The isometrics of ethyl ether from a specific volume of 2.5 to 35 cc. per g. and from 175° to 325° have been measured. It was found that from 15 cc. per g. to the smallest densities the isometrics were substantially straight within the experimental error of the measurements. At densities greater than 15 cc. per g. the isometrics show a curvature which becomes greater as the density increases.

From the experimental data the Keyes equation of state for ether vapor was determined. This is $p = \frac{1.1074}{v-\delta}T - \frac{5709}{(v+0.734)^2}$; $\log_{10}\delta = 0.77325 - \frac{2.4240}{v}$; $T = t°\text{C.} + 273.13$.

A modification of the last term of the Keyes equation, suggested by H. B. Phillips has been examined and found to hold as well as or slightly better than the original form. In this case the equation is $p = \frac{1.1074}{v-\delta}T - \frac{5709}{v^2}e^{-\frac{1.468}{v}}$ where $\log v^2\phi = 3.75656 - \frac{0.6375}{v}$, ϕ being the last term on the right hand side of the equation. In these equations v is the specific volume in cc. per gram, and p the pressure in atmospheres of 760 mm. of mercury at 0° and under standard conditions of gravitation.

The equation reproduces the measured pressures with great accuracy from the largest specific volumes to 15 cc. per g., that is, in the region of straight isometrics. At greater densities the equation in its present particular form cannot be used. The form which the equation takes in this region, where presumably the molecular species is changing (association or dissociation occurring) will be examined in a later article.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY, HARVARD UNIVERSITY]

A COMPARISON OF THE ATOMIC WEIGHTS OF TERRESTRIAL AND METEORIC COBALT. V. THE ANALYSIS OF COBALTOUS CHLORIDE

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The question of the identity of elementary material from different sources has received considerable attention at various times.

Even before the existence of isotopes was suspected many such comparisons were carried out.[1] More recently the matter has received especial

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[1] See especially copper: Richards, *Proc. Am. Acad. Arts Sci.*, **23**, 178 (1887); nickel: Richards and Cushman, *ibid.*, **33**, 102 (1897); calcium: Richards, THIS JOURNAL, **24**, 374 (1902); sodium and silver: Richards and Wells, *Carnegie Inst. Pub.*, **28**, 13, 17 (1905).

attention in the case of elements whose isotopes are products of radioactive disintegration,[2] in the case of certain elements found in meteorites,[3] and in the case of chlorine[4] and mercury.[5] All of these comparisons have yielded the same result. Except in the case of the products of radioactive disintegration, the elements seem always to be the same wherever found, in the earth's crust, or in meteorites. A single exception to the foregoing statement should be made. Muzaffar[6] claims to have discovered a difference between samples of antimony from different sources.

We have pursued this study further with respect to cobalt, although for some time it has been suspected and predicted[7] that cobalt is a simple element. Moreover, Aston[8] recently has found its mass spectrum to indicate the existence of only a single cobalt atom, of mass 59. In view of the latter fact the likelihood of finding more than one variety of cobalt in nature is small, but the following comparison of terrestrial and meteoric cobalt had been practically completed when Aston's announcement was made. In any case the evidence which has been obtained of the identity of the two sorts of material is of some corroborative value. Furthermore, the atomic weight of cobalt has been found to be slightly lower than the current one.

The method of comparison was to prepare pure anhydrous cobaltous chloride from both sorts of material and to analyze the chloride by comparison with silver.

Purification of Meteoric Cobalt

Water, reagents and gases were purified as previously described in many papers from this Laboratory.[9]

The iron meteorite from which the cobalt was obtained is the property of Professor Emeritus John E. Wolff who very kindly presented to us a generous supply of material. The history of the meteorite is unknown beyond the fact that it was probably found in the western part of the United States. It is not impossible that it is a fragment of the Cañon Diablo meteorite. There is nothing about its composition to contradict this possibility. At any rate, there is no question of its meteoric nature. The Widmanstättian figures and other general features of appearance and composition leave no doubt on this point. Preliminary examination showed it to contain about 0.5% of metallic cobalt.

