VI. *Researches on the Atomic Weight of Thallium.* *By* William Crookes, *F.R.S. &c.*

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Contents.

In June 1862, and in February 1863, I had the honour to lay before the Royal Society communications on the subject of the then newly discovered metal, Thallium. In these I gave an account of its occurrence, distribution, and the method of extraction from the ore, together with its physical characteristics and chemical properties; also

I discussed the position of thallium among elementary bodies, and gave a series of analytical notes.

In the pages of the 'Journal of the Chemical Society' for April 1, 1864, I collated all the information then extant, both from my own researches and from those of others, introducing qualitative descriptions of an extended series of the salts of the metal. I propose in the present paper to lay before the Royal Society the details and results of experiments which have engrossed much of my spare time during the last eight years, and which consist of very laborious researches on the atomic weight of thallium. In these researches I owe much to the munificence of the Royal Society for having placed at my disposal a large sum from the Government Grant. Without this supplement to my own resources it would have been difficult for me to have carried out the investigation with such completeness.

Section I.—ON THE DETERMINATION OF ATOMIC WEIGHTS.

In determining accurately the atomic weight of a metal that stands so high in the scale as thallium, difficulties and sources of error which are comparatively small with elements of low atomic weight are magnified to serious proportions, and require more than ordinary care for their elimination. When so large a proportion of the compound under analysis or synthesis consists of the body itself whose atomic weight is the one unknown quantity, it is evident that the almost unavoidable errors occasioned by impurity in the materials employed, the losses incident to imperfect manipulation, or the inaccuracies arising during the weighing from the omission of the corrections required by temperature, pressure, &c., will all find their way into the number which is finally considered to represent the atomic weight of the metal.

Nearly fourteen years ago, on taking the chair of the Chemical Section of the British Association at Leeds, the late Sir John Herschel called attention to the necessity which there then was for the introduction of greater accuracy into the determination of atomic weights. Speaking of the numerical relations which appear to exist between certain groups of elements, he considered that all these speculations took for granted a principle with which chemists had allowed themselves to be far too easily satisfied, viz. that all the atomic numbers are multiples of that of hydrogen. "Not until these numbers," he continues, "are determined with a precision approaching that of the elements of the planetary orbits—a precision which can leave no possible question of a tenth or a hundredth of a per cent., and in the presence of which such errors as are at present regarded tolerable in the atomic numbers of even the best determined elements shall be considered utterly inadmissible—I think can this question be settled; and when such gigantic consequences—so entire a system of nature—are to be based on a principle, nothing short of such evidence ought, I think, to be held conclusive, however seductive the theory may appear. I do not think such precision unattainable; and I think I perceive a way in which it might be attained, but one that would involve an expenditure of time, labour, and money, such as no private individual could bestow on it." Before this

remarkable sentence was written Professor STAS had commenced his classical researches on the atomic weights; and in 1861 he gave to the world the results of ten years' experiments, which had been conducted with a care and perseverance never surpassed in the history of experimental investigation. These researches of Professor STAS, and others which he has since made public, constitute a standard of excellence which chemists who are engaged on the important task of the determination of atomic weights should strive to attain. They are, in my opinion, the most noteworthy chemical memoirs that have ever been written: not only have they determined in the most definite and unassailable manner atomic weights about which scarcely any two chemists have agreed since the time of BERZELIUS, but they have raised the standard of accuracy in all chemical laboratories, and have set an example which, if followed, cannot fail to exert an important influence on the progress of chemical science.

It has been with these researches before me that I have endeavoured to determine in a manner which should approach them in accuracy the atomic weight of thallium.

In the determination of an atomic weight analysis is inferior to synthesis; and especially is this the case when the number sought is amongst the highest known. The method followed should be one in which as few chemical elements as possible are employed, so as to reduce to a minimum the errors arising from inaccuracy in the determination of their atomic weights,—which errors, whilst they might on the one hand balance each other, on the other might accumulate in the same direction, and become a total error of exceeding magnitude in the atomic weight of the metal under investigation. The method adopted should also be one in which there is the greatest possible difference of weight between the substance taken for the starting-point and the one ultimately obtained; for the greater the amount of this difference, other things being equal, the less likely are the unavoidable errors incidental to the method, and which may be looked upon as constant, to injuriously affect the atomic weight obtained. For these reasons processes in which a weighed quantity of the metal itself is taken and converted into one of its salts seemed likely to afford the best results; and this accordingly is the principal method which I have adopted.

Every substance employed in such a determination is liable to introduce errors proportionate to its own want of purity. The most extraordinary pains have therefore been taken to secure the absolute purity both of the thallium employed and of the agents used to act upon it. The glass and other apparatus have been specially constructed for these researches, and the balances and weights have been of an accuracy never before surpassed in any research. Whilst nearly every other branch of manipulative chemistry has advanced to an accuracy vieing with astronomical observation, the operation of weighing, as almost universally carried out, is attended with grave imperfections. For ordinary analytical work, and perhaps even for more refined and accurate researches, the errors attending the ordinary process of weighing are unimportant; but in determining an equivalent so high as that of thallium no precaution whatever which can either reduce an error to a minimum or eliminate it altogether should be neglected. I am anxious to

avoid the imputation of over-refinement in this research; but considering the fallibility of human operations, and especially those of so complicated a nature as I am about to describe, I have considered it better to err on the side of too great than of too little precaution, both in the purification of the chemicals, the arrangement of the apparatus, the time devoted to each separate determination, the removal of the errors incidental to the weighings, and the subsequent calculations. These latter have been especially tedious, as the numbers have generally extended to too many places of figures to allow the use of logarithms; each calculation has, moreover, been duplicated by different persons.

I have attempted two entirely different methods of arriving at the atomic weight of thallium. Had the results of these determinations differed materially, I should have extended the research to other methods; but as they nearly agree it appeared unnecessary to incur so great an additional expenditure of time and material with no reasonable prospect of getting any but confirmatory results.

The first method, and that which I shall describe, consists in taking a known quantity of metallic thallium, dissolving it in nitric acid, and weighing the nitrate of thallium produced.

The second method consists in dissolving known quantities of sulphate of thallium in water, and ascertaining how much nitrate of barium is necessary to precipitate the sulphuric acid as sulphate of barium.

In the prosecution of these two methods, the materials employed, the transferences from one vessel to another, and the weighings are reduced to a minimum, while several precautions have been introduced into the operations of weighing which are not usually adopted. No correction has been neglected that is not many times less than the probable error of a single observation; and, as I have stated, especially has attention been paid to such corrections as always influence in one direction, as in that for weight of air displaced. Errors sometimes in excess and sometimes in defect tend to disappear from the mean of a great number of observations.

I have for the foregoing reasons thought it necessary to dwell thus far upon the care I have bestowed upon my work. In the succeeding section I shall describe accurately the apparatus employed, including the balance and weights, and the necessary arrangements for weighing *in vacuo*. In the third section I shall enumerate the chemicals and the methods of preparing them and pure thallium. The fourth section will be devoted to the process determining the atomic weight and the weights obtained. The concluding section will consist of a calculation and discussion of results.

Section II.—APPARATUS EMPLOYED.

The absolute weight of any substance may be found by calculation from its apparent weight in an atmosphere balancing 30 inches of mercury, and from its apparent weight under, say, 25 inches of mercury; but the errors of observation, more especially those relating to the maintaining of a partial vacuum, will largely affect the result. Weighings

obtained in atmospheres balancing 30 inches of mercury and 5 inches of mercury respectively will give a more accurate result; but the best weighings whereby the absolute weight of a substance may be calculated are undoubtedly one in air at ordinary pressure and temperature, and one in a highly rarefied atmosphere,—it cannot be said *in vacuo*, owing to the difficulty of working under such a difference of pressure between the atmosphere of the balance and that surrounding it.

The Balances.

Two balances were used. That which I shall call the *air*-balance was made by Messrs. KEISSLER and NEU expressly for this work, and will clearly indicate a difference of 0·0001 of a grain when loaded with 1000 grains in each pan*. It is always kept in a dry room of tolerably uniform temperature, away from draught, artificial heat, or chemical vapours, and was (in the most accurate experiments) only used when no fire had been in the room for at least twelve hours.

The second balance, which I shall call the *vacuum*-balance, is almost a duplicate of the first, of 14-inch beam, with agate knife-edges and planes, made by OERTLING. It is enclosed in a cast-iron case connected with an air-pump, and so arranged that I can readily weigh any substance in air of any desired density, the rarefaction being measured by a barometer-gauge. The accompanying diagram (Plate XIV.) shows the method of the connexions. The upper and lower portions of the iron case are connected by flanges and bolts; while to ensure that the joint shall be air-tight, there is cemented to each flange a band of thick unvulcanized india-rubber, a lead wire being laid between the two pieces of india-rubber. By this means, and by causing the arm by which the riders are adjusted and the key liberating the pans and beam to work in a double-packed stuffing-box, a nearly perfect vacuum can be maintained. The openings in the metal work, through which observations are made, are fitted with clear stout plate glass; that to the left of the centre of the case, for the introduction of the apparatus &c., is closed with an iron door, clamped and fitted with washers. The apparatus, when attached to the air-pump and exhausted to 25 inches of mercury, seldom allows the column of mercury to sink at a greater rate than 0·01 inch in an hour. A plug of gold-leaf is inserted in the tube connecting the barometer-gauge with the vacuum-chamber, in order to absorb any mercury vapour that might otherwise be carried over.

* M. STAS employed four balances. One of them when loaded with 1000 grammes turns with $\frac{5}{10}$ of a milligramme; another when loaded with 5000 or 6000 grammes turns with 1 milligramme, and with 2000 or 3000 grammes in each pan turns with $\frac{3}{10}$ or $\frac{4}{10}$ of a milligramme. The third balance loaded with 500 grammes turns with $\frac{2}{10}$ of a milligramme; the fourth laden 25 grammes turns to $\frac{1}{33}$ of a milligramme. Reducing these weights to grains, we find that—

No. 1 loaded with		15,432 grains	turns with	0·0077 grain.
„ 2	„	92,592	„	0·0154 „
„ 2	„	46,296	„	0·0060 „
„ 3	„	7,716	„	0·0030 „
„ 4	„	386	„	0·0005 „

Even with moderate rarefaction the iron case of the balance showed at first a certain amount of porosity, due to the "kish" or graphite, carbide, and silicide diffused through the metal like a sponge. Cast-brass and even drawn-brass tubes exhibit a similar porosity. This porosity in the casing of the balance admits of easy remedy, by painting the whole surface with two or three thin coats of white-lead paint mixed with boiled linseed-oil or fine copal-oil varnish, allowing each coat to dry before the next is laid on. The vessel should be painted when it is partially exhausted; the multitude of small holes then appearing in the smooth surface of the paint as it is forced inwards by the pressure of the outer air should be covered carefully with thin coats of paint. When this effect ceases, a final thin coat should be given and allowed to dry.

The iron flanges were first planed true with the planing-machine, and then "fined off" by WHITWORTH'S process of scraping, generally employed for such work as slides of engines &c. The lead wire laid between the flanges of the iron case in india-rubber, becoming compressed when the bolts are tightened, effectually precludes the entrance of air. The washers of the iron door to the left of the case are of well-greased leather, while the glass plates in the other parts of the apparatus are cemented into double frames with red lead.

At first it was attempted to put nearly the correct weight into the pan, and then make the final adjustment by means of the rider. It was, however, soon found that the more accurate method was to introduce a certain weight, and then to alter the pressure of the air until the balance shows equilibrium. Thus, supposing a glass vessel weighing in air 625·1200 grains has to be weighed *in vacuo*, calculation estimates the probable weight (*in vacuo*) at 625·3700. I therefore introduce rather less (625·3600) than this weight, and exhaust until the balance attains equilibrium, when the gauge shows an atmospheric pressure equal (say) to 3·75 inches of mercury. When this is obtained the weight is slightly increased or diminished with the rider, and the exhaustion varied until a fresh equilibrium is established. Two weighings at different degrees of atmospheric pressure, varying by a considerable interval, give data upon which to calculate with great accuracy what the weight would be in a perfect vacuum.

With a rider there is some difficulty in estimating the exact point at which it rests, and it is necessary to note the oscillations, placing the rider as exactly as possible on one of the divisions of the beam. The best weighings, perhaps, will be taken when the arc is not very small.

Temperature has an effect upon the air-balance, rendering it less sensitive when increasing. This is perhaps due to the varying expansibility of the arms and the knife-edges upon which the pans are hung, or the superior and inferior parts of the beam may expand unequally. The two arms of the balance at times expand unequally; and in finding the true value of the weights employed in the determination, this cause of error is eliminated by following GAUSS'S method of interchanges—the constant friction of the forceps against the weights in transferring them from one pan to another being obviated by employing hooks of thin wire attached to the agate plane, upon which the

suspension-wires of the pans could be hung. This required that the pans should not differ from each other by a quantity greater than one thousandth of a grain.

In heavy weighings it is found convenient to remove one of the pans; but as the case is one of determining a weight and its increase after certain operations, the removal of the pan does not affect the result, provided the weight of the pan is accurately ascertained and this weight allowed for, the apparatus weighed appearing lighter to an amount equal to this weight. Always when weighing different metals, or glass, or some chemical against metal, it is necessary to correct for the weight of air displaced, reference being at the same time made to the temperature and air-pressure; for assuming that there are to be weighed 7000 grains of bronze against 7000 grains of platinum, there will arise an error of nearly 0·6 of a grain unless this precaution be attended to, for 7000 grains of bronze displace roughly 1 grain of air, while 7000 grains of platinum displace only 0·4 grain.

At each weighing at diminished air-pressure care must be taken to allow the balance to remain at rest for at least half an hour, and preferably for several hours, in order to allow the temperature to become uniform after the alteration caused by the exhaustion. The weighings were always repeated a second time after every thing had been allowed to remain at rest for one hour; and when the final weighing was made, the case had been unopened for six hours, the adjustment being made by slightly altering the density of the enclosed air.

One of the greatest difficulties occurred in endeavouring to illuminate the scale and pointer of the balance without heating sufficiently to introduce a cause of error. The concentrated rays of a lamp were found to be unsuited in several ways. The use of a small vacuum-tube suspended inside the iron case was finally decided upon, sufficient light being obtained with two Grove's cells actuating a small induction-coil placed some distance from the apparatus, the electricity being conveyed by fine conducting-wires of good copper, carefully insulated*. These wires pass into the case through grooves filed in the flanges and well protected with india-rubber bands, and in no way interfere with the obtaining of a vacuum.

To prevent parallax the scale and pointer are viewed through a small telescope having a vertical wire in the focus of the eyepiece. The observer is therefore able to be situated some eight or ten feet from the balance during accurate observations, thus reducing to a minimum the disturbance due to the temperature of the body. It is inexpedient to estimate the value of a division on the ivory scale over which the pointer of the balance travels, as its value varies with the length of arc of vibration, with the weight in the pans, and slightly with the temperature. It is also evident that GAUSS'S method of weighing in alternate pans is inapplicable when weighing in a rare atmosphere, owing to the number of times the case would have to be opened, and the consequent liability to other sources of error. BORDA'S method, as described by PÉCLET in his

* At high rarefactions this method of illumination fails, owing to the induced current passing between the wires outside the vacuum-tube.

'Cours de Physique,' gives the most accurate results with the least expenditure of time. The weights are placed in the left-hand pan, and the object to be weighed in the right. At the last three consecutive oscillations of the pointer along the divided scale the division reached by the pointer is recorded, and

$$\frac{a+c+2b}{4}=$$

the reading of the scale when the balance attains equilibrium. It is better to allow the first oscillation to occur unnoticed, and to record only the next three consecutive oscillations, while the first can be employed to check the result if required.

Finally, the balance-case contains a jar of pure oil of vitriol exposing a large surface, and another of caustic potash. The air is admitted through long U-shaped tubes, one filled with chloride of calcium, and the other with platinized asbestos.

For each weighing all necessary observations of the barometer and thermometer were made, as will be found noted in the fourth and fifth sections of this memoir.

I would here ask whether chemists in their analytic analyses sufficiently allow for barometric variation. The temperature at the time of weighing is generally recorded: chemists have known the influence of pressure on the boiling-point, and its effect upon gases, yet they appear to neglect reference to the barometer when weighing solids, forgetting that they are weighing in a gas which itself possesses weight. Weighings are repeated after some operation, such as expelling moisture, at intervals sufficiently long to admit of considerable variation in atmospheric pressure, and the increase or decrease of a few milligrammes in weight is considered to determine the gain or loss of certain constituents. It remains to be seen whether a neglect of variation in barometric pressure would not account for these minute differences.

An approximation to the true weight of bodies, that is their weight *in vacuo*, may be obtained by the following formula, when their specific gravity and weight in air of 760 millims. pressure of mercury at 0° C. is known.

Let W = weight in grains; then the weight of air displaced is

$$\frac{\mathrm{W}}{\text{sp. gr.}}\times 0{\cdot}00122.$$

This weight plus the value of the weights *in vacuo* balancing the substance is its true weight *in vacuo*.

Let the weight of 800 grains of water in 200 grains of glass be required from two assistants, the one weighing against brass, the other against platinum weights, neglecting (1) the weight of air displaced and (2) its variation in weight from barometric disturbances.

(1) The true value of 800 grains of water weighed in air (bar 760 millims., 0° C.) $=800{\cdot}976$ grains.

That of 200 grains of glass . . =200·0976 grains.
Weight of air displaced by water =0·976 grain.
„ „ glass =0·0976 „

A brass weight of 1000 grains in use in my laboratory displaces 0·1462 grain of air; a 1000-grains platinum weight, 0·058271 grain of air.

The weight of glass and water . . .	=1000·0000	grains.
„ air displaced by them .	= 1·9736	„
Weight of glass and water	1001·9736	

Glass and water	=1001·9736	grains.
Less air displaced by weight (brass) .	= 0·1462	„
	1001·8274	grains = the true value

of the water and apparatus received from the assistant employing brass weights.

Glass and water	=1001·973600	grains.
Less air displaced by weight (platinum) .	= 0·058271	„
	1001·915329	grains = the true value

of the water and glass received from the assistant employing platinum weights.

