XVII. *On the Atomic Weight of Glucinum (Beryllium).*

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[Plate 45.]

I. *Introductory.*

Ever since the discovery of glucinum by Vauquelin, in 1798, its atomic weight has been a disputed matter amongst chemists. Its discoverer considered that its oxide was a monoide, an opinion which was however strongly opposed by Berzelius, who wrote the oxide Gl_2O_3 and the atomic weight 13·7 ($O=16$). The researches of Awdejew[*] and Debray[†] again turned the scale in favour of the earlier view, and as an atomic weight of 9·2 suited the properties of the metal in the tables of periodicy constructed by MM. Mendeleef and Lothar Meyer, this atomic weight has, up to quite recently, been generally accepted by chemists. As a welcome confirmation to this came a determination of the specific heat of the metal by Professor E. Reynolds,[‡] who found that for its atomic heat to be near the normal number 6·0, its atomic weight must be 9·2 and not 13·8. Almost immediately afterwards a second determination of the specific heat was made by MM. Nilson and Petterson,[§] who, however, obtained a result agreeing not with the lower atomic weight but with the higher.

The reasons for these conflicting opinions are to be found—first, in the anomalous position of glucinum among the elements; secondly, in the difficulties which surround the preparation of even small quantities of the free metal in a tolerably pure condition; and thirdly, in the fact that no volatile compound of glucinum is known of which the vapour density might be easily determined.

The constitution of the compounds of glucinum cannot be inferred from any physical or chemical similarities with analogous compounds of other metals. Its compounds most closely resemble those of magnesium and aluminium, but also differ from these in the most striking manner. None are isomorphous with any similar compounds of these

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[*] Pogg. Ann., lvi., 101.

[†] Ann. Chim. and Phys. [3], xliv., 5.

[‡] Phil. Mag. [5], iii., 38; Chem. News, xlii., 273.

[§] Berl. Ber. xi., 381, 906.

two metals, if we except the result of EBELMEN,[*] who is said to have obtained the oxide isomorphous with alumina. The volatility of its chloride, its tendency to form basic compounds, its stable double fluorides with potassium and sodium, as well as the solubility of its hydrate in caustic soda or potash, all point to analogy with aluminium; while its carbonates, its double sulphate with potassium, and the greater simplicity of some of its double compounds when its oxide is written as a monoxide show similarity with magnesium.

A correct solution of this long-vexed question can therefore be only obtained either from the specific heat of the element or from the vapour density of some of its volatile compounds. Two determinations of the specific heat have been made, as referred to above, but with quite contradictory results; and, as far as I am aware, no determination of the vapour-density of glucinum chloride, nor of its compounds with ethyl and propyl, discovered by CAHOURS, has yet been made. The metal used by Mr. REYNOLDS in his experiments was prepared in a platinum crucible, and was apparently impure. His calorimeter, or as he prefers to call it, *atometer*, was "essentially a spirit thermometer with a test-tube sealed in the bulb." In the absence of any detailed description of his apparatus, and especially of the means adopted for its graduation, it cannot be definitely decided whether accurate results were possible or not. M. NILSON used iron vessels to prepare his metal and carefully determined its composition. It contained 13 per cent. of various impurities, which were allowed for in calculating the actual specific heat of the metal. The determinations were made with BUNSEN'S accurate and delicate ice-calorimeter.

The researches detailed in this paper were undertaken to obtain, if possible, a purer metal than M. NILSON'S, and to redetermine its specific heat. The vapour-density of volatile glucinum compounds I hope to refer to in a later paper.

II. *Extraction of glucina.*

Of the various methods recommended for the extraction of the earth from its commonest mineral beryl, I shall here only allude to two. The first consists in decomposing the finely-powdered mineral by fusion with potassium carbonate, disintegration of the fused mass with sulphuric acid, evaporation to dryness, to render the silica insoluble, concentration to separate most of alumina, as alum, and treatment with ammonium carbonate as in the second method. This process, otherwise a good one, is objectionable, because of the high temperature necessary to decompose the mineral, and because the fused mass is only very slowly attacked by the sulphuric acid. I have usually followed a different method, due to SCHEFFER,[†] which consists in decomposing the mineral by hydrofluoric acid. Briefly, the process is as follows:—The finely-powdered mineral is mixed with excess of powdered fluor spar and sulphuric acid

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[*] Ann. d. Ch. u. Pharm., lxxx., 211.

