

Citation:

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b'_k for β''_k indicated there, only some types lead to simple results¹⁾, among others also (with some restriction, see later on) the exponential type proposed already before by KAMERLINGH ONNES:

$$b = b_g - (b_g - b_0)e^{-\alpha(v-v_0)}$$

Already in 1901 (Archives Teyler (2) T. VII, Troisième partie) I tested (see p. 14 et seq.) the values of b for H_2 and CO_2 , by this equation²⁾, and found a good agreement. But that I then found deviations with respect to the critical quantities is simply owing to this that I at the time did not take b_g variable with the temperature, and that therefore observations of H_2 at 0° C. can by no means give a final decision about the quantities at -241° C.

It is of course only of formal importance, when in the above relation and others at last b_g and v_0 are replaced by critical quantities, so that the relations (21) are satisfied. But this will be discussed in a subsequent paper.

Fontainivent sur Clarens, January 1914.

Physics. — “An apparatus for the determination of gas isotherms up to about 3000 Atm.” (Continuation.) VAN DER WAALS-fund researches N^o. 6. By Prof. PH. KOHNSTAMM and K. W. WALSTRA. (Communicated by Prof. J. D. VAN DER WAALS.)

(Communicated in the meeting of January 31, 1914).

B. *The volume measurement.* (Continuation).

CONVEYANCE OF THE GAS INTO THE MEASURING TUBE.

In the previous communication the question was answered how the volume is determined of a quantity of gas which is in the measuring tube, above mercury. Now we shall have to describe how we get the gas quantity that is to be measured, in this position. For this the most intricate part of the apparatus is required.

As is known AMAGAT's measuring tubes consisted of piezometers

¹⁾ Also v. d. WAALS' relation in the general form $\frac{b-b_0}{v-b} = f \left[1 - \left(\frac{b-b_0}{b_g-b_0} \right)^n \right]$ with b_0 constant gives perfectly impossible results, among others n varying between 8 and 30.

²⁾ It is easy to see that the relation used there, viz.

$$b = b_\infty \left(1 - \theta e^{-\beta \frac{v}{b_\infty}} \right)$$

by the application of suitable substitutions for θ and β is identical with the above relation.

of the well-known CAILLETET form. The quantity of gas is measured at low pressure, the piezometer is placed in a steel vessel filled for the greater part with mercury and further with a transmission liquid; and by then forcing up this liquid by means of a hydrostatic press we expel the gas from the piezometer reservoir, and convey it to the calibrated stem. Through this way of procedure, however, we are compelled to confine ourselves to a comparatively small quantity of gas. For if we should want to start from e.g. 1 l. of gas under normal circumstances, the steel pressure vessel must itself have at least a capacity of 2 l. And to construct a vessel of such a capacity, which can be perfectly closed, and does not leak at 3000 atm., is, if feasible, so expensive that its execution is entirely out of the question. Yet it is very desirable not to work with small quantities that the volumes may not become too small at high pressure. To enable us to work with a quantity of gas of 1 l. without the parts of the apparatus exposed to high pressures becoming of too large dimensions, an apparatus was constructed which allows us to compress the quantity of gas to be measured first to from 50 to 100 atm., and then convey it to the measuring tube proper.

A first requirement is that throughout the experiment the measuring tube must be continually exposed to the same pressure outside and inside, because else the thin glass tube of course at once gives way. Originally it was the intention to convey the quantity of gas quantitatively into the measuring tube, after its normal volume had been determined. Owing to unforeseen difficulties, to which we shall revert further on, we have not yet succeeded in realizing this quantitative transference, so that in the experiments which will be described in what follows, the quantity of gas which was worked with, has been only determined by a measurement of its volume e.g. at 100 atm., the compressibility between 1 and 100 atm. having to appear from separate determinations. We shall discuss this more extensively later on in the description of the experiments, and shall now first proceed to give a description of the apparatus, used for the conveyance of the gas into the measuring tube.