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[2] Lead: Baxter and Grover, THIS JOURNAL, **37**, 1027 (1915).

[3] Iron: (a) Baxter and Thorvaldson, *ibid.*, **33**, 337 (1911). (b) Baxter and Hoover, *ibid.*, **34**, 1657 (1912). Nickel: (c) Baxter and Parsons, *ibid.*, **43**, 507 (1921); (d) Baxter and Hilton, *ibid.*, **45**, 694 (1923).

[4] Curie, *Compt. rend.*, **172**, 1025 (1921). Gleditsch and Samdahl, *ibid.*, **174**, 746 (1922). Dorenfeldt, THIS JOURNAL, **45**, 1577 (1923).

[5] Brönsted and Hevesy, *Z. anorg. allgem. Chem.*, **124**, 22 (1922).

[6] Muzaffar, THIS JOURNAL, **45**, 2009 (1923).

[7] Harkins, *ibid.*, **45**, 1426 (1923).

[8] Aston, *Nature*, **112**, Sept. 22 (1923).

[9] See, for example, Baxter and Grover, THIS JOURNAL, **37**, 1027 (1915).

The entire meteorite weighed about 75 kilograms. A fragment weighing approximately 7 kg. was cut off by means of a power hack saw, the cuttings being rejected. Several nodules of troilite were encountered, some as much as 3 cm. in diameter. A large proportion of the troilite was chipped out of the metallic mass and preserved for subsequent examination. Other nodules of troilite exposed during solution of the metal also were set apart.

After solution of the metal in nitric acid the greater part of the iron was separated by crystallization of ferric nitrate. Various devices were tried in order to hasten solution of the metal, such as varying the concentration and temperature of the acid, making the metal strongly anodic, reversing the poles, using alternating current. The most rapid action was secured at boiling temperature with nitric acid diluted with 30 to 40% of water. As soon as a given portion of acid had dissolved a considerable amount of meteorite it was decanted, concd. nitric acid was added to lower the solubility of the ferric nitrate, and the solution was allowed to cool and crystallize. The mother liquor was successively evaporated and allowed to deposit ferric nitrate until nickel nitrate crystals began to appear on crystallization. The ferric nitrate crystals, weighing nearly 50 kg., were all twice recrystallized from concd. nitric acid and the three mother liquors were united. These mother liquors contained, besides approximately 35 g. of cobalt, about 700 g. of nickel and the same amount of iron.

Since ferric hydroxide carries down nickel hydroxide and especially cobalt hydroxide when precipitated from mixed solutions by ammonia, and because of the difficulty of handling large amounts of ferric hydroxide, the cobalt and nickel were separated from the iron by precipitation of the sulfides and extraction with dil. hydrochloric acid. The solution of the mixed nitrates was evaporated to expel some of the excess of acid, and then was made alkaline with ammonia. Scrubbed hydrogen sulfide was passed in until precipitation was complete. Then, after the solution had stood for some time, hydrochloric acid was added until the solution was about 1% in this substance. After a short time the undissolved cobalt and nickel sulfides were filtered out and washed.

Solution of the sulfides in nitric acid was followed by filtration to remove sulfur and evaporation to eliminate much of the excess acid. Potassium nitrite and potassium chloride were next added until apparently the potassium cobaltinitrite was completely precipitated.

Since the hydrochloric acid extract of the sulfides contained a small quantity of cobalt it was concentrated from 40 to 5 liters. Thereupon several hundred grams of ferric phosphate separated. This was set aside for future examination. The solution was treated with ammonium acetate and potassium nitrite, and a further precipitate of the cobalt complex was obtained.

The combined cobaltinitrite precipitates were thoroughly washed by decantation, with centrifugal settling to increase the efficiency of each washing. Next, all the precipitate was dissolved in hydrochloric acid, and the solution was evaporated until a large portion of the excess of acid had been expelled. Upon saturation of the solution with hydrogen sulfide little or no precipitate formed, but by adding a small amount of potassium hydroxide a sulfide fraction consisting chiefly of cobalt sulfide was precipitated and removed by filtration.

