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THE CHEMISTRY AND CRYSTALLOGRAPHY OF SOME FLUORIDES OF COBALT, NICKEL, MANGANESE AND COPPER.[1]

BY FLOYD H. EDMISTER AND HERMON C. COOPER.

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Introduction.

The fluorides of the bivalent heavy metals, such as cobalt, nickel and copper, have never been fully investigated; neither have their compositions and crystalline forms, including isomorphous relations, been satisfactorily established. An examination of the description of these compounds in the handbooks[2] leaves one in doubt as to the facts and relationship.

In 1824 Berzelius[3] prepared the fluorides of cobalt, nickel and copper and regarded them as so similar that he described them together. "If the carbonate (of the metal) is treated with hydrofluoric acid, it will dissolve with effervescence, but soon a salt is precipitated as a heavy powder. If more and more of the carbonate be added, the effervescence continues, but the salt already formed decomposes, especially if warmed, and

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[1] A more detailed account of this work was submitted to the Faculty of the Graduate School of Syracuse University by Floyd H. Edmister in May, 1918, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] *E. g.*, "Gmelin-Kraut."

[3] Berzelius, *Pogg. Ann.* I, **1824**, p. 28; *Ann. chim. phys.* [2] **24**, 61 (1823).

there results a pulverulent basic salt. If the addition and decomposition of the carbonate be stopped before this salt (powder) forms and the solution be evaporated, there separates out a crystalline crust. * * * In this process there is given off the excess of acid which the dissolved salt contains. If the crystallized salt be covered with a very small amount of water and the mixture be allowed to stand for a long time at room temperature, there results a saturated solution which will deposit these same crystals on evaporation. If, however, the mixture is heated to boiling with much water, decomposition occurs, part of the salt dissolving in the liberated acid and another part remaining undissolved as a basic salt."

Berzelius selected the copper salt for analysis and found that on heating it with lead oxide there were given off 2 molecules of water, not in the least acid. The green pulverulent salt resulting from the decomposition of the neutral salt by boiling water proved, by the same method of analysis, to be a basic salt of the formula $CuO.CuF_2.H_2O$.

The 3 metals, cobalt, nickel and copper, were thus regarded by Berzelius as forming entirely analogous fluorides: a crystallized normal fluoride, $MF_2.H_2O$, and an amorphous basic fluoride.

About fifty years later F. W. Clarke[1] described the preparation of a supposedly new fluoride, made by evaporating a solution of nickel hydroxide in hydrofluoric acid, whereby a crystalline crust is formed. The analysis of this crust gave the formula, $NiF_2.3H_2O$.

In 1884 Balbaino[2] stated that he prepared the hydrated cupric fluoride ($CuF_2.2H_2O$) of Berzelius by dissolving copper carbonate in hydrofluoric acid and adding 95% alcohol, which precipitated a pale blue crystalline powder.

Poulenc[3] is credited with the first description of the anhydrous fluorides. They are only of incidental interest to us here, but it may be noted that, according to Poulenc, the anhydrous nickel fluoride is formed as an amorphous yellow powder or as green crystallized prisms. The anhydrous cobalt fluoride is either a rose-red amorphous powder or red prismatic crystals.

In 1905 Böhm[4] reviewed the work on the fluorides of the heavy metals, called attention to the lack of accurate investigations of well-crystallized material, and prepared, along with several other complex fluorides, the acid fluorides of cobalt, nickel and copper. He stated merely that he obtained these by dissolving the freshly precipitated hydroxides or carbonates of the metals in hydrofluoric acid and concentrating until crystals appeared. His cobalt and nickel fluorides are described as, respectively,

[1] Clarke, *Am. Chem. J.*, **13**, 290 (1887).

[2] Balbaino, *J. Chem. Soc.*, **2**, 1264 (1884).

[3] Poulenc, *Compt. rend.*, **114**, 1426 (1892); *Ann. chim. phys.*, [7] **2**, 47 (1894); *Ber.*, **25**, R. 662 (1892).

[4] Böhm, *Z. anorg. Chem.*, **43**, 330 (1905).

red and green prisms, having similar form and composition. They are stable in the air and easily soluble in water and dilute acids. The metal was determined by electrolysis from a sulfate solution, the fluorine by heating the salt with pure Iceland spar and the water by heating a mixture of the salt with lead chromate in a combustion tube. Böhm found the copper-fluoride crystals to be different from the others in that they soon lose their water of crystallization in the air and that they decompose completely when heated in a closed tube, water and hydrogen fluoride escaping, while copper oxide remains. In the case of copper fluoride the fluorine was determined by neutralizing with an excess of sodium hydroxide and titrating back with standard hydrochloric acid. The formulas assigned by Böhm for these fluorides are of a strongly acid fluoride type.

Purpose of the Investigation.

