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A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.[1]

PART III: ANALYSIS OF THE ALUMINUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM AND THALLIUM.

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Introduction.

This article is a continuation of a preceding one which appeared in an earlier number of this Journal in which were presented the first two parts of this system of qualitative analysis, dealing respectively with the preparation of the solution, and the analysis of the silver, copper, and tin groups.[2] For the purposes of this investigation, for the general considerations underlying it, and for various conventional matters relating to its presentation, the reader is referred to the introduction to the preceding paper.

Although the final form of the scheme of analysis of the groups here considered has been worked out during the past year by the authors of this article, much of the preliminary experimental work, especially that relating to the rarer metals, was carried on by others in this laboratory. It is unfortunately, scarcely practicable to indicate in just what respects each of these investigators has contributed to the final result; but we wish to express in a general way our great indebtedness to Messrs. Howard I. Wood, Bart E. Schlesinger and Charles Field, 3rd, for the assistance which their work has been to us.

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[1] Copyright, 1908, by Arthur A. Noyes.

[2] THIS JOURNAL, 29, 137 (1907).

The present publication deals with the analysis of the precipitate produced by ammonium hydroxide and sulphide in the filtrate from the hydrogen sulphide precipitate. In addition to the seven common elements (nickel, cobalt, iron, manganese, zinc, chromium and aluminum) considered in almost all schemes of qualitative analysis, we have included six of the especially important rarer elements, namely, beryllium, uranium, vanadium, thallium, titanium and zirconium. The portions of the procedure and of the notes referring to these rarer elements are, however, marked with asterisks, so that they may be readily omitted by any one interested only in the common elements.

The general features of our scheme for the analysis of this solution will be most readily comprehended by an examination of the tabular outline presented in Tables VII to IX. The considerations which have led to the adoption of this procedure will be discussed in the next chapter entitled "General Discussion," and the detailed process and the explanations of it will be presented in the following one entitled "Procedure and Notes." Later chapters, as in the preceding publication, will be devoted to the "Test Analyses and to Confirmatory Experiments and References."

General Discussion.

(1) With respect to the original precipitation of these elements, schemes of qualitative analysis differ as to whether ammonium hydroxide and ammonium sulphide be used successively with a filtration between, or whether they be added together so that all the elements are contained in a single precipitate. The former of these methods has the serious disadvantage that the separation with ammonium hydroxide of the trivalent elements, aluminum, chromium and ferric iron, from the bivalent elements, nickel, cobalt, manganese and zinc, while satisfactory enough when certain combinations of these elements are present is not so for other combinations. Thus even 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 to the manganic state, and it will be completely precipitated when phosphate is present in the solution. It is therefore necessary to provide for the detection of zinc and manganese both in the hydroxide and in the sulphide precipitate; and thus the scheme is complicated rather than simplified by precipitating separately with these reagents.

We have therefore adopted the plan of a single precipitation by simultaneous addition of both reagents, provision being made, however, for observing the effect of the addition of ammonium hydroxide alone for the sake of the indications which it may furnish. If care be taken to avoid an unnecessary excess of both the hydroxide and sulphide, all the elements in question are completely precipitated by these reagents even in moderately dilute solution, with the exception of a little of the nickel and a variable proportion of the vanadium. The nickel can be removed from the filtrate by boiling. Even a large quantity of vanadium remains completely in solution when it is present alone; but on the other hand it may be almost completely precipitated, probably as a hypovanadate or vanadate, when certain other elements of these groups are present. Many experiments were made in this laboratory by Mr. Charles Field, 3rd, to devise a practical method of reducing vanadium to a vanadous salt (corresponding to the oxide V_2O_3), in which state it is completely precipitated by ammonium hydroxide. In accordance with the results of Gooch and Curtis[1] hydriodic acid (best in the form of a mixture of ammonium iodide and hydrochloric acid) was found to be the only available agent, but even with the aid of this reagent reduction and precipitation were never quite complete and sometimes did not take place at all. For this reason it was not considered worth while to use this reagent, especially since the vanadium can be removed from the ammonium sulphide filtrate by acidifying, adding ferric chloride and making alkaline with ammonia.

(2) The ammonium sulphide precipitate in all the schemes of analysis known to us is first treated with cold dilute hydrochloric acid, in order to separate nickel and cobalt from the other elements. In spite of the general use of this process, we have become convinced that it does not fulfil the requirements of exact qualitative analysis; for not only is it true, as is generally known, that a considerable quantity of nickel and cobalt dissolves in a mixture of 1 volume of HCl (1.12) with 5 volumes of water when there is a large residue containing these elements, but our experiments have shown that a moderate quantity of either of them (up to at least 5 mg.) may *completely* dissolve and thus escape detection when it was originally disseminated through a large precipitate of iron sulphide. We have therefore eliminated this treatment as a method of separation; and, after adding hydrochloric acid at first to decompose such of the sulphides as it will act upon and to get an indication as to the presence of much nickel or cobalt, nitric acid is added, so as to bring all the elements into a single solution. Incidentally it may be mentioned that our experiments support the view that the fact that nickel and cobalt sulphides, though not precipitated by hydrogen sulphide from a slightly acid solution, yet dissolve difficultly in a much stronger acid, is due to an abnormally slow rate of solution of these sulphides, which are in fact relatively soluble substances, at least in the freshly precipitated state. For these experiments have shown that nearly all of a

[1] *Am. J. Sci.* (4), 17, 45 (1904).

portion of precipitated nickel sulphide dissolves when treated with successive portions of cold dilute HCl (1 volume HCl (1.12) with 5 volumes of water) even when the acid is kept saturated with hydrogen sulphide, and that solution continues to take place even after considerable nickel (30 mg. in 30 cc.) has passed into solution. When, therefore, the surface exposed to the acid is greatly increased, either, by the residue being a large one or by a small residue being left in a finely divided state by the dissolving out of iron sulphide, a considerable quantity of nickel and cobalt passes into solution in a comparatively short time. It is interesting to note that the reverse reaction, the precipitation of nickel sulphide by hydrogen sulphide in acid solution, also takes place very slowly, for Baubigny[1] has observed that in the presence of acetic acid, or of very small amounts of sulphuric or hydrochloric acids, the precipitation is a slow but continuous process.

(3) Having now all the elements together in solution, the next step in our process is to divide them into two main groups by the addition of sodium hydroxide and peroxide, followed by subsequent boiling. This method has been previously applied by other authors to the separation of certain of the common elements, but not, we believe, as a general means of subdivision. These reagents cause the complete precipitation of iron, nickel, cobalt and thallium, as hydroxides of the trivalent form, and of manganese, titanium and zirconium as hydroxides of the quadrivalent form. We shall designate all these elements so precipitated as the "iron group." All the remaining elements, namely, aluminum, beryllium, zinc, chromium, uranium and vanadium, remain in solution in the form of sodium salts of the corresponding acids, namely, as aluminate, zincate, chromate, peruranate and vanadate. We shall designate all these elements so dissolved as the "aluminum group." 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 only 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. This makes it necessary to provide for the detection of zinc in the analysis of the precipitate when it is large, but this is not attended with special difficulty. The use of sodium peroxide has the distinct advantage over that of sodium hydroxide alone, that chromium, uranium and vanadium are taken completely into solution whereby not only a division of these elements between the precipitate and filtrate is avoided, but also the carrying down of zinc into the precipitate is made less common and less considerable.

(4) Since, owing to the possible presence of phosphate, oxalate, or

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[1] Baubigny, *Compt. rend.*, 94, 963, 1183, 1251, 1417, 1473, and 1715 (1882), and 95, 35 (1882).

hypovanadate in the original solution, the alkaline-earth elements may be precipitated by ammonium hydroxide and sulphide, sodium carbonate is added with the hydroxide and peroxide, in order to ensure the complete precipitation of these elements (more especially barium) with the iron group. The presence of phosphate and carbonate does not affect at all the separation of the elements of the aluminum and iron groups from each other.

(5) The separation of the elements of the aluminum group from each other is very simple when only the common elements, chromium, aluminum and zinc, are to be provided for, and the process recommended below for this case offers no original features. It consists in precipitating the aluminum hydroxide from the solution with ammonium hydroxide after acidifying with nitric acid, the chromate in the filtrate with barium chloride after acidifying with acetic acid, and the zinc with hydrogen sulphide in the filtrate from the barium chromate.

(6) The presence of beryllium does not involve any complication, since it goes with the aluminum in the process just referred to, and can be separated from it as described below. When, however, uranium and vanadium are to be provided for, this process is entirely inadequate, for upon the addition of ammonium hydroxide after acidifying, vanadium divides between the filtrate and precipitate wherever uranium is present, owing to the insolubility of uranyl vanadate; uranium itself will divide owing to the presence of H_2O_2 formed on acidifying the sodium peruranate solution; and vanadium, when present in large amount, again divides upon the addition of barium chloride to the acetic acid solution, owing to the slight solubility of barium vanadate; finally vanadium interferes with the test for zinc with H_2S in acetic acid solution, since a precipitate of sulphur is always formed and sometimes one of black vanadium sulphide. Moreover, the uranium precipitate obtained with ammonium hydroxide will in general be mixed with aluminum, beryllium and vanadium, so that the difficult part of the separation still remains to be accomplished. After much experimenting, guided by the conception that under proper conditions of alkalinity it might be possible to separate the more basic elements, zinc, aluminum and beryllium, from those present as constituents of acid radicals, chromium, uranium and vanadium, it was finally found that this could be accomplished in a hot solution of sodium hydrogen carbonate, provided care be taken to prevent loss of carbon dioxide by heating the solution in an open vessel only to 90°, or better in a closed bottle to 100°. Under these conditions the separation is a fairly satisfactory one. A small amount of uranium may, however, be carried down almost completely when a large amount of aluminum or beryllium is present, making it necessary to test for uranium in the pre-

cipitate. Moreover, when uranium and vanadium are simultaneously present, each in large quantity (about 100 mg.), some uranyl vanadate precipitates, but a large quantity of both elements remains in the solution, so that their detection is not interfered with.

(7) The separation of the zinc from the aluminum and beryllium in the precipitate is readily effected by dissolving it in hydrochloric acid and adding a small excess of ammonium hydroxide. For the separation of the aluminum and beryllium from each other we studied what seemed to be the two most promising methods mentioned in the literature. The first of these was that described by Parsons and Barnes,[1] which consists in boiling for a short time a solution of the two elements to which enough sodium hydrogen carbonate is added to make a 10 per cent. solution, whereby aluminum is precipitated and beryllium dissolved. We found, however, that though this method is satisfactory for the detection of beryllium when a moderate amount of aluminum is present, yet with a large quantity of aluminum (say 100-500 mg.) 2-5 mg. of beryllium are almost completely retained in the precipitate, which may cause it to escape detection, and which at any rate leads to an incorrect estimate of its quantity. The second method investigated was that proposed by Havens[2] which consists in saturating a solution of the chlorides of the two elements in a mixture of ether and strong hydrochloric acid with hydrogen chloride gas, whereby aluminum is precipitated and beryllium remains in solution. It was found that this method gives entirely satisfactory results; even 0.5 mg. of aluminum is precipitated, as $AlCl_3.6H_2O$. provided care be taken to use a sufficient proportion of ether and to saturate completely with the gas; even 100 mg. of beryllium remain wholly in solution, and 0.5 mg. is not carried out with a large quantity of aluminum. This method was, therefore, adopted for the separation, it being supplemented by a confirmatory test for beryllium based on the process of Parsons and Barnes.

(8) The separation of the chromium, vanadium and uranium, which are present together in the filtrate from the sodium hydrogen carbonate precipitate, also required much investigation. It was soon decided that there was more promise of effecting a separation of the first two of these elements in the state of chromate and vanadate, in which they already exist, than in a lower stage of oxidation; and it was found that the lead salts differed sufficiently in solubility in nitric acid to enable 0.5 mg. of chromium to precipitate while retaining 100 mg. of vanadium in solution. A separation based on this fact was therefore adopted. The excess of lead added is subsequently removed by saturating the filtrate with hydrogen sulphide. To avoid the addition and removal

[1] THIS JOURNAL, 28, 1589 (1906).

[2] Z. anorg. Chem., 16, 15 (1898).

of lead when chromium is absent, a preliminary test for chromate with hydrogen peroxide is introduced. The uranium is separated from the vanadium (after oxidation to the vanadic state) by precipitating it as uranyl ammonium phosphate in acetic acid solution—a method that was found to give satisfactory results for the limiting case of a large proportion of uranium and a small proportion of vanadium, and also in the converse case. Vanadium is tested for by making the filtrate strongly alkaline with ammonia and saturating with hydrogen sulphide, whereby a violet-red solution of a vanadium sulpho-vanadate is formed.

(9) We will next consider the analysis of the precipitate produced by sodium peroxide, which contains the manganese, iron, nickel, cobalt, thallium, titanium and zirconium, the alkaline-earth elements, and possibly phosphate. The main problems connected with this were the separation of the manganese from the other elements, that of the alkaline-earth elements from phosphate and that of the titanium and zirconium from the iron and from each other.

(10) In almost all schemes of qualitative analysis it is thought sufficient to test a portion of the precipitate for manganese by fusing it with sodium carbonate or by boiling it with lead dioxide and nitric acid, without isolating the manganese. These color tests give, however, but little idea of the quantity of the element present. Moreover, aside from this objection, the large number of the elements contained in the precipitate in this scheme makes their separation necessary. The one reaction of manganese which seemed in every way suited for this purpose is that frequently employed in iron and steel analysis consisting in the conversion of the manganese into the dioxide by the action of chloric acid and concentrated nitric acid. For this is not only a behavior highly characteristic of this element; but, since the separation is carried out in a strongly acid solution, it might be anticipated that the other elements, which are not oxidizable to insoluble peroxides, would not be retained in the precipitate to an important extent. Our experiments have shown that this is, in general, the case; but one exception has been discovered. It has been found, namely, that titanium, which is quadrivalent like manganese in the dioxide, when present even in considerable quantity (up to 50 mg.) may be completely precipitated with a large quantity of manganese (500 mg.), and that a large proportion, though not all of the zirconium is likewise carried down. The method is, however, otherwise so satisfactory that we have adopted it, special provision being made for this unusual case in a way that need not be described here. The procedure consists in dissolving the whole sodium peroxide precipitate in strong hydrochloric acid, in evaporating with excess of nitric acid, adding concentrated nitric acid and

potassium chlorate, heating, and filtering off the manganese dioxide on an asbestos filter.

(11) Owing to the fact mentioned above that zinc is carried down in considerable quantity by manganese in the Na_2O_2 precipitation, experiments were made with the view of previously removing manganese by introducing this chloric acid procedure at the beginning of the analysis of this group. It was found, however, that vanadium, which is not carried down in the sodium peroxide procedure, is, like titanium, precipitated in large quantity with the manganese in the chloric acid procedure. It was found also that some zinc (1–4 mg.) may be carried down completely in the Na_2O_2 precipitate by iron, nickel and cobalt, so that it would be still necessary to provide for the detection of zinc in the iron group. For these reasons, it is evidently best to have the sodium peroxide precipitation precede the treatment with chloric acid.

(12) The filtrate from the chloric acid precipitate is first tested for phosphate. When it is not present, the iron, thallium, titanium and zirconium are separated from the other elements by the addition of ammonium hydroxide. When phosphate is present, in order to separate it from the alkaline-earth elements, the basic acetic precipitation is employed, ferric chloride being first added, if necessary. The provision here made for the case that phosphate is present is thought to have many advantages over the methods ordinarily employed in schemes of qualitative analysis, where the phosphate is removed by tin in nitric acid solution, by ferric chloride and barium carbonate, or by ferric chloride and ammonium acetate in the first stages of the analysis of the group. Of these three processes, the basic acetate is much more rapid and simple of execution; but it does not give a separation which is at all satisfactory when applied to a solution containing all the elements of the aluminum and iron groups; thus chromium and zinc may in certain combinations of elements be found either in the precipitate or filtrate, and manganese also divides, unless great care is taken to make the precipitation in a large volume at the proper acid concentration. In the scheme of analysis here presented, this basic acetate separation has been introduced only after these troublesome elements have already been removed, for the presence of phosphate involves no complications in the preceding steps of the process. Under these circumstances it is no more difficult to secure accurate results in this separation than in the precipitation with ammonium hydroxide. Indeed, by adopting this process for all cases the complication of the alternative procedure and the special test for phosphate might be removed; but since the operations require a somewhat longer time, it has seemed best to retain the

ammonium hydroxide precipitation for the case that phosphate is not present.

(13) The iron might be separated from the titanium and zirconium by the well-known method of boiling a solution of the elements kept slightly acid with sulphurous acid; but it is difficult to secure complete precipitation of the titanium and zirconium and at the same time to prevent the carrying down of iron. Besides this, the operation is a long one, involves large dilution, and makes it necessary to use hydrofluoric acid in redissolving the precipitated hydroxides. On the other hand, the removal of the iron by the method of Rothe,[1] which consists in shaking it out of a strong hydrochloric acid solution by means of ether, is extremely simple and rapid, gives a perfect separation, and leaves the titanium and zirconium in solution. We have therefore unhesitatingly employed this method in our scheme of analysis. Moreover, in this process the thallium, which is present as thallic chloride, is extracted together with the ferric chloride by the ether; it can be readily detected, after evaporating off the ether and reducing the ferric and thallic salts with sulphurous acid, by the formation with potassium iodide of the characteristic yellow precipitate of thallous iodide.

(14) For the separation of the titanium and zirconium from each other we have adopted the process of Hillebrand,[2] which consists in adding sodium phosphate to a slightly acid solution containing hydrogen peroxide, whereby the zirconium is precipitated and the titanium remains in solution. The latter is shown to be present by the color of the solution, but it can also be precipitated as phosphate by destroying the hydrogen peroxide with sulphurous acid after filtering off the zirconium compound.

(15) The analysis of the ammoniacal solution containing nickel, cobalt and perhaps zinc and the alkaline-earth elements, is carried out along the conventional lines. The first three elements are precipitated by the addition of ammonium sulphide, and the zinc is extracted, if the precipitate is large, by treating it with cold dilute hydrochloric acid, or if it is small by dissolving the precipitate completely and treating again with sodium peroxide. Instead of separating the nickel and cobalt from each other, it was found to be shorter and more conclusive to divide the solution of the sulphides into two parts and to test one portion for nickel by adding potassium cyanide and sodium hypobromite and the other portion for cobalt with potassium nitrite. The conditions for securing the best results in the nickel test were fully studied. Finally, in the filtrate from the ammonium sulphide pre-

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[1] Rothe, Stahl und Eisen, 12, 1052 (1892), 13, 333 (1893).

[2] Bull. U. S. Geol. Survey, No. 176, p. 75 (1900).

cipitate the alkaline-earth elements are precipitated with ammonium carbonate as usual.

(16) Though no provision is made in the system of analysis for the separate detection of any of the rare-earth elements, yet a process has been described for determining whether any of them are present and for removing them when they are found to be in the solution. This process consists in evaporating the acid solution of the original ammonium sulphide precipitate, adding to the residue hydrofluoric acid and filtering. This converts the rare-earth elements completely into insoluble fluorides, and enables them to be separated from all the other elements of the aluminum and iron groups (except from a very large quantity of aluminum). When alkaline-earth elements are present, these are also precipitated as fluorides, wholly or in part, and are separated from the rare-earth elements by decomposing the fluorides with sulphuric acid, diluting, filtering off any alkaline earth sulphates that separate, and precipitating the rare-earths in the filtrate with ammonium hydroxide. This process of isolating the rare elements has been worked out in this laboratory by W. C. Arsem and H. I. Wood, for use as a group separation in the "System of Qualitative Analysis Including Nearly all the Metallic Elements."[1]

(17) Final confirmatory tests are given for almost all the elements; and much experimenting has been done on some of these tests in order to make them delicate and reliable; thus, this is true of the color tests for aluminum and zinc made by igniting the oxides with cobalt nitrate, of that for chromium with hydrogen peroxide and ether, of that for nickel with H_2S in an alkaline tartrate solution, and of that for vanadium made by adding H_2O_2 to an acid solution; also of the precipitation test for uranium with potassium ferrocyanide. No satisfactory tests have as yet been found for beryllium or zirconium. Many, but not all, of these confirmatory tests will be found superfluous and will be omitted by the experienced analyst, except in cases where a very small precipitate or one of doubtful character is obtained; but they will, we believe, be useful to those unfamiliar with this scheme, and they serve, in the case of students, the educational purpose of making them acquainted with additional reactions of the elements in question.

(18) It may be thought an objection to this scheme of analysis that it involves a number of manipulative operations unusual in qualitative analysis, such as heating in a closed bottle, saturating the acid-ether solution with hydrogen chloride gas (in the separation of aluminum and beryllium), filtering through an asbestos filter (in the separation of manganese), and shaking out with ether in the separation of iron from

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[1] Two parts of this "System" have already been published. Technology Quarterly, **16**, 93-132 (1903); **17**, 214-257 (1904).

titanium and zirconium. These operations, when they have been once executed, are found to be little if any more troublesome than the ordinary operations of precipitation and filtration. They are, moreover, mostly employed only in connection with the detection of the rarer elements, where the difficulties in finding any satisfactory method are so great that a little additional trouble is an insignificant factor. And finally, from an educational standpoint, they introduce the student to new kinds of processes, thus enlarging his knowledge and diminishing the force of the objection that the ordinary study of qualitative analysis is too limited in its scope.

Tabular Outline.

In the tables below the enclosure of a symbol in brackets shows that the element may divide itself between the residue and the solution in the operation immediately preceding.

Procedure and Notes.

Procedure 51.—Boil the filtrate from the H_2S precipitate (P. 21)[1] till the H_2S is expelled. Transfer it to a flask, add NH_4OH (0.96) until the mixture after shaking smells of it, and then 2–4 cc. more. Note whether there is a precipitate. Add ammonium monosulphide slowly (or if nickel is likely to be present pass in H_2S), until, after shaking, the vapors in the flask blacken a piece of filter-paper moistened with lead acetate solution. To coagulate the precipitate shake the mixture or heat it nearly to boiling. Filter, and wash the precipitate, first with water containing about 1 per cent. of the $(NH_4)_2S$ reagent and then with a little pure water. If the filtration is slow, keep the funnel covered with a watch glass so as to prevent oxidation. To the filtrate add a few drops $(NH_4)_2S$, boil the mixture for a few seconds, or longer if it is dark colored (till it becomes colorless or light yellow); filter if there is a precipitate, uniting it with the preceding one. (Precipitate, P. 52; filtrate, P. 71, or first by *P. 51*a*, if vanadium is to be tested for.)

Notes.—(1) The H_2S is boiled out, and the effect of the addition of NH_4OH alone is noted because it often gives a useful indication as to what elements are present. To save time the expulsion of the H_2S may be omitted when this indication is considered unimportant. Ammonium monosulphide is used, rather than polysulphide, in order to prevent as far as possible the dissolving of NiS, and in order not to introduce sulphur into the precipitate, or polysulphide into the filtrate; for this gives to the filtrate a deep yellow color, and causes in the subsequent analysis separation of sulphur on standing or on heating. Excess of the monosulphide is avoided, for the same reasons, since it rapidly oxidizes in the air to polysulphide. By passing H_2S into the ammoniacal solution instead of adding $(NH_4)_2S$, the dissolving of NiS is entirely prevented; therefore, though the operation takes a little longer, the use of H_2S is to be preferred when nickel is likely to be present. The mixture is shaken in order

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[1] For this and similar references to former procedures, see the previous article, THIS JOURNAL, 29, 137.

TABLE VII.

ANALYSIS OF THE ALUMINUM AND IRON GROUPS FOR COMMON ELEMENTS.

To the filtrate from the H_2S precipitate add NH_4OH and $(NH_4)_2S$ (P. 51).

<table>
<tr><td colspan="8">Precipitate: $Al(OH)_3$, $Cr(OH)_3$, ZnS, MnS, FeS, Fe_2S_3, NiS, CoS.
Dissolve in HCl or $HCl + HNO_3$, evaporate, add $NaOH$, Na_2O_2 and Na_2CO_3 (P. 52).</td><td rowspan="10">Filtrate: Alkaline-earth and alkali elements.</td></tr>
<tr><td colspan="3">Filtrate: $NaAlO_2$, Na_2CrO_4, Na_2ZnO_2.
Acidify with HNO_3, add NH_4OH (P. 53).</td><td colspan="5">Precipitate: $MnO(OH)_2$, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$, $Ni(OH)_3$, $[ZnO_2H_2]$.
Dissolve in HCl, evaporate, heat with HNO_3 and $KClO_3$ (P. 61).</td></tr>
<tr><td>Precipitate: $Al(OH)_3$.
Dissolve in HNO_3, add $Co(NO_3)_2$, evaporate, ignite (P. 54).</td><td colspan="2">Filtrate: *Add $HC_2H_3O_2$ and $BaCl_2$ (P. 55).*</td><td>Precipitate: MnO_2.
Boil with HNO_3 and PbO_2 (P 62).</td><td colspan="4">Solution.[1] *Add NH_4OH (P. 64).*</td></tr>
<tr><td>Blue residue: $Al_2O_3.xCoO$.</td><td>Precipitate: $BaCrO_4$.
Dissolve in dilute HNO_3, add ether and H_2O_2 (P. 56).</td><td>Filtrate: Salt of Zn.
Pass in H_2S (P. 57).</td><td>Violet color: $HMnO_4$.</td><td>Precipitate: $Fe(OH)_3$.
Dissolve in HCl, add $KSCN$.</td><td colspan="3">Filtrate: $Co(NH_3)_x(NO_3)_2$, $Ni(NH_3)_4(NO_3)_2$, $Zn(NH_3)_4(NO_3)_2$.
Pass in H_2S (P. 66).</td></tr>
<tr><td></td><td>Blue coloration of ether layer: H_3CrO_7.</td><td>White precipitate: ZnS.
Dissolve in HNO_3, add $Co(NO_3)_2$, ignite (P. 57).</td><td></td><td>Red solution: $Fe(SCN)_3$.</td><td colspan="3">Precipitate: ZnS, CoS, NiS.
Treat with cold dilute HCl (P. 67).</td></tr>
<tr><td></td><td></td><td>Green residue: $ZnO.xCoO$.</td><td></td><td></td><td colspan="2">Solution: $ZnCl_2$, $[CoCl_2]$, $[NiCl_2]$.
Add $NaOH$ and Na_2O_2 (P. 67).</td><td>Residue: NiS CoS.</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td>Solution: Na_2ZnO_2.
Add $HC_2H_3O_2$ and H_2S (P. 57).</td><td colspan="2">Precipitate: $Co(OH)_3$, $Ni(OH)_{2\text{-}3}$.
Dissolve, evaporate, add $NaOH$.</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td>White precipitate: ZnS.</td><td>*To one-half add KNO_2 and $HC_2H_3O_2$ (P. 69).*</td><td>*To other half add KCN, digest, add $NaBrO$ (P. 70).*</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td>Yellow precipitate: $K_3Co(NO_2)_6$.</td><td>Black precipitate: $Ni(OH)_3$.</td></tr>
</table>

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[1] Test for phosphate at this point (P. 63); if present, follow Table IX.

TABLE VIII.

ANALYSIS OF THE ALUMINUM GROUP FOR COMMON AND RARE ELEMENTS.

Filtrate from Na_2O_2 treatment: Na_2CrO_4, sodium peruranate, Na_3VO_4, Na_2ZnO_2, $NaAlO_2$ Na_2BeO_2.
*Add HNO_3, dilute, add $NaHCO_3$, heat in a closed bottle (*P. 58a).*

<table>
<tr><td colspan="4">Filtrate: salts of chromic, uranic and vanadic acids.
*Add HNO_3 and $Pb(NO_3)_2$ (*P. 58 b).*</td><td colspan="4">Precipitate: $ZnCO_3$, $Al(OH)_3$, basic $BeCO_3$.
*Dissolve in HCl, add NH_4OH (*P. 58f).*</td></tr>
<tr><td rowspan="5">Yellow precipitate:
$PbCrO_4$.</td><td colspan="3">Filtrate: $UO_2(NO_3)_2$, H_3VO_4, $[Pb(NO_3)_2]$.
Pass in H_2S.</td><td>Filtrate:
$Zn(NH_3)_4Cl_2$.
Add $HC_2H_3O_2$, pass in H_2S.
(P. 57).</td><td colspan="3">Precipitate: $Al(OH)_3$, $Be(OH)_2$.
*Dissolve in HCl, add ether, saturate with HCl gas (*P. 58g).*</td></tr>
<tr><td rowspan="4">Precipitate:
PbS.
Reject.</td><td colspan="2">Filtrate: *Add bromine, neutralize, add $HC_2H_3O_2$ and Na_2HPO_4 (*P. 58c).*</td><td rowspan="4">White precipitate:
ZnS.</td><td rowspan="4">White precipitate:
$AlCl_3 6H_2O$.</td><td colspan="2">Filtrate: *Evaporate, add 10 per cent. $NaHCO_3$ solution, boil, pass in H_2S (*P. 58h).*</td></tr>
<tr><td>Precipitate:
$UO_2NH_4PO_4$.
Dissolve in HCl, evaporate, add NaCl and $K_4Fe(CN)_6$.
*(*P. 58d).*</td><td>Filtrate: H_3VO_4.
*Add NH_4OH, saturate with H_2S (*P. 58e).*</td><td>Filtrate: *Acidify, boil, add NH_4OH.*</td><td rowspan="3">Precipitate:
$Al(OH)_3$, Fe_2S_3.
Reject.</td></tr>
<tr><td rowspan="2">Brown precipitate:
$(UO_2)_2Fe(CN)_6$.</td><td>Red solution:
Sulphovanadate.
*Acidify (*P. 58e).*</td><td rowspan="2">White precipitate:
$Be(OH)_2$.[1]</td></tr>
<tr><td>Black precipitate:
V_2S_{4-5}.</td></tr>
</table>

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[1] Filter, and test the precipitate for uranium (*P. 58*h*).

TABLE IX.

ANALYSIS OF THE IRON GROUP FOR THE RARE ELEMENTS, AND FOR THE COMMON ELEMENTS IN THE PRESENCE OF PHOSPHATE.

Precipitate from Na_2O_2 treatment: $MnO(OH)_2$, $Fe(OH)_3$, $Tl(OH)_3$, $ZrO(OH)_2$, $TiO(OH)_2$, $Co(OH)_3$, $Ni(OH)_2$, $Ni(OH)_3$, $[Zn(OH)_2]$; $CaCO_3$, $SrCO_3$, $BaCO_3$, $MgCO_3$; and phosphates of these elements.

Dissolve in HCl, evaporate, heat with HNO_3 *and* $KClO_3$ *(P. 61).*

<table>
<tr><td rowspan="4">Brown precipitate: MnO_2.</td><td colspan="6">Solution.[1] <i>Test a portion for iron; to the remainder add</i> NH_4OH <i>till nearly alkaline, then</i> $NH_4C_2H_3O_2$ <i>and</i> $FeCl_3$, <i>dilute and boil (P. 65).</i></td></tr>
<tr><td colspan="4">Precipitate: Basic acetates, hydroxides, and phosphates of Fe, Tl, Zr, Ti. <i>Dissolve in HCl (1.12), shake with ether (*P. 65a).</i></td><td colspan="2">Solution: Salts of Co, Ni, Zn, Ca, Sr, Ba, Mg. <i>Add</i> NH_4OH, <i>pass in</i> H_2S <i>(P. 66).</i></td></tr>
<tr><td colspan="2">Ether layer: $FeCl_3$, $TlCl_3$. <i>Evaporate, dissolve in dilute</i> H_2SO_4, <i>add KI and</i> Na_2SO_3 <i>(*P. 65d).</i></td><td colspan="2">Water layer: $TiCl_4$, $ZrCl_4$. <i>Add</i> H_2SO_4, <i>evaporate, add</i> H_2O_2 <i>and</i> Na_2HPO_4 <i>(*P. 65b).</i></td><td rowspan="2">Precipitate: NiS, CoS, ZnS. See Table VII.</td><td rowspan="2">Filtrate: Salts of Ca, Sr, Ba, Mg.</td></tr>
<tr><td>Solution: $FeSO_4$.</td><td>Yellow precipitate: TlI.</td><td>White precipitate: $Zr(OH)PO_4$.</td><td>Orange-yellow filtrate: TiO_3. <i>Add</i> Na_2SO_3 <i>(*P. 65c).</i> White precipitate: $Ti(OH)PO_4$.</td></tr>
</table>

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[1] Test for phosphate at this point (P. 63); if found absent, make the solution alkaline with NH_4OH (omitting the addition of ammonium acetate and $FeCl_3$), and filter.

to coagulate the precipitate, and make it filter more readily. Heating also promotes the coagulation of the precipitate, and it is recommended when the precipitate does not coagulate and settle quickly on shaking. The filtrate is boiled for a few moments to ensure the complete precipitation of $Cr(OH)_3$, or longer to ensure that of NiS, whose presence is indicated by a brown or nearly black color of the filtrate. Finally it is directed to wash with water containing a little $(NH_4)_2S$, and to keep the filter covered, in order to avoid the oxidation of the sulphides by the air, by which soluble sulphates may be formed.

(2) Under the conditions of the procedure, which provides for a small excess of NH_4OH in the presence of NH_4Cl, aluminum, chromium, iron, titanium, zirconium, and beryllium are completely precipitated as hydroxides and uranium as ammonium diuranate, $(NH_4)_2U_2O_7$. All of these precipitates are white, except those of chromium, uranium, and iron; $Cr(OH)_3$ is grayish-green, and $(NH_4)_2U_2O_7$ is yellow. The color of the precipitated hydroxide of iron varies with the state of oxidation of the iron, pure ferrous salts yielding a white precipitate, and ferric salts a reddish-brown one, while mixtures of them yield green or black precipitates. In the alkaline mixtures the precipitate is rapidly oxidized by the oxygen of the air and undergoes corresponding changes in color. Manganous salts are also oxidized rapidly, with the result that brown $Mn(OH)_3$ separates. Under the conditions of the procedure zinc and nickel when present alone, are completely dissolved; the same is true of cobalt except when it is present in large quantity; but zinc is precipitated when chromium is also present. The ammoniacal solution of nickel is blue and that of cobalt of a reddish color, which darkens rapidly on exposure to the air owing to oxidation. If a smaller excess of NH_4OH is used than is directed, some zinc hydroxide, as well as cobalt hydroxide, may remain undissolved when large amounts of these elements are present; but this has no effect on the subsequent analysis. If, however, a much larger excess of NH_4OH is employed, a few milligrams of aluminum and chromium may be dissolved, the latter giving a pink colored solution.

(3) The presence of a considerable quantity of NH_4Cl, such as is formed by the neutralization of the acid already in the solution, serves to prevent the precipitation of $Mg(OH)_2$ (and of $Mn(OH)_2$), and also to lessen the amount of $Al(OH)_3$ dissolved by the NH_4OH.

(4) The influence of an excess of the NH_4OH and of the presence of NH_4Cl on the solubilities of the various hydroxides is explained by the mass-action law and ionic theory as follows: In order that any hydroxide, say of the type MO_2H_2, may be precipitated, it is necessary that the product $C_M.C^2_{OH}$ of the concentrations of the ions M^{++} and OH^- in the solution in question attain the value known as the solubility-product. This varies, of course, with the nature of the hydroxide; but for all the elements of the iron group and also for magnesium it has so small a value that, even in a solution containing in 50 cc. only one milligram of the element and a slight excess of NH_4OH, the product $C_MC^2_{OH}$ exceeds it, and precipitation results. When, however, much NH_4Cl is also present, this greatly reduces, in virtue of the common ion effect, the ionization of the NH_4OH and therefore the OH^- concentration in the solution, so that now for certain elements the product $C_MC^2_{OH}$ does not reach the solubility value, even when C_M is moderately large (say 500 mg. in 50 cc.). This is true of magnesium and manganese; but in the cases of aluminum, chromium, and ferric iron the solubility of the hydroxides in water is so slight that even in NH_4Cl solution the solubility is not appreciable.

