STUDIES OF VARIOUS METHODS FOR THE SEPARATION OF THE COMMON ELEMENTS INTO GROUPS

THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN SOLUTIONS CONTAINING SODIUM DITHIONATE AND PERCHLORIC ACID

Thesis

by

Robert C. Barton

In partial fulfillment of the requirements
for the degree of Doctor of Philosophy

California Institute of Technology

Pasadena, California

1933

ABSTRACT

Studies of Various Methods for the Separation of the Common Elements into Groups

I. Data are presented for the separation of chromium, aluminum and iron from manganese, nickel, cobalt and zinc by the various modifications of the ammonia separation. Under the best possible conditions it was found that the separation of nickel, cobalt and zinc from chromium and aluminum was unsatisfactory for quantitative work although the Ardagh modification of the method improved the aluminum separations.

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

III. It has been found that zinc, cobalt, nickel and iron (the Zinc Group) can be separated from aluminum, chromium and manganese (the Aluminum Group) by precipitation with hydrogen sulfide from a solution having a controlled excess of sodium hydrocarbonate and sufficient oxalate to prevent the precipitation of aluminum and chromium. The separations are very satisfactory quantitatively.

The Activity Coefficients of Hydrochloric Acid in Solutions Containing Sodium Dithionate and Perchloric Acid.

The effects of added sodium dithionate and added perchloric acid upon the activity coefficients of hydrochloric acid in aqueous solution were determined at 25°C up to an ionic strength somewhat greater than unity.

[Reprint from the Journal of the American Chemical Society, 54, 2219 (1932).]

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 304]

STUDIES OF VARIOUS METHODS FOR THE SEPARATION OF THE COMMON ELEMENTS INTO GROUPS.

I. THE PRECIPITATION BY AMMONIUM HYDROXIDE

BY ERNEST H. SWIFT AND R. C. BARTON

RECEIVED JANUARY 2, 1932 PUBLISHED JUNE 6, 1932

Introduction

During the course of an attempt to develop a system of qualitative analysis for the so-called common elements which would provide more quantitative information than that usually obtained, it became one of the first problems to examine the methods commonly used for the qualitative separation of these elements into groups. The extensive investigations of Noyes and Bray and their co-workers[1,2,3] have furnished much information as to the qualitative value of many of these separations, with special reference to the detection of very small amounts of one element in the presence of large amounts of the other, but very little information with respect to the completeness of the separation when each element is present in moderate or large amounts. Although these same separations are used in quantitative methods, surprisingly little systematic information of this nature seems to be collected in texts or reference works; while that in the original literature is widely scattered, gathered under such varying conditions as to be difficult to correlate, and apparently quite incomplete. Therefore it has seemed worth while to present the results of these studies in this series of papers.

The Precipitation by Ammonium Hydroxide.—The precipitation by ammonium hydroxide can well be termed one of the classical analytical separations and, as is stated by Hillebrand and Lundell,[4] "One of the commonest operations the analyst has to perform ..., with the object either of weighing the precipitated compound or of effecting a joint separation of two or more metals from others." That it may be inadequate even as a qualitative separation in certain cases is shown by the experiments of Noyes and Bray[5] in which, with large amounts of aluminum or ferric iron (100–200 mg.) and with amounts of cobalt, zinc or nickel up to 20 mg., from 75 to 99% of the latter elements were found to be carried down

---

[1] Noyes and Bray, THIS JOURNAL, **29**, 137 (1907).

[2] Noyes, Bray and Spear, *ibid.*, **30**, 481 (1908).

[3] Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, **1927**.

[4] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, p. 69.

[5] Ref. 3, pp. 153–155.

in the precipitate. Noyes, Bray and Spear[6] also state that "a large quantity of zinc may be quantitatively precipitated by ammonium hydroxide when a larger proportion of chromium is present; and manganese will in any case be partially precipitated by that reagent owing to its oxidation by the air." In a careful study of the conditions necessary for securing complete precipitation of aluminum by ammonia, Blum[7] has found that these are attained by carefully neutralizing the solution, using methyl red (or rosolic acid) as indicator, and avoiding an excess of ammonia. Concerning its separation from other elements the following statement is made: "It is well recognized that the separation of aluminum from such elements as zinc, manganese, nickel and cobalt by means of ammonia is unsatisfactory since the alkalinity required for the resolution of their hydroxides is such as to cause appreciable solution of the aluminum hydroxide also. Moreover, it was found that even in solutions just alkaline to methyl red, oxidation and precipitation of the manganese occurred so rapidly as to preclude a quantitative separation."

However, Lundell and Knowles[8] in an extensive series of experiments, in which the precipitations were carried out according to the procedure developed by Blum,[7] show that moderate amounts of iron and aluminum can be separated from manganese and nickel quite satisfactorily; under the same conditions considerable amounts of cobalt, copper and zinc were found in the precipitates. It was also found that an excess of ammonia, although apparently improving the separation of aluminum and iron from copper and zinc, made the separation of these two elements from manganese, nickel and cobalt less satisfactory. The striking experiments of Noyes and Bray, cited above, in which a relatively large excess of ammonia was present, seem to confirm this latter observation and to raise considerable question as to whether a more effective separation is obtained by having an excess of ammonia present. This would seem to depend upon whether the bivalent elements remain in solution due to the solubility of their hydroxides (as is most probable with manganese) or due to the formation of the soluble ammonia complexes, and, furthermore, to the relative tendency of these two molecular types to be carried down with the precipitate. The effect of the *P*H of the solution upon the adsorbing tendency of the precipitate has also to be considered. In spite of this uncertainty, the proper attention apparently has not been given, in qualitative procedures (or in quantitative methods where the complete precipitation of aluminum is not involved), to the effect of making a careful neutralization or of exactly adjusting the excess of ammonia. It will be shown in the experiments to be presented that the proper control of the excess of am-

---

[6] Ref. 2, p. 482.

[7] Blum, This Journal, **38**, 1291 (1916).

[8] Lundell and Knowles, *ibid.*, **45**, 676 (1923).

monia is a most important feature in the separations which have been included in the present investigation, and that many of these separations are quite inadequate even for crude qualitative separations unless the neutralization with ammonia is carefully performed.

This study has been restricted mainly to the elements iron, aluminum, chromium, manganese, nickel, cobalt and zinc; however, since in the qualitative analysis of the common elements, the ammonium hydroxide separation is likewise used to separate bismuth from copper and cadmium, a few experiments are shown to indicate the sharpness of these separations. The effect of phosphate has not been included in this paper. It has not seemed worth while to give separate references to all of the previous work dealing with each of the individual separations here studied. In most cases these can be found, with a brief discussion, in the reference work of Rüdisüle.[9]

Experimental Procedure

The separations were carried out according to three general procedures. The first of these, designated Procedure I, was designed to conform to usual qualitative technique, and, except where explained by notes, was as follows.

To a boiling solution containing the elements to be separated and 60 milli-equivalents of hydrochloric acid in a volume of 100–125 ml., 6 normal ammonium hydroxide was slowly added until red litmus paper just turned a distinct blue color. The mixture was then boiled for one to three minutes and filtered; it was kept hot during the filtration. The precipitate was washed with hot water until the washings were colorless or had no perceptible effect on red litmus.