It is hardly possible that the conclusions of Berzelius, Clarke and Böhm can all be correct, since all of them offer different formulas for salts prepared by methods which should yield the same type of fluoride for a single metal. It is reasonable to suspect that the old master, Berzelius, drew too hasty conclusions from his brief experiments.

Notwithstanding the slight experimental foundation on which the existence of the normal fluorides is based, one is inclined to prefer a normal salt formula to an acid salt formula for a halide obtained from the hydroxide or carbonate and acid, because it is in this way that the most familiar normal chlorides and bromides are prepared.

We have undertaken a combined chemical and crystallographic study of these fluorides, not merely to ascertain the facts in question, but to see whether an isomorphous series is involved.

Preparation of Materials.

The following general methods were investigated. (1) Treating the hydroxide of the metal with an excess of hydrofluoric acid. The excess is necessary for avoiding the formation of the basic salt. (2) Decomposing the carbonate with hydrofluoric acid. In either of these cases the resulting solution is evaporated until crystals appear. Both methods yield satisfactory results. (3) "Dissolving" the metal in hydrofluoric acid. In most cases the action was so slow that only a very small concentration could be obtained. (4) Treating a salt of the metal (the acetate) with hydrofluoric acid. (5) Double decomposition of an alkali fluoride and a salt of the metal. A complex fluoride resulted.

The first general method was ordinarily employed. The hydroxides were precipitated from the acetate solution with sodium hydroxide, the precipitate being washed repeatedly by decantation with cold water and finally with hot water, until the filtrate gave no color with phenolphthalein. The washing must be very thorough, since the gelatinous hydroxide adsorbs the alkali greedily. An excess of alkali was avoided and the precipitate was heated in an excess of water to boiling repeatedly before bringing it upon the filter. The moist hydroxide was then dissolved in C. P. hydrofluoric acid in a platinum basin and the solution was filtered through a wax funnel into a wax bottle, from which it was taken as needed.

Böhm specifies that the solution should be evaporated in a vacuum desiccator over sulfuric acid until crystals appear. Attempts to follow this procedure resulted in the formation, not of crystals, but of a crystalline crust on the sides and bottom of the container and an arborescent creeping growth extending often over the sides of the vessel. The walls of the container and the desiccator were bedewed with a strongly acid solution, which was not absorbed by the sulfuric acid. If the evaporation took place in the open air, the crust was drier and harder and more difficultly soluble.

Under the microscope this crust looked different according to the conditions under which the evaporation took place. In some cases the crust was only a mass of nodules, while in others it appeared to be a mixture of amorphous material and of small but fairly definite crystals. In the case of copper the crust was, fortunately, almost wholly crystalline.

In view of the fact that the analyses of Berzelius and Clarke were made on material prepared in this way, special attention was given to preparing a product which could be regarded as suitable for analysis, but examination with the petrographic microscope showed the preparations—except in the case of the copper salt—to be either amorphous and of indefinite water content or mixtures of amorphous and crystalline material. Analyses of these products were made and indicated roughly a ratio of cobalt or nickel to fluorine of 1 : 2, but the character of the crystals was too indefinite to warrant careful investigation of their composition.

Recrystallization.—If this crust is placed in about an equal weight of water, the crystalline portion can be seen to dissolve out, while the amorphous portion remains. If the amount of water is increased and the temperature raised, all of the material dissolves. Except in the case of cobalt no well-defined crystals, capable of measurement, were obtained from the original solution of the hydroxide in hydrofluoric acid. All of the crystals used for analysis and measurement have been obtained from the water extract of the crystalline crust, the extract being allowed to evaporate slowly in the air. Even then some of the crust is nearly always formed around the crystals and a second recrystallization is necessary to free them entirely from the crust. Each recrystallization reduces the acid concentration until in the third it is practically negligible.

We hesitated to recrystallize from pure water because of the possibility of hydrolysis and, particularly, because of the possible loss of acid in case the salts should be acid fluorides, as our investigation as well as

Böhm's disclosed. Contrary to expectations, the proportion of amorphous material lessened, rather than increased, with decreasing acidity, indicating that it is not a basic salt. The acid concentration, however, appears to control the equilibrium involving the crystal and amorphous phases.

Preparation of Cobalt Fluoride.—Our first preparation of cobalt fluoride was by treating the hydroxide with hydrofluoric acid. Because of the tendency of the cobalt (ous) hydroxide to oxidize in the air during the long washing process to cobaltic hydroxide, which is insoluble in hydrofluoric acid, we generally used the carbonate instead. It is permanent in the air, filters more quickly and is more easily washed. It is, however, less soluble than the cobaltous hydroxide. To be sure, the carbonate, when added to the hydrofluoric acid, is decomposed as long as there is any acid present, but, as Berzelius stated, there is precipitated a fine rose-red powder, which is dissolved only upon the addition of more acid and water.

