

Determination of End-Points in Hydrolytic Potentiometric Titrations in the $\text{Ca}^{2+} - \text{F}^-$ System *

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Mathematical modelling of a multi-component titration system of hydrolytic titrations of metal ions is described. A comparison of the calculated and experimental titration curves and end volumes in the $\text{Ca}^{2+} - \text{F}^-$ system at different pH values of titrated solutions is presented. The determination of the end-point of titrations by several approximation and mathematical methods is described.

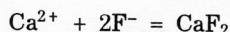
INTRODUCTION

Hydrolytic potentiometric titrations of metal ions present an unconventional titration system, characterized by the double role of the titrant.

The described observations present a basis for a number of titration processes that have been carried out /determination of calcium in drinking water,¹ wine,² sulphate in drinking river and mineral waters,³ lead in aluminium alloys.⁴ They present an extension of the usability of glass electrode, the most universal sensor excelling in great precision and selectivity in the new field of potentiometric titrations. Studies of these titrations by means of conventional methods are made more difficult by the fact that neither the changes of concentration of metal ion nor those of titrant ion are observed during titrations, but only the changes of pH value as a result of parallel hydrolytic reaction are observed.

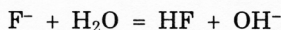
The presented model, based on the observation of chemical balances acting in the titration process, represents a quantification of the course of titrations curves; a comparison of the calculated and experimental curves explains, however, the primarily applied empirical procedure of determining the end-point of titration.

After the precipitation phase of metal ion:



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hydrolytic reaction of the anion of weak acid takes place after exceeding the end-point of titration:



This reaction results in a quick increase in the pH value of titrated solution, thus enabling instrumental indication of the end-point of titration by means of glass electrode. Optimal titration conditions depend on the solubility product of the sparingly soluble salt and dissociation constant of the weak acid produced by hydrolysis. With the initial pH value of titrated solution and by adding a less polar solvent, we optimize the linear slope of titration curve in both phases of titration as well as the change of curve slope in the end-point. The end-point was determined empirically by the point of intersection of tangents placed on both parts of the titration curve.⁵⁻⁷

Mathematical Model

If C_{A^-} , $C_{M^{2+}}$, C_{H^+} represent the initial concentrations of reactants before the titration reaction, and $[A^-]$, $[M^{2+}]$, $[H^+]$ are final concentrations at any point of titration, and if V_1 is the volume of the additional titrant and V_2 the volume of the titrated solution, the contents of reactants can be expressed by the number of moles as follows:

$$\begin{aligned} n_{M^{2+}}^0 &= C_{M^{2+}} \cdot V_2, & n_{M^{2+}} &= [M^{2+}] \cdot (V_1 + V_2) \\ n_{A^-}^0 &= C_{A^-} \cdot V_1, & n_{A^-} &= [A^-] \cdot (V_1 + V_2) \\ n_{H^+}^0 &= C_{H^+} \cdot V_2, & n_{H^+} &= [H^+] \cdot (V_1 + V_2) \end{aligned} \quad (1)$$

The application of the law of constant molar ratios shows the relationship:

$$n_{A^-} - n_{A^-}^0 = 2 \cdot (n_{M^{2+}} - n_{M^{2+}}^0) + (n_{H^+} - n_{H^+}^0)$$

and by observing expression (1), we obtain

$$\begin{aligned} [A^-] \cdot (V_1 + V_2) - C_{A^-} \cdot V_1 &= (V_1 + V_2) \cdot (2[M^{2+}] + [H^+]) - \\ &- V_2 \cdot (2C_{M^{2+}} + C_{H^+}) \end{aligned} \quad (2)$$

In practical conditions of hydrolytic titrations, the equilibrium is regulated with constants

$$K_1 = [M^{2+}] [A^-]^2 \quad K_2 = \frac{[HA]}{[H^+] \cdot [A^-]}$$

and by taking into consideration that

$$\frac{C_{H^+}}{v} - [H^+] = [HA] \quad v = \frac{V_1 + V_2}{V_2}$$

one gets, for A^- and M^{2+} at any point of titration, the expressions

$$[\text{A}^-] = \frac{C_{\text{H}^+} - [\text{H}^+]}{K_2 * [\text{H}^+]}$$

$$[\text{M}^{2+}] = \frac{K_1 * K_2^2 * [\text{H}^+]^2}{\left[\frac{C_{\text{H}^+}}{v} - [\text{H}^+] \right]^2}$$

