CXVI.—*Differential Potentiometric Titration. Part II. Refined Methods (Methods II and III).*

By Bernard Cavanagh.

1. *An Equation to the Titration Curve.*—In considering the procedure by which the highest degree of precision is to be obtained, it will be convenient to confine attention in the first place to the typical case of the titration of a chloride by means of silver nitrate.

The extension to other titrations depending on the combination or interaction of ions of like valency will then be obvious.

If s^2 is the activity product of silver chloride (so that s is practically the solubility in pure water), c' and c are the concentrations and γ' and γ the activity coefficients of silver and chloride ions, respectively,

$$c \cdot \gamma \cdot c' \cdot \gamma' = s^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

So long as the reagent can be considered to react completely with the titrated solution, no appreciable amount of silver ion remaining free, the quantity M c.c. of reagent still required must be chemically equivalent to the whole of the free chloride ion, *i.e.*, there must be Mn mg.-equivs. of free chloride ion present, n being the normality of the reagent solution. In view of the presence of a precipitate, however, it cannot be assumed that the whole of this is *in solution*, for a certain fraction of it $(1 - \theta)$, will, in general, be adsorbed by the precipitate [although in the titration of very dilute solutions, to which the refined method chiefly applies, the amount of precipitate is slight and the fraction $(1 - \theta)$ probably very small—compare preceding paper, Section 7]. The concentration c will therefore be $Mn\theta/V$, V being the volume of solution, *i.e.*,

$$Mn = cV/\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

When the end-point is closely approached, however, the free silver ion can no longer be neglected. Suppose the fraction $(1 - \theta')$ of the total free silver ion is in the adsorbed condition, then the amount of reagent required will be reduced by the corresponding amount $c'V/\theta'$, so that

$$Mn = cV/\theta - c'V/\theta' \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The potential of a (reversible) silver electrode dipping in the solution is (at constant temperature)

$$E = \text{constant} - RT/F \, . \log c'\gamma' \quad . \quad . \quad . \quad (4)$$

whilst that of a chloride electrode is

$$E = \text{constant} + RT/F \, . \log c\gamma \quad . \quad . \quad . \quad . \quad (5)$$

and from equations (1), (3), and *either* (4) or (5), one obtains rigorously,

$$\frac{Mn\sqrt{\gamma\gamma'\theta\theta'}}{2s(V_e - M)} = \sinh\left[\frac{F}{RT}(E - E_e) + \tfrac{1}{2}\log\frac{\gamma'\gamma_e}{\gamma\gamma_e'} + \tfrac{1}{2}\log\frac{\theta'\theta_e}{\theta\theta_e'} \pm \log\frac{s}{s_e}\right] \quad (6)$$

where the suffix e denotes the end-point value of a quantity, and, of the alternative signs, the positive is obtained by using equation (4) and the negative by using equation (5). In this equation, apart from s and the coefficients γ, γ', θ, θ', whose variations can be kept small, the only variables at constant temperature are M and E, and both variables may have any values, positive or negative.

This exact and complete equation to the titration curve is of the form

$$X = \sinh U \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which lends itself to mathematical treatment, with results which are immediately useful, since hyperbolic functions are fully tabulated. It is applicable (when suitable electrodes are available) to (*a*) other precipitations of insoluble uni-univalent salts if the appropriate activity product s is used; (*b*) precipitations of ν-ν-valent insoluble salts if νF and n/ν are substituted for F and n, respectively; (*c*) the titration of strong acid and alkali (in the complete absence of carbon dioxide, ammonia, quinhydrone, etc.)—the adsorption factors disappear, and s represents the activity product of water; and (*d*) the last titration in the presence of carbon dioxide, etc., with certain limitations.

2. For present purposes equation (6) may be written in the simplified form

$$Mn/2S(V_e - M) = \sinh F(E - E_e)/RT \quad . \quad . \quad (8)$$

where

$$S^2 = s^2/\gamma\gamma'\theta\theta' \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

S^2 being, as it were, an " apparent " solubility product of silver chloride (including both dissolved and adsorbed) in the solution at the stage under consideration. This approximation involves neglecting (*a*) the term $\pm \log s/s_e$, which allows for variation in s during the course of a titration (due, for instance, to change in the condition of the precipitate), and (*b*) the other two logarithmic terms.

In the case chiefly considered here, that of the silver chloride titration, it would seem reasonable to expect that the presence of the silver chloride-coated electrodes (see J., 1927, 2207) would tend to accelerate the establishment of true equilibrium (with the minimum value of s) and make s effectively a constant, and this appears to be borne out by the steadiness and permanence of the potentials rapidly set up. In the case of the bromide titration, conditions are almost equally good (with the silver bromide-coated electrodes), but in the iodide titration, in the neighbourhood of the end-point the establishment of a permanent potential is very slow.

As regards the other two neglected terms it may be noted that γ'/γ, for instance, is the ratio of the activity coefficients of univalent ions in the same solution, and that the first logarithmic term, representing half the relative change in this ratio on passing over to the end-point, will always be very small. Similar considerations apply to the second logarithmic term.

TABLE I.

Figures in heavy type, sinh $(F/RT) \, . \, E$. Figures in ordinary type, sech $(F/RT) \, . \, E$ (at 17°).

