periments, corresponding to an atomic weight for calcium of 40.074, if silver is 107. 88.

This value equals almost exactly the average of all the Harvard work upon the subject, 40.075, and may be taken for the present as the most probable atomic weight of calcium.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

A DETERMINATION OF THE RATIO BETWEEN CHLORINE AND BROMINE AND SODIUM.

BY JACOB S. GOLDBAUM.

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Introduction.

Before the National Academy of Sciences, Wolcott Gibbs, in 1880, first suggested the use of mercury as cathode in electro-analysis. His experiments, although purely qualitative, were sufficient to indicate the correctness of the principle involved. The subsequent development of the mercury cathode cell in metal determinations furnishes an important chapter in the history of analytical chemistry, but it is to its extension into the domain of anion estimation that especial attention is now directed.

Vortmann[1] and later Specketer[2] had published brief accounts of halogen fixation, but the activities of Edgar F. Smith and his students in the use of an attackable silver anode with a mercury cathode, made for sure and steady advance in this phase of our science. Within the last decade much has been published of results obtained in this laboratory in the analysis of alkali and alkaline earth salts, with particular emphasis upon the halides of these metals. The advent of the "double cup" as devised by Hildebrand was important and timely. By its use many analyses and separations of decided interest have been effected, as is evident by reference to the work of Hildebrand,[3] McCutcheon,[4] McCutcheon and Smith,[5] Lukens and Smith,[6] Kollock and Smith,[7] and Goldbaum and Smith.[8]

Extreme accuracy has always been a feature of the values obtained in the papers mentioned above. It seems, however, that in the hands of other investigators, difficulty in duplicating results is being encountered

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[1] *Elektrochem. Z.*, **1**, 137.

[2] *Z. für Elektrochem.*, **4**, 539.

[3] THIS JOURNAL, **29**, 447.

[4] *Ibid.*, **29**, 1445.

[5] *Ibid.*, **29**, 1460.

[6] *Ibid.*, **29**, 1455.

[7] *Proc. Am. Philos. Soc.*, **46**, 341.

[8] THIS JOURNAL, **30**, 1705; **31**, 900; and **32**, 1468.

from time to time. In the manipulation of the method there are many points of detail that heretofore have not been fully discussed. These have been more thoroughly studied in the present work. It is hoped that with the publication of this paper the mode of procedure will be made clear and the reliability of the method established beyond further doubt. This paper aims to indicate the application of electrolysis in general, and of the method in particular, to the highly exacting field of atomic weight work, itself the severest test to which any analytical procedure can be subjected. Full appreciation is held of the remarkably trustworthy character of the present values of the atomic weights of the halogen elements. It was, therefore, not in a spirit of revision, but rather with the idea of attacking the problem from an entirely different and novel standpoint that this work was undertaken.

Fundamentally the principle employed is extremely simple. An aqueous solution of common salt, for example, is electrolyzed with a weighed silver anode and mercury cathode. Sodium as cation forms an amalgam, chlorine attaches itself firmly to the silver, and the increase in weight of the anode represents the halogen content of the salt. In his monumental work on atomic weights, Berzelius always laid especial stress on "simplicity of analysis or synthesis of the simplest compounds." This dictum furnishes the keynote of the present investigation.

The many publications of atomic weight values of chlorine and bromine made within quite recent years contain admirable résumés of all methods heretofore employed, together with a listing of the results obtained by various investigators. It is hence deemed unnecessary to adopt a like procedure in this paper, and reference to "A Recalculation of the Atomic Weights," by F. W. Clarke,[1] is recommended.

Experimental Part.

Apparatus.—The electrolytic cell resembles in principle that used in the Castner-Kellner process for the decomposition of salt. It consists of a glass crystallizing dish 16 cm. in diameter, 6 cm. high, in which is placed a bottomless beaker 5 cm. high and 7 cm. in diameter. An equilateral triangle of thin glass rod with one angle left open acts as a spring to hold the beaker firmly in the center of the outer dish and likewise permits of easy adjustment of the lower rim of the beaker to within about 4 mm. from the bottom of the crystallizing dish. A layer of mercury 1 cm. in thickness (depth) placed in this immediately forms a two-compartment cell with the mercury as a seal. Extending around the inside of the outer compartment, about 1 cm. above the level of the mercury, is a ring of platinum wire holding a prong of the same metal which dips in the mercury. A stout platinum wire, partially encased in glass and held in position by a support clamped to a glass stand, serves as cathode connection for the

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[1] Smithsonian Institution Publication, 1910.

mercury with the negative pole of the circuit. The cell is covered with two semi-circular, well-fitting glass plates. The center of each plate is notched and ground to admit the anode when the cover glasses are in position. Actual contact of the ground glass with the platinum anode is prevented by a protective platinum foil.

