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III. *On the Specific Heats of Gases at Constant Volume.*—Part I. *Air, Carbon Dioxide, and Hydrogen.*

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Communicated by Professor FITZGERALD, *M.A., F.R.S., F.T.C.D.*

[PLATE 6.]

Introduction.

THIS paper is occupied with a consideration, from a purely experimental point of view, of the specific heats of three gases : (1) of air, chosen as being typical of the sensibly perfect gas, and one the properties of which have entered more into thermo-dynamical considerations than those of any other fluid ; (2) of carbon dioxide, as typical of the imperfect gas, in the case of which there is also the advantage of an already extensive knowledge of its other properties ; (3) of hydrogen, as a gas whose behaviour, as regards BOYLE's law, suggests that it occupies a peculiar position among perfect gases.

The specific heats of these gases are, in this first notice, treated over pressures ranging approximately from 7 to 25 atmospheres. The range of temperature is not sensibly varied, the lower limit being that of the prevailing atmospheric temperature, the upper that of steam at ordinary pressures. The question of the relation between the specific heats of gases and their temperatures I hope to make the subject of a future notice.

For advice and assistance in all matters of difficulty, more especially in the consideration of the nature of the corrections to be applied to the experiments, I have to thank Professor FITZGERALD. Where my work touched on chemical science I had the friendly assistance of Professor EMERSON REYNOLDS, and must thank him for his readiness to help me. In this connection, my thanks are also due to Mr. E. WERNER. The labour of reducing the results of the experiments was much lightened by the kind help of Mr. H. H. DIXON, of Trinity College.

The Board of Trinity College, in providing a suitable room for my experiments, have rendered it possible for me to attain a far higher degree of consistency in my

results than was previously possible. Some only of the experiments recorded in this paper shared this advantage; their results lead me to hope that future work will possess a higher degree of accuracy.

The Government Grant Committee have enabled me to meet the expenses attending the construction of apparatus.

To the personal care which Messrs. YEATES and SON have devoted to the construction of the apparatus the practicability of the experiments may be said to be due. It is sufficient, as testimony of this, to refer to the qualities displayed by the vessels they constructed for holding the gases.

On the Possibility of Accurate Determinations.

In two previous communications made to the Royal Society,* I have inquired into the accuracy of the method of condensation as a means of investigating the specific heats of substances. I claimed for it a high degree both of truth and sensibility, comparing favourably with, if not transcending, that of all other methods. I might also have claimed for it the quality of elasticity in an important degree. With a delicate balance, the smallest mass may be dealt with. Increasing the power of the balance and the dimensions of the calorimeter, it is easy to deal with large masses or with bulky vessels impossible of treatment by other methods.

This is the method employed in the following investigations on the specific heats of gases. For its principles and for its mode of employment specially with reference to gases, I must refer to my paper on the Steam Calorimeter (*loc. cit.*), in which a plate will be found illustrating the large differential calorimeter used in my experiments. The spherical copper vessels, one of which in an experiment will contain the gas under a greater or less degree of pressure, are shown suspended in the calorimeter. The essential detail of construction, whereby the freedom of the wires suspending the vessel from the balance is secured, is figured in the adjoining plate given in that paper. There will be no need of further description of the apparatus here.

I assume here, on my former proofs, the reliability of the method, and pass on to the question of the degree of accuracy possible of attainment in this application of it. The possibility of such experiments has always been a question of degree. For with the amount of stress to which any suitable material for enclosing the gas may be safely subjected, the weight of the vessel must many times transcend that of the gas, so that, in spite of the rather high specific heat to be ascribed to the latter, the calorific capacity of the gas must remain only a fraction of that of the containing vessel. Nor by increasing the size of the vessel is the disproportion diminished. For, supposing the vessel spherical, the rate of stress on a great circle for a given pressure will increase as the diameter; the weight of the vessel as the square of the diameter,

* " On the Method of Condensation in Calorimetry " ('Roy. Soc. Proc.,' vol. 41, p. 352, *et seq.*); and " On the Steam Calorimeter " ('Roy. Soc. Proc.,' vol. 47, p. 218, *et seq.*).

if the thickness be maintained constant. But, assuming in each case the spherical vessel to be charged to the limiting safe stress, an increase in the diameter necessitates an increase in the thickness of the material proportional to the increase of stress, that is, proportional to the increase of diameter. Thus, finally, the weight of a vessel which is always at its limiting safe stress increases as the cube of the diameter; and this is the rate of increase of its volume or of the weight of the contained gas.

An inferior limit to the size of the vessel is, however, fixed in the case of the present experiments, by the sensibility of the ordinary chemical balance in estimating the small weight of steam which is condensed due to the thermal capacity of the contained gas; a superior limit by the increased risk on a chance explosion and the inconvenience of providing large quantities of steam for filling the calorimeter rapidly at the commencement of an experiment.

After various trials and experiments on larger vessels, two spheres of copper having an external diameter of about 6·7 cms. were designed. One, " A," to stand a test pressure of 500 lbs. on the square inch and a working pressure up to 250 lbs. The other, " B," to stand a test of 1000 lbs. and a working pressure of 500 lbs. A smaller margin of safety than this was not considered advisable as, at the temperature of the steam, a decreased resistance of the vessel was to be expected. The thickness of the walls of these vessels would be, by calculation, closely one-half and one millimetre respectively. And to these dimensions the spheres were as accurately as possible constructed.

Now if we take the case of sphere B and supposing it filled with air to a pressure of some 22 atmospheres at $t°$, rising to 30 atmospheres at $t_2°$ or 450 lbs. per square inch, the following proportion obtains between the weight of steam thrown down by the vessel and the weight of steam precipitated by the contained air :—

B and its catchwater weigh nearly 100 grms. Its specific heat may be taken as 0·094. Over the range of 85° the condensation of B is therefore just 1·5 grms. The air in B weighs 4·2854 grms. Its condensation is 0·116 grm. Thus one-thirteenth of the precipitation is due to the air. But as we must be content to use the sphere B at pressures lower than this but still too high for sphere A, it is necessary to regard the ratio as descending as low as one to eighteen.

Forestalling speculations on the possibility of dealing with this one-thirteenth, say, to one per cent. of its value—or to $\frac{1}{1300}$th of the whole condensation, I give the results of an entire series of six experiments in which this ratio holds, in fact the series from which—taken at random—I have borrowed the foregoing figures. The mass of air, 4·2854 grms., affords over the mean range of 84°·52 a precipitation of 0·11629 grm. There is a want of balance between the thermal capacities of the vessels, making the observed precipitation 0·15217 grm. These are the mean results of the six experiments. To compare the experiments among themselves I divide the weights of precipitation observed in each case by the range of temperature for that experiment. The six numbers thus obtained represent the weight of steam thrown

down in each experiment per degree of range. The consistency of the experiments is thus truly represented by these numbers. They are :—

$$0\cdot017941$$
$$0\cdot018009$$
$$0.018070$$
$$0\cdot018080$$
$$0\cdot017906$$
$$0\cdot018016$$

Mean precipitation divided by mean range

$$0\cdot018004.$$

(See among the experiments, Air VIII.)

The departure from the mean in one case only amounts to so much as half per cent.

From these figures it is evident that close measurements are practicable.

Regarding the mode in which these measurements are effected, I may in the first place refer to a former statement of my own that by this method of calorimetry observations of the thermal capacity may be carried to the one-thousandth part. This was based on experiments on minerals where surface conditions were varied by breaking up the specimens between successive observations.* Now, although it is probable that this degree of accuracy would not obtain in the case of successive experiments on large objects of low density, effected in the ordinary way, on the other hand the effect of the simultaneous differential arrangement is to limit or banish several sources of error. Any source of error common to the two spheres and to the gas is not accumulated on the gas. The gas simply bears its own share. Thus a mis-reading of temperature affects the result for the gas simply by the amount of the error, and will not, as in the case of successive differential experiments, by falsifying the specific heat of a mass thirteen times as effective, thermally, as the gas, throw thirteen times the error upon the gas when the allowance for the thermal effect of the sphere subsequently comes to be made. With this class of error are eliminated to a great extent effects of radiation and effects due to buoyancy. Theoretically, indeed, in the use of the simultaneous differential method, there is reason to consider the entire sensibility of the method directed to the evaluation of the effects of the gas as if isolated from its containing vessel. Practically this will not be fully attained. But it appears evident from all considerations that this application of the method to the calorimetry of gases is not straining the method; and the expectation is, I think, justified that in the use of this method the old difficulties will be found to be overcome. In the tables of experiments, given further on, discrepancies in many cases occur. But these cannot all be laid to the charge of the calorimetry. In the case of hydrogen

* "On the Method of Condensation," *loc. cit.*, p. 362.

nearly all these discrepancies are very certainly due to varying amounts of impurities in the samples of gas. Again the earlier experiments on air were made under difficulties which it would be needless to enumerate. The principal one, that of insufficient supply of steam, arising from an inadequate gas main, was not overcome till after the experiments on carbon dioxide were concluded. I did not think it necessary to repeat these, for their agreement *inter se* was fairly satisfactory, but in the case of the far more difficult problem, the variation of the specific heat of air, I did repeat, under the improved conditions. The results, from the present point of view, go to show the degree of precision attainable in the careful application of the method. I allude to experiments VIII.–XI., which are seen plotted on the diagram of experiments on air, Plate 6.

The method is delicate in its results. It is, I think, capable of dealing with some subtle questions in calorimetry, but, as in other methods of measurement, when the higher resources of the method are called upon, care and judgment are needed to guard against the entry of error.

The Vessel for Holding the Gas.

The earlier attempts at effecting the measurements of the specific heat were confined chiefly to efforts at overcoming two principal difficulties :—the construction of a vessel sufficiently light, strong, and staunch to contain the gas, and when this was accomplished, to secure the filling of it with *dry* gas at the requisite degree of pressure.

As regards the first difficulty it was soon found that vessels constructed of more than one piece were only reliable when joined with very carefully *brazed* joints. Several explosions, which but for precautions might have been disastrous, occurred owing to various forms of soft and hard soldered, overlap joints tearing open in the steam.

The ordinary form of stop-cock for admitting the gas proved useless. At high pressures it was impossible to avoid leakage. A screw valve was accordingly designed. This has proved very satisfactory, and may be so contrived as to add hardly more than one gramme to the mass of the sphere. Finally, copper was found to be so satisfactory in all respects that its use was decided upon. It is surprisingly tough, not scattering on explosion, but tearing open, and admits of being spun into very thin hemispheres. So far as thermal capacity is concerned, there is not much choice, the densities of metals being about inversely as their specific heats.

Spheres A and B are built up of hemispheres meeting within a narrow belt of their own thickness. This belt is widened at one point, and here the screw valve is soldered in its place. For this soft soldering is permissible and convenient. The belt is brazed in with the utmost care to secure a deep and staunch joint. The screw valve is shown in section in the cut (fig. 1). The valve is opened by screwing back the central pin, which is of hard tempered steel, terminating at one end in a burnished conical point,

which crushes into the soft brass when the valve is closed.   The other end of the pin is fitted with a little eye for suspending the whole from the wire in the calorimeter. The sphere can be attached to the compression pump by the side tubulure.   While being filled there will be leakage along the thread of the valve pin, if the thread be not choked by strong wax or shellac run in while the valve is warmed with a spirit flame.   To avoid this trouble, and to still further lighten the valve, I devised the second form (fig. 2).   In this the valve, as introduced into the calorimeter, terminates with the cross-hatched part of the figure.   The remainder is a fitting for attaching it to the pump.   The central spindle is surrounded by a stuffing box, and consists of a forked key for gripping and turning the valve pin.   A longitudinal slot in the latter, extending just to the cone, allows of the free entry or exit of gas when the cone is lifted from its bed.
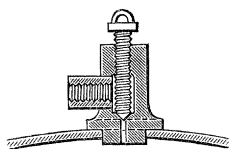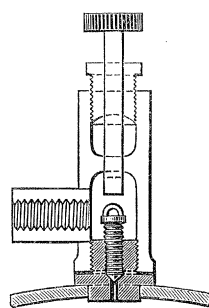
Fig. 1.   Fig. 2.

The sphere before use is attached to a small hydraulic hand-pump carrying a metallic gauge, and tested to the requisite pressure by pumping water into it.   In this process the form of the vessel visibly becomes more spherical; the internal volume may increase nearly three per cent.   Leakages are now detected and marked.   Subsequently these are staunched with soft solder, applied while a vacuum is maintained in the sphere.   The sphere will now probably be quite gas-tight, but it must be further tested when filled with gas by immersing it in water, and observing for some time if any bubbles grow upon its surface.

The catchwater of platinum foil with which each sphere is provided, is arranged to be easily removed.   It is, in fact, hooked on to two little wire loops soldered to the sides of the sphere.

The idle sphere, or counterpoise, is not, of course, tested.   It is only necessary to make sure that it is perfectly air-tight.   It is closed when full of air at normal pressure, and is as similar to the active sphere as regards material, weight, and volume, as possible.   The equality of volume should not be departed from to an extent exceeding three or four cubic centimetres.   Their thermal values are adjusted by inserting calculated weights of copper wire into the idle sphere.   It is easy to secure that this in the first instance shall be the lighter of the vessels.   More than an approximate equality in the thermal capacities of the vessels is hardly requisite.

Differential experiments on the thermal behaviour of the spheres are in any case requisite at intervals during a research.

The Storage of the Gas.

The gas—the earlier experiments were on air—was at first pumped into the sphere by a single acting vertical-cylinder pump, of the kind formerly much in use for liquefying carbonic acid gas. It was found that the gas, although supplied dry to the pump, not only took up moisture from the oil lubricating the piston, but took up the oil itself. Two series of experiments, effected in the single calorimeter by the successive differential method, were carried out at this time on air. A filtering tube had been inserted between pump and sphere, but the odour of oil from the air when being released proved that this had failed to clean the air. The experience with the single calorimeter, too, showed that some improvement in dealing with the bulky vessels was desirable. The calculations for the error of buoyancy involving the density of the steam, of the air, and of the hygrometric state of the latter, as well as the thermal expansion of the sphere, were risky and laborious. And so the differential calorimeter was devised.

A larger and more effective filtering tube was next attached above the pump, and the experiments appearing in a preliminary note* were carried out. It was subsequently found that the dryness of air so stored was open to doubt, and it was resolved to seek some different means of storing the gas. The apparatus at present in use was accordingly designed.

This apparatus consists of a receiving apparatus and an oil pump. The compression pump formerly in use was converted into an oil pump by adding above the cylinder suitable valves and an expansion chamber, after the manner of the ordinary force-pump. The pump is driven by a flywheel turned by hand, and can pump oil up to pressures of 35 or 40 atmospheres. This pump is attached to the receiving apparatus (fig. 3) by the two tubes leading to the right of the figure.