From the filtrate the double nitrite was again precipitated, the precipitate was thoroughly washed, and then the precipitation was thrice repeated. The mother liquor of the last precipitation gave no test for nickel with dimethyl glyoxime and no test for iron with ferrocyanide. Since heavy metals had been eliminated as sulfide, there remained only the alkalies to be removed. This was done in large part by electrolysis.

The double nitrite was dissolved in freshly distilled sulfuric acid and the sulfate solution was evaporated nearly to dryness to eliminate nitric and nitrous acids. After the residue had been dissolved in water, distilled ammonia was added in excess and the solution was electrolyzed in platinum dishes. The metal from several portions of electrolyte was deposited one layer after another upon a single dish. The deposited cobalt was washed with water, dissolved in sulfuric acid by making the dish the anode, an excess of ammonia was added, and the solution was again electrolyzed. The electrolytic process was then repeated a second time.

The final deposit of metal was dissolved in redistilled hydrochloric acid, a sulfide fraction was removed in order to eliminate platinum, and the solution was evaporated to crystallization in a quartz dish. Saturation with hydrogen chloride, made by boiling concd. hydrochloric acid, conducting the gas to the solution through a quartz tube and cooling with ice, materially increased the yield. Two further crystallizations of the chloride followed, although even the second mother liquor was free from sulfate. The thrice crystallized product is Sample M_1. The mother liquors were worked up by two crystallizations for Sample M_2. Here also the second mother liquor was sulfate-free.

Several samples of terrestrial cobalt were purified in substantially the same manner. Sample A was prepared from commercial "nickel-free" cobalt nitrate. About 0.5 kg. of crystals was dissolved, the solution was filtered, and potassium cobaltinitrite was precipitated by potassium nitrite and acetic acid. The mother liquor gave tests for both nickel and iron. The precipitate was washed by decantation five times with water, with centrifugal settling. Only after dissolving and reprecipitating the double nitrite twice more was the mother liquor wholly free from nickel and iron.

In order to remove alkalies and silica the attempt was next made to electrolyze the solution obtained by dissolving the double nitrite in nitric acid and adding an excess of ammonia. Owing to continual separation of the cobaltammine nitrate this was not successful.

Recrystallization of the ammine from ammonia was given up on account of its low solubility. Finally, the ammoniacal solution was boiled until the greater part of the cobalt was precipitated as a mixture of cobaltous and cobaltic hydroxides. This precipitate was washed thoroughly with pure water, with centrifugal settling. From the mother liquor considerable cobalt was recovered as sulfide, and after solution of the sulfide in nitric acid was precipitated with ammonia and washed as above. The combined precipitates were dissolved in nitric acid containing a small amount of hydrogen peroxide, and again the hydroxide was precipitated by a slight excess of ammonia. Thorough washing followed. Up to this point all operations were carried on in Jena or Pyrex vessels.

The precipitate of hydroxide was now placed in a quartz dish and dissolved in nitric acid which had been distilled through a quartz condenser. Upon evaporation of the solution to dryness and solution of the residue in water a precipitate of silica was evident. This was removed by filtration through a platinum-sponge Gooch crucible, into a platinum dish. After evaporation to the point of crystallization, the solution was cooled and the crystals were centrifugally drained in platinum. The crystals were twice recrystallized from concd. nitric acid, in which they are considerably less soluble than in water. Further crops of nitrate which had been four times crystallized were obtained from the mother liquors by the usual process of fractional crystallization, in which the mother liquors of a purer fraction are used to dissolve the crystals from a less pure fraction. Although no test for alkali was made, it seems reasonable to expect that the two precipitations as hydroxide together with the crystallization of the nitrate had effectually removed potassium.

All the recrystallized nitrate was now decomposed by heating the crystals in a platinum dish on an electric hot plate. After being powdered in an agate mortar the mixture of oxide and basic nitrate was still further heated to redness in a platinum boat in a porcelain electric muffle.