(2) In a note to the translation of DESCHANEL'S 'Natural Philosophy'* by Professor EVERETT, it is said, "In strictness the weight in grammes of a litre of air under the pressure of 760 millimetres of mercury is different in different localities, being proportional to the intensity of gravity—not because the force of gravity in the litre of air is different (for though this is true, it does not affect the numerical value of the weight when stated in grammes), but because the pressure of 760 millimetres of mercury varies as the intensity of gravity. So that more air is compressed into the space of a litre as gravity increases. The *weight in grammes* is another name for the *mass*. The force of gravity on a litre of air under the pressure of 760 millims. is proportional to the square of the intensity of gravity. This is an excellent example of the ambiguity of the word *weight*, which sometimes denotes a mass, sometimes a force; and though the distinction is of no practical importance so long as we confine our attention to one locality, it cannot be neglected when different localities are compared." In one locality we have to deal with differences of air-pressure alone. Assumed that we are weighing at Greenwich, where gravity is to that of Paris as 3457 to 3456, the weight of a litre of dry air at Paris being 1·293167 grm. at 0° C. at a barometric height of 760 millims., the weight of a litre of air at Greenwich at the same barometric and thermometric heights will be 1·293561 grm. Knowing the weight of a litre of air at 760 millims. barometric height, at a lower height of the mercurial column the weight will be proportionately less, the temperature beings upposed constant; so that the weight of air displaced with the barometer at 740 millims. by the glass apparatus and water will be 1·9216 grain, and at 715 millims. 1·8890 grain. The brass weight will displace 0·1424

* Part I. p. 141.

grain of air at 740 millims. and 0·1385 grain at 715 millims.; the platinum weight will displace 0·56737 grain of air at 740 millims., and 0·054666 grain at 715 millims. The assistant weighing with brass weights would give then

Under 760 millims. an error of 1·8276 grain
„ 740 „ „ 1·7792 „
„ 715 „ „ 1·7505 „
} on the 1000.

The assistant weighing with platinum weights would give

Under 760 millims. an error of 1·915329 grain
„ 740 „ „ 1·864863 „
„ 715 „ „ 1·834334 „
} on the 1000.

Proceed on another supposition. Let the apparatus be weighed on two days, the barometer readings being respectively 740 millims. and 715 millims. Weighed on, say, the first day at 715 millims., on the second day there would be an apparent increase of nearly 0·029 grain; and if weighed again on a third day at 760 millims. an increase of 0·0771 grain, or against platinum weights nearly 0·081 grain.

Had a specifically lighter fluid than water been taken, or exceptional cases exemplified, it would have been possible to have largely increased these numbers; but they are a fair average of the errors unrecognized in ordinary manipulation.

To select another instance. In the determination of the amount of carbonic acid yielded by an organic body under combustion, the weight of the potash and bulbs is always sufficiently great to introduce an error arising from neglect of barometric variation. Thus, taking the potash and bulbs to weigh 600 grains, there would be displaced 0·336 grain of air at 760 millims. pressure, 0·327 grain at 740 millims., and 0·316 grain at 715 millims. Between 715 and 760 millims. there is an increase of weight of 0·02 gr., or, supposing 3·5 grs. of the substance under analysis had been taken, an increase of nearly 0·6 per cent. Again, a chloride-of-calcium tube, weighing, with its contents, 350 grs., displaces 0·2135 gr. of air at 760 millims. pressure. Between 715 and 760 millims. there will be an increase of 0·0127 gr., or of 0·36 per cent. Thus, in the estimation of the carbonic acid and of the water yielded by the organic body, the total error introduced by barometric variation is nearly 1 per cent. I need not quote illustrations of the effect of such an error upon the formula deduced; it will perhaps account for the difference from theory often obtained in the results of carefully conducted analyses.

The preceding calculations show that a simple formula may be stated which shall include the corrections on a certain volume of air for pressure and for temperature. It is

$$W = 1{\cdot}293651 \text{ grm. } V \frac{1}{1+0{\cdot}00367\,T} \cdot \frac{P}{760},$$

where W is the weight in grammes of a volume (V) of air at a pressure P and temperature T, 0·00367 being the coefficient of the expansion of air. For accurate experi-

ments, it will be necessary to substitute the weight of a litre of air in the locality of the laboratory for the coefficient of V. The formula, as it now stands, is calculated for the volume in litres; if a cubic centimetre be taken, the coefficient of V becomes 0·001293651; if a cubic decimetre, 0·01293651. For laboratory purposes, the ratio of the pressures might be tabulated; this is scarcely necessary, however, if the ratio 759 : 760 be taken = 0·9987 as sufficiently accurate, for a tabular difference of 0·0013 will enable the operator to speedily determine the ratio he requires.

In particularly describing the vacuum-balance, I have one peculiarity to note in relation to the effect of heat in diminishing the weight of bodies. That a hot body should appear to be lighter than a cold one has been considered as arising from the film of air or aqueous vapour condensed upon or adhering to the surface of the colder body, or from the upward currents of air caused by the expansion of the atmosphere in the vicinity of the heated body. But neither hypothesis can be held when the variation of the force of gravitation occurs in a vacuum as perfect as the mercurial gauge will register, and under other conditions which I am now supplying, and which I purpose embodying in a paper to be submitted to the Royal Society during a subsequent session.

The Weights.

A set of weights as ordinarily supplied by even the best instrument-makers is never absolutely exact; however carefully they may be adjusted, the pieces of metal which respectively represent 1000 grs., 100 grs., 10 grs., &c. are only more or less approximations to the true weights. In most chemical analyses, the error arising from such inaccuracies in the weights used is so small, in comparison to errors of manipulation or to imperfections inherent in the chemical processes adopted, that it may generally be disregarded; but when the chemist has for his object the determination of an atomic weight, or is engaged in other researches demanding the highest refinement of accuracy which chemistry and physics can supply, then he is bound to neglect no correction which will increase the precision of the results. That chemists, whose well-trained reasoning powers allow them to take for granted nothing which is not capable of experimental verification, and who insist upon the utmost attainable precision in their balances, should, as a rule, neglect the probable errors which the inaccuracies of their weights may introduce, is somewhat inconsistent. But in considering these eliminations in my memoir, I must disclaim any originality in the process, the description of the method I employed being intended solely to place others on the same footing as myself in their judgment of the possible inaccuracies of my investigations and their effect on the result.

Professor W. H. Miller, of Cambridge, in his valuable researches on the determination of the standard pound (Philosophical Transactions for 1856, pp. 811, 827, 937), has given full directions for attaining a similar object. These, however, will not exactly apply to the systems of weights used by chemists; for, of the three cases described by him, the former two concern a peculiar system of weights, and in the

third, two sets of weights (one for the Exchequer, the other for the Royal Mint) were compared at the same time. To this paper, as well as to the learned author himself, I am indebted for a valuable store of information on the subject of weights and weighings.

The weights employed were of platinum, made expressly for these investigations by Messrs. JOHNSON and MATTHEY. The platinum was quite pure; it was fused, cast, and then well hammered. The weights were adjusted by myself during May, June, July, and August 1864: they were first roughly adjusted, and then the specific gravity of each weight was taken. The weights were heated to redness in a bath of magnesia previous to ascertaining their specific gravity. The density of the larger weights was ascertained to the second place of decimals, and that of the smaller ones to the first place. The record of the final adjustment of these weights will be sufficient to show the method I adopted.

In taking the specific gravity of the weights, the distilled water was contained in a glass beaker of about 250 cubic inches capacity. Each weight was suspended by a fine platinum wire to be attached to the pan of the balance. With this wire affixed the weight was introduced into a small glass vessel filled with water, and heated over a spirit-lamp to the boiling-point. When all the air-bubbles had been expelled by this process, the small jar containing the weight was lowered into the water in the beaker, the weight, on removing the small jar, being perfectly free from any adhering bubbles of air. After the temperature had sunk to the proper point, the specific gravity was taken.

The 1000-grain weight was selected as the standard; for in nearly every process in which weights are used in chemistry, the object is not to ascertain the *absolute* weight of a substance in terms of a grain or gramme, but to determine its *relative* weight in comparison with that which it possessed at some other time before it was submitted to certain analytical or synthetical operations. If the weighings are performed with the same weights, it does not at all matter whether the weights are absolutely of the value which they profess to be; but it is very important that they should bear a known proportion to each other. This must be understood as referring only to ordinary chemical research in synthesis or analysis. In many physical investigations it is of great importance that the 1000-grain weight should really represent 1000 normal grains, or that its deviation from that value should be accurately determined; but I confess I do not know where a standard weight suitable for such a comparison is to be met with. The weights at first tried were far from accurate among themselves. I accordingly ascertained their errors by the method described below, and then adjusted them myself according to the corrections thus found necessary. The residual errors in the weights were then finally taken in the following manner:—

The balance being brought into equilibrium and the temperature and barometrical pressure carefully noted, the 1000-grain weight was placed in the left pan, and in the right the 600, the 300, and the 100-grain weights. It was now found that, to bring the balance back to equilibrium, a slight additional weight had to be placed on the

right side to supplement the three weights already in that pan. This was noted. The weights were then removed to the opposite sides, the 1000 grains being on the right and the three smaller weights on the left. It was now found that a small weight had to be subtracted from the side carrying the three weights in order to produce equilibrium. The weights were removed and interchanged in this manner ten times, so as to eliminate, as far as possible, the errors arising from observation, or the unequal expansion by heat of the arms of the balance; and by applying the method of least squares to the results obtained, the following equation was arrived at:—

$$(1000)=(600)+(300)+(100) \quad + \quad 0{\cdot}01000 \quad . \; . \; . \quad a,$$

the figures within parentheses representing the nominal value of the actual pieces of platinum stamped 1000, 600, 100 grains, &c.

In a similar manner the values of the remaining weights were ascertained; thus,—

$(600)=(300)+(200)+(100)$	$+$	$0{\cdot}00777$	$b.$
$(300)=(200)+(100)$	$+$	$0{\cdot}00991$	$c.$
$(200)=(100)+(60)+(30)+(10)$	$+$	$0{\cdot}01577$	$d.$
$(100)=(60)+(30)+(10)$	$-$	$0{\cdot}00030$	$e.$
$(60)=(30)+(20)+(10)$	$-$	$0{\cdot}00522$	$f.$
$(30)=(20)+(10)$	$+$	$0{\cdot}00154$	$g.$
$(20)=(10)+(6)+(3)+(1)$	$+$	$0{\cdot}00355$	$h.$
$(10)=(6)+(3)+(1)$	$+$	$0{\cdot}00052$	$i.$
$(6)=(3)+(2)+(1)$	$-$	$0{\cdot}00102$	$j.$
$(3)=(2)+(1)$	$+$	$0{\cdot}00165$	$k.$
$(2)=(1)+(\cdot6)+(\cdot3)+(\cdot1)$	$-$	$0{\cdot}00312$	$l.$
$(1)=(\cdot6)+(\cdot3)+(\cdot1)$	$-$	$0{\cdot}00508$	$m.$
$(\cdot6)=(\cdot3)+(\cdot2)+(\cdot1)$	$-$	$0{\cdot}00260$	$n.$
$(\cdot3)=(\cdot2)+(\cdot1)$	$+$	$0{\cdot}00225$	$o.$
$(\cdot2)=(\cdot1)+(\cdot06)+(\cdot03)+(\cdot01)$	$-$	$0{\cdot}00100$	$p.$
$(\cdot1)=(\cdot06)+(\cdot03)+(\cdot01)$	$-$	$0{\cdot}00802$	$q.$
$(\cdot06)=(\cdot03)+(\cdot02)+(\cdot01)$	$-$	$0{\cdot}00607$	$r.$
$(\cdot03)=(\cdot02)+(\cdot01)$	$-$	$0{\cdot}00642$	$s.$
$(\cdot02)=(\cdot01)+(\cdot01r'')$*	$-$	$0{\cdot}00118r'$	$t.$
$(\cdot01)=(\cdot01r'')$	$+$	$0{\cdot}00413r'$	$u.$
$(\cdot01)=(\cdot01r')$	$+$	$0{\cdot}00410r''$	$v.$

* r', r'' represent riders, two of which were adjusted in this manner.

We have now the data for ascertaining the absolute values of the weights in terms of the (1000) weight taken as standard. Adding the equations a and b gives

$$(1000)=2(300)+(200)+2(100)+0{\cdot}01777.$$

Multiplying equation c by 2 gives

$$2(300)=2(200)+2(100)+0{\cdot}01982.$$

Subtracting e from d gives

$$(200)=2(100)+0{\cdot}01607.$$

Now by $(a+b)+2c+3(d-e)$ we get

$$(1000)=10(100)+0{\cdot}01777+0{\cdot}01982+0{\cdot}04827;$$

$$\therefore (1000)=10(100)+0{\cdot}08580;$$

$$\therefore \tfrac{(1000)}{10}= (100)+0{\cdot}008580;$$

$$\therefore (100)= 100-0{\cdot}008580;$$

$$\therefore (100)=99{\cdot}991420 \text{ grains.} \quad \ldots\ldots \text{A.}^*$$

Substituting this value for the (100) weight, we get from equation e,

$$99{\cdot}991420=(60)+(30)+(10)-0{\cdot}00030;$$

$$\therefore (60)+(30)+(10)=99{\cdot}991720. \quad \ldots\ldots \text{B.}$$

From equation d we therefore get

$$(200)=99{\cdot}991420+99{\cdot}991720+0{\cdot}01577;$$

$$\therefore (200)=199{\cdot}998910. \quad \ldots\ldots \text{C.}$$

From equation c we get

$$(300)=199{\cdot}998910+99{\cdot}991420+0{\cdot}00991;$$

$$\therefore (300)=300{\cdot}000240. \quad \ldots\ldots \text{D.}$$

From equation b we get

$$(600)=300{\cdot}000240+199{\cdot}998910+99{\cdot}991420+0{\cdot}00777;$$

$$\therefore (600)=599{\cdot}998340. \quad \ldots\ldots \text{E.}$$

Again, adding e and f,

$$(100)=2(30)+(20)+2(10)-0{\cdot}00552;$$

$\therefore$ from A,

$$99{\cdot}991420=2(30)+(20)+2(10)-0{\cdot}00552.$$

Multiplying g by 2,

$$2(30)=2(20)+2(10)+0{\cdot}00308.$$

* Although these decimals are carried to the sixth place, the balance would not indicate beyond the fourth place. By taking the mean of ten interchanged weighings, I could obtain a fifth place. The calculated values of the weights were carried to a sixth decimal, in order to avoid inaccuracy in the fourth and fifth places when several values were summed.

Subtracting i from h,

$(20)=2(10)+0{\cdot}00303.$

By adding e, f, twice g, and thrice the last equation, we get

$99{\cdot}991420=10(10)+0{\cdot}000665;$

$$\therefore (10)=9{\cdot}998477. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{F.}$$

From equation i we get

$9{\cdot}998477=(6)+(3)+(1)+0{\cdot}00052;$

$$\therefore (6)+(3)+(1)=9{\cdot}997957. \quad . \quad . \quad . \quad . \quad . \quad \text{G.}$$

Substituting these values in h we get

$(20)=9{\cdot}998477+9{\cdot}997957+0{\cdot}00355;$

$$\therefore (20)=19{\cdot}999984. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{H.}$$

From g we get

$(30)=19{\cdot}999984+9{\cdot}998477+0{\cdot}00154;$

$$\therefore (30)=29{\cdot}999991. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{I.}$$

From f we get

$(60)=29{\cdot}999991+19{\cdot}999984+9{\cdot}998477-0{\cdot}00522;$

$$\therefore (60)=59{\cdot}993232. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{J.}$$

Again, adding i and j,

$(10)=2(3)+(2)+2(1)-0{\cdot}00050.$

Multiplying k by 2,

$2(3)=2(2)+2(1)+0{\cdot}00330.$

Subtracting m from l,

$(2)=2(1)+0{\cdot}00196.$

Then $(i+j)+2k+3(l-m)$ gives

$(10)=10(1)+0{\cdot}00868;$

$$\therefore 9{\cdot}998477=(10)1+0{\cdot}00868;$$

$$\therefore 0{\cdot}9998477=(1)+0{\cdot}000868;$$

$$\therefore (1)=0{\cdot}9989797. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{K}$$

From equation m we have

$0{\cdot}9989797=(\cdot6)+(\cdot3)+(\cdot1)-0{\cdot}00508;$

$$\therefore (\cdot6)+(\cdot3)+(\cdot1)=1{\cdot}0040597. \quad . \quad . \quad . \quad . \quad \text{L.}$$

From l,

$(2)=0{\cdot}9989797+1{\cdot}0040597-0{\cdot}00312;$

$$\therefore (2)=1{\cdot}9998394. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{M.}$$

From k,

$(3)=1{\cdot}9998394+0{\cdot}9989797+0{\cdot}00165$;

$\therefore (3)=3{\cdot}0004691$. . . . . N.

From j,

$(6)=3{\cdot}0004691+1{\cdot}9998394+0{\cdot}9989797-0{\cdot}00102$;

$\therefore (6)=5{\cdot}9982682$. . . . . O.

Again, adding m and n,

$(1)=2(\cdot3)+(\cdot2)+2(\cdot1)-0{\cdot}00768$.

Multiplying o by 2 we get

$2(\cdot3)=2(\cdot2)+2(\cdot1)+0{\cdot}00450$.

Subtracting q from p,

$(\cdot2)=2(\cdot1)+0{\cdot}00702$.

Then $(m+n)+2o+3(p-q)$ gives

$(1)=10\ (\cdot1)+0{\cdot}01788$;

$\therefore 0{\cdot}9989797 =10(\cdot1)+0{\cdot}01788$;

$\therefore 0{\cdot}09989797= \ (\cdot1)+0{\cdot}001788$;

$\therefore (\cdot1)=0{\cdot}09810997$. . . . . P.

From q we get

$0{\cdot}09810997=(\cdot06)+(\cdot03)+(\cdot01)-0{\cdot}00802$;

$\therefore (\cdot06)+(\cdot03)+(\cdot01)=0{\cdot}10612997$. . . . Q.

From p,

$(\cdot2)=0{\cdot}09810997+0{\cdot}10612997-0{\cdot}00100$;

$\therefore (\cdot2)=0{\cdot}20323994$. . . . . R.

From o,

$(\cdot3)=0{\cdot}20323994+0{\cdot}09810997+0{\cdot}00225$;

$\therefore (\cdot3)=0{\cdot}30359991$. . . . . S.

From n we get

$(\cdot6)=0{\cdot}30359991+0{\cdot}20323994+0{\cdot}09810997-0{\cdot}00260$;

$\therefore (\cdot6)=0{\cdot}60234982$. . . . . T.

Again, adding q and r,

$(\cdot1)=2(\cdot03)+(\cdot02)+2(\cdot01)-0{\cdot}01409$.

Multiplying s by 2 we get

$2(\cdot03)=2(\cdot02)+2(\cdot01)-0{\cdot}01284$.

