FURTHER STUDY OF THE ATOMIC WEIGHT OF MERCURY, THROUGH THE ANALYSIS OF MERCURIC BROMIDE.

By C. W. Easley and B. F. Brann.

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Two previous contributions[1] relative to the atomic weight of mercury described work which resulted, within narrow limits, in the same value of this constant. The methods employed, entirely different in character, dealt with the same material, mercuric chloride. While such a procedure probably indicated that the error of method was sufficiently small to be negligible, doubt pertaining to the nature of the material analyzed was not removed. It remained, then, to prepare material of a different character and it was decided to attempt a redetermination of the atomic weight from a study of the bromide since there seemed to be no reason why this compound should not be prepared in a pure state. It would be ideal to attack the question through the use of the oxide but, from preliminary experiments, the preparation of this compound seems exceedingly doubtful.

The problem with the bromide presented many points of similarity to that of the chloride. Owing to the solubility of silver bromide in mercury salts, instead of treating a solution of mercuric bromide directly with silver nitrate, the mercury was first removed. This was accomplished in two ways, each leading to practically the same results: first, by means of hydrazine hydrate in weak alkaline solution and, second, with hydrogen peroxide under similar conditions. Like results from the use of the two reducing agents would seem to preclude the possibility of any considerable error arising from the use of either. The mean value of the atomic weight found does not differ essentially from the results reported in previous communications.

Pure Mercuric Bromide.

It is well known that bromine may be readily made very pure by the methods of Stas[2] and the modifications proposed by others[3] and, in a previous paper,[4] several methods for the preparation of pure mercury were described. Thus, since the elements unite easily, it is possible to prepare the bromide of mercury without the intermediate use of water. This is probably important as it was shown in the preparation of the chloride that that salt could not have had contact with water without the production of basic material during the subsequent process of sublimation. There was no reason to expect a different result with the bromide so that recrystallization of the salt was not resorted to, especially when

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[1] Easley, This Journal, 31, 1207 (1909) and 32, 1117 (1910).

[2] *Oeuvres Complètes*, 1, 587.

[3] Richards, *Proc. Amer. Acad.*, 25, 199. Scott, *J. Chem. Soc.*, 77, 649. Baxter, This Journal, 28, 1322 (1906).

[4] Easley, This Journal, 31, 1216 (1909).

the alternative and preferable procedure of bringing pure bromine and pure mercury together in an indifferent medium of nitrogen at the temperature of sublimation was practicable. The bromide thus prepared is probably free from the bromides of other metals for the process was carried out at a temperature in the neighborhood of 300°, conditions under which other compounds, most likely to be present, would not be perceptibly volatil.

In detail, the process consisted in passing a stream of nitrogen through liquid bromine, thus sweeping the vapor into a chamber containing mercury maintained at a temperature of 300°. The apparatus is shown in Fig. 1. The nitrogen was sent through a purifying and drying train constructed of glass alone and the exit tubes were so arranged by means of branches and glass stopcocks that the gas could either first bubble through the bromine in a wash bottle or pass directly into the reaction chamber *C* as shown in Fig. 1. Solutions of potassium hydroxide, some containing lead oxide in solution, were used for purifying the nitrogen while the gas was dried by means of sulfuric acid in towers filled with glass beads. Phosphorus pentoxide, resublimed in a stream of dry air, by contact served to dry the liquid bromine. After pure mercury had been introduced through the tubulature *T* by means of a funnel reaching to the bottom of the chamber *C*, the air in the apparatus was displaced by nitrogen and this in turn by a mixture of nitrogen and bromine. The bulb was then heated to a temperature around 300°. The fact that the metal was covered with transparent, colorless, fused bromide showed that a sufficient excess of bromine was present. When the mercury was entirely converted and carried into the receiver *R* in the adjacent compartment, the latter was raised to a temperature of 235°, a point where the salt began to show a considerable vapor pressure. During the latter operation, nitrogen, without bromine, was passing through the apparatus, completely sweeping out the excess of bromine and liberating, probably, any that might possibly have adhered to the salt at the lower temperature. Air ovens, entirely separate from each other, were used for heating the compartments and these were constructed of asbestos, with glass windows. The temperature was regulated by means of burners below the ovens. After cooling in the same atmosphere, dry air was admitted and the salt was transferred by holding the receiving funnel *R* over the mouth of the

