potassium perchlorate. To remedy this difficulty Caspari[1] has already suggested solution of the precipitate after preliminary washing, and re-evaporation, with subsequent washing as above. This was done in the following experiments in which the total volume of washing liquid used was 135–140 cc. The salt was dissolved after once washing by decantation.

TABLE IV.

Weight of KClO₄ taken.	Weight of NaCl taken.	Weight of KClO₄ found.	Difference. G.
0.3006	0.05	0.3010	+0.0004
0.3024	0.1	0.3028	+0.0004
0.3053	0.3	0.3062	+0.0009
0.3047	0.5	0.3063	+0.0016

The results suggest that a second solution of the precipitate with evaporation is desirable to avoid inclusion of sodium salt. Possibly if the preliminary washing is more thorough and if the quantity of sodium is not large one solution is sufficient.

The recommendations which we have to offer for the determination of potassium as perchlorate in the presence of sodium are as follows:

1. The use of absolute alcohol.

2. The use of a low temperature in washing (0°).

3. The use of a platinum-sponge crucible.

We support the suggestion of Davis, of using a washing liquid already saturated with potassium perchlorate. This may be prepared most easily by dissolving a suitable proportion of salt in the alcohol at a high temperature before adding the perchloric acid; also that of Caspari of dissolving the precipitate, after preliminary washing, and again evaporating to dryness before the final washing.
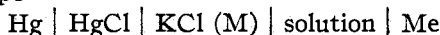
CAMBRIDGE, MASS.

THE TITRATION OF SOME BIVALENT METAL SULFATES BY THE CONDUCTANCE METHOD.

BY HERBERT S. HARNED.

In recent years, two important physical chemical methods have been employed in determining the end point in volumetric analysis. The first of these depends on measuring the change in electromotive force of a cell of the type

$$\text{Hg} \mid \text{HgCl} \mid \text{KCl (M)} \mid \text{solution} \mid \text{Me}$$

on adding a standardized titrating solution to the solution containing the substance to be determined. Behrend[2] used a silver concentration cell

[1] *Z. angew. Chem.*, **7**, 71 (1893).

[2] *Z. physik. Chem.*, **11**, 466 (1893).

in determining the silver or chlorine content of a solution; Böttger,[1] and Hildebrand[2] have employed the hydrogen electrode in acidimetric and alkalimetric titrations. Oxidation electrodes have also been employed by many workers.[3] The theory and practice of this form of titration will not be mentioned here; it is treated fully in the literature above referred to. Few of the many possible combinations have been worked out and many which have been tried have not been tested for accuracy. For this reason, there remains much to be done in this field from the analytical standpoint.

The first attempt to determine a metal by means of the hydrogen electrode was made by Hildebrand and Harned,[4] who found that it was possible to determine the magnesium in a solution containing calcium by titrating with a sodium hydroxide solution. If the plot of electromotive force against cc. of sodium hydroxide in this paper be consulted, it is seen that, owing to the gradual change in electromotive force, it is difficult to determine the inflection point at which all the magnesium has been precipitated as hydroxide. The final results on a sample of dolomite varied considerably. The present communication is the result of a search for a titration method which could be used in titrating metals with alkali or alkaline earth hydroxides and which would be more accurate than those previously employed.

The second general physical chemical method for determining the end point of a reaction in solution employs the change in conductance of the solution on the addition of a titrating agent. This method is recommended in laboratory text-books of physical chemistry[5] for use in titrating acids and bases. It has proved to be particularly useful in determining the end points in colored solutions in which an indicator could not be used. Küster, Grüters and Geibel[6] showed the accuracy of this method as applied to neutralization reactions. Recently, van Suchtelen and Itano[7] have applied the conductance method for the determination of the end point in various reactions, such as those between potassium chloride and silver nitrate, potassium sulfate and barium nitrate, ammonium phosphate and uranyl acetate. More results than the few given by them would be necessary to prove the accuracy of these titrations. The present

[1] Z. physik. Chem., 24, 253 (1897).

[2] THIS JOURNAL, 35, 847 (1913).

[3] Crotogino, Z. anorg. Chem., 24, 225 (1900); Forbes and Bartlett, THIS JOURNAL, 35, 1527 (1913); Kelley and Conant, "The Electrometric Titration of Vanadium," Ibid., 38, 341 (1916).

[4] Comm. Eighth Intern. Congr. Appl. Chem., 1, 217; also Hildebrand, Loc. cit.

[5] Findlay, "Practical Physical Chemistry;" Ostwald-Luther, "Physiko-Chemische Messungen."

[6] Z. anorg. Chem., 42, 225 (1904).

[7] THIS JOURNAL, 36, 1793 (1914).

investigation contains some results obtained for the purpose of testing
whether the conductance method can be employed in the determination
of metals and what degree of accuracy can be obtained. Incidentally,
some interesting facts regarding the precipitation of a few metallic hy-
droxides have been observed.

Theory.

