THE ATOMIC WEIGHT OF CALCIUM CONTAINED IN A VERY OLD POTASSIUM-RICH DEPOSIT OCCURRING AT PORTSOY, BANFFSHIRE.

Thesis for the Degree of Ph.D.

Presented by

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CONTENTS

INTRODUCTION.

Physical evidence of the transformation of the K_{41} isotope. 1.

Chemical evidence of the transformation. 5.

EXPERIMENTAL.

Outline of procedure. 8.

Balance and weighing. 9.

Preparation of pure materials. 11.

Extraction of calcium from the mineral and preparation of pure calcium chloride. 17.

Fusion and weighing of the chloride. 22.

Neutrality of the chloride. 26.

Precipation and gravimetric titration. 27.

Typical determination. 34.

Table of results. 37.

DISCUSSION. 38.

SUMMARY. 42.

The Atomic Weight of Calcium contained in a very old potassium-rich deposit occurring at Portsoy, Banffshire.

INTRODUCTION:-

The radioactivity of potassium was discovered by Campbell and Wood (Proc. Cam. Phil. Soc., 14, 15, 1906). Since the β -ray activity shown by all the potassium salts investigated was very small, the suspicion naturally arose that this activity was due to a trace of radioactive impurity and not to the potassium itself. All tests for the presence of an emanation gave, however, negative results and the conclusion was drawn that the observed emission of the β- radiation was a property of the potassium atom itself. The subsequent investigations of Campbell (Proc. Camb. Phil. Soc., 14, 211, 557, 1907) and of Hoffman (Zeit. für Phys., 25, 177, 1924), whose attempts to alter the activity by chemical operations were unsuccessful, supported this conclusion, as did also the work of Biltz and Marcus, who prepared specimens of potassium sulphate from potassium minerals of different geological ages and found that the activity of the preparations per atom of potassium was always the same. Similar remarks apply to the element rubidium which, like potassium, also emits β- rays.

From the rate of emission of β-rays a rough estimate has been made of the half-transformation period of potassium. The measurements are difficult on account of the very slight activity exhibited and the half-value period, 1.5×10^{12} years, put forward by Holmes and Lawson (Phil. Mag. 2, 1218, 1926) after a general survey of the question, is only an approximate one. This estimate based on the assumption that all the atoms of the element are similar in their radioactive behaviour, has now been altered to accord with the results of other work.

Aston had demonstrated that potassium consists of two isotopes of masses 39 and 41 and subsequent experiments showed that only the isotope of mass 41 emits β-rays. Hevesy (Nature 120, 838, 1927) subjected liquid potassium to a series of ideal distillations; the heavy end-fraction was collected and an atomic weight determination by Hönigschmid yielded a value 0.005 unit higher than that of ordinary potassium. The activity of this heavy end-fraction was determined by Biltz and Ziegert (Phys. Zeit., 29, 197, 1928) and found to be about four per cent greater than that of ordinary potassium. It is concluded therefore that the isotope of mass 41 is mainly, if not entirely responsible for the β- radiation of potassium. Now the isotope of mass 41 forms only one-twentieth of ordinary potassium and thus if this isotope is responsible for all the observed activity it will have a half-value period of 7.5×10^{10} years.

Recent work by Muhlhoff (Ann. Phys., 1930, (v) 7, 205), and also by Hevesy, Seith and Pahl (Zeit. Phys. Chem., 1931, Bodenstein Festband, 309), has shown that the above figure is probably too low, their estimate of the half-value period being 1×10^{12} years. In the above paper Hevesy, Seith and Pahl demonstrated, in accordance with their earlier work, that the radioactivity of ordinary potassium could not be ascribed to an isotope of mass 40. Of the two values suggested for the half-transformation period of potassium, very recent work to be described presently tends to support the former estimate of Holmes and Lawson.

Since the emission of a β-particle raises the nuclear charge by one unit, the potassium isotope of mass 41 should change into a calcium isotope of mass 41. Such an isotope is at present unknown; only those of masses 40 and 44 have been recognised experimentally. The important point emerges however, that the existence of this Ca41 isotope might be established by an atomic weight determination on the calcium contained in very old potassium-rich minerals, especially if they contain only a small percentage of calcium, for under these conditions it is quite possible that enough of the potassium isotope of mass 41 had changed into the Ca41 isotope to raise the resultant atomic weight of the calcium above the normal value 40.076.

Turning again to the values proposed for the half-transformation period of K41 we may show that if the former is correct, then since the consolidation of the earth's crust about 0.1 per cent of potassium has changed into calcium, while if the second value is the true one this percentage falls to 0.01.

A magneto-optic method discussed by Allison (Phys. Rev., 40, 1015, 1932) makes possible the detection of Ca41 in potassium from minerals of practically any age. Examination for Ca41 in samples of sylvine disclosed the presence of a minimum of light intensity intermediate in the scale between the minima due to Ca40 and Ca44 and appropriate to Ca41. This minimum presumably due to Ca41 was sought for in fourteen commercial calcium salts and in only six of them was it observed. Thus the minimum is not due to a third isotope of ordinary calcium. Further, prolonged search failed to reveal the presence of a third isotope of ordinary potassium which might be responsible for the activity of the element. Remarkable results were obtained in the determination of the approximate percentage of Ca41, a sample of sylvine from Stassfurt giving a Ca41 percentage of 0.2. All the results obtained by Allison are thus in harmony with the assumption that the transformation product of the K41 isotope is a calcium isotope of mass 41 and that the half-value period is approximately that suggested by Holmes and Lawson.