The original solution was evaporated on a water-bath until solid appeared, whereupon it was removed to a heat-insulated box of the Swedish box, or fireless cooker type, and allowed to cool slowly. No crystals formed. Even after standing in the box until half of it had evaporated, the solution continued to yield a brittle crystalline crust, the last portion being the same as the first.

The next trial was made in the open air, using the mother liquor from this crust, but no real crystals were obtained. The same method was tried, starting with a dilute solution and allowing it to evaporate slowly at an even temperature, with no better results. Böhm's method of letting stand in an evacuated desiccator over sulfuric acid was then tried. The evaporation proceeded slowly because, as stated above, the escaping vapor was not absorbed by the sulfuric acid but condensed upon the inner wall of the desiccator. Solid fluoride formed upon the sides of the basin and then crept over the edge. Under the microscope this crust appeared to have no crystal form and no definite composition.

The cobalt fluoride crust, however formed, is slowly soluble in very dilute hydrofluoric acid. For this reason a few drops of hydrofluoric acid were added to the water on dissolving. Upon evaporation the same results were obtained as in the first evaporation. Since the crust appeared to consist of more than one form of material, differing in solubility, a comparatively large amount was treated with a small quantity of water and warmed. The filtered solution upon standing for 6 hours began to deposit crystals which, though accompanied by crust, were sufficiently distinct from it to be separated mechanically. When these crystals were recrystallized from slightly acid water, very clean, well-defined crystals were obtained.

Preparation of Nickel Fluoride.—For the preparation of nickel fluoride either the hydroxide or the carbonate may be used, since the hydroxide, unlike that of cobalt, is stable in the air. The first product was a crystalline crust, as for cobalt. The crust forming on the surface of the evaporating solution is identical in appearance under the microscope with that deposited on the bottom. Satisfactory crystals were obtained in the same way as for cobalt, the cleanest ones resulting from a second recrystallization from water.

Preparation of Manganese Fluoride.—Of all the fluorides investigated that of manganese is the most difficult to prepare. The hydroxide is less stable in the air than that of cobalt; so that, before it can be thoroughly washed, much of it has become insoluble in hydrofluoric acid; but a more serious difficulty is the comparatively slight solubility of the manganous hydroxide in hydrofluoric acid. The carbonate likewise dissolves only to about 10%; further addition of the carbonate produces a marked effervescence and the precipitation of a fine powder, which does not dissolve upon the addition of more acid and water. The solution of the fluoride is consequently very dilute.

If the manganous fluoride solution be heated on the water-bath, the fluoride precipitates as the powder, so that all evaporation must be done at room temperatures, requiring on the average 6 weeks to produce crystals. The crust also forms as in the case of cobalt and nickel, but decomposes when digested with water. We attempted to obtain manganese fluoride by dissolving the metal in hydrofluoric acid, but obtained only manganese dioxide, which was formed by an unusually vigorous reaction between the metal and acid.

Preparation of Copper Fluoride.—For the preparation of copper fluoride the hydroxide is to be preferred to the carbonate, since the hydroxide reacts faster with hydrofluoric acid. Although it forms a basic salt upon standing in the air, the product is soluble in more acid. If the copper fluoride solution be evaporated slowly, small irregular blue crystals form on the bottom of the basin; while, if the evaporation takes place on the water-bath, the fluoride appears as a clear crystalline crust of constant composition. Both the small crystals and the crystalline crust were free from the granular, amorphous material so persistent in the deposition of cobalt and nickel fluorides. They were regarded as sufficiently well defined for analysis. The analyses showed the 2 products to be identical in composition, *viz.*, to be a normal fluoride.

These normal fluoride crystals are difficultly soluble in water, a white coat forming upon the surface. If an excess of water is added and the solution is heated, the filtrate yields upon evaporation well-defined 3- or 6-sided prismatic crystals. These are very soluble in water and, strange to say, have the composition of an acid fluoride. On exposure to the air they effloresce rapidly. If they are heated, water and hydrogen fluoride are evolved, leaving copper oxide in the tube. Presumably the hydrogen fluoride is driven off first, whereupon the water of crystallization hydrolyzes the copper fluoride.

Observations on Dissociation.

The crystal fluorides of cobalt, nickel, manganese and copper all evolve hydrogen fluoride when exposed to the air. After a portion of one of these substances is washed and dried and set aside on the watch glass the latter is found to be etched in 3 minutes. The gradual loss of hydrogen fluoride is a very important property of these fluorides. It means that the compound cannot be preserved with certainty of its retaining its original composition and that analyses must be made with the freshest possible product. This phenomenon will be referred to in the discussion of the analysis. It would be interesting to determine the rate of decomposition, but no work has been done upon it thus far.

The crystals are soluble in water and dilute acids. When heated, they give off water and hydrofluoric acid and are themselves converted to the oxides, as stated by Böhm, for the copper salt.

Analysis of the Fluorides.