It consists of three pressure stages: an (unprotected) glass part for the pressures below two atmospheres; a part that serves to compress the gas from 2 to 50 or 100 atm.; and the measuring part proper. The glass part consists of a vessel *A* of a capacity of ± 1 l.¹⁾, placed in a copper thermostat with glass windows (repre-

¹⁾ As we have not made use of the accurate capacity of this vessel for the experiments which will first be described, we shall not enter into a description of its calibration as yet.

sented schematically in fig. 6). At its bottom the vessel *A* passes into a tube *B*, which is in connection by means of a side tube with a GAEBDE-airpump and other auxiliary apparatus to be used in the filling. The tube *B* passes through the bottom of the thermostat, and is connected with a large pear-shaped mercury bulb by means of a rubber tube.

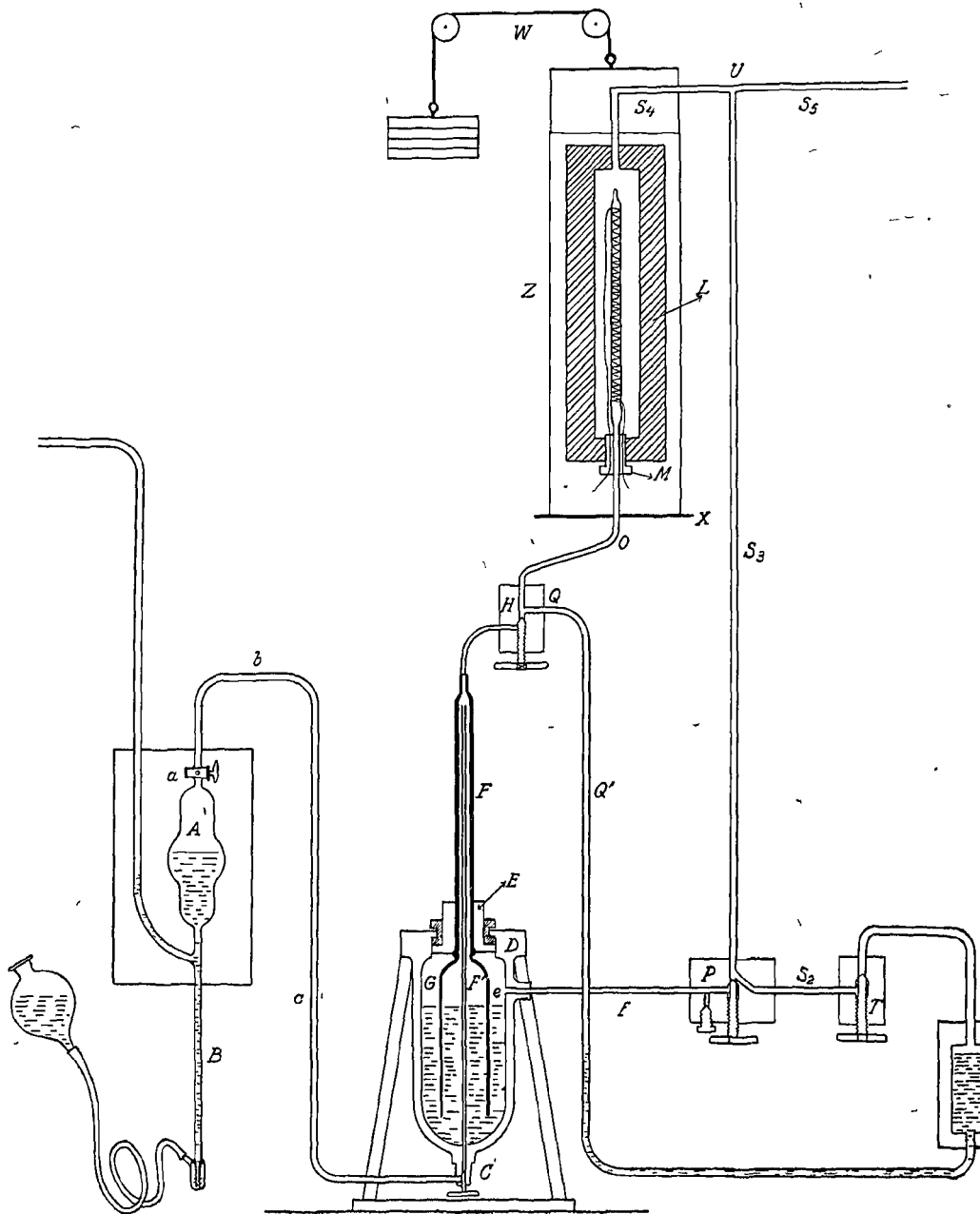


Fig. 6.

