to water at 4°, is found to be 4.385, and that of manganous chloride under the same conditions is found to be 2.977.

We are deeply indebted to the Carnegie Institution of Washington for funds which have made this investigation possible, and also to Dr. Wolcott Gibbs and the Cyrus M. Warren Fund for Research in Harvard University for many indispensable platinum vessels.

CHEMICAL LABORATORY OF HARVARD COLLEGE,
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF COBALT.

BY GREGORY PAUL BAXTER AND FLETCHER BARKER COFFIN.

Received August 13, 1906.

FOURTH PAPER.—THE ANALYSIS OF COBALTOUS CHLORIDE.

SOME years ago the atomic weight of cobalt was investigated in this laboratory by the determination of the ratios of cobaltous bromide to silver and to silver bromide,[1] and of cobaltous bromide,[2] cobaltous chloride,[3] and cobaltous oxide[3] to cobalt. From these investigations the probable value for the atomic weight of cobalt was found to be 58.995 (Ag = 107.930), the most satisfactory results being obtained through the analysis of cobaltous bromide.

The determination of the cobalt in cobaltous chloride was effected by reduction of the salt in a current of hydrogen. The salt was not obtained in a state of absolute purity, and it was necessary to apply corrections for the impurities, so that at the time very little value was attached to the result, 59.072.[4] In the present investigation it has been found possible with the help of the newly available quartz apparatus to prepare the salt in a state of greater purity, and the analysis of this new material confirms

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[1] Richards and Baxter: Pr. Am. Acad. 33, 115 (1897).

[2] Ibid. 34, 351 (1899).

[3] Ibid. 35, 61 (1899).

[4] The value found from two analyses was 59.044, upon the assumption that the atomic weight of chlorine is 35.456 (Ag = 107.930). Recent determinations in this laboratory by Richards and Wells (Publications of the Carnegie Institution, No. 28, 1905) have shown that the value of the latter constant is as high as 35.473. This change in the atomic weight of chlorine produces an increase in the atomic weight of cobalt of 0.028.

satisfactorily the previous analyses of cobaltous bromide, as well as the doubt concerning the earlier results with the chloride.

PURIFICATION OF MATERIALS.

Cobaltous Chloride.—The simplest method of freeing cobaltous salts from the salts of other metals was previously found to be precipitation of purpureo-cobalt chloride. This substance is only slightly soluble in cold hydrochloric acid solutions, but readily soluble in hot ammonia. It was prepared by bubbling air for several days through an ammoniacal solution of commercial cobalt chloride, and then adding hydrochloric acid in excess. The purpureo-chloride thus precipitated was collected and the mother-liquor removed as completely as possible by filtration upon a large porcelain Gooch crucible. It was then dissolved in hot redistilled ammonia, and the solution was filtered into a concentrated, distilled hydrochloric acid solution. The product, after washing with hydrochloric acid, was collected upon a Gooch crucible as before.

The final purification consisted in recrystallizing the amine three times by solution in the purest redistilled ammonia in a platinum dish, and filtration with a platinum funnel into a quartz dish containing hydrochloric acid which had been distilled with a quartz condenser. Care was taken always to have an excess of acid in the quartz dish, while the acid solution was never allowed to come in contact with platinum since it probably contained free chlorine. The product of the third precipitation was dried on a steam-bath, and was then converted into cobaltous and ammonium chlorides by heating to about 200° in a quartz crucible in an air-bath. For the latter purpose platinum proved to be unsuited, since it was slightly attacked during the decomposition of the amine, while the quartz crucible remained unchanged in weight. A temperature high enough to fuse the amine was very carefully avoided. The ammonium chloride still contained by the cobaltous chloride was eliminated during the final heating of the salt in a current of hydrochloric acid gas. During this final heating also care was taken to increase the heat very gradually, so as to avoid fusion of the salt and consequent possible enclosure of ammonium chloride in masses of fused cobaltous chloride.[1] Cobaltous chloride prepared in this way was designated Sample I.

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[1] Z. physik. Chem. 46, 194 (1903).