Procedure II, conforming more closely to the procedure outlined by Blum, was as follows.

To a boiling solution, which contained 10 g. of ammonium chloride and 6–12 milli-equivalents of hydrochloric acid in a volume of approximately 250 ml., 6 normal ammonium hydroxide was added dropwise until a color change was noted using methyl red, or in a few cases rosolic acid, as the indicator. Where the color of the solution prevented the use of the internal indicator, litmus test papers were used and the ammonia added until the color of the litmus matched that obtained from a similar solution of ammonium chloride and hydrochloric acid to which ammonium hydroxide had been added until the methyl red (or rosolic acid) color transition occurred. Extreme care was taken in these neutralizations; if the color transition was over-run, the mixture was made acid and the process repeated. The mixture was boiled for one to two minutes and filtered; it was kept hot until the filtration was completed. To expedite filtering and washing two separate filters were used in most cases. The precipitate was washed with a hot 2% solution of ammonium chloride until the washings gave no appreciable precipitate when tested with ammonium sulfide solution.

Procedure II differs from Procedure I in that the solution was diluted to a larger volume, a larger quantity of ammonium chloride was present and extreme care was taken to avoid an excess of ammonium hydroxide.

---

[9] Rüdisüle, "Nachweis, Bestimmung und Trennung der chemischen Elemente," Max Drechsel, Bern.

In order to compare more exactly the effect of an excess of ammonium hydroxide the experiments labeled III were performed. These duplicated Procedure II except that after carefully neutralizing with ammonia an excess of 2 ml. of 6 normal solution was added.

In each of the experiments 250 milligrams of one of the elements listed in the first column of the table was precipitated from a solution which also contained 250 milligrams of one of the elements listed at the top of the four major columns. Observations and variations from the procedures outlined above are contained in the notes to the table. The precipitate was then analyzed in order to determine the amount of the soluble element carried down. Limitation of space has made it necessary to omit a detailed description of the methods used in analyzing these precipitates. In every case the precipitate was so treated as to separate the two elements—thus the ferric hydroxide precipitates were dissolved in hydrochloric acid, the concentration of the acid properly adjusted and the iron removed by repeated extraction with ether—or the element carried down was converted into a form in which it could be directly estimated; for example, the manganese in the aluminum precipitate was converted directly into manganese dioxide, or, when very small in amount, oxidized to permanganate. The methods used were checked by blanks and by confirmatory analyses of prepared mixtures. The results of these experiments, showing the amount of co-precipitation in each separation, have been collected in Table I. It is felt that significance should be attached to the general magnitude, rather than the exact value for any individual experiment, as it is impossible to duplicate exactly all the conditions, such as local concentration of the precipitant during precipitation, and as in many cases the results are apparently highly dependent upon such conditions.

TABLE I

THE SEPARATION OF CHROMIUM, ALUMINUM AND IRON FROM MANGANESE, NICKEL, COBALT AND ZINC BY PRECIPITATION WITH AMMONIA

In these experiments 250 mg. of one of the elements in the first column was precipitated from a solution containing 250 mg. of one of the elements listed at the top of the four major columns.

	Manganese				Nickel			
Element precipitated	Expt.	Procedure	Mn in ppt. mg.	Notes	Expt.	Procedure	Ni in ppt., mg.	Notes
Chromium	1	I	55	1	6	I	114	
	2	II	0.8		7	I	163	4
	3	II	0.4	2	8	I	150	5
	4	II	0.5	3	9	II	28	
	5	III	18	2	10	II	26–28	6
					11	III	35	
Aluminum	19	I	4.0		23	I	230	
	20	II	0.2		24	II	10	
	21	II	0.3		25	III	190	
	22	III	2.5					
Ferric iron	35	I	2.0		39	I	16	
	36	II	1.5		40	II	3–4	6
	37	II	0.8		41	III	8–10	6
	38	III	2.7		48	III	13	10,11
					49		13	10,11

TABLE I (*Concluded*)

	Cobalt				Zinc			
Element precipitated	Expt.	Procedure	Co in ppt., mb.	Notes	Expt.	Procedure	Zn in ppt., mg.	Notes
Chromium	12	I	160		16	I	212	
	13	II	34		17	II	41	
	14	II	61	7	18	III	165	
	15	III	90					
Aluminum	26	I	230		31	I	214	
	27	I	216		32	II	75	
	28	II	8		33	III	121	
	29	III	166		34	II	68	9
	30	I, II	23	8				
Ferric iron	42	I	16		45	I	106	
	43	II	4		46	II	11	
	44	III	8		47	III	27	
					50	III	21	10
					51		19	10

NOTES TO TABLE I

1. The manganese in this precipitate was separated by precipitation as dioxide by addition of potassium chlorate to a nitric acid solution. The precipitate was washed free of chromate and chlorate and the manganese determined iodometrically.

2. The chromium hydroxide precipitate obtained in Expt. 3 required about 100 ml. of wash solution. However, the precipitate in Expt. 5 required 500 ml. The washings were tested for manganese by addition of ammonia and hydrogen peroxide.

3. In this neutralization a slight excess of ammonia was added, so 6 normal hydrochloric acid was added until the methyl red was distinctly pink and the neutralization repeated.

4. A slightly larger excess of ammonia was added in Expts. 7 and 8 than in 6.

5. Five grams of ammonium chloride was used in addition to that formed by neutralization of the hydrochloric acid.

6. The nickel was estimated by comparing with standards the precipitate produced by dimethylglyoxime in one-tenth the filtrate.

7. The solution was made just neutral to litmus without using a reference solution with an internal indicator. Probably slightly more ammonia was added than in Expt. 13.

8. The volume and other conditions were as in Procedure I. Neutralization was made and an excess of ammonia avoided as in Procedure II.

9. Only 160 mg. of zinc was taken.

10. In Expts. 49 and 51 an excess of 5 ml. of 15 normal ammonia was added; otherwise Expts. 48 and 49 and Expts. 50 and 51 were carried out in exact duplicate to note the effect of the larger excess of ammonia.

11. Expts. 48 and 49 were carried out in this Laboratory by Mr. Francis Hunter and Mr. Elvin Lien.

Discussion of the Data of Table I

An inspection of the data in Table I would seem to lead to two general conclusions: first, in about half of the separations studied the separation is quite unsatisfactory even under the most favorable conditions. Second, in every case studied the separation is more effective when an excess of ammonia is avoided and, in most cases, unless this excess is avoided the separation is so imperfect that little is gained by reprecipitations; thus, under the conditions studied, when an excess of ammonia is added, more than 50% of the nickel, cobalt or zinc is carried out by either chromium or aluminum. This would seem to indicate that the ammonia separation is more effectively carried out, at least in dilute solutions, as a process of selective hydrolysis and not as one depending on the formation of the soluble complex ammino ions. In support of this it is to be noted that manganese, where the tendency toward this complex formation is least, is much less co-precipitated than nickel, cobalt or zinc.