The receiving apparatus consists of two strong glass vessels—one placed at a level higher than the other. These receivers are 11 mm. thick in the walls. The internal volume of the upper one is 335 c.c., of the lower one 344 c.c. It is desirable that there should be this disparity of volume between them. These vessels, which are about 5 cms. in internal diameter, have, at the lowest estimate, assuming the glass to be well annealed, a bursting strength of some 180 atmospheres.

The glass receivers are carried in cast iron frames, furnished each with two slow-threaded screws, placed with their axes truly in line. The extremities of these screws are rounded, and bear against cast iron stoppers closing the ends of the receivers. In this way the uniform bearing of the stoppers against the ends of the receivers is secured. Leather washers, soaked in wax, are interposed next the glass. With this

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* ' Roy. Soc. Proc.,' vol. 45, p. 33.

arrangement, by screwing down the upper milled-headed screws, and without resort to the more powerful screws below, perfect immunity from leakage at the highest pressures is attained.

Fig. 3.
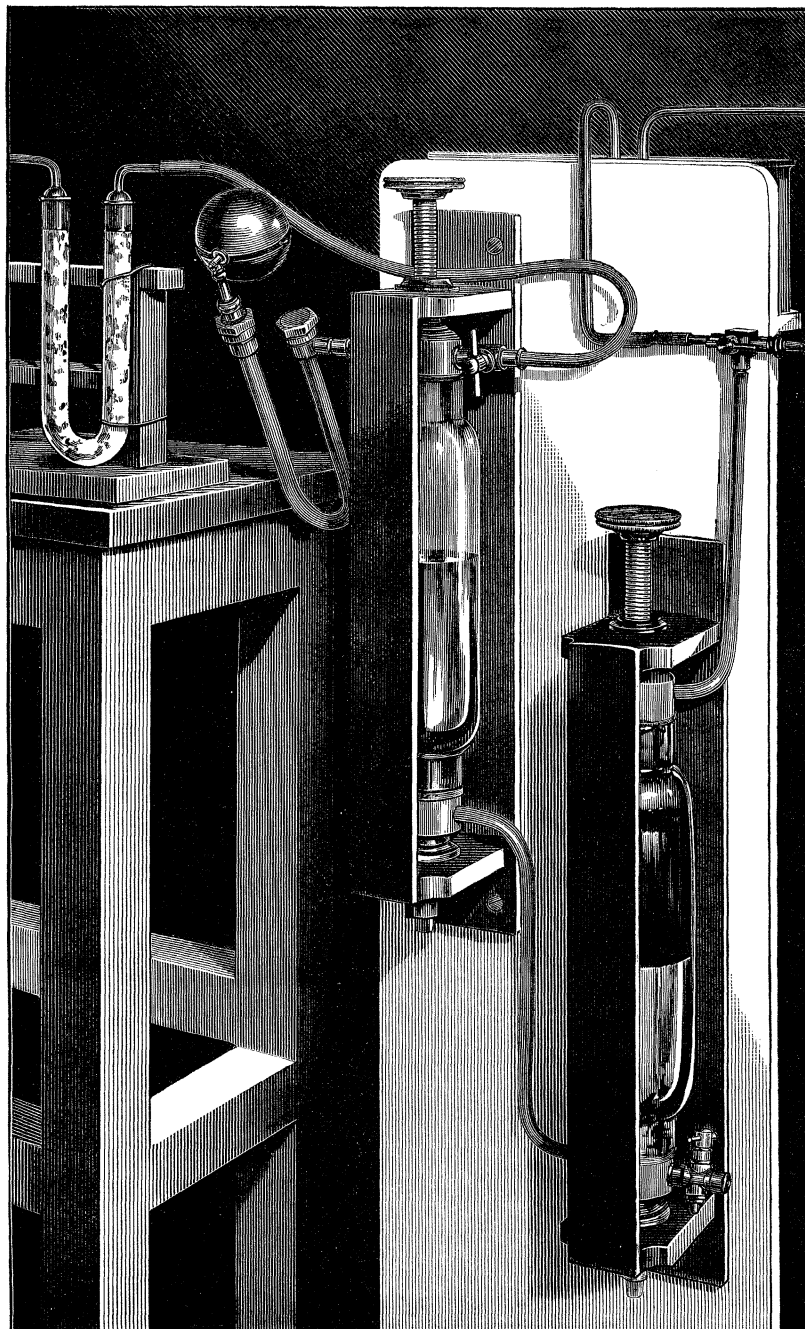
All the connections are effected through the stoppers, as is seen in the figure. The receivers communicate one with another by a bent wrought-iron tube, connecting the two undermost stoppers. The upper stopper of the lower receiver has a single con-

nection with an upright wrought-iron tube, terminating in a three-way stop-cock. Through this the lower receiver is put in connection with the high-pressure tube (of lead) leading to the oil pump, or through a glass tube with the little oil tank, placed above, and only partially seen in the figure protruding from behind the apparatus. Or the high-pressure tube from the pump may by this stop-cock be placed in connection with the oil-tank directly, the receiver being then closed. The lower stopper of this receiver is fitted with a wrought-iron stop-cock, for commanding the filling or emptying of the receiver with mercury.

The second and uppermost receiver has two stop-cock connections above; one, to the right, with the train of drying and purifying tubes through which the gas to be pumped is drawn before it enters this receiver; the other, to the left, leads to a high-pressure wrought-iron drying tube, of narrow bore (1 cm. *q.p.*), at the further extremity of which is the screw fitting for taking the tubulure on the valve of the copper sphere. Care is taken to keep the passages which are drilled in this uppermost stopper of the higher receiver, fine in bore, about 1 mm.

The method of applying the apparatus is as follows :—Clean dry mercury is let into the lower receiver. When this is just filled the mercury rises in the lower neck of the upper receiver. The tank must now be supposed to be filled with clean Rangoon oil, and the three-way cock connecting the pump and the receiver. On now working the pump oil is drawn from the tank through a glass tube (this is the higher right hand tube in the figure), and returned by the pump into the receiver. The mercury in this is displaced into the upper vessel, expelling the gas in it into the drying-tube and sphere. When the higher receiver is quite filled with mercury, owing to the greater content of the lower vessel, some three or four centimetres' depth of mercury remains in the latter. Closing now the left hand stop-cock of the upper receiver, setting the three-way cock to permit the oil in the lower one to flow into the tank, and finally opening the stop-cock connecting the upper receiver with the train of drying-tubes, the mercury flows back quietly by its own weight into the lower receiver, and gas is as quietly drawn into the upper one, to be again expelled, by the same operations, into the sphere.

The volume of the sphere being some 160 c.c. and of the drying-tube 31 c.c., one operation of the pump displaces sufficient gas to raise the pressure in the sphere by 1·6 atmospheres. In the knowledge of this I have dispensed with a pressure gauge in the use of this pump. But a gauge of small capacity attached between the pump and the high-pressure drying-tube is undoubtedly desirable, in case of leakage or of a mistake in reckoning the number of operations.

In the use of this pump the air only comes in contact with the mercury and glass of the upper receiver. After the pump has been in use some time, however, the mercury, judging from a certain dimming of the glass at the lower part of the receiver, appears to become to some extent greasy. This is much retarded by screwing a short tubulure of soft wood into the central perforation of the under stopper of the lower

vessel, extending some 2 cms. up into the mercury, which has all to flow out through this tubulure.   This greasiness only does harm in so far as it may communicate moisture to the gas.   No volatile hydrocarbon is taken up.   To investigate this question a careful experiment was kindly carried out by Mr. WERNER in the chemical laboratory. A quantity of $2\frac{1}{2}$ litres of air compressed into the sphere, and which before entering the pump had been passed through a potash bulb to free it to a great extent from the normal CO_2 of the atmosphere, was very slowly allowed to escape through a heated combustion tube 40 cms. in length, filled with platinised asbestos, in order to burn any hydrocarbons into carbon dioxide.   The issuing gas was bubbled slowly through baryta water.   At the end of the operation a hardly appreciable opalescence (soluble in hydrochloric acid) was visible.   As a small proportion of the normal CO_2 in air, escaping the potash bulb, would have caused the slight precipitation observed, there are no grounds for suspecting any appreciable impurity contracted in the receiver. The air compressed in this apparatus is, also, I may observe, quite free from odour.

The final drying of the compressed air is, however, necessary.   Before the addition of the drying-tube (which is filled with dried asbestos and phosphoric anhydride), an experiment was made by passing 4·340 grms. of air (which had been dried through three large U-tubes of phosphoric anhydride, and compressed directly from the receiver into the sphere) through a carefully counterpoised drying-tube, which throughout the operation was maintained suspended upon the balance.   An increase of 4·2 milligrammes in the weight of the tube was obtained.   As some 2 milligrammes would, on received principles, saturate the volume occupied by the air in the sphere, this error could not be suffered to remain.   The tube was therefore added.   The experiment was subsequently repeated, 4·3527 grms. of air being passed through the carefully equilibrated drying-tube.   The result was absolutely *nil*.   Later, the experiment was again repeated on 2·331 grms. of air.   The result in this case was unexpected.   There was a slight, but appreciable, *loss* of weight.   This can only be explained in the more complete drying of a minute plug of cotton wool placed in the tubulure of the drying-tube to hinder the free entry of air while the weighing was being effected.

It may be assumed from these observations, I think, that the various gases compressed in this pump, if delivered pure into the receiver, derived no impurity in being transferred to the copper sphere; and it will only be necessary to dwell in each case on the means taken for generating and purifying the gases.

Procedure in Making the Experiments.

The sphere having been repeatedly "washed out" with the gas to be dealt with, in a dry, pure state, is hung from the wire in the calorimeter against its counterpoise, the idle sphere, and the difference in weight observed.   In the process of "washing out" the sphere is both heated (by a spirit flame) and exhausted between each

admission of the pure gas. During the first equilibration it is filled with the pure gas at normal pressure. It is now screwed up to the pump and the requisite quantity of gas pumped into it. It is then returned to the calorimeter, and when all is cold the added weight of gas—subject to a small correction—found by difference.

An experiment cannot be performed till the thermometer is stationary—meaning thereby a state in which the motion of the thermometer cannot be perceived in observations made at intervals of some ten minutes. All openings in the calorimeter are now closed and the balance set in active vibration to keep the air in the calorimeter stirred, and thus secure greater uniformity of temperature. I have lately in order to attain the same end used a small stirring apparatus consisting of a little fan driven round by clockwork. This is mounted at the extremity of a stopper which enters the calorimeter by the wide opening at the back, through which the steam is admitted. It is withdrawn at the moment of turning the current of steam into the calorimeter. The motion of the fan keeps the air in the calorimeter in active motion, while all openings are closed against the ingress of external air.

While steam is being got up in the boiler the thermometer is observed at intervals. It will generally be found to rise a little. The final reading before admitting steam is taken as that of the spheres. The variation will be small, seldom more than $\frac{1}{20}$th of a degree.

The observation of the behaviour of the spheres in the steam takes about five minutes. If loose weights have been inserted in the idle sphere it will be found that its final assumption of the steam temperature will probably be delayed beyond that of the filled sphere. The inequality in the rate of heating reveals itself in the gradual acquisition of weight of the idle sphere. This effect was remarkably conspicuous in the experiments upon hydrogen—a result depending, doubtless, on the high conductivity of that gas.* In the course of $3\frac{1}{2}$ minutes the rate of increase of the idle sphere is diminished so as to be no longer perceptible, but the balance is observed till the fifth minute closes. This supposes no " increment." The increment generally indicates a weak burner, or leaky joints, so that the steam is impure—not free from mist—or a preponderance of the radiation of one sphere over the other. The first evil is met by the use of a powerful burner, close-fitting joints and long preliminary clearing (7 to 10 minutes) of the boiler and steam ways with the live steam. The second evil is generally caused by one of the spheres becoming greasy from handling (generally the filled one, the other is seldom touched), and is met by freeing the surface from grease by washing well with dilute ammonia. Although occasionally troubled in my earlier experiments by this evil, I have now for many

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* It might be suggested that this difference in the rate of heating of the spheres would give rise to an error in estimating the initial temperature, except in the case where this was actually stationary. I may observe, however, that a comparison of a number of the results of observations in the cases where t_1 was rising with the cases where t_1 was falling revealed no settled difference in one direction. The rate of change of t_1 is very slow.

months, using the calorimeter from twice to four times in the day, without inter-mission of a day, only observed it on two or three occasions. It can, indeed, be eliminated—very closely—by calculations based on continued observation of its value ("On the Steam Calorimeter," *loc. cit.*), but this necessitates the retention of the vessels in the steam an excessive time, which is to be avoided as the stress on the active sphere is then often very great.

The upper limit of temperature is most conveniently observed by a thermometer which is inserted in the calorimeter, in place of the low-range one, just before steam is let in.

When the experiment is concluded the spheres are simply dried in a soft clean cloth and laid aside to cool. The heat remaining in them completes the drying of their surfaces very thoroughly without further trouble.

When all is again cold, the spheres are restored to the calorimeter and an observa-tion made on their equilibration. This is an assurance against leakage having occurred during the experiment. Absolute return to the former equilibration is, perhaps, exceptional, but the departure from it is generally small, some two or three-tenths of a milligramme, and will as often appear to indicate loss from the one sphere as from the other. When the number of experiments deemed requisite is completed a careful equilibration of the spheres is made and some or all of the gas let out. If it is desired to make a further investigation upon this sample of gas at a lower pressure, the desired amount is retained by suffering the escape of gas to occur slowly while the sphere is hung from the balance, the weights being so adjusted that there will be equilibrium when the proper amount of gas remains in the sphere.

Finally, after a series of investigations, by the addition of all the weighed quantities which have been suffered to escape, the weight of gas put in in the first instance is found. This value, as might be expected, is often found to differ by a small quantity from the first determined value of the weight. The difference is generally negligible, except in the case of hydrogen, where the total weight is small. In this case, as the second determination of W is more reliable than the first, it is accepted. In the first determination there is evidently some chance of the vessel contracting some impurity upon its surface in the process of filling.

The thermal comparison of the spheres at normal pressures is now effected. I have generally thought it inadvisable to increase the weight of gas dealt with by exhausting the active sphere. In the process of exhaustion there was risk of spoiling the weighings by contamination of the surface of the sphere. There was also the risk of a back-leakage of air into the sphere during the process; injurious, either by the fact that it was undried or as an impurity if other gas was being dealt with.