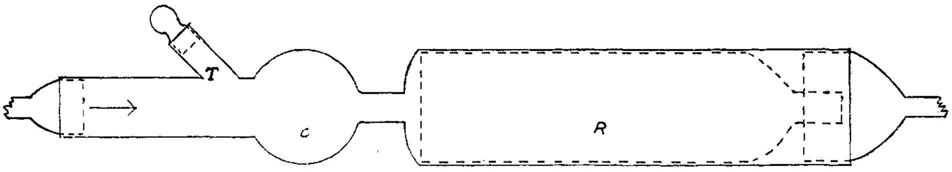

Fig. 1.

weighing bottle and pushing the crystals into the latter with a well-rounded glass rod. At times, the end of the receiver nearest the chamber *C* was heated to such an extent by conduction that a portion of the crystals fused and adhered somewhat to the glass. No attempt was made to dislodge such material so that the collected salt must have been entirely free from silica and other matter originating in the glass. The transfer of the salt to the weighing bottle was made in air, for it was shown that exposure to the air of the laboratory did not sensibly affect its weight. In proof, a light tube, sufficiently small to rest on the balance pan, was sealed at one end to another tube of smaller bore through which either dry air or bromine vapor could be admitted. The other end was fitted with a hollow stopper which could be closed by means of a stopcock. A quantity of mercury was converted into the bromide within this tube and as a stream of dry air was passing, it was effectually sealed, at one end by means of the flame and at the other by turning the stopcock. When counterpoised by a similar tube on the balance pan, the stopper was removed and for the first time the salt was exposed to the air of the laboratory.

The salt collected in the receiver in beautiful needle-like masses. The fact that bromine was present in excess during the preparation and that the bromine, mercury, nitrogen and air were free from water would preclude the formation of either calomel or basic salts. The complete solubility of the salt prepared by this method, in fact, shows no impurities of this character.

Preparation of Bromine.

Three samples of bromine were prepared, two being made by well-tried methods in which a solution of calcium bromide was depended upon to react with chlorine and fractional distillation, after transformation to hydrobromic acid, to remove the iodine. The bulk of the mercuric bromide was made with such bromine, but it was decided to use more exhaustive means in the purification of a third sample so that its value could not be doubted. The methods adopted were so laborious that only a small amount of this sample was obtained. The analyses showed that the mean atomic weight does not differ from the mean of any series in which a particular sample of bromine was used, by more than one part in ten thousand.

Sample 1.—Commercial bromine was dissolved in a solution of calcium bromide which was prepared from marble and hydrobromic acid. The marble had not been exposed to the fumes of the laboratory while the acid had been prepared from the original bromine by reduction. The bromine was distilled by placing the solution in a glass-stoppered flask whose side arm was sealed to the condensing system. All save the first fraction of this bromine was covered with sufficient water to form the constant boiling mixture of hydrobromic acid corresponding to the amount of bromine used. Hydrogen sulfide, from ferrous sulfide and dilute sulfuric acid, was next passed until nearly the whole of the bromine was converted into hydrobromic acid. Hydrochloric acid was removed from the gas by a train of wash bottles, the first of the series being filled with alkaline sulfides and the final ones with pure water. When the sulfur had been separated by filtration through glass wool, the acid was distilled, the free bromine and iodine passing over in the first fraction.

At this stage, the purity of the bromine was investigated. Accordingly, a weighed amount of silver was converted into silver bromide by using some of the hydrobromic acid prepared above after it had been treated with a slight excess of ammonia. The silver was prepared following the ammonium formate method of Stas, with subsequent fusion on lime. Using all precautions, three determinations were made in which 18.32765 grams of silver formed 31.89761 grams of silver bromide. This results in a ratio of 57.457 whereas the theoretical one is 57.445. An excess of chlorine in the bromine is thus indicated. During the next process, however, in converting the acid to bromine, any free chlorine would be in contact with a solution of potassium and manganese bromides and must have been effectually removed.

The oxidation of the acid to bromine was accomplished with potassium permanganate. Kahlbaum's highest grade was found to contain such small amounts of chlorine that several recrystallizations removed all save the merest traces. In fact, tests on the mother liquor of the last crystallization showed a maximum of one part of chlorine in forty thousand parts of salt. The hydrobromic acid dropped from a separatory funnel upon the permanganate in a flask whose connections with the condensing system and funnel were all of glass. The contents of the flask were kept at a temperature such as would liberate the bromine. A first small fraction was discarded. The remainder was freed as much as possible from water by means of a separatory funnel after which it was preserved in a bottle with phosphorus pentoxide, the preparation of which has been described before.

