

CCCCXXXIII.—*A Simple Method of Conductometric Titration.*

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THE conductometric method of analysis offers no advantages over ordinary chemical methods in many cases, but, on the other hand, it has great possibilities in cases involving coloured or turbid solutions, the neutralisation of weak acids with weak bases, or the titration of extremely dilute solutions.

Duboux (*Chem.-Ztg.*, 1913, **37**, 879), Duboux and Dutoit (*Compt. rend.*, 1908, **147**, 134), Dutoit (*Bull. Soc. chim.*, 1910, **7**, 1; *J. Chim. physique*, 1910, **8**, 12, 27), and Kolthoff (*Z. anorg. Chem.*, 1920, **111**, 1, 28, 52; 1921, **112**, 155, 172, 187, 196; *Z. anal. Chem.*, 1922, **61**, 171, 229, 332, 369, 433; 1923, **62**, 1, 97, 161, 209) have worked out many neutralisation and precipitation titrations, and their work, together with that of Thiel and Roemer (*Z. anorg. Chem.*, 1908, **63**, 711), represents the most important contributions to the subject.

The fact that the method has not attained wider application is doubtless due to the troublesome nature of the series of conductivity determinations necessary during the course of the titration. Improvements in experimental technique have been made by Callan and Horobin (*J. Soc. Chem. Ind.*, 1928, **47**, 329T), and Jander and Pfundt (*Z. anorg. Chem.*, 1926, **153**, 219) have already simplified the process considerably. The present method simplifies the procedure so that a titration and the necessary graph can be completed in 15—20 minutes, and at the same time gives results which are of the same order of accuracy as those obtainable by the conductometric method.

E X P E R I M E N T A L.

Apparatus.—Instead of the ordinary Wheatstone bridge, the Dionic Water Tester of Evershed and Vignoles is used. This instrument contains a continuous-current dynamo driven by the turning of a handle: it is fitted with a constant-speed clutch which slips when the dynamo handle turns above a certain speed (about 100 r.p.m.). With the aid of this device, the voltage is maintained constant at 100 ± 0.25 volts. The instrument contains three fixed resistances, the cell resistance being the fourth: the magnitude of the last determines the current which flows through the current meter, which is graduated to read in terms of conductivity—the one made for the author has a range from 0 to 200,000 reciprocal megohms. A current actually flows through the cell during a determination; its magnitude is not greater than 4 milliamps. and it is not applied for more than 2—3 secs.

With this apparatus and a suitable cell, the measurement of a conductivity merely consists in turning the handle until the clutch begins to slip and then reading the position of the pointer on the scale.

Since it is desirable to cover the most commonly occurring cases in ordinary practice, the titration cell has been designed to deal with 25 c.c. of an $N/10$ -solution.

The cell is a circular glass trough 20 cm. in diameter and 12 cm. high; on the top of this rests a piece of ebonite 23 cm. long, 4.5 cm. wide, and 1 cm. thick: it is prevented from slipping by two small screws projecting 1.3 cm. below and just inside the edges of the trough. The electrodes are of bright platinum foil, 0.7×2.0 cm., and are sealed into glass tubes 16 cm. long. These tubes fit tightly through holes 17.5 cm. apart in the ebonite, and are fixed by means of sealing wax. The lower edges of the electrodes are near the bottom of the cell. A glass stirrer in the shape of an L with the horizontal part 5 cm. long, is placed at one side so that it just clears the side of the glass and is equidistant from the electrodes; the stirrer is turned by a small motor at a speed of about 150 r.p.m.

Method.—20 or 25 C.c. of the solution are measured into the glass vessel, and a litre of distilled water is added, completely covering the electrodes; the stirrer is started, and the first reading taken. The titrating liquid in the burette is adjusted exactly to the zero and any adhering drop is removed from the tip. This liquid is added in successive exact amounts of 4 c.c.; readings may be taken at once without stopping the stirrer. When sufficient observations have been made, meter readings are plotted as ordinates against volumes of reagent added as abscissæ. The intersection of the two lines so obtained gives the end point of the titration in c.c.