Solution in hydrochloric acid which had been redistilled in quartz followed, in a quartz dish, to prevent difficulty from the presence of chlorine liberated by cobaltic oxide or residual nitrate. The solution was evaporated to dryness to expel chlorine, and the residue was dissolved in the smallest possible quantity of constant-boiling hydrochloric acid. The solubility of the chloride was then lowered by saturating the solution at 0° with hydrogen chloride. The crystals were drained centrifugally in platinum Gooch crucibles and washed with constant-boiling hydrochloric acid. In all, the chloride was crystallized thrice. It is designated Sample A_1. Sample A_2 was obtained from the mother liquors and was four times crystallized.

The earlier analyses which were made with this material yielded an unexpectedly low result for the atomic weight of cobalt; therefore a second sample of chloride was made from the mother liquors of the nitrate and chloride crystallizations. The salts were changed to sulfate by repeated evaporation with an excess of sulfuric acid which had been distilled in quartz. The residue was then dissolved, the solution was made strongly ammoniacal, and after filtration the cobalt was deposited electrolytically on platinum vessels. Solution of the metal in hydrochloric acid and evaporation of the solution to dryness in quartz was followed by treatment with hydrogen sulfide to remove a possible trace of platinum or other heavy metals. After the hydrogen sulfide had been expelled from the solution the chloride was thrice crystallized as described before. The third mother liquor gave no test for sulfate. This material is designated Sample B.

Sample C was made from a specimen of cobalt foil remaining from the purification by Baxter and Coffin.[10] This had been purified by crystallization of the purpureo-cobalt chloride. The foil was converted to chloride by heating in a current of pure dry hydrogen chloride in a quartz tube at a temperature high enough to sublime the chloride.

It is reasonable to expect that the process of precipitation as hydroxide or that of electrolysis should have been effective in eliminating alkalies and silica. It is to be remembered that sodium lowers but potassium raises the apparent atomic weight of cobalt. So far as the silica is concerned recent experience has shown that material handled in silica vessels is likely to contain this substance, especially in the case of hot concentrated solutions. However, the cobalt chloride was all sublimed in a current of hydrogen chloride as described below, and it is certain that this process eliminated the last trace of silica.

Sublimation and Drying of Cobaltous Chloride

To prepare the cobaltous chloride for analysis it was first dried and sublimed in a current of dry hydrogen chloride. Then it was fused in a weighed quartz boat and weighed.

The crystallized salt, which had been partially dehydrated in the desiccator where it had been preserved, was placed in two quartz boats in a quartz tube connected with a supply of dry hydrogen chloride, nitrogen and air. At first the salt was heated by means of an aluminum block furnace, in a current of hydrogen chloride, at about 50° to avoid melting, until the first two molecules of water of crystallization had evaporated. Then the temperature was raised to 120° where the remainder of the water of crystallization evaporated, and next to about 300° for some time. Fusion of the salt by means of an electrically-heated sleeve followed and then, after all moisture had been expelled from the tube, the salt was sublimed from the boats to the tube. As in similar experiments with nickelous chloride already described,[11] a slight residue of silica remained in the boats.

[10] Baxter and Coffin, This Journal, **28**, 1582 (1906).

[11] Ref. 3d, p. 697.

Upon resublimation of the salt no silica was left, although in the case of nickelous chloride several sublimations were necessary to free the salt from silica. The difference lay in the fact that since cobaltous chloride fuses before sublimation, the silica coagulates in the melted salt and remains in the receptacle. Nickelous chloride sublimes without melting and the fluffy silica residue is apparently blown along in the current of gases. As soon as it was found that a second sublimation was unnecessary, the salt used in the analyses was sublimed only once.

After the sublimation of the salt the hydrogen chloride was displaced by dry nitrogen and this gas in turn by air. The sublimed salt was easily removed from the tube with a long platinum spatula. Then it was again fused in a current of hydrogen chloride in a weighed silica boat contained in a quartz tube which formed part of a Richards and Parker bottling apparatus.[12] After the apparatus had cooled, the hydrogen chloride was displaced by dry nitrogen, and this in turn by air. The boat was transferred to the bottle, in which it had been weighed, and the bottle was stoppered, all without exposing the salt to moisture for an instant. The bottle and boat were then reweighed. The boat was heated in a current of air in the bottling apparatus and was bottled in dry air before the initial weighing of the empty boat.