Special attention must be paid to the form of anode used. As finally adopted this consists of three circular discs of platinum gauze 5 cm. in diameter and 30 meshes per cm., the circumference of each being slightly fused. They are mounted 8 mm. apart on a platinum rod 1 mm. in diameter and 10 cm. long which passes through the centers of the discs perpendicular to them. The silver plating of the anode will be discussed later. Rotation of the anode is accomplished by fastening it into the shaft of the special kind of motor used for all rotating work in this laboratory.[1] The chuck of the shaft with which the anode came in contact is lined with new platinum foil. The shaft of the motor is connected by ordinary annunciator wire to the positive pole of the battery.

A Weston milliammeter, a Weston voltmeter (graduated to 0.5 v.) and a very efficient Ward-Leonard rheostat are placed in the circuit. The current is derived from a battery of ordinary storage cells.

An electric oven for drying the anode was constructed as follows: Two ordinary iron tripods were fastened bottom to bottom to form a hollow cylinder 22 cm. long and 8 cm. in diameter. "Nichrome" ribbon, $^1/_{16}$ inch wide, 0.0035 inch thick, with a resistance of 2 ohms per foot, was then wound round the asbestos-insulated tripod rods, and the cylinder, with suitable precautions, covered with previously ignited sheets of asbestos. The whole was subsequently placed in a wooden box 28 cm. high and 20 cm. square. On the bottom of the box were four stout corks on which rested a square of asbestos board. The oven was placed on this, and the sides of the box tightly packed with a mixture of plaster of Paris and calcined magnesia. The bottom of the oven proper was covered with a sheet of ignited muscovite and the interior space of the oven protected from the "nichrome" wire by sheets of the same material. Mica likewise formed the cover of the heating device. The oven had a resistance of 60.0 ohms, so that when connected with the ordinary lighting circuit of 110 volts d. c., it gave a temperature suitable for the purpose. This temperature was, of course, cumulative, and in the course of two hours rose steadily to 400°. The insulation served so well that the encasing wooden box was at all times comfortable to the touch. By means of an ordinary screw clamp held on a retort stand, the anode may be lowered into the clean interior of the oven. New platinum foil protected the rod of the anode from the iron screw clamp.

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[1] See Smith's "Electro-Analysis," 4th ed., p. 58. The motor used was of the type listed by Greiner and Friederichs as No. 2159.

A nephelometer as devised and described by Richards and Wells[1] served to determine the amount of dissolved silver halide.

The balance used was of an excellent Troemner design. It was kept in a room isolated from the rest of the laboratory. Successive weighings on it of the same object gave concordance to within 0.03 mg. The weights used were of exceptionally good make, the corrections as applied from the calibration according to the method of Richards[2] being quite small.

Preparation of Pure Materials.

Water.—The distilled water of the laboratory, on examination, contained no chlorides. Traces of organic matter present were destroyed by redistillation from a weakly alkaline permanganate solution, using a block-tin condenser. The first part of the distillate was rejected and the subsequent portions collected in Jena flasks. This water was then again distilled just as needed and was never in contact with the glass for more than twenty-four hours before use.

Sodium Chloride.—Richards and Wells[3] have conclusively shown that the preparation of pure sodium chloride is comparatively easy. The sodium chloride used in this work was obtained from the J. T. Baker Company and was of exceptionally high grade. It was dissolved in pure water and saturated with HCl gas (made from the purest commercial hydrochloric acid and pure concentrated sulfuric acid). The crystals of sodium chloride were then filtered and separated from the mother liquor by centrifugal drainage, using a very efficient home-made centrifuge. They were again dissolved and the entire operation twice repeated. After centrifuging on a large platinum cone, the salt was crystallized four times from platinum and then the dry material was fused in platinum, with the aid of a blast lamp, the products of combustion being suitably deflected. The clear, colorless salt was removed in lumps about the size of a pea and preserved in weighing bottles with well-fitting stoppers.

Sodium Bromide.—The purest bromide furnished by the J. T. Baker Chem. Co. was used as the source of raw material. On careful examination it was found to be free of sulfates, phosphates, carbonates, bromates and iodides, and to contain but a faint trace of chloride. A comparatively large amount of suspended iron was found. This was easily removed by filtration. The filtrate was colorless and free of iron. The sodium bromide from it was recrystallized in platinum six times, each time with efficient centrifugal drainage. Examination at this point failed to reveal any chloride, and the colorless crystals were then recrystallized eight more times from pure water. The salt was now regarded as pure.

It was fused in platinum, and while quite hot was removed from the

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[1] *Am. Chem. J.*, **31**, 235.

[2] THIS JOURNAL, **22**, 144.

[3] *Ibid.*, **27**, 459.

crucible and quickly placed in very warm, dry weighing bottles. Absolutely clear, colorless, brilliant lumps of bromide, somewhat larger than the size of a pea, were obtained and preserved. The hygroscopic nature of sodium bromide necessitated this procedure and the clarity of the lumps of bromide was an indication of its sufficiency.