Also, the P_{H} values at which these divalent elements are precipitated from solution are given by Britton[10] as follows: zinc, 5.2; nickel, 6.7; cobalt, 6.8; and manganese, 8.5–8.8. It is seen that the co-precipitation in the experiments carried out by Procedure II in every case varies in amount in this same order—zinc, the least soluble hydroxide, showing the greatest tendency to be carried with the precipitate. The same order in general holds for the experiments by Procedures I and III, which is somewhat surprising, as, with an excess of ammonia present, it would be expected that the formation of the soluble ammonia complexes would be a more deciding factor; for the same reason it would have been predicted that the large excess of ammonia added in Expts. 49 and 51 would have decreased markedly the amount of co-precipitation; however, the difference is within the experimental variations. That the effect is due to an adsorption process and not to mechanical inclusion or local precipitation is indicated by the experiments of Ibbotson and Brearly[11] and of Noyes and Bray,[12] showing that when an ammoniacal solution of the bivalent element is added to a suspension of the freshly precipitated hydroxide, the effect approaches that obtained by precipitation in the presence of the bivalent element. That the complex ammonia compounds are not extensively carried down was shown by the fact that relatively little ammonia was found upon analyzing an aluminum precipitate, produced by Procedure III, which had co-precipitated with it about 200 mg. of nickel. Further studies are being made of certain of these separations in which the co-precipitation is pronounced in an attempt to ascertain the various factors affecting it and the mechanism of the phenomenon.

Specifically, in addition to confirming the results of Lundell and Knowles that, by proper methods of neutralization, a satisfactory separation of manganese from aluminum and from iron is obtained, it is shown that under these same conditions manganese can be separated from chromium. However, it is to be noted that the co-precipitation of manganese is in-

---

[10] Britton, "Hydrogen Ions," D. Van Nostrand Co., New York, 1929, p. 254, 278.

[11] Ibbotson and Brearly, *Chem. News*, **81**, 193 (1900).

[12] Ref. 3, p. 154.

creased much more by an excess of ammonia in the separation from chromium than it is in the separation from either aluminum or iron. The separations of nickel from aluminum and chromium show from 50 to 90% of this element brought down when an excess of ammonia is added, demonstrating the futility of reprecipitations; the same general behavior is obtained with these elements and cobalt. Even under the most favorable conditions these separations are hardly adequate for quantitative work. The separations of nickel and cobalt from iron, made from carefully neutralized solutions, show about 2% co-precipitation so that a reprecipitation would probably reduce this to satisfactory limits. The separation of zinc under these conditions is unsatisfactory regardless of methods of neutralization. It is to be noted that the co-precipitation in method I is usually greater than that in method III, showing the favorable effect of an increased volume with thereby a decrease in the concentration of the co-precipitated substance.

It is perhaps worthy of note that the procedure, almost universal in qualitative textbooks, which directs that a *slight excess* of ammonia be added to a relatively small volume of solution, produces conditions which are apparently the *least* favorable of those studied for the separations desired.

The Ardagh Method of Carrying out the Ammonia Separation.— Recognizing the inadequate nature of the conventional ammonia precipitation for the separation of iron (and aluminum) from zinc, Ardagh and his co-workers[13,14] have devised a procedure for carrying out the separation which employs radically different conditions from those existing in any of the procedures thus far described. In it the precipitation is made by the addition of a large excess of 15 N ammonium hydroxide to a very small volume of an acid solution which has been previously saturated with solid ammonium chloride. These conditions produce a more compact and granular precipitate than that usually formed and a satisfactory separation of zinc from iron or aluminum is obtained by a single precipitation. An extension of this method to other separations would seem desirable and, since no such data seemed available, such a study was made and the results are shown in Table II. The general procedure used was as follows. A hydrochloric acid solution of the elements to be separated was evaporated to a volume of 3 to 5 ml., cooled and 5 g. of solid ammonium chloride then intimately mixed with the solution. Following this 10 ml. of 15 N ammonium hydroxide was added, the resulting mixture thoroughly mixed with a stirring rod, 25 ml. of water added and the precipitate filtered, usually equally dividing it between two separate filters in order to facilitate washing. The precipitates were washed with a solution containing 5 g. of ammonium chloride and 5 ml. of 15 N ammonium hydroxide in a volume of 100 ml.

---

[13] Ardagh and Broughall, *Can. Chem. Met.*, **7**, 198 (1923).

[14] Ardagh and Bongard, *Ind. Eng. Chem.*, **16**, 297 (1924).

Variations from this procedure are explained in the notes accompanying the table. It should be mentioned that chromium cannot be precipitated under the conditions of this procedure as it remains to a large extent in solution due to the formation of complex ammines. Also from 2–5 milligrams of aluminum is dissolved and has to be recovered subsequently from the filtrate.

In these experiments 250 milligrams of one of the elements listed in the first column of the table was taken together with 250 milligrams of one of the elements listed at the top of the four major columns. Observations and variations from the outlined procedure are contained in the notes to the table.

TABLE II

THE SEPARATION OF ALUMINUM AND IRON FROM MANGANESE, NICKEL, COBALT AND ZINC BY THE ARDAGH METHOD OF PRECIPITATION WITH AMMONIA

In each experiment 250 mg. of one of the elements in the first column was taken with 250 mg. of one of the elements listed at the top of the four main columns

	Manganese			Nickel			Cobalt			Zinc		
Element precipitated	Expt.	Found in ppt. mg.	Notes	Expt.	Found in ppt., mg.	Notes	Expt.	Found in ppt., mg.	Notes	Expt.	Found in ppt., mg.	Notes
Aluminum	1	64	1	3	4	3	4	4	4	5	15	5, 8
	2	105	2							6	8	6, 8
										7	2	7, 8
											0–0.4	14
Iron	8	25		10	0.1–0.2		11	25	10	14	0.5	12
	9	8	9	16	0.7–0.9	13	12	5	10	15	0.6	13
							13	6	11		0.2–0.5	14

NOTES TO TABLE II

1. The precipitate was equally divided between two filters and each half required 150–200 ml. of wash solution; it darkened during the washing.
2. Only 5 cc. of 15 *N* ammonium hydroxide was used.
3. Found 5 mg. of aluminum in the filtrate.
4. Filtration and washing difficult; 200 ml. wash solution required.
5. Only 2 ml. of 15 *N* ammonium hydroxide was added and the mixture was diluted to 50 ml. before filtering. Less than 0.5 mg. of aluminum remained in the filtrate.
6. Only 3 ml. of ammonia added, mixture diluted to 25 ml. 1–2 mg. of aluminum found in filtrate.
7. Only 5 ml. ammonia added. 2–3 mg. of aluminum in filtrate.
8. In Expts. 5, 6, 7 only 125 mg. of aluminum was taken with 250 mg. of zinc.
9. Only 5 ml. of ammonia added.
10. In this experiment (No. 11) the original solution was evaporated to 3–4 ml. and this solidified upon cooling. Two ml. of 6 *N* hydrochloric acid was added to dissolve this residue. Upon adding the ammonium chloride this solution was absorbed and even after long maceration with a stirring rod the mixture did not seem homogeneous. In Expt. 12 the original solution was evaporated to 5 ml. and after adding the ammonium chloride, 6 *N* hydrochloric acid was added (2 cc.) until a homogeneous, thoroughly wet mixture was obtained.
11. A repetition of Expt. 12, except that the mixture was heated to 70–80° before filtering and the wash solution was also heated. The precipitate was more difficult to wash, requiring 500 ml. of wash solution.

