VIII.—*On the Atomic Weights of Cobalt and Nickel.*

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1.—*Cobalt.*

WHEN oxide of cobalt is ignited in the air, no constant compound is obtained, the weight of oxide varying more or less after each ignition. Sometimes the weight approaches very nearly that required by the supposition that the oxide has the composition Co_3O_4 ; at other times it diminishes so as only slightly to exceed the weight it would have if the whole of it were pure protoxide. This alteration in weight may be made to take place at pleasure by varying the intensity of the heat, and the rate at which the oxide is cooled. When the oxide is strongly ignited over a blast-lamp, and rapidly cooled, its composition agrees very nearly with that of the protoxide, but when slowly cooled or less strongly heated, it is found to contain a larger amount of oxygen. It appears probable from these facts, that the higher oxides of cobalt are decomposed at a high temperature, and reproduced to a greater or less extent as the oxide cools.

Again, if oxide of cobalt is strongly heated in a crucible filled with carbonic acid, and allowed to cool without coming in contact with the air, it undergoes a complete change of colour, passing from black to a rather light brown. This change of colour was first mentioned to me by my friend Dr. Dexter. I have carefully examined this brown substance, and have proved by numerous analyses that it is pure protoxide of cobalt. To show the constancy of this compound, and the ease with which it may be formed, I cite the following experiments:—1·3971 grms. of black oxide of cobalt were heated for five minutes in a platinum crucible over a blast-lamp in a current of carbonic acid, then allowed to cool in an atmosphere of this gas, and weighed. Its weight was 1·3017. This same portion of oxide was then heated in the air, so to reconvert it into black oxide, and then again heated in carbonic acid: it now weighed 1·3015.

No. of Experiment.	Quantity taken.	Weight after ignition in CO_2 .	CoO per cent.
1.	1·3971	1·3017	93·17
1.	do. (reheated)	1·3015	
2.	1·1114	1·0357	93·18
3.	1·0103	0·9414	93·19

The last column shows the percentage amount of protoxide contained in this specimen of black oxide, as deduced from these experiments.

In order to ascertain whether the oxide would undergo any further change by being heated for a longer time in carbonic acid, a weighed portion of the brown oxide was heated over the blast-lamp for three-quarters of an hour, and the heat rendered as intense as possible by surrounding the platinum crucible with a black lead one; but this produced not the slightest alteration in the weight of the oxide. Again, that this brown oxide is unmixed with any of the higher oxides of cobalt, is proved by dissolving it in hydrochloric acid and distilling the acid into water containing iodide of potassium and starch, when no trace of blue colour is produced.

The composition of this compound was ascertained by reducing known weights of it by means of hydrogen. The first two experiments for instance gave the following results:—

1.2612 grms. of brown oxide gave 0.9915 of metal.

0.8193 grms.   do.   do. 0.6441   do.

From these we deduce the following percentage:—

Composition, 1st expr. Cobalt, 78.61.

2nd „   do. 78.61.

These experiments were made soon after Schneider* published his paper on the Atomic Weight of Nickel and Cobalt; and as they differ so widely from the number 78.94, which should have been obtained, had his equivalent of 30 been correct, I was induced to undertake a series of experiments to establish, if possible, the true atomic weight of this metal. The difficulty which had previously existed in preparing a pure oxide of cobalt, prevented the atomic weight being obtained by so simple a method as that of the reduction of the oxide by hydrogen. The method adopted by Rothoff, who, I believe, was the first to make any experiments on the atomic weight of cobalt, was to estimate the amount of chlorine in a known weight of chloride of cobalt by precipitation with nitrate of silver. The atomic weight he deduced from his experiments was 29.45. Schneider, by estimating the amount of cobalt and carbon in the oxalate, deduced the number 30 as the true atomic weight. Dumas†, who has still more recently investigated this subject, adopted a process

* Pogg. Ann., 101, 387.

