The author takes this opportunity to thank Professor J. N. Brönsted for facilities placed at his disposal and for his constant advice and encouragement during the course of the work. It is also a pleasure to thank Mr. E. Güntelberg, also of this Laboratory, for discussions of the subject matter.

Summary

1. The activity coefficients of several slightly soluble complex cobalt-ammine salts of the simpler valence types have been determined in pure methyl alcohol by the solubility method. These data have been utilized to test the validity of the simple Debye and Hückel equations.

2. The important conclusion to be drawn is that in sufficiently dilute methyl alcohol solution and using saturating and solvent salts of the simpler valence types, the general ideal equations of Debye and Hückel are obeyed. It seems probable that the range of applicability of the theory will depend also upon the solute used.

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DIFFERENTIAL POTENTIOMETRIC TITRATION. III. AN IMPROVED APPARATUS AND ITS APPLICATION TO PRECISION MEASUREMENTS

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Received November 8, 1928 Published April 5, 1929

Introduction

Since the first paper on this subject by MacInnes and Jones[1] several articles have appeared[2] which contain criticisms of the method or offer suggestions as to changes in the apparatus. An objection to the original arrangement has been that the electrode and shield as used by MacInnes and Jones is complicated and difficult to construct. There are, we have found, additional disadvantages. In the first place, as originally designed

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[1] (a) MacInnes and Jones, This Journal, **48**, 2831 (1926); (b) MacInnes, *Z. physik. Chem.*, (Cohen-Festband), 217 (1927).

[2] (a) W. A. Roth, *Z. Electrochem.*, **33**, 127 (1927); (b) Rabinowitch and Kargin, *ibid.*, **34**, 311 (1928); (c) Hall, Jensen and Baeckström, This Journal, **50**, 2217 (1928). In two recent papers Erich Müller [(d) *Z. physik. Chem.*, **135**, 102 (1928); (e) *Z. angew. Chem.*, **41**, 1153 (1928)] claims first publication of the idea of a retarded electrode and, by implication at least, of the method of differential titration. As evidence he refers to a paper [(f) *Z. Electrochem.*, **31**, 323 (1928)] in which data on pairs of bimetallic titrations are given. In one of each pair one electrode was wrapped with asbestos, thus hindering diffusion. We consider Müller's claim to priority on this evidence as rather fantastic. The first differential titrations were performed by Cox, This Journal, **47**, 2138 (1925).

it is difficult to make a shield in which the retained solution will not be disturbed by vigorous stirring. Also quite a number of up and down movements of the cap shielding the retarded electrode are necessary, after a reading, to make sure that the concentration of the solution around the two electrodes is the same. This has the effect of slowing up a determination. A still more serious disadvantage is that the sheltered electrode is permanently attached to the apparatus with the result that it cannot be changed if "poisoned," or if it is necessary to change the type of electrode used.

The New Apparatus

In order to overcome these defects we have designed and tested the differential apparatus shown in Fig. 1. The retarded electrode E is surrounded by a tube A having a capillary outlet C at the bottom. Solution from the beaker is circulated over the electrode by means of a simple gas lift L operated by a stream of gas passing through the tube G. By stopping the gas stream the portion of the solution in the tube A is isolated from the bulk of the solution, and does not react when the titrating solution is added from the buret B. On restarting the gas stream the solution in A is soon mixed with that in the beaker and the composition of the solution in this tube is made uniform with the bulk of the solution. The construction of the gas lift pump is easily within the powers of the amateur glass blower. The small hole H prevents the solution from running over the top of Tube A in case the gas stream is too rapid. The capillary C may be quite fine, but should not be small enough to be readily clogged. An advantage of this arrangement is that the electrodes E and E′ can be of any convenient form, are not attached to the apparatus, and can be changed, even, if necessary, in the course of a titration. The two electrodes may be fastened together using a small separator, and can then be placed astraddle the tube A.

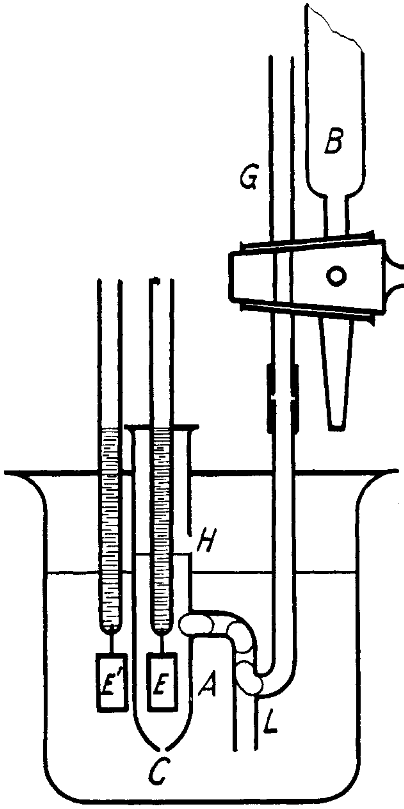

Fig. 1.