E in m.v.	·0.	·1.	·2.	·3.	·4.	·5.	·6.	·7.	·8.	·9.
	0·000	**0·004**	**0·008**	**0·012**	**0·016**	**0·020**	**0·024**	**0·028**	**0·032**	**0·036**
0	1·000	1·000	1·000	0·999$_9$	0·999$_9$	0·999$_8$	0·999$_7$	0·999$_6$	0·999$_5$	0·999$_4$
	0·040	**0·044**	**0·048**	**0·052**	**0·056**	**0·060**	**0·064**	**0·068**	**0·072**	**0·078**
1	0·999$_2$	0·999	0·998$_8$	0·998$_6$	0·998$_4$	0·998$_2$	0·998	0·997$_7$	0·997$_4$	0·997$_1$
	0·080	**0·084**	**0·088**	**0·092**	**0·096**	**0·100**	**0·104**	**0·108**	**0·112**	**0·116**
2	0·996$_8$	0·996$_5$	0·996$_1$	0·995$_8$	0·995$_4$	0·995	0·994$_6$	0·994$_2$	0·993$_8$	0·993$_3$
	0·120	**0·124**	**0·128**	**0·132**	**0·136**	**0·140**	**0·145**	**0·149**	**0·153**	**0·157**
3	0·992$_8$	0·992$_4$	0·991$_9$	0·991$_3$	0·990$_8$	0·990$_3$	0·989$_7$	0·989$_1$	0·988$_6$	0·988
	0·161	**0·155**	**0·169**	**0·173**	**0·177**	**0·181**	**0·185**	**0·189**	**0·193**	**0·197**
4	0·987$_3$	0·986$_7$	0·986$_1$	0·985$_4$	0·984$_7$	0·984	0·983$_3$	0·982$_6$	0·981$_8$	0·981$_1$
	0·202	**0·205**	**0·210**	**0·214**	**0·218**	**0·222**	**0·226**	**0·230**	**0·234**	**0·238**
5	0·980$_3$	0·979$_5$	0·978$_8$	0·977$_9$	0·977$_1$	0·976$_3$	0·975$_4$	0·974$_6$	0·973$_7$	0·972$_8$
	0·242	**0·246**	**0·251**	**0·255**	**0·259**	**0·263**	**0·267**	**0·271**	**0·275**	**0·280**
6	0·971$_9$	0·971	0·970	0·969$_1$	0·978$_1$	0·967$_1$	0·966$_1$	0·965$_1$	0·964$_1$	0·963$_1$
	0·284	**0·288**	**0·292**	**0·296**	**0·300**	**0·305**	**0·309**	**0·313**	**0·317**	**0·331**
7	0·962	0·961	0·959$_9$	0·958$_8$	0·957$_7$	0·956$_6$	0·955$_5$	0·954$_4$	0·953$_2$	0·952$_1$
	0·325	**0·330**	**0·334**	**0·338**	**0·342**	**0·347**	**0·351**	**0·355**	**0·359**	**0·304**
8	0·950$_9$	0·949$_7$	0·948$_5$	0·947$_3$	0·946$_1$	0·944$_9$	0·943$_6$	0·942$_4$	0·941$_1$	0·939$_6$
	0·368	**0·372**	**0·376**	**0·381**	**0·385**	**0·389**	**0·394**	**0·398**	**0·402**	**0·406**
9	0·938$_5$	0·937$_2$	0·935$_9$	0·934$_6$	0·933$_2$	0·931$_9$	0·930$_5$	0·929$_2$	0·927$_8$	0·926$_4$
	0·411	**0·415**	**0·419**	**0·424**	**0·428**	**0·432**	**0·437**	**0·441**	**0·446**	**0·450**
10	0·925	0·923$_6$	0·922$_2$	0·920$_7$	0·919$_3$	0·917$_8$	0·916$_4$	0·914$_9$	0·913$_4$	0·911$_9$
	0·454	**0·459**	**0·463**	**0·468**	**0·472**	**0·476**	**0·481**	**0·485**	**0·490**	**0·494**
11	0·910$_4$	0·908$_9$	0·907$_4$	0·905$_9$	0·904$_3$	0·902$_8$	0·901$_2$	0·899$_7$	0·898$_1$	0·896$_5$
	0·499	**0·503**	**0·508**	**0·512**	**0·517**	**0·521**	**0·526**	**0·530**	**0·535**	**0·539**
12	0·894$_9$	0·893$_3$	0·891$_7$	0·890$_1$	0·888$_5$	0·886$_8$	0·885$_2$	0·883$_5$	0·881$_9$	0·880$_2$
	0·544	**0·548**	**0·553**	**0·557**	**0·562**	**0·566**	**0·571**	**0·576**	**0·580**	**0·585**
13	0·878$_5$	0·876$_8$	0·875$_2$	0·873$_5$	0·871$_7$	0·870	0·868$_3$	0·866$_6$	0·864$_9$	0·863$_1$
	0·590	**0·594**	**0·599**	**0·604**	**0·608**	**0·613**	**0·618**	**0·622**	**0·627**	**0·632**
14	0·861$_4$	0·869$_6$	0·857$_9$	0·856$_1$	0·854$_3$	0·852$_5$	0·850$_8$	0·849	0·847$_2$	0·845$_4$
	0·637	**0·641**	**0·646**	**0·651**	**0·656**	**0·660**	**0·665**	**0·670**	**0·675**	**0·680**
15	0·843$_6$	0·841$_7$	0·839$_9$	0·838$_1$	0·836$_3$	0·834$_4$	0·832$_6$	0·830$_7$	0·828$_9$	0·827
	0·685	**0·690**	**0·694**	**0·699**	**0·704**	**0·709**	**0·714**	**0·719**	**0·724**	**0·729**
16	0·825$_2$	0·823$_3$	0·821$_4$	0·819$_5$	0·817$_7$	0·815$_8$	0·813$_9$	0·812	0·810$_1$	0·808$_2$
	0·734	**0·739**	**0·744**	**0·749**	**0·754**	**0·759**	**0·764**	**0·769**	**0·774**	**0·779**
17	0·806$_3$	0·804$_4$	0·802$_5$	0·800$_6$	0·798$_6$	0·796$_7$	0·794$_8$	0·792$_8$	0·790$_9$	0·789
	0·784	**0·789**	**0·794**	**0·799**	**0·804**	**0·809**	**0·815**	**0·820**	**0·825**	**0·830**
18	0·787	0·785$_1$	0·783$_1$	0·781$_2$	0·779$_2$	0·777$_3$	0·775$_3$	0·773$_4$	0·771$_4$	0·769$_4$
	0·835	**0·840**	**0·846**	**0·851**	**0·856**	**0·862**	**0·867**	**0·872**	**0·877**	**0·883**
19	0·767$_5$	0·765$_5$	0·763$_5$	0·761$_6$	0·769$_6$	0·757$_6$	0·755$_6$	0·753$_7$	0·751$_7$	0·749$_7$
	0·888	**0·894**	**0·899**	**0·904**	**0·910**	**0·915**	**0·920**	**0·926**	**0·931**	**0·937**
20	0·747$_7$	0·745$_7$	0·743$_7$	0·741$_7$	0·739$_7$	0·737$_8$	0·735$_8$	0·733$_8$	0·731$_8$	0·729$_8$
	0·942	**0·948**	**0·953**	**0·959**	**0·964**	**0·970**	**0·976**	**0·981**	**0·987**	**0·992**
21	0·727$_8$	0·725$_8$	0·723$_8$	0·721$_8$	0·719$_8$	0·717$_8$	0·715$_8$	0·713$_8$	0·711$_8$	0·709$_8$
	0,998	**1·004**	**1·009**	**1·015**	**1·021**	**1·027**	**1·032**	**1·038**	**1·044**	**1·050**
22	0·707$_8$	0·705$_8$	0·703$_8$	0·701$_5$	0·699$_8$	0·697$_8$	0·695$_8$	0·693$_8$	0·691$_8$	0·689$_8$
	1·055	**1·061**	**1·067**	**1·073**	**1·079**	**1·085**	**1·091**	**1·097**	**1·102**	**1·108**
23	0·687$_8$	0·685$_8$	0·683$_8$	0·681$_8$	0·679$_8$	0·677$_8$	0·675$_8$	0·673$_8$	0·671$_9$	0·669$_9$
	1·114	**1·120**	**1·126**	**1·132**	**1·139**	**1·145**	**1·151**	**1·157**	**1·163**	**1·169**
24	0·667$_9$	0·665$_9$	0·663$_9$	0·661$_9$	0·659$_9$	0·657$_9$	0·656	0·654	0·652	0·650
	1·175	**1·181**	**1·188**	**1·194**	**1·200**	**1·206**	**1·213**	**1·219**	**1·225**	**1·232**
25	0·648$_1$	0·646$_1$	0·644$_1$	0·642$_1$	0·640$_2$	0·638$_2$	0·636$_2$	0·634$_3$	0·632$_3$	0·630$_4$
	1·238	**1·244**	**1·251**	**1·257**	**1·264**	**1·270**	**1·276**	**1·283**	**1·289**	**1·296**
26	0·628$_4$	0·626$_4$	0·624$_5$	0·622$_5$	0·620$_6$	0·618$_7$	0·616$_7$	0·614$_8$	0·612$_8$	0·610$_9$
	1·303	**1·309**	**1·315**	**1·322**	**1·329**	**1·336**	**1·342**	**1·349**	**1·356**	**1·363**
27	0·609	0·607	0·605$_1$	0·603$_2$	0·601$_3$	0·599$_3$	0·597$_4$	0·595$_5$	0·593$_6$	0·591$_7$
	1·369	**1·376**	**1·383**	**1·390**	**1·397**	**1·403**	**1·410**	**1·417**	**1·424**	**1·431**
28	0·589$_8$	0·587$_9$	0·586	0·584$_1$	0·582$_2$	0·580$_3$	0·578$_4$	0·576$_5$	0·574$_6$	0·572$_7$
	1·438	**1·445**	**1·452**	**1·459**	**1·466**	**1·474**	**1·481**	**1·488**	**1·495**	**1·502**
29	0·570$_9$	0·569	0·567$_1$	0·565$_3$	0·563$_4$	0·561$_5$	0·559$_7$	0·557$_8$	0·556	0·554$_1$
	1·509	**1·517**	**1·524**	**1·531**	**1·539**	**1·546**	**1·553**	**1·561**	**1·568**	**1·576**
30	0·552$_3$	0·550$_4$	0·548$_6$	0·546$_8$	0·544$_9$	0·543$_1$	0·541$_3$	0·539$_5$	0·537$_7$	0·535$_9$
	1·583	**1·591**	**1·598**	**1·606**	**1·613**	**1·621**	**1·629**	**1·636**	**1·644**	**1·652**
31	0·534	0·532$_2$	0·530$_4$	0·528$_6$	0·526$_9$	0·525$_1$	0·523$_3$	0·521$_5$	0·519$_7$	0·517$_9$
	1·659	**1·667**	**1·675**	**1·683**	**1·691**	**1·698**	**1·706**	**1·714**	**1·722**	**1·730**
32	0·516$_3$	0·514$_4$	0·512$_6$	0·510$_9$	0·509$_1$	0·507$_4$	0·505$_6$	0·503$_9$	0·502$_1$	0·500$_4$
	1·736	**1·746**	**1·754**	**1·762**	**1·770**	**1·779**	**1·787**	**1·795**	**1·803**	**1·811**
33	0·498$_7$	0·497	0·495$_2$	0·493$_5$	0·491$_8$	0·490$_1$	0·488$_4$	0·486$_7$	0·485	0·483$_3$
	1·820	**1·828**	**1·836**	**1·845**	**1·853**	**1·862**	**1·870**	**1·879**	**1·887**	**1·896**
34	0·481$_6$	0·479$_9$	0·478$_2$	0·476$_6$	0·474$_9$	0·473$_2$	0·471$_5$	0·469$_9$	0·468$_2$	0·466$_6$

TABLE I (*contd.*).

