

Automatic Titration by Stepwise Addition of Equal Volumes of Titrant

Part VII.* Potentiometric Precipitation Titrations

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The method used throughout this series to add the titrant stepwise with equal volumes each time is well suited to precipitation titrations. The advantage that one has to wait for equilibrium to be reached at only a few points is of special importance.

Two methods for calculation of the equivalence volume in precipitation titrations have been evaluated. One is based on the solution of a set of linear equations and the other is an extended version of the Gran I method. The methods are characterised by the following facts: (1) side-reactions can be accounted for; (2) the values of the solubility product and the stability constants of complexes may be unknown; (3) the solutions may be so dilute that a complete precipitation is not obtained; and (4) no accurate calibration of the electrode couple is required.

The calculation methods have been tested on the determination of chloride by titration with silver nitrate solution. The two methods agree closely and the errors in the calculations are negligible. The over-all errors in the determinations are 0.1–0.2% at chloride concentrations down to 10^{-4} M. At lower concentrations the relative errors are greater.

The methods have also been tested on the determination of sodium fluoride with lanthanum nitrate in (a) neutral and unbuffered solution, (b) acidic solution, (c) solution buffered with acetic acid - acetate and (d) solution buffered with formic acid - formate. The calculations were performed on experimental curves according to Lingane. For (a) and (b) good agreement between calculated and expected values were obtained. In the acetate-buffered solution too high a value was obtained in spite of the fact that acetate and mixed acetate - fluoride complexes were considered. For (d) the buffer capacity was too small to give satisfactory results.

Keywords: Gran I method; potentiometric precipitation titrations; sodium fluoride determination; chloride determination

Previous parts of this series have covered calculations of the equivalence volume in acid-base titrations. In Part III¹ a program, EKVOL, was presented, which utilises a system of linear equations with a maximum of three unknown variables. In Parts V² and VI³ a method was described based on an extended Gran I method.⁴ In order to make it easy to refer to the new method we have named it QUOTEQ.

These two methods can be used also for the calculation of the equivalence volume in a precipitation titration. A program that could be used for all types of precipitation titrations would be difficult to develop. It is therefore more practical to adapt a program to the actual problem. In order to illustrate the method of evaluation of a precipitation titration, we have chosen a special example, namely the titration of a chloride ion solution with a standard silver nitrate solution in which the course of the titration is followed with a silver-silver chloride electrode.

The titrant is added stepwise with equal volumes each time (a principle used throughout this series). This method is also well suited for precipitation titrations. The advantage that it is necessary to wait for equilibrium to be reached at only a few points is of special importance in this type of titration.

If the reaction were complete and as simple as $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl(s)}$, the calculation of the equivalence volume would be very simple. Before the equivalence point, the chloride ion concentration would decrease linearly with the addition of titrant and after the equivalence point the silver ion concentration would increase linearly with the addition of titrant.

* For details of Part VI of this series, see reference list, p. 1118.

A graph of $(V_0 + V)[\text{Cl}^-]$ versus V would be a straight line, intersecting the volume axis at $V = V_e$, where V_0 is the volume of the sample solution at the start of the titration, V is the volume of the titrant added and V_e is the equivalence volume. After the equivalence point a graph of $(V_0 + V)[\text{Ag}^+]$ would be a straight line intersecting the volume axis and the graph of $(V_0 + V)[\text{Cl}^-]$ versus V at $V = V_e$.

This method of determining the equivalence volume has been described by Gran.⁵ It has to be assumed that the precipitation is complete and that no side-reactions take place. Such an assumption is virtually true if the initial concentration of chloride ions in the titrand is 10^{-3} M or higher. This is illustrated in Fig. 1 for the titration of 100 ml of 0.001 M chloride solution with 0.01 M silver nitrate solution. The S-shaped graph shows e.m.f. values versus titrant volumes. The corresponding Gran II plot is a straight line intersecting the volume axis at $V = 10.07$ ml close to the correct equivalence volume of 10.04 ml.

This method of evaluation gives less accurate results when a 10^{-4} M chloride solution is titrated in the same manner with 0.001 M silver nitrate solution. It is difficult to observe a potential jump at the equivalence point and the Gran II plot gives an erroneous result (Fig. 2). This is due to the fact that precipitation at the equivalence point is not complete. The solubility product of silver chloride is about $10^{-9.4}$ and therefore about 20% of the chloride ions are not precipitated at the equivalence point if the initial chloride ion concentration is 10^{-4} M. A correct evaluation method has to consider this fact and also take into account the side-reactions that may occur.