If these were the only effects involved, the greater the excess of NH_4OH added, the less would be the solubility of any hydroxide; but other influences come into play with certain of the elements. These influences are of two kinds. The first of these is shown by zinc, nickel, and cobalt. In the case of these elements, just as with silver and copper, the excess of ammonia combines with the simple cathion M^{++} forming complex cathions of the types $M(NH_3)_2^{++}$ and $M(NH_3)_4^{++}$, thereby removing the simple cathion from the solution and making it necessary for more of the hydroxide to dissolve, in order to bring back the value of $C_MC^2_{OH}$ to that of the solubility-product. In such a case, the presence of NH_4Cl increases the solubility still further, since it greatly decreases C_{OH} and slightly increases C_{NH_4OH} and C_{NH_3}, owing to the common ion effect on the ionization of the NH_4OH. Chromium also forms similar ammonia complexes, but in much smaller proportion.

The second effect is exhibited in the case of AlO_3H_3. This hydroxide is a so-called amphoteric substance,—*i. e.*, is one which behaves both as a base and as an acid in consequence of its being appreciably ionized both into $3(OH^-) + Al^{+++}$ and into $H^+ + AlO_3H_2^-$ (or AlO_2^- and H_2O). With the H arising from the latter form of ionization, the OH^- coming from the excess of NH_4OH combines to form H_2O thus causing more AlO_3H_3 to dissolve until the value of $C_{AlO_2}.C_H$ again attains that of the solubility-product. Since $C_{AlO_2}.C_H = \text{const.}$ in any solution saturated with AlO_3H_3 and since the equilibrium equations $C_H.C_{OH} = K_W$ and $C_{NH_4}C_{OH} = K_3C_{NH_4OH}$ must be satisfied, it follows from combination of these equations that $C_{AlO_2}/C_{OH} = \text{const.}$ and that $C_{AlO_2} = \text{const.} \times C_{NH_4OH}/C_{NH_4}$. The first equation shows that the quantity of aluminum dissolved is proportional to the concentration of hydroxide-ion in the solution, and that therefore it would be much greater in a solution of a largely ionized base like NaOH than in that of a slightly ionized base like NH_4OH. The second equation shows that the solubility in solutions containing NH_4OH and NH_4Cl (or other ammonium salt) is proportional to the ratio of the concentration of the base to that of the salt; so that the presence of ammonium salts tends to neutralize the solvent action of an excess of the hydroxide. All these conclusions are in accordance with the facts. BeO_2H_2 behaves in the same way as AlO_3H_3, forming the cation Be^{++} and the anion BeO_2^{--} or $HBeO_2^-$.

(5) It follows from the statements in the preceding notes that if the NH_4OH produces no precipitate it proves the absence of as much as one milligram of aluminum, iron, beryllium, uranium, titanium, and zirconium; also of chromium, if the mixture is heated to boiling after the addition of NH_4OH. Care must be taken not to overlook a small precipitate which might otherwise escape detection on account of its transparency. The mixture should therefore be well-shaken and allowed to stand 2 or 3 minutes in order that the precipitate may collect in flocks. This treatment also oxidizes the iron when present in small quantity, and thus enables it to be more readily detected; for its precipitation in the ferric state is more complete.

(6) When phosphate is present, magnesium, calcium, strontium, barium, and manganese may be partially, or even completely precipitated by NH_4OH. It is therefore necessary, when phosphate is present, to provide for the detection of the alkaline earth elements in the analysis of this precipitate. The normal phosphates and the monohydrogen phosphates of these elements are difficultly soluble in water, but dissolve readily in acids, owing to the formation in solution of the much more soluble dihydrogen phosphates or of free phosphoric acid, for example, according to the equations:

$$(Ca^{++})_3(PO_4^{---})_2 + 4H^+Cl^- = 2Ca^{++}(Cl^-)_2 + Ca^{++}(H_2PO_4^-)_2$$
$$Ca^{++}(H_2PO_4^-)_2 + 2H^+Cl^- = Ca^{++}(Cl^-)_2 + H_3PO_4.$$

Upon the addition of sodium or ammonium hydroxide to such a solution the hydrogen-ion in equilibrium with the $H_2PO_4^-$ and H_3PO_4 is removed, and these dissociate into $HPO_4^{=}$ and $PO_4^{\equiv}$, thus causing precipitation of the corresponding salts. When other elements, like iron, forming more insoluble phosphates are also present, it is evident that they will combine with the phosphate radical, thus leaving the alkaline earth elements in solution. On the other hand, when a soluble carbonate, or a large excess of a strong base, is also present, the alkaline earth phosphates will be partially converted into carbonates or hydroxides, leaving phosphate in solution.

(7) The presence of any other acid radical which forms with the alkaline earth elements salts soluble in dilute acids but insoluble in ammonia may also cause their precipitation at this point. Such radicals are fluoride, borate, oxalate, and hypovanadate. The fluoride will ordinarily have been removed in the evaporation with acids in the preparation of the solution. The borates of the alkaline earth elements, though somewhat difficultly soluble, are not sufficiently so to cause them to be precipitated, except when present in very large quantity. Oxalate and hypovanadate, even if present, do not make any change necessary in the usual process of analysis; for, in the course of it, vanadate and much of the oxalate are separated from the alkaline earths in P. 52, and the remainder of the oxalate is destroyed in P. 61.

(*8) Vanadium when present alone in moderate quantity may remain in solution, but when present in large quantity is partially precipitated by NH_4OH as a dark gray hydroxide, $VO(OH)_2$. This compound corresponds to the state of oxidation (oxide VO_2) to which vanadic acid (oxide V_2O_5) is partially or completely reduced by H_2S. It is an amphoteric substance which forms with acids soluble blue salts such as $VOCl_2$, vanadyl dichloride, and $VOSO_4$, vanadyl sulphate, and with bases hypovanadates such as $Na_2V_2O_5$ and $Na_2V_4O_7$. When other elements of this group are also present the vanadium may be completely precipitated with them, since their hypovanadates and vanadates are in general difficultly soluble substances.

(*9) When a base is added to a uranyl salt (for example UO_2Cl_2), uranyl hydroxide, $UO_2(OH)_2$, is first formed, but this is an amphoteric substance, and it is converted by the excess of base into salts of diuranic acid, $H_2U_2O_7$, of which even the alkali salts are insoluble.

(10) $(NH_4)_2S$ precipitates ZnS, MnS, NiS, CoS, and Tl_2S, and converts $Fe(OH)_2$ into FeS, $Fe(OH)_3$ into Fe_2S_3, and $(NH_4)_2U_2O_7$ very slowly into UO_2S. The hydroxides of aluminum, chromium, titanium, zirconium, and beryllium are not affected by the $(NH_4)_2S$. Whether a hydroxide precipitate is converted into a sulphide precipitate or whether the reverse reaction takes place depends on the relative solubilities of the two compounds and on the relative concentrations of sulphide-ion and hydroxide-ion in the solution. Since in the solution the concentration of the sulphide-ion greatly exceeds that of the hydroxide-ion, even difficultly soluble hydroxides would be converted into more soluble sulphides, provided that the difference in solubility were not too great. In the case of hydroxides, like $Al(OH)_3$, which are not so changed, their sulphides are so much more soluble that they do not form in aqueous sulphide solutions.

(11) The sulphides of iron, nickel, and cobalt are black; Tl_2S and UO_2S are dark brown; ZnS is white; and MnS is flesh colored, but turns brown on standing in the air owing to oxidation to hydrated Mn_2O_3.

(12) When nickel is present alone, or in large proportion in the $(NH_4)_2S$ precipitate, several milligrams of it usually pass into the filtrate making it dark colored, and some NiS also passes through the filter with the wash water. In this case it is useless to try to remove the NiS by filtering again; but it can be coagulated by boiling for several minutes. This behavior of nickel, as stated above, can be avoided altogether by passing H_2S into the NH_4OH solution to precipitate the sulphide, instead of adding $(NH_4)_2S$. The formation of this brown solution depends upon the presence of ammonium polysulphide, for nickel may be completely precipitated by

ammonium monosulphide in the absence of air. The nature of the brown solution is not known.

***Procedure 51a.**—To the filtrate from the $(NH_4)_2S$ precipitate (P. 51) add 5 cc. NH_4OH (0.90) and completely saturate the solution with H_2S. (Pink or violet-red color, presence of *vanadium.*)

If no red color results, boil the solution for several minutes in a casserole to expel most of the NH_4OH and $(NH_4)_2S$, filter off the sulphur, and treat the filtrate by P. 71.

If the solution assumed a pink or red color, acidify it with HCl (1.12), heat it to boiling, and filter. Boil the filtrate in a casserole to expel H_2S, add 0.5–5 cc. 10 per cent. $FeCl_3$ solution, and NH_4OH (0.96) until the mixture after shaking smells of it, and filter. (Filtrate, P. 71.) Heat the HCl precipitate (with the filter, if necessary) with 5–10 cc. HNO_3 (1.20) until the black precipitate is dissolved, and filter. (If the red coloration produced by H_2S was slight, evaporate the filtrate to about 2 cc.) Add to the solution a few drops of 3 per cent. H_2O_2. (Orange-yellow or orange-red color, presence of *vanadium.*) Dissolve the NH_4OH precipitate by pouring a small portion of HNO_3 (1.20) repeatedly through the filter, and test for vanadium with H_2O_2 in the same way, first adding a little water to the HNO_3 solution if it has a red color owing to the presence of much ferric nitrate.

Notes.—(1) An ammoniacal solution of a vanadate or hypovanadate quickly becomes yellowish red when H_2S is led into it, and this color slowly deepens as more H_2S is absorbed; but the characteristic, brilliant violet-red color is obtained only when the solution is completely saturated with H_2S. The presence of ammonium salts tends to prevent the formation of this red compound, but their influence is overcome by the addition of a large excess of NH_4OH. These facts make it probable that this red compound is an ammonium sulpho vanadate, from which the sulphur is readily split off as SH^- ion, owing to hydrolysis. Under the conditions of procedure, 0.2 mg. V can be easily detected, the solution then having a pink color.

(2) Upon the addition of HCl the sulpho salt is immediately decomposed, with formation of a black precipitate of V_2S_4 or V_2S_5. This precipitation is far from complete under these conditions, only about half the vanadium being thrown down. More or less sulphur will also be precipitated, but the dark color of the sulphide is apparent even when less than 0.5 mg. V is present. Acetic acid may be used instead of HCl, but the proportion of vanadium precipitated as sulphide is not much increased.

(3) When a three- to fivefold excess of a ferric salt is present and NH_4OH is added, the remainder of the vanadium is precipitated (probably as hypovanadate) together with the $Fe(OH)_3$.

(4) The confirmatory test for vanadium with H_2O_2 depends upon the formation of pervanadic acid, HVO_4. 0.1 to 0.2 mg. V may be detected in a volume of 5 cc., provided that this solution is strongly acid. A very large excess of H_2O_2 is to be avoided, for this decreases the intensity of the color, and may even decolorize the solution completely if very little acid is present, probably owing to the formation of a colorless compound of pervanadic acid with hydrogen peroxide.

(5) Molybdenum, if not completely precipitated by H_2S in P. 21, and tungsten, if it passed into the original acid solution (owing to the presence of phosphate or ar-

senate) in P. 3, may also be present in the filtrate from the $(NH_4)_2S$ precipitate. Upon saturating with H_2S molybdenum also gives a deep red color which would obscure the test for vanadium and might be mistaken for it; but tungsten gives no color. Upon acidification with HCl, tungsten divides between the pecipitate and filtrate, but molybdenum is thrown down completely as black MoS_3. (If the cold solution is acidified with acetic acid, the sulphomolybdate remains undecomposed for some time and the MoS_3 is not completely precipitated even on boiling.) In the final confirmatory test with H_2O_2 tungsten gives no color; and molybdenum, even when a large quantity is present, gives only a pure yellow color but not an orange or red one.

Procedure 52.—Transfer the $(NH_4)_2S$ precipitate (P. 51) with the filter if necessary to a casserole; add 5–20 cc. HCl (1.12), stir for a minute or two in the cold, and then boil the mixture for two or three minutes; if a black residue still remains, add a few drops HNO_3 (1.42) and boil again. Dilute with a little water, filter off the sulphur residue, and evaporate the filtrate to a small volume to remove the excess of acid.

*In order to detect rare earth elements, and to remove them if present, treat this solution by *P. 52*a*.

*If uranium and vanadium are to be tested for later by *P. 58*a–h*, evaporate twice with a little HNO_3 (1.42), to destroy HCl.

Dilute the solution to 10 or 20 cc.; make alkaline with NaOH solution, avoiding a great excess; add 10–20 cc. more water if so large a precipitate separates that the mixture becomes almost gelatinous. Cool by placing the casserole in cold water, and add 0.5–3 gram solid Na_2O_2, in small portions with constant stirring. Then add 5 cc. 10 per cent. Na_2CO_3 solution; boil for two or three minutes to decompose the excess of Na_2O_2, cool, dilute with an equal volume of water, filter with the help of suction and wash with hot water. (Precipitate, P. 61; filtrate, P. 53, or if uranium or vanadium is to be tested for, *P. 58*a*.)

Notes.—(1) All the hydroxides and all the sulphides, except NiS, CoS, usually dissolve readily in cold HCl. If, therefore, there is considerable black residue after adding the HCl, it shows the presence of nickel, or cobalt (or possibly vanadium); a very small black residue may, however, be due to FeS enclosed within sulphur. The fact that there is no such dark colored residue does not, however, prove that nickel and cobalt are absent, for a considerable quantity of them (even 5 mg.) may dissolve completely in the HCl when large quantities of other elements, especially iron, are also present.

(2) The fact that NiS and CoS dissolve so much less readily in dilute acids than do the other sulphides of this group seems to be due not to a lesser solubility in water, but to an unusually slow rate of solution, for nickel and cobalt are not precipitated by H_2S even from a much more weakly acid solution, and their sulphides obtained by precipitation with an alkaline sulphide continue to dissolve in dilute acids without reaching a limit determined by the concentration of the H_2S and the nickel-ion or cobalt-ion in the solution, as would be the case if the phenomena were that of the solubility of a difficultly soluble sulphide.

(3) The $(NH_4)_2S$ precipitate is first treated with HCl, partly in order to furnish the indication just referred to of the presence of nickel or cobalt but mainly because much more free sulphide and sulphate would be formed by oxidation if HNO_3 or *aqua*

regia were used at the start. The presence of the sulphate in considerable quantity in the solution interferes with the subsequent test for chromate (with $Ba(NO_3)_2$ in P. 55 or with $Pb(NO_3)_2$ in *P. 58*b*). If NiS, CoS, or V_2S_5 is present in the residue, HNO_3 must, however, be subsequently added, to ensure the solution of these sulphides. *The HCl is destroyed by evaporation with HNO_3, since chloride interferes with the test for chromate with $Pb(NO_3)_2$ in *P. 58*b*.

(*4) If the $(NH_4)_2S$ precipitate be allowed to stand for a long time before treating it with acid, or if the mixture be heated for a long time after the precipitation, $TiO(OH)_2$ and $ZrO(OH)_2$ may remain in part undissolved even by the boiling concentrated acids, owing to the fact that the hydroxides at first precipitated become partially dehydrated, in which state they are very difficultly soluble. If this happens at this point or in dissolving hydroxide precipitates obtained later in the analysis, the residue may be dissolved in a little HF in a platinum dish, and the HF then expelled by evaporating two or three times with HNO_3 (or HCl) nearly to dryness.

(5) By NaOH, iron, manganese, nickel, cobalt, *titanium, *zirconium, and *uranium are completely precipitated and do not dissolve in moderate excess; while aluminum, chromium, zinc, *vanadium, and *beryllium, remain in solution or dissolve when a sufficient excess is added, owing to the fact that their hydroxides are amphoteric substances (see P. 51, Note 3), and form with the NaOH soluble aluminate ($NaAlO_2$), chromite ($NaCrO_2$), zincate (Na_2ZnO_2), vanadate (Na_3VO_4), and beryllate (Na_2BeO_2). Thallium in the thallous state also remains in solution since TlOH is a readily soluble substance. When zinc and chromium are simultaneously present, they are precipitated in the form of a double compound ($ZnCr_2O_4$). Chromium would also be completely precipitated, owing to hydrolysis and the formation of a less soluble solid hydroxide, if the NaOH solution were boiled before adding Na_2O_2. It will be observed that NaOH precipitates manganese, nickel and cobalt while NH_4OH does not. This occurs with manganese because of the far greater concentration of hydroxide-ion in the NaOH solution, and with nickel and cobalt partly on this account and partly because there is no complex formation, as there is with NH_4OH. $Mn(OH)_2$ is white, but rapidly turns brown, owing to oxidation to $Mn(OH)_3$; $Ni(OH)_2$ is light green; $Co(OH)_2$ is pink, but from cobalt solutions a blue basic salt is first precipitated in the cold. If a large excess of NaOH be added, a little $Co(OH)_2$ dissolves yielding a blue solution, doubtless forming a salt such as Na_2CoO_2. This is to be avoided since then the cobalt will not be completely oxidized and precipitated upon the subsequent addition of Na_2O_2.

(6) By the addition of Na_2O_2, $Fe(OH)_2$ is changed to dark red $Fe(OH)_3$, $Mn(OH)_2$ to brown hydrated MnO_2, $Co(OH)_2$ to black $Co(OH)_3$, $Ni(OH)_2$ partially to black $Ni(OH)_3$, and thallium is precipitated as dark red $Tl(OH)_3$, all of which are insoluble in excess of NaOH and remain, together with $TiO(OH)_2$ and $ZrO(OH)_2$, in the precipitate. Chromium and uranium, which after the addition of NaOH are present as soluble sodium chromite or as insoluble sodium diuranate ($Na_2U_2O_7$), are converted by Na_2O_2 into chromate (Na_2CrO_4) and peruranate which are soluble compounds and remain in solution, together with the zinc, beryllium, and vanadium, which are still present as zincate, beryllate, and vanadate. The separation is more satisfactory, especially in the case of uranium when a large amount Na_2O_2 is used

(7) Even a cold solution of Na_2O_2 decomposes rapidly with evolution of oxygen, and this decomposition takes place with explosive violence when the solution is hot. The peroxide is therefore added in small portions to the cold solution. A steady evolution of gas continuing after the mixture has been well-stirred is an indication that sufficient peroxide has been added. The mixture is finally boiled in order to destroy the excess of Na_2O_2 and to cause the complete precipitation of titanium, some

of which first passes into solution, probably as the pertitanate. The solution is cooled because $Tl(OH)_3$ is somewhat more soluble in the hot solution than in the cold one. Even in the cold when thallium is present alone about 0.5 mg. will usually pass into the filtrate but precipitation is complete when elements of the iron group are also present. The solution is diluted before filtering in order to avoid the disintegration of the filter paper; it is often advantageous to support the filter by folding it together with a small hardened filter.

(8) The Na_2CO_3 is added to cause the complete precipitation of the alkaline-earth elements, whose hydroxides, especially that of barium, are somewhat soluble even in the presence of NaOH. $ZnCO_3$, though insoluble in a dilute solution of Na_2CO_3 alone, dissolves when much NaOH is present, owing to the nearly complete conversion of the zinc-ion into zincate-ion by the reaction $Zn^{++} + 4OH^{-} = ZnO_2^{=} + 2H_2O$. The Na_2CO_3 also serves to decompose the chromates of the alkaline-earth elements; if it is not added, chromium may remain in the precipitate and escape detection. It is unnecessary to add the Na_2CO_3 when the alkaline-earth elements are known to be absent.

(9) Phosphate or oxalate, if present, divides itself in this procedure between the precipitate and solution in a proportion which depends on the nature and quantities of the metallic elements. (See P. 51, N. 6.) Their presence does not cause any of the elements to precipitate which would not otherwise do so, in spite of the slight solubility of aluminum, zinc, and beryllium phosphates. This is due to the fact that the cathions of these elements (Al^{+++}, Zn^{++}, Be^{++}) are present in the NaOH solution only at an extremely small concentration, owing to their combination with the OH ion to form anions (AlO_2^{-}, $ZnO_2^{=}$, $BeO_2^{=}$).

(10) Even when less than 1 mg. Cr is present as chromate, it imparts a distinct yellow color to the alkaline solution, so that when a colorless solution results, it proves the absence of this element. Uranium in small quantity also gives a yellow color to the solution, which is noticeable with 1 or 2 mg.; a moderate amount (about 10 mg.) gives a red color, which is intense with still larger quantities. Alkaline solutions containing vanadium are colorless after boiling.

(11) This separation with NaOH, Na_2O_2, and Na_2CO_3 is a very satisfactory one, except in the case of zinc. This element, when present in small quantities, is completely carried down in the precipitate when much iron, nickel, or cobalt, or especially manganese, is present. Provision for the detection of zinc in the precipitate must therefore be made.

(12) If Na_2O_2 is not available, sodium hypobromite, NaBrO (prepared by mixing NaOH and bromine, as described in P. 70 N. 3), may be used as the oxidizing agent, but it is not quite so satisfactory as Na_2O_2, for it does not oxidize $Cr(OH)_3$ so readily, and it is apt to oxidize some of the manganese to $NaMnO_4$ (especially if there is not a sufficient excess of NaOH present).

***Procedure 52a.**—To detect rare earth elements, and to remove them, if present, transfer the acid solution (P. 52) to a platinum dish (after destroying HNO_3, if any has been added, by evaporating in porcelain once or twice with HCl (1.20)), and evaporate just to dryness. Add to the residue 45 per cent. HF solution, little by little, until the residue has been dissolved, or until about 25 cc. have been added, stirring with a platinum rod after each addition, and finally boiling gently under a hood for a minute or two if there is still a residue. Collect the residue on a filter supported on a platinum ring or in a celluloid funnel; collect the filtrate in a platinum dish; wash the residue thoroughly with water.

To the filtrate add 3–5 cc. HCl (1.20), and evaporate it just to dryness; add a little HCl and evaporate again, and repeat these operations a third time. Dissolve the residue in a little water, adding HCl if necessary; transfer to a casserole, and treat the solution by the last paragraph of P. 52, first evaporating with HNO_3 to destroy HCl if chromium, uranium and vanadium are to be tested for by *P. 58*a*–*e*.

Transfer the residue insoluble in HF to a platinum crucible; if the filter has been added, ignite to destroy it. Add 2–5 cc. H_2SO_4 (1.20), heat until sulphuric acid fumes are given off, cool, add 10–20 cc. water, heat and filter. Treat the precipitate (which can consist only of $CaSO_4$, $SrSO_4$ or $BaSO_4$) with concentrated Na_2CO_3 solution by P. 6. To the H_2SO_4 solution add ammonia until alkaline. (White precipitate, presence of *rare earth elements.*) Filter and test the filtrate for calcium and magnesium. Wash the precipitate thoroughly, dissolve it in a little HCl, evaporate just to dryness in a platinum dish, dissolve in a little water, and add 5–10 cc. HF. (White precipitate, presence of *rare-earth elements.*)

Notes.—(1) Among the so-called rare earth elements are included thorium, cerium, lanthanum, praesodymium, neodymium, yttrium, ytterbium, and a number of other similar elements. These elements, like the alkali earth elements, are characterized by the insolubility of their fluorides; but differ from the alkali earth elements in that their hydroxides are precipitated by ammonia, and that their sulphates are not precipitated by sulphuric acid. It is upon these facts that the separation described in the above procedure is based. If there is no residue after the treatment with HF, it shows of course that the rare earth elements are absent; if, on the other hand, there is a residue, it does not necessarily show their presence, except when it is known that alkaline earth elements cannot be present. (See P. 51, N. 6 and 7.) The further treatment described in the procedure serves to eliminate the latter.

(2) Owing to the fact that aluminum and chromium fluorides are somewhat difficultly soluble in HF, care must be taken to use a rather large quantity of this acid when a residue remains. It is also obvious that the fluoride residue must be thoroughly washed, if the formation of a precipitate with ammonia is to be considered a conclusive indication of rare earth elements. The final treatment of the NH_4OH precipitate is recommended to eliminate the possibility of error from these sources.

(3) The HF solution, which may contain all the elements of the aluminum and iron groups, is evaporated repeatedly with HCl to expel the HF, which is especially apt to be retained when titanium and zirconium are present.

The Aluminum Group.

Procedure 53.—Acidify the alkaline solution (P. 52) with HNO_3 (1.42), avoiding a large excess; add NH_4OH (0.96) until the mixture after shaking smells of it, and then add 2–3 cc. more. Heat almost to boiling in order to coagulate the precipitate, filter, and wash thoroughly with hot water. (White, flocculent precipitate, presence of *aluminum* (or **beryllium*); colorless solution, absence of *chromium.*) (Precipitate, P. 54, or to detect beryllium, *P. 58*g* and *h*; filtrate, P. 55.)

Notes.—(1) The alkaline solution is acidified with HNO_3, instead of with HCl, because the latter acid might reduce chromic acid, especially if a large quantity were added, or if the acid solution were heated. A moderate excess of NH_4OH must be added in order to keep the zinc in solution, which it does because of the production of $Zn(NH_3)_4{}^{++}(NO_3{}^{-})_2$; but a large excess is to be avoided, since it dissolves $Al(OH)_3$, owing to formation of $NH_4{}^{+}AlO_2{}^{-}$. The zinc is dissolved even when carbonate, phosphate, or oxalate is present.

(2) Since aluminum and silica are very likely to be present in the NaOH and Na_2O_2 used as reagents, and since they may be taken up from the dishes, a blank test for these impurities should be made whenever new reagents are employed for the first time, by following P. 52 and 53 and comparing the NH_4OH precipitate with that obtained in any regular analysis. It is also well at the same time to test for zinc by acidifying the NH_4OH solution with acetic acid and following P. 57.

Procedure 54.—Dissolve the precipitate (P. 53), or a small portion of it if it is large, in 5 cc. HNO_3 (1.20). From the appearance of the precipitate estimate the number of milligrams of aluminum which have been dissolved, and to the solution add about one-fourth as much cobalt as cobalt nitrate, using, however, not less than 0.2 mg. Evaporate almost to dryness in a casserole, add a drop or two of water, and soak up the solution in a small piece of filter-paper. Make a small roll of the paper, wind a platinum wire around it to form a spiral, and incinerate the paper in a small flame, finally heating the residue strongly. (Blue residue, presence of *aluminum.*)

Notes.—(1) This confirmatory test for aluminum should always be tried when the NH_4OH precipitate is small, for general reasons, inasmuch as the precipitation by NH_4OH of an element whose hydroxide is soluble in NaOH is not very characteristic (lead, antimony, tin, and beryllium showing a similar behavior), but also especially to guard against mistaking SiO_3H_2 for $Al(OH)_3$, for the former substance, if not entirely removed by proper dehydration in the process of the preparation of the solution (in P. 3, Part I), will appear at this point. A gelatinous precipitate which does not dissolve in HNO_3 indicates silica; it may be tested for by P. 5.

(2) The test described in this procedure depends upon the formation of a blue compound, whose formula is not definitely known; but it is doubtless a compound of the two oxides $CoO.xAl_2O_3$, and may be simply cobalt aluminate, $Co(AlO_2)_2$. It may be formed in various ways; but the process described in the procedure seems to be the most suitable one for making the test for aluminum reliable and delicate. It is of the utmost importance to have the aluminum present in excess; for, otherwise, the blue color is obscured by the black oxide of cobalt. In order that a small enough amount of cobalt may be added, it is convenient to use a very dilute solution of cobalt nitrate, say one that contains one-tenth of a milligram of cobalt per cubic centimeter.

(3) When the test is properly made, the ash retains the form in which the filter paper was rolled, and the whole mass, or a large part of it is colored blue. The presence of an equivalent amount of phosphate does not spoil the test. When sodium or potassium salts are also present, the ash fuses together, and the test is very unsatisfactory. For this reason the sodium salts present should be all washed out of the NH_4OH precipitate before dissolving it in HNO_3. No other element gives a blue color

to the ash, but certain elements, especially iron, obscure the test, so that it can be applied only after other elements have been removed in the regular process of analysis. 0.5 mg. Al may be easily detected, and even 0.2 mg. after a little practice.

(4) Another very good confirmatory test for aluminum consists in dissolving the NH_4OH precipitate in HCl (1.12), adding one and one-half volumes of ether, and saturating the mixture in the cold with HCl gas, as described in *P. 58 *g*. Under these conditions aluminum separates in the form of the crystalline compound $AlCl_3.6H_2O$; but no other element of the aluminum group is precipitated, except chromium, which if present in quantity greater than 10–20 mg. gives a violet precipitate. Moreover, silica does not interfere with this test. By this process, moreover, beryllium is quantitatively separated from aluminum, and may be tested for in the filtrate.

Procedure 55.—Acidify the NH_4OH solution (P. 53) with 30 per cent. acetic acid solution, avoiding an excess of more than 2 cc.

If the solution is colorless, treat it by P. 57.

If it is at all yellow, add about 10 cc. 10 per cent. $BaCl_2$ solution, allow the mixture to stand for at least five minutes and filter. (Yellow precipitate, presence of *chromium*.) (Precipitate, P. 56; filtrate, P. 57.)

Notes.—(1) The presence of less than 0.5 mg. chromium as chromate in a volume of 50 cc. makes the solution distinctly yellow, and the addition of $BaCl_2$ is therefore unnecessary when the solution is perfectly colorless. It is to be avoided, since $BaSO_4$ may be precipitated and has then to be removed by filtration. In doubtful cases the color of the solution should be compared with that of water. The color test is, of course, not delicate by artificial light.

(2) Since some sulphate may be present, the formation of a white precipitate with $BaCl_2$ does not prove the presence of chromium. Whether the precipitate is pure white or yellow should therefore be carefully noted. The yellow color of a small $BaCrO_4$ precipitate is most apparent when the precipitate has settled or when it has been collected on the filter. If there be sufficient sulphate present to obscure the yellow color of a little $BaCrO_4$, the confirmatory test for chromium described in the next procedure should be tried.

Procedure 56.—Pour repeatedly through the filter a 5–10 cc. portion of a mixture of 1 volume of HNO_3 (1.20) with 9 volumes of water; to the cold solution in a test-tube add about 2 cc. of ether and 1 cc. 3 per cent. H_2O_2, and shake. (Blue coloration of ether layer, presence of *chromium*.)

Notes.—(1) This blue compound which is formed by the action of H_2O_2 on chromic acid is one of the perchromic acids. It has the formula H_3CrO_7, and appears to be an addition product of H_2O_2 and a higher oxide of chromium. It is a very unstable substance; by its decomposition oxygen is evolved and the chromium is reduced to a chromic salt. Its decomposition is greatly accelerated by an excess of H_2O_2, by the presence of much acid, and by raising the temperature. It is therefore important not to add too much H_2O_2, and to use dilute acid, as directed in the procedure. If, in dissolving the precipitate, the filter be heated with HNO_3, the paper causes the chromate to be reduced to a chromic salt; but when the cold acid is merely poured through the filter this reduction does not take place. If a green solution should be obtained, the chromium must be reoxidized with Na_2O_2 in alkaline solution before making the test. Under proper conditions 0.2 mg. Cr may be detected, but the test may fail with a much larger amount if the directions are not followed.

Procedure 57.—Warm the acetic acid solution (P. 55 or *P. 58*f*) to 50° or 60°, saturate it in a small flask with H_2S, cork the flask and allow it to stand for five or ten minutes if no precipitate separates at once. (White flocculent precipitate, presence of *zinc.*) Filter through a double filter (two filters folded together), wash once with a little water. Reject the filtrate.

To confirm the presence of zinc, pour a 5–10 cc. portion of HNO_3 (1.20) two or three times through the filter containing the H_2S precipitate. To the solution add an amount of cobalt as cobalt nitrate equal to about one-fourth of the amount of zinc estimated to be present, using, however, not less than 0.2 mg. cobalt. Evaporate in a casserole almost to dryness to expel the acid, neutralize with 10 per cent. Na_2CO_3 solution, and add about 0.5 cc. in excess. Evaporate to dryness, ignite gently until the purple color due to the cobalt disappears, and allow the casserole to cool. (Green color, presence of *zinc.*)

Notes.—(1) ZnS precipitates more rapidly, and in a somewhat more flocculent form, from a warm solution. Very small quantities of zinc (less than 1 mg.) may be missed unless a short time be allowed for the precipitate to coagulate; but, since sulphur may then separate, the appearance of a white turbidity is not sufficient proof of the presence of zinc. The precipitate may be allowed to settle, in order that the amount of zinc present may be better estimated. A double filter is used, since the ZnS is apt to pass through the filter.

(2) The immediate formation of a white flocculent precipitate with H_2S in acetic acid solution is so characteristic as to be a sufficient test for zinc. Manganese is the only other element of this group that forms a light colored sulphide; and this, owing to its greater solubility in water, does not precipitate from an acetic acid solution. The confirmatory test described in the last paragraph of the procedure is, however, useful when only a small non-coagulating precipitate, which may be sulphur, results, or when owing to the presence of a small quantity of other elements the precipitate is dark colored.

(3) The green compound obtained in the confirmatory test is doubtless a compound of cobalt and zinc oxides, perhaps cobalt zincate $CoZnO_2$. The conditions under which the zinc and aluminum compounds of cobalt are formed are very different. As we have seen, the aluminum compound is formed only at very high temperatures, and the test is not at all delicate in the presence of a salt of an alkali-element. On the other hand, the zinc compound is obtained at comparatively low temperatures, and the presence of an alkali is essential. Excess of cobalt must, of course, be avoided, for the black cobalt oxide completely obscures the green color. A larger proportion of cobalt than is recommended in the procedure may be added without danger, but the test is very satisfactory even when a large excess of zinc is present.

***Procedure 58a.**—To the filtrate from the Na_2O_2 precipitate (P. 52), add HNO_3 (1.20), keeping the solution cool, until it reacts slightly acid and any precipitate just redissolves upon shaking. (See note 1.) Dilute the solution to 100 cc. and transfer it to a strong 200 cc. bottle. Add solid $NaHCO_3$, a little at a time, until the mixture after shaking no longer turns blue litmus paper red at once; finally add 1.0–1.5 grams solid $NaHCO_3$ (weighed out roughly). Close the bottle with a tightly fitting cork, wire it in, wrap a cloth around the bottle, place it in a vessel of warm water, and boil the water gently for twenty or thirty minutes. Cool the bottle to at least 50° (best by slowly adding cold water to the bath), remove the cork, filter at once, and wash, using suction if the precipitate is large. (Filtrate, *P. 58*b*; precipitate, *P. 58*f*.)

Notes.—(1) If up to this point in the analysis there has been no indication of any of the elements that are to be tested for in the alkaline solution, time may often be saved by determining before treating with $NaHCO_3$ whether any of them are present by proceeding as follows: to one-fourth of the solution, which has been acidified with HNO_3, add NH_4OH (0.96) in small excess, note whether a precipitate forms, and then add a few drops of $(NH_4)_2S$ solution. Even if there is no precipitate, vanadium may be present; to test for this, add 3 cc. NH_4OH (0.90) and completely saturate with H_2S. (See *P. 51*a*.) If the results of these tests show that any of these elements are present, treat the remainder of the HNO_3 solution by the regular procedure. If, on the other hand, the results are negative, no further treatment is necessary.