12. 5 g. of ammonium nitrate was used instead of ammonium chloride.

13. A nitric acid solution was evaporated to 3–4 ml. and 8 g. of ammonium nitrate used instead of the ammonium chloride. Ammonium nitrate was substituted for ammonium chloride in the wash solution.

14. Values taken from experiments of Ardagh and Bongard[14] using about 200 mg. of iron and zinc.

Discussion of the Data of Table II

An inspection of the data of Table II, and a comparison with Table I, shows, as was to be expected, that the Ardagh method cannot be used for separations involving manganese, due to the oxidation of this element in the more alkaline solution. The separation of nickel from aluminum is improved and the separation of nickel from iron is so nearly perfect that only one precipitation would be required for most quantitative work. The separation of cobalt from aluminum is more complete than by any method of precipitation by ammonia in a dilute solution; although the separation of cobalt from iron is fairly satisfactory it is no more complete than that obtained by a careful neutralization. Where, as is the case in many qualitative systems, it is desired to separate iron from nickel, cobalt and zinc, the Ardagh method of precipitation offers decided advantages.

Attempts to reduce the amount of aluminum dissolved by decreasing the ammonia concentration caused, in the separation from zinc, an increase in the co-precipitation of that element (Expts. 5, 6, 7). This indicates that in this separation, contrary to those studied in Table I, the bivalent elements are held in solution mainly due to the formation of the ammonia complexes. That, in spite of the use of small volumes and more concentrated solutions, better separations are obtained by this method, is probably due to this more complete conversion of the bivalent elements into the ammonia complexes and, in addition, to the more granular and less hydrous nature of the precipitates obtained, these physical characteristics usually indicating a less effective adsorbing agent.[15] Experiments 14, 15 and 16 show that the substitution, in the cases studied, of an equivalent amount of ammonium nitrate for ammonium chloride has relatively little effect, indicating that the presence of chloride ion is not highly essential to the separation.

The Separation of Bismuth from Copper and Cadmium

In most systems of qualitative analysis this separation follows the detection and removal of lead as sulfate. In precipitating lead the solution is fumed with sulfuric acid, then cooled and diluted. To conform to these conditions the procedure used was as follows: to 250 mg. each of bismuth and of copper or cadmium (as the nitrates), was added 10 ml. of 6 *N* sulfuric acid and the volume made from 80–100 ml. There was then added

---

[15] Weiser, "The Hydrous Oxides," The McGraw-Hill Book Co., New York, 1926, p. 1.

6 *N* ammonia until in one case the solution was just neutral to litmus or, in the alternative case, there was 5 ml. of ammonia in excess. The precipitates were washed with 2% ammonium sulfate solution and then analyzed for the copper and cadmium present. In the separations in which the solution was made just neutral and an excess of ammonia was avoided, 150–180 mg. of copper and 2 mg. of cadmium were found in the bismuth precipitates; in the separations with the 5 ml. excess of ammonia added 0.5 mg. of copper and 2 mg. of cadmium were found. This indicates, as would be expected from the *P*H value at which copper precipitates, that the separation of copper from bismuth in a sulfate solution requires an excess of ammonia sufficient to form the complex ammine; on the other hand, the separation of cadmium, due to the greater solubility of the hydroxide, is equally effective with or without an excess of ammonia.

Summary

Data are presented for the separation of chromium, aluminum and iron from manganese, nickel, cobalt and zinc by various modifications of the ammonia separation.

It is shown that when working with the usual dilute solutions the separation is more effective when a careful neutralization is made using methyl red (or its equivalent) as indicator, and an excess of ammonia avoided. Under these conditions, with 250 mg. of each element present, the chromium precipitate carried out only 0.4–0.8 mg. of manganese, but 30–40 mg. of nickel, cobalt or zinc; the aluminum precipitate carried out only 0.2–0.3 mg. of manganese, but 8–10 mg. of nickel or cobalt and 75 mg. of zinc; the iron precipitate carried out 0.8–1.5 mg. of manganese, 3–4 mg. of cobalt or nickel and 11 mg. of zinc.

When an excess of ammonia is used the separation is so imperfect, regardless of the presence of a large amount of ammonium chloride, that in the majority of cases it is not recommended even for qualitative purposes.

When the precipitation is made by addition of concentrated ammonium hydroxide to a small volume (3–5 ml.) of a solution saturated with ammonium chloride, even with 250 mg. of each element present, less than a milligram of the soluble element was co-precipitated in separating iron from nickel or zinc, or aluminum from zinc, and 4–5 mg. was co-precipitated in separating iron from cobalt, or aluminum from nickel or cobalt. Under the conditions of the procedure aluminum dissolves to the extent of about 5 mg., and chromium is very soluble.

When separating bismuth from copper in a dilute sulfate solution an excess of ammonia is required; the separation from cadmium can be made either from a carefully neutralized solution or one containing an excess of ammonia.

PASADENA, CALIFORNIA

[Reprint from the Journal of the American Chemical Society, 54, 4155 (1932).]

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 321]

STUDIES OF VARIOUS METHODS FOR THE SEPARATION OF THE COMMON ELEMENTS INTO GROUPS. II. THE SEPARATION BY MEANS OF SODIUM HYDROXIDE AND SODIUM PEROXIDE

BY ERNEST H. SWIFT AND R. C. BARTON

RECEIVED JUNE 11, 1932 PUBLISHED NOVEMBER 5, 1932

Introduction.—As stated in the first paper of this series, the data here presented were collected during the course of an attempt to develop a system of qualitative analysis for the so-called common elements which would provide more quantitative information than that usually obtained.

The use of sodium hydroxide and sodium peroxide as a group reagent in a qualitative system seems to have been first suggested by Parr,[1] who used it to effect the separation of iron, manganese, nickel and cobalt from aluminum, chromium and zinc and it was later adopted by Noyes, Bray and Spear[2] in their system which included many of the less common elements. The process has also been used extensively in qualitative systems, and in quantitative methods for the separation of the individual elements of one of these groups from those of the other. Frequently in quantitative methods other oxidizing agents, such as bromine, chlorine or persulfate, are substituted for the peroxide but these are not as convenient as the peroxide or may introduce objectionable ions into the analysis.