For the *metal* the following general methods are applicable: (1) precipitation as the hydroxide or sulfide with subsequent reduction in a stream of hydrogen; (2) evaporation with sulfuric acid and weighing as the anhydrous sulfate; (3) heating at red heat to convert the fluoride into the oxide; (4) electrolytic deposition.

The *total fluorine* can be determined volumetrically by adding an excess of standard alkali and titrating back with standard acid. In this case the precipitated hydroxide is filtered off before the titration, else it will obscure the end-point. With nickel and copper, using phenolphthalein as an indicator, a very good end-point can be obtained if the alkali be added slowly to the warm solution until the free hydrofluoric acid is neutralized and the hydroxide of the metal is precipitated.

The gravimetric determination of fluorine is based upon its precipitation as an insoluble fluoride. A number of metals form insoluble fluorides, calcium being the one most commonly used. Lead chloride precipitates the fluorine as the double halide, $PbFCl$,[1] and lithium chloride is said to give accurate results.[2] In our work with the fluorides lead chloride gave results uniformly low and lithium chloride failed in some cases to give a precipitate. The difficulties of precipitation are well known. Calcium fluoride is an extremely finely divided, slimy precipitate, which passes through nearly all filters the first time. Refiltering through the same filter proved to be exceedingly tedious, and washing was impracticable because of the time consumed in filtration of the solution. However, a

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[1] G. Starck, *Z. anorg. Chem.*, **70**, 173 (1911); *J. Chem. Soc. Abs.*, **100**, ii, 436 (1911).

[2] Deladrier, *J. Chem. Soc.*, **86**, 440 (1904).

number of determinations for fluorine were made by precipitating it with calcium chloride or calcium acetate. While the results were not accurate, they afforded independent confirmation of those obtained by other methods so far as the interpretation was concerned.

The purpose of adding the carbonate to the fluoride in the calcium fluoride method (Berzelius) is to assist in the filtration. A modification of this procedure has given good results in our work. Instead of adding sodium carbonate we made the solution slightly acid with acetic acid. An amount of standard ammonium oxalate was then added so that the calcium oxalate precipitated would be approximately the same as the weight of calcium fluoride. The 2 precipitates were then filtered off together in a Gooch crucible, dried and weighed. The difference between the weight of the combined precipitate and the weight of the calcium oxalate, corresponding to the ammonium oxalate added, gave the calcium fluoride. The decided advantage lies in the elimination of the decomposition and, furthermore, it does not necessitate a second filtration. The calcium oxalate serves the same purpose as the calcium carbonate and does it equally well. None of the absorption methods was used in the analysis for fluorine.

The determination of *crystal hydrate water* is the most difficult, since a temperature sufficiently high to expel the last traces will cause a loss of at least a part of the hydrogen fluoride. The method used by Böhm—heating the fluoride with lead oxide—is the only one described as being satisfactory. In the analyses that follow the water determinations were so variable that they were used only as rough indications of the amount present. For calculating formulas use was made of the percentage of water by difference.

Cobalt Fluoride Analysis.—The fluorine of the cobalt fluoride was determined by adding an excess of standard alkali to the water solution. The precipitate was 4 times washed by decantation with hot water, whereupon it was brought upon the filter and washed with hot water until the washings gave no test for alkali with phenolphthalein. The filtrate was then titrated with standard hydrochloric acid and the weight of sodium hydroxide used was calculated. In order to check this method determinations were made by precipitating the fluorine with calcium acetate. The results were lower than by titration and are not considered reliable.

All of the general methods were used for determining cobalt metal. The first method employed was that of precipitating with sodium hydroxide, filtering the precipitate and washing it with hot water. The dried hydroxide was ignited and the oxide decomposed with conc. sulfuric acid. This acid solution was then evaporated to dryness and the anhydrous cobalt sulfate weighed.

Another method used for cobalt was to treat the fluoride with sulfuric acid and evaporate. This should volatilize all of the constituents except the metal. Consistent results were obtained by this method which agree with the electrolytic determinations. The reaction with sulfuric acid is vigorous and complete within a few minutes. The sulfuric acid is then driven off in an air-bath, the residue heated for 5 minutes and eventually weighed as anhydrous cobalt sulfate.

In electrolytic deposition cobalt does not behave ideally; it does not always form a good coating on the cathode, but often scales off before the deposition is complete. We carried out the electrolysis as specified by Treadwell-Hall.[1] Our experience has been that, if the voltage exceeds 1.5 volts, the cobalt will precipitate as the hydroxide and, if the solution is not kept strongly alkaline, a black ring will be deposited, particularly around the edge. A voltage of 1.0 to 1.5 and an amperage of 1.0 to 1.3 gave the best results. A 100-cc. platinum basin served as the cathode. It is not necessary to precipitate the hydroxide of cobalt, but the crystals may be dissolved in water, ammonium hydroxide added and the solution electrolyzed directly. The possibility of contamination with alkali is eliminated and accurate results are to be expected, but no determination of fluorine can be made on the same sample.