(2) The alkaline solution is kept cold during the neutralization and an excess of HNO_3 is avoided because chromate in the presence of H_2O_2 and an acid is rapidly reduced to a chromic salt, especially when the solution is hot. This reduction, if complete, would prevent the detection of chromium in the subsequent test. H_2O_2 will, to be sure, not be present, since Na_2O_2 is very rapidly destroyed by the boiling of the alkaline solution in P. 52, except when uranium is also present; in this case the peruranate which is formed by the treatment with Na_2O_2 is not decomposed upon boiling, but breaks up into a uranyl salt and H_2O_2 upon acidification.

(3) The success of this separation depends upon securing the proper concentration of the $NaHCO_3$. Since the $NaHCO_3$ may be at first used up in precipitating zinc, aluminum, and beryllium as well as in neutralizing the free acid, the weighed amount of $NaHCO_3$ is added only after the solution ceases to react distinctly acid. A much larger concentration of $NaHCO_3$ than 1.0 to 1.5 per cent. would not prevent the complete precipitation of zinc or of aluminum, but it would interfere with that of beryllium. Thus with a volume of 100 cc. the precipitation of the beryllium is complete when the concentration of the $NaHCO_3$ is 1 per cent., and 1 mg. can usually be detected when it is 2 per cent., but 3 mg. remain dissolved in a 3 per cent. solution, about 15 mg. in a 5 per cent. solution, and about 150 mg. in a 10 per cent. solution. A smaller concentration of $NaHCO_3$ and a smaller volume than 100 cc. are avoided, in order to prevent as far as possible the precipitation of uranyl vanadate, which may otherwise occur when large quantities of uranium and vanadium (about 100 mg. of each) are simultaneously present. The presence of phosphate or oxalate (or chromate) does not cause the precipitation of uranium, nor otherwise interfere with the analysis. When only small amounts of the elements of this group are present, the separation can be made in a smaller volume, care being taken that the concentration of the $NaHCO_3$ rather than the quantity taken be that prescribed.

(4) If it is desired, the separation may be made in an open flask; but in this case the solution must not be boiled and the $NaHCO_3$ solution should not be stronger than 1 per cent. The process is then best carried out by digesting the mixture on a water bath for 20 to 30 minutes in a flask covered with a watch glass. Under these condi-

tions neither zinc nor beryllium dissolve in significant quantity; but one to two milligrams of aluminum may be completely dissolved. The mixture must not be boiled, for a larger amount of aluminum may then dissolve (as much as five milligrams on one minute's boiling).

(5) When a large amount of aluminum or beryllium is present, two to five milligrams of uranium may be carried down almost completely in the $NaHCO_3$ precipitate, so that in this case uranium has to be tested for in the analysis of the precipitate.

(6) In a dilute solution of $Na^+HCO_3^-$ saturated with CO_2, the hydrogen ion and hydroxyl ion concentrations are both very small and are nearly the same as in pure water. AlO_3H_3, basic $BeCO_3$ and $ZnCO_3$ are completely precipitated because the solubility of these substances is not much increased through removal of the OH^- or $CO_3^{=}$ by combination with H^+ with formation of H_2O or HCO_3^- (leaving the cathions Al^{+++}, Be^{++} or Zn^{++} in the solution). or through removal of the metal ions by combination with the OH^- with the formation of AlO_2^-, $BeO_2^{=}$ or $ZnO_2^{=}$. The higher hydroxides of chromium, and vanadium (chromic and vanadic acids) are soluble polybasic acids, which are so much more highly ionized than H_2CO_3 that they displace it from its salt $NaHCO_3$, forming mainly sodium hydrogen chromate or vanadate. The fact that uranium is not precipitated, even though $Na_2U_2O_7$ is difficultly soluble, may be due to the formation of a complex sodium uranyl carbonate.

***Procedure 58b.**—To the $NaHCO_3$ filtrate add HNO_3 (1.20) until the solution is distinctly acid, avoiding an excess of more than 1 cc. (Colorless solution, absence of *chromium.*) Unless the solution is as colorless as pure water, test one-fourth of it for chromium by adding to the cold solution in a test-tube 2 cc. ether and 0.5–1.0 cc. 3 per cent. H_2O_2 solution. (Blue coloration of the ether layer, presence of *chromium.*) To this mixture add about 5 cc. HNO_3 (1.42). (Red coloration of water layer, presence of *vanadium.*)

If chromium is not present, treat the HNO_3 solution or the part of it not tested with H_2O_2 by *P. 58*c.*

If chromium is present, exactly neutralize the remainder of the HNO_3 solution with NaOH, add 2 cc. HNO_3 (1.20) and then 20 cc. 20 per cent. $Pb(NO_3)_2$ solution; allow the mixture to stand for fifteen to twenty minutes, and filter. (Yellow precipitate, presence of *chromium.*) Saturate the filtrate with H_2S, filter off and reject the precipitate; boil the filtrate for two or three minutes to expel H_2S and to coagulate any sulphur that may separate; filter off and reject the precipitate. In order to oxidize vanadyl salts to vanadate, add bromine water (or if much is required, liquid bromine) until the solution has a permanent reddish color. Boil in a casserole until the bromine is expelled and treat the solution by *P. 58*c.*

Notes.—(1) The $NaHCO_3$ filtrate should not be heated after acidifying because some H_2O_2 may still be present (even though most of it is decomposed in the heating with $NaHCO_3$), which would cause the reduction of chromate, and might thus prevent the detection of even several milligrams of chromium. (See *P. 58*a*, N. 2.)

(2) It is desirable to determine in advance, by making a preliminary test if neces

sary, whether or not chromium is present, for, if it is absent, the addition of the lead salt, and the subsequent removal of the lead with H_2S may be omitted. If lead be added, its removal is necessary before the tests for uranium and vanadium can be made. If the acid solution is perfectly colorless, an amount of chromium exceeding 0.5 milligram may safely be pronounced absent. Uranium and especially vanadium in moderate quantity (20 to 50 mg.) also give yellow solutions. A yellow solution is therefore tested for chromate with H_2O_2. In regard to this test, see P 56, N. 1. The test can be made in only a small portion (one-fourth) of the solution, for it is so delicate that the presence of 0.1 milligram chromium in this portion can be detected. The portion in which the test is made is rejected, because chromium, if present, is reduced to the chromic state by the H_2O_2 in the acid solution, and would therefore not be precipitated by the lead nitrate.

(3) When vanadium is present even in moderately small quantity, the water layer, on the addition of H_2O_2, becomes orange-yellow to orange-red in color, owing to the formation of pervanadic acid. This test for vanadium becomes more delicate when the solution is made strongly acid as is directed; a distinct color is then obtained even when only 0.5 mg. vanadium is present in the portion tested, corresponding to about 2 mg. in the whole solution. (Compare *P. 51*a*, N. 4.) The test is not essential since vanadium is always tested for later; it is introduced here, where it can be made in a moment's time, as an additional confirmation of the presence or absence of that element.

(4) The separation of chromium from vanadium and uranium by $Pb(NO_3)_2$ depends on the relatively small solubility of lead chromate in dilute HNO_3 in the presence of a large quantity of $Pb(NO_3)_2$. Under the conditions described in the procedure, over 100 mg. of vanadium yield no precipitate and only 0.1 to 0.3 mg. of chromium usually remains in solution, though this amount is somewhat increased when a very large quantity of $NaNO_3$ has been introduced. To secure these results, however, care must be taken to use the prescribed quantities of HNO_3 and $Pb(NO_3)_2$, for lead vanadate is also a difficultly soluble substance, and would be quantitatively precipitated in the presence of a much weaker acid, such as acetic acid in the presence of ammonium acetate. Lead uranate would also be precipitated from a neutral or slightly alkaline solution.

(5) The presence of much chloride or sulphate would cause the precipitation of white $PbCl_2$ or $PbSO_4$, which might obscure the yellow color of a small quantity of $PbCrO_4$ and prevent the estimation of the amount of chromium present. These anions will, however, not be present in harmful quantity, if in dissolving the original $(NH_4)_2S$ precipitate (P. 51) the acids are used in the way prescribed, and if in acidifying the solutions in *P. 58*a* and *b*, HNO_3 and not HCl is used, as directed.

(6) The lead which is added to precipitate the chromate must be removed before testing for uranium with Na_2HPO_4 (in *P. 58*c*), since it would give a precipitate of $Pb_3(PO_4)_2$. It is precipitated with H_2S, rather than with $(NH_4)_2SO_4$, because in the latter case enough lead (about 1 mg.) still remains in solution to give a precipitate with Na_2HPO_4.

(7) By the H_2S, vanadic acid is reduced to vanadyl nitrate $VO(NO_3)_2$ slowly in the cold but more rapidly on heating the solution, so that sulphur may be precipitated on boiling the filtrate to expel H_2S. This must be re-oxidized to vanadic acid, for otherwise vanadyl ammonium phosphate would be precipitated with the uranium phosphate in *P. 58*c*. The oxidation by bromine does not take place instantaneously; and a considerable excess of bromine must therefore be used, and the mixture allowed to stand for a few minutes.

***Procedure 58c.**—Make the solution obtained in *P. 58*b* neutral with NH_4OH, add 5 cc. 30 per cent. acetic acid, 1–2 grams solid $(NH_4)_2SO_4$ (or NH_4NO_3), and then 2 grams solid $Na_2HPO_4.12H_2O$, and heat to boiling. (White precipitate, presence of *uranium.*) Allow the mixture to stand ten to fifteen minutes to coagulate the precipitate, filter, and wash the precipitate with a 5–10 per cent. solution of $(NH_4)_2SO_4$ (or NH_4NO_3). (Precipitate, *P. 58*d*; filtrate, *P. 58*e.*)

Notes.—(1) The precipitation of white uranyl ammonium phosphate, $UO_2NH_4PO_4$, is a delicate test provided the solution be made only moderately acid with acetic acid and a sufficient excess of Na_2HPO_4 be added. The separation from vanadium as vanadic acid is a very satisfactory one; for vanadium, even when present in large quantity (100 mg.), does not precipitate, nor is a small quantity carried down by uranium; on the other hand 0.5 mg. uranium gives a distinct precipitate. The test is a somewhat more delicate one if made in a smaller volume, say 40 cc.; in this case the same quantities of reagents may still be used, and the separation is perfectly satisfactory.

(2) The formation of a precipitate at this point is not sufficient evidence of the presence of uranium, for aluminum, beryllium, and lead will separate as phosphates if they have not been completely removed in previous procedures, and vanadium will precipitate as vanadyl ammonium phosphate if the oxidation by bromine was incomplete. On the other hand a slight turbidity may correspond to an appreciable amount of uranium (0.2 to 0.5 mg.). Therefore the confirmatory test for uranium (*P. 58*d*) should always be tried.

(3) When the solution is made alkaline with NH_4OH a pale yellow precipitate of uranyl ammonium vanadate may separate, and may not dissolve when the acetic acid is added. This, however, has no effect on the separation, since, on boiling, it is converted into the less soluble uranyl ammonium phosphate and vanadic acid.

(4) In the absence of ammonium salts uranium is precipitated as uranyl hydrogen phosphate, UO_2HPO_4, which often separates as a very finely divided precipitate that runs through the filter. The ammonium salt is added to cause the uranium to precipitate as uranyl ammonium phosphate, which coagulates and filters more readily.

***Procedure 58d.**—Dissolve the Na_2HPO_4 precipitate (*P. 58*c*) by pouring a small portion of hot HCl (1.12) repeatedly through the filter, evaporate the solution nearly to dryness, add about 10 cc. nearly saturated NaCl solution, pour into a test-tube, cool, and add 5 cc. 10 per cent. $K_4Fe(CN)_6$ solution. (Dark red precipitate or coloration, presence of *uranium.*)

Notes.—(1) The precipitation of the dark red uranyl ferrocyanide $(UO_2)_2Fe(CN)_6$ is a very characteristic and also a very delicate test for uranium, provided care be taken to avoid any excess of acid. The solution must, however, be distinctly acid, for otherwise the precipitate may not form, owing to the small concentration of the uranyl ion, UO_2^{++}. Uranyl ferrocyanide tends to form a colloidal solution, but the presence of NaCl and HCl soon causes it to coagulate.

Procedure 58e.—Neutralize the filtrate from the Na_2HPO_4 precipitate (*P. 58*c*) with NH_4OH (0.90) and add at least 5 cc. more. Saturate the solution completely with H_2S by passing the gas through it in a small flask for ten or fifteen minutes. (Pink or violet red color, presence of *vanadium.*) Pour the solution through a filter; make it distinctly acid with acetic acid (or HCl) and heat nearly to boiling. (Dark precipitate, presence of *vanadium.*)

Notes.—(1) In regard to the formation of the sulphovanadate of vanadium in the strongly alkaline solution, the partial precipitation of vanadium sulphide on acidifying, and the action of H_2O_2 on vanadic acid, see the Notes on *P. 51*a*.

***Procedure 58f.**—Heat the $NaHCO_3$ precipitate (*P. 58*a*) with 10–30 cc. HCl (1.06) in a casserole, or dissolve it by pouring the acid two or three times through the filter, boil the solution to expel CO_2, add NH_4OH (0.96) until the solution after shaking smells of it and then 2–3 cc. in excess. Heat the mixture nearly to boiling, filter and wash the precipitate, using suction if it seems desirable. (Precipitate, *P. 58g; filtrate, acidify with acetic acid and test for zinc by P. 57.)

Notes.—(1) The zinc remains in the ammoniacal filtrate as a complex ammonia salt, chiefly $Zn(NH_3)_4^{++}Cl_2^{-}$. Aluminum and beryllium are precipitated as hydroxides. The precipitate will also contain any uranyl vanadate that was precipitated in the $NaHCO_3$ separation.

***Procedure 58g.**—Dissolve the NH_4OH precipitate (*P. 58*f*) by pouring a hot 5–15 cc. portion of HCl (1.12) repeatedly through the filter, using another portion of acid, if necessary. Add a volume of ether equal to one and a half times that of the solution. Pass into the mixture in a small flask HCl gas until a single layer results, and until fumes of HCl are copiously evolved, cooling the flask in running water during the progress. Cover the flask and let the mixture stand for fifteen minutes even if no precipitate has separated. (White crystalline precipitate, presence of *aluminum.*) Filter through an asbestos filter (see P. 61) or an ordinary filter supported by a small hardened filter folded with it, after first moistening the filter with a mixture of two volumes of HCl (1.20) and three of ether previously saturated with HCl gas; wash the precipitate once with this mixture. During the filtration and washing keep the funnel covered with a watch glass to prevent evaporation of the ether. (Precipitate, P. 54 to confirm the presence of aluminum; filtrate, *P. 58*h*.)

Notes.—(1) Aluminum chloride, $AlCl_3.6H_2O$, is only slightly soluble in concentrated HCl solutions and the precipitate is complete when ether is added and the mixture saturated with HCl. 0.5 mg. of aluminum can be easily detected in 30 cc. The test is therefore a delicate one. It is also very characteristic; for no other elements of the aluminum group is precipitated by this treatment, except chromium when it is present in moderate quantity.

(2) The ethereal solution of HCl, unlike the concentrated aqueous solution, does not disintegrate filter-paper rapidly, and the filtration can almost always be made with an ordinary filter supported by means of a hardened filter. This filtration is apt to be slow, and it is often advantageous to filter through asbestos with the help of suction.

(3) When the NH_4OH precipitate is small (corresponding to less than 30 mg. Al), it need not be treated by this procedure, but it may be dissolved in a little HCl, and treated directly by *P. 58*h*.

***Procedure 58h.**—Evaporate the filtrate from the HCl precipitate (*P. 58*g*), first on a water-bath under a hood until the ether is expelled, and then over a flame, almost to dryness until nearly all the HCl is expelled; add a little water, make alkaline with NH_4OH, avoiding a large excess, and heat nearly to boiling. (No precipitate, absence of *beryllium.*)

If there is a precipitate, dilute to 30 cc., add enough solid $NaHCO_3$ to make a 10 per cent. solution, heat to boiling, boil for one minute, cool, pass in H_2S for a few seconds, and filter after a few minutes if there is a precipitate. Acidify the filtrate with HCl, boil for two or three minutes to expel CO_2, make the solution alkaline with NH_4OH, and heat nearly to boiling. (White flocculent precipitate, presence of *beryllium*, yellow precipitate, presence of *uranium.*)

Treat this precipitate or a portion of it corresponding to about 20 mg. of beryllium by *P. 58*d.* (Dark red precipitate, presence of *uranium.*) Filter and to the filtrate add NH_4OH. (White precipitate, presence of *beryllium.*)

Notes.—(1) The filtrate from the HCl precipitate may contain besides beryllium, uranium or vanadium (carried down in the treatment with dilute $NaHCO_3$ in *P. 58*a*), aluminum (if care was not taken in precipitating and filtering aluminum chloride), and a little iron (introduced from the reagents). This solution is first tested with NH_4OH to determine if any further treatment is necessary. The treatment with the hot concentrated $NaHCO_3$ solution serves to precipitate the aluminum completely and to dissolve the beryllium and uranium. This method of separation of aluminum and beryllium is a satisfactory one, when, as in the present case, only a small amount of aluminum is present; a large quantity of aluminum, however, retains almost completely a small quantity of beryllium. The $NaHCO_3$ solution must not be boiled for a long time, because, owing to the escape of CO_2 and the formation of free NaOH, the solution becomes alkaline enough to dissolve some aluminum. The reason for the great solubility of beryllium hydroxide in concentrated $NaHCO_3$ solutions is not known. H_2S is passed in to remove the iron, since a small amount of it remains dissolved in the concentrated $NaHCO_3$ solution; the filtrate is sometimes dark green even after repeated filtration, due to the presence of colloidal iron sulphide; to precipitate this, add a small amount of a ferrous salt (say 2 to 4 mg. Fe), shake, allow the mixture to stand several minutes, and then filter, finally passing more H_2S into the filtrate to make sure that the iron has been all removed.

(2) The treatment with $K_4Fe(CN)_6$ described in *P. 58*d* gives a satisfactory separation of beryllium from uranium (and vanadium) provided the amount of beryllium in the solution does not exceed 20 milligrams. When more beryllium is present a gelatinous precipitate separates; on this account it is directed to use only a portion of the NH_4OH precipitate when it is large, but even in this case a small amount of uranium can still be detected, owing to the delicacy of the ferrocyanide test. Vanadium, if present owing to its having been precipitated as uranyl vanadate in the treatment with dilute $NaHCO_3$ (*P. 58*a*), remains with uranium and is precipitated as greenish yellow vanadyl ferrocyanide, but does not obscure the dark red color of the uranium precipitate. It is not necessary to provide for the detection of vanadium at this point, since a large quantity always dissolves in the $NaHCO_3$ treatment.

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Procedure 61.—Transfer the Na_2O_2 precipitate (P. 52) to a casserole together with the filter if necessary, add 5–30 cc. HCl (1.12), boil gently till the precipitate is dissolved, filter to remove the paper, and evaporate the filtrate to 1 or 2 cc. To decompose the HCl add about 5 cc. HNO_3 (1.42), and boil as long as oxides of nitrogen are given off. Add 5–20 cc. HNO_3 (1.42), heat to boiling, add about 0.5 gram of solid $KClO_3$ and boil gently, adding more $KClO_3$ in small portions if a large precipitate forms. (Dark brown or black precipitate, presence of *manganese.*) Boil gently for a minute or two, and filter through an asbestos filter, made by pouring a suspension of washed asbestos over a compact wad of glass wool in a glass funnel. (See note 4.) Heat the filtrate to boiling, add more $KClO_3$, boil, and filter through the same filter if more of the precipitate separates. Wash two or three times with HNO_3 (1.42) which has previously been freed from the oxides of nitrogen by warming with a little $KClO_3$. Evaporate the filtrate to about 5 cc., but not further, dilute to 20 or 30 cc., and filter the solution if it is turbid. (Precipitate, P. 62; filtrate, P. 63).

Notes.—(1) HCl is used for dissolving the Na_2O_2 precipitate rather than HNO_3. Pure concentrated HNO_3 does not dissolve hydrated MnO_2 except in the presence of filter paper, whereby the HNO_3 is reduced to lower oxides; the action is more rapid with HCl (for the MnO_2 is thereby quickly reduced to manganous chloride with evolution of chlorine.)

(2) By $HClO_3$ in HNO_3 solution (but not by HNO_3 alone) manganous salts are rapidly oxidized to hydrated MnO_2 with formation of chlorine dioxide (ClO_2), which escapes as a yellow gas. The HCl must previously be completely removed by evaporation and boiling with HNO_3, since the oxides of nitrogen resulting from its action on the HNO_3 would continuously dissolve the precipitate.

(3) The separation of manganese in this way from the other metals of this group is entirely satisfactory with the following exceptions. A small quantity of iron (up to 1 mg.) may be completely carried down with a large quantity (500 mg.) of manganese. The same is true in a much higher degree of titanium, of which even 50 mg. may be entirely precipitated with 500 mg. of manganese. Much zirconium is also carried down, but never quite completely. Provision is therefore made (in *P. 62*a*) for the detection of these three elements in the precipitate (if it is large) as well as in the filtrate. If it is not thought necessary to test for zirconium in the precipitate, the certain detection of titanium can be much more quickly accomplished just before precipitating the manganese, by diluting the HNO_3 solution, from which the HCl has been removed, with once or twice its volume of water, and adding 3 cc. of 3 per cent. H_2O_2 solution. An orange-yellow or orange-red color shows the presence of titanium. (See *P. 65*b*, N. 1.) In the absence of HCl iron does not interfere with this test, nor does even a large quantity of nickel or cobalt prevent a distinct change of color from being seen.

(4) In filtering the MnO_2 a cylindrical glass funnel with a small delivery tube is usually employed in quantitative analysis. An ordinary conical funnel is, however, satisfactory, provided the wad of glass wool is made compact and enough asbestos

is used. Filtration will, to be sure, be slow if the glass wool is packed very tightly or if the asbestos mat is very thick, but in that case suction may be applied.

(5) On evaporating the HNO_3 filtrate, titanium and zirconium oxides may separate out, especially if the solution be evaporated almost to dryness. For this reason the solution is evaporated only to about 5 cc., but even then a small white precipitate will sometimes be obtained when these elements are present in large amount.

Procedure 62.—Transfer the whole of the $HClO_3$ precipitate (P. 61) if it is small (containing less than 5 mg. Mn), or 5–10 mg. of it if it is large, to a casserole; add 1 or 2 grams solid PbO_2, and about 10 cc. HNO_3 (1.20); boil for about two minutes in a casserole covered with a watch glass; pour the mixture into a test-tube, and allow the PbO_2 to settle. (Violet red solution, presence of *manganese.*)

If the precipitate is large, dissolve the remainder in hot HCl (1.12) in a casserole, or by pouring a 10–15 cc. portion repeatedly through the filter, and boil the solution to expel chlorine. To one-tenth of this solution add 5 cc. KCNS solution. (Deep red color, presence of *iron.*) Treat the remainder of the HCl solution by *P. 62*a* to recover any titanium and zirconium that may be present.

Notes.—(1) This confirmatory test for manganese is usually superfluous since the precipitation of MnO_2 by $HClO_3$ is highly characteristic. In order that the PbO_2 test may be satisfactory, the HNO_3 used must be fairly concentrated and the boiling continued for two or three minutes.

***Procedure 62a.**—To the HCl solution (P. 62), without evaporating it, add NH_4OH (0.96) until the mixture is barely alkaline, avoiding the addition of more than two or three drops in excess; heat nearly to boiling for two or three minutes, filter at once, and wash with hot water. Reject the filtrate. Dissolve the precipitate in a little hot HCl (1.12) (without diluting it with water), reserve it, and unite it with the main HCl solution to be treated in *P. 65*a*.

Notes.—(1) In order to avoid as far as possible the precipitation of manganese by NH_4OH, the OH^- concentration is kept small by avoiding an excess of NH_4OH and by having a large quantity of ammonium salt present. Under these conditions the oxidation by the air to the manganic state is slow. If, however, much NH_4OH be added, oxidation takes place rapidly and much manganese may be precipitated as $Mn(OH)_3$, yielding a brown precipitate. Even at best a little manganese will come down, but a moderate amount does not interfere with the subsequent tests for titanium and zirconium.

Procedure 63.—Add about one-tenth of the HNO_3 solution (P. 61) to three or four times its volume of ammonium molybdate reagent, and heat to 60–70°. (Yellow, finely crystalline precipitate, presence of *phosphate.*) If there is no precipitate, or only a very small one, treat the remainder of the HNO_3 solution by P. 64; otherwise by P. 65.

Notes.—(1) Phosphate is tested for at this point because a different treatment is necessary when it is present in significant amount, in order to separate from it alkaline-earth elements and to provide for their detection. When phosphate is not present, iron, thallium, titanium, and zirconium can be separated from nickel, cobalt, and the alkaline-earth elements by NH_4OH (as in P 64); but, when considerable phosphate is present, the alkaline-earth elements would be partly or wholly precipitated in combination with it. (See P. 51, N. 6.)

(2) In order that the phosphate test may be delicate and may appear immediately, a large proportion of the molybdate reagent must be used and the solution must be warmed. The precipitate of ammonium phosphomolybdate is of complicated and somewhat variable composition; it contains ammonium phosphate and molybdic acid, approximately in the proportion $(NH_4)_3PO_4:12MoO_3$.

Procedure 64.—If phosphate is absent, make the HNO_3 solution (P. 62) strongly alkaline with NH_4OH (0.96) using an excess of 3–5 cc. (Dark red precipitate, presence of *iron.*) Filter, and wash the precipitate, using suction if the precipitate is large, and sucking it as dry as possible.

Treat the filtrate by P. 66.

Dissolve the precipitate in HCl (1.12), warming if necessary, taking care not to dilute the acid by wash water. To about one-tenth of the solution add 5 cc. KCNS solution. (Dark red color, presence of *iron.*) *Treat the remainder of the solution by *P. 65*a*.

Notes.—(1) If titanium and zirconium are to be tested for, it is important to dissolve the NH_4OH precipitate in HCl of a specific gravity 1.12 (24 per cent. HCl) and to avoid dilution, for the separation in *P. 65*a* depends on the concentration of the HCl.

(2) The red color obtained on adding KCNS is due to the formation of un-ionized ferric thiocyanate, $Fe(CNS)_3$. This test may be made in the presence of much HCl, for the acid HCNS is also a highly dissociated acid, which is therefore not displaced from its salt. Much HNO_3 must not, however, be present; for, by its action on KCNS, NO_2 may be formed and this also gives a deep red color with KCNS. This test for iron is an extremely delicate one; and if only a faint color is obtained, the acids used in the process must be tested for iron.

Procedure 65.—When phosphate is present, test one-tenth of the HNO_3 solution (P. 63) for iron, by evaporating it just to dryness, adding 1–2 cc. HCl (1.20), evaporating again to decompose the HNO_3, diluting to 5 or 10 cc. and adding 5 cc. KCNS solution. (Permanent red color presence of *iron.*) To the remainder of the solution add NH_4OH (0.96) until the precipitate formed by the last drop does not redissolve on shaking. If, owing to the addition of too much NH_4OH the solution becomes alkaline or a large precipitate separates, make it distinctly acid with acetic acid. Add 5 cc. of a 50 per cent. solution of ammonium acetate, and, unless the mixture is already of a brownish red color, add 10 per cent. $FeCl_3$ solution drop by drop until such a color is produced. Add enough water to make the volume about 100 cc., boil in a 250 cc. flask for five minutes, adding more water if a very large precipitate separates, and let the mixture stand for a minute or two. Filter while still hot, and wash with hot water. Add 3–5 cc. more ammonium acetate solution to the filtrate, boil it again, and collect on a separate filter any further precipitate. Make the filtrate alkaline with NH_4OH, adding an excess of 2–3 cc., filter off and wash any precipitate, uniting it with the main precipitate. (Filtrate, P. 66; precipitate, reject or dissolve in hot HCl (1.12), and treat by *P. 65*a*.)

Notes.—(1) With regard to the test for iron with KCNS and the necessity of removing the HNO_3, see P. 64, N. 2.

(2) This method of separation depends on the facts that, upon boiling an acetic acid solution containing much acetate, ferric iron and titanium are completely precipitated, and thallic thallium and zirconium nearly so, in the form of a basic acetate or hydroxide; and that all the phosphate present combines with these elements when they are present in excess, and therefore it then passes completely into the precipitate, leaving the bivalent elements in solution. This behavior of the phosphate is due to the fact that the solubility in acids of the phosphates of the trivalent and quadrivalent elements is much smaller than that of the phosphates of the bivalent elements.

(3) If upon adding the ammonium acetate the solution becomes of a reddish color, it shows that iron is present in quantity more than sufficient to combine with the phosphate; for a cold solution containing ferric acetate is of a deep red color. If, on the other hand, a colorless solution results (either with or without a precipitate), it shows that there is no excess of iron, and $FeCl_3$ is therefore added, which causes the precipitation of $FePO_4$ as a yellowish white precipitate. Upon boiling, the excess of iron separates completely as a dark red gelatinous precipitate of basic ferric acetate, leaving the supernatant liquid colorless, except when nickel or cobalt is present.

(4) The solution is diluted to at least 100 cc., owing to the large volume of the precipitate, and it must be heated in a capacious flask owing to its tendency to boil over.

(*5) Zirconium may not be completely precipitated under the conditions of this procedure, 1–5 mg. sometimes remaining in solution, especially when considerable acetic acid is present. To ensure its complete separation, the filtrate is made alkaline with NH_4OH.

(*6) The precipitation of thallium in this procedure is not quite complete, but there is no danger of losing even 0.5 of a milligram when iron is also present, as is always the case.

***Procedure 65a.**—To the HCl solution (P. 64 or 65, and *62*a*) which should be of specific gravity of 1.11–1.12, add 10–20 cc. more HCl (1.12), transfer the (cold) solution to a separating funnel, add an equal volume of ether, shake vigorously several times (preferably after inverting the funnel and opening the cock), and then allow the two layers to separate. Draw off the layers separately, and rinse out the funnel with a little ether. Return the aqueous layer to the funnel and treat it with ether as before; if necessary, repeat this treatment once or twice until the ether layer remains colorless. (Water solution, *P. 65*b*; first ether solution, *P. 65*d*; remaining ether solutions, reject.)

Notes.—(1) If the directions are followed, 97 to 99 per cent. of the $FeCl_3$ present passes into the ether layer in each extraction. It is evident from this statement, that even when 500 mg. of iron are present, substantially all of it will be removed in three extractions. But it is important that the concentration of the HCl solution in contact with the ether layer lie within the narrow limits of 20 to 22 per cent. HCl, corresponding to a specific gravity of 1.10 to 1.11 at 15°. This concentration is realized in the procedure, even though a little stronger acid is used, for some of the HCl passes into the ether layer. The extraction of the $FeCl_3$ is less complete both with stronger and weaker HCl solutions; thus with HCl containing initially either 18 or 25 per cent. about 94 per cent. of the $FeCl_3$ passes into the ether layer; while with 8 per cent. HCl only 4 or 5 per cent. of the $FeCl_3$ was extracted in each shaking. Almost all the thallium, which is present as $TlCl_3$, also passes into the first ether extract.

(2) The following are probably the principles involved in this ether extraction. Since iron passes into the ether layer only in the form of $FeCl_3$, the quantity of it extracted by the ether increases, in accordance with the distribution law, the larger the proportion of un-ionized anhydrous $FeCl_3$ in the water layer. This proportion is, however, increased by increasing the concentration of HCl both in virtue of the reduction of the ionization by the common-ion effect and of the reduction of the hydrolysis of the ferric salt by the free acid. It is doubtless true that the strong acid has also a dehydrating effect, thereby increasing the anhydrous $FeCl_3$ in the water layer. As the HCl becomes very concentrated, however, another effect, opposite in character, comes into play; namely ether dissolves in large quantities in the aqueous layer, and HCl and water dissolve in large quantity in the ether layer, thus making the two layers more nearly alike, and doubtless decreasing the distribution-ratio for the $FeCl_3$ between the ether and water layers. With respect to this explanation, it should be added that it is uncertain to what extent complex acids ($HFeCl_4$, etc.) may be involved.

(3) Since the color of the ether layer is a sensitive indication of iron, the treatment with ether may be discontinued as soon as a nearly colorless ether extract is obtained. When titanium is present the water layer may remain distinctly yellow, owing to the presence of hydrogen peroxide as impurity in the ether; such a color does not, therefore, show that iron is still present.

(4) Titanium and zirconium remain completely in the water layer. When much zirconium is present some of it may be precipitated out, as chloride; but this remains suspended in the water layer.

(5) Phosphoric acid does not interfere with this separation, and the iron can therefore be extracted even after the basic acetate procedure.

***Procedure 65b**.—Heat the HCl solution (*P. 65*a*) on a waterbath until the ether is expelled, add 1 cc. H_2SO_4 (1.20), evaporate almost to dryness until the H_2SO_4 begins to fume, adding 1 cc. more H_2SO_4 (1.20) if the residue is solid. If the residue is dark colored, owing to organic matter, add a few drops HNO_3 (1.42) and evaporate again until the H_2SO_4 begins to fume. Cool, add 5 cc. water, 10 cc. 3 per cent. H_2O_2 solution, and then 10 cc. 10 per cent. $Na_2HPO_4.12H_2O$ solution. (Orange-yellow to orange-red solution, presence of *titanium;* white, flocculent precipitate, presence of *zirconium.*) Let the mixture stand for at least an hour, filter, and wash the precipitate. (Filtrate, if colored, *P. 65*c*; precipitate, note 3.)

Notes.—(1) By the addition of H_2O_2 titanium is converted into a sulphate corresponding to the higher oxide TiO_3, the red color being due to the cathion. This color test is an extremely delicate one, even 0.1 mg. Ti imparting a distinct, yellow color to the solution.

(2) By the Na_2HPO_4, zirconium is precipitated as a basic phosphate, $Zr(OH)PO_4$. Its precipitation is slow; but, if nothing has separated after half an hour, it is safe to conclude that less than 0.5 zirconium is present, provided care has been taken not to use more H_2SO_4 than is directed in the procedure. If the titanium had not been

oxidized by the addition of H_2O_2, it would also give an entirely similar precipitate of $Ti(OH)PO_4$; but from a solution containing H_2O_2 in excess when titanium is alone present none of it separates even on standing several hours. When zirconium and titanium are present together, a small proportion of the titanium is carried down with the zirconium and the phosphate precipitate may then have a distinct, yellow color.

(3) Some of the rare earth elements, such as thorium, may also be precipitated as phosphate at this point, if these elements have not been proved absent or removed in *P. 52*a*. In such a case the presence of zirconium may be proved by pouring a portion of dilute HF several times through the filter (supported in a celluloid funnel or a platinum ring), evaporating with H_2SO_4 in a platinum dish, diluting, and adding NH_4OH. The rare-earth phosphate would be left undissolved by the HF.

(4) Besides titanium and zirconium, the solution from *P. 65*a* will sometimes contain uranium, manganese, and cobalt (carried down in the precipitates in P. 52, *P. 62 *a*, and P. 64, respectively); but not in sufficient amount to interfere with the zirconium and titanium tests. The only other element of the aluminum and iron groups that gives a similar color with H_2O_2 in acid solution is vanadium; but this, aside from the fact that it should not be present, would give no precipitate with Na_2HPO_4 (not even on the addition of Na_2SO_3 in *P. 65*c*).