Accordingly, if a suitable mineral can be found, it should be possible to prove the existence of Ca 41, by showing that the calcium contained in the mineral has a higher atomic weight than ordinary calcium. Further, if the age of the mineral is known then the atomic weight difference, especially if this be large, will furnish a more exact estimate of the half-transformation period of the K_{41} isotope.

Two attempts have been made to discover if these atomic weight differences actually exist, one having been made by A. and O. Frost (Nature, 125, 48, Jan. 1930), and the other by Hönigschmid and Kempter (Zeit. Anorg. Chem. 195, 1 1931). Of these two, only the latter deserves extensive mention since tha atomic weight determinations in the former case were in error to the extent of 0.25 per cent and this was the order of difference found in the atomic weight values.

Hönigschmid and Kempter used as their starting material calcium oxalate derived from sylvine, performing as well a parallel series of experiments with ordinary calcium, following closely the methods due to Richards and Hönigschmid (Jour. Amer. Chem. Soc. 32, 12, 1910) which will be given in detail later.

After a long series of determinations the value, 40.085 ± 0.0006 was put forward as the atomic weight of ordinary calcium.

In the case of the calcium oxalate from sylvine, two precipitations as oxalate preceded the usual method of purification, which was shown to be inadequate since the two mean values found, 40.194 and 40.226, were proved to be in error attributable to the presence of strontium.

Removal of strontium by the only method apparently successful, namely by repeated precipitation as oxalate, led to a final value of the atomic weight of 40.091.

This atomic weight difference, although small, is quite definite. The source of the calcium which yielded this result was sylvine, the age of which has been estimated to be of the order 2×10^8 years: a larger atomic weight difference is to be expected by the choice of a much older mineral. The source of calcium for the present research was pegmatite, the age of which has been given as 6×10^8 years. This mineral had also the added advantage that it contained a large percentage of potassium, and only a very small content of calcium, the actual figures being, potassium 7.5 per cent, calcium 0.20 per cent. (Geological Survey, "Summary of Progress for 1919", pp. 43-44.).

EXPERIMENTAL:-

In determining the atomic weight of calcium, either, or both of the two classical methods used by Stas, Richards and others may be adopted. However, since the object of the present experiment was to determine the magnitude of a possible atomic weight difference it seemed better to employ only the method known to be more accurate, namely, the determination of the ratio $CaCl_2 : 2Ag$. The ratio $CaCl_2 : 2AgCl$ gives less accurate results and the experiments are more troublesome to perform than in the above case. The ratio $CaBr_2 : 2Ag$ might have been measured but the work of Richards (Jour. Amer. Chem. Soc., 32, 12, (1910) demonstrated that the results were scarcely as consistent as with the ratio $CaCl_2 : 2Ag$, and further, hydrobromic acid is more troublesome to prepare in large quantities than hydrochloric acid.

OUTLINE OF THE PROCEDURE:-

A weighed amount of pure, fused, calcium chloride is dissolved in a small quantity of pure water, when colorimetric comparison with a solution of pure neutral calcium chloride of the same concentration indicates the very small correction to be applied for any slight departure from neutrality of the solution of the fused salt. An exactly equivalent quantity of pure silver is weighed out and converted into silver nitrate by the addition of a slight excess of pure nitric acid. The silver nitrate solution diluted to about one per cent strength is then slowly added with constant shaking to the chloride solution, diluted to a liter, and contained in a three liter flask fitted with ground-glass stopper. The silver chloride and solution is allowed to stand for a day after which it is shaken vigorously to coagulate the precipitate and yield a clear supernatant solution. The question as to whether chloride or silver is in excess in the solution is then settled by the use of the nephelometer. When the appropriate correction is made to the weight of calcium chloride or silver, the atomic weight of calcium can be calculated from the numerical value of the weight ratio $2Ag : CaCl_2$, since the atomic weights of silver and chlorine are known.

BALANCE AND WEIGHING:-

The Kuhlmann balance used in the present research was easily sensitive to 0.01 milligram. This balance, with a beam only 70 mm. in length, has a sensitivity practically constant, whether unloaded or carrying its maximum load of twenty grams. As a consequence of the improvement in the methods of grinding the knife edges, due to Kuhlmann, combined with extreme precaution in manipulation, it was found possible to standardize the set of weights according to the methods of Richards (Jour. Amer. Chem. Soc. 22, 144, 1900), with an accuracy of ± 0.005 milligram.

The balance was protected carefully from local sources of heating, e.g., direct incidence of electric light or sunshine, and the temperature of the balance room was maintained at 18° ± 0.5°. The balance was illuminated from a distance of six feet by electric light which had passed through a twenty per cent solution of potassium chromate. Since all weighings were made by substitution, using a counterpoise similar to the object being weighed, the weights required were never large and the influence of changes in atmospheric conditions was nearly always negligible.

Since the specific gravity of the platinum-covered brass weights was 8.3 and the temperature of the balance room was 18° C the following vacuum corrections per gram were applied.

	Density	Vacuum Corrections
Silver	10.49	-0.000030
Calcium Chloride	2.15	+0.000377

The fractional weights were of aluminium of density 2.6 and to them the corrections per gram were:-

	Density	Vacuum Correction
Silver	10.49	-0.000350
Calcium Chloride	2.15	+0.000097

In the case of the correction of brass to calcium chloride and aluminium to silver a graphical relation was drawn up between the barometric pressure and the necessary vacuum correction. In the other two cases this was not done since the corrections are very small.

