Chapter 5

Principles of Titrimetric Analyses According to Generalized Approach to Electrolytic Systems (GATES)

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.69248

Abstract

The generalized equivalent mass (GEM) concept, based on firm algebraic foundations of the generalized approach to electrolytic systems (GATES), is considered and put against the equivalent "weight" concept, based on a "fragile" stoichiometric reaction notation still advocated by IUPAC. The GEM is formulated a priori, with no relevance to a stoichiometry. GEM is formulated in a unified manner, and referred to systems of any degree of complexity with special emphasis put on redox systems, where generalized electron balance (GEB) is involved. GEM is formulated on the basis of all attainable (and preselected) physicochemical knowledge on the system in question, and resolved with use of iterative computer programs. It is possible to calculate coordinates of the end points taken from the vicinity of equivalence point. This way, one can choose (among others) a proper indicator and the most appropriate (from analytical viewpoint) color change of the indicator. Some interpolative and extrapolative methods of equivalence volume V_{eq} determination are recalled and discussed. The GATES realized for GEM purposes provides the basis for optimization of analytical procedures a priori. The GATES procedure realized for GEM purposes enables to foresee and optimize new analytical methods, or modify, improve, and optimize old analytical methods.

Keywords: equilibrium analysis, mathematical modeling, redox titration curves, equivalence volume, Gran methods

1. Introductory remarks

Titrimetry reckons to the oldest analytical methods, still widely used because of high precision, accuracy, convenience, and affordability [1]. Nowadays, according to *Comité Consultatif pour la*

Quantité de la Matière (CCQM) opinion [2], it is considered as one of the primary methods of analysis i.e., it fulfills the demands of the highest metrological qualities. Titration is then perceived as a very simple and reliable technique, applied in different areas of chemical analysis. A physical chemist may perform a titration in order to determine equilibrium constants, whereas an analytical chemist performs a titration in order to determine the concentration of one or several components in a sample.

In a typical titration, V_0 mL of titrand (D) containing the analyte A of an unknown (in principle) concentration C_0 is titrated with V mL of titrant (T) containing the reagent B (C); V is the total volume of T added into D from the very beginning to a given point of the titration, where total volume of D + T mixture is $V_0 + V$, if the volume additivity condition is fulfilled. Symbolically, the titration T → D in such systems will be denoted as $B(C,V) \rightarrow A(C_0,V_0)$. Potentiometric acid-base pH titrations are usually carried out by using combined (glass + reference) electrode, responding to hydrogen-ion activity rather than hydrogen-ion concentration. Potentiometric titrations in redox systems are made with use of redox indicator electrodes (RIE) e.g., combined (Pt + reference) electrode [3–5]. For detection of specific ions in a mixture, ion-selective electrodes (ISE) are also used [5]. The degree of advancement of the reaction between B and A is the fraction titrated [6], named also as the degree of titration, and expressed as the quotient $\Phi = n_B/n_A$ of the numbers of mmoles: $n_B = C \cdot V$ of B and $n_A = C_0 \cdot V_0$ of A, i.e.,

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \tag{1}$$

We refer here to visual, pH, and potentiometric (E) titrations. The functional relationships between potential E or pH of a solution versus V or Φ, i.e., $E = E(V)$ or $E = E(\Phi)$ and $pH = pH(V)$ or $pH = pH(\Phi)$ functions, are expressed by continuous plots named as the related titration curves. The Φ provides a kind of normalization in visual presentation of the appropriate system. In the simplest case of acid-base systems, it is much easier to formulate the functional relationship $\Phi = \Phi(pH)$, not $pH = pH(\Phi)$. In particular, the expression for Φ depends on the composition of D and T, see Appendix.

The detailed considerations in this chapter are based on principles of the generalized approach to electrolytic systems (GATES), formulated by Michałowski [9] and presented recently in a series of papers, related to redox [7–26] and nonredox systems [27–32] in aqueous and in mixed-solvent media [33–37]. The closed system separated from its environment by diathermal walls secure a heat exchange between the system and its environment, and realize dynamic processes in a quasistatic manner under isothermal conditions.

The mathematical description of electrolytic nonredox systems within GATES is based on general rules of charge and elements conservation. Nonredox systems are formulated with use of charge (ChB) and concentration balances $f(Y_g)$, for elements/cores $Y_g \neq$ H, O. The description of redox systems is complemented by generalized electron balance (GEB) concept, discovered by Michałowski as the Approach I to GEB (1992) and the Approach II to GEB (2006); GEB is considered as a law of a matter conservation, as the law of nature [7, 9, 11, 13, 25].

http://dx.doi.org/10.5772/intechopen.69248

Formulation of redox systems according to GATES principles is denoted as GATES/GEB. Within the Approach II to GEB, based on linear combination $2{\cdot}f(O) - f(H)$ of the balances: $f(H)$ for H and $f(O)$ for O, the prior knowledge of oxidation degrees of all elements constituting the system is not needed; oxidants and reductants are not indicated. Moreover, the linear independency or dependency of $2{\cdot}f(O) - f(H)$ from other balances: ChB and $f(Y_g)$, is the general criterion distinguishing between redox and nonredox systems. Concentrations of the species within the balances are interrelated in a complete set of equations for equilibrium constants, formulated according to the mass action law principles. The GATES and GATES/GEB in particular, provide the best possible tool applicable for thermodynamic resolution of electrolytic systems of any degree of complexity, with the possibility of application of all physicochemical knowledge involved.

Several methods of equivalence volume (V_{eq}) determination are also presented in terms of the generalized equivalence mass (GEM) [8] concept, suggested by Michałowski (1979), with an emphasis put on the Gran methods and their modifications. The GEM concept has no relevance to a chemical reaction notation. Within GATES, the chemical reaction notation is only the basis to formulate the expression for the related equilibrium constant.

2. Formulation of generalized equivalent mass (GEM)

The main task of titration is the estimation of the equivalence volume, V_{eq}, corresponding to the volume $V = V_{eq}$ of T, where the fraction titrated (1) assumes the value

$$\Phi_{eq} = \frac{C \cdot V_{eq}}{C_0 \cdot V_0} \tag{2}$$

In contradistinction to visual titrations, where the end volume $V_e \cong V_{eq}$ is registered, all instrumental titrations aim, in principle, to obtain the V_{eq} value on the basis of experimental data $\{(V_j, y_j) \mid j = 1,\ldots,N\}$, where y = pH, E for potentiometric methods of analysis. Referring to Eq. (1), we have

$$C_0 \cdot V_0 = 10^3 \cdot m_A/M_A \tag{3}$$

where m_A [g] and M_A [g/mol] denote mass and molar mass of analyte (A), respectively. From Eqs. (1) and (3), we get

$$m_A = 10^{-3} \cdot C \cdot M_A \cdot V/\Phi \tag{4}$$

The value of the fraction V/Φ in Eq. (4), obtained from Eq. (1),

$$V/\Phi = C_0 \cdot V_0/C \tag{5}$$

is constant during the titration. Particularly, at the end (e) and equivalence (eq) points, we have

$$V/\Phi = V_e/\Phi_e = V_{eq}/\Phi_{eq} \tag{6}$$

The V_e [mL] value is the volume of T consumed up to the end (e) point, where the titration is terminated (ended). The V_e value is usually determined in visual titration, when a preassumed color (or color change) of D + T mixture is obtained. In a visual acid-base titration, pH_e value corresponds to the volume V_e (mL) of T added from the start for the titration and

$$\Phi_e = \frac{C \cdot V_e}{C_0 \cdot V_0} \tag{7}$$

is the Φ-value related to the end point. From Eqs. (4) and (6), one obtains:

$$m_A = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_e} \tag{8a}$$

$$m_A = 10^{-3} \cdot C \cdot V_{eq} \cdot \frac{M_A}{\Phi_{eq}} \tag{8b}$$

This does not mean that we may choose between the two formulas: (8a) and (8b), to calculate m_A. Namely, Eq. (8a) cannot be applied for the evaluation of m_A: V_e is known, but Φ_e unknown; calculation of Φ_e needs prior knowledge of C_0 value; e.g., for the titration NaOH $(C,V) \rightarrow HCl(C_0,V_0)$, see Appendix, we have

$$\Phi_e = \frac{C}{C_0} \times \frac{C_0 - \alpha_e}{C + \alpha_e} \text{ where } \alpha(\text{Appendix}), \text{ and } \alpha_e = \alpha(pH_e) \tag{9}$$

However, C_0 is unknown before the titration; otherwise, the titration would be purposeless. The approximate pH_e value is known in visual titration. Also Eq. (8b) is useless: the "round" Φ_{eq} value is known exactly, but V_{eq} is unknown; V_e (not V_{eq}) is determined in visual titrations.

Because Eqs. (8a) and (8b) appear to be useless, the third, approximate formula for m_A, has to be applied, namely:

$$m_A' \cong 10^{-3} \cdot C \cdot V_e \cdot M_A/\Phi_{eq} = 10^{-3} \cdot C \cdot V_e \cdot R_A{}^{eq} \tag{10}$$

where Φ_{eq} is put for Φ_e in Eq. (8a), and

$$R_A{}^{eq} = \frac{M_A}{\Phi_{eq}} \tag{11}$$

is named as the equivalent mass. The relative error in accuracy, resulting from this substitution, equals to

$$\delta = (m_A' - m_A)/m_A = m_A'/m_A - 1 = V_e/V_{eq} - 1 = \Phi_e/\Phi_{eq} - 1 \tag{12}$$

http://dx.doi.org/10.5772/intechopen.69248

For $\Phi_e = \Phi_{eq}$, we get $\delta = 0$ and $m_A' = m_A$; thus $\Phi_e \cong \Phi_{eq}$ (i.e., $V_e \cong V_{eq}$) corresponds to $m_A' \cong m_A$. A conscious choice of an indicator and a pH-range of its color change during the titration is possible on the basis of analysis of the related titration curve. From Eqs. (10) and (8b), we get

$$m_A = m_A'/(1+\delta) = m_A' \cdot \left(1 - \delta + \delta^2 - \ldots\right) \tag{13}$$

3. Accuracy and precision

In everyday conversation, the terms "accuracy" and "precision" are often used interchangeably, but in science—and analytical chemistry, in particular—they have very specific, and different definitions [38].

Accuracy refers to how close a result of measurement, e.g., expressed by concentration x (as an intensive variable), agrees with a known/true value x_0 of x in a sample tested. In N repeated trials made on this sample, we obtain x_j ($j = 1, \ldots, N$) and then the mean value $\overline{x}$ and variance s^2 are obtained

$$\overline{x} = \frac{1}{N} \cdot \sum_{j=1}^{N} x_j,\ s^2 = \frac{1}{N-1} \cdot \sum_{j=1}^{N} (x_j - x_0)^2 \tag{14}$$

The accuracy can be defined by the absolute value $|\overline{x} - x_0|$, whereas precision is defined by standard deviation, $s = (s^2)^{1/2}$; the accuracy and precision are brought here into the same units.

Accuracy and precision are the terms of (nearly) equal importance (weights: 1 and $(1 - 1/N)$ for the weighted sum of squares [39]) when involved in the relation [40, 41]

$$\frac{1}{N} \cdot \sum_{j=1}^{N} (x_j - x_0)^2 = 1 \cdot (\overline{x} - x_0)^2 + (1 - 1/N) \cdot s^2 \tag{15}$$

where x_j — experimental ($j = 1, \ldots, N$) and true (x_0) values for x, $\overline{x}$ — mean value, s^2 — variance. The problem referred to accuracy and precision of different methods of V_{eq} determination has been raised, e.g., in Refs. [42, 43].

Accuracy and precision of the results obtained from titrimetric analyses depend both on a nature of D + T system considered and the method of V_{eq} evaluation. Herein, the kinetics of chemical reactions and transportation phenomena are of paramount importance.

4. The $E = E(\Phi)$ and/or $pH = pH(\Phi)$ functions

Relatively simple, functional relationships for $\Phi = \Phi(pH)$, ascribed to acid-base D + T systems, are specified in an elegant/compact form in Refs. [6, 27, 28, 30], see Appendix.

In acid-base systems occurred in aqueous media, pH is a monotonic function of V or Φ. From the relation,

$$\frac{dpH}{d\Phi} = \frac{dpH}{dV} \cdot \frac{dV}{d\Phi} = \frac{C_0 \cdot V_0}{C} \cdot \frac{dpH}{dV} \tag{16}$$

it results that the $\Phi = \Phi(pH)$ and $pH = pH(\Phi)$ relationships are mutually interchangeable, $C_0V_0/C > 0$. The relation (16) can be extended on other plots.

Explicit formulation of functional relationships: $\Phi = \Phi(pH)$ and $E = E(\Phi)$, is impossible in complex systems, where two or more different kinds (acid-base, redox, complexation, precipitation, liquid-liquid phase equilibria [44, 45]) of chemical reactions occur sequentially or/and simultaneously [8]. The E values are referred to SHE scale.

Monotonicity of $pH = pH(\Phi)$ and/or $E = E(\Phi)$ is not a general property in electrolytic redox systems. In **Figure 1**, the monotonic growth of $E = E(\Phi)$, i.e., $dE/d\Phi > 0$, is accompanied by monotonic growth of $pH = pH(\Phi)$, i.e., $dpH/d\Phi > 0$ [20].

In **Figure 2**, the monotonic drops of $E = E(\Phi)$, i.e., $dE/d\Phi < 0$, are accompanied by nonmonotonic changes of $pH = pH(\Phi)$ [9, 46, 47].

From inspection of **Figure 2B**, it results that the neighboring, *quasi* linear segments of the line (at $C_{Hg} = 0$) intersect at the equivalent points $\Phi_{eq1} = 2.5$ and $\Phi_{eq2} = 3.0$. So, it might seem that the pH titration is an alternative to the potentiometric titration method for the V_{eq} detection. It should be noted, however, that there are small changes within the pH range, where the characteristics of glass electrode is nonlinear, and an extended calibration procedure of this electrode is required. The opportunities arising from potential E measurement are here incomparably higher, so the choice of potentiometric titration is obvious.

In **Figure 3**, the nonmonotonic changes of $E = E(V)$ are accompanied by nonmonotonic changes of $pH = pH(V)$ [16].