Example.—24.99 C.c. of 0.10205*N*-hydrochloric acid were measured out, and 1100 c.c. of distilled water added; the solution was then titrated with 0.0966*N*-sodium hydroxide with the following results:

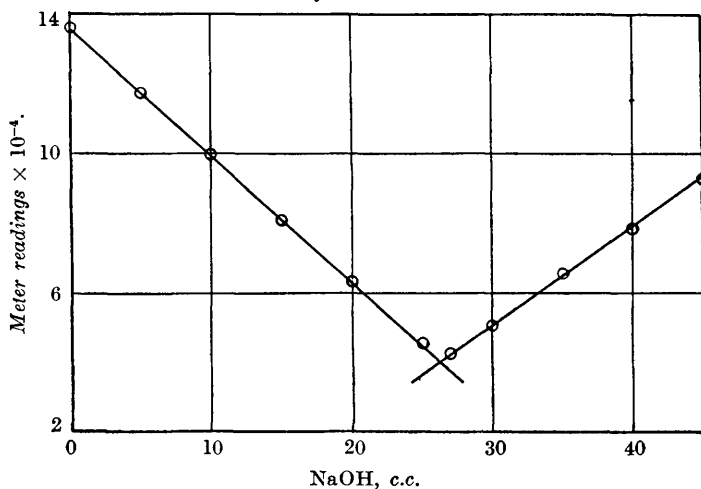
NaOH, c.c.	Meter reading.	NaOH, c.c.	Meter reading.	NaOH, c.c.	Meter reading.
0	136,000	20	63,500	35	66,000
5	117,500	25	46,000	40	79,000
10	99,500	27	43,000	45	93,000
15	81,000	30	51,000		

These data are plotted in Fig. 1 and give the end point as 26.36 c.c., whence the concentration of the acid is 0.1019*N*.

The method has been applied in a number of cases with the results given below. The mean error E is calculated from the mean of four determinations, and the average deviation from the mean is denoted by Δ .

Table I compares the true concentration of hydrochloric acid with the results obtained on titration with various alkalis. With sodium hydroxide or carbonate separately the error is not greater than the limit of the method, *viz.*, about 0.25%. With their mixtures, however, a larger error is obtained, which increases with the amount of carbonate. This error is caused by regarding the curves as

FIG. 1.
Titration of HCl with NaOH.



straight lines, whereas in reality, there is a flat portion of the curve near the end point which tends to escape notice when the amount of carbonate is small.

TABLE I.
Titration of hydrochloric acid with alkali.

Conc. of alkali, <i>N</i> .	Conc. of acid, <i>N</i> ,		Δ , %.	<i>E</i> , %.
	actual.	found.		
NaOH = 0.0966	0.1021	0.1022	± 0.1	+0.1
NaOH = 0.0966 } Total	0.1021	0.1027	± 0.1	+0.6
Na ₂ CO ₃ = 0.0050 / 0.1016				
NaOH = 0.0966 } Total	0.1021	0.1045	± 0.1	+2.4
Na ₂ CO ₃ = 0.0693 / 0.1659				
Na ₂ CO ₃ = 0.1103	0.1018	0.1015	± 0.4	-0.3
NaHCO ₃ = 0.1011	0.1018	0.1010	± 0.2	-0.8

Table II summarises the results for the reverse titration, *i.e.*, that of the same alkalis with hydrochloric acid. With sodium hydroxide, the alkali concentration found is low: this result is found to be general (see p. 3146): it is probably due to the presence of a little carbonate in the caustic alkali. The second example shows the

TABLE II.

Titration of alkali with N/10-hydrochloric acid.

Conc. of alkali, N,				
actual.		found.	Δ , %.	E , %.
NaOH	= 0.0966	0.0956	± 0.25	-1.0
NaOH	= 0.0966	0.0992	± 0.1	-2.4
Na ₂ CO ₃	= 0.0050 } Total			
NaOH	= 0.0966	0.1663	± 0.2	+0.25
Na ₂ CO ₃	= 0.0693 } Total			
Na ₂ CO ₃	= 0.1103	0.1109	± 0.1	+0.6
NaHCO ₃	= 0.1011	0.1018	± 0.2	+0.1

increase in this error with an increase in the amount of carbonate. The third case shows a smaller error because now the amount of carbonate is large enough to enable its individual curve to be plotted separately from that relating to the neutralisation of the caustic soda. The high result obtained with sodium carbonate alone may be connected with the effect of dissolved carbonic acid set free during the titration.

Table III (a) shows the results of titrating with sodium hydroxide a series of monobasic acids of gradually decreasing strength. The results are seen to be accurate to one part in 400 parts in the case of the first five acids: since only 5% of the common monobasic acids are weaker than acetic acid, this result is very satisfactory. With the remaining acids errors up to 2% are obtained except in the case of phenol, where the error is so large that the method is inapplicable.

TABLE III.

