PRECIPITATION AND SEPARATION BY WEAK ORGANIC BASES.

BY E. T. ALLEN.

A LARGE number of organic bases are known, which may serve as quantitative precipitants of many metallic hydroxides, though they usually present no advantage over ammonia or the fixed alkalies. Of late, more especially,[1] some of them have found use for analytical separations, where the inorganic reagents are not applicable. We have, between the organic and inorganic bases, a nearly complete analogy. The tetrammonium compounds are well known to be highly dissociated in aqueous solution, giving, in a marked degree, the characteristic hydroxyl reactions, like the hydroxides of the alkalies and thallium. A second weaker class of bases comparable, in general, with ammonia are the paraffin amines. These also are strongly alkaline in reaction and capable of precipitating all but the strongest metallic bases, whose solubility products are too high to be reached by such concentrations of hydroxyl as these reagents afford.

A third class of bases in which the aromatic amines, quinoline, naphthyl-amine, phenyl-hydrazine, etc., may be named, have no soluble analogues in the inorganic field, though they are akin to the bases formed by the metals of the third and fourth groups of the periodic system.

With indicators they give either a faint alkaline reaction or none at all. When a metallic salt is precipitated by such a base, say aniline, the solution remains acid even when a considerable excess of the reagent has been added. It is plain, therefore, that only those bases which can be thrown down in acid solution, can be precipitated here. All chemists are familiar with the precipitation of certain hydroxides by the action of water alone. Such reactions are always reversible. We may instance the case of titanium sulphate.

$$Ti(SO_4)_2 + 4H_2O = 2H_2SO_4 + Ti(OH)_4.[2]$$

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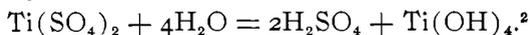
[1] This Journal, 24, 540, and 21, 776.

[2] The principle involved is the same whether the precipitate be a hydroxide, or a basic salt.

The complete precipitation of the titanium evidently depends on the reduction of the concentration of free acid to a point where the titanium hydroxide is no longer appreciably soluble. Let us suppose the precipitation to be incomplete. If now we should add to the system a weak base like aniline, a certain quantity of the free acid would be converted into neutral salt, and thus the concentration of the acid would be diminished, though an appreciable quantity would always remain unless a very great excess of reagent were used, for, according to the principles of hydrolysis, the salt of a weak base must be partially decomposed by water into free base and free acid. Thus:

$$C_6H_5NH_3Cl = C_6H_5NH_2 + HCl.$$
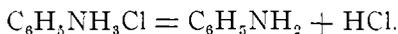
The precipitation of titanium will therefore go further, in fact, to completion when a proper quantity of aniline has been added, because in small concentrations of acid, titanium hydroxide is practically insoluble. The degree of the hydrolysis of the aniline hydrochloride is conditioned by temperature, by the degree of dilution, and by excess of free base. Speaking in general of this class of weak bases, it is, of course, true that the degree of hydrolysis, in other words the concentration of free acid in solutions of their salts, depends on the strength of the base. Some organic bases are so weak that they would doubtless be of no service for any quantitative precipitation, but those whose hydrochlorides are hydrolyzed to an extent of several per cent. in dilute solutions form a group well adapted for the separation of weak from strong metallic bases. For the strong bases like magnesia, the alkaline earths, etc., are incapable of existence with free acid, while the weak ones, whose salts are more or less hydrolyzed in aqueous solution, are practically insoluble in such concentrations of acid as one can readily obtain by the above means. This is the principle of most analytical separations by weak organic bases, and the most important one involved in the experimental part of this paper. Of course there are cases in which the precipitate by an organic base redissolves in excess. Thus several paraffin amines redissolve the hydroxides of aluminum, copper, silver, zinc, etc., and it is possible some of the weaker bases may yield separations on this principle, though no cases of the kind are known to me.[1]

[1] In her statement that phenylhydrazine throws down, from thorium nitrate, a "canary-yellow precipitate, easily soluble in excess," Miss Jefferson appears to be in error. See this Journal, **24**, p. 546.

In the study of the separations in the sequel, it seemed of interest, not merely to determine the necessary empirical conditions, but also to inquire how much acid is freed from the salts of certain weak bases—the precipitants—under definite conditions of dilution, temperature and excess of the base. Thus the hydrolytic constant,

$$K = \frac{BOH \times HCl}{V(BCl)},$$

of aniline, and of phenylhydrazine hydrochloride was determined in $N/10$ solutions at a temperature of $40°$ C. In this way could be made an approximation to the concentration in free acid possessed by the solutions in which the separations were made—concentrations in which certain weak metallic bases remain without dissolving appreciably.

SEPARATION OF ALUMINUM FROM IRON.

Several years ago Campbell and Hess[1] described a method for precipitating aluminum in the presence of iron after the latter had been reduced to the ferrous state by sulphurous acid. The reagent used was phenylhydrazine. The results appeared satisfactory, and, as a good method for the direct determination of aluminum in the presence of iron was needed, Dr. W. F. Hillebrand suggested that I study this separation more closely, especially in regard to its application to rock analysis, where titanium is nearly always present, and sometimes zirconium. I desire in this place to express to Dr. Hillebrand my best thanks for this suggestion.

In brief, my results indicate that it is practically impossible to separate the iron completely in one precipitation. With a double precipitation, the results are good. When the quantity of precipitated alumina is large, there is apt to be a loss, which I ascribe to the long contact with the faintly acid wash solution which is necessary to remove the iron. Thus I have obtained on certain rocks results which were considerably lower than those carefully determined by difference in the usual way. On the other hand from mixtures of iron, aluminum, titanium, and zirconium salts made up from standard solutions the results have been satisfactory. This discrepancy has not thus far been explained. The method is excellently adapted to the separation of very small quantities of aluminum, such as a milligram or even less, from a

[1] This Journal, 21, 776.

large excess of iron, a point of considerable practical importance.

In the following tests, standard solutions of ferric and aluminum chlorides were used. The former was prepared from piano wire by dissolving in pure hydrochloric acid, filtering, oxidizing with chlorine, and driving out the excess from the hot solution by a current of air. No alumina or other bases of similar strength could be detected in this solution. It was standardized by precipitation with ammonia. The aluminum chloride was prepared by dissolving "C. P." metal in hydrochloric acid, filtering off the silicon and diluting. The exact strength was determined by precipitation with ammonia. The solution contained only a trace of iron.

