351. *The Composition and Properties of Precipitated Nickel and Cobalt Sulphides. Part I.*

By A. W. Middleton and A. M. Ward.

Although nickel and cobalt sulphides are not precipitated from mineral acid solutions, yet the precipitated sulphides are only sparingly soluble in these media; this peculiar behaviour has not been accounted for satisfactorily. The sulphides precipitated from alkaline sulphide solutions are usually written as NiS and CoS, but there is meagre evidence in support of the formulæ. The results of Thiel and Gessner (*Z. anorg. Chem.*, 1914, **86**, 56) agreed fairly closely with this formula for nickel sulphide; Baubigny (*Compt. rend.*, 1882, **94**, 1417) had, however, found the atomic proportion Ni : S to be *ca.* 1 : 1·14. Thiel and Gessner concluded that nickel sulphide exists in three forms, all NiS: the first (α), precipitated in absence of air, dissolves readily in cold 2*N*-hydrochloric acid with evolution of hydrogen sulphide, the second (β) is soluble in boiling 2*N*-acid, and the third (γ) is insoluble but dissolves in presence of an oxidising agent. They considered that the transformation of the α- into the β- and the γ-form was accelerated by dilute acetic acid in absence of air, or by exposure to air. Herz (*Z. anorg. Chem.*, 1901, **27**, 390; **28**, 342) observed that, in presence of air, wet freshly precipitated cobalt or nickel sulphide evolved hydrogen sulphide on treatment with *N*-hydrochloric acid, but it slowly became insoluble, and after several days the wet sulphide had become partly oxidised to sulphate. Although they appear to have neglected this aspect of the problem in the interpretation of their results, Thiel and Gessner stressed the fact that nickel sulphide precipitated in presence of air is oxidised very readily (cf. also Ephraim, *Ber.*, 1923, **56**, 1885, on oxidation of nickel ammonium sulphides).

In the present study, sulphides were prepared from solutions of nickel, cobaltous, hexamminocobaltous and hexamminocobaltic chlorides, by means of hydrogen sulphide, both in presence and in absence of air. The sulphide preparations to which air had access at any stage before drying was complete contained oxygen, hydrogen, and small amounts of nitrogen. The values of *x*, *y*, and *z* in the empirical formula, $MS_xO_yH_z(NH_3)_w$, of the air-dried sulphides are shown in Table I. The totals of the individual percentages of the elements on which the formulæ are based are shown in the last column.

TABLE I.

Preparation.	*x*.	*y*.	*z*.	Total, %.
From $NiCl_2$, *p*	1·16	1·17	1·76	100·8
r	1·19	1·63	1·52	99·7
,, $CoCl_2$, *q*	1·35	1·62	1·61	100·7
p	1·28	1·59	1·18	100·3
r	1·15	2·10	1·37	99·1
r	1·39	2·22	1·70	100·4
,, $Co(NH_3)_6Cl_2$, *r*	1·28	2·95	2·36	100·4
,, Co stearate	1·27	1·72	1·31	99·9
,, $Co(NH_3)_6Cl_3$, *p*	1·75	2·83	1·87	101·9
q	1·56	3·19	2·22	100·7
r	1·64	6·39	3·76	101·6

In experiments marked *p*, the sulphides were precipitated in nitrogen and dried in air, the results being the mean of a number of determinations with different preparations; preparations marked *q* were as in *p*, except that the sulphides were precipitated in presence of air; preparations *r* were as in *q*, but the complete analyses were made on a single sample.

In all cases the proportion of sulphur was considerably greater than required for NiS or CoS, and for the tervalent cobalt complexes it exceeded that for Co_2S_3. Determinations of uncombined sulphur in the precipitates showed a negligible amount to be present. The atomic proportion of oxygen was never less, and usually considerably greater, than that of sulphur, becoming particularly high in the sulphides derived from tervalent cobalt. The sulphide made from hexamminocobaltous chloride, which is readily transformed into cobaltic compounds, contained oxygen comparable in amount with the cobaltic series. The atomic proportion of hydrogen was usually intermediate between that of sulphur and oxygen. Its presence may be due to combined water, hydroxyl or hydrosulphide radicals. Water of crystallisation is not usually present in very sparingly soluble substances, and the sulphides did not undergo any marked change in weight when the temperature at which they were dried was raised from 110° to 150°. In all preparations in aqueous media, ammonia and, in consequence, hydroxyl ions were present. Accordingly another sample was prepared by passing dry hydrogen sulphide into a solution of cobaltous stearate in dry benzene; after being washed with benzene and dried in an air-oven, it agreed closely in general type with sulphides prepared in presence of water and of hydroxyl ions. Support is therefore given to the view that hydrogen is initially present as the hydrosulphide radical. Manchot and Gall (*Ber.*, 1929, **62**, 678) formulated a sulphide initially formed in water as $Ni(SH)_2$.