The evaluation methods derived were also tested on the titration of sodium fluoride with lanthanum nitrate using experimental curves according to Lingane.⁶

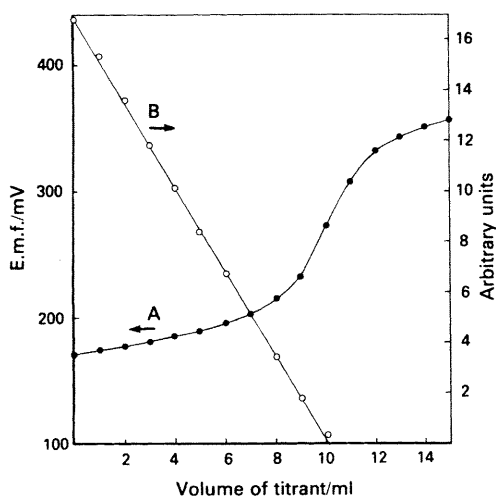


Fig. 1. Titration of 100 ml of 1.005×10^{-3} M chloride ion solution with 1.000×10^{-2} M silver nitrate solution. Graph A is e.m.f. in mV (left-hand scale) versus added volume of titrant; graph B is the Gran II plot in arbitrary units (right-hand scale).

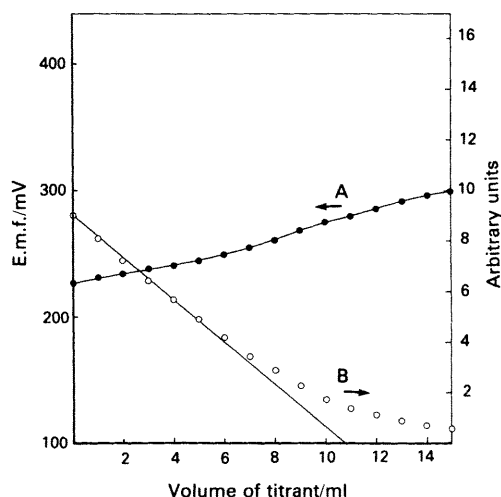


Fig. 2. Titration of 100 ml of 1.005×10^{-4} M chloride ion solution with 1.000×10^{-3} M silver nitrate solution. Graph A is e.m.f. in mV (left-hand scale) versus added volume of titrant; graph B is the Gran II plot in arbitrary units (right-hand scale). The straight line through the first few points gives a very imprecise value of V_e .

Theoretical

The Titration Curve

Assume that V_0 ml of a C_0 M chloride solution is titrated with C_B M silver nitrate solution. After addition of V ml of titrant, P mmol of silver chloride have been precipitated and therefore

$$(V_o + V)[\text{Cl}^-]_{\text{tot}} = V_o C_o - P \quad \dots \quad (1)$$

$$(V_o + V)[\text{Ag}^+]_{\text{tot}} = V C_B - P \quad \dots \quad (2)$$

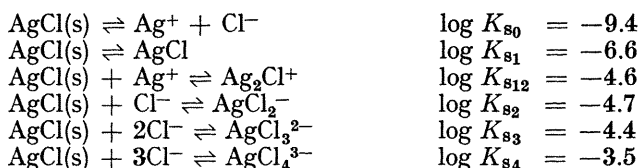
where $[\text{Cl}^-]_{\text{tot}}$ and $[\text{Ag}^+]_{\text{tot}}$ are the total concentrations of chloride and silver ions in the solution. If V_e is the equivalence volume, then by definition

$$V_o C_o = V_e C_B \quad \dots \quad (3)$$

Combination of equations (1), (2) and (3) gives

$$V - \frac{V_o + V}{C_B} ([\text{Ag}^+]_{\text{tot}} - [\text{Cl}^-]_{\text{tot}}) - V_e = 0 \quad \dots \quad (4)$$

The following equilibrium conditions are valid⁷:



By combining these equilibrium conditions with equation (4) the following expression is obtained (for convenience, charge signs have been omitted):

$$V - \frac{V_o + V}{C_B} \cdot [\text{Ag}] (1 + K_{s12}) + \frac{V_o + V}{C_B} \cdot [\text{Cl}] (1 + K_{s2} + 2K_{s3} [\text{Cl}] + 3K_{s4} [\text{Cl}]^2) - V_e = 0 \quad \dots \quad (5)$$

The values of the parentheses are close to unity. In other types of titrations where the constants are unknown, it may be safe to consider the constants for the first complexes, *i.e.*, K_{s12} and K_{s2} . The concentrations of the higher complexes usually are too low to interfere in any practical titration.

