CXV.—*Differential Potentiometric Titration. Part I. Simple Method (Method I).*

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The potential of a suitable electrode dipping into a titrated solution has been used for the detection of the end-point according to two distinct principles. The more obvious principle, that a particular *value* of the potential marks the end-point, came into use comparatively recently with the methods of Pinkhof, Treadwell, and Müller (Müller, " Electrometrische Massanalyse," 4te Aufl., Berlin; see also Cavanagh, J., 1927, 2207). In earlier methods the end-

point was detected by a *rapid change* in the potential, or, more precisely, by a maximum in the value of $\Delta E/\Delta M$ (where E is the potential, and M the amount of reagent used). This " differential " indication is intrinsically less sensitive than the other, but has the advantage at present of wider application. Moreover, in some of the cases where the more convenient " absolute " principle is applicable, the exact determination of the particular potential which marks the end-point depends ultimately on the use of the differential principle.

The methods described in this and the following paper depend upon a broader conception of the differential principle and, while retaining the advantage of wide applicability, appear to be an improvement upon the usual methods, both in convenience and in precision. Instead of the customary process of making a large number of small additions of reagent with corresponding potential measurements in order to detect the maximum value of $\Delta E/\Delta M$, it has been found possible to determine the result of the titration with higher precision from two or three measurements of the potential, corresponding to one or two *large* additions of the reagent, without necessarily finishing the titration in the ordinary sense. Indeed the simple method now described depends on the assumption that the added reagent reacts completely with the titrated solution, which implies that the end-point is not quite reached. This sets a limit to the absolute precision attainable by this method with given electrodes. For example, in the titration of a chloride by means of silver nitrate, if the electrodes are trustworthy as regards constancy to $\pm$ 0·25 millivolt, so that the change of potential is defined to $\pm$ 0·5 millivolt, the maximum absolute precision is about one-seventh of the solubility of silver chloride, *i.e.*, about $\pm$ 0·2% in the titration of an $N/1000$ solution. About five times this degree of absolute precision is obtainable, with electrodes of the same constancy, by the use of methods II and III which take account of the incompleteness of the reaction in the neighbourhood of the end-point (see Part II, following paper).

1. *Principle of Method I.*—The potential of a reversible electrode dipping into a solution of the corresponding (univalent) ion, concentration c, is given by the formula

$$E = \text{constant} + RT/F.\log c\gamma \quad . \quad . \quad . \quad . \quad (1)$$

where γ is the activity coefficient of the ion. Suppose this ion is to be titrated by means of a standard reagent of normality n, and that the solution is chemically equivalent to M_0 c.c. of the reagent, so that the object of the titration is to determine M_0. If the volume

of the solution is V_0 c.c., the concentration c is equal to nM_0/V_0, and the initial potential of the electrode is

$$E_0 = \text{constant} + RT/F.\log nM_0\gamma_0/V_0 \quad . \quad . \quad . \quad (2)$$

Suppose now that any quantity, m c.c. (less than M_0) of the reagent is added to the solution, reacting completely. The solution is now equivalent to $(M_0 - m)$ c.c., and the volume is increased to $(V_0 + m)$ c.c. The potential of the electrode will therefore be

$$E = \text{constant} + RT/F.\log nM\gamma/V \quad . \quad . \quad . \quad (3)$$

where $M = (M_0 - m)$, $V = (V_0 + m)$, and γ is the activity coefficient under the changed conditions. The potential *change*, ε, due to the addition of m c.c. of reagent is therefore

$$\varepsilon = RT/F.\log nM_0\gamma_0/V_0 - RT/F.\log nM\gamma/V \quad . \quad . \quad (4)$$
$$= RT/F.\log M_0\gamma_0/V_0 - RT/F.\log M\gamma/V \quad . \quad . \quad (5)$$

As a first approximation we can put $\gamma_0 = \gamma$, and if m is assumed to be negligibly small in comparison with V_0, we can put $V = V_0$; then

$$\varepsilon = RT/F.\log M_0/M = RT/F.\log (1 + m/M). \quad . \quad (6)$$

Thus, at constant temperature, ε is a function of m/M; and conversely, *the ratio* M/m *is a function of* ε; explicitly (see Table I)

$$M/m = f(\varepsilon) = \tfrac{1}{2}(\coth F\varepsilon\, 2RT - 1) \quad . \quad . \quad . \quad (7)$$

Thus the measurement of a single potential change (ε), produced by the addition of the arbitrary quantity of reagent (m c.c.) suffices with the aid of Table I to determine M, and therefore M_0, the result of the titration.

2. *Correction for the Changing Volume of the Solution, and for Change in the Activity Coefficient.*—The foregoing approximations can be dispensed with, however, for ε (equation 5) can be divided into three additive parts,

$$\varepsilon = \varepsilon_m + \varepsilon_v - \varepsilon_\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where

$$\varepsilon_m = RT/F.\log M_0/M = RT/F.\log (1 + m/M) \quad . \quad . \quad (9)$$
$$\varepsilon_v = RT/F.\log V/V_0 = RT/F.\log (1 + m/V_0) \quad . \quad . \quad (10)$$
$$\varepsilon_\gamma = RT/F.\log \gamma/\gamma_0 = RT/F.\log [1 + (\gamma - \gamma_0)/\gamma_0] . \quad (11)$$

and comparison with equations (5) and (6) shows that

$$M/m = f(\varepsilon_m) = f(\varepsilon - \varepsilon_v + \varepsilon_\gamma) \quad . \quad . \quad . \quad (12)$$
$$V_0/m = f(\varepsilon_v) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$
$$\gamma_0/(\gamma - \gamma_0) = f(\varepsilon_\gamma) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Thus M/m can be obtained from ε_m exactly as (in neglecting m and $\gamma - \gamma_0$) it was obtained from ε, and the " corrections," ε_v and ε_γ,

can be estimated by using Table I in the inverse way—as in finding an antilogarithm from a table of logarithms. (But see also sections 11 and 12.)