At the top of the glass vessel there is a cock a , which, opened, gives access to the glass tubing bc , which leads to the steel high pressure cock C . This cock has been specially constructed for the quantitative transference of gases, as was described in these Proceedings already before.¹⁾

With this cock we reach the second "pressure stage". It consists chiefly of a large cast-iron vessel D of more than 2 l . capacity, which can be closed at the top with a heavy iron piece E with bayonet joint and leather packing. This piece E is bored through and a heavy glass tube F , of more than barometer height, has been cemented in it. On its bottom this tube F is attached to a glass jar G , of about 1 l . capacity, at its top it passes with a sealing-wax joint into a steel capillary, which gives a connection with the high-pressure-cock H , which can shut off the third "pressure stage".

The said cock C is fastened to the bottom of the iron vessel D ; the vertical opening is in connection with a thin glass tube F' , of a length of at least 80 cm. When the piece E with the glass jar G is placed into the iron vessel, the tube F' gets inside F , as is shown in the figure. Through an aperture e the vessel D is further in connection with a steel tube f , which connects D with the high pressure-three-way-cock P , where the third pressure stage begins again. The tube f is again connected with D by means of a steel-to-steel closure, as was already described in this series of communications²⁾. On the steel tube f , the end-piece of which is ground conical, a double steel cone g is screwed, which is in its turn pressed against D by means of a flange plate h with bolts, fastened in the iron vessel D' and nuts. (Cf. fig. 7). The closure of E in D is elucidated by fig. 7a and 7b. A steel ring E_2 is pressed into a leather ring E_3 , which is V-shaped in section by means of a plate E_1 fastened with screws on E (see the figure). The leather ring extends through the pressure, presses therefore against E and D , and effects in this way the closure. E is held in its place by a piece D_1 with bayonet joint. When the projecting sectors D_2 are rotated so that they get before the opening D_3 of the rim D_4 (see fig. 7b), the piece D_1 can be taken out, and with it the piece E and G .

The highest pressure stage consists in the first place of the observation vessel proper L , a heavy steel tube of ± 1 m. length and

¹⁾ These Proc. XI, p. 915.

²⁾ These Proc. XV, p. 1024 and fig. 2.

1,65 cm. bore, which is calculated to resist a pressure of 4000 atm and is suspended on the ceiling by means of rods. At the bottom

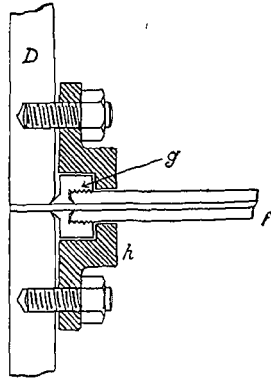


Fig. 7.

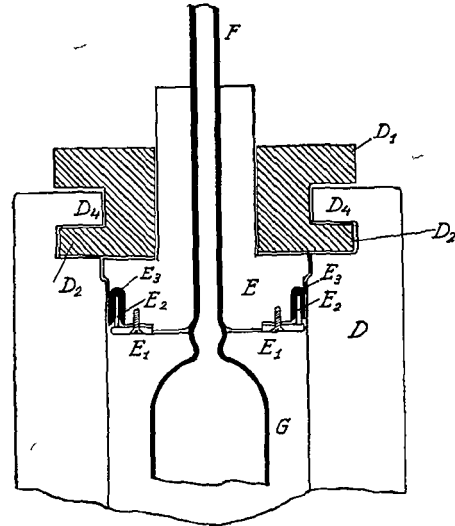


Fig. 7a.

L is closed by a shutter piece *M*, the construction of which we shall discuss presently. *M* is bored through, and this boring terminates in a steel tube *N* (fig. 11), to which the glass observation tube is

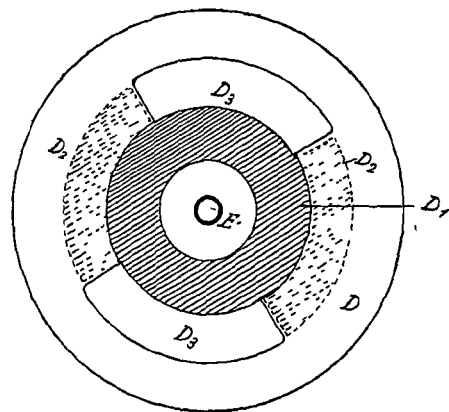


Fig. 7b.