Procedure 65c.—To the H_2O_2 solution (*P. 65*b*), if colored, add powdered Na_2SO_3 little by little until the solution is decolorized, and let the mixture stand twenty or thirty minutes. (White flocculent precipitate, presence of *titanium.*)

Notes.—(1) This test serves to confirm the presence of titanium and to enable the quantity of it to be better estimated. H_2O_2 and the sexivalent titanium compound are rapidly reduced by the action of H_2SO_3, even in the cold, and titanium then precipitates as $Ti(OH)PO_4$. As in the case of zirconium, the precipitation takes place slowly. When there was only a faint color with H_2O_2, no precipitate will be obtained; but 0.5 mg. of titanium is easily detected, if the concentration of the sulphuric acid does not exceed 1 cc. H_2SO_4 (1.20) in 25 cc. solution.

***Procedure 65d.**—Evaporate the first ether extract (*P. 65*a*) on a waterbath, and dissolve the residue in 3–5 cc. H_2SO_4 (1.20) and 3–5 cc. water. To the cold solution in a test-tube add 2–3 cc. 1 per cent. KI solution and powdered Na_2SO_3 a little at a time until the iodine color has permanently disappeared. (Yellow precipitate, presence of *thallium.*) Filter, using preferably a hardened filter when the precipitate is small. Collect a little of the precipitate on a clean platinum wire and introduce the wire into a colorless gas flame. (Momentary green flame, presence of *thallium.*)

Notes.—(1) The precipitation of thallium as TlI is practically complete, provided that the volume of the solution is small, say less than 15 cc. The presence of iron does not prevent a good blank being obtained, nor does its presence in large quantity (500 mg.) prevent the detection of 0.5 mg. of thallium. TlI is readily oxidized to the soluble TlI_3 by iodine; therefore an excess of sulphite must be present.

(2) Any quantity of thallium in excess of 10–15 mg. is precipitated in **P.** 11, except when the solution there treated with HCl contains the thallium in the thallic state.

(3) The green flame test is a very delicate and characteristic test, but, on account

of the volatility of the thallium compound, the green color is seen only at the moment in which the wire is introduced into the flame. A hardened filter is recommended when the precipitate is small, because the precipitate can be more readily collected on the wire on account of the smooth surface of the filter.

Procedure 66.—Into the ammoniacal solution (P. 64 or P. 65) pass H_2S gas until the mixture after shaking blackens lead acetate paper held above it. (Black precipitate, presence of *nickel* or *cobalt*.) Filter, and wash the precipitate with water containing a very little $(NH_4)_2S$. (Precipitate, P. 67; filtrate, P. 81.)

Notes.—(1) In precipitating NiS, the use of H_2S has the advantage that the nickel is all thrown down at once, while with $(NH_4)_2S$ some of it usually remains in the solution, giving it a dark brown color. If found more convenient, $(NH_4)_2S$ can of course be used, the filtrate being boiled to throw down the unprecipitated nickel, as described in P. 51.

(2) The filtrate is in general tested for the alkaline earth elements, for these may be precipitated with the aluminum and iron groups when phosphate or certain other acid radicals are present, as discussed in P. 51 N. 6 and 7.

Procedure 67.—Transfer the H_2S precipitate (P. 66) with the filter to a casserole, and add 10–30 cc. of a cold mixture of 1 volume HCl (1.12) and 5 volumes of water. Digest in the cold for five minutes, stirring the mixture frequently, and filter.

Treat the residue by P. 68.

Boil the HCl solution until the H_2S is completely expelled, add 10 per cent. NaOH solution until the mixture is slightly alkaline, transfer to a casserole, cool, and add 0.5–1 gram Na_2O_2 a small portion at a time. Boil for several minutes to decompose the excess of Na_2O_2 and cool the mixture; filter off the precipitate, and treat it by P. 68, uniting with it the residue already obtained in the HCl treatment. Make the solution acid with acetic acid, warm it to about 60°, and pass in H_2S for two or three minutes. (White flocculent precipitate, presence of *zinc*.) Apply to the precipitate the confirmatory test as described in P. 57.

Notes.—(1) This treatment with dilute HCl serves to extract almost completely the zinc which may be present in this precipitate, owing to its having been carried down in the Na_2O_2 precipitate as described in P. 52, N. 11. A small proportion of the nickel and cobalt present (5 to 20 per cent.) always dissolves in the dilute HCl, and the subsequent treatment with Na_2O_2 serves to separate them from the zinc. This separation is satisfactory when, as in this case, the nickel and cobalt are present in such small quantity that only an insignificant quantity of zinc is carried down with them. When, therefore, the H_2S precipitate is small, it may, instead of being treated with dilute HCl, be dissolved at once in *aqua regia* and the solution treated directly as described in the last paragraph of the procedure.

(2) This procedure must always be followed in order to determine whether or not zinc is present in the substance, except in the case that a satisfactory test for it has already been obtained in P. 57, or in the case that the original Na_2O_2 precipitate (P. 52) was small.

Procedure 68.—Transfer the residue insoluble in dilute HCl, and the

Na_2O_2 precipitate (P. 67), with the filters to a casserole, add 5–15 cc. HCl (1.12) and a few drops HNO_3 (1.42), warm until the black precipitate is dissolved, and filter off the paper. Evaporate the solution nearly to dryness to expel most of the acid, add about 5 cc. water, and then NaOH solution drop by drop until the mixture is neutral, or until a permanent precipitate just forms. Test one-half of this mixture for cobalt by P. 69, and the remainder for nickel by P. 70.

Procedure 69.—To one-half of the neutral solution (P. 68) add 15 cc. 30 per cent. acetic acid, and then 50 cc. 30 per cent. KNO_2 solution; dilute to 100 cc., and allow the mixture to stand at least half an hour if no precipitate forms sooner. (Yellow, finely divided precipitate, presence of *cobalt.*) Filter, and wash with KNO_2 solution. If the precipitate is very small, incinerate the filter. Introduce a portion of the precipitate, or of the ash, into a borax bead made in the loop of a platinum wire, and heat strongly, adding more of the precipitate or ash if no color is obtained. (Deep blue color, presence of *cobalt.*)

Notes.—(1) The yellow precipitate is potassium cobalti-nitrite, $K_3Co(NO_2)_6$, which in solution dissociates into K^+ and the complex anion $Co(NO_2)_6^{\equiv}$. The precipitate is somewhat soluble in water but very difficultly soluble in a concentrated KNO_2 solution, owing to the common ion effect of the potassium ion. In the formation of this substance the cobaltous salt is oxidized to the cobaltic state by the nitrous acid displaced from its salt by the acetic acid, the cobaltic salt combining as fast as formed with the potassium nitrite, according to the equations:

$$Co^{++}(NO_2^-)_2 + 2HNO_2 = Co^{+++}(NO_2^-)_3 + H_2O + NO \text{ and}$$
$$Co^{+++}(NO_2^-)_3 + 3K^+NO_2^- = K_3Co(NO_2)_6.$$

(2) The formation of the $K_3Co(NO_2)_6$ precipitate takes place slowly, but even when very little cobalt is present (0.1 to 0.2 mg.) a distinct test is obtained within ten minutes; but the complete precipitation of a large amount of cobalt requires several hours, so that the method is ill-adapted for the removal of cobalt before testing for nickel. Moreover, when nickel is present, some of it is carried down with the cobalt, and this is true even when the total amount of nickel is small. For these reasons the test for nickel is made in a separate portion.

(3) Nickelous salts are not oxidized by nitrous acid, and are not precipitated by KNO_2 except in a very concentrated solution, when a dark yellow to dark red precipitate of potassium nickelous nitrite, $K_4Ni(NO_2)_6$, may separate. By making the volume large, as directed in the procedure, there is no danger of the precipitation of nickel.

Procedure 70.—To the remainder of the neutral solution (P. 68) add 10 per cent. KCN solution, a few drops at a time, until all or nearly all of any precipitate that may form at first redissolves; then add 0.5–3 cc. more (according to the amount of the KCN precipitate). Heat to 50° or 60° in an open casserole, with frequent stirring, for five minutes, or longer if the solution has not become light-colored. Filter off and reject any small precipitate that may remain. To the filtrate, preferably in a test-tube, add freshly prepared, concentrated NaBrO solution (see note 3) until a piece of filter paper moistened with KI and starch solutions, when dipped into the solution, is colored blue or brown. Allow the mixture to stand five to ten minutes, and filter. (Brown to black precipitate, presence of *nickel.*)

Wash the precipitate; dissolve a small portion of it, if it is large, in 2–3 cc. HNO_3 (1.20); add 3–5 cc. 10 per cent. tartaric acid solution, neutralize with 10 per cent. NaOH solution, and add 3 or 4 cc. in excess. Pass in H_2S for about one minute, filter out any precipitate that may form and saturate the filtrate with H_2S. Filter again if there is a precipitate. (Brown coloration, presence of *nickel.*)

Notes.—(1) The reactions involved in the first test for nickel are as follows: When a little KCN is added to the neutral solution, precipitates of (green) $Ni(CN)_2$ and (dark brown) $Co(CN)_2$ result except when only small amounts of these elements are present. The addition of more KCN causes the precipitate to dissolve owing to the formation of soluble complex cyanides, as $K_2^{+}[Ni(CN)_4]^{=}$ and $K_4^{+}[Co(CN)_6]^{==}$. The complex nickel salt is stable in the air, but the cobalt salt is very readily oxidized according to the equation:

$$2K_4^{+}[Co(CN)_6]^{==} + O + H_2O = 2K_3^{+}[Co(CN)_6]^{\equiv} + 2K^{+}OH^{-}$$

(Potassium cobaltocyanide) (Potassium cobalticyanide)

The first action of the NaBrO is to decompose the excess of KCN, chiefly with formation of KCNO. It then oxidizes the nickel to the nickelic state, whereupon the nickel is immediately precipitated as brownish-black $Ni(OH)_3$ by the NaOH present. The cobalt, though already in the cobaltic state, is not precipitated as $Co(OH)_3$, because the complex ion, $[Co(CN)_6]^{\equiv}$, is so slightly ionized into its constituent-ions (Co^{+++} and 6 CN^{-}) that the concentration of the Co^{+++} does not suffice to produce with the OH^{-} present the solubility-product for the $Co(OH)_3$, and that of the CN^{-} is so small that it is only very slowly oxidized by the NaBrO.

(2) In executing this procedure the following precautions should be observed: A very large excess of the strong KCN solution over that required to redissolve the precipitate should not be added, for the excess must be destroyed by the NaBrO before the nickel can be oxidized and precipitated by it. Yet there must be sufficient KCN added, not only to combine with all the cobalt, but to furnish a moderate excess in order that the oxidation to the cobalticyanide may take place rapidly. Care must also be taken to heat the solution long enough in the air to complete this oxidation, before the NaBrO is added, for otherwise the latter reagent after destroying the free KCN will oxidize the decomposable cobaltocyanide with precipitation of $Co(OH)_3$, just as it does the nickelocyanide; the completion of the oxidation by the air is indicated by the disappearance of the dark color in the solution. Finally one must make sure (by applying the iodide-starch test) that an excess of NaBrO over that required to oxidize both the cyanide and the nickel has been added. If these precautions are observed, there is no difficulty in securing a precipitate with 0.2 mg. of nickel nor in causing 300 mg. of cobalt to remain entirely in solution.

(3) The hypobromite reagent is prepared by adding liquid bromine to a known volume of 10 per cent. NaOH solution until the solution becomes distinctly red, owing to the presence of excess of bromine; and then adding half as much more NaOH solution. This solution may be filtered through a hardened filter. It decomposes fairly rapidly, with formation of bromate and bromide, and also with evolution of oxygen, and should therefore not be used when more than a few days old. Instead of this

reagent, bromine water and NaOH solution may of course be used. The concentrated hypobromite solution is recommended because a much smaller volume of it is required to decompose the large excess of cyanide used in the procedure.

(4) When an alkaline tartrate solution containing a small amount of nickel (even 0.1 to 0.2 mg. in 20 cc.) is saturated with H_2S a clear brown solution is obtained. With somewhat larger amounts of nickel (10 to 20 mg.) the liquid is opaque but runs through a filter very readily. The condition of the nickel in this solution is not known. The presence of the tartrate serves merely to prevent the precipitation of $Ni(OH)_2$ by the NaOH solution, owing to the formation of a complex salt containing the nickel in the anion. The brown color does not appear until the alkaline solution is nearly saturated with H_2S, so that care must be taken to use an excess of H_2S.

(5) This confirmatory test for nickel is not interfered with by moderate amounts of other elements of this group, such as cobalt and iron (which, however, should not be present at this point), for on leading H_2S into an alkaline tartrate solution containing these elements, they are completely precipitated as sulphides and may be filtered off, yielding a filtrate which in the absence of nickel remains clear when saturated with H_2S, or becomes dark brown when it is present in even small amounts.

Test Analyses.

Numerous analyses were made to test the efficiency of the process above described. Nearly all of those which were made after the procedure assumed final form are reproduced in the tables below. Almost all the analyses relating to the common elements alone were made before the procedures for the rare elements had been worked out, but the process for the analysis of mixtures containing only the common elements was at that time substantially the same as given above. In these tables the numbers in each vertical column show the weights in milligrams of the various elements which the solution submitted to analysis contained. The results of the tests for each element are shown by the letters following these numbers. That the result was satisfactory is indicated by the letter S; that is, when the element was present, that the test for it, however small, was unmistakable, and therefore conclusive; and when the element was absent, that a good blank test was obtained. When the test was very small, especially in comparison to the quantity of the element present, though still unmistakable, this is sometimes indicated by the symbol S–. When in the presence of the element the test failed, or in its absence a result was obtained that might be thought to indicate its presence, the letter F is used. When the result was doubtful or inconclusive, owing to the appearance or small size of the precipitate, this is indicated by the letter D. When the test was not tried, if the element was present a dash is used in place of a letter; or, if the element was not present, dots are inserted.

Common Elements.

The following analyses (Nos. 114–119) were begun at P. 51; P. 61 was introduced before P. 52.

T. A. No.	114.	115.	116.	117.	118.	119.
Mn	10 S	2 S	1 S	500 S	500 S	0 S^{4}
Al	10 S	2 S	1 D^{1}	0 D^{1}	2 S	0 D^{1}
Cr	10 S	2 S	1 S	0 S	2 F^{3}	0 S
Zn	10 S	2 S	1 S	0 S	2 S	0 S
Fe	10 S	2 S	1 S	0 S	2 S	500 S
Ni	10 S	2 S	1 S	0 S	2 S	0 S
Co	10 S	2 S	1 S	0 S	....	0 S

Analyses 120–125 were begun at P. 61.

T. A. No.	120.	121.	122.	123.	124.	125.
Mn	500 S	500 S	100 S	1 S	....	.....
Fe	0 S	1 S–	1 S	100 S	500 S	500 S
Ni	2 S	1 S	....	....	3 S	1 S–

Analyses 125–127 were made by P. 69; analyses 128–130 by P. 70.

T. A. No.	126.	127.	128.	129.	130.
Co	0 S	0.5 S	150–	150–	150–
Ni	250–	250–	0 S	0.3 S	0.15 S

The following analyses (Nos. 131–143) were begun at P. 52.

T. A. No.		131.	132.	133.	134.	135.	136.
Al		0 S^{2}	0 S^{2}	0 S^{2}	0 S^{2}	0 S^{2}	0 S^{2}
Cr		2 S	1 S	0 S	....	0 S	1 S
Zn	in P. 57	2 F	4 F	10 F	20 S–^{5}	5 F	0 S
	in P. 67	S	S	S	S	S	S
Mn		500 S	500 S	500 S	500 S	0 S	2 S
Fe		0 S	0 S	0 S	0 S	500 S	500 S
Ni		0 S	0 S	0 S	0 S	0 S	2 S

T. A. No.		137.	138.	139.	140.	141.	142.	143.
PO$_4$		....	....	....	....	....	200 S	200 S
Zn	in P. 57	5 F	5 S–^{7}	10 S–^{6}	3 F	5 S–^{5}	5 F^{8}	10 F^{8}
	in P. 67	S	S	–	–	–	–	S
Fe		500 S	500 S	500 S	....	....	....	....
Ni		....	....	...	250–	250–	250–	250 S
Co		....	....	....	250–	250–	250–	250 S

The following analyses (Nos. 144–155) were begun at P. 52; P. 61 was omitted.

T. A. No.		144.	145.	146.	147.	148.	149.
Al		0 S^{2}	3 S	3 S	0 S^{2}	0 S^{2}	0 S^{2}
Cr		0 S	2 S	1 S	1 S	0 S	10 S
Zn	in P. 57	0 S	5 S–^{5}	3 F	3 S–	3 F	20 S–^{5}
	in P. 67	S	S	S	S	S	S
PO$_4$		0 S	200 S	200 S	100 S	100 S	100 S
Fe		500 S	500 S	500 S	100 S	100 S	100 S
Ni		0 S	2 S	1 S	0 S	....	....
Co		0 S	2 S	1 S	0 S	100 S	100 S
Ba		0 S	2 S	1 S–	0 S	0 S	0 S
Ca		0 F^{9}	0 F^{9}	0 F^{9}	4 S	0 F^{9}	100 S
Mg		0 S	2 S	1 S	2 S	2 S	100 S

T. A. No.	150.	151.	152.	153.	154.	155.
Cr	2 S	....	0 S	....	2 S	1 S[10]
Zn in P. 57	3 F	5 S	0 S	1 F	....	....
Zn in P. 67	–	S	S	S	....	....
PO_4	100 S	100 S	....	....	....	....
Fe	100 S	100 S	0 S	....	....	....
Co	100 S	100 S	500 S	500 S	....	....
Ba	2 S	1 F	....	....	100 S	100 S

Mixtures Containing the Rarer Elements.

Analyses 156–161 were begun at *P. 58*a*.

T. A. No.	156.	157.	158.	159.	160.	161.
Cr	0 S	0 S	2 S	1 S[11]	....	....
U	100 S	0 S	100 S	100 S	100 S	1 S
V	0 S	100 S	100 –	100 –	1 S	100 S

Analyses 162–165 were begun at *P. 58*f*.

T. A. No.	162.	163.	164.	165.
Al	500 S	500 S	1 S	1 S
Be	0 S	2 S[12]	0 S	100 S

Analyses 166–170 were begun at *P. 58*a*.

T. A. No.	166.	167.	168.	168*a*.	169.	170.
Zn	....	....	....	....	200–	200 S
Al	200–	200–	....	....	....	200 S
Be	....	....	50–	50 S	....	....
U in *P. 58*c–d*	2 F	3 S–	2 F	2 S–	2 S	2 F
U in *P. 58*h*	–	–	–	S–	S–	S

Analyses 171–176 were begun at P. 64; analysis 176 at P. 52.

T. A. No.	171.	172.	173.	174.	175.	176.
Al	....	....	....	....	....	200–
Mn	....	....	....	....	....	200 S
Fe	500 S	500 S	0.5 S	500 S	500 S	200 S
Ti	0 S	1 S	5 S	....	....	....
Zr	0 S	1 S	....	....	....	....
Tl	0 S	....	....	1 S	0.5 S	1 S[13]

The following analyses (Nos. 177–181) were made by Mr. R. D. Gale, who had had no previous experience in connection with the process. The first analysis was with a known mixture, the remaining four were with unknowns. Mr. Gale received no assistance while making an analysis (except in T. A., No. 179), but all the precipitates and solutions were preserved in order that the causes of mistakes might afterwards be investigated. The process was practically in its final form with exception of the procedures relating to the separation of chromium, uranium and vanadium (*P. 58*b–e*), which were revised on account of the results of these analyses; moreover, uranium was not tested for in *P. 58*h*. Test analyses 156–161 and 166–170 were made at a later date to test these procedures in their final form.

T. A. No.	177.		178.		179.		180.		181.	
Begun at—	P. 52.		P. 51.		P. 51.		P. 52.		P. 51.	
Cr	2	S	1	S–[15]	1	S	1	S	2	F[14]
U	3	S	1	F[16]	1	F[16]	0	S	100	S
V	3	S	1	S	1	S	0	S	100	S[21]
Zn in P. 57	3	S	1	F	1	S	1	F	100	S[22]
Zn in P. 67		D		S–		..		S–		S
Al	3	S	200	S	1	S[17]	0	S	0	S
Be	3	S	1	S	0.5	S	0	S	0	S
Mn	3	S	1	S	1	S	200	S	300	S
PO_4	....		....		....		320	S	....	
Fe	3	S	200	S	1	S	1	S[18]	1	S[19]
Ti	3	S	1	S	0.5	S	1	S	0	S
Zr	3	S	1	S–	1	S	1	F[23]	0	S
Ni	3	S–[20]	1	S	1	S	200	S	1	I
Co	3	S–[20]	200	S	1	S	1	S	1	S
Ca	....		....		....		200	S	....	
Ba	....		....		....		2	S	....	

Notes.—(1) The presence of aluminum in the reagents made the result doubtful.

(2) A distinct precipitate of $Al(OH)_3$ was obtained in P. 53, but not more than with the reagents alone.

(3) Excess of HCl was added in P. 53 and the solution boiled, as a result of which the chromic acid was reduced. On analyzing another mixture, and using HNO_3, a satisfactory test for chromium was obtained.

(4) The absence of manganese was confirmed by fusing some of the iron salt on platinum foil with Na_2CO_3 and KNO_3: no green color was obtained.

(5) A small precipitate of ZnS was obtained in P. 57, which did not contain more than 1 mg. Zn. See C. E., P. 52, N. 11.

(6) A small precipitate of ZnS was obtained in P. 57, corresponding to 2 or 3 mg. Zn.

(7) In this analysis a large excess of alkali was added before the Na_2O_2 in P. 52, and the mixture was well stirred.

(8) This analysis was repeated except that the acid solution in P. 42 was poured slowly into an excess of hot alkali before adding Na_2O_2: a distinct test for zinc was then obtained in P. 57.

(9) A distinct test for calcium was obtained (except possibly in T. A. No. 148): the iron salt was found to contain about 2 mg. Ca with 500 mg. Fe.

(10) This analysis was repeated except that no Na_2CO_3 was added in P. 52: the test for chromium failed.

(11) See C. E., *P. 58*b*, N. 2.

(12) The precipitate of $Be(OH)_2$ obtained in *P. 58*h* was large and corresponded to 2 mg. Be, thus showing that much smaller amounts could be easily detected.

(13) The basic acetate procedure (P. 65) was used instead of P. 64: good tests for thallium were obtained both in the precipitate and in the filtrate. (Compare C. E., P. 65, N. 6.)

(14) Chromium was lost in *P. 58*a*, owing to the presence of H_2O_2 (from the peruranate, see C. E., P. 52, N. 6 and *P. 58*b*, N. 2) and the addition of a large excess of acid.

(15) A slight blue coloration was obtained with H_2O_2 in *P. 58*h*, corresponding to not more than 0.5 mg. Cr. No lead nitrate was added.

(16) The directions in *P. 58*c* were faulty: too little phosphate was added to precipitate 1 mg. U.

(17) A good test for aluminum was obtained in *P. 58*g*, but the confirmatory test (P. 54) failed.

(18) The test for iron in P. 65 was a failure: the iron was found with the manganese in P. 62.

(19) Satisfactory tests for iron were obtained in P. 62 and in P. 64.

(20) $(NH_4)_2S$ was used instead of H_2S in precipitating the sulphides in P. 66, and some nickel was lost in the brown solution. Nickel and cobalt were also lost in P. 67 in the treatment with dilute HCl, owing to the rejection of the Na_2O_2 precipitate.

(21) Only a few milligrams of vanadium were found in the filtrate from P. 51.

(22) About twice as much zinc was found in P. 57 as in P. 67.

(23) Owing to the insolubility of $Zr(OH)PO_4$ it is scarcely possible for zirconium and phosphate to occur together in the analysis of the aluminum and iron groups. The zirconium was undoubtedly lost in dissolving the precipitates obtained in P. 52–65.

Although all possible combinations of small and large quantities of the elements have not been investigated, the test analyses are sufficiently varied to justify general conclusions as to the reliability of the method of separation and detection of the elements.

An examination of these analyses shows that 1 mg. of any of the seven common elements in various combinations with one another and in the presence of the rarer elements was detected in almost all cases, even when the element was associated with a large quantity of other elements. Zinc frequently escaped detection in the analysis of the aluminum group (in P. 57), but was then always found in the analysis of the iron group (in P. 67) when tested for (see T. A. 131–153, 178, 180). One mg. is, however, near the limit of detectability when the elements of the iron group are present in large quantity. Two mg. of chromium were lost in two cases (T. A. 118, 181) owing to the reduction of the chromate; these analyses served to emphasize the necessity of added precautions, which have since been provided for in the directions. One mg. of iron in the presence of a large quantity of manganese would have been overlooked (in T. A. 180) if it had not been tested for in the solution of the chloric acid precipitate, as directed in P. 62. In the case of aluminum, owing to its being contained in the reagent, it was sometimes difficult (see T. A. 116, 117, 119, 131–136, 144–149) to determine with certainty whether or not 1 mg. was present.

It will be seen from T. A. 142–151 and 180 that the presence of much phosphate does not interfere with the detection of 1 mg. of any of the common elements of these groups. It does, however, cause a larger quantity of zinc to be completely precipitated by sodium peroxide (compare T. A. 141 with 142 and 143). It is shown by 144–146, 150, 151 and 180 that 2 mg. of barium and 1 mg. of magnesium are detected in the process, showing that adequate provision is made for the recovery of the alkaline-earth elements when carried down with these groups, through the presence of phosphate.

The analyses with the rarer elements (T. A. 156 to 181) show that the process led to the detection of 1 mg. of each of these and even of 0.5 mg. of beryllium and titanium in all cases except the following: In T. A. 180 zirconium was missed, owing to the simultaneous presence of much phosphate; but, even in the absence of phosphate, 1 mg. is not far from the limit of detectability in a complete analysis. In T. A. 166, 168, 170 and 178 uranium was missed in the usual place (in *P.58*c* and *d*) owing to the fact that it was carried down with aluminum or beryllium in the treatment with dilute $NaHCO_3$ (*P. 58*a*), but T. A. 168 and 170 and a number of special experiments with mixtures of beryllium and uranium show that in such cases uranium can be detected in *P. 58*h*.

CONFIRMATORY EXPERIMENTS AND REFERENCES.

G. D., Section 1: Precipitation of Zinc with Chromium on adding NH_4OH.—10 mg. Zn as $ZnCl_2$ and 100 mg. Cr as $KCr(SO_4)_2$ were dissolved in 4 cc. HCl (1.12) and 96 cc. water; 10 cc. NH_4OH (0.96) were added a little at a time to the cold mixture (giving an excess of about 3 cc. NH_4OH); after 3 or 4 minutes the precipitate was filtered off, the filtrate, which had a very faint pink color was heated to boiling; and the precipitate that separated (estimated to contain 2 or 3 mg. Cr) was filtered off. H_2S was finally passed into the alkaline filtrate: no precipitate separated, thus showing that the zinc had been completely carried down with the $Cr(OH)_3$. The precipitates were united and dissolved in HCl, and the solution treated by P. 52 to 57; the zinc was precipitated as ZnS in P. 57.

For the preparation and properties of $ZnCr_2O_4$, see Chancel, *Compt. rend.*, 43, 927 (1856); Viard, *Bull. de la soc. chim.* (3), 2, 331 (1889).

Action of NH_4OH and $(NH_4)_2S$ on Nickel Solutions, and Precipitation of NiS on Boiling the Brown Solution.—See C. E., P. 51, N. 12.

The Test for Vanadium with H_2S.—See C. E., P. 51*a*, N. 1.

The Slow Reduction of Vanadic Acid to Hypovanadic Acid by H_2S.—50 mg. V as H_3VO_4 were dissolved in 4 cc. HCl and 100 cc. water; the mixture was saturated with H_2S in the cold. After about 10 mintues the mixture was filtered several times to remove the sulphur that had separated, and the blue filtrate was heated to boiling: a large precipitate of sulphur separated, showing that reduction was more rapid at higher temperatures. The mixture was filtered and the hot filtrate again saturated with H_2S: a large precipitate of sulphur separated. After 10 minutes the mixture was boiled, filtered and again saturated with H_2S: sulphur separated, showing that the reduction was still incomplete. The treatment of the hot solution with H_2S was repeated, the sulphur filtered off, the mixture was boiled in a casserole to expel H_2S, and 1 g. KI was added: no iodine was liberated, showing that the reduction to hypovanadic acid was complete.—The first experiments were repeated with 3 cc. HNO_3 (1.20) in 100 cc: the results were the same.

Reduction of Vanadic Acid to Hypovanadic Acid by HCl (1.20).—See Gooch and Curtis, *Am. J. Sci.* (4) 17, 41 (1904). The reaction is slow in the cold but rapid on heating. When a moderate amount of vanadium is present, the reduction is not absolutely complete unless a more concentrated HCl solution is used than that obtained on evaporating. Compare C. E. *P. 58*d*, N. 1.

Action of NH_4OH on a Hypovanadate.—100 mg. V as Na_3VO_4 were treated with H_2S by P. 21 to reduce it to the hypovanadic state; the solution was evaporated to about 40 cc. and made alkaline with NH_4OH: a dirty gray precipitate separated.—50 mg. V as Na_3VO_4 were boiled with concentrated HCl (1.20) to reduce the vanadium; the mixture was diluted to 100 cc. and made alkaline with NH_4OH: a small gray precipitate, with a greenish shade, separated. Several cc. NH_4OH were added: the precipitate dissolved.

Precipitation of Vanadium in P. 51 or by NH_4OH alone when Iron or Zinc is Present.—500 mg. Fe as $FeSO_4$ and 100 mg. V as Na_3VO_4 were treated with H_2S by P. 21, evaporated to 40 cc. and treated by P. 51; the filtrate was tested for vanadium by *P. 51*a*: less than 1 mg. V was found.—The experiment was repeated with 500 mg. Fe and 10 mg. V: no vanadium was found in the filtrate.

500 mg. Fe as $FeCl_3$ and 100 mg. V as Na_3VO_4 were dissolved in 40 cc. containing 4 cc. HCl (1.12), the solution was made alkaline with NH_4OH, and (without adding $(NH_4)_2S$) the mixture was filtered, and the filtrate was tested for vanadium by *P. 51*a*: only a trace of vanadium was found.—The experiment was repeated with 500 mg. Fe as $FeSO_4$ and 100 mg. V as Na_3VO_4; the mixture was allowed to stand and

shaken frequently in order that the iron might be completely precipitated: no vanadium was found in the filtrate.—50 mg. Fe as $FeCl_3$, 15 mg. V as hypovanadic acid and several grams NH_4Cl were dissolved in a little HCl and 100 cc. water; the solution was made alkaline with NH_4OH, and the filtrate was evaporated to dryness, ignited, dissolved in a little NCl and tested for vanadium by P. 51*a*: only a trace of vanadium was found.—Therefore vanadium is almost completely carried down when a three- to fivefold excess of iron is present.

300 mg. Zn as $ZnCl_2$ and 10 mg. V as H_3VO_4 were treated with H_2S by P. 21, evaporated to 30 cc. and treated by P. 51; the filtrate was tested for vanadium by *P. 51*a*: 3 or 4 mg. V were found. The ZnS precipitate was analyzed by the regular procedure: the remainder of the vanadium was found.

Reduction of Vanadic Acid by HI and its Subsequent Behavior with the Group Reagents.—According to Gooch and Curtis (*Am. J. Science* (4) **17**, 45, 1904), the first stage of the reduction, that to V_2O_4, took place rapidly in a dilute HI solution, but the second stage, that to V_2O_3, takes place slowly and only in hot concentrated solutions. When a mixture containing 60 mg. V_2O_3, 1 g. KI and an excess of HCl was evaporated to 2 cc., about 97 per cent. of the vanadium was reduced to a salt corresponding to V_2O_3.

In our experiments 1 mg. V as Na_3VO_4 was dissolved in 15 cc. HCl (1.20) in a 50 cc. round bottom flask; 1 g. NH_4I was added, and the mixture was evaporated carefully to 2 or 3 cc., a capillary ebullator tube being used to prevent bumping. The mixture was diluted with 10 cc. water, and NH_4OH (0.96) was added until the solution after shaking smelled distinctly of it: a dark green precipitate formed. A few drops colorless ammonium sulphide were added: the precipitate did not dissolve. It was filtered off and dissolved in a little HNO_3; a large excess (5 to 10 cc.) of NH_4OH (0.90) was added and the mixture saturated with H_2S: the solution became red, showing the presence of vanadium. The filtrate from the NH_4OH precipitate was tested for vanadium in the same way: only a very small amount was found.—The experiment was repeated, except that the evaporated mixture was diluted to 20 cc: more vanadium was found in the filtrate than in the precipitate.—The experiment was repeated, the mixture being diluted to 40 cc.: all the vanadium was found in the filtrate.

The experiment was repeated several times with 100 mg. V, the mixture being diluted to 20 cc. after the evaporation: on adding NH_4OH a dark colored (brown) precipitate separated, but it dissolved completely or in large part on adding a few drops of colorless $(NH_4)_2S$.

The experiment was repeated with 50 mg. V; after the first evaporation 15 cc. HCl (1.20) and 1 g. NH_4I were added, and the evaporation repeated; the mixture was diluted to 50 cc: a large dark greenish colored precipitate separated on the addition of NH_4OH, and it did not dissolve on adding several drops $(NH_4)_2S$. The filtrate was evaporated nearly to dryness; an excess of 5 cc. NH_4OH (0.90) was added, and the mixture saturated with H_2S: not more than 0.5 mg. V was found in the filtrate. The last experiment was repeated with 5 and with 10 mg. V: in the experiment with 5 mg. only a very slight precipitate was obtained on adding NH_4OH and it quickly redissolved; with 10 mg. a precipitate was obtained but about half the vanadium was found in the filtrate. Therefore in a volume of 50 cc. the precipitation is fairly satisfactory for large amounts of vanadium but not for small amounts. The above results were not perfectly reproducible, but each of them was obtained several times.

A number of attempts were made to reduce 50 to 100 mg. V as Na_3VO_4 by evaporating as described above with 10 to 15 cc. pure concentrated HI, and to precipitate the vanadium with NH_4OH after diluting to 40 or 50 cc.; but the precipitation was much less complete than after the reduction with NH_4I and HCl, probably owing to the larger proportion of iodine found to be retained in the solution in the former case.—The experiments were repeated with HI that had been exposed to the air and contained much iodine: the precipitation was still less complete.

Rate of Oxidation of Trivalent Vanadium in the Presence of NH_4OH, and of $(NH_4)_2S$.—50 mg. V was reduced twice by evaporation with 15 cc. HCl (1.20) and 1 g. NH_4I to 2 or 3 cc.; the residue was diluted to 50 cc., and made alkaline with NH_4OH. The mixture was divided into two parts; one was filtered at once and the second after half an hour; both filtrates were tested for vanadium by *P. 51*a*: a very poor test was obtained in the first filtrate, and a good one in the second. The experiment was repeated, except that the second portion was filtered after 2 hours: the first filtrate gave a slight test for vanadium; the second contained 2 to 4 mg. V. Therefore the oxidation takes place slowly in the presence of NH_4OH.

The experiments were repeated except that several drops colorless $(NH_4)_2S$ were also added: the filtrates obtained at once, after 1/2 hour, and after 2 hours gave only slight tests for vanadium. Therefore the addition of a little $(NH_4)_2S$ does not cause the vanadium hydroxide to dissolve, and the rate of oxidation is slower in the presence of $(NH_4)_2S$ than in that of NH_4OH alone.

The oxidation, by the oxygen of the air of the trivalent vanadium after dilution is therefore much too slow to account for the abnormal results, such as the nearly complete precipitation of 50 to 100 mg. V in one experiment, and the non-precipitation in another performed under apparently the same conditions.