The activity coefficient of an ion in a mixed salt solution depends, to a first approximation, on the "ionic strength" of the whole solution (see Lewis and Randall, "Thermodynamics," McGraw-Hill, New York), which may be defined as "half the sum of the equivalent concentrations of all the ions present multiplied respectively by their valencies." In the course of a titration, one ion is gradually substituted for another in the titrated solution, while at the same time the volume of the solution is increased. When the "exchanged" ions are of the same valency (as in the titration of halides by means of silver nitrate, or of acids by sodium hydroxide), the ionic strength changes only on account of the increasing volume, to which it is inversely proportional, and even if the volume is doubled the relative change in γ is only 2—4%. The corresponding value of ε_γ is therefore less than 1 millivolt—generally much less. When, as in titration with barium hydroxide, a bivalent ion is being substituted for a univalent, the effect of the increasing volume upon the ionic strength of the solution is partly or wholly counterbalanced, and ε_γ is still smaller. Thus, ε_γ is almost always negligible, so that (12) may then be abbreviated to

$$M/m = f(\varepsilon_m) = f(\varepsilon - \varepsilon_v) \quad . \quad . \quad . \quad . \quad (15)$$

The dilution correction, ε_v, on the other hand, may be quite large; *e.g.*, if the added volume of reagent is equal to the initial volume of the titrated solution, $V_0/m = 1$, and ε_v (see Table I) = 17·3 millivolts.

3. The *precision of the determination* is limited ultimately by the inherent variability of the electrodes which appears (multiplied by 2) in ε as an uncertainty which is "absolute," *i.e.*, independent of the magnitude of ε. The consequent absolute uncertainty in the determination of M_0 is therefore found by differentiating M_0 partially with respect to ε, ε_v and m being treated as constants; thus

$$-\partial M_0/\partial\varepsilon = FM_0M/RTm = 0{\cdot}04M_0M/m \text{ (at } 17°) \quad (16)$$

and the *relative* uncertainty per millivolt of uncertainty in ε

$$-(\partial M_0/\partial\varepsilon)/M_0 = 0{\cdot}04(M_0/m - 1) \quad . \quad . \quad . \quad (17)$$

Thus the relative uncertainty in M_0 corresponding to an uncertainty of $\pm$ 0·5 millivolt in ε is roughly 20% when m is 10% of M_0, 2% when m is 50% of M_0, and 0·2% when m is 90% of M_0.

The importance of having removed the limitation upon the value of m is now plain, for the precision of the result increases rapidly

with m. It is still essential, however, that m should be less than M_0. If the result of the titration (M_0) is approximately known beforehand, m may be made large at once, and a precise result obtained from the measurement of a *single potential change*. Otherwise the reagent must be added in two or even three stages with corresponding potential measurements, the process being one of successive approximation (see examples below).

4. It is not necessary that ε and m should be measured always from the beginning of the titration. Any stage may be taken as the starting point, for at any stage (so long as the reaction may be regarded as complete), if M' is the volume of reagent still required, and the volume of the solution is V' c.c., the concentration of the titrated ion is nM'/V', the potential of the electrode is

$$E' = \text{constant} + RT/F.\log nM'\gamma'/V' \quad . \quad . \quad (18)$$

and if ε and m are measured from this stage,

$$\varepsilon = RT/F.\log M'\gamma'/V' - RT/F.\log M\gamma/V \quad . \quad (19)$$

$$= \varepsilon_m + \varepsilon_v - \varepsilon_\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where

$$\left.\begin{aligned} M/m &= f(\varepsilon_m) = f(\varepsilon - \varepsilon_v + \varepsilon_\gamma) \\ V'/m &= f(\varepsilon_v) \\ \gamma'/(\gamma - \gamma') &= f(\varepsilon_\gamma) \end{aligned}\right\} \quad . \quad . \quad . \quad (21)$$

or, when ε_γ is negligible,

$$M/m = f(\varepsilon_m) = f(\varepsilon - \varepsilon_v) \quad . \quad . \quad . \quad . \quad (22)$$

Then, instead of (17), a more general expression for the relative uncertainty in the determination of M_0 is obtained, *viz.*,

$$-\frac{1}{M_0}\cdot\frac{\partial M_0}{\partial\varepsilon} = -\frac{1}{M_0}\cdot\frac{\partial M}{\partial\varepsilon} = 0{\cdot}04\,.\,\frac{M'M}{mM_0} = 0{\cdot}04\left(1+\frac{M}{m}\right)\frac{M}{M_0} \quad (23)$$

$$= 0{\cdot}04[1 + f(\varepsilon_m)]M/M_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

which shows that precision depends on the smallness of M relative to M_0, and also *up to a point* on the smallness of M/m or $f(\varepsilon_m)$. But when ε_m is 60 millivolts or more, $f(\varepsilon_m)$ is less than 0·1, and the factor $[1 + f(\varepsilon_m)]$ cannot be much diminished by further increasing ε_m, so that precision then depends chiefly on the smallness of M/M_0, which is independent of the stage from which m is reckoned. On the other hand, the temperature correction (see Section 5) is proportional to ε, and the correction, ε_γ, for variation in the activity coefficient increases with m. Hence it is sometimes advantageous to reduce the final values of ε and m somewhat by reckoning them from the second, or even from a third, stage in the titration (see Example 1, Section 10).

5. *Temperature Correction.*—Table I (as also Tables II and II*a*) is strictly applicable only at 17°, and the potential change if measured at any other temperature ($t°$) ought to be corrected to 17° by the addition of the small (positive or negative) correction, $(17 - t)\varepsilon/300$, which, however, is often smaller than the experimental uncertainty in ε.

A moderate constancy of temperature is assumed, for, without knowledge of the temperature coefficients of the electrodes, the effect of any slight change of temperature between the measurements of the two potentials E' and E cannot be predicted, and must be included in the experimental uncertainty of ε.

The measurements recorded in Section 10 were obtained without the use of a thermostat.

6. *Applicability of the Method.*—The method as described is applicable to the titration of univalent ions, *e.g.*, $Ag^{\cdot}$, $H^{\cdot}$, Cl', Br', I', OH', etc., to which a corresponding reversible electrode can be found. In the case of a bivalent ion, it would only be necessary to multiply all potentials by 2.