If the concentration of free silver ions is measured, $K_{s0}/[\text{Ag}]$ is substituted for $[\text{Cl}]$ and equation (5) becomes

$$V - \frac{V_o + V}{C_B} \cdot K_1 [\text{Ag}] + \frac{V_o + V}{C_B} \cdot \frac{K_2}{[\text{Ag}]} - V_e = 0 \quad \dots \quad (6)$$

where $K_1 = (1 + K_{s12}) \approx 1$ and $K_2 = (1 + K_{s2})K_{s0} \approx K_{s0}$. In equation (6) K_1 , K_2 and V_e are unknown, V_o , V and C_B are known and $[\text{Ag}]$ is measured.

If a silver electrode combined with a reference electrode is used for following the titration, the e.m.f. (E) between the electrodes will depend on the concentration of silver ions in the solution:

$$E = E'_o + Q \log [\text{Ag}] \quad \dots \quad (7)$$

where E'_o is the conditional standard potential of the electrode pair, including the reference electrode potential and the activity coefficient, Q is the Nernst factor $= (RT \ln 10)/F = 59.158$ at 25 °C and $[\text{Ag}]$ is the silver ion concentration (not the activity), as the electrode pair is calibrated using solutions with known silver ion concentrations. This means that the activity factors must be kept constant, *i.e.*, it is necessary to carry out the titration in a solution of constant ionic strength. From equation (7) we obtain

$$[\text{Ag}] = 10^{(E - E'_o)/Q} \quad \dots \quad (8)$$

As an actual value of E'_o may be difficult to determine, it is practical to assume that the values of the silver ion concentrations calculated from equation (8) may contain a constant but unknown error, so that

$$[\text{Ag}] = f[\text{Ag}'] \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (9)$$

where $[\text{Ag}]$ is the correct silver ion concentration and $[\text{Ag}']$ is the silver ion concentration obtained by using an incorrect value of E'_0 . If this expression is inserted in equation (6), the following equation is obtained:

$$\frac{(V_0 + V)[\text{Ag}']}{C_B} \cdot K'_1 - \frac{V_0 + V}{[\text{Ag}']C_B} \cdot K'_2 + V_e - V = 0 \quad \dots \quad \dots \quad (10)$$

where $K'_1 = K_1 f$ and $K'_2 = K_2/f$.

Calculation of the Equivalence Volume

Equation (10) may be used for calculating the equivalence volume. The quantities V_0 , V and C_B are known and $[\text{Ag}']$ is measured. Two different calculation procedures, EKVOL and QUOTEQ, have been used for the evaluation. The procedures require pairs of measurements (volumes of titrant *versus* e.m.f.) plus initial volume, titrant concentration, temperature and a rough value of the conditional standard potential.

Calculation with the aid of EKVOL

No preliminary estimates of equivalence volume or of the constants K'_1 and K'_2 are required in this procedure. Equation (10) is a linear equation with three unknowns, K'_1 , K'_2 and V_e . To determine the values of these unknowns a set of at least three equations is required, *i.e.*, at least three data pairs (V_i ; $[\text{Ag}']_i$) are needed. With more than three measurement points, a least-squares treatment should be used.

For a certain data pair (V_i ; $[\text{Ag}']_i$) equation (10) may be written as

$$A(1,i) K'_1 + A(2,i) K'_2 + A(3,i) V_e + A(4,i) = 0 \quad \dots \quad \dots \quad (11)$$

where

$$\begin{aligned} A(1,i) &= (V_0 + V_i)[\text{Ag}']_i/C_B \\ A(2,i) &= -(V_0 + V_i)/([\text{Ag}']_i C_B) \\ A(3,i) &= 1 \\ A(4,i) &= -V_i \end{aligned}$$

The computer program EKVOL¹ can carry out these calculations. Initially it calculates the different $[\text{Ag}']_i$ values using a rough value of E'_0 . The values of V_0 , V_i , C_B and the calculated $[\text{Ag}']_i$ are then used to calculate the coefficients in the set of linear equations (11). A least-squares procedure is then used to calculate the coefficients in the normal equations and these equations are solved.

The resulting values of K'_1 , K'_2 and V_e include random errors and some systematic errors derived from errors in V_0 , V , E'_0 and E . Accurate pipetting will make volume errors practically negligible. A constant error in E'_0 will influence the values of K'_1 and K'_2 but not the value of the equivalence volume, V_e . As $K'_1 K'_2 = K_1 f K_2 / f$, it follows that $K'_1 K'_2 = K_1 K_2$, which means that the solubility product, K_{s0} , is roughly equal to $K_1 K_2$.