Silver Nitrate.—The purest silver nitrate obtainable was recrystallized three times in platinum. This was regarded as sufficient for nephelometric work, since values obtained by its use were solely relative.

Nitric Acid.—This was kindly furnished by Dr. W. H. Chapin, who had purified it for his work on the "Atomic Weight of Tantalum." It was entirely free of chlorides.

Ammonium Oxalate.—The colorless crystals of commerce were dissolved in pure water and recrystallized twice.

Ammonia Water.—Ordinary ammonia water was heated and the vapors absorbed in pure water.

Mercury.—Ordinary distilled mercury of commerce was thoroughly washed with potassium dichromate and sulfuric acid, then dried and doubly distilled in Hulett and Minchin's glass distilling apparatus.[1]

Preparation of the Silver Anode.—In the previously published work on anion determinations with the double cup and silver anode, the anode was prepared by plating the gauze discs in a bath of $KAg(CN)_2$ under a voltage of five and an amperage of one. The anode was then washed with water, dried and gently heated, after which it was ready for a determination. Examination by the writer showed that with this procedure there was still some possibility of enclosed cyanide, and so the expedient of dipping the plated gauze in dilute HCl was tried. The HCl formed KCl, which was easily washed out with distilled water. The gauze was then heated to incipient redness and was ready for weighing. Repeated tests showed no trace of soluble matter. The weighed anode could be immersed in boiling water, and re-ignited, without showing any loss in weight, and since after electrolysis the weight of the halogen is determined directly by difference, the above method of preparing the anode plate was obviously satisfactory. However, for the final work in this investigation, recourse was had to the double oxalate of silver and ammonia electrolyte. This was done only because the silver from such a bath was of a more porous character, and hence presented greater surface to the action of the ionic halogen during the electrolysis. The platinum gauze was made the cathode in the oxalate electrolyte, and with the use of a clean platinum rod as anode, a current of 1 ampere at 1.5 volts was sent through the solution. The gauze rotated at about 200 r. p. m. This low current admits of a close, coherent coating on the platinum. It was then gradually increased to four amperes and an extremely heavy porous deposit of silver

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[1] *Phys. Review*, **21**, 388.

finally obtained. The proper plating of the gauze requires constant attention for about five hours, because the gas bubbles evolved during the electrolysis collect on the gauzes, act as non-conducting cushions and thus prevent an even coating. The gauze must, therefore, be lifted out of the bath from time to time in order to break the bubbles and hence insure a satisfactory deposit. This deposit is then dipped in dilute HCl and very thoroughly washed with pure water, after which it is heated in the Bunsen flame to incipient redness, cooled in a desiccator and weighed. Repeated ignition with subsequent immersion in water showed no change in weight. This method of preparing the silver anode is therefore adequate.

Mode of Procedure.—Since pure fused chloride of sodium is perfectly stable, its weighing was a very simple matter. The lumps of salt for each determination were transferred from a weighing bottle into a small weighed beaker and the increase in weight of the latter observed, of course using an almost identical beaker for a counterpoise. The weighed beaker containing salt was then carried in a desiccator to the electrolytic cell.

Fused sodium bromide is, however, hygroscopic; and a variation in the above procedure was therefore adopted. The bromide was contained in an exceedingly well-ground weighing bottle, and was weighed against a similar bottle containing bromide. The stopper of the bottle was then removed, about the required amount of salt shaken out into a clean beaker, and the stopper replaced, after which the bottle was ready to be reweighed, the decrease in its weight, of course, representing the apparent weight of the salt used. The operation of removal of salt never consumed over fifteen seconds and the glass was handled through linen gloves. The construction of the stopper of the weighing bottle was such that there was no possibility of loss of bromide in transference. When clear, fused masses of sodium bromide are exposed to the action of ordinary air for even forty-five seconds, the surface becomes clouded and the transparence is lost. Investigation of the increase in weight of the hygroscopic bromide when exposed to the air in the balance case gave the following results: Five grams of bromide were carefully weighed in a closed weighing bottle, the stopper was then removed and the increase in weight noted. In one minute no increase was observed; in three minutes 0.03 mg.; in five minutes 0.06 mg.; in ten minutes 0.13 mg. It is quite obvious that in an actual determination there was no likelihood of error in the weight of the sodium bromide, because of the fifteen seconds or less during which the weighing bottle was open. Furthermore, each successive quantity of sodium bromide removed from the weighing bottle was as brilliant in appearance as the very first taken out.

All weighings were made by substitution. Since the counterpoise was always almost exactly similar to the object weighed, the weights required were never large in amount, and thus errors due to atmospheric conditions were greatly minimized. All weighings were, of course, reduced to a vacuum standard, with a consideration of density at 20°.