Statements in the literature as to the effectiveness of these individual separations are somewhat incomplete and often not definite. Noyes, Bray and Spear state that: "The separation of the two groups by this process is entirely satisfactory, at any rate, from the standpoint of qualitative analysis, with the single exception that when 5 or 10 mg. of zinc are present this may be carried down completely when elements of the iron group (especially manganese) are present in large quantity." However, there appears to be a certain amount of distrust of the method which is perhaps explained by the statement of Hillebrand and Lundell:[3] "The use of sodium hydroxide for precipitations has not been in good repute among analysts because of the uncertain quality of the reagent and the slimy character of the solution and precipitate." It is explained, however, that the first objection is not as well founded today as in the past, that the difficulty in filtering about 5% solutions is not serious, and that: "In the hands of one of us (L.) the method has proved very satisfactory."

The confirmatory experiments and test analyses of Noyes, Bray and

---

[1] Parr, THIS JOURNAL, 19, 341 (1897).

[2] Noyes, Bray and Spear, *ibid.*, 30, 484 (1908).

[3] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., 1929, p. 76.

Spear give quite complete information as to the qualitative value of the separation, as they perform it, in the detection of small amounts of an element in the presence of even large amounts of others; however, very meager systematic data seem to be available showing the completeness of the individual separations when considerable amounts of each element are present. Such data have been collected and are presented in this paper.

This study has been restricted to the common elements which may be found in the ammonium sulfide precipitate and therefore includes only the separation of iron, manganese, nickel and cobalt from aluminum, chromium and zinc. For more general statements concerning certain of the individual separations, as well as for references to the original literature, one is referred to Hillebrand and Lundell[3] and to Rüdisüle.[4]

Experimental Procedure

The separations have been carried out according to two general procedures. The first of these, called Procedure I, conforms closely to that given by A. A. Noyes[5] and by Noyes and Bray,[6] and more nearly represents the usual qualitative technique. It was as follows.

To a solution of the elements to be separated, containing 1–2 ml. of 6 *N* hydrochloric acid and having a volume of 30–40 ml., was added 6 *N* sodium hydroxide until the solution was alkaline to litmus, and then 5 g. of sodium peroxide. The sodium peroxide was sprinkled in very gradually and the mixture kept cold during the addition. Then the mixture was boiled until the sodium peroxide was decomposed, diluted to 60 ml. and filtered through hardened filters; in order to facilitate washing, two separate filters were used if the precipitate was bulky. The precipitate was washed with hot water until the washings no longer turned red litmus blue.

In Procedure II certain modifications were used which are recommended as giving more quantitative separations. It was as follows.

To a solution of the elements to be separated, containing 1–2 ml. of 6 *N* hydrochloric acid and having a volume of 15–20 ml., 6 *N* sodium hydroxide was added dropwise until the first permanent turbidity was produced. To this was added 20 ml. of 3% hydrogen peroxide and the resulting solution poured dropwise into 100 ml. of 5% sodium hydroxide which was kept just boiling during this addition. The mixture was then cooled and kept cool during the slow addition of 5 g. of sodium peroxide. Finally the mixture was boiled until the sodium peroxide was decomposed and then filtered, two separate papers being used in most cases. Hardened filters were not necessary in filtering these solutions. The precipitate was washed with 50 ml. of hot 5% sodium hydroxide and then with a hot 1% solution until no test for the soluble element being separated was obtained.

The slightly acid solution containing the hydrogen peroxide was poured into the hot sodium hydroxide solution since there appears to be general agreement that a better

---

[4] Rüdisüle, "Nachweis, Bestimmung und Trennung der chemischen Elemente," Max Drechsel, Bern.

[5] Noyes, "Qualitative Chemical Analysis," The Macmillan Company, New York, 1922, 9th ed., p. 95.

[6] Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Company, New York, 1927, pp. 164, 168.

separation results from this order of mixing.[7] Qualitative experiments also indicated that a more rapid and complete oxidation of chromium was obtained when hydrogen peroxide was present in the acid solution; when sodium peroxide was added to an alkaline solution, as in Procedure I, or upon adding an acid solution without peroxide to a hot sodium hydroxide solution, a precipitate which oxidized slowly was obtained. The acid solution could be added to a cold sodium peroxide solution; however, the preparation of a solution of sodium peroxide, even when it is kept cold, results in excessive loss of peroxide due to its decomposition. Furthermore, the precipitate produced upon addition of the acid solution to the hot hydroxide seemed more readily handled than that formed by precipitating in the cold and then heating.

In most of the experiments 250 mg. of the element to be precipitated was taken with 250 mg. of one of the soluble elements. The precipitate was then analyzed in order to determine the amount of the soluble element carried down. The results of these experiments, showing the amount of the soluble element carried down in each case, have been collected in Table I which is shown below. Observations and variations from the procedure outlined above are contained in the notes to the table. For the reason stated in the first paper of this series,[8] it is felt that significance should be given to the general magnitude, rather than the exact value, obtained in any individual experiment.

Methods of Analyzing the Precipitates.—The general methods used in analyzing the precipitates are here described. Changes or modifications in individual experiments are given in the notes which follow Table I.

The precipitates were in all cases dissolved in hot hydrochloric acid, sodium sulfite or hydrogen peroxide being used to help dissolve the manganese and cobalt precipitates.

The aluminum was recovered from the solution of the manganese precipitates by carefully neutralizing the boiling solution with ammonium hydroxide, avoiding an excess. The amount of aluminum in the precipitate thus obtained was estimated by comparing it with standard precipitates prepared under strictly similar conditions. The chromium in the manganese precipitate was recovered from the reduced hydrochloric acid solution by careful neutralization with ammonium hydroxide. The chromium hydroxide precipitate was dissolved and treated with sodium peroxide; any manganese dioxide present was filtered out and the chromate in the filtrate determined iodometrically. Zinc was recovered from the hydrochloric acid solution by fuming it with sulfuric acid, carefully neutralizing it, adding the proper excess of sulfuric acid and precipitating the zinc as sulfide. The precipitate was washed and introduced into an excess of ferric sulfate solution. The ferrous iron thus produced was titrated with standard permanganate solution.

After dissolving the ferric hydroxide precipitates in 6 *N* hydrochloric acid, the iron was removed by extraction with ether. The elements remaining in the aqueous solution were then estimated as indicated above.

The aluminum was recovered from the solution of the cobalt precipitates by carefully neutralizing the boiling solution with ammonium hydroxide;

---

[7] Ref. 4, Vol. V, pp. 96, 900, 1105; Ref. 3, p. 77.

[8] THIS JOURNAL, 54, 2219 (1932).

the precipitate thus obtained was dissolved, reprecipitated and compared with standards. The chromium, after reduction, was precipitated with ammonium hydroxide; this precipitate was dissolved and treated with sodium peroxide to remove the co-precipitated cobalt and to oxidize the chromium; after filtering out the cobalt oxide, the chromium was determined iodometrically. The zinc was recovered by precipitation as sulfide from a sulfuric acid solution. This precipitate was dissolved and treated with sodium peroxide to remove the co-precipitated cobalt. The zinc was again precipitated as the sulfide and determined as indicated above.

The aluminum in the hydrochloric acid solution of the nickel precipitates was recovered by carefully neutralizing with ammonium hydroxide; the aluminum hydroxide precipitate thus obtained was treated with sodium hydroxide and potassium persulfate to remove the nickel carried down, a final precipitation of the aluminum with ammonium hydroxide made, and this precipitate compared with standards. The chromium and zinc were recovered by the methods used in analyzing the solution containing cobalt.