Subtracting u from t,

$(\cdot 2)=2(\cdot 01)-0\cdot 00531.$

Then $(q+r)+2s+3(t-u)$ gives

$(\cdot 1)=10(\cdot 01)-0\cdot 04286,$

$\therefore 0\cdot 09810997 =10(\cdot 01)-0\cdot 04286,$

$\therefore 0\cdot 009810997=(\cdot 01)-0\cdot 004286,$

$$\therefore (\cdot 01)=0\cdot 014096997. \quad \text{U.}$$

From u we get

$0\cdot 014096997=(\cdot 01r'')+0\cdot 00413,$

$$\therefore (\cdot 01r'')=0\cdot 009966997. \quad \text{V.}$$

From t we get

$(\cdot 02)=0\cdot 014096997+0\cdot 009966997-0\cdot 00118,$

$$\therefore (\cdot 02)=0\cdot 022883994. \quad \text{W.}$$

From s we get

$(\cdot 03)=0\cdot 022883994+0\cdot 014096997-0\cdot 00642,$

$$\therefore (\cdot 03)=0\cdot 030560991. \quad \text{X.}$$

From r we get

$(\cdot 06)=0\cdot 030560991+0\cdot 22883994+0\cdot 014096997-0\cdot 00607,$

$$\therefore (\cdot 06)=0\cdot 061471982. \quad \text{Y.}$$

From v we get

$0\cdot 014096997=(\cdot 01r')+0\cdot 00410,$

$$\therefore (\cdot 01r')=0\cdot 009996997. \quad \text{Z.}$$

The value of the weights thus given was, however, their weight in *air* of the ordinary pressure; it became therefore necessary to ascertain their value in a vacuum. All bodies displace a bulk of air equal to their own volume, and the weight of this air is of course greater as their specific gravity diminishes. In delicate investigations this loss of weight is important. The reduction of the platinum weights to their true value *in vacuo* I calculated by the following formula:—

Let W = weight in air,

w = „ „ water,

a = specific gravity of air as compared with water;

then

$$x, \text{ or weight } in\ vacuo, = \frac{W-aw}{1-a},$$

where

$a=0\cdot 001225$, and

$1-a=0\cdot 998775.$

The following Table shows the final results of these adjustments:—

Nominal value of weights.	True value in air at 30 in.* 62° F.	Weight of air displaced.	Volume in water of maximum density.
grs.	grs.	gr.	grs.
1000·00	1000·000000	0·058271	47·5100
600·00	599·998340	0·035533	28·9700
300·00	300·000240	0·017501	14·2700
200·00	199·998910	0·011664	9·5100
100·00	99·991420	0·005887	4·8000
60·00	59·993232	0·003483	2·8400
30·00	29·999991	0·001668	1·3600
20·00	19·999984	0·001104	0·9000
10·00	9·998477	0·000490	0·4000
6·00	5·998268	0·000355	0·2900
3·00	3·000469	0·000171	0·1400
2·00	1·999839	0·000113	0·1000
1·00	0·998980	0·000055	0·0400
0·60	0·602350	0·000035	0·0300
0·30	0·303600	0·000017	0·0200
0·20	0·203240	0·000011	0·0100
0·10	0·098110	0·000005	0·0040
0·06	0·061472	0·000003	0·0030
0·03	0·030561	0·000002	0·0020
0·02	0·022884	0·000001	0·0010
0·01	0·014097	0·000001	0·0004
0·01′	0·009997	0·000001	0·0004
0·01″	0·009967	0·000001	0·0004

The value of each weight in air, plus the weight of air displaced, is, of course, the weight *in vacuo*.

Having ascertained their true value, the weights were carefully preserved; and as, being of platinum, there was no accumulation of tarnish on their surface, and as they were lifted with ivory-tipped forceps to prevent wear, they have showed up to the present time, whenever compared, absolutely no alteration.

The Glass.

The flasks and vessels used were of the hardest Bohemian glass, and as thin as they could be employed. When practicable, vessels of old green German glass were used; neither this nor Bohemian glass is practically affected by reagents.

Liquids were generally kept sealed up in glass bulbs and globes, but sometimes in stoppered green German glass flasks or in "bromine" bottles. When liquids were kept in these bottles for a few days only, they were not found to have contracted any saline impurity from the glass, but after remaining for some weeks they were found to leave a visible residue on evaporation.

No cork or luting was employed in the distillations &c.; in most cases the apparatus was blown in one piece, and the operations performed in a vacuum. The pieces of apparatus which were weighed were entirely composed of glass suspended with platinum loops. The fingers were not allowed to touch them after the first weighing.

The weight of tubes, bulbs, and flasks, even of hard Bohemian glass, constantly diminishes when the glass is long heated in a spirit- or gas-flame; this loss may amount

* The cistern of the barometer is 115 feet above the approximate mean water-level at Somerset House.

to several thousandths of a grain in the space of two hours when a bulb of Bohemian glass three inches in diameter is exposed to a decided red heat in a gas-flame. Following the suggestion of Professor STAS, I have obviated this source of error by employing a bath of pure magnesia; and find that the weight remains constant even at a nearly white heat. Baths of lime have sometimes been employed with similar satisfactory results.

The special apparatus that I have used will be described in the processes in which they were required; I need scarcely say that in no case were materials of untried purity employed.

Improved Sprengel Vacuum-pump.

[Before detailing the processes of the determination, it will be requisite to describe the means of producing a vacuum in the flasks and bulbs employed. In proceeding with the determinations, several additions and improvements have been made to the Sprengel pump as generally found in the laboratory. Working so much with this pump, I have endeavoured to avoid the inconveniences attending the usual mode of raising the mercury from the lower to the upper reservoir.

The mercury is contained in a closed glass reservoir A (fig. 2, Plate XV.), perforated with a fine hole at the top. This reservoir is attached to a block, capable of free movement in a vertical line, and running in grooves, and connected with the lower reservoir by a flexible tube, *g*.

When the whole of the mercury has run from the reservoir A, the reservoir and slide can be lowered by liberating the teeth of the cog-wheel K from the detent *m*; at the same time a friction-brake is pressed against the cylinder. The aim of this arrangement is to permit the slide-block to fall steadily, swiftly, and without any injurious shock upon the block L. H is a glass reservoir, which receives the mercury after flowing through the pump. When the reservoir A is emptied and has been lowered to the block L, the mercury from H is admitted into A by opening the tap I. *f* is another tap, to regulate the flow of mercury through the pump, whilst a third tap is at R. *g* is a flexible india-rubber tube, strengthened to withstand the pressure by being constructed of concentric layers of rubber and canvas. *b* is a tube filled with small glass beads and containing concentrated sulphuric acid to absorb moisture*; it is attached to *l* by means of a mercury joint. *c*, *c*, *c* are mercury joints, it being inconvenient to have the apparatus in one piece of glass tubing. *e e* is a barometer dipping into the same vessel as the gauge-barometer P, the two thus forming a differential system, by which the rarity of the atmosphere in the apparatus to be exhausted can be easily estimated. *d d* is a scale attached to the gauge.

* Since writing the above description I have soldered a small glass tube to the lower part of *b*, turned up and terminating in a funnel-shaped mercury stopper. This enables me to draw off the old acid when weakened by absorption of moisture and to replace it by fresh acid, and also to pass different gases into any apparatus I may have under experiment.—W. C., July 1873.

The reservoir A being filled with mercury, the tap I is turned off and the reservoir is raised to the top of the slide, where it is supported by the piece T.

On opening the tap *f* the mercury rises in the tube *fh*, and falling through the chamber N, carries with it the air contained in the tube R and in the apparatus or bulbs attached to the tube *b*, as in the ordinary Sprengel pump. At N the tubing is enlarged in order that the mercury may not be forced up the tube R, as otherwise frequently happens if the apparatus or mercury gets soiled. This liability of the mercury to run up is further obviated by raising the tube R above the level of the upper reservoir A.

J, J are iron brackets supporting the apparatus. S is a large inverted glass receiver to collect the small portions of mercury which are unavoidably and constantly being spilled; it contains a little weak solution of carbonate of sodium. The part of the tubing *gfh* N forms a barometric siphon arrangement, which effectually prevents air getting into the enlargement N from the reservoir A, when the mercury has completely run out: in this case no harm whatever is done to the operation, the vacuum is not injured, and the exhaustion proceeds immediately on retransferring the mercury from the reservoir H to the reservoir A, and raising A again into its place. The apparatus, as thus arranged, is readily manageable with certainty of obtaining a barometric vacuum.

The mercury fall-tube of a pump in constant use frequently wants cleaning. I find the most effectual means of doing this is to put oil of vitriol into the funnel stopper *h*, and then, by slightly loosening the glass stopper, allow a little of the strong acid to be carried down the tube with the mercury. With care this can be effected without interfering with the progress of exhaustion. The residual acid in the chamber N does good rather than harm. When sufficient sulphuric acid has run into the fall-tube, the funnel stopper can be perfectly closed by filling it with mercury.

The preceding description is that of the apparatus with the most recent improvements. During the determination of the atomic weight of thallium a pump was employed similar in detail, with the exception that, instead of the movable reservoir and flexible rubber tubing, a glass funnel with tubing of glass was used. The mercury passing from the funnel was broken up in its fall and freed from adhering air-bubbles by the insertion of two silk-covered thin iron wires extending from the funnel to the base of the tube. As equally perfect results can be obtained by both methods, the details should be considered as improvements for the sake of convenience rather than for accuracy.—29 *November*, 1872.]

Section III.—THE CHEMICALS.

In this section I shall detail the methods adopted in the preparation of thallium and the reagents in a chemically pure state.

Water.

Ordinary distilled water is mixed with a little crystallized permanganate of silver, and boiled for about half an hour. An excess of sulphuric acid is next added, and it is again

boiled for half an hour. The supernatant solution is then transferred to a German green glass retort, and distilled over a water-bath at the rate of about one drop a minute. The end of the neck of the retort is drawn out, and fitted tightly into the mouth of the flask used as a receiver. The first portions of water which distil over are always to be rejected, and the distillation is stopped when about three fourths of the contents of the retort have come over. The product of this distillation is then mixed with freshly precipitated oxide of silver, and allowed to stand, with frequent agitation, until a few drops of the decanted clear solution exhibit an alkaline reaction. The water is then introduced into an apparatus shown at fig. 1, Plate XVI. *a*, *b*, *c* are three globes made of hard German glass, *a* and *c* holding about half a pint each, *b* holding about four ounces; they are connected by tubes as shown, the tubes being contracted at the places *d*, *e*, *f*. The water, containing a little oxide of silver dissolved in it, is introduced through *d* into the globe *a*, until *a* is nearly full. The contracted part at *d* is then sealed up before the blowpipe, the end *g* is put into connexion with the Sprengel pump from which the U-tube containing sulphuric acid has previously been removed, and the mercury set running. Heat is applied to the globe *a* containing the water, until gentle ebullition (under diminished pressure) sets in, the globes *b* and *c* being kept cold with ice. This is continued until no more air, either from the apparatus or from the water, is carried down by the falling mercury. When this is the case, the globe *a* is allowed to cool, and the tube is sealed up at *f*, the vacuum being maintained as perfect as possible. By inclining the tube and globes, any water which may have distilled over from *a* into *b* or *c*, is now poured back into *a*. The two end globes *a* and *c* are then placed in water-baths, whilst the centre globe, *b*, is immersed in melting ice. A gentle heat being applied to the water-bath containing *a*, distillation rapidly proceeds without actual ebullition, and water condenses in *b*, its condensation in *c* being prevented by warming the water-bath in which *c* is immersed. When about one fourth of the contents of *a* has thus distilled over, the operation is stopped, and the bulb *b* removed by sealing the contracted part of the tube at *h*; any trace of ammonia which might happen to be in the water as introduced into *a* will thus have been collected in the bulb *b* and removed. The apparatus now has the appearance shown at fig. 2, Plate XVI. The globe *c* is now cooled in melting ice, and gentle heat being applied to the bath containing the globe *a*, distillation again proceeds, the condensation this time being into *c*. The first portions of water which come over into *c* are used to rinse out that globe, a dexterous movement throwing it all over the inner surface without throwing any of the liquid out of *a*. After two such rinsings, distillation is allowed to proceed without ebullition until four fifths of the water has distilled from *a* to *c*. The tube is then sealed at the contracted part *e*, and the globe *c* (fig. 3), containing what I believe to be absolutely pure water *in vacuo*, may be set aside for future use. It will be observed that the water, almost chemically pure to begin with, has in this manner been distilled and further purified in the entire absence of atmospheric air. When some of this water is required for use, the glass tube is touched at *f* with a blowpipe-flame. As soon as the glass softens, the atmo-

spheric pressure forces the glass in, forming a fine hole. In this way no fragments of glass get into the water, as might be the case if the end of the tube were broken off after scratching with a file in the usual manner. As much water as is needed is driven out by warming the globe, and the water remaining unused may be sealed up again.

Water purified in this manner was employed in the final crystallizations of all the salts used in the investigation, in rinsing out the apparatus, and generally in all operations where its employment was likely to increase the accuracy of the result.

Nitric Acid.

The apparatus in which the nitric acid was prepared is represented in the accompanying figure (fig. 4, Plate XVI.). *a*, *b*, *c*, *d* are glass globes, *a* being about 4 inches and the others about 2 inches diameter; they are connected by fusion with glass tubes bent as represented in the drawing, and contracted at the points *o*, *p*, *q*, *r*, *s*. The cylindrical tube *e* is connected by means of a flexible joint, *iiii* (fig. 4 *b*), to the Sprengel pump: this joint consists of several pieces of glass tube held closely together by means of india-rubber tubing; the pieces of tubing are fastened with two or three turns of silk-covered iron wire. A little glycerin smeared over a joint of this description renders it quite air-tight, whilst the apparatus is capable of considerable movement. A mixture of glacial phosphoric acid and nitrate of silver in atomic proportions, and coarsely ground together in an agate mortar, is introduced into the globe *a* until about half-full, the cylinder *e* having previously been filled through the opening *g* with pieces of caustic soda. The tubes *f* and *g* are now sealed up at the contracted portions, and the Sprengel pump is connected to *h*. Exhaustion is proceeded with, the apparatus being gently warmed at the same time until moisture is no longer visible, and the mercury is as high as the vapours present will allow it to rise. The bulb *b* is then immersed in a freezing-mixture, and heat is cautiously applied to the bulb *a*. The nitrate of silver and phosphoric acid soon fuse together to a clear liquid, and vapours of nitric acid mixed with nitrous acid are copiously evolved. The mixture froths considerably, and care must be taken that none rises so high as to pass into the bulb *b*. In this and the other bulbs nearly all the vapours condense, the small quantity that escapes being caught by the caustic soda in *e*. If, through spirting or inadvertence, some of the solid matter is carried over from *a* into *b*, the contents of *b* are easily decanted back into *a* by tilting the apparatus into such a position that the line *k l* would become horizontal: owing to the curvatures of the connecting-tubes, no liquid which might be in the bulbs *c* or *d*, and none of the pieces of caustic soda in *e*, can get out of their place. When the reaction between the phosphoric acid and nitrate of silver has been pushed as far as convenient (too strong a heat must not be applied, or the nitric acid is in part decomposed as it is liberated), the tube connecting *a* and *b* is sealed in a spirit-lamp, and the globe *a* drawn off. The bulb *c* is now thoroughly washed out with nitric acid by distilling a little over from *b*, letting it condense in *c*, and then pouring it back by inclining the apparatus so that the vertical line *m n* would become horizontal. The bulbs *b* and *d* are now warmed

in water-baths, whilst the bulb *c* is immersed in a freezing-mixture. Distillation rapidly proceeds without ebullition, the acid almost entirely condensing into *c*. When about four fifths of the contents of *b* are distilled into *c*, the tube is sealed up at *q* before the blowpipe and the bulb *b* drawn off.

The next operation is to clear the acid in *c* and the rest of the apparatus from nitrous vapours. For this purpose the mercury of the Sprengel pump is set gently in motion, and the apparatus is very moderately heated from time to time until the vacuum is as perfect as the tension of nitric-acid vapour will admit*. When this is effected, the bulb *c* is gently warmed in a water-bath, whilst *d* is immersed in a freezing-mixture. The temperature of *c* is so adjusted that distillation proceeds slowly without ebullition. When four fifths of the contents of *c* have come over, the mercury-pump working slowly all the time, the connecting-tube is sealed before the blowpipe at *r*, and *c* is drawn off. The flame being then applied at the contracted part *s*, the bulb *d*, containing the pure nitric acid, and having the appearance shown at Plate XVI. fig. 4 *a*, is removed. The acid may be kept unchanged for any length of time, provided it be not exposed to the light. When required for use, the end of one of the tubes is perforated with a blowpipe-flame, as described above under the heading "Water." By heating the bulb, any desired quantity of acid is driven out, when the remainder can again be sealed up.

Oxalic Acid.

Commercial purified oxalic acid is gently heated in a flat dish until the water of crystallization is removed. Bibulous paper is then placed over it, a paper cap over that, and the heat is increased until the oxalic acid sublimes. The sublimed crystals are removed from the inside of the paper cap, and introduced into the lower portion, *a*, of the glass apparatus shown in the diagram (Plate XVI. fig. 5). The tubes are contracted at *b* and *c*, and the end *d* is connected by means of an india-rubber connector with the Sprengel pump. The air is now completely exhausted from the apparatus, and it is immersed in a paraffin-bath to a little above the first contraction, *b*; a thermometer is also immersed in the bath.

The temperature is first raised to 200° F., and the exhaustion continued until all moisture disappears from the inside of the tube. The bath is then gradually raised to 250°, and kept at that temperature till the oxalic acid has risen in vapour and condensed in the wide portion of the tube between *b* and *c*. The paraffin-bath is then taken away, and when the tube is cold it is removed from the pump by applying a blowpipe-flame to the contraction *c*; this being repeated at *b*, leaves the sublimed oxalic acid perfectly pure in the bulb *b c*, and in a vacuum.

In this apparatus oxalic acid commences to sublime below 200° F. If the temperature of the paraffin-bath be kept below 278° F. no permanent gas is evolved, and no

* If acid vapours pass into the tubes of the Sprengel pump they do no harm, being carried down at once. The small quantity which condenses in the tubes may be afterwards removed by passing some distilled water through the pump, and then drying with warm air, or by passing oil of vitriol through the pump.

formic acid is obtained; above that temperature the barometer-gauge of the pump commences to sink; but the mercury descends very slowly until 330° is reached, when the decomposition of the oxalic acid into formic and carbonic acids becomes more rapid.

Sulphuric Acid.

After many attempts to prepare sulphuric acid free from arsenic by the distillation at a red heat of alkaline bisulphates, by dissolving sulphuric anhydride in water, and by decomposing sulphate of silver with sulphuretted hydrogen, I finally adopted BLOXAM'S method of preparing it by means of sulphurous and nitrous acids (Journ. Chem. Soc. vol. xv. p. 52).

The sulphurous acid is evolved from well-crystallized sulphite of sodium by the action of sulphuric acid, keeping the temperature as low as possible. The current of gas is first passed through a washing-bottle of water containing a little oxide of silver in suspension (which becomes converted into sulphite of silver, and then into a mixture of sulphate of silver and metallic silver), then through two U-tubes filled with small pieces of pumice-stone moistened with water. The pumice-stone should be previously purified from chlorides and fluorides by STAS'S method of igniting it twice with sulphuric acid.

The nitrous acid is prepared by gently heating together nitrate of potassium, ferrous sulphate (both purified by repeated crystallization), and dilute sulphuric acid.

The sulphurous acid and nitrous acid are conducted simultaneously by tubes into a large glass globe, a third tube serving for the introduction of steam. The three tubes pass into the globe through a glass plate in which three holes have been perforated. The glass plate and mouth of the glass globe are fitted to each other by grinding. No lute being used, sufficient air finds its way into the globe to keep up the reaction. By regulating the ingress of nitrous acid, of sulphurous acid, and of steam, the operation can be carried on continuously for many hours.