To the conditions laid down by Campbell and Hess a few additions might be made. The volume of the solution may vary, according to the quantity of alumina to be precipitated, from 100 to 200 cc. It should be heated and reduced by adding saturated ammonium bisulphite. From 5 to 20 drops, according to the quantity of iron, may be used. If the solution turns deep red (ferric sulphite) it is not acid enough, and a few drops of hydrochloric acid should be added, for the sulphite itself does not reduce ferric salts, at least not with rapidity. Now quickly bring to neutrality with ammonia, and then add several drops of dilute hydrochloric acid. If this last operation is done too slowly, the oxygen of the air helps to form a little ferric hydroxide which does not always readily dissolve in the dilute acid. Finally add from 1 to 3 cc. phenylhydrazine,[1] according to the weight of the alumina to be precipitated. If too little has been used, a few drops added to the filtrate will disclose the mistake. Stir until the precipitate has become sufficiently flaky and allow to settle. The supernatant liquid will now be plainly acid to litmus. One need not be disturbed if the precipitate has a brownish color, for it is not due to ferric hydroxide but to the coloring-matter contained by all phenylhydrazine which has not been freshly distilled. When the determinations are allowed to stand too long, the air increases this oxidation product, and a brown insoluble scum forms on the surface of the liquid and on the sides of the vessel, which is rather troublesome to the analyst. Fortunately equilibrium appears to be

[1] NOTE.—The reagent should, of course, be free from inorganic impurities which could disturb the results. The author found one sample, which, after persistently giving high results, was proved to contain tin, which had probably been used in its preparation.

established in a short time. The vessels need not stand more than an hour at any rate.[1]

PRECIPITATION OF ALUMINA ALONE BY PHENYLHYDRAZINE.

1 cc. $AlCl_3 = 0.005001$ gram Al_2O_3.

	Taken.	Found. Gram.	Error. Gram.
I	50 cc. $= 0.2500$ gram Al_2O_3	0.2487	—0.0013
	25 cc. $= 0.1250$ gram Al_2O_3	0.1236	—0.0014
	5 cc. $= 0.0250$ gram Al_2O_3	0.0254	+0.0004

The tendency toward low results is here plainly visible.

SEPARATION OF SMALL QUANTITIES OF ALUMINA FROM EXCESS OF IRON.

The first precipitation in the following series was made in a nearly neutral solution of about 150 cc. volume. After washing out most of the iron by the phenylhydrazine sulphite solution, the precipitate was dissolved on the filter in a few cubic centimeters of hot, dilute hydrochloric acid, washed through with hot water, neutralized with ammonia and acidulated with 2 or 3 drops $1:1$ HCl. The precipitate which is thrown down in a small volume of liquid by 0.5 cc. phenylhydrazine, is washed with the sulphite solution till free from iron. After blasting, the precipitate is usually pure white.

No.	FeCl₃ taken.		AlCl₃ taken.		Al_2O_3 found. Gram.	Error. Gram.
1	35 cc. $= 0.2189$ gr. Fe_2O_3	0.1 cc. $= 0.0005$ gr. Al_2O_3			0.0005	0.0000
2	35 " $= 0.2189$ " "	0.2 " $= 0.0010$ " "			0.0014	+0.0004
3	35 " $= 0.2189$ " "	0.6 " $= 0.0030$ " "			0.0031	+0.0001
1′	35 " $= 0.2189$ " "	0.7 " $= 0.0007$ " "			0.0008	+0.0001
2′	35 " $= 0.2189$ " "	1.2 " $= 0.0012$ " "			0.0013	+0.0001
3′	33 " $= 0.1867$ " "	2.0 " $= 0.0020$ " "			0.0019	—0.0001

SEPARATION OF TITANIUM FROM IRON.

As solutions of titanium chloride are quite unstable, a standard solution of the sulphate was prepared as follows: Potassium titano-fluoride of the market was twice crystallized from hot water and dried at 105° C. A weighed quantity of this compound was then heated in a large platinum crucible with excess of sulphuric acid, until free from fluorine. A very low flame should be used, or insoluble basic sulphate may form. The cooled sulphate was

[1] The precipitate is washed by a solution of phenylhydrazine sulphite, made by adding cold saturated sulphurous acid to a little phenylhydrazine until the crystalline sulphite first formed, dissolves in the excess. The solution has an acid reaction. Five to 10 cc. of this are used in 100 cc. hot water. See Campbell and Hess : *Loc. cit.*

then poured into excess of cold water, precipitated by ammonia, washed, and redissolved in a quantity of sulphuric acid 5 or 10 per cent. in excess of that demanded by theory, to prevent hydrolysis.

Phenylhydrazine gives a practically complete separation of titanium from iron, in two precipitations. I have never found more than traces of titanium remaining with the iron. It was sought for as follows. The iron, with any titanium it might contain after the precipitation with phenylhydrazine, was removed from the solution by ammonium sulphide, washed a few times and dissolved in nitric acid, from which solution it was subsequently precipitated by ammonia and weighed. The weighed oxide was now tested for titanium by the method described in Bulletin 176, U. S. Geol. Survey, p. 67.

TiO_2 found in Fe_2O_3.

I.	II.	III.	IV.	V.
0.00017 gram	None	0.0002	0.0002	Trace

The same details apply to this separation as were laid down for the separation of aluminum from iron, except that here the solution may be considerably more acid before adding the phenylhydrazine. If much titanium is present, a considerable precipitate will form before the solution is completely neutralized by ammonia. When the neutral point is reached, a half dozen drops of 1 : 1 hydrochloric acid may be added. This quantity is frequently insufficient to redissolve all the titanium precipitate but that is a matter of no consequence.

No.	cc. =	FeCl$_3$ taken. Gram Fe$_2$O$_3$.	Fe$_2$O$_3$ found. Gram.	Error. Gram.	cc. =	Ti(SO$_4$)$_2$ taken. Gram TiO$_2$.	TiO$_2$ found. Gram.	Error. Gram.
1	35	0.1748	.....	....	2	0.0020	0.0022	+0.0002
2	5	0.0250	0.0254	÷0.0004	25	0.0246	0.0237	—0.0009
3	2	0.0100	0.0104	+0.0004	25	0.0246	0.0254	·+0.0008
4	25	0.1248	.....	....	1	0.0010	0.0011	+0.0001
5	10	0.0499	.....	....	50	0.0492	0.0501	÷0.0009
6	3	0.0140	.....	....	50	0.0492	0.0502	+0.0010

SEPARATION OF ZIRCONIUM FROM IRON.

A standard solution of zirconium sulphate was used in these experiments. The raw material consisted of picked crystals of North Carolina zircon,[1] which were converted into potassium zircono-fluoride after the excellent method of Marignac.[2]

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[1] My thanks are due to Mr. Wirt Tassin, assistant curator of the National Museum, from whom the zircon, as well as a supply of beryl, was obtained.

[2] *Ann. chim. phys.* (3), 60, 260.