Table I

The Separation of Manganese, Iron, Cobalt and Nickel from Aluminum, Chromium and Zinc by Precipitation with Sodium Hydroxide and Peroxide

In these experiments 250 mg. of one of the elements in the first column was precipitated from a solution containing 250 mg. of one of the elements listed at the top of one of the three major columns.

Element precipitated 250 mg. taken	Aluminum, 250 mg. taken				Chromium, 250 mg. taken				Zinc, 250 mg. taken			
	Expt.	Method	Al found in ppt., mg.	Notes	Expt.	Method	Cr found in ppt., mg.	Notes	Expt.	Method	Zn found in ppt., mg.	Notes
Manganese	1	I	12–15	1, 2	3	I	50–70	3	29	I	65	6
	2	II	2–3		4	II	51	4, 5	5	II	60	6
					25	I	7	10				
Iron (ferric)	6	I	1–2	1, 2					9	I	103	7
	7	II	1–2		8	II	56		10	II	37	6
					24	I	37		32	II	47	
					24	I	0.2	10	33	II	46	
									34		67	11
									35		62	11
Cobalt	28	I	20–25		12	I	65–80	8	30	I	50	6
	11	II	12–15		13	I	65		16	II	88	6
					14	I	87	9				
					15	II	21					
					23	II	1	10				
Nickel	17	I	30–35		27	I	44		31	I	30	6
	18	II	30–40		19	II	42		21	II	25	
					22	II	0.5–1	10				

Notes to Table I

1. Only 125 mg. of aluminum was taken.
2. The aluminum was recovered from the precipitate by dissolving it in hydrochloric acid, repeating the sodium hydroxide–sodium peroxide treatment, acidifying this filtrate, making it just alkaline with ammonium hydroxide and comparing the aluminum hydroxide precipitate obtained with standards.
3. The chromium was recovered from the precipitate by dissolving it in hydro-

chloric acid, repeating the sodium hydroxide–sodium peroxide treatment, making this filtrate just acid with acetic acid and precipitating the chromate as lead chromate. The precipitate was matched with standards. Method uncertain due to retention of chromium in second precipitate and to uncertainty in matching the size of the precipitate of lead chromate.

4. The color of the solution indicated that the chromium was completely oxidized upon pouring the acid solution containing hydrogen peroxide into the sodium hydroxide.

5. Difficulty was had in washing the precipitate free of chromate.

6. Only 160 mg. of zinc was taken.

7. The zinc was estimated by precipitation as carbonate, dissolving this in an excess of standard acid and titrating back with standard base.

8. The chromium was estimated by repeating the sodium hydroxide–sodium peroxide treatment, precipitating the chromium in the second filtrate as lead chromate and matching the precipitate. See note 3.

9. The hydrochloric acid solution of the precipitate was evaporated, a large excess of 16 *N* nitric acid added, 4 g. of potassium chlorate slowly sprinkled in, and the solution boiled until the excess chlorate appeared to be decomposed. The solution was made alkaline with ammonium hydroxide, then just acid with acetic acid, and the chromate precipitated as lead chromate. This was filtered out, dissolved in hydrochloric acid and the chromate determined iodometrically.

10. The chromium was taken as potassium chromate and no hydrogen peroxide was added to the acid solution, otherwise a duplication of Expt. 19.

11. Duplicates of Expts. 32 and 33, except that the sodium hydroxide was added to the acid solution instead of the reverse order.

Discussion of the Data of Table I.—From the cases studied it would seem that, in general, the separations obtained by the two procedures are not strikingly different. To test the effectiveness of the method of adding the acid solution to the sodium hydroxide, Expts. 32–35 were carried out by Mr. Elvin Lien and Mr. James Radford. In all of these the conditions of Procedure II were duplicated, except that in Expts. 34 and 35 the 5% sodium hydroxide was added to the acid solution containing the hydrogen peroxide; this resulted in a definite increase in the zinc carried out. Where better separations are obtained by Procedure I, it seems probable that the higher concentration of sodium hydroxide at first obtained in that procedure is the deciding factor. It has been found in practice, however, that the results obtained in repeating the same separation by Procedure I vary more than do those by Procedure II.

More specifically, the separation of aluminum from manganese and iron can be made sufficiently complete for qualitative and for most quantitative work; with the amounts of each element here used, from 4 to 5% of the aluminum is left with the cobalt precipitate and from 12–14% with the nickel precipitate; this latter difficulty is generally recognized.[9,10]

The separation of chromium, beginning with chromic ion and using sodium peroxide as the oxidizing agent, is unsatisfactory in every case

---

[9] Ref. 4, Vol. V, p. 242.

[10] Ref. 3, pp. 77, 391.

regardless of method. That this is due to incomplete oxidation of the chromium by the peroxide is shown by Expts. 20–23, where, beginning with the chromium as chromate, satisfactory separations are obtained except in the case of manganese and there the co-precipitation is reduced from 20% to about 3%. We are indebted to Mr. Harrison Backus for the following experiments showing that only trivalent chromium is co-precipitated.

To 250 mg. of chromium and 250 mg. of nickel, as the chlorides, in 50 ml. of a solution containing 4 ml. of 6 *N* hydrochloric acid, was added 6 *N* sodium hydroxide until the first turbidity appeared, then 10 ml. of 3% hydrogen peroxide; this was slowly poured into a cold solution of 20 ml. of 6 *N* sodium hydroxide and 10 ml. of 3 *N* sodium carbonate to which had been added 1 g. of sodium peroxide. An additional gram of sodium peroxide was added during the mixing of the solution, then 3 g. more was slowly sprinkled in; finally, the mixture was boiled for three minutes after no more oxygen bubbles seemed to be evolved.

The precipitate was filtered out, washed thoroughly with hot water, dissolved in sulfuric acid and this solution made alkaline with ammonia; a precipitate of chromium hydroxide was obtained which was estimated to contain about 50 mg. of chromium. No test for chromate could be obtained in the solution. Further experiments showed that under the conditions of the above experiment chromium, when *alone*, was completely oxidized—the oxidation was slow in a cold solution, but proceeded rapidly when the mixture was heated. Also, it was found that when chromate was added to a nickel precipitate produced by sodium peroxide under the conditions of this experiment and this mixture then acidified with sulfuric acid, less than one milligram of the chromium was reduced, thus showing that the reduced chromium originally obtained could not have been due to peroxide held by the nickel precipitate. The adsorption of colloidal hydrous chromic oxide by precipitates of iron, manganese, cobalt and nickel frequently has been noted,[11] and it would be expected that the chromium thus held would be oxidized with difficulty. It is therefore recommended that chromium be oxidized to chromate in an acid solution before using the sodium hydroxide–sodium peroxide separation.