The condensed liquid is next introduced into an apparatus blown from hard German glass, as shown in Plate XVI. fig. 6. *a*, *b*, and *c* are three bulbs about 3 inches diameter. The dilute sulphuric acid is introduced into the bulb *a* by means of the neck *d*, which is then sealed before the blowpipe at the contracted part. The end of the tube *e* is then connected with the Sprengel pump, the end *f* temporarily stopped up, and the whole is exhausted. The bulb *b* is immersed in a water-bath kept at the boiling-point, and *a* being gently heated the excess of water in the sulphuric acid goes off, and partly condenses in the bulb *c*, which is kept cold, and partly becomes carried down through the pump by the falling mercury.

Concentration of the acid proceeds rapidly; and as soon as all excess of water has been thus eliminated, and the gauge of the pump shows that only aqueous vapour is present, the bulb *c*, containing water, is removed by applying a blowpipe-flame to the contracted portion of the tube *g*. Air is now admitted, the tube *f* is connected with the Sprengel pump, and exhaustion again proceeded with. The bulb *b* is now kept cool, and the bulb *a* heated in a sand-bath. The atmospheric pressure must not be altogether removed,

or the bumping of the acid in *a* will be very violent. If the exhaustion is such that the mercury in the gauge stands at about 15 inches, the oil of vitriol distils quietly from the bulb *a* to *b* without bumping; but if the exhaustion is raised to above 16 inches, the ebullition becomes percussive. When most of the acid has distilled over into *b* the source of heat is removed, the mercury in the pump is again allowed to run until a vacuum is produced, and the bulb *b*, containing pure distilled sulphuric acid, is sealed up and removed by the application of a blowpipe-flame to the contracted portions of the tubes *h* and *i*.

Carbonic Acid.

Calc-spar is dissolved in pure hydrochloric acid. An excess of the spar is added, and the solution warmed; to it is added lime-water made from pure or nearly pure lime, until the solution is alkaline to test-paper. This solution is filtered, and after heating it to at least 160° F., precipitated with carbonate of ammonium*. The carbonate of calcium thus precipitated is thrown on a filter and well washed with pure water. Thus prepared, the carbonate of calcium is a dense powder and perfectly pure; or, if it contain any impurity, it will be a trace of carbonate of barium or strontium, which in no way interferes with its use in preparing carbonic acid.

The dense granular carbonate of calcium is then strongly compressed in a steel diamond mortar into the form of coherent lumps. These lumps are introduced into a WOULFE'S bottle, and pure oil of vitriol poured over them. A continuous and not too rapid evolution of carbonic acid commences and is continued for some time. When the disengagement of gas becomes sluggish, a few drops of water restore the action. Large bottles must be used for this operation to avoid the inconvenience of the foaming to which the acid is liable.

The carbonic acid is washed by passing through solution of sulphate of silver containing carbonate of silver in suspension to the consistency of thin cream, and it is then passed through a U-tube containing purified pumice-stone moistened with oil of vitriol.

Ammonia.

Ammonia is prepared in two ways:—

1. Nitrate of potassium heated to incipient decomposition, and then crystallized three times from pure water, is dissolved to saturation in water, and put into a retort. Sodium amalgam containing about 1 per cent. of sodium is then added, and the whole allowed to stand in a cool place for twelve hours. Gentle heat being now applied to the retort, ammonia (from the reduction of the nitric acid) is driven over with the first

* This precaution, which was first suggested by Professor J. LAWRENCE, of Louisville, must not be overlooked, as it is desirable to obtain the precipitated carbonate of calcium as dense as possible. If the carbonate of ammonium be added to the cold solution, the precipitate, at first gelatinous, will ultimately become much more dense and settle readily; the same is true if the mixture be heated after the addition of the carbonate of ammonium; but in neither case will it be as dense as when the carbonate is added to the hot solution of chloride of calcium.

portions of water, and is condensed in a receiver cooled with ice. The temperature of the liquid in the retort is not allowed to rise to the point of ebullition, and the operation is stopped when one fourth of the liquid in the retort has distilled over.

2. Ammonia is also prepared by a method recommended by Professor STAS. Nitrite of potassium is mixed with strong solution of caustic potash, and the liquid poured into a large glass balloon containing a mixture of zinc (free from carbon*) and iron wire which has been first oxidized by heating in the air and then reduced by hydrogen. After standing for seventy-two hours, the liquid is decanted from the residue into a retort, which is then gently heated on a sand-bath. The arrangement for condensing the ammonia consists of two flasks fitted up as WOULFE'S bottles containing pure water. The distillation is effected very slowly below the boiling-point of the liquid, and the condensers are cooled with ice.

Hydrogen.

The method pursued in the preparation of pure hydrogen is as follows:—The gas is generated in one of a series of WOULFE'S bottles by pouring warm caustic potash over a mixture of granulated zinc and iron scraps. The gas thus generated (the method is due to RUNGE, POGG. Ann. xvi. p. 130) is inodorous. It is next passed into another WOULFE'S bottle containing protochloride of tin; then through tubes containing pumice-stone moistened with a concentrated solution of pyrogallic acid in caustic potash, and again through tubes containing pumice moistened with sulphuric acid, the object in passing the gas through the protochloride of tin and through the pyrogallic acid being to remove the oxygen diffused into the apparatus from the atmosphere.

Thallium.

It may not be out of place here to note the most usual sources of thallium as it is ordinarily prepared.

Thallium is a very widely distributed constituent of iron and copper pyrites. Upon examining a large collection of pyrites from different parts of the world, it was found present in more than one eighth. It is not confined to any particular locality. Amongst those ores in which it occurs most abundantly (although in these cases it does not constitute more than from the 100,000th to the 4000th of the bulk of the ore), may be mentioned iron pyrites from Theux, near Spa in Belgium, from Namur, Philipville, Alais, the south of Spain, France, Ireland, Cornwall, Cumberland, and different parts of North and South America; in copper pyrites from Spain, as well as in crude sulphur prepared from this ore; in blende and calamine from Theux; in blende, calamine, metallic zinc, sulphide of cadmium, metallic cadmium, and cake sulphur from Nouvelle-Montagne; in native sulphur from Lipari and Spain; in bismuth, mercury, and antimony ores, as well as in the manufactured products from these minerals (frequently in so-called pure medicinal preparations of these metals); in commercial selenium and tellurium (probably as selenide and telluride).

* Zinc is obtained free from carbon by fusing it with a mixture of carbonate of sodium and nitre.

Thallium is likewise frequently present in copper and commercial salts of this metal. In Spain a very impure copper is prepared in the following way:—Copper pyrites is allowed to oxidize in the air, and the resulting sulphate of copper is washed out; scrap iron is now placed in the liquid, which causes the copper to precipitate in the powdery state. The metal is then collected together, dried, strongly compressed, and heated to the melting-point. It is brought over to this country in the form of rectangular cakes, weighing about 20 lbs. each, and is called "cement copper." The sulphide of thallium, oxidizing to sulphate along with the sulphide of copper, is washed out by the water, and precipitated with the copper by the iron. The two metals alloy together.

Thallium is present in tolerable quantity in lepidolite from Moravia, and in mica from Zinnwald. It has likewise been found in the deliquescent "sel à glace" from the mother-liquors of the salt-works at Nauheim. This consists of a mixture of the chlorides of magnesium, potassium, and sodium, with relatively considerable quantities of chlorides of rubidium and cæsium, and sensible traces of chloride of thallium. Thallium is also met with in the mother liquors in the sulphate-of-zinc works at Gozlar, in the Harz.

Nordenskjöld has found in the copper-mine of Skrikerum, in Norway, a native selenide of copper, silver, and thallium, containing about 18 per cent. of thallium. It occurs in the form of lead-grey compact masses, having the hardness of copper glance and a spec. grav. of 6·9. This mineral has been named *Crookesite* by its discoverer. From the general association of selenium, copper, silver, and thallium in iron and copper pyrites it is probable that the thallium is here present in the form of Crookesite disseminated through the mass.

The optical process of detecting thallium in a mineral is very simple. A few grains of the ore are crushed to a fine powder in an agate mortar, and a portion taken up on a moistened loop of platinum wire. Upon gradually introducing this into the outer edge of the flame of a Bunsen's gas-burner, and examining the light by means of a spectroscope, the characteristic green line will appear as a continuous glow, lasting from a few seconds to half a minute or more, according to the richness of the specimen. By employing an opaque screen in the eyepiece of the spectroscope to protect the eye from the glare of the sodium line, thallium may be detected in half a grain of mineral, when it is present only in the proportion of 1 to 500,000. The sensitiveness of this spectrum reaction is so great that no estimate can be arrived at respecting the probable amount of thallium present.

Many samples of commercial sulphuric acid and yellow hydrochloric acid contain thallium. The source in these cases is evidently the pyrites used in the sulphuric-acid works.

PREPARATION OF COMMERCIALLY PURE THALLIUM.

a. From the Flue-dust of Pyrites-burners.—This is by far the most economical source of thallium at present known. In burning thalliferous pyrites for the purpose of manufacturing sulphuric acid, the thallium oxidizes along with the sulphur, and is driven off

by the heat. If the passage leading from the burners to the leaden chambers is only a few feet long, the greater portion of the thallium escapes condensation, and is carried into the leaden chambers; it there meets with aqueous vapours, sulphurous and sulphuric acids, and becomes converted into sulphate of the protoxide of thallium. This being readily soluble both in water and dilute sulphuric acid, and not being reduced by contact with the leaden sides, remains in solution and accompanies the sulphuric acid in its subsequent stages of concentration, &c. If, on the other hand, the passage connecting the burners and chambers is 10 or 15 (or more) feet in length, nearly the whole of the thallium is condensed, together with the multiplicity of other bodies which constitute "flue-dust." Accompanying the thallium have been found mercury, copper, lead, tin, arsenic, antimony, iron, zinc, cadmium, bismuth, lime, and selenium, together with ammonia, sulphuric, nitric, and hydrochloric acids. The amount of thallium in these flue-deposits is very various: in many specimens it is not present at all, and in very few it amounts to as much as $\frac{1}{4}$ per cent., although in some as much as 8 per cent. of thallium has been found.

The following is the best plan for extracting thallium from the dust:—The dust is first heated to very dull redness, so as to allow the excess of sulphuric acid to drive off any hydrochloric acid which may be present, and is then mixed in wooden tubs with an equal weight of boiling water, and well stirred; after this the mixture is allowed to rest for twenty-four hours for the undissolved residue to deposit. The liquid is then siphoned off, and the residue is washed, and afterwards treated with a fresh quantity of boiling water. The collected liquors which have been siphoned off from the deposit are allowed to cool, precipitated by the addition of a considerable excess of strong hydrochloric acid, and the precipitate, consisting of very impure chloride of thallium, is allowed to subside. The chloride obtained in this way is then well washed on a calico filter, and afterwards squeezed dry. Three tons of flue-dust treated in this way yielded as much as 68 lbs. of this crude chloride.

The next step consists in treating the crude chloride in a platinum dish with an equal weight of strong sulphuric acid, and afterwards heating the mixture to expel the whole of the hydrochloric acid. To make sure of this, the heat must be continued until the greater part of the excess of sulphuric acid is volatilized. After this the mass of bisulphate of thallium is dissolved in about twenty times its weight of water, nearly neutralized with chalk, and then filtered. On the addition of hydrochloric acid to the filtrate, nearly pure chloride of thallium is thrown down; this is collected on a filter, well washed, and then dried. The crude protochloride of thallium obtained by either of the above methods is added by small portions at a time to half its weight of hot oil of vitriol in a porcelain or platinum dish, the mixture being constantly stirred and the heat continued till the whole of the hydrochloric acid and the greater portion of the excess of sulphuric acid are driven off. The fused bisulphate is now to be dissolved in an excess of water, partially neutralized with carbonate of sodium, and an abundant stream of sulphuretted hydrogen passed through the solution. The precipitate, which may contain

tin, arsenic, antimony, bismuth, lead, mercury, and silver, is separated by filtration, and the filtrate is boiled till all free hydrosulphuric acid is removed. The liquid is now to be rendered alkaline with ammonia and boiled; the precipitate of iron and alumina, which generally appears in this place, is filtered off, and the clear solution evaporated to a small bulk. Sulphate of thallium will then separate out on cooling in the form of long, clear prismatic crystals. As sulphate of ammonium is much more soluble than sulphate of thallium, the latter can readily be separated from the small quantity of the former salt present. The two salts do not crystallize together.

In order to avoid the inconvenience of driving off the excess of oil of vitriol in the decomposition of chloride of thallium, it is less troublesome, although not quite so economical, to proceed as follows:—Boil the chloride of thallium in solution of sulphide of ammonium for five minutes: decomposition takes place readily. Filter and wash with sulphuretted water till no more chlorine can be detected in the filtrate; then dissolve the sulphide on the filter in dilute sulphuric acid, and treat the solution with ammonia &c., as above directed.

In order to obtain the metal when working on small quantities of material, sulphate of thallium is dissolved in twenty times its weight of water; the liquid is acidulated with sulphuric acid, and a current of electricity from two or three cells of GROVE's batteries is passed through it, platinum terminals being used. The appearance presented when a tolerably strong solution of thallium is undergoing reduction is very beautiful. If the energy of the current bears a proper proportion to the strength and acidity of the liquid, no hydrogen is evolved at the negative electrode, but the metal grows from it in large crystalline fern-like branches, spreading out into brilliant metallic plates, and darting long needle-shaped crystals, sometimes upwards of an inch in length, towards the positive pole, the appearance being more beautiful than with any other metal. Some of the tabular crystals, as seen in the liquid, are beautifully sharp and well defined; considerable difficulty, however, is met with in disengaging them from the electrode, and removing them in a perfect state from the liquid. So long as thallium is present in the solution, no hydrogen is evolved with a moderate strength of current; as soon as bubbles of gas are evolved, the reduction may be considered complete. The crystalline metallic sponge may now be squeezed into a mass round the platinum terminal, disconnected from the battery, quickly removed from the acid liquid, rinsed with a jet from a wash-bottle, and transferred to a basin of pure water. The metal is then carefully removed from the platinum, and kneaded with the fingers into as solid a lump as possible. It coheres readily by pressure, and will be found to retain its metallic lustre perfectly under water.

When considerable quantities of thallium are to be reduced to the metallic state, it is convenient to employ metallic zinc for the purpose. In the course of twenty-four hours I have reduced upwards of a quarter of a hundredweight of the metal in the following way:—Plates of pure zinc (which should leave no residue whatever when dissolved in sulphuric acid) are arranged vertically round the sides of a deep porcelain dish holding a gallon. Crystallized sulphate of thallium, in quantities of about seven pounds at a

time, is then placed in the dish, and water poured over to cover the salt. Heat is applied, and in the course of a few hours the whole of the thallium will be reduced to the state of a metallic sponge, which readily separates from the plates of zinc on slight agitation. The liquid is poured off, the zinc removed, and the spongy thallium washed several times. It is then strongly compressed between the fingers, and preserved under water until it is ready for fusion.

The metal is readily obtained in the coherent form by fusing the sponge. This is most conveniently performed under cyanide of potassium on the small scale, and under coal-gas when working with large quantities. In the former case the sponge, strongly compressed and quite dry, is broken into small pieces, which are dropped one by one into cyanide of potassium kept fused in a porcelain crucible. They rapidly melt, forming a brilliant metallic button at the bottom. When cold, the cyanide of potassium may be dissolved in water, when the thallium will be left in the form of an irregular lump, owing to its remaining liquid and contracting after the cyanide has solidified.

On the large scale, the fusion is best effected in an iron crucible. This is placed over a gas-burner, and a tube is arranged so that a constant stream of coal-gas may flow into the upper part of the crucible. Lumps of the compressed sponge are then introduced, one after the other as they melt, until the crucible is full of metal. It is then stirred up with an iron rod; and the thallium may either be poured into water and obtained in a granulated form or cast into an ingot. Thirty or forty fusions have been performed in the same crucible without the iron being appreciably acted upon by the melted thallium.

b. From Iron Pyrites.—The richest pyrites which I have yet met with comes from Oneux, near Theux; it contains about 1 part of thallium in 4000. Two tons of this ore were worked in the following manner:—

The pyrites, broken up into pieces of the size of a walnut, is distilled in hexagonal cast-iron pipes, closed at one end, and arranged in a reverberatory furnace. Conical sheet-iron tubes are luted on to the open ends, and the retorts are kept at a bright red heat for about four hours. At the end of the operation the receivers are found to contain from 14 lbs. to 17 lbs. of dark green or grey-coloured sulphur for every 100 lbs. of ore used. The whole of the thallium originally in the pyrites will be found in this sulphur, from which it has now to be separated. The sulphur may be dissolved out by means of bisulphide of carbon, which leaves the sulphide of thallium behind; or it may be extracted by boiling with caustic soda. The former plan occasions less loss of thallium, but, owing to the inconvenience of working with large bulks of bisulphide of carbon, the soda process is preferable. 12 lbs. of caustic soda, 18 lbs. of the thalliferous sulphur, and $1\frac{1}{2}$ gallon of water are boiled together till the sulphur has dissolved; 6 gallons of water are added, and the clear liquid, when cool, is decanted from a voluminous black precipitate, which has been separated from the sulphur. The precipitate is then collected on a calico filter and washed. It contains the greater portion of the thallium in the form of sulphide, together with iron, copper, mercury, zinc, &c. Some thallium,

however, remains dissolved in the alkaline liquid, and is lost. The black precipitate is then dissolved in hot dilute sulphuric acid, to which a little nitric acid is added, and the liquid is diluted with water and filtered. Hydrochloric acid and a reducing agent, such as sulphite of sodium, will now throw down the nearly insoluble white protochloride of thallium, which is to be filtered off and washed.

c. From Sulphur or Pyrites in the Wet Way.—The material is boiled in nitro-hydrochloric acid until nothing but bright yellow sulphur is left; water is then added, and the filtrate is evaporated with sulphuric acid until it is nearly dry, and sulphuric vapours are copiously evolved. The residue is dissolved in a large excess of hot water, and carbonate of sodium is added to alkaline reaction, and then cyanide of potassium (free from sulphide of potassium). The liquid is then heated gently for some time, and filtered. The precipitate contains the whole of the lead and bismuth which may be present, as carbonates, whilst the thallium is in solution. A current of sulphuretted hydrogen being now passed through the alkaline liquid precipitates all the thallium, whilst the copper, antimony, tin, and arsenic remain dissolved. The precipitated sulphide is filtered off, washed, and dissolved in dilute sulphuric acid, and the thallium is precipitated by means of hydrochloric acid as chloride, from which the metal is extracted in the way previously described.

d. From the Saline Residues of the Salt-works at Nauheim.—Dr. Böttger adds an insufficient quantity of bichloride of platinum to the strong solution, and boils the precipitate five or six times with three times its weight of water. The insoluble residue consists of the platinum-salts of cæsium, rubidium, and thallium. Upon boiling these with a weak solution of potash and a little hyposulphite of sodium, the solution soon becomes clear, whereupon cyanide of potassium and sulphuretted hydrogen are added. This precipitates the thallium as sulphide. The liquid is then to be filtered, the residue washed and dissolved in sulphuric acid, and the metal precipitated by metallic zinc.

e. From Commercial Hydrochloric Acid.—Many samples of yellow hydrochloric acid contain thallium. It may be separated by neutralizing with an alkali and adding sulphide of ammonium. The black precipitate contains the thallium, together with iron and some other metallic impurities of the acid. It is to be dissolved in sulphuric acid, and the thallium precipitated with hydrochloric acid as protochloride. This is afterwards reduced as already described.

f. From the Mother-liquors of the Sulphate-of-Zinc Works at Goslar.—Each kilogramme of these liquors is said to yield as much as half a gramme of chloride of thallium. A sheet of zinc is plunged into the liquid, whereby the thallium, copper, and cadmium are precipitated. The metallic sponge is then removed from the zinc, washed, and treated with cold dilute sulphuric acid, which dissolves the cadmium and thallium with disengagement of hydrogen, whilst the copper is left behind. The filtrate from the copper is then mixed with hydrochloric acid, which precipitates the nearly insoluble chloride of thallium. If only a small quantity of thallium is present, iodide of potassium may be used as a precipitant, as the iodide of thallium is insoluble in water.