G. D., Section 2: Action of HCl on NiS or CoS.—Herz (*Z. anorg. Chem.*, **27**, 390 and **28**, 343, 1901) treated sulphides which had been kept on filters for several days after precipitation with 0.5 normal HCl (1 vol. HCl (1.12) and 12 vols. water) and found that the evolution of H_2S could not be detected by odor or by action on paper moistened with a lead salt. On the other hand, he found H_2S to be evolved fairly rapidly by the action of 0.5 normal HCl on freshly precipitated sulphides. He concludes that there are two allotropic forms of the sulphides, one that is soluble in 0.5 normal HCl, and one that is not. As Glixelli (*Z. anorg. Chem.*, 55, 297, 1907) has pointed out, this evidence of decreased solubility is not very conclusive, for the reaction with the old sulphides may simply be much slower. The following experiments show that NiS, at any rate while freshly precipitated, is not a mixture of two sulphides differing markedly in solubility.

200 mg. Ni as NiS, precipitated in the cold by passing H_2S into NH_4OH solution, was digested in the cold for a known time with about 30 cc. dilute HCl (1 vol. HCl (1.12) and 5 vol. water). The HCl was first saturated with H_2S, and H_2S was passed through the mixture in a small flask during the treatment. The mixture was filtered, and the experiment repeated several times with the NiS residue. The amount of nickel dissolved in each treatment was estimated by adding NH_4OH and precipitating the nickel as NiS by passing in H_2S. In the first treatment of 15 min. about 20 mg. Ni dissolved; in each of the next four treatments of 15 min. each, steadily decreasing amounts of Ni dissolved, and in the 5th treatment the amount was estimated to be 10 mg. Ni. The 6th and 7th treatments were each for half an hour: somewhat more nickel dissolved than in the 5th treatment of 15 minutes. The 8th treatment was for 4 hours: nearly as much dissolved as in the first treatment (say 18 mg.). Over night, without passing the current of H_2S, about 20 mg. Ni dissolved. In a last treatment for 6 hours, 25 or 30 mg. dissolved. The final residue contained only about 30 mg. Ni.—A similar series of experiments was performed, except that the HCl was not saturated with H_2S and no H_2S was passed through the mixture: the results were

similar, except that the NiS dissolved more slowly owing to the fact that the mixture was very little stirred.

100 mg. Ni as NiS (precipitated by H_2S in NH_4OH solution) were digested with 30 cc. dilute HCl (1 vol. HCl (1.12) and 3 vols. of water) for 5 minutes: about 5 mg. Ni dissolved.—The experiment was repeated with HCl (1.12): the amount of Ni that dissolved was not much greater than in the preceding experiment.—The last experiment was repeated with 1 mg. Ni: only a small proportion of the nickel dissolved.

Action of HCl on NiS when Other Sulphides are also Present.—500 mg. Fe as $FeSO_4$ and 5 mg. Ni as $NiSO_4$ were dissolved in 50 cc. water containing 2 cc. H_2SO_4 (1.84), and the solution treated at about 40° with NH_4OH and $(NH_4)_2S$ as described in P. 51: the filtrate was clear and light colored, showing that it contained no nickel. The precipitate was dried by suction, and treated in a casserole with 30 cc. cold dilute HCl (1 vol. HCl (1.12) and 5 vols. water), with frequent stirring, for 5 minutes: only a very small black residue remained, which was found to contain about 0.5 mg. Fe but no nickel.—The experiment was repeated, except that ferric chloride was used instead of ferrous sulphate: the residue contained 1 or 2 mg. Fe and a mere trace of nickel.—Both experiments were repeated, except that the sulphides were precipitated at about 90° by passing H_2S into NH_4OH solutions. In the experiment with ferrous iron the residue insoluble in dilute HCl contained nearly 1 mg. Fe and less than 1 mg. Ni; in the experiment with ferric iron the residue contained about 1 mg. Fe and nearly all the nickel.—The last experiment was repeated with 500 mg. Fe as $FeCl_3$ and 2 mg. Ni as $NiSO_4$: the residue insoluble in cold dilute HCl contained a little iron and nearly all the nickel.—The first of the above experiments was repeated with 500 mg. Fe as $FeSO_4$ and 10 mg. Ni as $NiSO_4$; the residue insoluble in dilute HCl and also the filtrate were tested for iron and nickel: the residue contained about 1 mg. Fe and 5 mg. Ni; the HCl solution contained also about 5 mg. Ni.—The experiment was repeated except that the sulphides were precipitated at about 90° by passing H_2S into an NH_4OH solution: the residue insoluble in dilute HCl contained about 0.5 mg. Fe and .3 or 4 mg. Ni.

500 mg. Mn as $MnSO_4$ and 5 mg. Ni as $NiSO_4$ were dissolved in 2 cc. H_2SO_4 (1.84) and 50 cc. water, and the solution was treated with NH_4OH and $(NH_4)_2S$ as described in P. 51; the filtrate was clear, showing the absence of nickel. The precipitate was digested with 30 cc. cold dilute HCl (1 vol. HCl (1.12) and 5 vols. water), with frequent stirring, for 5 minutes: the small dark colored residue on analysis was estimated to contain 3 or 4 mg. Ni; the HCl solution contained only about 0.5 mg. Ni.

The experiment was repeated with 500 mg. Zn as $ZnSO_4$ and 2 mg. Ni as $NiSO_4$: after 10 minutes treatment with the dilute HCl a very large residue remained; the HCl solution contained only about 100 mg. Zn, and no Ni. The 2nd treatment with HCl lasted over night: about 300 mg. Zn and no Ni dissolved. The third treatment lasted two days: the residue was small and dark colored, and contained over 1 mg. Ni and little or no Zn; the HCl solution contained about 100 mg. Zn and a little Ni. The experiment was repeated with HCl (1.12): a black residue remained.

These experiments show that small amounts of NiS may be dissolved completely when distributed throughout a large precipitate of iron sulphide, but that they are not readily dissolved in the presence of ZnS or MnS. They also show that ZnS dissolves slowly in dilute HCl just as NiS does.

G. D., Section 6: Precipitation of Vanadium by Alkaline Hydroxides when Uranium is Present.—For the insolubility of uranyl vanadate, see v. Klecki, *Z. anorg. Chem.*, 5, 381 (1894); Carnot, *Compt. rend.*, 104, 1850 (1887); also C. E. *P. 58*a*, N. 3.

50 mg. V as Na_3VO_4 and about 250 mg. U as $UO_2(NO_3)_2$ were dissolved in 3 or 4 cc. HNO_3 (1.20) and 30 cc. water; the solution was made alkaline with NH_4OH (0.96):

a large yellow precipitate separated. This was filtered off and the solution was tested for vanadium by *P. 58*e*: not more than 1 mg. was found. In this experiment there was just sufficient uranium to form $UO_2NH_4VO_4$. The precipitate obtained in the preceding experiment was dissolved in a little HNO_3, diluted to about 15 cc. and poured into about 20 cc. 10 per cent. NaOH solution: a large yellow precipitate separated, This was filtered off and the filtrate tested for vanadium by *P. 58*e*: only 5 to 10 mg. V were found.

Separation of Zinc and Vanadium by Hydrogen Sulphide.—H_2S was passed into a solution containing H_3VO_4 and acetic acid: the solution slowly became blue and sulphur separated, which rapidly became dark colored owing to the precipitation of some V_2S_4.

1 mg. V as Na_3VO_4 and 50 mg. Zn as $Zn(NO_3)_2$ were dissolved in 30 cc., a little acetic acid was added, and an excess of about 3 cc. NH_4OH (0.90). The clear solution was saturated with H_2S. A heavy precipitate of ZnS separated at once, and the solution slowly became deep red in color, which color was very distinct after filtering.—The experiment was repeated with *1* mg. Zn and 50 mg. V: a precipitate of ZnS was obtained, which was confirmed by the last paragraph of P. 57.

Action of NH_4OH on Uranium Solutions containing H_2O_2.—100 mg. U as $UO_2(NO_3)_2$ were treated by P. 52. The red (peruranate) solution was made acid with HNO_3. Without heating, the acid solution (which contained H_2O_2, see C. E., P. 52, N. 6) was made alkaline with NH_4OH: a large yellow precipitate of $(NH_4)_2U_2O_7$ separated, but the filtrate was yellow. The filtrate was acidified with HNO_3, boiled for two or three minutes, and again made alkaline with NH_4OH: a large yellow precipitate separated, which was nearly as large as the first NH_4OH precipitate. The colorless filtrate was again acidified, boiled, and then made alkaline with NH_4OH: no precipitate separated. Therefore uranium, if present, will divide in P. 53.

To a nitric acid solution containing 200 mg. U as $UO_2(NO_3)_2$ and 40 mg. V as H_3VO_4 in 40 cc. were added about 20 cc. 3 per cent. H_2O_2; the mixture was made alkaline with NH_4OH: no precipitate separated, showing that the precipitation of $UO_2NH_4VO_4$ and of $(NH_4)_2U_2O_7$ is prevented by the presence of an excess of H_2O_2.

Action of $BaCl_2$ on Uranate Solutions.—100 mg. U as $UO_2(NO_3)_2$ were treated by P. 52 and 53. The yellow filtrate from the NH_4OH precipitate, which contained about half the uranium, was treated by P. 55: a moderately large precipitate separated. After standing over night the precipitate was filtered off and the filtrate tested for uranium by adding HNO_3, boiling and adding NH_4OH: a small yellow precipitate separated, which was estimated to contain 2 mg. U. Therefore barium uranate (or peruranate) may be precipitated nearly completely in P. 55.

Action of $BaCl_2$ on Vanadate Solutions.—100 mg. V as Na_3VO_4 were treated by P. 52 and 53. See C. E., P. 52, N. 10. The NH_4OH solution, which had a volume of about 40 cc., was made just acid with acetic acid and $BaCl_2$ solution was added in the cold as described in P. 55: no precipitate separated from the yellow solution in 5 minutes.—The experiment was repeated with 300 mg. V: no precipitate appeared when the $BaCl_2$ was first added, but in 10 minutes a large orange precipitate of barium vanadate had separated. This was filtered off and the filtrate allowed to stand over night: a large precipitate formed. The precipitate was collected on a filter and washed with water: much of it dissolved, showing that barium vanadate is fairly soluble in water. A portion of the filtrate which was still slightly yellow was tested for vanadium by *P. 58*e*: much vanadium was found, showing that the precipitation of barium vanadates take place slowly, and that large amounts of vanadium remain in the filtrate in the cold.—A solution containing 100 mg. V as Na_3VO_4 and a little NH_4OH in 40 cc. was made acid with acetic acid; 10 cc. 10 per cent. $BaCl_2$ solution were added, and the mixture was boiled for a minute or two: a large nearly white precipitate separated, and the solution became perfectly colorless. The precipitate was filtered off and the filtrate tested for vanadium by *P. 58*e*: the filtrate was found to contain not more than a few milligrams of vanadium, thus showing that a large proportion of the vanadium had been precipitated on boiling.—The last experiment was repeated except that the acetic acid solution was made alkaline with NH_4OH before boiling: the filtrate was found to be nearly free from vanadium.—The last experiment was repeated with a mixture of 100 mg. V and 10 mg. Zn as nitrate: only about 3 mg. Zn were found in the filtrate, showing that a large part of it had been precipitated with the vanadium, probably as zinc vanadate.

Action of NH_4OH on Solutions containing Zinc and Vanadium as Vanadate.—500 mg. Zn as nitrate and 100 mg. V as Na_3VO_4 were treated by P. 52: only a very small precipitate remained and the solution was colorless. The filtrate was acidified with HNO_3 (1.20), an excess of about 2 cc. being added; and the solution was made just alkaline with NH_4OH: a large precipitate separated. 4 cc. NH_4OH (0.96) were added: the precipitate dissolved completely. The NH_4OH solution was neutralized with acetic acid: a large precipitate separated but it dissolved when a small excess of acetic acid was added. The acetic acid solution was boiled for a minute or two: a large precipitate separated leaving a clear solution, which, however still contained considerable zinc and vanadium.

Separation of Zinc and Uranium by NH_4OH.—1 mg. Zn as $Zn(NO_3)_2$ and 100 mg. U as $UO_2(NO_3)_2$ were dissolved in 4 cc. HNO_3 (1.20) and 100 cc. water; the mixture was made alkaline with NH_4OH and an excess of about 3 cc. added; the yellow precipitate was filtered off and the solution tested for zinc with H_2S: a small nearly white precipitate separated.—The experiment was repeated with 50 mg. Zn and 100 mg. U: the filtrate contained nearly all the zinc. The precipitate was washed, dissolved in HNO_3, diluted to 100 cc. and treated again with NH_4OH: the filtrate contained only about 2 mg. Zn. The NH_4OH precipitate was again treated in the same way: the filtrate contained no zinc.

Action of NH_4OH on Solutions containing Uranium and Chromate.—4 mg. Cr as K_2CrO_4 and 100 mg. U as $UO_2(NO_3)_2$ were treated as described in the preceding paragraph: the filtrate from the NH_4OH precipitate contained nearly all the chromium; the second NH_4OH filtrate was colorless.—The experiment was repeated with 50 mg. Cr and 100 mg. U: the filtrate after the second NH_4OH precipitation was nearly colorless, thus showing that little or no chromium was carried down with the uranium.

G. D., Section 13: The Separation of Titanium and Zirconium by Boiling with Sulphurous Acid.—With regard to the unsatisfactory nature of the process usually employed, see Hillebrand, *Bull. U. S. Geol. Sur.*, 176, 72–3 (1900). A fairly satisfactory quantitative separation of titanium from iron is obtained by boiling a solution of a volume of about one liter containing acetic and sulphuric acids. This large volume is impracticable in qualitative analysis, and H. I. Wood and B. E. Schlesinger (Theses M. I. T. 1901, 1902) devised the following method: "Heat the HCl solution (volume 10 to 20 cc.) to boiling, remove the flame, add at once carefully NH_4OH until litmus paper is turned distinctly blue; add 30 to 40 cc. H_2SO_3 solution, and place on the water-bath for 15 to 20 minutes." This method was carefully tested by us. The results were satisfactory with titanium or zirconium alone, and small quantities of these elements were easily detected. But when iron was also present, some of it was carried down. In an experiment with 3 mg. Fe, 100 mg. Ti and 100 mg. Zr as chlorides, no test for iron was obtained in the filtrate, thus showing that this amount of iron had been completely carried down. Also when 500 mg. alone (as $FeCl_3$) of Fe were present, some of the $Fe(OH)_3$ precipitated by NH_4OH did not dissolve in the H_2SO_3 solution; and even when ferrous iron was used, some $Fe(OH)_3$ sometimes precipitated during the heating on the waterbath. Moreover, the precipitation of titanium and zirconium was usually incomplete when much of these elements were present, more especially if the solution was not made distinctly alkaline with NH_4OH. This method is therefore a very unsatisfactory one.

G. D., Section 17: Precipitation of Beryllium Phosphate as a Confirmatory Test.—See B. E. Schlesinger, Thesis, M. I. T. 1902; Classen, Ausgewählte Meth. d. Analyt. Chemie, 5th Ed., 1, 715.

1 mg. Be as $BeCl_2$ was in each of three experiments dissolved in water containing a little HCl; 1 cc. 10 per cent. citric acid and 2 cc. 10 per cent. ammonium phosphate solutions were added, the mixture was made strongly alkaline with ammonia, and it was boiled gently for about 5 minutes in a small flask: a small white crystalline precipitate separated.—The experiment was twice repeated with 2 mg. Al as $AlCl_3$: no precipitate separated.—The experiment was repeated with 0.5 mg. Be: no precipitate resulted (4 experiments). Therefore this confirmatory test is hardly delicate enough, especially since beryllium has a very low atomic weight.

Test for Zirconium with Turmeric Paper.—The following procedure recommended by B. E. Schlesinger (Thesis, M. I. T., 1902) was tested: "Dissolve the phosphate precipitate in HF (1: 5), evaporate to one or two drops, and dip a piece of turmeric paper into it; heat the paper at 100° until dry." (Pink color, presence of *zirconium.*) In agreement with the results of Schlesinger, 1 mg. was found to be the limit of detectability. Even with 2 mg. the test was not a striking one. Moreover, titanium also caused a pink coloration of the turmeric paper, and the test was more delicate than in the case of zirconium. The blank test with strong HF was not perfectly satisfactory. The results obtained when HCl, instead of HF, was used were practically the same.

P. 51, N. 2: Precipitation of Small Amounts of Various Elements by Ammonia.—0.5 and 1 mg. of Al, Be, U, and Zr as nitrate, of Fe as $FeSO_4$, of Cr as $Cr_2(SO_4)_3$, of Ti as $TiCl_4$ were dissolved in separate experiments in 4 cc. HCl (1.12) and 30 cc. water in small conical flasks; the solutions were neutralized with NH_4OH (0.96) and about 1 cc. excess added; the mixtures were shaken several times and then allowed to stand a few minutes: in each case the solution was transparent after the NH_4OH was added, but a distinct flocculent precipitate was observed after the shaking and standing. The precipitates were more difficult to see with chromium, aluminum, and uranium, than with the other substances, but even in these cases 0.5 mg. was easily detected.

The experiments with aluminum, uranium, and chromium were repeated in a volume of 100 cc. containing 4 cc. HCl (1.12): 1 mg. Al was near the limit of detectability in a cold solution, but 0.5 mg. could be easily detected if the solution were heated nearly to boiling and allowed to stand. With uranium the limit of detectability was 1 to 2 mg. in a cold solution, and with chromium it was 2 mg. in a cold solution, but with 0.5 mg. Cr the solution became turbid on heating the NH_4OH solution to boiling.

2 mg. Cr as $KCr(SO_4)_2$ were dissolved in 4 cc. HCl (1.12) and a little water; the solution was boiled, diluted to 100 cc., cooled, and made alkaline with NH_4OH (0.96): a very small precipitate was seen after shaking and standing. This was filtered off, and the nearly colorless filtrate was heated to boiling: a finely divided, light green precipitate then separated, showing that precipitation of $Cr(OH)_3$ by NH_4OH in the cold is incomplete.

Solubility of Zinc and Nickelous Hydroxides in Solutions containing NH_4Cl and NH_4OH.—To a number of solutions containing 500 mg. Zn as $ZnCl_2$ and varying amounts of HCl in 30 cc. of solution, known amounts of NH_4OH (0.96) were gradually added, 1.0 cc. HCl (1.12) being equivalent to about 1.5 cc. NH_4OH (0.96). The following table shows the amount of NH_4OH that had to be added (1) before a large precipitate was formed, (2) before a distinct odor of NH_4OH persisted after shaking, and (3) before the precipitate dissolved to give a colorless solution.

HCl (1.12) present.	NH_4OH (0.96) required to give a large precipitate.	to give a distinct odor.	to dissolve the precipitate.
2 cc.	3 cc.	8 cc.	11 cc.
4 cc.	7 cc.	11 cc.	14 cc.
6 cc.	11 cc.	14 cc.	16 cc.
8 cc.	no precipitate.	17 cc.	....

The experiment was repeated in a volume of 100 cc. containing 4 cc. HCl (1.12): the result was practically the same as in the corresponding experiment with an initial volume of 30 cc.

The experiments were repeated with 500 mg. Ni as $NiCl_2$, the initial volume being 30 cc.: the solution became blue when an excess of NH_4OH was added, but no precipitate separated even when only 2 cc. HCl were used. In an experiment with no acid, a large green precipitate resulted, which dissolved on adding about 6 cc. excess NH_4OH after the odor of NH_4OH was persistent.

Precipitation of Cobalt Hydroxide.—The foregoing experiments were repeated with 500 mg. $CoCl_2$ and 4 cc. HCl (1.12) in 30 cc.: when the NH_4OH was added slowly a moderately large green precipitate was always obtained, which did not dissolve on adding a large excess of NH_4OH; the supernatant solution was reddish brown. The experiments were repeated with 4 and 6 cc. HCl (1.12), the ammonia (3–4 cc. excess) being added all at once: no precipitate was obtained, but the solution was red colored, and darkened on standing owing to oxidation. The experiments were repeated in a volume of 100 cc. containing 4 cc. HCl (1.12): the results were the same, except that the amount of green precipitate formed was greater than in the smaller volume and that a larger excess of NH_4OH was necessary, in order to prevent the separation of a precipitate when the excess of NH_4OH was added all at once.

Solubility of Aluminum Hydroxide in Excess of Ammonia.—To a solution containing 10 mg. Al as nitrate and 4 cc. HCl (1.12) in 100 cc. were added in the cold 17 cc. NH_4OH (0.96); *i. e.*, an excess of about 10 cc. and the mixture was shaken; the precipitate of $Al(OH)_3$ was filtered off after about five minutes, and the filtrate was boiled for several minutes to expel the excess of NH_4OH: a precipitate of $Al(OH)_3$ separated which was estimated to contain about 3 mg. Al. The experiment was repeated, except that an excess of only 2 or 3 cc. NH_4OH (0.96) was used: the filtrate on boiling became turbid, but the amount of aluminum that separated did not exceed 0.5 mg.

P. 51, N. 3 and 4: Solubility of $Mg(OH)_2$ in NH_4Cl Solutions.—The solubility of $Mg(OH)_2$ in water is about 2×10^{-3} mols. per liter. For evidence that the non-precipitation of $Mg(OH)_2$ in moderately dilute solutions containing an ammonium salt depends solely on the driving back of the dissociation of NH_4OH, see Lovén, *Z. anorg. Chem.*, 11, 404 (1896); Treadwell, *Z. anorg. Chem.*, **37**, 326 (1904); Herz and Muhs, *Z. anorg. Chem.*, **38**, 138 (1904).

The following experiments show that enough ammonium salt is produced by the neutralization of the 4 cc. HCl (1.12) originally present to prevent the precipitation of $Mg(OH)_2$ even when 500 mg. are present. A solution containing 500 mg. as $MgCl_2$ and 4 cc. HCl (1.12) in 100 cc. was neutralized with NH_4OH (0.96) (6 cc.), and more NH_4OH was added. No precipitate formed when 40 cc. in all had been added, but the addition of 10 cc. more gave a precipitate.—The experiment was repeated with an initial volume of 30 cc. instead of 100 cc.: 30 cc. NH_4OH produced no precipitate, even after several minutes, but 40 cc. did.—The experiment was repeated with 2 cc. HCl and a volume of 30 cc.: 15 cc. NH_4OH (0.96) produced no precipitate, but 20 cc. did.

Complex Zinc Ammonia Cathion.—$Zn(NH_3)_4^{++}$. See Herz, *Z. anorg. Chem.*, **25**, 225 (1900); Gaus, *Z. anorg. Chem.*, 25, 236 (1900); Euler, *Ber.*, **36**, 3400 (1903); Bonsdorff, *Z. anorg. Chem.*, **41**, 132 (1904).

Complex Nickel Ammonia Cathion.—$Ni(NH_3)_4^{++}$. See Dawson and McCrae, *J. Chem. Soc.*, **77**, 1239 (1900); Konowaloff, *Chem. Centralblatt*, **1900** I, 646; and especially Bonsdorff, *Z. anorg. Chem.*, **41**, 132 (1904).

Behavior of Chromium towards Ammonium Hydroxide.—To a solution containing in 30 cc. 3 or 4 cc. HCl (1.12) and 250 mg. Cr as $CrCl_3$ freshly prepared by boiling K_2CrO_4 with concentrated HCl, was added NH_4OH (0.96) until after shaking the odor was distinct. The mixture was divided into two parts; one part was filtered at once; to the other part 10 cc. NH_4OH (0.96) were added, and it was immediately filtered: the former had only a very faint pink color, and on boiling not more than 0.5 mg. Cr precipitated as $Cr(OH)_3$; the latter was distinctly pink, and on boiling 2 to 3 mg. Cr precipitated as $Cr(OH)_3$.—The experiment was repeated, except that an excess of 2 cc. NH_4OH was added after the odor of NH_4OH was distinct, and that in addition 5 g. solid NH_4Cl were added to one-half of the mixture, and both portions were filtered at once: each filtrate was faintly pink, and on boiling that containing no excess of NH_4Cl there resulted a precipitate of $Cr(OH)_3$ estimated to contain 0.5 mg. Cr, while on boiling the other filtrate no precipitate separated, and the solution remained pink.—The last experiment was repeated, except that the mixtures were allowed to stand 20 hours before filtering: the filtrate containing no excess of NH_4Cl was faintly pink but did not contain more than 1 mg. Cr. The second filtrate was highly colored and on boiling 5 to 10 mg. Cr precipitated as $Cr(OH)_3$, but the precipitation was not quite complete. These results show that both NH_4OH and NH_4Cl increase the amount of the pink chromium compound formed, and therefore prove that this compound is a complex ammonia salt and not a chromite. For the proof that these solutions are unstable, even at room temperatures, see Herz, *Z. anorg. Chem.*, **31**, 357 (1902).

P. 51, N. 6: Precipitation of Phosphates of Calcium, Barium, Magnesium and Manganese by Ammonium Hydroxide.—To solutions containing 2 mg. PO_4 as Na_2HPO_4 and 4 cc. HCl (1.12) in 30 cc., were added in separate experiments varying amounts of manganese, barium, and magnesium, as chloride and of calcium as nitrate. The solutions were then neutralized with NH_4OH (0.96) and about 2 cc. excess added, making 8 cc. in all, after which the mixtures were shaken and allowed to stand: 2 and 3 mg. Mn gave small precipitates after a minute or two, but 1 mg. gave no precipitate; 10 and 20 mg. Ca gave large precipitates at once but 5 mg. gave no precipitate even in half an hour. 100 mg. Ba gave a large precipitate at once, and 50 mg. gave no precipitate in half an hour. 1, 3 and 5 mg. Mg. gave precipitates on shaking. —The experiment was repeated with 10 mg. PO_4 and varying amounts of barium. 60 mg. Ba gave a large precipitate at once, but 40 mg. gave no precipitate, or only a very small one, in half an hour.—The experiment was repeated with 2 mg. Ca and varying amounts of phosphate: with 30 mg. PO_4 a precipitate was obtained at once, with 20 mg. after several minutes, and with 10 mg. no precipitate appeared in half an hour. On repeating the experiment with 1 mg. Ca a precipitate was obtained with 30 mg. PO_4 after a few minutes but not with 20 mg.

P. 51, N. 7: Solubility of the Borates of the Alkaline Earth Elements.—500 mg. BO_2 as H_3BO_3 and 20 mg. Ca as chloride were dissolved in 4 cc. HCl (1.12) and 36 cc. water, and NH_4OH (0.96) were added until the mixture after shaking just smelled of it: no precipitate separated.—The experiment was repeated with 200 mg. Ba as chloride; no precipitate separated.—The experiment was repeated with 300 mg Ba; a small precipitate formed, but it dissolved on adding a little concentrated NH_4Cl solution.—The experiment was repeated with 500 mg. Mg as chloride: no precipitate resulted.

P. 51, N. 9: Action of Ammonium Hydroxide on Uranyl Solutions.—See Kern. *J. Am Chem. Soc.*, **23**, 701–5 (1901).—1 and 3 mg. U as $UO_2(NO_3)_2$ were dissolved in separate experiments in 20 cc. water, and a few drops NH_4OH (0.96) were added: no precipitate separated on standing, nor on boiling. A small quantity of solid $NaNO_3$ was added to the cold solutions: pale yellow precipitates separated at once, showing that the uranium had been present in the colloidal form.—The experiment with 1 mg. U was repeated, except that a little NH_4Cl instead of $NaNO_3$ was added: a yellow precipitate separated.

P. 51, N. 9: Uranyl Salts and Diuranates.—See Dittrick, *Z. physik. Chem.*, 29, 449–90 (1899); Kern, *J. Am. Chem. Soc.*, 23, 686–726 (1901).

P. 51, N. 10: Completeness of Precipitation of the Sulphides of the Iron Group.—In each of the following experiments the quantity of the element given below was dissolved in 4 cc. HCl (1.12) and 96 cc. water; to this solution in the cold were added 9–10 cc. NH_4OH (0.96), and then $(NH_4)_2S$ solution drop by drop until an excess was present. The mixtures were well shaken and then filtered, generally through a double filter. The results were as follows: With 5 mg. Mn as $MnCl_2$, a light colored precipitate was formed at once; the filtrate was clear after two filtrations. With 0.5 mg. Mn as $MnCl_2$, the result was the same. With 0.25 mg. Mn as $MnCl_2$, the solution became turbid in two or three minutes. The filtrate in the first two experiments was evaporated almost to dryness; HNO_3 (1.42) was added; the mixture was evaporated to 5 cc., $KClO_3$ was added, and the mixture boiled: no precipitate of MnO_2 separated, showing that the precipitation of MnS had been complete.

With 1 mg. Zn as $Zn(NO_3)_2$, the mixture became turbid at once, and was readily filtered. With 0.5 mg. Zn, the result was the same. The filtrate in the first experiment was evaporated to 5 cc., made alkaline with NH_4OH and $(NH_4)_2S$ was added: only an insignificant turbidity appeared, showing that the precipitation of ZnS was practically complete.

With 0.5 mg. Co as $Co(NO_3)_2$, a black precipitate formed at once, which was readily filtered off. With 0.1 mg. Co, the solution became dark colored at once.

With 0.2 mg. Fe as $FeSO_4$, the solution became dark colored at once and the precipitate was easily filtered off. With 0.5 mg. Fe as $FeSO_4$, the result was the same. The filtrate was evaporated to 5 cc.; NH_4OH and $(NH_4)_2S$ were added: the solution remained colorless.

With 0.3, 0.5 and 1.0 mg. Tl as Tl_2SO_4, the solutions became dark brown at once and yielded clear filtrates, which when evaporated almost to dryness and tested for thallium by *P. 65*d*, gave no precipitate of TlI.

With 0.5 and 1.0 mg. U as $UO_2(NO_3)_2$, distinct flocculent precipitates could be seen after the addition of $(NH_4)_2S$; the filtrates were clear, and the precipitate, when collected on the filter, was yellow in color. With 0.3 mg. U as $UO_2(NO_3)_2$, a slight coloration was seen on the filter, but the precipitate could scarcely be seen before filtration. With 5 mg. U as $UO_2(NO_3)_2$, the result was the same. The filtrate was evaporated almost to dryness, and was tested for uranium by *P. 58*d* with $K_4Fe(CN)_6$: no brown coloration was observed. The last experiment was repeated except that the filtrate was evaporated to 5 cc. and NH_4OH and $(NH_4)_2S$ added: no precipitate formed, showing that the precipitation as sulphide in 100 cc. had been complete.

Nature of the Uranium Precipitate Produced by Ammonium Sulphide.—20 mg. U as $UO_2(NO_3)_2$ were dissolved in 4 cc. HCl (1.12) and 96 cc. water, about 9 cc. NH_4OH were added and $(NH_4)_2S$ drop by drop in the cold, until a distinct excess was present. The precipitate was flocculent and had a bright yellow color. After two hours it was light brown and in six hours dark brown in color.—The experiment was repeated except that a much larger excess of $(NH_4)_2S$ was added: the precipitate darkened more rapidly. It is evident that $(NH_4)_2U_2O_7$ is first precipitated contrary to the statements in some text books, and that the conversion of this substance into UO_2S takes place slowly.

The Existence of Ferric Sulphide (Fe_2S_3).—That Fe_2S_3 is formed when $(NH_4)_2S$ is added to suspension of $Fe(OH)_3$ in dilute NH_4OH has been proved by Stokes, *J. Am. Chem. Soc.*, **29**, 304 (1907). When, however, an acid solution is first saturated with H_2S and then made alkaline with NH_4OH, FeS and not Fe_2S_3 is formed.

P. 51, N. 11: Dark Color of Sulphide Precipitate as Evidence of Iron, Nickel, or Cobalt.—To solutions containing 500 mg. Zn as nitrate, 4 cc. HCl (1.12) and 30 cc. H_2O were added in separate experiments 1 and 2 mg. Ni as nitrate, 1 and 2 mg. Co as nitrate, 1 mg. Fe as $FeSO_4$ and 1 mg. Fe as $FeCl_3$. The mixtures were neutralized with NH_4OH (0.96) and 3 or 4 cc. excess added, making 10 cc. in all: A large white precipitate of $Zn(OH)_2$ remained which was estimated to contain at least 100 mg. Zn. Colorless $(NH_4)_2S$ was then added as described in P. 51 and the color of the precipitates was compared with that obtained with 500 mg. pure zinc; the precipitates containing 1 mg. Fe were nearly black with a greenish tinge; those containing 2 mg. Ni and Co were much darker than the pure ZnS, but those with 1 mg. Ni and Co were only very slightly darker.—The experiments were repeated except that 4 cc. more NH_4OH were added in order to dissolve the $Zn(OH)_2$: the results were substantially the same.—A solution containing 500 mg. Ca and 1 mg. Ni as nitrates, 1 g. PO_4 as $(NH_4)_2HPO_4$, 4 cc. HCl (1.12) and 35 cc. H_2O was made alkaline with NH_4OH (0.96) and 1 cc. colorless $(NH_4)_2S$ was added: the large white precipitate of phosphate became dark colored as soon as the sulphide was added.

P. 51, N. 12: Behavior of Nickel towards Ammonium Monosulphide and Polysulphide.—See Lecrenier, *Chem. Ztg.*, **13**, 431, 449 (1889); Anthony and Magri, *Gazz. chim. ital.*, **31**, II, 265 (1901). By boiling the brown solution in the absence of air the last-named authors have prepared NiS_4. The composition of the brown solution is unknown; it may be ammonium sulpho-nickelate, $(NH_4)_2NiS_{2+x}$, or colloidal nickel persulphide.

That in absence of air nickel is completely precipitated as NiS and the filtrate is colorless, thus proving that the brown solution is due to the presence of polysulphide, has been shown by Lecrenier. *Chem.-Ztg.*, **13**, 431, 449 (1889) and Villiers, *Compt. rend.*, **119**, 1263 (1894). The presence of NH_4OH tends to prevent the precipitation of NiS, and it is possible to obtain colorless (or bluish) solutions, containing a small excess both of $(NH_4)_2S$ and of nickel. In the presence of air we have found it almost impossible, when working with large amounts of a pure nickel salt, to prevent some nickel from passing into the filtrate, giving a brown solution. The amount of nickel in the filtrate increased with the excess of ammonium sulphide used and with the length of exposure to the air.

Some of the brown solutions obtained in these experiments were boiled in small flasks for 3 to 10 minutes, and then filtered: in each case the filtrate was colorless after a single filtration.

Precipitation of Nickel in Ammoniacal Solution by Hydrogen Sulphide.—In several experiments 500 mg. Ni as $Ni(NO_3)_2$ were dissolved in 30 cc. water and 4 cc. HCl (1.12); NH_4OH (0.96) was added until the odor could be detected after shaking and then 3 cc. more, and H_2S was led into the mixture for 15 minutes: the precipitates were always granular, and the filtrates clear and colorless; when the precipitates were washed with water containing either H_2S or a little $(NH_4)_2S$ the wash water was invariably clear.

**P. 51a, N. 1: Test for Vanadate with H_2S in Alkaline Solution.*—To separate solutions containng 3 g. NH_4Cl and 5 cc. NH_4OH (0.90) in a volume of 110 cc. were added 0.1, 0.3 and 0.5 mg. V as vanadate, and the mixtures were saturated with H_2S: in the experiments with 0.3 and 0.5 mg. V the solutions quickly became dark yellow, then reddish yellow and finally pink; in that with 0.1 mg. V the solution finally became faintly pink, but the test was a poor one. Therefore, the limit of detectability under these conditions is 0.1 to 0.2 mg.