It was found, by adding the cobalt solution to a considerable excess of aqueous hydrogen sulphide, that negatively charged cobalt sulphide sols were formed. They were coagulated by continued addition of cobalt ions, or their co-ordinated forms. The presence of small amounts of ammonia ($w = 0{\cdot}02$—$0{\cdot}09$) in the precipitates is accounted for by the presence of adsorbed amminated cobalt or nickel.

The presence of oxygen most probably was due to oxidation of the hydrosulphide initially formed. The sulphides were therefore prepared, dried, and weighed with oxygen exclusion, and the total percentages of metal and sulphur were thus greatly increased as shown in Table II, in which values of *x* relate to the sulphide MS_x.

TABLE II.

Sulphide.	Nickel sulphide.					
Total MS_x, %	94·2	94·5	94·6	96·9	97·7	98·7
x	1·22	1·18	1·14	1·18	1·12	1·08
	Cobaltous sulphide.			Cobaltic sulphide.		
Total MS_x, %	92·0	92·7		88·6	89·6	95·7
x	1·07	0·91		1·52	1·56	1·47

Generally, the higher the total percentage of metal plus sulphur, the more nearly did the precipitates approach the compositions NiS, CoS, and Co_2S_3, but the ratios of sulphur to metal were usually greater than required by these formulæ. It is difficult to prepare and keep water free from dissolved oxygen, for this gas is almost instantaneously absorbed to saturation (Mears and Evans, *J. Soc. Chem. Ind.*, **1933**, **52**, 349T), and the introduction of this factor during manipulations probably accounts for the deviations.

The behaviour of the various sulphides towards hydrochloric acid has received a preliminary examination. The percentages of total metal in the air-dried sulphides dissolved in successive extractions (indicated by Roman numerals) with 2*N*- and then with 12*N*-acid, during one or more days, are shown in Table III.

TABLE III.

Sulphide.	Prepn.*	2*N*-Acid.				12*N*-Acid.		
		I.	II.	III.	IV.	V.	VI.	VII.
Nickel	(A) (1) (*b*)	62	9	8	7	8		
Cobaltous	(B) (1) (*c*) (i)	49·5	3·5	6	3		11	
	(ii)	56·5	8	5	3·5	3	3·5	
	(iii)	56	2·5	5	4		8	
	(B) (1) (*d*)	47·5	15	6	5·5		14·5	
Cobaltic	(C) (1) (*b*)	84	9		0·5		1·75	

* See pp. 1464—1465.

Sulphur dissolved mainly as sulphate; possibly small amounts of free sulphur were liberated, and traces only of hydrogen sulphide were detected. The largest portion of metal dissolved in the first extract, and the amount of metal dissolved from the cobalt sulphides ran parallel to the oxygen content of the sulphide. In the initial extraction, the ratio metal to sulphur generally considerably exceeded that required for MSO_4, but in the subsequent extractions it was generally less than required by this formula. The dry sulphides were oxidised almost completely to sulphates after exposure to air at room temperature for 2 years.

The wet sulphides, prepared from nickel and cobaltous solution, and kept in nitrogen, dissolved rapidly and extensively in 2*N*-hydrochloric acid; the solubility of cobaltic sulphide was much lower. They all became less soluble, however, with increasing time; the results on 12 preparations of sulphides, showing the percentages soluble after standing for 1½ or 30 mins., are given below :

Sulphide.	Nickel.	Cobaltous.	Cobaltic.
% Soluble after 1·5 mins.	87·7, 83·6	92·6, 88·4	56·1, 52·1
,, ,, 30 ,,	71·1, 62·1	84·1, 81·1	45·8, 44·4

The cause of this ageing effect, whether it be due to chemical change or to physical (as postulated by Thiel and Gessner), has not yet been examined.