The number of observations made on the thermal equilibrium of the "empty" spheres is some five or six generally. In the earlier experiments these observations were more frequent, as trifling alterations on the valve or for leakage, &c., were then often necessitated.

Corrections to be Applied to the Experimental Results.

The direct results of experiment are subject to some corrections before they can be applied to the calculation of the specific heat of the gas. The conditions of experiment involve that the two spherical vessels have their specific heats compared when each is filled with gas at the pressure of one atmosphere, and again when a further weight (W grammes) of gas is compressed into one of them. It is necessary to inquire whether the presence of the added quantity of gas does not give rise to any thermal effect other than that due simply to its capacity for heat at constant volume between the limits t_1 and t_2.

1. *Correction for Thermal Expansion of the Vessel.*—The volume of the sphere increases during the experiment by the thermal expansion of the copper. The gas in the sphere is not, in fact, maintained at absolutely constant volume. The thermal effect of this on the added quantity of gas, W, is evidently that which is to be considered.

The initial pressure due to W is affected negatively by the increased volume of the sphere, positively by the rise of temperature. Work, ϵ, is done by the expansion of the gas through the increased volume of the sphere, and the thermal equivalent of this must be deducted from the experimental result. Calling the initial volume V_1, and the initial pressure P_1, at any moment during the rise of temperature.

$$P = \frac{P_1 V_1}{V} \left(1 + \alpha t\right) \quad \text{and} \quad V = V_1 \left(1 + \beta t\right),$$

where α is the coefficient of increase of pressure at constant volume, and β the coefficient of thermal expansion of copper. From this a complete formula for the correction is found—

$$\epsilon = P_1 V_1 \left[\alpha \left(t_2 - t_1\right) + \frac{\beta - \alpha}{\beta} \cdot \log \frac{1 + \beta t_2}{1 + \beta t_1}\right].$$

But for this an approximation may be substituted. A good approximation is found to be—

$$\epsilon = \left\{P_1 V_1 \beta \left(t_2 - t_1\right)\right\} \left\{1 + \alpha - \beta \tfrac{1}{2} \left(t_2 - t_1\right)\right\}.$$

The correction is subtractive. A numerical estimate of its value is given further on.

2. *Effect of the Elastic Distension of the Vessel.*—In considering the last correction it was assumed, for the sake of simplicity, that the copper sphere is so rigid as not to yield to the increased pressure exerted by the gas as it rises in temperature.

To obtain exact data in calculating this correction, experiments were made on the shrinkage of the spheres when a known weight of gas was liberated. These experiments consisted in carefully weighing the sphere in water with a sinker before and after releasing a certain weight of air. These are given later, with other data connected with the spheres.

If the increase of volume by distension is estimated for the change of pressure $P_2 - P_1$, the usual equation for work of expansion gives the amount of the correction when reduced to its heat measure as a weight of steam precipitated. The correction is subtractive.

3. *Thermal Effect of Stretching the Material of the Sphere.*—The increased pressure of the gas in the sphere has the effect of distending the copper sphere, as just seen; this, according to well known principles, results in a cooling of the copper. Experiments have been made by JOULE, EDLUND, and others, on the amount of this cooling in wires exposed to suddenly-applied traction. The cooling of the copper in the present case is made good by the condensation of steam. An estimation, however, of the amount of this correction in an extreme case showed that it was too small to merit consideration. It is not, therefore, further considered.

4. *Correction for Buoyancy due to Distension in the Steam.*—The distension in the calorimeter has also to be considered, as occasioning another correction. The increased displacement in the steam will tend to decrease the apparent weight of the sphere, and so diminish the amount observed as the weight of steam precipitated due to the gas. The amount of the correction is the increase of volume due to rise of pressure multiplied by the absolute density of steam at the temperature t_2. It is additive.

5. *Correction for Buoyancy due to Distension at t_1.*—In that series of experiments in which the one sphere is filled with gas at high pressure, the air-to-steam displacement effect of the filled sphere is greater than it is in the series of experiments in which both spheres are at the same pressure. The distension due to W grammes of gas at t_1 is multiplied into the relative density of air and steam. As the correction results in a greater apparent increased weight of the filled sphere on the admission of steam into the calorimeter, the correction is subtractive.

6. *Correction for Unequal Thermal Capacity of the Spheres.*—This correction has been already alluded to. It is effected on a series of experiments the mean results of which are taken, giving a correction of $\pm \omega_1$ grammes of steam over a range $t_2 - t_1$. In applying it the amount of ω is adjusted for the mean temperature range of the series of experiments under consideration. It must be effected before the next correction.

7. *Reduction of the Weight of Precipitation to Vacuo.*—By multiplying the observed weight of precipitation less ω_1 (6) into the absolute density of steam, this correction is effected. It is additive.

The analogous correction for the displacement in air of the weights added to the balance to equilibrate the precipitated steam is unnecessary, if the weights are, as usual, of platinum or gold.

The total result of these corrections is to reduce the direct measurement by about 0·7 per cent. In estimating the relative importance of these corrections a few figures will be of service. I take the case of the series Air II., in which the stronger sphere B was used.

The data are :—

Volume of sphere B at 15° and 760 mm. internal pressure $= 159{\cdot}826$ c.c. (by experiment).

Distension due to $4{\cdot}3525$ grms. of air at 12° C. ($22{\cdot}01$ atmospheres) $= 0{\cdot}1732$ c.c. (by experiment).

In the series Air II. :—

$$\text{Mean } t_1 = 11{\cdot}72, \quad \text{Mean } t_2 = 99{\cdot}73, \quad \text{Weight of air} = 4{\cdot}8064 = \text{W}.$$

V_1 has first to be found, by a subtractive correction for temperature (of $0{\cdot}024$ c.c. using the coefficient of expansion $\beta = 0{\cdot}00004998$, applied to the measured volume at 15°, and by an additive correction for distension effected on a first rough estimate of pressure at t_1; 24 atmospheres in this case. This last correction amounts to $0{\cdot}191$ c.c. Finally therefore the value V_1 is found to be $159{\cdot}993$ c.c.

In estimating P_1, the weight of a volume of air $= V_1$, at the temperature $11°{\cdot}7$ and at the pressure 760 mm. is divided into W. This gives the approximate pressure P_1, due to W, as $24{\cdot}266$ atmospheres.

The thermal expansion over the range $t_2 - t_1$, is calculated to be $0{\cdot}702$.

From these values the correction (1) is first calculated. This reduced to its thermal equivalent in grammes of steam precipitated is found to amount to a correction of $- 0{\cdot}00090$.

To estimate the second correction, that for the effect of elastic distension of the sphere, the pressure at the temperature t_2 is found by the coefficient of increase of pressure, α (REGNAULT). It is found to be $32{\cdot}54$, and the distension due to the increase is, by calculaton, $0{\cdot}065$ c.c. Taking V_1' as $160{\cdot}695$ and V_2' as $160{\cdot}760$, the correction is calculated and found to be $- 0{\cdot}0000658$ grm. of steam.

The buoyant effect of the distension in the steam (4) is found to be $+ 0{\cdot}000039$ grm. ; and the correction for the air-to-steam displacement effect of the distension due to P_1 (5) is $- 0{\cdot}000140$ grm.

In this series, Air II., the weight of precipitation due to the unequal thermal values of the spheres is, on four experiments, found to be $0{\cdot}00310$ over the range $87{\cdot}92$. As this excess is on the idle sphere it is a $+$ correction. Calculating the proportional correction over the range $t_2 - t_1$ and adding this to the observed precipitation, the correction for displacement of the precipitation in the steam is with sufficient accuracy applied to the result. It is $+ 0{\cdot}000083$ grm. The final result is a correction of $- 0{\cdot}000920$ grm., which is taken as 1 milligrm., as the balance reads reliably no closer than to the fourth place of decimals. The true weight of precipitation to be ascribed to the calorific capacity of the air enclosed at constant volume, can now be arrived at.

Having calculated thus the corrections for one series of experiments effected in a particular vessel, the labour of future calculations may be much lightened by basing the new corrections on the old, proportionately to pressure and range of temperature.

In the calculation of the corrections in the case of carbon dioxide, which departs very sensibly from BOYLE's law, the estimation of pressure is based on the results of the experiments of ANDREWS ('Roy. Soc. Proc.,' vol. 24, p. 458) on the departure of this gas from conformity with BOYLE's law, and on its coefficient of expansion at constant volume at various pressures and temperatures. The last data are not as full as would be desirable.

8. A correction on the apparent weight of gas compressed into the sphere is necessary in the case of hydrogen where the total weight of gas is small. The correction arises from the distension of the sphere due to the pressure P_1, and is equal to the amount of distension multiplied into the density of the air at the time the weighing is effected. Whether it is positive or negative will depend upon whether the weight has been determined upon the occasion of filling the sphere or emptying it. It is negligible in the case of a gas so dense as air. Thus in the numerical example I have given the distension 0·191 c.c. affords a correction of 0·00023 grm. This, in a weight of gas of 4·8064 grms., is outside the value to five figures of the specific heat. In the case of hydrogen the same distension would arise for a weight of but one-third of a gramme. The correction has therefore been applied in all cases to the weights of hydrogen.

Calculation of the Density and Pressure.

On Plate 6 will be found charts giving a graphic representation of the results of the experiments. In these the mean result of each series is taken as ordinate, the mean absolute density (mass of one cubic centimetre) of the gas as abscissa.

The mean absolute density is the ratio W/V, where W is the *total* weight of gas enclosed in the sphere, V the mean volume during experiment. The total weight of gas is obtained with sufficient accuracy by adding to the measured weight of gas the calculated weight of a volume of the gas equal to the volume of the sphere, and at the temperature and pressure (approximately) obtaining in the "empty" sphere at the time when the weight of gas was being determined. The volume is obtained from the standard observations on the sphere, corrected for thermal expansion to the temperature $\frac{1}{2}(t_2 - t_1)$ (*i.e.*, to the mean temperature of the experiment), and for the distension due to the *total* weight of enclosed gas at the mean temperature of experiment as before.

This is a troublesome estimation, as it has to be independently calculated for each series.

Simultaneously with calculating the last constant we arrive easily at an estimate of the *actual* or total pressure in the sphere at the temperature $\frac{1}{2}(t_2 - t_1)$, that is, the pressure due to the total weight of gas in the sphere, as above, at the actual mean volume, as above, and at the mean temperature of experiment. The numbers obtained for the pressures in the sphere can only be considered as approximate. This

more especially applies to the case of carbon dioxide, for which gas I used, however, as far as possible the determinations of ANDREWS, as in the calculations (*ante*) of pressure and density for the evaluation of the errors.

Particulars of the Spheres used to contain the Gas and other particulars.

Sphere A.—Weight 41·105 grms., 0·4 grm. lighter than its counterpoise; internal volume 161·560 c.c. at 15°. This sphere appears to have increased permanently in volume from the effects of the experiments. The above is from a recent observation, and, although no comparably accurate observation was made before the experiments, a reliable observation of the difference between its external volume and the external volume of its counterpoise, made before the experiments, afforded 1·7 c.c.; one made recently gave 3·545 c.c., an increase of 1·845 in external volume.

Its shrinkage was determined recently in two experiments. In one the release of 2·5284 grms. of air at 14°·3 afforded a shrinkage of 0·2636 c.c.; in the second experiment the air released weighed 1·6046, and the shrinkage was 0·1723. Temperature of the air 16°. These results agree closely, and a mean result is accepted.

Sphere B.—Weight without catchwater 92·4 grms.; internal volume, measured June, 1890, = 159·826 at 15°; measured May, 1889 (before the experiments recorded in this paper) = 159·829 at 14°. There has therefore been no permanent set in the distension of this sphere. Its volume differs from that of its counterpoise by 0·580 c.c.; its weight by 6 grms.

Its distension has been measured by two experiments; one, in October, 1889, affording 0·1732 c.c. for a pressure of 22·01 atmospheres, or a weight of air 4·3525 at 12°. A second experiment (June, 1890) showed a shrinkage of 0·1013 for the release of 2·5728 grms. of air at 15°·4. These agree very closely; the first is taken for calculating the corrections.

The Thermometer.—The thermometer used in obtaining the initial temperatures throughout, is one of NEGRETTI and ZAMBRA's, divided openly to tenths of a degree, and standardised at Kew. At the close of the experiments it was compared with a recently standardised thermometer, when no appreciable error was detected.

The upper limit of temperature was in the earlier experiments obtained from observation of a fine barometer corrected for capacity by a movable scale. Subsequently a standardised thermometer of NEGRETTI and ZAMBRA's, reading to tenths, was used. Comparing its indications with the readings derived from the barometer, no appreciable difference was found to obtain.

Value ascribed to the Latent Heat of Steam.—The latent heat of steam is assumed to have the values determined by REGNAULT, and is derived from his formula, for each experiment. This constant has been investigated by ANDREWS (535·9 at 100°), BERTHELOT (636·2 at 100°, total heat), FAVRE and SILBERMANN (537·77 at 99°·81). These agree closely, but all are a little lower than REGNAULT's results (536·5 at 100°),

and would tend to lower the results of the experiments by a very slight (inappreciable) amount.

The Experiments on Air.

The results of the first experiments[*] on air effected in the differential calorimeter, were to ascribe to it a somewhat higher specific heat than subsequent experiments have revealed. The air in these experiments was compressed in contact with oil, and hence moisture and impurities in the air are probably the source of difference. These experiments, too, appeared to indicate invariability of the specific heat over a considerable range of pressure. Subsequent experiments, which from the very fact of the existence of the discrepancy have been multiplied in number, disprove this result. There is an undoubted diminution of the specific heat with decreasing pressure or density. A plausible explanation of the first result exists in the very certain presence of moisture in the gas, taken in conjunction with the course of procedure adopted.

The lower pressures were obtained in fact by releasing a certain quantity of the gas between the first and second series of experiments. Now if moisture be present, the effect of this procedure is to concentrate the impurity at the lower pressure, for on the moment of release there is an intense chilling of the vessel, which will have the effect of precipitating any moisture in suspension in the gas. A small thing will conceal the decrement of thermal capacity, as will be judged from the succeeding experiments. I may point out here that over and above the quantity of moisture (calculated to be some 2 milligrammes) necessary to saturate the volume of 160 c.c. of air at the normal temperature, t_1, the effect of moisture is to cause very serious error. Water, in the form of a liquid, within the sphere must, in fact, be conceived as adding its latent heat of vaporisation to intensify the error. For every milligramme of water evaporating within, there will be thrown down externally a corresponding milligramme of steam. I have already described the results of observations which showed that even with the use of a much safer apparatus for effecting the compression of the gas, a considerable weight of water was, in some way, taken up by the gas in its passage through the pump; so that it was found essential to re-dry the gas immediately before its entrance into the sphere. The presence of moisture in the preliminary experiments is therefore very probable.