E in m.v.	·0.	·1.	·2.	·3.	·4.	·5.	·6.	·7.	·8.	·9.
35	**1·904** 0·464$_9$	**1·913** 0·463$_3$	**1·922** 0·461$_6$	**1·930** 0·460	**1·939** 0·458$_4$	**1·948** 0·456$_7$	**1·956** 0·455$_1$	**1·965** 0·453$_5$	**1·974** 0·451$_9$	**1·983** 0·450$_3$
36	**1·992** 0·448$_7$	**2·001** 0·447$_1$	**2·010** 0·445$_5$	**2·028** 0·443$_9$	**2·028** 0·442$_3$	**2·037** 0·440$_7$	**2·046** 0·439$_1$	**2·055** 0·437$_5$	**2·064** 0·436	**2·073** 0·434$_4$
37	**2·083** 0·432$_8$	**2·092** 0·431$_3$	**2·101** 0·429$_7$	**2·111** 0·428$_2$	**2·130** 0·426$_6$	**2·129** 0·425$_1$	**2·139** 0·423$_6$	**2·148** 0·422	**2·158** 0·420$_5$	**2·167** 0·419
38	**2·177** 0·417$_5$	**2·186** 0·415$_9$	**2·196** 0·414$_4$	**2·206** 0·412$_9$	**2·215** 0·411$_4$	**2·225** 0·409$_9$	**2·235** 0·408$_4$	**2·245** 0·406$_9$	**2·255** 0·405$_5$	**2·264** 0·404
39	**2·274** 0·402$_5$	**2·284** 0·401	**2·294** 0·339$_6$	**2·304** 0·398$_1$	**2·314** 0·396$_6$	**2·324** 0·395$_2$	**2·335** 0·393$_7$	**2·345** 0·392$_3$	**2·355** 0·390$_8$	**2·365** 0·389$_4$
40	**2·376** 0·388	**2·386** 0·386$_5$	**2·396** 0·385$_1$	**2·407** 0·383$_7$	**2·417** 0·382$_3$	**2·428** 0·380$_9$	**2·438** 0·379$_5$	**2·449** 0·378$_1$	**2·459** 0·376$_7$	**2·470** 0·375$_3$
41	**2·481** 0·373$_9$	**2·491** 0·372$_5$	**2·502** 0·371$_1$	**2·513** 0·369$_7$	**2·524** 0·368$_4$	**2·535** 0·367	**2·546** 0·365$_6$	**2·556** 0·364$_3$	**2·567** 0·362$_9$	**2·579** 0·361$_6$
42	**2·590** 0·360$_2$	**2·601** 0·358$_9$	**2·612** 0·357$_6$	**2·623** 0·356$_2$	**2·634** 0·354$_9$	**2·646** 0·353$_6$	**2·657** 0·352$_2$	**2·668** 0·350$_9$	**2·680** 0·349$_6$	**2·691** 0·348$_3$
43	**2·703** 0·347	**2·714** 0·345$_7$	**2·726** 0·344$_4$	**2·738** 0·343$_1$	**2·749** 0·341$_8$	**2·761** 0·340$_5$	**2·773** 0·339$_3$	**2·784** 0·338	**2·796** 0·336$_7$	**2·808** 0·335$_5$
44	**2·820** 0·334$_2$	**2·832** 0·332$_9$	**2·844** 0·331$_7$	**2·856** 0·330$_4$	**2·868** 0·329$_2$	**2·881** 0·327$_9$	**2·893** 0·326$_7$	**2·905** 0·325$_5$	**2·917** 0·324$_2$	**2·930** 0·323
45	**2·942** 0·321$_8$	**2·955** 0·320$_6$	**2·967** 0·319$_4$	**2·980** 0·318$_2$	**2·992** 0·317	**3·005** 0·315$_8$	**3·018** 0·314$_6$	**3·030** 0·313$_4$	**3·043** 0·312$_2$	**3·056** 0·311
46	**3·069** 0·309$_8$	**3·082** 0·308$_6$	**3·095** 0·307$_5$	**3·108** 0·306$_3$	**3·121** 0·305$_2$	**3·134** 0·304	**3·147** 0·302$_8$	**3·160** 0·301$_7$	**3·174** 0·300$_5$	**3·187** 0·299$_4$
47	**3·200** 0·298$_2$	**3·214** 0·297$_1$	**3·227** 0·296	**3·241** 0·294$_8$	**3·255** 0·293$_7$	**3·268** 0·292$_6$	**3·282** 0·291$_5$	**3·296** 0·290$_4$	**3·309** 0·289$_3$	**3·323** 0·288$_1$
48	**3·337** 0·287	**3·351** 0·285$_9$	**3·365** 0·284$_9$	**3·379** 0·283$_8$	**3·393** 0·282$_7$	**3·408** 0·281$_5$	**3·422** 0·280$_5$	**3·436** 0·279$_4$	**3·456** 0·278$_4$	**3·465** 0·277$_3$
49	**3·479** 0·276$_2$	**3·494** 0·275$_2$	**3·508** 0·274$_1$	**3·523** 0·273$_1$	**3·538** 0·272	**3·552** 0·271	**3·577** 0·269$_9$	**3·582** 0·268$_9$	**3·597** 0·267$_9$	**3·622** 0·266$_8$
50	**3·627** 0·265$_8$	**3·642** 0·264$_8$	**3·657** 0·263$_8$	**3·672** 0·262$_7$	**3·688** 0·261$_7$	**3·703** 0·260$_7$	**3·718** 0·259$_7$	**3·734** 0·258$_7$	**3·749** 0·257$_7$	**3·765** 0·256$_7$
51	**3·780** 0·255$_7$	**3·796** 0·254$_7$	**3·812** 0·253$_8$	**3·827** 0·252$_8$	**3·843** 0·251$_8$	**3·859** 0·250$_8$	**3·875** 0·249$_9$	**3·891** 0·248$_9$	**3·907** 0·247$_9$	**3·924** 0·247
52	**3·940** 0·246	**3·956** 0·245$_1$	**3·972** 0·244$_1$	**3·989** 0·243$_2$	**4·005** 0·242$_2$	**4·022** 0·241$_3$	**4·038** 0·240$_4$	**4·055** 0·239$_4$	**4·072** 0·238$_5$	**4·039** 0·237$_6$
53	**4·106** 0·236$_7$	**4·122** 0·235$_7$	**4·139** 0·234$_8$	**4·157** 0·233$_9$	**4·174** 0·233	**4·191** 0·232$_1$	**4·208** 0·231$_2$	**4·225** 0·230$_3$	**4·248** 0·229$_4$	**4·260** 0·228$_5$
54	**4·278** 0·227$_6$	**4·216** 0·227$_7$	**4·313** 0·225$_9$	**4·331** 0·225	**4·349** 0·224$_1$	**4·367** 0·223$_2$	**4·385** 0·222$_4$	**4·403** 0·221$_5$	**4·421** 0·220$_6$	**4·439** 0·219$_8$
55	**4·457** 0·218$_9$	**4·475** 0·218$_1$	**4·494** 0·217$_2$	**4·512** 0·216$_4$	**4·531** 0·215$_5$	**4·549** 0·214$_7$	**4·568** 0·213$_8$	**4·587** 0·213	**4·606** 0·212$_3$	**4·624** 0·211$_4$
56	**4·643** 0·210$_5$	**4·662** 0·209$_7$	**4·682** 0·208$_9$	**4·701** 0·208$_1$	**4·720** 0·207$_3$	**4·739** 0·206$_5$	**4·759** 0·205$_6$	**4·778** 0·204$_8$	**4·798** 0·204	**4·817** 0·203
57	**4·837** 0·202$_4$	**4·857** 0·201$_7$	**4·877** 0·200$_9$	**4·897** 0·200$_1$	**4·917** 0·199$_3$	**4·937** 0·198$_5$	**4·957** 0·197$_7$	**4·977** 0·197	**4·998** 0·196$_2$	**5·018** 0·195$_4$
58	**5·039** 0·194$_7$	**5·059** 0·193$_9$	**5·070** 0·193$_1$	**5·101** 0·192$_4$	**5·122** 0·191$_6$	**5·142** 0·190$_9$	**5·163** 0·190$_1$	**5·185** 0·189$_4$	**5·206** 0·188$_6$	**5·227** 0·187$_9$
59	**5·248** 0·187$_2$	**5·270** 0·186$_4$	**5·291** 0·185$_7$	**5·313** 0·185	**5·334** 0·184$_3$	**5·356** 0·183$_5$	**5·378** 0·182$_8$	**5·400** 0·182$_1$	**5·422** 0·181$_4$	**5·444** 0·180$_7$
60	**5·466** 0·180	**5·489** 0·179$_2$	**5·511** 0·178$_5$	**5·533** 0·177$_8$	**5·556** 0·177$_1$	**5·578** 0·176$_4$	**5·601** 0·175$_8$	**5·624** 0·175$_1$	**5·647** 0·174$_4$	**5·670** 0·173$_7$
61	**5·693** 0·173	**5·716** 0·172$_3$	**5·739** 0·171$_6$	**5·763** 0·171	**5·786** 0·170$_3$	**5·810** 0·169$_6$	**5·833** 0·169	**5·857** 0·168$_3$	**5·881** 0·167$_6$	**5·905** 0·167
62	**5·929** 0·166$_3$	**5·953** 0·165$_7$	**5·977** 0·165	**6·001** 0·164$_4$	**6·026** 0·163$_7$	**6·050** 0·163$_1$	**6·075** 0·162$_4$	**6·099** 0·161$_8$	**6·124** 0·161$_2$	**6·149** 0·160$_5$
63	**6·174** 0·159$_9$	**6·199** 0·159$_2$	**6·224** 0·158$_6$	**6·250** 0·158	**6·275** 0·157$_4$	**6·300** 0·156$_8$	**6·326** 0·156$_1$	**6·352** 0·155$_5$	**6·377** 0·154$_9$	**6·403** 0·154$_3$
64	**6·429** 0·153$_7$	**6·455** 0·153$_1$	**6·482** 0·152$_5$	**6·508** 0·151$_9$	**6·534** 0·151$_3$	**6·561** 0·150$_7$	**6·587** 0·150$_1$	**6·614** 0·149$_5$	**6·641** 0·148$_9$	**6·668** 0·148$_3$
65	**6·695** 0·147$_7$	**6·722** 0·147$_1$	**6·749** 0·146$_6$	**6·776** 0·146	**6·804** 0·145$_4$	**6 831** 0·144$_8$	**6·859** 0·144	**3·887** 0·143$_7$	**6·915** 0·143$_1$	**6,943** 0·142$_6$
66	**6·971** 0·142	**6·999** 0·141$_4$	**7·027** 0·140$_9$	**7·056** 0·140$_3$	**7·084** 0·139$_8$	**7·113** 0·139$_2$	**7·142** 0·138$_7$	**7·171** 0·138$_1$	**7·200** 0·137$_6$	**7·229** 0·137
67	**7·258** 0·136$_5$	**7·288** 0·135$_9$	**7·317** 0·135$_4$	**7·347** 0·134$_9$	**7·376** 0·134$_3$	**7·406** 0·133$_8$	**7·436** 0·133$_3$	**7·466** 0·132$_7$	**7·496** 0·132$_2$	**7·527** 0·131$_7$
68	**7·557** 0·131$_2$	**7·588** 0·130$_7$	**7·618** 0·130$_1$	**7·649** 0·129$_6$	**7·680** 0·129$_1$	**7·711** 0·128$_6$	**7·742** 0·128$_1$	**7·774** 0·127$_6$	**7·805** 0·127$_1$	**7·837** 0·126$_6$
69	**7·868** 0·126$_1$	**7·900** 0·125$_6$	**7·932** 0·125$_1$	**7·964** 0·124$_6$	**7·996** 0·124$_1$	**8·028** 0·123$_6$	**8·061** 0·123$_1$	**8·093** 0·122$_6$	**8·126** 0·122$_1$	**8·159** 0·121$_7$
70	**8·192** 0·121$_2$	**8·225** 0·120$_7$	**8·258** 0·120$_2$	**8·292** 0·119$_8$	**8·325** 0·119$_3$	**8·359** 0·118$_8$	**8·392** 0·118$_3$	**8·426** 0·117$_8$	**8·461** 0·117$_4$	**8·494** 0·116$_9$
71	**8·529** 0·116$_5$	**8·563** 0·116	**8·598** 0·115$_5$	**8·632** 0·115$_1$	**8·667** 0·114$_6$	**8·702** 0·114$_2$	**8·737** 0·113$_7$	**8·772** 0·113$_3$	**8·808** 0·112$_8$	**8·843** 0·112$_4$
72	**8·879** 0·111$_9$	**8·915** 0·111$_5$	**8·951** 0·111	**8·987** 0·111$_6$	**9·023** 0·110$_1$	**9·059** 0·109$_7$	**9·096** 0·109$_3$	**9·133** 0·108$_8$	**9·170** 0·108$_4$	**9·207** 0·108
73	**9·244** 0·107$_6$	**9·281** 0·107$_1$	**9·318** 0·106$_7$	**9·356** 0·106$_3$	**9·394** 0·105$_9$	**9·431** 0·105$_4$	**9·470** 0·105	**9·508** 0·104$_6$	**9·546** 0·104$_2$	**9·584** 0·103$_8$
74	**9·623** 0·103$_6$	**9·662** 0·102$_9$	**9·701** 0·102$_5$	**9·740** 0·102$_1$	**9·779** 0·101$_7$	**9·819** 0·101$_3$	**9·858** 0·100$_9$	**9·898** 0·100$_5$	**9·938** 0·100$_1$	**9·978** 0·099$_7$