After two crystallizations it was dried carefully at 105° C., and then changed into sulphate by a method similar in all details to that given for the titanium compound. 1.0470 grams of the above preparation, thus treated and afterwards precipitated by ammonia, thoroughly washed, dissolved in hydrochloric acid and again precipitated and washed as before, ignited and finally blasted, gave 0.4508 gram ZrO_2 instead of 0.4529 gram required for K_2ZrF_6. The details of the separation of zirconium from iron are the same as those for the separation of titanium. The following results show that a single precipitation is not always sufficient to remove all the iron.

SINGLE PRECIPITATION.

	FeCl$_3$ taken.		Zr(SO$_4$)$_2$ taken.		ZrO$_2$ found.	Error.
No.	cc. =	Gram Fe$_2$O$_3$.	cc. =	Gram TiO$_2$.	Gram.	Gram.
I	30	0.1876	2	0.0020	0.0023	+0.0003
2	4	0.0250	23	0.0229	0.0230	+0.0001
3	I	0.0062	25	0.0249	0.0255	+0.0006
4	35	0.2189	I	0.0010	0.0016	+0.0006
5	10	0.0625	50	0.0498	0.0520	+0.0022
6	I	0.0062	50	0.0498	0.0530	+0.0032

DOUBLE PRECIPITATION.

	FeCl$_3$ taken.		Zr(SO$_4$)$_2$ taken.		ZrO$_2$ found.	Error.
No.	cc. =	Gram Fe$_2$O$_3$.	cc. =	Gram TiO$_2$.	Gram.	Gram.
I	50	0.2997	50	0.0500	0.0496	—0.0004
2	50	0.2997	I	0.0010	0.0011	+0.0001
3	5	0.0300	25	0.0249	0.0247	—0.0002

In the following series of determinations, aluminum, zirconium, and titanium in varying quantities were separated from iron as already described, and weighed together. The standard solutions used have already been described.

SEPARATION OF ALUMINUM, TITANIUM, AND ZIRCONIUM FROM IRON.

No.	Fe$_2$O$_3$ taken. Gram.	Al$_2$O$_3$ taken. Gram.	TiO$_2$ taken. Gram.	ZrO$_2$ taken. Gram.	Al$_2$O$_3$ + TiO$_2$ + ZrO$_2$ taken. Gram.	Al$_2$O$_3$ + TiO$_2$ + ZrO$_2$ found. Gram.	Error. Gram.
I	0.0999	0.1500	0.00985	0.00492	0.1648	0.1654	+0.0006
2	0.1249	0.1650	0.01477	0.00196	0.1817	0.1816	—0.0001
4	0.1748	0.0500	0.0197	0.00287	0.0726	0.0717	—0.0009
4	0.0749	0.1000	0.0049	0.00098	0.1059	0.1063	+0.0004
5	0.1748	0.0250	0.0197	0.0148	0.0595	0.0603	+0.0008

Average, +0.00016

In a recent paper by Miss A. M. Jefferson[1] it is stated that zirconium is not precipitated by phenylhydrazine. Now zirconia is certainly a weaker base than alumina, and, according to the principles stated in the beginning of this paper, ought to be precipitated by phenylhydrazine, the more so since, according to Miss Jefferson, it is precipitated by aniline, a base which my experiments indicate to be somewhat weaker than phenylhydrazine. It should be noted, however, that Miss Jefferson employed a cold solution of zirconium nitrate, while the experiments I have described were performed with solutions containing sulphates and chlorides or chlorides alone. As theory indicates the possibility of a difference, the following tests were undertaken: Zirconium hydroxide was prepared from the sulphate and then dissolved in dilute nitric acid. The solution was freed from most of the acid by evaporating to a volume of a few cubic centimeters, and diluted with cold water so that 1 cc. contained about 1 mg. ZrO_2. The solution contained no sulphate. In the first test, a portion of it was precipitated by a large excess of phenylhydrazine, 5 cc. to 25 cc. of the solution. After standing more than twenty-four hours, the precipitate was filtered, washed, ignited and blasted.

	Found.	By ammonia.
$ZrO_2 =$	0.0251	0.0245

Twenty-five cc. of the solution with 1 cc. of the reagent gave $ZrO_2 = 0.0241$ gram. Ammonia gave no precipitate with the filtrate. I could not discover that the zirconium hydroxide had any tendency to dissolve in excess of phenylhydrazine. The same statement may be made of aniline, which also precipitates zirconium completely.

It was thought to be of some interest to determine the behavior of phenylhydrazine with the remaining elements of this natural family, thorium and cerium.

PHENYLHYDRAZINE AND THORIUM.

A solution of thorium nitrate was prepared from the pure dioxide. The latter was brought into solution by fusion with potassium acid sulphate from which it was precipitated by ammonia in a form soluble in dilute nitric acid. A double precipitation was necessary to remove sulphate entirely. The nitrate was evaporated to crystallization and dissolved in cold water.

[1] This Journal, **24**, 543.

Three portions of 25 cc. each were then precipitated as follows: No. 1 was precipitated by ammonia, washed, ignited and weighed as in an ordinary determination. No. 2 was nearly neutralized with ammonia, precipitated hot and washed with hot water. No. 3 was treated as No. 2, except that a smaller amount of reagent was added to the cold solution and the precipitate was washed with cold water. In all cases the precipitate was blasted before weighing.

ThO_2 found.

1 25 cc. contained 0.0477 gram average of three determinations by NH_3.
2 25 " hot by phenylhydrazine 0.0477 gram.
3 25 cc. cold by phenylhydrazine 0.0475 gram.

The precipitated thoria was white or nearly so.

Regarding Miss Jefferson's statement[1] that phenylhydrazine throws down, from a solution of thorium nitrate, "a canary-yellow precipitate, easily soluble in excess," I can say that if the solution contains much free nitric acid, the precipitate is colored yellow, evidently by an oxidation product of the phenylhydrazine. The precipitate may be obscured by an excess of reagent, but there is no tendency to redissolve. Thus, in one test I employed 5 cc. of the reagent to a small volume of the thorium solution. I was at first in doubt about the result, but a careful examination showed that no thorium passed through an ordinary filter.

PHENYLHYDRAZINE AND CERIUM.

The remaining element in the family under consideration is cerium. It differs from the other three members, in that it is easily reducible from the quadrivalent to the trivalent state. Phenylhydrazine fails to precipitate it except in a partial way from its ceric salts, not because it is a more basic element than the rest but because it is an oxidizing agent which phenylhydrazine easily reduces to the cerous condition, and cerous oxide is a much stronger base. These statements were proved by the following experiments:

Ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6.1\frac{1}{2}H_2O$, was made from a preparation of cerous nitrate furnished by Merck. To separate it from any neodymium and praseodymium, it was twice precipitated by caustic potash and oxidized by a stream of chlorine, the ceric hydroxide being thor-

[1] This Journal, 24, 546.

oughly washed after each treatment. The ceric hydroxide was now changed to ceric ammonium nitrate by the addition of dilute nitric acid and a little ammonium nitrate. A comparatively concentrated solution of this salt, containing considerable free acid, at once oxidized both phenylhydrazine and aniline with marked color changes, and no excess of either produced, thereafter, any precipitate.[1] With a dilute and nearly neutral solution, the results were different. Such a solution was obtained by evaporating one like the above to dryness in a vacuum desiccator with lime and sulphuric acid.