Sample 2.—This sample was prepared in the same manner as Sample 1 save for the fact that sulfur dioxide instead of hydrogen sulfide was used as the reducing agent. The gas was furnished from a cylinder containing the liquid and was allowed to run through several wash bottles containing sodium acid sulfite and then through pure water. This method obviates the contamination of the hydrobromic acid with precipitated sulfur, a source of considerable difficulty combined with loss of material whenever the hydrogen sulfide method was used.

Sample 3.—A quantity of Kahlbaum's best bromine was allowed to remain in contact with a solution of the potassium and manganese bromides which were saved in the process of oxidizing the hydrobromic acid of Samples 1 and 2. The mixture was frequently shaken and finally distilled. Reduction to hydrobromic acid was carried out as in Sample 2 but only the middle fraction of the distillate was retained. To a very dilute solution of this acid, pure silver nitrate was added and the precipitate was washed many times, first with cold and then with hot water. Mercuric nitrate, prepared from mercury and halogen-free nitric acid, was added and allowed to remain in contact with the precipitate for 48 hours. A strong solvent action is thus exerted upon the silver halides[1] and, as the solution of the nitrate was about normal, amounts of chlorine and iodine which analysis revealed in Sample 1 would have been removed when the residue was washed free from the mercuric nitrate. The silver bromide was next suspended in water and converted to hydrobromic acid by well-washed hydrogen sulfide. A reserve supply of the silver bromide used up the excess of hydrogen sulfide. When the sulfide had been separated from the acid, the latter was distilled and oxidized to bromine precisely as in the case of the other samples.

Preparation of Mercury.

Sample 1.—This consisted of a small amount of mercury remaining from previous work.[2] Its preparation has been described.

Sample 2.—The starting point was the same mercuric chloride whose analysis,[3] after sublimation, has already been reported. It was exceedingly pure. After sublimation in a stream of pure, dry air, the salt was dissolved in water and treated directly with an ammoniacal solution of hydrogen peroxide. The resultant globule was given the same treatment as the one to be described under Sample 3.

Sample 3.—The same material used in Sample 2 served as the basis of this sample. The salt was resublimed, dissolved in a large amount of water and treated with sulfur dioxide, thoroughly washed. The precipitated calomel was washed many times with pure water and finally subjected to the action of ammonia. After washing out the excess of ammonia, a necessary process to prevent the formation of large amounts of soluble compounds[4] from which mercury could not be separated by the method used, sulfur dioxide was again added. During the latter process, the mass was maintained at a temperature of approximately 100°. Metallic mercury separated in globular form. The globule was washed with water and then shaken with a dilute ammoniacal solution of hydrogen peroxide to remove all suspicion of reducible, surface impurities. The metal was dried by quickly heating to the boiling point.

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[1] Morse, *Z. physik. Chem.*, 38, 705.

[2] THIS JOURNAL, 31, 1217 (1909). See sample 3.

[3] *Ibid.*, 32, 1125 (1910).

[4] P. de Saint-Gilles, *Annalen der Chemie*, 84, 266.

Traces of foreign material, of the nature of finely-divided silica, were separated by filtering the metal through a small funnel, the drawn-out stem of which was filled with fine glass threads. In spite of these precautions, after the metal had been converted to the bromide in the apparatus shown in Fig. 1 and the bromide had been distilled, there sometimes remained a slight residue. As no less than 15 grams of mercury was ever used and as the residue seemed unweighable, no error could have crept into the results from this source. No matter how long the residue was heated, no volatilization was apparent. In several cases the residue was certainly silica. At another time, black material remained. This may have been a basic salt of mercury with an inappreciable vapor pressure at the temperature used. How it might have formed is not clear.

Reagents.

Hydrazine Hydrate.—Hydrazine sulfate was treated with an excess of sodium hydroxide and the liberated hydrate was separated by distillation in a copper retort. The product was subjected to a second distillation in a system made entirely of glass. A product almost entirely free from chlorine resulted. When treated with silver nitrate, 0.00003 gram of silver chloride was found in every gram of the hydrate.

