

solution by filtration through paper filters is so small as to be inappreciable in its effect on qualitative or most quantitative separations.

The separation of zinc from the elements precipitated by sodium hydroxide is unsatisfactory in every case studied, from 10–50% of the zinc remaining in the precipitate.

Summary

An experimental study of the separation of manganese, iron, cobalt and nickel from aluminum, chromium and zinc by means of sodium hydroxide and sodium peroxide has been made.

With 250 mg. of each element present, from 1–3 mg. of aluminum remains with the manganese or the iron, from 12–15 mg. with the cobalt, and 30–40 mg. with the nickel.

The separation of trivalent chromium from these elements is unsatisfactory due to incomplete oxidation of the chromium. When the chromium is originally present as chromate, not over 1 mg. is carried down by any of the precipitates except manganese, where 7 mg. was co-precipitated.

The separation of zinc is unsatisfactory, from 10–40% of it being carried down with the precipitates.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 322]

STUDIES OF VARIOUS METHODS FOR THE SEPARATION OF THE COMMON ELEMENTS INTO GROUPS. III. A NEW METHOD FOR THE SEPARATION OF ZINC, COBALT, NICKEL AND IRON FROM ALUMINUM, CHROMIUM AND MANGANESE

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Introduction

The two methods most frequently used in systems of qualitative analysis for dividing into sub-groups the elements found in the ammonium sulfide precipitate are: (1) the ammonium hydroxide precipitation, and (2) the sodium hydroxide–sodium peroxide treatment. The results of studies of these separations have been presented in the two preceding papers of this series,¹ and the data show that many of the individual separations obtained by either of these methods are so incomplete as to make their use unsatisfactory in a qualitative system in which it was desired to stress the quantitative information that could be obtained. Accordingly, other methods for separating these elements into groups were investigated.

¹ (a) Swift and Barton, *THIS JOURNAL*, **54**, 2219 (1932); (b) Swift and Barton, *ibid.*, **54**, 4155 (1932).

It had been found by Mr. F. N. Laird² that the well-known precipitation by ammonium sulfide from an ammonium tartrate solution provided exceptionally fine separations of iron and zinc from aluminum and chromium and later experiments showed that the separation of cobalt from either aluminum or chromium was equally satisfactory—these being separations which are surprisingly imperfect by either the ammonium hydroxide or sodium hydroxide-peroxide methods. However, there seems to be some uncertainty as to the complete precipitation of manganese and nickel; and, in addition, the removal of the tartrate from the filtrate by fuming with sulfuric and nitric acids and the resolution of the anhydrous chromic sulfate which formed proved so tedious and time-consuming that the method was considered as undesirable.

It is known that oxalate tends to form complex compounds with all of these elements and many of these compounds have been studied.³ Very stable ions of the type $\text{M}(\text{C}_2\text{O}_4)_3$ are formed with aluminum⁴ and chromium⁵ (as well as with ferric iron),⁶ and ions, apparently somewhat less stable, of the type $\text{M}(\text{C}_2\text{O}_4)_2$ are formed with manganese,⁷ zinc,⁸ nickel⁹ and cobalt.¹⁰ Although oxalate can be much more easily oxidized and removed from a solution, its use as a substitute for tartrate does not seem to have been adequately investigated. Carnot¹¹ states that the presence of a sufficient concentration of oxalate will prevent the precipitation of nickel by ammonium or sodium sulfide while under the same conditions cobalt is completely precipitated. It is also proposed that zinc be separated from nickel and cobalt by precipitation as sulfide from a weakly acid solution containing an excess of oxalate. No experimental data are given in support of the method and, as will be shown below, we have not been able to confirm the results reported.

Mr. Laird² had also found that moderate amounts of aluminum or chromium could be held in an ammoniacal solution if sufficient oxalate

² Laird, unpublished experiments carried out in this Laboratory.

³ A review of these compounds with bibliographies will be found in Abegg and Auerbach, "Handbuch der anorganischen Chemie," S. Herzl, Leipzig, and in Gmelin-Kraut "Handbuch der anorganischen Chemie," Carl Winters, Heidelberg. Because of this only a few of the individual references will be given below.

⁴ Plessy, *Compt. rend.*, **97**, 1033 (1887); Wahl, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, **4**, 1-9 (1927).