For preparing the second sample of cobaltous chloride, cobaltamine, which had been at least once dissolved in ammonia and reprecipitated with hydrochloric acid, was heated on a steam-bath with an excess of sulphuric acid, until all chlorine and hydrochloric acid had been expelled. The cobaltous sulphate thus formed was then dissolved in water, the solution was filtered and a large excess of ammonia was introduced. In order to free the cobalt from alkalies and silica this ammoniacal solution was then electrolyzed in a platinum dish, a platinum wire serving as anode, and the dish as cathode. The deposit of cobalt was washed thoroughly with pure water and dissolved in hydrochloric acid which had been freshly distilled through a quartz condenser. The solution was next evaporated to crystallization, and the product was twice recrystallized. In the third crystallization the salt was drained with a centrifugal machine in which platinum Gooch crucibles served as baskets and platinum crucibles as receivers. Any trace of sulphate occluded by the electrolytic metal was effectually eliminated in this way, for the mother-liquors from the second recrystallizations, when tested for sulphates, always yielded negative results.

After superficial moisture had been eliminated in a desiccator over potassium hydroxide, the salt was powdered in an agate mortar and heated in a platinum dish in an air-bath to expel the water of crystallization. The first molecules of water are lost below 50° and by keeping the temperature below this point it was possible to avoid melting the salt. It has been pointed out by Richards[1] that a salt dried in this way is left in the form of a skeleton which allows the escape of vapor from its inmost recesses, while if fusion takes place during drying, a portion of the original salt may be so enclosed within an impervious coating of anhydrous salt that escape of water is impossible. Except in Analyses 3 and 11 the remaining water of crystallization was expelled during the final heating of the cobaltous chloride in a stream of dry nitrogen and hydrochloric acid gases. Here also the temperature was at first so low that melting of the salt was completely avoided. The temperature was raised to 400° only after apparently all the water was expelled. In Analyses 3 and 11 all the water was expelled in the air-bath.

Silver.—Pure silver was prepared in the fashion usually em-

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[1] Z. physik. Chem. 46, 194 (1903).

ployed in this laboratory as follows: To a dilute solution of silver nitrate an excess of hydrochloric acid was added. The silver chloride was shaken many times with pure water and was then reduced to metallic silver by means of a solution of sodium hydroxide and invert sugar. After the metal had been thoroughly washed with water, it was fused on charcoal with a blowpipe, and the lumps of silver were cleaned by scrubbing with sand and etching with nitric acid. Next they were dissolved in redistilled nitric acid, the excess of nitric acid was neutralized with redistilled ammonia, and the metal was precipitated with ammonium formate which had been made from redistilled formic acid. After the silver had been washed with pure water until free from ammonia, it was again fused in a boat of pure lime before a blowpipe. The buttons of silver were then cleaned with nitric acid and washed with water. Finally the silver was deposited electrolytically, the buttons in turn serving as the anode, a piece of the purest silver as the cathode, and a concentrated solution of one of the buttons in nitric acid as the electrolyte. The electrolytic crystals were washed with water and ammonia, dried, and fused in a boat of pure lime in a porcelain tube in a current of electrolytic hydrogen. The ingots were then cut into pieces of convenient size by means of a jeweler's saw, and were subjected to prolonged cleansing with successive portions of dilute nitric acid, until the acid no longer gave a test for iron, traces of which on the surface of the buttons had been introduced from the saw. The pieces were further cleaned with ammonia and with water, dried in air, and then heated to 300° and cooled in a vacuum. They were preserved in a desiccator containing solid potassium hydroxide.

METHOD OF ANALYSIS.

The cobaltous chloride, contained in a platinum boat, was first heated in a current of hydrochloric acid gas in a hard glass tube. An apparatus consisting of a series of towers which supplied either pure dry hydrochloric acid gas, nitrogen or air was constructed wholly of glass by Dr. M. A. Hines for work upon the atomic weights of cadmium[1] and manganese,[2] and was kindly loaned for this investigation. The hydrochloric acid gas was

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[1] Baxter and Hines: This Journal, **27**, 222 (1905); Baxter, Hines and Frevert: Ibid. **28**, 770 (1906).