The unusual shape of the respective plots for $E = E(\Phi)$ and $pH = pH(\Phi)$ is shown in **Figure 4** [13].

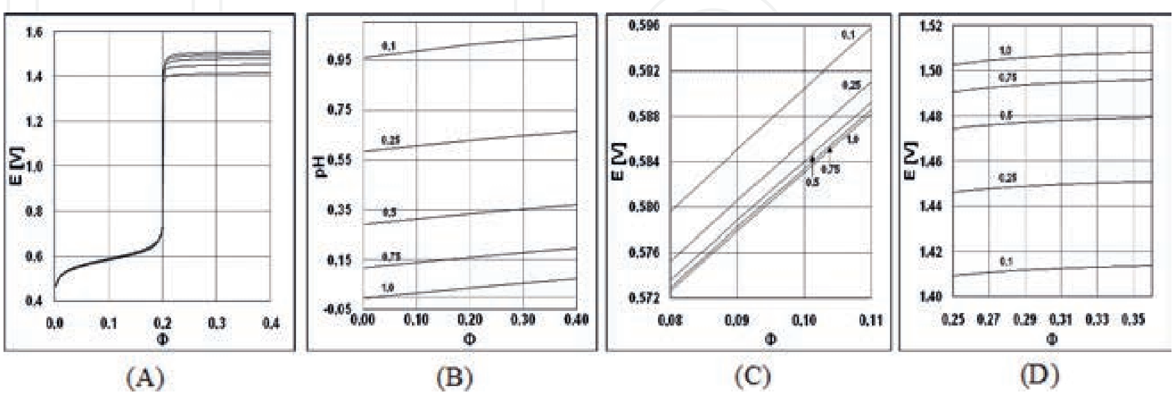

Figure 1. The collected (A) $E = E(\Phi)$ and (B) $pH = pH(\Phi)$ curves plotted for D + T system $KMnO_4$ (C) → $FeSO_4$ (C_0) + H_2SO_4 (C_{01}) at $V_0 = 100$, $C_0 = 0.01$, $C = 0.02$, and different C_{01} values, indicated in Figures (B), (C), and (D) (in enlarged scales), before and after $\Phi = \Phi_{eq} = 0.2$.

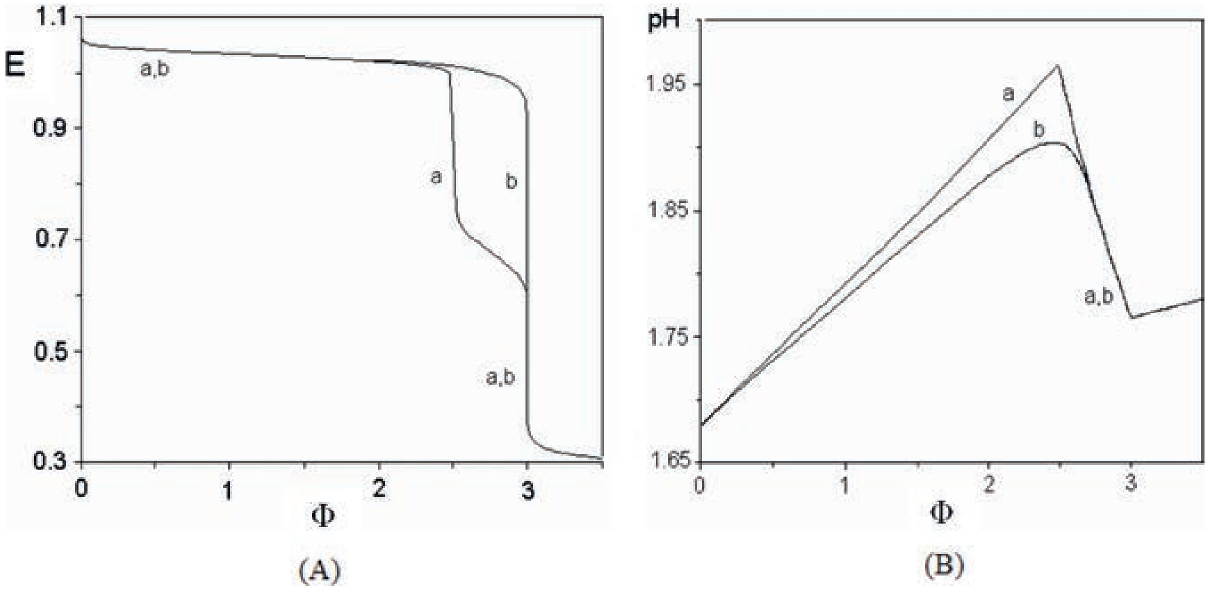

Figure 2. The theoretical plots of (A) E = E(Φ) and (B) pH = pH(Φ) functions for the D + T system, with KIO_3 ($C_0 = 0.01$) + HCl ($C_{01} = 0.02$) + H_2SeO_3 ($C_{Se} = 0.02$) + $HgCl_2$ (C_{Hg}) as D, and ascorbic acid $C_6H_8O_6$ (C = 0.1) as T; $V_0 = 100$, and (a) $C_{Hg} = 0$, (b) $C_{Hg} = 0.07$.

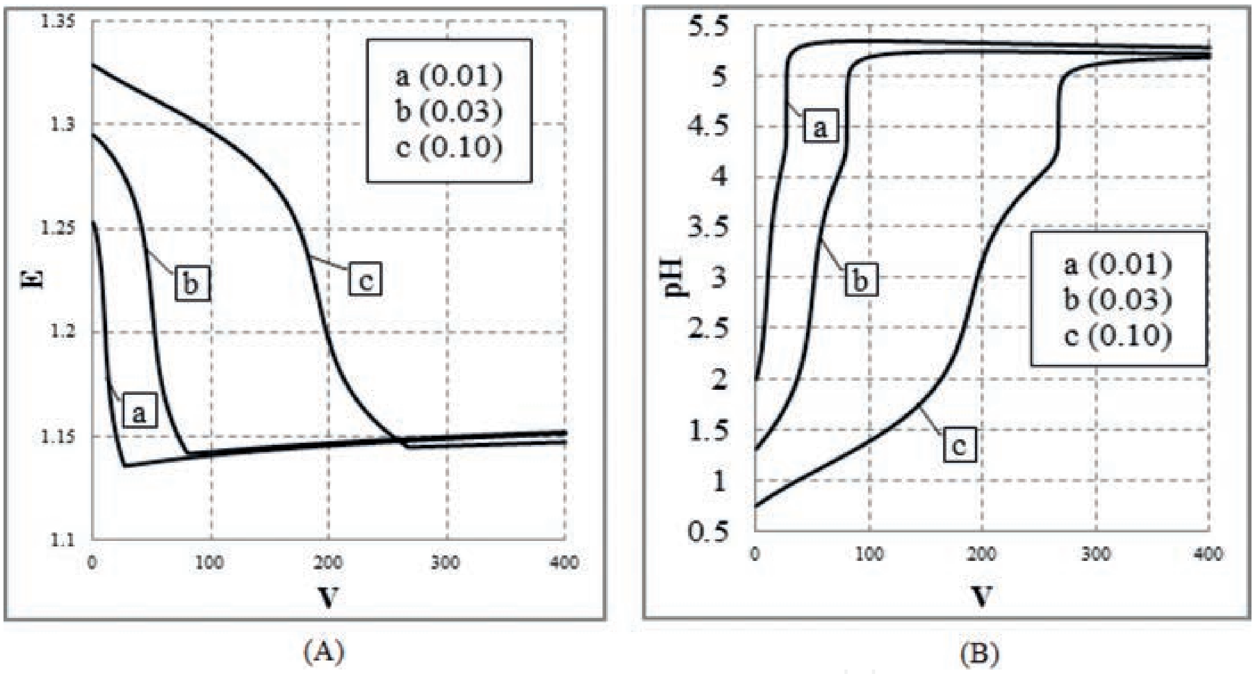

Figure 3. The theoretical plots of (A) E = E(V) and (B) pH = pH(V) functions for the system with $V_0 = 100$ mL of NaBr ($C_0 = 0.01$) + Cl_2 (C_{02}) as D titrated with V mL of $KBrO_3$ (C = 0.1) as T, at indicated (a, b, c) C_{02} values.

Other examples of the nonmonotonicity were presented in Refs. [7, 9, 46–49]. The nonmonotonic pH versus V relationships were also stated in experimental pH titrations made in some binary-solvent media [33]. Then, the Gran's statement "all titration curves are monotonic" [50] is not true, in general.

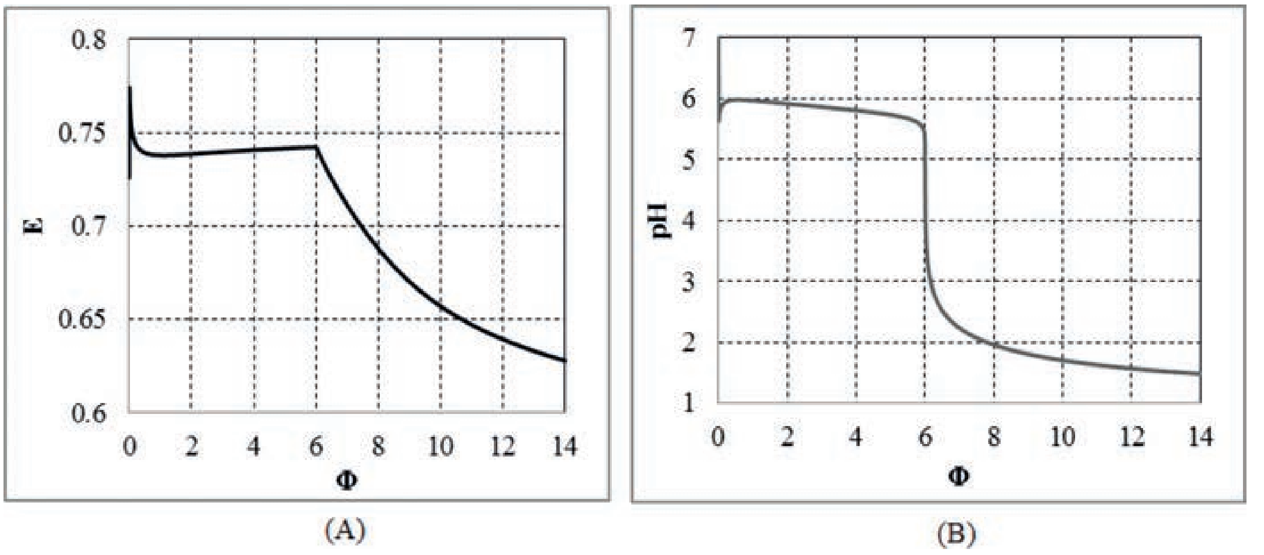

Figure 4. The plots of (A) $E = E(\Phi)$ and (B) $pH = pH(\Phi)$ functions for the system HI ($C = 0.1$) → KIO_3 ($C_0 = 0.01$).

5. Location of inflection and equivalence points

Some of the $E = E(\Phi)$ and/or $pH = pH(\Phi)$ (or $E = E(V)$ and/or $pH = pH(V)$) functions have inflection point(s), and characteristic S-shape (or reverse S-shape) is assumed within defined Φ (or V) range [51].

Generalizing, let us introduce the functions $y = y(V)$, where $y = E$ or pH and denote $V = V_{IP}$, with the volume referred to inflection point (IP) [52, 53], i.e., the point (V_{IP}, y_{IP}) of maximal slope $|\eta|$

$$\eta = \frac{dy}{dV} = \frac{1}{dV/dy} \tag{17}$$

on the related curve $y = y(V)$ ($y = E$, pH), plotted in normal coordinates (V, y) or their derivatives: $dy/dV = y_1(V)$ and $d^2y/dV^2 = y_2(V)$ on the ordinate. We have, by turns [54],

$$\frac{d^2y}{dV^2} = -\frac{1}{(dV/dy)^3} \cdot \frac{d^2V}{dy^2} \tag{18a}$$

$$\frac{d^2y}{dV^2} + \eta^3 \cdot \frac{d^2V}{dy^2} = 0 \tag{18b}$$

At $\eta \neq 0$, from Eq. (18b), we get $d^2V/dy^2 = 0$. Analogously to Eq. (16), we have

$$\frac{dE}{d\Phi} = \frac{C_0 \cdot V_0}{C} \cdot \frac{dE}{dV}$$

At the inflection point on the curve $y = y(V)$, we have maxima for $dy/d\Phi$ and $d^2y/dV^2 = 0$, see **Figure 5** for $y = E$ [55].

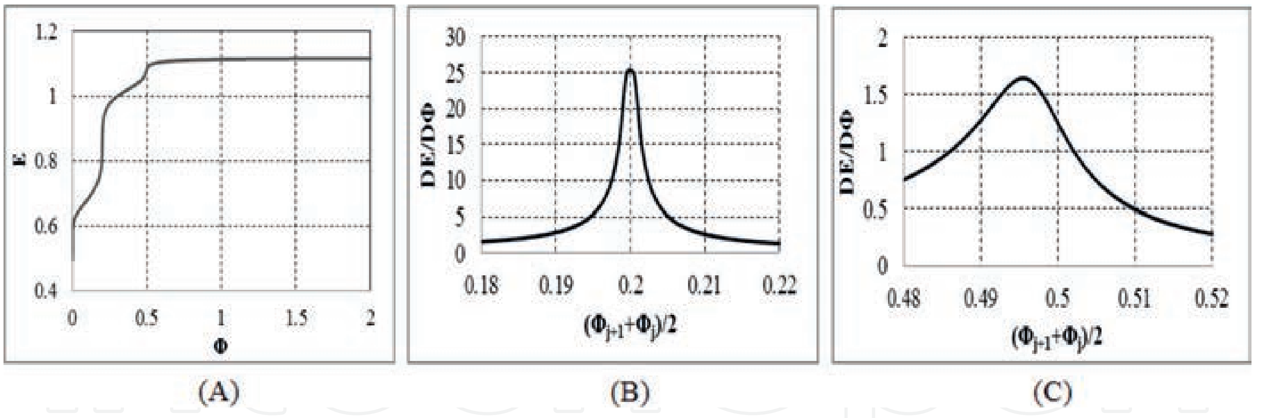

Figure 5. The function (A) $E = E(\Phi)$ and the difference quotient $DE/D\Phi = (E_{j+1} - E_j)/(\Phi_{j+1} - \Phi_j)$ versus $(\Phi_{j+1} + \Phi_j)/2$ relationships in the vicinity of $\Phi = 0.2$ (B) and $\Phi = 0.5$ (C) plotted for the system KIO_3 ($C = 0.1$) –> KI ($C_0 = 0.01$) + HCl ($C_{01} = 0.2$).