The beautiful orange crystals, with the small excess of ammonium nitrate they contained, were then put into solution by cold water, and after standing a day or two, filtered from a slight precipitate which had formed. The concentration of this solution was not far from 1 mg. CeO_2 per cubic centimeter (20 cc. gave 0.0161 gram). 15 cc. of the solution were treated with a little phenylhydrazine and set away for twenty-four hours. Some little precipitate, composed partly of organic matter, apparently an oxidation product of the reagent, had formed, but the filtrate yielded with ammonia 0.0078 gram CeO_2 out of a total quantity of 0.0121 gram originally contained in the solution. Aniline being a weaker reducing agent gave a practically complete precipitation with this solution. Only two or three very small flakes were obtained from the filtrate by ammonia.

PHENYLHYDRAZINE AND FERRIC SALTS.

Ferric salts follow ceric salts in their behavior, except that phenylhydrazine gives with the former almost no precipitate. This is true, at least, with both strong and weak solutions of ferric chloride. With one containing about 1 mg. per cubic centimeter, phenylhydrazine at first brings down some brown hydroxide which dissolves when the liquid is shaken, leaving only a little insoluble tarry matter. Aniline, however, gives a complete precipitation; at least the filtrate is colorless and gives no precipitate with ammonia.

SEPARATION OF TITANIUM FROM BERYLLIUM.

It has been shown that the elements of the quadrivalent family, Ti-Th, are, with the exception of Ce, separable from iron by

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[1] See also Gmelin-Kraut, Vol. II, part 1, p. 508.

phenylhydrazine. Beryllium forms a much weaker base than ferrous iron, but it may be separated from titanium and zirconium in a fairly satisfactory manner by similar means. The tendency is for the beryllium also to be partly precipitated, and with sulphate solutions, especially where the quantities of the elements to be separated are considerable, satisfactory results are not obtained by two precipitations. The standard solution of beryllium employed in the work was the chloride. The source of it was beryl from Chester County, Pennsylvania. I transformed this into the double fluoride by the method which Marignac used in extracting zirconia from zircon, viz., by fusing the powdered mineral with two to three times its weight of potassium fluoride. For convenience in handling, the fused mass may be poured out in a thin sheet into a platinum basin and subsequently powdered. It is then boiled several times with successive portions of water, to which should be added at first some hydrofluoric acid. The double fluorides which silicon and aluminum form with potassium are nearly insoluble in water containing potassium fluoride, and are thus for the most part left behind. The solution is now evaporated to a small volume and allowed to crystallize. The salt is then recrystallized several times. It dissolves rather slowly in boiling water. Each time the last portion should be rejected. The compound still retains iron, which may be entirely removed by passing hydrogen' sulphide through the aqueous solution, which is, of course, alkaline. The crystals may finally be dried at $105°$ C. It is a difficult matter to be sure of the complete absence of alumina, but the following determination indicates that the compound thus prepared is essentially pure. A weighed portion was changed into sulphate by heating with sulphuric acid, thence through the hydroxide to chloride, and finally to hydroxide again, which was ignited and weighed. To be sure that the beryllium oxide was free from sulphate, the precipitation with ammonia was, in fact, made three times. All the filtrates were evaporated to a small volume and treated with a little ammonia, which brought down a little beryllia, which was filtered and washed separately and added to the main portion. 1.2996 grams gave 0.2008 gram BeO ; calculated for K_2BeF_4, 0.1993. I am not aware that this method has been used previously to extract beryllium from beryl. For the determinations which follow, a solution of beryllium chloride was prepared as above indicated.

To separate titanium and zirconium from beryllium, it is not, of course, necessary to add any soluble sulphite. The acid solutions are merely brought nearly to neutrality with ammonia and then acidified with several drops of dilute hydrochloric acid. A double precipitation was made, and water only was used for washing. The solutions were heated but not boiled. As previously stated, the results were not so exact as in the separation of titanium and zirconium from ferrous iron.

SEPARATION OF TITANIUM FROM BERYLLIUM—DOUBLE PRECIPI-

TATION.

No.	BeCl$_2$ taken.		BeO found. Gram.	Error. Gram.	Ti(SO$_4$)$_2$ taken.		TiO$_2$ found. Gram.	Error. Gram.
	cc. = Gram BeO.				cc. = Gram TiO$_2$.			
I	10	0.0101	.....	....	10	0.0096	0.0096	0.0000
2	10	0.0101	.....	....	10	0.0096	0.0096	0.0000
3	5	0.0050	.....	....	25	0.0239	0.0247	—0.0008
4	30	0.0302	.....	....	5	0.0048	0.0069	+0.0021
5	100	0.1006	0.0960	—0.0046	100	0.0958	0.0996	+0.0038
6	95	0.0956	0.0951	—0.0005	5	0.0048	0.0054	+0.0006
7	5	0.0050	0.0049	—0.0001	95	0.0910	0.0911	+0.0001

The beryllium was determined in the filtrate from titanium by ammonia as in an ordinary determination of aluminum. Subsequent experiments showed that phenylhydrazine precipitates a large fraction of the beryllium from a solution of the *sulphate*, but none from the *chloride*. It follows that a double precipitation by phenylhydrazine from a chloride solution would give a more exact separation from titanium, than those recorded above.

SEPARATION OF TITANIUM FROM BERYLLIUM BY ANILINE.

No.	BeO taken. Gram.	TiO$_2$ taken. Gram.	TiO$_2$ found. Gram.	Error. Gram.
1	0.050	0.1416	0.1422	—0.0006
2	0.075	0.0944	0.0950	—0.0006

The solutions used were beryllium chloride and titanium sulphate. The mixtures were first changed to chlorides by precipitation with ammonia and subsequent solution in hydrochloric acid. From the chloride solution, a double precipitation was made by aniline.

SEPARATION OF ZIRCONIUM FROM BERYLLIUM.

Everything that has been said as regards the separation of titanium from beryllium applies equally well here.