⁵ Werner, *Ber.*, **45**, 865 (1912).

⁶ Rieger, *Z. Electrochem.*, **7**, 871 (1901); Schäfer, *Z. anorg. Chem.*, **45**, 293 (1905); Scholz, *Wein. Monatsk.*, **29**, 439 (1908).

⁷ Rüst, *Z. anal. Chem.*, **41**, 606 (1902); Hauser and Wirth, *J. prakt. Chem.*, [2] **79**, 358 (1909).

⁸ Kunschert, *Z. anorg. Chem.*, **41**, 337 (1904).

⁹ Rammelsberg, *Pogg. Ann.*, **95**, 198 (1855).

¹⁰ Benedict, *THIS JOURNAL*, **28**, 171 (1906).

¹¹ Carnot, *Compt. rend.*, **166**, 329-333 (1918).

were present; however, it was later found that the precipitation of manganese as sulfide from such solutions was quite incomplete, as much as 50 mg. of manganese being present before a precipitate was obtained, also that in slightly acid solutions a precipitate of manganese oxalate was obtained. On neutralizing the solution with sodium hydrocarbonate, no precipitate of manganous oxalate formed when an excess of oxalate was present, and it was found possible to have even large amounts of manganese present without formation of a precipitate upon saturating the solution with hydrogen sulfide. These results seemed to warrant further investigation, and this paper presents experiments showing the results which may be obtained in precipitating zinc, nickel, cobalt and iron as sulfides from such solutions containing aluminum, chromium or manganese, and a study of some of the factors affecting these separations.

Experimental

Behavior of Manganese.—In order to study the conditions under which manganese could be kept in solution, the experiments recorded in Table I were performed. In these 70 millimoles of ammonium oxalate was added to a solution containing 30 millimoles of hydrochloric acid and the amount of manganese, as sulfate, shown in the second column. This amount of oxalate was found in preliminary experiments to

TABLE I
THE PRECIPITATION OF MANGANESE SULFIDE FROM HYDROCARBONATE SOLUTIONS CONTAINING OXALATE

Expt.	Manganese taken, mg.	Excess NaHCO ₃ added, g.	Volume of solution, ml.	H ₂ S Treatment Time, min.	Temp., °C.	Mn precipitated as sulfide, mg.	Remarks
1	570	1	60	20	60-80	0	
2	570	2	60	45	60-80	182	No precipitate for 15 min.
3	570	3	60	45	60-80	250	No precipitate for 5 min.
4a	500	1	120	10	60-80	0	
4b	500	2*	120	15*	60-80	0	* 1 g. NaHCO ₃ added to solution from 4a; treated with H ₂ S for 15 min. longer
4c	500	3*	120	10*	60-80	250	* 1 g. NaHCO ₃ added to solution from 4b; treated with H ₂ S for 10 min. longer
5	500	1	120	30	70-90	0	After standing 4 days 11 mg. Mn had pptd.
6	500	2	120	30	70-90	0	Precipitate began to form slowly 10 min. after finish of H ₂ S treatment. After standing four days 133 mg. of Mn had precipitated
7	570	1	120	30	60-80	0	After standing 4 days 77 mg. Mn had pptd.
8	570	2	120	15	60-80	0	After 20 min. precipitate formed rapidly; after standing 4 days 130 mg. Mn had pptd.

TABLE I (Concluded)

Expt.	Manganese taken, mg.	Excess NaHCO ₃ added, g.	Volume of solution, ml.	H ₂ S Treatment Time, min.	Temp., °C.	Mn precipitated as sulfide, mg.	Remarks
9	250	2	120	30	60-80	0	After standing 5 days 63 mg. Mn had pptd.
10	570	2	120	120	20	<1	93 mg. after standing 4 days
11	570	1	200	30	60-80	0	0.5 mg. after standing 2 days
12a	570	1	200	20	65	0	
12b	570	1	200	24 hrs.*	20	2-5	* Solution from (a) stood under pressure
12c	570	1	200	24 hrs.*	20	20	* Soln. from (b) stood with slow stream passing
12d	570	1	200	30*	60-70	51	Filtrate from (c). Very rapid stream of H ₂ S. Ppt. formed slowly
13	500	1	200	45	60-70	0	100 mg. pptd. after 5 days
14	570	2	200	30	60-80	0	57 mg. pptd. after 2 days
15a	570	2	200	20	60-70	0	
15b	570	2	200	24 hrs.*	20	0	* Solution from (a) stood under pressure
15c	570	2	200	24 hrs.*	20	15	* Soln. from (b) stood with slow stream passing
15d	570	2	200	30*	60-70	67	* Filtrate from (c), very rapid stream. Precipitate formed rapidly
16	500	2	200	20	60-70	1	Very rapid stream H ₂ S
				45	60-70	52	
17a	500	4	400	20	60-80	0	
17b	500	5*	400	10	60-80	Large ppt.	* 1 g. NaHCO ₃ added to (a); treated with H ₂ S 10 min. longer