In most of what follows, S is treated as constant during the course of any one titration, and the approximation in this form seems to be justified by experiment (see Section 11), but this point is further discussed in Section 13.

3. Equation (7) may be regarded as a substituted form of (8), where

$$X = Mn/2S(V_e - M) = Mn/2SV \qquad (10)$$

$$U = F(E - E_e)/RT = 0{\cdot}04(E - E_e)_{17^\circ} \qquad (11)$$

so that X represents the amount of reagent required, expressed in terms of the unit $2SV/n$, whilst U represents the potential of the electrode reckoned from the end-point and in terms of the unit RT/F (which is just 25 millivolts at 17°). Similarly for an *earlier* stage (M', V', E', as in Part I),

$$X' = X + x = \sinh(U + u) \qquad (12)$$

where

$$X' = M'n/2S(V_e - M') = M'n/2SV' \qquad (13)$$

$$U + u = F(E' - E_e)/RT = F(E - E_e + \varepsilon)/RT \qquad (14)$$

and, for the differences, x and u,

$$u = F\varepsilon/RT = 0{\cdot}04\,\varepsilon_{17^\circ} \qquad (15)$$

$$\text{and } x = mnV_e/2SVV' = mn(1 + M/V)/2SV' \qquad (16)$$

which (when M/V is negligible) becomes

$$x \approx mn/2SV' \qquad (17)$$

so that u is the potential change in terms of the unit RT/F and is virtually an experimental quantity ($0{\cdot}04\,\varepsilon_{17^\circ}$), whilst x is the corresponding addition of reagent expressed in terms of the unit $2SVV'/nV_e(\approx 2SV'/n)$, and is known, at least approximately, if S is known. For the precise evaluation of x when M/V is not negligible, a rough estimate of M is required (see Section 5). Finally, if $r = X/x$,

$$r = MV'/mV_e = M(V - m)/m(V + M) \qquad (18)$$

or

$$M = rm/[1 - m(1 + r)/V] \text{ [compare Part I, equation (30)]} \qquad (19)$$

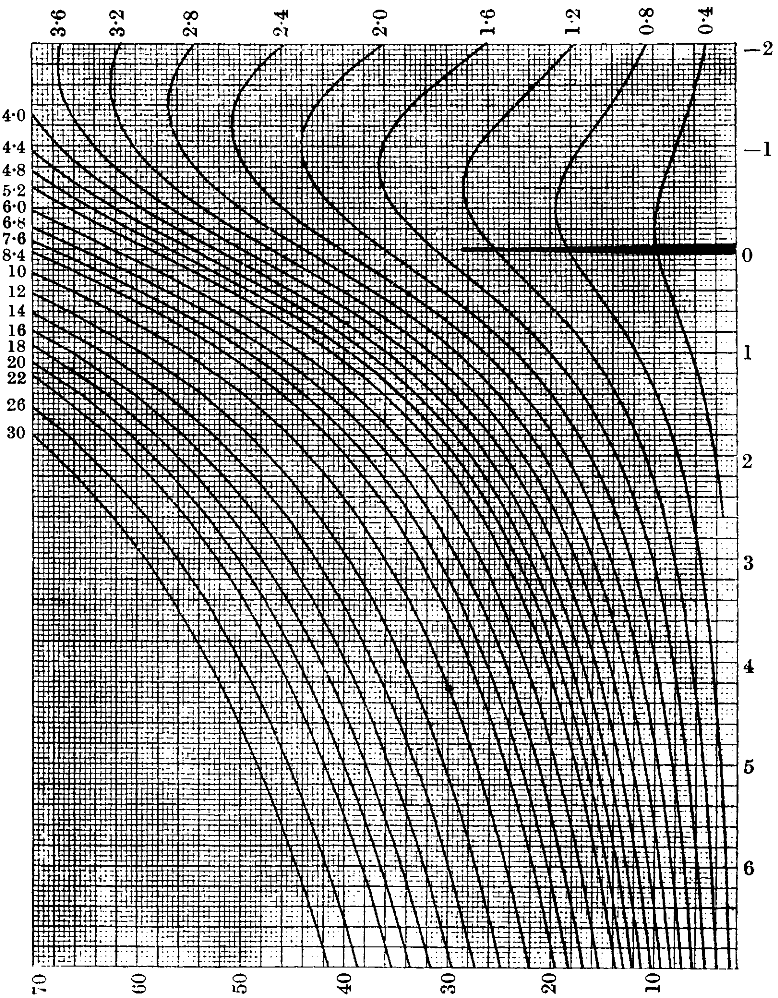
$$\approx rm(1 + m/V) \text{(when } m/V \text{ is small)} \qquad (20)$$

Thus M, and therefore the result of the titration, is obtainable from the ratio r without knowledge of S. It is alternatively obtainable from X if S is known [see (10)].