PREPARATION OF CHEMICALLY PURE THALLIUM.

a. Commercial sulphate of thallium is dissolved in water, and the cold solution deluged with sulphuretted hydrogen. It is then filtered, heated to ebullition, and poured into boiling dilute hydrochloric acid. The solution is filtered whilst hot and then allowed to cool. The chloride of thallium which crystallizes out on cooling is washed by decantation until the washings are free from sulphuric acid, and further purified by recrystallizing twice from water. The chloride of thallium thus obtained is dried, mixed with pure carbonate of sodium, and projected by small portions at a time into pure cyanide of potassium kept in a state of fusion in a white unglazed crucible. The chloride is rapidly reduced to the metallic state; the crucible is then allowed to cool, and the contents exhausted with water. The resulting ingot of metal is well boiled in water, dried and fused over a spirit-lamp* in an unglazed porcelain crucible with free access of air, stirred with a porcelain rod to facilitate oxidation, and finally cast in a porcelain mould. It may be preserved under water which has been boiled to expel the air. This metal was used in the determinations A and B.

b. Ordinary metallic thallium is fused in contact with the air, in an iron crucible made nearly red-hot, and then poured into water. The granulated metal is then exposed to a warm atmosphere to facilitate oxidation, the oxide being frequently removed by boiling out with water. When a considerable quantity of oxide (mixed with carbonate) has been obtained, the solution is heated to ebullition, and a rapid current of carbonic-acid gas passed through until the liquid is quite cold, and the excess of carbonate of thallium has crystallized out. The resulting salt is recrystallized and projected into pure cyanide of potassium kept in a state of fusion in a porcelain crucible at a dull red heat; carbonic acid escapes with effervescence, and the metal is reduced to the metallic state. The whole is then allowed to cool, the soluble salts boiled out with water, and the lump of thallium fused over an alcohol-lamp in a lime crucible and cast in a lime mould as described further on. With this ingot of thallium the determination C was effected.

c. Carbonate of thallium, obtained as in process *b*, is covered with a small quantity of water, and decomposed by the current from six GROVE'S cells. Much peroxide of thallium is deposited, which is removed† and preserved for the preparation of thallium by another method. The reduced thallium is then squeezed into a hard cake, melted in a lime crucible heated by means of a spirit-lamp, and cast in a lime mould. This metal was employed in the determination D.

d. A third portion of carbonate of thallium, obtained as in process *b*, is crystallized several times from water, carbonic acid being passed through during the cooling of the solution. After six crystallizations the carbonate is perfectly white. It is then placed in a porcelain dish, covered with a little water, and decomposed by four GROVE'S cells.

* A spirit-flame is preferable to one of coal-gas, as the latter contains sulphur.

† The operation requires this peroxide of thallium to be constantly removed from the positive pole, or the passage of the current will be retarded and ultimately stopped.

The spongy metal is washed, boiled in pure water, tied up in a linen cloth, and compressed between steel plates in a vice. The hard lump is broken up, put into a porcelain crucible and melted over a spirit-lamp, no flux being used other than the thallium oxide formed on heating. The metal is constantly stirred with a piece of unglazed porcelain and cast in a warm porcelain mould. With thallium prepared in this manner the synthetical operations E and F were performed.

e. The peroxide of thallium obtained by the electrolysis of the carbonate (processes *c* and *d*) is dissolved in purified sulphuric acid, evaporated to dryness, and heated strongly to decompose any sulphate of peroxide; it is then dissolved in water and recrystallized twice. The sulphate of thallium is then reduced to the metallic state by three of GROVE'S cells, platinum terminals being employed. The metal is squeezed into a lump and melted under hydrogen in a porcelain crucible, and cast in a polished steel mould, the heat in this case being produced by the combustion of pure hydrogen gas. The thallium purified as above was used in the operation G.

f. Chloride of thallium, as obtained by method *a*, is boiled in nitric acid till most of it is converted into sesquichloride. This is washed by decantation until it begins to decompose with separation of peroxide of thallium, and purified by twice recrystallizing. The purified sesquichloride of thallium is dissolved in boiling water and poured into dilute ammonia. The precipitated peroxide of thallium is washed by decantation till chlorine is no longer detected in the washings, and then boiled in a little water with pure sublimed oxalic acid till the whole is converted into oxalate of thallium. This is dried and heated in a crucible until the whole is decomposed into a mixture of metallic thallium and oxide of thallium; the reduced metal is then cast in a mould of polished steel. The ingot was employed in the determination H.

g. Ordinary thallium is dissolved in nitric acid, and the excess of acid driven off by heat, the residue is dissolved in water, and the solution saturated with sulphuretted hydrogen. A slight black precipitate is generally formed, the solution is filtered cold, and is then freed from sulphuretted hydrogen by boiling. Ammonia is then added, which generally produces a faint precipitate of sesquioxide of iron and peroxide of thallium; it is then filtered, and the solution is mixed with oxalate of ammonium and concentrated till the oxalate of thallium crystallizes out. This is freed from nitrate of ammonium by recrystallizing, and the oxalate of thallium decomposed by heat, as in process *f*. The thallium thus obtained is again fused in a lime crucible, a blowpipe-flame being directed downwards on to the surface of the fused metal for about five minutes, till the slag of thallium oxide has united with the lime, forming a semifluid pasty mass. The metal is then cast in a lime mould, washed when cold, and kept under boiled distilled water or very dilute acetic acid. With metal purified in this manner the estimations I and K were performed.

Purification of Thallium by Fusion in Lime.

A piece of well burnt, very dense quick-lime, prepared from black marble, is cut out

so as just to fit a porcelain crucible; a hole is then turned in the centre of the lime, and a lump of lime cut into the form of a stopper. This apparatus is then raised to a temperature above the melting-point of thallium over a spirit-lamp, and the cavity in the lime is gradually filled with the metal, previously purified by one of the above processes, which is introduced in lumps. The stopper is then put on, and the heat raised to dull redness and kept so for half an hour; after which the melted metal is poured into a lime mould, and preserved in a well-stoppered bottle under boiled water or very dilute acetic acid.

The ingots of thallium purified by the various methods above described were kept separate, and were employed in the synthetical operations described further on.

Section IV.—PROCESSES AND RESULTS.

The processes and manipulation necessary to the determination of an atomic weight are at all times difficult and delicate, but especially so in the case of a metal such as thallium, so readily oxidizable. This strong tendency to combine with oxygen renders the ordinarily exact processes of weighing out pure metals inapplicable to the present purpose. The chances of contact with the oxygen of the atmosphere must be reduced to a minimum, and to this end the following modes of operation were devised. The method found to be the most accurate, and that adopted in repeating the determinations, will receive a description more detailed than the first and what may be termed approximative methods.

Process of the Conversion of Thallium into Nitrate of Thallium.

Thallium being a metal of very high atomic weight, the change in weight in the interconversion of its compounds is comparatively too small to be estimated with any approximation to accuracy. For instance, the conversion of acetate of thallium into chloride of thallium is an operation hardly to be effected without such loss as would seriously interfere with the calculated result*. The immediate conversion of the metal into one of its salts is therefore the method affording results less liable to be affected by errors in observation; and the conversion of thallium into its nitrate has been that ultimately adopted.

Pure thallium, obtained as described, is cut up into small bars with a very sharp steel knife, and dropped into a dish of pure water slightly warmed, and forming the substratum to an atmosphere of carbonic acid in a vessel large enough to admit both hands easily. In this bath the original surface of the ingot is removed and rejected. The bars are then well rubbed with fine cambric to smooth down all sharp edges. Any pieces which contain pores are rejected†.

A stoppered tube (Plate XVI. fig. 7) is half filled with water and weighed. The bars

* An error of 0·05 grain in the weighing accumulates to an error of 0·95 in the atomic weight.

† The upper surface of the fused lump is full of pores for a depth of one sixteenth of an inch; one quarter inch is therefore removed for greater certainty.

of thallium are then quickly removed from the warm water of the carbonic-acid bath, rapidly wiped dry with warm cambric while in the carbonic acid, and put into the weighed tube of water. It is found that no appreciable oxidation takes place during this transference, and that the whole of the moisture can be removed. The tube and its contents are then weighed again.

Fig. 8 represents a vessel for the conversion of thallium into its nitrate, the pure metal as weighed in the manner described above in a tube of water being placed in the bulb *a*, and the pure nitric acid in *b*. The tubes are accurately ground and fitted to each other at *c*. *d* is a permanent stopper to the upper bulb, well ground. *e* and *f* are platinum wires for the support of the flask in the balance. The process of converting the thallium into its nitrate coincides in detail with this apparatus with the process ultimately adopted, and particularly described in the succeeding pages. With an apparatus of this kind the determination A was performed, the metal being purified by the process already described under *a* (p. 308).

Fig. 9 is a further improvement. The nitric acid in acting upon the metal in *a* evolves fumes, which mechanically carry off traces of nitrate of thallium. In the vessel shown in fig. 8 these fumes are washed in the nitric acid, offering, however, no great advantage; but in the series of bulbs shown in fig. 9, *b* contains the nitric acid, which can, by means of the tap *c*, be admitted in the required quantity to the metal. The fumes are washed in the water contained in *g*, the water being evaporated to obtain the nitrate of thallium held in solution. In this apparatus, and with metal purified by the process described under the letter *a*, the determination B was effected. The metallic thallium is weighed sealed up in hydrogen in the following manner:—

The lump or ingot of pure metallic thallium prepared by the process *a*, already described, is cut up into parallelograms, all the original surface being removed with a very sharp steel knife. The parallelograms, immersed and boiled in very dilute sulphuric and hydrochloric acids, are subsequently washed, boiled repeatedly in water, and then transferred to the glass tube *a*, fig. 10. Into this tube pass and are fused the platinum wires *b*, *c*, these wires being the reducing and oxidizing electrodes respectively in connexion with two GROVE'S elements. At *d* the tube is drawn out to a fine orifice, and at *e* is passed in a current of pure hydrogen prepared as before described, as shown in fig. 10 A. The electric current being passed through the water, to preserve the pure metallic surface of the thallium, heat is applied until the water is entirely volatilized. At this point, and while the tube is very hot, the dry hydrogen still passing, the end of the tube at *d* is sealed up, and then the tube at *h*, previously much contracted, is closed before the blowpipe. The metal is thus enclosed hermetically in an atmosphere of pure hydrogen. The tube and its contents are then cooled for six hours, and when cooled, weighed first in air and then in the vacuum-balance. The tube is now cut across the middle with a cutting diamond, wrapped up in smooth platinum-foil to secure any splinters of glass which might be thrown off, and then broken with a sharp blow opposite the cut. The thallium is carefully removed from the pieces of tube, and introduced

into the apparatus where the subsequent operations are to take place. The pieces of tube, with any splinters which may have broken off, are weighed, first in air and then in a highly rarefied atmosphere. The difference between the weighings of the full and empty tube, after correcting for the hydrogen contained at first, gives the weight of thallium taken.

These two forms of apparatus were found to answer the purpose tolerably well. Several improvements, however, suggested themselves whilst the determinations were in progress, and they were finally embodied in the apparatus shown in Plate XVI. figs. 11, 12, & 13. In this several refinements of manipulation can be introduced which were impracticable with the former apparatus—notably the ease with which a definite quantity of metal is introduced into the apparatus without the chance of oxidation, the simplifications introduced in the weighings consequent on having the apparatus vacuous, and the facilities obtained for the employment of the Sprengel and Bunsen pump at different stages of the operations.

Although each determination with this improved apparatus still took many weeks for its successful performance, a great saving of time was effected when compared with that required for a determination in the apparatus first used, where months were consumed in the evaporations. As this form of apparatus was the one in which most of the determinations were effected, and as the manipulations were attended with greater chances of accuracy than were those at first employed, I will describe the apparatus, its employment, and the several processes performed in it somewhat in detail.

Some of the metallic thallium prepared by one of the methods already described is cut by means of a sharp steel knife into prisms about one eighth inch square and half an inch long, no particular care being taken to avoid oxidation. The prisms are boiled in dilute hydrochloric acid to remove any trace of iron which the knife might have communicated. They are then washed in water, dried with blotting-paper, and introduced into the cylindrical portion *a*, fig. 11, of the apparatus. The outer extremity of *a* is then drawn out and sealed before the blowpipe. The end *c* is also sealed up and the horizontal tube *e* is connected to the Sprengel pump and a vacuum obtained, the apparatus and the thallium being kept warm to drive off any moisture which might have been introduced with the thallium. When the vacuum is perfect the tube is sealed at *f*. The apparatus, sealed up and entirely free from air, is now laid on its side, and the cylinder *a* and the bulb *b* imbedded in a bath of magnesia held in a copper vessel heated by gas. The temperature is then raised to above the fusing-point of thallium (561° F.), when by careful manipulation the oxide may be separated from the liquid metal and the greater part of the oxide collected at the closed end of the cylinder *a*. The magnesia is then removed from about the narrow part of the tube *d* (which should be somewhat long and very much contracted), and by a dexterous movement the magnesia-bath containing the apparatus is suddenly tilted up and the liquid metal allowed to run through the contracted part into the bulb *b*. In some instances portions of oxide or of metal stick in the channel, then the operation is lost and a fresh attempt has to

be made with another apparatus; but if the channel is entirely or in great part clear, it may be sealed up at the contraction, care being taken to apply the heat at such a place that no particles of metal or oxide are entangled in the fused glass.

The apparatus has now the form shown in fig. 12. It is hermetically sealed, entirely free from air, and contains a certain quantity of pure metallic thallium entirely free from oxide and as brilliant as mercury.

The next operation is to ascertain the combined weight of the apparatus and metal. It is washed on the outside with dilute sulphuric acid to remove any particles of magnesia that might adhere to it, and after rinsing with water is dried and gently warmed. Its weight is then taken in the air-balance—not necessarily with extreme accuracy, but to enable a calculation to be made as to how much it will probably weigh in the vacuum-balance at a greatly reduced atmospheric pressure. As the substance weighed consists of thallium and glass in unknown proportions, the vacuum-weight cannot be calculated with any approach to accuracy; but it is generally easy to arrive at some approximation to the relative proportions of thallium and glass, and in this manner the probable vacuum-weight may be estimated.

The apparatus is now transferred to the vacuum-balance, and weights put which it is judged will balance it at an atmospheric pressure a few barometric inches short of a vacuum. The balance-case is then sealed up, and the exhaustion proceeded with. As the rarefaction proceeds, the beam is occasionally liberated until it is found that the apparatus and weight are in equipoise. If the barometer-gauge shows a rarefaction not equal to 25 inches of mercury, the air had better be let in, the requisite additional weight added, and the exhaustion recommenced; but if, when the balance is in equilibrium, the rarefaction is above 25 inches, the weighing may be continued.

Two sources of error have now to be guarded against:—1. The alteration of temperature inside the iron case consequent on the rarefaction. 2. The slow and almost unavoidable leakage of air into the balance through the iron, the numerous joints, and the stuffing-boxes. This leakage should not exceed 0·1 inch in an hour.

Equilibrium having been obtained, two or three extra strokes are made with the air-pump, and the exhaustion raised to such a point that by about six hours' leakage the balance is again in equipoise. The weights will at first appear lighter than the apparatus. The balance is allowed to remain well protected from external thermal influences, until the time has nearly arrived when the leakage of air into its interior has reduced the rarefaction to the point at which the weights and apparatus will be exactly in equilibrium. The observer now enters the room, and after liberating the beam and setting it in oscillation, watches the movements of the index through a telescope fixed 10 feet off. By reason of the gradual leakage of air the inequality of the oscillations gradually diminishes, until at last the arcs are of the same value. At this moment the temperature inside and outside the balance-case, the height of the barometer-gauge, and the reading of the standard barometer are observed.

Six hours are generally sufficient to restore the temperature reduced by the exhaus-

tion; but if the inner and external thermometers differ, I again rarefy by a few strokes of the pump, and repeat the observation after waiting for a few hours longer.

Having obtained the accurate weight in a rarefied atmosphere, the next step is to weigh the apparatus in air of the ordinary density. Air is allowed slowly to enter the balance through the U-tubes at the side, and in a few hours, when the inner and outer temperatures are uniform, the weight is again taken.

For the final adjustment of the weight the rider may be used. I, however, prefer, as being more accurate, to place a weight slightly in excess in the pan opposite to the apparatus to be weighed, and then, having sealed up the balance, to exhaust a little beyond the point of equilibrium of weight, and continue the operation exactly as in weighing in a rare atmosphere. By taking care that the air contained in the balance shall only be half an inch or so rarer than the external atmosphere, the data afforded by the two weighings will be sufficient to enable the true vacuum-weight of the apparatus to be calculated with accuracy.

This method of ascertaining minute differences of weight, not by the addition to, or subtraction of, material weights from one arm of a balance, but by varying the density of the air in which the operation is performed, is, I believe, attended with a greater approach to accuracy than the method generally adopted. It can, however, only be adopted when the weights and the substance weighed differ in specific gravity.

The data for ascertaining the weight of the apparatus and the thallium it contains have now been obtained. The next operation is to convert the thallium into nitrate. For this purpose, the tube *g* (Plate XVI. fig. 12) must be opened; and to effect this without any risk of losing particles of glass, I gently warm the extremity in a spirit-lamp, and then apply the tip of a blowpipe-flame to the warm glass at *g*. The atmospheric pressure outside acting against the vacuum inside, immediately perforates a small hole through the glass, into which the air rushes.

Some nitric acid, purified in the manner described, is now removed from the bulb in which it has remained sealed up, and a little is introduced into the bulbs *h* and the globe *b*; this is readily effected by alternately warming and cooling *b*, the perforation *g* dipping under the acid. Sufficient nitric acid must be introduced to three quarters fill the two lower bulbs, and also to moisten the thallium in the globe *b*. The apparatus is then placed in a horizontal position, and the quantity of acid in the bulbs is regulated so as to allow air-bubbles to pass in either direction and be washed without spirting acid out.