7. *Correction for Adsorption of the Titrated Ion.*—In the case of precipitation titrations, the possible adsorption of the titrated ion by the precipitate has to be considered (compare Part II, Section 1). If at the stage (M, V), the fraction (1—θ) of the total amount of the ion is adsorbed, the concentration in the solution will be reduced to $nM\theta/V$, and similarly at the earlier stage (M', V'), (1—θ′) being the fraction adsorbed, the concentration will be $nM'\theta'/V'$, so that in the complete expression for ε (equation 8) an additional term, $\varepsilon_\theta = RT/F.\log\theta'/\theta$, will be introduced. For small values of $(1 - \theta)$, $\varepsilon_\theta \approx RT(\theta' - \theta)/F$. If further, as a first approximation, the fraction can be regarded as independent of the concentration of the ion and proportional to the ratio of the amount of precipitate to the volume of solution, so that $(1 - \theta) \propto n(M_0 - M)/V$, then $\varepsilon_\theta \propto nmV_0/VV'$, which means (*a*) that ε_θ will be greater in titrating stronger solutions, and (*b*) that it can be minimised by the procedure of Section 4.

It would be possible to eliminate this source of error almost entirely by filtering off and washing the precipitate with small quantities of water, making the necessary allowance in ε_v for the increased volume of the solution. In the measurements recorded in Section 10, the correction ε_θ, like ε_γ, has been neglected, so that it was probably very small in these cases.

Modification for Oxidation–Reduction Titrations.—The method can be adapted to oxidation–reduction titrations such as the titration of ferrous or titanous ions. In these cases the dilution correction, ε_v, does not occur, but a correction $\varepsilon_{m'}$ has to be made for change in

the concentration of the oxidised ion. If m' c.c. is the total amount of reagent already added before the further addition of m c.c., and if M c.c. is the unknown amount still required one finds

$$\varepsilon = \varepsilon_m + \varepsilon_{m'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where [compare (21) and (22)]

$$\left\{ \begin{array}{l} M/m = f(\varepsilon_m) = f(\varepsilon - \varepsilon_{m'}) \quad . \quad . \quad (26) \\ m'/m = f(\varepsilon_{m'}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (27) \end{array} \right.$$

so that a very similar procedure appears to be applicable. In other cases both ε_v and $\varepsilon_{m'}$ would occur.

9. *The Limit of Precision.*—The method depends on the condition that the reagent added to the solution *reacts completely*, removing from the solution a chemically equivalent quantity of the titrated ion. In the strict sense of course this condition would never be fulfilled, but it holds to a close approximation except in the immediate neighbourhood of the end-point. For example, when silver nitrate is added to a solution of a chloride the residual concentration of silver ion, which remains in solution, thereby failing to remove its equivalent of chloride ion from the solution, is inversely proportional to the chloride-ion concentration, inasmuch as the solubility product ($S^2 = C_{Ag} \cdot C_{Cl}$) is constant. To a first approximation the consequent relative error in the found value of M is C_{Ag}/C_{Cl} or S^2/C^2_{Cl} (*i.e.*, S^2V^2/M^2n^2).

Now with electrodes of the constancy described above, the potential change is defined to within $\pm 0{\cdot}5$ millivolt, and the minimum relative uncertainty in the found value of M is $\pm 0{\cdot}5F/RT$, or $\pm 0{\cdot}02$, which will be exceeded by the error due to the neglect of C_{Ag} unless $C_{Cl} > 7S$ (*i.e.*, $M > 7SV/n$). This sets a limit to the closeness of approach to the end-point, and therefore to the absolute precision (in terms of concentration) attainable by this method, with such electrodes. The minimum absolute uncertainty will be, in fact, rather more than one-seventh of the solubility of silver chloride ($0{\cdot}02 \times 7S$), that is to say, about $\pm 2 \times 10^{-6}$ (*i.e.*, about $\pm 0{\cdot}2\%$ in the titration of $N/1000$-chloride solution with a relatively concentrated reagent).

The considerations of this section apply also to other titrations to which the method is applicable, if the appropriate ionic product is inserted in place of $C_{Ag} \cdot C_{Cl}$, and the limit of absolute precision is estimated accordingly.

For exceptional purposes a somewhat higher order of absolute precision can be obtained with the same electrodes by approaching the end-point more closely, taking into account the incompleteness of the reaction (see Part II).

As a first approximation the correction S^2V^2/M^2n^2 may be subtracted from the found value of M when the latter is less than about $10SV/n$, but the limit $7SV/n$ (about) should not be appreciably overstepped.

10. *Results.*

A few typical titrations by this method are recorded below. The dilute solutions of known relative strength were prepared in the manner described in a previous paper (*loc. cit.*). The same pointer galvanometer was used. A good potentiometer and checked standard cell were actually employed, but it should be observed that since the method depends only on *differences* of potential of the order of 0·1 volt or less, precision better than say, 0·1%, either in the standard cell or in the calibration of the potentiometer, is generally superfluous. The electrodes were silver-halide–quinhydrone pairs, as described in the cited paper, so that the uncertainty of a liquid-junction potential had not to be considered. At the same time the use of these electrodes necessitated the doubling of the dilution correction ε_v, since the potentials of both electrodes were equally affected by the changing volume of the solution. A small measured quantity of the reagent was, in most cases, added *before* the first measurement of the potential (Stage 0), as it was found that the initial potential was more trustworthy if obtained in the presence of a trace of precipitate. In the first example, where the temperature was markedly different from 17° and a rather large value of ε was obtained at Stage III, the advantage of reducing ε, by reckoning ε and m from Stage II, is illustrated (indicated by "III—II"; see also examples 5 and 6). Example 6 illustrates one peculiar advantage of this method, *viz.*, that it is *independent of the immediate neighbourhood of the end-point.* The establishment of a steady and reproducible potential in the case of the iodide electrode is very slow near the end-point, whereas, at a distance from the end-point, measurements can be made quickly and yield an accurate result.

In the examples, col. 2 shows the total number of c.c. of reagent present; col. 3, the volume added after stage 0 (or between the stages indicated); col. 5, the values of $2\varepsilon_v$ (in millivolts) as obtained from Table I; col. 6, the measured potential, E, in millivolts; col. 7, ε, the potential change from stage 0 (or between the stages indicated); col. 8, the difference $\varepsilon - 2\varepsilon_v = \varepsilon_m$; the values in col. 9 are obtained from Table I; col. 10 gives the number of c.c. still required; col. 11, the successive approximations to M_0; and col. 12, the percentage error, Δ.