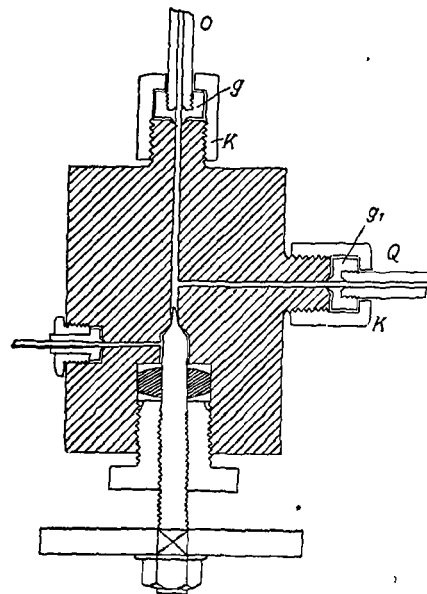


Fig. 8. Cock H.

fastened. The other side of the channel in the shutter piece M is connected through a cone and nut K^1) with a steel capillary tube O , which leads to the before mentioned cock H . The construction of this cock appears from fig. 8. The tube O always remains in communication with the righthand side opening, which opens again into a steel tube Q' , which leads further to the mercury vessel R . By opening or closing the cock H we can, however, bring O in connection with, resp. shut off from the glass jar G in the iron vessel D . The mercury vessel R is by means of a steel tube S_1 in communication with a high pressure cock T , which can effect or prevent the communication with the steel tube S_2 . And finally this tube S_2 again leads to the before mentioned high pressure three-way cock P . The construction of this cock appears from fig. 9. The stopper t only serves to shut off an opening, through which at the end of an experiment when one wants to lead back the gas into the jar G , oil can escape. It is seen that S_2 is always in communication with a third tube S_3 , but that a communication can be made or broken off of S_3 and S_2 with the tube f and so with the second pressure stage by the opening or the closure of P . S_2 terminates in a τ -piece U , which on one side is in communication through the tube S_4 with the upper side of the observation vessel L in entirely the same way as the tube O with the bottom side,

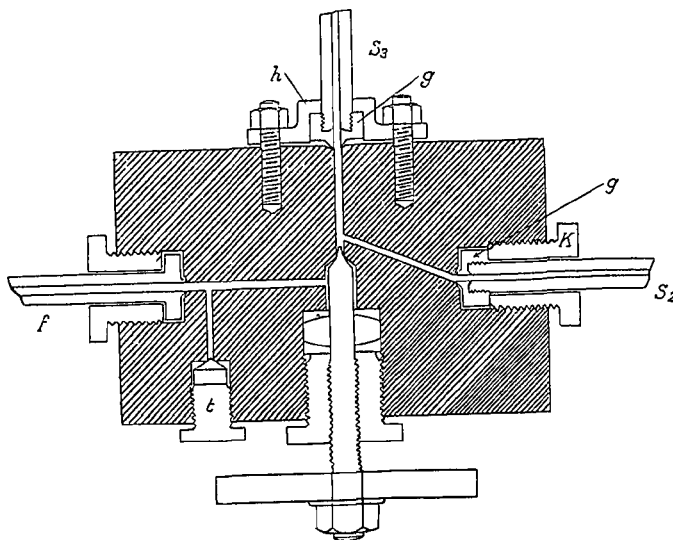


Fig. 9. Cock P .

on the other side through S_4 with the hydrostatic press, which causes the pressure.

¹⁾ Cf. the description of these connections lower down.

By the aid of this arrangement it is now possible to fill the measuring tube, which is fastened at N on the piece M with the gas that is to be measured, this glass tube being always subjected to the same pressure on the inside and on the outside.