† Ann. Ch. Pharm., 113, 20.

similar to that used by Rothoff, only using a standard solution of nitrate of silver instead of weighing the chloride of silver formed. He deduces from his experiments, which vary from 29·50 to 29·57, the number 29·5 as the probable atomic weight of cobalt.

The properties of this brown protoxide of cobalt well adapt it for being used as a means of determining the atomic weight. It is easily obtained, is of very definite composition, but slightly hygroscopic, and easily reduced to the metallic state. At ordinary temperatures, it appears to undergo but very slight alteration in composition; some specimens of it have been kept for many weeks without absorbing any trace of oxygen; another specimen prepared some eight or nine months ago, has now been found to contain a trace of some higher oxide.

It naturally suggested itself as an interesting question whether the carbonic acid acts otherwise than merely mechanically, simply preventing the contact of oxide, after it has been heated, with the air, or whether the presence of a foreign atmosphere is the principal cause of the ready giving off of the excess of oxygen. The experiments I have made on this subject show that the carbonic acid is not necessary to the formation of the protoxide, but that it is a question of temperature, all the higher oxides of this metal being decomposed when strongly heated. I proved this in the following manner:—A small platinum crucible was nearly filled by pressing into it oxide of cobalt, and strongly heated over a blast-lamp for ten minutes; it was then very rapidly cooled by immersing the crucible in cold water. When quite cold, the oxide was turned out of the crucible, and it was found that, although the surface was black, the interior portion had the characteristic brown colour. By this process also, I have obtained an oxide which analysis has shown not to vary above $\frac{1}{10}$ or $\frac{2}{10}$ per cent. from the oxide prepared by the help of the carbonic acid.

In the following experiments on the atomic weight of cobalt, three different specimens of the black oxide were used. They were sold as being nearly pure, but contained a considerable amount of impurity, the nature and quantity of which varied in each specimen. The following is the process which was adopted to purify them:—The oxide was first dissolved in hydrochloric acid, then evaporated to dryness, and heated for several hours. The chloride was then dissolved up in water containing a few drops of hydrochloric acid, and the insoluble silica filtered off. This process was repeated to ensure the removal of the silica. A

considerable amount of sulphurous acid was now passed into the solution of the chloride, and the liquid allowed to stand for some days in a warm place. The sulphurous acid was then removed by boiling, and after adding hydrochloric acid, the liquid was thoroughly saturated with hydrosulphuric acid, and again allowed to stand for several days in a warm place. If more than a very small amount of precipitate was obtained with the first specimen of cobalt, the iron was then precipitated by ammonia; and the remaining metals were converted into sulphides, and digested for some length of time with dilute hydrochloric acid to remove the manganese. The cobalt was next converted into Claudet's salt, and then boiled with strong hydrochloric acid for some days, the acid being changed from time to time. In order to purify still further this salt, it was dissolved in water slightly acidulated with hydrochloric acid and recrystallized. The salt was now heated first in air and afterwards in hydrogen; the metal was then dissolved in nitric acid, and the solution was evaporated to dryness, and strongly heated. The carbonic acid used was prepared from white marble, and purified and dried by passing, first through two wash-bottles containing pumice-stone and a solution of carbonate of potash, then through another wash-bottle containing sulphuric acid, and lastly through a U-tube containing pumice-stone moistened with sulphuric acid.

The hydrogen was prepared by using thin sheet-zinc, which appeared to be free from arsenic, and was passed, first through a wash-bottle containing a dilute solution of caustic potash, then through one containing a solution of nitrate of silver, and afterwards dried by passing through a third bottle partly filled with sulphuric acid, and lastly through a U-tube containing pumice moistened with sulphuric acid. To break up the stream of gas, small pieces of pumice-stone were placed in all the bottles.