Referring to examples presented in **Figures 1A** and **2A**, we see that the inflection points (Φ_{IP}, E_{IP}) have the abscissas close to the related equivalence points (Φ_{eq}, E_{eq}), namely:

(0.2, 1.034)—see **Table 1** and **Figure 1A**;

(2.5, 0.903), (3.0, 0.414)—see **Table 2** and the curve a in **Figure 2A**;

(3.0, 0.652)—see **Table 2** and the curve b in **Figure 2A**;

Then we can consider Φ_{eq} (Eq. (2)) as a ratio of small natural numbers: p and q, i.e.,

$$\Phi_{eq} = \frac{p}{q} \quad (p,\ q \in N) \tag{19}$$

e.g., $\Phi_{eq} = 1$ (=1/1) for titration in D + T system with A = HCl and B = NaOH (see Eq. (9)); $\Phi_{eq} = 1/5 = 0.2$ in **Figure 1A** (see **Table 1**); $\Phi_{eq} = 5/2 = 2.5$ or $\Phi_{eq} = 3/1 = 3$ in **Figure 2A** (see **Table 2**).

Φ	**E**
0.19800	0.701
0.19900	0.719
0.19980	0.761
0.19990	0.778
0.19998	0.820
0.20000	1.034
0.20002	1.323
0.20010	1.365
0.20020	1.382
0.20200	1.442

Table 1. The (Φ, E) values related to $C_{01} = 0$ and other data presented in legend for **Figure 1A**.

$C_{Hg} = 0$				$C_{Hg} = 0.07$	
Φ	**E**	**Φ**	***E***	**Φ**	***E***
2.45	1.004	2.95	0.632	2.95	0.97
2.475	1	2.975	0.62	2.975	0.96
2.49	0.995	2.99	0.607	2.99	0.947
2.492	0.994	2.992	0.604	2.992	0.944
2.494	0.992	2.994	0.6	2.994	0.94
2.496	0.989	2.996	0.595	2.996	0.935
2.498	0.983	2.998	0.586	2.998	0.926
2.5	0.903	3	0.414	3	0.652
2.502	0.809	3.002	0.38	3.002	0.379
2.504	0.791	3.004	0.371	3.004	0.371
2.506	0.781	3.006	0.365	3.006	0.365
2.508	0.774	3.008	0.362	3.008	0.362
2.51	0.768	3.01	0.359	3.01	0.359
2.525	0.744	3.03	0.345	3.03	0.345
2.55	0.727	3.06	0.336	3.06	0.336

Table 2. The (Φ, E) values related to the data presented in legend for **Figure 2A**.

As we see (Eq. 12), the Φ_e values are compared each time with the "round" $\Phi_{eq} = p/q$ value for Φ_e due to the fact that just Φ_{eq} is placed in the denominator of the expression for the equivalent mass, $R_A{}^{eq}$ (Eq. (11)).

The Φ_e values, presented in **Tables 1** and **2** refer—in any case—to the close vicinity of the Φ_{eq} value(s), see e.g. $\Phi_{eq1} = 2.5$ and $\Phi_{eq2} = 3.0$.

Then from **Figures 1A** and **2A**, it results that location of IP is an interpolative method and $V_{IP} \cong V_{eq}$ [56], but in practice, this assumption may appear to be a mere fiction, especially in context with accuracy of measurements.

6. The case of diluted solutions

The V_{eq} and V_{IP} do not overlap in the systems of diluted solutions. For titration of V_0 mL of HB (C_0) with V mL of MOH (C), we have [6, 57]

$$V_{eq} - V_{IP} = \frac{x_{IP}}{1 + x_{IP}} \cdot (C_0/C + 1) \cdot V_0 \tag{20}$$

where

http://dx.doi.org/10.5772/intechopen.69248

$$x_{IP} = \frac{8K_W}{C^2} + \left(\frac{8K_W}{C^2}\right)^2 + \ldots \tag{21}$$

and $K_W = [H^{+1}][OH^{-1}]$. Similar relationship occurs for $AgNO_3$ (C,V) → NaCl (C_0,V_0) system; in this case, the relations [57]: Eq. (20) and

$$x_{IP} = \frac{8K_{sp}}{C^2} + \left(\frac{8K_{sp}}{C^2}\right)^2 + \ldots \tag{22}$$

where $K_{sp} = [Ag^{+1}][Cl^{-1}]$, are valid.

7. Some interpolative methods of V_{eq} determination

7.1. The Michałowski method

Two interpolative methods, not based on the IP location, were presented by Fortuin [58] and Michałowski [6, 57]. The Fortuin method is based on an nomogram; an extended form of Fortuin's nomogram was prepared by the author of Ref. [6]. The Michałowski and Fortuin methods are particularly applicable to NaOH (C,V) → HCl (C_0,V_0) and NaOH (C,V) → HCl (C_0,V_0) systems. However, the applicability of the Michałowski method is restricted to diluted D and T, where the Fortuin method is invalid. In the Michałowski method, V_{eq} is the real and positive root of the equation

$$(1-2a)\cdot {V_{eq}}^3 + (2-3a)\cdot V_0 \cdot {V_{eq}}^2 + {V_0}^2 \cdot V_{eq} - a \cdot {V_0}^3 = 0 \tag{23}$$

where

$$a = \frac{1}{3}\cdot\frac{3A_0 - 2V_0A_1 + {V_0}^2A_2}{A_0 - V_0A_1 + {V_0}^3A_3} \tag{24}$$

and A_0, A_1, A_2, A_3 are obtained from results $\{(V_j, E_j) \mid j = 1,\ldots, N\}$ of potentiometric titration, after applying the least squares method (LSM) to the function

$$\left(1+\frac{V}{V_0}\right)^3 \cdot E = \sum_{i=0}^{3} A_i \cdot V^i \tag{25}$$

A useful criterion of validity of the V_{eq} value are: pK = – log K (K = K_W or K_{sp}) and standard redox potential (E_0), calculated from the formulas [59]:

$$pK = \log\left(\frac{24}{C^2}\right) + \log\left(-\frac{a_3}{a_1}\right);\ E_0 = a_0 + \frac{RT}{2F}\cdot \ln 10 \cdot pK \tag{26}$$

where

$$a_3 = \frac{V_0{}^3}{3V_{eq}} \cdot \frac{3A_0 - 2V_0A_1 + V_0{}^2A_2}{(V_0 + V_{eq})^2};\ a_1 = \frac{3a_3V_{eq}}{2V_0{}^2} \cdot (V_0 - V_{eq}) + \frac{V_0}{2} \cdot \frac{3A_0 - A_2V_0{}^2}{V_0 + V_{eq}};\ a_0 = V_0{}^3 \cdot A_3 + a_1 + a_3 \tag{27}$$

7.2. The Fenwick–Yan method

The Yan method [59] is based on Newton's interpolation formula

$$f(x) = f(x_0) + \sum_{i=1}^{n} f_i(x_i) \cdot \prod_{j=0}^{i-1} (x - x_j) \tag{28}$$

where

$$f_1(x_j) = \frac{f(x_j) - f(x_0)}{x_j - x_0} \text{ for } j = 1, 2, \ldots, n$$

$$f_i(x_j) = \frac{f_{i-1}(x_j) - f_{i-1}(x_{i-1})}{x_j - x_{i-1}} \text{ for } j = i, \ldots, n$$

and on the assumption that $V_{eq} \cong V_{IP}$. Putting $n = 3$ in Eq. (28) and setting $d^2f(x)/dx^2 = 0$ for IP, after rearranging the terms one obtains

$$x_{IP} = \frac{1}{3} \cdot \left(x_0 + x_1 + x_2 - \frac{f_2(x_2)}{f_3(x_3)} \right) \tag{29}$$

Let $x_j = V_{k+j}$, $f(x_j) = y_{k+j}$, j = 0, 1, 2, 3; y = pH or E. According to Yan's suggestion, $x_{IP} \cong V_{eq}$. Then, on the basis of 4 experimental points (V_{k+j}, y_{k+j}) (j = 0, 1, 2, 3) taken from the immediate vicinity of V_{eq}, we get

$$V_{eq} = \frac{1}{3} \cdot \left(V_k + V_{k+1} + V_{k+2} - \frac{f_2(V_{k+2})}{f_3(V_{k+3})} \right) \tag{30}$$

Volumes V_{k+j} of T added were chosen from the immediate vicinity of V_{eq}. The best results are obtained if $V_{k+1} < V_{eq} < V_{k+2}$. The error in accuracy may be significant if $V_k < V_{eq} < V_{k+1}$ or $V_{k+2} < V_{eq} < V_{k+3}$. Moreover, the following conditions are also necessary for obtaining the accurate results: (i) volume increments $V_{k+i+1} - V_{k+I}$ (ca. 0.1 mL) are small and rather equal and (ii) concentrations of reagent in T and analyte in D are similar.

When the titrant is added in equal volume increments ΔV in the vicinity of the equivalence point, then $V_{k+j} - V_{k+i} = (j - i)\cdot\Delta V$, and Eq. (30) assumes the form

$$V_{eq} = V_{k+1} + \frac{y_k - 2y_{k+1} + y_{k+2}}{y_k - 3y_{k+1} + 3y_{k+2} - y_{k+3}} \cdot \Delta V \tag{31}$$

identical with one obtained earlier by Fenwick [60] on the basis of the polynomial function

$$y = A_0 + A_1 \cdot V + A_2 \cdot V^2 + A_3 \cdot V^3 \tag{32}$$

(compare it with Eq. (25)). In Ref. [6], it was stated that a simple equation for $x \cong V_{eq}$ can be obtained after setting n = 4 in Eq. (28). Then one obtains the following equation

$$6f_4(V_{k+4}) \cdot V_{eq}{}^2 + 3\left(f_3(V_{k+3}) - \beta \cdot f_4(V_{k+4})\right) \cdot V_{eq} + f_2(V_{k+2}) - \sigma \cdot f_3(V_{k+3}) + \gamma \cdot f_4(V_{k+4}) = 0 \tag{33}$$

where the parameters:

$$\sigma = V_k + V_{k+1} + V_{k=2}, \beta = \sigma + V_{k+3}, \gamma = \sum_{i>j=0}^{3} V_{k+i} \cdot V_{k+j}$$

are obtained on the basis of 5 points $\{(V_{k+j}, y_{k+j}) \mid j=0,\ldots,4\}$ from the close vicinity of V_{eq}.

8. Standardization and titrimetric analyses

The amount of an analyte in titrimetric analysis is determined from the volume of a titrant T (standard or standardized solution) required to react completely with the analyte in D. Titrations are based on standardization and determination steps. During the standardization, the titrant T with unknown concentration C of the species B is added into titrand D containing the standard S (e.g., potassium hydrogen phthalate, borax) with mass the m_S (g) known accurately. In this context, different effects involved with accuracy of visual titrations will be discussed.

Discussion on the formula 12 in context with Eq. (15) will be preceded by detailed considerations, associated with (1°) selection of an indicator (pH_e), (2°) volume V_0 of titrand D, (3°) concentration C_{0In} of indicator in D, (4°) buffer effect, and (5°) drop error, being considered as a whole. These effects will be considered first in context with nonredox systems. One should also draw attention whether the indicator is present in D as the salt or in the acidic form [61]; e.g., methyl orange is in the form of sodium salt, $NaIn = C_{14}H_{14}N_3NaO_3S$, more soluble than $HIn = C_{14}H_{15}N_3O_3S$.

To explain the effects 1° and 2°, we consider first a simple example, where the primary standard sample S is taken as an analyte A, A = S.

Example 1. We consider first the titration of n_S = 1 mmole of potassium hydrogen phthalate KHL solution with C = 0.1 mol/L NaOH. The equation for the related titration curve

$$\Phi = \frac{C}{C_0} \cdot \frac{(1 - \overline{n}) \cdot C_0 - \alpha}{C + \alpha} \tag{34}$$

is valid here [62], where α is specified in Appendix,

$$\overline{n} = \frac{2 \cdot [H_2L] + [HL^{-1}]}{[H_2L] + [HL^{-1}] + [L^{-2}]} = \frac{2 \cdot 10^{7.68-2pH} + 10^{4.92-pH}}{10^{7.68-2pH} + 10^{4.92-pH} + 1} \quad (35)$$

and $C_0 = 1/V_0$ (V_0 in mL). The values for the corresponding equilibrium constants are: $pK_W = 14$ for H_2O (in α), and $pK_1 = 2.76$, $pK_2 = 4.92$ for phthalic acid (H_2L).

The $\Phi = \Phi_e$ values in **Table 3** are calculated from Eq. (34) at some particular pH_e values, which denote limiting pH-values of color change for phenol red (6.4 ÷ 8.0), phenolphthalein (8.0 ÷ 10.0), and thymolphthalein (9.3 ÷ 10.5). A (unfavorable) dilution effect, expressed by different V_0 values, is involved here in context with particular indicators; at $pH_e = 6.4$, the dilution effect is insignificant, but grows significantly at higher pH_e values e.g., 10.5. As we see, at $pH_e = 8.0$, the $\Phi = \Phi_e$ value is closest to 1, assumed as Φ_{eq} in this case. At $pH_e = 6.4$ and 10.5, the Φ_e values differ significantly from 1. At $V_0 = 100$ and phenolphthalein used as indicator, at first appearance of pink color (pH ≈ 8.0), from Eq. (34) we have $\Phi_e = 0.9993 \Rightarrow \delta = -0.07\%$. The dilution practically does not affect the results of NaOH standardization against potassium hydrogen phthalate if pH titration is applied and titration is terminated at $pH_e \approx 8.0$ (**Table 3**).

A properly chosen indicator is one of the components of the D + T system in visual titrations. As a component of D having acid-base properties, the indicator should be included in the related balances [6, 62, 63]. The indicator effect, involved with its concentration, is considered in Examples 2 and 3. Moreover, the buffer effect is considered in Example 3.