Not at first fully recognising the probability of error in the first results, it was some time before I recognised the possibility of a variation of the specific heat with pressure. The ordinary contention that from REGNAULT's experiments on air at constant pressure the conclusion is legitimate that at constant volume there is no variation of specific heat, was so (apparently) forcible, that any other result was deemed improbable. In truth, however, the assumption of perfectness for air is at variance with the facts, and it is probable that the variation of specific heat is an outcome of its imperfectness. Later on, the experiments on carbon dioxide, a typically

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[*] " On the Specific Heats of Gases at Constant Volume (Preliminary Note)," *loc. cit.*

imperfect gas, revealed a much more marked variation of specific heat with density, which by analogy tends to confirm the results on air. A still more remarkable evidence is afforded by the behaviour of hydrogen, as will be seen later.

The first two series of experiments on air succeeding those published, effected on separate samples of air, brought down the specific heat by some 2 per cent. (The results in the Preliminary Note are not corrected for errors of expansion, &c.), and revealed a variation following the density. With the improved conditions under which my experiments are now carried on, the more recent results are again somewhat at variance with these two, the first effected with the use of the improved pump. I think it best, in the case of each gas, to give the experiments in order of date.

To effect the drying and purifying of the air in these and the succeeding experiments, it is passed through a train of U-tubes, consisting of a tube containing pumice soaked in strong caustic potash, a tube containing pumice soaked in strong sulphuric acid, and then through three tubes packed with dried asbestos fibres, separated by layers of phosphoric anhydride. These tubes are closed with ground stoppers, are some 2 cms in diameter, and afford an effective length of 40 cms. each.

Finally, between receiver and sphere, the high-pressure drying tube, having a length of 40 cms., and a capacity of 31 c.c., also containing phosphoric anhydride, removes what moisture may be taken up in the receiver.

Regarding the mode of tabulating the results of the experiments, it should be mentioned for clearness, that the column headed ω gives the total apparent weight in grammes of precipitation observed in each experiment. The amounts of the corrections, in grammes, to be applied in each case, are given below the columns, as well as the mean of the column ω adjusted for all corrections. This is designated ϖ. On this number, on W (the weight of gas), on the mean of the column λ (the latent heat of steam), and on the mean range, the final result is calculated, which is given at the foot of the table. The number given as the specific heat is the specific heat compared weight for weight with water.

The last column, $\omega \div (t_2 - t_1)$, is added for the purpose of affording a means of judging of the agreement of the experiments *inter se*.

AIR I.—W = 4·3527 grammes.   Mean Absolute Density, 0·028406.   Mean
Pressure, 26·45 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	13·42	99·82	536·6	86·40	0·1332	15417
2	13·60	99·76	536·7	86·16	0·1335	15494
3	13·04	99·36	536·9	86·32	0·1333	15442
	13·35	99·64	536·7	86·29	0·13333	15451

Rate of correction for spheres = − 0·0106 for 86°·52.   Sphere B.
Corrections for thermal expansion, &c. = − 0·00090. ϖ = 0·12185.

Deduced specific heat = 0·17411.

At the conclusion of this series, the air enclosed was passed out through a weighed
drying tube, and assurance of the freedom (sensibly) from moisture of the air thereby
obtained, as previously described.

Three experiments on the spheres at normal pressures were made after the release
of the air.

CORRECTION for Spheres (Air I.).

No.	t_1.	t_2.	w.
1	13·11	99·22	− 0·0109
2	12·37	99·14	− 0·0106
3	12·72	99·41	− 0·0103

Mean range, 86·52.
Mean w = − 0·0106.

In the table the sign of ω indicates whether the excess precipitation is on the active
or on the idle sphere; when in the former it is marked —, being then subtractive
as a correction.

AIR II.—W = 4·8064 grammes. Mean Absolute Density, 0·031201. Mean
Pressure, 29·586 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	11·70	99·56	536·8	87·86	0·1356	15434
2	11·27	99·88	536·6	88·61	0·1360	15348
3	12·30	99·83	536·6	87·53	0·1340	15309
4	11·60	99·64	536·7	88·04	0·1358	15425
	11·72	99·73	536·7	88·01	0·13535	15379

Rate of correction for spheres = + 0·0031 for 87°·92. Sphere B.
Corrections for thermal expansion, &c. = − 0·00100. ϖ = 0·13745.

Deduced specific heat = 0·17439.

Some alterations having been made to the spheres, a fresh set of observations on their state of thermal equilibrium was necessitated for obtaining the correction for the last experiments.

CORRECTION for Spheres (Air II.).

No.	t_1.	t_2.	w.
1	12·39	99·98	+ 0·0028
2	12·30	99·98	+ 0·0029
3	11·71	99·70	+ 0·0032
4	11·37	99·79	+ 0·0035

Mean range 87·92.
Mean w = + 0·0031.

These two series of experiments will be found plotted as the highest points on the Air Diagram, Plate 6. They show a fall of specific heat with diminishing density, but from after results it appears the rate of decrement is somewhat exaggerated. In subsequent experiments the number of observations in each series was increased.

An attempt was now made to fix points in the line of specific heat at lower pressures. The sphere A was taken into use for the purpose. The number obtained in series III. for the specific heat agrees fairly with the later observations. The succeeding series, IV. and V., are still more in harmony with the best observations made some months later. Although, on the small masses of air used in these series, very definite conclusions as to the exact position of the true line cannot be drawn ;

yet, from the number of experiments made and their agreement among themselves, it is probable that they are a fair approximation to the truth.

A glance at the diagram shows that what is very probably the true line passes fairly well through the mean of IV. and V.

In the series III., IV., and V., the air was separately compressed for each series, and in the case of series III. it was examined for the presence of moisture in the manner before described.

AIR III.—W = 2·3334 grammes.   Mean Absolute Density, 0·015654.   Mean Pressure, 14·58 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
1	9·80	100·32	536·3	90·52	0·0686	0·000 75784
2	9·20	100·18	536·4	90·98	0·0702	77160
3	10·70	100·07	536·4	89·37	0·0691	77319
4	10·43	99·76	536·6	89·33	0·0688	77018
5	11 51	99·74	536·7	88·23	0·0685	77638
	10·33	100·01	536·5	89·68	0·06903	76974

Rate of correction for spheres = — 0·0012 for 90°·77.   Sphere A.
Corrections for thermal expansion, &c. = — 0·00053. w = 0·06729.

Deduced specific heat = 0·17252.

CORRECTION for Spheres (Air III.).

No.	t_1.	t_2.	w.
1	10·25	99·41	— 0·0012
2	8·60	99·82	— 0·0012
3	8·54	99·96	— 0·0009
4	9·17	99·85	— 0·0016
5	8·48	99·85	— 0·0012

Mean range = 90°·77.
Mean w = — 0·00122.

AIR IV.—W = 1·4728 grammes.   Mean Absolute Density, 0·010335.   Mean Pressure, 9·56 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·000
1	8·97	100·35	536·2	91·38	0·0446	48807
2	9·44	100·41	536·2	90·97	0·0440	48368
3	9·95	100·41	536·2	90·46	0·0451	49856
4	10·42	100·29	536·3	89·87	0·0442	49182
5	11·26	100·29	536·3	89·03	0·0444	49871
6	12·16	100·29	536·3	88·13	0·0439	49813
7	9·36	99·73	536·7	90·37	0·0454	50238
8	9·63	99·70	536·7	90·07	0·0451	50072
	10·15	100·18	536·36	90·03	0·04459	49528

Rate of correction for spheres = − 0·00196 for 90°·36.   Sphere A.
Corrections for thermal expansion, &c. = − 0·00033. x = 0·04230.

Deduced specific heat = 0·17111.

CORRECTION for Spheres (Air IV.).

No.	t_1.	t_2.	w.
1	9·30	99·97	− 0·0010
2	9·90	99·91	− 0·0019
3	10·50	100·09	− 0·0031
4	9·18	100·49	− 0·0019
5	10·10	100·49	− 0·0020
6	10·37	100·44	− 0·0022
7	9·94	100·44	− 0·0016

Mean range = 90°·36.
Mean w = − 0·00196.

Air V.—W = 0·9766 gramme.   Mean Absolute Density, 0·00728.   Mean Pressure, 6·81 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$	w.	$w \div (t_2 - t_1)$.
						0·000
1	9·40	99·40	536·9	90·00	0·0302	33555
2	9·60	99·45	536·9	89·85	0·03075	34224
3	8·96	99·87	536·5	90·91	0·0301	33110
4	9·40	99·86	536·5	90·46	0·0300	33164
5	9·74	100·03	536·5	90·29	0·0304	33669
6	10·00	100·06	536·4	90·06	0·03075	34144
7	8·90	99·81	536·6	90·91	0·0311	34210
8	9·51	99·67	536·7	90·16	0·0308	34161
9	8·60	100·07	536·4	91·47	0·0304	33235
	9·34	99·80	536·6	90·46	0·03050	33717

Rate of correction for spheres = − 0·0019 for 89°·32.   Sphere A.
Corrections for thermal expansion, &c. = − 0·000217. ϖ = 0·02832.

Deduced specific heat = 0·17202.

CORRECTION for Spheres (Air V.).

No.	t_1.	t_2.	w.
1	10·16	100·03	− 0·0017
2	10·40	99·96	− 0·0019
3	10·65	99·71	− 0·0026
4	10·27	99·89	− 0·0025
5	11·10	99·83	− 0·0014
6	10·30	99·78	− 0·0016
7	10·50	99·72	− 0·0021
8	10·51	99·93	− 0·0020
9	9·60	99·29	− 0·0017

Mean range 89°·32.
Mean w = − 0·0019.

Some months after the completion of the foregoing observations, when under more favourable conditions (see *Introduction*) the results of experiments were visibly improved in consistency, and more experience had been obtained, I resumed the observations on air. The series VI., VII., VIII., and IX. were carried out. In these the sphere B alone was used. VI. and VII. are on the one sample of air; so are VIII. and IX. That is, the air for the low density series was in each case provided from that used at higher pressure by suffering part of the latter to escape. As great precautions were taken

(by the use of freshly filled tubes, &c.) to secure effective drying of the air, this procedure was probably not productive of error (see p. 90). In the interval between the series VII. and VIII., experiments on the equilibrium of the vessels were made.

Air VI.—W = 3·7463 grammes.   Mean Absolute Density, 0·024591.   Mean Pressure, 23·35 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	ω.	$\omega \div (t_2 - t_1)$.
						0·00
1	14·29	100·30	536·3	86·01	0·1401	16289
2	14·58	100·31	536·3	85·73	0·1393	16249
3	13·74	100·40	536·2	86·66	0·1402	16178
4	14·44	100·40	536·2	85·96	0·1399	16275
5	15·03	100·37	536·3	85·34	0·1392	16311
	14·41	100·35	536·26	85·94	0·13974	1·6260

Rate of correction for spheres = − 0·0353 for 85°·36.   Sphere B.
Corrections for thermal expansion, &c. = − 0·00078. ϖ = 0·10340.

Deduced specific heat = 0·17223.

Air VII.—W = 2·0923.   Mean Absolute Density, 0·014281.   Mean Pressure, 13·563 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	ω.	$\omega \div (t_2 - t_1)$
						0·00
1	13·96	100·32	536·3	86·36	0·0937	10850
2	14·78	100·25	536·3	85·47	0·0936	10951
3	14·12	100·30	536·3	86·18	0·0939	10896
4	14·46	100·31	536·3	85·85	0·0932	10856
5	14·45	100·34	536·3	85·89	0·0936	10898
6	13·51	100·40	536·2	86·89	0·0949	10922
	14·21	100·32	536·3	86·11	0·09382	10895

Rate of correction for spheres = − 0·0353 for 85°·36.   Sphere B.
Correction for thermal expansion, &c. = − 0·000439. ϖ = 0·05776.

Deduced specific heat = 0·17193.

CORRECTION for Spheres (Air VI., VII., VIII., IX.).

No.	t_1.	t_2.	w.
1	14·40	100·35	— 0·0358
2	13·87	100·20	— 0·0358
3	14·78	100·17	— 0·0356
4	15·20	100·01	— 0·0348
5	14·60	99·90	— 0·0352
6	15·38	99·78	— 0·0347

Mean range = 85°·36.
Mean w = — 0·0353.

AIR VIII.—W = 4·2854 grammes.   Mean Absolute Density, 0·027944.   Mean Pressure, 26·62 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	15·60	99·93	536·5	84·33	0·1513	17941
2	14·96	100·03	536·5	85·07	0·1532	18009
3	15·82	100·05	536·5	84·23	0·1522	18070
4	16·50	100·02	536·5	83·52	0·1510	18080
5	15·01	100·18	536·4	85·17	0·1525	17906
6	15·48	100·29	536·3	84·81	0·1528	18016
	15·56	100·08	536·45	84·52	0·15217	18004

Rate of correction for spheres = — 0·0353 for 85°·36.   Sphere B.
Correction for thermal expansion, &c. = — 0·000902. ϖ = 0·11629.

Deduced specific heat = 0·17225.

AIR IX.—W = 2·2558 grammes.   Mean Absolute Density, 0·015297.
Mean Pressure, 14·53 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1.)$
						0·00
1	14·78	100·36	536·3	85·58	0·0977	11416
2	14·40	100·55	536·1	86·15	0·0980	11376
3	15·40	100·57	536·1	85·17	0·0982	11530
4	15·40	100·55	536·1	85·15	·0·0977	11474
5	14·44	100·30	536·3	85·86	0·0979	11402
6	15·60	100·13	536·4	84·53	0·0962	11381
7	15·64	100·10	536·4	84·46	0·0964	11414
8	15·16	100·14	536·4	84·98	0·0969	11403
	15·10	100·33	536·26	85·23	0·097375	11425

Rate of correction for spheres = — 0·0353 for 85°·36.   Sphere B.
Correction for thermal expansion, &c. = — 0·000474. ϖ = 0·06164.

Deduced specific heat = 0·17192.

Omitting the first two experiments as anomalous, and therefore, probably containing some error or inaccuracy, the results for air stand thus :—

No.	C_v.	Pressure in atmospheres.	Absolute density.
III.	0·17252	14·58	0·015654
IV.	0·17111	9·56	0·010335
V.	0·17202	6·81	0·00728
VI.	0·17223	23·35	0·024591
VII.	0·17193	13·56	0·01428
VIII.	0·17225	26·62	0·027944
IX.	0·17192	14·53	0·015297
Means .	0·171997	15·57	0·016483

From these it is, I think, well established that the mean specific heat at the mean pressure of 15 atmospheres has the value to three figures very closely of 0·172. Taking the means of the last four—by far the most reliable results—*the specific heat of air at constant volume to four figures is* 0·1721, *for the mean absolute density* 0·0205, *and mean pressure* 19·51 *atmospheres*. The close agreement of the experimental numbers is a strong reason for accepting these last four results as reliable.