Cobalt hydroxide was also reduced to the metal by the Rose method. Unfortunately, the ignited precipitate was always in masses, which would not reduce unless removed from the crucible and ground. If this was not done, the reduction was incomplete and the results were too high.

Nickel Fluoride Analysis.—In the nickel fluoride the fluorine was determined as in the case of cobalt. The metal also was determined (1) as the anhydrous sulfate, after evaporating the fluoride crystals with sulfuric acid; (2) by electrolysis; and (3) as the oxide. Unlike cobalt oxide nickel oxide has a constant composition and the metal can be calculated from the weight of the oxide.

Anhydrous nickel sulfate is hygroscopic and must be weighed quickly after removal from the desiccator. The electrolysis was conducted in a strongly alkaline solution with a voltage of about 1.5 and an amperage of 1.5. In all cases the platinum basin was used as the cathode.

No analyses for nickel were made by the Rose method.

Copper Fluoride Analysis.—The copper is best determined (1) by electrolysis in the water solution of the crystals, which are acid with hydrofluoric acid, unless the fluorine is to be determined in the same sample. In the latter case the copper is precipitated as the hydroxide, dissolved in dil. nitric acid and subjected to electrolysis. Copper was also determined (2) by evaporating the crystals with sulfuric acid. (3) When the copper fluoride crystals are heated alone, they give off water and hydrofluoric acid and are converted to the oxide. The weight of copper calculated

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[1] Treadwell-Hall, "Analytical Chemistry" II, 1915, p. 138, 4th Ed., N. Y.

from the oxide thus obtained agrees approximately with that obtained by other methods.

Manganese Fluoride Analysis.—The fluorine was determined by the same method as for the other fluorides. The metal was determined (1) by decomposing with sulfuric acid, and (2) by converting to the pyrophosphate. For the latter method the manganese is first precipitated as the hydroxide, washed free from alkali and dissolved in dil. sulfuric acid.

The Analytical Data.—The results of the analyses are tabulated in the following tables. The numbers in the first column are analytical reference numbers; the method employed in the analysis is indicated in the second column; the weights of salt and constituent, respectively, are given in the next 2 columns; the computed percentage is found in the fifth column; while the last column is used for memoranda that might aid in the appraisal of the results.

COBALT FLUORIDE.

Prepared by the action of HF on the hydroxide or carbonate, no difference being seen in the products.

Reference No.		Salt. G.	Fluorine. G.	%.
6	Pptd. as CaF_2	0.3000	0.1214	39.97
3	Titration	0.5000	0.1310	41.30
63	Titration	0.3000	0.1221	40.78
64	Titration	0.4007	0.1695	41.45
90	Titration	0.3000	0.1285	42.85[a]
130	Pptd. as CaF_2 + CaC_2O_4	0.2934	0.1458	42.79[a]
131	Pptd. as CaF_2 + CaC_2O_4	0.2280	0.1232	43.79[a]

Reference No.		Salt. G.	Metal. G.	%.	
37	Dissolved hydroxide in H_2SO_4 and electrolyzed	0.3026	0.0591	19.53	Crystals were washed in alcohol
39	Dissolved hydroxide in H_2SO_4 and electrolyzed	0.4483	0.0864	19.27	
50	Decomposed with H_2SO_4 and weighed as $CoSO_4$	0.3520	0.1793	19.36	
63	Electrolysis	0.3000	0.0571	19.40	
78	Electrolysis	4.4007	0.7840	19.40	Very clean crystals
93	Electrolysis	0.3000	0.0590	19.60	Dissolved in water and electrolyzed
51	Electrolysis	0.2544	0.0484	19.03	Dehydrated

[a] Taken from solution, washed, dried and analyzed immediately.

Reference No.		Salt. G.	Metal. G.	%.
51	Heating and collecting the water	0.2544	0.1036	40.70
130	Heating and collecting the water	0.3024	0.1195	39.52
133	Heating with PbO	0.3313	0.1363	41.14
135	Heating with PbO	0.1853	0.7440	41.15
137	Heating and collecting the water	0.2107	0.8650	41.05

Nickel Fluoride.

Prepared from the hydroxide and hydrofluoric acid.

Reference No.		Salt. G.	Fluorine. G.	%.	
58	Titration	0.3000	0.1259	41.99	Washed in alcohol
80	Titration	0.3000	0.1658	41.36	Old crystals
89	Titration	0.3000	0.1296	43.27	Clean crystals fresh from solution
96	Titration	0.3000	0.1292	43.05	Clean crystals fresh from solution
97	Titration	0.3000	0.1248	41.67	Old crystals
131	Pptd. as CaF_2 + CaC_2O_4	0.1876	0.0914	43.76	Crystals fresh from solution

Reference No.		Salt. G.	Metal. G.	%.
54	Electrolysis	0.3070	0.0677	19.80
58	Electrolysis	0.3000	0.0584	19.60
62	Electrolysis	0.3000	0.0574	19.50
64	Electrolysis	0.2497	0.0489	19.58
91	Electrolysis	0.3000	0.0478	19.26

Reference No.		Salt. G.	Water. G.	%.
110	Heating and collecting water in H_2SO_4	0.2764	0.1149	41.50

Manganese Fluoride.