Example 2. The equation of the titration curve for titration of V_0 mL of D containing $n_S = 1$ mmole of borax in the presence of C_{0In} mol/l methyl red ($pK_{In} = 5.3$) as an indicator with C = 0.1 mol/L HCl as T, is as follows [49, 62]

$$\Phi = \frac{C}{C_{0S}} \cdot \frac{(4\overline{n} - 10) \cdot C_{0S} + (1 - \overline{m}) \cdot C_{0In} + \alpha}{C - \alpha} \quad (36)$$

where α (Appendix), $C_0 = C_{0S} = 1/V_0$, and

$$\overline{n} = \frac{3 \cdot [H_3BO_3] + 2 \cdot [H_2BO_3] + [HBO_3]}{[H_3BO_3] + [H_2BO_3] + [HBO_3] + [BO_3]} = \frac{3 \cdot 10^{35.78-3pH} + 2 \cdot 10^{26.54-2pH} + 10^{13.80-pH}}{10^{35.78-3pH} + 10^{26.54-2pH} + 10^{13.80-pH} + 1} \quad (37)$$

pH_e	Φ_e		
	$V_0 = 50$	$V_0 = 100$	$V_0 = 200$
6.4	0.9679	0.9679	0.9678
8.0	0.9992	0.9993	0.9994
9.3	1.0012	1.0022	1.0051
10.0	1.0060	1.0010	1.0260
10.5	1.0190	1.0349	1.0825

Table 3. The Φ_e values for different $pH = pH_e$, calculated from Eq. (34), at C_0 and C values assumed in *Example* 1.

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$$\overline{m} = \frac{[HIn]}{[HIn] + [In]} = \frac{1}{1 + 10^{pH-5.3}} \tag{38}$$

It should be noted that the solution obtained after introducing 1 mmole of borax into water is equivalent to the solution containing a mixture of 2 mmoles of H_3BO_3 and 2 mmoles of NaH_2BO_3; $Na_2B_4O_7 + 5H_2O = 2H_3BO_3 + 2NaH_2BO_3$, resulting from complete hydrolysis of borax [62]. The results of calculations are presented in **Table 4**.

In context with **Table 4**, we refer to the one-drop error. For this purpose, let us assume that the end point was not attained after addition of V' mL of titrant T, and the analyst decided to add the next drop of volume ΔV mL of the T. If the end point is attained this time, i.e., $V_e = V' + \Delta V$, the uncertainty in the T volume equals ΔV. Assuming ΔV = 0.03 mL and applying Eq. (1), we have:

$\Phi' = C \cdot V'/(C_0 \cdot V_0)$, $\Phi_e = C \cdot V_e/(C_0 \cdot V_0)$ and then $\Delta\Phi = \Phi_e - \Phi' = C \cdot V_e/(C_0 \cdot V_0) - C \cdot V'/(C_0 \cdot V_0) = C \cdot \Delta V/(C_0 \cdot V_0)$. At V_0 = 100 mL, C_0 = 0.01 mol/L, C = 0.1 mol/L, and ΔV = 0.03 mL, we have

$$\Delta\Phi = C \cdot \Delta V/(C_0 \cdot V_0) = 0.003 \tag{39}$$

Taking the value Φ_e = 2.0048 in **Table 4**, which refers to V_0 = 100 mL, C_0 = 0.01 mol/L, C = 0.1 mol/L, $C_{0In} = 10^{-5}$ mol/L and pH_e = 4.4, we see that |2.0048 – 2| = 0.0048 > 0.003 i.e., the discrepancy between Φ_{eq} and Φ_e is greater than the one assumed for ΔΦ = 0.003; it corresponds to ca. 1.5 drop of the titrant. At pH_e = 6.2 and other data chosen as previously, we get |1.9973 – 2| = 0.0027 < 0.003 i.e., this uncertainty falls within one–drop error.

The indicator effect stated in **Table 4**, for V_0 = 100, C_0 = 0.01, C = 0.1 and pH_e = 4.4 equals in Φ-units: |2.0048 – 2.0047| = 0.0001 at $C_{0In} = 10^{-5}$ or |2.0058 – 2.0047| = 0.0011, i.e., it appears to be insignificant in comparison to ΔΦ = 0.003, and can therefore be neglected.

pH_e	Φ_e			
	C_{0In}	$V_0 = 50$	$V_0 = 100$	$V_0 = 200$
4.4	0	2.0027	2.0047	2.0087
	10^{-5}	2.0028	2.0048	2.0089
	10^{-4}	2.0033	2.0058	2.0109
5.3	0	1.9999	2.0001	2.0006
	10^{-5}	2.0001	2.0006	2.0016
	10^{-4}	2.0024	2.0051	2.0106
6.2	0	1.9964	1.9964	1.9965
	10^{-5}	1.9968	1.9973	1.9983
	10^{-4}	2.0008	2.0053	2.0142

Table 4. The Φ_e values calculated from Eqs. (36) to (38) for different pH = pH_e, C_{0In} and V_0 (mL) values assumed in Example 2. The pH_e values are related to the pH-interval <4.4 ÷ 6.2> corresponding to the color change of methyl red (HIn).

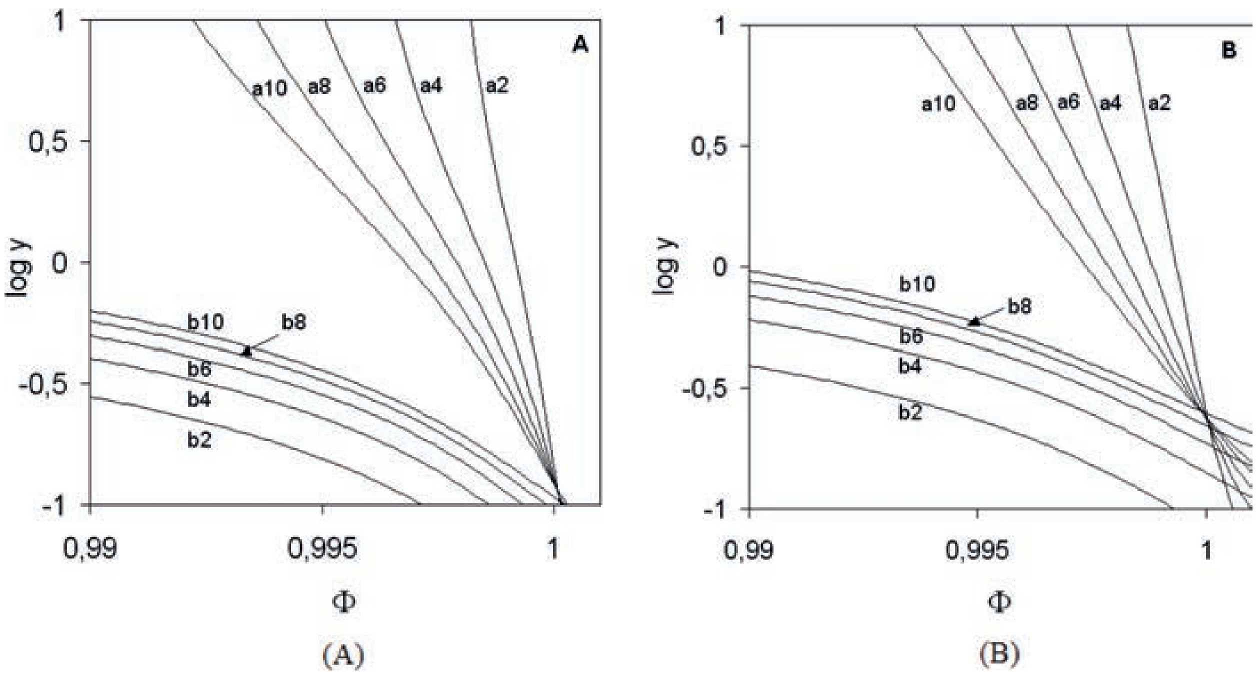

Figure 6. The logy versus Φ relationships in the close vicinity of $\Phi_{eq} = 1$, for $C_{In} = p \cdot 10^{-5}$ mol/L (p = 2, 4, 6, 8, 10); curves ap correspond to $C_{NH3} = 0.1$ mol/L, curves bp correspond to $C_{NH3} = 1.0$ mol/L; (A) refers to $r = 1$, (B) refers to $r = 4$.

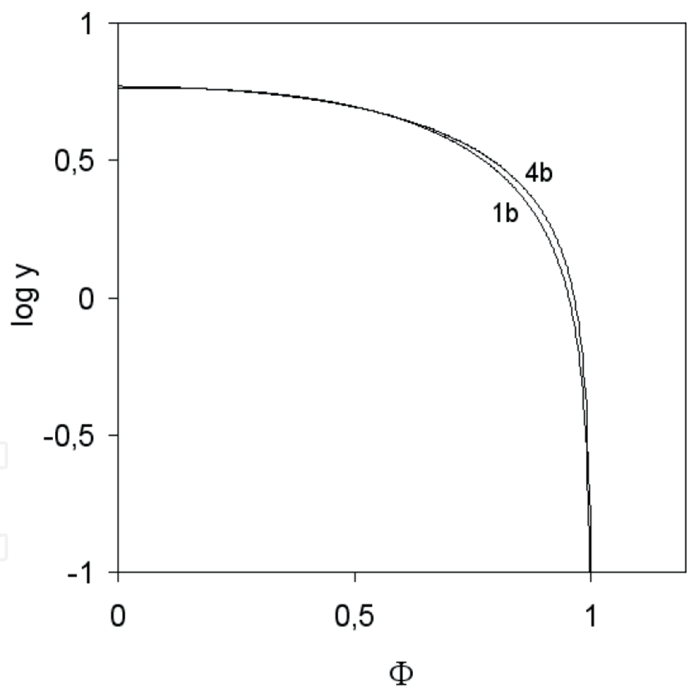

Figure 7. The logy versus Φ relationships plotted at $C_N = 1$ mol/L and $r = 1$ (curve 1b), and r = 4 (curve 4b).

Example 3. The solution of $ZnCl_2$ ($C_0 = 0.01$) buffered with NH_4Cl (C_1) and NH_3 (C_2), $C_1 + C_2 = C_N$, $r = C_2/C_1$, is titrated with EDTA ($C = 0.02$) in presence of Eriochrome Black T ($C_{In} = p \cdot 10^{-5}$, p = 2, 4, 6, 8, 10) as the indicator changes from wine red to blue color. The curves of logy versus Φ relationships, where

http://dx.doi.org/10.5772/intechopen.69248

$$y = \frac{x_2}{x_1} \text{ and : } x_1 = \sum_{i=0}^{3} [H_iIn],\ x_2 = [ZnIn] + 2[ZnIn_2]$$

are plotted in **Figure 6**, where (A) refers to r = 1, (B) refers to r = 4. It is stated that at $C_N = 0.1$, the solution becomes violet (red + blue) in the nearest vicinity of $\Phi_{eq} = 1$, and the color change occurs at this point. At $C_N = 1.0$, the solution has the mixed color from the very beginning of the titration (**Figure 7**). At $C_N > 1.0$, the solution is blue from the start of the titration. This system was discussed in more details in Refs. [9, 37, 49, 62].

9. Intermediary comments

If a concentration C of the properly chosen reagent B in T is known accurately from the standardization, the B (C mol/L) solution can be used later as titrant T, applied for determination of the unknown mass m_A of the analyte A in D. The B (C) reacts selectively with an analyte A (C_0 mol/L) contained in the titrand (D). This way, NaOH is standardized as in Example 1, and HCl is standardized as in Example 2. In Example 3, the standard solution of EDTA can be prepared from accurately weighed portion of this preparation, without a need for standardization, if EDTA itself can be obtained in enough pure form.

The reaction between A and S, B and A, or S and A should be fast i.e., equilibrium is reached after each consecutive portion of T added in the titration made with use of calibrated measuring instrument and volumetric ware.

In pH or potentiometric (E) titration, the correct readout with use of the proper measuring instrument needs identical equilibrium conditions at the measuring electrode and in the bulk solution, after each consecutive portion of T added in a *quasistatic* a priori manner under isothermal conditions assumed in the D + T system.

The quasistaticity assumption is fulfilled only approximately; however, the resulting error in accuracy is affected by a drift involved with retardation of processes occurred at the indicator electrode against ones in the bulk solution, where titrant T is supplied. Then, the methods based on the inflection point (IP) registration give biased results, as a rule. This discrepancy can be limited to a certain degree, after slowing down the titrant dosage. Otherwise, the end point lags behind the equivalence point because of a slow response of the electrode.

In modern chemical analysis, titrations are performed automatically and the titrant is introduced continuously. In this context, the transportation factors concerning the response of the indicating system are of paramount importance. At low concentration of analyte, the degree of incompleteness of the reaction is the highest around the equivalence point, and then the methods based on the inflection point registration give biased results, as a rule. The results like ones obtained with precision 0.02% within 5 min of the potentiometric titration performed with use of an ion–selective electrode or alike (according to some literature reports), can be considered only as a mere fiction.

In this context, for the reasons specified above, it is safer to apply extrapolative methods of titrimetric analyses. Such a requirement is fulfilled by some methods applied in potentiometric analysis; the best known ones are the Gran methods considered e.g., in Refs. [3, 6, 65, 77]. The Gran methods of V_{eq} determination can replace the currently used first-derivative method in the potentiometric titration procedure.

In the mathematical model applied for V_{eq} evaluation, it is tacitly assumed that activity coefficients and electrode junction potentials are invariable during the titration. The slope of indicator electrode should be known accurately; the statement that the slope should necessarily be Nernstian [66] is not correct. In reference to acid-base titrations, T and D should not be contaminated by carbonate; it particularly refers to a strong base solution used as T [67, 68].

10. The Gran methods

10.1. Introductory remarks

The Gran methods is an eponym of the well–known methods of linearization of the S–shaped curves of potentiometric E or pH titration [69–71]. In principle, there are two original Gran methods, known as Gran I method (abbr. G(I)) [72] and Gran II (abbr. G(II)) method [73, 74].