Example 1. 100 C.c. $N/100$-KCl titrated (at 13°) by $N/100$-$AgNO_3$.

(Actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/1000$.)

$V_0 = 101$.

(1) Stage.	(2) M_0-M.	(3) m.	(4) V_0/m.	(5) $2\epsilon_v$.	(6) E.	(7) ϵ.	(8) ϵ_m.	(9) $f(\epsilon_m)$.	(10) M.	(11) M_0.	(12) Δ.
0	1				307·2						
I	11	10	10·1	4·7	299·4	7·8	3·1	7·6	76	87	−12
II	71	70	1·44	26·3	250·5	56·7	30·4	0·421	29·5	100·5	+ 2
III	96	95	1·06	33·1	184·9	122·3	89·2	0·0290	2·75	98·75	+ 0·25
			Correcting to 17°, $\epsilon_{17°}$ =			123·9	90·8	0·0272	2·58	98·58	+ 0·08
III—II	96	25		6·8	$\epsilon_{13°}$ =	65·6	58·8	$0·105_2$	2·63	98·63	+ 0·13
			Correcting to 17°, $\epsilon_{17°}$ =			66·5	59·7	$0·101_1$	2·53	98·53	+ 0·03

Example 2. 100 C.c. $N/400$-KCl titrated (at 16·5°) by $N/100$-$AgNO_3$.

(Actually known to be equivalent to 24·62 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/1000$.)

$V_0 = 101$.

Stage.	M_0-M.	m.	V_0/m.	$2\epsilon_v$.	E.	ϵ.	ϵ_m.	$f(\epsilon_m)$.	M.	M_0.	Δ.
0	1				252·8						
I	11	10	10·1	4·7	233·8	19	14·3	1·30	13	24	− 2·5
II	23	22	4·6	9·8	175·5	77·3	67·5	0·072	$1·58_5$	$24·58_5$	− 1·4

Example 3. 1000 C.c. $N/1000$-KCl titrated (at 14·5°) by $N/100$-$AgNO_3$.

(Actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/2500$.)

$V_0 = 1010$.

Stage.	M_0-M.	m.	V_0/m.	$2\epsilon_v$.	E.	ϵ.	ϵ_m.	$f(\epsilon_m)$.	M.	M_0.	Δ.
0	10				222·0						
I	40	30	33·7	1·5	210·4	11·6	10·1	2·01	60·3	100·3	+ 1·8
II	85	75	13·5	3·6	172·2	49·8	46·2	0·187	14·0	99·0	+ 0·5
			Correcting to 17°, $\epsilon_{17°}$ =			50·2	40·6	$0·183_5$	13·75	98·75	+ 0·25
Approximate correction for incomplete reaction = $-\frac{S^2V^2}{n^2M} \simeq -0·1$ →									13·65	98·65	+ 0·15

Example 4. 100 C.c. $N/1000$-KCl titrated (at 20°) by $N/1000$-$AgNO_3$.

(Actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/4000$.)

$V_0 = 105$.

Stage.	M_0-M.	m.	V_0/m.	$2\epsilon_v$.	E.	ϵ.	ϵ_m.	$f(\epsilon_m)$.	M.	M_0.	Δ.
0	5				250·7						
I	25	20	5·25	8·7	236·3	14·4	5·7	3·9	78	103	+4·5
II	75	70	1·5	25·6	190·4	60·3	34·7	$0·332_6$	23·28	98·28	−0·22
			Correcting to 17°, $\epsilon_{17°}$ =			59·7	34·1	$0·343_5$	24·05	99·05	+0·55
Approximate correction for incomplete reaction = $-\frac{S^2V^2}{n^2M} \simeq -0·2$									23·85	98·85	+ 0·35

Example 5. 500 C.c. of $N/5000$-KBr titrated (at 19°) by $N/1000$-$AgNO_3$. (Actually known to be equivalent to 90·8 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/10{,}000$.)

$V_0 = 500$.

Stage.	M_0-M.	m.	V_0/m.	$2\epsilon_v$.	E.	ϵ.	ϵ_m.	$f(\epsilon_m)$.	M.	M_0.	Δ.
0	0				340·5						
I	50	50	10	4·7	315·2	25·3	20·6	0·78	39	89	−2
II	80	80	6·25	7·4	279·1	61·4	54·0	$0{\cdot}130_5$	10·44	90·44	−0·4
III	88	88	5·7	8·1	243·7	96·8	88·7	$0{\cdot}0296_5$	2·61	90·61	−0·2
			Correcting to 17°, $\epsilon_{17°}$ =			96·2	88·1	0·0304	2·68	90·68	−0·13
III—I	88	38		3·4	$\epsilon_{19°}$ =	71·5	68·1	0·0702	2·67	90·67	−0·14
			Correcting to 17°, $\epsilon_{17°}$ =			71·0	67·6	0·0718	2·73	90·73	−0·08
III—II	88	8	Uncorrected ϵ_m (at 19°) =			34·7	0·333		2·66	90·66	−0·15

Example 6. 1000 C.c. of $N/10{,}000$-KI titrated (at 19·5°) by $N/1000$-$AgNO_3$.

(Actually known to be equivalent to 111·1 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/20{,}000$.)

$V_0 = 1000$.

Stage.	M_0-M.	m.	V_0/m.	$2\epsilon_v$.	E.	ϵ.	ϵ_m.	$f(\epsilon_m)$.	M.	M_0.	Δ.
0	0				440·5						
I	50	50	20	2·4	422·7	17·8	15·4	1·17	58·5	108·5	−2·5
II	100	100	10	4·7	377·5	63·0	58·3	$0{\cdot}107_8$	10·76	110·76	−0·3
			Correcting to 17°, $\epsilon_{17°}$ =			62·5	57·8	0·110	11·0	111·0	−0·09
II—I	100	50	Uncorrected ϵ_m (at 19·5°) =			42·9	0·219		10·95	110·95	−0·1

Addendum.