[2] Baxter and Hines: Ibid. **28**, 1560 (1906).

generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid, and was dried by passing through five towers filled with beads moistened with concentrated sulphuric acid. Nitrogen was produced by passing a mixture of air with an excess of ammonia over heated rolls of copper gauze. It was freed from ammonia and further purified by passing through three wash-bottles containing dilute sulphuric acid, a tower filled with beads moistened with a solution of silver nitrate to remove sulphur compounds taken from rubber connections at the beginning of the apparatus, a tower filled with solid potassium hydroxide, then through three towers filled with beads moistened with concentrated sulphuric acid and finally through a tube containing resublimed phosphorus pentoxide. The air was purified by passing through a tower filled with solid potassium hydroxide, then through four towers filled with beads moistened with concentrated sulphuric acid, and finally through a tube containing phosphorus pentoxide.

In preliminary experiments in which cobaltous chloride was fused in an atmosphere of pure hydrochloric acid gas, the platinum boat containing the salt was always seriously alloyed on the surface with metallic cobalt. This phenomenon was probably due to partial dissociation of the cobaltous chloride vapor which was invariably formed in considerable quantities when the salt was heated barely to fusion. It was possible to reach a temperature of 400° without meeting the above difficulty, consequently this temperature was employed in the preparation of all samples for analysis, although the salt was not fused at this temperature.

The salt was heated very gently at first in a current of hydrochloric acid gas containing a small quantity of nitrogen until the greater part of the ammonium chloride or water had been expelled, without melting the salt. Then the temperature was increased until finally the salt was maintained at about 400° for at least an hour, usually much longer. After the heating had ceased, the mixture of nitrogen and hydrochloric acid was displaced by nitrogen, and this in turn by dry air, and the boat was transferred to a weighing-bottle without exposure to moist air by means of the bottling apparatus which has frequently served for a similar purpose in many atomic weight investigations in this laboratory.[1]

The weighing-bottle containing the boat and salt was weighed, after it had stood in a desiccator beside the balance case for some time. Then the boat was transferred to a flask containing about 250 cc. of pure water, and the weighing-bottle was rinsed with water, the rinsings being added to the solution in the flask. A trace of insoluble matter was collected by filtering the solution through a tiny filter into a glass-stoppered precipitating flask, and the filter was ignited in a weighed platinum crucible. This residue, which consisted chiefly of cobalt oxide, never amounted to as much as two-tenths of a milligram. In Analyses 1, 2, 9 and 10 a slight increase in the weight of the boat was caused by incipient dissociation of the salt and alloying of the boat. The increase was only 0.05 mg. in the case of Analyses 1 and 9, 0.66 mg. in the case of Analyses 2 and 10. In these cases the weight of the boat after solution of the cobaltous chloride in water, washing and drying at 100° was determined and used in the calculations. These two analyses yielded results essentially identical with the remainder.

From the corrected weight of cobaltous chloride very nearly the requisite quantity of pure silver was calculated. This silver was weighed out, and dissolved in redistilled nitric acid diluted with an equal volume of water in a small flask provided with a column of bulbs to prevent loss by spattering. After the solution had been diluted with an equal volume of water, the nitrous fumes were expelled by gentle heat. Then the solution of silver nitrate, after dilution until its concentration was about 1 per cent., was poured slowly, with constant agitation, into the solution of cobaltous chloride, which also had been diluted to a like concentration in the precipitating flask, and the flask was shaken for some time. The precipitation and subsequent filtration of the silver chloride were carried out in a cupboard made of ruby glass.

After the solution had stood for about two days with occasional agitation, and after the supernatant liquid had become perfectly clear, 25 cc. portions of the solution were tested with hundredth-normal solutions of silver nitrate and potassium chloride in a

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[1] Richards and Parker: Pr. Am. Acad. 32, 59 (1896).

nephelometer[1] for excess of chloride or silver, and, if necessary, either standard silver nitrate or potassium chloride solution was added, and the process of shaking and testing repeated, until the amounts of silver and chloride were equivalent. The test solutions were always returned to the flask since they contained an appreciable amount of silver chloride and the weight of silver chloride subsequently obtained was corrected for the quantity thus introduced.