An additional convenience, but not altogether necessary for the operation of the apparatus, is the type of buret stopcock S as shown in Fig. 1. This stopcock is arranged so as to regulate the gas stream as well as the titration fluid. As shown the buret is closed and the flowing of the gas stream is producing circulation through the tube A. If, however, the stopcock is turned through a small angle the gas stream is turned off, thus isolating the solution in A. On turning still further the titrating fluid runs out of the buret. If the stopcock is turned back just enough to stop the flow of titrating fluid, the gas stream will not start and a reading of the potential between the electrodes E and E′ may be made. A short turn further causes the gas to flow again and renews the circulation.

Since this circulation soon produces uniformity in concentration throughout the apparatus the potential difference between the electrodes E and E′ should rapidly reach zero. If the electrodes are well adapted to the titration in hand this is found to be the case, except in the immediate region of the end of the titration where a short delay in attaining zero difference may be observed. We have found that observations of the speeds with which the zero is reached are of greatest use in determining the relative advantages for a particular titration of electrodes of different designs.

Titrations can be much more rapidly carried out if the operator does not have to set a potentiometer for each reading. The potential can be read directly in deflections of a galvanometer without polarizing the electrodes by means of one of the various forms of apparatus involving radio tubes. Arrangements for carrying out titrations in this manner have been described by Goode,[3] Treadwell[4] and others. A difficulty with most arrangements of this kind is that the zero is constantly shifting due to the sensitiveness of the radio tubes to slight changes in the current used for heating the filament. We have, however, found that the amplifier for ionization currents designed by Wynn-Williams[5] largely overcomes this difficulty and has far more than the necessary sensitivity for our measurements. Some measurements were also carried out with a potentiometer in the usual way.

The Combined Direct and Differential Procedure

An unexpected advantage of the apparatus shown in Fig. 1 is that the tube A can serve as a temporary reservoir for a small portion of the solution while a rough idea of the end-point is being obtained. To find this preliminary end-point the gas stream is stopped and the titrating solution is added until a large potential difference is found between the electrodes E and E′. This amounts to making a preliminary non-differential titration in the manner described by Müller.[2d] The potential during the titration, for instance, of an acid by a base follows a course like that shown by the dotted line O–x–a in Fig. 2. Now if the titration has not been carried too far beyond the point of inflection x of this curve and the solution has not become too basic it can be brought back to the acid side of the end-point by starting the gas stream. The material in the tube A will

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[3] Goode, THIS JOURNAL, **44**, 26 (1922).

[4] Treadwell, *Helv. Chim. Acta*, **8**, 89 (1925).

[5] Wynn-Williams, *Proc. Camb. Phil. Soc.*, **23**, 811 (1927); *Phil. Mag.*, **6**, 325 (1928).

then mix with the bulk of the solution and the difference between the two electrodes will return to zero. The exact end-point can then be found by the differential method as described above. At the final end-point the potential goes through a sharp maximum, as shown by the typical curve b–c–d. This procedure unites the advantages of the direct and differential methods, since the great bulk of the solution can be added rapidly and the precision and convenience of the newer method are retained. Ordinary titrations carried out by this method take very little more time than titrations involving the usual indicators, the limiting factor being the rapidity with which the electrodes respond to changes in concentration.

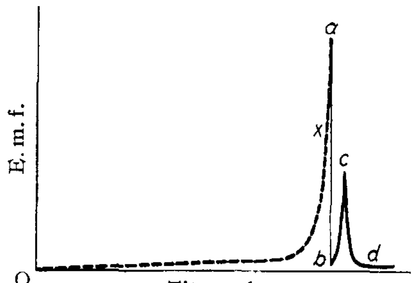

Fig. 2.