prevent the precipitation of even 500 milligrams of aluminum or chromium. The acid was nearly neutralized with ammonium hydroxide, solid sodium hydrocarbonate added in 0.1-g. portion until the solution was just neutral to litmus, and then the amount of sodium hydrocarbonate indicated in the third column of Table I was added in excess. It should be noted that 1 g. excess of the hydrocarbonate gives the solution a distinct alkaline reaction to litmus even after treatment with hydrogen sulfide. The solution was diluted to the volume indicated in the fourth column, then a rapid stream of hydrogen sulfide passed through it for the time indicated in the fifth column. The solution was maintained at the temperature shown in the sixth column. The amount of manganese in any precipitate obtained is given in the seventh column. The manganese was estimated by dissolving the sulfide precipitate with hydrochloric acid and reprecipitating the manganese as dioxide with sodium peroxide or by dissolving the sulfide precipitate with nitric acid and reprecipitating the manganese with chlorate; in either case the manganese dioxide precipitate was dissolved in an excess of potassium iodide and hydrochloric acid, and the iodine thus formed was titrated with standard thiosulfate solution.

Discussion of the Data of Table I.—It is seen from the data given that the precipitation of manganese sulfide from these solutions is dependent upon the excess of hydrocarbonate added, upon the volume of the solution, upon the time for which the hydrogen sulfide is passed, and, after this, upon the time for which the solution is allowed to stand. It is also apparent that with large quantities of manganese the separations attained may depend considerably upon maintaining a supersaturated solution. Other sulfide separations depending upon similar conditions are known. Thus the studies of Glixelli¹² and of Kolthoff and Pearson¹³ show that the separation in acid solutions of the sulfides of the copper and tin group elements from zinc is due, at least in part, to the slow rate of precipitation of zinc sulfide. It would be expected that the precipitation of other sulfides from the solution would induce the precipitation of manganese sulfide. Although conclusive studies have not been made of this effect, it will be shown below that other sulfides can be precipitated and surprisingly sharp separations obtained from solutions which are probably supersaturated with respect to manganese sulfide; thus with 250 milligrams of each element present in a volume of 120–150 milliliters, the amount of manganese co-precipitated is insignificant even when the operations of precipitation and filtering extend over several hours.

A detailed study of the buffering action caused by the hydrocarbonate in these solutions has not been made. It is probable that on prolonged passage of hydrogen sulfide the carbon dioxide is quite completely swept out and the hydrocarbonate converted into hydrosulfide. Approximate calculations indicate that this conversion would result at no time in more than a two-fold change in the hydrogen-ion concentration of the solution; also that the sulfide-ion concentration would not be increased by more than about four-fold upon sweeping a solution, containing hydrocarbonate and saturated with both hydrogen sulfide and carbon dioxide, with hydrogen sulfide until the carbon dioxide has been removed and the hydrocarbonate converted into hydrosulfide.

The Precipitation of Zinc, Nickel, Cobalt and Iron as Sulfides from Oxalate Solutions.—Experiments showed that the precipitation of zinc from solutions having a volume of 120 ml. and containing 70 millimoles of ammonium oxalate and 30 millimoles of ammonium chloride was almost complete when the solution was just acid to litmus and that quantitative precipitation was obtained from neutral solutions. The zinc sulfide precipitated under these conditions was compact and readily filtered, while a precipitate from a solution containing an excess of 2 ml. of 6 *N* ammonium hydroxide was finely divided and difficult to filter.

¹² Glixelli, *Z. anorg. Chem.*, **55**, 297 (1907).

