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**XLII. On a Method of Determining the Absolute Density of a Gas.** By J. JOLY, B.E., M.A.\*

THE method still in general use for the accurate determination of the density of a gas is that of Regnault, improved from the conception of Biot and Arago, by the addition principally of the counterpoising vessel. This method is not free from objections.

The gas is weighed in the vessel in which its volume is measured, and as this is necessarily a large vessel, of considerable weight, the weight of the gas bears but a very small proportion to the total weight observed. Again, from the great bulk and surface of the containing vessel, it is in itself a difficult object to weigh with a high degree of accuracy, more especially when exposed, as it is, between the first and second weighings, to the manipulation incident in filling it at a known temperature.

Further, in the determination of the volume of this vessel there arises, as Lord Rayleigh has lately shown†, an error due to the variation of pressure within the vessel when it is weighed, vacuum in the first instance, full in the second. This error, which escaped Regnault, is very considerable in this method.

If, again, there is an object in economizing the gas, Regnault's method is wasteful, as the "washing out" of so large a vessel with the gas necessitates a far greater expenditure of gas than is subsequently required for the actual determination. Without referring again to these objections to the method of Regnault, it will be seen that they are either much reduced in importance or eliminated in the method to be described.

In this new method the measurements of the volume and of the weight of the gas are effected in separate vessels. That in which the gas is weighed is small, the gas being under high pressure within it. That in which the volume is subsequently measured may, on the other hand, be as large as may be desired. We are not concerned with its weight.

The vessel which I have in use for holding the gas, when being weighed, is of copper, spherical in form, about 6·7 centim. in diameter, made up of two hemispheres, the walls being about 1 millim. in thickness. The hemispheres are brazed (not soft-soldered) together within a belt of copper about

\* Reprinted from the Scientific Proceedings of the Royal Dublin Society, June 18, 1890.

† Proc. Roy. Soc. xliii. p. 356.

$4\frac{1}{2}$  millim. wide, and 1 millim. in thickness. The vessel must be quite staunch. Its internal volume is just 160 cub. centim. It is closed by a small screw-valve, having a side tubulure for attachment to the various apparatus. The valve-spindle of steel works through a small stuffing-box to prevent the escape of gas along the shaft of the spindle when the vessel is being filled or emptied.

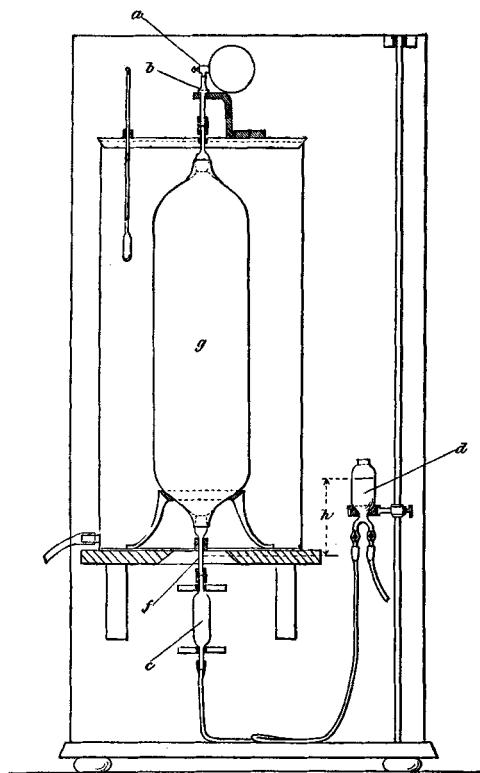
This vessel is tested hydraulically to 1000 lb. in the square inch. It may be safely filled to pressures of 20 or 25 atmospheres. I am daily using such vessels in the steam calorimeter in determining the specific heats of gases; here they are raised to the temperature of  $100^{\circ}$  C., bringing the pressure to near 30 atmospheres in many cases. For the purpose of compressing the gas into this vessel I use a pump of special construction, a description of which I hope shortly to publish. But, obviously, any compression-pump which will deliver the gas without contamination of oil or moisture will answer.

A counterpoising sphere of the same bulk and weight approximately is required. Against this, after the required quantity of gas has been inserted in the weighing-sphere, the latter is equilibrated. This operation is readily performed in an ordinary chemical balance to an accuracy of one tenth or one twentieth of a milligram. The weight of a copper vessel of the strength described will be from 80 to 90 grammes. It will be seen later that one sufficiently strong to hold 2 litres safely need not exceed some 40 grammes in weight.