[†] Jahres. Ber. 1859, 139.

in a large leaden dish, which is furnished with a leaden lid, and is heated on a water-bath for two or three hours. The remaining sulphates are next heated in an iron crucible to expel the excess of acid and any traces of silica, then dissolved in warm water and the calcium sulphate filtered off. To the filtrate, sufficient potassium sulphate is added to form alum with the alumina present, and the solution evaporated down to crystallize. The mother-liquor, from which nearly the whole of the alumina has been thus removed, is then slowly dropped, best by a separating funnel, into a large excess of warm concentrated ammonium carbonate solution, with constant stirring. About ten times as much of the salt is necessary as the quantity of glucina supposed to be present. The whole is then placed in stoppered bottles, and allowed to stand for four or five days, after which no change appears to take place. At the end of this time the solution, which contains nearly the whole of the glucina, some alumina, and often not inconsiderable quantities of iron, is then filtered, and colourless sodium sulphide added as long as ferrous sulphide is thrown down. If the quantity of iron present produces only a coloration, but no precipitate, it is well to add a little ferric chloride, and then completely precipitate with sodium sulphide. This is the only method I know of, except fusion with acid potassium fluoride, which removes every trace of iron. In the filtered solution the ammonium carbonate is now to be decomposed by boiling, but if the concentrated solution is heated directly over the flame very violent bumping cannot be avoided. A better plan is either to dilute freely with water (to about three times the bulk), or else to warm for about two hours over a water-bath, and when most of the ammonium carbonate has been decomposed, then to boil over the flame. The final traces of the carbonate are removed by acidulating with hydrochloric acid, yielding a solution from which ammonia precipitates the hydrate. By repeating the process the glucina is obtained nearly pure. Absolutely pure it can only be prepared from the double potassium fluoride, K_3GlF_6, by fusion with acid potassium fluoride, and recrystallizing the double fluoride from hot water. The quantity of the acid fluoride required by theory (6 : 1) should be used, not only 2 : 1, as recommended by Dr. WOLCOTT GIBBS, who, I believe, first introduced the process. The purified double fluoride is then readily decomposed by the requisite quantity of concentrated sulphuric acid in a platinum dish, and the hydrate precipitated with ammonia in the usual manner.

A very good yield may be obtained from beryl by this hydrofluoric acid process, provided the mineral is sufficiently finely powdered. Fairly pure compounds of glucinum may, however, be now obtained from some continental manufacturing chemists, which only require once purifying with ammonium carbonate for all ordinary purposes.

III. *Separation of metallic glucinum.*

Metallic glucinum may be obtained either from its double fluoride with potassium or from its chloride, of which the latter is decidedly the most suitable compound.

The double fluoride, K_3GlF_6, melts at a low red-heat without decomposition.

In the fused state it readily conducts an electric current with the formation of metallic glucinum at the negative pole. The metal so obtained is, however, largely contaminated with impurities derived from the vessel in which the experiment is conducted, which is strongly attacked by the free fluorine. In one experiment with platinum electrodes—the positive electrode being a platinum crucible in which the salt was fused—the crucible lost two decigrammes in weight. The double fluoride may also be decomposed by fusion with sodium or potassium, but in this case also only a very impure product results, owing to corrosion of the vessels employed. It is possible that by using an *iron* crucible a purer metal might be obtained.

The metal used in the determination of its specific heat was prepared from its chloride, which compound was obtained in the usual way by heating a mixture of the oxide and sugar charcoal in dry chlorine. I have found it better to employ starch paste (made of pure wheaten-starch) in place of the oil which is commonly recommended for mixing the oxide and charcoal. If starch paste is used a much more compact mass is obtained after the subsequent glowing in charcoal powder, but which is still sufficiently porous to allow the chlorine to penetrate into the interior. It is advisable to employ a hard glazed porcelain tube for heating the mixture in the stream of chlorine, this being far less attacked by the chloride than hard glass. Absolute purity of the oxide used to prepare the chloride is not necessary, as, owing to the high temperature at which glucinum chloride condenses, any traces of aluminium or silicon which may be present are carried, with traces of the chloride, to the less heated portions. If, however, iron is present, it is not completely removed.

Glucinum chloride melts at about 600° (CARNELLY) to a brown liquid, of which the electric resistance is so great that it is apparently not decomposed even by a powerful current. On connecting the wires from a battery of forty quart BUNSEN cells in series with platinum electrodes dipping in fused glucinum chloride and with a galvanometer, no deflection of the needle of the instrument was observed. I can therefore confirm NILSON'S result that the chloride is practically a non-conductor of electricity. The fused or gaseous chloride is readily decomposed by sodium, but if vessels of platinum, porcelain, or glass are used the metal obtained is largely contaminated with impurities derived from the vessels. To overcome this difficulty DEBRAY* used lime. He constructed boats of a mixture of lime and alumina, placed sodium in the first and the chloride in the second, then introduced them into a tube of hard glass through which was passed a stream of dry hydrogen. The boat containing the sodium was first heated, then that containing the chloride, so that its vapour was carried by the stream of hydrogen over the fused sodium. The metallic glucinum so obtained was a compact, fibrous, crystalline mass, and was probably purer than any prepared in platinum vessels. NILSON and PETTERSON first proposed iron vessels for the reduction of the chloride. They heated equivalent quantities of the chloride and sodium in a massive iron cylinder and thus obtained a metal resembling DEBRAY'S, and comparatively pure.