¹³ Kolthoff and Pearson, *J. Phys. Chem.*, **36**, 549 (1932).

The precipitation of nickel from a slightly acid solution is quite incomplete and when the solution is just neutral to litmus the precipitate forms very slowly. However, from a solution containing 1 g. of sodium hydrocarbonate in excess the precipitation is fairly rapid, is complete, and, if the formation of disulfide is avoided, the precipitate is obtained in a coarse granular form that can be filtered and washed by decantation. The effect of the presence of disulfide is very pronounced. If ammonium sulfide containing only a small amount of disulfide is added or if during the treatment with hydrogen sulfide the solution is allowed to stand in contact with the air, the dark brownish colloidal solution, characteristic of nickel sulfide when it is precipitated by ammonium sulfide solution, is formed. This can be prevented by first boiling the solution to remove dissolved oxygen, then sweeping the flask with hydrogen sulfide and thereafter keeping a continuous flow of the gas through the mixture until precipitation is complete. Once formed this colloidal solution can sometimes be coagulated by very vigorous shaking of the stoppered flask or, this failing, by filtering out the coagulated portion of the precipitate, then making the filtrate distinctly acid to litmus, heating it almost to boiling and again shaking it. The precipitate thus coagulated, which usually contains less than 1 mg. of nickel, does not appreciably redissolve in the acid solution and can be readily filtered.

The precipitation of cobalt is complete, although slow, if the solution is made neutral to litmus with hydrocarbonate. With a 1-g. excess of sodium hydrocarbonate the precipitation is rapid and the precipitate is compact and easily filtered.

From 2 to 5 mg. of iron remain in a solution made neutral with hydrocarbonate. In solutions containing an excess of 1 g. of sodium hydrocarbonate the precipitate forms in a finely divided state and from 0.2–0.4 mg. may pass through the filter, giving the filtrate a greenish or even dark color. This is readily coagulated by shaking the solution, heating it, or passing in more hydrogen sulfide; with 2 g. of sodium hydrocarbonate precipitation is quite complete.

The Effect of Phosphate and of Alkaline Earth Elements.—Experiments showed that the presence of considerable phosphate caused manganese, but not aluminum or chromium, to precipitate. Alkaline earth elements would be more or less completely precipitated as oxalates. It is therefore necessary to remove phosphate and alkaline earth elements before applying this method as a general group separation.

Procedure for the Separation of the Zinc Group from the Aluminum Group.—From the above experiments it is indicated that from ammonium oxalate solutions containing a small concentration of sodium hydrocarbonate zinc, nickel, cobalt and iron (these elements will hereafter be designated the zinc group) can be precipitated as their sulfides and thus

separated from aluminum, chromium and manganese (these elements to be designated the aluminum group). Accordingly, two series of experiments were carried out to test the qualitative and quantitative value of this separation. The general procedure for these experiments was as follows.

To a solution containing 30 millimoles of hydrochloric acid and the elements to be separated in a volume of 100 ml., 6 *N* ammonium hydroxide was added until the solution was just acid to litmus or until any local precipitate which formed just redissolved. Ten grams (70 millimoles) of ammonium oxalate was added, the solution heated until the ammonium oxalate dissolved, cooled, and then solid sodium hydrocarbonate added, 0.1 g. at a time, until the solution was neutral to litmus, that is, turned both blue and red litmus to an intermediate purplish color. A rapid stream of hydrogen sulfide was passed through the solution for three to five minutes, then, while a slow stream of the gas was kept flowing, the mixture heated to 60–80°. The solution was tested with litmus (preferably without interrupting the flow of gas) and, if it had become acid, again neutralized with sodium hydrocarbonate, an excess of exactly 1.0 g. of the solid added, and hydrogen sulfide again passed through the solution for three to five minutes. This process was repeated until the solution remained slightly alkaline to litmus. In no case were more than three one-gram portions of the sodium hydrocarbonate required. It was found that when iron was present, or when nickel was present and disulfide had been allowed to form, the coagulation of the precipitate was facilitated by tightly closing the flask with a rubber stopper and vigorously shaking the hot mixture. The mixture was filtered immediately through a paper filter and the precipitate washed with a hot solution made by dissolving 1 g. of ammonium oxalate in 100 ml. of hot water and saturating it with hydrogen sulfide. When washing precipitates of iron sulfide it was found advantageous to add 0.5 g. of sodium hydrocarbonate to this wash solution before treating it with hydrogen sulfide.