In the inner compartment of the double cup was placed the salt under analysis. The total dilution never exceeded 65 cc. The weighed, silver-plated anode supported in the platinum-protected chuck of the motor shaft was placed centrically in the inner beaker. The lowest gauze was about 1 cm. above the surface of the mercury. About 5 cc. of a saturated aqueous solution of common salt was then put in the outer compartment and this was diluted with water to about 200 cc. The circle of thin platinum wire was thus completely covered. The rod of platinum serving as cathode connection with the mercury was then put in position and the cover glasses replaced. The anode was rotated at a speed of 200 r. p. m. and the current applied. Decomposition of the salt was instantly visible. The anode darkened because of silver halide. The sodium passed into the mercury as amalgam and was decomposed in the outer cell. This oxidation was greatly facilitated by the introduction of the circle of platinum described, for, in reality, a secondary cell entirely independent of the main electrolytic circuit was established. In this, the elements were amalgam, platinum and the solution of sodium chloride. The purpose of the sodium chloride introduced into the outer compartment is thus to act as a conducting medium at the beginning of the decomposition. Hydrogen bubbles "break" from the platinum wire in a continuous steady stream until the end of the electrolysis.

During the progress of the electrolysis the amperage gradually decreases because of the removal of salt from the inner cell. When the ammeter needle has fallen to below 0.03 amp. the current is interrupted. The anode is raised from the cell, is thoroughly washed with pure water, dried in the electric oven, cooled in a desiccator and weighed. Treatment of the liquid remaining in the inner cup will be described later.

Previous analyses made in the double cup were of quantities of salt rarely exceeding 0.15 gram, and excellent results were obtained, if no decomposition of amalgam occurred in the inner cup. Quite evidently such decomposition would give rise to the formation of sodium hydroxide which would undergo electrolysis with the consequent deposition of silver oxide on the anode. This contaminates the silver chloride alone desired and vitiates the value of the increase in weight of the anode. One cannot foretell just when decomposition of amalgam in the inner cup will or will not take place. Even working with the most scrupulous cleanliness does not necessarily insure complete absence of decomposition in the inner cell, although under such conditions the secondary decomposition would be minimized. This secondary electrolysis is therefore possible and quite likely, and to this cause may, in part, be attributed irregular values occasionally obtained heretofore. Silver oxide, however, decomposes at 250° with the liberation of oxygen, whereas silver chloride is stable at a much higher temperature. Thus if the anode after electrolysis, containing AgCl contaminated with Ag_2O, be heated to above 250° the oxide is decomposed, and the anode consists substantially of silver and silver chloride exactly as is desired. This condition was effectually brought about by recourse to the electric oven described above. The temperature ranged from 330 to 400°, and was thus quite sufficient to decompose the oxide. It is noteworthy that the oxide appears on the anode only near the end of the electrolysis and after practically all of the sodium chloride has been decomposed. (Its decidedly brown tinge distinguishes it from the bluish black chloride.) It is thus a superficial formation, and hence can be easily and completely decomposed. It is readily seen that with the use of the drying oven at elevated temperatures, the old bugbear of concomitant oxide formation on the anode is entirely dispelled.

Quite naturally larger quantities than 0.1 g. of material are necessary for atomic weight work, and on increasing this amount considerable difficulty was encountered. With the use of over a gram of salt in solution and an initial voltage of 3.5 the increasing resistance in the cell caused the pressure to rise of itself to 6.5 volts. Complete decomposition of the salt occurred, but a black scum invariably appeared on the surface of the liquid in the inner cup. This black scum was identical with small quantities of a loosely adherent deposit on the silver anode. Examination proved it to be oxide of silver. Quantitative determinations of halogen content under such conditions were, of course, absurd. Continued experimentation led to the adoption and maintenance of a low voltage as a means of preventing the formation of the loose oxide. A voltage of 3.5, kept constant throughout the electrolysis, insured a perfectly adherent deposit. And still the values of halogen obtained were very low. Trial after trial was made with varying conditions, but with no apparent advance.