As soon as the exact end-point had been found, about one decigram of silver nitrate in excess was added, in order to produce as complete precipitation of the silver chloride as possible, and the flask was again shaken and allowed to stand until clear. The precipitate of silver chloride was collected upon a Gooch crucible, after it had been washed several times with a dilute solution of silver nitrate and finally ten times with pure water. Then it was heated in an electric oven for five hours at 180°, cooled in a desiccator and weighed.

In order to determine the moisture still retained by the dried silver chloride, in each case it was transferred as completely as possible to a porcelain crucible and weighed. Then the salt was fused by heating the small covered crucible contained in a large crucible and again weighed.

Although the filtrate and silver nitrate wash-waters were nearly free from dissolved silver chloride, the aqueous washings contained appreciable quantities of this substance. The amount of dissolved salt in both filtrate and wash-waters was determined by comparison with standard chloride solutions in a nephelometer. It has recently been found in this laboratory by Richards and Stähler that if the solution is made slightly alkaline with ammonia and then is acidified immediately before being tested, more accurate results are obtained.[2] This procedure was followed in the greater part of our analyses. The testing took place very shortly after the filtration, so that suspended material had no time to settle.

After the filtrate and wash-waters had been analyzed for dissolved silver chloride, they were filtered through a tiny filter to collect a small quantity of asbestos mechanically detached from the Gooch crucible. This filter was washed with ammonia to

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[1] Richards and Wells: Am. Ch. J. 31, 220 (1904).

[2] Ibid. 35, 512 (1906).

eliminate the silver chloride, which might have been collected and which had been determined in the nephelometric test, and was ignited in a weighed platinum crucible.

For most of the work a new short-armed Troemner balance, sensitive to a fiftieth of a milligram with a load of 50 grams, was used. The gold-plated brass weights were three times carefully standardized to hundredths of a milligram and were used for no other work. Weighings were made by substitution with counterpoises as nearly like the objects to be weighed as possible.

In order that the proper vacuum correction for cobaltous chloride might be applied, the density of this substance was determined by Dr. M. A. Hines in connection with similar work upon manganese. The salt was first fused in a platinum boat in a current of hydrochloric acid gas, and then the toluene displaced was determined with a pycnometer previously described.[1]

Density of $CoCl_2$.

Density of Toluene = 0.86166.

Weight of $CoCl_2$ in vacuum. Grams.	Weight of toluene displaced in vacuum. Grams.	Density of $CoCl_2$. 25°/4°.
4.8719	1.2522	3.352
4.6520	1.1991	3.343
	Average,	3.348[2]

The following vacuum corrections were applied: Cobaltous chloride, +0.000215; silver, —0.000029; silver chloride, +0.000073.

Evidence of the purity of the silver and of the absence of appreciable occlusion by the silver chloride may be obtained from the relation between the amount of silver used in the titrations and the corresponding amount of silver chloride formed. In all, 29.46524 grams of silver produced 39.14905 grams of silver chloride, a ratio of 100.000 to 132.865. Richards and Wells found this ratio to be 100.000 to 132.867.

Attention should be called to the fact that if the salt made from the amine still contained appreciable amounts of ammonium chloride after being heated, the observed value for the atomic weight of cobalt would have been too low. On the other hand, if the cobaltous chloride made from the crystallized salt retained traces of water, the result would have been too high. The average

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[1] Baxter and Hines: Am. Ch. J. 31, 220 (1904).

[2] Playfair and Joule obtained the value 2.937.. Landolt-Bornstein: Physikalisch-Chemische Tabellen, 3rd Ed., p. 238.

THE ATOMIC WEIGHT OF COBALT.

Series I. $CoCl_2 : 2Ag$.

Ag = 107.930 Cl = 35.473.