After the whole system of tubes and all the cocks etc. have been cleaned, the mercury vessel R is filled entirely, and the vessel D half with mercury. By the application of a slight pressure the mercury in Q rises, and fills the whole tube Q up to the cock H . Then the cock T is closed, so that the mercury in Q cannot move up and down any longer. When this pressure is applied, the vessel L outside the glass tube has filled with the oil, which is used as pressure transmission liquid. Now all the cocks except T are opened, and the whole system $AabcF'FON$ is exhausted by means of the GAËDE-pump. Then the mercury from D rises in the jar G and reaches barometric height between F and F' . Now the apparatus may be rinsed once or twice with gas by admitting gas at B by means of the mercury reservoir, and then making a vacuum with the GAËDE-pump. If we now want to bring a definite measured quantity of gas into the measuring tube, we close a , and admit a quantity of gas into A . When the mercury reservoir is then raised, a quantity of gas is isolated in A , the pressure, the volume, and the temperature of which can be determined. If now the glass cock a is opened, the gas flows into the exhausted space cF' . Now the mercury in F falls, and by raising the mercury reservoir which is in communication with B , we can now expel the gas from A to D . If we want to do this quantitatively, we must raise the mercury reservoir so much that the mercury overflows at b , and fills the whole tube bc , and that at last it becomes visible at the upper end of F . C is then closed. The gas is then under a pressure of about one atmosphere in the jar D , and further in FON and in the measuring tube.

By the hydrostatic press, resp. through the way S_5US_5Pfe we now increase the pressure. The mercury in D then descends outside the jar G and rises inside it, and expels the gas more and more from the jar towards F . The pressure in the measuring tube then rises, of course. But U being in communication with L through S_4 , the pressure inside and outside the measuring tube is always the same. If we want to convey quantitatively, the pressure must be raised so high that the gas has been entirely expelled by mercury from G and F , and the mercury has reached the steel capillary above F and finally H . Then H is closed. Now the communication between the inside and the outside of the measuring tube is broken.

We should, therefore, take care that in this condition no great variations of pressure can take place, which might make the measuring tube burst. This is controlled by a spring manometer, which is in connection with the hydrostatic press. In the operation it appears, however, that a few atmospheres' difference of pressure is not yet dangerous to the measuring tube. The dimensions of the measuring tube must be so chosen in proportion to the jar G that all the gas has been expelled from G and F by mercury before 80 to 100 atm. have been reached, as the unprotected glass tube F cannot resist a higher pressure. Now P is closed. This separates the high pressure division, in which the measurements take place, entirely from the second pressure stage, D etc. For H has already been closed (see above). Now T is opened. This opens again the communication (by the way S_4 , US_3 , PS_2 , TS_1 , $RQHO$) between the inside and the outside of the measuring tube. If we now continue to raise the pressure by the hydrostatic press, the mercury rises in H resp. O , and pushes the gas further and further above it, till at last the mercury reaches the tube N and then the measuring tube. Still further increase of pressure then brings the mercury into contact with the platinum contacts in the measuring tube one after another. All through the measuring tube remains constantly exposed to the same pressure on the inside and on the outside. When we want to suspend the measurements temporarily, this continues to be the case. For then a cock in the hydrostatic press is closed which shuts the conduit S_4 . The closure of the apparatus is so perfect that when this cock is closed the high pressure stage ($LHRTPU$, and the connecting system of tubes) can be left at a few hundreds of atm.'s pressure for weeks, without a trace of leakage being observed.

This perfect closure is obtained by the application of steel-to-steel closure everywhere. Only in the cock T it is inevitable that liquid under high pressure is in contact with packing material. (In the cocks P and H there is of course also packing material, but this packing material belongs to the second "pressure stage").

All the couplings are again of the system indicated in fig. 7 and 8, of course modified according to circumstances at the different places. Thus the couplings for the cock P are represented by fig. 9. A steel cone g is always found, which is then pressed against the piece with which it is to be connected by a nut K or the flange plate h . In the former case the thread of the screw is left-handed, so that when the nuts K are turned on, the cone is screwed tighter, instead of being unscrewed. This precaution is unnecessary in case of a

flange plate (fig. 7 and 9). The flange plate is pressed tight by bolts and nuts.

We must discuss the piece M , on which the glass measuring tube is fastened, somewhat more fully. This fastening seemed an insuperable difficulty for a long time. We have said up to now that the pressure inside and outside the measuring tube was the same; this is true, however, only by approximation. For the way $RQOMN$ is filled with mercury, the way $RS_1S_2S_3S_4$ with oil, and the difference of height of the measuring tube and R certainly amounting to 1.5 m., there prevails a pressure inside the measuring tube of about 2 atm. less than outside it. The different kinds of cement which we used to fasten the measuring tube on N (CAILLETET cement, with or without shellac, sealing wax, also packing material put between, such as ivory) were always cracked by the pressure, even though sometimes only invisible cracks arose. On account of the excess of pressure outside, oil then entered the tube from the outside, and rendered the measurements impossible by contamination of the mercury.