All this work was done with a "six-decker" platinum gauze especially devised to pick up larger quantities of anions. Examination of the silver plate under a lens led to the discovery of a non-uniform coating, indeed minute spaces of platinum were exposed. Here, then, might be a reason for the low values obtained. If platinum is made the anode in a solution of sodium chloride, some NaClO and $NaClO_3$ are formed, lost, and quantitative retention of halogen as halide is impossible. The nature of the six-gauzed anode used prevented the deposition of a thick adherent plate of silver. The wires of each gauze were too fine in diameter, the gauze was too fine in mesh and the gauzes themselves were too close together. Thus, in attempting the plating of a very heavy deposit the meshes would be closed up, giving even less anodic surface and defeating the original purpose of the many-disc electrode. A triple-disc anode, made and prepared as described above, was finally adopted. The proper preparation of the silver anode is most essential to the success of each determination. At no time during the electrolysis must the anion be permitted to come in contact with the platinum. If only small amounts of halide are used, then a comparatively thin coating of silver suffices to retain all the halogen. But in the case of much larger quantities great care must be taken to procure a uniform silver plate of considerable thickness, so that as the chloride ion, for example, converts the surface silver to halide and works its way to the core of the deposit, there should be sufficient silver at all times to protect the platinum base. If the deposit is not uniformly thick, it is readily seen that at the places of this deposit the ionic halogen will soon meet the platinum, even though there be sufficient silver in bulk on the rest of the gauze; and when the platinum becomes the anode, then the very disturbing secondary formations arise. It is very likely that this phenomenon is the chief cause of uncertain values in anion estimations obtained occasionally by various investigators. Emphasis must be laid on the necessity of a satisfactory silver plate. In the present work a deposit of 10 to 15 grams of silver generally obtained. The use of a pure silver anode is, of course, ideal. A three-disc pure silver anode, of the same dimensions as the platinum gauze anode, with sand-blasted and perforated surface, was later used for several determinations and gave excellent satisfaction.

A peculiar phenomenon noted in the course of this work was the appearance, after drying in the oven, of a dark, purplish "sublimate" on the silver-plated rod of the platinum anode, at a place just below the upper limit of the silver coating. Continued heating of the anode showed no loss in weight. Indeed, direct ignition of the "sublimate" had no effect. Since constant weight was obtained, the first thought of a volatil chloride or subchloride of silver, had to be laid aside. It was then believed that the electrolyte was, to a slight degree, drawn up the anode rod by capillarity. This would explain the presence of the apparent sublimate which, on solution in potassium cyanide and reprecipitation by nitric acid, proved itself to be a chloride of silver. The expedient of forming a very coarse deposit of metallic silver immediately above the gauzes proved the correctness of the capillarity assumption. The spongy, though perfectly adherent, deposit really acted as a sponge, and prevented the electrolyte's creeping up the rod and eventually coming in contact with the platinum above.

Silver chloride is, to a slight degree, soluble in water, and so account must be taken of the silver chloride present in the inner-cup liquid after electrolysis. This was done by precipitation of the dissolved chloride with an excess of silver nitrate in the presence of nitric acid and determination of the turbidity thus produced by means of a nephelometer.[1] In addition to the dissolved silver chloride, there was also some sodium hydroxide, due to decomposition of amalgam in the inner cup. This had no effect on the nephelometric work, since the silver oxide formed when silver nitrate is added to the inner-cup solution is completely dissolved by the nitric acid added to catalyze the formation of the chloride opalescence. The determination of the silver chloride in solution was carried out as follows:

A standard solution of pure sodium chloride was prepared by dissolving 0.0414 gram NaCl in 250 cc. water. This was solution A. One cc. of it was equivalent to 0.0001 gram Cl. Solution B, 250 cc. in volume, was then made by diluting one cc. of solution A with pure water. A solution of silver nitrate was prepared by dissolving 10 grams silver nitrate in 250 cc. pure water. A 1 : 10 aqueous solution of nitric acid was likewise at hand.

The liquid remaining in the inner cup (never more than 70 cc. in vol.) was pipetted into a calibrated 250 cc. flask, and the inner cup was washed six times with small amounts of pure water, pipetting each washing into the flask. The original wash waters obtained in washing the anode after removal from the inner cup were then added to the contents of the flask and the whole made up to the mark with pure water. These 250 cc. therefore contained all the dissolved silver chloride and since the volume was identical with that of solution B, a direct comparison of the halide content of the two solutions could be made. To this end, one cc. of the silver nitrate solution and one cc. of the nitric acid were added to each of two 6-inch test tubes. One tube was then filled with the solution to be examined, the other with the solution B of known strength. The solutions were thoroughly agitated with clean glass rods and placed in the nephelometer. Constant reading was had after a lapse of fifteen minutes. The ratios of the respective turbidities furnished a direct determination of the halide present in the test solution. For example, if the nephelometric ratio was as 8 is to 4, *i. e.*, the reading of the tube containing the standard was 8.0, whereas the reading of the test solution gave 4.0, then, according to the scale of the instrument, there was twice as much turbidity in the test as in the standard, and consequently twice as much halide.

Although the solubility of silver chloride in water varies, it is less than 2 mg. per liter, so that if the 65 cc. of solution in the inner cup were saturated with AgCl there could only be about 0.1 mg. of the salt in solution; hence an accuracy of only 10 per cent. in the nephelometer would be quite sufficient for the purpose. However, the nephelometer admits of much greater precision, and hence permitted the following variation

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[1] *Am. Chem. J.*, **31**, 235.

in the electrolytic procedure. Instead of conducting an electrolysis to the complete analysis of the sodium chloride, the current was interrupted, while traces of undecomposed salt still remained, and these traces were nephelometrically determined, using the same procedure just described. It was a source of great satisfaction that, with the widely varying amounts of chloride determined by the nephelometer, the total halogen obtained gave uniform atomic weight figures. The identical method of nephelometric tests was used in the bromine estimations.