If it be asked how far this agrees with theory, it may be answered that theory has more than one value to ascribe to the specific heat, for the data with which theory has to deal are not invariable.

Taking the value of the specific heat at constant pressure as 0·2375 (REGNAULT), and the value of R/E (CLAUSIUS, 'Mechanical Theory of Heat') as 0·0691, the number 0·1684 is obtained; assuming C_p to be 0·2389 (WIEDEMANN), the number becomes 0·1698. But further, in the fraction R/E the exact value of E (the mechanical equivalent of heat) is still in question. CLAUSIUS assumes 423·55, but a recent discussion of the results of ROWLAND[*] and others appears to indicate more nearly a value 426·8.[†] This brings the fraction R/E to 0·06858; which, applied to REGNAULT's result gives 0·1698 as the value of C_v; applied to WIEDEMANN's result (the most reliable), gives 0·1712 as C_v. These are supposed to be the values at 760 mm. pressure.

Basing speculations on the value of γ and WIEDEMANN's result for C_p, the number 0·1692 is found for C_v. Finally it may be calculated on the values γ, R, and E only, and if the last is taken as 426·8, C_v is found to be 0·1689.

Of the above results that value which appears most directly based on the most reliable experimental results assigns 0·1712 as the value of C_v at the pressure of one atmosphere. Now, assuming that the specific heat is a linear function of the pressure, the experimental data, VI., VII., VIII., and IX., afford the value 0·17154 for C_v at the pressure of one atmosphere.

On the reality of the variation of the specific heat with change of pressure I may observe that the experiments free of error are almost unanimous in showing such a variation. The coincidence (I might say the *identity*) of the slope of VI. and VII. with the slope of VIII. to IX. is remarkable. It may be objected that the difference of the actual numbers is very small. I find that the "probable error" of the specific heat (so far as the series of values of $\omega \div (t_2 - t_1)$ indicates) is $\pm$ 0·00018 in the case of IX., and $\pm$ 0·00019 in the case of series VIII. If the coincidence of a $+$ error on the lower result with a $-$ error on the higher result for the specific heat be assumed, the numbers just coincide. The lower becomes 0·17210, the higher 0·17206. But the same coincidence has to be assumed for the series VI. and VII. There is, further, the analogy with carbon dioxide, in which case there is no room for doubt as to the variability of the specific heat. In the case of hydrogen it will subsequently be seen there is also very certain variability of the specific heat, but in the *opposite direction*; that is, while in the case of air and carbon dioxide the specific heat increases with increasing density, in the case of hydrogen it diminishes. Now this for all three gases agrees with their behaviour as regards BOYLE's law at the pressures covered by the experiments. It is well known that in the case of air and carbon dioxide the imperfectness of the gases is revealed by departures from BOYLE's law, small in the one case, large in the other, but in the *opposite direction* to that which is apparent in the case of hydrogen, whose deviation from the law is, as in the case of air, small.

These facts, taken together, are, I think, a strong confirmation of the reality of the

[*] "On the Mechanical Equivalent of Heat," 'Amer. Acad. Proc.,' 1880.

[†] 'Thermodynamics,' by DE VOLSON WOOD, New York, 1889, p. 25 *et seq.*

variation observed in the experiments on air. For if there is no corresponding reality to the variation shown by nearly all the experiments on air, it is necessary to suppose some source of error varying in the one direction with the pressure. Considered now in connection with the other two gases it is necessary to suppose this error *increasing* in intensity for the more imperfect gas and *reversed in direction* for the super-perfect gas.

It appears therefore that:—

The specific heat of air at constant volume is not constant under variation of pressure, but increases with increase of pressure, between the limits of pressure 10 *to* 30 *atmospheres (which the experiments sufficiently cover) at the mean temperature of* 50° *C.*

If we assume that the function connecting density and specific heat over the range of observation is a linear one, the equation

$$C_v = \rho \times 0.02788 + 0.17151 . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

affords the specific heat as a function of the absolute density ρ, in agreement with the experiments VI. to IX.

The Experiments on Carbon Dioxide.

The gas used in these experiments was generated by the action of " pure " dilute sulphuric acid on bicarbonate of soda. It was stored in a large glass holder under a head of about 50 cms. of water. From the holder it passed through two U-tubes containing sulphuric acid on pumice, and three U-tubes filled with phosphoric anhydride packed with asbestos. Through these the receiver drew the gas as required, and passed it on into the sphere through the high-pressure drying-tube filled with phosphoric anhydride. I give the results in the order in which they were obtained.

It is my intention shortly to endeavour to trace the specific heat of this gas more minutely throughout, and up to its state as a liquid. The spheres for this purpose have indeed already been completed.

CARBON Dioxide I.—W = 2·9283 grammes.   Mean Absolute Density, 0·019950.
Mean Pressure, 12·2 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·000
1	8·30	100·13	536·4	91·86	0·0902	98193
2	9·05	100·03	536·5	91·02	0·0896	98440
3	8·97	99·96	536·5	90·99	0·0885	97263
4	9·73	99·97	536·5	90·24	0·0887	98293
5	9·70	99·97	536·5	90·27	0·0886	98150
6	9·80	99·74	536·7	89·94	0·0875	97287
	9·26	99·97	536·5	90·72	0·08885	97939

Rate of correction for spheres = — 0·00395 for 89°·84.   Sphere A used.
Correction for thermal expansion, &c. = — 0·00043. ϖ = 0·08439.

Deduced specific heat = 0·17054.

CORRECTIONS for Spheres (Carbon Dioxide I.–III.).

No.	t_1.	t_2.	w.
1	10·32	99·60	— 0·0026
2	9·24	99·40	— 0·0034
3	9·62	99·38	— 0·0037
4	9·10	100·18	— 0·0041
5	10·70	100·12	— 0·0040
6	10·72	99·90	— 0·0045
7	10·41	99·77	— 0·0040

Mean range = 89°·84.
Mean w = — 0·00395.

This series of experiments on the spheres also applies to the ensuing two series, II. and III.   The same sample of gas is used in II. and III.

CARBON Dioxide II.—W = 2·9016 grammes.   Mean Absolute Density, 0·019786.
Mean Pressure, 12·1 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$\omega \div (t_2 - t_1)$.
						0·000
1	10·80	99·33	537·0	88·53	0·0843	95222
2	11·35	99·33	537·0	89·98	0·0852	96840
3	9·20	99·28	537·0	90·08	0·0870	96581
4	10·40	99·22	537·0	88·82	0·0858	95600
	10·25	99·33	537·0	88·85	0·08558	96320

Rate of correction for spheres = − 0·00395 for 89°·84.   Sphere A used.
Correction for thermal expansion, &c. = − 0·00043. ϖ = 0·08115.

Deduced specific heat = 0·16922.

CARBON Dioxide III.—W = 1·5622 grammes.   Mean Absolute Density, 0·011530.
Mean Pressure, 7·2 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$\omega \div (t_2 - t_1)$.
						0·000
1	10·37	99·49	536·9	89·12	0·0475	53299
2	10·40	99·50	536·8	89·10	0·0483	54209
3	9·70	99·50	536·9	89·80	0·0476	53007
4	10·86	99·50	536·9	88·82	0·04785	53873
5	10·66	99·52	536·8	88·86	0·0474	53342
6	9·86	99·86	536·6	90·00	0·0479	53222
7	11·16	99·87	536·6	88·71	0·0476	53658
8	10·84	99·87	536·6	89·03	0·0481	54027
	10·46	99·64	536·7	89·18	0·04786	53667

Rate of correction for spheres = − 0·00395 for 89°·84.   Sphere A used.
Correction for thermal expansion, &c. = − 0·00022. ϖ = 0·04367.

Deduced specific heat = 0·16841.

In the next three series the high-pressure sphere is taken into use. The experiments on the thermal equilibrium of the spheres, applying to all three, were made after IV. The gas in V. and VI. is from the same sample.

CARBON Dioxide IV.—W = 5·5524 grammes. Mean Absolute Density, 0·036529.
Mean Pressure, 20·90 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	10·00	99·76	536·7	89·76	0·2010	22393
2	10·86	99·76	536·7	88·90	0·1986	22340
3	10·64	99·80	536·6	89·16	0·1998	22409
4	10·55	99·70	536·7	89·15	0·1988	22300
5	9·70	99·76	536·7	90·06	0·2010	22319
6	9·80	99·76	536·7	89·96	0·2004	22277
	10·26	99·76	536·7	89·50	0·19993	22339

Rate of correction for spheres = − 0·0390 for 89°·35. Sphere B used.
Correction for thermal expansion, &c. = − 0·000637. ϖ = 0·16023.

Deduced specific heat = 0·17305.

CORRECTION for Spheres (Carbon Dioxide IV.–VI.).

No.	t_1.	t_2.	w.
1	10·22	99·13	− 0·0379
2	10·58	99·10	− 0·0401
3	9·40	99·51	− 0·0390
4	10·00	99·60	− 0·0389
5	10·35	99·63	− 0·0381
6	10·16	99·86	− 0·0389

Mean range = 89°·35.
Mean w = − 0·0390.

CARBON Dioxide V.—W $= 5.757$ grammes.   Mean Absolute Density, 0.037802.
Mean Pressure, 21.66 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	10·51	99·96	536·5	89·45	0·2066	23097
2	10·79	100·01	536·5	89·22	0·2056	23044
3	11·00	100·00	536·5	89·00	0·2057	23112
4	11·10	100·00	536·5	88·90	6·2056	23127
5	10·77	100·08	536·5	89·31	0·2064	23110
	10·83	100·01	536·5	89·18	0·20598	23097

Rate of correction for spheres $= - 0.0390$ for $89°.35$.   Sphere B used.
Correction for thermal expansion, &c. $= - 0.000661$. $\varpi = 0.16638$.

Deduced specific heat $= 0.17386$.

CARBON Dioxide VI.—W $= 4.2654$ grammes.   Mean Absolute Density, 0.028498.
Mean Pressure, 16.87 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	11·16	100·08	536·5	88·92	0·1605	18050
2	10·47	100·11	536·5	89·64	0·1615	18017
3	10·93	100·10	536·5	89·17	0·1610	18055
4	11·00	100·13	536·5	89·13	0·1609	18052
5	10·52	100·40	536·2	89·88	0·1624	18068
	10·82	100·16	536·5	89·34	0·16126	18050

Rate of correction for spheres $= - 0.0390$ for $89°.35$.   Sphere B used.
Correction for thermal expansion, &c. $= - 0.000510$. $\varpi = 0.12175$.

Deduced specific heat $= 0.17141$.

The foregoing experiments are plotted in the diagram for carbon dioxide, Plate 6.
On the purity of the gas I may observe that, in the course of compressing the gas
for one of the experiments, I drew off some of the gas and tested its purity by
absorption with caustic potash. A *very small* bubble of air (presumably) remained
over. It was impossible, in the tube used, to ascertain its volume ; but as this was
the impurity in 80 c.c., and as from the approximation of specific heats and, indeed,
of densities, a small impurity would not affect the result, I did not think it necessary
to delay over its exact estimation.

Connecting, on the diagram, the mean of Experiments I. and II. with the mean of Experiments IV. and V. gives a line probably expressing closely the true locus of the specific heat. From this line the equation for the specific heat as a function of the density is found to be

$$C_v = \rho \times 0 \cdot 2064 + 0 \cdot 16577 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Taking again the means of Experiments I. and II., IV. and V., as affording reliable results, which seems justifiable, the specific heat of carbon dioxide at constant volume is $0 \cdot 16988$ at the pressure $16 \cdot 71$ atmospheres and density $0 \cdot 01987$, and $0 \cdot 17345$ at the pressure $21 \cdot 28$ atmospheres and density $0 \cdot 03716$; both at the mean temperature of 55° C.

These numbers differ by so considerable an amount as to render it most improbable that the experiments express other than a real variation of the specific heat of carbon dioxide. And the conclusion seems justified that *the specific heat of carbon dioxide is not constant, but increases very appreciably with increase of density throughout the range of pressure 10 to 25 atmospheres at the mean temperature of 55° C.*

I add for convenience a table of the experiments.

EXPERIMENTS on Carbon Dioxide.

No.	C_v.	Pressure in atmospheres.	Absolute Density.
I.	0·17054	12·20	0·019950
II.	0·16922	12·10	0·019786
III.	0·16841	7·20	0·011530
IV.	0·17305	20·90	0·036529
V.	0·17386	21·66	0·037802
VI.	0·17141	16·87	0·028498

The specific heat at the pressure of one atmosphere is by calculation $0 \cdot 16552$. The number obtained by CLAUSIUS from the experiments of REGNAULT is $0 \cdot 172$. But apparently CLAUSIUS' result applies to REGNAULT's experiments in C_p over the range 11° to 214°. If CLAUSIUS' formula* be applied to REGNAULT's results over the range 15° to 100°, a result departing from the experimental value of C_v in the opposite direction is obtained, *i.e.*, $0 \cdot 157$. The amendment of CLAUSIUS' formula for the value of E raises the last number by a trifling amount. The cause of the discrepancy of these results is not apparent. It is suggestive that in the case of the more perfect gases, air and hydrogen, the deduction of the one specific heat from the other is attended by no such wide discrepancy.

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* 'Mechanical Theory of Heat,' p. 55. London, 1879.

The Experiments on Hydrogen.

The difficulties in the way of obtaining this gas in a sufficiently pure state proved so great, that what can only be considered as *qualitative* results have been obtained from the experiments up to the present. It is true that as the procedure of generating and storing the gas was refined upon, results closely agreeing with the theoretical value of the specific heat were obtained, but always so far differing from each other as to show *some* difference in the purity of the samples of gas dealt with. It has, hence, been impossible to assign with certainty a definite experimental value to the specific heat.

The earlier experiments are rejected as having been effected on very impure hydrogen, affording values entirely too low. A very small impurity by volume will seriously affect the result of experiment. The error due to an admixture with another gas is, in fact, very nearly proportional to the percentage of impurity by weight.

The hydrogen was generated from granulated distilled zinc, under the action of dilute " pure " sulphuric acid. It was purified, in the case of the immediately succeeding experiments, by passing it through a tube containing pumice and a solution of silver nitrate, and then dried by passage through a tube containing sulphuric acid on pumice, and three tubes of phosphoric anhydride, passing through a fourth tube of the same nature between receiver and sphere. From the generating bottle it passed into a glass gas-holder under a head of about half a metre of water for the supply of the pump.

