CCXCIV.—*A New Method of (Absolute) Potentiometric Titration.*

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THE following is an account of a new method of titration which combines great simplicity with the highest precision and with other special advantages. No potentiometer or standard cell is required, no normal electrode or reference "half-cell" and no mechanical stirrer, neither is any sort of liquid junction involved. Small quantities of solution can be rapidly titrated in an ordinary flask, with the aid only of a rheostat or resistance, a key, and a pointer-galvanometer. Yet the sensitivity and precision are the highest attainable by electrometric methods, and, in addition to its convenience for ordinary titrations, the method is especially suited for the titration of (*a*) very dilute solutions and (*b*) very small volumes (micro-titration).

This paper deals with the titration of the following ions: $H^{\bullet}$, $Ag^{\bullet}$, OH', Cl', Br', I'. The underlying principles will first be discussed.

1. The fundamental idea consists in the application to electrometric titration of the long-known principle of the Helmholtz cell, or cell without liquid junction. A familiar example of this type of cell is that consisting of a hydrogen electrode and either a calomel or a silver chloride electrode in one and the same solution of hydrochloric acid. The *E.M.F.* of this cell at the temperature T is given by

$$E = E_0 + 2RT/F \,.\, \log_e C\gamma,$$

where E_0 is a constant and C is the concentration of hydrochloric acid; or, if for the present we ignore the correction factor γ, *i.e.*, the "activity coefficient," and consider a particular temperature, *e.g.*, 16°, we may write

$$E = E_0 + 0{\cdot}1147 \log_{10} C \quad . \quad . \quad . \quad . \quad (1)$$

More generally, if for pure hydrochloric acid we substitute a mixed electrolyte containing hydrogen ions and chlorine ions at different concentrations, C_H and C_{Cl}, then the *E.M.F.* of the cell will be

$$E = E_0 + 0{\cdot}05735 \log (C_H \times C_{Cl}) \quad . \quad . \quad . \quad (2)$$

It is plain, therefore, that if we know E_0 and *one* of the factors C_H or C_{Cl}, we can determine the other by measuring E. This would be an example of what is commonly called a "physical" method of analysis.

Alternatively, we may gradually remove one of the ions from the solution by means of a standard reagent, the *residual* concentration of the ion being, at each stage, indicated by the value of E, until that residual concentration either (*a*) can be neglected or (*b*) (for refined titration) reaches a certain value known to characterise the exact end-point of the titration. For instance, at the end-point in the titration of a chloride against silver, the value of C_{Cl} is equal to the solubility, S_{AgCl}, of silver chloride. The *E.M.F.* at the end-point would therefore be, in accordance with equation (2):

$$E = (E_0 + 0{\cdot}05735 \log S_{AgCl}) + 0{\cdot}05735 \log C_H \quad . \quad . \quad (3)$$

the bracketed expression being a known constant, so that the end-point *E.M.F.* depends on C_H, the acidity of the solution. A rough knowledge of C_H, however, is sufficient to permit high precision in the titration. Thus, even if C_H were estimated at *twice* its true value, the error produced in the end-point would be only $1{\cdot}5 \times 10^{-7}$ g.-equiv. per 10 c.c. of solution, which is only 1·5% in the titration of $N/1000$-solution, so that only when high precision in the most dilute solutions is required, will C_H have to be known more accurately.

Similarly, at the end-point in the titration of a strong acid by a strong base the value of C_H is equal to the acidity, h, of distilled water under the conditions prevailing. (The value of h depends ordinarily on the amount of carbon dioxide in the air and may be between 2×10^{-6} and 3×10^{-6}.) We obtain therefore a formula for the end-point potential of the same type as (3), *viz.*,

$$E = (E_0 + 0{\cdot}05735 \log h) + 0{\cdot}05735 \log C_{Cl} \quad . \quad . \quad (4)$$

so that in this case we need a rough knowledge of C_{Cl}.

It is plain that we have here a means of absolute * potentiometric titration in a single vessel without a liquid junction, and it may be observed that the resistance can thus easily be kept low, so that the method is peculiarly useful for the titration of dilute solutions without the employment of a refined galvanometer. It seems probable that the principle may be widely applicable.

