A DETERMINATION OF THE DENSITY OF HELIUM BY MEANS OF A QUARTZ MICRO-BALANCE.

By T. S. Taylor.

Introduction.

THE present investigation was undertaken for the purpose of determining the density of helium more accurately than had been done previously by the use of a quartz micro-balance after the type which was first described by Steele and Grant[1] and later used by Gray and Ramsay[2] in their determination of the density of radium emanation. Some time after the present investigation was begun Aston[3] described a simple form of a micro-balance for comparing the densities of small quantities of gases with considerable accuracy.

Several balances were constructed similar to the ones used by Steele and Grant[4] and by Gray and Ramsay[5] and it was found that these balances having knife edge and plane supports failed to have an entirely reliable zero position of equilibrium under similar conditions. It was therefore decided to try a balance of the Nernst type and the one herein described and used was found to be entirely reliable and satisfactory for accurate comparison of the densities of gases.

Apparatus and Method.

The balance consisted essentially of two parts: a framework of small quartz rods having a bulb and counterpoise, and a large quartz rod bent up in the shape of a flattened U between the legs of which the framework was suspended by quartz fibers. A sketch of the balance is shown in Fig. 1.

The framework, which constituted the main part of the balance, was made in the shape of a flattened rhomboid of small quartz rods about three fourths of a millimeter in diameter. A hollow bulb *H* about one centimeter in diameter was attached at one end of the longer diagonal of this framework, and a solid mass of quartz *I* was attached at the

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[1] Proc. Roy. Soc., 1909 A, Vol. 82, p. 580.

[2] Proc. Roy. Soc., 1910 A, Vol. 84, p. 536.

[3] Proc. Roy. Soc., 1913 A, Vol. 89, p. 439.

[4] Loc. cit.

[5] Loc cit.

opposite end of the same diagonal as a counterpoise. Such a framework is readily made by placing the quartz rods, bulb, and counterpoise in a form of the desired dimensions previously cut in a flat slab of graphite and then fusing the rods together by means of the oxy-gas flame. The entire mass of framework including the bulb and counterpoise was slightly under one gram. From the ends of the rod *LN*, which was perpendicular to the plane of the framework at its mid point, fine quartz fibers were drawn out and being stretched taut their ends were fused at *F* and *E* to the legs of the flattened U made of a heavy quartz rod. Thus the framework upon which the bulb *H* and the counterpoise *I* were attached was supported by the quartz fibers *FL* and *NE* with its plane of figure vertical and at right angles to the line joining *F* and *E*.

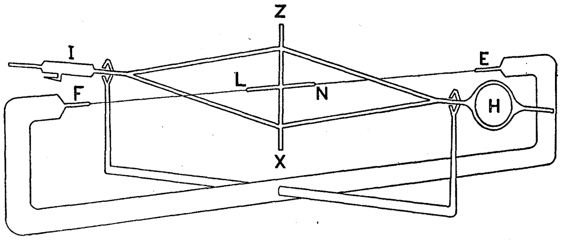

Fig. 1.

The balance was adjusted so that its center of gravity was very slightly below the line *LN*. This is readily done by adding small quantities of quartz to the ends of the rods *X*, *Z* or those attached to *I* and *H*. The final adjustment is obtained by holding the desired end of a rod for a few seconds in the oxy-gas flame, thus volatilizing a very small quantity of quartz. Quartz rods were fused at right angles to the mid point of the support rod and to these were attached the forked supports near *I* and *H*, as shown in Fig. 1. These supports prevented the balance from producing too great a torsion on the supporting fibers when a considerable difference in the buoyancy upon counterpoise and bulb existed, and also permitted the balance to move but slightly from what might be called the equilibrium position. The equilibrium position is that for which the line drawn through the center of the bulb *H* and the counterpoise *I* is horizontal.