Calculation with the aid of QUOTEQ

The titration data are divided into two groups: (1) before the equivalence point where $[\text{Ag}]$ is small and thus the term $(V_0 + V)K'_1[\text{Ag}']/C_B$ in equation (10) is small, and (2) after the equivalence point where $[\text{Cl}] = K'_2/[\text{Ag}']$ and thus the term $(V_0 + V)K'_2/([\text{Ag}']C_B)$ in equation (10) is small. Before the equivalence point has been reached, the following equation can be applied:

$$(V_e - V)C_B = \frac{K'_2}{[\text{Ag}']} (V_0 + V) \quad \dots \quad \dots \quad \dots \quad (12)$$

For two additions of titrant, V_i and V_j , the following expressions are obtained:

$$(V_e - V_i) C_B = \frac{K'_2}{[Ag']_i} (V_o + V_i) \quad \dots \quad (13)$$

and

$$(V_e - V_j) C_B = \frac{K'_2}{[Ag']_j} (V_o + V_j) \quad \dots \quad (14)$$

Divisions of equation (13) by equation (14) and rearrangement as in Part V² gives

$$V_e = V_j + \frac{V_j - V_i}{\frac{V_o + V_i}{V_o + V_j} \cdot \frac{[Ag']_j}{[Ag']_i} - 1} \quad \dots \quad (15)$$

After the equivalence point the following expression is obtained in a similar way:

$$V_e = V_j - \frac{V_i - V_j}{\frac{V_o + V_i}{V_o + V_j} \cdot \frac{[Ag']_i}{[Ag']_j} - 1} \quad \dots \quad (16)$$

In neither of the instances is it necessary to know the value of the solubility product. All values, except V_e , are known or may be measured. Note also that only ratios of silver ion concentrations are used, which means that the calculations are independent of the value of f .

In dilute solutions equations (15) and (16) will not give sufficiently accurate results. In such instances it is necessary to use the complete expression (10). The following equation is obtained:

$$V_e = V_j + \frac{V_j - V_i}{\frac{V_o + V_i}{V_o + V_j} \cdot \frac{K'_2/[Ag']_i - K'_1[Ag']_i}{K'_2/[Ag']_j - K'_1[Ag']_j} - 1} \quad \dots \quad (17)$$

In this equation K'_1 , K'_2 and V_e are unknown. However, if the calibration of the electrode couple is not too bad, the factor f has a value close to unity and it is possible to use $K'_1 \approx K_1 \approx 1$ and $K'_2 \approx K_2 \approx 10^{-9.4}$ as a first approximation. In fact, it is even possible to start by setting $K'_1 = K'_2 = 0$. The program will still calculate the values for the three unknowns.

As in the similar method described in Parts V² and VI,³ V_j should be as close as possible to the expected V_e value. As the equivalence potential is known to be approximately 270 mV, it is fairly easy to choose a value for V_j (*cf.*, reference 8). Other titration points are used as V_i .

In order to refine the value of V_e and to calculate values for K'_1 and K'_2 an iterative procedure is used, in which K'_1 and K'_2 are calculated from

$$K'_1 = \frac{C_B}{[Ag']_\omega} \cdot \frac{V_\omega - V_e}{V_o + V_\omega} + \frac{K'_2}{[Ag']_\omega^2} \quad \dots \quad (18)$$

and

$$K'_2 = C_B [Ag']_\alpha \cdot \frac{V_e - V_\alpha}{V_o + V_\alpha} + K'_1 [Ag']_\alpha^2 \quad \dots \quad (19)$$

In these two equations (V_α ; $[Ag']_\alpha$) is chosen from one of the very first points and (V_ω ; $[Ag']_\omega$) from one of the last points in the titration. By doing so, the value of K'_1 is least influenced by the value of K'_2 , and *vice versa* for the calculation of K'_2 .

The calculation program is thus built up around three fixed data pairs (V_α ; $[Ag']_\alpha$), (V_j ; $[Ag']_j$) and (V_ω ; $[Ag']_\omega$). For each data pair (V_i ; $[Ag']_i$) a $V_{e(i)}$ is calculated, where the iteration is carried on until two consecutive values for $V_{e(i)}$ do not deviate by more than, *e.g.*, 10^{-5} ml. The first data pair (V_i ; $[Ag']_i$) used normally requires several iterations. The subsequent data pairs usually require only a few, as all values of $V_{e(i)}$, K'_1 and K'_2 are very close to the values to be found in the next iteration.

The QUOTEC program also includes the possibility of making a linear regression of the various $V_{e(i)} = a + bV_i$. This line is then intersected by the line $V_{e(i)} = V_i$ to give a final value for V_e , *i.e.*, $V_e = a/(1 - b)$, see Table I.