No reaction, or scarcely any, between strong nitric acid and thallium takes place in the cold; but on applying gentle heat the metal is attacked, and becomes rapidly converted into nitrate. The quantity of acid which is allowed to act at a time must be very limited; and the temperature should not be higher than is sufficient to prevent the nitrate of thallium formed crystallizing on the metal and interfering too much with the action. As soon as the action ceases, a little nitric acid from the washing-bulbs is allowed to run into the globe, its place being supplied with fresh acid. When cold, the crystallization

of the nitrate of thallium entirely prevents the reaction between the metal and acid, but on warming, the salt dissolves and the action proceeds. The vapours of nitric and nitrous oxide, which are evolved in abundance, are washed by passing through the system of bulbs, and the reaction must be only just sufficient to cause them to pass through slowly.

In course of time the whole of the thallium is dissolved, and the most tedious part of the process then commences—the evaporation of the excess of free acid.

For this purpose an apparatus is used represented in Plate XVII. *a* is the apparatus connected by a wide tube, *b*, and a narrower glass tube with a bottle, *c*. This is in connexion with a BUNSEN'S water-pump, *d*, having 18 feet fall of water, and capable of producing an exhaustion equal to 10 inches of mercury. The water is supplied to this pump by an independent pipe and tap attached to a large cistern, so that it can be allowed to work continuously day and night without interfering with the ordinary water-supply of the laboratory. The apparatus *a* is enclosed in a glass case, and stands in an air-bath, the temperature of which can be kept constant by means of a gas-regulator. The water of the pump being set in motion, and a temperature of about 250° F. being maintained in the air-bath, evaporation of the nitric acid commences, the vapour partly condensing in the bottle *c*, and partly being carried away through the pump. As the evaporation of the acid proceeds the temperature is gradually raised, until ultimately it becomes as high as 380° F., which must not be exceeded in this stage of the operation. In course of time (varying from a few days to as many weeks, according to the quantity of acid to be drawn off, and the size of the perforation through which it is to pass) the nitrate of thallium is left in the form of dry white crystals.

The pump is then stopped, and air allowed to enter the apparatus by opening the pinch-cock, *e*, connected with the chloride-of-calcium tubes, *f*. The apparatus being cooled, water is added to the nitrate of thallium in the proportion of bulk for bulk, about 1 grain of oxalic acid* being dissolved in the water. Heat is then applied, and the solution boiled until all the nitrate of thallium is dissolved, forming a clear colourless liquid, which deposits on cooling brilliantly white crystals of nitrate of thallium†.

The nitric acid having been previously removed from the bottle *c* and the rest of the tubes, the apparatus is again fitted to the pump. It is heated in the air-bath, and the water gradually drawn out under diminished pressure, the temperature being kept a little below the point of ebullition of the liquid. When apparently dry the heat is very carefully raised to 394° F., at which temperature the crystals of nitrate of thallium melt; a little froth at first breaks the surface, but this soon disappears, and the liquid becomes as clear and colourless as water. If sufficient oxalic acid has been added to decompose

* If the action of nitric acid on thallium is allowed to become too violent, or if the nitrate of thallium is long heated with excess of nitric acid, a little pernitrate of thallium is formed, which on subsequent fusion of the nitrate deposits a brown powder of peroxide of thallium. The oxalic acid is therefore added to decompose the pernitrate of thallium. The excess of oxalic acid disappears with the last traces of free nitric acid and water.

† Nitrate of thallium is soluble in 9·4 times its weight of water at 60° F., and in less than one fourth of its bulk of boiling water. The crystals deposited on cooling are anhydrous.

the pernitrate of thallium, no deposit whatever is visible in the liquid; but should any be seen, a fraction of a grain of oxalic acid must be added with the water in the next operation.

As soon as the nitrate is in the form of a clear liquid the apparatus is allowed to cool *, and after being disconnected from the pump is weighed in the air-balance, no particular precautions being taken, however, and the air having free access to the interior of the apparatus.

Water is again added, the nitrate of thallium is dissolved and allowed to crystallize out, and the operation of evaporating the water under diminished pressure in the air-bath is repeated exactly as already described.

The dry nitrate is again fused at 394° F., and after the whole apparatus is heated to about 420° F. for a few minutes it is allowed to cool, and is again weighed. If there has been loss of weight, the operation must be repeated till the weights are constant.

When this is the case the apparatus must be disconnected from the Bunsen water-pump and attached by its extremity *g*, Plate XVI. fig. 12, to the Sprengel mercury-pump. The air is now exhausted as perfectly as possible, and when quite vacuous the tube is sealed up at *i* (fig. 12) by the application of a small spirit-flame. Care must be taken in doing this to lose no particle of glass, as the end of the tube *g* which is drawn off, having been included in the first weighing, must be carefully preserved and weighed along with the apparatus in all the subsequent weighings.

The apparatus is now of the form shown in fig. 13. It contains nothing but the pure nitrate of thallium produced from the action of nitric acid on the thallium at first introduced, and is entirely free from air. It is now, with the loose piece of tube *g* belonging to it, to be weighed in the vacuum-balance at two different atmospheric pressures, with all the precautions already adopted in the previous weighings.

When the data for ascertaining the weight of the glass apparatus and the nitrate of thallium are correctly obtained, the weight of the glass apparatus by itself has to be taken. For this purpose a hole is perforated in the tube *i*, as before described, by means of a blowpipe-flame, and water being introduced the nitrate of thallium is dissolved out, and by repeated washings ultimately removed. The completion of the operation is ascertained by evaporating some of the washing water almost to dryness, and testing by means of the spectroscope. The apparatus is then dried, connected with the Sprengel pump, and after complete exhaustion it is sealed up at *h*, the same precautions being taken to preserve the piece of tube now removed as were adopted in the previous sealing up.

The empty apparatus is now to be weighed at different atmospheric pressures in the vacuum-balance with all necessary precautions, the two loose pieces of glass tube *g* and

* If a considerable bulk of fused nitrate of thallium is allowed to solidify in a thin bulb, the glass is almost certain to crack, owing to unequal contraction. Many of my operations were spoilt by this cause. By keeping the apparatus in motion during solidification, so as to allow the nitrate to line the greater part of the inner surface of the bulb, this source of danger is avoided.

ih being now included, and from the data thus obtained its true weight is calculated. There have thus been obtained:—

α. The weight of the glass+thallium.

β. The weight of the glass+nitrate of thallium.

γ. The weight of the glass alone.

From these data the atomic weight of thallium can be calculated by the formulæ given in the next section.

Section V.—CALCULATION OF THE RESULTS.

The succeeding results must not be regarded as embodying all the attempts to determine the atomic weight; for, as stated in the preceding section, many of the apparatus were broken at various stages of the operation. The calculations, however, serve to illustrate the weighings which came to a successful issue.

For the accurate determination of the weighings, it will be seen that it is necessary to ascertain the density of the ordinary atmosphere at the place where the weighings are made. Ritter has deduced from Regnault's observations that in Paris, lat. 48° 50′ 14″, at 60 metres above the level of the sea, a litre of dry atmospheric air at 0° C. and 760 millims. pressure weighs 1·2932227 gramme. It is well established that if G represents the force of gravity at the mean level of the sea in lat. 45°, the force of gravity in lat. λ at the mean level of the sea$=G(1-0{\cdot}0025659\cos 2\lambda)$.

The force of gravity in a given latitude at a place on the surface of the earth at a height z above the mean level of the sea

$$=\left\{1-\left(2-\frac{3}{2}\frac{\varsigma'}{\varsigma}\right)\frac{z}{r}\right\}$$

multiplied by the force of gravity at the level of the sea in the same latitude, r being the radius of the earth$=63966198$ metres, ς its mean density, and ς' the density of that part of the earth which is above the mean level of the sea; and if the ratio $\varsigma' : \varsigma$ be taken as 5 : 11, then

$$2-\frac{3}{2}\frac{\varsigma'}{\varsigma}=1{\cdot}32 \text{ nearly.}$$

Continuing the reasoning, Professor Miller has shown that a litre of dry atmospheric air, containing the average amount of carbonic acid, at 0° and 760 millims. pressure, at the height z above the mean level of the sea in lat. λ, weighs in grammes

$$1{\cdot}2930693\left(1-1{\cdot}32\frac{z}{r}\right)(1-0{\cdot}0025659\cos 2\lambda).$$

It has been shown by Regnault and others that, between 0° and 50°, the ratio of the density of air at 0° to its density at $t°$ is $1+0{\cdot}003656t$, and that the density of the vapour of water is 0·622 of that of air. Therefore the weight in grammes of a litre of air will be

$$\frac{1{\cdot}2930693}{1+0{\cdot}003656t}\,\frac{b-0{\cdot}378v}{760}\left(1-1{\cdot}32\frac{z}{r}\right)(1-0{\cdot}0025659\cos 2\lambda),$$

where t is the temperature of the air, b the barometric pressure, v the pressure of the vapour (of water) present in the air, both expressed in millimetres of mercury at 0°, z the height above the mean level of the sea, λ the latitude. My laboratory at Mornington Road, Regent's Park, where the atomic weight of thallium was determined, is in lat. 51° 32′ 6″, at a height of 35·05 metres above the mean level of the sea. The expression consequently becomes

$$\frac{1{\cdot}2930693}{1+0{\cdot}003656t}\cdot\frac{b-0{\cdot}378v}{760}\,(\cdot99999289815)\,(1{\cdot}0005802549).$$

As a litre is the volume of 1000 grammes of water at its maximum density, the division of this expression by 1000 gives the ratio of the density of air to the maximum density of water. By the addition of the logarithm of $b-0{\cdot}378v$ in millimetres to $\log A_t$ we obtain the logarithm of the ratio of the density of air at $t°$ to the maximum density of water.

TABLE A.—Calculated for Mornington Road, Regent's Park.

t.	$10+\log A_t$.	Diff.	t.	$10+\log A_t$.	Diff.
			15	4·207868	
0	4·231055				1502
		1585	16	4·206366	
1	4·229470				1498
		1579	17	4·204868	
2	4·227890				1492
		1574	18	4·203376	
3	4·226317				1487
		1567	19	4·201889	
4	4·224750				1483
		1563	20	4·200406	
5	4·223187				1477
		1556	21	4·198925	
6	4·221631				1471
		1551	22	4·197458	
7	4·220980				1468
		1545	23	4·195990	
8	4·218535				1462
		1540	24	4·194528	
9	4·216995				1457
		1535	25	4·193071	
10	4·215460				1452
		1529	26	4·191618	
11	4·213931				1447
		1524	27	4·190171	
12	4·212407				1443
		1518	28	4·188728	
13	4·210889				1438
		1513	29	4·187290	
14	4·209376				1433
		1508	30	4·185857	
15	4·207868				

These logarithms, when increased by 0·000030, agree with those employed by Professor MILLER in his determination of the value of the new standard pound (see Phil. Trans. for 1856) when working in the cellar under the Mineralogical Museum at Cambridge, in lat. 52° 12′ 18″, about 8 metres above the mean level of the sea; increased by 0·000002 they can be used in reducing weighings in Somerset House, lat. 51° 30′ 40″, 29·56 metres above sea-level; or diminished by 0·000102 for weighings made in Paris.

We have next to consider the influence exerted by the hygrometric state of the atmosphere, or, in other words, the influence of the vapour of water suspended in the atmosphere. It is clear that the moist air is nothing more than a mixture of v cubic inches of dry air at $t°$ under a pressure minus that of the vapour, and of v cubic inches of vapour at $t°$ and the pressure resulting from the hygrometric condition. BIOT, REGNAULT, and BIANCHI have ascertained that the pressure of vapour in an ordinary dry room is two thirds of the maximum pressure due to the temperature.

TABLE B.—Values of $0{\cdot}378 \times \frac{2}{3} v_t$, where v_t is the maximum pressure of vapour at the temperature t, in millims. of mercury at 0°, according to REGNAULT'S observations*.

t.	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
0	1·16	1·17	1·18	1·18	1·19	1·20	1·21	1·22	1·23	1·24
1	1·25	1·25	1·26	1·27	1·28	1·29	1·30	1·31	1·32	1·33
2	1·34	1·35	1·36	1·37	1·37	1·38	1·39	1·40	1·41	1·42
3	1·43	1·44	1·45	1·46	1·47	1·48	1·49	1·50	1·51	1·53
4	1·54	1·55	1·56	1·57	1·58	1·59	1·60	1·61	1·63	1·64
5	1·65	1·66	1·67	1·68	1·69	1·70	1·72	1·73	1·74	1·75
6	1·76	1·78	1·79	1·80	1·81	1·82	1·84	1·85	1·86	1·87
7	1·89	1·90	1·91	1·93	1·94	1·95	1·96	1·98	1·99	2·01
8	2·02	2·03	2·05	2·06	2·08	2·09	2·10	2·12	2·13	2·15
9	2·16	2·17	2·19	2·21	2·22	2·24	2·25	2·27	2·28	2·29
10	2·31	2·32	2·34	2·35	2·37	2·39	2·40	2·42	2·44	2·45
11	2·47	2·48	2·50	2·52	2·53	2·55	2·57	2·58	2·60	2·62
12	2·64	2·65	2·67	2·69	2·71	2·72	2·74	2·76	2·78	2·80
13	2·81	2·83	2·85	2·87	2·89	2·91	2·93	2·94	2·96	2·98
14	3·00	3·02	3·04	3·06	3·08	3·10	3·12	3·14	3·16	3·18
15	3·20	3·22	3·24	3·26	3·28	3·31	3·33	3·35	3·37	3·39
16	3·41	3·43	3·46	3·48	3·50	3·52	3·54	3·57	3·59	3·61
17	3·63	3·66	3·68	3·71	3·73	3·75	3·78	3·80	3·82	3·85
18	3·87	3·90	3·92	3·95	3·97	4·00	4·02	4·04	4·07	4·09
19	4·12	4·15	4·17	4·20	4·22	4·25	4·28	4·30	4·33	4·36
20	4·38	4·41	4·44	4·47	4·49	4·52	4·55	4·58	4·61	4·63
21	4·66	4·69	4·72	4·75	4·78	4·81	4·84	4·87	4·90	4·92
22	4·95	4·99	5·02	5·05	5·08	5·11	5·14	5·17	5·20	5·23
23	5·26	5·30	5·33	5·36	5·39	5·43	5·46	5·49	5·52	5·56
24	5·59	5·62	5·66	5·69	5·73	5·76	5·80	5·83	5·87	5·90
25	5·93	5·97	6·01	6·04	6·08	6·12	6·15	6·19	6·22	6·26
26	6·30	6·34	6·37	6·41	6·45	6·49	6·53	6·56	6·60	6·64
27	6·68	6·72	6·75	6·79	6·83	6·87	6·91	6·95	6·99	7·03
28	7·08	7·12	9·17	7·21	7·25	7·29	7·34	7·38	7·42	7·46
29	7·51	7·55	7·59	7·64	7·68	7·73	7·77	7·82	7·86	7·91
30	7·95	8·00	8·04	8·09	8·14	8·18	8·23	8 28	8·23	8·37

The formula employed for the calculation of the true weight of a substance *in vacuo*,

* Annales de Chimie, 1845, 3me série, tome xv. p. 138.

from data given by two weighings, one at ordinary and one at a greatly diminished air-pressure, is as follows:—

Let H denote the substance to be weighed, and
h its true weight (*in vacuo*) in grains.

First Weighing in Air of Ordinary Density.

Let W denote the material weight which balances H,
w „ „ true weight of W observed in air,
x „ „ weight of air displaced by W,
t „ „ temperature,
p „ „ pressure, in height of mercury, reduced to 32° F.,
b „ „ bulk of W in grs. of water at max. density,
k „ „ weight of air displaced by H:

w, x, t, p, b being given, required to find k,

$$h-k=w-x.$$

Second Weighing in a Rare Atmosphere.

Let γ denote the weights which balance H,
y „ „ true weight of γ in air of ordinary density,
z „ „ weight of air displaced by γ,
t' „ „ temperature,
p' „ „ pressure, in height of mercury, reduced to 32° F.,
$b'=\frac{y}{w}b$ „ bulk of γ in grains of water at max. density,
l denote the weight of air displaced by H:

y, t', p', b' being given, to find l and z,

$$h-l=y-z;$$

hence $k-l=y-w+x-z$.

By Tables A and B,

$$\log\frac{\text{density rare air}}{\text{max. den. water}}=\log(p'-0{\cdot}378\tfrac{2}{3}v_t)+\log\frac{0{\cdot}001293893}{1+0{\cdot}003656}\cdot\frac{1}{760};$$

$$\therefore \log b'+\log\frac{\text{density rare air}}{\text{max. density water}}=\log z,$$

$$\frac{l}{k}=\frac{\text{density rare air}}{\text{density common air}}=n \text{ (suppose)}.$$

Let $m=y-w+x-z$; then $k-l=m$, $\frac{l}{k}=n$.

Hence $l=nk$, $k-nk=m$, $k=\frac{m}{1-n}$, $l=\frac{mn}{1-n}$.

Hence $h=w-x+\frac{m}{1-n}$; or $h=y-z+\frac{mn}{1-n}$.

To illustrate the application of this formula, I will reduce the weighings of one of the determinations (E).

Substance weighed.	Balance used.	Weights, actual.	True value in air.
(H)		(W)	(w)
Glass apparatus.	Vac.	765·8081	765·814578
(H)		(γ)	(y)
Glass apparatus.	Vac.	766·1133	766·122626

Weight of air displaced.	Temperature.	Bar. (reduced to 32° F.).
(x)	(t)	(p)
0·044547 (vol. in water max. density=36·326)	65° F.=18°·5 C.	29·848 (758·125 millims.)
	(t')	(p')
0·044546	63° F.=17° C.	1·173 in. (29·79 millims.)

CALCULATION OF VACUUM-WEIGHT OF FLASK FROM ABOVE WEIGHINGS.

Let h=true weight in vacuum of flask,

w=765·814578,

x= 0·044547,

t=65° F.=18°·33 C.,

p= 29·848 in.=758·12 millims.,

b= 36·326,

y=766·122626,

t'=63° F.=17°·2 C.,

p'= 1·173 in.=29·79 millims.

$$\log \frac{\text{density atmospheric air}}{\text{max. density water}} = \log 758{\cdot}12 - 4{\cdot}00 + 4{\cdot}204149 - 10;$$

$$\therefore \quad \text{,,} \quad = \quad 2{\cdot}8774430 + 4{\cdot}204149 - 10;$$

$$\therefore \quad \text{,,} \quad = \quad 7{\cdot}0815920 - 10.$$

$$\log b' = \log 766{\cdot}122626 - \log 765{\cdot}814578 + \log 36{\cdot}326;$$

$$\therefore \; b' = 2{\cdot}8842970 - 2{\cdot}8841230 + 1{\cdot}5602176;$$

$$\therefore \; b' = 1{\cdot}5603916.$$

$$\log \frac{\text{density rare air}}{\text{max. den. water}} = \log (29{\cdot}79 - 3{\cdot}63) + 4{\cdot}204898 - 10;$$

$$\therefore \quad \text{,,} \quad = \quad 1{\cdot}4176377 + 4{\cdot}204898 - 10;$$

$$\therefore \quad \text{,,} \quad = \quad 5{\cdot}6225357 - 10.$$

$\log z = 1{\cdot}5603916 + 5{\cdot}6225357 - 10$;

$\therefore\ z = 7{\cdot}1829373 - 10$;

$\therefore\ z = 0{\cdot}001524$.