The conductance of a solution depends on three factors: the concentra-
tion of the electrolyte, the degree of ionization of the electrolyte and the
mobilities of the ions in the solution. Hence, from data relating to these
three factors, titrating reagents may be selected, which, when added to
the solution to be titrated, will give the maximum change of conductance
at the end point. The following examples are given to illustrate the
application of conductance theory to titrations of this kind. The titra-
tion of hydrochloric acid by sodium hydroxide is given in Fig. 1a, in which
cc. of sodium hydroxide are plotted against the conductance of the solu-
tion. The conductance of a hydrochloric acid solution is high, owing to

a
Titration of HCl by NaOH

b
Titration of CH₃COOH
by NaOH

c
Titration of MgSO₄
by NaOH

d
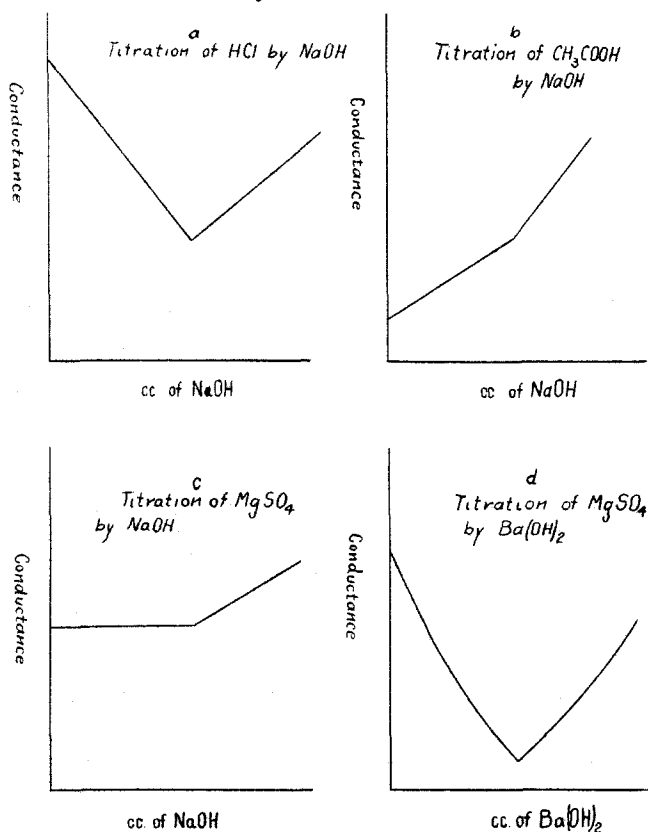Titration of MgSO₄
by Ba(OH)₂

Fig. 1.

the high mobility of the hydrogen ion and the high degree of dissociation of hydrochloric acid.   When sodium hydroxide is added, water is formed and the sodium ion is substituted for the hydrogen ion.   Since the degrees of dissociation of hydrochloric acid and sodium chloride are nearly identical, the number of sodium ions formed in the solution will equal the number of hydrogen ions removed.   The conductance will decrease because the sodium ion of low mobility is substituted for the fast moving hydrogen ion.   At the equivalent point, the solution contains only sodium ions and chlorine ions in quantity along with the negligible quantity of hydrogen and hydroxyl ions from the dissociated water molecules.   On adding an excess of sodium hydroxide, the conductance rises because of the rapid addition of the fast moving hydroxyl ion.   Fig. $1b$ gives the plot of the titration of acetic acid with sodium hydroxide.   Although acetic acid yields hydrogen ions to the solution, its slight degree of dissociation causes its conductance to be low.   Since the degree of dissociation of sodium acetate is high, the addition of sodium hydroxide causes the substitution of a large number of sodium ions for a relatively small number of hydrogen ions and the conductance rises slowly.   After the equivalent point is reached, excess of sodium hydroxide causes a relatively greater increase in conductance owing to the addition of the highly mobile hydroxyl ion.   From these illustrations, it is obvious that, from the simple data referred to above, it is easy to predict the nature of the plots, and to choose a titrating agent which will give a distinct end point.

If to a solution of magnesium sulfate, a sodium hydroxide solution of known normality is added, the reaction

$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4$$
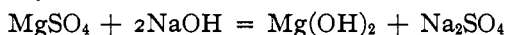
takes place.   During the course of the addition of sodium hydroxide, the magnesium ion is being precipitated as hydroxide, the sodium ion is being substituted for it while the concentration of the SO_4^{--} remains the same.   The ionic mobilities of the magnesium and sodium ions are nearly the same, the degrees of dissociation of magnesium sulfate and sodium sulfate are nearly the same; therefore, neglecting the volume change of the solution, the conductance should change little if at all during the course of the reaction.   After the reaction has been completed, or when an amount of sodium hydroxide equivalent to the magnesium sulfate has been added, sodium hydroxide is simply being added to the sodium sulfate solution, and, owing to the high mobility of the hydroxyl ion, the conductance is increased.   (Fig. $1c$.)   This titration gives only a fairly easily detectable end point for the change in direction of the plot before and after the end point is not great.   A reagent must, therefore, be sought which will increase the difference in the slopes of the plots at the end point.   It is obvious that if a reagent is added which will precipitate both ions of magnesium sulfate from the solution, the conductance will fall

rapidly during the course of the reaction and will rise rapidly after the reaction has been completed. Such a reagent is barium hydroxide, when the solution contains a sulfate of a metal which possesses a difficultly soluble hydroxide (see Fig. 1d). It is extremely important to note the large change in the direction of the plot at the end point. This should make the end point easily detectable and the method very accurate. In this communication, a report of the titration of a few bivalent metals by a barium hydroxide solution is presented.