11. Although ε_v may be obtained from V_0/m or V'/m as explained on p. 846, it is desirable to have a table which reads directly and not inversely; the function derived from equation (10) is more suitable for tabulation in terms of m/V_0 (or m/V') than in terms of V_0/m, and Table II gives ε_v in millivolts for values of m/V_0 up to 2·1, *i.e.*, over the range usually required. When, as is often the case, V_0 is a simple number such as 10, 20, 50, the ratio m/V_0 is readily evaluated, and Table II provides the easiest way of "correcting to constant volume" all the measured potentials. Alternatively, Table IIA is more convenient when V (instead of V_0 or V') is a simple number.

12. More generally, the measured potentials may readily be "corrected" to any arbitrarily chosen simple volume by means of Tables II and IIA. For example, if 73·7 c.c. of solution are titrated and 20, 35, 7, and 1·5 c.c. are the successive additions of reagent, the five measured potentials can be "corrected" to 100 c.c. volume as follows, the correction when positive being made in the *same* direction as the change of potential during the titration.

Stage.	Volume, V c.c.	$(100 - V)$.	$\frac{(100 - V)}{100}\cdot$	Corr. (millivolts).	
0	73·7	+26·3	+0·263	+7·6	from Table IIA.
I	93·7	+ 6·3	+0·063	+1·6	
II	128·7	−28·7	−0·287	−6·3	from Table II.
III	135·7	−35·7	−0·357	−7·6	
IV	137·2	−37·2	−0·372	−7·9	

TABLE I.

$f(\epsilon) = \frac{1}{2}(\coth F\epsilon/2RT - 1)$.

ϵ is given in millivolts; $T = 290°$ Abs.

ϵ.	·0.	·1.	·2.	·3.	·4.	·5.	·6.	·7.	·8.	·9.
0	∞	250	125	83	62	50	41	35.2	30.8	27.8
1	24.5	22.2	20.3	18.7	17.3	16.2	15.1	14.2	13.4	12.7
2	12	11.1	10.3	10.4	9.93	9.51	9.13	8.77	8.44	8.13
3	7.84	7.58	7.33	7.09	6.88	6.65	6.46	6.27	6.09	5.93
4	5.76	5.61	5.47	5.33	5.2	5.07	4.95	4.84	4.72	4.62
5	4.52	4.42	4.33	4.23	4.15	4.06	3.98	3.9	3.83	3.76
6	3.69	3.63	3.55	3.48	3.43	3.37	3.31	3.25	3.2	3.15
7	3.095	3.045	2.996	2.949	2.902	2.858	2.815	2.772	2.731	2.691
8	2.652	2.613	2.576	2.54	2.504	2.469	2.436	2.403	2.37	2.339
9	2.308	2.278	2.248	2.219	2.191	2.163	2.135	2.11	2.084	2.058
10	2.033	2.009	1.985	1.961	1.938	1.915	1.894	1.872	1.851	1.83
11	1.809	1.789	1.769	1.75	1.731	1.712	1.694	1.677	1.658	1.64
12	1.623	1.606	1.59	1.573	1.557	1.542	1.526	1.511	1.496	1.481
13	1.468	1.453	1.438	1.424	1.41	1.397	1.383	1.37	1.357	1.345
14	1.332	1.32	1.308	1.296	1.284	1.273	1.262	1.249	1.238	1.227
15	1.216	1.205	1.195	1.185	1.174	1.164	1.154	1.144	1.135	1.125
16	1.115	1.106	1.097	1.088	1.079	1.07	1.061	1.052	1.043	1.035
17	1.027	1.019	1.01	1.002	0.994	0.986	0.979	0.971	0.963	0.956
18	0.948	0.941	0.934	0.927	0.92	0.913	0.906	0.899	0.892	0.885
19	0.878	0.872	0.865	0.859	0.852	0.846	0.84	0.834	0.828	0.822
20	0.816	0.81	0.804	0.798	0.793	0.787	0.782	0.776	0.77	0.765
21	0.76	0.754	0.749	0.744	0.739	0.734	0.729	0.724	0.719	0.714
22	0.709	0.704	0.699	0.694	0.69	0.685	0.681	0.676	0.671	0.667
23	0.662	0.658	0.654	0.65	0.646	0.642	0.637	0.633	0.629	0.625
24	0.6205	0.6165	0.6126	0.6085	0.6047	0.6009	0.597	0.5932	0.5894	0.5857
25	0.582	0.5788	0.5747	0.5711	0.5675	0.564	0.5605	0.557	0.5535	0.5501
26	0.5467	0.5433	0.540	0.5367	0.5334	0.5308	0.5269	0.5237	0.5205	0.5174