The case in which the balance was placed was a bronze casting having its internal cavity in the form of a cross, the same as that of the balance and of such size as to allow the balance to be slipped readily into it. The case being made in this shape made it possible to use a relatively small volume of gas. It was so constructed that it could be evacuated or withstand considerable internal pressure and remain gas tight.

The balance was adjusted in the manner mentioned above, so that when it was placed in air at a pressure of about one sixth of an atmosphere, it was in equilibrium position. This position could be observed by looking through a window in the case at the small tip of quartz below the counterpoise *I*. This was done by means of a low-power micrometer microscope. The reading of the microscope which corresponded to equilibrium position was 26.00. The balance thus adjusted was cleaned by boiling in nitric acid and washing in distilled water. It was thoroughly dried in an oven and placed in the case. The case was then made tight by waxing and screwing down its cover.

In order to determine the density of helium in terms of oxygen, say, it was only necessary to measure the pressures required to keep the balance in equilibrium position when the case contained oxygen and helium respectively provided the temperature was the same in both cases. Their densities are to each other inversely as the corresponding equilibrium pressures. It was not possible to adjust the pressure of the gas in the balance case so as to bring the pointer below *I* (Fig. 1) to the zero position which was 26.00, as indicated by the microscope, but the observed pressure could be reduced to equilibrium pressure from the sensibility and the number of scale divisions the pointer deviated from the zero position. The density of helium was determined in terms of both oxygen and hydrogen. By the use of these gases the accuracy of the results obtained could be checked up, as their densities are well known. The sensibility of the balance was determined very carefully and it was found that a displacement of one scale division from the zero position corresponded to a change of one two hundred and seventy-fifth of one per cent. of the pressure required to keep the balance at the equilibrium position. If the temperatures of the gases were not the same when the pressures were measured, the observations could be reduced to the same temperature, say 0° C., by using the pressure coefficients for the respective gases. This assumes that the volume of the bulb *H* (Fig. 1) remained constant for slight changes in temperature and for considerable differences in pressure. This assumption is without doubt justified since the coefficient of expansion of quartz is so very small and since the walls of the bulb were sufficiently thick as to be unaffected by even very great pressures.

This investigation was carried out in a constant temperature room which had a large heat capacity and hence its temperature was not affected by small changes. For instance, it was found that one could go into the room, take a set of observations requiring two or three minutes, and not change the temperature to such an extent but that it would have come to an equilibrium temperature within an hour after leaving the room. This greatly facilitated carrying on the experiment. A large number of observations of the constancy of the room temperature showed that the temperature did not change more than two tenths of a degree during the course of a day even when the variation in the outside temperature was quite pronounced.

The method of introducing the gas into the balance case and of determining the pressure of the same can be seen by referring to Fig. 2. The balance case was joined to the system shown in this figure at *M*. The entire system shown in Fig. 2 including the balance case was evacuated. The charcoal bulb *E* was sealed off at the constriction just above the stopcock. When working with hydrogen and helium the liquid air was left on the bulb *N*. The gas in the container *D* was admitted and forced over into the balance case by means of the transfer pump *B*. After sufficient gas had been admitted the mercury was raised so as to come up in the cut-off *U*. The exact pressure to bring up the bulb to the equilibrium position was obtained by changing the reservoir *H* which was so arranged as to be moved through very small distances or considerable ones as desired thus changing the volume occupied by the gas in *L*.

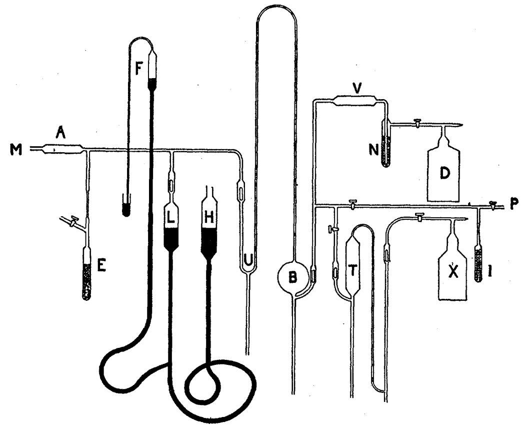

Fig. 2.