THE PREPARATIONS OF MATERIALS:-

The most efficient methods of purification may fail to yield a pure product unless extreme care is paid to the exclusion of dust and the various gases sometimes contained in the air of the laboratory. The air of the room was therefore kept as pure as possible, while all operations of transference or evaporation were performed under a large, clean glass plate supported by stout glass rods and placed inside a fume cupboard which had been thoroughly cleaned. When crystallizations had to be performed or solutions evaporated the heating was conducted electrically, the platinum basins used, being placed on pyrex-beakers wound with nichrome ribbon and heated to about 450° . All vessels containing pure materials were always kept covered and under bell-jars when not in use.

The vessels used in purifying materials were nearly always of quartz or platinum. In only one case, and this a permissible one, was pyrex glass used.

Water. The best distilled water of the laboratory was distilled from alkaline permanganate, rejecting the first and last parts of the distillate. The apparatus used was of pyrex, and consisted of a 5 litre flask with ground-in condenser and ground-in receiving flask. The water obtained by this method is absolutely dust-free and suitable for all nephelometric work: it was preserved in 5 litre Jena glass bottles fitted with ground-in stoppers. No water was kept unless its conductivity was below 1×10^{-6} r.o. In special cases, e.g., in the crystallization of calcium nitrate, the water obtained by the above process was distilled and then condensed and collected wholly in quartz, dust being carefully excluded. The water was always distilled as short a time as possible before use.

Nitric Acid. The purest nitric acid of commerce was shaken with a little barium nitrate and silver nitrate to remove possible traces of sulphuric acid and hydrochloric acid. The filtered acid was then distilled from a pyrex flask with ground-in condenser, rejecting the head and tail fractions of the distillate. Two other distillations completed its purification. It was kept in a carefully stoppered Jena glass bottle in a dust-free atmosphere.

Hydrochloric Acid. Traces of hydrobromic and hydriodic acids were removed from ordinary hydrochloric acid by boiling with a little potassium permanganate. The acid was then distilled and condensed in pyrex glass rejecting the first and last portions of the distillate. Another distillation in pyrex followed this. The acid thus produced is pure enough for the preparation of hydrochloric acid gas, but before being used for the conversion of calcium carbonate to calcium chloride it was condensed and collected in quartz vessels.

Ammonium Carbonate. The purest ammonium carbonate obtainable was dissolved in water and then distilled once, using a silica condenser. Any impurities in the resultant product must have been volatile ones and these are not detrimental in the present case.

Ammonium Formate. A. R. formic acid was distilled once, using a silica condenser ground into a litre pyrex flask, and then neutralized with a pure ammonia solution prepared by passing pure ammonia into freshly prepared distilled water.

Calcium Oxide. This substance is used as a support for silver during the fusion of the latter in a current of hydrogen. Its purity is therefore a matter of great importance.

A. R. calcium nitrate was dissolved in water and then boiled with a little calcium oxide to precipitate any trace of iron present. The solution was then passed through a filter of sintered Jena glass and the calcium nitrate crystallized three times from the purest water, with thorough separation of the crystals from the mother liquor each time. The calcium nitrate was then converted into calcium carbonate by means of a solution of ammonium carbonate prepared in the above way. The dried calcium carbonate, packed in long porcelain boats, was then heated in a silica tube to a temperature of 1050° in a current of pure hydrogen. The calcium oxide is thus produced as a firm mass which forms an ideal support for silver.

Silver. The problem of preparing absolutely pure silver was first solved by Richards and Wells (Carnegie Inst. Washington, Publ. 28). The silver prepared by Stas was shown to contain a small amount of oxygen derived from the oxidising flux under which the silver was fused. Of the several methods described by Richards and Wells the following is recognised to be the best and most convenient, and was the one adopted in the present research.

The purest silver nitrate obtainable was dissolved in the minimum quantity of pure water and the solution passed through a sintered Jena glass filter to remove any trace of dust suppended in the liquid. The salt was then crystallized eight times from the purest water, every precaution being taken to exclude dust. The resultant pure silver nitrate, dissolved in pure water, was then reduced to silver by adding hot ammonium formate prepared in the manner described above. The precipitation and also the crystallization of the nitrate were conducted in vessels of pyrex glass. The heavy white precipitate was washed thoroughly with the purest water and then dried at 300° C. As Richards demonstrated, the silver is extremely pure at this stage, the only possible impurity being a trace of silver nitrate occluded during the reduction: this important impurity can be eliminated only by fusion.

The question as to the support for the silver during fusion, as well as the environing atmosphere, was first given a satisfactory answer by Richards and Wells (loc. cit.). As mentioned above, pure lime was found to be the ideal support for the silver, since experiment established the fact that the amount of calcium oxide dissolved by molten silver was less than 0.0001 per cent. The best environing atmosphere was found to be pure hydrogen, for not only is this gas insoluble in molten silver, but it also removes by chemical combination the small amount of oxygen contained in the silver, and derived from the fused, occluded, silver nitrate.

The silver used in the present research was then fused in a wide silica tube in the manner recommended. By marking a series of holes of various sizes on the lime boat, the molten silver was obtained in globules of different weights: these were very convenient when definite quantities of silver had to be weighed out. The pure hydrogen required was obtained by the action of pure hydrochloric acid on A.R. zinc. The gas was passed through two wash-bottles containing copper sulphate solution, through two towers containing soda-lime and finally over a layer of phosphorus pentoxide.

The silver, produced as explained above, was then warmed with pure dilute nitric acid to remove the surface film and dissolve away a possible trace of lime adhering to the surface. This done, the metal was washed many times with pure water and finally dried by heating to 400° in small, covered, pyrex glass beakers supported inside the electrically heated beakers.

As an added test of the purity of the silver, the mother liquors from the sixth crystallization furnished enough silver nitrate to yield twenty grams of silver by the above methods. If these two smaples of silver yield the same ratio $2Ag:CaCl_2$ with two similarly prepared specimens of calcium chloride, this may be taken as convincing proof of the purity of both samples of silver. The metal was preserved in stoppered weighing bottles in a desiccator containing sticks of sodium hydroxide.