Apparatus and Manipulation.

In using barium hydroxide as a titrating agent, it is necessary to remove all carbon dioxide from the solution and to keep the solution free from carbon dioxide during the course of the titration. Hence, the titrating apparatus should be so constructed as to permit boiling of the solution under reduced pressure. Secondly, the electrodes should remain stationary with respect to each other and in respect to their position in the solution. Thirdly, the titrating solution must be run into the cell without coming in contact with carbon dioxide. After many trials, the cell shown in Fig. 2 was constructed and found to be satisfactory. A is a round bottom
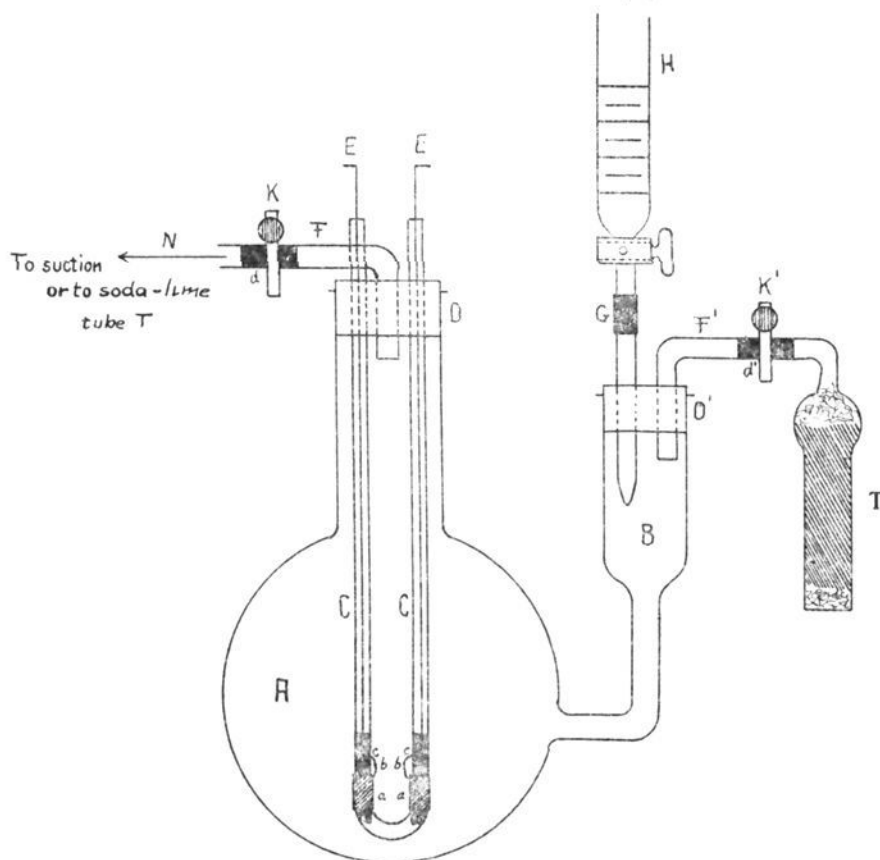

Fig. 2.

flask into the side of which a tube, B, of the shape shown was sealed. The electrode apparatus CC consisted of a narrow glass U-tube sealed in such a way at the bend that the inner compartments of the two sides were

separated.   The electrodes *aa* were made of sheet platinum fused to platinum wires *bb* which were in turn sealed in through the glass at *cc*. The two ends of the U-tube passed through a rubber stopper, D, which fitted tightly in the neck of the flask.   This held the electrodes stationary. The connections to the leads EE were made by mercury.   F and F' were exit tubes joined to soda-lime tubes TT' by the rubber tubes *dd'* which could be clamped by the screw clamps K and K'.   G was a rubber connection which joined the cell with the buret H so as to permit the tilting and the shaking of the whole titrating apparatus.   The conductance of such a cell was measured by the simplest kind of a conductance apparatus, amply described in books relating to physical-chemical measurements.[1]

In making a determination, the following procedure was adopted: The solution to be titrated is introduced into the flask, the rubber stopper D is pressed in tightly, as is the stopper D'.   The clamp K' is closed and suction is applied at N while the solution is boiled.   After all the carbon dioxide has been expelled, the clamp K is closed and a soda-lime tube, T, is placed at N.   Then the clamps KK' are opened and air passes into the titrating flask through the soda-lime tubes T and T'.   This prevents any carbon dioxide from entering the apparatus.   The barium hydroxide solution is run into A through B from the buret H and readings of the conductance are taken at each successive addition of the titrating solution. Near the end point, it is advisable to take readings at successive additions of from 0.3 to 0.5 cc. of the titrating solution.   Any titrating solution remaining in B can be washed into A by tilting the apparatus.