The vessel in which the volume is determined is next to be considered. It is lettered *g* in the diagram, where it is shown connected with the weighing-sphere, the latter screwed to the steel connexion *b* provided for it, and through the fine bore (1 millim.) of which it delivers its contents into *g*. The volumenometer is of glass, cylindrical, closed at each end by ground stoppers with tubulures attached. The upper tubulure is of fine bore, hardly 1 millim., the lower tubulure of some 3 or 4 millim. bore. The volumenometer is surrounded by a copper jacket, having two large openings cut in its cover for the admission of broken ice or water, and also a tubulure for admitting a thermometer. A fine mark is etched on the lower tubulure at *f*, and this tubulure is continued by attachment to a smaller vessel *c*, as shown. This again is connected by a rubber-tube connexion with the vessel *d*, which can be raised or lowered, as will be understood from the diagram. The volume of the volumenometer is best determined with water. If water is subsequently to be used in it the procedure is as follows:—

The coupling *b* is removed and the vessel *g* inverted in the copper jacket. The wide tubulure is now uppermost, the narrow one below. This is attached to *d*, and the upper one to an air-pump, and distilled air-free water drawn into *g* through the lower tubulure till it is quite full. The vessel *d* is now raised, the connexion with the air-pump removed, and when *d* is so high that water is just welling out of the tubulure this is closed with a short pinched rubber tube.

Broken ice is now filled in round the volumenometer, and after the lapse of some hours the connexion below with *d* is



broken and the fine tubulure closed with a little piece of wax. The upper tubulure is now opened, and the level in the tubulure lowered by applying bibulous paper till it sinks to the mark etched upon the glass. It is then closed with rubber tubing as before. The ice being next removed, *g* is lifted out, dried carefully, and weighed. This done it is replaced

in the copper cylinder, this time in its normal position, and the water allowed to run out. The ice is now returned to the jacket, and after the lapse of some time the volumenometer is closed as before, when the height  $H$  of the barometer is read. Another weighing is now made, and by difference the weight of water at  $0^{\circ}\text{C.}$  which has quitted the vessel is calculated, allowing for the weight of saturated air at  $0^{\circ}\text{C.}$  and  $H$  contained in the vessel at the second weighing. One or more such operations may be performed, and from the known density of water at  $0^{\circ}\text{C.}$  the volume at the temperature  $0^{\circ}\text{C.}$  calculated. To this must be added, for the complete volume, the volume at ordinary temperatures of the small steel connexion with the sphere. It is obvious that the error arising from the inconstant temperature of this fine tube or of the short tubulure exposed at  $f$  need not be attended to.

If mercury is subsequently to be employed in the volumenometer the volume should be determined on a slightly different procedure. Water should still be used, however—not mercury, or a distending effect, due to the great weight of the latter, might give rise to error—but the weight of the vessel, when containing air, should be *first* ascertained when the walls within are dry. In this way the capacity of the *dry* volumenometer is obtained, which is that required with the use of mercury. It is evident that the use of mercury is on this account much preferable to water in subsequent work, as the volume of residual water in the vessel from one experiment to another will not be accurately constant. Again, no hygrometric correction on the pressure of the gas contained in the volumenometer will be requisite.

The volume of this vessel (which is but an enlarged Sprengel tube) being ascertained once for all at the temperature  $0^{\circ}\text{C.}$ , it follows that it will afford a ready means of dealing with a gas contained in the weighing-sphere. It is filled with mercury or water, and surrounded by ice. The vessel  $d$  is then raised till the liquid in the volumenometer has risen to the top of the fine steel tubulure  $b$ , the weighing-sphere removed from the balance, screwed on to  $b$ , and the vessel  $d$  lowered. The valve at  $a$  is next screwed back a little till the mercury is seen to rise in  $d$ . The right-hand stop-cock on  $d$  is now opened, and the mercury let flow into a tall graduated or marked vessel, so that it may be known about when the operation of filling  $g$  is approaching completion. Presently, the surface level of the mercury sinks into the vessel  $c$ . This possesses such capacity as to give time to close the valve of the sphere before any gas is lost;  $d$  is now raised slowly, till the overflow gas in  $c$  is compressed back into