Reference No.		Salt. G.	Fluorine. G.	%.	
76	Titration	0.3537	0.1313	43.02	Crystals fresh from solution
69	Titration	0.3004	0.1190	39.63	
92	Titration	0.3020	0.1220	40.68	

Reference No.		Salt. G.	Metal. G.	%.
76	Heating with H_2SO_4 and weighing as $MnSO_4$	0.0365	0.1817	18.09
60	Heating with H_2SO_4 and weighing as $MnSO_4$	0.3537	0.1810	18.89
77	Heating with H_2SO_4 and weighing as $MnSO_4$	0.2892	0.1457	18.35

Reference No.		Salt. G.	Water. G.	%.
127	Heating with PbO and collecting the water	0.3171	0.1221	38.2

COPPER FLUORIDE (Crystals).

Reference No.		Salt. G.	Fluorine. G.	%.	
43	Titration	0.3000	0.1282	42.76	
59	Titration	0.3000	0.1281	42.71	
65	Titration	0.4220	0.1808	43.05	
127	Precipitation	0.3612	0.1519[b]	42.20	[b] $CaF_2 + CaC_2O_4$

Reference No.		Salt. G.	Metal. G.	%.
59	Electrolysis	0.3000	0.0610	20.30
60	Electrolysis	0.3000	0.0602	20.07
61	Electrolysis	0.3009	0.0604	20.06
79	Electrolysis	0.4112	0.0838	20.38

COPPER FLUORIDE (Crystalline Crust).

Reference No.		Salt. G.	Fluorine. G.	%.	
52	Titration	0.6087	0.1692	27.80	These two are the same preparation
53	Titration	0.6896	0.1270	27.00	
56	Titration	0.5000	0.1437	28.75	
74	Titration	1.1751	0.3323	28.28	
83	Titration	0.9401	0.2646	28.13	

Reference No.		Salt. G.	Metal. G.	%.
52	Electrolysis	0.0609	0.2814	46.10
53	Electrolysis	0.6896	0.3158	45.80
82	Electrolysis	0.8219	0.3767	45.83
83	Electrolysis	0.9401	0.4306	45.82
49	Electrolysis	0.3621	0.1643	45.40

Calculations.—In the computation of the formulas for the fluorides use was made of the analyses on crystals which were taken from the solution, washed, dried and analyzed immediately. The average of these analyses was used.

In the case of fluorine results from the precipitation by calcium chloride alone were discarded, as they had been proven to be inaccurate. The results used are the average of the fluorine determinations by titration and by precipitation by calcium chloride in the presence of calcium oxalate.

For the metal the calculations in the case of cobalt, nickel and copper are the average of results obtained from the anhydrous sulfate and by electrolysis, with emphasis upon the latter, since in this method the sources of error are reduced to a minimum. For manganese metal the calculations are based upon the weight found in the anhydrous sulfate and in the pyrophosphate.

For the water use was made of the percentage difference.

In some cases only selected determinations were utilized for the calculations. The selection is given in the last column of the following tables. A great many more determinations were made than are recorded in the preceding tables, in order to familiarize ourselves with the possible sources of error.

FORMULAS.

Cobalt Fluoride.

Co = 19.40 ÷ 58.97 = 0.3291 = 1.000. All determinations.
F = 43.14 ÷ 19.00 = 2.2705 = 6.899. Nos. 90, 130, 131.
H_2O = 36.06 ÷ 18.00 = 2.0033 = 6.087. By difference.
H = 1.6.
The formula is $CoF_2.5HF.6H_2O$.

Nickel Fluoride.

Ni = 19.50 ÷ 58.68 = 0.3323 = 1.0000. All determinations.
F = 43.32 ÷ 19.00 = 2.2800 = 6.8610. Nos. 89, 96, 131.
H_2O = 35.58 ÷ 18.00 = 1.9767 = 5.9485. By difference.
H = 1.6.
The formula is $NiF_2.5HF.6H_2O$.

Manganese Fluoride.

Mn = 18.09 ÷ 55.00 = 0.3283 = 1.000. No. 76.
F = 43.02 ÷ 19.00 = 2.2640 = 6.889. No. 76.
H_2O = 35.58 ÷ 18.00 = 2.0772 = 6.327.
H = 1.5.
The formula is $MnF_2.5HF.6H_2O$.

Copper Fluoride.

(Crystals by recrystallization from water.)