The experiment with 0.5 mg. V was repeated except that, instead of 5 cc. NH_4OH (0.90) 1, 2.5 and 10 cc. respectively were used: with 1 cc. and with 2.5 cc. NH_4OH the pink color was scarcely noticeable; with 10 cc. a good color was obtained as with 5 cc. NH_4OH, but only after passing in H_2S for a longer time. These experiments show that a fairly large excess of NH_4OH is necessary.

20 mg. V as Na_3VO_4 were added to 20 cc. NH_4OH (0.96) and H_2S passed in: the color quickly became brown and slowly turned red, becoming after 5 or 6 minutes a deep cherry-red. The solution was divided into two parts. To the first was added an equal volume of water: the red color disappeared in 2 or 3 minutes, but appeared again on resaturating with H_2S. To the second part of the red solution was added an equal volume of NH_4OH (0.96): the color faded slowly (in 4 or 5 minutes) but reappeared on passing in H_2S. These experiments show that the solution must be saturated with H_2S.

1 mg. V as Na_3VO_4 was dissolved (*a*) in 20 cc. NH_4OH (0.90), (*b*) in 20 cc. NH_4OH (0.96), (*c*) in 5 cc. NH_4OH (0.96) and 15 cc. water, (*d*) in 2 cc. NH_4OH (0.96) and 38 cc. water, (*e*) in 2 cc. NH_4OH (0.96) and 98 cc. water. Each solution was saturated with H_2S: a good color was obtained in every case, showing that in the absence of ammonium salts the test may be obtained in any concentration of NH_4OH.

A solution containing 1 mg. V as Na_3VO_4 and 3 cc. HNO_3 (1.42) in 10 cc. was neutralized with NH_4OH (0.90) and 1 or 2 cc. in excess added: on saturating with H_2S a very faint color was obtained.—The experiment was repeated, except that the acid solution was first evaporated to dryness and ignited: a very good test was obtained, showing that the presence of ammonium salts interferes with test for vanadium.

0.5 mg. V as Na_3VO_4 was added to some HCl (1.20) and the mixture was evaporated twice nearly to dryness to reduce the vanadic acid to hypovanadic acid; 4 cc. HCl (1.12) were added and 96 cc. water; the mixture was neutralized with NH_4OH (0.90), an excess of 5 cc. was added, and H_2S passed in for 10 to 15 minutes: the solution darkened quickly, became reddish yellow and finally pink; the color was exactly the same as in the experiment described above with 0.5 mg. V as Na_3VO_4.—The experiment was repeated with 25 mg. V, which was reduced to hypovanadic acid by long continued treatment of the hot solution with H_2S: the solution darkened and then became deep red very quickly; the color was the same as in the experiment described above with 50 mg. V as Na_3VO_4.

1 mg. V as Na_3VO_4 was dissolved in 18 cc. water, 2 cc. 10 per cent. NaOH solution were added, and the mixture saturated with H_2S: a deep red color was finally obtained which was almost the same as that obtained when NH_4OH was used. The experiment was repeated with 20 cc. undiluted NaOH solution: the final color was the same, but the solution remained colorless for a long time while the H_2S was being passed through it. Therefore the formation of the red compound does not depend on the presence of NH_4OH or NH_4^+ ion.

**P. 51a, N. 2: Action of Acids on Sulphovanadate.*—0.5 mg. V as sodium vanadate was dissolved in 100 cc. containing about 3 g. NH_4Cl; 5 cc. NH_4OH (0.90) were added, and the mixture saturated with H_2S; the pink solution was filtered, and then acidified in the cold with acetic acid, stirred, and filtered: a small black precipitate containing sulphur was obtained. This was dissolved by boiling with a little HNO_3 (1.20); the solutions were evaporated to about 2 cc. and 1 to 2 cc. 3 per cent. H_2O_2 were added: an orange-yellow color resulted, showing the presence of a small amount of vanadium. —The experiment was repeated with sodium hypovanadate: the results were the same.

The experiment was repeated with 25 mg. V: on boiling the filtrate from the precipitate of vanadium sulphide it became blue and sulphur separated. To it 50 mg. Fe as $FeCl_3$ were added and then an excess of NH_4OH; the mixture was filtered, the filtrate was evaporated to dryness, the residue ignited and dissolved in a very little HNO_3, and a few drops H_2O_2 solution were added: no color appeared, showing that the vanadium in excess of 0.1 mg. had been carried down with the $Fe(OH)_3$. The sulphide and hydroxide precipitates were dissolved separately in HNO_3, H_2O_2 was added together with and 20 to 30 cc. water, and the intensities of the colors compared: it was estimated that about 10 mg. V were precipitated as sulphide, and the remaining 15 mg. V with the $Fe(OH)_3$.—The experiment was repeated with 50 mg. V, a larger amount of $FeCl_3$ being used: the results were similar, thus showing that under these conditions less than half the vanadium is precipitated as sulphide. —In other experiments in which the volume was only 20 to 30 cc., and the relative proportion of ammonium salt to NH_4OH was smaller, 80 to 90 per cent. of the vanadium was found to be precipitated as sulphide by acetic acid. Even when NaOH was used instead of NH_4OH, it was not possible to precipitate the sulphide completely.

The experiment with 50 mg. V described in the last paragraph was repeated, except that HCl was used to acidify the cold solution: it was estimated that roughly one-half of the vanadium was precipitated as sulphide and the other half with the $Fe(OH)_3$. —The last experiment was repeated, except that the mixture containing HCl was boiled for about 1 minute: somewhat less than half the vanadium was found in the HCl precipitate.

**P. 51a, N. 3: Complete Precipitation of Vanadium by Ammonium Hydroxide in the Presence of Iron.*—See preceding section, and C. E., G. D., Section 1.

P. 51a, N. 4: Pervanadic Acid.*—See Scheuer, *Z. anorg. Chem.*, **16, 284 (1898); Pissarjewsky, *Z. phys. Chem.*, **43**, 171 and 173 (1903), and **40**, 368 (1902).

Action of H_2O_2 on Vanadic Acid.—In a series of 6 test tubes, each of which contained 1 mg. V as Na_3VO_4, were placed 0, 0.5, 2, 5, 10, and 20 cc. H_2SO_4 (1.20); each solution was diluted to 20 cc. and 2 cc. 3 per cent. H_2O_2 added: no change was observed in the tube with no acid; the solution became orange to orange-red in the remaining tubes, and the intensity of the color increased greatly as the concentration of the acid increased. The experiments were repeated with HNO_3 (1.20): the results were the same. All the tubes were allowed to stand over night: no changes in the colors were observed. Ether was added to a number of the solutions and the mixtures shaken: the ether layer remained colorless.

To solutions containing 1 mg. V as Na_3VO_4 dissolved in 1 cc. HNO_3 (1.20) were added, (*a*) 1 cc. 3 per cent. H_2O_2 and 8 cc. water, (*b*) 3 cc. H_2O_2 and 6 cc. water, and (*c*) 9 cc. H_2O_2: the first two solutions were orange-red, but the third solution was practically colorless, thus showing that a large excess of H_2O_2 spoils the test. To the third solution were added 3 cc. HNO_3 (1.20): the orange-red color reappeared, thus proving again that the test is more easily obtained in the presence of a large excess of acid. To this solution was then added 7 cc. H_2O_2: the color became much fainter.

The first series of experiments with varying amounts of HNO_3 (1.20) and a total volume of 20 cc. was repeated, except that 0.1 mg. V as Na_3VO_4 was used instead of 1 mg.: all the solutions remained colorless, showing that 0.1 mg. V cannot be detected in 20 cc.—This series of experiments was repeated with 0.3 mg. V: a distinct yellow color could be seen on looking down the tubes in the experiments with 5, 10, and 20 cc. HNO_3, a light color with 2 cc. HNO_3, and none with 0.5 cc.—This series was repeated with 0.5 mg. V: with 0.5 cc. HNO_3, the solution was colorless, with 2 cc. it was slightly yellow, and in the remaining experiments a slight but distinct orange-yellow color was observed. Therefore the limit of detectability of vanadium with H_2O_2 in HNO_3 solution is about 0.5 mg. V in 20 cc., and the solution must contain at least 1 volume HNO_3 (1.20) to 3 volumes of water.

**P. 51a, N. 5: Tungstic Acid Dissolves in Acids when Phosphate or Arsenate is Present.—Tech. Quart.*, 16, 122 (1903).

Partial Precipitation of Tungsten on Acidifying a Solution of Sulphotungstate.—See *Tech. Quart.*, 17, 253–5 (1904).

Action of H_2S on Tungstate Dissolved in Excess of NH_4OH.—50 mg. W as $(NH_4)_2WO_4$ and 3 g. NH_4Cl were dissolved in 100 cc. water, 5 cc. NH_4OH (0.90) were added, and the mixture was saturated with H_2S: the solutions remained nearly colorless for over 10 minutes, but finally became slightly yellow, probably owing to the formation of polysulphide.

Action of H_2O_2 on Tungstic and Molybdic Acids.—See *Tech. Quart.*, 17, 251 (1904).—20 mg. Mo as $(NH_4)_2MoO_4$ were dissolved in 5 cc. HNO_3 (1.20) and 2 cc. H_2O_2 added: a lemon-yellow color resulted. On account of the absence of an orange tint there is no difficulty in distinguishing between this color and that of pervanadic acid.

Action of H_2S on Molybdate Dissolved in Excess of NH_4OH.—A solution containing 6 mg. Mo as $(NH_4)_2MoO_4$ and 4 cc. HCl (1.12) in 30 cc. was treated by P. 51: no precipitate formed with NH_4OH, nor with $(NH_4)_2S$. To the nearly colorless filtrate were added 5 cc. NH_4OH (0.90), and H_2S was led through the solution in a test tube for 20 minutes: after 3 minutes the solution was dark yellow, after 5 minutes it had a reddish color, after 10 minutes it was brilliant red, and the color did not change in the next 10 minutes. The color was not the same as in the case of vanadium, but might be mistaken for it if a comparative test were not made.—50 mg. Mo as $(NH_4)_2MoO_4$ and 3 g. NH_4Cl were dissolved in 100 cc. water, 5 cc. NH_4OH (0.90) were added, and the solution was saturated with H_2S: the colors obtained were the same as in the preceding experiment.—The last experiment was repeated with 1 mg. Mo: the solution finally became deep orange in color.

Action of Acids on Sulphomolybdate.—50 mg. Mo as $(NH_4)_2MoO_4$, 3 g. NH_4Cl, and 5 cc. NH_4OH (0.90) were dissolved in 100 cc. water, and saturated with H_2S. The red solution was filtered and then made distinctly acid with acetic acid: the color remained nearly the same; on filtering, a very small black precipitate was obtained which contained less than 1 mg. Mo. The solution was allowed to stand for one hour: it remained clear. After 3 hours a small precipitate had separated which contained only 2 or 3 mg. Mo. The mixture was then boiled for 5 minutes and filtered: about 2/3 of the molybdenum precipitated as MoS_3 and the filtrate was still deep orange. The filtrate was evaporated to a small volume and 10 cc. HCl (1.20) added: a large black precipitate of MoS_3 separated, but the solution was found to still contain 1 or 2 mg. Mo.

The foregoing experiment was repeated, except that HCl was added to the cold solution: a large black precipitate separated at once. The filtrate was evaporated to 30 cc. and tested for Mo by *P. 43*e*: none was found.—The experiment was repeated except that the mixture was boiled after adding HCl: the result was the same, not more than a trace of molybdenum being found in the filtrate.

P. 52, N. 3: The Formation of Sulphate on Dissolving NiS in Acids.—In two experiments 300 mg. Ni as freshly precipitated NiS were treated by P. 52, the sulphur was filtered off, and $BaCl_2$ was added to the filtrate: small precipitates of $BaSO_4$ separated, each of which was estimated to contain 5–10 mg. Ba.—In another series of experiments the NiS was first treated in the cold for several minutes with mixtures of 5 cc. HNO_3 (1.20) with 20 to 20 cc. water and the residue was dissolved by evaporating the solution to concentrate the HNO_3, and then adding a few drops HCl (1.20): precipitates of $BaSO_4$ resulted, estimated to contain 20–50 mg. Ba. In each of these experiments and especially when the precipitate was first treated with HNO_3 considerable sulphur separated and the NiS enclosed in it did not dissolve readily.

P. 52, N. 4: Action of HCl on Titanium and Zirconium Hydroxides.—Acid solutions containing 100 mg. Ti and 100 mg. Zr as chlorides in volumes of about 100 cc. were treated in the cold with NH_4OH; the precipitates were filtered off and treated with 20 cc. cold HCl (1.12): they dissolved completely in a minute or two.—The experiments were repeated, except that the solutions were heated to boiling, and the NH_4OH was added to the hot solutions: on pouring 20 cc. HCl (1.12) repeatedly through the filters containing the hydroxide precipitates, almost all of the $TiO(OH)_2$ dissolved, but only a small portion of the $ZrO(OH)_2$ (8–10 mg. Zr). On pouring a 20 cc. portion of hot HCl (1.12) repeatedly through the filters, the remainder of the titanium, but only about half the zirconium dissolved. The remainder of the $ZrO(OH)_2$ was boiled in a casserole with HCl (1.12) for several minutes: it dissolved completely.

P. 52, N. 5: Complete Precipitation of Titanium and Zirconium in the Sodium Peroxide Procedure.—1 mg. Ti as $TiCl_4$ was treated with NaOH and Na_2O_2 by P. 52, the mixture being boiled for about 4 minutes after the Na_2O_2 was added: a white precipitate separated. The filtrate was made acid with HCl; one-half of it was tested for titanium by adding H_2O_2: no color appeared, showing that the titanium had been completely precipitated. The other half of the filtrate was tested for H_2O_2 by adding excess of $TiCl_4$: no color appeared, showing that the Na_2O_2 had been completely decomposed.—The experiment was repeated with 500 mg. Ti: the filtrate contained 1 or 2 mg. Ti. The precipitate was treated with HCl (1.12): nearly all dissolved in the cold and the remainder on warming. The solution was reddish yellow, showing that the precipitate contained some TiO_3.—The HCl solution obtained in the last experiment (containing nearly 500 mg. Ti) was treated with NaOH and Na_2O_2 by P. 52; the mixture containing Na_2O_2 was boiled for less than 1 minute: the filtrate contained at least 5 mg. Ti.—These experiments show that the amount of titanium that remains in the filtrate may be greatly lessened by long continued boiling.

1 mg. Zr as $ZrCl_4$ was treated with NaOH and Na_2O_2 by P. 52: a distinct precipitate separated.—The experiment was repeated with 100 mg. Zr; the large precipitate was filtered off, and the filtrate was tested for zirconium by acidifying with HNO_3, evaporating almost to dryness, and adding Na_2HPO_4 solution: only a trifling precipitate separated, thus proving that the precipitation of the zirconium had been complete.

Action of NaOH on Uranyl Salts.—A solution containing 5 mg. U as UO_2Cl_2 and a little HCl in 15 cc. was neutralized with 10 per cent. NaOH solution, and an excess of 2 or 3 cc. was added: a small yellowish precipitate separated. This was filtered off and the filtrate was tested for uranium by acidifying and adding NH_4OH: a small precipitate separated, which was estimated to contain 2 or 3 mg. U. The experiment was repeated, except that the mixture containing NaOH was boiled for a minute or two: nearly all of the precipitate which had formed in the cold was redissolved. Therefore the uranium is not completely precipitated by a small excess of NaOH.—50 mg. U as $UO_2(NO_3)_2$ were added to 30 cc. 10 per cent. NaOH solution, and the mixture was heated to boiling, cooled, and poured through a hardened filter;

half of the filtrate was tested for uranium as above: only a small precipitate of $(NH_4)_2U_2O_2$ separated, showing that the uranium had been nearly completely precipitated by the alkali.

Composition of Sodium Aluminate, Zincate, Beryllate and Chromite.—For the evidence that sodium aluminate in solution has the formula, $Na^+AlO_2^-$, see Noyes and Whitney, *Z. physik. Chem.*, 15, 694 (1894); Hantzsch, *Z. anorg. Chem.*, 30, 296 (1902). Hantzsch has shown by means of conductivity measurements that a solution of the empirical composition Na_3AlO_3 contains mainly NaOH and $NaAlO_2$ and some colloidal $Al(OH)_3$.

Hantzsch, *Z. anorg. Chem.*, 30, 298, 303 (1902), concluded from conductivity measurements that a 1/200 molal solution of sodium zincate, even in the presence of a sevenfold excess of NaOH, is almost completely hydrolyzed into NaOH and $Zn(OH)_2$ and that the latter is present as a colloid. Fisher and Herz, *Z. anorg. Chem.*, 31, 355 (1902), confirmed this by dialysis experiments. Kunchert, *Z. anorg. Chem.*, 41, 343–8 (1904), working with a larger excess of alkali, and using Bodländer's electromotive force method, proved, however, that the solutions contained chiefly $ZnO_2^{=}$ and some $HZnO_2^-$. Förster (*Z. Elektrochem.*, 6, 301, 1899) has prepared solid $NaHZnO_2$.

Hantzsch (*Loc. cit.*) concludes that H_2BeO_2 is a very weak acid, weaker than $HAlO_2$, but much stronger than H_2ZnO_2.

From dialysis and conductivity experiments Fisher and Herz (*Loc. cit.*) conclude that in alkaline chromite solutions chromium is present almost solely as colloidal $Cr(OH)_3$.

Behavior of Cobalt Hydroxide towards NaOH.—See Donath, *Z. analyt. Chem.*, 40, 137 (1901).—An acid solution containing 100 mg. Co as nitrate in 30 cc. was neutralized with 10 per cent. NaOH and an excess of 15 cc. added; 2 g. Na_2O_2 were added a little at a time to the cold solution, the mixture was boiled for two or three minutes, cooled, and filtered: the filtrate had a deep blue color. It was acidified, made alkaline with NH_4OH, and H_2S was passed into it: a precipitate separated which was estimated to contain 5 to 8 mg. Co.—The experiment was repeated, except that no excess of NaOH was added: the filtrate was colorless and no cobalt was found in it.—This last experiment was repeated except that 4.5 g. Na_2O_2 were used instead of 2 g.: again the filtrate contained no cobalt. Therefore the blue (soluble) cobalt compound is formed only by the action of concentrated alkali on a *cobaltous* salt, and the cobalt is completely precipitated if it is first oxidized to the cobaltic state by Na_2O_2 in a weakly alkaline solution.

The first experiment with the large excess of NaOH was repeated with 100 mg. Ni instead of Co: no nickel was found in the filtrate.

P. 52, N. 6: Formation of Peruranates. See P. Melikow and L. Pissarschewsky, *Z. physik. chem.*, 28, 556 (1899). A large number of salts are known in the solid state; *e. g.*, $UO_4.2Na_2O_2.8H_2O$; $UO_4.2BaO_2.8H_2O$; $UO_4.2BaO_2.10H_2O$; etc. The salts of the alkali elements are soluble in water, the others insoluble. These salts may be regarded as compounds of peruranic anhydride, UO_4, with peroxides of the other elements. They were prepared by the action of H_2O_2 on solutions of uranyl salts in the presence of the hydroxides of the other elements.

A HNO_3 solution containing 100 mg. U as $UO_2(NO_3)_2$ in 25 cc. was treated by P. 52: the solution was yellow when acid, and a yellow precipitate separated on adding NaOH; on adding Na_2O_2 (3 g.) and boiling, a deep red solution resulted. This solution was acidified with HNO_3: it became yellow. To a portion of it was added a little $TiCl_4$ in HCl solution: an orange-red color resulted, proving the presence of free H_2O_2. Therefore the uranium is oxidized by Na_2O_2 to a soluble "peruranate," which is stable in the strong alkali, but apparently decomposes readily in the acid solution with formation of H_2O_2 and a uranyl salt.—The experiment was repeated except that only about 0.5 g. Na_2O_2 was added: a yellow uranium precipitate remained, but the solution contained a large proportion of the uranium.

P. 52, N. 7: Complete Decomposition of Na_2O_2 by Boiling.—2 g. Na_2O_2 were added to a neutral solution containing 0.5 g. NaCl in 30 cc., the mixture was heated to boiling, boiled for one minute, cooled, acidified with HNO_3, and tested with $TiCl_4$ solution for H_2O_2; the solution remained colorless.—The experiment was repeated with 100 mg. Mn as $MnCl_2$, the MnO_2 being filtered off before the filtrate was made acid: it contained no H_2O_2.—The experiment was repeated with 100 mg. V as Na_3VO_4: the result was the same. See the preceding paragraph as to the effect of uranium.

Precipitation of Thallium by Sodium Peroxide.—1, 3, and 20 mg. Tl as $Tl(NO_3)_3$ were treated in separate experiments by P. 52: brown precipitates separated in each case on adding NaOH, and remained after the treatment with Na_2O_2. The solutions, which were filtered off almost immediately after diluting, were found to contain about 0.5, 1, and 2 to 3 mg. respectively.—1 mg. Tl as Tl_2SO_4 was treated by P. 52: no precipitate separated on adding NaOH; there was a slight coloration on adding Na_2O_2, but no precipitate remained upon boiling; when, however, the solution was set aside to cool, a good precipitate separated in 10 or 15 minutes, and the filtrate was found to contain only 0.2 to 0.4 mg. Tl.—A mixture containing 1 mg. Tl as TlCl, 200 mg. Fe as $FeCl_2$, 200 mg. Mn as $MnCl_2$ and 200 mg. Al as $AlCl_3$ was treated by P. 52; the filtrate was evaporated nearly to dryness and tested for thallium by *P. 65*d*: no precipitate of TlI separated.

P. 52, N. 8: Necessity of Adding Na_2CO_3 to Precipitate Barium.—1 and 2 mg. Ba as $BaCl_2$ were treated by P. 52, the final volume being about 30 cc.: on boiling, a precipitate which was proved to contain barium appeared in both experiments, but it was very slight in that with 1 mg.—These experiments were repeated, except that no Na_2CO_3 was added: no precipitate appeared on boiling.

2 mg. Cr and 100 mg. Ba as chlorides were treated by P. 52, except that no Na_2CO_3 was added: the filtrate was colorless, and the solution obtained on dissolving the precipitate in HNO_3 was yellow, showing that the chromium had been precipitated as $BaCrO_4$.—The experiment was repeated with 1 mg. Cr and 100 mg. Ba, except that Na_2CO_3 was added: the filtrate was yellow, showing that the addition of Na_2CO_3 causes chromium to pass into the filtrate even when a large amount of barium is present.

Solubility of Zinc Carbonate in NaOH.—50 mg. Zn as nitrate were dissolved in 20 cc. water and an equivalent amount of Na_2CO_3 added: a white precipitate separated. 5 cc. more 10 per cent. NaOH solution were added: the precipitate dissolved. 5 cc. more NaOH and 10 cc. 10 per cent. Na_2CO_3 solution were added, and the mixture heated to boiling: no precipitate separated. More Na_2CO_3 was added: a precipitate finally formed.

P. 52, N. 9: Solubility of the Phosphates of Aluminum and Zinc in NaOH.—100 mg. Zn and 100 mg. Al as phosphates were dissolved in separate experiments in 25 cc. water and a very little HNO_3 (1.20); 10 per cent. NaOH was added slowly: precipitates separated but dissolved when an excess of about 4 cc. had been added.

Partial Decomposition of Phosphates on Treating with Sodium Hydroxide.—50 mg. Mg, 50 mg. Ca, and 20 mg. (ferric) Fe, all as freshly precipitated phosphates were boiled separately with about 30 cc. 4 per cent. NaOH solution for 3 or 4 minutes in covered casseroles; the mixtures were filtered, the precipitates being washed with dilute NaOH. The filtrates were made strongly acid with HNO_3, and the precipitates were dissolved in HNO_3. Each solution was evaporated to a small volume and treated with several cc. ammonium molybdate solution. The amount of phosphate in each solution was estimated by the amount of yellow precipitate that had separated out after several hours: in the case of magnesium only a very small proportion of the phosphate remained in the precipitate; in the case of the iron about one-fifth remained in the precipitate; and in the case of calcium the phosphate was about equally divided between precipitate and filtrate.

Behavior of Calcium Borate and Oxalate towards Sodium Hydroxide.—A mixture containing 100 mg. Ca as $CaCl_2$ and 80 mg. BO_2 as H_3BO_3 was treated by P. 52; the precipitate was tested for borate by adding to it in a casserole H_2SO_4 (1.84) and alcohol, igniting the alcohol and stirring vigorously: no green color appeared. The filtrate was acidified with H_2SO_4, evaporated, and tested in the same way: a large amount of borate was found. A trial experiment showed that 5 mg. BO_2 could easily be detected in this way.

A mixture containing 500 mg. Fe as $FeCl_3$, 500 mg. C_2O_4 as oxalic acid, and 100 mg. Ca as $CaCl_2$ was treated by P. 52; the filtrate was analyzed for oxalate by acidifying, adding NH_4OH and $CaCl_2$: a very large precipitate of calcium oxalate separated.—The experiment was repeated with 300 mg. Ca and 500 mg. C_2O_4 (but no iron): the result was the same. The precipitate was tested for oxalate by dissolving it in HCl and adding NH_4OH: a small precipitate separated, showing that a large proportion of the oxalate had passed into the filtrate.

Decomposition of Oxalic Acid by Acids.—10 and 100 mg. oxalic acid were treated separately by P. 61, about 1 g. $KClO_3$ being added to the concentrated HNO_3 solution. The solutions were finally evaporated to almost 5 cc., diluted to 30 cc., neutralized with NH_4OH, and tested for oxalate by adding 10 cc. of 10 per cent. $Ca(NO_3)_2$ solution: no precipitate separated in either experiment.—The experiment with 10 mg. oxalic acid was repeated, except that no $KClO_3$ was added to the HNO_3 solution: a precipitate containing about 3 mg. oxalic acid resulted.—10 mg. oxalic acid were added to 15 cc. HCl (1.20), the mixture was evaporated to 2 or 3 cc., diluted and tested for oxalic acid as above: a precipitate of calcium oxalate separated that was estimated to correspond to 3 or 4 mg. oxalic acid.—The experiment was repeated with aqua regia instead of HCl (1.20): somewhat more oxalic acid was decomposed, but at least 2 mg. remained.—These experiments prove that the decomposition of oxalic acid is very rapid in a hot mixture of HNO_3 and $HClO_3$, much slower in aqua regia, and still slower in HCl (1.20) or HNO_3 (1.42).

P. 52, N. 10: Color of an Alkaline Solution of Sodium Chromate and Peruranate.—1 mg. Cr as $KCrSO_4$ was treated by P. 52, the final volume being about 30 cc.: the yellow color of the solution was easily seen.

1 mg. U as $UO_2(NO_3)_2$ was treated by P. 52, the final volume being about 15 cc.: the solution was distinctly yellow.—The experiment was repeated with 5 mg. U; the solution had a reddish tinge. It was diluted to 30 cc.: the reddish color changed to yellow.

Color of Vanadium Solutions.—100 mg. V as Na_3VO_4 were added to a little concentrated HCl, and the mixture was evaporated to a small volume: the solution was at first orange-yellow but turned greenish blue on evaporation with HCl, showing reduction of the vanadium to the quadrivalent state. Excess of concentrated HNO_3 was added and the mixture again evaporated to a small volume: the solution rapidly became yellow and the concentrated solution was deep red, doubtless owing to the presence of free vanadic acid (See below). On diluting to about 20 cc., it became yellow. The solution was neutralized with 10 per cent. NaOH solution: a small yellow precipitate separated during the neutralization but dissolved on the addition of a little more NaOH; the alkaline solution was of a deeper yellow color than the dilute HNO_3 solution. Na_2O_2 was added: no change was observed. The mixture was boiled for 1 minute: the solution became colorless. The solution was cooled and made acid with HNO_3: it became yellow, the color being deepest at the neutral point. To a portion of this acid solution were added 50 mg. Ti as $TiCl_4$: no change in color was observed, showing that the Na_2O_2 had been completely decomposed and that no pervanadate had remained in the alkaline solution after boiling. Düllberg, *Z. physik. Chem.*, 45, 172 (1903), considers that the yellow color is due to $H_4V_6O_{17}$, an ion of the tetrabasic hexavanadic acid, $H_4V_6O_{17}$ (see C. E., *P. 58*a*, N. 6).

P. 52, N. 11: Division of Zinc in the Sodium Peroxide Treatment.—500 mg. Fe as $FeSO_4$ and 10 mg. Zn as $ZnCl_2$ were treated by P. 52, the final volume being about 30 cc.; the filtrate was tested for zinc by P. 53 and 57: only about 3 mg. Zn were found, showing that the remainder had been carried down with the $Fe(OH)_3$.—The experiment was repeated with 5 mg. Zn as $ZnCl_2$: only a trace of zinc was found in the filtrate.—The last experiment (with 5 mg. Zn) was repeated except that a large excess of NaOH was added before the Na_2O_2: 1 to 2 mg. Zn were found in the filtrate. The precipitate of $Fe(OH)_3$ was analyzed by P. 64, 66 and 67: the remainder of the zinc was found.

500 mg. Mn as $MnCl_2$ and 10 mg. Zn as $ZnCl_2$ were treated by P. 52, and the filtrate was tested for zinc by P. 53 and 57: no zinc was found.—The experiment was repeated with 20 mg. Zn: a very small precipitate of ZnS was obtained in P. 57 which contained less than 0.5 mg. Zn. On analyzing the precipitate by P. 61, 64, 66 and 67 the zinc was found. Therefore nearly 20 mg. zinc may be completely carried down when 500 mg. Mn are present.—The experiment was repeated with 10 mg. Zn, except that the acid solution was poured into a fairly concentrated NaOH solution in P. 52: about 0.3 mg. Zn was found in the filtrate, showing that a little zinc remains in the filtrate in this case.

For the fact that zinc is carried down with nickel and cobalt, see T. A., No. 140–143.

Separation of Vanadium from Manganese.—A mixture containing 250 mg. Mn as nitrate and 1 mg. V as Na_3VO_4 was treated by P. 52; the filtrate was tested for vanadium by *P. 58*e*: a very good test was obtained.

P. 53, N. 1: Solubility of Zinc Phosphate, Carbonate, and Oxalate in Ammonium Hydroxide.—100 mg. Zn as $ZnSO_4$ along with an equivalent amount of sodium phosphate, sodium carbonate or oxalic acid were dissolved in separate experiments in about 30 cc. cold water and about 2 cc. HNO_3 (1.20). The solutions were neutralized with NH_4OH (0.96) and an excess of about 3 cc. added: clear solutions were obtained in each case.

P. 54, N. 1–3: Confirmatory Test for Aluminum.—See Knoevenagel, *Prakticum des anorg. Chemikers*, p. 160.

0.5 mg. Al and 0.2 mg. Co as nitrates were treated by P. 54: the ash retained the form in which the filter paper was rolled and had a brilliant blue color.—The experiment was repeated with 0.2 mg. Al and 0.1 mg. Co: the residue was distinctly blue. —The experiment was repeated with 0.1 mg. Al and 0.1 mg. Co: no blue color was apparent.

Effect of Other Elements upon the Confirmatory Test for Aluminum.—0.5 mg. Al and 0.2 mg. Co as nitrates were treated by P. 54, except that 1 mg. Fe as $Fe(NO_3)_3$ was also added: the residue was brown.—This experiment was repeated with 1 mg. Al: the residue was partly blue.—The experiment was repeated with 2 mg. Fe and 1 mg. Al: the blue color could scarcely be distinguished.

The experiment with 0.5 Al was repeated in the presence of 1 mg. Be as $Be(NO_3)_2$: the residue was blue.—The experiment was repeated with 5 mg. Be: a satisfactory test for aluminum was obtained.—The experiment with 1 mg. Al was repeated in the presence of 5 mg. Be and also of 10 mg. Be as nitrate: a fair test for aluminum was obtained in the presence of 5 mg. Be but none with 10 mg. Be. In the latter case the paper and ash disintegrated.

1 mg. Al as nitrate was treated by P. 54, in the presence of 1, 2, and 5 mg. U as $UO_2(NO_3)_2$ respectively: a slight test for aluminum was obtained in the first experiment, a very poor one in the second, and none in the third.—The experiment was repeated with 0.5 Al and 1 mg. U: the test was very poor.

The experiment was repeated with 1 mg. Al and 5 mg. V as Na_3VO_4: the residue was distinctly blue.

0.5 mg. Al as $Al_2(PO_4)_3$ and 0.2 mg. Co as nitrate were treated by P. 54: the residue was blue.

1 mg. Al as nitrate was precipitated by adding to it $NaHCO_3$ solution and boiling. The precipitate was filtered off, washed once and treated by P. 54: the ash fused together into a small mass and no blue color was apparent.—1 mg. Al and about 5 mg. Na as nitrates were then treated by P 54: the result was the same, showing that the failure in the first experiment had been due to the presence of a sodium salt.

50 mg. SiO_2 as Na_2SiO_3 were dissolved in about 2 cc. HNO_3 (1.20) and 30 cc. water, heated to boiling, and made alkaline with NH_4OH: the solution slowly became turbid, and a gelatinous precipitate separated. This was collected on a filter, washed, and a portion of hot HNO_3 (1.20) was poured through the filter two or three times: the silica did not dissolve. The HNO_3 solution was tested for aluminum by P. 54, 0.5 mg. Co as nitrate being added: the residue was black.—The experiment was repeated except that 2 mg. Al as nitrate were also present: a fair test for aluminum was obtained.

P. 56, N. 1: Test for Chromate with Hydrogen Peroxide.—For the constitution and properties of the perchromic acid, and of other perchromates, see Riesenfeld, *Ber.*, 38, 1885, 3380, 4578, and 4068 (1905).

In a series of test tubes, each of which contained 0.3 mg. Cr as K_2CrO_4, were placed 0, 0.5, 2, 5, 10, and 20 cc. HNO_3 (1.20); each solution was diluted to 20 cc.; 3–5 cc ether and 2 cc. H_2O_2 (3 per cent.) were added, and the solutions were shaken: in the solution containing no acid, and in the solutions containing 5, 10, and 20 cc. acid, no blue color was obtained, but the remaining two solutions became blue at once, and the blue compound was extracted by the ether on shaking. In the solution containing 2 cc. HNO_3, the color in the ether layer in contact with the solution disappeared in about half an hour on standing; the color was more brilliant and remained for a longer time in the experiment with 0.5 cc. HNO_3.—The experiment was repeated with H_2SO_4 (1.20) instead of HNO_3: no color was obtained with no acid or with 10 and 20 cc. of it; the most brilliant and most permanent color was obtained in the experiment with 0.5 cc. acid.—The experiment was repeated with 30 per cent. acetic acid: in this case the best tests were obtained in the solutions containing 10 and 20 cc. of acid; with the more delicate solutions only a faint blue color was obtained.

Another series of experiments was performed with solutions that contained 0.3 mg. Cr as K_2CrO_4, and 2 cc. HNO_3 (1.20) in about 20 cc.; 3 cc. ether and varying amounts of H_2O_2 (3 per cent.) were added: with 10 cc. H_2O_2 no test was obtained, with 5 cc. a slight one, with 2 cc. a good test, but with 0.5 cc. H_2O_2 a much better one.

In all of these experiments in which the blue perchromic acid was formed, the blue color disappeared completely in less than 1 hour. In some of them the solution was warmed to 50 or 60°: the blue color disappeared very rapidly. These experiments prove that perchromic acid is a very unstable substance even in the absence of an excess of H^+ or of H_2O_2 and is still more so at higher temperatures.

Delicacy of the Confirmatory Test for Chromate.—To a solution containing 0.5 cc. Cr as K_2CrO_4 in 100 cc. was added a little ammonium acetate solution, 2 cc. acetic acid, and 1 g. $BaCl_2$: a yellow precipitate separated at once. This was collected on a filter, and treated by P. 56: upon the addition of H_2O_2 and ether, a distinct blue color resulted. The experiment was repeated with 0.2 mg. Cr: a slight but distinct precipitate and color were obtained.