the volumenometer. All must now be let to stand till  $t_0^\circ$  is attained (half-an-hour will suffice), and the final adjustment of the mercury level to the mark  $f$  then effected. By means of a cathetometer the height  $h$ , the difference of level between the surfaces at  $d$  and  $f$ , is read. This will only be some 5 or 6 millim. in general. For this a temperature correction is hardly required; but a capillary correction, ascertained experimentally once for all, must be applied owing to the different areas of the surfaces in the two tubes. This might be eliminated in the construction by conferring an equally small area on  $d$ , but it is probably more convenient to make the simple correction required. The barometer is now read, and the pressure of the gas in  $g$  computed. Its temperature is  $0^\circ \text{C.}$ , and its volume that of the vessel,  $= V$ . The sphere is now returned to the balance, re-weighed, and the weight of gas, subject to a small correction, found by difference.

The correction mentioned is due to the shrinkage of the copper sphere on the relief of pressure, and corresponds to that occurring in the case of Regnault's glass vessel. Experiments (two, closely agreeing, have been made on this sphere) reveal a shrinkage which may be taken as  $0.1732$  cub. centim. on the removal of  $4.3525$  grammes of air at the temperature  $12^\circ \text{C.}$ , a fall of pressure of  $22.01$  atmospheres, closely. At  $760$  millim. this weight of air occupies about  $3.367$  litres. This would be a needlessly large volume to confer on the volumenometer, except for very special work. Even in the case of hydrogen (1 litre at  $760$  and  $0^\circ \text{C.}$ , weighing  $0.0895$  gram.) two litres will suffice for a very accurate estimation of the weight of gas dealt with. At the pressure corresponding to the compression of two litres into the sphere of  $160$  cub. centim. capacity, a much lighter weighing-sphere than that previously described will suffice. Thus I use one weighing but  $41$  grammes, which has been tested up to  $500$  lb. in the square inch. The thickness of its walls is somewhat less than half a millimetre, its volume a little greater than  $160$  cub. centim. There is no difficulty in weighing such a vessel to the one-twentieth of a milligram., or closer. Using the heavier vessel the correction for shrinkage will be the shrinkage due to two litres, *i. e.*  $0.1029$  cub. centim. multiplied into the normal density of air. This gives a displacement effect of  $0.000127$ . This correction is on a weight of  $2.5878$  gram. of air or the correction on  $w$ , which is subtractive, is for air one part in  $25,000$  q.p. In the case of hydrogen one part in  $1790$ . Assuming the use of the lighter sphere the experimentally determined shrinkage is  $0.26359$  cub. centim. for a lowering of pressure of  $12.82$  atmospheres,

a little more than the pressure due to two litres. The shrinkage is, in fact, closely 0.257 cub. centim., and the correction on the weight of gas released is 0.000318. This is higher than with the heavier sphere, but the correction is perfectly definite [and easily ascertained once for all by successive weighings, before and after emptying, in distilled water]\*; and on the other hand the use of the lighter vessel will probably confer still greater accuracy on the weighings.

Turning our attention to the volumenometer it appears possible that a similar correction may arise in the assumption made as to its capacity. For, in the experiments in which its volume is determined, its walls are exposed to the pressure due to the weight of the water contained in it; subsequently, when it is occupied by a gas, this pressure does not obtain. Hence there might be reason to fear some small excess in the value ascribed to its capacity. To make this a matter of experiment, I filled the jacket with water, and provided a wide tube dipping into it, syphon-wise, enabling the water to be all run off within a short space of time. The volumenometer within was filled with air, the upper tubulure was closed, the lower one being arranged to dip into a vessel of water, the water standing some little height in the tube, nearly to the etched mark. Thick baize was now folded round and over the jacket, and after the lapse of some time the cross wire of a cathetometer was brought to read the level of the water in the lower tubulure. A few minutes' observation sufficed to show when this level was stationary. The syphon was now put into operation; and while the water was running out of the jacket the level of the liquid on the tubulure was observed. No movement was perceivable. It is thus, I think, legitimate to conclude that no appreciable error arises from this source, the experiment being a delicate one.

Comparing the previous figures with those obtained in the exact experiments of Lord Rayleigh, using Regnault's method, which experiments may be fairly taken as representative of modern refinement on the method, the following numbers are obtained, assuming the same weight of hydrogen to be dealt with in the present method as was used by Lord Rayleigh, and the lighter sphere to be used.