The pressure exerted by the gas in the balance case was determined from the observations of the level of the mercury in the vessels *L*, *H* and *F* by means of a cathetometer. The vessel *F* together with the capillary tube attached constituted a special barometer having as its mercury reservoir the mercury in *L* to which it was attached by means of a flexible rubber tube as shown in the figure. This barometer could be raised or lowered at will and thus allow the mercury in *F* to be kept at the same relative position. The pressure of the gas was then obtained in two ways: First from the levels of the mercury in *F* and *L* and second from the difference in the mercury levels in *L* and *H* together with the reading of a separate barometer. The glass vessels *F*, *L* and *H* were sufficiently large so that the effect of surface tension on the level of the mercury was entirely negligible. After having finished an experiment with any one gas it could be pumped out of the system by means of the transfer pump and collected in a reservoir such as *X*. The tubes *A* and *V* of Fig. 2 contained P_2O_5.

Preparation and Purification of the Gases.

Helium.—The helium was separated by Professor Boltwood from thorianite obtained from the Galle Province, Ceylon. It was purified in the apparatus shown in Fig. 3. The system being carefully evacuated the helium was introduced from a container such as *D*. The tube *M* contained fused calcium chloride. *A* was made of hard glass containing copper and copper oxide and was enclosed in an electric furnace. The tubes *L*, *H* and *F* contained P_2O_5. A charcoal trap *N* immersed in liquid air was inserted as shown. The transfer pump *T* was used to circulate the gas through the system. The gas when purified was collected in the container *E*. By repeatedly circulating the helium through this system the impurities would be taken out by the heated copper, copper oxide, the drying substances and the charcoal. After circulating the gas for some time it was all collected in the container *E* and that absorbed in *N* was pumped out of the system through *P* after heating *N*. After reëvacuating with liquid air and charcoal joined at *P* the gas in *E* was circulated again. By several repetitions of this process the helium was thoroughly purified. This was observed by noting the nature of the spectrum in the discharge tubes *V*.

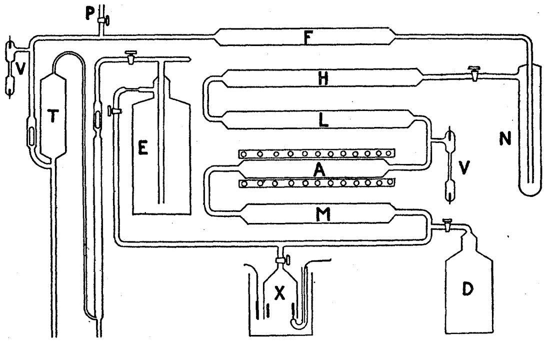

Fig. 3.

Hydrogen.—The hydrogen was also purified by the apparatus shown in Fig. 3. It was generated in the cell X between nickel electrodes by the electrolysis of a fifteen per cent. solution of sodium hydroxide. After passing slowly through the system it was collected in a container E. The tube A in the electric furnace contained only copper in this case.

Oxygen.—This was also produced by the electrolysis of the same solution as the hydrogen and was purified by the same method except that the tube A contained only copper oxide and the charcoal trap N was omitted in the system shown in Fig. 3.

RESULTS.

A series of observations which were obtained when the balance case contained oxygen is given in Table I. The first column contains the values of the pressures, corrected for temperature, required to keep the balance in equilibrium. The temperatures of the room corresponding to the pressures given in column 1 are recorded in column 2. This temperature was determined by two thermometers one graduated in tenths of a degree and the other in fifths of a degree. Smaller fractions of a degree could be estimated. These two thermometers were compared with a standard Reichsanstalt thermometer and the temperature readings corrected accordingly. Column 3 gives the reading of the pointer below I (Fig. 1) as measured by the micrometer microscope. The last column gives the pressures that would be required to keep the balance in equilibrium position (the pointer at 26.00) if the temperature were 0° C. The reduced equilibrium pressures are calculated from the relation

TABLE I.