Both these gases passed along the same tube into the crucible containing the cobalt, this tube being connected by means of a T-piece with both apparatus. There was also another means of escape for the gases, namely, by a tube passing through the cork of the last washing bottle, and bent down so as to dip some distance into sulphuric acid. Thus, when the sides of either of the caoutchouc tubes connecting the T-piece with the last drying of either apparatus were pressed together by a clamp, the gas then escaped, bubbling up through the sulphuric acid. By this contrivance, either gas could be passed into the crucible

without admitting the air. The reason for adopting this method was the difficulty and loss of time experienced in cooling the platinum crucible full of hydrogen, the platinum causing the gas to burn, and in some cases the moisture thus formed was found even to affect the weight of the cobalt. To obviate this, the oxide of cobalt, after being reduced by hydrogen, was allowed to cool in an atmosphere of carbonic acid.

The oxide of cobalt was weighed in a small cup made of platinum foil; the foil was first heated in nitric acid to remove any foreign metal adhering to its surface, and before being used, it was proved that the weight of the cup remained unaltered after being heated both in air and in hydrogen. In order to heat this cup without bringing it in contact with the gas flame, it was placed inside a platinum crucible in the bottom of which there was a piece of pipeclay; this prevented the direct contact of the two platinum surfaces, which, after being strongly heated, are apt to adhere together with considerable force. A cover of platinum foil was carefully fitted on to the crucible, and a hole in the centre admitted the tube conveying the gas. To prevent, however, the stream of gas playing directly on the oxide, a small piece of platinum-foil was fastened in front of the orifice, so that the gas striking against it was more uniformly spread over the interior of the cup, and any mechanical carrying away of the oxide was prevented.

The general process adopted in the experiments was as follows: The weight of the platinum cup was first carefully ascertained, then, after introducing the necessary quantity of black oxide, the cup was placed inside the crucible, and the air thoroughly expelled by carbonic acid. The crucible was now heated as strongly as possible over a blast-lamp for about a quarter of an hour, then allowed to cool, a brisk current of carbonic acid being kept up the whole time. The cup was afterwards removed to the balance case, the bottom of which was covered with a layer of chloride of calcium, and carefully weighed. By repeating this operation two or three times, a constant weight of the protoxide was obtained. The reduction by hydrogen was effected, first at a comparatively low temperature, the crucible being heated only by a single Bunsen's burner for half to three-quarters of an hour, and then by a blast-lamp for about a quarter of an hour; in this way the metal was obtained in a dense form and hardly at all hygroscopic.

The first specimen of cobalt gave the following results when treated as above described :—

No. of Experiment	Protoxide taken	Weight of Metal found	Amount of Metal in 100 parts of Protoxide
1.	2·1211	1·6670	78·591
2.	2·0241	1·5907	78·588
3.	2·1226	1·6673	78·550
4.	1·9947	1·5678	78·598
5.	3·0628	2·4078	78·614
			Mean 78·588

After making these determinations, the remaining portion of the oxide was again dissolved in hydrochloric acid, and subjected a second time to a process of purification similar to the one it had already undergone. The following are the results obtained from the oxide thus treated :—

Cobalt.

Specimen No. 1—2nd Purification.

No. of Experiment	Protoxide taken	Weight of Metal found	Amount of Metal in 100 parts of Protoxide
1.	2·1167	1·6638	78·603
2.	1·7717	1·3924	78·591
3.	1·7852	1·4030	78·591
			Mean 78·595

Again, the remaining portion of this oxide was subjected to a third purification, and the amount of metal in the oxide determined.

Cobalt.

Specimen No. 1—3rd Purification.

No. of Experiment	Protoxide taken	Weight of Metal found	Amount of Metal in 100 parts of Protoxide
1.	1·6878	1·3264	78·588
2.	2·2076	1·7350	78·592
			Mean 78·590

The second specimen of cobalt, after being treated in the same manner as the first, gave the following results:—

Cobalt.

Specimen No. 2.

No. of Experiment	Protoxide taken	Weight of Metal found	Amount of Metal in 100 parts of Protoxide
1.	2·6851	2·1104	78·597
2.	2·1461	1·6868	78·598
			Mean 78·597

The third specimen gave the following results:—

Cobalt.