All subsequent plots were obtained by plotting the bridge wire readings against the number of cc. of the titrating agent.   The end point of the reactions is just as easily determined by this method and the calculation of the conductance from the bridge wire readings is eliminated.

The Titration of Magnesium Sulfate.

A solution of magnesium sulfate behaved normally.   The weighed sample was dissolved in about 50 cc. of water in the titrating vessel; any dissolved carbon dioxide was expelled by boiling and suction, and the solution was allowed to cool.   The barium hydroxide solution, made free from barium carbonate[2] and standardized against 0.1 *M* hydrochloric acid, was then added and the titration was carried out as outlined.   Table I gives the results obtained.   Fig. 3*a* gives a typical curve obtained from one of these titrations.   Bridge wire readings (denoted B. W. R.) are plotted against cc. of barium hydroxide solution.   A discussion of the accuracy will be reserved until later.

[1] A good description is given by Findlay, "Practical Physical Chemistry," 3rd edition, pp. 165–205.

[2] Findlay, "Practical Physical Chemistry," pp. 162–164.

TABLE I.

Titration of Magnesium Sulfate Using 0.1709 Normal Barium Hydroxide.

A sample of $MgSO_4.7H_2O$ was employed. Three gravimetric determinations of the magnesium as pyrophosphate in the sample used, made at the beginning, middle, and end of this series of determinations, gave 9.98%, 9.98% and 9.95%, respectively.

Expt. No.	$MgSO_4.7H_2O$ used.	Mg present. G.	Mg found by conductance.	
			G	%.
1	1.5396	0.1537	0.1548	10.06
2	1.0678	0.1066	0.1072	10.04
3	0.9925	0.0991	0.0988	9.95
4	1.2581	0.1256	0.1240	9.86
5	1.3506	0.1348	0.1353	10.02
6	0.8992	0.0897	0.0886	9.85
7	0.6497	0.0648	0.0642	9.91
8	0.8248	0.0822	0.0821	9.95
9	0.7114	0.0710	0.0710	9.98
10	0.7862	0.0785	0.0785	9.98
11	0.9250	0.0923	0.0929	10.04
12	0.7548	0.0753	0.0759	10.05
13	0.8112	0.0810	0.0818	10.08
14	0.6977	0.0696	0.0699	10.01
15	0.8533	0.0852	0.0852	9.99

If, at the start, the solution contained sulfuric acid along with the magnesium sulfate it could be neutralized with the barium hydroxide solution until the pink color of phenolphthalein just appeared and then the magnesium sulfate could be titrated by the conductance method. That this is true will be shown as the discussion continues.

The question whether it is possible to titrate magnesium sulfate in the presence of calcium sulfate is naturally suggested at this point. If a barium hydroxide solution is added to a solution containing both calcium sulfate and magnesium sulfate, the magnesium sulfate will be precipitated first and the conductance will fall. When all the magnesium has been precipitated as hydroxide, the barium hydroxide will react with the calcium sulfate giving the soluble calcium hydroxide and barium sulfate and the conductance will rise. The presence of calcium sulfate, however, will cause the end point to be less sharp. There will be relatively much less change in conductance. Table II gives the results obtained.

TABLE II.

Titration of Magnesium Sulfate in the Presence of Calcium Sulfate, using 0.1417 N Barium Hydroxide.

Expt. No.	$MgSO_4$ solution. Cc.	$CaSO_4$ solution (saturated). Cc.	$Ba(OH)_2$ solution. Cc.	Mg.	
				Present. G.	Found. G.
1	10.00	...	94.55	0.1608	0.1607
2	10.00	...	94.35	0.1608	0.1604
3	10.00	25.00	94.85	0.1608	0.1612[1]
4	10.00	50.00	94.70	0.1608	0.1609[2]

[1] The plot of this titration is given in Fig. 3b.
[2] The plot of this titration is given in Fig. 3c.