Sulphides, prepared without contact with oxygen, dissolve with evolution of hydrogen sulphide. The percentages of sulphides dissolving on treatment with 2*N*-acid, based upon the estimation of M, and the value of x in the formula MS_x derived from the estimation of the metal and the hydrogen sulphide evolved, are shown below :

Sulphide.	Nickel.	Cobaltous.	Cobaltic.
% Soluble	58·6, 49·1, 30·1, 45·5	56·0, 35·3	30·0, 30·8
x	— — 0·48, 0·31	0·72, 0·57	0·82, 0·82

The relatively low solubilities are probably due in part to the ageing effect, for varying times were needed for manipulation—in all cases greater than those required in the preceding experiments. The low relative value of sulphur to metal may be due to presence of oxygen in the water and acid used in this set of experiments; a part of the sulphide would thereby be oxidised and dissolve with production of metal and sulphate ions, whilst the non-oxygenated part would dissolve with production of metal and sulphide ions. To illustrate further this effect of oxygen in diminishing the value of x, precipitates prepared in nitrogen were exposed to air for 30 mins. and then treated with $2N$-hydrochloric acid :

Sulphide.	% Soluble.	x.
Nickel	44·6	0·15
Cobaltous	36·1	0·05
Cobaltic	31·1	0·04

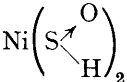
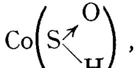
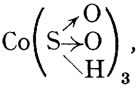
Discussion and Summary of Results.

The experimental results are consistent with the following mechanisms, which will be made the basis of the development of the study of these reactions.

(1) Sulphides are formed, with air exclusion, by reactions $\mathrm{Ni}^{\cdot\cdot} + 2\mathrm{HS}' \longrightarrow \mathrm{Ni(SH)_2}$ (and similarly for $\mathrm{Co}^{\cdot\cdot}$) ; $\mathrm{Co}^{\cdot\cdot\cdot} + 3\mathrm{HS}' \longrightarrow \mathrm{Co(SH)_3}$.

The metallic ions reacting are doubtless amminated, and interaction in part with S'' ions probably proceeds with formation of NiS, CoS, and $\mathrm{Co_2S_3}$.

(2) These sulphides, dried in nitrogen, are NiS, CoS, and $\mathrm{Co_2S_3}$.

(3) In presence of oxygen, variable addition takes place initially at the sulphur atoms, *e.g.*,  $\mathrm{Ni}\left(\mathrm{S}\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{H}\end{smallmatrix}\right)_2$,  $\mathrm{Co}\left(\mathrm{S}\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{H}\end{smallmatrix}\right)_3$, accompanied by intramolecular rearrangement. Further addition can proceed at the sulphur atom, *e.g.*,  $\mathrm{Co}\left(\mathrm{S}\begin{smallmatrix}\nearrow\mathrm{O}\\ \rightarrow\mathrm{O}\\ \searrow\mathrm{H}\end{smallmatrix}\right)_3$, and mixed forms can be obtained.

Under the conditions of formation employed in presence of air, cobaltous cobalt tends to change into the cobaltic state, and this accounts for the greater variability in composition of " cobaltous sulphide " than of " nickelous sulphide," and the similarity of results in some cases between analyses of " cobaltous sulphide " and of " cobaltic sulphide."

(4) Drying the oxygenated sulphides results in a partial elimination of hydrogen sulphide and of water, and further oxygenation may proceed.

(5) The undried sulphides $\mathrm{M(SH)_2}$ initially formed are soluble in dilute acid with generation of hydrogen sulphide : $\mathrm{M(SH)_2} + 2\mathrm{H}^{\cdot} \longrightarrow \mathrm{M}^{\cdot\cdot} + 2\mathrm{H_2S}$. Similarly, $\mathrm{Co(SH)_3}$ affords $\mathrm{Co}^{\cdot\cdot\cdot} + 3\mathrm{H_2S}$ accompanied by the reaction $2\mathrm{Co}^{\cdot\cdot\cdot} + \mathrm{H_2O} \longrightarrow 2\mathrm{Co}^{\cdot\cdot} + 2\mathrm{H}^{\cdot} + \mathrm{O}$, and the available oxygen oxygenates a part of the sulphide, which then dissolves as under (7).