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* *Loc. cit.*

I first attempted DEBRAY'S method, but owing to the difficulty of procuring compact boats of lime or of a mixture of lime and alumina of sufficient size, no good results were obtained. Nor did I get good results with NILSON'S process. I found considerable difficulty in excluding the oxygen of the air; the tubes could scarcely be unscrewed again when cold, as the sodium chloride had solidified in the thread, and when opened it was not easy to extract the metal without contamination from the outside scale. A modification of the two methods was therefore adopted, which answers admirably.

Iron boats were constructed of pieces of tubing partly filed away, and with end pieces screwed on. They were about 200 millims. long and 20 millims. in diameter. In order to prevent any contact of the reduced metal with the glass of the tubes, the boats were enclosed in slightly longer pieces of entire iron tubing, and in these cases were introduced into a wide tube of hard glass. As in DEBRAY'S method, the first boat contained about the requisite quantity of sodium, the second the glucinum chloride. When the tube had been filled with dry hydrogen, the boat containing the sodium was heated until the metal was fused, the heating was then continued backwards to the chloride, the vapour of which thus passed, mixed with the excess of hydrogen, over the molten sodium. After the somewhat violent reaction had ceased and the tube was again cold, the boat containing the reduced glucinum, together with the sodium chloride produced and the excess of sodium, was placed in a vessel of crude alcohol until hydrogen ceased to come off. It was then removed to water to dissolve out the sodium chloride. Compact crystalline masses of glucinum were thus obtained, always, however, mixed with more or less basic chloride and oxide, even when the experiment was most carefully conducted. The larger pieces of metal could be easily removed from the liquid and purified by washing with cold dilute caustic soda, which dissolves out any oxide, but is without action on the metal. The residue was then likewise treated with caustic soda, and preserved separately as being less pure. The iron boats and tubes were not attacked during the reaction, except that blisters were raised on the outer tubes which, unlike the boats themselves, were of steel. The metal was of a steel-grey colour not so white as aluminium, but considerably harder, and can be beaten into thin sheets under the hammer. Compressed in a steel mortar it yielded a compact disc of metal—0·7 gramme thus treated gave a disc 15 millims. in diameter and 3 millims. thick. Its specific gravity at 10° C. was found to be 1·84, or making allowance for the impurities present, 1·70. As it was suspected that the metal so compressed might still contain air, it was first boiled for half an hour in water before determining its specific gravity. All attempts to fuse the metal were without any good result. It remained apparently unaltered when heated to bright redness in the air, and probably became covered with a thin coating of the oxide. Heated under sodium chloride in a lime crucible by the oxyhydrogen flame imperfect fusion was obtained. When similarly heated and exposed to the air it burnt with a dazzling, bluish light. The metal dissolved readily in dilute acids leaving a minute trace of insoluble matter, quite imponderable. When 3 centigrammes were dissolved, the residue could not have been as much as 0·1 milligramme. To determine the amount of iron contained in it, 0·0341 gramme was dissolved in dilute sulphuric acid in a stream of carbonic acid, and then required 1·4 cc. of a potassium permanganate solution of which 1 cc. was equivalent to 0·32 milligramme iron, which gives the percentage of iron present to be 1·32. The oxide mixed with the metal was found by dissolving 0·0340 gramme of the metal in dilute hydrochloric and precipitating the hydrate with ammonia and weighing, after thorough washing, as oxide. The amount taken gave 0·0883 gramme oxide, corresponding to a percentage of 4·71. The composition of my metal was therefore :—

Gl . . . . = 93·97
Gl_2O_3 . . . . = 4·71
Fe . . . . = 1·32
SiO_2 . . . . = traces

100·00

That obtained by M. Nilson, the only other sample which has been analysed, had the composition :—

Gl . . . . = 87·09
Gl_2O_3 . . . . = 9·84
Fe . . . . = 2·08
SiO_2. . . . . = 0·99

100·00

I believe it is possible by using purer chloride to obtain a metal almost chemically pure by the method described above.