At the conclusion of the Series I. a portion was allowed to escape and a second series of experiments made on the residue. The gas released from the sphere was in part passed into a eudiometer having a capacity of 50 c.c. and burned with an excess of electrolytically prepared oxygen. The residual oxygen was then treated first with caustic potash (which revealed no carbon dioxide) and then with pyrogallic acid. A small quantity, estimated later (by weighing a bead of mercury occupying the same volume in the tube) as 0·11 c.c., remained. The error by volume was estimated as 1 in 350, or, if the impurity was nitrogen, 1 in 25 by weight. This will be nearly the maximum error to be ascribed to the thermal result. The eudiometric experiment, however, is not satisfactory, as there is, I am informed, a liability to the evolution of carbon monoxide from the alkaline pyrogallol. It was, indeed, frequently found, in subsequent tests of like nature, that it was possible to obtain a second ignition on passing a spark when the absorption had reached a certain stage and apparently ceased. I decided in consequence to discontinue these tests, and had hoped to substitute determinations of density as tests of purity in future experiments, taking Lord RAYLEIGH's recent researches for comparison in judging of the degree of purity. The method I had intended to use for the determination of density only necessitated the use of a large volumenometer into which the gas from the sphere

might be passed, the weight of the gas being determined by successive weighings of the sphere. This method is described in a forthcoming number of the 'Proceedings of the Royal Dublin Society.'* It surmounts or reduces many of the sources of error arising in the application of REGNAULT's method. However, so far as the present experiments are concerned, I regret to say I have not been able to apply it, as the construction of the volumenometer was not completed in time. Some preliminary experiments on the application of this method appear to show that it is capable of a high degree of accuracy.

The degree of purity of the gas in the experiments from III. onwards must only be inferred from the increasing precautions taken to guard against the entrance of impurities. That higher degrees of purity were obtained as the experiments advanced may, indeed, partly be inferred from the results of the experiments themselves by the observed rise in the deduced specific heats. My subsequent attempts to test for impurities by absorption were so unsatisfactory and contradictory as to be valueless.

HYDROGEN I.—W = 0·3312 gramme.   Mean Absolute Density, 0·0021514.
Mean Pressure, 29·12 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	10·76	100·19	536·4	89·43	0·1680	18786
2	10·01	100·20	536·4	90·19	0·1691	18750
3	11·43	100·20	536·4	88·77	0·1666	18768
4	10·41	100·06	536·5	89·65	0·1675	18684
5	11·41	100·10	536·4	88·69	0·1656	18672
	10·80	100·15	536·4	89·35	0·16736	18731

Rate of correction for spheres = − 0·0359 for 88°·10.   Sphere B.
Correction for thermal expansion, &c. = − 0·000990. ϖ = 0·12997.

Deduced specific heat = 2·3559.

* 'Roy. Dublin Soc. Proc.,' vol. 6, p. 534.

HYDROGEN II.—W $= 0.2370$ gramme.   Mean Absolute Density, 0.0015646.
Mean Pressure, 21.15 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_1 - t_1)$.
						0.00
1	10.67	100.00	536.5	89.33	0.1295	14497
2	11.99	100.04	536.5	88.05	0.1286	14605
3	10.50	100.12	536.4	89.62	0.1297	14472
4	11.90	100.10	536.4	88.20	0.1288	14603
	11.26	100.06	536.45	88.80	0.12915	14544

Rate of correction for spheres $= - 0.0359$ for $88°.10$.   Sphere B.
Correction for thermal expansion, &c. $= - 0.000709$. $\varpi = 0.09224$.

Deduced specific heat $= 2.3512$.

HYDROGEN III.—W $= 0.3274$ gramme.   Mean Absolute Density, 0.0021271.
Mean Pressure, 28.79 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0.00
1	10.80	99.86	536.6	89.06	0.1661	18650
2	11.81	99.84	536.6	88.03	0.1638	18607
3	11.30	99.84	536.6	88.54	0.1643	18557
4	11.19	99.78	536.7	88.59	0.1652	18647
5	10.87	99.69	536.7	88.82	0.1653	18611
6	11.70	99.67	536.7	87.97	0.1654	18575
	11.28	99.78	536.65	88.50	0.16468	18608

Rate of correction for spheres $= - 0.0359$ for $88°.10$.   Sphere B.
Correction for thermal expansion, &c. $= - 0.000980$. $\varpi = 0.12760$.

Deduced specific heat $= 2.3633$.

HYDROGEN IV.—W = 0·2191 gramme.   Mean Absolute Density, 0·0014525.
Mean Pressure, 19·670 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	11·51	99·68	536·7	88·17	0·1206	13678
2	10·69	100·01	536·5	89·32	0·1228	13748
3	11·87	100·05	536·5	88·18	0·1223	13869
4	11·60	100·10	536·4	88·50	0·1229	13887
5	10·62	100·26	536·3	89·64	0·1244	13878
6	12·10	100·22	536·4	88·12	0·1213	13765
7	10·50	100·12	536·4	89·62	0·1239	13825
8	11·45	100·08	536·5	88·63	0·1217	13731
	11·29	100·06	536·5	88·77	0·12249	13799

Rate of correction for spheres = − 0·0359 for 88·°10.   Sphere B.
Correction for thermal expansion, &c. = − 0·000656. ϖ = 0·08564.

Deduced specific heat = 2·3623.

CORRECTION for Spheres (Hydrogen I.–VII.).

No.	t_1.	t_2.	w.
1	12·03	100·00	− 0·0359
2	10·97	99·95	− 0·0361
3	12·40	99·97	− 0·0351
4	12·76	100·00	− 0·0360
5	11·68	100·09	− 0·0360
6	11·70	100·10	− 0·0366

Mean range = 88°·10.
Mean w = − 0·0359.

As seen by the estimation of the nitrogen present in the gas used in I. and II., a maximum error of 5 per cent. may affect these results.   But this is very probably excessive.   For the succeeding series, III. and IV., further precautions were taken in dealing with the hydrogen.   Glass tubes were substituted for rubber as far as possible, the tubes being brought end to end and connected by a thick rubber, varnished externally.   A test for the presence of sulphuretted hydrogen, by passing the gas into a tube containing a filter paper soaked in acetate of lead, revealed no trace of that impurity.   The next two series, V. and VI., are upon the one sample of gas.

HYDROGEN V.—W = 0·2094 gramme.   Mean Absolute Density, 0·0013919.
Mean Pressure, 18·82 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	11·74	100·00	536·5	88·26	0·1191	13494
2	12·20	100·00	536·5	87·80	0·1174	13371
3	12·28	100·00	536·5	87·72	0·1182	13475
4	11·50	99·91	536·5	88·41	0·1183	13381
	11·93	99·98	536·5	88·05	0·11825	13430

Rate of correction for spheres = − 0·0359 for 88°·10.   Sphere B.
Correction for thermal expansion, &c. = − 0·000628. x = 0·08172.

Deduced specific heat = 2·3779.

HYDROGEN VI.—W = 0·1007 gramme.   Mean Absolute Density, 0·00071402.
Mean Pressure, 9·66 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·000
1	12·41	99·89	536·6	87·48	0·0752	85962
2	12·86	99·86	536·6	87·00	0·0753	86552
3	11·92	99·86	536·6	87·94	0·0751	85399
4	13·02	99·85	536·6	86·83	0·0749	86261
5	12·80	99·85	536·6	87·05	0·0754	86617
6	11·80	99·81	536·6	88·01	0·0762	86581
7	12·53	99·80	536·6	87·27	0·0748	85711
	12·48	99·85	536·6	87·37	0·07527	86151

Rate of correction for spheres = − 0·0359 for 88°·10.   Sphere B. 0·03937.
Correction for thermal expansion, &c. = − 0·000302. x = 0·03937.

Deduced specific heat = 2·4012.

The Series V. and VI. show a fall in the specific heat with increase of density.   The specific heat, too, is raised above that obtained in the preceding series.   Undoubtedly purer hydrogen had been obtained.   What greatly conduced to this was an addition to the arrangements whereby the connection of the gas-holder with the generating bottle could be maintained throughout the operation of pumping.   Previously the coupling with the bottle had to be transferred to the high-pressure receiver.   The new

arrangement providing for a supply of gas not limited to the capacity of the gas-holder, enabled a much greater quantity to be used as a wash-out in the first instance.

The difficulty of obtaining concordant observations on different samples of hydrogen having become very apparent, I resolved to continue the system of making two observations upon the one sample of gas. It appeared to me, indeed, that a point of far higher interest than the actual value to be ascribed to the specific heat of the gas was the question as to the nature of its variation with change of pressure.

In the very next series, VII., however, my intention of duplicating the experiments was frustrated. In releasing the gas, in fact, at the conclusion of the series, I detected an odour of nitrous fumes, which induced me to seek the source of the impurity and start a fresh series. The source of the impurity turned out to be the tube containing the nitrate of silver, which was probably becoming affected by acid carried by the gas. The tube was suppressed, and a tube containing copper potassium tartrate, carried on pumice, substituted. The use of this tube entirely removed the odour of H_2S which the gas quitting the generating bottle had to some extent, and, in fact, the gas passed on quite free from smell.

It is improbable that VII. is affected appreciably by the amount of oxide of nitrogen present. A very small quantity would have sufficed to impart the odour.

HYDROGEN VII.— W = 0·2350 gramme. Mean Absolute Density, 0·0015513.
Mean Pressure, 20·99 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	12·01	99·82	536·6	87·81	0·1282	14600
2	12·69	99·81	536·6	87·12	0·1270	14578
3	13·00	99·78	536·7	87·78	0·1268	14612
4	13·00	99·80	536·6	86·80	0·1280	14747
5	13·28	99·80	536·6	86·52	0·1273	14713
6	12·12	99·90	536·6	87·78	0·1288	14673
	12·68	99·82	536·6	87·14	0·1277	14655

Rate of correction for spheres = − 0·0359 for 88°·10.   Sphere B.
Correction for thermal expansion, &c. = − 0·000705. ϖ = 0·0915.

Deduced Specific Heat = 2·3975.

The next two series, VIII. and IX., are on the one sample of gas. This would appear to have been the purest sample of gas prepared. The specific heat has risen quite to the theoretic value, and the fall of specific heat with increasing density is well marked.

Series X., XI. and XII. are all on the one sample. The extremes X. and XII. agree with the testimony of all the latter experiments as to the nature of the variation of the specific heat with density, but the central series is discordant.

HYDROGEN VIII.—W = 0·2979 gramme. Mean Absolute Density, 0·0019432. Mean Pressure, 26·412 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	13·50	99·74	536·7	86·24	0·1522	17648
2	12·22	99·86	536·6	87·64	0·1544	17618
3	12·97	99·81	536·6	86·84	0·1535	17676
4	13·46	99·78	536·7	86·32	0·1510	17493
5	12·20	99·95	536·5	87·75	0·1536	17504
6	13·08	99·98	536·5	86·90	0·1527	17572
	12·90	99·85	536·6	86·95	0·1529	17585

Rate of correction for spheres = − 0·0352 for 86°·09. Sphere B.
Correction for thermal expansion, &c. = − 0·000897. ϖ = 0·11646.

Deduced specific heat = 2·4120.

HYDROGEN IX.—W = 0·1737 gramme. Mean Absolute Density, 0·0011693. Mean Pressure, 15·876 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_1 - t_1)$.
						0·00
1	12·90	100·00	536·5	87·10	0·1040	11940
2	12·98	100·04	536·5	87·06	0·1045	12003
3	12·50	100·04	536·5	87·54	0·1044	11926
4	13·20	100·04	536·5	86·84	0·1045	12034
5	13·67	100·05	536·5	86·38	0·1050	12156
6	12·98	100·08	536·5	87·10	0·1049	12044
	13·04	100·04	536·5	87·00	0·10455	12017

Rate of correction for spheres = − 0·0352 for 86°·09. Sphere B.
Correction for thermal expansion, &c. = − 0·000523. ϖ = 0·06849.

Deduced specific heat = 2·4320.

HYDROGEN X.—W = 0·3050 gramme.   Mean Absolute Density, 0·0019874.
Mean Pressure, 26·848 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	12·93	99·70	536·7	86·77	0·1546	17817
2	13·13	99·74	536·7	86·61	0·1543	17815
3	13·50	99·72	536·7	86·22	0·1533	17780
4	12·85	99·82	536·6	86·97	0·1544	17753
	13·10	99·74	536·6	86·64	0·15415	17792

Rate of correction for spheres = — 0·0352 for 86°·09.   Sphere B.
Correction for thermal expansion, &c. = — 0·000914. ϖ = 0·11784.

Deduced specific heat = 2·3928.

HYDROGEN XI.—W = 0·2100 gramme.   Mean Absolute Density, 0·0013955.
Mean Pressure, 18·938 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·00
1	12·61	99·97	536·5	87·36	0·1176	13462
2	13·17	99·96	536·5	86·79	0·1178	13573
3	13·40	99·95	536·5	86·55	0·1168	13495
4	13·24	99·78	536·7	86·54	0·1169	13508
5	13·66	99·78	536·7	86·12	0·1166	13539
6	13·94	99·78	536·7	85·84	0·1167	13595
7	13·20	100·09	536·5	86·89	0·1171	13477
	13·32	99·90	536·6	86·58	0·11707	13522

Rate of correction for spheres = — 0·0352 for 86°·09.   Sphere B.
Correction for thermal expansion, &c. = — 0·000632. ϖ = 0·08104.

Deduced specific heat = 2·3917.

HYDROGEN XII.—W = 0·1087 gramme.   Mean Absolute Density, 0·0007632.
Mean Pressure, 10·396 Atmospheres.

No.	t_1.	t_2.	λ.	$t_2 - t_1$.	w.	$w \div (t_2 - t_1)$.
						0·000
1	14·10	100·14	536·4	86·04	0·0768	89261
2	13·34	100·40	536·2	87·06	0·0776	89134
3	14·18	100·40	536·2	86·22	0·0774	89770
4	14·56	100·40	536·2	85·84	0·0780	90867
5	13·86	100·38	536·2	86·52	0·0773	89344
6	14·59	100·35	536·3	85·76	0·0780	90951
7	14·75	100·32	536·3	85·57	0·0773	90335
8	14·69	100·31	536·3	85·62	0·0776	90633
9	13·82	100·27	536·3	86·45	0·0779	90110
	14·22	100·33	536·3	86·11	0·07754	90048

Rate of correction for spheres = — 0·0352 for 86°·09.   Sphere B.
Correction for thermal expansion, &c., = — 0·000329. ϖ = 0·04201.