(6) The sulphides (1) formed initially change on ageing into much less soluble forms.

(7) The dried and undried oxygenated sulphides, which are the substances usually obtained in qualitative analytical procedure, dissolve without hydrogen sulphide evolution—the metal by direct acid attack, and the sulphur by further oxidation to sulphate.

EXPERIMENTAL.

Materials.—Nickel and cobalt chlorides (iron-free) were the purified commercial salts. Hexamminocobaltic chloride was prepared as described by Biltz and Biltz (" Übungsbeispiele aus der Unorganischen Experimentalchemie," 1920, p. 168, 1*b*).

Hexamminocobaltous chloride was obtained in almost quantitative yield from a solution of cobaltous chloride (10 g.) in cold ethyl alcohol (100 ml.) placed in *A* (Fig. 1); *B* was replaced by a tube, dipping into the solution, through which ammonia gas was introduced, the apparatus being first filled with nitrogen. After precipitation was complete and the liquid had cooled, the precipitate was filtered off into *D* in an atmosphere of nitrogen, washed with ether, quickly transferred to a vacuum desiccator, and dried at room temperature. Surface discoloration took place when it was placed in the desiccator.

In the preparation of cobaltous stearate, stearic acid (53 g.) was dissolved in *iso*propyl alcohol (750 ml.), and water (200 ml.) added. The stirred solution, after neutralisation by N-potassium hydroxide, was treated dropwise at 60° with a solution of cobaltous chloride (25 g.) in water (200 ml.) and *iso*propyl alcohol (250 ml.). The cobaltous stearate was filtered off, washed with boiling water, and then with hot *iso*propyl alcohol. It was dried at 105°, and finely powdered; yield 45 g.

The nitrogen used was the commercial gas, washed through alkaline pyrogallol, and then passed through an empty trap.

Hydrogen sulphide was prepared from sodium sulphide and phosphoric acid in an atmosphere of nitrogen, and, after passing through water and a cooled trap to remove spray, it was absorbed in air-free water contained in a blackened flask *C*; this was then closed and attached as shown in Fig. 1. The concentration of the hydrogen sulphide solution varied from about 0·05 to 0·15*N*, and changed but slightly after several months' storage in contact with nitrogen.

Composition of Precipitates.

(A) *Nickel Sulphides.*—1. *Dried in air.* (*a*) The apparatus shown in Fig. 1 was used; *A* was of 300 ml. capacity. Nickel chloride (0·2—0·5 g.) and ammonium chloride (1—3 g.) were weighed into a float, which was placed in *A*. The apparatus was evacuated, then filled with nitrogen, and the operations thrice repeated. Freshly boiled and cooled water (60 ml.) and 2*N*-ammonia (1·25—3·5 ml.) were added from *E*, and, after the salts had dissolved, hydrogen sulphide solution (50—120 ml.; 0·06*N*) was added dropwise and with swirling from *B*. After standing for 30 mins., the precipitate was filtered off, washed with 6 portions of 60 ml. of boiled water, and then with alcohol and ether; all operations were carried out in an atmosphere of nitrogen. The crucible was detached and dried in an air-oven at 110° for 3—4 hrs. One preparation weighed 0·0861, 0·0860, and 0·0856 g. after 1, 1½, and 5½ hrs.' drying at 110°, whilst in a second experiment at 110° the weights were 0·1015, 0·1014, and 0·1023 g. after ¾, 2, and 6½ hrs.' drying.

The dried precipitate was powdered with 5 ml. of a 30% w./v. solution of bromine in carbon tetrachloride. After it had stood for 10 mins., 5 ml. of concentrated nitric acid were added, and when the initial vigorous reaction had subsided, the solution was evaporated nearly to dryness; concentrated hydrochloric acid (10 ml.) was then added and the evaporation repeated. The cold diluted solution (700 ml.) was precipitated by means of barium chloride, and after standing over-night, the barium sulphate was filtered off and weighed. Nickel dimethylglyoxime was precipitated from the filtrates (Found: Ni, 46·3, 43·1, 50·4, 49·6; S, 30·4, 29·4%).