TABLE I
TITRATION OF 10^{-4} M CHLORIDE SOLUTION

99.88 ml of a 1.005×10^{-4} M hydrochloric acid solution were titrated with a 1.000×10^{-3} M silver nitrate solution. The supporting electrolyte was 0.1 M in potassium nitrate and 0.1 M in nitric acid. The temperature was 25 °C. E_o was assumed to be 555 mV. Pipette volume, 1.0021 ml.

Value No.	Experimental values*		V_e /ml		
	V /ml	E /mV	Calculated from equation (10)	Calculated from equations (17), (18) and (19)	
0	0	228.6		10.0754	10.0833
1	1.002	231.5	10.108	10.0759	10.0731
2	2.004	234.6	10.072	10.0763	10.0660
3	3.006	237.9	10.071	10.0764	10.0657
4	4.008	241.6	10.055	10.0766	10.0614
5	5.010	245.6	10.072	10.0764	10.0659
6	6.013	250.2	10.062	10.0767	10.0622
7	7.015	255.2	10.087	10.0760	10.0728
8	8.017	260.9	10.091	10.0757	10.0770
9	9.019	267.2	10.086	10.0757	10.0766
10	10.021	273.8	10.081		10.0758
11	11.023	280.3	10.078	10.0758	
12	12.025	286.3	10.082	10.0761	10.0649
13	13.027	291.7	10.077	10.0759	10.0718
14	14.029	296.4	10.079	10.0760	10.0709
15	15.031	300.5	10.081	10.0761	10.0704
16	16.034	304.1	10.081	10.0760	10.0708
17	17.036	307.3	10.073	10.0759	10.0731

* Using the experimental data in columns 2 and 3 the following values were obtained with the aid of EKVOL: $V_e = 10.079$ ml, standard deviation = 0.011; $\log K'_1 = 0.004$; $\log K'_2 = -9.497$. These values for the constants were used to calculate the individual V_e values in column 4 using equation (10).

From the same experimental data values for V_e , K'_1 and K'_2 were calculated by iteration of equations (17), (18) and (19). In columns 5 and 6 individual V_e values are given for $j = 10$ ($V_j = 10.206$ ml) and $j = 11$ ($V_j = 11.227$ ml), respectively. Linear regression on column 5 gives $V_e = 10.0761 - 9.068 \times 10^{-6} V_i$, which, with $V_i = V_e$, gives $V_e = 10.076$ ml, standard deviation = 0.0003 ml; $\log K'_1 = -0.004$; $\log K'_2 = 9.498$, in good agreement with the corresponding values obtained by the EKVOL program.

Evaluation of the Programs

Synthetic Titration Data

The programs were first evaluated using synthetic data, which were calculated from the titration equation (10). The sample volume was 100 ml, $\log K'_1 = 0.2$, $\log K'_2 = -9.6$ and $V_e = 10$ ml. C_o was varied from 10^{-2} to 10^{-6} . In all instances correct values were obtained.

Experimental Data

The e.m.f. measurements were carried out with a silver - silver chloride electrode (according to Brown⁹) combined with a Radiometer K701 reference electrode and a digital millivoltmeter. Titrant aliquots of 1.0021 ml were added with a pneumatically driven pipette. The titration vessel was immersed in a bath maintained at 25.0 ± 0.1 °C.

The chloride solutions were prepared from a 0.1005 M stock solution of hydrochloric acid. The titrant solutions were prepared from a 0.1000 M solution of silver nitrate. The concentrations of the two stock solutions were determined by precipitation and weighing as silver chloride. Five different concentrations of hydrochloric acid were used:

- (1) 100 ml 10^{-2} M chloride titrated with 0.1 M silver nitrate solution;
- (2) 100 ml 10^{-3} M chloride titrated with 0.01 M silver nitrate solution;

(3) 100 ml 10^{-4} M chloride titrated with 0.001 M silver nitrate solution;

(4) 100 ml 5×10^{-5} M chloride titrated with 0.001 M silver nitrate solution;

(5) 100 ml 10^{-5} M chloride titrated with 0.001 M silver nitrate solution.

All solutions were 0.1 M in potassium nitrate and 0.1 M in nitric acid.

An approximate value of \bar{E}_0 was determined by measuring the e.m.f. of the electrode pair in the 10^{-3} M silver nitrate solution. The value found was $\bar{E}_0 = 555$ mV and this value was used throughout all calculations.

Example 1

Three titrations of a 0.01 M chloride solution were performed. The results were $V_e = 10.118$, 10.060 and 10.040 ml using EKVOL and $V_e = 10.053$, 10.053 and 10.057 ml using QUOTEQ. The values for $\log K_{s0} = \log K'_1 + \log K'_2$ were -9.41 to -9.43 .