2. *Elimination of the Potentiometer.*—The use of a potentiometer has been implied since we have to determine when the potential between the two electrodes reaches a certain end-point value. The instrument, it is true, need be only of simple pattern, and may be set for the end-point *E.M.F.*, so that the end of the titration is shown in practice by the reversal of the galvanometer deflexion; but we can eliminate the necessity for a potentiometer if we can

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* The end-point is marked by the *E.M.F.* attaining a particular absolute value. This is the case also in the methods of Treadwell and of Müller. In all other nethods, the end-point is marked by the attainment of a maximum value by the differential dE/dx, the rate of change of potential. It can be shown that the intrinsic sensitivity of the " absolute " methods is the higher.

construct a cell that will develop the required end-point *E.M.F.*, which might be done by imitating the composition which the titrated cell should have at the end-point. For instance, for the titration of a chloride, we might take a solution having the same acidity as the titrated solution, and shake it with some well-washed, precipitated silver chloride. A hydrogen electrode and a silver chloride electrode dipping into such a solution should develop the required end-point *E.M.F.* This procedure would bear the same relation to the (alternative) use of the potentiometer as the method of Treadwell bears to that of Müller.

A much simpler and more trustworthy procedure is available, however, for comparison of (1) and (3) shows that they become identical when $C^2 = S_{AgCl} \times C_H$; and it follows that if we take some hydrochloric acid of approximately the concentration C, where

$$C = \sqrt{S_{AgCl} \times C_H} = 0{\cdot}0031\sqrt{C_H} \quad . \quad . \quad . \quad (5)$$

(C_H being, as before, the acidity of the *titrated* solution), then a hydrogen and a silver chloride electrode dipped into this solution will develop the end-point *E.M.F.* This is more trustworthy than the other form of end-point cell because, the concentrations of both ions being considerable, there is less liability to polarisation during the titration. It follows from the relation (5) that, just as C_H need not be accurately known (see p. 2208), so C, the concentration of the hydrochloric acid in the end-point cell, does not require accurate adjustment.

In just the same way, for the titration of a strong acid by a strong base we obtain from (1) and (4) the relation $C^2 = hC_{Cl}$, and adopting $2{\cdot}5 \times 10^{-6}$ as a mean value for h (see p. 2208), we have

$$C = 0{\cdot}0016\sqrt{C_{Cl}} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

as the strength of the hydrochloric acid solution required, in terms of the chloride concentration. (In the total absence of carbon dioxide, the numerical coefficient would be 0·0003.)

3. *The Silver Chloride–Quinhydrone Cell.*—Of late, the hydrogen electrode has been superseded for many purposes by the more convenient " quinhydrone electrode," since Biilmann showed that, for solutions not distinctly alkaline, the presence of a trace of quinhydrone in solution caused a smooth platinum electrode to behave as a reversible hydrogen electrode.

It appeared possible that an exceedingly simple form of the Helmholtz cell might be obtained by merely dipping a smooth platinum electrode and a silver chloride electrode into a solution containing hydrogen ions, chlorine ions, and a little quinhydrone, providing always that the electrodes did not interfere with one another.

In the first experiments, a plain silver wire was used, in the presence of a visible precipitate of silver chloride, but the results were unsatisfactory owing possibly to some slight catalysis of the quinhydrone reaction on the metallic surface. When, however, the silver was coated electrolytically with silver chloride, excellent and quickly reproducible results were obtained.

Many measurements were made with cells containing various proportions and concentrations of the two ions, and the results, substituted in the more exact form of equation (2), *viz.*,

$$E = E_0 + 0{\cdot}05735 \log a_{\mathrm{H}} a_{\mathrm{Cl}} \quad . \quad . \quad . \quad . \quad (7)$$

(a_{H} and a_{Cl} being " corrected concentrations " or activities) gave the mean value 0·4740 for E_0. The measurements covered the whole range of the titrations of both ions, up to and beyond the end-points, leaving no doubt as to the practicability of using this very simple form of cell. In fact, the results were so uniformly good as to prompt an investigation, now in progress, of the suitability of this type of cell as a means of " physical " analysis.