The results of the qualitative tests obtained have been collected in Table II. In the experiments shown in that table an excess of one gram of sodium hydrocarbonate was provided in all of the experiments; where a large precipitate formed, it was necessary to add two or three one-gram portions. However, it is to be noted that there was never more than 1 g. of sodium hydrocarbonate in excess at any one time. Completeness of precipitation was tested for by adding more sodium hydrocarbonate and again treating the solution with hydrogen sulfide for a considerable length of time. The aluminum group elements in the filtrates were detected by evaporating it to a small volume, adding an excess of concentrated nitric acid, repeating the evaporation, then adding solid potassium chlorate and nitric acid until the oxalate was completely decomposed and any manganese precipitated

as the dioxide. This was filtered out and the filtrate made just alkaline with ammonia in order to precipitate the aluminum. The filtrate from this precipitate was made just acid with acetic acid and tested for chromium by addition of lead acetate. The zinc group precipitates were dissolved in hydrochloric and nitric acids, and the solutions made just alkaline with ammonia to precipitate the iron. An excess of sodium hydroxide was added to this filtrate, the ammonia boiled out, then sodium peroxide added and the mixture boiled until the peroxide was decomposed. The nickel and cobalt oxides were filtered out and hydrogen sulfide passed

TABLE II

THE QUALITATIVE SEPARATION OF THE ZINC GROUP FROM THE ALUMINUM GROUP

The solution contained 70 millimoles of oxalate, and an excess of approximately 1 g. of sodium hydrocarbonate was maintained.

Expt.	Elements taken, mg.	Elements found		Notes
		Pre- cipitate	Filtrate	
1	Zn 500	Zn		
	Al 1		Al	
	Cr 1		Cr	
	Mn 1		Mn	
2	Ni 500	Ni		No Ni found in filtrate
	Al 1		Al	Precipitate coagulated; easily filtered
	Cr 1		Cr	
	Mn 1		Mn	
3	Co 500	Co		
	Al 1		Al	
	Cr 1		Cr	
	Mn 1		Mn	
4	Fe* 500	Fe	Fe†	* Taken as FeCl ₃ ; reduced by H ₂ S in slightly acid solution
	Al 1		Al	† 0.1 mg. Fe found in filtrate
	Cr 1		Cr	
	Mn 1		Mn	
5	Zn 1	Zn		No Al found in precipitate
	Ni 1	Ni		
	Co 1	Co	*	* Filtrate not analyzed
	Fe 1	Fe		
	Al 500			
6	Zn 1	Zn		No Cr found in precipitate
	Ni 1	Ni		† About 0.5 mg. Fe found
	Co 1	Co	*	* Filtrate not analyzed
	Fe 1	Fe†		
	Cr 500			
7	Zn 1	Zn		
	Ni 1	Ni		
	Co 1	Co		
	Fe 1	Fe		
	Mn 500	Mn*		* 5-6 mg. Mn found in precipitate

into the filtrate to test it for zinc. The sodium peroxide precipitate was dissolved in hydrochloric acid, the solution divided into equal portions and the cobaltinitrite test made for cobalt in one portion and the dimethylglyoxime test for nickel made on the other. Unless otherwise stated in the notes, the tests obtained indicated that no considerable fraction of the element had been lost in the separation.

The Quantitative Separation of the Elements of the Zinc and Aluminum Groups.—In order to ascertain the quantitative value of this method, especially when large amounts of each of the elements to be separated were present, the experiments collected in Table III were performed. The procedure was essentially that used in carrying out the qualitative experiments, except that varying amounts of ammonium oxalate and of the excess of hydrocarbonate were used; these are given in the third and fourth columns of the table. Other departures or variations are included in the column headed Remarks or in the Notes.

In each of these experiments 250 mg. of an element of the zinc group and 250 mg. of an element of the aluminum group were taken. The precipitate obtained was then analyzed to determine the amount of the soluble element which had been carried down; the results of these analyses are shown in the sixth column.