Example 2

A titration of a 0.001 M chloride solution is shown in Fig. 1. A Gran II plot gives $V_e = 10.07$ ml. A numerical evaluation of this titration and a duplicate one gave $V_e = 10.023$ and 10.024 ml (EKVOL) and 10.038 and 10.037 ml (QUOTEQ). All four evaluations gave $\log K_{s0} = -9.49$.

Example 3

A Gran II plot of a titration of a 10^{-4} M chloride solution gives completely wrong results (Fig. 2). However, a numerical evaluation gives correct results. Duplicate titrations gave $V_e = 10.08$ and 10.03 ml (EKVOL) and $V_e = 10.07$ and 10.03 ml (QUOTEQ). Impurities in the supporting electrolyte could be calculated to consume about 0.03 ml of 0.001 M silver nitrate solution. The V_e values obtained thus agree well with the expected value of 10.04 ml. The four evaluations gave $\log K_{s0} = -9.48$ to -9.50 . See Table I for further details.

Example 4

Even a chloride solution as dilute as 5×10^{-5} M can be evaluated with good results. EKVOL gave $V_e = 5.18$ and 5.18 ml and QUOTEQ gave $V_e = 5.20$ and 5.20 ml.

Example 5

The results of titrations of 10^{-5} M chloride solutions with 10^{-3} M silver nitrate solution were 1.1, 1.4, 1.5 and 1.6 ml (all obtained with the EKVOL program). $\log K_{s0}$ varied between -9.40 and -9.45 . The QUOTEQ program did not work, as too narrow an e.m.f. range was obtained. However, if average values for K'_1 and K'_2 , taken from examples 2 and 3, were used in the QUOTEQ program, the results were $V_e = 1.47$, 1.40, 1.38 and 1.59 ml. It is obvious that at this very low concentration the results are scattered.

Discussion

In general, evaluations by the EKVOL and the QUOTEQ programs give results that agree fairly well; only for the first titration in example 1 a small difference is found: QUOTEQ gave $V_e = 10.053$ ml, close to the expected value of 10.04 ml, whereas EKVOL gave $V_e = 10.118$ ml. This discrepancy can be explained as follows. EKVOL is based on the solution of a system of linear equations. All data therefore have the same weight, and if some data are bad this shows up in the result. In the first titration some data are bad because the solution was not stirred effectively enough to prevent some precipitate from adhering to the electrodes. In QUOTEQ $V_e = V_j + \text{quotient}$; with $j = 10$, i.e., $V_j = 10.021$ ml, the quotient is only 0.055 ml, and for $j = 11$, i.e., $V_j = 11.023$ ml, V_e was calculated to be 10.071 ml and the quotient was -0.952 ml. In QUOTEQ the V_j term normally dominates and the value of the quotient should not exceed the volume of the titrant pipette, V_p . It is suitable to use two V_j values, one on each side of V_e , in the calculations.

The over-all errors in the determinations are 0.1–0.2% down to chloride concentrations of 10^{-4} M. The errors due to the evaluation are negligible.

Other Titrations

In order to illustrate the evaluation of more complicated precipitation titrations we have chosen the titration of sodium fluoride with lanthanum nitrate. These titrations have been

studied by Lingane,⁶ who used a lanthanum fluoride membrane electrode to follow the change in the fluoride ion activity during the titration. The main reaction is



However, the fluoride and lanthanum ions may also take part in a number of side-reactions. In acidic solutions HF may be formed, as hydrofluoric acid is a weak acid. Further, HF_2^- may be formed. At the start of the titration, F^- , HF and HF_2^- may be present in the sample solution. The total concentration of fluoride ions in the solution is thus

$$[\text{F}] (1 + K_{\text{HF}}[\text{H}] + 2K_{\text{HF}_2}[\text{H}][\text{F}]) \quad \dots \quad (21)$$

where K_{HF} is the stability constant for the reaction $\text{H}^+ + \text{F}^- = \text{HF}$ and K_{HF_2} is the stability constant for the reaction $\text{H}^+ + 2\text{F}^- = \text{HF}_2^-$. $\log K_{\text{HF}}$ is about 3.5 and $\log K_{\text{HF}_2}$ is about 4.0.

In dilute fluoride solutions, the term $2K_{\text{HF}_2}[\text{H}][\text{F}]$ can be neglected and thus equation (21) is reduced to

$$[\text{F}](1 + K_{\text{HF}}[\text{H}]) \quad \dots \quad (22)$$

The factor $(1 + K_{\text{HF}}[\text{H}])$ can be replaced with a constant K_1 if the hydrogen ion concentration is kept constant or if it is low, *e.g.*, $\text{pH} > 5$. In the titration of unbuffered fluoride solutions the pH is usually 5–6 and then K_1 is very close to unity.