So, the basic equation (2) can be put down in a more distinct form showing the relation between the volume of the titrant and the measured parameter pH

$$\frac{C_{\text{A}^-} * V_1}{V_2 * (2 * C_{\text{M}^{2+}} + C_{\text{H}^+})} - 1 = \frac{v}{(2 * C_{\text{M}^{2+}} + C_{\text{H}^+})} \left[\frac{C_{\text{H}^+}}{v} - [\text{H}^+] \right] - \frac{2 * K_1 * K_2^2 * [\text{H}^+]^2}{\left[\frac{C_{\text{H}^+}}{v} - [\text{H}^+] \right]^2} - [\text{H}^+]$$

In equivalent point, the following condition is fulfilled:

$$\frac{C_{\text{H}^+}}{v} - [\text{H}^+] - \frac{2 * K_1 * K_2^2 * [\text{H}^+]^2}{\left[\frac{C_{\text{H}^+}}{v} - [\text{H}^+] \right]^2} - [\text{H}^+] = 0$$

EXPERIMENTAL

Apparatus

A digital pH meter ISKRA MA 5730 was used with a glass combination electrode at constant temperature 298 ± 0.2 K. Calculations were done on a VAX 8800 computer. Comparative spectrometric determination was performed with the Atomic Absorption spectrometer PERKIN ELMER Model 1100 B. Comparative titrations with fluoride ISE were performed on the Expandable Ion Analyzer EA 920 (ORION).

Reagents

All chemicals used were of analytical grade. Solutions were made with redistilled water. The solution of Ca^{2+} ions was prepared from $\text{Ca}(\text{NO}_3)_2$ and was standardized complexometrically with EDTA. The solution of F^- ions was prepared from NaF. It was standardized potentiometrically with Ca^{2+} solution by using the fluoride ion-selective electrode (ORION) as an indicator electrode and the saturated calomel electrode with a salt bridge filled with 0.1 mol/l KNO_3 as a reference electrode.

Titration

The pH of the solution was adjusted to the required value by addition of 0.1 mol/l and resp. 0.01 mol/l HNO_3 . The titrant was added at 0.2 cm^3 intervals. The pH value at every addition was read after establishing the equilibrium.

RESULTS AND DISCUSSION

The model was tested by means of Ca^{2+} ions with NaF as titrant. Figure 1 presents the experimental and calculated pH values for titration curves at initial pH = 3.00. For the calculations of pH values in the model equation (2) we first used the solubility product and thermodynamic stability constant stated in literature ($K_1 = 4.9 \cdot 10^{-11}$ and $K_2 = 1.48 \cdot 10^3$).⁸ To solve equation (2), we used one of the numerous iteration methods, *i.e.* the method of half interval. According to this method, the equation is solved by halving pH during iteration until the interval becomes smaller than 0.001 pH. This method is applicable because it requires only real solutions having a physical meaning.⁹