Deduced specific heat = 2·4135.

CORRECTION for Spheres (Hydrogen VIII.--XII.).

No.	t_1.	t_2.	w.
1	12·30	99·91	— 0·0359
2	12·68	99·80	— 0·0360
3	14·50	100·21	— 0·0355
4	14·78	100·20	— 0·0339
5	14·20	100·15	— 0·0354
6	15·10	100·13	— 0·0349
7	14·70	100·14	— 0·0350
8	13·90	100·23	— 0·0347

Mean range = 86°·09.
Mean w = — 0·0352.

The diagram for Hydrogen, Plate 6, is a sufficient résumé of the foregoing experiments.   It will be understood that the lines throughout the diagram connect experiments effected on gas of the same purity.

The two lines low down on the diagram depict the first four series in which there was very certainly a greater degree of impurity than in subsequent series.   The impurity consisting almost certainly of air, its effect will be to conceal the true varia-

tion of the specific heat with density; and, in fact, the impurity has done so and even reversed it; less in the cases of III. and IV., than in I. and II.

The next two series are higher on the diagram, and a well marked (probably excessive) downward slope of the line is apparent. The lines connecting VI. and V., X. and XII., agree as regards the negative variation of the specific heat with increased density. X. and XI. are discordant.

Nearly all the experiments on the purer gas being at one upon this point, it is, I think, allowable to assume that these experiments prove that *the specific heat of hydrogen is not constant, but varies with the density, diminishing with increase of density, and vice versâ.*

As already remarked, this seems in harmony with the nature of the departure of this gas from BOYLE's law.

The theoretic value assigned by CLAUSIUS to the specific heat of hydrogen is 2·411. Experiment VIII. is just this number, IX. rises above it. The rest lie less or more below it.

Conclusion.

The principal result of these first experiments on gases is the broad fact of the departure of the specific heat at constant volume from constancy. Some such result might have been, perhaps, anticipated from the known imperfectness of all gases. But the invariability of the two specific heats is in text books most generally insisted on. It is probable that a gas whose molecules were without action upon one another would show invariability of specific heat. As it is, it appears that the mutual influence of the molecules of some gases being of a positive nature, that of others (hydrogen molecules at least) may be of a negative nature. But the subject is only touched upon in this first paper. Many questions remain to be answered. Is the specific heat dependent on temperature limits? If the perfectness of a gas depends upon its temperature, how will this affect the nature of the relation between specific heat and density? Will the rate of variation alter? Presumably it will. It is not improbable that at very high temperatures the slope of the line for air (or even for carbon dioxide), after approaching more and more nearly to parallelism with the axis of density, will take up the position of a perfect gas, and even assume the negative inclination of the super-perfect gas. Similarly with rise of temperature the slope of the line for hydrogen may become intensified; or, if we suppose the range to be sinking, the opposite may be the course of events, hydrogen ultimately falling into agreement with the behaviour of the other gases.

There may be for each gas a temperature, such that for it the gas behaves in all respects as a truly perfect gas, in which neither a positive nor a negative latent heat would become apparent at high densities. But, again, it may be that a truly perfect gas is not possible in nature, that is, with molecules of the one kind. For

t is evident that a gas undistinguishable in its thermal behaviour from a perfect gas could be compounded out of a mixture, in the proper proportions, of say air and hydrogen.

For dealing, at least to some extent, with the question of the influence of temperature on the specific heat, arrangements are being made, and I am in hopes that reliable quantitative measurements will be found attainable.

Other questions—as that of the mutual influence, thermally, of different intermixed gases, will suggest themselves, probably, as fields of research in which the present method may find application.

Diagram of Experiments on Air.

The points on the diagram
are,

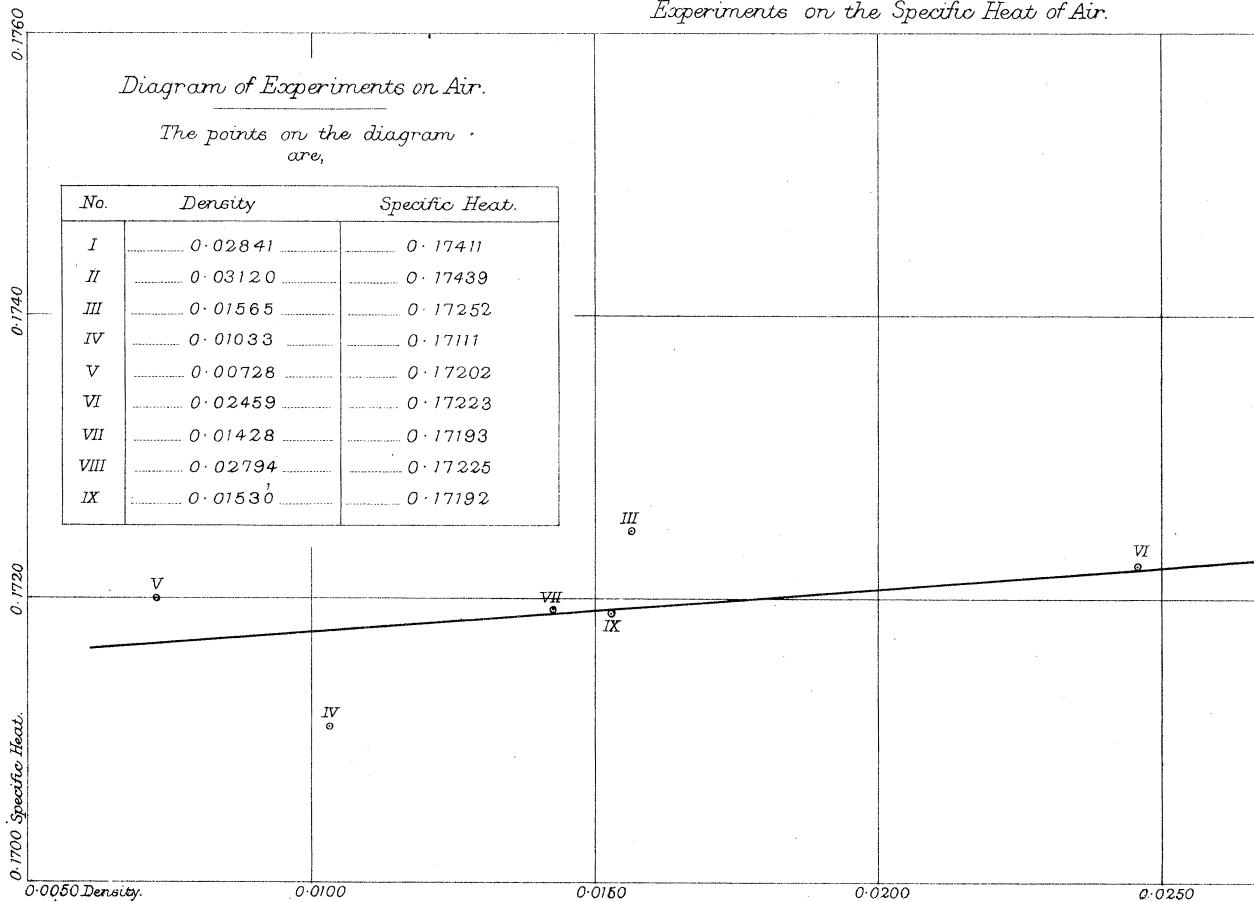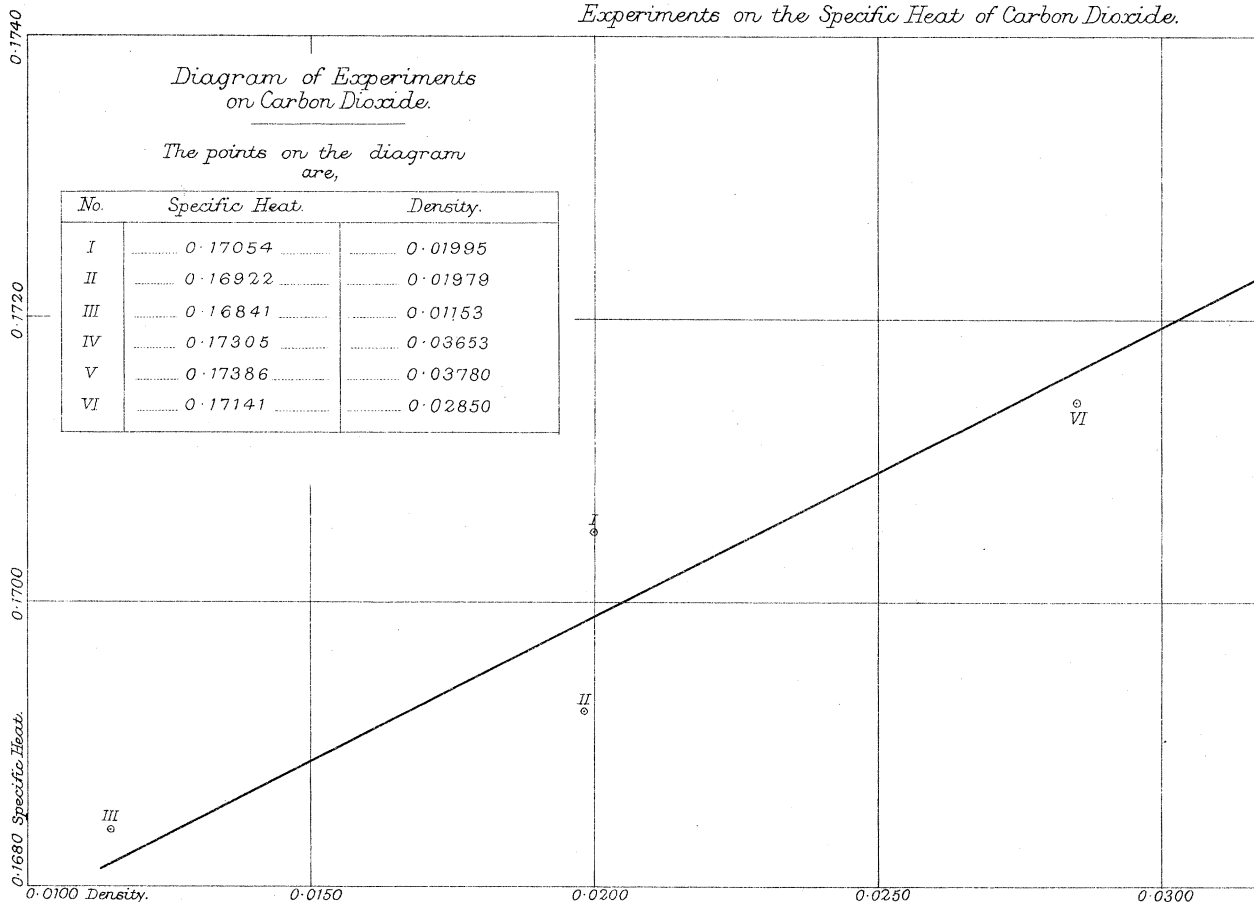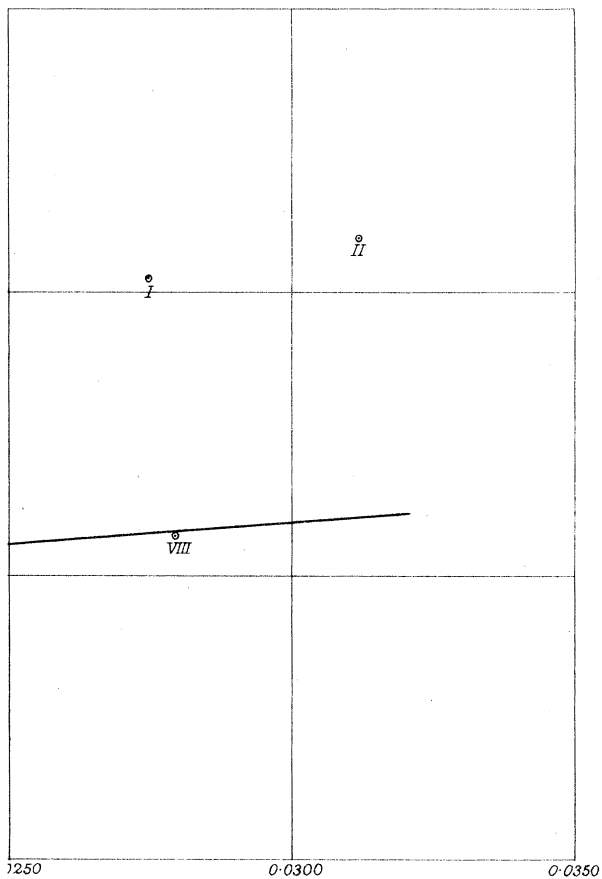| No.	Density	Specific Heat.
I	0.02841	0.17411
II	0.03120	0.17439
III	0.01565	0.17252
IV	0.01033	0.17111
V	0.00728	0.17202
VI	0.02459	0.17223
VII	0.01428	0.17193
VIII	0.02794	0.17225
IX	0.01530	0.17192

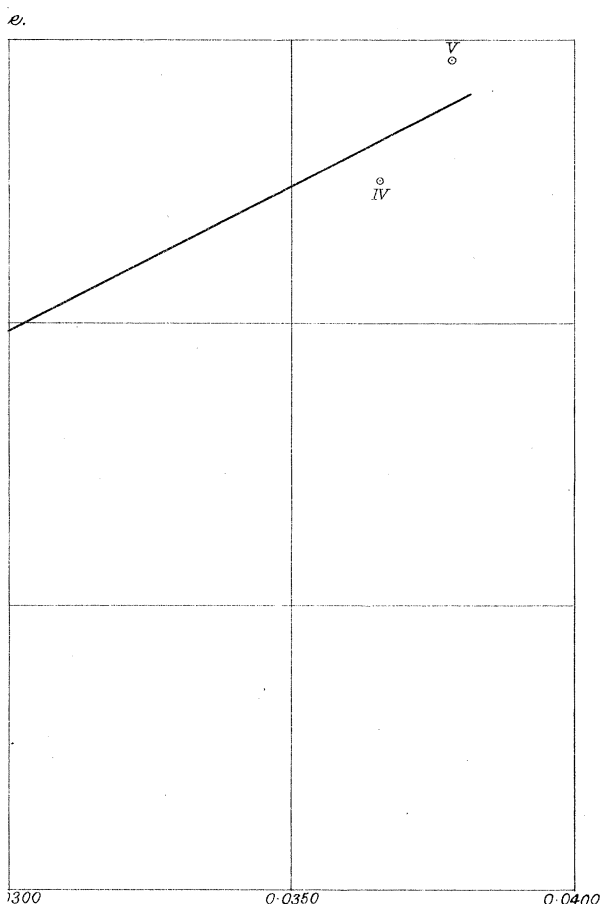## Diagram of Experiments on Carbon Dioxide.
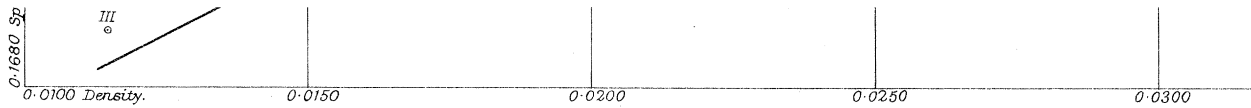
The points on the diagram
are,