Observed Pressure.	Temperature.	Position of Pointer.	Reduced Equilibrium Pressure.
109.12	19.24	26.05	101.91
109.05	19.30	25.91	101.89
109.07	19.30	26.12	101.82
109.19	19.32	26.30	101.86
109.08	19.34	25.87	101.91

$$p_0 = p_t\left[\frac{1}{1 + at}\right]\left[\frac{100}{100 + \frac{x}{275}}\right],$$

where a is the average pressure coefficient over the range of temperature and pressures respectively, and the last part in brackets is the correction term to reduce the pressure for the reading in question to the equilibrium position of pointer. The values of a for the three gases used are: oxygen

0.0036652, hydrogen 0.0036621 and helium 0.0036626. The factor x in the last term is the number of divisions of the microscope reading above or below 26.00. It is positive when the reading is greater than 26.00 and negative when less. The factor 1/275 is the sensibility as defined above. As can be seen from the reduced values, the equilibrium is remarkably good.

Similar sets of observations consisting of from 3 to 5 measurements were obtained for each of the gases, oxygen, helium, and hydrogen, and the pressures for equilibrium at 0° C. calculated in each case as above. The results are all recorded in Table II.

Table II.

Oxygen.	Hydrogen.	Helium.
101.91	1620.2	815.54
101.89	1620.0	815.70
101.82	1619.5	815.58
101.86	1619.7	815.83
101.91	1620.5	815.77
101.89	1620.1	814.45
101.84	1619.6	815.68
101.96	1619.5	815.65
101.86	1619.2	815.49
101.90	1619.9	815.61
101.86	1619.82 ± 0.083	815.57
101.84		815.65
101.88		815.618 ± 0.0243
101.84		
101.93		
101.83		
101.878 ± 0.0067		

The column headed oxygen represents results from four separate experiments, the hydrogen column two and the helium three. After each set of observations such as the one given in Table I. for oxygen, the gas was removed, the vessel reëvacuated and a different gas let in.

From the mean values of the reduced pressures given in Table II. the value of the density of helium was calculated with respect to both oxygen and hydrogen. Taking the density of oxygen = 1.42900 ± 0.000034 the calculated density of helium = 0.17850 ± 0.000015 and taking the density of hydrogen = 0.089873 ± 0.0000027 the calculated density of helium = 0.17848 ± 0.000012.

By use of the relation which states that the molecular weights of gases are to each other as their ideal densities

$$\frac{M_1}{M_2} = \frac{d_1(1 - a_1)}{d_2(1 - a_2)},$$

it is possible to calculate the molecular weight of helium in terms of oxygen, it being taken as 32.00. In the relation M, d, and a refer to the molecular weight, density, and compressibility coefficient of the gas respectively. The values of $(1 - a)$ for the gases are as follows: Oxygen 0.99903, hydrogen 1.00077 and helium 1.00000. Substituting the values in this expression the molecular weight of helium is found to be 4.0008 ± 0.0005. This value is in good agreement with that found by Heuse,[1] who gives the molecular weight of helium = 4.002. His calculation was made in the same manner from his determinations of the density of helium by direct weighing. His value of the density of helium is 0.17856 ± 0.00008, which is practically the same as the one found in the present experiments.

SUMMARY.

1. The density of helium has been determined by the use of a quartz micro-balance with reference to both hydrogen and oxygen and the values found are 0.17848 ± 0.000012 and 0.17850 ± 0.000015 respectively.

2. The molecular weight of helium has been calculated in terms of oxygen as 32 and found to be 4.0008 ± 0.0005.

In conclusion I wish to express my indebtedness to Professor Boltwood, who furnished the raw helium, and to Professor Bumstead, as director of the laboratory, for the facilities for carrying on the investigation.

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[1] Ber. d. D. phys. Ges., 15, 518, 1913.