The Method Adapted to Precision Measurements

The main object of this investigation was, however, to continue the study commenced by MacInnes[1b] of the differential method as a means of making titrations of high precision. In such measurements the solution to be titrated was accurately weighed out into the beaker from a weight buret. With the gas stream stopped the titrating fluid was run from another weight buret until a point corresponding to a of Fig. 2 was attained. The titration was then continued by means of the differential procedure using, in the buret B of Fig. 1, the titrating fluid diluted in a known ratio, say 1 to 10 or 1 to 20. The success and accuracy of this procedure can best be judged by the results from the two different types of titrations outlined below.

The Titration of Ferrous Sulfate with Potassium Dichromate.— In a previous paper[1b] a failure was reported in the attempt to get accurate titrations of solutions containing ferrous ions, using the earlier differential technique, although the method yielded results of high accuracy for iodimetry and for the reaction between oxalic acid and potassium permanganate. The difficulty was probably due to an oxidation, catalyzed by the platinum electrodes, of the ferrous ions by atmospheric oxygen. We have, however, obtained excellent results by carrying out the titrations in an atmosphere of carbon dioxide. To this end a stream of that gas operated the lift pump and another stream bubbled through the solution to be titrated. A tall beaker was used in order to have a layer of the heavy gas between the solution and the air. The solution titrated was approximately 0.1 N ferrous ammonium sulfate. This was kept strongly acidified in an atmosphere of carbon dioxide during the measurements, and the volume of the solution drawn out of the container was replaced by that gas which was not, however, specially purified. The electrodes E and E′ were of smooth platinum gauze. Sixty to eighty grams of the acidified solution was weighed out into the beaker and 0.1 *N* potassium dichromate was added from a weight buret until the point a of Fig. 2 was obtained. The gas lift was then started and the titration continued with 0.01 *N* potassium dichromate, using increments of 0.1 cc., each of which corresponds to about 0.01%. However, the curve b–c–d is, in this case, extraordinarily sharp and definite, so that the true maximum could readily be interpolated to 0.002 or 0.004%. The data from a series of titrations are given in Table I, which is mostly self-explanatory. The figures in Col. 5 are the corrections to the weight of potassium dichromate solutions obtained from readings of the volumetric buret. The figures in Col. 6 show that there is a gradual increase in the ratio of the weight of the iron solution to the corrected weight of the dichromate solution. However, if these ratios are plotted against the times at which the individual titrations were carried out, a remarkably straight line is obtained. This result would follow if a slow oxidation of the ferrous sulfate solution occurred under the conditions of our experiments.

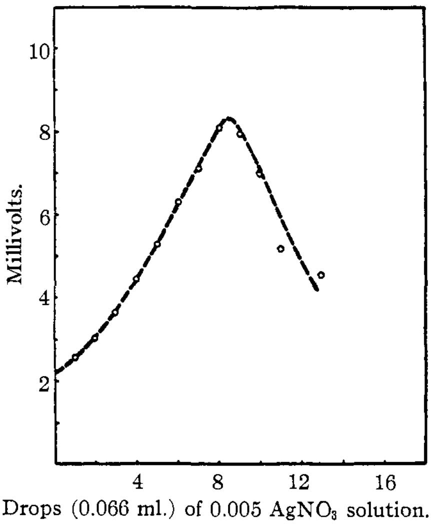

Fig. 3.

TABLE I

TITRATION OF FERROUS SULFATE BY POTASSIUM DICHROMATE

Expt.	Time, hours	Weight of ferrous soln., g.	Weight of $K_2Cr_2O_7$, g.	Corr. to wt. of (4)	Ratio, wt. Fe/$K_2Cr_2O_7$	Ratio at zero, time
1	0	86.064	76.284	0.067	1.12722	1.1272_2
2	26	62.070	54.694	.266	1.12937	1.1270_2
3	30	63.081	55.673	.115	1.12991	1.1271_9
4	31.5	66.429	58.740	.048	1.12998	1.1271_2
5	122	60.500	53.115	.044	1.13810	1.1270_3
6	123.5	65.119	57.180	.031	1.13822	1.1270_2
7	126	76.718	67.331	.051	1.13855	1.1271_2

An idea of the accuracy of the measurements can be obtained by correcting all the ratios to zero time by means of the slope of the line just described. The ratios thus corrected, given in Col. 7 of the table, show a maximum variation of 0.02%. Apparently no rapid reaction with the oxygen of the air took place during a determination, as was found in the earlier experiments.