27	0.5142	0.5111	0.5081	0.505	0.502	0.499	0.496	0.493	0.4901	0.4872
28	0.4843	0.4815	0.4786	0.4756	0.473	0.4703	0.4675	0.4647	0.462	0.4593
29	0.4567	0.454	0.4514	0.4488	0.4473	0.4436	0.4411	0.4388	0.436	0.4336
30	0.431	0.4286	0.4261	0.4237	0.4218	0.4189	0.4166	0.4142	0.4119	0.4096
31	0.4073	0.405	0.4027	0.4005	0.3982	0.396	0.3938	0.3916	0.3894	0.3873
32	0.3851	0.383	0.3809	0.3788	0.3767	0.3747	0.3726	0.3706	0.3685	0.3665
33	0.3645	0.3626	0.3606	0.3586	0.3567	0.3548	0.3528	0.3509	0.349	0.3472
34	0.3453	0.3435	0.3416	0.3398	0.338	0.3362	0.3344	0.3326	0.3308	0.3291
35	0.3275	0.3256	0.3239	0.3222	0.3205	0.3188	0.3171	0.3154	0.3138	0.3121
36	0.3105	0.3089	0.3073	0.3057	0.3041	0.3025	0.3009	0.2994	0.2978	0.2963
37	0.2948	0.2933	0.2917	0.2902	0.2887	0.2872	0.2856	0.2843	0.2828	0.2814
38	0.280	0.2785	0.2771	0.2757	0.2746	0.2729	0.2715	0.2701	0.2688	0.2674
39	0.2661	0.2647	0.2634	0.2621	0.2607	0.2594	0.2581	0.2568	0.2555	0.2542
40	0.253	0.2517	0.2505	0.2493	0.248	0.2468	0.2455	0.2443	0.2431	0.2419
41	0.2407	0.2395	0.2383	0.2371	0.236	0.2348	0.2336	0.2325	0.2314	0.2302
42	0.2291	0.228	0.2269	0.2257	0.2246	0.2235	0.2225	0.2214	0.2203	0.2192
43	0.2181	0.2171	0.216	0.215	0.2139	0.2129	0.2119	0.2109	0.2098	0.2088
44	0.2078	0.2068	0.2058	0.2048	0.2038	0.2029	0.2019	0.2009	0.200	0.199
45	0.1981	0.1971	0.1982	0.1952	0.1942	0.1934	0.1925	0.1916	0.1906	0.1897
46	0.1888	0.1879	0.187	0.1862	0.1854	0.1844	0.1835	0.1827	0.1818	0.1809
47	0.1801	0.1792	0.1784	0.1776	0.1767	0.1758	0.1751	0.1743	0.1734	0.1726
48	0.1718	0.171	0.1702	0.1694	0.1688	0.1677	0.1671	0.1663	0.1655	0.1647
49	0.164	0.1632	0.1625	0.1617	0.161	0.1602	0.1595	0.1587	0.158	0.1573
50	0.1565	0.1558	0.1551	0.1544	0.1537	0.153	0.1523	0.1516	0.1509	0.1502
51	0.1495	0.1488	0.1481	0.1474	0.1468	0.1461	0.1454	0.1448	0.1441	0.1434
52	0.1428	0.1421	0.1415	0.1408	0.1402	0.1396	0.1388	0.1382	0.1377	0.1371
53	0.1364	0.1358	0.1352	0.1346	0.134	0.1334	0.1328	0.1322	0.1316	0.131
54	0.1304	0.1298	0.1292	0.1286	0.128	0.1275	0.1269	0.1263	0.1258	0.1252
55	0.1246	0.1241	0.1235	0.123	0.1224	0.1219	0.1215	0.1209	0.1205	0.1199
56	0.1192	0.1186	0.1181	0.1176	0.1171	0.1165	0.116	0.1155	0.115	0.1145
57	0.1140	0.1135	0.1130	0.1125	0.1120	0.1115	0.1110	0.1105	0.1100	0.1095
58	0.1090	0.1085	0.1080	0.1076	0.1071	0.1066	0.1062	0.1057	0.1052	0.1048
59	0.1043	0.1038	0.1034	0.1029	0.1025	0.1020	0.1016	0.1011	0.1007	0.1002
60	0.0998	0.0994	0.0989	0.0985	0.0981	0.0976	0.0972	0.0968	0.0963	0.0959
61	0.0955	0.0951	0.09465	0.09425	0.0938	0.0934	0.0930	0.0926	0.0922	0.0918
62	0.0914	0.0910	0.0906	0.0902	0.0898	0.08945	0.08905	0.08866	0.08825	0.0879
63	0.0875	0.0871	0.08675	0.08635	0.0860	0.0856	0.08525	0.0849	0.0845	0.08415
64	0.0838	0.0834	0.08305	0.0827	0.08235	0.0820	0.08165	0.0813	0.08095	0.0806
65	0.08025	0.0799	0.07955	0.0792	0.07885	0.0785	0.0782	0.07785	0.0775	0.0772
66	0.07685	0.0765	0.0762	0.07585	0.07555	0.0752	0.0749	0.07455	0.07425	0.07395
67	0.0736	0.0733	0.0730	0.07265	0.07235	0.07205	0.07175	0.07145	0.0711	0.0708
68	0.0705	0.0702	0.0699	0.0696	0.0693	0.06905	0.06875	0.06845	0.06815	0.06785
69	0.06755	0.0673	0.0670	0.0667	0.0664	0.06615	0.06585	0.0656	0.0653	0.0650