Reduction of Chromic Acid by Filter Paper.—10 mg. Cr as K_2CrO_4 were precipitated as lead chromate, and the mixture filtered. The precipitate, with the filter, was placed in a casserole; 10 cc. water, and 5 cc. HNO_3 (1.20) were added, and the mixture was boiled. The solution turned green in about 1 minute, thus showing that reduction takes place readily.

P. 57, N. 3: Ignition Test for Zinc with Cobalt Nitrate.—0.1, 0.2 and 10 mg. Zn as $Zn(NO_3)_2$ were treated as described in the second paragraph of P. 57, 0.2 mg. Co as nitrate being used in each experiment: a distinct green color resulted in the experiment with 0.1 mg. Zn, a deeper color with 0.2 mg. and an intense color with 10 mg. —1 mg. Zn and 2 mg. Co as nitrates were treated as described in the last paragraph of P. 57: the residue was green. The residue was then heated strongly: it turned black, showing that when an excess of cobalt is present the test is more delicate if the mixture is not heated strongly.—The experiment was repeated with 2 mg. Cr and 1 mg. Zn: a green color resulted which remained after the residue had been heated strongly.

A solution containing 5 mg. Zn and 0.5 mg. Co as nitrates was evaporated to dryness in a casserole and the mixture was ignited, first gently and then strongly: the residue was black owing to the presence of cobalt oxide.—0.3 mg. Zn and 0.2 mg. Co as nitrates were treated by the last paragraph of P. 57, except that 5 cc. of 10 per cent. Na_2CO_3 solution were added in excess: only a very faint green color resulted. —The experiment was repeated except that only 3 drops Na_2CO_3 solution were added in excess: the green color was mixed with black.—The experiment was repeated, with an excess of 1 cc. and also with an excess of 0.5 cc. Na_2CO_3 solution: a good green color was obtained.—These experiments show that some Na_2CO_3 must be added, but only a moderate quantity.

A solution containing 0.3 mg. Zn and 0.2 mg. Co as chlorides and an excess HCl was treated by P. 57 (last par.), no HNO_3 being added: the residue had no distinct color, showing that HCl cannot be substituted for HNO_3.

P. 58a, N. 3: Composition of the Zinc and Beryllium Precipitates Produced by Sodium Hydrogen Carbonate.*—500 mg. Zn as nitrate were treated by *P. 58*a*, using a total volume of 100 cc. The precipitate was carefully washed with water, and tested for carbonate in the usual way by treating with acid in a flask and passing the gas evolved through $Ba(OH)_2$ solution. A large precipitate of $BaCO_3$ was obtained which corresponded to at least 200 to 300 mg. Zn.—The experiment was repeated with 200 mg. Be: a large amount of carbonate was also found in the beryllium precipitate, the precipitate of $BaCO_3$ being about twice as large as in the experiment with zinc. Parsons states, *J. Am. Chem Soc.*, **28, 557 (1906), that the precipitate obtained in a dilute ammonium carbonate solution is a basic carbonate of beryllium.

Precipitation of Aluminum in Hot Sodium Hydrogen Carbonate Solutions in a Closed Bottle.—Solutions containing 2 mg. Al as nitrate in 100 cc. were placed in pressure bottles, and 2, 5 and 10 mg. $NaHCO_3$ added: each of the three solutions quickly became turbid in the cold. The bottles were heated at about 95° in a water bath for half an hour: a flocculent precipitate formed in each case in less than 5 minutes, and settled in less than 20 minutes. The bottles were cooled and the precipitates filtered off; the filtrates were evaporated with excess of HNO_3 and tested for aluminum with NH_4OH: little or no precipitate separated, showing that the precipitation of the aluminum had been practically complete in each case.—The experiments were repeated with 1, 1/4, 1/16, and 1/32 g. $NaHCO_3$: the results were the same except that the precipitation was not complete with 1/32 g. $NaHCO_3$.—The experiment was repeated with 1/64 g. $NaHCO_3$: no precipitate was obtained.—These experiments were repeated, except that the solution was thoroughly saturated with CO_2 gas before adding the $NaHCO_3$: the results were nearly the same.

A solution containing 500 mg. Al as nitrate in 100 cc. was placed in a bottle and 4 g. $NaHCO_3$ added: there was a violent evolution of CO_3 gas, a small precipitate formed, and the solution still reacted acid to litmus. One g. more $NaHCO_3$ was added: a very large precipitate separated, very little gas came off, and the solution after shaking did not turn blue litmus red. The mixture was heated in the closed bottle at 95° in a waterbath for half an hour, cooled, and filtered: the filtrate was found to contain no aluminum. Therefore 500 mg. Al are completely precipitated when about 5 g. $NaHCO_3$ are added in 100 cc. of solution.

Precipitation of Zinc Carbonate in Hot Sodium Hydrogen Carbonate Solutions.—Four solutions, each containing 2 mg. Zn as nitrate dissolved in 100 cc., were poured into strong 200 cc. bottles; to these were added 1, 2, 3 and 5 g. respectively of solid $NaHCO_3$; the bottles were corked and shaken until the $NaHCO_3$ dissolved; they were then heated in a waterbath at 90 to 95° for half an hour: all the solutions became slightly turbid in the cold and after heating for 5 minutes precipitates could be seen in suspension. After the half hour's heating the bottles were allowed to cool to about 40°, and the solutions containing 1 and 5 g. $NaHCO_3$ were filtered and tested for zinc by evaporating with HNO_3, adding NH_4OH and acetic acid and passing in H_2S: only a trace of zinc was found in each filtrate, thus showing that the precipitation was practically complete in both 1 per cent. and 5 per cent. $NaHCO_3$ solutions.—The experiments with 1 and 2 g. $NaHCO_3$ were repeated except that the solutions were thoroughly saturated with CO_2 gas at room temperature before the $NaHCO_3$ portions were added: the results were the same.

The experiment was repeated with a solution containing 500 mg. Zn as nitrate in 100 cc., 2 g. $NaHCO_3$ being added: no precipitate of ZnS separated. The experiment was repeated with 500 mg. Zn and 1.5 g. $NaHCO_3$: about 5 mg. Zn were found in the filtrate, showing that 1.5 g. $NaHCO_3$ is not quite sufficient to precipitate 500 mg. Zn completely.

Precipitation of Beryllium in Hot Sodium Hydrogen Carbonate Solutions in a Closed Bottle.—A solution containing 1 mg. Be as nitrate in 100 cc. was placed in a 200 cc. bottle, 1 g. $NaHCO_3$ was added, and the mixture was digested in the tightly stoppered bottle at about 95° in a waterbath for half an hour: the solution became turbid in less than 5 minutes and a precipitate separated in 10 minutes; on standing in the cold for an hour the precipitate seemed to redissolve to a small extent. The experiment was repeated with a solution that was saturated with CO_2 gas before the $NaHCO_3$ was added: the result was the same.—These experiments were repeated with 1 mg. Be and 2 g. $NaHCO_3$: the mixture that had been saturated with CO_2 was distinctly turbid in 15 minutes while the other was only very slightly turbid after half an hour. The solutions cleared on standing for an hour in the cold.—The last experiments were repeated with 2 mg. Be and 2 g. $NaHCO_3$: distinct precipitates were obtained corresponding to about 1 mg. Be but these redissolved to a considerable extent in the cold.

These experiments were repeated with solutions containing 3 to 10 g. $NaHCO_3$ in 100 cc. of solution and varying quantities of beryllium: in the 3 per cent. $NaHCO_3$ solution 3 mg. Be gave no precipitate, but a larger amount did so; in the 5 per cent. solution, about 15 mg. Be just remained in solution in 100 cc.; and in the 10 per cent. solution, about 75 mg. Be gave a small precipitate in 50 cc., while 50 mg. Be gave only a negligible precipitate.

Solubility of Uranyl Vanadate in Sodium Hydrogen Carbonate Solutions.—Solutions containing 100 mg. U as $UO_2(NO_3)_2$ and 60 mg. V as Na_3VO_4 were mixed, a few drops HNO_3 (1.20) were added to dissolve the precipitate, the mixture was diluted to 100 cc., 2 g. $NaHCO_3$ were added, and the mixture was digested in a closed bottle at 95° for half an hour: no precipitate separated. The mixture was cooled down, 40 mg. V as Na_3VO_4 were added, making 100 mg. in all, and the mixture was again heated at 95° for half an hour: no precipitate separated in the hot solution, nor in the cold on standing several days.—The experiment was repeated with 100 mg. U and 100 mg. V, except that the mixture was first treated with NaOH and H_2O_2 by P. 52, and that 1.5 g. $NaHCO_3$ were used instead of 2 g.: the result was nearly the same.—100 mg. U as $UO_2(NO_3)_2$, 100 mg. V as Na_3VO_4, and 3 g. $NaNO_3$ were treated by *P. 58*a*, 1 g. excess of $NaHCO_3$ being added: a precipitate formed on adding $NaHCO_3$ and a considerable one remained after heating the mixture at 100° in a closed bottle for 30 minutes. The precipitate and filtrate were analyzed for uranium and vanadium by *P. 58*c–e:* the filtrate was found to contain 35–40 mg. of uranium and all but 10 or 15 mg. of the vanadium.

The last experiment was repeated except that the mixture was warmed in a flask at 95° (without allowing it to boil) for 30 minutes: the precipitate that remained was smaller, and contained only 10 to 20 mg. U and 2 to 5 mg. V.—The last experiment was repeated except that the mixture was boiled for 1 minute in an open flask: the precipitate dissolved completely, and no precipitate formed on cooling even in 24 hours, showing that uranyl vanadate is more soluble in slightly alkaline carbonate solutions than in those from which the CO_2 is prevented from escaping.

An acid solution containing 50 mg. V as Na_3VO_4, and 50 mg. U as $UO_2(NO_3)_2$ was diluted to 100 cc. and neutralized by adding a little powdered $NaHCO_3$. Then 0.5 g. $NaHCO_3$ was added, and the mixture was heated in a pressure bottle at 95° for half an hour: on heating a large precipitate remained.—To a solution containing 100 mg. V as Na_3VO_4, 20 mg. U as $UO_2(NO_3)_2$ and a known excess of HNO_3 (1.20) in 50 cc. (instead of 100 cc.) was added just sufficient $NaHCO_3$ to leave 1 g. undecomposed $NaHCO_3$. The mixture was heated in a closed bottle at 95° for half an hour: no precipitate separated.—To this solution after cooling, was added 20 mg. more U and the mixture was again heated at 95°: a large precipitate separated in the cold and remained on heating.—The experiment was repeated with 100 mg. U and 10 mg. V: no precipitate separated. 10 mg. more V were added and the heating repeated: a large precipitate separated in the cold and remained on heating.—The last experiment was repeated with 100 mg. V and 100 mg. U and the precipitate and filtrate were analyzed for uranium and vanadium by *P. 58*c* to *e:* the filtrate was found to contain 20 or 30 mg. of uranium and all but a few mg. of the vanadium.

Non-Precipitation of Uranyl Chromate, Phosphate, and Oxalate in the $NaHCO_3$ Procedure.—To a solution containing 100 mg. U as $UO_2(NO_3)_2$ 200 mg. Cr as K_2CrO_4, and a known (small) amount of HNO_3 (1.20) in 100 cc. was added enough $NaHCO_3$ to leave 1 g. of the undecomposed carbonate; the mixture was heated in a closed bottle at 95° for half an hour: no precipitate separated.—A solution containing 100 mg. U as $UO_2(NO_3)_2$ and 100 mg. PO_4 as $NaHPO_4$ was treated by P. 52 and then by *P. 58*a:* no precipitate separated in the $NaHCO_3$ procedure. After cooling an additional 250 mg. portion of PO_4 was added, and the heating repeated: no precipitate separated. —The experiment was repeated with 100 mg. V as Na_3VO_4 and 200 mg. oxalic acid: no precipitate separated.

**P. 58a, N. 4: Precipitation of Aluminum, Zinc, and Beryllium in Hot Sodium Hydrogen Carbonate Solutions in Open Flasks.*—2 mg. Al as nitrate and 3 g. $NaNO_3$ were dissolved in 100 cc. water; a little $NaHCO_3$ was added until the mixture after shaking just ceased to react acid to litmus paper; 1 g. more was added; the mixture was heated to about 90° and digested at this temperature in a covered flask on a waterbath for half an hour: the precipitate slowly dissolved, except a few small flakes. The mixture was filtered while hot, and the filtrate tested for aluminum by acidifying with acetic acid, adding Na_2HPO_4 and heating to boiling: almost all the aluminum was found in the filtrate.—This experiment was repeated twice with 2 mg. and with 1 mg: the results were the same.—The experiment was repeated twice with 20 mg. Al: the filtrate contained less than 1 mg. Al.

The experiments with 2 and 20 mg. were repeated, except that CO_2 gas was passed through the mixture: the results were nearly the same, except that the filtrate may have contained somewhat more aluminum, showing that there is no advantage in using CO_2 gas.

The experiment with 20 mg. Al was repeated except that the mixture was boiled for one minute: the filtrate contained 3 or 4 mg. Al.—The experiment was repeated except that the mixture was allowed to cool before filtering: the filtrate contained about 1 mg. Al.—The experiment was repeated with 4 mg. Al: the precipitate disappeared completely on boiling, but a precipitate separated out on cooling.—The experiment was repeated with 6 mg. Al: a very small precipitate remained on boiling 1 minute.

1 mg. Zn as nitrate and 2 g. $NaNO_3$ were dissolved in 100 cc., 1 g. excess $NaHCO_3$ was added, and the mixture boiled in a flask for one minute: the precipitate did not dissolve and was proved to contain zinc by P. 53–57.—The experiment was repeated with 20 mg. Zn; the filtrate being tested for zinc by acidifying with HNO_3, boiling, adding NH_4OH and passing in H_2S: no precipitate formed, showing that the zinc was completely precipitated.

10 mg. Be as chloride and 2 g. $NaNO_3$ were dissolved in 100 cc. water, $NaHCO_3$ was added until the mixture after shaking just ceased to react acid to litmus paper; 1 g. more was added; the mixture was boiled for 1 minute, and filtered while hot; the filtrate was acidified with HNO_3, evaporated to about 15 cc. and tested for beryllium by adding NH_4OH: the filtrate contained only about 0.1 mg. Be.—The experiment was repeated except that the mixture was allowed to cool before filtering: the filtrate contained about 0.3 mg. Be.—The experiment was repeated with 1 mg. Be: the precipitate remained on boiling for one minute, and did not disappear on standing in the cold for several hours.

These experiments were repeated with solutions containing from 1.5 to 5 g. $NaHCO_3$ in 100 cc. of solution and varying quantities of beryllium: in a 1.5 per cent. $NaHCO_3$ with 1 mg. Be little or no precipitate remained on boiling 1 minute; in a 2 per cent. solution no precipitate remained with 2 mg. Be, but one remained with 4 mg.; in a 3 per cent. solution 40 mg. Be dissolved almost completely, but 50 mg. gave a large precipitate. A comparison of these results with those obtained in a similar series of experiments in closed bottles (C. E., N. 3, above) shows that considerably more beryllium dissolves in concentrated $NaHCO_3$ solutions when the CO_2 is allowed to escape.

**P. 58a, N. 5: Precipitation of Uranium with Aluminum or Beryllium in Hot Dilute Sodium Hydrogen Carbonate Solutions.*—See T. A., No. 171 to 175. In an analysis with 200 mg. Al and 10 mg. U, starting at *P. 58*a*, 1 or 2 mg. U were found in *P. 58*c–d*.

**P. 58a, N. 6: Dissociation Relations of Carbonic Acid.*—See McCoy, *Am. Chem. J.*, 29, 437 (1903).

Dissociation Relations of Chromic Acid.—See Spitalsky, *Z. anorg. Chem.*, 54, 265 (1907) and Sherrill, *J. Am. Chem. Soc.*, 29, 1641 (1907). The work of the latter shows that H_2CrO_4 dissociates in steps, first into $HCrO_4^-$ and then into $CrO_4^{=}$, that the $HCrO_4^-$ is a very weak acid, and that the latter even in dilute solution is converted by dehydration in large measure but by no means wholly, into dichromate-ion (Cr_2O_7)

Condition of Vanadic Acid in Solution.—See Düllberg, *Z. physik. Chem.*, 45, 129–181 (1903). He considers that in a solution of the composition of Na_3VO_4, which reacts strongly alkaline, the salt is largely hydrolyzed according to the reaction $2Na_3VO_4 + H_2O = 2NaOH + Na_4V_2O_7$, but his evidence is not convincing. On adding HCl slowly the results indicate the presence of a tetrabasic acid, $H_4V_6O_{17}$. This is a strong acid, two of the hydrogens splitting off nearly completely in dilute solutions, and the third one to a considerable extent. The yellow color is probably due to the ion $HV_6O_{17}^{\equiv}$. The transition of one form of vanadic acid into another takes place readily, the final equilibrium state being reached fairly quickly. Conductivity and freezing-point determinations make it probable that the formula of sodium metavanadate is $(Na^{+})_3V_3O_9^{\equiv}$

**P. 58b, N. 1: Partial Decomposition of H_2O_2 in the $NaHCO_3$ Treatment.*—A mixture containing 100 mg. U as $UO_2(NO_3)_2$ and 100 mg. V as Na_3VO_4 was treated by P. 52 and *P. 58*a* and then was acidified with HNO_3: the acid solution before adding the $NaHCO_3$ was red owing to the presence of pervanadic acid, indicating the presence of much H_2O_2; on neutralizing with $NaHCO_3$ it became yellow; and the final HNO_3 solution was also pale yellow. The solution was tested for H_2O_2 with a titanium solution: a distinct color was obtained. These results show that much but not all of the H_2O_2 had been decomposed.

**P. 58b, N. 2: Detection of Chromic Acid in the Presence of Uranium and Vanadium by H_2O_2.* —A mixture containing 1 mg. Cr, 100 mg. U, 100 mg. Zn and 100 mg. Al as nitrates, and 100 mg. V as Na_3VO_4 was treated with NaOH and Na_2O_2 by P. 52: a deep red solution resulted and there was no residue. The solution was made acid with HNO_3, being cooled carefully during the process. Just enough acid was added to dissolve the precipitate that formed. To about one-fourth of the solution in a test-tube was added a little ether and about 1 cc. H_2O_2: the ether layer became blue. The water layer was red before H_2O_2 was added, showing the presence of pervanadic acid. —The experiment was repeated with 2 mg. Cr, 100 mg. U and 100 mg. V: the result was the same. After testing for chromium the remainder of the solution was treated by *P. 58*a*, the solution was cooled, made just acid with HNO_3, and one-tenth of it tested for chromic acid with H_2O_2: a good blue color was obtained. The remainder of the solution was made somewhat more strongly acid and evaporated to half its volume; the test for chromic acid was then made with half the solution: no blue color was obtained, showing that the chromic acid had been reduced on boiling.

Action of H_2O_2 on Uranium Salts.—To 10 mg. U as $UO_2(NO_3)_2$ in 20 cc. were added 1 cc. HNO_3 (1.20), 1 cc. 3 per cent. H_2O_2, and a little ether: the yellow color of the solution did not change, and the ether layer remained colorless.

**P. 58b, N. 4: Precipitation of Chromate by Lead Nitrate.*—Several solutions each containing 0.5 mg. Cr as K_2CrO_4, 2 g. $NaNO_3$, and 1 g. $NaHCO_3$ in 100 cc. or 70 cc. were made distinctly acid with HNO_3, shaken to expel CO_2, and neutralized exactly with NaOH; varying amounts of HNO_3 (1.20) were added, and finally known volumes of a 20 per cent. lead nitrate solution. The results are shown in the following table:

Initial volume.	Volume of HNO_3 (1.20).	Volume of lead nitrate solution.	
100 cc.	1.5 cc.	10 cc.	precipitate in 1 or 2 min.
100 cc.	2.5 cc.	20 cc.	precipitate in 3 or 4 min.
100 cc.	5.0 cc.	30 cc.	no precipitate in 30 min.
70 cc.	1.5 cc.	10 cc.	precipitate in 2 or 3 min.
70 cc.	2.5 cc.	10 cc.	precipitate very slowly.
70 cc.	2.5 cc.	20 cc.	precipitate in 3 to 5 min.

The last two experiments were repeated with 6 g. $NaNO_3$ (instead of 2 g.): only very small precipitates were obtained in half an hour, even with 20 cc. $Pb(NO_3)_2$ solution, showing that the presence of much $NaNO_3$ prevents the precipitation of $PbCrO_4$.

Behavior of Vanadate and Uranate towards Lead Nitrate. — Several solutions, each containing 100 mg. V as Na_3VO_4, 2 g. $NaNO_3$ and 1 g. $NaHCO_3$, in 100 cc., were acidified with HNO_3, shaken, and then neutralized exactly with NaOH; 1.5 to 3 cc. of HNO_3 (1.20) and 10 to 30 cc. of a 20 per cent. lead nitrate solution were added and the mixture allowed to stand 30 minutes: with 3 cc. HNO_3 there was no precipitate even with 30 cc. $Pb(NO_3)_2$; with 1.5 and 2 cc. HNO_3 there was none with 10 cc. $Pb(NO_3)_2$; but a small one with 20 cc., which was however very slight when 2 cc. HNO_3 were used. The experiments were repeated with an initial volume of 70 cc.: the results were nearly the same, except that the precipitates when formed were somewhat larger.

A solution containing 100 mg. U as $UO_2(NO_3)_2$, 2 g. $NaNO_3$, and 1 g. $NaHCO_3$ in 100 cc. was neutralized with HNO_3, and an excess of 1 cc. HNO_3 (1.20) was added; finally 20 cc. 20 per cent. $Pb(NO_3)_2$ were added: no precipitate separated in several hours.

*Precipitation of Aluminum, Beryllium or Lead by Sodium Phosphate in *P. 58c.*— 0.5, 1, and 2 mg. Al as nitrate, in solutions containing 2 g. $NaNO_3$, 2 g. NH_4NO_3, and 5 cc. 30 per cent. acetic acid in a total volume of 100 cc. were heated to boiling: flocculent white precipitates separated in each case, the results showing that this is a very good method of estimating small amounts of aluminum.

The experiments were repeated with 0.5, 1 and 2 mg. Be as chloride: flocculent white precipitates resulted except in the experiment with 0.5 mg. The filtrate in the experiment with 2 mg. was estimated to contain about 0.5 mg. Be.

The experiments were repeated with 1 and 2 mg. Pb as nitrate: a distinct precipitate was obtained with 2 mg. but only a very small one with 1 mg. Pb.

Oxidation of Hypovanadic Acid by Bromine.—50 mg. V as Na_3VO_4 and 1 g. Pb as $Pb(NO_3)_2$ were dissolved in 2.5 cc. HNO_3 (1.20) and 100 cc. water; the mixture was saturated with H_2S in the cold, filtered, and the filtrate was boiled: the cold solution had a blue color, but on boiling sulphur separated and the color became deeper. The sulphur was filtered off, bromine water added until the bromine odor was distinct after shaking, and the mixture was boiled: the color was still blue. A small excess of bromine was again added: the solution was still blue.—The experiment was repeated except that several drops liquid bromine were added, and the mixture shaken, and allowed to stand two or three minutes; the bromine was then boiled off: the solution was yellow. The filtrate was treated by *P. 58*c*: no precipitate separated.

Behavior of Vanadyl Salts and Vanadates towards Sodium Phosphate.—50 mg. V as Na_3VO_4 and 1 g. Pb as $Pb(NO_3)_2$ were dissolved in 2.5 cc. HNO_3 (1.20) and 100 cc. water; the mixture was saturated with H_2S, filtered, boiled and filtered again. The blue filtrate was treated by *P. 58*c*, 2 g. $(NH_4)_2SO_4$ and 2 g. Na_2HPO_4 being added: on warming, a large, flocculent, bluish white precipitate separated.—The experiment was repeated except that the vanadyl salt was first oxidized with liquid bromine as described in P. 58*b*: no precipitate separated in *P. 58*c*.

P. 58c, N. 1: Precipitation of Uranyl Ammonium Phosphate.*—See Kern, *J. Chem. Soc.*, **23, 705–10 (1901).

Detection of Small Amounts of Uranium.—0.3, 0.5 and 1 mg. U as $UO_2(NO_3)_2$ were dissolved in separate experiments in 100 cc. water containing 5 cc. 30 per cent. acetic acid and 3 g. $NaNO_3$, and treated by P. 58*c*: white flocculent precipitates separated in each case, but that with 0.3 mg. was very small. The precipitates were filtered off and tested by P. 58*d*: in the experiment with 0.3 mg. U the ferrocyanide test failed, but was very satisfactory in the other two cases.—The experiment with 0.3 mg. U was repeated except that 0.5, 4, and 6 g. respectively $(NH_4)_2SO_4$ (instead of 2 g.) were added: very small precipitates of uranyl ammonium phosphate were obtained in each case, but the ferrocyanide test failed. This shows that there is no advantage in adding more than 2 g. $(NH_4)_2SO_4$.—The experiments with 0.5 and 1 mg. U were repeated, except that no ammonium salt was added: with 1 mg. the result was satisfactory, but with 0.5 mg. the confirmatory failed.

The first experiments with 0.3, 0.5 and 1.0 mg. U were repeated in a volume of 40 cc. instead of 100 cc.: a distinct phosphate precipitate resulted in each case, and the ferrocyanide test was satisfactory, even with 0.3 mg. With 0.2 mg. a small phosphate precipitate formed but the confirmatory test failed.—The experiment was repeated with 1.0 mg. U, except that 0.3 g. $Na_2HPO_4.12H_2O$ was added instead of 2 g.: the confirmatory test failed, showing that a large excess of Na_2HPO_4 is necessary.—The experiment with 0.3 mg. U was repeated except that 10 cc. acetic acid was used instead of 5 cc.: the confirmatory test failed, showing that a large excess of acetic acid makes the phosphate precipitation less complete.

Separation of Uranium and Vanadium by Phosphate:—100 mg. U as $UO_2(NO_3)_2$, 50 mg. V as Na_3VO_4, and 1 g. NH_4NO_3 were dissolved in a few drops HNO_3 and 30 cc. water. The mixture was neutralized with NH_4OH: a large pale precipitate of uranyl ammonium vanadate separated. 10 cc. 30 per cent. acetic acid were added: the precipitate did not dissolve. 5 cc. 10 per cent. ammonium phosphate were added, the mixture was heated to boiling, allowed to stand for 15 minutes, and filtered. The filtrate was tested for vanadium by *P. 58*e*: a large quantity was found. The precipitate was washed with dilute NH_4NO_3 solution, dissolved in dilute hydrochloric acid, and the phosphate precipitation repeated: less than 1 mg. V was now found in the filtrate. The phosphate precipitate was treated in the same way: less than 0.2 mg. V was found in it.—The complete experiment was repeated except that the mixture containing the uranium ammonium vanadate precipitate and the acetic acid was heated to boiling, cooled, and allowed to stand over night before the phosphate was added: the result was the same, showing that the vanadium passes into the filtrate even when it is first precipitated in combination with the uranium.

P. 58c, N. 4: Precipitation of Uranyl Hydrogen Phosphate.*—See Kern, *J. Am. Chem. Soc.*, **23, 705 (1901).

**P. 58d, N. 1: Behavior of Uranyl Salts towards Potassium Ferrocyanide.*—Known amounts of $K_4Fe(CN)_6$ solutions were added to solutions containing 0.5 mg. U as $UO_2(NO_3)_2$, 1 cc. HCl (1.12), and 10 cc. nearly saturated NaCl solution: with 4 cc. of a 3 per cent. ferrocyanide solution a brown color appeared only after 40 minutes, with 10 cc., a brown precipitate separated in about 10 minutes, while with 10 cc. of a 10 per cent. ferrocyanide solution a precipitate separated in a minute or two, showing that a large excess of $K_4Fe(CN)_6$ is needed to make the test delicate.—The experiment was repeated except that 0.5 cc. HCl (1.12) was added, instead of 1 cc., 10 cc. 3 per cent. ferrocyanide solution being added: a brown precipitate separated in a minute or two.—This experiment was repeated with 0.1 and 0.05 cc. HCl (1.12): brown precipitates separated at once.—The experiment was repeated without the addition of any acid: no brown color appeared.—The experiment was repeated, adding 5 cc. HCl (1.12): no brown precipitate separated in 1 hour, but the solution became blue and a blue precipitate separated slowly on account of the decomposition of the ferrocyanide.—These experiments show that a little acid must be present, but that much acid makes the test less delicate.

0.1 and 0.2 mg. U as $UO_2(NO_3)_2$ were treated by *P. 58*d*, a few mg. PO_4 as Na_2HPO_4 being added: a good test was obtained with 0.2 mg., but only a very poor one after several minutes with 0.1 mg., showing that 0.1 mg. is about the limit of detectability, and that phosphate does not interfere with the detection of 0.2 mg. U.

The experiment with 0.5 mg. U and 0.5 cc. HCl (1.12) was repeated, except that water was added instead of NaCl solution: a dark red color resulted, and no precipitate separated out in 1 hour, showing that NaCl is needed to coagulate the colloid.

Behavior of Vanadyl Salts and Vanadic Acid towards Potassium Ferrocyanide.—5 mg. V as Na_3VO_4 after evaporation with HCl (whereby it is reduced to vanadyl chloride) were treated by *P. 58*d:* a greenish yellow precipitate separated. The precipitate was filtered off and the filtrate tested for vanadium by *P. 58*e:* only a very faint pink color resulted, showing that the precipitation of the vanadium by the ferrocyanide is nearly complete.—The experiment was repeated except that only two drops of HCl were added and the solution was not evaporated: no precipitate separated in half an hour, showing that a small quantity of vanadium in the form of vanadic acid is not precipitated by $K_4Fe(CN)_6$.

**P. 58e: Non-interference of Lead with the Vanadium Test.*—A solution containing 2 mg. Pb as $Pb(NO_3)_2$, and 0.5 mg. V as Na_3VO_4 and 2 g. NH_4NO_3 was treated by P. 58*e* and the black precipitate of PbS formed was filtered off: on saturating completely with H_2S, the filtrate had the characteristic violet-red color due to vanadium.

**P. 58g, N. 1: Separation of Aluminum and Beryllium.*—See Havens, *Z. anorg. Chem.*, 16, 15 (1898).

Precipitation of Aluminum as $AlCl_3.6H_2O$.—0.5 mg. Al as $AlCl_3$ was treated by *P. 58*g*, the total volume of the acid ether mixture being about 15 cc.: on saturating with HCl gas no precipitate could be seen, but on standing about 15 minutes a distinct crystalline precipitate separated out.

100 and 500 mg. Al as $AlCl_3$ were treated by *P. 58*g:* the filtrates, which had a total volume of about 70 cc., were evaporated to about 20 cc. and made alkaline with NH_4OH: no precipitate separated, but in the second experiment there was a faint turbidity corresponding perhaps to 0.1 mg. Al.

Behavior of Beryllium, Uranium and Chromium in the Hydrochloric Acid Ether Process.—100 mg. Be as $BeCl_2$ were treated by *P. 58*g*, the final volume being about 30 cc.: a small precipitate remained. This was filtered off, washed twice, dissolved in a little water, and proved to contain aluminum but no beryllium by boiling in a 10 per cent. $NaHCO_3$ solution as described in *P. 58*h*.

500 mg. Al and 2 mg. Be as chlorides were treated by *P. 58*g* in a volume of 60 cc. and the filtrate was treated by *P. 58*h:* a good test for beryllium was obtained and the amount of beryllium in the filtrate was estimated to be 1 or 2 mg., showing that very little beryllium was retained by the $AlCl_3.6H_2O$.

100 mg. U as UO_2Cl_2 were treated by *P. 58*g*, the total volume being 50 cc.: a clear yellow solution was obtained.

20 mg. Cr as K_2CrO_4 were boiled with HCl (1.20) to reduce the chromium to the chromic state, and the green solution was treated by *P. 58*g*, in a volume of about 30 cc.: the green color quickly disappeared and a violet precipitate separated. This was filtered off after several hours and the filtrate tested for chromium by evaporating, adding NH_4OH, and boiling: a precipitate estimated to contain 5–10 mg. Cr separated.

P. 58h, N. 1: Separation of Beryllium and Aluminum in Strong Sodium Hydrogen Carbonate Solution.*—See Parsons and Barnes, *J. Am. Chem. Soc.*, **28, 1589 (1906).

200 mg. Al as nitrate were dissolved in 20 cc. water, and added to a warm solution of 10 g. $NaHCO_3$ in 80 cc. water, the mixture was heated to boiling in a flask, boiled for 1 minute, and filtered; the filtrate was acidified with HNO_3, evaporated to about 20 cc. and made alkaline with NH_4OH: no precipitate separated on warming gently, nor on standing.

100 mg. Al and 1 mg. Be as nitrates were dissolved in 50 cc. water and 6 g. $NaHCO_3$ were added; the mixture was heated to boiling, boiled for 1 minute, and filtered while still hot; the filtrate was made acid with HNO_3, evaporated to about 10 cc. and made alkaline with NH_4OH: a very small precipitate separated which was estimated to contain 1/20 mg. Be.—The experiment was repeated with 2 mg. Be: the result was the same.—The experiment was repeated with 5 mg. Be: scarcely 1 mg. Be was found in the filtrate.—Therefore small amounts of beryllium cannot be completely separated from 100 mg. Al by this method.

The precipitate obtained in the experiment with 1 mg. Be was treated by *P. 58*g*–*h*: the beryllium present was estimated to be nearly 1 mg., showing that this separation with HCl and ether is more satisfactory than that with 10 to 12 per cent. $NaHCO_3$.

Behavior of Iron in Strong Sodium Hydrogen Carbonate Solution, and its Precipitation as Sulphide.—2 and 5 mg. Fe as $FeCl_3$ were treated by the last paragraph of *P. 58*h*: small precipitates of $Fe(OH)_3$ were formed in the $NaHCO_3$ solutions, but the precipitation was incomplete, for after acidifying the filtrates and adding NH_4OH, precipitates of $Fe(OH)_3$ were obtained, each of which was estimated to contain over 1 mg. Fe.—The experiment with 5 mg. Fe was repeated except that 5 cc. NaOH were added to the $NaHCO_3$ filtrate: no precipitate resulted in the cold, but about 0.5 mg. Fe as $Fe(OH)_3$ precipitated on boiling. The precipitation was still incomplete for about 0.5 mg. Fe was found in the solution on acidifying and adding NH_4OH.

0.5 mg. Fe as $FeSO_4$ and in a second experiment as $FeCl_3$, was boiled with 30 cc. 10 per cent. $NaHCO_3$, for 1 minute, the mixtures were poured through filters, cooled, and H_2S was passed in for about 3 seconds: the solutions became dark colored at once. After about 5 minutes the mixtures were filtered: the filtrates were clear, with a faint greenish shade corresponding to an insignificant amount of iron; more H_2S caused no further darkening.—The experiment with 0.5 mg. Fe as $FeCl_3$ was repeated, except that the $NaHCO_3$ solution was not cooled before passing in H_2S: a dark green solution was obtained which ran through the filter, showing that it is better to add the H_2S in the cold. To this solution (which was now cold) was added 2 or 3 mg. Fe as $FeSO_4$: on filtering after several minutes the filtrate was nearly colorless, and more H_2S gave no precipitate nor color.