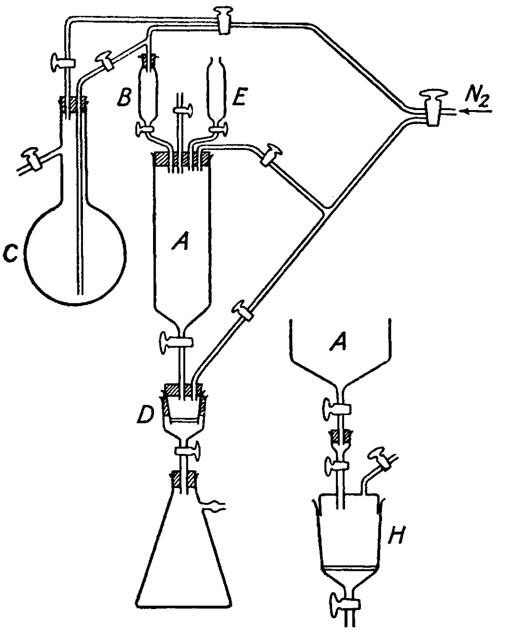


FIG. 1. FIG. 2.

For the determination of oxygen, the sulphide (*ca.* 0·1 g.) was weighed in a copper boat and heated in a silica tube in a current of hydrogen; the hydrogen was purified from oxygen by passing over platinum gauze and was then dried through phosphoric oxide. The silica tube was packed beyond the boat with copper wire to retain any hydrogen sulphide or sulphur liberated; blank determinations on pure sulphur showed that it was completely retained by the copper. The water evolved was collected in a U-tube containing phosphoric oxide, followed by a guard tube. All the analytical results for oxygen, hydrogen, and ammonia immediately following relate to separate sulphide preparations (Found: O, 21·3, 22·4, 21·6, 21·2%).

In the determination of hydrogen, the sulphide (approx. 0·1 g.) contained in a copper boat was mixed with 3—4 g. of dried red lead, and heated in a hard-glass tube, containing a plug of asbestos (Borphy, *Ind. Eng. Chem., Anal.*, 1931, **3**, 13), in a current of dry oxygen. The water was collected as above (Found: H, 1·70, 1·25%).

Ammonia was estimated by heating the weighed sulphide (*ca.* 0·1 g.) with concentrated sulphuric acid (3 ml.) and potassium sulphate (1 g.) for ½ hr., and then transferring the solution to a micro-Kjeldahl distillation apparatus (Found: NH_3, 0·49, 0·17%).

Chloride was tested for by heating the sulphide with concentrated sulphuric acid, and collecting the gases in sodium hydroxide solution, which was then made acid with nitric acid and silver nitrate added; a precipitate was not obtained in any experiment.

(*b*) A single preparation was made and analysed completely. Nickel chloride (4 g.) and ammonium chloride (20 g.) were dissolved in water (2½ l.) containing 2*N*-ammonia (25 ml.). Hydrogen sulphide was passed through the solution for ½ hr.; after standing for ½ hr., the liquid was decanted from the precipitate, which was thrice washed by decantation. It was filtered off, and well washed first with water and finally with alcohol and ether. After drying at 110° for 5 hrs., it was powdered and analysed as above (Found : Ni, 46·79; S, 30·48; O, 20·80; H, 1·29; N, 0·37; Total 99·73%).

2. *Prepared and dried in nitrogen.* The sintered-glass crucible *D* and attachments were replaced by *H* (Fig. 2), which was made entirely of glass with a sintered diaphragm. The funnel *E* was replaced by a tube connected to a flask containing water which had been boiled, cooled, stored, and transferred to the apparatus in contact with nitrogen.