No.	BeCl$_2$ taken.		BeO found. Gram.	Error. Gram.	Zr(SO$_4$)$_2$ taken.		ZrO$_2$ found. Gram.	Error. Gram.
	cc.	= Gram BeO.			cc.	= Gram ZrO$_2$.		
1	5	0.0050	.....	....	95	0.0925	0.0961	+0.0036
2	95	0.0956	.....	....	5	0.0049	0.0061	+0.0012
3	5	0.0066	0.0040	—0.0026	45	0.0438	0.0458	+0.0020
4	45	0.0591	0.0590	—0.0001	5	0.0049	0.0052	+0.0003
5	15	0.0196	0.0187	—0.0009	45	0.0438	0.0443	+0.0005
6	35	0.0458	0.0445	—0.0013	35	0.0341	0.0359	+0.0018
7	100	0.1305	0.1290	—0.0015	50	0.0506	0.0520	+0.0014

An inspection of these tables makes it plain that a little beryllium is sure to be carried down with the quadrivalent metal, where sulphate solutions are used, but here too, as in the case of beryllium and titanium, we may confidently predict more accurate results, if chloride solutions are taken.

SEPARATION OF THORIUM FROM BERYLLIUM.

	BeO taken. Gram.	ThO$_2$ taken. Gram.	ThO$_2$ found. Gram.	Error. Gram.
1	0.025	0.2863	0.2847	—0.0016
2	0.025	0.1909	0.1895	—0.0014

The solutions used were beryllium chloride and thorium nitrate. Separation 1 was made with phenylhydrazine, separation 2 with aniline. Double precipitations were made in both cases. Thoria is, of course, a stronger base than titania or zirconia. From the above solutions it did not precipitate until a boiling temperature was reached and the precipitate was very slimy, like alumina when precipitated under the same circumstances. This may account for the fact that the results are a little low.

Attempts to separate aluminum from beryllium, and chromium from beryllium, and from ferrous iron, all failed. Usually the bivalent metal was carried down in considerable quantities with the trivalent one. Chromium chloride does not easily precipitate with phenylhydrazine. Many experiments tried along the above lines show that two elements when too near the same basicity can not be separated by this method, though just why the bivalent element should be partly precipitated in the presence of the trivalent is not perfectly clear.

THE HYDROLYSIS OF ANILINE AND PHENYLHYDRAZINE HYDRO-CHLORIDES.

The degree of hydrolysis which a salt suffers in aqueous solution, may be estimated from its conductivity, the values observed

being compared with those shown by salts of the same type in which hydrolysis is negligible; or it may be calculated from the velocity of certain chemical actions which are caused by the free acid present in the salt solution. The best examples of the latter are the inversion of cane-sugar, and the saponification of methyl acetate. The last-named method[1] was selected in this work. A medium temperature of 40° C. was chosen. It was maintained by a thermostat of the Ostwald type, of 100 liters' capacity, which could be held within limits of about 0.2° C. for long periods. All the experiments were made with $N/10$ solutions of the hydrochlorides of the two bases, phenylhydrazine and aniline. Several preparations were used that there might be reasonable certainty that the saponification constants were not affected in any considerable degree by impurities. Two different samples of "C. P." phenylhydrazine hydrochloride were purified by dissolving in alcohol and precipitating by ether. One specimen of aniline hydrochloride was prepared in a similar way, and another was made from pure aniline by evaporating with pure hydrochloric acid on the water-bath. All the preparations stood a long time in desiccators with lime and sulphuric acid, before use. The reaction vessels consisted of 8-inch test-tubes which were first treated for some time with steam, then boiled with concentrated hydrochloric acid and finally very thoroughly washed and dried.[2] $N/10$ solutions of the hydrochlorides were employed in the saponification as representing on the average about the concentration of these salts in those solutions in which the separations were made. In detail, the proper quantities of the salts, *viz.*, 0.324 gram $C_6H_5.NH_3Cl$, and 0.361 gram $C_6H_5.N_2H_4Cl$, were first weighed out and transferred to the reaction tubes. The latter were then constricted in the flame at a distance of 2 or 3 inches from the open end, after which 1 cc. methyl acetate was introduced by a pipette about 2 mm. in diameter, followed by 250 cc. water free from carbonic acid. The tubes were then sealed, cooled, shaken to mix the contents, and placed in the bath. After a sufficient interval, a tube was withdrawn, chilled and opened. Its contents were then tested as follows: 1 cc. was removed by a pipette, added to a small volume of water free from carbonic acid and titrated with $N/20$ soda, phenolphthaleïn serving as an indicator. The

[1] Walker : *Ztschr. phys. Chem.*, **4**, 319.

[2] Ley : *Ibid.*, **30**, 229; Walker : *J. Chem. Soc.*, **65**, 577.

errors in measurement were reduced to a minimum by using narrow instruments. The pipette was about 2 mm. in diameter and the 10 cc. burette, about 8 mm. During the titration, the contents of the burette were protected from the outer air by a soda-lime tube. The sodium hydroxide was prepared according to Ley,[1] and was proved free from carbon dioxide by titrating against $N/10$ hydrochloric acid, first with the aid of phenolphthaleïn, then with methyl orange.

1. Phenolphthaleïn used as indicator: 5 cc. HCl = 9.58, 9.59, 9.58, 9.60 cc. NaOH; mean, 9.59 cc.

2. Methyl orange used as an indicator: 5 cc. HCl = 9.59, 9.52, 9.58, 9.59 cc. NaOH; mean, 9.57 cc.

SAPONIFICATION OF METHYL ACETATE BY $N/10$ HYDROCHLORIC ACID AT $40°$ C.

25 cc. acid and 1 cc. methyl acetate were used in each test. 1 cc. acid = 0.00374 gram hydrochloric acid, as determined by sodium carbonate. The process was carried out in sealed tubes as described above:

a_0 = 1 cc. of the original mixture in terms of $N/20$ soda = 2.10.

a_∞ = 1 cc. of the mixture when saponification was complete = 9.50.

$a = a_\infty - a_0 = 7.4 =$ the original mass of methyl acetate in terms of $N/20$ soda.

Then the saponification constant for a reaction of the first order = $K = \frac{1}{t} \log_e \frac{a}{a-x}$.

Here, of course, $t =$ the time, in this case measured in minutes, and $x =$ quantity of methyl acetate changed, or acid liberated in the time t, again in terms of the soda solution. The Briggs logarithms were used in the calculation.

$t_1 = 131\ m$	$x_1 = 2.25$	$K_1 = 0.001204$
$t_2 = 235\ m$	$x_2 = 3.55$	$K_2 = 0.001207$
$t_3 = 324\ m$	$x_3 = 4.33$	$K_3 = 0.001180$
$t_4 = 363\ m$	$x_4 = 4.70$	$K_4 = 0.001206$
		Average = 0.00120

[1] *Ztschr. phys. Chem.*, **30**, 205.

Corrected for volume, since 1 cc. methyl acetate was added to the 25 cc. acid, $K = 0.00120 \times \dfrac{26}{25}$.

