Mr. BLOM. In the first place in the "commutator" fig. 3, the contacts of the circuit and the mercury in the glass apparatus are obtained by platinum wires sealed into the tubes C_1 , C_2 , C_3 . Further the apparatus is mounted on a little board p, which can turn easily round an axis x. When turned to the left c_1 and c_2 , when turned to the right c_2 and c_3 are in contact. In the position represented in the figure the circuit is broken. The platinum contacts consist of interwoven thin platinum wire, the connecting pieces of the tube C and the small brass blocks b, being therefore very flexible. The latter are insulated by ebonite, and joined to the rest of the circuit. If the juncture of the platinum, enamel and glass is not absolutely tight, as appears at the mercury pump, this is remedied by putting on some shellac. The glass is previously cleaned in the manner described in § 4 and is exhausted with the mercury-pump and then filled with mercury; afterwards dry air is admitted, which serves as cushion for the mercury when the commutator is reversed; the auxiliary tubes which are used in this operation are afterwards sealed off. Owing to these precautions the mercury-surfaces are now after several years just as clean as at the moment the apparatus was delivered. Care has been taken that the resistance along c_1, c_2 is the same as along c_2, c_3 ; the small difference which remains is constant and may be measured and taken into account if necessary.

The "current-reverser" fig. 4 is constructed on the same principle as the commutator. In the bent tube a,

in the position A fig. 5, the mercury makes contact between the mercury tubes d_1 and d_4 , and between d_2 and d_3 which open out into a; in the position Cthere is contact between d_1 and d_2 and between d_3 and d_4 . In the position B the contact is broken. The apparatus is again mounted with cork fig. 4, k, on a little board p, which can be turned round the axis xby a slight movement of the finger The tube l (fig. 4 and separately fig. 6 in the original state when the tubes for cleaning, exhausting and filling are not yet sealed off), forms the connection between the different branches of the tube a, and in this manner forms a continuous space above the different mercury levels. Again care is taken that the resistances along C_1 , C_2 and C_3 C_4 are the same as those along C_1 C_3 and C_2 C_4 and here also the difference that might still exist is constant and can be measured.

The apparatus including the wires is packed in cottonwool in a large box, which is further carefully protected against heat radiation and conduction; it is placed in the room for magnetic measurements, where of course care is taken to assure a constant temperature.

13. Galvanometer. In the measurements a galvanometer made by BRAUN (cat. 1894 n^o. 371) was used. As suspending wire a beautiful quartz fibre is used. I have to thank this fibre to the special kindness of Prof. V. A. JULIUS, who at my request made this fibre in the desired dimensions and a number of similar ones as a reserve.

The suspensive contrivance of the galvanometer was modified as represented in fig. 2 and requires no further explanation. To fasten the fibre its terminal, supported by

suitable small clipstands, is brought near the little cylinder which is also held in a small stand; with a needle



the fibre is pointed into the fine groove, which has been drawn on the flat side of the halfcylinder in the direction of the axis; a piece of shellac is laid on it and the end of the small cylinder is heated until the shellac melts. 1) At the other end in the same manner a small eye is attached, on which also a groove has been drawn. This is done by laying it on a mica plate and heating on the other side with a small soldering bolt. When the shellac is completely hardened the bellmagnet is suspended from the fibre; it has never happened that the connection gave way. The considerable

Fig. 2.

and often irregular changes which occur when silk fibres are used in consequence of change, of moisture and temperature are excluded by the use of the quartz fibre.

The middle ring of the galvanometer is easily adjusted in the meridian by a little mirror leaning against this ring and a magnetic theodolite. The galvanometer is provided with the bobbins the coil of which has a resistance of 3 ohms. The four coils are connected in two parallel sets of two in series.²) They are pressed against the middle

²) The soft iron rings are not applied. The galvanometer therefore is not aperiodic but the changes of zero and sensibility may be better studied, also in reference to the changes of terrestrial magnetism.

ring and in order to attain a good fit they are surrounded by india-rubber rings; little corks are thrust into the openings of the bobbins. Over the top of the galvanometer a glass bell is fixed (see fig. 3) by means of a cork

Nº677

Fig. 3.