Hydrogen Peroxide.—Merck's 30% solution of hydrogen peroxide was redistilled and diluted to an approximately 3% solution. In every 100 cc. used, an amount of chlorine corresponding to 0.00007 gram of silver chloride was found and duly corrected for.

Sodium Hydroxide.—Very pure sodium was converted into the hydroxide by standing on platinum gauze over a platinum dish in a water-laden atmosphere free from carbon dioxide. The required quantity of hydroxide for one determination was prepared at a time and a portion of this material was always examined for chlorine. When treated in the nephelometer[1] with silver nitrate, the different samples showed varying amounts of silver chloride but in no case was an amount present exceeding 0.0001 gram per 5 grams of sodium hydroxide.

Other reagents: The water, nitric acid and ammonia were all redistilled, the first twice from permanganate solution. All were chlorine-free. Silver nitrate was made from the metal and acid and the solution was evaporated to dryness. The metallic silver was prepared by the action of ammonium formate on silver nitrate.

The Method of Analysis.

The plan pursued consisted in treating a weighed amount of mercuric bromide in solution with sodium hydroxide, adding such an amount of a reducing agent as would precipitate the mercury, leaving the bromine in the form of bromide ions. The mercury being filtered off and the solu-

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[1] Richards and Wells, *Am. Chem. J.*, 31, 235 (1904).

tion being rendered alkaline, silver nitrate was used to form silver bromide which was weighed. The value of the ratio $HgBr_2$: $2AgBr$ is thus determined.

In order to keep the amount of solution at a minimum, the bromide was not entirely dissolved in water when the calculated amount, plus 0.25 or 0.30 gram, of sodium hydroxide was added. The object was not to unduly dilute the reducing agents in which case more mercury might remain in solution and also to avoid the filtration of large quantities of solution. This practice, on the other hand, lengthened the time required for the completion of the reaction since the undissolved crystals of bromide could give rise to an amount of oxide only proportional to their surface. With hydrazine hydrate, the reduction proceeded with relative rapidity at room temperature but in the case of hydrogen peroxide, a temperature of 70° was required to have the reaction progress at a moderate rate. The oxide, successively formed, remained as a crust on the crystals until reacted upon by the reducing agent. Hydrazine hydrate was employed in some of the preliminary work on the analysis of mercuric chloride but no actual analyses were made. It has proven a most effective reagent in the case of the bromide, the mercury forming with perhaps less unglobulized material than in the case of hydrogen peroxide. This, perhaps, is explained by the fact that the reaction is completed more quickly and therefore less silica is formed by the action of the slightly alkaline solution. Again, the temperature was lower. The rate of the reaction was so regulated that the nitrogen was expelled quietly carrying no spray beyond the catch system. A very small amount of mercury must have remained in solution as invariably silver bromide was detected after an excess of silver nitrate had been added. The determination of this dissolved material will be described later. The amount of silver bromide in this condition never exceeded 0.001 gram per liter of solution. When the reduction was complete, the contents of the flask were brought to the boiling point in order to decompose the greater portion of the peroxide. This was done even in the experiments where hydrazine hydrate was used, for the excess of the latter was destroyed by the addition of hydrogen peroxide.

The flask, with the system for introducing the reagents and the tube for the escape of the liberated gases, is shown in Fig. 2. It is of the Erlenmeyer form, holds 500 cc. and is made of Bohemian glass. The tube passing through the ground-glass stopper is branched above. Through one branch the reagents are added and the amount added at any time is gauged by means of the stopcock; through the other, the liberated gases pass. In the latter arm, the tubing is bent so as to form a trap, *T*, beyond which it is widened and filled with beads kept wet with pure water. As the trap is always full of water, a most effective means of preventing loss through spray is at hand. Any material collecting on the inner walls of the branches found its way into the flask during the rinsing process at the completion of the reduction. It was found very difficult in the work on the chloride to entirely separate the mercury from the solution. The extremely fine particles refused to be globulized and some of these particles either passed through the filter paper of the most compact texture or crept over its side. The present work was not unlike the previous case in this respect. Better results were obtained by decreasing the rate of filtration by placing a globule of mercury in the apex of the filter. The difficulty was not entirely overcome, however, so that more than one filtration was often necessary. In spite of the character of the paper used, some shreds were loosened and passed into the filtrate, owing perhaps to the hot, slightly alkaline solution. The amount was very small but it was found later in the fused silver bromide as a small patch of surface scum. It was impossible to determin its amount accurately, but there is little doubt but that the correction would be exceedingly small. All danger of losing any of the solution by leakage from the lip of the flask during filtration was avoided by the use of a protecting cup around the neck of the flask as shown in the figure at *C*. The cup was thoroughly rinsed after all traces of solution had been removed from the flask itself. It is safe to say that there was no appreciable loss of material due to the process of filtration. Many rinsings were made, no danger of adding too much water being feared since there is less danger of including material in the precipitated silver bromide if the solution is dilute. The solution was filtered directly into a flask of Jena glass and was acidified with an amount of nitric acid slightly in excess of that found necessary from the known excess of sodium hydroxide used at the outset. A slight excess over the theoretical quantity of silver nitrate was added to precipitate the bromine. Both the bromide and silver solutions were approximately tenth-normal. After standing over night in the glass-stoppered flask, the solution could be easily separated from the precipitate by the use of the Neubauer crucible. Only a small portion of the silver bromide found its way into the crucible during the filtering process, the greater portion remaining in the flask so that the washing might be more effective. The first stage of the latter process consisted in making