TABLE I (*contd.*).

ϵ.	·0.	·1.	·2.	·3.	·4.	·5.	·6.	·7.	·8.	·9.
70	0·0647$_5$	0·0644$_5$	0·0642	0·0639$_5$	0·0636$_5$	0·0634	0·0631	0·0628$_5$	0·0626	0·0623
71	0·0620$_5$	0·0618	0·0615$_5$	0·0612$_5$	0·0610	0·0607$_5$	0·0605	0·0602$_5$	0·0600	0·0597$_5$
72	0·0594$_6$	0·0592	0·0589$_5$	0·0587	0·0584$_5$	0·0582$_5$	0·0580	0·0577$_5$	0·0575	0·0572$_5$
73	0·0570	0·0567$_5$	0·0565$_5$	0·0563	0·0560$_5$	0·0558	0·0556	0·0553$_5$	0·0551	0·0549
74	0·0546$_6$	0·0544	0·0542	0·0539$_5$	0·0537$_5$	0·0535	0·0533	0·0530$_5$	0·0528$_5$	0·0526
75	0·0524	0·0522	0·0519$_5$	0·0517$_5$	0·0515	0·0513	0·0511	0·0509	0·0506$_5$	0·0504$_5$
76	0·0502$_5$	0·0500$_5$	0·0498	0·0496	0·0494	0·0492	0·0490	0·0488	0·0486	0·0484
77	0·0481$_5$	0·0479$_5$	0·0477$_5$	0·0475$_5$	0·0473$_5$	0·0471$_5$	0·0470	0·0468	0·0466	0·0464
78	0·0462	0·0460	0·0458	0·0456	0·0454$_5$	0·0452$_5$	0·0450$_5$	0·0448$_5$	0·0447	0·0445
79	0·0443	0·0441	0·0439$_5$	0·0437$_5$	0·0435$_6$	0·0434	0·0432	0·0430$_5$	0·0428$_5$	0·0426$_5$
80	0·0425	0·0423	0·0421$_5$	0·0419$_5$	0·0418	0·0416	0·0414$_5$	0·0412$_5$	0·0411	0·0409$_5$
81	0·0407$_5$	0·0406	0·0404	0·0402$_5$	0·0401	0·0399	0·0397$_5$	0·0396	0·0394$_5$	0·0392$_5$
82	0·0391	0·0389$_5$	0·0388	0·0386	0·0384$_5$	0·0383	0·0381$_5$	0·0380	0·0378	0·0376$_5$
83	0·0375	0·0373$_5$	0·0372	0·0370$_5$	0·0369	0·0367$_5$	0·0366	0·0364$_5$	0·0363	0·0361$_5$
84	0·0360	0·0358$_5$	0·0357	0·0355$_5$	0·0354	0·0352$_5$	0·0351	0·0349$_5$	0·0348	0·0346$_5$
85	0·0345$_5$	0·0344	0·0342$_5$	0·0341	0·0339$_5$	0·0338	0·0337	0·0335$_5$	0·0334	0·0332$_5$
86	0·0331$_5$	0·0330	0·0328$_5$	0·0327	0·0326	0·0324$_5$	0·0323	0·0322	0·0320$_5$	0·0319
87	0·0318	0·0316$_5$	0·0315$_5$	0·0314	0·0312$_5$	0·0311$_5$	0·0310	0·0309	0·0307$_5$	0·0306$_5$
88	0·0305	0·0304	0·0302$_5$	0·0301$_5$	0·0300	0·0299	0·0297$_5$	0·0296$_5$	0·0295	0·0294
89	0·0292$_5$	0·0291$_5$	0·0290$_5$	0·0289	0·0288	0·0287	0·0285$_5$	0·0284$_5$	0·0283	0·0282
90	0·0281	0·0280	0·0278$_5$	0·0277$_5$	0·0276$_5$	0·0275	0·0274	0·0273	0·0272	0·0270$_5$
91	0·0269$_5$	0·0268$_5$	0·0267$_5$	0·0266$_5$	0·0265	0·0264	0·0263	0·0262	0·0261	0·0260
92	0·0259	0·0257$_5$	0·0256$_5$	0·0255$_5$	0·0254$_5$	0·0253$_5$	0·0252$_5$	0·0251$_5$	0·0250$_5$	0·0249$_5$
93	0·0248$_5$	0·0247$_5$	0·0246$_5$	0·0245$_5$	0·0244$_5$	0·0243$_5$	0·0242$_5$	0·0241$_5$	0·0240$_5$	0·0239$_5$
94	0·0238$_5$	0·0237$_5$	0·0236$_5$	0·0235$_5$	0·0234$_5$	0·0233$_5$	0·0232$_5$	0·0231$_5$	0·0230$_5$	0·0230
95	0·0229	0·0228	0·0227	0·0226	0·0225	0·0224	0·0223$_5$	0·0222$_5$	0·0221$_5$	0·0220$_5$
96	0·0219$_5$	0·0219	0·0218	0·0217	0·0216	0·0215	0·0214$_5$	0·0213$_5$	0·0212$_5$	0·0211$_5$
97	0·0211	0·0210	0·0209	0·0208$_5$	0·0207$_5$	0·0206$_5$	0·0206	0·0205	0·0204	0·0203$_5$
98	0·0202$_5$	0·0201$_5$	0·0201	0·0200	0·0199	0·0198$_5$	0·0197$_5$	0·0196$_5$	0·0196	0·0195
99	0·0194$_5$	0·0193$_5$	0·0193	0·0192	0·0191	0·0190$_5$	0·0189$_5$	0·0189	0·0188	0·0187$_6$
ϵ.	+0.	+1.	+2.	+3.	+4.	+5.	+6.	+7.	+8.	+9.
100	0·0186$_5$	0·0179	0·0172	0·0165	0·0158$_5$	0·0152	0·0146	0·0140$_5$	0·0135	0·0129$_5$
110	0·0124$_5$	0·0119$_5$	0·0114$_5$	0·0110	0·0105$_5$	0·0101$_5$	0·0097$_5$	0·0093$_5$	0·0090	0·0086$_5$
120	0·0083	0·0079$_5$	0·0076$_5$	0·0073$_5$	0·0070$_5$	0·0068	0·0065	0·0062$_5$	0·0060	0·0057$_5$
130	0·0055$_5$	0·0053$_5$	0·0051	0·0049	0·0047	0·0045$_5$	0·0043$_5$	0·0042	0·0040	0·0038$_5$
140	0·0037	0·0035$_5$	0·0034$_5$	0·0033	0·0031$_5$	0·0030$_5$	0·0029	0·0028	0·0027	0·0026
150	0·0025	0·0024	0·0023	0·0022	0·0021	0·0020$_5$	0·0019$_5$	0·0019	0·0018	0·0017$_5$
160	0·0016$_5$	0·0016	0·0015$_5$	0·0015	0·0014	0·0013$_5$	0·0013	0·0012$_5$	0·0012	0·0011$_5$
170	0·0011	0·0010$_5$	0·0010$_5$	0·0010	0·0009$_5$	0·0009	0·0009	0·0008$_5$	0·0008	0·0008
180	0·0007$_5$	0·0007	0·0007	0·0006$_5$	0·0006$_5$	0·0006	0·0006	0·0005$_5$	0·0005$_5$	0·0005
190	0·0005	0·0005	0·0004$_5$	0·0004$_5$	0·0004$_5$	0·0004	0·0004	0·0004	0·0003$_5$	0·0003$_5$

TABLE II.

$$\epsilon_v = f^{-1}(1/x) = RT/F.\ \log\,(1 + x).$$

$x = m/V'$ or m/V_0; $T = 290°$ Abs.