These results show conclusively that the magnesium in magnesium sulfate can be titrated even when calcium sulfate is present in the solution. Since this is the case, the magnesium in a dolomite should be accurately and rapidly titrated by this method. To this end, a sample of dolomite is placed in a small round bottom flask, just a little more than enough sulfuric acid is added to decompose the mineral and then the carbon dioxide is expelled by boiling under reduced pressure. A safety trap is inserted to prevent loss of solution due to bumping. After cooling, a few drops of phenolphthalein are added and a barium hydroxide solution is run in until the pink color just appears. No note is made of the quantity of barium hydroxide added. This causes the neutralization of the free sulfuric acid, precipitates any iron present as hydroxide, and, if any free carbon dioxide remains in the solution, it has now been converted to barium bicarbonate. The solution is then transferred to the titrating vessel and boiled under suction. The acid carbonate of barium, if present, is converted to the neutral carbonate which precipitates. The insoluble portion contains
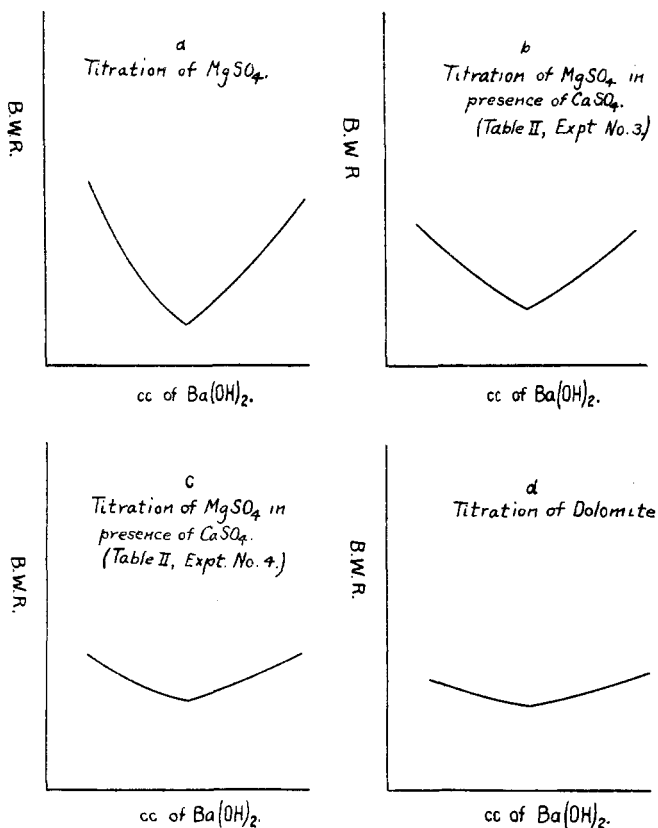

Fig. 3.

gangue, iron hydroxides, calcium sulfate, barium sulfate, and barium carbonate, and there remains in the solution all the magnesium sulfate and some of the calcium sulfate. This solution is then directly titrated quantitatively without the removal of the insoluble material. Table III gives some of the results thus obtained. Fig. 3d gives a typical plot.

TABLE III.

Titration of Dolomite using 0.1417 N Barium Hydroxide.

Expt. No.	Wt. of sample. G.	Mg. present. G.	Mg found by conductance.	
			G.	%.
1	0.3002	0.0595	0.0597	19.87
2	0.3000	0.0595	0.0590	19.66
3	0.3206	0.0636	0.0636	19.83
4	0.3656	0.0725	0.0727	19.88
5	0.3349	0.0654	0.0656	19.56
6	0.3458	0.0675	0.0675	19.52
7	0.3312	0.0646	0.0650	19.63
8	0.3612	0.0705	0.0701	19.40
9	0.3510	0.0685	0.0687	19.57
10	0.3334	0.0651	0.0647	19.43

Expts. 1–4 inclusive were made on a dolomite whose magnesium content was found, from a mean of a number of gravimetric determinations, to be 19.83%. Expts. 5–10 inclusive were made on a dolomite whose magnesium content was found to be 19.52%.

It is not easy to determine the percentage error from these measurements, because the error seems to be independent of the amount of magnesium present and depends only on obtaining the end point. The results in Table I were the first obtained. In this series, there are three in which the magnesium found by conductance varied from the magnesium present by more than one milligram. The results in Tables II and III are thought to be more accurate than these. It is safe to say that by this method, the magnesium content of the above solutions can be obtained to within ± 1 mg. of magnesium independent of the amount of magnesium present. The results obtained by Hildebrand and Harned[1] varied 7 mg. in magnesium content, which gives an error of ± 3.5 mg.

Although experience with this type of titration will be necessary before results like the above are obtained, it is thought that, if proper considera- tion and time be expended, it may prove to be of technical value. As many as four determinations have been made by the author within three hours.

The Titration of Copper Sulfate.

Previous to any attempt to titrate copper sulfate by means of a barium hydroxide solution, a sodium hydroxide solution was employed. It was found that when a quantity of sodium hydroxide less than that required

---

[1] *Loc. cit.*

to completely convert the copper sulfate to the hydroxide was added, all the copper was precipitated. This indicated obviously the precipitation of an oxysulfate or of solid solutions of the hydroxide and copper sulfate of variable composition. Electrometric titrations at 20° using a cell of the type

$$Cu \mid CuO \mid CuSO_4 \mid KCl(M) \mid HgCl \mid Hg^1$$
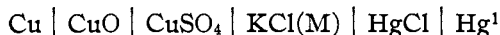
gave an end point when six-sevenths of the equivalent quantity of sodium hydroxide was added. It is not thought that this figure has any significance. Although many oxysulfates of copper have been reported and formulas such as $CuSO_4.3CuO.4H_2O$, $2CuSO_4.5Cu(OH)_2$ have been given[2] to the naturally occurring substances langit and brochantite, respectively, proof is lacking that these exist as chemical compounds. A recent communication[3] shows conclusively that the earlier workers were mistaken, mainly because of the fact that it takes three months for the system CuO–$CuSO_4$–H_2O to come to equilibrium. A closer application of the phase rule to this system would be necessary in order to clear up these difficulties.