The Titration of Chloride Solutions with Silver Nitrate.—We have, however, been more interested in developing a rapid, convenient method for titrating chlorides as the necessity for this analysis occurs frequently in our work. Lange and Schwartz[6] describe, in a most excellent paper from which we have obtained many useful suggestions, a research in which they carried out direct electrometric titrations the results of which showed mean variations of only 0.003%. To get this precision required, however, elaborate precautions to prevent diffusion of chloride from the calomel half cell, and of the solution to be titrated into the salt bridge. They found it necessary to use an opposing flow of chloride-free ammonium nitrate solution to overcome the effects of these diffusions.

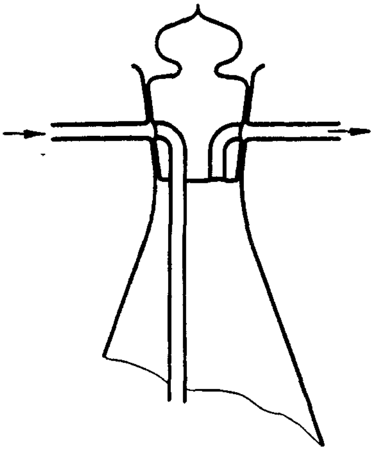

Fig. 4.

The procedure in our titrations followed that already described for the ferrous sulfate solutions with necessary changes to be outlined below. The solution to be titrated was an accurately prepared tenth (weight) normal potassium chloride solution made from the fused sodium-free salt. The titrating solution was approximately 0.1 N silver nitrate. The last part of the titrations was carried out with this solution diluted in the ratio 1 to 20. Following the suggestions of the authors just mentioned the titration was made with the beaker immersed in an ice-bath, and the solution in it was kept down to the smallest possible volume. Some of the electrodes used in this titration were made by coating a platinum wire with a paste of silver oxide and heating,[7] and with others the platinum was silver plated. The latter form of electrode is apparently the better for this purpose. To prevent slowing up of the electrode reaction due to an adherent coating of precipitated silver chloride, the upper part of the electrodes was given a vigorous tapping from the hammer of an electric bell. This tapping was also found necessary to keep the gas lift pump from clogging by the precipitated silver chloride. The entry tube of the solution to the gas lift was also given a slight constriction for the same reason. In these titrations a potentiometer was used instead of the Wynn-Williams bridge. A typical series of readings around an end-point are plotted in Fig. 3, indicating the magnitudes of the potentials and the definiteness of the curve.

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[6] Lange and Schwartz, *Z. Electrochem.*, **32**, 240 (1926).

[7] Lewis, THIS JOURNAL, **28**, 166 (1906).

The solutions were kept in two-liter Erlenmeyer flasks the necks of which were arranged as shown in Fig. 4. These flasks are particularly useful if it is desired to control the atmosphere above a solution. If the gas enters in the direction of the arrow it will bubble through the solution and eventually displace the air originally in the flask. To transfer the solution to another container the stopper is given a half turn. A flow of the gas in the same direction as before will then force the solution out of the flask. A quarter turn of the stopper will prevent the flow of either gas or solution. In the present work the air used to displace the solution was first bubbled through a solution of the same composition as that in the flask.

(a) **The Titration of Potassium Chloride Solution.**—The results of a series of titrations are given in Table II, with the ratios of the weights of the potassium chloride and silver nitrate solutions in the last column.

TABLE II

THE TITRATION OF 0.1 *N* POTASSIUM CHLORIDE WITH 0.1 *N* SILVER NITRATE

No.	Wt. KCl soln., g.	Wt. $AgNO_3$ soln., g.	Corr. to $AgNO_3$ soln.	Ratio $\frac{\text{wt. KCl soln.}}{\text{wt. AgNO}_3\text{ soln.}}$
1	38.858	39.441	0.030	0.98447
2	31.399	31.807	.088	.98445
3	39.875	40.359	.142	.98455
4a	25.589	25.970	.022	.98449
4b	25.639	25.970	.069	.98464
5	38.5304	39.0203	.1138	.98458

Of these determinations, that numbered 4b was made by adding more potassium chloride solution to the beaker and then going once more through the end-point, after the determination 4a had been made. Determination 5 was made with a separately prepared potassium chloride solution. The average of the last four figures was used in the computations which follow. The mean deviation (0.003%) is the same as that of Lange and Schwartz's measurements.