At last it was resolved to platinize the measuring tube over some centimeters' distance on the bottom side, to coat this with copper, and then to solder it to the copper tube k fastened on the steel piece N (Fig. 10). Now it seemed that a solution was found, but a new difficulty presented itself. When pressure brought the mercury into the tube, it could come in contact with the tin when it passed the place of soldering, and the amalgam formed contaminated the measuring tube. To prevent this the tube was lengthened at the bottom by a conical piece l , which fitted in a conical part of the steel pipe N . Though it was tried, besides, to improve this closure with zapon lac, the place of soldering was not yet sufficiently protected. We then drew out the measuring tube some centimeters into a point m . When the gas is compressed in the tube, part of it will be enclosed in the small space n outside the drawn-out point. We must then for the present give up the thought of a quantitative transference of a quantity of gas. Besides, care should always be taken that during the measurement of isotherms the mercury does not get below the drawn-out point m , because then the quantity of gas in the measuring tube might change. But that the soldering place now remains separated from the mercury by gas up to high pressures, is at present an indispensable advantage.

In the steel piece M there are four passages p , and through each of them passes an insulated wire. The passages end at the top in a conical widening. In this fits a conical ivory ring r , and in this a copper cone q . The wire insulated by the passage is soldered to the

bottom side of the cone. The upper side of two of these cones is connected with beginning and end point of the volume wire. Only

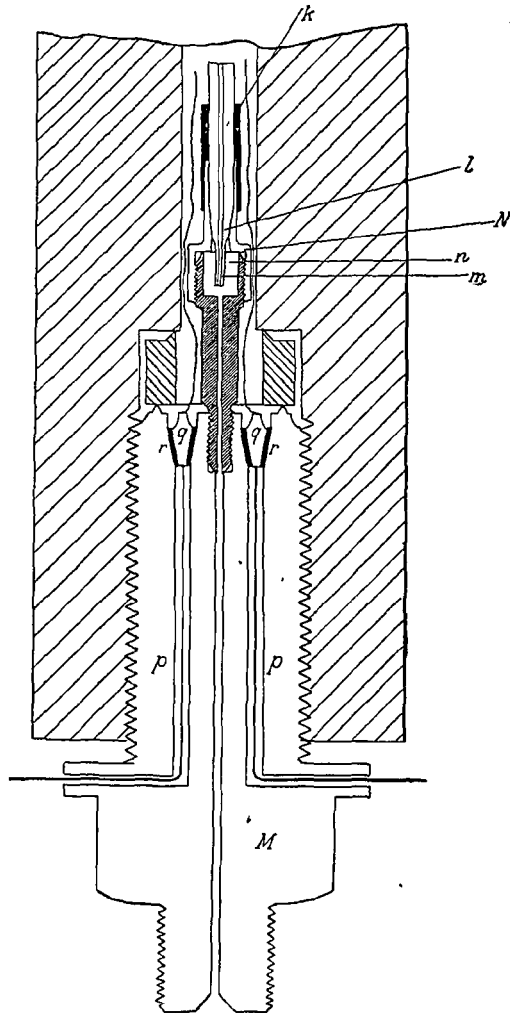


Fig. 10.

the upper side is under pressure, and everything is close fitting on account of the conical form, so that now we have an insulated electrical connection with the measuring tube.

A glass tube closed at the top, on which a platinum wire is wound bifilarly is hung on the measuring tube. The ends of the wire are connected with the two other copper cones.

We shall come back to this in the description of the temperature measurement.

The hydrostatic press.