4. *The Silver–Quinhydrone Cell and the Solubility of Silver Chloride.*—It is of interest that, *beyond* the end-point in the chloride titration, we have in effect the rather remarkable one-solution cell, Ag | Ag^+, H^+ (quinhydrone) | Pt, or, if we regard the quinhydrone electrode as a hydrogen electrode, Ag | Ag^+, H^+ | H_2, of which the *E.M.F.* is given by

$$E = E'_0 + RT/F \, . \log a_{\mathrm{Ag}}/a_{\mathrm{H}} \quad . \quad . \quad . \quad . \quad (8)$$

and is thus practically unaffected by the addition of water.

The results in this region were very good and yielded the value 0·1009 for E'_0. Now the activity-product of silver chloride, and hence its true solubility in pure water, S_{AgCl}, is readily obtained from E_0 and E'_0, for

$$-\,2RT/F \, . \log S_{\mathrm{AgCl}} = E_0 + E'_0 = 0{\cdot}5749 \text{ (at } 16^\circ\text{)},$$

whence $S_{\mathrm{AgCl}} = 0{\cdot}97 \times 10^{-5}$ at 16°, with a probable accuracy of $\pm 2\%$.

5. *Final Simplification : Elimination of the End-point Cell.*—It is evident, therefore, that the method of titration outlined in Sections 1 and 2 is fully applicable with the more convenient silver chloride–quinhydrone cell. A final simplification of apparatus and procedure, however, now becomes possible, arising out of the value of E_0, given above.* Substituting 0·4740 for E_0 and $0{\cdot}97 \times 10^{-5}$ for

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* This simplification is *not* available if the hydrogen electrode is used, because of the *negative* value of E_0 in that case.

S_{AgCl} in equation (3), we have, for the end-point potential in the titration of a chloride,

$$E_{Cl} = 0{\cdot}1866 + 0{\cdot}05735 \log C_H \quad . \quad . \quad . \quad . \quad (9)$$

this being the formula required when a potentiometer is used (see Section 12). Now calculation shows that E_{Cl} vanishes when $C_H = 5{\cdot}6 \times 10^{-4}$, *i.e.*, if the acidity of the solution is roughly $N/1800$, the end-point potential will be zero, and we require neither a potentiometer nor a second pair of electrodes to balance it. One pair of electrodes and a galvanometer is then all the physical apparatus required for the titration.

Similarly, for the acid–alkali titration, substituting for E_0 and for h in equation (4), we obtain for the end-point potential

$$E_H = 0{\cdot}153 + 0{\cdot}05735 \log C_{Cl} \quad . \quad . \quad . \quad . \quad (10)$$

which vanishes when $C_{Cl} = 2{\cdot}2 \times 10^{-3}$ (or $N/450$).

6. *The Bromide and the Iodide Cells.*—From similar series of measurements with the corresponding silver bromide (or iodide)–quinhydrone cells, the values 0·6235 and 0·8460, respectively, have been obtained for E_0, and $5{\cdot}6 \times 10^{-7}$ and $6{\cdot}5 \times 10^{-9}$ for the solubilities of the bromide and iodide. Hence we obtain for the end-point potentials :

$$E_{Br} = 0{\cdot}261 + 0{\cdot}05735 \log C_H \quad . \quad . \quad . \quad . \quad (11)$$
$$E_I = 0{\cdot}3725 + 0{\cdot}05735 \log C_H \quad . \quad . \quad . \quad (12)$$

which vanish, respectively, when $C_H = 2{\cdot}8 \times 10^{-5}$ or $3{\cdot}2 \times 10^{-7}$.

When the end-point cells are required in the titration of bromide and iodide, it is convenient still to use the hydrochloric acid cell, of which the *E.M.F.* is

$$E_{HCl} = 0{\cdot}4740 + 0{\cdot}1147 \log C \quad . \quad . \quad . \quad . \quad (13)$$

C being the concentration of the acid. Equating this in turn to E_{Br} and E_I, we obtain for the bromide $C = 0{\cdot}013\sqrt{C_H}$ (14), and for the iodide $C = 0{\cdot}12\sqrt{C_H}$ (15).