Method of Analysis

The boat and contents were transferred to a 3-liter glass-stoppered precipitating flask and covered with a few hundred cubic centimeters of pure water. The weighing bottle and stopper were rinsed and the rinsings added to the flask. As soon as the cobaltous chloride had dissolved, the boat was removed from the flask and carefully rinsed, and the solution was diluted until the concentration of cobaltous chloride was approximately 1%.

Pure silver equivalent to the chloride within a few tenths of a milligram was weighed, dissolved in nitric acid, and diluted until the concentration was approximately 1%. The silver solution was then added to the chloride solution in small portions with frequent shaking, and the flask was allowed to stand at room temperature for some days with occasional agitation. The clear supernatant solution was next tested in a nephelometer for excess of chloride or silver, by adding equivalent amounts of 0.01 *N* silver nitrate and potassium chloride solution to separate portions. The estimated deficiency of either was added in the form of 0.01 *N* solution, the solution was again shaken, allowed to clarify, and tested as before, and the process was repeated until exactly equivalent quantities of silver and chloride had been used. The end-points were finally adjusted nearly six months after the commencement of the analyses, so that occluded material had abundant opportunity to be leached out.

[12] Richards and Parker, *Proc. Am. Acad. Arts Sci.*, **32**, 59 (1896).

In order to avoid difficulty from variations in atmospheric density, the bottle and boat were weighed by substitution for a counterpoise of similar weight, shape and volume. The silver was weighed by substitution for weights.

A high sensitivity balance was used, and the relative values of the weights were found to hundredths of a milligram by the Richards[13] substitution method.

The following vacuum corrections were applied.

	Sp. Gr.	Vacuum corr. per g.
Weights	8.3	....
$CoCl_2$	3.348[14]	+0.000214
Ag	10.49	−0.000031

TABLE I

RESULTS. THE ATOMIC WEIGHT OF COBALT

$CoCl_2$:2 Ag Ag = 107.880 Cl = 35.458

Analysis	Sample $CoCl_2$	Wt. of $CoCl_2$ in vac. G.	Wt. of Ag in vac. G.	Wt. of Ag added or subtracted G.	Corr. wt. of Ag in vac. G.	Ratio $CoCl_2$:2Ag	At. wt. of cobalt
1	A_2	5.37099	8.92147	+0.00206	8.92353	0.601891	58.948
2	A_1	5.54240	9.20624	+ .00335	9.20959	.601807	58.930
3	A_1	6.85503	11.38657	+ .00380	11.39037	.601827	58.934
4	C	4.25562	7.07078	+ .00036	7.07114	.601829	58.935
5	B	7.76501	12.90195	− .00141	12.90054	.601914	58.953
6	B	6.51902	10.83117	+ .00050	10.83167	.601848	58.939
7	B	9.64093	16.01614	+ .00220	16.01834	.601868	58.943
					Av.	.601855	58.940
8	M_1	8.02742	13.33720	+ .00030	13.33750	.601868	58.943
9	M_1	6.02652	10.01254	+ .00035	10.01289	.601876	58.945
10	M_2	8.28996	13.77371	+ .00060	13.77431	.601842	58.937
					Av.	.601862	58.942
					Av. of all	.601857	58.941

Discussion

In Analysis 5 the solution of the cobaltous chloride was not absolutely clear, apparently owing to the presence of a trace of basic salt. If this presumption is correct, the atomic weight of cobalt found in this experiment is too high. As a matter of fact the result of this analysis is slightly higher than those of the others, but to omit this result would lower the average by 0.002 unit only.

Certainly, there is no evidence that meteoric cobalt differs in the least from terrestrial cobalt, for not only are the observed average atomic weights of both very nearly the same, but also the extreme values with the meteoric sample are well within the extremes found with the terrestrial.

[13] Richards, THIS JOURNAL, **22**, 144 (1900).

[14] Ref. 10, p. 1587.

Furthermore there is no evidence of dissimilarity among the three samples of terrestrial material.