In the titration of pure fluoride solutions, only LaF_3 and LaF_2^+ have to be considered, but in buffered solutions many different complexes can be formed in addition to these two. If an acetate buffer is chosen, the pH is so high that the formation of HF and HF_2^- can be neglected. The addition of acetate ions leads to the formation of acetate complexes in addition to the fluoride complexes and further mixed complexes may be formed.

During the titration in an acetate-buffered solution, varying amounts of F^- , La^{3+} , LaFAc^+ , LaAc_2^+ , LaF_2^+ , LaAc_3 , LaF_2^+ and LaF_3 are present. Anfält *et al.*¹⁰ used the program HALTAFALL¹¹ to calculate the equilibrium concentrations of the various species formed during the titrations. They used the experimental values from Lingane's paper⁶ and equilibrium constants from "Stability Constants"¹² and other sources in their calculations. In this way it is possible to decide which species will dominate and which can be neglected.

In the determination of the equivalence point the method of maximum slope of the titration curve cannot be used. In these titrations,¹³ the equivalence point and the point of maximum slope do not coincide. Anfält and co-workers^{10,14} and Eriksson¹⁵ determined the equivalence volume by the Gran II method. By applying the same principles as in the chloride titration above, the following equation, corresponding to equation (5), can be deduced:

$$\begin{aligned} & \frac{V_0 + V}{3C_B} [\text{F}](1 + K_{\text{HF}}[\text{H}]) - \frac{V_0 + V}{3C_B} \cdot \frac{3K_{80}}{[\text{F}]^3} - \frac{V_0 + V}{3C_B} \cdot \frac{2[\text{Ac}]^2}{[\text{F}]^2} \cdot K_{80}K_{112} - \\ & \frac{V_0 + V}{3C_B} \cdot \frac{2}{[\text{F}]^2} \cdot K_{80}K_{\text{LaF}} - \frac{V_0 + V}{3C_B} \cdot \frac{[\text{Ac}]}{[\text{F}]} \cdot K_{80}K_{121} + V - V_e = 0 \quad \dots \quad (23) \end{aligned}$$

where K_{LaF} , K_{112} and K_{121} are the stability constants for the formation of the complexes LaF_2^+ , LaFAc_2 and LaF_2Ac , respectively.

If the hydrogen and acetate ion concentrations can be considered to be constant, the following titration equation, corresponding to equation (10), is obtained:

$$\begin{aligned} & \frac{V_0 + V}{3C_B} \cdot [\text{F}'] \cdot K_1 - \frac{V_0 + V}{3C_B} \cdot \frac{K'_2}{[\text{F}']^3} - \frac{V_0 + V}{3C_B} \cdot \frac{K'_3}{[\text{F}']^2} - \\ & \frac{V_0 + V}{3C_B} \cdot \frac{K'_4}{[\text{F}']} + V - V_e = 0 \quad \dots \quad (24) \end{aligned}$$

The constants K'_1 , K'_2 , K'_3 and K'_4 are thus conditional constants in which both the error factor f and stoichiometric coefficients are included. Equation (24) is linear with five unknowns and can in principle be solved, *e.g.*, by the program EKVOL, if sufficiently many accurate measurement data are available. However, in practice, a few terms dominate and the contribution from the other terms is so slight that they do not influence the data. In the choice among the terms a knowledge of the approximate values of the stability constants is a good help; otherwise, one has to resort to the trial and error method.

This technique has been tested on the evaluation of four titrations shown in Fig. 6 in Lingane's paper.⁶ In all four titrations 100 ml of 0.004 M sodium fluoride solution were titrated with 0.03189 M lanthanum nitrate solution, *i.e.*, $V_e = 4.18$ ml. The experimental data were read from the figure, which of course involved a high risk of inaccuracy. $E'_o = -170$ mV was chosen for the calculation of the fluoride concentrations.

Titration 1: unbuffered neutral solution

It can be assumed that $[F^-]$ dominates before the equivalence point and $[LaF_3]$ after the equivalence point. Some LaF^{2+} may be formed.

Result: $V_e = 4.15 \pm 0.05$ ml, $K'_1 = 0.93$, $\log K'_2 = -17.70$ and $\log K'_3 = -13.2$. Nearly the same results were obtained even if the K'_2 term was omitted: $V_e = 4.19 \pm 0.07$ ml, $K'_1 = 1.04$ and $\log K'_2 = -17.53$.

A calculation on the same titration using a QUOTEQ program gave $V_e = 4.20 \pm 0.04$ ml, $K'_1 = 1.04$ and $\log K'_2 = -17.52$.