Two points must be mentioned with regard to the iodide cells, *viz.*, first, that the acidity must be kept very low—below $N/100$—because at higher concentrations the hydriodic acid reacts with the quinhydrone producing free iodine; and, secondly, that in the immediate neighbourhood of the end-point, equilibrium (and hence a reproducible potential) is only obtained after standing for $\frac{1}{4}$—$\frac{1}{2}$ hour with occasional shaking. Thus when high precision is required the titration of an iodide cannot be very expeditious.

7. "*Corrected Concentrations*" : *Activities.*—For the sake of simplicity, the correction factors or activity coefficients, by which the concentrations are multiplied in the exact forms of the equations

given, have been ignored up to this point. It is, in fact, only when high precision is aimed at, and the most dilute solutions are titrated, that these factors need be considered; in such cases every symbol C, with or without subscript, representing a concentration (but not the symbols h, S_{AgCl}, S_{AgBr}, etc., which already represent activities), is to be multiplied by the appropriate activity coefficient, to make the formulæ exact.

EXPERIMENTAL.

8. *The Electrodes.*—The simpler the form of the electrodes the more easily is the surface layer of solution kept uniform with the rest by shaking.

The platinum electrodes are best free from glass so that they may the more easily be cleaned occasionally in hot sulphuric–chromic acid, and " blanked " by heating to redness for a minute or two in an alcohol flame. A form which has been found effective consists of a strip of thin foil, bent along its length to give a little rigidity, and fixed in a binding screw.

The silver halide electrodes have been made from pieces of stout silver wire about 15 cm. long by coating them, along a length of, say, 5 cm. from one end, with the appropriate halide. The wire is made the anode in the electrolysis of a dilute solution of the sodium or potassium salt, and a current of 2—3 milliamps. per sq. cm. is passed for about an hour. The wire should be turned once or twice to secure an even coating. Several electrodes can be prepared at one time, and they may be preserved in the dark for a week or more in corked tubes full of distilled water. In use, a silver halide electrode is fixed in a binding screw, and mounted in an ordinary clamp, vertically alongside and close to a platinum electrode, so that the pair will easily pass through the neck of a conical flask. We may speak of a " chloride-pair " of electrodes or a bromide- or iodide-pair, according to the nature of the silver halide electrode.

9. *The Reference Ion.*—We have seen that the potentials with which we have to deal in this method depend always on two ions, and the essential principle is that if we know the concentration of one of these ions roughly, we can titrate the other exactly. It will be convenient to speak of the ion of which the concentration must be roughly known as " the reference ion." Thus, in the titrations of the three halides the reference ion is the hydrogen ion, whilst in the titration of hydrogen ions (acids) it might be any of the three halides, but most commonly the chloride. Now in most cases, so long as the solution to be titrated is not weaker than about $N/100$ —the limit is lower in the case of bromide or iodide—*only the order of magnitude of the reference-ion concentration need be known* (see p. 2208). If, however, we are aiming at the highest precision in the

end-point, as in titrating extremely dilute solutions, we may need to know the reference-ion concentration to within a few units %, and a rough titration may be necessary to determine this.

If the reference ion is absent or nearly so, then we can easily introduce it in whatever concentration we require, by adding a little of a standard solution of sodium chloride (for Cl$'$) or of nitric or sulphuric acid (for H$^{\bullet}$).

It should be observed that, strictly speaking, it is the concentration at the end-point that has to be known or adjusted, and when the highest precision is required some allowance must be made for the dilution caused by the volume of reagent to be added; this can easily be done after a rough preliminary titration.

10. *The Method in its Simplest Form.*—The simplest form of procedure is applicable when the reference-ion concentration approximates to (see p. 2212), or can be adjusted roughly to, the values calculated from equations (9)—(12). All the physical apparatus required is a sturdy pointer-galvanometer (which will just detect, say, 10^{-7} amp.) in series with a rheostat, a tapping-key or plug, and one appropriate pair of electrodes, *viz.*, a chloride-pair for the titration of chloride or acid, a bromide- or an iodide-pair for the corresponding halide titrations. The deflexions of the galvanometer should be minimised by means of the rheostat so as to avoid any tendency to polarise the electrodes.