If a barium hydroxide solution is used, it is to be expected that any oxysulfate formed would be more easily broken up, owing to the formation of barium sulfate. This is the case, but at 20°, the results are still low; less barium hydroxide is required than that necessary to completely convert all the sulfate to hydroxide. In order to obtain analytical results, the titration was carried out at a temperature just under the boiling point of the solution. Under these conditions, copper oxide formed and the "so-called" oxysulfates were decomposed. Table IV contains the results obtained. The plot is similar to Fig. 3a. A sample of $CuSO_4.5H_2O$ was used which was known to contain the theoretical amount of copper.

TABLE IV.

Titration of Copper Sulfate using a 0.1709 N Barium Hydroxide Solution.
The theoretical percentage of copper in the sample used was 25.48%.

Expt. No.	Wt. sample. G.	Cu present.	Cu found by conductance.	
			G.	%.
1.....................	0.7544	0.1922	0.1934	25.64
2.....................	0.7171	0.1827	0.1822	25.41
3.....................	0.8917	0.2272	0.2262	25.36
4.....................	0.8917	0.2272	0.2264	25.39
5.....................	0.6140	0.1564	0.1564	25.47
6.....................	0.6168	0.1572	0.1577	25.55

In this series of results, the variation is about 1% of the amount of copper present.

[1] Made by Dr. J. Bennett Hill in this laboratory.
[2] Graham, *Lieb. Ann.*, 29, 29 (1839); Becquerel, *Compt. rend.*, 34, 573 (1852).
[3] Young and Stearn, THIS JOURNAL, 38, 1947 (1916).

The Titration of Nickel and Cobalt Sulfates.

It is not easy to obtain crystals of nickel or cobalt sulfate which are entirely free from sulfuric acid. A barium hydroxide solution added to a solution containing nickel sulfate with a slight excess of sulfuric acid will first neutralize the acid and then react with the sulfate. A sharp end point should occur when a quantity of barium hydroxide just equivalent to all the sulfuric acid and nickel sulfate is added. When the titration is carried out cold, low results are obtained which are due to "so-called" oxysulfates. However, when the titration is carried out hot, such substances cease to exist and the minimum in conductance is reached when the barium hydroxide has reacted with both the sulfuric acid and nickel sulfate to form only nickel hydroxide and barium sulfate. The same is true of cobalt sulfate.

In these experiments, solutions of nickel and cobalt sulfates containing slight excesses of sulfuric acid were made up. Gravimetric analysis showed that 10 cc. of the nickel solution contained an excess of sulfuric acid equivalent to 1.4 cc. of the barium hydroxide solution and that 10 cc. of the cobalt solution contained an excess of sulfuric acid equivalent to 2.0 cc. of the barium hydroxide solution. The nickel and cobalt in these solutions were determined by electrolysis in a mercury cup. Tables V and VI give the results obtained. Fig. 4a and b give the plots.

TABLE V.

Titration of Nickel Sulfate using a 0.1610 N Barium Hydroxide Solution.

(10 cc. of solution used in each of the following experiments:)

Expt. No.	Ni by electrolysis.	Cc. Ba(OH) used for NiSO$_4$ and H$_2$SO$_4$.	Cc. Ba(OH)$_2$ used NiSO$_4$ alone.	Ni by conductance.
1..........	0.3420	73.25	71.85	0.3413
2..........	0.3413	73.60	72.20	0.3429
3..........	..	73.55	72.15	0.3427
4..........	..	73.35	71.95	0.3418
5..........	..	73.25	71.85	0.3413

TABLE VI.

Titration of Cobalt Sulfate using a 0.1602 N Barium Hydroxide Solution.

(10 cc. of solution used in each of the following experiments:)

Expt. No.	Co by electrolysis.	Cc. of Ba(OH)$_2$ used for CoSO$_4$ and H$_2$SO$_4$.	Cc. Ba(OH)$_2$ for CoSO$_4$ alone.	Co by conductance. G.
1..........	0.3625	78.40	76.40	0.3617
2..........	0.3627	78.60	76.60	0.3627
3..........	0.3620	78.65	76.65	0.3629
4..........	..	78.60	76.60	0.3627
5..........	..	78.45	76.45	0.3619

The error in these series of results is about 0.15% of the total amount of nickel or cobalt present.