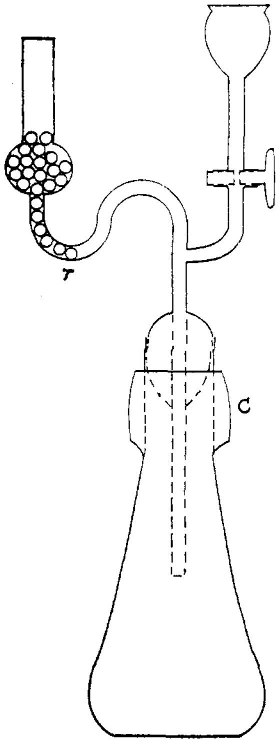

Fig. 2.

eight or ten additions of water containing a slight amount of silver nitrate and nitric acid, decanting each in turn. About the same number of washings were then made with water containing nitric acid alone. The latter washings contained dissolved silver bromide. The amount was determined in the nephelometer and found to average 0.0002 gram per liter. When the precipitate had been completely transferred the crucible with its contents was dried in an air oven, protected from outside fumes, at a temperature ranging from 150–160°, after which it was weighed. The greater portion of the precipitate being transferred to a weighed porcelain crucible and fused, the expelled water was determined by another weighing. The fused mass was transparent, save for a small patch due to filter shreds referred to before, and greenish yellow in color. No difference appeared in the results whether a fused sample contained the above-mentioned impurity or not so that the error from this source is too small to be feared. Since tests on the contaminated portions for silver were negative, it is doubtful if any chemical change had resulted. More likely, the shreds merely entangled and kept separate small portions of silver bromide.

A correction, of small though positive value, became necessary through the observation that bromine was present in the filtrate, after the separation of the silver bromide, even after an excess of silver nitrate was added. This never amounted to more than 0.001 gram of silver bromide per liter, generally considerably less, but a measurable quantity was invariably present. In most cases, the atomic weight would hardly be changed one unit in the second decimal place by this factor but it was determined in every case to guard against larger error. A similar result was found in the analysis of mercuric chloride. At that time, it was assumed to be due to the presence of mercury salts in solution. While no other supposition is put forward here, it is difficult to understand how such small quantities of mercury as are present (none has been shown in tests) could have such a strong solvent action. It is not impossible that some of the finely-divided mercury escaped notice and was dissolved by the very dilute nitric acid added to neutralize the solution. That bromine was present, however, was proven by carrying out a blank test at the same time the solution was examined. The two sets, one with the solution, the other with pure water, were treated alike in every detail and although halogens were always found in the blank due to the reagents, yet larger amounts were always found in the solution. The method of determination consisted in the precipitation of the heavy metals in slightly ammoniacal solution by means of hydrogen sulfide. A small amount of alum in the solution assisted in securing a clear filtrate. Boiling served to drive off most of the hydrogen sulfide and the remainder was oxidized to sulfuric acid by means of hydrogen peroxide. On acidifying the solutions, tests for the presence of halogens were made with the aid of the nephelometer.