(b) **The Analysis of Constant-Boiling Hydrochloric Acid.**—Since we have, in this Laboratory, made much use of constant-boiling hydrochloric acid as a source of acid of known strength, it seemed desirable to determine whether the acid as we were preparing it had the strength assigned to it by the research of Foulk and Hollingsworth.[8] We have repeatedly proved the reproducibility of the concentration of successive distillations of the acid by means of conductance measurements. These showed that variations are not greater than 0.01%. The still, however, differs from that of the authors named in that it has a greater capacity (2 liters) and a larger condenser tube (1 cm. internal diameter). Also the rate of distillation was somewhat greater (7 cc. per min.) than they

[8] Foulk and Hollingsworth, THIS JOURNAL, **45**, 1220 (1923).

used. The rate per unit of surface of acid is, however, within their recommended range.

Titrations of the middle fraction of the acid were carried out using the technique described in the last section, except that the acid had first to be neutralized. For this purpose a very nearly chloride-free alkali was prepared by recrystallizing sodium hydroxide twice from water. The resulting material, when neutralized, gave a barely perceptible turbidity with silver nitrate, certainly too little to affect the result. For analysis the constant-boiling acid was first diluted to 0.1 *N* and weighed portions of the dilute solution were titrated with the silver nitrate solution, standardization of which, against fused potassium chloride, is decribed in the previous section. The results of two titrations are given in Table III.

TABLE III

ANALYSIS OF CONSTANT-BOILING HYDROCHLORIC ACID

No.	Wt. const.-boiling acid, g.	Wt. $AgNO_3$ soln., g.	Corr.	% HCl 768.2 mm.	% HCl Corr. to 750 mm.
1	0.74385	41.8985	0.0823	20.2051	20.249
2	.71066	40.0368	.0676	20.2034	20.247
				Av.	20.248
				From Foulk and Hollingsworth	20.245

The column headed "weight of constant-boiling acid" is computed from the weight of the 0.1 *N* solution used by the accurately known factor of dilution. The last two columns contain the percentage of hydrogen chloride in the constant-boiling acid at 768 mm. and at 750 mm., the latter being obtained from the former by means of the factor (−0.0024%/mm.) used by Foulk and Hollingsworth. The usual corrections were applied to our barometer readings. The average of our determinations agrees remarkably closely with the value 20.245 given by those authors, whose measurements, however, ranged 0.004% above and below this. Foulk and Hollingsworth analyzed their solutions gravimetrically using the precautions, including the use of a nephelometer, developed at Harvard for atomic weight determinations. The outcome of this comparison of the gravimetric method with the differential potentiometric method is gratifying.

Conclusions and Comment

The differential potentiometric method using the improved apparatus has thus been shown to be suitable for rapid titrations of ordinary accuracy, and also for titrations of high precision. We feel sure that, using the technique already developed, still greater accuracy can readily be obtained.

Unless the counter-current method of Lange and Schwartz is used to overcome diffusion or convection of solution into the salt bridge, accuracy such as we have demonstrated cannot be obtained by the direct potentiometric method. Even with that device the solution is continually gaining in concentration of the solution used for the salt bridge. It is a desirable feature of the differential procedure that it introduces no extraneous material into the solution to be titrated. Another paper from this Laboratory will deal with the method as modified for the use of hydrogen electrodes.

From published comment[2b] it appears that there is uncertainty in the minds of some readers concerning the error involved in retaining a small proportion of the solution in the space around the retarded electrode, as, for instance, in Tube A of Fig. 1. A short consideration will show that the error E cannot be greater than

$$\frac{\Delta T}{T} \times \frac{v}{V} > E$$

in which ΔT is the last increment of titrating solution, T is the total volume of this solution used and v and V are, respectively, the volume retained around the retarded electrode and the total volume. This is true because the final portion of titrating fluid reacts with all of the solution except a small proportion given by v/V. However, this small proportion of solution is only the fraction $\Delta T/T$ removed from the end-point. Thus if 50 ml. of solution are used with 0.1-ml. increments, and the tube A holds 4 ml. out of the 200 ml. in the beaker, the error will be

$$\frac{0.1}{50} \times \frac{4}{200} \times 100 = 0.004\%$$

Since such measurements are ordinarily made to one drop of solution, or about 0.1%, this error is negligible. In our work with weight burets the ratio $\Delta T/T$ is around 1/10,000 and the corresponding error is about 0.0002%, which is, of course, well within the experimental error.

Summary

An improved apparatus for differential potentiometric titration, involving a simple gas lift pump, is described. The usefulness of the method in analyses of high precision is shown in the titration of ferrous sulfate with potassium dichromate and of potassium chloride with silver nitrate. An analysis of constant-boiling hydrochloric acid, which agrees closely with the results of Foulk and Hollingsworth, has also been carried out.

NEW YORK, N. Y.