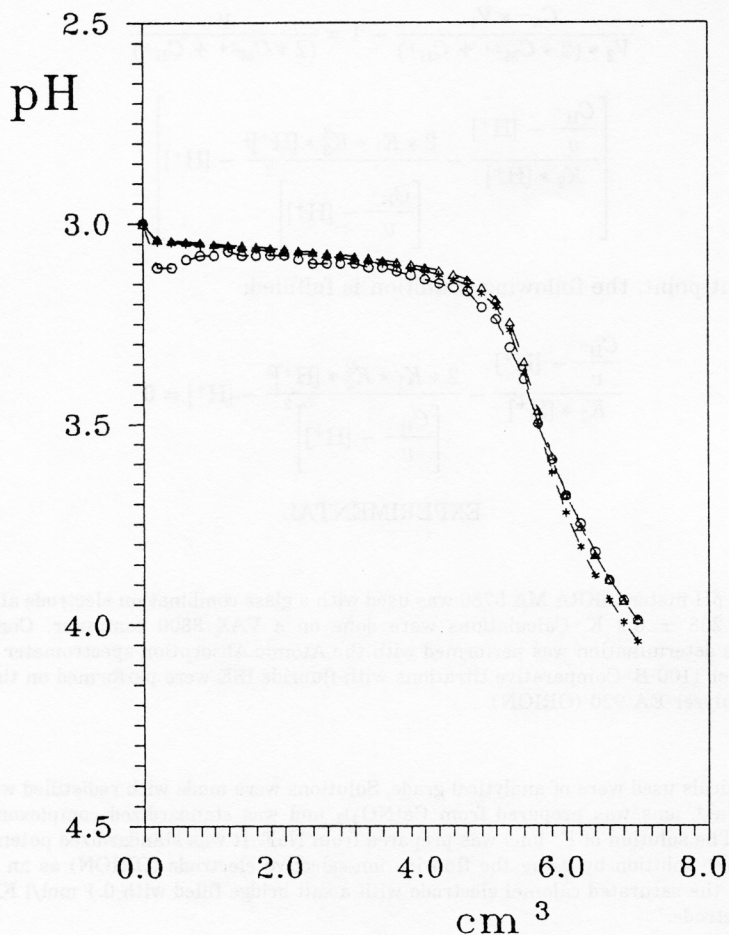


Figure 1. Titration curves of titrations of 50 cm³ 0.01 M Ca^{2+} with 0.200 M NaF at initial pH 3.0. (O)—experimental, (Δ)—calculated K_{cond} . (*)—calculated $K_{\text{thermodyn}}$.

The number of iterations N is defined, depending on how precise the result should be, according to the equation: $N = 1.44 \ln \gamma$. The value γ is obtained by the ratio between the desired degree of accuracy and the whole pH range. If we wish the experimental pH values to agree with the calculated ones at an accuracy of 0.001 pH, we choose the interval in which we assume to find the solution (for instance between $\text{pH} = 0$ and $\text{pH} = 14$), and calculate the value of γ from the ratio between the accuracy required for the calculation and the entire pH range. In our case, 17 iterations were necessary.

In order to describe the actual state in the titrated solution, we used the same numerical method of half interval to calculate the conditional stability constants. The