Nickel chloride, ammonium chloride, and ammonium hydroxide were introduced as in (*a*), and precipitation was similarly effected. After the precipitate had been filtered off and well washed, the taps of *H* were closed. It was transferred to an air-oven, reconnected to the nitrogen supply, and dried for about 4 hrs. at 110° in a current of the gas. The apparatus, with taps closed, was weighed, the precipitate transferred to a tared beaker, and the apparatus re-weighed; the precipitate (*ca.* 0·1 g.) gained 1—5 mg. in weight during 15 mins.' contact with air. It was dissolved, and sulphate determined, as previously. Nickel was estimated in an aliquot portion of the filtrate by adding 2*N*-sodium hydroxide to the boiling solution until a precipitate just formed, followed immediately by 50 ml. of a 20% w./v. solution of ammonium acetate to dissolve the precipitate. 12 Ml. of a 2% solution of 8-hydroxyquinoline in *N*-acetic acid, diluted with 50 ml. of 2*N*-ammonia, were stirred in. After 10 mins.' boiling, the nickel complex was filtered off, well washed with hot water, and estimated volumetrically (Fleck, Greenane, and Ward, *Analyst*, 1934, **59**, 325) (Found : Ni, 62·1, 60·6; S, 36·6, 37·1%, respectively in two preparations). In four experiments in which water was stored under nitrogen but poured into *E* which had been swept out with the gas, the nickel content was lower (Found : Ni, 56·0, 59·0, 58·3, 57·5; S, 38·2, 37·9, 36·3, 37·0%).

(B) *Cobaltous Sulphides.*—1. *Dried in air.* (*a*) The procedure for precipitation, filtration, and drying was as in (A) 1. (*a*). The precipitate, dried at 100° for 3, 5, and 10 hrs., weighed 0·1172, 0·1133, and 0·1145 g.; it was then heated at 150° for 5 hrs., and weighed 0·1104 g. No free sulphur could be extracted from the precipitate by carbon disulphide.

The precipitate was dissolved and the sulphur determined as for nickel sulphide. Excess barium was precipitated from the filtrate, cobalt was then removed as cobaltic hydroxide, well washed, dissolved in hydrochloric acid, the solution evaporated, and cobalt determined electrolytically (Found : Co, 44·4, 47·7; S, 32·6, 32·4%).

(*b*) Preparations were also made from about 0·2 g. of cobaltous chloride and ammonium chloride (20 g.) in water (100—250 ml.) by reaction with hydrogen sulphide gas or solution. The precipitates from 7 preparations were each dried and analysed as above (Found : Co, 46·0, 44·2, 45·7, 47·5, 42·4, 44·4, 43·3; S, 30·8, 28·2, 36·3, 36·5, 34·3, 39·6, 38·4%). To determine if the composition changed during drying, two analyses were made of the wet sulphide immediately after it had been washed (Found : Co : S = 1 : 1·69, 1·61). The ratios in the above series vary from 1·18 to 1·64.

The amounts of oxygen found in individual preparations by procedures (*a*) and (*b*) were :

Procedure	*a.*	*a.*	*a.*	*b.*	*b.*	*b.*	*b.*	*b.*	*b.*
O, %	23·2	20·6	16·0	21·1	20·2	18·5	22·9	19·6	17·4

The percentages of hydrogen in the precipitates varied from 1·04 to 1·52, and of nitrogen from 0·71 to 0·99. Chlorine was absent in all cases.

(*c*) (i) A single preparation for analysis was made from cobaltous chloride (6·5 g.) as in (A) 1. (*b*) (Found : Co, 41·71; S, 31·63; O, 25·06; H, 1·29; N, 0·69; Total, 100·38%).

(ii) The preparation was repeated, but the cobaltous chloride (6·5 g.) was contained in 800 ml. of solution (Found : Co, 44·47; S, 27·81; O, 25·26; H, 1·13; N, 0·47; Total, 99·14%).

(iii) The sulphide was also prepared from hexamminocobaltous chloride (4 g.), water (2 l.), and ammonium chloride (20 g.) (Found : Co, 39·28; S, 27·33; O, 31·46; H, 1·70; N, 0·59; Total, 100·36%).

Cobalt in this set of experiments was determined by conversion of the sulphide into sulphate by evaporation with concentrated sulphuric acid.

(*d*) Hydrogen sulphide, dried by means of warm glycerol and phosphoric oxide, was passed into a solution of cobalt stearate (0·4—8 g.) in benzene (50—1000 ml.) at 70°; the solution was contained in a flask, the outlet tube of which was attached to tubes containing phosphoric oxide. The cobalt sulphide was washed by decantation with dry benzene, filtered off, washed with dry benzene, and dried in an air-oven at 110° for 1 hr. (Found, in four preparations: Co, 39·4, 39·8, 40·8, 39·5; S, 21·7, 24·8, 26·0, 28·4% respectively). A fifth preparation was analysed completely (Found: Co, 45·8; S, 31·7; O, 21·4; H, 1·02; Total, 99·9%).