All electrolyses heretofore made with the double cup were conducted in the presence of sunlight or artificial yellow light, and no effort was put forth to prevent the coloration of the silver halide as formed. It seemed desirable in the present work to carry out several analyses of sodium chloride and of sodium bromide in a dark room and to note any variation in effect. Three experiments were accordingly made at night, in complete darkness, except for the occasional use of a red lamp to illuminate the measuring instruments. The dried anode, holding supposedly pure undecomposed silver halide, was then weighed in red light. Reference to the table of results shows the difference in weight to be inappreciable. The photo-chemical change of silver halide is, perhaps, insignificant in this work because of the large excess of silver present with the silver salt. In any case, the comparative values obtained, indicate the use of ordinary light to be quite safe.

In three electrolyses of sodium chloride conducted especially for the purpose, the liquid in the inner cup, after the current had fallen to 0.05 A., was examined for hypochlorites and chlorates. None was found in any tests. The halogen seemed to be present as halide only. The absence of a significant amount of silver from the electrolyte by solution of the silver anode is consequently proved. For in all the electrolyses only absolutely clear solutions prevailed, and the amount of silver ions in the presence of the excess of chloride must have been extremely small. The maximum solubility of silver chloride in water at 20° is 1.06×10^{-5} moles per liter, hence its solubility product in moles per liter is 1.12×10^{-10}. In determination No. 9, for example, the chlorine found by the nephelometer was 0.00026 gram. Since the volume in which this was contained was 50 cc., the chlorine concentration in moles per liter was 1.5×10^{-4}. The amount of silver ions present in a clear chloride solution of such concentration cannot exceed 1.12×10^{-10} divided by 1.5×10^{-4}, or 0.75×10^{-6} moles per liter or 0.35×10^{-5} grams of silver in 50 cc. (the volume of the liquid in the inner cup).

Moreover, the same lot of mercury was used as cathode in all the determinations. This was distilled until only a small residue remained. The residue was carefully examined for silver. A nephelometric test revealed the presence of 0.0003 gram of the metal. Since this was the total quantity of silver transferred in more than fifty analyses of salt, it is quite evident that the effect of transference of silver from anode to cathode in a single electrolysis is negligible.

The matter of occlusion of salt solution in the constantly increasing deposit on the anode was of vital importance and required careful consideration. It seemed quite possible, especially in the concentrated solution that obtained in the beginning of each electrolysis, for the silver halide in its formation to enclose minute quantities of the surrounding liquor; and although the mechanically enclosed water might probably be driven off by drying in the oven, the occluded sodium halide would exert its detrimental effect on the weight of the anode, and consequently vitiate the method for accurate work. The following experiments were therefore carried out. The dried anode after electrolysis was immersed in pure water saturated with distilled ammonia. Solution of the silver chloride resulted, and the anode was thoroughly washed with the ammonia water. Any occluded sodium chloride would be in the ammoniacal solution. On the addition of pure HNO_3 and on boiling, silver chloride was precipitated, but only the chloride ion of the original silver chloride would be affected; any sodium chloride originally occluded would be in the filtrate. (Of course, the usual precautions in filtering silver chloride were observed.) This filtrate was made up to definit volume and its turbidity (extremely slight) determined by the nephelometer. This gave the zero point, so to speak, and to the solution was then added an excess of silver nitrate; a nephelometric reading was taken and the increase in turbidity noted. In three separate instances the maximum opalescence produced did not exceed 0.005 mg., an entirely negligible quantity, indicating quite definitly the absence of occluded chloride. Richards and Wells have conclusively demonstrated that occlusion of mother liquor in precipitates is a function of the concentration of the medium in which the precipitation occurs. Acting on this, in two electrolyses only very dilute solutions obtained; that is, the salt was added in small quantities from time to time, when the fall of the ammeter needle indicated that only minute amounts of salt were undergoing analysis. There was, in these atomic weight values, no significant variation from those resulting on electrolysis of more concentrated solutions, thus again pointing to the absence of salt occlusions.

In three cases the anode, after the usual drying in the oven, was placed in a previously ignited and weighed porcelain evaporating dish, and heated by a protected Bunsen flame until complete fusion of the silver halide resulted. Cooling and reweighing the dish and anode with a suitable counterpoise gave substantially the same values. In two determinations the loss in weight was 0.02 mg., while in the third the balance detected no change in weight. This procedure dispelled the thought of permanent retention of water in the dried deposit, and demonstrated the efficacy of the ordinarily employed method of drying the anode. Moreover, the concordance in values obtained by the use of widely different amounts of salt, strengthens the basic thesis that the increase in weight of the anode represents only the halogen content of the salt under analysis.