Corrected for concentration, since the acid was not exactly $N/10$, $K = 0.00120 \times \dfrac{26}{25} \times \dfrac{3645}{3740} = 0.001216 = 1.22 \times 10^{-3}$.

Walker[1] found for the velocity constant of the same reaction at $25°$ C., $K = 0.00315$, using normal hydrochloric acid. Ley[2] found at $99.7°$ C., $K = 0.00158$ as the average for $N/500$ hydrochloric acid, and 0.00307, average for $N/250$ hydrochloric acid.

If these constants are made comparable by multiplying them by their corresponding concentrations, we have:

$$kv = 0.00315 \text{ at } 25° \text{ C.} - Walker.$$
$$\text{''} = 0.01216 \text{ at } 40° \text{ C.} - Allen.$$
$$\text{''} = 0.782 \text{ (average) at } 99.7° \text{ C.} - Ley.$$

Strictly these quantities should, of course, be multiplied by 2.3, because the natural logarithms were not used in the calculations.

Van't Hoff has shown that we may get some light on the change of reaction velocity with temperature if we resolve the equation $\dfrac{d \log_e K}{d T} = \dfrac{q}{RT^2}$ (where $K =$ the equilibrium constant, $\dfrac{k}{k'}$, of any reaction, $T =$ the absolute temperature, and $q =$ the heat of reaction) into two others, viz., $\dfrac{d \log_e k}{d T} = \dfrac{A}{T^2} + B$, and $\dfrac{d \log_e k'}{d T} = \dfrac{A'}{T^2} + B$. B is unknown, but often seems to be negligible, in which case, assuming also that q is constant, we have $\log_e k = -\dfrac{A}{T} + C$ or $\log_e \dfrac{k_2}{k_1} = A \left(\dfrac{T_2 - T_1}{T_1 T_2} \right)$. By the aid of this equation, we may correlate the various values of k found at different temperatures.

Substituting for k_2, k_1, t_2 and t_1, 0.01216, 0.00315, 298 and 313 respectively, $A = 8397$.

Substituting 0.782, 0.01216, 372.7 and 313, $A = 8132$.

Considering the difference in dissociation of the different concentrations of acid, the slight variation of q, etc., the agreement seems satisfactory. K_T (the saponification constant of methyl

[1] Ztschr. phys. Chem., **4**, 324.

[2] Ibid., **30**, 230.

acetate by hydrochloric acid) may thus be approximately reckoned from the equation

$$K_T = \frac{K_{298}}{V} e^{8264 \left[\frac{T - 298}{298\ T} \right]}$$

SAPONIFICATION OF METHYL ACETATE BY ANILINE HYDROCHLORIDE AT 40° C.

$a_0 = 1.81 =$ acid in 1 cc. mixture, at the beginning, in terms of N/20 soda.

$a_\infty = 9.30 =$ free acid in 1 cc. mixture after one month in the thermostat at 40° C.

$a = a_\infty - a_0 = 7.49$ total acid freed by saponification in 1 cc. mixture, equivalent to the original mass of the methyl acetate in terms of soda.

$$K = \frac{1}{t} \log_e \frac{a}{a-x}$$

$t_1 = 1330\ m \qquad x_1 = \begin{cases} 2.35 \\ 2.31 \\ 2.32 \end{cases}$

$\qquad\qquad\qquad\qquad \overline{2.33} \quad - \quad 1.81 = 0.52$

$t_2 = 2450\ m \qquad x_2 = \begin{cases} 2.80 \\ 2.85 \\ 2.81 \end{cases}$

$\qquad\qquad\qquad\qquad \overline{2.83} \quad - \quad 1.81 = 1.02$

$t_3 = 4290\ m \qquad x_3 = \begin{cases} 3.61 \\ 3.60 \end{cases}$

$\qquad\qquad\qquad\qquad \overline{3.61} \quad - \quad 1.81 = 1.80$

$t_4 = 5683\ m \qquad x_4 = \begin{cases} 4.20 \\ 4.23 \end{cases}$

$\qquad\qquad\qquad\qquad \overline{4.22} \quad - \quad 1.81 = 2.41$

1 $\quad K = 2.35 \times 10^{-5} \times \frac{26}{25} = 2.45 \times 10^{-5}.$

2 $\quad K = 2.60 \times 10^{-5} \times \frac{26}{25} = 2.70 \times 10^{-5}.$

3 $\quad K = 2.78 \times 10^{-5} \times \frac{26}{25} = 2.89 \times 10^{-5}.$

4 $\quad K = 2.97 \times 10^{-5} \times \frac{26}{25} = 3.09 \times 10^{-5}.$

Now if it be remembered that the rate of reaction depends **on**

the concentration of free hydrochloric acid, it will be seen that the percentage of aniline salt which is hydrolyzed may be obtained by dividing these results by the constant for hydrochloric acid at the same dilution.

$$2.45 \times 10^{-5} \div 1.22 \times 10^{-3} = 2.0 \text{ per cent.}$$
$$2.70 \times 10^{-5} \div 1.22 \times 10^{-3} = 2.2 \text{ per cent.}$$
$$2.89 \times 10^{-5} \div 1.22 \times 10^{-3} = 2.4 \text{ per cent.}$$
$$3.09 \times 10^{-5} \div 1.22 \times 10^{-3} = 2.5 \text{ per cent.}$$

As there is always a constant ratio between the undecomposed part of the salt, multiplied by the volume in which it is contained, and the product of the decomposed parts, we have the well-known equation $\dfrac{x^2}{V(1-x)} = C$, where x is the percentage hydrolyzed, V is the volume in which 1 gram-molecule is dissolved, and C is the hydrolytic constant. If we take the average of x as 2.3, $C = 5.4 \times 10^{-5}$, or if 2 is more nearly correct, $C = 4.1 \times 10^{-5}$.

The strength of aniline has previously been determined by two different observers. Bredig,[1] using the conductivity method, concluded that 2.63 per cent. of aniline hydrochloride was decomposed in N/32 solution at 25° C., while Walker,[2] by the use of the sugar inversion method, obtained the value 4.5 per cent. at 60° C. in N/30 solution.

If we calculate these results to N/10 dilution by the use of the equation $C = \dfrac{x^2}{v(1-x)}$, we have :

1.48 per cent. hydrolyzed at 25° C.—*Bredig*.
2.00 " " " " 40° C.—*Allen*.
2.63 " " " " 60° C.— *Walker*.

These results indicate a nearly regular increase in hydrolysis with increasing temperature. Regarding this point not much is known, but Madsen's[3] results indicate that the increase may be very considerable.

SAPONIFICATION OF METHYL ACETATE BY PHENYLHYDRAZINE
HYDROCHLORIDE AT 40° C.