EXTRACTION OF CALCIUM FROM THE MINERAL AND PREPARATION OF PURE CALCIUM CHLORIDE.

Since the mineral contains 0.20 per cent of calcium and at least 80gms. have to be obtained, it is clear that a sodium carbonate fusion as a method of extraction is out of the question. A recent article in the patent literature by Calcagni, (Annali Chim. Appl., 1930, 20, 522-527) describes how potassium and aluminium may be extracted from leucite by the action of nitric acid, A method of removing potassium must remove the Ca_{41} produced from it, and since there is a possibility of the preferential extraction of Ca_{41} by this procedure, the effect of various acids on the mineral was tried. A weighed quantity of the finely ground rock was heated with a weighed amount of the acid, and the calcium extracted, determined quantitatively as oxalate. By using three parts of constant-boiling hydrochloric acid, to one part of the pulverized rock, it was found possible to extract 30 per cent of the calcium by boiling the mixture gently for six hours. The other acids gave less satisfactory results.

Enough mineral to yield 180 grams of calcium oxalate was then heated in kilogram portions with the necessary amounts of hydrochloric acid, in five litre pyrex flasks fitted with reflux condensers. The extract with the excess acid was decanted off and the residue washed twice with distilled water. The excess acid was then distilled off, the solution diluted and the iron precipitated by adding to the hot solution a slight excess of dilute ammonia. The filtrate, made slightly acid, was saturated with chlorine and the trace of iron left was precipitated by again adding a slight excess of ammonia to the hot solution. It was found that the iron could be removed completely only by this process, involving as it does, the oxidation of the trace of ferrous salt to the ferric state. The calcium was then precipitated from the filtrate by the addition of a hot dilute solution of A.R. ammonium oxalate in the usual analytical manner.

When about 180grams of calcium oxalate had been obtained in this manner, the process of purification was started. Since no barium or strontium was found in the complete analysis of the mineral, the main impurity present at this stage is magnesium oxalate. This may easily be eliminated by reprecipitation of the oxalate because the magnesium salt is much more soluble in water than the calcium one. The calcium oxalate was therefore dissolved in hot distilled water containing the minimum quantity of A.R. hydrochloric acid and precipitated again by the slow addition of dilute A.R. ammonia. After settling, the precipitate was well washed with distilled water and then filtered off. The process was repeated another four times, taking every precaution to exclude dust.

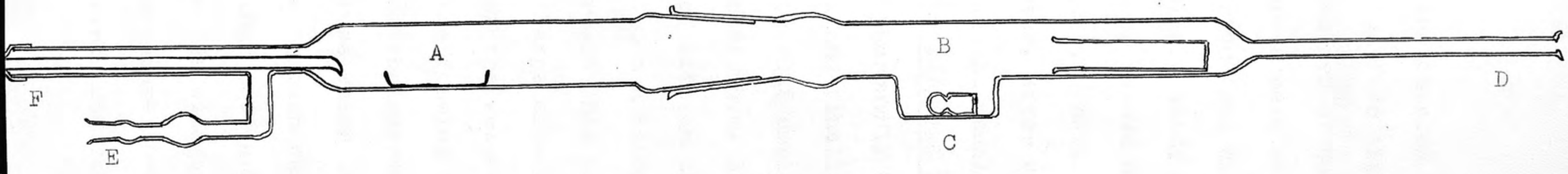
The calcium oxalate is now very pure, all the magnesium being completely removed. Further the above procedure was shown by Hönigschmid and Kempter (loc. cit.) to lead to the complete removal of traces of barium and strontium, so that even if the original calcium oxalate had contained traces of these elements they would now be absent in the final product. The oxalate was then converted into the oxide by heating to 700° in platinum basins. The oxide was transformed into the nitrate by the addition of pure nitric acid, and the resulting solution was filtered through the Jena glass Gooch crucible.

A trace of titanium is present in the mineral and a faint possibility exists that the oxalate precipitations may have failed to remove it. The most delicate chemical tests failed, however, to indicate its presence. Nevertheless the solution of calcium nitrate was electrolysed for 24 hours using pure platinum electrodes and a very small current: it was then filtered and the calcium nitrate crystallized five times using the purest water. From the time of the electrolysis to the production of pure calcium chloride, the calcium salts came into contact with nothing but platinum or silica. The pure calcium nitrate was next dissolved in water and calcium carbonate precipitated by adding a slight excess of distilled ammonium carbonate solution. As Richards (loc. cit.) pointed out, the well washed carbonate if heated to 300° is absolutely pure except for a trace of calcium nitrate brought down during the precipitation. This trace of nitrate may easily be removed in the following manner.

The calcium carbonate is dissolved in the minimum quantity of pure, dilute hydrochloric acid and reprecipitated by adding a slight excess of ammonium carbonate solution. The well-washed precipitate is again dissolved in hydrochloric acid and the above process repeated. The carbonate, heated to 300° in platinum basins to remove traces of volatile ammonium salts, is then converted into the chloride by adding an equivalent quantity of pure hydrochloric acid. The filtered chloride solution is then evaporated in a dust-free atmosphere and the crystals of calcium chloride produced are then dried by placing in a desiccator containing lime and evacuated by means of a Hyvac pump. This last filtration is very necessary, for in spite of all precautions an extremely small amount of dust may have found its way into the preparation. The filtering medium was pure finely-divided platinum contained in a platinum Gooch crucible.