The position of glucinum in the electro-chemical series is a peculiar one, and deserves passing notice. In dilute acids (hydrochloric, nitric or sulphuric) glucinum is strongly electro-negative to magnesium, and feebly positive to aluminium. In caustic potash or caustic soda, the series is different, and glucinum is now negative to both metals, feebly to magnesium, strongly to aluminium ; while in ammonium carbonate the series is the same as for dilute acids. These results may be thus tabulated :—

(i.) Dilute acids and ammonium carbonate.

$$+\text{Mg, Gl, Al}-$$

(ii.) Caustic alkalies.

$$+\text{Al, Mg, Gl}-$$

IV. *Determination of specific heat.*

The most accurate method for determining the specific heat of substances of which small quantities only are available is undoubtedly that devised by BUNSEN, in which, as is well known, the quantity of ice at 0° which is melted by a given weight of the substance heated to a high temperature is measured by the diminished volume which the water produced occupies. Unless, however, the whole apparatus is kept exactly at the freezing-point, accurate results are not possible, and even under the most favourable conditions there is usually a mean error of nearly one per cent. BUNSEN originally immersed his instrument in a large box of pure freshly-fallen snow to preserve it accurately at 0°—a proceeding which has been somewhat simplified by SCHULLER and WARTHA, who coat the exterior vessel with a thick layer of ice, and work in ice-cold water. But even with this modification it is scarcely possible to use the apparatus in England, and especially on the west coast, where frost in the winter is the exception rather than the rule.

Several kinds of rough calorimeters based on the same principle have been proposed in which the heated substance produces an expansion in a liquid at a definite temperature. Among these are the *atometer* of Mr. REYNOLDS, which was used to determine the specific heat of his glucinum, and a similar form described by Professor BALFOUR STEWART.* No instrument of this description can, however, give accurate results unless most carefully shielded from external sources of heat and carefully calibrated, especially when a liquid expanding so irregularly as alcohol is used. As far as can be judged by the published results, no calibration has been attempted, and therefore the results obtained cannot be of much value.

A very simple form of apparatus has been devised by KOPP† who places the substances in a glass tube with naphtha, and heats in a bath of mercury. Considerable dexterity must be requisite to remove the heated substance from the bath of mercury to the calorimeter in exactly equal times, and a further objection is the small range of temperature through which the substances can be heated. His results, too, do not agree so closely with one another as those obtained by BUNSEN'S or REGNAULT'S methods, especially when only small quantities are used.

To overcome these various objections a modification of REGNAULT'S method of mixtures has been adopted, which with small quantities of the substances (0·7 to 7 grammes) gives results with a mean error of one per cent. or less, and which can be easily worked by one person without assistance. The errors in REGNAULT'S apparatus have been pointed out by NEUMANN and PAPE.‡ They showed how a cooling effect must be produced by an upward current of cold air when the heating arrangement was opened at the top, and explained that, in many cases, the water equivalent of the

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* Proceed. of the Phys. Soc., iv., 52, 342.

† Phil. Trans., 1865, 71.

‡ POGG. Ann., cxx., 337, 579.

casing of brass wire gauze used to contain the substances was greater than that of the substances themselves. As far as possible these errors have been avoided in the following modification of REGNAULT's method. The apparatus consists of two parts—that for raising the substance to a high temperature, and the calorimeter proper.

The *heater* is an annular brass vessel of 32 millims. internal and 64 millims. external diameter, and is 115 millims. high (Plate 45, fig. A.). Its lid screws on firmly and is made steam-tight by indiarubber packing, freed from sulphur by previous boiling in caustic soda. Three tubes pass through the lid of the heater, the central one carrying a thermometer (T_1), which gives the temperature of the interior air bath, while the other two enclose platinum wires connected with the arrangement for supporting the substance and for allowing it to fall into the calorimeter at the correct instant. All connexions in the lid are made as air-tight as possible to prevent any upward current of cold air into the heater. The substance is supported in a small platinum capsule (B) attached by a hinge to one of the platinum wires referred to above, and this capsule is held in a horizontal position by the second platinum wire, the end of which is bent at right angles to its length. To the upper end of this platinum wire is fixed a strip of wood, so that the wire can be easily turned through a small angle, the catch released, and the substance allowed to fall into the calorimeter. The heater is completely covered by a double coating of thick baize, and is placed in a wooden box (not shown in the figure). In the bottom of this wooden box is a small slider (C) which is connected with an electro-magnet and can be opened or closed at will. Two tubes (D, D) connect the annular space of the heater with a boiler containing water, placed on the other side of a tin screen, and with the air. The whole heating arrangement stands on a larger box (E) open at one side and with a long base board, and this again is supported on a suitable wooden stand.