x.	·00.	·01.	·02.	·03.	·04.	·05.	·06.	·07.	·08.	·09.
0·0	0·00	0·2$_5$	0·5	0·7$_4$	0·9$_8$	1·2$_2$	1·4$_6$	1·6$_9$	1·9$_2$	2·1$_5$
0·1	2·3$_8$	2·6$_1$	2·8$_3$	3·0$_6$	3·2$_8$	3·4$_9$	3·7$_1$	3·9$_3$	4·1$_4$	4·3$_5$
0·2	4·5$_6$	4·7$_7$	4·9$_7$	5·1$_8$	5·3$_8$	5·5$_8$	5·7$_8$	5·9$_8$	6·1$_7$	6·3$_7$
0·3	6·5$_6$	6·7$_5$	6·9$_4$	7·1$_3$	7·3$_2$	7·5	7·6$_9$	7·8$_7$	8·0$_5$	8·2$_3$
0·4	8·4$_1$	8·5$_9$	8·7$_7$	8·9$_4$	9·1$_2$	9·2$_9$	9·4$_6$	9·6$_3$	9·8	9·9$_7$
0·5	10·1$_4$	10·3	10·4$_7$	10·6$_3$	10·7$_9$	10·9$_6$	11·1$_2$	11·2$_8$	11·4$_4$	11·5$_9$
0·6	11·7$_5$	11·9$_1$	12·0$_6$	12·2$_1$	12·3$_7$	12·5$_2$	12·6$_7$	12·8$_2$	12·9$_7$	13·1$_2$
0·7	13·2$_7$	13·4$_1$	13·5$_6$	13·7	13·8$_5$	13·9$_9$	14·1$_3$	14·2$_7$	14·4$_2$	14·5$_6$
0·8	14·6$_9$	14·8$_3$	14·9$_7$	15·1$_1$	15·2$_4$	15·3$_8$	15·5$_1$	15·6$_5$	15·7$_8$	15·9$_1$
0·9	16·0$_5$	16·1$_8$	16·3$_1$	16·4$_4$	16·5$_7$	16·7	16·8$_2$	16·9$_5$	17·0$_8$	17·2
1·0	17·3$_3$	17·4$_5$	17·5$_8$	17·7	17·8$_2$	17·9$_5$	18·0$_7$	18·1$_9$	18·3$_1$	18·4$_5$
1·1	18·5$_5$	18·6$_7$	18·7$_9$	18·9	19·0$_2$	19·1$_4$	19·2$_5$	19·3$_7$	19·4$_8$	19·6
1·2	19·7$_1$	19·8$_3$	19·9$_4$	20·0$_5$	20·1$_6$	20·2$_7$	20·3$_8$	20·4$_9$	20·6	20·7$_1$
1·3	20·8$_2$	20·9$_3$	21·0$_4$	21·1$_5$	21·2$_5$	21·3$_6$	21·4$_7$	21·5$_7$	21·6$_8$	21·7$_8$
1·4	21·8$_9$	21·9$_9$	22·0$_9$	22·2	22·3	22·4	22·5	22·6$_1$	22·7$_1$	22·8$_1$
1·5	22·9$_1$	23·0$_1$	23·1$_1$	23·2$_1$	23·3	23·4	23·5	23·6	23·6$_9$	23·7$_9$
1·6	23·8$_9$	23·9$_8$	24·0$_8$	24·1$_7$	24·2$_7$	24·3$_6$	24·4$_6$	24·5$_5$	24·6$_5$	24·7$_4$
1·7	24·8$_3$	24·9$_2$	25·0$_2$	25·1$_1$	25·2	25·2$_9$	25·3$_8$	25·4$_7$	25·5$_6$	25·6$_5$
1·8	25·7$_4$	25·8$_3$	25·9$_2$	26·0$_1$	26·1	26·1$_3$	26·2$_7$	26·3$_6$	26·4$_1$	26·5$_3$
1·9	26·6$_2$	26·7	26·7$_9$	26·8$_8$	26·9$_6$	27·0$_5$	27·1$_3$	27·2$_1$	27·3	27·3$_8$
2·0	27·4$_7$	27·5$_5$	27·6$_3$	27·7$_1$	27·8	27·8$_8$	27·9$_6$	28·0$_4$	28·1$_2$	28·2

This table gives ε_v (in millivolts), the change in the potential E due to the dilution of the solution from V' c.c. to $(V' + m)$ c.c., the change being in the same direction as the change due to adding the reagent.

TABLE IIA.

$$\varepsilon_v = f^{-1}(1/x - 1) = -RT/F.\log(1 - x).$$

$x = m/V$; $T = 290°$ Abs.

x.	·00.	·01.	·02.	·03.	·04.	·05.	·06.	·07.	·08.	·09.
0·0	0·00	$0·2_5$	0·5	$0·7_6$	$1·0_2$	$1·2_8$	$1·5_5$	$1·8_1$	$2·0_8$	$2·3_6$
0·1	$2·6_3$	$2·9_1$	3·2	$3·4_8$	$3·7_7$	$4·0_6$	$4·3_6$	$4·6_6$	$4·9_8$	$5·2_7$
0·2	$5·5_8$	$5·8_9$	$6·2_1$	$6·5_3$	$6·8_6$	$7·1_9$	$7·5_3$	$7·8_7$	$8·2_1$	$8·5_6$
0·3	$8·9_2$	$9·2_8$	$9·6_4$	$10·0_1$	$10·3_9$	$10·7_7$	$11·1_6$	$11·5_5$	$11·9_5$	$12·3_6$
0·4	$12·7_7$	$13·1_9$	$13·6_2$	$14·0_5$	14·5	$14·9_5$	15·4	$15·8_7$	$16·3_5$	$16·8_3$
0·5	$17·3_3$	$17·8_3$	$18·3_5$	$18·8_8$	$19·4_1$	$19·9_6$	$20·5_2$	21·1	$21·6_9$	$22·2_9$

This table gives ε_v (in millivolts), the change in the potential E due to dilution of the solution from $(V - m)$ c.c. to V c.c., the change being in the same direction as the change due to adding the reagent.

13. There is an alternative way of allowing for the change in the volume of the solution, which is of interest in that it completes the connexion between the simple method now described and the more refined methods of Part II. Equation (19) may be written,

$$\begin{aligned} \varepsilon &= RT/F.\log V(M + m)/M(V - m) \\ &= RT/F.\log[1 + m(V + M)/M(V - m)] \end{aligned}$$

i.e., $$f(\varepsilon) = r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where $$r = M(V - m)/m(V + M) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

whence $$M = rm/[1 - m(1 + r)/V] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

[compare Part II, equation (19)], which reduces to equation (7) when m/V is negligible (constant volume). This way of allowing for the changing volume of the solution seems, however, to be less simple and expeditious than the application of the correction ε_v to the measured potential change (Sections 2 and 11), or the correction of the measured potentials according to Sections 11 and 12.

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