While waiting for the arrival of the triple gauze anodes a preliminary series of determinations was made with the ordinary double gauze electrode. In all other respects, the apparatus and materials were identical for both series of values. Greater concordance in the final series is to be ascribed to the use of larger quantities of salt as well as to more experience in the manipulation of the method.

The atomic weight of sodium, as given by the International Committee on Atomic Weights for 1910, was taken as 23.00.

In calculating vacuum corrections the following table was used:

	Density at 20°.	Correction for 1 gram of substance at 20°, 760 mm.
NaCl	2.14	+0.000418
NaBr	3.1	+0.000244
Ag	10.49	+0.000029
AgCl	5.56	+0.000073
AgBr	6.39	+0.000046
Brass weights	8.4	

Wt. of 1 cc. of air = 0.0012 gram.

By calculating from the approximate amount of halogen present the silver necessary to combine with it, the necessary vacuum correction for silver and silver halide was obtained, since only that weight of the anode actually undergoing change is to be considered in applying the vacuum correction. Thus, the approximate weight of chlorine times 3.04 gives the weight of silver actually attacked, and the correction is made for this and not for the whole anode.

The data for one single determination will be given in detail, to illustrate the mode of procedure. Subsequent record will be made of only the final figures necessary to establish the ratio of sodium to halogen.

WEIGHING OF SODIUM CHLORIDE.

0.070 gram = wts. on pan excess over counterpoise.
+0.00085 gram = rider reading.
0.07085 gram = total weights used.
+0.00003 gram = correction for weights used.
0.07088 gram = apparent excess weight of empty beaker over counterpoise.
1.079 grams = wts. on pan excess over counterpoise.
—0.00062 gram = rider reading.
1.07838 grams ≐ total wts. used.
+0.00001 gram = correction for weights used.
1.07839 grams = apparent excess weight of beaker and NaCl over counterpoise.
—0.07088 gram = apparent excess weight of beaker over counterpoise.
1.00751 grams = apparent weight of NaCl.
+0.00042 gram = vacuum correction.
1.00793 grams = correct weight of NaCl.

0.61 gram = approximate weight of Cl present in NaCl taken.
0.61 × 3.04 = 1.85 grams = approximate weight of silver combined with chlorine.
0.61 + 1.85 = 2.46 grams = approximate weight of silver chloride formed.
1.85 × —0.00003 = vacuum correction for silver = —0.00006 gram.
2.46 × 0.000073 = vacuum correction for silver chloride = 0.00018 gram.

WEIGHING OF ANODE.

3.150 grams = wts. on pan in excess of counterpoise anode.
+0.00024 gram = rider reading.

3.15024 grams = total wts. used.
+0.00010 gram = correction for weights.

3.15034 grams = apparent excess weight of silver anode over counterpoise.
—0.00006 gram = vacuum correction for silver attacked.

3.15028 grams = corrected excess of anode over counterpoise.
3.760 grams = wt. on pan in excess of counterpoise anode.
+0.00097 gram = rider reading.

3.76097 grams = total weights used.
+0.00016 gram = correction for weights.

3.76113 grams = apparent excess weight of silver chloride anode over counterpoise
+0.00018 gram = vacuum correction for silver chloride formed.

3.76131 grams = corrected excess of anode over counterpoise.
—3.15028 grams = corrected excess of anode over counterpoise.

0.61103 gram = correct weight of chlorine found on anode.

NEPHELOMETER READINGS.

Standard.	Test.	Ratio.
5.0	1.9	3.80
7.8	3.0	3.84
9.1	3.5	3.84

Correction for chloride in solution = 0.00038 gram chlorine.

ELECTRICAL READINGS.

	Beginning of electrolysis.				End of electrolysis.
Voltage....	3.5	3.5	3.5	3.5	3.5
Amperage..	0.91	0.52	0.22	0.12	0.038
Time......	9.8	9.20	9.45	10.15	10.46

(hence 1 hour, 38 minutes)

0.61103 gram Cl found on anode.
+0.00038 gram Cl determined in nephelometer.

0.61141 gram total chlorine found.
1.00793 grams NaCl taken.

1.00793 : 0.61141 = 23.00 + X : X. X = atomic weight of chlorine.
$X = (23.00)\ (0.61141)/1.00793 - 0.61141$
$X = 35.465.$

Determinations 10, 12 and 24 were carried out in darkness as mentioned above. After drying and weighing as usual, the halides on anodes in determinations 9, 11 and 20 were fused as previously described. No significant change of weight was observed. In determinations 17, 18, 19 and 27, the pure silver disc anode was used.

PRELIMINARY SERIES.

SODIUM CHLORIDE.