In current laboratory practice, only G(II) is applied mainly in alkalinity [75] (referred to seawaters, as a rule) and acid–base titrations, in general. The presumable reasons of G(I) factual rejection (this statement was nowhere pronounced in literature) were clearly presented in the chapter [65], where G(I) and G(II) were thoroughly discussed. It was stated that the main reason of rejection was too high error, inherent in the simplified model that can be brought to the approximation

$$\ln(1+x) \cong x \tag{40}$$

to the first term of the related Maclaurin's series [76]

$$\ln(1+x) = \sum_{j=1}^{\infty} (-1)^{j+1} \cdot x^j/j$$

The relation Eq. (40) is valid only at $|x| \ll 1$. To extend the x range, Michałowski suggested the approximation [6]

$$\ln(1+x) = \frac{x}{1+x/2} \tag{41}$$

that appeared to be better than expansion of ln(1+x) into the Maclaurin series, up to the 18th term at $|x| \leq 1$ [65], see **Figure 8**.

It is noteworthy that some trials were done by Gran himself [50] to improve G(I), but his proposal based on some empirical formulas was a kind of "prosthesis" applied to the defective model. In further years, the name "Gran method" (in singular) has been factually limited to G(II) i.e., in literature the term "Gran method" is practically perceived as one tantamount with G(II).

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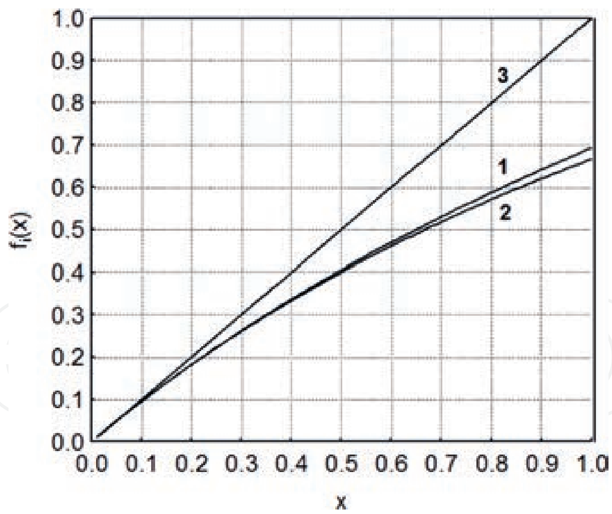

Figure 8. Comparison of the plots for: (1) $f_1(x) = \ln(1 + x)$, (2) $f_2(x) = x/(1 + x/2)$, and (3) $f_3(x) = x$ at different x-values, $0 < x \leq 1$.

10.2. The original Gran methods: G(I) and G(II)

The principle of the original Gran methods can be illustrated in a modified form [6], starting from titration of V_0 mL of C_0 mol/L HCl with V mL of C mol/L NaOH, taken as a simplest case. From charge and concentration balances, and $C_0V_0 = CV_{eq}$ i.e., $\Phi_{eq} = 1$ in Eq. (2), we get

$$([H^{+1}] - [OH^{-1}])(V_0 + V) = C \cdot (V_{eq} - V) \tag{42}$$

Applying the notations: $h = \gamma \cdot [H^{+1}]$, $ph = -\log h$, at $[H^{+1}] >> [OH^{-1}]$ (acid branch) i.e., $V < V_{eq}$, from Eq. (42) we have the relations:

$$(V_0 + V) \cdot 10^{-ph} = G_1 \cdot (V_{eq} - V) \tag{43}$$

$$ph \cdot \ln 10 = \ln(V_0 + V) - \ln G_1 + \ln\left(V_{eq} - V\right) \tag{44}$$

10.2.1. G(I) method

Applying Eq. (44) to the pair of points: (V_j, pH_j) and (V_{j+1}, pH_{j+1}), we have, by turns,

$$\ln 10 \cdot (pH_{j+1} - pH_j) = \ln \frac{V_0 + V_{j+1}}{V_0 + V_j} - \ln \frac{V_{eq} - V_{j+1}}{V_{eq} - V_j} \tag{45}$$

$$= \ln(1 + x_{1j}) - \ln(1 - x_{2j}) \tag{45a}$$

where:

$$x_{1j} = \frac{V_{j+1} - V_j}{V_0 + V_j} \tag{46a}$$

$$x_{2j} = \frac{V_{j+1} - V_j}{V_{eq} - V_j} \tag{46b}$$

Applying the approximation Eq. (40), we have:

$$\ln(1 + x_{1j}) \cong x_{1j};\ \ln(1 - x_{2j}) \cong -x_{2j} \tag{47}$$

Then we have, by turns,

$$\ln 10 \cdot (pH_{j+1} - pH_j) = x_{1j} + x_{2j} = (V_{j+1} - V_j) \cdot \frac{V_0 + V_{eq}}{(V_0 + V_j)(V_{eq} - V_j)} \tag{48}$$

$$y_j = G_1 \cdot (V_{eq} - V_j) + \varepsilon_j \tag{49}$$

$$y_j = P_1 - G_1 \cdot V_j + \varepsilon_j \tag{50}$$

where $P_1 = G_1 V_{eq}$, and

$$G_1 = \frac{\ln 10}{V_0 + V_{eq}} \tag{51}$$

$$y_j = \frac{1}{V_0 + V_j} \cdot \frac{V_{j+1} - V_j}{pH_{j+1} - pH_j} \tag{52}$$

From Eq. (50) and LSM, we get the formula

$$V_{eq} = \frac{P_1}{G_1} = \frac{\sum y_j V_j \cdot \sum V_j - \sum y_j \cdot \sum V_j^2}{N \cdot \sum y_j V_j - \sum y_j \cdot \sum V_j} \tag{53}$$

where $\sum = \sum_{j=1}^{N}$, and y_j is expressed by Eq. (52); it is the essence of G(I).

10.2.2. G(II) method

Eq. (43) can be rewritten into the regression equation

$$y_j = P_2 - G_2 \cdot V_j + \varepsilon_j \tag{54}$$

where:

$$G_2 = \gamma \cdot C \tag{55a}$$

$$P_2 = \gamma \cdot C \cdot V_{eq} = G_2 \cdot V_{eq} \tag{55b}$$

$$y_j = (V_0 + V_j) \cdot 10^{-ph_j} \tag{56}$$

Applying LSM to ph titration data {(V_j, ph_j) | j=1,…,N}, from (55b) we get

$$V_{eq} = \frac{P_2}{G_2} = \frac{\sum y_j V_j \cdot \sum V_j - \sum y_j \cdot \sum V_j^2}{N \cdot \sum y_j V_j - \sum y_j \cdot \sum V_j} \tag{57}$$

similar to Eq. (53), where y_j is expressed by Eq. (56) at this time; it is the essence of G(II).

10.3. The modified Gran methods

10.3.1. MG(I) method

Applying Eq. (41) to Eqs. (45a) and (46), we have

$$\ln(1 + x_{1j}) \cong \frac{x_{1j}}{1 + x_{1j}/2} = \frac{\frac{V_{j+1} - V_j}{V_0 + V_j}}{1 + \frac{V_{j+1} - V_j}{2(V_0 + V_j)}} = \frac{V_{j+1} - V_j}{V_0 + \frac{V_j + V_{j+1}}{2}} \tag{58a}$$

$$\ln(1 - x_{2j}) \cong \frac{-x_{2j}}{1 - x_{2j}/2} = \frac{-\frac{V_{j+1} - V_j}{V_{eq} - V_j}}{1 - \frac{V_{j+1} - V_j}{2(V_{eq} - V_j)}} = \frac{-(V_{j+1} - V_j)}{V_{eq} - \frac{V_j + V_{j+1}}{2}} \tag{58b}$$

From Eqs. (58) and (45a) we have, by turns,

$$\ln 10 \cdot (pH_{j+1} - pH_j) \cong (V_{j+1} - V_j) \cdot \left(\frac{1}{V_0 + V_j^*} + \frac{1}{V_{eq} - V_j^*} \right) = \frac{(V_{j+1} - V_j) \cdot (V_0 + V_{eq})}{(V_0 + V_j^*) \cdot (V_{eq} - V_j^*)} \tag{59}$$

$$y_j^* = G_1 \cdot (V_{eq} - V_j^*) + \varepsilon_j$$

$$y_j^* = P_1 - G_1 \cdot V_j^*) + \varepsilon_j \tag{60}$$

where G_1 and V_j^* are as in Eq. (51), and:

$$V_j^* = \frac{V_j + V_{j+1}}{2} \tag{61}$$

$$y_j^* = \frac{1}{V_0 + V_j^*} \cdot \frac{V_{j+1} - V_j}{pH_{j+1} - pH_j} \tag{62}$$

$$V_{eq} = \frac{P_1}{G_1} = \frac{\sum y_j^* V_j^* \cdot \sum V_j^* - \sum y_j^* \cdot \sum V_j^{*2}}{N \cdot \sum y_j^* V_j^* - \sum y_j^* \cdot \sum V_j^*} \tag{63}$$

Application of V_j^* in Eqs. (59) and (62), suggested in Ref. [6], improves the results of analyses when compared with Eqs. (50) and (52).

10.3.2. New algorithms referred to $Fe^{+2} + MnO_4^{-1}$ system

The algorithms applied below are referred to the system, where V_0 ml of the solution containing $FeSO_4$ (C_0) and H_2SO_4 (C_{01}) as D is titrated with V ml of $KMnO_4$ (C). The simplest form of GEB related to this system has the form [3, 46]

$$
\begin{aligned}
&\left[Fe^{+2}\right] + \left[FeOH^{+1}\right] + [FeSO_4] - \left(5\left[MnO_4^{-1}\right] + 4\left[MnO_4^{-2}\right] + \left[Mn^{+3}\right] + \left[MnOH^{+2}\right]\right) \\
&= (C_0V_0 - 5CV)/(V_0 + V) = (1 - 5\Phi)C_0V_0/(V_0 + V)
\end{aligned} \tag{64}
$$

Concentration balance for Fe has the form

$$
\begin{aligned}
&\left[Fe^{+2}\right] + \left[FeOH^{+1}\right] + [FeSO_4] + \left[Fe^{+3}\right] + \left[FeOH^{+2}\right] + \left[Fe(OH)_2{}^{+1}\right] + 2\left[Fe_2(OH)_2{}^{+4}\right] \\
&+ \left[FeSO_4{}^{+1}\right] + \left[Fe(SO_4)_2{}^{-1}\right] = C_0V_0/(V_0 + V)
\end{aligned} \tag{65}
$$

On the basis of **Figure 9**, at $\Phi < \Phi_{eq} = 0.2$ and low pH-values, Eqs. (64) and (65) assume simpler forms:

$$\left[Fe^{+2}\right] + [FeSO_4] = (1 - 5\Phi) \times C_0V_0/(V_0 + V) \tag{66}$$

$$\left[Fe^{+2}\right] + [FeSO_4] + \left[Fe^{+3}\right] + \left[FeSO_4{}^{+1}\right] + \left[Fe(SO_4)_2^{-1}\right] = C_0V_0/(V_0 + V) \tag{67}$$

These simplifications are valid at low pH-values (**Figure 6**). Eqs. (66) and (67) can be rewritten as follows:

$$\left[Fe^{+2}\right] \cdot b_2 = (1–5\Phi)C_0V_0/(V_0 + V) \tag{68}$$

$$[Fe^{+2}] \cdot (b_2 + f_{23} \cdot b_3) = C_0 \cdot V_0/(V_0 + V) \tag{69}$$

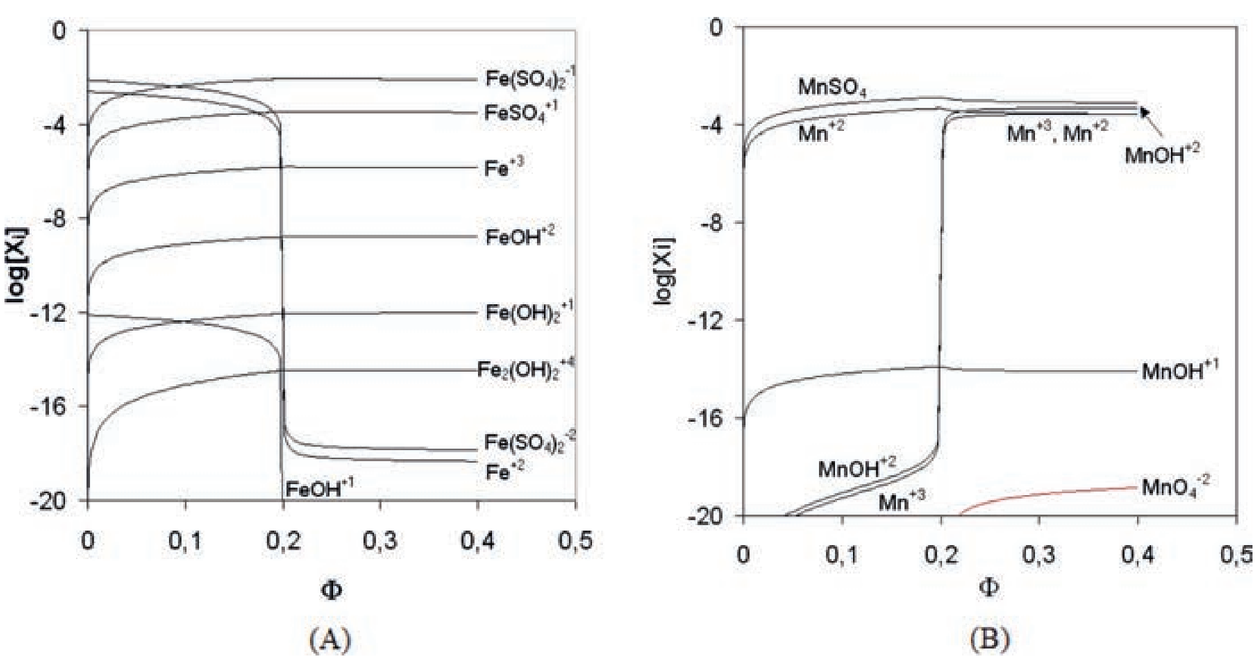

Figure 9. Dynamic speciation curves plotted for (A) Fe-species; (B) Mn-species in D + T system where $V_0 = 100$ mL of T ($FeSO_4$ ($C_0 = 0.01$) + H_2SO_4 ($C_{01} = 1.0$) is titrated with V ml of $KMnO_4$ (C = 0.02).