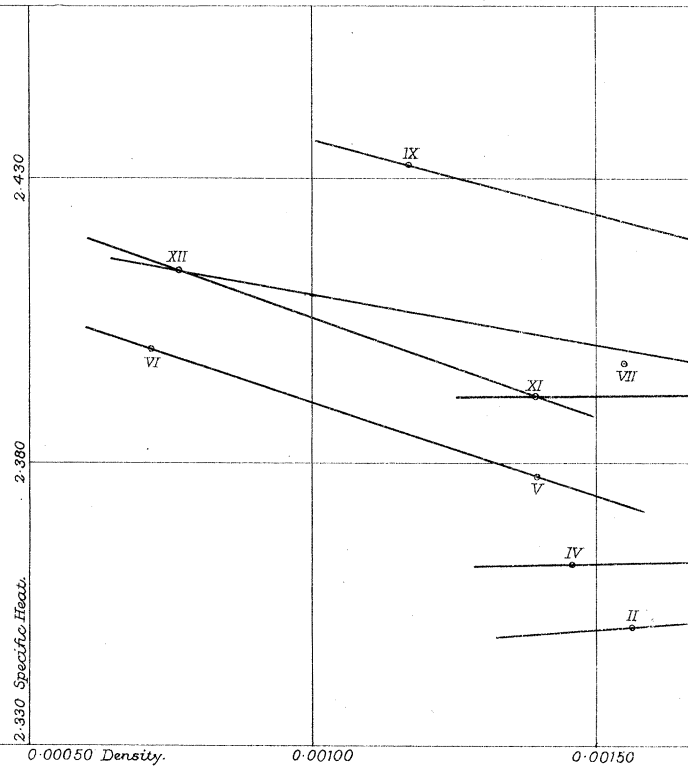| No.	Specific Heat.	Density.
I	0.17054	0.01995
II	0.16922	0.01979
III	0.16841	0.01153
IV	0.17305	0.03653
V	0.17386	0.03780
VI	0.17141	0.02850

July.

I
II
VIII

0250   0·0300   0·0350

e.

V
IV

0300   0·0350   0·0400

0·1680 Sp

III

0·0100 Density.   0·0150   0·0200   0·0250   0·0300

Experiments on the Specific Heat of Hydrogen.

The Experiments on Hydrogen.

The points on the diagram are,

No.	Specific Heat.	Density.
I	2·3559	0·002151
II	2·3512	0·001565
III	2·3633	0·002127
IV	2·3623	0·001452
V	2·3779	0·001392
VI	2·4012	0·000741
VII	2·3975	0·001551
VIII	2·4120	0·001881
IX	2·4320	0·001169
X	2·3928	0·001987
XI	2·3917	0·001395
XII	2·4135	0·000763

2·430   2·380   2·330 Specific Heat.

IX   XII   VI   XI   VII   V   IV   II

0·00050 Density.   0·00100   0·00150

0·0300   0·0350   0·0400

VIII

VII   X

III   I

II

0·0150   0·00200   0·0250

Phil. Trans. 1891. A. Plate 6.

Experiments on the Specific Heat of Air.

Diagram of Experiments on Air.

The points on the diagram are,

No.	Density	Specific Heat
I	0·02841	0·17411
II	0·03120	0·17439
III	0·01565	0·17252
IV	0·01033	0·17111
V	0·00726	0·17202
VI	0·02459	0·17223
VII	0·01428	0·17193
VIII	0·02794	0·17225
IX	0·01530	0·17192

Experiments on the Specific Heat of Carbon Dioxide.

Diagram of Experiments on Carbon Dioxide

The points on the diagram are,

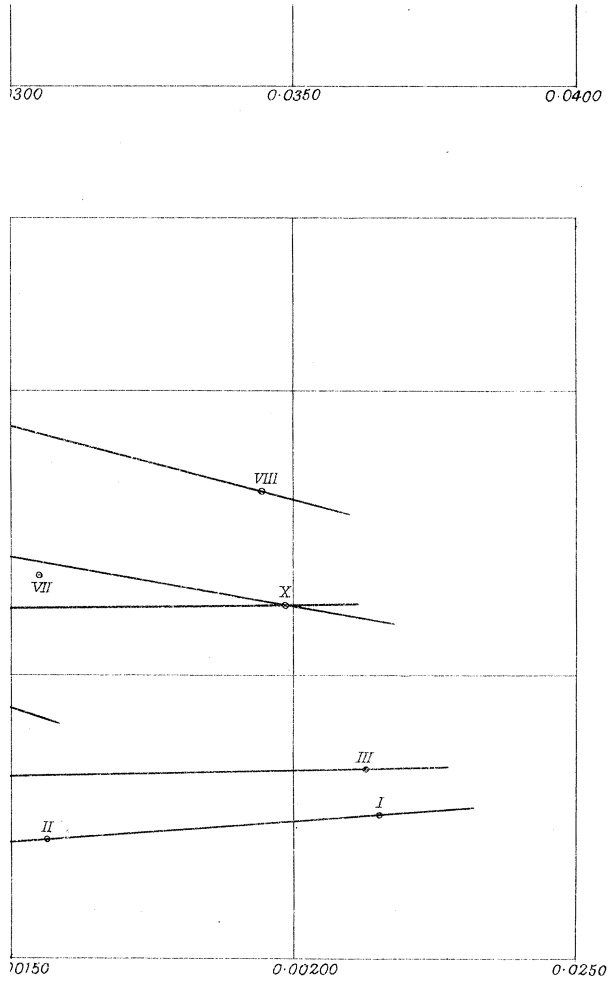| No.	Specific Heat	Density.
I	0·17054	0·01995
II	0·16922	0·01979
III	0·16841	0·01153
IV	0·17305	0·03653
V	0·17386	0·03780
VI	0·17141	0·02850

Experiments on the Specific Heat of Hydrogen.
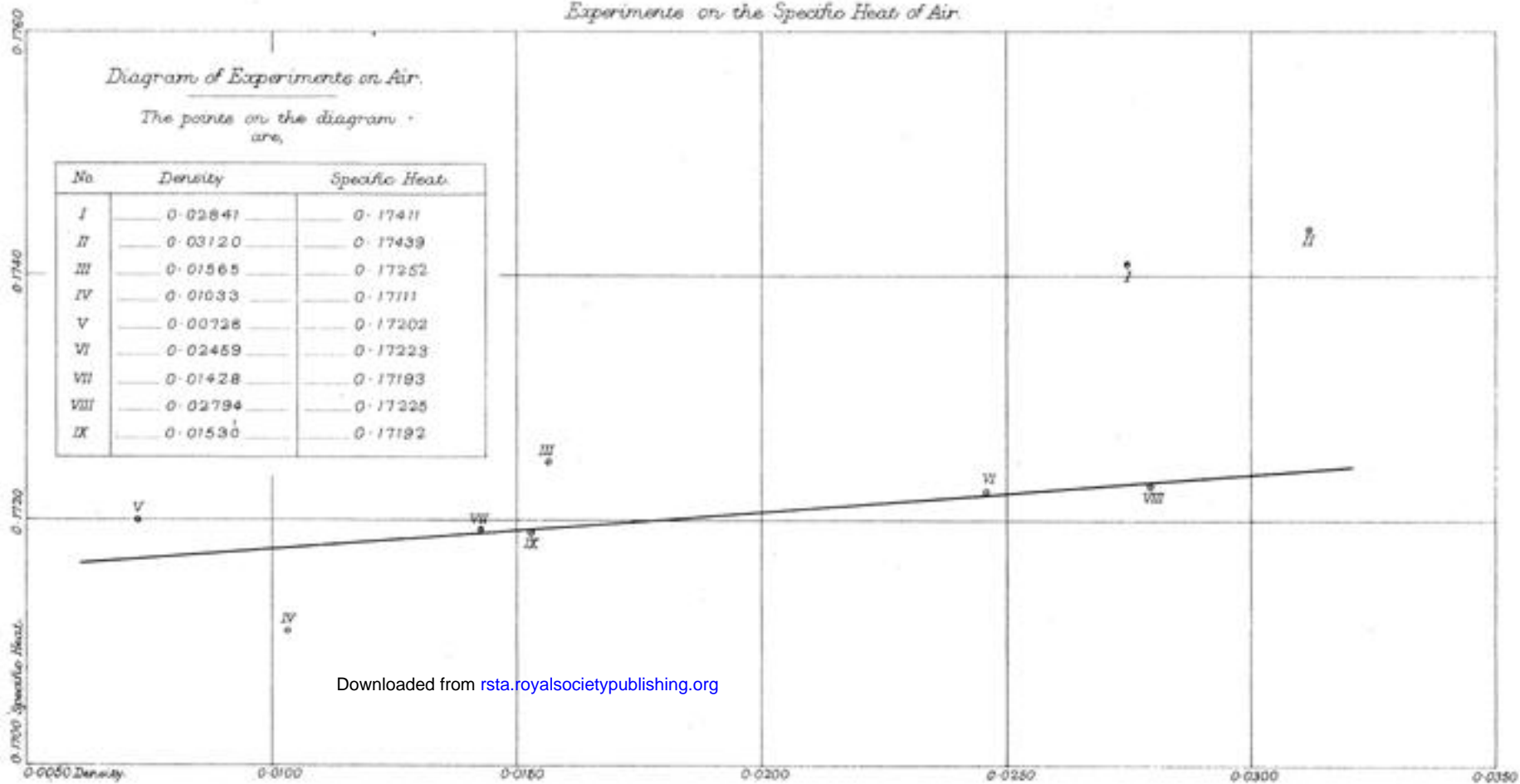
The Experiments on Hydrogen.

The points on the diagram are,

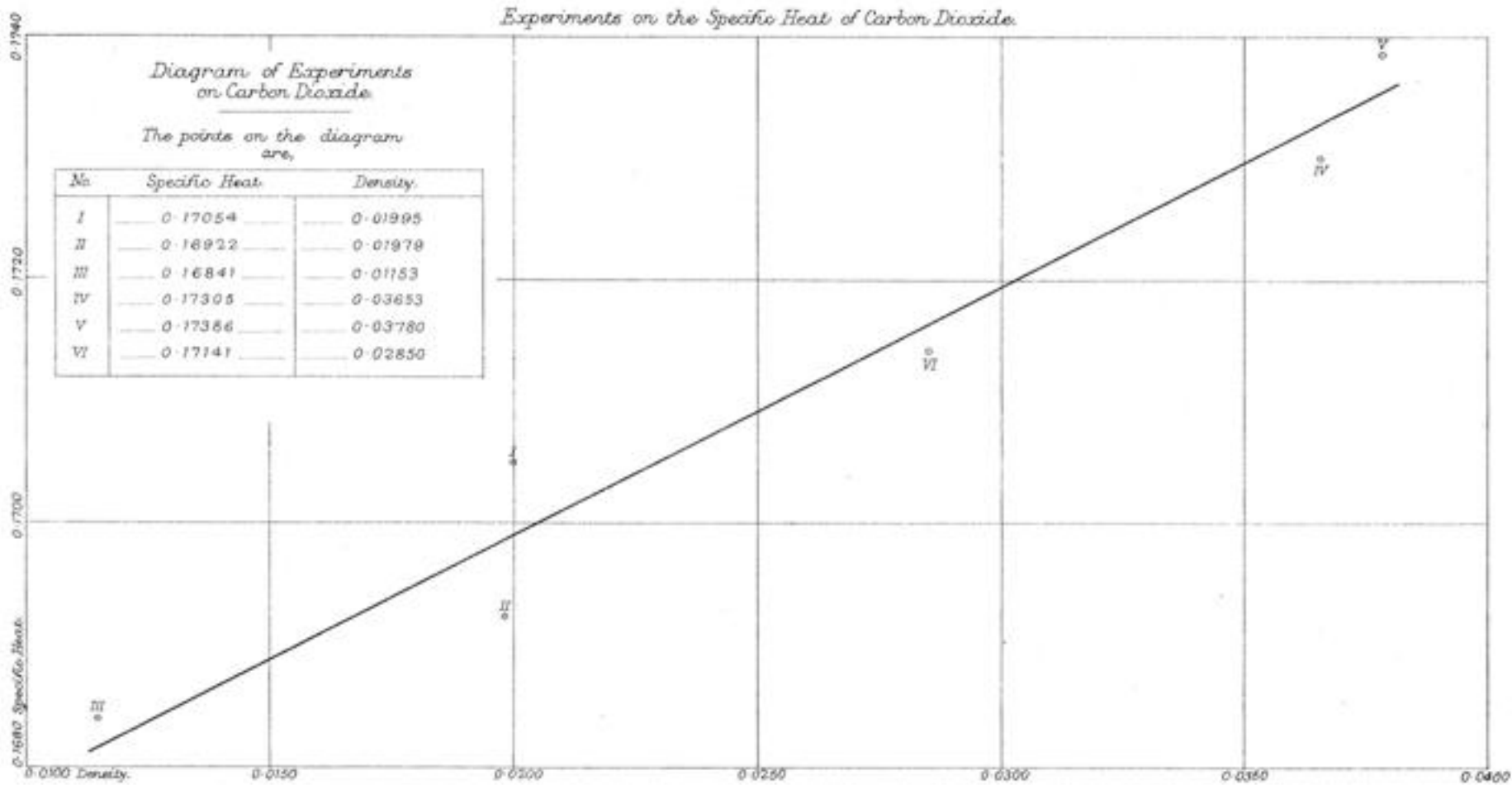| No.	Specific Heat	Density.
I	2·3559	0·002151
II	2·3512	0·001565
III	2·3633	0·002127
IV	2·3623	0·001452
V	2·3779	0·001392
VI	2·4012	0·000741
VII	2·3975	0·001551
VIII	2·4120	0·001681
IX	2·4320	0·001169
X	2·3926	0·001987
XI	2·3917	0·001395
XII	2·4135	0·000763