4. *Method II. Refined Method* (S *known*).—In Fig. 1, X is represented graphically as a function of x and ε_{17° ($=25\,u$). In a somewhat different manner, Fig. 2 represents the ratio r as a function of the same quantities, the curves being curves of constant r. (The experimental values of x and ε_{17° fix a point on this diagram, whose position on the scale formed by the curves gives the value

of *r*.) In this way Method I is extended to and beyond the end-point, provided x is known, *i.e.*, provided S is known.

FIG. 1.



Curves of constant x, the value of x being given by the number at the right-hand end of each curve; x is a quantity of reagent added, expressed in terms of the unit $2SVV'/nV_e(\simeq 2SV'/n)$. Ordinates represent the resulting potential change ϵ_{17° (roughly corrected to 17°) in millivolts, and abscissæ the further amount (X) of reagent still required to reach the end-point ($X = 0$), expressed in terms of the unit $2SV/n$. For a given value of x, the corresponding curve (interpolated if necessary) enables the distance (X) from the end-point to be deduced from the potential change observed.

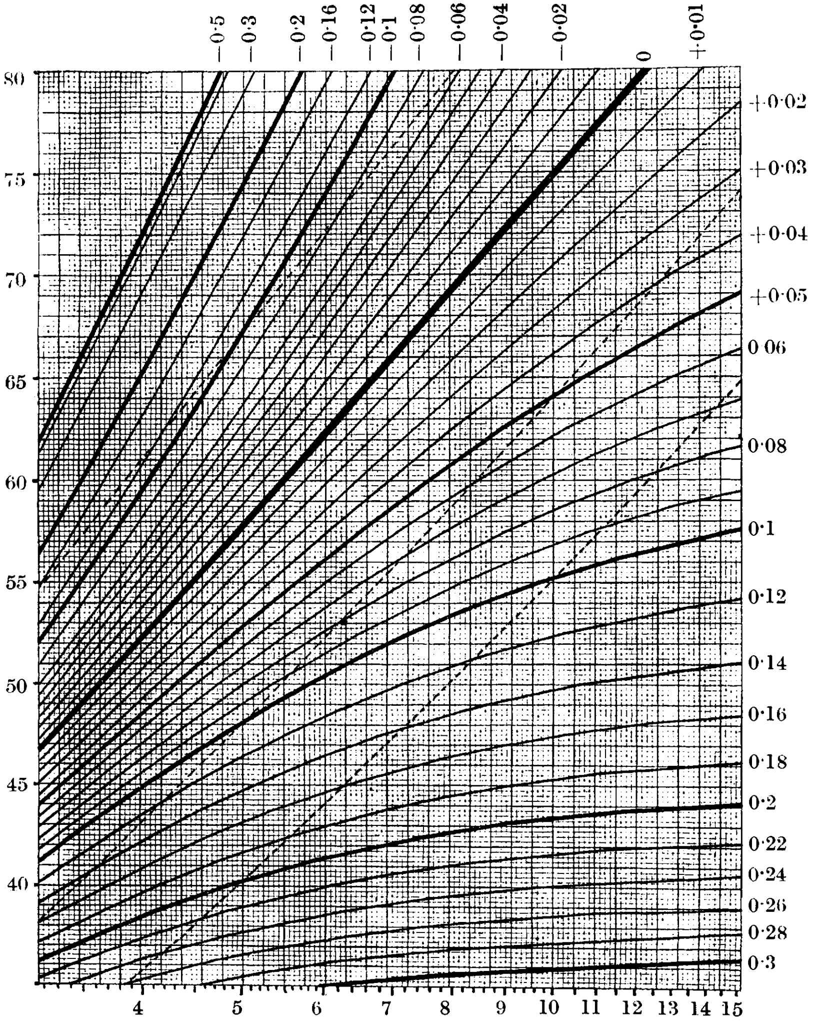
The functions represented in Figs. 1 and 2, *viz.*,

$$X = \pm\ \tfrac{1}{2}[x^2 \coth^2 u/2 - 4 \cosh^2 u/2]^{\frac{1}{2}} - x/2 \quad . \quad (21)$$

and the same divided through by x, are not convenient for the purpose of calculation, but by means of the relation

$$\operatorname{sech}\,(U + u/2) = (\sinh u/2)/\tfrac{1}{2}x \quad . \quad . \quad . \quad (22)$$

FIG. 2.



Curves of constant r, forming a numbered scale, the value of r being given at the right-hand end of each curve. Abscissæ are proportional to $\log_{10} x$, which ranges from 0·5 to 1·18, but a numbered scale of x is provided. Ordinates represent ϵ_{17°.

obtained from (7) and (12), U, and therefore x, is easily obtained. Conveniently, the substituted form (in millivolts)

$$\operatorname{sech}\,[0{\cdot}04\{(E - E_e)_{17^\circ} + \tfrac{1}{2}\varepsilon_{17^\circ}\}] = \sinh\,[0{\cdot}04(\tfrac{1}{2}\varepsilon_{17^\circ})]/\tfrac{1}{2}x \quad . \quad (22a)$$

may be employed with the aid of Table I, which contains a useful range of values of the hyperbolic sine and secant, tabulated in parallel against 25 times the argument, so that sinh u and sech u, for instance, are to be found (in heavy and ordinary type, respectively) against ε_{17°. sinh $\frac{1}{2}u$ is first found (against $\frac{1}{2}\varepsilon_{17^\circ}$) and divided by $\frac{1}{2}x$, and the quotient, which is sech $(U + \frac{1}{2}u)$, is sought in the body of the table (figures in ordinary type). Then on moving back $\frac{1}{2}\varepsilon_{17^\circ}$ millivolts in the table, sinh U, which is X, is found in the figures in heavy type.

This is the most exact form of the method, but the accuracy of the diagrams, particularly of Fig. 2, is in most cases as great as is justified by the precision with which x and ε are known.

5. There is theoretically an ambiguity in the determination, as may be seen from the symmetry of the curves in Fig. 1, or the alternative signs in equation (21). The found values of X and r might, in reality, be the values of $-(X + x)$, and $-(r + 1)$, respectively; but this would mean that the end-point had been overstepped by a very large amount, *viz.*, *more* than $\frac{1}{2}x$, and in practice the doubt will not arise, because an approximate determination will already have been made by Method I (see examples, Section 11). The latter will also enable the small correction $Mmn/2SV'V$, by which the exact form of x differs from the approximate form $mn/2SV'$, to be applied with sufficient precision (it is often negligible). The result of the titration (M_0), as determined by Method II, depends upon (*a*) the quantities $(M_0 - M)$, m, V, and n, which may be regarded as accurately known; (*b*) the measured potential change ε, in which there is an absolute uncertainty dependent on the behaviour of the electrodes (Part I, Section 3); and (*c*) the assumed value of S.

Supposing S to be correctly known, it is clear that for a given absolute error in ε_{17°, the precision of the result, in terms of concentration, will be proportional to the absolute sensitivity of ε_{17° to change in X, *i.e.*, to the steepness of the curve in Fig. 1 at the point from which the reading would be taken. It can be shown that this sensitivity (the tangent of slope of these curves, in millivolts per unit of X) is $25[\operatorname{sech} U - \operatorname{sech}(U + u)]$, which has a maximum value of 25 when $X = 0$ and x is infinite; but Fig. 1 shows that this theoretical maximum sensitivity can be closely approached if X is small and x fairly large, *i.e.*, if the final measurement of the potential of the electrode is made within about $\frac{1}{2}$ unit (of reagent) of the end-point, and x is reckoned from a stage at least 5 or 6 units earlier.