Methods of Analyzing the Precipitates.—As the amount of the aluminum group element found in the precipitate was in all cases small, these quantities were estimated by a comparison with a known quantity of that element after treating it by a similar process. When a negative test for one of these elements was obtained in a solution, the latter was then divided into equal portions and one milligram or less of the element being tested for added to one portion and the test then repeated. Care was taken always to ensure that any oxalate remaining in the sulfide precipitates was completely decomposed before applying the tests indicated below. The individual methods used are briefly outlined. The precipitates were usually dissolved in nitric acid containing potassium chlorate in order to destroy any oxalate present. Aluminum was precipitated from the acid solutions by very careful neutralization with ammonia. Iron, when present, was previously separated by two precipitations with sodium hydroxide. Blanks were made on the reagents used. Chromium was oxidized in the nitric acid solution by means of the potassium chlorate. This solution was neutralized with ammonia, made just acid with acetic acid and lead acetate added. Manganese was precipitated as dioxide by potassium chlorate or, more usually, the nitric acid solution treated with a large excess of sodium bismuthate.

The filtrates were tested for completeness of precipitation and the amount of the zinc group element found indicated under the column of remarks.

TABLE III

THE QUANTITATIVE SEPARATION OF THE ELEMENTS OF THE ZINC AND ALUMINUM GROUPS

Expt.	Elements taken (250 mg. of each)		Oxalate added (milli-moles)	Excess of NaHCO ₃ added, g.	Final volume, ml.	Found in precipitate, mg.	Remarks
1	Zn	Al	70	0 ¹	120	Al 1	Precipitation started in an acid solution
2	Zn	Al	30	Note 2	100	Al 5	Precipitate difficult to filter and wash
3	Zn	Al	70	1 ⁴	130	Al 0.4-0.6	See note 3
4	Zn	Cr	57	0	120	Cr 0	
5	Zn	Mn	30	0	100	Mn 2	
6	Zn	Mn	70	2	400	Mn 0.5	
7	Zn	Mn	70	1	130	Mn 1 ⁵	Note 3
8	Ni	Al	57	1	125	Al 0	Ppt. slightly colloidal
9	Ni	Al	70	1	130	Al 0.8-1	Note 3
10	Ni	Cr	70	1	100	Cr 0	
11	Ni	Cr	70	1	130	Cr 0.1-0.6	Note 3
12	Ni	Mn	35	0	70	Mn 1	Ppt. colloidal, coagulated by shaking
13	Ni	Mn	70	1	130	Mn 0-0.2	Note 3
14	Co	Al	30	0	100	Al 0	Precipitate coagulated rapidly
15	Co	Al	70	1	130	Al 1-2	Note 3
16	Co	Cr	70	0	90	Cr 0.1	
17	Co	Cr	70	1	130	Cr 0	Note 3
18	Co	Mn	30	0	80	Mn 0	
19	Co	Mn	70	1	130	Mn 0.2-0.5	Note 3
20	Fe ⁵	Al	70	1	100	Al 0.2	0.5 mg. Fe found in filtrate
21	Fe	Al	70	1	130	Al 1-2	Note 3
22	Fe ⁵	Cr	70	1	120	Cr 0	0.3 mg. Fe found in filtrate
23	Fe	Cr	70	1	130	Cr 0-0.2	Note 3. 0.1-0.2 mg. Fe in filtrate
24	Fe ⁵	Mn	70	1	100	Mn 2	No Fe found in filtrate
25	Fe	Mn	70	2	400	Mn 0	No Fe found in filtrate
26	Fe	Mn	70	1	130	Mn 0.3-0.4	Note 3. Filtrate stood 3 days; no MnS formed

NOTES

1. Where this value is zero the solution was made neutral to litmus with sodium hydrocarbonate, then tested during the precipitation and, if acid, again made just neutral by addition of sodium hydrocarbonate.

2. Two ml. of 6 *N* ammonium hydroxide was added in excess; no sodium hydrocarbonate.

3. Part of a group of experiments performed by a section of sophomore students in analytical chemistry. The procedure was provided in typed form and the separation carried out independently by the student. The sodium hydrocarbonate was added as a one formal solution; because of this the final volumes are somewhat uncertain. In most

cases the range in values for the amount of the aluminum group element found in the precipitate is that obtained from several experiments.

4. The solution was tested during precipitation, made neutral if acid, and a 1-g. excess of sodium hydrocarbonate added. This process was repeated until the solution remained neutral or, usually, slightly alkaline.