http://dx.doi.org/10.5772/intechopen.69248

valid for $\Phi < \Phi_{eq} = 0.2$, where:

$$b_2 = 1 + K_{21} \times \left[SO_4^{-2}\right] \tag{70a}$$

$$b_3 = 1 + K_{31} \times \left[SO_4^{-2}\right] + K_{32} \times \left[SO_4^{-2}\right]^2 \tag{70b}$$

$$f_{23} = \frac{[Fe^{+3}]}{[Fe^{+2}]} = 10^{A(E - E_0)} \tag{71a}$$

$$A = \frac{F}{R \cdot T \cdot \ln 10} = \frac{1}{a \cdot \ln 10} \tag{71b}$$

$$a = \frac{RT}{F} \tag{71c}$$

and $[FeSO_4] = K_{21}[Fe^{+2}][SO_4^{-2}]$, $[FeSO_4^{+1}] = K_{31}[Fe^{+3}][SO_4^{-2}]$, $[Fe(SO_4)_2^{-1}] = K_{32}[Fe^{+3}][SO_4^{-2}]^2$. From Eqs. (68) and (69), we have, by turns,

$$1 + f_{23} \cdot \frac{b_3}{b_2} = \frac{1}{1 - 5\Phi} \tag{72a}$$

$$10^{A(E - E_0)} \cdot \frac{b_3}{b_2} = \frac{5\Phi}{1 - 5\Phi} \tag{72b}$$

$$E = E_0 - a \cdot \ln\left(\frac{b_3}{b_2}\right) + a \cdot \ln(5\Phi) - a \cdot \ln(1 - 5\Phi) \tag{72c}$$

As results from **Figure 10**, the term $\ln(b_3/b_2)$ drops monotonically with Φ (and then V) value

$$\ln\left(\frac{b_3}{b_2}\right) = \alpha - \gamma \cdot \Phi \tag{73a}$$

$$\ln\left(\frac{b_3}{b_2}\right) = \alpha - \beta \cdot V \tag{73b}$$

The value for β in (73b) is small for higher C_{01} values, ca. 1 mol/L; in Ref. [77], it was stated that $\beta = 1.7 \cdot 10^{-3}$ at $C_{01} = 1.0$ mol/L; this change is small and can be neglected over the V-range covered in the titration. The assumption $\ln(b_3/b_2) = \text{const}$ is applied below in the simplified Gran models. For lower C_{01} values, this assumption provides a kind of drift introduced by the model applied, and then in accurate models, the formula Eq. (72c) is used.

From Eqs. (1) and (2), we have $\Phi/\Phi_{eq} = V/V_{eq}$; at $\Phi_{eq} = 0.2$, we get $5\Phi = V/V_{eq}$. Then applying Eq. (71b), we have

$$E = \omega - a \cdot (\alpha + \beta \cdot V) + a \cdot \ln\frac{V}{V_{eq}} - a \cdot \ln\left(1 - \frac{V}{V_{eq}}\right) \tag{74}$$

valid for $V < V_{eq}$, with the parameters: ω, α, β and a assumed constant within the V-range considered.

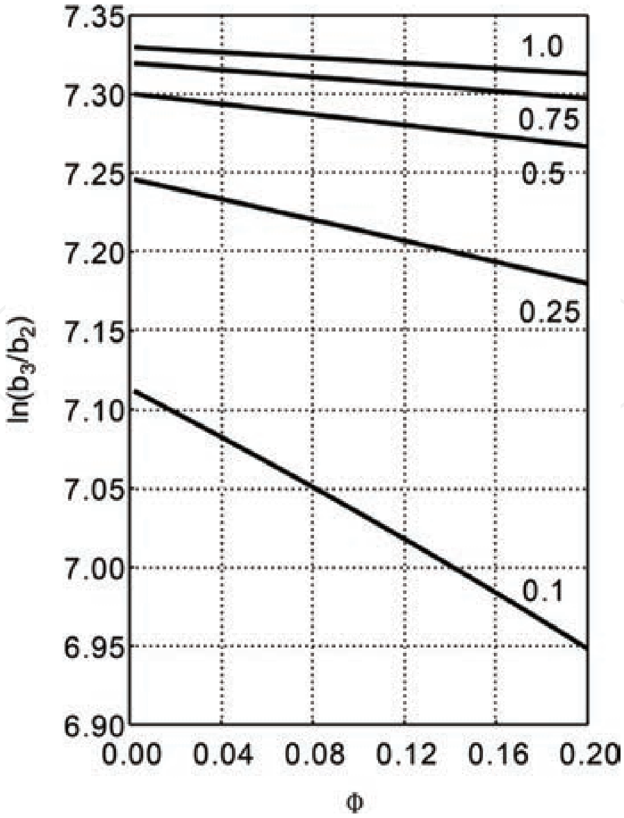

Figure 10. The $\ln(b_3/b_2)$ versus Φ relationships for the D + T system where $V_0 = 100$ mL of T ($FeSO_4$ ($C_0 = 0.01$) + H_2SO_4 (C_{01}) is titrated with V ml of $KMnO_4$ ($C = 0.02$). The lines are plotted at different concentrations (C_{01}) of H_2SO_4, indicated at the corresponding curves.

10.3.3. Simplified Gran I method

For jth and j+1th experimental point, from Eq. (72) we get:

$$\begin{aligned} E_j &= E_0 - a \cdot \ln\frac{b_3}{b_2} + a \cdot \ln(5\Phi_j) - a \cdot \ln(1 - 5\Phi_j); \\ E_{j+1} &= E_0 - a \cdot \ln\frac{b_3}{b_2} + a \cdot \ln(5\Phi_{j+1}) - a \cdot \ln(1 - 5\Phi_{j+1}) \\ E_{j+1} - E_j &= a \cdot \ln\frac{\Phi_{j+1}}{\Phi_j} - a \cdot \ln\frac{1 - 5\Phi_{j+1}}{1 - 5\Phi_j} \end{aligned} \tag{75}$$

Applying in Eq. (69) the identities: $\Phi_{j+1} = \Phi_j + \Phi_{j+1} - \Phi_j$ and $1 - 5\Phi_j = 1 - 5\Phi_{j+1} + 5(\Phi_{j+1} - \Phi_j)$ we have

$$E_{j+1} - E_j = a \cdot \ln(1 + x_{1j}) - a \cdot \ln(1 - x_{2j}) \tag{76}$$

where:

$$x_{1j} = (\Phi_{j+1} - \Phi_j)/\Phi_j \quad \text{and} \quad x_{2j} = 5(\Phi_{j+1} - \Phi_j)/(1 - 5\Phi_j) \tag{77}$$

Applying the approximation Eq. (41) [6] for $x = x_{1j}$ and $x = -x_{2j}$ in Eq. (69) and putting $\Phi_j = C \cdot V_j/(C_0 \cdot V_0)$, $\Phi_{j+1} = C \cdot V_{j+1}/(C_0 \cdot V_0)$, we get, by turns,

$$\ln(1 + x_{1j}) = \frac{\Phi_{j+1} - \Phi_j}{(\Phi_j + \Phi_{j+1})/2} = \frac{V_{j+1} - V_j}{V_j^*} \quad \text{and} \quad -\ln(1 - x_{2j}) = \frac{5(\Phi_{j+1} - \Phi_j)}{1 - 5(\Phi_j + \Phi_{j+1})/2} = \frac{V_{j+1} - V_j}{V_{eq} - V_j^*} \tag{78}$$

$$\frac{1}{V_j^*} \cdot \frac{V_{j+1} - V_j}{E_{j+1} - E_j} = G_1 \cdot (V_{eq} - V_j^*) + \varepsilon_j \tag{79}$$

$$y_j^* = P_1 - G_1 \cdot V_j^* + \varepsilon_j \tag{80}$$

where V_j^* (Eq. (61)), and

$$y_j^* = \frac{1}{V_j^*} \cdot \frac{V_{j+1} - V_j}{E_{j+1} - E_j} \tag{81}$$

$$P_1 = \frac{1}{a}, G_1 = \frac{1}{a \cdot V_{eq}} \tag{82}$$

$$V_{eq} = \frac{P_1}{G_1} \tag{83}$$

P_1 and G_1 in Eq. (80) are obtained according to LSM, as previously described.

10.3.4. Accurate Gran I method

Applying analogous procedure based on Eqs. (67) and (68), we get, by turns,

$$E_{j+1} - E_j = a \cdot \gamma \cdot (\Phi_{j+1} - \Phi_j) + a \cdot \ln(1 + x_{1j}) - a \cdot \ln(1 - x_{2j}) \tag{84}$$

$$E_{j+1} - E_j = a \cdot \gamma \cdot (\Phi_{j+1} - \Phi_j) + a \cdot \frac{(\Phi_{j+1} - \Phi_j)}{(\Phi_{j+1} + \Phi_j)/2} + a \cdot \frac{5 \cdot (\Phi_{j+1} - \Phi_j)}{1 - 5(\Phi_{j+1} + \Phi_j)/2} \tag{85}$$

$$\frac{E_{j+1} - E_j}{V_{j+1} - V_j} = B + \frac{a}{V_j^*} + \frac{a}{V_{eq} - V_j^*} + \varepsilon_j \tag{86}$$

where

$$B = \frac{a \cdot \gamma}{5V_{eq}} \tag{87}$$

The parameters: B, a and V_{eq} are then found according to iterative procedure; V_j^* is defined by Eq. (61).

10.3.5. Simplified Gran II method

From Eqs. (1), (2) and (72a), we have, by turns

$$f_{23} \cdot \frac{b_3}{b_2} = \frac{\Phi}{\Phi_{eq} - \Phi} = \frac{V}{V_{eq} - V} \tag{88}$$

In this case, the fraction b_3/b_2 is assumed constant. From Eqs. (88) and (71a), we get, by turns,

$$V \cdot 10^{-A \cdot E} = \frac{b_3}{b_2} \cdot 10^{-A \cdot E_0} \cdot (V_{eq} - V) \tag{89}$$

If b_3/b_2 is assumed constant, then $G_2 = b_2/b_3 \cdot 10^{-A \cdot E_0} =$ const, and

$$V_j \cdot 10^{-A \cdot E} = P_2 - G_2 \cdot V_j + \varepsilon_j \tag{90}$$

Then

$$V_{eq} = \frac{P_2}{G_2} \tag{91}$$

where P_2 and G_2 are calculated according to LSM from the regression equation (90).

10.3.6. MG(II)A method

At $\beta \cdot V << 1$, we write

$$\frac{b_3}{b_2} = e^{\alpha} \cdot e^{-\beta V} \cong e^{\alpha} \cdot (1 - \beta \cdot V) \tag{92}$$

From Eqs. (89) and (92), we get

$$\Omega = \Omega(\vartheta, V) = V \cdot 10^{-E/\vartheta} = G_2 \cdot (V_{eq} - V) \cdot (1 - \beta \cdot V) \tag{93}$$

where $G_2 = e^{\alpha} \cdot 10^{-A \cdot E_0} =$ const and real slope ϑ of an electrode is involved, after putting $1/\vartheta$ for A. From Eq. (93), we have

$$\Omega = \Omega(\vartheta, V) = V \cdot 10^{-E/\vartheta} = P \cdot V^2 - Q \cdot V + R \tag{94}$$

where:

$$P = G_2 \cdot \beta \tag{95a}$$

$$Q = G_2 \cdot (\beta \cdot V_{eq} + 1) \tag{95b}$$

$$R = G_2 \times V_{eq} \tag{95c}$$

The P, Q, and R values in Eqs. (95a,b,c) are determined according to LSM, applied to the regression equation

$$\Omega_j = P \cdot V_j^2 - Q \cdot V_j + R + +\varepsilon_j \tag{96}$$

where

$$\Omega_j = V_j \cdot 10^{-E_j/\vartheta} \tag{97}$$

Then we get, by turns,

$$\frac{R}{P} = \frac{V_{eq}}{\beta};\ \frac{Q}{R} = \beta + \frac{1}{V_{eq}}; P \cdot V_{eq}{}^2 - Q \cdot V_{eq} + R = 0 \tag{98}$$

$$V_{eq} = \frac{Q - \sqrt{Q^2 - 4 \cdot P \cdot R}}{2 \cdot P} \tag{99}$$

Eq. (96) is the basis for the modified G(II) method in its accurate version, denoted as MG(II)A method [77]. This method is especially advantageous in context of the error of analysis resulting from greater discrepancies $|\vartheta_c - \vartheta_p|$ between true (correct, ϑ_c) and preassumed (ϑ_p) slope values for RIE has been proved; the error in V_{eq} is significantly decreased even at greater $|\vartheta_c - \vartheta_p|$ values [77].

Numerous modifications of the Gran methods, designed also for calibration of redox indicator electrodes (RIE) purposes, were presented in the Refs. [4–6, 77]. Other calibration methods, related to ISE electrodes, are presented in Ref. [5].

10.4. Modified G(II) methods for carbonate alkalinity (CA) measurements

The G(II) methods were also suggested [28] and applied [78] for determination of carbonate alkalinity (CA) according to the modified CAM method. The CAM is related to the mixtures $NaHCO_3 + Na_2CO_3$ (system I) and $Na_2CO_3 + NaOH$ (system II), see **Table 5**. In addition to

No.	pH interval	Gran type functions	
		System I	System II
a	$pH > pK_2 + \Delta$	–	$(V_0 + V) \cdot 10^{ph} = C/K_W^* \cdot (V_a - V)$
b	$pK_2 - \Delta < pH \approx pK_2$	$(V_b + V) \cdot 10^{ph} = (K_2^*)^{-1} \cdot (V_c - V)$	$(V - V_a) \cdot 10^{ph} = (K_2^*)^{-1} \cdot (V_b - V)$
c	$pK_1 - \Delta \le pH \le pK_1 + \Delta$	$(V_d - V) \cdot 10^{-ph} = K_1^* \cdot (V - V_c)$	$(V_d - V) \cdot 10^{-ph} = K_1^* \cdot (V - V_c)$
d	$pH < pK_1 - \Delta$	$(V_0 + V) \cdot 10^{-ph} = \gamma \cdot C \cdot (V - V_d)$	$(V_0 + V) \cdot 10^{-ph} = \gamma \cdot C \cdot (V - V_d)$
Sequence of operations		d → c and b	d → c and b, a
Relationships		$V_d = V_{eq1} + V_{eq2}$	$V_d = V_{eq2} + V_{eq3}$
		$V_c = V_{eq2}/2$	$V_c = V_b = V_{eq2}/2 + V_{eq3}$
		$V_b = V_{eq1}$	$V_a = V_{eq3}$

Table 5. The modified Gran functions (CAM) related to the systems I and II (see text).

the determination of equivalence volumes, the proposed method gives the possibility of determining the activity coefficient of hydrogen ions (γ). Moreover, CAM can be used to calculate the dissociation constants (K_1, K_2) for carbonic acid and the ionic product of water (K_W) from a single pH titration curve. The parameters of the related functions are calculated according to LSM.