Cu = 20.09 ÷ 63.57 = 0.316 = 1.000. All determinations.
F = 42.70 ÷ 19.00 = 2.250 = 7.100. All determinations.
H_2O = 35.61 ÷ 18.00 = 1.978 = 6.260. By difference.
H = 1.6.
The formula is $CuF_2.5HF.6H_2O$.

Copper Fluoride.

(Small crystals and crust deposited slowly from original mixture.)

Cu = 45.82 ÷ 63.57 = 0.747 = 1.000.
F = 28.13 ÷ 19.00 = 1.480 = 2.036.
H_2O = 26.05 ÷ 18.00 = 1.440 = 2.000.
The formula is $CuF_2.2H_2O$.

We append here the results of a few determinations and calculations on the crust or powder formed in the preparation of crystals of cobalt and nickel fluorides.

Cobalt Fluoride—Crystalline Crust.

Reference No.	Fluorine. %.	Metal.	Ratio.	
84	25.09	33.99	1.0 : 2.29	
			Powder.	
104	24.42[a]	35.19	1.0 : 2.154	
		Nickel Fluoride—Powder.		
100	Not det'd.	34.51		
101	25.46	34.66	1.0 : 2.26	Made by boiling the crust.

[a] Average of 2 determinations on the same material; fluorine also determined on same powder.

The results approximate the neutral salt formula and correspond to the result for the copper fluoride crust. We do not, however, feel warranted in assigning formulas.

Crystallography.

From the second recrystallization in the open air crystals were obtained in ample quantity for crystallographic investigation and analysis. Some of them were as large as 20 × 8 mm. Measurements were made with a Goldschmidt reflecting goniometer. In general, the specimens were found to be extensively etched because of their high solubility. The etching caused so much dispersion of light that the reflected image was not as sharp as was desirable; therefore the readings were only reliable to about 30 seconds.

Cobalt Fluoride, $CoF_2.5HF.6H_2O$, Rhombohedral.—The cobalt fluoride is orange-red; equivalent wave-length 610 $\mu\mu$ for a plate 2 mm. thick.[1] The crystals are flattened hexagonal prisms capped by 2 rhombohedrons of the opposite order to the prisms. The average angle between the prism faces *m:m′* is 60° 0′. For the rhombohedrons the angles from the base are 30° 59′ and 50° 6′, both within ±8′. From the measurements $\acute{c} = 1.039$; $c \wedge r\ (10\bar{1}1) = 50° 9'$ and $c \wedge e\ (01\bar{1}2) = 30° 55'$. Distinct prismatic cleavage was observed. Optically the crystals are uniaxial postive with approximate refractive indices measured by immersion: $\omega = 1.38(5)$, $\epsilon = 1.39(7)$. Extinction is parallel. The sp. gr. by the Jolly balance, using alcohol as immersion liquid, is 2.0445.

It does not seem worth while to make drawings of the crystals because of their distortion, which was probably due to their growing attached by one side to the dish.

Nickel Fluoride, $NiF_2.5HF.6H_2O$, Rhombohedral.—The nickel fluoride is blue-green; equivalent wave-length 510 $\mu\mu$ for a plate 2 mm. thick; non-pleochroic, with habit, cleavage and general optical properties like cobalt fluoride. Measurements of the rhombohedrons gave the same angles as the coblat salt. Refractive indices measured on a small prism gave the following results for the mercury lines; the other values are interpolated:

	ω.	ϵ.
Hg 436	1.398	1.413
F	1.395	1.410
Hg 578	1.392	1.408
D	1.392 −	1.408 −
C	1.390	1.406

Sp. gr. in alcohol, 2.006.

Manganese Fluoride, $MnF_2.5HF.6H_2O$.—The manganese fluoride is light red with habit and general optical properties like those of cobalt fluoride. The average angle between the prism faces *m:m′* is 60° 8′. The pyramid faces were so poorly developed that it was impossible to measure them. Sp. gr. in alcohol, 1.921.

Copper Fluoride, $CuF_2.5HF.6H_2O$, Monoclinic.—The copper fluoride is blue-green-blue, equivalent wave-length 490 $\mu\mu$ for a plate 2 mm. thick., and is distinctly pleochroic. The crystals were not perfect enough to determine by form. Microscopically they apparently show 3 cleavages, to one of which they extinguish parallel. This cleavage seems to be parallel to a set of faces. The extinction observed against another apparent cleavage is very oblique. A few elongated rough crystals and cleavage fragments were elongated in the direction of α'. Good biaxial interference figures showed $-2E = 48° \pm 2°$, with no observable axial dispersion. The refractive indices were measured carefully under the microscope by immersion as follows: $\alpha = 1.395$, $\beta = 1.440$, $\gamma = 1.444$. Therefore $-2V = 32°$. α is least absorbed.

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[1] A considerable number of these observations were made or confirmed by H. E. Merwin, of the Geophysical Laboratory, to whom we are accordingly greatly indebted.