Specimen No. 3.

No. of Experiment	Protoxide taken	Weight of Metal found	Amount of Metal in 100 parts of Protoxide
1.	3·4038	2·6752	78·595
2.	2·2778	1·7901	78·589
3.	2·1837	1·7163	78·596
			Mean 78·593

The following numbers are the means of each of the foregoing series of determinations:—

78·588
78·595
78·590
78·597
78·593
Mean..... 78·5926

If now we take this last mean as representing the true amount of metal in the oxide, and calculate from it the atomic weight of cobalt, we find it is represented by the number 29·370.

II.—NICKEL.

For determining the atomic weight of this metal, three different specimens of nickel were employed. The following is the method adopted for obtaining the metal in a pure state. The first part of the process is similar to that already described for the purification of the cobalt, namely, dissolving in hydrochloric acid, and separating the silica, arsenious acid, and other metals precipitable from an acid solution by hydrosulphuric acid. Having removed any of these impurities that might be present, the solution was diluted very considerably and saturated with chlorine, carbonate of baryta added, and the excess of this salt removed by dilute sulphuric acid. The nickel was then precipitated by means of pure oxalic acid prepared by decomposing oxalate of ethyl with water. The oxalate of nickel thus obtained was dissolved in ammonia, and then allowed slowly to deposit from this solution. It was then washed and dried, and, after being strongly heated, was dissolved in nitric acid, the solution evaporated to dryness, and the nitrate decomposed by heat. As the oxide of nickel obtained in this way is generally regarded as the pure protoxide, and as I found that on heating it over a Bunsen's burner in a platinum capsule, in the same way as that adopted in heating the cobalt, the weight of the oxide and capsule remained constant, I supposed the oxide to be pure protoxide. For instance, three consecutive experiments gave the following numbers as the amount of metal in the oxide: 78·461, 78·472, and 78·465. The oxide in this case was prepared by heating the nitrate to a red heat for several hours, and well stirring it, and although these three specimens were heated for different lengths of time, still this produced no appreciable difference of composition, as is shown by these numbers; it was found, however, that if different temperatures were employed, considerable variations in the amount of metal contained in the oxide occurred. If, for instance, the oxide were prepared by employing a dull red heat, four consecutive experiments showed that it contained only the following amounts of metal, 78·418, 78·421, 78·442 and 78·418, and however long the heat was continued it did not change the composition; in fact, the second of these four specimens was heated for twelve hours longer than the first. Further, on boiling the oxide prepared in

this way with hydrochloric acid, and passing the products of the distillation into a solution of iodide of potassium, free iodine was always liberated. I next tried whether I could obtain a pure protoxide by employing a much higher temperature, and was quite successful in so doing. When oxide of nickel is very strongly heated over a blast-lamp, all the higher oxides are decomposed and pure protoxide remains behind. On dissolving the oxide thus obtained in hydrochloric acid no chlorine is liberated. This complete decomposition of the higher oxides is however not very easily effected; the heating must be continued for a considerable length of time, the oxide occasionally stirred, and the heat of the blast-lamp rendered as intense as possible. In several instances I traced by analysis this gradual loss of oxygen by continued heating, the amount of metal in the oxide increasing till, as will be seen in the following experiments, it reached 78.59, and then, however long the heating was continued, no further alteration took place. This continued heating produces a very marked change in the oxide: it diminishes greatly in bulk, and assumes, I believe, always when pure a bright green colour.

This pure protoxide of nickel was at first prepared by heating the ordinary oxide in carbonic acid in the same way as that adopted in preparing the oxide of cobalt; but it was found that the carbonic acid was in no way necessary, the oxide of nickel differing from that of cobalt in having no tendency to reabsorb, on cooling, the oxygen which it has lost at a high temperature. This difference of property of the two oxides is well shown by the following experiment made with the pure oxide of nickel:—

Weight of the oxide after heating over blast-lamp	1.8296
Do. do. exposed to low red heat for $1\frac{1}{2}$ hours	1.8296
Do. do. do. $\frac{1}{2}$ hour	1.8296

Neither did this continual heating at a low temperature produce the least change in the green colour of the oxide.