For the reasons given above, another sample of calcium chloride was prepared in a similar way from the calcium nitrate occurring in the mother liquors from the third crystallization. By leaving the calcium chloride in the vacuum desiccator for a few weeks at a temperature below its transition point, 29°, the substance received a preliminary drying which enables it to be heated and fused, without spattering, during the atomic weight determinations. During all these operations the greatest care was taken to exclude dust and the various gases present as impurities in the atmosphere: in the case of the carbonate this is especially important and it was preserved in a platinum basin, in a desiccator containing lime made from the purest marble.

The source of normal calcium was Bermuda limestone. Except for a preliminary incineration to remove the organic matter present, followed by filtration, the procedure for obtaining two pure specimens of calcium chloride was the same as that given above for the calcium chloride from the mineral. In the case of the limestone, however, the nitrate was crystallized four times and the confirmatory sample was taken from the mother liquors from the third crystallization. If both of these samples of calcium chloride give the same atomic weight, then an even stronger case is made out for the purity of the calcium chloride from the



BOTTLING APPARATUS FOR THE FUSION OF CALCIUM CHLORIDE.

rock, as the calcium nitrate from the mineral was crystallized five times.

A specimen of Ca Cl_2 was also prepared for preliminary atomic weight determinations. Calcite was converted into calcium nitrate by the addition of A.R. nitric acid; the solution was then boiled with lime to remove any trace of iron and filtered. The nitrate was next crystallized six times using the purest water, after which it was converted into the chloride in the usual way.

FUSION AND WEIGHING OF THE CHLORIDE.

The thoroughly effloresced chloride was further dehydrated and finally fused in a piece of apparatus similar to that employed by Richards and Willard (Jour. Amer. Chem. Soc., 32, 4, 1910), for the melting of lithium chloride.

The tube A is of quartz, one inch in diameter and is ground into the pyrex glass tube B containing a bulb C large enough to hold the ground-glass stopper of the weighing bottle used, the weighing bottle itself being placed in the position indicated. The end of the narrow tube D is carefully ground into another tube which is sealed on to the system of purifiers through which the entering gases pass. The platinum boat containing the calcium chloride is heated in the wide quartz tube and the gases passing through A escape through the end of E, which is ground into a pyrex tube connected to an absorption tower.

The end of tube F is fitted with a small piece of rubber tubing and through this passes the glass rod employed for pushing the platinum boat into its weighing bottle. By rotation of the tube B the stopper can also be inserted in the weighing bottle. By the use of this simple piece of apparatus the calcium chloride can be dried, fused and finally preserved for weighing in the appropriate gas atmosphere.

The calcium chloride contained in the platinum boat was slowly heated to a temperature of about 400° in a current of pure nitrogen. The latter was obtained by passing ordinary cylinder nitrogen through a long tube packed with bright copper gauze and heated to about 600°, through an alkaline solution of pyrogallol and over solid sodium hydroxide, after which the gas was passed through glass beads moistened with sulphuric acid and finally over phosphorus pentoxide. After an hour all the air in the tube had been displaced and the salt was practically free from water. By turning the appropriate stop-cock pure dry hydrochloric acid gas was next admitted and as soon as all the nitrogen had been displaced the temperature of the chloride was raised to its melting point, about 800°.

The pure hydrochloric acid gas was obtained by dropping concentrated sulphuric acid into pure hydrochloric acid and drying the gas by passing through wash-bottles containing glass beads covered with concentrated sulphuric acid. Phosphorus pentoxide was not used for drying this gas. The acid gas was, of course, passed through the apparatus in an all-glass train, ground-glass junctions being employed throughout.

After fusion for fifteen minutes nitrogen was again passed through the tube and the chloride was kept in the molten condition until the greater part of the acid gas had been displaced. The fusion was then continued in nitrogen for another five minutes. As Richards and Hönigschmid proved, this last precaution prevents the somewhat explosive crystallization of the chloride on cooling.

When the chloride had cooled to about 100° the nitrogen was displaced by a current of pure air obtained by passing laboratory air through purifiers containing solid sodium hydroxide, concentrated sulphuric acid and finally phosphorus pentoxide. After forty five minutes the boat and its contents were pushed into the weighing bottle and the stopper inserted. The weighing bottle was then transferred to a desiccator (containing pure lime) which was allowed to stand near the balance for six hours before weighing.

In order to avoid the errors introduced by weighing under varying meteorological conditions, a weighing bottle similar in every respect to the above weighing bottle was employed as counterpoise.

The empty platinum boat had previously been treated in the same way as during a fusion of calcium chloride. The weighing bottle employed as counterpoise contained a small piece of rounded glass rod which thus brought up its weight to almost exactly that of the other weighing bottle plus the empty platinum boat. The weight of the calcium chloride is then found as a difference which is independent of atmospheric conditions.

The platinum boat was attacked to a slight extent by the hydrochloric acid gas during the fusion. The average loss in weight during an experiment was, however, only 0.08 milligram, and as Richards pointed out this amount of platinum very probably reverted to the metallic state during the fusion in the neutral atmosphere. The original weight of the boat was therefore taken as the true one. After weighing, the calcium chloride was transferred to a wide-necked, 250 cc pyrex-glass flask with a ground-in stopper, the weighing bottle and its stopper being thoroughly washed with about 150 cc of the purest water.

NEUTRALITY OF THE CALCIUM CHLORIDE.