$\log \frac{l}{k} = 5{\cdot}6225357 - 7{\cdot}0815920$;

$\therefore\ \frac{l}{k} = 8{\cdot}5409437 - 10$;

$\therefore\ n = \frac{l}{k} = 0{\cdot}034749$;

$\therefore\ 1 - n = 0{\cdot}965251$.

$m = 766{\cdot}122626 - 765{\cdot}814578 + 0{\cdot}044547 - 0{\cdot}001524$;

$\therefore\ m = 0{\cdot}351071$.

$k = \frac{m}{1-n} = \frac{0{\cdot}351071}{0{\cdot}965251}$;

$\therefore\ k = 0{\cdot}3638$.

$h = 765{\cdot}814578 - 0{\cdot}044547 + {\cdot}3638$;

$\therefore\ h = 766{\cdot}133831$.

WEIGHING OF GLASS APPARATUS + NITRATE OF THALLIUM.

Vacuum-balance.

In air. Left pan removed. Platinum weights.

After third heating (to fusion) and cooling:—

Weights.	True value in air.	Weight of air displaced.	Volume in water at max. density.
600	599·998340	0·035533	28·970
100	99·991420	5887	4·800
60	59·993232	3483	2·840
30	29·999991	1668	1·360
6	5·998268	355	·290
3	3·000469	171	·140
·06	0·061472	3	·003
·0031	0·003099	0	·000
799·0631	799·046291	0·047100	38·403
Pan=206·3733	206·379646	0·012040	9·824
1005·4364	1005·425937	0·059140	48·227

Therm.=73° F.=22°·7 C.

Barom.=29·891 in. at 0° C.=759·22 millims.

1005·425937

765·814578=weight of glass apparatus (see *w*, preceding).

239·611359=weight of thallium nitrate in air.

The weight of air displaced &c. is taken separately for each weight in all cases, but is omitted in subsequent examples (the sum being given), to prevent the introduction of useless figures.

WEIGHING OF GLASS APPARATUS + NITRATE OF THALLIUM IN RARE ATMOSPHERE.

Vacum-balance.

Exhausted. Left pan removed. Platinum weights.

	Weights.	True value in air.	Weight of air displaced.	Volume in water at max. density.
	799·3600	799·346792	0·047117	38·423
Pan =	206·3733	206·379646	0·012040	9·824
	1005·7333	1005·726438	0·059157	48·247

Therm. = 69°·5 F. = 21° C.
Barom. = 29·775 in. = 756·27 millims. at 0° C.
Gauge = 25·141 in. = 638·57 millims. at 0° C.

756·27
638·57
117·70 millims. pressure.

Weight of left scale-pan of air-balance, which was removed to relieve the beam in weighing the heavier pieces of apparatus:—

Weight.	True value in air.	Weight of air displaced.	Volume in water at max. density.
179·7365	179·719377	0·010429	8·513

Weight of left scale-pan of vacuum-balance taken in air-balance:—

Weight.	True value in air.	Weight of air displaced.	Volume in water at max. density.
206·3733	206·3719646	0·012040	9·824

Weight of air displaced by scale-pan = 0·02403 gr.
Volume in water of maximum density = 24·244 grs.

CALCULATION OF VACUUM-WEIGHT OF GLASS APPARATUS + NITRATE OF THALLIUM FROM GIVEN DATA.

First Weighing in Air of Ordinary Density.

By Table A,

$$\log \frac{0{\cdot}00129381}{1+0{\cdot}03656t} \cdot \frac{1}{780} \text{ for } 22°{\cdot}7 \text{ C.}$$

t 22° is 4·197488−10
t ·7 is 1027
4·198515−10

By Table B,

$$0{\cdot}378\tfrac{2}{3}\,v \text{ for } t=22{\cdot}7=5{\cdot}17 \text{ millims.}$$

$$759{\cdot}22-5{\cdot}17=753{\cdot}05;$$

$$\log(753{\cdot}05)=(2{\cdot}8768238-10)+4{\cdot}198515=$$

$$\log 7{\cdot}0753388-10=\log\frac{\text{dens. atmos. air}}{\text{max. dens. water}}.$$

Second Weighing in a Rare Atmosphere.

By Table A the value of

$$\log\frac{0{\cdot}0012938}{1+0{\cdot}00365t}\cdot\frac{1}{768} \text{ for } t=21^\circ\text{C.}=(4{\cdot}198959-10)+2{\cdot}0532321=6{\cdot}2521911-10=$$

$$\log\frac{\text{dens. rare air}}{\text{max. dens. water}}.$$

Value of $0{\cdot}378\frac{2}{3}\,v$ for $t=21^\circ$ C.$=4{\cdot}66$ millims.:

$$117{\cdot}70 \text{ millims. (pressure)}-4{\cdot}66=113{\cdot}04=p'-0{\cdot}378\tfrac{2}{3}\,v,$$

$$\log b'=1{\cdot}6834703+6{\cdot}2521911-10=7{\cdot}9356614-10;$$

$$\therefore\ {\cdot}0086231=z=\text{weight of rare air displaced by } \gamma.$$

The data now are,—

$$w=1005{\cdot}425937,$$

$$x=\ \ 0{\cdot}059140,$$

$$y=1005{\cdot}726438,$$

$$z=\ \ 0{\cdot}0086231,$$

$$\log\frac{l}{k}=6{\cdot}2521911-7{\cdot}07653388=9{\cdot}1768523-10.$$

Hence $n=\frac{l}{k}={\cdot}15026$:

$$1-n={\cdot}84974,$$

$$y-w=1005{\cdot}726438-1005{\cdot}425937={\cdot}300501,$$

$$x-z={\cdot}059140-{\cdot}008623+={\cdot}050517;$$

$$\therefore\ m-y-w+x-z={\cdot}351018.$$

$$k=\frac{m}{1-n}=\log{\cdot}351018-\log{\cdot}84974={\cdot}5453418-{\cdot}9292861={\cdot}6160557=k={\cdot}4131,$$

$$w-x=1005{\cdot}425937-{\cdot}059140=1005{\cdot}366797.$$

$(w-x)-k=1005{\cdot}366797-{\cdot}4131=1005{\cdot}779897=h$ = true weight of glass apparatus plus nitrate of thallium *in vacuo*.

$1005{\cdot}779897-766{\cdot}133831$ (weight of glass apparatus *in vacuo*)$=239{\cdot}646066=$ weight of nitrate of thallium *in vacuo*.

$239{\cdot}646066-239{\cdot}611359$ (weight of nitrate of thallium in air) $={\cdot}034707=$ increase in weight for vacuum.

WEIGHT OF THALLIUM*.

Weight of thallium taken	=183·783921
Air displaced by thallium	= 0·018907
	183·802828
Deduct air displaced by weights . . .	= 0·012596
True weight of thallium *in vacuo* . . .	183·790232

Collecting the data, we have

† True weight of thallium *in vacuo*	=183·790232 grs.
„ „ nitrate of thallium *in vacuo* . .	=239·646066 „
„ „ glass *in vacuo*	=766·133831 „

The reduction of the atomic weight from data obtained in the manner of the preceding weighings becomes a case of simple proportion; but the values found are absolute in so far only as the atomic weights of nitrogen and oxygen are correct. The atomic weights of nitrogen and oxygen have been usually represented by the numbers 14 and 16; but Professor STAS found these elements represented, according to observation, by 14·009 and 15·960. Therefore, oxygen (O_3)=47·880, and nitrogen =14·009, or NO_3 =61·889. According to the old equivalents, NO_6=62.

Taking as data the series of weighings *in vacuo*, the quantity of NO_3 required to convert the thallium into nitrate is

(239·646066−183·790232=)55·855834 grms.

We have, then, with Professor STAS's determination of the atomic weights of nitrogen and oxygen, the following proportion:—

Weight of NO_3.		Weight of thallium.		Atomic weight of NO_3.		Atomic weight of thallium.
55·855834	:	183·790232	::	61·889	:	x;

$$\therefore\ x=203{\cdot}642.$$

This number, it will presently appear, represents the atomic weight of thallium as nearly as the possibility of error will allow.

Let us see what would be the atomic weight of thallium if one or other of the corrections introduced into the above determination had been omitted. The use of the old equivalent (=62) for NO_6, with the data derived from the weighings *in vacuo*, gives

55·855834 : 183·790232 :: 62 : 204·007

as the atomic weight; but I cannot admit this number to be so correct as 203·642.

If we take the corrected weighings in air of ordinary density, we have with NO_3=61·889,

55·827438 : 183·783921 :: 61·889 : 203·738.

* To save needless repetition, I only give the results of these calculations.

† In this determination the thallium and afterwards the nitrate of thallium were weighed in the same glass apparatus as described.

With $NO_6=62$,

55·827438 : 183·783921 :: 62 : 204·103.

Accepting the uncorrected weights observed in air, we have, with $NO_3=61·889$,

55·8184 : 183·8099 :: 61·889 : 203·800.

With $NO_6=62$,

55·8184 : 183·8099 :: 62 : 204·166.

The several atomic weights would therefore be

203·642	204·007
203·738	204·103
203·800	204·166

The error of the last deduction, +·524, is sufficiently large to show the necessity of neglecting no precaution in chemical manipulation, especially in a determination of this character. The largeness of these errors has an immediate bearing upon quantitative analysis; for it shows that from data ordinarily given, very varying results may be obtained. Chemists have to deal with much smaller quantities than a quarter per cent., particularly in organic analysis, where, as I have shown, such a difference from the truth may lead to very erroneous reasoning.

RESULTS.

Ten results of the most trustworthy weighings (with $NO_3=61·889$) are*:—

Determination.	True Weights *in vacuo*. Weight of thallium taken.	Weight of nitrate of thallium + glass.	Weight of glass.	Calculated atomic weight from these data.
	grs.	grs.	grs.	grs.
A.	497·972995	1121·851852	472·557319	203·666
B.	293·193507	1111·387014	729·082713	203·628
C.	288·562777	971·214142	594·949719	203·632
D.	324·963740	1142·569408	718·849078	203·649
†E.	183·790232	1005·366796	766·133831	203·642
F.	190·842532	997·334615	748·491271	203·636
G.	195·544324	1022·176679	767·203451	203·639
H.	201·856345	1013·480135	750·332401	203·650
I.	295·683523	1153·947672	768·403621	203·644
K.	299·203036	1159·870052	769·734201	203·638

* It should be noted that the arithmetic mean of *all* the readings, including the highest as well as the lowest result, in which doubt might arise as to success in manipulation, is 203·6.

† Fully illustrated in the preceding text.

I wish it to be noted that I have made determinations with considerable weights of thallium. In ordinary analysis chemists are satisfied to take 5 or 10 grains of the substance under investigation: here I have gone to the very highest weight that can be entrusted, with safety, to the balance. The lowest weight of thallium taken is 183·790232 grains, the heaviest 497·972995 grains, the remaining determinations varying between these limits. It is hardly necessary to say that the purpose has been to eliminate the error arising from manipulation with small quantities, and to produce such variety in the results as to render the chances of coincidence of very small value.

Let me now tabulate the results of the determination, with the view to ascertain severally their degree of approximation to the arithmetic mean:—

A.	203·666	+·024
B.	203·628	−·014
C.	203·632	−·010
D.	203·649	+·007
E.	203·642	·000
F.	203·636	−·006
G.	203·639	−·003
H.	203·650	+·008
I.	203·644	+·002
K.	203·638	−·004

The arithmetic mean of the ten observations is

$$\alpha=\frac{2036\cdot424}{10}=203\cdot642.$$

But does this average represent the truth? Or, rather, how nearly does it represent the truth?

According to the theory of probabilities, the "weight" of α may be determined by means of the formula

$$w=\frac{n^2}{2\Sigma e^2},$$

where $n=$ the number of observations, and $\Sigma e^2=$ the sum of the squares of the successive differences, obtained by subtracting *each* observation from the arithmetic mean of the *whole*.

The arithmetic mean of the ten weighings is $\alpha=203\cdot642$.

The sum of the squares of the ten differences between α and each individual observation is:—

e.	e^2.
+·024	·000576
+·008	·000064
+·007	·000049
+·002	·000004
·000	·000000
−·003	·000009
−·004	·000016
−·006	·000036
−·010	·000100
−·014	·000196
	Σe^2=·001050

Hence the "weight" of α is

$$w=\frac{(\text{number of observations})^2}{2\Sigma e^2}$$

$$=\frac{100}{\cdot 0021}$$

$$=47619.$$

The largeness of this figure indicates the high degree of probability that α is very near to the true value sought. But the question, What is the true value? does not admit of absolute answer; for one of the observations was as low as 203·628, and one as high as 203·666. The number of possible values between 203·628 and 203·666 is infinite, the arithmetic mean α being but one of these values; and although more likely than any other that could be *named*, it is not more likely than *one or other* of all the possible values. The odds are many to one that α is *not* the truth; but they are also many to one that α is very near the truth. The question "How near?" cannot be answered; alter the question to "What is the probability that the truth is comprised within the limits $\alpha\pm k$?" and the answer may be easily given, *however small k may be.* Thus if k=·01,—in other words, if the question be "What is the degree of likelihood that the truth lies between 203·632 and 203·652?"—the answer is given by the formulæ

$$\left.\begin{aligned}\pi&=\mathrm{H},\\ t&=k\sqrt{w},\end{aligned}\right\}$$

having recourse to tables calculated from the celebrated Definite Integral,

$$\mathrm{H}_t=\frac{2}{\sqrt{\pi}}\cdot\int_0^t e^{-t}\,.\,dx.$$

Let

$$k = \cdot 01,$$
$$w = 47619,$$
$$\sqrt{w} = 218,$$
$$\therefore\ t = k\sqrt{w} = 2 \cdot 18,$$
$$\therefore\ \pi = \mathrm{H}_{2 \cdot 17} = \cdot 99795.$$

(See Table I., at end of Professor De Morgan's 'Essay on Probabilities'.)

The result, $= \cdot 99795$, is so near to unity, the measure of *certainty*, that for every practical purpose it may be considered *certain* that the truth is really comprised within the limits named.

By Table II. in Professor De Morgan's Essay, we can test the correctness of the preceding deductions; for

$$\frac{62}{130\sqrt{w}} = \text{the probable error},$$

$$\frac{k}{\text{probable error}} = t.$$

Then K, answering to t in Table II., is the probability required.

Hence

where $w = 47619$,

„ $\sqrt{w} = 218$,

$$\frac{62}{130\sqrt{w}} = \cdot 0022,$$

$$\frac{k}{\cdot 0022} = \frac{\cdot 01}{\cdot 0022} = 4 \cdot 6 = t,$$

to which corresponds in Table II. K = 99808, against 99795, as before.

I may therefore conclude that, within the limits of error (as small as possible) of observation, the

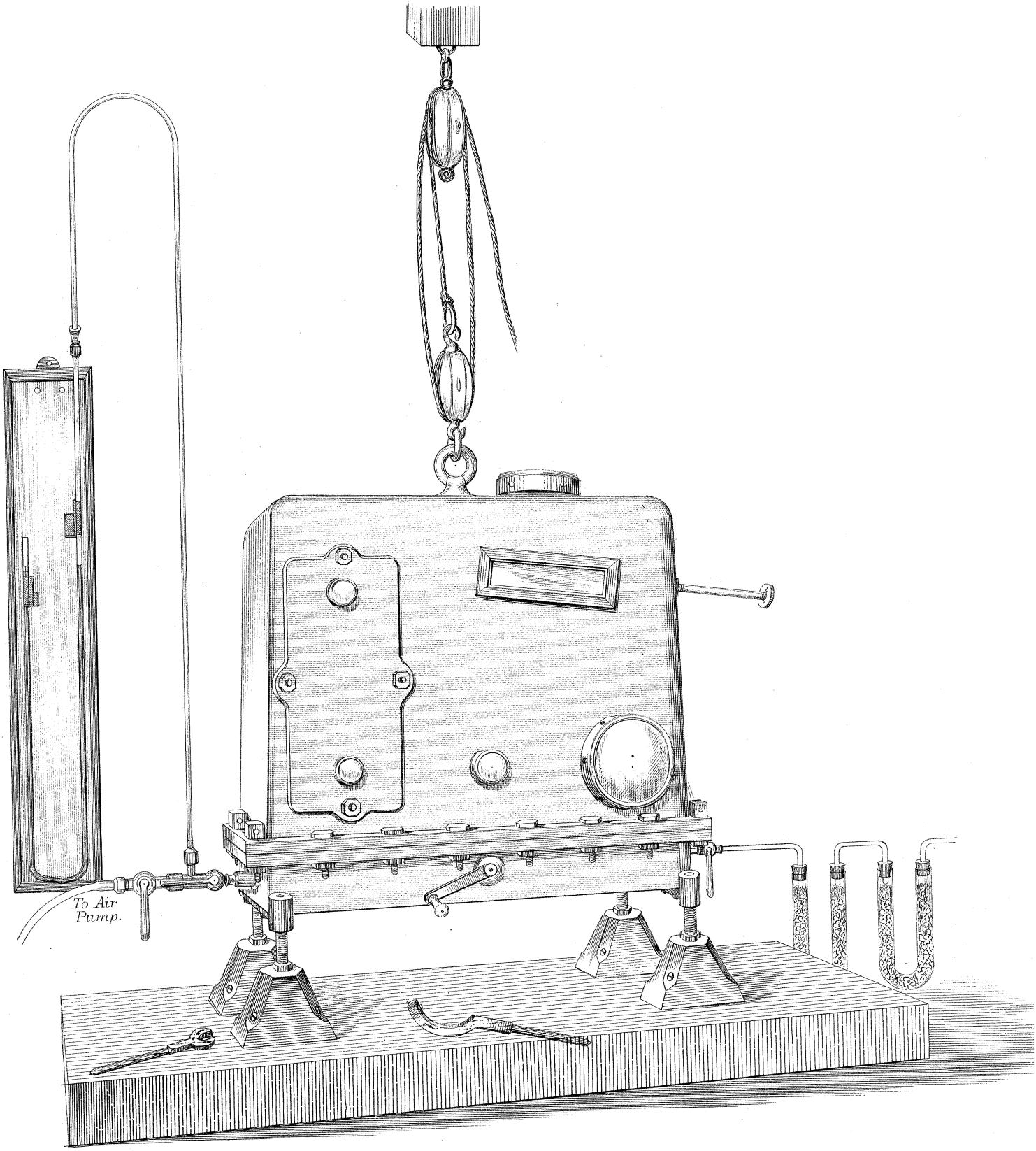
ATOMIC WEIGHT OF THALLIUM = 203·642.