The *calorimeter* itself (F) is a small thin platinum vessel of 50 millims. in diameter and 60 millims. in height, and containing therefore when full about 100 cc. It is furnished with an agitator of two discs of thin perforated platinum, soldered with gold to two thin platinum wires, one of which terminates about 15 millims. below the lid of the brass casing in a hook. To this hook a silken string (G) is attached, which passes over pulleys and is kept stretched by a small weight. The two discs of the agitator have perforations at one side for the bent thermometer (T_2), which gives the temperature of any liquid contained in the calorimeter. The advantages of using platinum for calorimeters have been pointed out by BERTHELOT. It always remains bright and of constant weight, and from its low specific heat corresponds to a very small equivalent of water. The weight of my calorimeter and agitator is 74·40 grammes, and its water equivalent 2·41 grammes, but it might have been made very much thinner. The calorimeter stands on three boxwood cones in a brass casing, which is fixed by three pieces of cork to a sliding board. This brass casing is 85 millims. high and 77 millims. in diameter, and its movable lid is furnished with a small slider which can be opened or closed by two iron armatures working in the two solenoïds (H and H) placed one on each side. The wires from those solenoids terminate in four points of German silver at the end of the board (only one of which, J, is shown in the figure), which when the calorimeter is drawn up into its place under the heater come into contact with four springs of the same metal (K) connected with the battery and a switch. The board on which the calorimeter and its appurtenances are fixed can be moved by strings from the position shown in the figure to that exactly under the heater and back again.*

To obtain accurate readings of the different temperatures, two standard thermometers were first constructed, with a millimeter scale, and calibrated by GAY-LUSSAC's method, using Mr. F. D. BROWN's excellent little instrument.† These two read between about 5° and 105° C., and 1 millim. is about equivalent to 0°·2 C. They were compared with one another for every half degree between 8° and 20° C., in a large bucket of water, kept suitably agitated, and in only one instance differed by more than 0°·02 from one another. The bent thermometer (T_2) was more open, and 1 millim. was about equal to 0°·1 C. It was very carefully compared, by two series of experiments, with the two standard thermometers together, and the mean temperature taken when they differed from one another. The thermometer T_1, used for the heater, read accurately to 0°·05 C., was corrected for the boiling point, but not calibrated; the correction for the exposed thread was determined experimentally, and was found to be 0°·03 less than given by the usual formula :—

$$C = m\,(T - t)\,n.$$

The water-equivalent of the thermometer T_2 was calculated, from the weight of mercury which it contained, and the weight of glass immersed, to be 0·5 gramme, which agreed with experimental results.

Readings of the temperature to which the substance was heated are thus correct to at least 0°·1 C., and of the calorimeter to 0°·01 C.

The liquid used in the calorimeter is French turpentine, purified and redistilled. Taking the specific heat of this liquid as 0·4, and its specific gravity as 0·87, about 28 small calories are requisite to raise the temperature of 80cc. through one degree, and only a small weight of the substance is required. Thus, for silver, the quantity necessary would be $\frac{28}{80 \times 0{\cdot}057} = 6$ grammes (circâ), and for aluminium $\frac{28}{80 \times 0{\cdot}2} = 1{\cdot}7$ gramme (circâ) for a fall in temperature of 80°: much smaller weights than are required for any other accurate method, except BUNSEN's. With a temperature difference of 1°·00, and reading to 0°·01, the mean error cannot well be smaller than 1 per cent., and with the instrument in its present form, this is, in fact, the limit of error. More accurate results might be possible with a still smaller calorimeter, and a still more open thermometer.

One possible objection to the use of turpentine was loss by evaporation during the

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* A battery-power of four quart BUNSEN or GROVES' cells is necessary. More convenient than this is a bichromate battery so arranged that the zincs can be lowered into the liquid when required.

† Phil. Mag. [5], xiv., 57.

experiment; this, however, was found to be too small to affect the results to any appreciable extent. The loss between two experiments, even after removing the substance, never exceeded 0·1 gramme, and a difference of 0·05 gramme would only produce a much smaller error than a difference of 0°·01 in reading the bent thermometer. In order to still further test the evaporation, the calorimeter was left open, exposed to the air of a warm room for 16 hours, and then only lost 0·26 gramme. Provided, therefore, that the agitator or substance does not rise above the level of the liquid, the loss by evaporation during an experiment can be very safely neglected.