There is considerable evidence that alkaline solutions of chromate may be reduced by filter paper,[12,13,14] the effect apparently being dependent upon the quality of the paper, the temperature of the solution and the time of contact. To note the extent of this effect experiments were carried out by Mr. Backus in which solutions containing 250 mg. of chromium as chromate in 15 ml. of 4 *N* sodium hydroxide were heated to boiling and then filtered through four different types of paper filters—two qualitative papers of different price, a quantitative paper and a hardened paper. The solutions were kept hot and the rate of flow restricted so that the filtrations required from 6 to 10 minutes. There was no apparent color change of the solutions on the filters or in the filtrates. The filtrates were then acidified with sulfuric acid. There was produced in the filtrate from the cheaper qualitative paper a considerable precipitate of what appeared to be paper pulp; the filtrate from the other qualitative paper became slightly cloudy, while the other filtrates remained quite clear. The acid solutions were filtered and then made just alkaline with ammonium hydroxide. None of the solutions produced an observable precipitate. This indicates that the reduction of an alkaline chromate

---

[11] Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, p. 90.

[12] Jervis, *Chem. News*, **77**, 133 (1898).

[13] Allison, *ibid.*, **96**, 1 (1907).

[14] Mellor, "A Treatise on Quantitative Inorganic Analysis," Griffin, London, p. 477.

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.

Pasadena, California

[Reprint from the Journal of the American Chemical Society, 54, 4161 (1932).]

[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

BY ERNEST H. SWIFT, R. C. BARTON AND H. S. BACKUS

RECEIVED JUNE 11, 1932   PUBLISHED NOVEMBER 5, 1932

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. Laird[2] 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 $^{\equiv}M(C_2O_4)_3$ are formed with aluminum[4] and chromium[5] (as well as with ferric iron),[6] and ions, apparently somewhat less stable, of the type $^{=}M(C_2O_4)_2$ are formed with manganese,[7] zinc,[8] nickel[9] 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. Carnot[11] 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. Laird[2] 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. Herzel, 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, Commentations Phys.-Math.*, **4**, 1–9 (1927).

[5] Werner, *Ber.*, **45**, 865 (1912).

[6] Rieger, *Z. Electrochem.*, **7**, 871 (1901); Shäfer, *Z. anorg. Chem.*, **45**, 293 (1905); Scholz, *Wein. Monatsh.*, **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_2S 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_2S for 15 min. longer
4c	500	3*	120	10*	60–80	250	* 1 g. $NaHCO_3$ added to solution from 4b; treated with H_2S 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_2S 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_2S Treatment Time, min.	H_2S Treatment 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_2S. 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_2S
				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_2S 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 Glixelli[12] and of Kolthoff and Pearson[13] 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
		Precipitate	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_2S in slightly acid solution
	Al 1		Al	
	Cr 1		Cr	† 0.1 mg. Fe found in filtrate
	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 (millimoles)	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[6]	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.

PASADENA, CALIFORNIA

THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN AQUEOUS SOLUTIONS CONTAINING PERCHLORIC ACID

THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN AQUEOUS SOLUTIONS CONTAINING PERCHLORIC ACID

The effect of added salts upon the activity of hydrochloric acid has been studied by a number of investigators.[1] All of these except Bates and Urmston[1d] and Murdoch[1e] have used added chlorides. In the present investigation the influence of perchloric acid was studied, that is, the effect of hydrogen ion was determined. This electrolyte is among the relatively few (except chlorides) which are suitable for this purpose.

The electromotive forces of cells of the type

$$H_2, HCl(m_1) + salt\ (m_2), \underline{AgCl} + \underline{Ag}$$

were determined at 25°. Except where noted the experimental procedures were similar to those of Bates and Urmston.[1d]

The perchloric acid solutions were prepared from the 60 percent C.P. product of the G.Frederick Smith Corporation. It had been redistilled in vacuo and was stated to contain not more than 0.004% non-volatile matter. The acid gave no test for chlorides, sulphates or lower oxy-acids.

All mixtures were made up by weight from stock solutions. All concentrations are expressed as mols per 1000 grams of water.

That dissolved aif has an effect upon the potential of the calomel electrode in acid solution due to a reaction between mercury, chloride ion, hydrogen ion, and oxygen, has been clearly demonstrated by Randall and Young.[2] The similar effect on the silver-silver chloride electrode is less serious. Guntelberg[1b] found some influence and removed oxygen from his solutions by means of nitrogen. Randall and Young, however, discovered no measurable affect upon silver-silver chloride spiral* electrodes in 0.1 M hydrochloric acid.

The change in the potential of the silver-silver chloride electrode due to the presence of oxygen is associated with the removal of chloride ion from the solution in immediate contact with the electrode, and is proportional to the fractional change in the activity of the chloride ion. Hence, other factors remaining the same, it is especially noticeable at low chloride concentrations. The removal of the chloride is facilitated by high hydrogen ion concentrations, and therefore increases with increasing acid concentration. Thus with solutions 0.01 M in hydrochloric acid and 0.09 M in perchloric acid, a decrease of about 1 millivolt was observed when oxygen-free solution was substituted for one which had been in equilibrium with air. With solutions in which the chloride content was 0.1 M or greater, the effect was always less than 0.1 millivolt. Hence for those solutions in which the chloride concentration was 0.1 M or less, the Linhart type of cell, in which the whole solution is saturated with hydrogen, was employed. Hydrogen was bubbled thru the cell for 24 hours before introducing the silver-silver chloride electrodes.

Further evidence that a reaction occurs between silver and hydrochloric acid in the presence of air was obtained by shaking a piece of bright silver wire with 0.5 M hydrochloric acid for twenty-four hours. At the end of that time the surface of the metal was covered with a characteristic coating of silver chloride which darkened upon exposure to light.

---

*Spiral electrodes may offer less silver surface and hence less opportunity for oxidation than do electrodes employing electrolytic silver crystals. The latter were used by Güntelberg and in this investigation.

EXPERIMENTAL RESULTS

The measured values of the electromotive forces at 25° and the activity coefficients are given in Table I.

TABLE I

Electromotive Forces and Activity Coefficients of Hydrochloric Acid

HCl	$HClO_4$	E.M.F.	Activity Coefficient
0.02498	0.02498	0.40304	0.837
.04821	.04821	.37140	.802
.1493	.1493	.31631	.758
.2570	.2570	.28849	.756
.3732	.3732	.26741	.758
.4961	.4961	.25059	.819
.02143	.02730	.42084	.841
.02445	.07337	.38849	.802
.09885	.2995	.31855	.765
.1881	.5644	.28420	.793
.2482	.7447	.26771	.829
.00988	.08985	.41072	.806
.04005	.3604	.34159	.771
.07087	.6378	.31116	.790
.09994	.8995	.29060	.834

The activity coefficients of hydrochloric acid α were calculated from the equation:

$$E - E^\circ = -\frac{RT}{F}\ln(m_1 + m_2)\, m_1\alpha^2.$$

Here m_1 and m_2 are the molal concentrations of the hydrochloric and perchloric acids respectively; E is the measured electromotive force of the cell containing both acids; E° is the molal electromotive force for the hydrogen silver-silver chloride cell. Here it is taken as 0.2221 volt.*

In Table II the data is shown interpolated to round values of hydrochloric acid and of added electrolyte.