-

cut in two pieces. In this manner the galvanometer is totally closed and disturbances by dust, small spiders, etc., that might otherwise be found cannot occur. The instrument with wires is packed in cotton-wool and protected by a pasteboard cap, in which a hole is made through which the readings are taken. In this manner the conditions are fulfilled, under which the galvanometer in a permanent position may be used for a long time without any change; a calibration of the sensibility in its dependance upon the deviation once made, remains correct for a long time and accidental disturbances are excluded. A very



¹) Comp. Boys, Phil. Mag. 37. 463. 1894.

firm disposition was obtained by placing the galvanometer on a marble slab fixed with plaster to an observation pillar, which in its turn was firmly fixed with plaster to the great pillar of the magnetic room. On this same pillar is placed the reading-apparatus, described Proceed. April '96. Comm. nº. 25, by which the deviations of the galvanometer mirror are read with great accuracy on a glass scale made by HARTMANN and BRAUN (compared with the standard metre). The great pillar (fig. 4) consists of a block of masonry erected on three rows of barrels with perch poles, which is built out sideways at the top and forms a continuous floor of great stability under the ordinary floor of the magnetic room. On this floor between the beams of the ordinary floor the proper observation pillars are erected. Galvanometer and scale are therefore mounted on the same mass of brickwork in an absolutely fixed relative position. The stability of the zero is excellent in consequence.

14. Standard cell for comparison. The sensibility of the galvanometer can be determined by absolute measurements; as a rule however for the determination of electromotive force in absolute measure a comparison with a standard CLARK-cell (now one constructed by FUESS) is made. To eliminate the changes in the sensibility of the galvanometer during the determinations of the temperature a thermoelement (newsilver copper) is used, of exactly the same construction as the observation-element and the junctures of which are placed in steam and in ice. It is a great convenience 37

especially in this case that this comparison-cell can itself be placed in ice and steam and stay there as long as is desired. The boiling point apparatus serving for this purpose is described in § 8 (Pl. I, fig. 2.) The velocity of evaporation is kept as constant as possible, so that only a correction for the change of the boiling point with the barometer has to be applied, for which correction use is made of a calibration performed with this element. The element for comparison is compared from time to time with the CLARK-cell. If it should appear by absolute measurement that the thermoelement, when treated always in the same manner, always gives the same electromotive force at the same temperature, one would be certain of the electromotive force within $\frac{1}{10000}$ after having made the aforesaid correction and the element itself might then be used as a standard for the measurement of electromotive forces. Although this constancy is highly probable, I have not been able to put it beyond all doubt so far.

In determining a temperature the reading of the deviation of the galvanometer produced by the observation element, is immediately followed by a reading with the comparison element. Pl. I fig. 2 shows the way in which use is made of the mercury-commutators for this purpose. Two commutators and one "current-reverser" are used to send the current of the observation element (oa, gh or if, od) and the comparison element successively (ob, gf or ih, od) through the galvanometer in two directions. The measurements are repeated with a second resistance.

Further by turning the commutator to the right

PLATE I.





Communication Nº. 27.









Communication Nº. 27.

Fig: 5. Nº 100.





PLATE V.



Communication N°. 27.

(oa, gh or if, oe) the connection of the wires being as given in the figure, the current of the two elements in series is sent through the galvanometer in two directions. If the copper connection at w is then reversed, the elements are placed in opposition (oa, gh or if, oe), the same result being obtained independently by changing the copper contacts at v (oa, gh and if, oe). In each of these measurements again two resistances are used successively.

Ultimately by shortcircuiting the wires, connected to the commutators at v and w, it may be tested whether the commutators are free of current.

In this manner data are obtained for different independent determinations of the same thermoelectric force, expressed in parts of the EMF of the comparison element between 0° and 100°.

By means of observations, made with the element at 0° and 100° it is possible to express the measured electromotive force in the EMF of the observation element at 0° and 100° .

Finally by replacing the observation element by the CLARK-cell at C_1 and C_8 it becomes possible to express the comparison element in terms of the standard cell and so, independently of the supposition as to the constancy of the comparison element, to compare different series of readings with the comparison element. The results of these measurements will be published in a subsequent communication.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

Director of the Laboratory.

No. 28. (REPRINT).

OP THE

Dr. J. VERSCHAFFELT. Measurements on capillary ascension of liquefied carbonic acid near the critical temperature. (With a plate). (Translated from: Verslagen en Mededeelingen der Kon. Akad. v. Wetenschappen te Amsterdam, 27 Juni 1896, p. 94-103).

EDUARD IJDO - PRINTER - LEIDEN.