The pressure is furnished by a SCHÄFFER and BUDENBERG hydrostatic press of the known construction, only heavier than usual according to the circumstances. This press is provided with 4 cocks

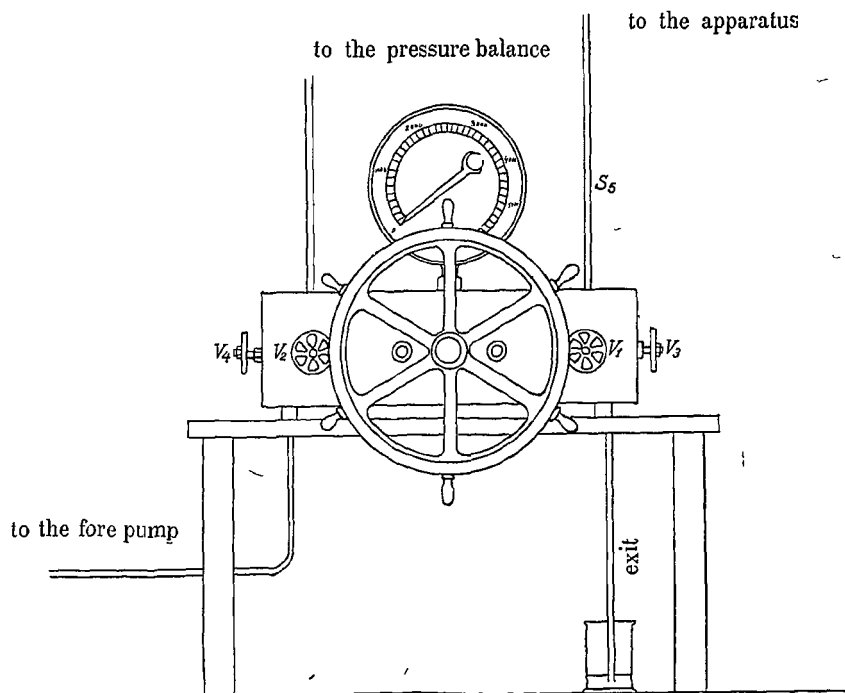


Fig. 11.

(fig. 11). The tube S_5 is in connection with one of them V_1 , and it is this cock that is turned off when in the evening the work is suspended after the measuring tube has been filled with gas. (cf. above p. 829). V_2 can open, resp. break off the communication with the large pressure balance. Here the tube ends, which joins the pump with the "head" A and the space C (fig. 1) of the pressure balance. All the couplings are effected steel to steel as above. V_3 is the exit-valve, V_4 bars the way to the fore pump. This fore pump is an ordinary oil suction- and forcing pump, which can carry the pressure up to 800 atm. So when the whole space beyond V_1 has been filled up to that pressure, V_4 is closed, and the pressure is further increased by means of the large wheel of the press. On the way between V_4 and the fore pump there is still a \perp -piece. The branch way which is formed here, may be shut off by a high-pressure cock of ordinary construction. This branch

way leads on one side to the "head" of the little pressure balance, on the other side to an accurate spring-manometer, which can indicate up to 300 atm. As has been said above, during the time that there is no communication between inside and outside of the measuring tube the pressure is regulated with the aid of this spring manometer.

On the large press stands a large spring manometer of SCHAFFER and BUDENBERG, which can be used up to 5000 atm.; it serves for a preliminary orientation about the prevailing pressure.

C. *The temperature measurement.*

It was originally the intention to measure the temperature immediately by the side of the measuring tube, so inside the vessel L . The third and fourth insulated wires in the piece M were at first destined for this purpose. But an accurate preliminary investigation, directed to this end, showed that no accurate temperature measurement could thus be attained. For as LISELI and LUSSANA have already demonstrated, the resistance of a metal wire does not only change in consequence of the temperature, but also through the pressure. And this latter variation appeared to be by no means regular. After increase of pressure a wire sometimes returned to its original resistance at atmospheric pressure, sometimes permanent changes of resistance appeared. Besides it would have to be ascertained empirically separately for every wire, how much the change of the resistance with the pressure is, for these changes are by no means equal for wires of seemingly the same material. It is, however, required for such a gauging of the resistance wire that the wire can be placed under different pressures in the pressure apparatus, the temperature being left constant. This can practically not be achieved in another way than by enclosing the whole pressure apparatus in a thermostat, and by taking, under the necessary precautions, the temperature of the thermostat for the temperature of the resistance wire under pressure. But then it is much simpler to apply the same thing directly in the measurements, and assume then too the temperature of the vessel L and its contents to be equal to that of the surrounding thermostat.