A series of blank experiments were next made to determine whether the calorimeter gained heat during the time that it was open to receive the substance. It was found that the shortest time possible in which the whole series of operations could be performed—the calorimeter run under the heater, the substance introduced, and the calorimeter returned to its original position—was five seconds, and during this time no change could be noticed in the thermometer T_2. If, therefore, the operations follow one another promptly the gain of heat to the calorimeter may be safely said to be within the unavoidable errors of reading. All readings were of course made through a telescope.*

The following is the course usually adopted in the experiments. The substance, weighed to milligrammes, is introduced into the heater from below, this part of the apparatus being removed from its stand for the purpose. The heater is then returned to its position, the wooden slider adjusted, and the two tubes connected with the boiler and waste pipe respectively. During the time that the substance is heating, about 70 grammes of turpentine are poured into the calorimeter and weighed to centigrammes. The calorimeter is then placed in its brass casing, the string attached to the agitator, the thermometer and electro-magnets adjusted, and then a large plate of glass placed in front of the whole apparatus. At the end of about an hour's *vigorous* boiling the thermometer in the heater becomes stationary, starting with all cold, or in about three-quarters of an hour if the instrument has been previously used. This maximum temperature is either higher or lower than the boiling-point, according to the size of the waste pipe. In the experiments already made the waste pipe was generally small and the maximum temperature slightly higher than the boiling-point. Longer heating appears unnecessary, owing probably to the small quantities used. As soon as thermometer T_1 is constant, continuous readings of it and the other thermometer (T_2) are made at regular intervals of one minute. Thermometer T_1 will be quite constant, and if the liquid in the calorimeter is at a temperature within 1° of that of the air, the other thermometer (T_2) should not oscillate through more than 0°·01 in five minutes. At the end of a given minute T_2 is read for the last time, giving the initial temperature of the calorimeter (t), while T_1, giving the temperature to which the substance was heated (T), has been read just before. The substance is

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* I should state that in using large weights, as with the 10 grammes of silver, there was sometimes a little splashing, though never exceeding 0·05 gramme.

now introduced, the calorimeter returned to its original position, the agitator worked a few times and a reading made at the end of the half minute. Renewed agitations and readings are then made for every half minute until the maximum temperature (θ) is reached. The time to reach this maximum for metallic substances, with which I have as yet only experimented, is about a half to one minute.

Although it is not intended to use the calorimeter with water, as the temperature difference would be too small for the small quantities employed, three experiments were made with pure silver, and two with commercial aluminium (re-fused under sodium chloride) to test the apparatus. The following results were obtained, in which T, t and θ have the meanings given above, t' is the temperature of the air, W the weight of water, together with the water equivalent of the calorimeter, agitator and thermometer (2·91 grammes), w the weight of the substance employed, and s the required specific heat.

Silver in water.

I. $W=84{\cdot}25$, $w=10{\cdot}205$, $T=101^\circ{\cdot}9$, $t=11^\circ{\cdot}09$, $\theta=11^\circ{\cdot}71$, $t'=10^\circ{\cdot}9$.

$$s=\frac{W(\theta-t)}{w(T-\theta)}=0{\cdot}05677.$$

II. $W=84{\cdot}03$, $w=10{\cdot}205$, $T=101^\circ{\cdot}9$, $t=11^\circ{\cdot}08$, $\theta=11^\circ{\cdot}69$, $t'=10^\circ{\cdot}7$.

$$s=0{\cdot}05568.$$

III. $W=84{\cdot}01$, $w=10{\cdot}205$, $T=101^\circ{\cdot}9$, $t=10^\circ{\cdot}86$, $\theta=11^\circ{\cdot}47$, $t'=10^\circ{\cdot}4$.

$$s=0{\cdot}05553.$$

Mean specific heat $=0{\cdot}05600$; mean error $= 0{\cdot}0003 = 0{\cdot}6$ per cent.

Aluminium in water.[*]

I. $W=85{\cdot}71$, $w=3{\cdot}502$, $T=98^\circ{\cdot}6$, $t=7^\circ{\cdot}59$, $\theta=8^\circ{\cdot}42$, $t'=8^\circ{\cdot}0$.

$$s=0{\cdot}2253.$$

II. $W=85{\cdot}25$, $w=3{\cdot}502$, $T=98^\circ{\cdot}5$, $t=8^\circ{\cdot}56$, $\theta=9^\circ{\cdot}37$, $t'=8^\circ{\cdot}5$.

$$s=0{\cdot}2212.$$

Mean specific heat $=0{\cdot}2232$; mean error $= 0{\cdot}002 = 1$ per cent.

It will thus be evident that results comparable in accuracy with the best determinations can be obtained with the apparatus, and, I need not add, working entirely without assistance. I intend shortly to make a series of more extended experiments,

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[*] Using a wider exit tube.

and if possible to modify the apparatus so that it can be used for higher temperatures than 100°.

The specific heat of the sample of turpentine was next determined, with results as follows, T, t, θ, and t' having the same significance as before, W being the weight of turpentine used, w the weight of silver, s its specific heat (taken as 0·057), and s' the required specific heat of the turpentine.