An equally sensitive potential change occurs *after the end-point has been passed, viz.*, between two stages, of which one is within $\frac{1}{2}$ unit of the end-point, and the other is at least 5 or 6 units later. This is the "ambiguous" case already mentioned. (This depends upon the use of the second half of the titration curve; but see Section 7.)

The prior use of Method I (upon the same sample of solution) enables these conditions to be fulfilled in a single titration. In this way, with ε defined to within $\pm$ 0·5 millivolt (compare Part I), the absolute uncertainty of the result of the titration can be reduced to little more than $\pm$ 0·02 unit (in terms of concentration $\pm 0{\cdot}04S$), provided S is known correctly. The *probable* error can be further reduced by making several potential measurements near the end-point, using them for independent calculations of M_0, and averaging the results.

6. Error in the assumed value of S, on the other hand, will have a one-way effect, not to be reduced by averaging. It will produce an equal relative error in x, whose effect on the result can be gauged by means of Fig. 2. In this diagram the curves are lines of constant r, and from r the result of the titration follows without reference to S. The abscissæ are proportional to $\log x$, one large square representing a change of about 5% in x, so that an error of 5% in the assumed value of S will produce an error of one large square in the abscissa of the representative point. It follows that the slope of these curves represents the error in ε which would just cancel an error of 5% in S. The effect of the possible error in S is thus obtained as an equivalent error in ε, which should of course be kept smaller than the experimental uncertainty in ε. In the diagram three dotted lines of constant X have been inserted, *viz.*, $X = 1$, $X = 0{\cdot}5$, and $X = -0{\cdot}5$ (they are roughly parallel to the line $X = r = 0$), and it is seen that the error in ε which is equivalent to a 5% error in S is about 0·35 millivolt when $X = 1$, nearly 0·7 millivolt when $X = 0{\cdot}5$, and about 1·25 millivolts at the end-point, while at half a unit past the end-point (when $X = -0{\cdot}5$) it is about 1·8 millivolts.

Thus on approaching within $\frac{1}{2}$ unit of the end-point with the object of obtaining the highest sensitivity in ε, it is necessary to know the value of S within $\pm$ 2%; and when the uncertainty in S is appreciably greater than this, the best result is obtained by not approaching the end-point so closely.

7. This method depends upon the experimental realisation of only one-half of the titration curve expressed by equation (8).

It is applicable, for instance, to acidimetry with a quinhydrone electrode, and in the presence of carbon dioxide. Its main disadvantage is the necessity for fairly precise knowledge of the constant S, in order to obtain the highest precision. When, as in the case of the silver–chloride titration for example, the whole of the titration curve conforms to equation (8), a method becomes available which is free from this disadvantage, no knowledge of S being required.

8. *Method III. Refined Method* (S *unknown*).—This depends upon the measurement of two successive potential changes, ε and ε', corresponding to two successive additions of reagent, m and m' c.c.; from these four quantities, together with the approximate volume of the solution at the intermediate stage, the result of the titration is calculated, without either assuming or determining the value of S. Thus three stages are involved, the two already considered (M', V', E', and M, V, E) to which equations (12) and (7) correspond, and a later stage ($M + m$, $V + m$, $E - \varepsilon'$), for which a similar equation may be written, *viz.*,

$$X - x = \sinh (U - u') \quad . \quad . \quad . \quad . \quad (23)$$

so that $u' = F\varepsilon/RT = 0{\cdot}04\,\varepsilon'_{17^{\circ}}$, and

$$x' = m'nV_e/2SV(V + m') \quad . \quad . \quad . \quad . \quad (24)$$

From equations (7) and (12), the relation

$$X/x = \tfrac{1}{2}[\tanh (U + \tfrac{1}{2}u) \coth \tfrac{1}{2}u - 1] \quad . \quad . \quad (25)$$

is derived, and from (7) and (23), similarly,

$$X/x' = \tfrac{1}{2}[\tanh (U - \tfrac{1}{2}u') \coth \tfrac{1}{2}u' + 1] \quad . \quad . \quad (26)$$

Between (25) and (26), U can be eliminated, giving

$$2X = (x \coth \tfrac{1}{2}\,u - x' \coth \tfrac{1}{2}\,u') \coth \tfrac{1}{2}\,(u + u') - (x - x') \quad . \quad (27)$$

By substituting for X, x, x', u, and u', making use of the function tabulated in Table I (Part I), and dividing throughout by nV_ϵ/SV^2, one obtains

$$\frac{M}{1 + M/V} = [1 + 2f(\varepsilon + \varepsilon')]\left[\frac{m\,.\,f(\varepsilon)}{1 - m/V} - \frac{m'\,.\,f(\varepsilon')}{1 + m'/V}\right] + f(\varepsilon + \varepsilon')\left[\frac{m}{1 - m/V} - \frac{m'}{1 + m'/V}\right] \quad . \quad . \quad (28)$$

When the values of ε, ε', m, m', and the approximate value of V are inserted (from experiment) this equation reduces to a linear equation for M (which gives the result of the titration).

In practice ($\varepsilon + \varepsilon'$) is of the order of 100 millivolts or more, and m and m' are not large fractions of V, so approximation gives

$$M\ (\text{app.}) = m_c\,.\,f(\varepsilon) - m_c'f(\varepsilon') \quad . \quad . \quad . \quad (29)$$

where $m_c = m + m^2/V$, and $m_c' = m' - m'^2/V$. The small terms neglected in this approximation are almost exactly

$$(\textit{Small terms}) \quad M^2\,(\text{app.})/V + [m^2/V^2 \,.\, m_c \,.\, f(\varepsilon) - m'^2/V^2 \,.\, m_c' \,.\, f(\varepsilon')] + f(\varepsilon + \varepsilon')[2M\,(\text{app.}) + (m_c - m_c')] \quad . \quad (30)$$

In the examples given in Section 11, these small terms are in each case roughly evaluated and added to the approximate result obtained by the use of (29), but, as may be seen, the correction is only of the same order of magnitude as the uncertainty of the result.

9. Alternatively a graphical method of calculation may be used. When divided throughout by $2x$, equation (27) gives (in terms of the function f)

$$r = X/x = [1 + 2f(\varepsilon + \varepsilon')][f(\varepsilon) - a \,.\, f(\varepsilon')] + f(\varepsilon + \varepsilon')[1 - a] \quad . \quad (31)$$

where $a = x'/x = m'(V - m)/m(V + m')$. This relation can be expressed graphically for any fixed value of a. Fig. 3 represents the case where $x' = x$, and

$$r = [1 + 2f(\varepsilon + \varepsilon')][f(\varepsilon) - f(\varepsilon')] \quad . \quad . \quad . \quad (32)$$

If the second addition of reagent (m') is made such that

$$m' = m/(1 - 2m/V) \quad . \quad . \quad . \quad . \quad . \quad (33)$$

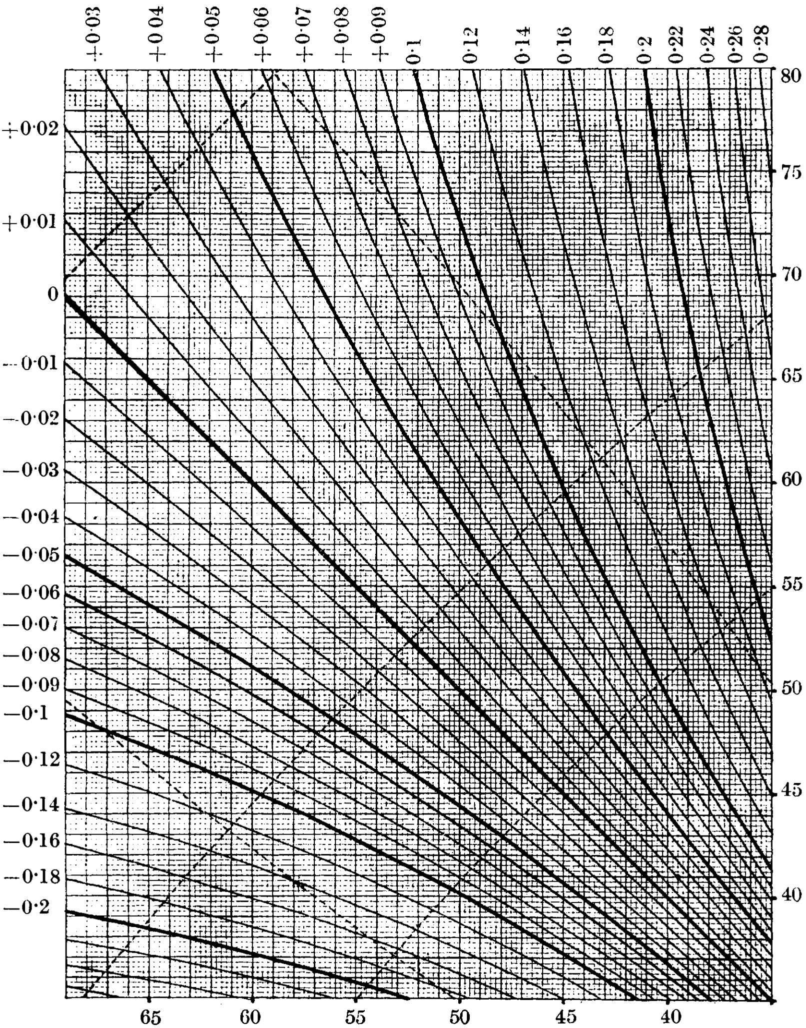
the condition $x = x'$ is fulfilled, and the measured potential changes ε and ε' (corrected to 17°) then fix a point on this diagram, whose position on the scale formed by the curves gives the value of r; whence the result of the titration follows by equation (19) or (20).