Number of determination.	NaCl taken in grams.	Cl found on anode.	Cl determined in nephelometer.	Cl total.	Atomic wt. of chlorine. Na = 23.00.
1....	0.81495	0.49423	0.00009	0.49432	35.460
2....	0.79370	0.48128	0.00007	0.48135	35.445
3....	0.88940	0.53952	0.00010	0.53962	35.483
4....	0.45642	0.27666	0.00013	0.27679	35.441
5....	0.43884	0.26612	0.00006	0.26618	35.458
6....	0.44239	0.26818	0.00010	0.26828	35.440
7....	0.64942	0.39381	0.00006	0.39387	35.449
8....	0.53706	0.32535	0.00046	0.32581	35.473
				Average =	35.456 ± 0.0037

FINAL SERIES.

SODIUM CHLORIDE.

Number of determination.	NaCl taken in grams.	Cl found on anode.	Cl determined in nephelometer.	Cl total.	Atomic wt. of chlorine. Na = 23.00.	Atomic wt. of sodium. Cl = 35.458.[1]
9....	1.02234	0.61988	0.00026	0.62014	35.463	22.997
10....	1.02221	0.61957	0.00049	0.62006	35.463	22.997
11....	2.43474	1.47654	0.00038	1.47692	35.466	22.996
12....	1.46370	0.88780	0.00009	0.88789	35.466	22.995
13....	0.56934	0.34522	0.00012	0.34534	35.460	22.999
14....	1.00793	0.61103	0.00038	0.61141	35.465	22.995
15....	1.06501	0.64579	0.00021	0.64600	35.459	22.999
16....	2.16720	1.31442	0.00018	1.31460	35.463	22.997
17....	2.75219	1.66904	0.00035	1.66939	35.460	22.999
18....	0.92900	0.56337	0.00012	0.56349	35.458	23.000
19....	1.83527	1.11294	0.00030	1.11324	35.462	22.998
				Average =	35.462 ± 0.0005	22.997 ± 0.0003

SODIUM BROMIDE.

Number of determination.	NaBr taken in grams.	Br found on anode	Br determined in nephelometer.	Br total.	Atomic wt. of bromine. Na = 23.00.	Atomic wt. of sodium. Br = 79.920.[1]
20....	1.05343	0.81775	0.00028	0.81803	79.927	22.998
21....	1.33360	1.03542	0.00019	1.03561	79.932	22.997
22....	1.95652	1.51875	0.00061	1.51936	79.936	22.995
23....	5.02976	3.90513	0.00073	3.90586	79.930	22.997
24....	2.09332	1.62545	0.00009	1.62554	79.925	22.998
25....	6.46697	5.02162	0.00016	5.02178	79.920	23.000
26....	5.54733	4.30740	0.00028	4.30768	79.923	22.999
27....	7.03901	5.46575	0.00031	5.46606	79.926	22.99[illegible]
				Average =	79.927 ± 0.0014	22.998 ± 0.0003

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[1] F. W. Clarke, *Loc. cit.*

Since the above article was published in separate form as a thesis, Dr. W. A. Noyes has called attention to the fact that the work is really a determination of the ratios between sodium and chlorine and sodium and bromine. The accepted value for the atomic weight of sodium, 23.00, is based on oxygen through either silver or chlorine or bromine and hence, as a piece of atomic weight work, the value of sodium is to be calculated. This was accordingly done and with the results given in the last column of the table. The value of chlorine was taken as 35.458, of bromine 79.920.[1]

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THE FRACTIONATION OF THE YTTRIUM EARTHS BY MEANS OF THE SUCCINATES.

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During the past decade material contributions have been made to the study of the yttrium group of the rare earths. Among these it has been shown by Lenher that, through the agency of the succinates, considerable rapidity can be arrived at in the process of separating various mixtures of these earths. The succinates of the yttrium group are finely divided crystalline precipitates, which are best formed by the addition of a solution of neutral ammonium or sodium succinate to a neutral nitrate solution of the yttrium earths. This precipitate is of especial interest because the time of formation is so greatly delayed that it is possible for equilibrium to become more readily established. Under these conditions the separation is more sharply performed than if precipitation took place instantaneously.

In order to test the applicability of the succinates as reagents in the yttrium group, the yttrium earths were extracted from a number of rare earth minerals of widely differing character and the separation studied in some detail.

Samarskite.—The yttrium earths were extracted from samarskite and studied in considerable more detail than previously reported.[2] The atomic weight determinations and the study of the absorption spectra were used as a continual control on the process of fractionation. The atomic weight determinations were carried out with sufficient accuracy by means of the oxalate method. The absorption spectra studies were made by means of a Steinheil grating spectroscope, similar to the one described by Dennis.[3] The earths having the highest atomic weights were precipitated first, showing that the succinates of the earths having

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[1] F. W. Clarke, *Loc. cit.*

[2] THIS JOURNAL, **30**, 575.

[3] *Ibid.*, **24**, 415.