Professor Stas has shown the hypothesis of Prout—that the atomic weights of the elements are severally multiples of the atomic weight of hydrogen—to be without the corroboration of experimental result. This view of the hypothesis is further borne out in the present investigation; for the number 203·642 cannot, within the limit of what has been shown to be the probable error, by any liberty be made to follow the hypothesis. Without doubt, when the atomic weights of all the metals are redetermined according to the standard of recent scientific method, it will be found that there are more exceptions to the hypothesis than are commonly considered. Marignac gives, in his confirmatory discussion of Stas's experiments and in his own results with calcium

(40·21), lanthanum (94·13), strontium (87·25), analogous opposed evidence, as in the case of the weight found for thallium.

In the preceding pages I have given the method by which I have arrived at the atomic weight of thallium, whilst I have endeavoured to show that experimental chemistry is strictly a science of precision. Accordingly the determination of the atomic weights of other of the elements (gold, chromium, platinum, rhodium, ruthenium, palladium, iridium, lithium, glucinum, cerium, and boron) is not a matter of supererogatory labour undertaken for the sake of verification merely, but is necessary to the progress of chemistry immediately as a science and technologically. For, until these elements shall have assigned to them more accurately their combining numbers, it will not be safe to enter into theoretical speculations respecting the interrelations between elementary bodies, nor possible to estimate them quantitatively without some error, which, small as it may be, yet remains an inaccuracy inadmissible to true science. One of the sources of error (that of neglecting the variation of atmospheric pressure during the weighings), it will have been seen, frequently introduces as much defect from the truth as impurity of the chemicals employed—a fact that has hitherto been greatly overlooked. Undoubtedly larger errors are sometimes admitted to general chemical manipulation from deficiency or excess in the weights employed than would obtain from the use of materials of ordinary purity, although in the latter case to notice effects of variable pressure, or the loss by weight of air displaced, would be labour wasted.

Bearing these teachings of experience in my mind, I have striven to eliminate all erroneous influence in the number I submit to the Royal Society as the Atomic Weight of Thallium; and I shall be amply rewarded for my long labour if I can know that the determination has secured to researches of this character a nearer approach to the standard of truth.

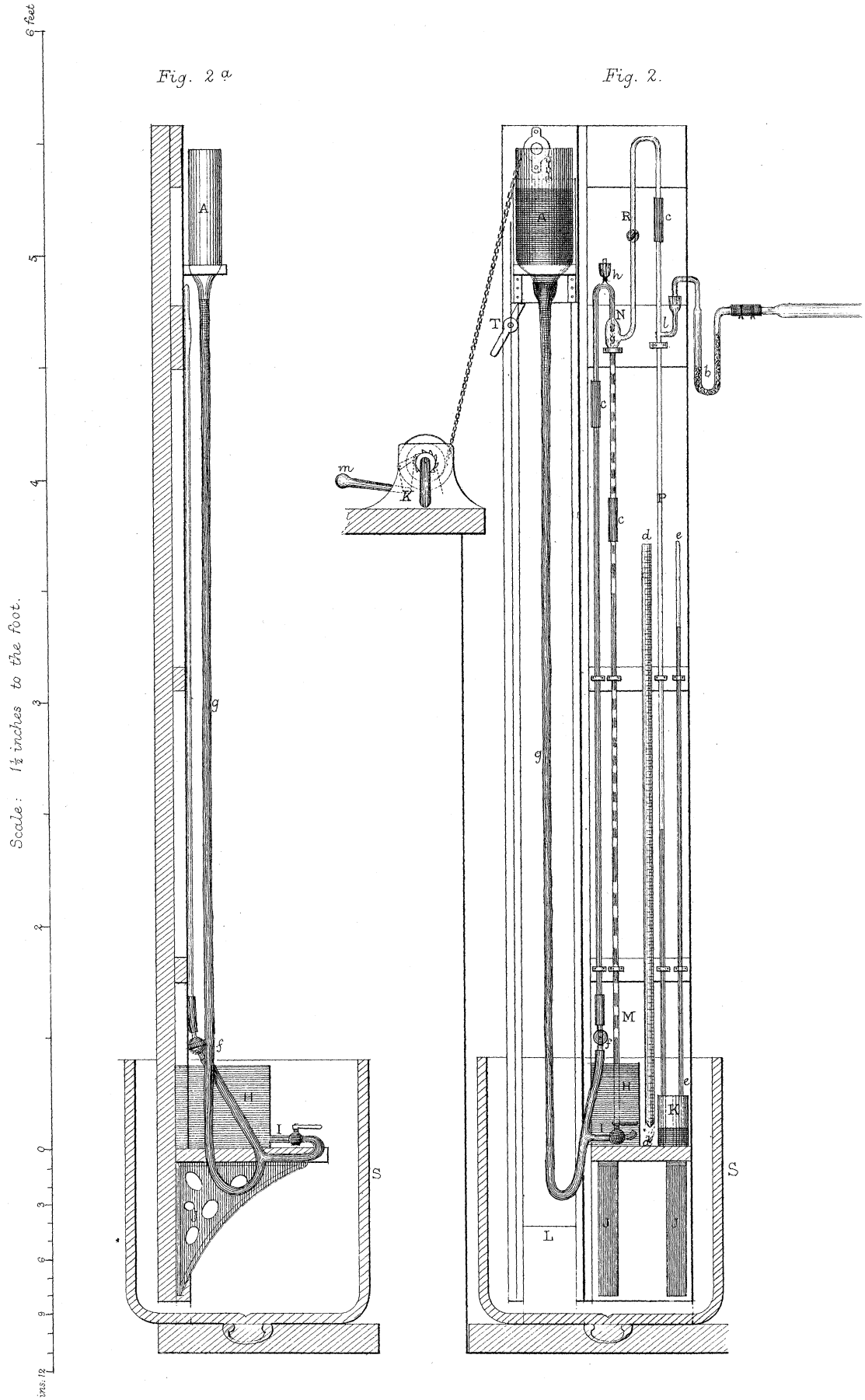


W.H.Wesley sc.

W.West & Co. imp.

Fig. 2 a

Fig. 2.


6 feet
5
4
3
2
1
0
ins. 12
Scale: 1½ inches to the foot.
A
g
f
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I
S
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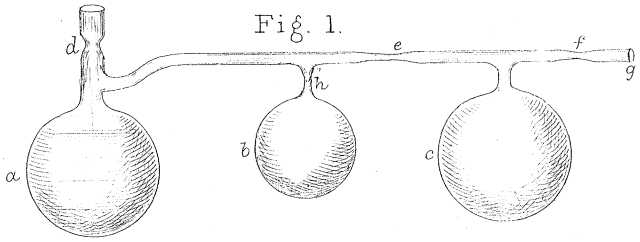
Fig. 1.



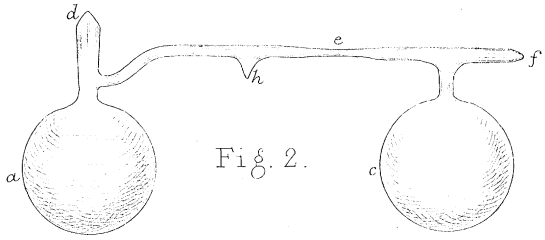


Fig. 2.

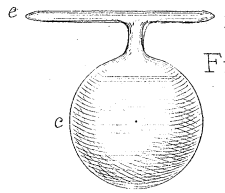


Fig. 3.

Fig. 4.

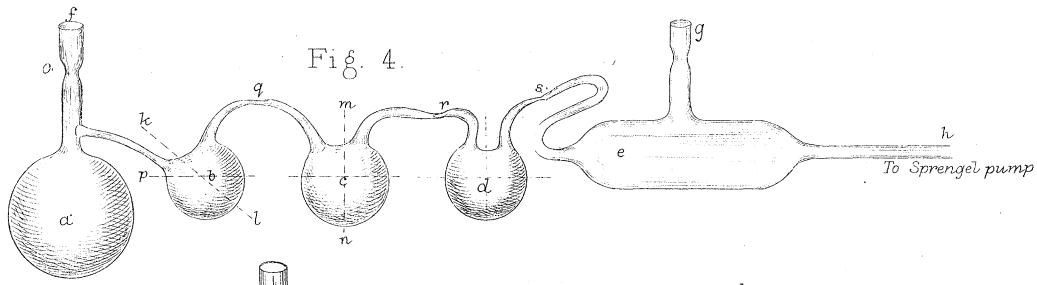


Fig. 4ª

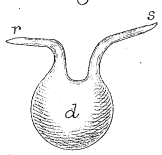
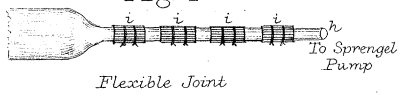


Fig. 4ᵇ



Flexible Joint

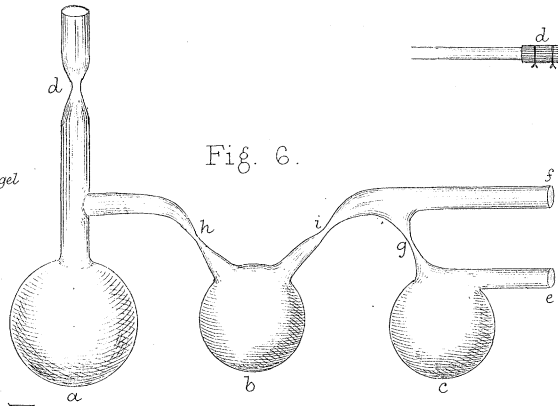


Fig. 6.

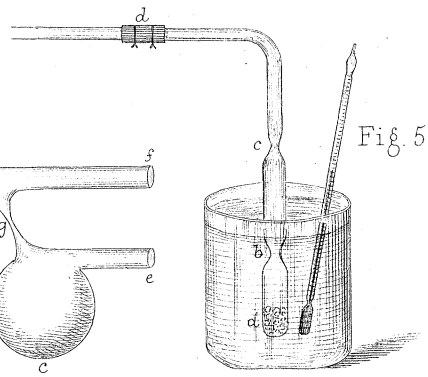


Fig. 5.

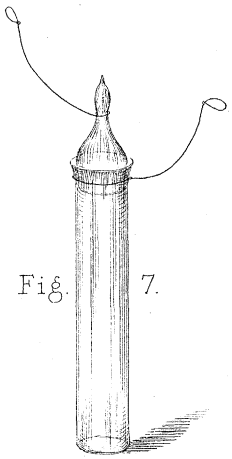


Fig. 7.

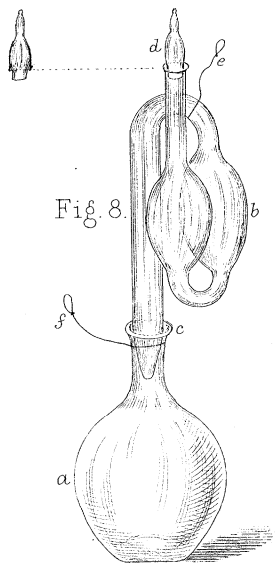


Fig. 8.

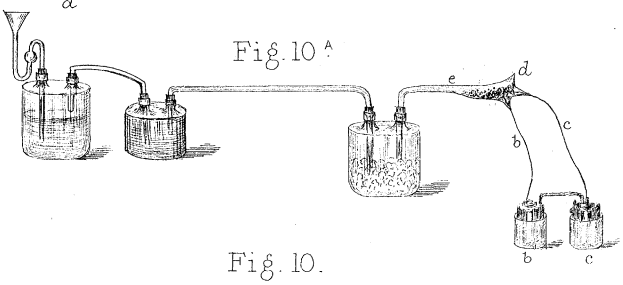


Fig. 10ᴬ

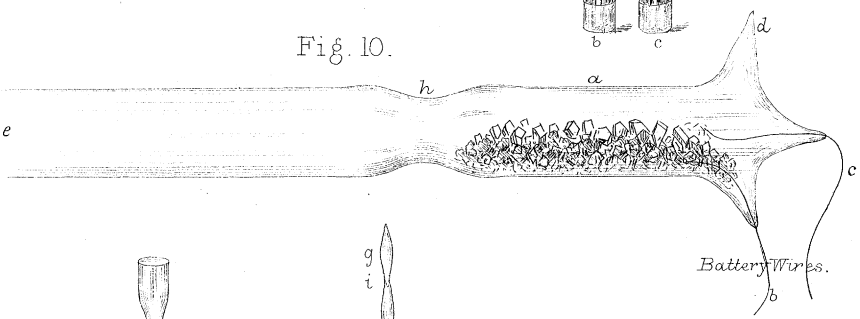


Fig. 10.

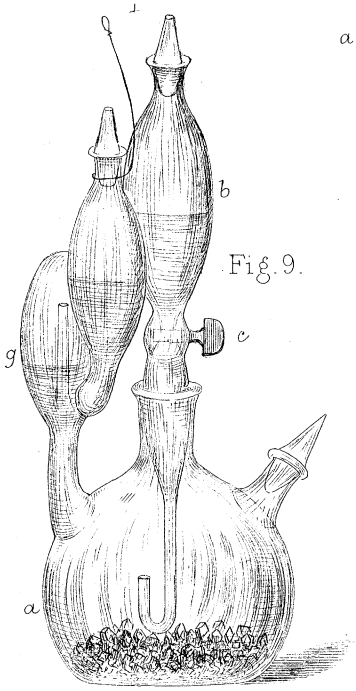


Fig. 9.

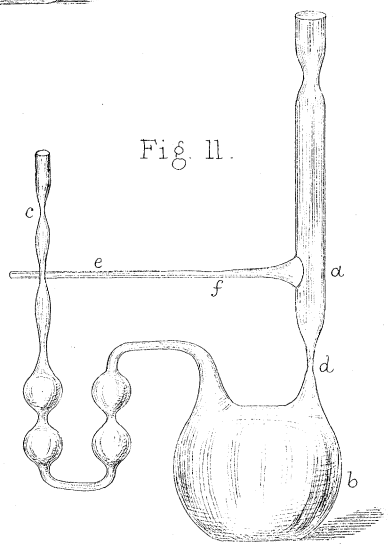
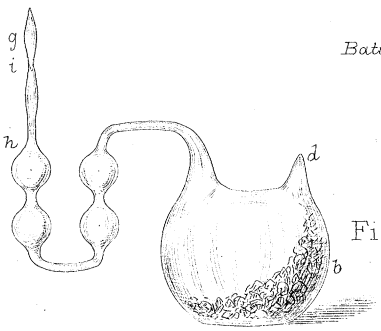


Fig. 11.



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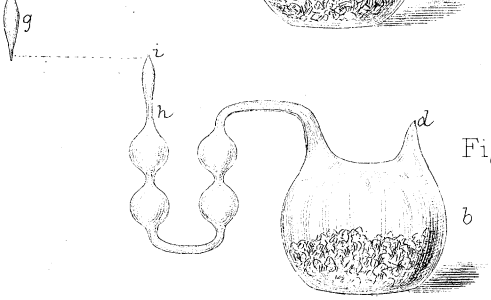
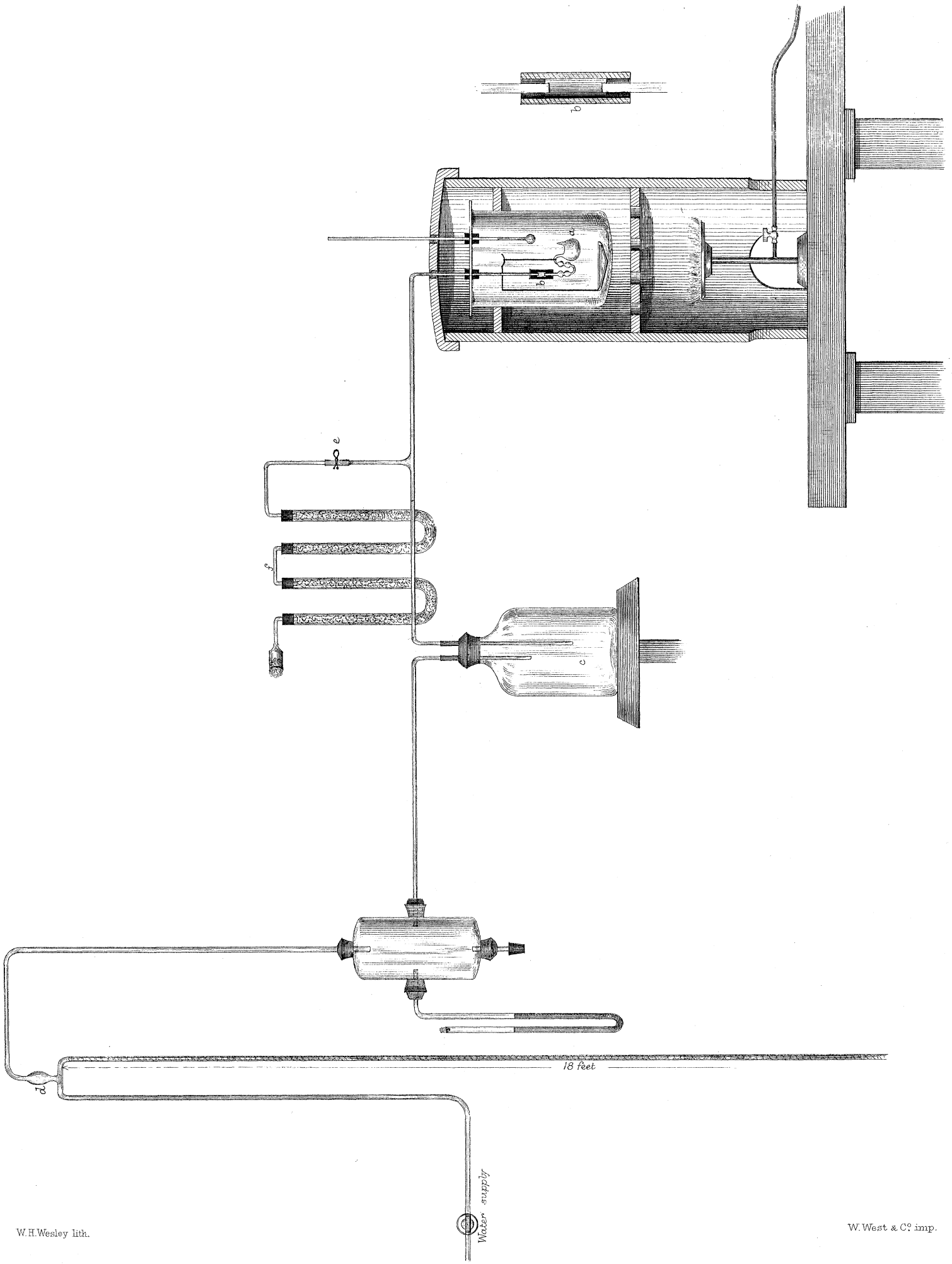


Fig. 13.



W. H. Wesley lith.

W. West & Co. imp.