\* Two experiments on the heavier sphere afforded: (1) a shrinkage of 0.1013 cub. centim. for the release of 2.5728 grammes of air at 15°.4; (2) a shrinkage of 0.1732 cub. centim. for 4.3525 grammes of air at 12° C.

Two experiments on the lighter sphere gave: (1) 0.1720 cub. centim. shrinkage for the release of 1.6046 grammes of air at 16°; and (2) a shrinkage of 0.2636 cub. centim. for 2.5284 grammes of air at 14°.3.

Volume of vessel in which the gas is weighed :—

For Regnault's method 1800 cub. centim.  
 „ new „ 160 „

Weight of vessel in which the gas is weighed :—

For Regnault's method 200 grams.  
 „ new „ 41 „

Error of buoyancy on the weight of gas :—

For Regnault's method 1 in 280.  
 „ new „ 1 in 560.

Ratio of weight of gas to weight of vessel in which it is weighed :—

For Regnault's method 1 to 1261.  
 „ new „ 1 to 258.

Regarding the last numbers I may observe that the case assumed is unfavourable to the new method. The compression of 1800 cub. centim. (at 760 millim.) in the sphere raises the pressure to 12·5 atmospheres, but it may safely be filled to 17, or, it will carry some 36 per cent. more gas than is assumed above.

The volumenometer which I am about to take into use in estimating the density of the samples of gas used in my experiments on the specific heats of gases has only lately been constructed. A first and hasty experiment on the density of dry air may, however, indicate the magnitudes dealt with, and the accuracy obtainable when restricted to the use of water in the volumenometer. The interior volume of the volumenometer determined by weighing it filled with water at 15°·67, and again filled with air, but wet on the walls, was found to be 1751·0 cub. centim. This is with great probability correct to unity, the first place of decimals being perhaps open to small error.

The data in the experiment on air density are as follows :—  
 Weight of air inserted = 2·1092 less 0·0001 for error of buoyancy = 2·1091. Temp. of water jacket = 15°·70. Bar. 760·32 reduced to 0° C. Head of water 0·388 inches (=  $h$ ) + 0·120 inches correction for capillarity (by subsequent experiment). Total press. 760·32 + 0·95 millim. = 761·27. Max. vapour tension of water at 15·7 = 13·3 millim.; hence the pressure, finally, is 747·97 millim. The volume for the experiment may be taken as 1751 cub. centim., neglecting the temperature effect of 0°·03.



From these data the density of dry air at 747·97 millim., and at the temperature 15·70, is found to be 0·0012046. The last figure is doubtful, as being beyond the limit of accuracy with which the volume is known.

If, for confirmation of this result, reference is made to accepted results from the *Tabellen* of Landholt and Börnstein, the density of dry air under the same conditions of pressure and temperature is deduced as 0·0012033. From Biedermann's *Chemiker-Kalender* (1888) is deduced the number 0·0012052. The mean of these two closely agrees with the experimental result, absolutely indeed to the fourth significant figure, the last reliable one in the determination.

In conclusion, I may point out that this method leaves the gas finally in a vessel, which, by the addition of a small side way to the connexion *b*, may be made a most convenient one for the subsequent transference of the gas into any apparatus for its analysis.

The present method may, as in the case of Regnault's, be by obvious procedures applied to the determination of the variation of the density with change of temperature, or change of pressure. And its application to the determination of vapour densities suggests itself. In this case the temperature of the volumometer would, perhaps, best be adjusted by the use of a vapour in the jacket, and an arrangement for controlling its pressure.

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**XLIII.** *On the Tension of Water Surfaces, Clean and Contaminated, investigated by the Method of Ripples.* By Lord RAYLEIGH, Sec. R.S.\*

**N**UMEROUS and varied phenomena prove that the tension of a water surface is lowered by the presence of even a trace of grease. In the case of olive-oil, a film whose calculated thickness is as low as 2 micro-millimetres is sufficient to entirely alter the properties of the surface in relation to fragments of camphor floating thereupon. It seemed to me of importance for the theory of capillarity to ascertain with some approach to precision the tensions of greasy surfaces; and in a recent paper † I gave some results applicable to the comparison of a clean surface with one just greasy enough to stop the camphor movements and also with one saturated with olive-oil. The method employed was that depending upon the

\* Read September 6 before Section A of the British Association at Leeds. Communicated by the Author.

† Proc. Roy. Soc. March 1890, vol. xlvii. p. 367.