In making the following analyses, it was however found convenient to pass a stream either of carbonic acid or of air into the crucible containing the oxide, while it was being heated, in order to prevent any reducing gases from the flame acting on the oxide; many analyses showed that the composition of the oxide was the same whichever of the gases was used.

The following determinations were made with the same precau-

tions and in the same way as that adopted with the oxide of cobalt. The oxide of nickel was heated so as to convert it into a very nearly, if not quite, pure oxide, before taking a weighed quantity for experiment.

Nickel.

1st Specimen.

No. of Experiment.	Oxide taken.	Weight of Metal found.	Amount of Metal in 100 parts of Oxide.
1.	2·0820	1·6364	78·597
2.*	—	—	—
3.	2·0956	1·6468	78·584
4.	2·0148	1·5838	78·608
Mean			78·596

The second specimen of nickel was purified three times by the process already described. Unfortunately, I have no determinations made after the first and second purifications; but the oxide, after having undergone the three purifications, gave the following results :—

Nickel.

2nd Specimen—3rd Purification.

No. of Experiment.	Oxide taken.	Weight of Metal found.	Amount of Metal in 100 parts of Oxide.
1.	2·2069	1·7342	78·581
2.	2·2843	1·7952	78·589
3.	2·1329	1·6761	78·583
Mean			78·584

A comparison of these two tables will show how very slight is the effect produced by increasing the number of purifications, the difference of the means of the two series being only ·012.

* The second experiment I have omitted in the table, owing to its not having been made at so high a temperature as the others, so that a trace of a higher oxide appears to have escaped decomposition. When making this experiment, I was not aware of the high temperature necessary. The results of the experiment are as follows :—

No. of Experiment.	Oxide taken.	Weight of Metal found.	Amount of Metal in 100 parts of Oxide.
2.	2·6921	2·1151	78·567

The third specimen of nickel, after one purification, gave the following results :—

Nickel.

3rd Specimen—1st Purification.

No. of Experiment.	Weight of Oxide taken.	Metal found.	Amount of Metal in 100 parts of Oxide.
1.	2·2783	1·7911	78·616
2.	2·1434	1·6845	78·590
3.	2·4215	1·9030	78·588
Mean			78·598

The mean of this series of experiments is almost identical with that of the first series. I therefore resolved to repurify the remainder of this oxide, in order to see if a decrease in the number would again take place. The following are the results obtained :—

Nickel.

3rd Specimen—2nd Purification.

No. of Experiment.	Weight of Oxide taken.	Metal found.	Amount of Metal in 100 parts of Oxide.
1.	2·1859	1·7179	78·590
2.	2·0088	1·5788	78·594
3.	2·0839	1·6379	78·597
4.	2·6560	2·0873	78·588
Mean			78·592

This second purification can hardly be said to have altered the mean result of these experiments. We have then the following numbers as the means of the different series of experiments :—

1st Specimen	78·596
2nd Specimen—3rd Purification	78·584
3rd Specimen—1st Purification	78·598
Ditto 2nd Purification	78·592

If now we allow the mean of each series of experiments to have an equal value, the general mean will be 78·592; and, taking this number as representing the true amount of metal in the oxide, it gives, as the atomic weight of nickel, the number 29·369.

From the foregoing experiments, it appears then that the atomic

weights of nickel and cobalt are identical and somewhat lower than the number hitherto in use.

As the alteration in the weights obtained would have been so slight, it was not thought worth while to reduce the weighings to what they would have been in a vacuum.

In conclusion, my best thanks are due to my assistant, Mr. Gill, for the very valuable aid he has given me in carrying out this research.