(a) *Monobasic acids titrated with N/10-sodium hydroxide.*(b) *N/10-Sodium hydroxide titrated with monobasic acids.*

Acid.	K.	Conc. of acid, N/10,			Δ , %.		E , %.	
		actual.	found (a).	found (b).	(a).	(b).	(a).	(b).
Trichloroacetic.....	2 $\times 10^{-1}$	0.966	0.967	0.979	± 0.1	± 0.25	+0.1	+1.3
Dichloroacetic	5.1 $\times 10^{-1}$	1.136	1.134	1.157	± 0.3	± 0.5	-0.2	+2.1
Monochloroacetic	1.55 $\times 10^{-1}$	0.736	0.734	0.755	± 0.8	± 0.4	-0.3	+2.5
Formic	2.14 $\times 10^{-2}$	0.997	0.998	1.030	± 0.5	± 1.0	+0.1	+3.3
Acetic	1.86 $\times 10^{-2}$	1.004	1.005	1.061	± 0.3	± 0.4	+0.05	+5.6
Trichlorophenol *	1 $\times 10^{-2}$	0.986	1.006	1.033	± 0.6	± 0.5	+2	+4.7
<i>p</i> -Nitrophenol	7 $\times 10^{-3}$	0.995	1.015	1.041	± 0.5	± 0.8	+2	+4.6
<i>m</i> -"	5.3 $\times 10^{-3}$	0.993	0.996	1.053	± 0.3	± 1.25	+0.3	+6.0
Phenol	1.3 $\times 10^{-10}$	0.960	0.81	0.986	?	+0.6	-15	+2.4

* Trichlorophenol solution...

Table III (b) shows the converse titration. It exhibits the general error (positive in terms of the acid concentration) which is considered to be due to the presence of carbonate ion in the alkali. This error increases as the strength of the titrating acid decreases, from +1% with the strongest acid to +5% with acetic acid, whereupon it becomes constant. Phenol may be approximately determined by this titration.

TABLE IV.
Titration of dibasic acids with alkali.

Acid.	pK_1 .	pK_2 .	ΔpK .	Acid conc., $N/10 \times$.	Average error, %.			
					Forward titration.		Reverse titration.	
					1st break.	2nd break.	1st break.	2nd break.
Sulphuric	0.4	1.52	1.12	0.796	—	0.0	+0.8	—
Dibromosuccinic* ...	1.47	2.80	1.33	0.749 ₅	— 2.4	—0.6	+9.1	—
Oxalic	1.40	4.53	3.13	0.735	+ 0.3	+0.9	+5.9	+11.2
Maleic	1.82	6.58	4.76	0.746	— 3.9	+0.5	+6.1	— 0.7
Selenious	2.52	7.22	4.70	0.828	— 3.3	—3.3	+5.5	— 1.1
Malonic	2.8	5.68	2.88	0.749	—10.8	+0.3	+6.4	— 0.1
Tartaric	3.01	4.16	1.15	0.748	—18	0.0	+2.5	+17.6
Fumaric*	3.00	4.52	1.52	0.750	—18	—0.8	+3.8	+ 7.9
Malic	3.4	5.05	1.65	0.748	—28	+0.5	+5.5	— 5.7
Succinic	4.18	5.55	1.37	0.750	—	—0.3	+3.5	—
Adipic	4.6	?	?	0.748	—	—0.9	+5.1	—
Camphoric	4.65	4.85	0.20	0.750	—	—2.5	+3.7	—
Telluric	6.21	10.4	4.2	0.375†	+ 2.5	—	—	+ 6.7
Salicylic	2.98	13.0	10.0	0.375†	— 0.9	—	—	+ 2.9

* In dilute alcoholic solution.

† Concentrations in terms of $M/10$.

Table IV shows the titration of dibasic acids with sodium hydroxide, and the reverse. Since these acids can be considered to be similar to mixtures of two monobasic acids of different strengths but in equivalent amounts, the results show what may be expected with mixtures of two monobasic acids of dissociation constants K_1 and K_2 ($pK = -\log K$ and $\Delta pK = pK_2 - pK_1$).

In the forward titration (acid with alkali) the important factor is the value of the second and smaller dissociation constant: this conditions the accuracy with which the second break in the curve can be found, the break corresponding to the formation of the normal salt. The table shows that when $pK_2 \gg 6$, an accuracy of one part in 200 parts may be expected. The position of the first break depends both on the value of pK_1 , and on that of ΔpK . It approximates to the correct position if $\Delta pK \ll 3$ and if $pK_1 > 2$; this favourable combination is uncommon in practice. When the second acid is extremely weak, as with telluric acid, the first break only is obtained, and the acid titrates like a monobasic acid. Similarly, when pK_2 is small, as with sulphuric acid, only the second break can be observed.

In the titrations of alkali with the acids, the first break is generally quite definite and is subject to the usual errors previously noticed in the titration with monobasic acids, the magnitude of the error being conditioned by the value of pK_2 . In general, the second point, corresponding to the formation of the acid salt, is apparent, but the angle of the break is so obtuse that the point cannot be fixed quantitatively.