10. *Conditions for Precision of Method III.*—If the second of the three stages concerned is within $\frac{1}{2}$ unit of the end-point (on either side of it), and the other two stages are at least 5 units earlier and later, respectively, both the potential changes will be of high sensitivity (see Section 5), and it is obvious that these are the conditions for high precision by this method (but see Section 13). Knowledge of the value of the constant S is not required, although a rough estimate of it is useful in arranging the conditions. It is really only necessary, however, that the intermediate stage should be as near as can be judged (by use of Method I) to the end-point, and that the two potential changes should be of the order of 50 millivolts or more.

11. *Results.*

Some examples of the application of Method III (chiefly) are recorded below. Apparatus and materials were essentially as in Part I, and the gradual fall of the potential of the quinhydrone electrode, due to dilution of the acid present by the added reagent, was allowed for by correcting the measured potentials to a constant volume such as 100 or 1000 c.c. (according to Part I, Section 11). This correction is given under the heading "Corr."

FIG. 3.



Curves of constant r, forming a numbered scale (the value of r is given at the right-hand end of each curve). Subject to the condition that $x' = x$, *i.e.*, that $m' = m/(1 - 2m/V)$, the ordinate represents the first of the two successive potential changes ($\epsilon_{17°}$), and the abscissa the second ($\epsilon'_{17°}$), and the position of the point so defined, on the scale of r formed by the curves, gives the value of r. The dotted lines are typical lines of constant X ($X = +0·5$ and $X = -0·5$) and of constant x ($x = 3$, 4, and 8).

Example 1. 1000 C.c. $N/1000$-KCl titrated by $N/100$-$AgNO_3$ (temp. $\approx$ 14·5°).

(Actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/2000$.)

By Method I (see Part I, Section 10, Example 3) from stages 0, I, and II, the number (M) of c.c. of reagent still required at Stage II, is found to be about 13·7. Hence 13 c.c. are now added, and afterwards a further 12 c.c. (the unit $2SV'/n$ being roughly 2·5 c.c.); the corresponding potentials are measured (Stages III and IV) and (together with E_{II}) corrected (*a*) to 17° by addition of the small correction, $E/120$ (see Part I, Section 5), and (*b*) to 1000 c.c. volume as regards the quinhydrone electrode.

Stage.	$M_0 - M$.	$\frac{M_0 - M}{1000}$.	Corr.	E (expt.)	$E_{17°}$.	E (corr.)
II	85	0·085	2·0	172·2	173·6	175·6
III	98	0·098	2·3	118·1	119·1	121·4
IV	110	0·110	2·6	58·3	58·8	61·4

Then from the potential changes, ε and ε' (Stages II—III and III—IV, respectively), and the corresponding additions of reagent, m and m', together with the approximate volume $V(= 1100$ at Stage III), the amount of reagent still required at Stage III [M (app.)] is calculated by equation (29), and so by addition of ($M_0 - M$), which is 98 at Stage III, the result M_0 (app.) is obtained. The small terms are then approximately evaluated by the formula (30) and added, to obtain the final M_0.

Stages.	ϵ.	$f(\epsilon)$.	m.	$\pm m^2/V$.	m_c.	$m_c \, . \, f(\epsilon)$.	$m^2/V^2 . \, m_c . \, f(\epsilon)$.
II—III	54·2	0·1292	13	+0·15	13·15	1·699	0·0002
III—IV	60·0	0·0998	12	−0·13	11·87	1·185	0·0001
		$f(\epsilon + \epsilon') =$ 0·0105		$(m_c - m'_c) =$	1·28	M (app.) = 0·51$_5$ M_0 (app.) = 98·51$_5$	Diff. = 0·0001

Small terms : {0·0003 + 0·0001 + 0·0105[2 × 0·515 + 1·28]} $\approx$ 0·025.

M_0 = 98·54. Error = +0·04%

Example 2. 100 C.c. $N/1000$-KCl titrated by $N/1000$-$AgNO_3$ (temp. $\approx$ 20°).

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

By Method I (see Part I, Example 4) the amount of reagent still required at Stage II is found to be about 24 c.c.; 21 c.c. are added (the unit $2SV/n$ being roughly 5 c.c.) followed by 4 c.c. and then a further 25 c.c., the corresponding potentials (Stages III, IV, and V) being measured, and corrections being made to 17° and 100 c.c.

Stage.	$M_0 - M$.	$\frac{M_0 - M}{100}$.	Corr.	E (expt.)	E_{17°.	E (corr.)
II	75	0·75	14·0	190·4	188·5	202·5
III	96	0·96	16·8	139·8	138·4	155·2
IV	100	1·0	17·3	120·5	119·3	136·6
V	125	1·25	20·3	68·4	67·7	88·0

Two independent calculations are now made, from Stages II—III—V and from Stages II—IV—V, respectively, each as in Example 1, and the results averaged.

(*a*) From Stages II, III, and V. $V = 196$ (Stage III).

Stages.	ϵ.	$f(\epsilon)$.	m.	$\pm m^2/V$.	m_c.	$m_c . f(\epsilon)$.	$m^2/V^2 . m_c . f(\epsilon)$.
II—III	47·3	0·1776	21	+2·25	23·25	4·13	0·047$_5$
III—V	67·2	0·0730	29	−4·29	24·71	1·80$_4$	0·039$_5$
	$f(\epsilon + \epsilon') = 0{\cdot}0104$			$(m_c - m'_c) = -1{\cdot}46$		M (app.) = 2·32$_6$ M_0 (app.) = 98·32$_6$	Diff. = 0·008

Small terms : $[0{\cdot}028 + 0{\cdot}008 + 0{\cdot}0104\{2 \times 2{\cdot}33 - 1{\cdot}46\}] \approx 0{\cdot}069$

$M_0 = 98{\cdot}39_5$. Error = − 0·11%.

(*b*) From Stages II, IV, and V. $V = 200$ (Stage IV).

II—IV	65·9	0·0772	25	+3·13	28·13	2·17$_1$	0·034
IV—V	48·6	0·1671	25	−3·13	21·87	3·65$_5$	0·057
	$f(\epsilon + \epsilon') = 0{\cdot}0104$			$(m_c - m'_c) =$ 6·26		M (app.) = −1·48$_4$ M_0 (app.) = 98·51$_6$	Diff. = −0·023

Small terms : $\{0{\cdot}011 - 0{\cdot}023 + 0{\cdot}0104[2 \times (-1{\cdot}48) + 6{\cdot}26]\} \approx 0{\cdot}02_2$

$M_0 = 98{\cdot}54$. Error = +0·04%.

Mean result from (*a*) and (*b*) : M_0 (mean) = 98·47. Error = −0·03%.

Example 3. 1000 C.c. $N/10{,}000$-KCl titrated by $N/1000$-$AgNO_3$ (temp. ≈ 17°).

(Actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/15{,}000$.)

The unit $2SV/n$ being approximately 25 c.c., Method I is inapplicable from the commencement, the end-point being too near. The first approximation is therefore obtained by Method II, on the assumption that the unit is about 25 c.c.; 15 c.c. of reagent are added and the initial potential is measured. Then 50 c.c. (2 units) more are added and the second potential is measured. The potentials are corrected to 1000 c.c. as regards the quinhydrone electrode, and subtracted. From the curve, $x = 2$ (Fig. 1), the value of X corresponding to the change of potential (ε) is read, and multiplied by 25, thus giving M (app.).