2. *Prepared and dried in nitrogen.* The technique was the same as for (A) (2), with the more rigid conditions of washing. Cobalt was determined by means of 8-hydroxyquinoline (Found: Co, 61·9, 58·1; S, 30·8, 33·9%, respectively).

(C) *Cobaltic Sulphides.*—1. *Dried in air.* (*a*) The sulphide was precipitated from an aqueous solution of hexamminocobaltic chloride by hydrogen sulphide solution, as in (B) 1. (*b*), but ammonium chloride and ammonia were not added in any of this series of experiments. Chlorine and free sulphur were absent from the precipitates. Cobalt and sulphur were determined in each dried sulphide prepared; figures in the same vertical column refer to the same specimen:

Co, %	38·3	46·1	35·7	33·1	32·8	26·4	44·4
S, %	37·2	35·5	32·7	22·1	22·4	40·3	21·8

The results for oxygen, hydrogen, and nitrogen on different preparations were: O, 29·3, 40·4, 29·6, 27·3; H, 1·28, 1·80; N, 0·80, 0·93, 0·70, 0·91, 0·66%.

(*b*) Hexamminocobaltic chloride (4 g.) was dissolved in water (2 l.) and hydrogen sulphide gas was passed into the solution until precipitation was complete (½ hr.). After standing for ½ hr., the precipitate was separated for analysis as in (A) 1. (*b*) (Found: Co, 27·4; S, 24·4; O, 47·5; H, 1·85; N, 0·48; Total, 101·6%).

2. *Prepared and dried in nitrogen.* The procedure was as in (B) 2., the results on 3 preparations being: Co, 53·1, 48·1, 45·9; S, 42·6, 40·5, 43·7%.

Solubilities of Precipitates.

Dried Oxygenated Sulphides.—The dried sulphides (0·1 g.), prepared as under (B) 1. (*c*) and (*d*), were extracted, with occasional swirling at room temperature, first with 3 successive portions of 50 ml. of 2*N*-hydrochloric acid, each for 1 or more days, and finally with 50-ml. portions of 12*N*-acid. The extraction vessel was attached to bulb-tubes containing aqueous sodium hydroxide; after reaction, the alkaline solution, when tested with lead acetate solution, did not form lead sulphide. In a further test, 0·2 g. of sulphide was boiled for 15 mins. with 30 ml. of 2*N*-hydrochloric acid, and the vapours were led into water. The slightly opalescent distillate, tested by means of lead acetate, contained 3γ of hydrogen sulphide; the opalescence was probably due to sulphur, for the solution after treatment with nitric acid became clear and a trace of sulphate was present.

The acid extracts were free from hydrogen sulphide, for, when they were made alkaline, cobalt or nickel sulphide was not formed. The acid solutions also remained clear after addition of mercuric chloride solution, and did not discharge the colour of iodine solution. The solution contained sulphate, which was estimated as barium sulphate; cobalt was determined electrolytically.

Results follow for the three preparations described under (B) 1. (*c*); the complete results

		2*N*-HCl.			12*N*-HCl.					
		I.	II.	III.	IV.	V.	VI.	VII.	In residue.	Total.
(i)	Days	1	1	1	3	1	3	6		
	Co, mg.	20·6	1·4	2·4	1·2	4·5			11·7	41·8
	S, mg.	5·6	2·2	1·9	1·3	1·4			7·8	20·2
	Co : S	2·0	0·35	0·7	0·5	1·75			—	—
(ii)	Days	3	2	2	3	2	2			
	Co, mg.	25·2	3·6	2·2	1·6	1·2	1·4		11·5	46·7
	S, mg.	6·2	0·8	0·6	0·4	0·3	0·4		8·2	16·9
	Co : S	2·2	2·45	2·0	2·2	2·2	1·9		—	—
(iii)	Days	1	1	1	3	1	3	6		
	Co, mg.	22·0	1·0	2·0	1·6	3·25			6·5	36·3
	S, mg.	6·7	2·0	1·9	6·6	1·4			5·0	23·6
	Co : S	1·8	0·3	0·6	0·13	1·25			—	—

Weights of residues, mg.: (i) 30·0; (ii) 27·9; (iii) 20·3.