As might be anticipated, calcium chloride fused in the above manner is not absolutely neutral. If the chloride is fused for a long time in hydrochloric acid gas and only a relatively short time in nitrogen, the calcium chloride reacts slightly acid on account of a trace of dissolved hydrogen chloride. Fusion for a long time in nitrogen leads to a very slight alkalinity on account of the presence of a trace of oxygen in that gas, and the resulting formation of an extremely small amount of calcium oxide. In both cases, however, the departures from neutrality are so slight that they can be accurately estimated only by colorimetric comparison with a neutral calcium chloride solution of the same concentration. The neutral chloride solution was prepared by crystallizing A.R. calcium chloride three times from the purest water. Such a solution is presumably neutral, for there is no evidence that either calcium oxide or hydrochloric acid tend to go into the crystals of calcium chloride to any appreciable extent.

The procedure is then straightforward. The neutral calcium chloride solution is prepared from the appropriate volume of the standard solution, which is then diluted to the same volume as the fused chloride solution. 10cc. of aqueous methyl red prepared from pure water and A.R. methyl red are then added to each of the two solutions and the colours equalised by adding either extremely dilute standard nitric acid or potassium hydroxide. The volume added gives an exact measure of the acidity or alkalinity of the fused chloride.

In the colour adjustment of the two solutions it was always possible to judge the amount of nitric acid to be added correctly to within two drops, which, with the solutions dealt with, meant a correction accurate to 0.01 milligram. The fused chloride always exhibited a very slight alkalinity because of its fusion for a short time in nitrogen but the average correction to the weight of chloride was only 0.3 milligram. The chloride solution was then transferred to a three litre pyrex-glass conical flask fitted with a well-ground glass stopper. A 12 centimetre filter-funnel placed in the neck of the large flask minimised the risk of loss of chloride solution during this operation. After thorough washing of the small flask and filter-funnel the solution in the three litre flask was diluted to a volume of about one litre.

PRECIPITATION AND GRAVIMETRIC TITRATION.

Silver in amount exactly equivalent to the quantity of calcium chloride in solution was weighed directly on the balance-pan and then carefully transferred to a litre pyrex-glass flask, whose ground-in upright condenser contained a series of bulbs which eliminated the possibility of loss of silver during its solution in the slight excess of pure dilute nitric acid. The equivalent quantity of silver could easily be weighed out almost exactly by choosing a series of suitable pieces of the metal. The last few hundredths of a milligram of silver were always added in the form of an extremely dilute standard solution, which in this case was one containing one milligram of silver in ten cubic centimetres of solution. When the nitric acid had been added to the silver in the flask, the condenser was inserted and the vessel gently warmed by placing it on a water-bath containing distilled water at 60°. After solution the temperature of the water-bath was raised to 95° in order to expel nitrous vapours, and the solution was then diluted to about 600 cc with water whose conductivity had been taken just before use. The water employed for diluting was, of course, also used for washing thoroughly the upright condenser and the sides of the flask.

The precipitation of silver chloride is then conducted in the red light of the dark room. The silver solution is added very slowly with continuous shaking to the chloride solution. Slow addition is very necessary because of the danger of the occlusion of silver nitrate by the precipitate of silver chloride. However, since the solutions were very dilute and every precaution was taken during the precipitation, the possibility of error in this connection was reduced to a minimum. When all the silver solution has been added, the flask and filter-funnel are thoroughly washed with about 500 cc of the purest water, the sides of the flask warmed with the bands and the stopper carefully inserted. When the stopper is withdrawn later the pressure difference caused by warming the flask prevents the expulsion of drops of solution held in the control space between the stopper and the neck of the flask. The flask is shaken very gently for another two minutes to promote complete mixing of the reactants and then allowed to stand 24 hours inside a black box in the dark room. Violent shaking is not practised at this stage, because this causes the precipitate to aggregate into impenetrable masses which may retain traces of either calcium chloride or silver nitrate. By leaving for 24 hours, however, time is given for the washing out of any excess of either reagent held by the spongy precipitate and equilibrium is established between the solution and the silver chloride.

The closely-stoppered flask is next shaken violently for fifteen minutes. This causes the precipitate to cohere and deposit itself completely after standing for a short time so that after cooling the flask for 24 hours in ice a perfectly clear supernatant liquid results. By cooling, the solubility of the silver chloride is greatly reduced and this leads to a more accurate determination of the end-point by the equal-opalescence method.

This method depends on the fact that pure silver chloride solution in presence of electrolyte, e.g., nitric acid, or calcium nitrate, gives equal turbidities with equivalent quantities of silver nitrate or calcium chloride, provided sufficient time is allowed for the formation of the opalescence. Stas adopted the method in his determination of the atomic weight of sodium, but it gave unsatisfactory results because he was unaware of the latter condition: only after the work of Richards and Wells (loc. cit.) was this method of estimating the end-point shown to be extremely accurate. These investigators proved (1) that an excess of electrolyte must be present, for this brings about the coagulation of the colloidal silver chloride and (2) that time must be given for the formation of the maximum opalescence, because in some instances the turbidities develop at different speeds. The time allowed must not, however, be too long, otherwise the precipitate may settle, when its presence can obviously not be detected by the nephelometer.. A time of five to eight hours is in general sufficient.

The nephelometer used in making the measurements was of the standard Klett type, special tubes being made for holding the test solutions. These were made from thin-walled flat-bottomed tubes, three inches long and three-quarters of an inch in diameter, whose ends were covered by close-fitting black vulcanite caps which, besides preventing light from being reflected through the bottoms of the tubes, formed also admirable supports for them when placed in the nephelometer. The vernier scales on the instrument gave measurements of the lengths of the columns of liquid accurate to 0.5 millimetre.

The accuracy with which the end-point can be determined by this method is almost inversely proportional to the concentration of the silver chloride remaining in solution after the precipitation, because the percentage accuracy of the nephelometer does not increase with increasing cloudiness. The solubility of silver chloride in water is four times as great at 34° as it is at 1.5° and it found that at this lower temperature the opalescences are so faint that the slightest excess of silver or calcium chloride is unmistakably evident.