Silver in turpentine.

$$\text{I. } \mathrm{W}=75{\cdot}30,\quad w=10{\cdot}205,\quad \mathrm{T}=102^{\circ}{\cdot}2,\quad t=10^{\circ}{\cdot}98,\quad \theta=12^{\circ}{\cdot}47,\quad t'=12^{\circ}{\cdot}8.$$

$$s'=\frac{ws(\mathrm{T}-\theta)-2{\cdot}91(\theta-t)}{\mathrm{W}(\theta-t)}=0{\cdot}4265.$$

$$\text{II. } \mathrm{W}=75{\cdot}19,\quad w=10{\cdot}205,\quad \mathrm{T}=102^{\circ}{\cdot}5,\quad t=13^{\circ}{\cdot}32,\quad \theta=14^{\circ}{\cdot}81,\quad t'=14^{\circ}{\cdot}5.$$

$$s'=0{\cdot}4165.$$

$$\text{III. } \mathrm{W}=74{\cdot}74,\quad w=10{\cdot}205,\quad \mathrm{T}=102^{\circ}{\cdot}4,\quad t=14^{\circ}{\cdot}56,\quad \theta=16^{\circ}{\cdot}00,\quad t'=15^{\circ}{\cdot}0.$$

$$s'=0{\cdot}4280.$$

Mean specific heat $=0{\cdot}4236$; mean error $=0{\cdot}0044=1$ per cent.

The result obtained by REGNAULT for turpentine at 10° was 0·4278, and by HIRN 0·4241.

Three determinations of the specific heat of the compressed disc of glucinum referred to above were then made, yielding the following closely concordant results, in which the letters have the same significance as before, except that W is the weight of the turpentine and W' its water equivalent + the water equivalent of the calorimeter, &c.

Glucinum in turpentine.

$$\text{I. } \mathrm{W}=72{\cdot}93,\quad \mathrm{W}'=33{\cdot}77,\quad w=0{\cdot}6575,\quad \mathrm{T}=102^{\circ}{\cdot}1,\quad t=11^{\circ}{\cdot}09,\quad \theta=11^{\circ}{\cdot}85,\quad t'=11^{\circ}{\cdot}1.$$

$$s=\frac{\mathrm{W}'(\theta-t)}{w(\mathrm{T}-\theta)}=0{\cdot}4326.$$

$$\text{II. } \mathrm{W}=72{\cdot}67,\quad \mathrm{W}'=33{\cdot}66,\quad w=0{\cdot}6568,\quad \mathrm{T}=102^{\circ}{\cdot}2,\quad t=10^{\circ}{\cdot}08,\quad \theta=10^{\circ}{\cdot}86,\quad t'=9^{\circ}{\cdot}9.$$

$$s=0{\cdot}4264.$$

$$\text{III. } \mathrm{W}=75{\cdot}12,\quad \mathrm{W}'=34{\cdot}69,\quad w=0{\cdot}6565,\quad \mathrm{T}=102^{\circ}{\cdot}3,\quad t=14^{\circ}{\cdot}26,\quad \theta=14^{\circ}{\cdot}98,\quad t'=14^{\circ}{\cdot}3.$$

$$s=0{\cdot}4357.$$

Mean specific heat of glucinum $=0{\cdot}4316$; mean error $=0{\cdot}0035=0{\cdot}9$ per cent.