A *thermoscope* inside L is, however, indispensable then. In consequence of the compression, resp. dilatation heat of the gas in the measuring tube, namely, variations of temperature of the magnitude of one degree occur inside L . If there is no *thermoscope* inside L , much time may be needlessly lost in making sure that the stationary

state has returned in L . The bifilarly wound wire now, placed on the top of the measuring tube (cf. p. 831) supplies the want of such a thermoscope. This resistance is led outside by the third and fourth insulated wires of the piece M , and brought in connection with a WHEATSTONE bridge. The galvanometer of this combination indicates if the stationary state has set in.

Separate experiments made at atmospheric pressure, so that a resistance thermometer can be put in the space inside L , and moved to and fro, have proved that when the stationary state in L has set in, the same temperature prevails everywhere in L ; at least for the temperature at the top and the bottom of L (making use of the thermostat which is to be described presently) no difference of $0^{\circ},01$ could be demonstrated.

It also appeared that the temperature measured within L and in the thermostat that surrounds L , agreed to within the same amount. This was, however, not the case until not only the whole piece L , but also the closing pieces M , projecting at the top and at the bottom, and a part of the adjoining tubes had been enclosed in the thermostat. In a smaller apparatus constructed first, in which the extremities of L projected outside the thermostat, differences of the order of magnitude of 1° could be demonstrated inside L .

The arrangement of the thermostat can be sketched in a few words. Round L on a steel cable W , which runs over pulleys fastened to the ceiling, hangs a plate-iron cylindre jacket Z balanced by counterpoises; it can be slid up and down a few d. m. On the tube O , which leads from the cock H to M is placed oiltight by means of a packing box an iron circular plate X , whose section is a little larger than that of the cylindre. At its bottom the cylindre carries a flange, which can be fastened by bolts and nuts on the plate, when the closing piece M and the tube O have been sufficiently screwed tight by means of the nut K belonging to it. A leather packing between flange and plate renders this closure oiltight. The cylindre jacket remains open at the top. An oil pump worked by the repeatedly mentioned transmission shaft then fills the whole thermostat with oil from the large iron store reservoir. By means of a stop-cock fastened in the plate X (not drawn) and a hard lead tubing connected with it, the oil can again be collected in this store reservoir. In a fixed position attached to the cylindre jacket, and therefore moving up and down with it is a stirrer, which when it has been put in its place can again be set going by the transmission shaft. Inside the cylindre a large toluol thermoregulator is suspended, which is in connection with a gas flame which plays against the

plate-iron cylindre jacket. By its aid the temperature can be easily kept constant to within $0^{\circ}.01$.

The temperature is determined by a platinum resistance thermometer, which is inserted in a WHEATSTONE bridge formed by a HARTMANN and BRAUN resistance box. The galvanometer is a HARTMANN and BRAUN mirror galvanometer. The image of the incandescent rod of a NERNST-lamp is thrown by a mirror and a lens on a large scale fastened on the wall. The sensitiveness of the instrument is such that a deviation of $0^{\circ}.01$ corresponds with a deviation of about 6 cm. on the scale. So it can be seen all through the room whether the temperature remains constant, resp. how much it changes. The indication of the thermoscope inside *L* is thrown on this screen in the same way (only the NERNST-burner has here two incandescent rods to distinguish it). Accordingly the observer, who is engaged with the pressure balance or some other part of the apparatus, can ascertain from far whether the stationary state has set in.

The resistance thermometer is gauged with the same leads and in the same bridge arrangement as that with which the measurements take place. For this purpose it is placed by the side of the chief-temperature-normal of the laboratory in a tube filled with oil in the thermostat which surrounds the vessel *A*; the temperature is here kept constant in the ordinary way.

Amsterdam.

Physical Lab. of the University.

Botany. — "*Experiments on Hybridisation with Canna indica.*"

By J. A. HONING. (Communicated by Prof. F. A. F. C. WENT.)

(Communicated in the meeting of January 31, 1914).

Among the plants which my Javanese gardener planted in the beginning of 1910 in order to make the empty space round the house look somewhat like a garden, there were two varieties of *Canna*, which occurred as escapes on the high bank of the Deli river. One of them had leaves entirely green, green bracts, a green stem, small red flowers, with yellowish labellum and fruits, which in an unripe condition are green. This variety completely corresponds to the plants, grown from seeds, which I received as *Canna indica* from the Botanic gardens of Buitenzorg. The other had somewhat darker leaves with a red edge and the flowers were also of a somewhat darker red. Further the stem was dark red as were the conical papillae on the unripe fruits.