11. A brief review of other papers involved with titrimetric methods of analysis

11.1. Isohydric systems

Simple acid-acid systems are involved in isohydricity concept, formulated by Michalowski [31, 32, 79]. For the simplest case of acid-acid titration HB (C,V) → HL (C_0, V_0), where HB is a strong acid, HL is a weak monoprotic acid (K_1), the isohydricity condition, pH = const, occurs at

$$C_0 = C + C^2 \cdot 10^{pK_1} \tag{100}$$

where $pK_1 = -\log K_1$.

In such a system, the ionic strength of the D + T mixture remains constant during the titration, i.e., the isohydricity and isomolarity conditions are fulfilled simultaneously and independently on the volume V of the titrant added. On this basis, a very sensitive method of pK_1 determination was suggested [31, 32]. The isohydricity conditions were also formulated for more complex acid-acid, base-base systems, etc.

11.2. pH titration in isomolar systems

The method of pH titration in isomolar D + T systems of concentrated solutions (ionic strength 2–2.5 mol/L) is involved with presence of equal volumes of the sample tested both in D and T. The presence of a strong acid HB in one of the solutions is compensated by a due excess of a salt MB in the second solution [80–90]. In the systems tested, acid-base and complexation equilibria were involved. The method enables to calculate concentrations of components in the sample tested together with equilibrium constants and activity coefficient of hydrogen ions. This method was applied for determination of a complete set of stability constants for mixed complexes [91–94].

11.3. Carbonate alkalinity, total alkalinity, and alkalinity with fulvic acids

Ref. [29] was referred to complex acid-base equilibria related to nonstoichiometric species involved with fulvic acids and their complexes with other metal ions and simpler species present in natural waters. For mathematical description of such systems, the idea of Simms constants was recalled from earlier issues e.g., Refs. [27, 28, 84–88], and the concept of activity/basicity centers in such systems was introduced.

http://dx.doi.org/10.5772/intechopen.69248

11.4. Binary-solvent systems

Mutual pH titrations of weak acid solutions of the same concentration C in D and T formed in different solvents were applied [33–35] to formulate the $pK_i = pK_i(x)$ relationships for the acidity parameters, where x is the mole fraction of a cosolvent with higher molar mass in D + T mixture. The $pK_i = pK_i(x)$ relationship was based on the Ostwald's formula [95, 96] for monoprotic acid or the Henderson-Hasselbalch functions for diprotic and triprotic acids. The systems were modeled with the use of different nonlinear functions, namely Redlich-Kister and orthogonal (normal, shifted) Legendre polynomials. Asymmetric functions by Myers-Scott and the function suggested by Michałowski were also used for this purpose.

11.5. pH-static titration

Two kinds of reactions are necessary in V_{eq} registration according to pH–static titration; one of them has to be an acid–base reaction. The proton consumption or generation occurs in redox, complexation, or precipitation reactions [47], for example in titration of arsenite(+3) solution with I_2 + KI solution [18]; zinc salt solution with EDTA [97]; cyanide according to a (modified) Liebig-Denigès method [65, 102, 103].

11.6. Titration to a preset pH value

A cumulative effect of different factors on precision of V_{eq} determination was considered in [98] for pH titration of a weak monoprotic acids HL with a strong base, MOH. The results of calculations were presented graphically.

11.7. Dynamic buffer capacity

The dynamic buffer capacity concept, β_V, involving the dilution effect in acid-base D + T system, has been introduced [99] and extended in further papers [27, 28, 30, 100].

11.8. Other examples

The errors involved with more complex titrimetric analyses of chloride (mercurimetric method) [101], and cyanide (modified) Liebig-Denigès method) [97, 102, 103]. A modified, spectro-pH-metric method of dissociation constant determination was presented in Ref. [104]. An overview of potentiometric methods of titrimetric analyses was presented in Ref. [64]. The titration of ammonia in the final step of the Kjeldahl method of nitrogen determination [105, 106] was discussed in Ref. [107].

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Three (complexation, acid-base, precipitation) kinds of reactions occur in the Liebig-Denigès method mentioned above. Four elementary (redox, complexation, acid-base, precipitation of I_2) types of reactions occur in the D + T system described in the legend for **Figure 2** and in less complex HCl → NaIO system presented in Ref. [21]. Other examples of high degree of complexity are shown in the works [9, 11, 12, 14–16]. One of the examples in Ref. [12] concerns a four-step analytical process with the four kinds of reactions, involving three electroactive elements.

12. Final comments

The Generalized Approach To Electrolytic Systems (GATES) provides the possibility of thermodynamic description of equilibrium and metastable, redox and non-redox, mono- and two-phase systems of any degree of complexity. It gives the possibility of all attainable/pre-selected physicochemical knowledge to be involved, with none simplifying assumptions done for calculation purposes. It can be applied for different types of reactions occurring in batch or dynamic systems, of any degree of complexity. The generalized electron balance (GEB) concept, discovered (1992, 2006) by Michałowski [11, 13] and obligatory for description of redox systems, is fully compatible with charge and concentration balance(s), and relations for the corresponding equilibrium constants.

The chapter provides some examples of dynamic electrolytic systems of different degree of complexity, realized in titrimetric procedure that may be considered from physicochemical and/or analytical viewpoints. In all instances, one can follow measurable quantities (potential E, pH) in dynamic and static processes, and gain the information about details not measurable in real experiments; it particularly refers to dynamic speciation. In the calculations made according to iterative computer programs, all physicochemical knowledge can be involved.

This chapter aims to demonstrate the huge/versatile possibilities inherent in GATES, as a relatively new quality of physicochemical knowledge gaining from electrolytic systems of different degrees of complexity, realizable with use of iterative computer programs.

Appendix

Expressions for Φ related to some D + T acid-base systems [6]; $M^{+1} = Na^{+1}$, K^{+1}; $B^{-1} = Cl^{-1}$, NO_3^{-1}; $k = 0,\ldots,n$ (nos. 1–10), $k = 0,\ldots,q - n$ (no. 11); $l = 0,\ldots,m$.

No.	A	B	$\Phi =$
1	HCl	MOH	$\frac{C}{C_0}\cdot\frac{C_0-\alpha}{C+\alpha}$
2	MOH	HB	$\frac{C}{C_0}\cdot\frac{C_0+\alpha}{C-\alpha}$
3	$M_kH_{n-k}L$	MOH	$\frac{C}{C_0}\cdot\frac{(n-k-\bar{n})\cdot C_0-\alpha}{C+\alpha}$
4	$M_kH_{n-k}L$	HB	$\frac{C}{C_0}\cdot\frac{(\bar{n}+k-n)\cdot C_0+\alpha}{C-\alpha}$

http://dx.doi.org/10.5772/intechopen.69248

No.	A	B	$\Phi =$
5	$(NH_4)_kH_{n-k}L$	MOH	$\frac{C}{C_0}\cdot\frac{(n-k\cdot\overline{n}_N-\overline{n})\cdot C_0-\alpha}{C+\alpha}$
6	$(NH_4)_kH_{n-k}L$	HB	$\frac{C}{C_0}\cdot\frac{(\overline{n}+k\cdot\overline{n}_N-n)\cdot C_0+\alpha}{C-\alpha}$
7	$M_kH_{n-k}L$	$M_lH_{m-l}Ł$	$\frac{C}{C_0}\cdot\frac{(\overline{n}+k-n)C_0+\alpha}{(m-l-\overline{m})C-\alpha}$
8	$M_kH_{n-k}L$	$(NH_4)_lH_{m-l}Ł$	$\frac{C}{C_0}\cdot\frac{(\overline{n}+k-n)\cdot C_0+\alpha}{(m-l\cdot\overline{n}_N-\overline{m})\cdot C-\alpha}$
9	$(NH_4)_kH_{n-k}L$	$M_lH_{m-l}Ł$	$\frac{C}{C_0}\cdot\frac{(\overline{n}+k\cdot\overline{n}_N-n)\cdot C_0+\alpha}{(m-l-\overline{m})\cdot C-\alpha}$
10	$(NH_4)_kH_{n-k}L$	$(NH_4)_lH_{m-l}Ł$	$\frac{C}{C_0}\cdot\frac{(\overline{n}+k\cdot\overline{n}_N-n)\cdot C_0+\alpha}{(m-l\cdot\overline{n}_N-\overline{m})\cdot C-\alpha}$

The symbols:

$$\overline{n}=\frac{\sum_{i=1}^{q} i\cdot[H_iL^{+i-n}]}{\sum_{i=0}^{q}[H_iL^{+i-n}]}=\frac{\sum_{i=1}^{q} i\cdot 10^{\log K_{Li}^H-i\cdot pH}}{\sum_{i=0}^{q}10^{\log K_{Li}^H-i\cdot pH}}$$

$$\overline{m}=\frac{\sum_{i=1}^{p} i\cdot[H_iŁ^{+i-m}]}{\sum_{i=0}^{p}[H_iŁ^{+i-n}]}=\frac{\sum_{i=1}^{p} i\cdot 10^{\log K_{Łi}^H-i\cdot pH}}{\sum_{i=0}^{p}10^{\log K_{Łi}^H-i\cdot pH}}$$

$$\overline{n}_N=\frac{[NH_4^{+1}]}{[NH_4^{+1}]+[NH_3]}=\frac{10^{\log K_{1N}^H-pH}}{10^{\log K_{1N}^H-pH}+1}$$

enable to get a compact form of the functions, where:

$[H_iL^{+i-n}]=K_{Li}^H\cdot[H^+]^i[L^{-n}]$ (i = 0,…,q); $[H_iŁ^{+i-m}]=K_{Łi}^H\cdot[H^+]^i[Ł^{-m}]$(i = 0,…,p) ; $[NH_4^{+1}]=K_{1N}^H[H^+][NH_3]$ ($\log K_{1N}^H=9.35$); $K_{L0}^H=K_{Ł0}^H=1$; $M^{+1}=K^{+1}$, Na^{+1} ; $[H^{+1}]=10^{-pH}$

and the ubiquitous symbol

$$\alpha=[H^{+1}]-[OH^{-1}]=10^{-pH}-10^{pH-pK_w}$$

termed as "proton excess" is used; $pK_W = 14.0$ is assumed here.

Notations

D, titrand; T, titrant; V_0, volume of D; V, volume of T; all volumes are expressed in mL; all concentrations are expressed in mol/L.

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References

[1] Dasgupta, PK, Tanaka H, Jo KD. Continuous on-line true titrations by feedback based flow ratiometry. Application to potentiometric acid-base titrations. Analytica Chimica Acta. 2001;**435**:289–297

[2] Felber H, Rezzonico S, Mariassy M. Titrimetry at a metrological level. Metrologia **40** (2003) 249–254

[3] Michałowski T, Baterowicz A, Madej A, Kochana J. An extended Gran method and its applicability for simultaneous determination of Fe(II) and Fe(III). Analytica Chimica Acta. 2001;**442**(2):287–293

[4] Ponikvar M, Michałowski T, Kupiec K, Wybraniec S, Rymanowski M. Experimental verification of the modified Gran methods applicable to redox systems. Analytica Chimica Acta. 2008;**628**(2):181–189

[5] Michałowski T, Pilarski B, Ponikvar-Svet M, Asuero AG, Kukwa A, Młodzianowski J. New methods applicable for calibration of indicator electrodes. Talanta. 2011;**83**(5):1530–1537

[6] Michałowski T. Some remarks on acid-base titration curves. Chemia Analityczna. 1981; **26**:799–813

[7] Michałowski T. The Generalized Approach to Electrolytic Systems: I. Physicochemical and Analytical Implications. Critical Reviews in Analytical Chemistry. 2010;**40**(1):2–16

[8] Michałowski T, Pietrzyk A, Ponikvar-Svet M, Rymanowski M. The generalized approach to electrolytic systems: II. The generalized equivalent mass (GEM) concept. Critical Reviews in Analytical Chemistry. 2010;**40**(1):17–29

[9] Michałowski T. Application of GATES and MATLAB for resolution of equilibrium, metastable and non-equilibrium electrolytic systems, chapter 1 (pp. 1–34). In: Applications of MATLAB in Science and Engineering. Michałowski T, editors. Rijeka: InTech—Open Access publisher in the fields of Science, Technology and Medicine; 2011

[10] Michałowska-Kaczmarczyk AM, Asuero AG, Michałowski T. "Why not stoichiometry" versus "Stoichiometry – why not?" Part I. General context. Critical Reviews in Analytical Chemistry. 2015;**45**(2):166–188

[11] Michałowska-Kaczmarczyk AM, Asuero AG, Toporek M, Michałowski T. "Why not stoichiometry" versus "Stoichiometry – why not?" Part II. GATES in context with redox systems. Critical Reviews in Analytical Chemistry. 2015;**45**(3):240–268

[12] Michałowska-Kaczmarczyk AM, Michałowski T, Toporek M, Asuero AG. "Why not stoichiometry" versus "Stoichiometry – why not?" Part III, extension of GATES/GEB on complex dynamic redox systems. Critical Reviews in Analytical Chemistry. 2015;**45**(4): 348–366

[13] Michałowski T, Toporek M, Michałowska-Kaczmarczyk AM, Asuero AG. New trends in studies on electrolytic redox systems. Electrochimica Acta. 2013;**109**:519–531

[14] Michałowski T, Michałowska-Kaczmarczyk AM, Toporek M. Formulation of general criterion distinguishing between non-redox and redox systems, Electrochimica Acta. 2013;**112**:199–211

[15] Michałowska-Kaczmarczyk AM, Toporek M, Michałowski T. Speciation diagrams in dynamic iodide + dichromate system. Electrochimica Acta. 2015;**155**:217–227