TABLE I
Titration of 50 cm³ 0.010 M Ca^{2+} with 0.200 M NaF

cm ³	pH = 4.00			pH = 3.50			pH = 3.00		
	pH _{exp.}	pH _{calc.} ^a	pH _{calc.} ^b	pH _{exp.}	pH _{calc.} ^a	pH _{calc.} ^b	pH _{exp.}	pH _{calc.} ^a	pH _{calc.} ^b
0.0	4.00	4.000	4.000	3.50	3.500	3.500	3.00	3.000	3.000
0.2	4.12	4.036	4.045	3.62	3.541	3.530	3.11	3.039	3.045
0.4	4.08	4.039	4.048	3.58	3.544	3.533	3.11	3.042	3.048
0.6	4.07	4.041	4.050	3.57	3.546	3.535	3.09	3.045	3.050
0.8	4.07	4.044	4.053	3.56	3.549	3.537	3.08	3.047	3.053
1.0	4.08	4.046	4.056	3.57	3.552	3.540	3.08	3.050	3.056
1.2	4.08	4.049	4.059	3.58	3.555	3.542	3.07	3.053	3.059
1.4	4.08	4.052	4.062	3.58	3.557	3.545	3.08	3.055	3.062
1.6	4.07	4.055	4.065	3.59	3.560	3.548	3.08	3.058	3.065
1.8	4.08	4.058	4.068	3.59	3.564	3.550	3.08	3.061	3.068
2.0	4.08	4.061	4.072	3.59	3.567	3.553	3.08	3.064	3.071
2.2	4.08	4.064	4.075	3.59	3.570	3.556	3.09	3.068	3.075
2.4	4.08	4.067	4.079	3.59	3.574	3.559	3.10	3.071	3.078
2.6	4.08	4.070	4.082	3.59	3.577	3.562	3.10	3.075	3.082
2.8	4.09	4.074	4.087	3.60	3.581	3.566	3.10	3.078	3.086
3.0	4.09	4.078	4.091	3.61	3.585	3.569	3.10	3.082	3.091
3.2	4.09	4.082	4.096	3.61	3.590	3.573	3.11	3.087	3.095
3.4	4.10	4.087	4.101	3.62	3.595	3.577	3.11	3.092	3.100
3.6	4.10	4.092	4.107	3.62	3.600	3.582	3.12	3.097	3.106
3.8	4.11	4.098	4.114	3.63	3.606	3.587	3.13	3.103	3.113
4.0	4.11	4.104	4.121	4.64	3.614	3.593	3.14	3.110	3.120
4.2	4.12	4.112	4.131	3.65	3.623	3.600	3.15	3.118	3.129
4.4	4.14	4.123	4.143	3.66	3.634	3.609	3.16	3.128	3.140
4.6	4.17	4.136	4.159	3.70	3.648	3.622	3.17	3.141	3.155
4.8	4.21	4.157	4.183	3.75	3.670	3.640	3.21	3.160	3.175
5.0	4.26	4.193	4.226	3.81	3.707	3.721	3.24	3.190	3.208
5.2	4.33	4.271	4.315	3.89	3.783	3.800	3.31	3.246	3.267
5.4	4.44	4.403	4.462	3.99	3.915	3.938	3.39	3.345	3.372
5.6	4.55	4.530	4.601	4.08	4.049	4.077	3.50	3.468	3.503
5.8	4.64	4.633	4.711	4.17	4.159	4.191	3.59	3.582	3.623
6.0	4.72	4.718	4.801	4.25	4.249	4.282	3.68	3.677	3.723
6.2	4.79	4.789	4.875	4.33	4.324	4.359	3.75	3.758	3.807
6.4	4.85	4.851	4.939	4.39	4.389	4.425	3.82	3.827	3.878
6.6	4.90	4.904	4.994	4.44	4.445	4.482	3.89	3.888	3.940
6.8	4.95	4.952	5.043	4.49	4.495	4.532	3.94	3.941	3.995
7.0	4.99	4.996	5.088	4.54	4.540	4.577	3.99	3.989	4.043

^apH values calculated with K_{cond} .

^bpH values calculated with $K_{\text{thermodyn}}$.

conditional constant depends on the composition of the titrated solution and is invariable for a certain group of real samples with a similar matrix, which is a noteworthy fact that extends the applicability of such titration procedures to analyses of real samples. Experimental pH values were inserted in the model equation and the conditional stability constants were calculated for each point after the equivalent point. The average conditional constant then serves as a basis for the calculation of new calculated pH values for the model equation. Measured pH values do not vary from these calculated ones by more than 0.05 pH in all the titration curves mentioned here (Table I).

The real value of metal ion concentration is calculated according to the method of »optimum overlapping«. By comparing the experimental pH values with the new