If, to a solution containing sulfuric acid, cobalt sulfate, and sodium sulfate, a barium hydroxide solution be added, the conductance will

fall in consequence of: first, the neutralization of the free acid, and secondly the precipitation of both ions of the cobalt sulfate. After a quantity of barium hydroxide equivalent to the free acid and sulfate is added, further addition of barium hydroxide causes the formation of barium sulfate and
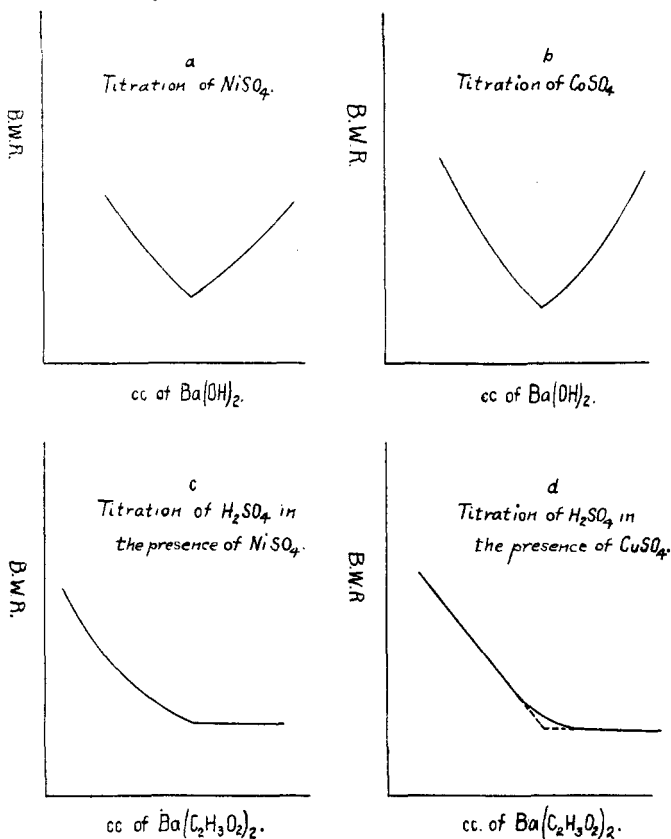

Fig. 4.

sodium hydroxide and the conductance rises. That this is true is shown in Table VII. A large excess of sodium sulfate may flatten the plot in such a way as to cause difficulty in determining the end point. The plot is similar to Fig. 3d.

TABLE VII.

Titration of Cobalt Sulfate in the Presence of Sodium Sulfate using a 0.1600 N Barium Hydroxide Solution.

Expt. No.	Cc. Ba(OH)$_2$ used.	Cc. Ba(OH)$_2$ used for CoSO$_4$.	Grs. of Na$_2$SO$_4$.	Co by conductance. G.
1.........	78.9	76.9	0.5	0.3633
2.........	78.8	76.8	1.0	0.3627

Furthermore, it would be important if a titrating agent could be found to titrate the free sulfuric acid. In this case, no indicator will give the

end point, because the nickel hydroxide begins to precipitate before any of the reliable indicators change color. Barium hydroxide and the conductance method cannot be used for the determination of the free sulfuric acid because the change caused in the conductance at the end point is so very small. Therefore, another titrating agent was sought. It was thought that a solution of barium acetate would serve the purpose, for, if such a solution be added to a solution containing nickel sulfate and sulfuric acid, barium sulfate and acetic acid should first form and the conductance should fall, owing to the slight dissociation of the acetic acid. After all the free sulfuric acid has been titrated, the barium acetate solution should react with the nickel sulfate to give barium sulfate and nickel acetate and the conductance should change little. Such a solution of barium acetate was made by running a barium hydroxide solution into acetic acid until the pink color of phenolphthalein just appeared. This solution was diluted, standardized against sulfuric acid of known strength by the conductance method and used. As shown by Fig. 4c, an end point which is not sharp is obtained. Table VIII gives the results.

TABLE VIII.

Titration of Free Sulfuric Acid in the Presence of Nickel Sulfate using a 0.100 N Barium Acetate Solution.

Expt. No.	Cc. of Ba(C$_2$H$_3$O$_2$)$_2$ required.	Cc. of Ba(C$_2$H$_3$O$_2$)$_2$ found.	Diff. in no. of cc.
1.............	7.57	7.30	0.27
2.............	14.10	13.60	0.50
3.............	20.64	19.90	0.74

Thus, in the presence of nickel sulfate, low results are obtained which increase with increasing amounts of the sulfuric acid originally present.
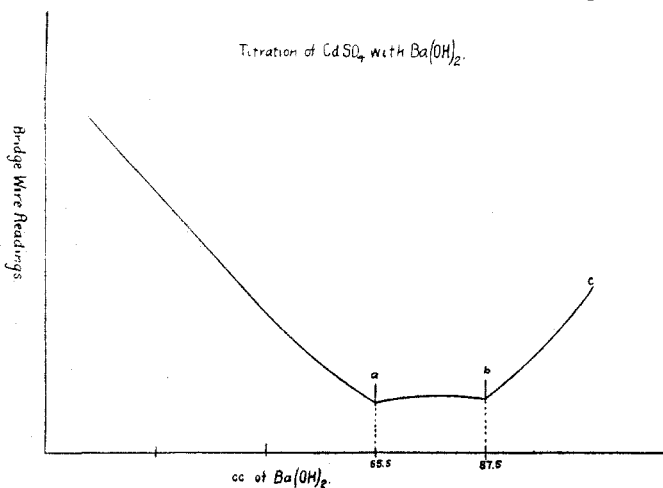

Fig. 5.