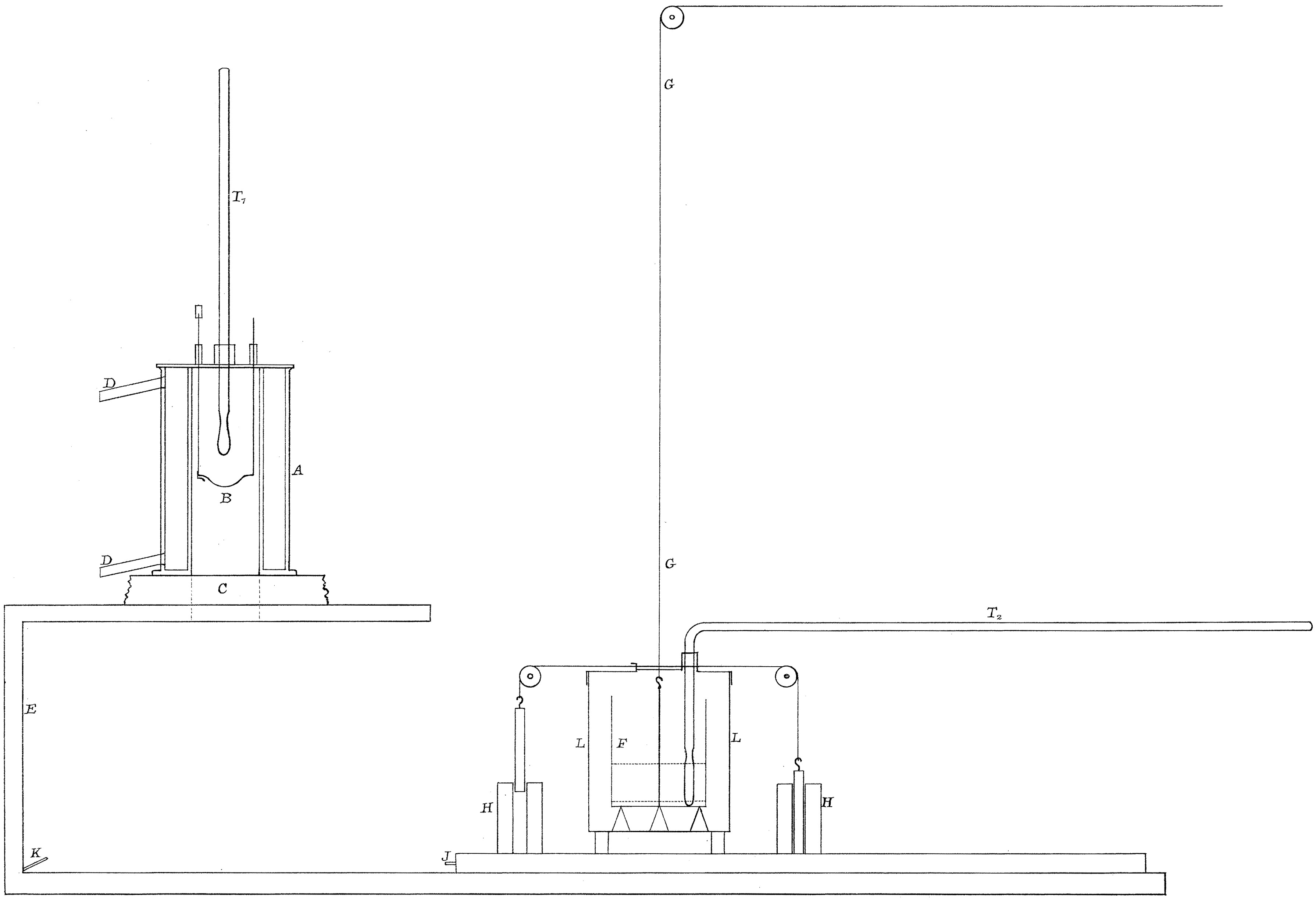
Making allowances for the impurities which the metal contained, the true specific heat (s') of the pure metal would be :—

$$s'=\frac{0·4316\times 100-1·32\times 0·114-4·71\times 0·247}{93·97}=0·4453,$$

taking the specific heat of iron as 0·114, and that of glucina as 0·247. Multiplying this number by the atomic weight of glucinum when its oxide is a sesquioxide, *i.e.*, 13·65, the atomic heat becomes 6·08, proving conclusively, if DULONG and PETIT'S law is true for this metal as it is for all others, that this is the true atomic weight, and not two-thirds of this number, or 9·1.

The specific heat, as above determined, is considerably higher than that found by NILSON (0·4079), and my results might be too great for two reasons. The compressed metal was somewhat porous, and heat might have been produced by the absorption of the turpentine in its pores, and there might be a further error from hygroscopic water. The former supposition could be only decided by enclosing the metal in some impervious envelope, which has not yet been done; the latter possible error was as far as practicable avoided by drying the glucinum for two hours at 150° before each experiment. But, even supposing the above results to be erroneous to the extent of 10 per cent., it is still certain that the specific heat of the metal is nothing near 0·6, as it ought to be if the atomic weight were 9·1.

The result is unfortunate for the periodic law, and is the first serious rebuff which this useful generalisation of facts has received. Glucinum, with the atomic weight of 9·1, finds its natural position as the first element of the magnesium group; but if its atomic weight is 13·65, it falls between carbon and nitrogen, and entirely contradicts the first principles upon which the tables have been constructed. With an atomic weight of less than 12 it might be easily introduced, and it is possible that when absolutely pure such a result might be obtained. NILSON has recently made some determinations with the sulphate which reduced the atomic weight from the number previously given 13·8 to 13·65, but it does not seem quite certain that his compounds were entirely free from aluminium, which would naturally increase the atomic weight. I hope shortly to re-determine this with the purest material it is possible to obtain.



Atomic weight of Glucinum: Calorimeter for determining specific heat of the metal.
(Scale: 5 m/m = 1 c/m.)

West, Newman & Co. lith.