$a_0 = 1.78$	$a_\infty = 10.90$	$a = 9.12$
$t_1 = 1330$	$x_1 = 0.37$	
$t_2 = 2419$	$x_2 = 0.57$	
$t_3 = 4290$	$x_3 = 1.55$	
$t_4 = 5683$	$x_4 = 2.33$	
$t_5 = 6960$	$x_5 = 3.02$	

[1] *Ztschr. phys. Chem.*, **13**, 322.
[2] *J. Chem. Soc.*, **67**, 582.
[3] *Ztschr. phys. Chem.*, **36**, 294.

$$K = 1.67 \times 10^{-5} \times \frac{26}{25} = 1.73 \times 10^{-5} \div 1.22 \times 10^{-3} = 1.4 \text{ per cent.}$$

$$K = 1.44 \times 10^{-5} \times \frac{26}{25} = 1.50 \times 10^{-5} \div 1.22 \times 10^{-3} = 1.2 \text{ per cent.}$$

$$K = 2.38 \times 10^{-5} \times \frac{26}{25} = 2.47 \times 10^{-6} \div 1.22 \times 10^{-3} = 2.0 \text{ per cent.}$$

$$K = 2.89 \times 10^{-3} \times \frac{26}{25} = 3.00 \times 10^{-5} \div 1.22 \times 10^{-3} = 2.5 \text{ per cent.}$$

$$K = 3.27 \times 10^{-5} \times \frac{26}{25} = 3.40 \times 10^{-5} \div 1.22 \times 10^{-3} = 2.8 \text{ per cent.}$$

Comparing these results with those for aniline hydrochloride, we note that there is an acceleration in the rate of saponification in both cases. With aniline hydrochloride, this is comparatively small; with the phenylhydrazine compound, considerable. If the periods of time had been successive instead of overlapping, the acceleration would be seen to be actually greater than the above figures indicate. If we compare the values for a, we have $a = $ N/10 hydrochloric acid, 7.4; N/10 aniline salt, 7.49; N/10 phenylhydrazine salt, 9.12.

This means that by some secondary reaction more acid has been formed than the methyl acetate could furnish. On this account it seems more rational to calculate the percentages hydrolyzed, from the earlier periods of the process. This leads us to the approximate values 1.5 per cent. for the phenylhydrazine salt and 2.0 per cent. for the aniline compound. Many other experiments on the saponification of methyl acetate were made with other preparations of the salts, but since all led to the same conclusions and the table given above contains the results obtained under the most carefully regulated conditions, no others have been quoted.

In calculating the values of $K = \frac{1}{t} \log_e \frac{a}{a-x}$ for the phenyl-hydrazine salt, a was taken equal to 7.4.

A similar case of acceleration in the saponification of methyl acetate was noticed by Ley,[1] when he employed solutions of aluminum and lanthanum chlorides.

He attributed the acceleration to a secondary action between the chloride and acetic acid, setting free the more highly dissociated hydrochloric acid.

If we compare aniline and phenylhydrazine in regard to their power to precipitate the weak inorganic bases, it appears that their strength is nearly the same, but that of aniline is slightly less.

[1] *Ztschr. phys. Chem.*, **30**, 231.

Salt.	Action of aniline.	Salt.	Action of phenylhydrazine.
$Be(NO_3)_2$	Trace of precipitate.	$Be(NO_3)_2$	Same as with aniline.
$BeSO_4$	No precipitate.	$BeSO_4$	Heavy precipitate, though not complete.
$Al(NO_3)_3$	Precipitation slow, but complete.	$Al(NO_3)_3$	Complete and much more rapid precipitation.
$Al_2(SO_4)_3$	Complete precipitation.	$Al_2(SO_4)_3$	Complete precipitation.
$Cr(NO_3)_3$	Complete, but slow precipitation.	$Cr(NO_3)_3$	Complete and rapid precipitation.
$Cr_2(SO_4)_3$	Complete precipitation.	$Cr_2(SO_4)_3$	Complete precipitation.
$Ti(NO_3)_4$	Complete precipitation.	$Ti(NO_3)_4$	Complete precipitation.
$Ti(SO_4)_2$	Complete precipitation.	$Ti(SO_4)_2$	Complete precipitation.
$Zr(NO_3)_4$	Precipitation complete, but slow.	$Zr(NO_3)_4$	Precipitation complete and considerably more rapid than with aniline.
$Zr(SO_4)_2$	Complete precipitation.	$Zr(SO_4)_2$	Complete precipitation.

These precipitations were all made in the cold, with solutions containing about 1 mg. of metallic oxide per cubic centimeter, and all were slightly acid. 15 cc. of each solution and about 1 cc. of the reagent, a large excess, were taken for each test. Where any difference is found in the behavior of the two bases, it is seen that phenylhydrazine precipitates more rapidly and in one instance, beryllium sulphate, it precipitates where aniline has no action. That both reagents bring down the same precipitates, one can scarcely doubt. They all closely resemble the hydroxides (or basic-salts), formed by ammonia, being flocculent and white or nearly so, when the reagents are free from color and the solutions are dilute. The color of phenylhydrazine is partly borne down by the precipitates. I have noticed that solutions containing free nitric acid in some quantity, form yellow or brown products which are probably oxidation products and which color the precipitates. The addition products which are formed by the action of the same bases on the chlorides of zinc, cadmium, and mercury, and by phenylhydrazine on the chlorides of cobalt and nickel as well, are entirely different in appearance; in fact they are crystalline.

Regarding the difference in the behavior of the nitrates and sulphates of the same elements, too little has been done to draw conclusions, but it will be noticed that where any difference exists, the sulphates precipitate more rapidly. The chlorides have not been systematically compared with the sulphates, but enough has been done to show that they behave similarly to the nitrates, in precipitating less rapidly and sometimes less completely than the

sulphates. This may be due to the formation of basic salts in the case of the sulphates, precipitates, which possess a different solubility from the hydroxides, or perhaps the sulphates of the organic bases are less dissociated than the chlorides.

CONCENTRATION OF FREE ACID IN THE SOLUTIONS PRECIPITATED BY ORGANIC BASES.

The solutions in which the previously described separations were made, are too complicated in composition to deal with directly. All contained an 'unmeasured quantity of ammonium salt, while some contained also several different acids. A few experiments were therefore carried out under simplified conditions.