TABLE II

Activity Coefficients of Hydrochloric Acid in Presence of Added Salts

Ionic Strength	Added $HClO_4$ Ratio $HCl:HClO_4$ 1:1	 1:3	 1:9
0.1	0.800	0.804	0.908
0.2	.769	.773	.780
0.5	.761	.767	.773
0.7	.779	.787	.792
1.0	.820	.828	.834

---

*Randall and Young (loc.cit), Carmody (J.Am.Chem.Soc., 542 188 (1932)) has recently arrived at the value 0.2223. Since the values used for the activity coefficients of pure hydrochloric acid are those of Randaly and Young, their values of E° is employed. The effect of any uncertainty in the values of these investigators is to change all activity coefficients by a constant factor.

DISCUSSION

In general, the results of this and similar investigations must, for the present at any rate, be considered chiefly from the empirical standpoint. On account of the physical complexity of the problem[3] and of mathematical difficulties[4] the treatment of pure electrolytes is, except for very dilute solutions, incomplete and the situation is more complicated in the case of mixtures. However, brief reference will be made to certain relations between the results of this and of other investigators.

In many mixtures of constant ionic strength μ, the activity coefficient α of hydrochloric acid has been found to be related to the concentration m of the acid in the mixture and to the activity coefficient α_0 of pure hydrochloric acid at the same ionic strengty by the equation (Ref. 1a)

$$\log \alpha = \log \alpha_0 + k(\mu - m)$$

In Figure 1 are plotted values of $\log \alpha$ against those of m at various ionic strengths for sodium dithionate (Ref. 1e) and perchloric acid mixtures. The above equation demands a linear relation. It will be seen that this relation is closely followed by the dithionate mixtures and is approximately obeyed by the perchloric acid mixtures. The values for the latter mixtures, particularly in dilute solutions, are, however, subject to somewhat greater uncertainty so that for both added electrolytes the above equation possibly holds with the experimental error.

This equation has been found to hold for dilute mixtures containing only univalent ions. The results of Randall and Breckenridge (Ref. 1c) show that it is not followed by mixtures containing

barium chloride or lanthanum chloride, but that the similar relation in which m, the concentration of the hydrogen ion constituent, is replaced by the geometric mean molality of the hydrogen and chloride ion constituents does hold. As these authors state, they give no derivation for this rule. Their relation does not hold for the data here presented for perchloric acid.

The comparative effects of increasing amounts of various salts upon the activity coefficient of the acid, whose concentration is maintained constant at 0.1 M, is plotted against the ionic strength for the added electrolytes lithium chloride, sodium chloride, potassium chloride, sodium perchlorate, barium chloride, sodium dithionate and perchloric acid in Figure 2. The figure shows that, as is to be expected, the minimum value for the activity coefficient is shifted most strongly to higher ionic strengths by those added salts which cause the greatest decrease in its value.

Of these added salts the activity coefficients of lithium chloride, sodium chloride, potassium chloride and barium chloride are known.[5] At a given ionic strength their activity coefficients decrease in the above order. Figure 2 shows that the effects of these salts on hydrochloric acid is in the same order. There is, however, no quantitative relation between the two sets of results. The comparative effects of sodium chloride and potassium chloride are somewhat anomalous since the activity coefficients of potassium chloride in its own pure solutions are but very slightly less than those of sodium chloride, while the activity coefficient of hydrochloric acid in the presence of the former is much less than in the presence of sodium chloride.

For those cases in which the activity coefficients of the salts in their own pure solutions are known, they are less, at the same ionic strength, than are those of hydrochloric acid in the mixture. From this it follows that the hydrogen ion has under certain conditions an unusually large tendency to escape from the solution. Thus, from the closely agreeing data of Harned and of Guntelberg there may be found by extrapolation the activity product $\alpha_H \alpha_{Cl}$ in the solution 0.1 <u>f</u> NaCl + 0.0 <u>f</u> HCl. Taking the activity coefficient of 0.1 <u>f</u> HCl as 0.796 (Ref. 2) this product in 0.1 <u>f</u> NaCl is $(0.789)^2$. In this same solution the product $\alpha_{Na} \alpha_{Cl}$ has the value[6] $(0.778)^2$. Hence $\alpha_H / \alpha_{Na} = 1.03$* in 0.1 <u>f</u> NaCl. That is, the hydrogen ion constituent has a greater tendency to be "salted out" from 0.1 <u>f</u> NaCl than has the sodium ion constituent. This difference is associated with the fact that the electrical forces acting upon these two ions are not the same, tho in both cases they are chiefly due to surrounding chloride ions. Thus the mean distances of the chloride ions will be different, for there is involved the diameters of the hydrogen and sodium ions, and the dielectric constant of the medium in their immediate neighborhood. In addition different proportions of these two ion-constituents may exist as free ions. The fact that the hydrogen ion has a relatively large activity coefficient may be related to its simple structure. It is less deformable and less polarizable than other ions. The effect is to exert a greater repulsive force and the ion tends to escape from the solution.

---

*Due chiefly to uncertainties in the values for pure HCl and pure NaCl solutions this figure may be about one percent in error.

SUMMARY

The effect of various amounts of added perchloric acid upon the activity coefficients of hydrochloric acid in aqueous solution were determined at 25° up to an ionic strength somewhat greater than unity.

The effect of perchloric acid, which is of a type not heretofore tested, is qualitatively the same as those of added chlorides of the alkali and alkaline earth elements. Thus, when added to a dilute solution of hydrochloric acid it causes the activity coefficient at first to decrease and then to increase with increasing ionic strength. The addition of perchloric acid increases the activity coefficient more than does that of any other electrolyte. In fact, the activity coefficient in these mixtures is greater than is that of pure hydrochloric acid at the same ionic strength.

The equation which has been found to hold for the effect of certain other electrolytes upon hydrochloric acid, namely $\log \alpha = \log \alpha_0 + k(\mu - m)$ is closely followed by mixtures containing perchloric acid.

REFERENCES

1. a. Harned, J.Am.Chem.Soc., 38, 1988 (1916); 42, 1808 (1920); 48, 326 (1926).
   b. Güntelberg, Zeit.physik.Chem., 123, 199 (1926).
   c. Randall and Breckenridge, J.Am.Chem.Soc., 49, 1435 (1927).
   d. Bates and Urmston, J.Am.Chem.Soc., (1933).
   e. Murdoch, Ph.D. Thesis, Calif.Inst.Tech. 1932.

2. Randall and Young, J.Am.Chem.Soc., 50, 989 (1928).

3. Bjerrum, Trans.Faraday Soc., 23, 445 (1927).

4. Gronwall, LaMer and Sandved, Physik.Zeit., 29, 350 (1928).

5. Lewis and Randall, "Thermodynamics" McGraw-Hill Book Co. N.Y. 1923 page 362.

6. Scatchard, J.Am.Chem.Soc., 47, 648 (1926).

ACKNOWLEDGMENT

I wish to acknowledge my indebtedness to Professor Ernest H. Swift and to Professor Stuart J. Bates and to thank them for their helpful advice and criticism during the course of these investigations.