To the solution to be titrated, contained in a conical flask, a trace of quinhydrone is added (not more than 1 mg. per c.c. of solution), and most of it dissolved by gentle shaking. On raising the flask so that the pair of electrodes dips into the liquid, shaking gently, and then depressing the key, a marked deflexion of the galvanometer pointer is obtained with a high resistance in circuit, indicating a high *E.M.F.* (of the order of 0·2—0·3 volt). Some of the standard reagent is now added, and the observation of the *E.M.F.* then repeated, and so on, until eventually the *direction* of the pointer deflexion is reversed, the *E.M.F.* having reached and passed zero. This marks the end of the titration.

The indication is very sharp and sensitive. Thus the change from a deflexion representing an *E.M.F.* of 5 millivolts to the same deflexion in the reverse direction is produced, in 10 c.c. of solution, by the following quantities of reagent:

In titration of acid	3×10^{-8} g.-equiv.
,, ,, ,, chloride (or silver)	1×10^{-7} ,,
,, ,, ,, bromide (or silver)	6×10^{-9} ,,
,, ,, ,, iodide (slowly, see p. 2211) ...	$6{\cdot}5 \times 10^{-11}$,,

11. *The Use of the End-point Cell.*—When the concentration of the reference ion cannot conveniently be adjusted to the appropriate

value given above, it becomes necessary to add to the apparatus *either* a simple potentiometer *or* a second pair of electrodes—a chloride-pair—connected in opposition (platinum to platinum) to the first pair. In the latter case the end-point cell is completed by diluting some roughly standard hydrochloric acid approximately to the concentration C given in equation (5), (6), (14), or (15), dissolving a little quinhydrone in this solution contained in a flask or beaker, and raising the vessel on a support so that the second pair of electrodes dips into the solution. The vessel should be gently shaken occasionally during the titration.

Otherwise the titration proceeds exactly as described in Section 10, the end-point being indicated by the reversal of direction of the galvanometer deflexion, and the sensitivity being of the same order. The end-point cell can be used repeatedly for the same type of titration so long as the reference-ion concentration (C_{Cl} or C_H) in the titrated solutions remains the same.

12. *Alternative Use of a Potentiometer.*—If it is preferred to use a simple form of potentiometer to produce the end-point potential, instead of the end-point cell, it will be convenient, by means of equations (9), (10), (11), and (12), to construct tables after the following manner, giving the end-point potential for various values of the reference-ion concentration.

End-point Potential in Titration of Chloride (or Silver).

Acidity, C_H ...	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
End-pt. *E.M.F.*	0·1866	0·1292	0·0719	0·0145	−0·0428	−0·1002

For intermediate values :

To {multiply divide} C_H by...............	1·25	1·6	2	2·5	3·2
Add to Subtract from} E the value ...	0·0055	0·0117	0·0173	0·0228	0·0290

These two tables, in conjunction with ordinary proportional interpolation, cover all probable values of C_H and E and similar tables are readily constructed for the other titrations. It would appear, however, that the second pair of electrodes, combined with a standard solution of hydrochloric acid and a measuring cylinder, constitutes a sort of " chemical potentiometer " which possesses advantages as regards bulk, cost, and immediate readiness for use over the simplest of physical instruments.

Results.

It would be superfluous to quote the results obtained in the more concentrated solutions, where the precision of the indication is greater than that of the volumetric apparatus. The results in

Table I, obtained with the more dilute solutions, indicate the limits of precision, and the order of accuracy attained requires no comment.

In order to provide a check on the *correctness* as well as the concordance of the results, the very dilute solutions were prepared by the precise dilution of carefully compared strong solutions. These gave the " calculated " results in the sixth column, from which the percentage deviations are given in the seventh column. $N/5$-Solutions of silver nitrate and the halides of potassium were compared by Volhard's method, and very good distilled water was used for the subsequent dilutions. The acid and alkali were compared at $N/2$-strength, and for the dilution of the baryta, conductivity water was used with a special arrangement to exclude atmospheric carbon dioxide.