As an illustration of the relative value of the corrections necessary in finding the amount of silver bromide which results from a given weight of mercuric bromide, we may take experiment No. 9. In this case, 11.28487 grams of mercuric bromide gave rise to 11.75970 grams of silver bromide, the latter weight being the sum of various factors as follows:

Weight of silver bromide dried at 150–160°		11.76077
Weight of silver bromide in filtrate (1225 cc.)		0.00025
Weight of silver bromide in wash water (1020 cc.)		0.00020
		11.76122
Water in silver bromide dried at 150–160° (loss on fusion)	0.00134	
Silver chloride, due to chlorine in hydrazine hydrate	0.00002	
Silver chloride, due to chlorine in sodium hydroxide	0.00016	
		0.00152
Corrected weight of silver bromide		11.75970

The weighings were made by the method of substitution by the use of a delicate Sartorius balance and the weights found in air have been converted to weights in a vacuum by the use of the following corrections:

+ 0.000067 gram per gram of mercuric bromide.

+ 0.000041 gram per gram of silver bromide.

The platinum plated weights were carefully calibrated and the corrections duly applied.

THE RESULTS.

No. of exp.	Sample Hg.	Sample Br.	Weight of $HgBr_2$.	Weight of AgBr.	The atomic weight[1] of Hg.
1	1	1	8.93958	9.31480	200.63
2	1	1	14.36691	14.96940	200.64
3	2	1	10.13638	10.56230	200.61
4	2	1	9.94452	10.36218	200.62
5	3	1	12.60142	13.13051	200.63
6	3	1	12.16157	12.67122	200.65
7	3	2	11.19762	11.66809	200.62
8	3	3	16.16607	16.84235	200.68
9	3	2	11.28487	11.75970	200.59
10	3	2	17.25074	17.97597	200.61
11	3	3	14.20924	14.80685	200.61
					Mean, 200.64

Any discussion of the results would practically be a repetition of that in the paper on the chloride. No evidence has been unearthed in the present work to allow a different view of the result. Hydrogen peroxide

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[1] These results are calculated with the values Br 79.92, Ag 107.88; THIS JOURNAL, 33, 1642 (1911).

was used as the reducing agent in eight experiments of the series; in Experiments 9, 10, and 11, hydrazine hydrate served this purpose. The mean result by each method is practically the same. This is strong evidence that there is little error connected with the removal of the mercury from mercuric bromide. The results are slightly but uniformly lower, however, in the cases where hydrazine hydrate was used. This would indicate that all the bromine from mercuric bromide had not been measured when hydrogen peroxide was used or, on the other hand, that foreign matter was weighed in the other series. The latter assumption would seem to be the more probable, if either carries any weight, for hydrazine hydrate, if any remained after the treatment with hydrogen peroxide, might reduce the silver nitrate and thus give an apparently large amount of silver bromide. This seems unlikely, however, for the solution was purposely made more strongly acid in this case than where the peroxide was used in order to counteract such a tendency. The effect is certainly small and should be connected with the accuracy of the second, rather than the first decimal place.

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RECENT WORK IN INORGANIC CHEMISTRY.

BY JAS. LEWIS HOWE.

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The past year has witnessed no startling discoveries in the field of inorganic chemistry, yet there has been great activity along every line, especially in working over old material in the light of new theories. Such work is often difficult and painfully slow, attracts little attention and adds little to reputation, but is vitally necessary if we are to broaden our generalizations. But one new element has been added to the list, Urbain's keltium (Ct) from the gadolinite earths, unless we are to believe the newspaper statements of a new platinum metal from the northwest, and while Ramsay has given radium emanation standing as niton, doubt has been thrown on Flint's companion to tellurium.

No attempt will be made to review the whole field, but rather to consider some of the most important papers which have appeared the past year. The order followed will be that of the periodic table.

Group III.—Further work has appeared from Biltz (*Z. anorg. Chem.*, **71**, 182, 427) on the sulfides of this group. Al_2S_3 is prepared by fusing together the metal and sulfur in a crucible and then igniting the mass by magnesium ribbon. The material is then sublimed, best in a vacuum. The felted product consists of fine needles, which are quite possibly isomorphous with corundum, and this is the more probable since the solidifying curve with alumina indicates the formation of mixed crystals ("Mischkrystalle"), though the intersolubility is not unlimited. Al_2S_3 is readily attacked by moisture, and seems to form one or more compounds with the Al_2O_3 formed. The product obtained by Regelsberger from alumina and sulfur in the electric furnace is a complex mixture, but one of its