Number of analysis.	Sample of $CoCl_2$.	Weight of $CoCl_2$ in vacuum. Grams.	Weight of residue. Gram.	Change in weight of boat. Gram.	Weight of silver in vacuum. Grams.	Weight of silver added or subtracted. Gram.	Corrected weight of $CoCl_2$. Grams.	Corrected weight of silver. Grams.	Atomic weight of cobalt.
1	I	1.09971	0.00007	+0.00005	1.82659	+0.00012	1.09959	1.82671	58.991
2	I	1.47808	0.00009	+0.00066	2.45404	−0.00006	1.47733	2.45398	59.005
3	II	3.84144	0.00011	0.00000	6.38106	−0.00025	3.84133	6.38081	59.005
4	II	3.64357	0.00015	0.00000	6.05223	+0.00009	3.64342	6.05232	58.999
5	II	2.96330	0.00015	....	4.92221	+0.00023	2.96315	4.92244	58.995
6	II	3.48435	0.00017	....	5.78776	+0.00039	3.48418	5.78815	58.991
7	II	3.29530	0.00007	....	5.47391	+0.00019	3.29523	5.47410	58.995
8	I	1.57670	0.00015	....	2.61889	+0.00016	1.57655	2.61905	58.992
								Average,	58.997

Series II. $CoCl_2 : 2AgCl$.

Number of analysis.	Sample of $CoCl_2$.	Weight of $CoCl_2$ in vacuum. Grams.	Weight of residue. Gram.	Change in weight of boat. Gram.	Weight of AgCl in vacuum. Grams.	Loss on fusion. Gram.	Weight of asbestos. Gram.	Weight of AgCl from wash-waters. Gram.	Corrected weight of $CoCl_2$. Grams.	Corrected weight of AgCl. Grams.	Atomic weight of cobalt.
9	I	1.09971	0.00007	+0.00005	2.42529	0.00011	0.00016	0.00142	1.09959	2.42676	59.009
10	I	1.47808	0.00009	+0.00066	3.25929	0.00028	0.00006	0.00188	1.47733	3.26095	58.988
11	II	3.84144	0.00011	0.00000	8.47596	0.00040	0.00000	0.00179	3.84133	8.47735	59.014
12	II	2.96330	0.00015	....	6.53901	0.00038	0.00035	0.00121	2.96315	6.54019	58.997
13	II	3.48435	0.00017	....	7.69032	0.00058	0.00017	0.00093	3.48418	7.69084	58.986
14	II	3.29530	0.00007	....	7.27146	0.00049	0.00018	0.00169	3.29523	7.27284	59.002
15	I	1.57670	0.00015	....	3.47946	0.00032	0.00011	0.00087	1.57655	3.48012	58.982

Average, 58.997

Average of Series I and II, 58.997

of all the results obtained with salt made from the amine is 58.995, and the average of the results with salt made from the crystallized chloride is 58.998. The very slight difference between these values lies within the experimental error of the determinations. Evidently, the salt was in all cases essentially free both from ammonium chloride and water. The almost complete absence of ammonium chloride was also shown by two experiments in which the amine was heated in a current of hydrochloric acid in the usual manner, and then the salt was dissolved in water and the cobalt was precipitated by the addition of ammonia-free sodium hydroxide. In one case where 1.76 grams of cobaltous chloride were used, the filtered solution, when tested with Nessler's reagent, showed the presence of 0.00025 gram of ammonium chloride, while in the other 2.13 grams of cobaltous chloride yielded 0.00005 gram of ammonium chloride. This proportion of impurity would have lowered the observed atomic weight 0.004 in the first case, and only 0.001 in the second. The average 0.003 is exactly the difference between the averages from the two samples of material. If this correction is applied in the analyses where the cobaltamine was used, the averages of both Series I and Series II are raised to 58.998, a negligible change.

Whether or not such a correction is applied the average of Series I and II confirms very closely the value 58.995 previously found by analysis of the bromide, hence the atomic weight of cobalt may, as before, be assumed to be 59.00 referred to silver 107.930.

We are deeply indebted to the Cyrus M. Warren Fund for Research in Harvard University for many platinum, quartz, and other vessels.

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SEPARATION AND ESTIMATION OF BERYLLIUM.

BY CHARLES L. PARSONS AND S. K. BARNES.

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THE separation of beryllium from other elements presents little difficulty except in the case of aluminum and iron. It will invariably be found with aluminum in the last instance, and the problem therefore becomes the determination of beryllium in such a mixture.