TABLE I.

Solution titrated.	Reagent.	*R.I.A.*	*E.P.C.*	Vol. of reagent (c.c.). Found.	Calc.	Error, %.
100 C.c. of $\frac{N}{400}$-KCl	$\frac{N}{100}$-$AgNO_3$	1·0	0·0031	25·13	25·12	+0·04
		0·09	0·00093	25·135		+0·06
		0·00056	None	25·12		±0
200 C.c. of $\frac{N}{1000}$-KCl	$\frac{N}{100}$-$AgNO_3$	0·09	0·00093	20·11	20·095	+0·07
		0·01	0·00031	20·07		−0·12
		0·00056	None	20·08		−0·07
1000 C.c. of $\frac{N}{10000}$-KCl	$\frac{N}{100}$-$AgNO_3$	0·25	0·00155	10·08	10·05	+0·3
		0·04	0·00062	9·94		−1·1
		0·00056	None	9·97		−0·8
100 C.c. of $\frac{N}{5000}$-KBr	$\frac{N}{1000}$-$AgNO_3$	1·0	0·013	20·535	20·55	−0·07
		0·04	0·0026	20·53		−0·1
		$2{\cdot}8 \times 10^{-5}$	None	20·56		+0·05
1000 C.c. of $\frac{N}{100000}$-KBr	$\frac{N}{1000}$-$AgNO_3$	0·09	0·0039	10·15	10·275	−1·25
		0·01	0·0013	10·22		−0·55
100 C.c. of $\frac{N}{5000}$-KI	$\frac{N}{1000}$-$AgNO_3$	0·01	0·012	20·04	20·01	+0·15
		0·0025	0·006	20·02		+0·05
1000 C.c. of $\frac{N}{100000}$-KI	$\frac{N}{1000}$-$AgNO_3$	0·0009	0·0036	9·95	10·005	−0·55
		$3{\cdot}2 \times 10^{-7}$	None	10·10		+0·1
100 C.c. of $\frac{N}{400}$-HNO_3	$\frac{N}{100}$-$Ba(OH)_2$	1·0	0·0015	25·92	25·90	+0·08
		0·04	0·0003	25·89		−0·04
		0·0022	None	25·905		+0·02
200 C.c. of $\frac{N}{1000}$-HNO_3	$\frac{N}{100}$-$Ba(OH)_2$	0·25	0·00075	20·70	20·72	−0·1
		0·09	0·00045	20·71		−0·05
		0·0022	None	20·745		+0·12
1000 C.c. of $\frac{N}{10000}$-HNO_3	$\frac{N}{100}$-$Ba(OH)_2$	0·36	0·0009	10·50	10·36	+1·4
		0·09	0·00045	10·37		+0·1
		0·0022	None	10·45		+0·9

In the titrations a cheap pointer galvanometer was used throughout. The resistance of the titrated solutions was diminished by the addition of small quantities of a 10% potassium nitrate solution, prepared from Kahlbaum's " for analysis " product, twice recrystallised.

The activity coefficients depended largely on the added potassium nitrate. They were derived mainly by the use of Lewis and Randall's data (" Thermodynamics," McGraw Hill, New York, p. 382). In the third column are given the " corrected concentrations " or *activities* of the reference ion (*R.I.A.*) which were adjusted to some representative rounded values, while in the fourth column are given the activities of the hydrochloric acid in the end-point cells (*E.P.C.*), except where none was required.

Finally, it may be observed that the possibility of using a pair of very simple electrodes fixed close together and a single simple vessel for titration is not only a convenience, but also a simplification which permits the application of this method in several special ways (*e.g.*, microtitration), whilst the closeness of the electrodes and absence of liquid junction make it comparatively easy to keep the electrical resistance within bounds even at the lowest concentrations. Moreover, the elimination of the uncertainty attaching to liquid-junction potentials must facilitate greater precision.

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