The procedure is then a straightforward application of the foregoing principles. The stopper is removed from the precipitation flask and 10cc. of the clear supernatant solution pipetted off into each of four nephelometer tubes. The stopper is replaced and the flask again immersed in the cooling bath. To each of two of the tubes one cubic centimetre of standard silver solution is added, and to the other two an equal volume of standard calcium chloride solution. The silver solution used in this work was prepared from the pure metal and pure nitric acid and contained one milligram of silver in one cubic centimetre of solution. The chloride solution prepared from the pure, fused salt was of an equivalent concentration. Each of the four test solutions was then stirred the same number of times with thin glass rods, after which the tubes were immediately covered with a small glazed-earthenware jar. This protects the solutions from all traces of light and, what is much more important, keeps them free from dust and the resulting serious errors. The nephelometer, as Richards pointed out, can easily detect 1/3000 of a milligram of chlorine, and a single mote of dust may contain this amount. Although during all the above processes active light had been carefully excluded, Richards and Wells (loc. cit.) proved that the end-point was exactly the same whether the silver chloride was pure white or had turned bluish by exposure to diffused daylight. By doing the tests in duplicate as mentioned above, much greater reliance may be placed on the results, for although there may be anomalous behaviour in the case of two of the tubes, it is not likely to be repeated in the other pair. If the observations on both sets accord as was usually the case, it is practically certain that each result is correct. A time of about five hours was allowed to elapse before the measurements were taken.

Two of the tubes are then placed in the nephelometer and moved until the plungers of the instrument are just beneath the surface in each case. A glance through the eye-piece shows at once which solution is more turbid. The opalescences are then adjusted to equality by moving one or other of the two tubes. In only one or two instances was this ratio not within the value 100:80. Because the volume of solution in the flask was about two litres and the temperature of the liquid was kept at about 0°C. the amount of silver or calcium chloride which had to be added to bring this ratio to the value 100:100 was practically constant, being either 0.2 milligram of silver in the form of silver nitrate solution, or the equivalent weight of calcium chloride. A ratio 100:90 was similarly adjusted to absolute equality by the addition of about 0.07 milligram of silver to the solution in the flask. This knowledge considerably hastened the completion of each experiment. When the ratio has been determined unequivocally, the appropriate amount of either silver or chloride solution is added to the 3 litre flask, which after vigorous shaking for five minutes to ensure thorough mixing is then packed in ice for 24 hours. The determinations are again carried out and the experiment is finished when both pairs of tubes give the same ratio to within two per cent; and this ratio falls in the region 100:97 to 100:100.

A simple calculation indicates the small correction which has to be applied to the weight of calcium chloride or silver, and the atomic weight of calcium is then found from the expression

$$A = \frac{215.76 \times w_1}{w_2} - 70.914$$

where A is the atomic weight of calcium, 215.76 twice the atomic weight of silver, 70.914 twice the atomic weight of chlorine, w_1, the weight of calcium chloride and w_2 the weight of silver.

TYPICAL DETERMINATION.

The calcium chloride used in this experiment was derived from Bermuda limestone, the calcium nitrate having been crystallized four times from pure water.

Weight of fused chloride in vacuo = 1.74559 grams.

Correction for alkalinity of the chloride = 2.10cc nitric acid.

For ease in calculation this pure nitric acid was made to contain an amount of acid per cubic centimetre equivalent to 0.1 milligram of chloride ion. Since the alkalinity of the chloride is due to the presence of calcium oxide, 2.10cc of the standard acid indicated 0.00016 gram of calcium oxide. This calcium oxide had no influence on the precipitation since it was at once converted into calcium nitrate by the excess of nitric acid also present.

Thus corrected weight of calcium chloride in vacuo = 1.74543. grams.

Amount of silver weighed out (in vacuo)=3.39301gms. 40cc. of the clear supernatant solution were then withdrawn for nephelometric tests as explained above. From the results obtained the mean value of the ratio was found to be 100:88, the tubes containing the excess of silver having the greater opalescence. A slight excess of chloride was therefore present in the solution in the precipitation flask. 1cc. of standard silver nitrate was added to this solution, after which the flask was shaken violently for five minutes and then immersed in the cooling bath for 24 hours. Another 40cc. of the liquid were withdrawn for tests and this time the ratio 100:98 was obtained as the mean value of the observations on both pairs of tubes.

Volume of solution in the precipitation flask = 1820cc.

Now 1cc. of silver nitrate solution (i.e., 0.1 milligram of silver) was added to the flask when the latter contained 1859cc. of solution, and the original volume of the solution was 1899cc.; hence the weight of silver required to neutralize the total excess of calcium chloride was $0.1 \times \frac{1899}{1859}$ milligram.

Thus 3.39311 grams of silver are equivalent to 1.74543 grams of calcium chloride.

Substituting in the above expression,

Atomic weight of Calcium = 40.074.

The following table gives the results obtained with the various samples of calcium chloride prepared as mentioned above.

Sample A is from calcite, B and C from Bermuda limestone, D and E from pegmatite. B and C are from third and fourth crystallisations of the nitrate, and D and E from fifth and third crystallisations respectively.