for the sulphides are summarised in Table III (p. 1461). Cols. I—VII show the successive extractions; the lines under each heading show, in order, the time of extraction in days, the number of mg. of cobalt and of sulphur extracted, and the atomic ratio of cobalt to sulphur. The last two cols. give first the weights (in mg.) of cobalt and sulphur found in the residues, and finally the total weights thus accounted for. The total cobalt found agrees well, for this kind of experiment, with the amount determined in the complete analyses of the precipitates (p. 1464), but the sulphur usually showed a considerable deficiency. This may be due to a partial loss as the free element (see above); it is known that sulphides are decomposed by treatment with ammonia or acids with liberation of sulphur (Gluud and Mühlendyck, *Ber.*, 1922, **55**, 952; 1923, **56**, 899; Gluud and Schonfelder, *ibid.*, 1924, **57**, 628; Dunn and Rideal, J., 1923, **123**, 1250).

Variation with Time in Solubilities of Sulphides (*Air Exclusion*).—The sulphides were precipitated as in (A) 2. A standardised solution of nickel chloride containing ammonium chloride was used. Aliquot portions of the solution, well-boiled immediately before use, and introduced boiling into the apparatus, were taken. The hydrogen sulphide solution was added dropwise during 3 mins. in quantity in excess of that required completely to precipitate the sulphide, and after the solution had stood for 1½ or 30 mins., 5*N*-hydrochloric acid, prepared and stored under nitrogen, was introduced, to give a total acidity of approx. 2*N*. After being swirled for 2 mins., the undissolved precipitate was filtered off and washed in contact with nitrogen. The filtrates were boiled until hydrogen sulphide was expelled, and nickel was determined by 8-hydroxyquinoline. The complete results for nickel, cobaltous and cobaltic solutions are given on p. 1461.

Two other experiments on the "ageing" of the sulphides were carried out as follows. Cobaltous chloride (0·35 g.) in air-free water (160 ml.) was contained in a distillation flask. A sealed, thin-walled, glass tube containing sodium sulphide (0·7 g. in 10 ml. of water) was placed in the solution. The neck of the flask was closed by a stopper through which passed a closed glass tube completely filled with 12*N*-hydrochloric acid (40 ml.), and holding a plunger with which to break the bottom of the container. The flask was evacuated and its side tube sealed. The sodium sulphide solution was mixed into the cobalt solution by gently agitating the flask. The precipitate was allowed to stand for a known time, and the hydrochloric acid was then introduced. After standing for 24 hrs., air was admitted to the flask, and cobalt determined in the solution. The percentage solubility was 93·6 after 4 mins.' standing and 76·5 after 15 mins.' standing.

Composition of Extracts from Undried Sulphides.—The sulphides were prepared, filtered, and washed as in (A) 1. (*a*). Nitrogen was then passed through the apparatus for 10 mins. to sweep out any hydrogen sulphide. Hydrochloric acid (2*N*; 180 ml.), which had just previously been boiled and cooled in contact with air, was added dropwise to the precipitate during 45—60 mins., and the filtrates were collected in a clean flask. Nitrogen was intermittently passed through the precipitate to remove hydrogen sulphide. The precipitate was finally washed by water (60 ml.) and by nitrogen. A Drechsel bottle containing *N*-sodium hydroxide was connected to the filter flask, to absorb hydrogen sulphide escaping from the acid solution. The two solutions were mixed and hydrogen sulphide was determined by means of *N*/10-iodine solution; the metal was estimated as its oxine complex. The insoluble residue from the acid extraction was dried in contact with air, tipped from the crucible as completely as possible, and analysed. The results for cobaltous chloride are shown below, and the complete data are summarised on p. 1461.

Co taken, g.	Soluble portion.		Insol. portion.			Solubility, %.
	S, g.	Co, g.	Wt., g.	S, %.	Co, %.	
0·0863	0·0191	0·0483	0·0783	25·7	42·7	56·0
0·0779	0·0084	0·0275	0·0985	29·8	45·5	35·3
0·0778	0·0008	0·0281	0·0995	28·8	47·5	36·1

In the third experiment, air was aspirated over the sulphide for 15 mins., and it was allowed to stand during a further 15 mins. before acid was added.

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