Stage.	$M_0 - M$.	$\frac{M_0 - M}{1000}$.	Corr.	E (expt.).	E (corr.).	ϵ.	m.	x.	x'.	M (app.).
0	15	0·015	0·4	167·9	168·3					
I	65	0·065	1·6	145·5	147·1	21·2	50	2	1·25	31·3

Addition of the correction ($MM'/V' \approx 2{\cdot}5$) for change in the unit gives $M = 33{\cdot}8$, $M_0 = 98{\cdot}8$.

Assuming, therefore, that about 34 c.c. of reagent are still required at Stage II, one adds, first, 25 c.c., then successively 10 c.c., 10 c.c., and 100 c.c., measuring the four corresponding potentials and correcting as before.

Stage.	$M_0 - M$.	$\frac{M_0 - M}{1000}$.	Corr.	E (expt.).	E (corr.).
II	90	0·09	2·2	126·0	128·2
III	100	0·10	2·4	116·1	118·5
IV	110	0·11	2·6	107·2	109·8
V	210	0·21	4·8	64·0	68·8

Then three calculations are made (from 0—II—V, from 0—III—V, and from 0—IV—V, respectively), each as in Example 1, and the results averaged.

(a) From Stages 0, II, and V. $V = 1090$ (Stage II).

Stages.	ϵ.	$f(\epsilon)$.	m.	$\pm m^2/V$.	m_c.	$m_c \, . f(\epsilon)$.	$m^2/V^2 \, . m_c f(\epsilon)$.
0—II	40·1	0·2517	75	+ 5·16	80·16	20·18	0·10
II—V	59·4	0·1025	120	−13·21	106·79	10·95	0·13
	$f(\epsilon + \epsilon') = 0{\cdot}019$			$(m_c - m'_c) = -26{\cdot}6$		M (app.) = 9·23	Diff. = −0·03
						M_0 (app.) = $99{\cdot}2_3$	

Small terms : $\{0{\cdot}08 - 0{\cdot}03 + 0{\cdot}019[2 \times 9{\cdot}2 - 26{\cdot}6]\} \approx -0{\cdot}11$

$M_0 = 99{\cdot}1$. Error = +0·06%.

(b) From Stages 0, III, and V. $V = 1100$ (Stage III).

0—III	49·8	0·1585	85	+ 6·57	91·57	14·51	0·09
III—V	49·7	0·1587	110	−11·00	99·00	15·71	0·16
	$f(\epsilon + \epsilon') = 0{\cdot}019$			$(m_c - m'_c) = -7{\cdot}4$		M (app.) = −1·2	Diff. = −0·07
						M_0 (app.) = 98·8	

Small terms : $\{0{\cdot}00 - 0{\cdot}07 + 0{\cdot}019[2 \times (-1{\cdot}2) - 7{\cdot}4]\} \approx -0{\cdot}26$

$M_0 = 98{\cdot}5_4$. Error = +0·04%.

(c) From Stages 0, IV, and V. $V = 1110$ (Stage IV).

0—IV	58·5	0·1066	95	+8·13	103·13	10·99	0·08
IV—V	41·0	0·2407	100	−9·01	90·99	21·90	0·18
	$f(\epsilon + \epsilon') = 0{\cdot}019$			$(m_c - m'_c) = +12{\cdot}1$		M (app.) = $-10{\cdot}9_1$	Diff. = −0·10
						M_0 (app.) = $99{\cdot}0_9$	

Small terms : $\{0{\cdot}11 - 0{\cdot}10 + 0{\cdot}019[2 \times (-10{\cdot}9) + 12{\cdot}1]\} \approx -0{\cdot}17$

$M_0 = 98{\cdot}9_2$. Error = $+0{\cdot}4_2$%.

Mean result from (a), (b), and (c) : M_0 (mean) = $98{\cdot}8_5$. Error = $+0{\cdot}3_5$%.

12. *Determination of the End-point Potential, and of the Constant* S.—The result of the titration is obtained without calculating either of these quantities. Both, however, may be calculated from the measurements if they are of interest, and this is probably the most exact method of determining them. Various formulæ might be given for the calculation of E_e. For instance from equation (25) the relation

$$f[\varepsilon_{17^\circ} + 2(E - E_e)_{17^\circ}] = [f(\varepsilon) - r]/(1 + 2r) \quad . \tag{34}$$

or, alternatively,

$$f(2E - 2E_e)_{17^\circ} = [1 + f(\varepsilon_{17^\circ})][f(\varepsilon_{17^\circ})/r - 1]/[1 + 2f(\varepsilon_{17^\circ})] \tag{34a}$$

is obtained, which enables E_e to be evaluated by means of Table I (Part I), the value of r being obtained either directly by equation (31), or from the result of the titration and equation (19).

When E_e is known, U is known, and S can then be calculated by the formula

$$2S = \frac{n(m + m')}{(V - m)\sinh(u + U) + (V + m')\sinh(u' - U)} \tag{35}$$

$$= \frac{n(m + m')}{(V - m)\sinh[0{\cdot}04\{\varepsilon_{17^\circ} + (E - E_e)_{17^\circ}\}] + (V + m')\sinh[0{\cdot}04\{\varepsilon'_{17^\circ} - (E - E_e)_{17^\circ}\}]} \tag{36}$$

the hyperbolic sines being obtained from Table I (this Part).

The precise measurement of E_e under standard conditions is of interest in connexion with " absolute " methods of potentiometric titration (see Part I and previous paper, *loc. cit.*), whilst the value of S is required in Method II, described above.

13. *Precision of Method III, and Dependence on the Constancy of* S.—Analytically the small error (dM) in M due to small errors, du and du', in u and u', can be estimated by the equation

$$\frac{n}{2SV} \, . \, dM = \frac{p \, . \, du' - du}{\Delta \operatorname{sech} U + p\Delta' \operatorname{sech} U} \quad . \quad . \quad . \tag{37}$$

where $\Delta \operatorname{sech} U$ and $\Delta' \operatorname{sech} U$ represent [$\operatorname{sech} U - (V/V') \operatorname{sech} (U + u)$] and [$\operatorname{sech} U - V/(V + m') . \operatorname{sech} (U - u)$] respectively, and

$$p = [\tanh (U + u) - \tanh U]/[\tanh U - \tanh (U - u)].$$

Thus p represents the relative importance of equal errors in u and u' (p is also the expression for the slope of the curves in Fig. 3). The conditions for high precision are easily deduced from equation (37). Under the ideal conditions ($X = 0$ and both x and x' are infinite), it reduces to $(n/2SV) \, . \, dM = \frac{1}{2} (du' - du)$, showing that (under these conditions) equal errors in u and u' will cancel if in the same direction, and if in opposite directions will have the same effect as a single error of the same magnitude as either in u in Method II. Thus the minimum absolute uncertainty is the same as for Method II, but the probable error is less, and also the precision is not dependent on knowledge of S.

With regard to the effect of slight variation of S during the course of a titration, it can be shown that if it changes by 1% between the first and second of the three stages the effect will be equivalent to an error of about 0·25 millivolt in the first potential change (ε); and similarly as between the second and third stages. The effects on the result are in the same direction when the variations in S are in the same direction.

Summary.

The methods described depend on the changes of the potential of the indicator-electrode, not on the particular values of the potential. Method I (see Part I) is applicable in all ordinary

cases, where an absolute uncertainty of the order of one-fifth or one-seventh of the solubility of silver chloride (or the corresponding constant) is permissible. A first tentative addition of reagent is made, and from the resulting potential change an approximate estimate of the amount still required is obtained by the use of Table I. Nearly this amount is then added, and the small residual deficiency is precisely evaluated by the same means. Precision depends chiefly on the closeness of approach to the end-point, which in the most dilute solutions is limited by the incompleteness of the reaction (which would invalidate the method) in the neighbourhood of the end-point.

The other two methods (Part II), essentially for very dilute solutions, are of a somewhat higher order of absolute precision. Method II is the extension of Method I to and beyond the end-point, depending upon fairly precise knowledge of the constant *S* (the solubility of silver chloride in the solution), and the use either of a set of accurately drawn curves (Figs. 1 and 2) or of a numerical table (Table I, Part II).

Method III is independent of knowledge of the constant *S*. From the two potential changes produced by two successive additions of reagent, the result of the titration is accurately obtained, either by a simple calculation with the aid of Table I or by the use of a set of curves (Fig. 3).

Methods II and III depend upon the conformity of the titration curve (on one side of the end-point, for Method II; on both sides for Method III) to a slightly simplified form of a general equation (Part II, Section 1) deduced (on the assumption of a reversible electrode) on thermodynamic grounds only.

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