Although no explanation is offered for this behavior, it is thought that there is some connection between this fact and the fact that it is hard to remove sulfuric acid from nickel sulfate. A possible explanation is that nickel sulfate forms complex acids with the free sulfuric acid.

In the presence of copper sulfate, however, the free sulfuric acid can be titrated as shown in Table IX. Fig. 4d gives the plot.

TABLE IX.

Titration of Free Sulfuric Acid in the Presence of Copper Sulfate using a 0.100 N Barium Acetate Solution.

Expt. No.	Cc. of $Ba(C_2H_3O_2)_2$ required.	Cc. of $Ba(C_2H_3O_2)_2$ found.
1	6.55	6.55
2	13.10	13.20
3	20.25	20.15
4	22.00	21.85

This last titration has no particular merit since the free sulfuric acid in copper sulfate solutions can be titrated using methyl orange as an indicator.[1]

The Titration of Cadmium Sulfate.

The titration of a cadmium sulfate solution with a barium hydroxide solution did not turn out to be accurate analytically. This was due to the fact that cadmium sulfate exhibits a strong tendency to form an oxysulfate. This titration was carried out at a temperature just below the boiling point of the solution. Table X gives the results, Fig. 5 the plot. The cadmium in the solutions used was determined by deposition on a platinum dish from an ammoniacal acetate electrolyte.

TABLE X.

The Titration of Cadmium Sulfate Using a 0.1627 N Barium Hydroxide Solution.

Expt. No.	Cc. Ba(OH)$_2$ 1st end point.	Cc. Ba(OH)$_2$ 2nd end point.	No. of cc. Ba(OH)$_2$ 2nd end point times $^3/_4$.	Cd (Calc. from 2nd end point).
1	65.5	87.5	65.7	0.7967
2	67.5	90.0	67.5	0.8203

10 cc. of the solution used were found to contain 0.8059 g. Cd.

It is to be noticed from these results and from the figure that the minimum in conductance is reached when just three-fourths of the quantity of barium hydroxide necessary to completely change the sulfate to the hydroxide is added. Then the conductance remains practically constant until an equivalent quantity of barium hydroxide is added; then further addition of barium hydroxide causes it to rise rapidly. A simple explanation of this is that an oxysulfate is formed having the composition $CdSO_4.3Cd(OH)_2$. This salt is difficultly soluble, and, for this reason, the conductance of the solution is low corresponding to the point a. Along the line ab this is gradually being changed to the hydroxide and at b all the sulfate of cadmium has been converted to the hydroxide. Along bc

[1] Wogrinz, *Chem. Ztg.,* **37,** 869 (1913).

an excess of barium hydroxide is be᷍ ᷍᷍ added and the conductance increases. A basic, difficultly soluble hydroxide of cadmium of the composition $CdSO_4.Cd(OH)_2$ was reported by Kühn.[1] This was obtained in triclinic needles by boiling a solution of cadmium sulfate with one-third of an equivalent of potassium hydroxide. No mention has been made of a compound of the composition $CdSO_4.3Cd(OH)_2$. Although the above titration would indicate the existence of this compound, a thorough investigation of equilibria in the system $CdO–CdSO_4$- H_2O would be necessary before definite proof would be obtained. The author wishes to express his thanks to Mr. Harry Beckerman for some of the first titrations of magnesium sulfate and copper sulfate.

Summary.

1. The use of a barium hydroxide solution has been suggested for the determination of metals in sulfate solutions by the conductance method.

2. A suitable apparatus has been constructed for carrying out such titrations in an atmosphere free from carbon dioxide.

3. The method as outlined in this paper has proved to be sound for the determination of magnesium in magnesium sulfate; also, for the determination of magnesium in a solution containing magnesium sulfate. calcium sulfate and sulfuric acid; and finally, an accurate and rapid method has been suggested and tested for the determination of magnesium in dolomite.

4. Copper sulfate, nickel sulfate, and cobalt sulfate can also be titrated by this method.

5. Titration of cadmium sulfate indicates the formation of an oxysulfate of the composition $CdSO_4.3Cd(OH)_2$.

PHILADELPHIA, PA.

THE INTERFERENCE OF THIOCYANATES, FERROCYANIDES AND FERRICYANIDES IN THE DETECTION OF IODIDES WITH PALLADIUM.

BY LOUIS J. CURTMAN AND BEN R. HARRIS.

In a recent paper of the authors[2] attention was called to the observations made by Kern[3] that thiocyanates, ferrocyanides and ferricyanides interfere with the precipitation of iodides as palladium iodide. Since Kern does not, however, supply detailed data to show the nature and extent of the several interferences, it was thought worth while to carry out the experiments recorded below for the purpose of furnishing such information.

[1] Ber., 436 (1847–48).

[2] THIS JOURNAL, 38, 2622 (1916).

[3] Chem. News, 32, 242 (1875); 33, 184 (1876).