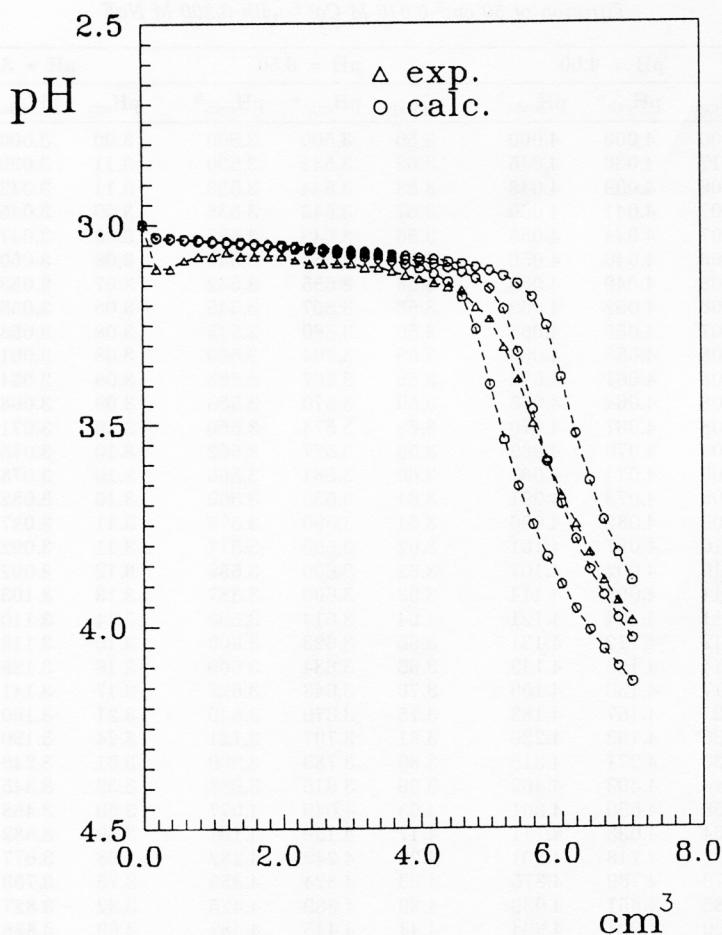


Figure 2. Titration curves of titrations of 50 cm³ 0.01 M Ca²⁺ with 0.200 M NaF at initial pH 3.0. (Δ)—experimental, (\circ)—calculated.

corrected calculated ones, we tried to determine the real value of metal ion concentration. If, in this model equation, the assumed concentration of metal ion is lower than the real value, the calculated curve is shifted to the left from the experimental curve. If, however, the concentration exceeds the real value, the curve lies to the right from the experimental curve (Figure 2). The concentration C_M of the metal ion in the model equation is varied until the square of the sum of differences between the measured and calculated pH values is reduced to minimum (least square minimization method) for all points measured after the equivalent point ($\sum(\text{pH}_{\text{exp.}} - \text{pH}_{\text{calc.}})^2 = \text{min.}$). The amplitudes of deviations between the experimental and calculated pH values indicate no systematic deviation but random deviation only.

The end-point of titration was evaluated in several ways (Table II). Due to the fact that the equivalent point indicates the content of the sum of metal and H^+ ions, the end-point is obtained by the following condition:

$$\frac{C_{\text{A}^-} * V_1}{V_2 * (2 * C_{\text{M}^{2+}} + C_{\text{H}^+})} - 1 = 0 \quad \text{in model equation}$$

The end-point of the titration, defined in this way, corresponds to the equivalent volume for the calculated model equation with a known concentration of Ca^{2+} ions

TABLE II

Comparison of end volumes for titration of 50 cm³ 0.01 M Ca²⁺ with 0.200 M NaF

Way of determination	Initial pH	End volume Ca ²⁺ + H ⁺	(cm ³) Ca ²⁺	mg Ca in 50 cm ³ sample
Method of optimum overlapping	3.0	5.300	5.050	20.240
	3.5	5.129	5.050	20.240
	4.0	5.075	5.050	20.240
Gran plot calculated curve	3.0	5.291	5.041	20.204
	3.5	5.139	5.060	20.280
	4.0	5.084	5.059	20.276
Gran plot experiment. curve	3.0	5.290	5.040	20.200
	3.5	5.140	5.061	20.284
	4.0	5.065	5.040	20.200
Inflection point by rational spline calculated curve	3.0	5.310	5.060	20.280
	3.5	5.138	5.059	20.276
	4.0	5.065	5.040	20.200
Inflection point by rational spline experiment. curve	3.0	5.260	5.061	20.284
	3.5	5.139	5.060	20.280
	4.0	5.064	5.039	20.196
Tangent method with 50% MeOH	3.0		5.060	20.280
	3.5		5.039	20.196
	4.0		5.040	20.200
Complexometric determination			5.030	20.160
Potentiometric determination in 50% MeOH with ISE			5.049	20.236
Spectrometric determination with AAS method				20.250

standardized beforehand. It was calculated for titration curves of initial pH values 3.0, 3.5, and 4.0 (Table I).