The most striking point in the results is the appreciable difference between the average value for the atomic weight of cobalt, 58.94, and the one found by Richards and Baxter,[15] and later confirmed by Baxter and Coffin,[16] 58.97. Richards and Baxter used cobalt material which had been purified in essentially the same way as that described in this paper, as well as material purified by precipitation as cobaltammine chloride. No difference was found between the two. The purified metal was converted to bromide by being heated in an atmosphere of hydrogen bromide and the bromide was sublimed. This process was conducted in porcelain tubes, and since these tubes were attacked it was necessary to make allowance for alkali bromide introduced from this source. No correction was made for silica, although it now seems likely that this substance must have contaminated the bromide to a slight degree at any rate. Silica would have raised the observed atomic weight by 0.03 unit, if present to the extent of 0.015%.

Baxter and Coffin prepared the chloride in two ways. In one the purpureo-chloride was decomposed at a high temperature in a current of hydrogen chloride, but the product was not fused. Although found free from ammonium salt this material probably retained a small proportion of moisture, since varied experience with other salts has shown that fusion is essential for complete drying.[17] Furthermore, the cobalt ammine was prepared in part in quartz vessels and probably contained a trace of silica, judging from our own experience and that of Baxter and Hilton.[3d] In the other preparation the hydrated chloride was prepared by solution of electrolytic metal in hydrochloric acid, and crystallization, and was dehydrated in a current of hydrogen chloride at a temperature below fusion. As suggested above, complete dehydration is hardly to be expected. Furthermore, the specimen of cobalt remaining from this research and used in preparing Sample C left a residue of silica upon being heated in hydrogen chloride. To produce the observed difference in the case of the chloride would require 0.023% of water and silica.

A possible cause for too low a value for the atomic weight of cobalt lies in the retention of hydrogen chloride by the salt. In similar cases no evidence of such retention has ever been obtained, although the *free halogens* are likely to be held by their salts to a very considerable extent. One might expect to diminish this difficulty by lowering the concentration of hydrogen chloride in the atmosphere in which the salt is fused and solidified. We attempted to do this in one experiment by diluting the hydrogen

[15] Richards and Baxter, *Proc. Am. Acad. Arts Sci.*, **33**, 115 (1897); **34**, 351 (1898); **35**, 61 (1899).

[16] Ref. 10, p. 1580.

[17] See especially Richards, *Proc. Am. Phil. Soc.*, **42**, 28 (1903).

chloride with a liberal supply of pure nitrogen. The experiment failed, however, since the cobaltous chloride thus prepared gave a very turbid solution.

The atomic weight of cobalt is interesting in connection with the general question of the deviation of the atomic weight of a simple element from a whole number. If the elements have been evolved from hydrogen (and helium), at present the atomic weights of the simple elements furnish the only means for determining whether a gain or loss in mass has occurred. It is very doubtful whether the proportions of isotopes in a mixture can be estimated with sufficient accuracy for the purpose. With the elements of higher atomic weight a loss seems to be the rule, scandium being the exception, but with those of low atomic weight the difference, though small, is usually in the opposite direction. Of course a difference in either direction may be due to the existence of undiscovered isotopes.

Table II gives the atomic weights of those elements which up to the present time have given no evidence of being isotopic mixtures.

TABLE II

ATOMIC WEIGHTS OF PURE ELEMENTS

Element	At. wt.	Element	At. wt.
H	1.008	Sc	45.1
He	4.00	Ti	47.9
Be	9.02	V	50.96
C	12.000	Cr	52.01
N	14.008	Mn	54.93
O	16.000	Co	58.94
F	19.00	As	74.96
Na	23.997	Sr	87.62
Al	26.96	Y	88.9
P	31.02	I	126.93
S	32.06	Cs	132.81

Summary

1. Meteoric and terrestrial cobalt are found to possess the same atomic weight.

2. The atomic weight of both varieties is found to be 58.94, if Ag = 107.880 and Cl = 35.458.

This value is 0.03 unit lower than the one previously found by Richards and Baxter, and by Baxter and Coffin.

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