Sample of Silver	Sample of Calcium Chloride	Weight of Calcium Chloride in vacuo.	Weight of Silver in vacuo.	Atomic Weight of Calcium.
1	A	1.73315	3.36509	40.082
		1.76657	3.43399	40.081
		2.08000	4.04339	40.081
1	B	1.77727	3.45491	40.077
		1.82493	3.54743	40.080
	C	1.81606	3.53030	40.077
		1.74543	3.39311	40.074
		1.75771	3.41695	40.075
1	D	1.70015	3.30465	40.089
		1.78487	3.46928	40.090
2		1.74779	3.39721	40.090
		1.69538	3.29562	40.087
1	E	1.87366	3.64188	40.089
		2.07253	4.02853	40.086

DISCUSSION:)

The results in the preliminary series were consistent, and the two samples of silver gave results essentially identical, thus establishing the purity of the metal. Samples B and C, D and E, yielded values of the atomic weight concordant to within the limit of experimental error. This may be taken as strong proof of the purity of all the calcium chloride used in the atomic weight determinations. The mean value of the atomic weight of ordinary calcium is 40.077 with a probable error of 0.0007 as calculated by means of the expression,

$$R = \frac{0.8453 \sum(+v)}{n(n-\ )^{\frac{1}{2}}}$$

where $\sum(+v)$ denotes the sum of the deviations of every observation from the mean, their sign being disregarded, R the probable error of the mean, and n the number of observations.

This estimate is very close to the value 40.074 put forward in 1910 by Richards and Hönigschmid (loc. cit.) but is noticeably different from the number 40.084 advanced by Hönigschmid and Kempter in 1931. These latter investigators, however, purified their ordinary calcium by a method which, as they themselves pointed out, failed to remove the last traces of strontium. There is a possibility therefore, that the value 40.084 is slightly high because of a small content of either strontium or barium. The calcium which gave the value 40.077 was purified by repeated precipitation of the oxalate, a procedure which Hönigschmid and Kempter proved to eliminate all strontium and barium.

The slightly high value obtained by Hönigschmid and Kempter could also be explained by assuming that the source of their calcium, viz., marble, had at some time been associated with deposits of potassium minerals and thus had acquired a very small amount of Ca_{41}. The average value, 40.081, obtained as the atomic weight of calcium from calcite shows that this possibility, although slight must be considered. The particular advantage of using Bermuda limestone as a source of normal calcium, rests in the fact that this substance is of oceanic origin and is thus comparatively recent. Since the ratio of potassium to calcium is much smaller than in the case of most mineral deposits, and because of the continuous circulation of the ocean waters, the limestone is elaborated by the marine organisms from what is essentially an average world calcium of recent origin.

The atomic weight of the "heavy" calcium is 40.089 ± 0.0004. The difference between these two values, 0.012 ± 0.001, is probably correct to within ten per cent and points to the fact that a partial transformation of K_{41} into Ca_{41} has taken place.

Using the above figures it becomes possible to calculate the numerical limits of the half-transformation period of the K_{41} isotope. If the percentage of Ca_{41} in the rock is w, which is found from the expression,

$$A = \frac{(0.20 - w) \times 40.077 + 41 w}{0.20}$$

A being the resultant atomic weight of all the calcium in the mineral, 0.20 the percentage of calcium and 40.077 the atomic weight of normal calcium; 6×10^{8} years the age of the rock, 0.067×7.5 the percentage of K_{41} in the mineral, then λ the half-value period is found from the expression,

$$\lambda = -\frac{2.303 \times 0.693 \times 6 \times 10^{8}}{\log_{10}\left(1 - \frac{w}{0.067 \times 7.5}\right)}$$

The treatment of the mineral led to the extraction of only one third of the available calcium, and the possibility exists that Ca_{41} was preferentially removed during this process: this assumption of the complete extraction of Ca_{41} and only partial removal of ordinary calcium leads to the value 1.3×10^{12} years for the half-period of K_{41}. The other limit 4.3×10^{11} years is obtained in a similar way by postulating that all the calcium in the rock has the atomic weight 40.089. Actually the true half-value period probably lies between these two estimates which, based as they are on the age 6×10^{8} years, of the pegmatite from Portsoy, confirm the results obtained by Hevesy, and by Muhlhoff (loc. cit.).

The results obtained by Mr. T.Tait, who has been engaged on a similar research, confirm all the above values. The source of normal calcium in this case was sea-shells, and the mineral employed to yield "heavy" calcium was a felspar occurring at Rhiconich, which contained 0.20 per cent of calcium and 7.8 per cent of potassium. The age of this rock had been estimated to be 1×10^{9} years. The two series of results are given in tabular form, those given under (2) referring to the numbers obtained by Mr. Tait.

	(1)	(2)
Normal Calcium.	40.077	40.076
"Heavy" Calcium.	40.089	40.092
Half-value Period.	4.3×10^{11}, 1.3×10^{12} years.	7.4×10^{11}, 2.2×10^{12} years.

The age of the pegmatite from Portsoy has been the subject of several discussions among geologists, but the above evidence tends to show that its age is of the same order as that of the felspar from Rhiconich, i.e., definitely pre-Cambrian.

If the difference 0.012 in the atomic weight values were partly due to the presence of strontium or barium, the estimate 7.5×10^{10} years of Holmes and Lawson is even more definitely precluded. It is intended to study the latter point in detail by deliberately adding small quantities of barium and strontium salts to ordinary calcium nitrate solution, purifying the nitrate and chloride by the methods given under experimental, and then determining the atomic weights of the specimens prepared.

SUMMARY:-

(1) The atomic weights of ordinary and "heavy" calcium have been determined and found to be 40·077, and 40.089 respectively, the latter value indicating that a partial transformation of K_{41} into Ca_{41} has taken place in the mineral investigated.

(2) The numerical limits, 1.3×10^{12}, 4.3×10^{11} years, have been suggested for the half-transformation period of the K_{41} isotope.

In conclusion, I desire to thank Professor Kendall, Sir James Walker, Dr. Frederick Walker and Professor Briscoe for helpful advice and criticism received during the research.