**P. 58h, N. 2: Behavior of Uranyl Salts in Strong Sodium Hydrogen Carbonate Solution, and on Passing in H_2S.*—50 mg. U as UO_2Cl_2 (and in another experiment as $UO_2(NO_3)_2$) were dissolved in a little water and added to a solution containing 5 g. $NaHCO_3$, the final volume being 50 cc.; the mixture was boiled for 5 minutes: no precipitate separated.—The experiment was repeated with 5 mg. U as UO_2Cl_2 in a volume of 30 cc. and 10 cc. 10 per cent. NaOH was added to the 10 per cent. $NaHCO_3$ solution after boiling: no precipitate separated.

To a mixture containing 100 mg. Be and 20 mg. U dissolved in 50 cc. 10 per cent. $NaHCO_3$ was added 1 g. NH_4Cl, and the mixture was boiled: no precipitate separated.

A mixture containing 100 mg. Be and 10 mg. U (but no iron) dissolved in 30 cc. 10 per cent. $NaHCO_3$ solution was saturated completely with H_2S gas: no precipitate separated.

The Separation of Uranium and Beryllium by Potassium Ferrocyanide.—15 and 25 mg. Be as chlorides in HCl solution were evaporated almost to dryness, 10 cc. saturated NaCl solution added, the mixture was cooled and 5 cc. 10 per cent. $K_4Fe(CN)_6$ solution were added: clear solutions resulted which were blue colored, owing to the presence of a small amount of iron in the beryllium; after standing several hours a gelatinous light colored precipitate had separated in the experiment with 25 mg. Be.—The experiment was repeated with mixtures of 1 mg. U as $UO_2(NO_3)_2$ and with 5, 10, 15 and 20 mg. Be: a dark red color appeared at once in the experiments with 5 and 10 mg. Be, and on standing dark red precipitates settled out. In the experiments with 15 and 20 mg. the color was somewhat obscured owing to the presence of the iron. —The experiment with 20 mg. Be and 1 mg. U was repeated, except that the iron was first removed from the beryllium solution by P. 52: a good test for uranium was then obtained.

P. 61, N. 1: Solubility of Manganic Peroxide in HNO_3 in the Presence of Filter Paper. —500 mg. Mn as $Mn(NO_3)_2$ were treated by P. 52; the $MnO(OH)_2$ precipitate was boiled with 30 cc. HNO_3 (1.20) in a covered casserole for several minutes: very little of the precipitate dissolved. The experiment was repeated except that the filter, as well as the precipitate, was treated with the nitric acid: on boiling, the filter disintegrated and the precipitate dissolved completely in 10 or 15 min.—The last experiment was repeated with HNO_3 (1.42): nearly all of the precipitate dissolved after 5 minutes' boiling, and the remainder on standing over night. The solution obtained in the last experiment was evaporated to a small volume and diluted to about 15 cc.; the paper was filtered off, and the filtrate was treated by P. 61: the manganese was completely precipitated.

P. 62, N. 2: Precipitation of Manganese by Chloric and Nitric Acids.—See Hannay, *J. Chem. Soc.*, 23, 269 (1878); Ford, *Trans. Inst. Min. Eng.*, 9, 397.

P. 62, N. 3: Separation of Other Elements from Manganese by Chloric and Nitric Acids.—See T. A., No. 117, 118.

Iron.—100 mg. Mn as $MnCl_2$ and 1 mg. Fe as $FeSO_4$ were treated by P. 52 and P. 61 and the filtrate was tested for iron by P. 64: a good test was obtained.—500 mg. Mn as $MnCl_2$ and 1 mg. Fe were treated by P. 52 and then by P. 61; the precipitate and filtrate were tested for iron by evaporating with excess of HCl, diluting, and adding KSCN solution: a distinct test for iron was obtained in the filtrate but much more iron was found in the precipitate than in the filtrate.

Titanium.—A mixture containing 500 mg. Mn and 1 mg. Ti as nitrates was treated by P. 61; the filtrate was evaporated and made alkaline with NH_4OH: no precipitate separated, proving that the titanium had been completely carried down with the MnO_2.—This experiment was repeated with 5 and with 50 mg. Ti: the result was the same in each case.—The experiment was repeated with 50 mg. Mn and 50 mg. Ti; the precipitate was analyzed by *P. 62*a*, and about half the titanium found in it; the filtrate was evaporated almost to dryness: some of the titanium separated during the evaporation as a white precipitate which did not dissolve readily in HCl, but did in HF.—The experiment was repeated with 50 mg. Ti in the absence of manganese: no precipitate separated on adding $KClO_3$, nor on evaporating to 5 or 10 cc.

Zirconium.—A mixture containing 500 mg. Mn and 2 mg. Zr as nitrates was treated by P. 61; the filtrate was evaporated and made alkaline with NH_4OH: only a very small precipitate separated, showing that not quite all of the zirconium had been carried down.—The experiment was repeated with 50 mg. Zr: the filtrate was found to contain 15 or 20 mg. Zr. The manganese precipitate was treated by *P. 62*a*: the rest of the zirconium was recovered.

Vanadium.—A mixture containing 250 mg. Mn as nitrate and 1 mg. V as Na_3VO_4 was treated by P. 61: the filtrate was treated by *P. 58*e* to test for vanadium: no trace of vanadium was found. For the fact that vanadium is not carried down by manganese in the Na_2O_2 procedure see C. E., P. 52, N. 11.—The experiment was repeated with 250 mg. Mn and 10 mg. V: a mere trace of vanadium was found.—The experiment was repeated with 50 mg. Mn and 10 mg. V: not more than 1 or 2 V mg. were found in the filtrate.—The experiment was repeated with 20 mg. Mn and 10 mg. V: the filtrate contained not more than 2 or 3 mg. V.

Uranium.—A mixture of 250 mg. Mn as $Mn(NO_3)_2$ and 1 mg. U as $UO_2(NO_3)_2$ was treated by P. 61: the filtrate was tested for uranium by *P. 58*d*: a good test for uranium was obtained.

Thallium.—15 mg. Tl as $Tl(OH)_3$ were treated by P. 61: no precipitate separated. 200 mg. Mn as $MnCl_2$ and 1 mg. Tl as $TlCl_3$ were treated by this procedure. The filtrate was tested for thallium by the regular procedure: a good test was obtained. The precipitate was dissolved in HCl (1.12) and treated by *P. 65*a–d*: a very small precipitate of TlI was obtained, which was estimated to contain not more than 0.1 mg. Tl, showing that thallium is not carried down with the manganese.

The Test for Titanium with H_2O_2 in the Presence of Iron, Cobalt, or Nickel.—500 mg. Fe as $FeCl_3$ were evaporated with a large excess HNO_3 (1.42) to 5 cc.; the dark red solution was diluted to 40 cc.: it became almost colorless. The solution was divided into two parts, and to one of these 0.5 mg. Ti as $TiCl_4$ solution was added; to both parts 2 or 3 cc. H_2O_2 were added: in both a deep yellow color very clearly indicated the presence of titanium.—The experiment was repeated, except that the HNO_3 solution was diluted to about 15 cc.: the test for titanium was distinct, although the ferric solution was not quite colorless.

500 mg. Co as $Co(NO_3)_2$ were evaporated with excess HNO_3 (1.42) to 5 cc.; the red solution was diluted to 15 cc. and divided into two parts, to one of which 1 mg. Ti was added: 2 cc. 3 per cent. H_2O_2 were added: the solution containing titanium acquired a reddish color of a distinct yellow tinge.

The experiment was repeated with 500 mg. Ni as $Ni(NO_3)_2$: the green color of the nickel solution containing titanium changed to olive when the H_2O_2 was added.

P. 62, N. 1: Confirmatory Test for Manganese with Lead Dioxide.—To 1 g. PbO_2 and 10 cc. HNO_3 (1.20) in a casserole were added in separate experiments 0.5, 0.2, 0.1 and 0.02 mg. Mn as $MnCl_2$. The mixtures were boiled gently for about 2 minutes, in covered casseroles, and then poured into test tubes: after the PbO_2 had settled, the color of $KMnO_4$ could be clearly seen, even in the last experiment.—The experiment was repeated without adding $MnCl_2$: a perfectly colorless solution was obtained.—The series of experiments was repeated, except that HNO_3 (1.42) was used: the color of $KMnO_4$ was easily distinguished in each case, but was not so pronounced as with the more dilute acid. Moreover, on standing the pink color faded slowly in the concentrated HNO_3.

To determine whether the test would be satisfactory when the manganese was initially present as MnO_2, 1 mg. Mn as $MnCl_2$ was treated by P. 61, and the precipitate collected on an asbestos filter. About 1/10 of it (*i. e.*, 0.1 mg. Mn) was treated by P. 62: the permanganate color was very distinct.

**P. 62a, N. 1: Separation of Titanium and Zirconium from Manganese by Ammonia.*—To a mixture containing 50 mg. Mn and 50 mg. Ti as nitrates and 4 cc. HCl (1.12) in 50 cc. was added NH_4OH (0.96) very carefully until the mixture was barely alkaline to litmus paper: a white precipitate formed. 2 drops more NH_4OH (0.96) were added, and the mixture was heated on a steambath for 10 minutes: the precipitate remained white. The solution was filtered. The filtrate was tested for titanium by adding more ammonia: no more precipitate separated at once, showing that the precipitation of the titanium was complete. The precipitate was dissolved in hot HCl, the process was repeated, and the filtrate was tested for manganese by adding $(NH_4)S_2$: a precipitate estimated to contain 3 or 4 mg. Mn separated. The titanium precipitate was again dissolved and treated in the same way: no manganese was found in the filtrate, showing that the manganese had been completely removed in two separations.—The experiment was repeated except that the 2 drops of ammonia in excess were not added: only about 2/3 of the titanium precipitated.—The experiment was repeated, except that NH_4OH was added until the odor after shaking was distinct: the NH_4OH precipitate was brown, showing the presence of a large amount of manganese.—The last experiment was repeated, except that 15 g. NH_4Cl were also added: the NH_4OH precipitate was white, and contained only about 1 mg. Mn.—These experiments prove that a satisfactory separation is obtained only when the hydroxide-ion concentration is very small.

A solution containing 500 mg. Mn and 1 mg. Ti as nitrates, and 10 cc. HCl (1.12) in 60 cc. was made barely alkaline to litmus paper by means of NH_4OH (0.96), an excess of two drops NH_4OH was added, and the mixture was heated for 10 minutes on a steambath: the precipitate was dark colored. The precipitate was dissolved in hot HCl and the separation repeated: a small white precipitate resulted, which was practically free from manganese. It was dissolved in HCl, and a little 3 per cent. H_2O_2 was added: the solution became deep yellow, showing the presence of titanium.—The experiment was repeated with 500 mg. Mn and 2 mg. Zr as nitrates: the results were the same. The final white precipitate was dissolved in hot HCl, the solution was evaporated to a few drops, and a piece of turmeric paper was dipped in it and dried over a small flame: it turned pink, proving the presence of zirconium.

Separation of Zirconium from Manganese by Ammonium Acetate.—A solution of 500 mg. Mn and 5 mg. Zr in 10 cc. HCl (1.12) was just neutralized with NH_4OH; 2 cc. 30 per cent. acetic acid were added, the mixture was diluted to 50 cc., 6 cc. 50 per cent. ammonium acetate were added, and the mixture was boiled: the precipitate was brown, showing that several milligrams of manganese were present and that the separation was unsatisfactory.

Complete Precipitation of Thallium by Ammonium Hydroxide.—20 mg. Tl as Tl_2SO_4 were treated with HNO_3 and $HClO_3$ by P. 61, and then with NH_4OH by P. 64: a dark red flocculent precipitate separated. This was filtered off, the filtrate was evaporated nearly to dryness and tested for thallium with KI by *P. 65*d*: no precipitate of TlI separated, showing that thallium had been completely precipitated by the NH_4OH. Since thallous hydroxide is soluble, it follows also that thallous compounds are completely oxidized by HNO_3 and $HClO_3$ in P. 61.

P. 64, N. 2: Action of Nitric Acid on Potassium Sulphocyanate.—In each of a number of test-tubes 1 cc. HNO_3 (1.42) was placed; varying amounts of water (from 0 to 15 cc.) and finally 5 cc. 10 per cent. KSCN solution were added: in each case a red color appeared slowly in the cold, more quickly on warming slightly, and more quickly in the more concentrated HNO_3 solutions. The red solutions were boiled in casseroles: the color disappeared quickly, and the solutions remained colorless on cooling. More KSCN was added: the color reappeared quickly.—The experiments were repeated with 0.1 mg. Fe as $FeCl_3$: a red color appeared at once in the cold, but on boiling, this color also disappeared in a minute or two. To one of these colorless solutions, after cooling, was added KSCN: the red color appeared at once. To another was added 0.1 mg. Fe as $FeCl_3$: the solution remained nearly colorless.—These experiments show that on boiling with HNO_3, the KSCN is completely decomposed, and therefore that the red color due to nitrous acid cannot be eliminated by boiling.

P. 65, N. 2, 5 and 6: Precipitation of Titanium, Zirconium, and Thallium in the Ammonium Acetate Procedure.—0.5 mg. Ti as $TiCl_4$ in 100 cc. was treated by P. 65: a small precipitate separated, which was proved to contain titanium by *P. 65*b*.—The experiment was repeated with 10 and with 500 mg. Ti; the filtrates were tested for titanium by evaporating with a little H_2SO_4 to fuming, cooling and adding H_2O_2: no color appeared.

A mixture containing 500 mg. Fe as $FeCl_3$ and 20 mg. Zr as $ZrCl_4$ was treated by P. 65: a large amount of zirconium was found in the precipitate, but on adding NH OH to the filtrate a white precipitate was obtained which was estimated to contain 3 to 5 mg. Zr.—10 mg. Zr as nitrate in HNO_3 solution were treated by P. 65, except that no $FeCl_3$ was added; NH_4OH was added only until a very small precipitate of zirconium hydroxide separated and the solution was still acid when the ammonium acetate was added; the filtrate from the basic acetate precipitate was made alkaline with NH_4OH to test for zirconium: a white precipitate separated, which was estimated to contain 1 or 2 mg. Zr.—The experiment was repeated with 1 and 2 mg. Zr, except that NH_4OH was added until the solution was neutral; the filtrate was made acid, evaporated to 20 cc. and then made alkaline with NH_4OH: no precipitate separated.—The last experiment was repeated with 5 mg. Zr as nitrate and 20 mg. PO_4 as Na_2HPO_4: no zirconium was found in the filtrate.—For the fact that zirconium is not precipitated in the presence of considerable acetic acid, and that it then prevents the complete precipitation of titanium, see Hillebrand, *Bull. U. S. Geol. Survey*, **176**, 72 (1900).

20 mg. Tl as $TlCl_3$ were treated by P. 65, except that no $FeCl_3$ was added: a brown precipitate separated on boiling and also on adding NH_4OH; the former was two or three times as large as the latter, thus showing that at least 5 mg. Tl were not precipitated till the NH_4OH was added. The filtrate was evaporated nearly to dryness; H_2SO_4 was added, and the solution when cold was tested for thallium with KI and Na_2SO_3 by *P. 65*d:* a small precipitate of TlI was obtained which was estimated to contain 0.5 to 1 mg. Tl.—The experiment was repeated with 1 mg. Tl: no precipitate resulted on boiling, nor on adding NH_4OH. The filtrate was proved to contain the thallium.—The experiment with 1 mg. Tl was repeated, $FeCl_3$ being added as directed in the procedure: no precipitate separated on adding NH_4OH to the filtrate. Both precipitate and filtrate were tested for thallium: about half of the thallium was found in the precipitate and the remainder in the filtrate.—The last experiment was repeated with 0.5 mg. Tl: a small but distinct test was obtained for thallium both in the precipitate containing the iron and in the filtrate.

P. 65a, N. 1 to 3: Extraction of $FeCl_3$ by Ether.*—See Rothe, *Stahl und Eisen*, **12, 1052 (1892); **13**, 333 (1893); Langmuir, *J. Am. Chem. Soc.*, 22, 102 (1900); Kern, *J. Am. Chem. Soc.*, **23**, 689 (1901).

To determine the best concentration of HCl to use in this extraction, a series of experiments was performed as follows: 500 mg. Fe as $FeCl_3$ were dissolved in 30 cc. HCl of known specific gravity and this solution was treated several times with about 35 to 40 cc. ether in a separating funnel as described in the procedure. The amount of $FeCl_3$ extracted in each treatment was estimated by evaporating the ether extract to dryness, adding HCl, and precipitating with NH_4OH. The results are given in the following table. Since the ether used contained initially no HCl, the amount of HCl in the water layer is somewhat decreased in each treatment. The proportion of $FeCl_3$ extracted in each treatment was 4 to 5 per cent. with 8 per cent. HCl (sp. gr., 1.04); 95 to 96 per cent. with 18 per cent. HCl (sp. gr., 1.09); 99 per cent. with 22 per cent. HCl (sp. gr., 1.11); and 94 per cent. with 25 per cent. HCl (sp. gr., 1.125).

With the 22 per cent. acid (sp. gr., 1.11) the first extraction took out nearly all the $FeCl_3$ (495 mg. Fe), the second extraction nearly all of 5 mg. Fe remaining, and the third only a fraction of a milligram. A similar result was obtained when 500 mg. Fe as $FeCl_3$ were precipitated with NH_4OH, the precipitate dried between filter papers, and dissolved in HCl (1.12). This result is in agreement with that of Rothe, who recommends an acid of sp. gr. 1.100 to 1.105, for he shook his ether with HCl of this strength before making the separation.

Molecular Formula of Ferric Chloride in Ether Solution.—See Beckmann, *Z. physik. Chem.*, 46, 860 (1903).

Extraction of Thallic Chloride by Ether.—15 mg. Tl as $Tl(OH)_3$ were treated by *P. 65*a:* the solution of $TlCl_3$ in HCl (1.12) had a yellow color, but this layer was colorless after it was shaken with ether; the ether layer had a yellowish color. The first ether extract contained nearly all the thallium, the second ether extract contained less than 1 mg., and the water layer after the two extractions was practically free from thallium.

**P. 65a, N. 4: Behavior of Titanium, Zirconium, and Uranium in the Ether Treatment.*—A solution of 50 mg. Ti as $TiCl_4$ in one experiment, and of 50 mg. Zr in another, in 30 cc. HCl (1.11) was shaken with an equal volume of ether; the ether layer was evaporated to dryness in a casserole on a waterbath, HCl (1.20) was added and heated, the solution was made alkaline with NH_4OH: no precipitate separated in either case, showing that no titanium or zirconium had dissolved in the ether layer. In the case of titanium the water layer became reddish yellow owing to the presence of H_2O_2 in the ether, and in the case of zirconium a white precipitate ($ZrCl_4$?) separated in the water layer, but when the ether was expelled by evaporation a clear solution resulted. A white precipitate was also found to result with titanium in an experiment in which 300 mg. PO_4 were also present.

For proof that uranium is not extracted, see Kern, *J. Am. Chem. Soc.*, **23**, 689 (1901).

**P. 65a, N. 5: Extraction of Iron by Ether in the Presence of Phosphate.*—500 mg. Fe as $FeCl_3$ and 300 mg. PO_4 as ammonium phosphate were dissolved in 30 cc. HCl (1.09) and treated with ether (35 cc.) as described in the procedure: about 95 per cent. of the iron was extracted in each treatment and the phosphate remained in the water layer.

P. 65b, N. 1: Nature of the Compound of Hydrogen Peroxide with Titanium.*—In regard to the colored solution, and the preparation of solid TiO_3, see Schönn, *Z. analyt. Chem.*, **9, 41 (1870); Classen, *Ber.*, **21**, 370 (1888); Levy, *Ann. chim. phys.* (6) **25**, 463 (1892); Melikoff and Pissarjewsky, *Ber.*, **31**, 953 (1898).

Mr. Chas. Field, 3rd, working in this laboratory, performed the following migration experiment. A colored solution was prepared by rotating for three hours pure TiO_3, which had been dried over P_2O_5, with a normal HNO_3 solution which contained 1 mol. H_2O_2 per liter. The resulting solution was 0.087 molal with respect to TiO_3. A large U tube which was partly filled with normal HNO_3 solution was placed in a thermostat at 25° and the titanium solution was carefully introduced through a tube at the bottom of the U. The surfaces of contact of the two solutions were sharply marked. After a current had passed for 8 hours, one of the surfaces of the red solution had moved 4 cm. upward toward the cathode, and the other boundary had moved away from the anode a nearly equal distance. This proves that the color is due to a cathion containing titanium.

Delicacy of the Hydrogen Peroxide Reaction for Titanium.—0.1 mg. Ti as chloride was treated by *P. 65*b:* a distinct yellow color appeared on adding the H_2O_2 solution.

P. 65b, N. 2: Precipitation and Separation of Titanium and Zirconium as Phosphate.*—See Hillebrand, *Bull. U. S. Geol. Survey*, **176, 75 (1900).

0.5 and 1 mg. Zr and a mixture of 1 mg. Zr and 100 mg. Ti as chloride were treated by *P. 65*b:* flocculent precipitates formed in every case within 10 minutes but were more distinct after half an hour.—100 mg. Ti alone were treated by *P. 65*b:* no precipitate separated in several hours.

10 mg. Zr as chloride were treated by *P. 65*b:* the precipitate was filtered off after half an hour, and the filtrate made alkaline with NH_4OH: a small precipitate estimated

to contain about 0.3 mg. Zr separated. The result was the same when the filtration was made after 20 hours.—The experiment was repeated, except that only 3 or 4 cc. phosphate solution were used: the filtrate contained 0.5 to 1.0 mg. Zr after half an hour and after 1 hour.—The experiment was repeated, using about 15 cc. phosphate solution; only 0.1 to 0.2 mg. Zr remained in the filtrate after 2 hours.

To a number of solutions, containing 1 mg. Zr as chloride and varying amounts of H_2SO_4 (1.20) in 15 cc., were added 5 cc. 7 per cent. $Na_2HPO_4.12H_2O$ solution: with 1 and 2 cc. of acid the solutions became turbid at once, and flocculent precipitates settled out within 20 minutes; with 5 cc. acid the solution remained clear for about 10 minutes, but after 1 hour there was a distinct precipitate; with 10 cc. acid the solution remained clear for a longer time and only a minute precipitate separated in 1.5 hours.

Precipitation of Titanium with Zirconium Phosphate.—10 mg. Zr and 10 mg. Ti as chlorides were treated by *P. 65*b*: the precipitate when collected on a filter was distinctly yellow and this color remained after washing with water for an hour. About 10 cc. 15 per cent. HF solution were poured through the filter in a celluloid funnel and the solution was treated again by *P. 65*b*: the phosphate precipitate was white, and the titanium in the solution was estimated from the color to be about 1 mg.—0.1 mg. Ti and 100 mg. Zr as chlorides were treated by *P. 65*b*: the solution became distinctly yellow on adding H_2O_2, and the filtrate from the phosphate precipitate was also yellow, showing that titanium is not completely carried down by the zirconium. (100 mg. Zr alone gave no color with H_2O_2.)

**P. 65b, N. 3: Precipitation of Thorium as Phosphate.*—2, 5, and 50 mg. Th as nitrate were treated by *P. 65*b*: white gelatinous precipitates separated on the addition of Na_2HPO_4, the precipitate being small and forming slowly in the experiment with 2 mg. Th. In the experiment with 5 mg. a 10 cc. portion of HF (1 volume 45 per cent. HF to 2 volumes water) was poured several times through the filter; the solution was evaporated with H_2SO_4 to fuming, cooled, diluted and excess NH_4OH added: no precipitate separated at once and only a very small one on standing an hour.

**P. 65b, N. 4: Behavior of Manganese, Cobalt, Uranyl and Vanadyl Salts in the Tests for Titanium and Zirconium.*—100 mg. Mn as $MnCl_2$ were treated by *P. 65*b–c*: with H_2O_2 no color resulted, and no precipitate formed when Na_2HPO_4 was added, nor on standing 1 hour. After the addition of just sufficient powdered Na_2SO_3 to reduce the H_2O_2 (determined by testing portions of the solution with Ti solution), no precipitate formed, but when about 1 g. more Na_2SO_3 was added a large precipitate separated.—The experiment was repeated separately with 100 mg. Co as $CoCl_2$ and with 5 mg. U as $UO_2(NO_3)_2$: there was no change of color with H_2O_2 and no precipitate with Na_2HPO_4 on adding enough Na_2SO_3 to destroy the H_2O_2.—The experiment was repeated with 100 mg. U as $UO_2(NO_3)_2$: the solution was distinctly yellow before the H_2O_2 was added, and a large white precipitate formed on adding just sufficient Na_2SO_3 to decompose the H_2O_2.

10 and 100 mg. V as Na_3VO_4 were treated in separate experiments by *P. 65*b–c*: with the 10 mg. the color obtained on adding H_2O_2 was similar to that obtained with 3 to 5 mg. Ti; with the 100 mg. however the color was of a much redder shade than that with titanium; on the addition of an excess of Na_2SO_3 the color changed at once to blue, showing the presence of a vanadyl salt, and no precipitate had separated in either case after several hours in the cold or on boiling.

*P. *65c, N. 1: Behavior of Titanium in Acid Solutions towards Sodium Phosphate.*—To a solution containing 0.5 mg. Ti as chloride and 2 cc. H_2SO_4 (1.20) in 10 cc. were added 10 cc. 7 per cent. $Na_2HPO_4.12H_2O$ solution: the solution remained clear for 10 minutes, but had become distinctly turbid in half an hour. Several solutions, containing 10 mg. Ti as chloride and varying amounts of H_2SO_4 (1.20) were treated in the same way; the flocculent precipitates were filtered off after 10 minutes, and the filtrates were made alkaline with NH_4OH: in the experiment with 2 cc. acid the filtrate contained 0.5 to 0.1 mg. Ti; in that with 3 cc. acid, 1 to 3 mg. Ti; in the experiment with 5 cc. acid, 3 to 4 mg. Ti.

10 mg. Ti as chloride were treated by *P. 65*b–c*, and after half an hour the mixture was filtered, and the filtrate made alkaline with NH_4OH: a very small precipitate was obtained containing about 0.5 mg. Ti.—The experiment was repeated with 0.5 mg. Ti: the solution became distinctly turbid on decolorizing with H_2SO_3. Half of the turbid solution was heated to boiling: a distinct, flocculent precipitate was obtained. The other half was allowed to stand in the cold for half an hour: the precipitate in this case also became somewhat flocculent.

**P. 65d, N. 1: Test for Thallium with KI.*—0.5, 0.2, and 0.1 mg. Tl as Tl_2SO_4 were treated by *P. 65*d*, the total volume being about 10 cc.: a distinct yellow finely divided precipitate of TlI was obtained in each experiment, even in that with 0.1 mg. Tl. For proof that 500 mg. ferric iron does not interfere with the test, see T. A., No. 174–6.

**P. 65d, N. 3: Flame Test for Thallium.*—0.5, 0.2, and 0.1 mg. Tl were precipitated by *P. 65*d* as TlI. The precipitates were collected on small filters and washed twice with a very little water. The moist filter was removed from the funnel, a looped platinum wire was drawn across its surface to collect a little of the precipitate, and introduced into a colorless gas flame: with 0.5 mg. Tl, the momentary green color was generally seen, but it was sometimes obscured by the yellow flame, due to sodium and to small fibers of paper; with 0.2 and 0.1 mg. Tl the green color could not be detected with certainty.—The experiments were repeated, except that the TlI precipitates were collected on hardened filters: the green flame was much more brilliant with 0.5 and 0.2 mg. Tl than in the corresponding experiments with ordinary filter paper; it could, however, scarcely be seen with 0.1 mg. Tl.

P. 69, N. 1: Potassium Cobaltic Nitrite.—See Fisher, *Pogg. Ann.*, **74**, 115 (1848); Sadtler, *Am. J. Sci.* (2), **49**, 196 (1870); Rosenheim and Koppel, *Z. anorg. Chem.*, **17**, 35 (1898).

P. 69, N. 2: Precipitation of Cobalt with Potassium Nitrite.—0.1 and 0.3 mg. Co as $CoCl_2$ were treated by P. 69: in each experiment the solution became distinctly turbid within 5 minutes.—The experiment was repeated in the absence of cobalt: the solution remained perfectly clear.—For the detection of 0.5 mg. Co in the presence of 250 mg. Ni in P. 69, see T. A., No. 127.

500 mg. Co as nitrate were treated by P. 69: the mixture was shaken well, allowed to stand, and filtered after about half an hour, and again allowed to stand: a considerable precipitate again separated.—The experiment was repeated except that the mixture was heated on a waterbath to 50 or 60° with frequent shaking for half an hour; it was allowed to cool and filtered: no precipitate separated in the filtrate even on standing over night.

Separation of Nickel from Cobalt with Potassium Nitrite.—500 mg. Co and about 5 mg. Ni as nitrates were treated by P. 69; after standing 20 hours the mixture was filtered; the filtrate was evaporated almost to dryness with HCl, and made alkaline with NaOH: only a very small green precipitate separated corresponding to not more than 2 mg. Ni. Half of the cobalt precipitate obtained was treated by P. 70: a very good test for nickel was obtained.—The experiment was repeated except that the mixture was heated on a waterbath for half an hour: less nickel was found in the filtrate than in the preceding experiment.

Precipitation of Potassium Nickelous Nitrite.—250 mg. Ni (previously freed from cobalt by a KNO_2 treatment) were treated by P. 69, except that the volume was cut down to 50 cc. without however altering the total amounts of reagents used: a distinct reddish colored precipitate separated within 20 minutes which was proved to contain nickel but no cobalt by the borax bead test.—For the action of HNO_2 on nickel salts and the formation of $K_4Ni(NO_2)_6$ see Lang, *J. prakt. Chem.*, 86, 299 (1862); Hampe, *Lieb. Ann.*, **125**, 346 (1863); and Reichard, *Chem.-Ztg.*, 28, 479, 885, 912 (1904).

P. 70, N. 2: Delicacy of Hypobromite Test for Nickel.—150 mg. Co free from nickel were treated by P. 70: no precipitate was observed, not even on filtering. The experiment was repeated except that 0.15 mg. Ni as $NiCl_2$ was added: the solution became dark colored on adding excess NaBrO, but no precipitate collected; it was easily seen, however, on the filter.—0.2 mg. Ni as $NiCl_2$ was treated by P. 70: a distinct precipitate was obtained on filtering.

Separation of Nickel from Cobalt by Hypobromite.—200 mg. Co and 0.5 mg. Ni as chlorides were treated by P. 70; the precipitate was tested for cobalt in the borax bead: no blue color was obtained.

A large number of experiments were performed to determine the proper conditions for making this separation. In working with cobalt free from nickel, it was found that a precipitate of $Co(OH)_3$ always formed when the NaBrO reagent (or bromine water and NaOH) was added very soon after the addition of KCN, and that the necessary interval of time was greatly shortened by increasing the excess of KCN added.

The following experiments show that excess of NaBrO is essential to the precipitation of nickel. 1 mg. Ni as $Ni(NO_3)_2$ was treated by P. 69; the NaBrO solution was added in small portions and after the addition of each portion the solution was tested with the starch KI paper: as long as this paper remained colorless no precipitate of $Ni(OH)_3$ separated, but after the precipitate formed the paper became blue when dipped into the mixture.—The experiment was repeated with 10 mg. Ni. As long as the precipitation was incomplete the paper remained colorless, or only a small brown ring was formed on the paper, but after complete precipitation all of the paper immersed in the solution became brown or blue.

P. 70, N. 4: Action of H_2S on Alkaline Tartrate Solutions Containing Nickel or Cobalt.—Villiers, *Compt. rend.* **119**, 1263 (1894); **120**, 46 (1895), found that when H_2S was passed into a NaOH containing freshly precipitated $Ni(OH)_2$ (but no tartrate) the hydroxide was quickly converted into black nickel sulphide, but that a portion of the nickel passed into solution giving a deep brown color, proving that the presence of tartrate is not essential for the formation of the brown solution.—0.5 mg. Ni as nitrate was treated by both parts of P. 70: a deep brown solution was obtained on saturating the alkaline tartrate solution in a test tube with H_2S.—0.1 and 0.2 mg. Ni as nitrate were dissolved in a little HNO_3 and treated by the second paragraph of P. 70, about 5 cc. of 10 per cent. tartaric acid and 5 cc. excess of NaOH being added: clear dark yellow solutions were obtained on saturating with H_2S.—The experiment was repeated with 1 mg. Ni: on passing in H_2S the solution remained nearly colorless for about 1 minute, but finally a clear dark brown solution resulted.—The experiment was repeated with 20 mg. Ni: on saturating with H_2S the liquid in the test-tube was opaque and almost black in color. The liquid was filtered: very little precipitate remained on the filter. It was allowed to stand several hours: a black precipitate separated but the filtrate was still black and opaque.

20 mg. Co as $CoCl_2$ in a little dilute HNO_3 were treated by the second paragraph of P. 70: a black precipitate separated as soon as the H_2S was led in and the cobalt was completely precipitated within 1 minute. The mixture was filtered, the filtrate was saturated with H_2S, and the test-tube corked and set aside: the solution remained colorless for several hours. A similar solution was exposed to the action of the air

in an open flask: it became dark yellow in about 1 hour owing to oxidation of the sulphide and consequent formation of polysulphide.—The experiment was repeated except that 1 mg. Ni as $NiNO_3$ was also present; the excess of 10 per cent. NaOH was 4 or 5 cc.; H_2S was led into the solution for about 1 minute and the CoS filtered off: the filtrate was nearly colorless. This was saturated with H_2S: it became brown, the color being such as to indicate that very little of the nickel had been carried down with the cobalt.—This experiment was repeated except that the H_2S was led through the solution for 5 minutes before the CoS was filtered off: the filtrate was of a lighter brown than before, indicating that over half the nickel had been carried down with the cobalt.—The experiment was repeated except that the CoS was not filtered off till after 10 minutes: the filtrate was almost colorless, and remained so on saturating again with H_2S.—The experiment was repeated, the CoS being filtered off after half an hour: the filtrate was colorless and contained no nickel.—In a similar series of experiments in which a smaller excess of NaOH than 4 to 5 cc. was added, the filtrate was light brown after 1 minute, and nearly colorless after 5 minutes, thus showing that there is more danger of losing nickel when the excess of alkali is small, in which case the brown solution is formed more quickly.—This result that NiS is deposited on CoS after the separation of the latter was confirmed by several experiments.

Similar experiments were made with a mixture of 20 mg. Fe as $FeCl_3$ and 1 mg. Ni, and with one of 20 mg. Mn and 1 mg. Ni: good tests for nickel were obtained in both cases.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE CARRYING DOWN OF SOLUBLE OXALATES BY OXALATES OF THE RARE EARTHS.

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In a recent investigation[1] it has been shown that neodymium oxalate, when precipitated in neutral or nearly neutral solution by means of ammonium oxalate, carries down considerable quantities of this salt, and that the amount carried down increases with increasing concentration of molecular ammonium oxalate at the moment of precipitation. Furthermore, it was shown that neodymium oxalate has no tendency to carry down molecular oxalic acid, and that occlusion of ammonium oxalate may be prevented by diminishing the molecular concentration of the latter salt with a strong acid before precipitation. Other rare earth oxalates were found to exhibit a like tendency to occlude ammonium oxalate. Since it seemed probable that the carrying down of sodium and potassium oxalates[2] would vary with conditions of precipitation in a similar manner, the following investigation was undertaken to test this point.

The method employed was to precipitate the rare earth oxalate under different conditions, and to analyze the precipitated oxalate by deter-

[1] Baxter and Griffin, THIS JOURNAL, 28, 1684 (1906).

[2] The well-known fact that the oxalates of the alkalis are carried down by the oxalates of the rare earths was first noted by Sheerer. Pogg. Ann. [2], **56**, 496 (1842).