5. The iron was taken as ferric chloride and this reduced by hydrogen sulfide while the solution was slightly acid.

6. In an experiment in which the zinc sulfide precipitate was allowed to stand for three days before it was filtered 10 mg. of manganese was found in the precipitate.

Discussion.—An inspection of the data collected in Tables II and III shows that by this method of separation 1 mg. of any element of either group can be detected in the presence of even 500 mg. of any element of the other group. Also, by properly adjusting the conditions, less than 1 mg. of any element of either group will be carried into the other group even when large amounts of both are present.

The precipitates of the zinc group sulfides are usually quickly coagulated and much more readily filtered and washed than those obtained by the conventional ammonium sulfide precipitation, in fact, in most cases washing by decantation can be used. Experiment 2, Table III, shows that, even with oxalate present, if an excess of ammonium hydroxide is used, the zinc sulfide is difficult to handle. Iron, of the zinc group sulfides, shows the greatest tendency to pass into the filtrate. Unless a one-gram excess of the hydrocarbonate is present, this tendency is pronounced; with that excess the amount lost can be made negligible. The coagulation of the iron sulfide is slow and unless time is given for this the filtrate will appear dark colored. Experiments have shown that the original valence state of the iron has no apparent effect on the completeness of the precipitation. In Expts. 20, 22 and 24 the iron was reduced before neutralizing or adding oxalate, in Expts. 21, 22, 25 and 26 this treatment was omitted. Contrary to expectation manganese was not carried down in large amounts even when filtration of the zinc group sulfide was delayed or when the filtrate was allowed to stand for several days. This is probably due to the final concentration of hydrocarbonate being somewhat less than that indicated because of the formation of acid during precipitation of the zinc group sulfide. However, it is recommended that, where large amounts of manganese are probable, the sodium hydrocarbonate be limited to an excess of not more than 1 g. and the volume of the solution be increased to from 200–400 milliliters.

Summary

It has been found that zinc, nickel, cobalt and iron can be separated from aluminum, chromium and manganese by precipitation with hydrogen sulfide from a solution having a controlled excess of sodium hydro-

carbonate and sufficient oxalate to prevent the precipitation of the aluminum or chromium.

The behavior of these individual elements has been studied and the method is proposed for the qualitative separation of these elements into two groups, to be designated the Zinc Group and the Aluminum Group, respectively.

Experiments have shown that by this method 1 mg. of any element of one group can be separated from as much as 500 mg. of any element of the other group.

As a quantitative method it has been shown that 250 mg. of any element of the zinc group can be precipitated quantitatively from a solution containing 250 mg. of any element of the aluminum group and that less than 1 mg. of any element of the aluminum group will be carried out in the precipitate.

The sulfide precipitates obtained under these conditions are readily coagulated, filtered and washed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE MECHANISM OF HYDROLYSIS OF DIALKYLAMINOMETHYL ETHERS

BY T. D. STEWART AND WILLIAM E. BRADLEY

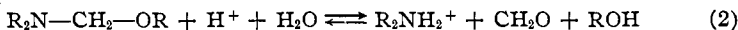
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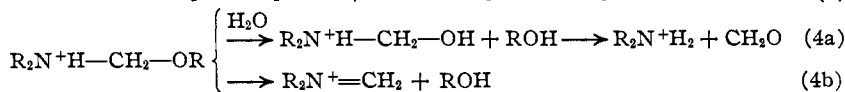
The aminomethyl ethers have been prepared by a modification of the method of McLeod and Robinson.¹



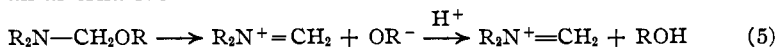
They are very rapidly hydrolyzed in dilute aqueous acid at room temperature, so that merely dissolving the ether in one equivalent or more of acid usually produces the reaction



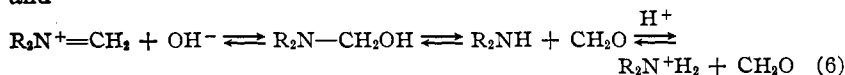
Possible successive steps in the hydrolysis reaction may be represented as



or as an alternative



and



¹ McLeod and Robinson, *J. Chem. Soc.*, 119, 1470 (1921).