The other method is Gran's linearization of titration curve. For calculation of the modified F function, the mathematical model, involving the reaction of precipitation and hydrolysis, is applied. This function was proposed by I. Hansson and D. Jagner,¹⁰ when high precision and accuracy are required. For determination of the end-point, only the measured points after the equivalent point are used. F is calculated according to the following equation:

$$F = (V_1 + V_2) * \left[\frac{\frac{C_{H^+}}{v} - [H^+]}{K_2 * [H^+]} - \frac{2 * K_1 * K_2' * [H^+]^2}{\left[\frac{C_{H^+}}{v} - [H^+] \right]^2} - [H^+] \right]$$

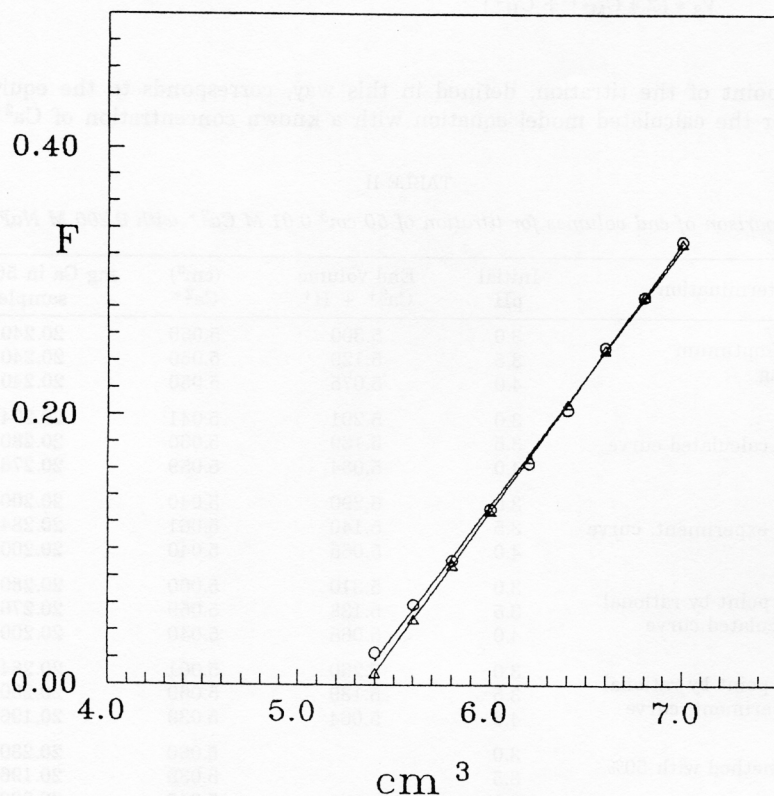


Figure 3. Gran plot for titrations of 50 cm³ 0.01 M Ca²⁺ with 0.200 M NaF at initial pH 3.0. (Δ)-experimental, (○)-calculated.

where K_2 represents the conditional stability constant of acid. Figure 3 shows that the experimental and calculated F functions coincide within the wide range of added volume in the zone after the equivalent point.

From the calculated F values from the zone after the equivalent point, a straight line equation is obtained by means of linear regression. By solving this equation, we get an intersection on the abscissa which is the end-point of the titration.

The inflection point of titration curves indicates the content of the sum of metal and hydrogen ions. By increasing the pH values of titrated solutions, the influence of H^+ ions on the position of the end-point disappears so that, in optimal titration conditions and in adequately chosen systems, the empirically determined end-point by means of the tangent method⁵⁻⁷ coincides with the inflection point of the curve¹¹ (Table II).

Table II shows the results of the average values of end-points as well as the calcium content for 5 titrations. The relative standard deviation is below 0.2% for all methods applied to determining the end-point. The table proves that in determining the end-point according to these methods the error is below 0.01 cm^3 , which lies within the limits of error in reading on a burette.

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SAŽETAK

Određivanje završne točke u hidrolitnim potenciometrijskim titracijama u sustavu $\text{Ca}^{2+} - \text{F}^-$

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Opisan je matematički model višekomponentnoga sustava hidroliznih potenciometrijskih titracija. Prikazana je usporedba izračunanih eksperimentalnih titracijskih krivulja te završnih volumena u sustavu $\text{Ca}^{2+} - \text{F}^-$ pri različitim početnim vrijednostima pH titriranih otopina. Opisano je računanje završne točke titracije različitim aproksimativnim računskim metodama.