Experiment 1.—100 cc. titanium sulphate, containing 0.0944 gram titanium dioxide, were precipitated with ammonia, and the washed precipitate was transferred by a jet of water to an empty beaker. A measured quantity of hydrochloric acid, greater than that theoretically demanded, was then introduced. After warming and stirring, a large part of the precipitate remaining undissolved, an excess of phenylhydrazine was poured in. The precipitate was then filtered, while the filtrate was carefully tested for traces of titanium. None was found. It is evident that we have here data which, with the value of the hydrolytic constant of phenylhydrazine hydrochloride, will enable us to calculate the quantity of free acid present. For if m equals the number of molecules of the phenylhydrazine salt, l equals the number of molecules of excess of base, v equals the volume of the solution in liters, k equals the hydrolytic constant, and a equals the degree of dissociation,

$$k = \frac{a(ma + l)}{v(1 - a)} \text{ and } a = -\frac{kv + l}{2m} + \sqrt{\frac{kv}{m} + \left(\frac{kv + l}{2m}\right)^2}.$$

Total weight of acid = 0.238.

Phenylhydrazine required = $0.238 \times \dfrac{108}{36.5} = 0.704$ gram = 0.006521 gram-molecule.

Phenylhydrazine used = 1 cc. = 1.09 gram.

Phenylhydrazine in excess = 1.09 − 0.704 = 0.386 gram = 0.003575 gram-molecule.

$m = 0.006521$ Hence $a = 0.001$, *i. e.*, we have $0.006521 \times 0.001 \times 36.5 =$
$l = 0.003575$ 0.2 milligram of free acid in 100 cc.
$k = 0.00002$
$v = 0.2$ liter.

Experiment 2.—In this experiment all the conditions were the same as in Experiment 1, except that only 0.8 cc. phenylhydrazine was used.

$m = 0.006521$ $a = 0.0027$, *i. e.*, we have 0.60 milligram of acid in 200 cc.
$l = 0.001555$
$k = 0.00002$
$v = 0.2$ liter.

Experiment 3.—To a quantity of freshly precipitated and washed alumina equivalent to 0.1257 gram Al_2O_3, was added a very slight excess of hydrochloric acid, *viz.*, 0.280 gram; all the precipitate dissolved. At a boiling temperature, 2 cc. phenyl-hydrazine gave a practically complete precipitation, but the precipitate was very slimy and the conditions were not adapted to practical work. The excess of phenylhydrazine here is quite large, but other experiments with a smaller excess failed to precipitate the alumina completely.

Here $m = 0.007672$ gram-molecule.
           $l = 0.01251$ gram-molecule.
           $k = 0.00002$.
           $v = 0.1$.

Hence $a = 0.00008$ and the free acid $= 0.007672 \times 0.00008 \times 36.5 = 0.02$ milligram per 100 cc.

The concentrations of free acid in the above cases were probably a little larger than those in the solutions with which the practical work was done, for in the latter cases there was an ammonium salt which must have tended to reduce dissociation.

It is quite certain that titanium hydroxide can be quantitatively precipitated in solutions more strongly acid, but we have here, no doubt, about the same amount of free acid as in the practical work.

There is some reason to believe that the calculated values given above are somewhat too small, for I found that blue litmus paper, while it was decidedly reddened by the solutions we have just considered, gave hardly any reaction with solutions prepared by adding the calculated amount of free acid to 100 cc. distilled water.[1]

I am unable to explain this discrepancy. Possibly the value 2×10^{-5} for the hydrolytic constant of phenylhydrazine hydrochloride is too small, though one would be inclined to suspect that the method used would give high rather than low results. At all events it appears probable, in view of all the facts, that the con-

[1] A sensitive litmus tincture, however, reacted strongly with these solutions.

centration of free acid in the solutions we have been considering is not greater than a few milligrams in 100 cc.

SUMMARY.

(1) The weak organic bases, such as show little or no alkaline reaction with indicators, on account of the hydrolysis of their salts, can, of course, never completely neutralize the acid of a metallic salt. They, therefore, cannot precipitate the strong metallic bases, but only the weak ones, which are practically insoluble in very dilute acid. The precipitate may be either the hydroxide or a basic salt. All the analytical separations with these weak bases, which have been devised thus far, seem to involve this principle. The strong reducing power of phenylhydrazine gives it a particular advantage in certain cases.

(2) The work described in this paper was done with phenylhydrazine and aniline. These two bases are of about the same strength, aniline being slightly weaker. This conclusion was arrived at by the study of the saponification of methyl acetate by their hydrochlorides, and also by their power to precipitate metallic hydroxides. The saponification constants in $N/10$ solutions at $40°$ C. were found to be 2.5×10^{-5} for the aniline salt, and 1.7×10^{-5} for the phenylhydrazine salt. These numbers lead us to the values 4×10^{-5} and 2×10^{-5}, respectively, for the hydrolytic constants. This means that about 2 per cent. of the former and 1.50 per cent. of the latter are decomposed into free base and free acid, under the conditions of dilution and temperature stated above.

(3) The concentration of free acid in solutions from which the metallic hydroxides were separated must be quite small. The calculated values amounted to but a few tenths of a milligram for such volumes as 100 to 200 cc. There is some reason to think these values are too small, but it is not likely that they reach above a few milligrams in the above volumes.

(4) Aniline quantitatively precipitates the quadrivalent and weakly basic elements, titanium, zirconium, cerium and thorium, as well as the trivalent elements Fe^{III}, Al, and Cr^{III} under certain conditions, from dilute and slightly acid solutions. The solutions may be chlorides, nitrates or sulphates. The same statements apply to phenylhydrazine, except that ceric and ferric salts are

reduced by this reagent to salts of comparatively strong bases which are precipitated incompletely or not at all.

Zinc, cadmium, mercury, cobalt and nickel, when sufficiently concentrated, form difficultly soluble addition products with phenylhydrazine. With aniline, also, zinc, cadmium and mercury give similar compounds. The strongly basic elements, magnesium barium, calcium, strontium, manganese and ferrous iron are not precipitated.[1]

Beryllium, when present alone, is not precipitated by aniline, nor by phenylhydrazine, except from sulphate solutions. Actual separations were worked out as follows: titanium and zirconium from iron; titanium, zirconium and thorium from beryllium. The separation of aluminum from iron proposed by Campbell and Hess was studied more closely. A double precipitaton is advisable in all these separations. The separations from ferrous iron depend upon the reducing power of phenylhydrazine as well as its weakly basic nature. Aniline can not be substituted for it here, but all the separations from beryllium may be done equally well with aniline.

(5) Phenylhydrazine will accurately separate minute quantities of alumina (and probably also the weaker bases) from large masses of iron.

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CHROM-MALONATES.

COMPLEX salts of organic acids are little known. The chrom-oxalates have been thoroughly studied from the days of Mitscherlich on, and in more recent time the complex oxalates of the metals of the platinum group have been investigated by Joly, Leidié, Vèzes, and their pupils. Few, if any, other organic acids than oxalic have been examined from the standpoint of the formation of complex salts.

Several years ago a preliminary qualitative examination was made in this laboratory, by Mr. G. B. Capito and Mr. W. E. Davis, of the relations of chromium to a number of organic acids, and it

his Journal, 21, 779.