The QUOTEQ program in this instance iterates the three equations

$$V_e = V_j + \frac{V_j - V_i}{\frac{V_o + V_i}{V_o + V_j} \cdot \frac{K'_1[F']_i - K'_2/[F']_i^3}{K'_1[F']_j - K'_2/[F']_j^3} - 1} \quad \dots \quad (25)$$

$$K'_1 = \frac{3C_B}{[F']_\alpha} \cdot \frac{V_e - V_\alpha}{V_o + V_\alpha} + \frac{K'_2}{[F']_\alpha^4} \quad \dots \quad (26)$$

and

$$K'_2 = 3C_B[F']_\omega^3 \cdot \frac{V_\omega - V_e}{V_o + V_\omega} + K'_1[F']_\omega^4 \quad \dots \quad (27)$$

Titration 2: acidified solution

This titration was performed in the same way as titration 1, except that 10 ml of 0.100 M hydrochloric acid solution was added to the 100 ml of neutral sample solution before the start of the titration. In this instance the formation of hydrofluoric acid cannot be disregarded.

Equation (23) then becomes

$$\frac{V_o + V}{3C_B} \cdot [F']K'_1 + \frac{V_o - V}{3C_B} \cdot [F'] [H] K'_{HF} - \frac{V_o + V}{3C_B} \cdot \frac{K'_2}{[F']^3} - V_e + V = 0 \quad (28)$$

where K'_1 is the error factor for $[F]$, *i.e.*, about 1.0 if the electrode couple is fairly well calibrated. As the K'_1 term is small in comparison with the other terms it is better not to calculate K'_1 but to assume that $K'_1 = 1.0$.

The hydrogen ion concentration is not constant, but it can of course be measured during the titration. However, it is also possible to calculate the hydrogen ion concentration if the total number of moles, $V_o[Cl]$, of hydrochloric acid added is known. In this instance the titration equation is changed to

$$\frac{V_o[Cl]}{3C_B} \cdot \frac{[F']}{1 + K'_{HF}[F']} \cdot K'_{HF} - \frac{V_o + V}{3C_B} \cdot \frac{K'_2}{[F']^3} - V_e + V + \frac{V_o + V}{3C_B} [F'] = 0 \quad \dots \quad (29)$$

As in principle, K'_{HF} is unknown the calculations must be iterated. In the first cycle of the iteration K'_{HF} in the denominator can be given an arbitrary value, *e.g.*, 1000.

Result: $V_e = 4.20 \pm 0.06$ ml, $\log K'_{HF} = 3.04$ and $\log K'_2 = -17.3$.

A calculation of the same titration using a QUOTEQ program gave $V_e = 4.18 \pm 0.02$ ml, $\log K'_{HF} = 3.01$ and $\log K'_2 = -17.1$. In this instance, the QUOTEQ equations, of course, were derived from equation (29).

Titration 3: acetate-buffered solution

This titration was performed as titration 2 except that the hydrochloric acid addition was replaced with 10 ml of 1 M acetate buffer solution of pH 4.88. The hydrogen ion concentration can be assumed to remain constant during the whole titration. The best precision in the results of the calculations of V_e was obtained when the K'_3 term in equation (24) was excluded, in which event the following result was obtained: $V_e = 4.52 \pm 0.06$ ml, $K'_1 = 1.08$, $\log K'_2 = -15.6$ and $\log K'_4 = -7.0$.

The equivalence volume obtained is much too high and the value for the solubility product which can be calculated from K'_2 , $\log K_{s0} = -15.8$, is not in accordance with accepted values. Titration of fluoride in acetate-buffered solution is therefore not suitable. Certainly, too far-reaching conclusions should not be drawn from these results, as the data obtained from Lingane's diagrams are rather uncertain. However, our results agree reasonably well with those obtained by Anfält and co-workers^{10,14,16} who studied the problem in more detail using Lingane's data and their own data. They found that acetate ions enter the solid phase during the titration. The precipitate is therefore not pure LaF_3 , which is a requirement for the calculation of a correct fluoride concentration.

Titration 4: formate-buffered solution

This titration resembled titration 3 except that the acetate buffer was replaced with 10 ml of 0.2 M formate buffer solution of pH 3.00. The result, $V_e = 4.40$ ml, is too high and the precision is too low, which may be due to too low a buffer capacity and thus to a changing hydrogen ion concentration. $K'_1 = 2.11$, which is in fair agreement with the expected value $K'_1 = (1 + K_{FH}[\text{H}]) = (1 + 10^{3.1} \times 10^{-3}) = 2.25$.

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NOTE—References 1, 2 and 3 are to Parts III, V and VI of this series, respectively.

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