The evidence of monoclinic symmetry is thus almost conclusive. The examination of the optical properties was rendered very difficult by the rapid loss of crystal hydrate water. Sp. gr. in alcohol, 2.4055.

The crystals of the normal fluoride, $CuF_2.2H_2O$, were too small to measure. Recrystallization yielded the acid fluoride.

Isomorphism.—The chemical and optical examination thus showed that the acid fluorides of cobalt, nickel and manganese are isomorphous, while the similarly prepared copper fluoride, of the same chemical formula, has a different crystal form. The first 3 are rhombohedral, forming flattened hexagonal prisms, capped by 2 rhombohedra of the opposite order to the prisms. All 3 showed prismatic cleavage, are uniaxial positive and give parallel extinction. The refractive indices of the cobalt and nickel fluorides differ by less than 1%. The indices of the manganese fluoride were not measured.

Summary.

The fluorides of cobalt, nickel, manganese and copper can be prepared by dissolving either the hydroxide or the carbonate of the metal in hydrofluoric acid, the same product being obtained, whichever is used. In all cases a crust-like product was obtained as the result of evaporating the original solution. From the water extract, slightly acidulated with hydrofluoric acid, crystals of the acid fluorides were formed and analyses and measurements of these crystals were made.

The formulas of all 4 fluorides are of the same acid fluoride type: $MF_2.5HF.6H_2O$. It was a surprise to obtain the acid fluoride by recrystallization from water, it being considered more likely that a basic salt would be obtained under these circumstances.

The acid fluorides are not permanent in the air but decompose, losing hydrogen fluoride, and in the case of copper losing water also, so that the crystals used for analyses must be carefully selected and preserved. Investigation of the rate of loss of hydrogen fluoride was not undertaken, but our analyses were made with crystals soon after being taken from the solution and in our opinion the results are the most reliable obtainable.

The formation of a hydrated, non-crystalline crust is distinct from that of the hydrated acid fluoride crystals. In this crust the ratio of metal to fluorine, for the cases of cobalt and nickel, was found to be, roughly, one to two, with varying water content. This crust differs from the crystals in solubility and form, as well as in composition. We have arrived at the conclusion that the crust described by Berzelius as containing 2 molecules of water, the crust later described by Clarke as containing 3 molecules of water, and the crust and powder obtained by use are the same, the water content being variable and the crystal form undeveloped. All were obtained in the same manner.

The acid fluorides of cobalt, nickel and manganese give rhombohedral crystals, with prismatic cleavage, parallel extinction and uniaxial positive character. Since they have the same type of chemical formula, the same crystal form and the same habit, cleavage and general optical properties, we consider that they constitute an isomorphous series.

The acid fluoride of copper has the same type of formula, but differs crystallographically.

From the original preparation of copper fluoride small crystals of the normal fluoride, $CuF_2.2H_2O$, were obtained, which were not good enough for measurement and which reverted unexpectedly to the acid fluoride on recrystallization from water.

The experimental work upon which this article is based was completed in May, 1918.

College of the City of New York,
New York, N. Y.

[Contribution from the Department of Chemistry of Columbia University. No. 332.]

A STUDY OF THE SATURATED POTASSIUM CHLORIDE CALOMEL CELL.

By Harold A. Fales and William A. Mudge.

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The increasing use of the electromotive force method for hydrogen-ion measurements, and the variety of combinations employed, have intensified the desirability of devising a single combination which will not only minimize, as far as possible, the inherent errors of this important method, but will give, in addition, an improved technique for working over a wide range of temperature, 5–60°.

The combinations which have been used to the greatest extent are those employing either the 0.1 N or N calomel cell in conjunction with either the 0.1 N,[1] N,[2] 3.5 N,[3] or saturated[4] potassium chloride salt bridge.

In the use of such combinations the difficulties are two-fold: (*a*) those due to the changes in value of the contact potentials brought about by the interdiffusion of the respective solutions at their several junctions; and (*b*) those due to the change in value of the calomel cell resulting from the diffusion of the potassium chloride of the salt bridge into the more dilute solution of the salt in the calomel cell.

Fales and Vosburgh,[5] in a study of Planck's formula for contact poten-

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[1] Loomis and Acree, *Am. Chem. J.*, 46, 585 (1911); Myers and Acree, *ibid.*, 50, 398 (1913); Harned, This Journal, 37, 2475 (1915); Fales and Vosburgh, *ibid.*, 40, 1302 (1918).

[2] Ostwald. Ostwald-Luther, "Physico-chemische Messungen," 3rd Ed., p. 445.

[3] Bjerrum, *Z. physik. Chem.*, 53, 430 (1905); Fales and Nelson, This Journal, 37, 2781 (1915).

[4] Loomis and Acree, *loc. cit.*; Harned, *loc. cit.*; Fales and Vosburgh, *loc. cit.*

[5] This Journal, 40, 1291 (1918).