[16] Toporek M, Michałowska-Kaczmarczyk AM, Michałowski T. Symproportionation versus disproportionation in bromine redox systems. Electrochimica Acta. 2015;**171**:176–187

[17] Michałowska-Kaczmarczyk AM, Michałowski T, Toporek M. Formulation of dynamic redox systems according to GATES/GEB principles. International Journal of Electrochemical Science. 2016;**11**:2560–2578

[18] Michałowski T, Ponikvar-Svet M, Asuero AG, Kupiec K. Thermodynamic and kinetic effects involved with pH titration of As(III) with iodine in a buffered malonate system. Journal of Solution Chemistry. 2012;**41**(3):436–446

[19] Michałowska-Kaczmarczyk AM, Michałowski T. Comparative balancing of non-redox and redox electrolytic systems and its consequences. American Journal of Analytical Chemistry. 2013;**4**(10):46–53

[20] Michałowska-Kaczmarczyk AM, Rymanowski M, Asuero AG, Toporek M, Michałowski T. Formulation of titration curves for some redox systems. American Journal of Analytical Chemistry. 2014;**5**:861–878

[21] Toporek M, Michałowska-Kaczmarczyk AM, Michałowski T. Disproportionation reactions of HIO and NaIO in static and dynamic systems. American Journal of Analytical Chemistry. 2014;**5**:1046–1056

[22] Michałowska-Kaczmarczyk AM, Michałowski T. Generalized electron balance for dynamic redox systems in mixed-solvent media. Journal of Analytical Sciences, Methods and Instrumentation. 2014;**4**(4):102–109

[23] Michałowska-Kaczmarczyk AM, Michałowski T. Compact formulation of redox systems according to GATES/GEB principles. Journal of Analytical Sciences, Methods and Instrumentation. 2014;**4**(2):39–45

[24] Michałowska-Kaczmarczyk AM, Michałowski T. GATES as the unique tool for simulation of electrolytic redox and non-redox systems. Journal of Analytical & Bioanalytical Techniques. 2014:**5**(4)

[25] Michałowski T. Generalized electron balance (GEB) as a law of preservation for electrolytic redox systems. The 65th Annual Meeting of the International Society of Electrochemistry, 31 August - 5 September, 2014, Lausanne, Switzerland, ise141331

[26] Meija J, Michałowska-Kaczmarczyk AM, Michałowski T. Redox titration challenge. Analytical and Bioanalytical Chemistry. 2017;**409**(1):11–13

[27] Asuero AG, Michałowski T. Comprehensive formulation of titration curves referred to complex acid-base systems and its analytical implications. Critical Reviews in Analytical Chemistry. 2011;**41**:151–187

[28] Michałowski T, Asuero AG. New approaches in modeling the carbonate alkalinity and total alkalinity. Critical Reviews in Analytical Chemistry. 2012;**42**:220–244

[29] Michałowska-Kaczmarczyk AM, Michałowski T. Application of Simms constants in modeling the titrimetric analyses of fulvic acids and their complexes with metal ions. Journal of Solution Chemistry. 2016;**45**:200–220

[30] Michałowska-Kaczmarczyk AM, Michałowski T. Dynamic buffer capacity in acid-base systems. Journal of Solution Chemistry. 2015;**44**:1256–1266

[31] Michałowski T, Pilarski B, Asuero AG, Dobkowska A. A new sensitive method of dissociation constants determination based on the isohydric solutions principle. Talanta. 2010;**82**(5):1965–1973

[32] Michałowski T, Pilarski B, Asuero AG, Dobkowska A, Wybraniec S. Determination of dissociation parameters of weak acids in different media according to the isohydric method. Talanta. 2011;**86**:447–451

[33] Pilarski B, Dobkowska A, Foks H, Michałowski T. Modeling of acid–base equilibria in binary-solvent systems: A comparative study. Talanta. 2010;**80**(3):1073–1080

[34] Michałowski T, Pilarski B, Dobkowska A, Młodzianowski J. Mathematical modeling and physicochemical studies on acid-base equilibria in binary-solvent systems. Wiadomości Chemiczne. 2010;**54**:124–154

[35] Michałowski T, Pilarski B, Asuero AG, Michałowska-Kaczmarczyk AM. Modeling of acid-base properties in binary-solvent systems, Chapter **9.4**. pp. 623–648. In: "Handbook of Solvents", Vol 1 Properties. Wypych G, editors. Toronto: ChemTec Publishing; 2014

[36] Michałowski T. Is the chemical equivalent due to the reaction equation notation? (in Polish). Orbital. 1999;**3/99**:174–176

[37] Michałowska-Kaczmarczyk AM, Michałowski T. Linear dependence of balances for non-redox electrolytic systems. American Journal of Analytical Chemistry. 2014;**5**:1285–1289

[38] https://en.wikipedia.org/wiki/Accuracy_and_precision

[39] https://en.wikipedia.org/wiki/Weight_function [accessed on August 5, 2017]

[40] Michałowski T, Rokosz A, Wójcik E. Optimization of the conventional method of determination of zinc as 8-oxyquinolinate in alkaline tartrate medium. Chemia Analityczna. 1980;**25**:563–566

[41] Michałowska-Kaczmarczyk M, Michałowski T. Simplex optimization and its applicability for solving analytical problems. Journal of Applied Mathematics and Physics. 2014;**2**:723–736

[42] Anfalt T, Jagner D. The precision and accuracy of some current methods for potentiometric end-point determination with reference to a computer-calculated titration curve. Analytica Chimica Acta. 1971;**57**:165–176

[43] Briggs TN, Stuehr JE. Simultaneous determination of precise equivalence points and pK values from potentiometric data. Single pK systems. Analytical Chemistry. 1974;**46**(11): 1517–1521

[44] Michałowski T, Lesiak A. Acid-base titration curves in disproportionating redox systems. Journal of Chemical Education. 1994;**71**(8):632–636

[45] Michałowski T. Effect of mutual solubility of solvents in multiple extraction. Journal of Chemical Education. 2002;**79**:1267–1268

[46] Michałowski T, Lesiak A. Formulation of generalized equations for redox titration curves. Chemia Analityczna (Warsaw). 1994;**39**:623–637

[47] Michałowski T, Rymanowski M, Pietrzyk A. Non-typical Brönsted's acids and bases. Journal of Chemical Education. 2005;**82**(3):470–472

[48] Michalowski T. Calculation of pH and potential E for bromine aqueous solutions. Journal of Chemical Education. 1994;**71**(7):560–562

[49] Michałowski T, N.Wajda, D.Janecki. A Unified quantitative approach to electrolytic systems. Chemia Analityczna (Warsaw). 1996;**41**:667–685

[50] Gran G. Equivalence volumes in potentiometric titrations. Analytica Chimica Acta. 1988;**206**:111–123

[51] Michałowska-Kaczmarczyk AM, Michałowski T, Asuero AG. Inflection points on some S-Shaped curves. Journal of Analytical Sciences, Methods and Instrumentation. 2014;**4**(1): 27–30

[52] Sigel H, Zuberbühler AD, Yamauchi O. Comments on potentiometric pH titrations and the relationship between pH-meter reading and hydrogen ion concentration. Analytica Chimica Acta. 1991;**255**(1):63–92

[53] http://www.titrations.info/acid-base-titration-polyprotics-and-mixtures [accessed on August 5, 2017]

[54] https://en.wikipedia.org/wiki/Inverse_functions_and_differentiation [accessed on August 5, 2017]

[55] https://en.wikipedia.org/wiki/Difference_quotient [accessed on August 5, 2017]

[56] Kolthoff IM, Furman NH. Potentiometric Titrations. 2nd ed. New York: Wiley; 1931

[57] Michałowski T, Stępak R. Evaluation of the equivalence point in potentiometric titrations with application to traces of chloride. Analytica Chimica Acta. 1985;**172**:207–214

[58] Fortuin JMH. Method for determination of the equivalence point in potentiometric titrations. Analytica Chimica Acta. 1961;**24**:175–191

[59] Yan JF. A method for the determination of equivalence point in potentiometric titrations using unequal volume increments. Analytical Chemistry. 1965;**37**(12):1588–1590

[60] Fenwick F. Rapid Method for Fixing End Point of Potentiometric Titration, Industrial and Engineering Chemistry. Analytical Edition. 1932;**4**(1):144–146

[61] https://en.wikipedia.org/wiki/PH_indicator [accessed on August 5, 2017]

[62] Michałowski T. Calculations in analytical chemistry with elements of computer programming (in Polish) PK, Cracow, 2001

[63] Michałowski T, Nizińska-Pstrusińska M, Sztark W, Baterowicz A. Laboratory trainings in analytical chemistry (in Polish). Wyd. PK, Kraków 2002

[64] Michałowski T. Potentiometric titration in acid-base systems; an overview of methods involved. Zeszyty Naukowe Uniwersytetu Jagiellońskiego. Prace Chemiczne. 1989;**32**:15–45

[65] Michałowski T, Toporek M, Rymanowski M. Overview on the Gran and other linearization methods applied in titrimetric analyses. Talanta. 2005;**65**(5):1241–1253

[66] Schwarz LM. Advances in acid-base Gran plot methodology. Journal of Chemical Education. 1987;**64**(11):947–950

[67] Michałowski T. Titration of monoprotic acids with sodium hydroxide contaminated by sodium carbonate. Journal of Chemical Education. 1988;**65**:181–182

[68] Michalowski T. Titrations of monoprotic acids with sodium hydroxide contaminated by sodium carbonate (the author replies). Journal of Chemical Education. 1990;**67**(12):1072

[69] Burns DT, Maitin BK, and Svehla G. Evaluation of equivalence points in the potentiometric titration of mixture of halides. Analyst. 1983;**108**:457

[70] Christian GD. Analytical Chemistry. 4th ed. Hong Kong: John Wiley & Sons; 1986, pp. 318–321

[71] Harris DG. Quantitative Chemical Analysis. 2nd ed. New York: W.H. Freeman & Co.; 1987. 243–244

[72] Gran G. Determination of the equivalent point in potentiometric titrations. Acta Chemica Scandinavica. 1950;**4**:559–577

[73] Gran G. Determination of the equivalence point in potentiometric titrations. Part II. Analyst. 1952;**77**:661–671

[74] Johansson A, Gran G. Automatic titration by stepwise addition of equal volumes of titrant. Part V. Extension of the Gran I method for calculation of the equivalence volume in acid-base titrations. Analyst. 1980;**105**:802–810

[75] Stumm W, Morgan JJ. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. 3rd ed. New York: John Wiley & Sons; 1996

[76] http://mathworld.wolfram.com/MaclaurinSeries.html [accessed on August 5, 2017]

[77] Michałowski T, Kupiec K, Rymanowski M. Numerical analysis of the Gran methods. A comparative study. Analytica Chimica Acta. 2008;**606**(2):172–183

[78] Pilarski B, Michałowska-Kaczmarczyk AM, Asuero AG, Dobkowska A, Lewandowska M, Michałowski T. A new approach to carbonate alkalinity. Journal of Analytical Sciences, Methods and Instrumentation. 2014;**4**:62–69

[79] Michałowski T, Asuero AG. Formulation of the system of isohydric solutions. Journal of Analytical Sciences, Methods and Instrumentation. 2012;**2**(1):1–4

[80] Michałowski T, Rokosz A, Tomsia A. Determination of basic impurities in mixture of hydrolysable salts. Analyst. 1987;**112**:1739–1741

[81] Michałowski T. Possibilities of application of some new algorithms for standardization purposes; Standardisation od sodium hydroxide solution against commercial potassium hydrogen phthalate. Analyst. 1988;**113**:833–935

[82] Michałowski T, Rokosz A, Negrusz-Szczęsna E. Use of Padé approximants in the processing of pH titration data; Determination of the parameters involved in the titration of acetic acid. Analyst. 1988;**113**:969–972

[83] Michałowski T, Rokosz A, Kościelniak P, Łagan J.M, J. Mrozek. Calculation of concentrations of hydrochloric and citric acids together in mixture with hydrolysable salts. Analyst. 1989;**114**:1689–1692

[84] Michałowski T. New Concepts of Analysis of Concentrated Solutions of Electrolytes with Use of Potentiometric Titration in Acid-Base Systems (in Polish), Kraków; 1989

[85] Michałowski T. Some remarks related to determination of free acids in presence of hydrolysable salts. Chemia Analityczna (Warsaw). 1990;**35**:375–390

[86] Michałowski T. Some new algorithms applicable to potentiometric titration in acid-base systems. Talanta. 1992;**39**(9):1127–1137

[87] Michałowski T, Gibas E. Applicability of new algorithms for determination of acids, bases, salts and their mixtures. Talanta. 1994;**41**(8):1311–1317

[88] Michałowski T, Rokosz A, Zachara M. Conventional method of determination of aminoacetic acid by pH-metric titration. Chemia Analityczna (Warsaw). 1994;**39**:217–222

[89] Michałowski T, Rokosz A, Gibas E. Standardization of sodium hydroxide against tartaric acid by pH-metric titration in isomolar systems. Acta Chimica Polonica. 1995;**37**:143–149

[90] Janecki D, Michałowski T, Zieliński M. A simple method of etidronate disodium determination in commercial preparations of the salt. Chemia Analityczna (Warsaw). 2000;**45**:659–666

[91] Janecki D, Doktór K, Michałowski T. Determination of stability constants of complexes of $M_iK_jH_kL$ type in concentrated solutions of mixed salts Talanta. 1999;**48**:1191–1197

[92] Janecki D, Doktór K, Michałowski T. Erratum to "Determination of stability constants of complexes of $M_jK_jH_kL$ type in concentrated solutions of mixed salts": [48 (1999) 1191] Talanta. 1999;**49**:943

[93] Janecki D, Michałowski T. Evaluation of equilibrium constants—a new approach. Chemia Analityczna (Warsaw). 1999;**44**:611–621

[94] Janecki D, Styszko-Grochowiak K, Michałowski T. The Catenation and Isomerisation effects on stability constants of complexes formed by some diprotic acids. Talanta. 2000;**52**:555–562

[95] Michałowska-Kaczmarczyk AM, Michałowski T. Ostwald's dilution law challenge. Analytical and Bioanalytical Chemistry. 2014;**406**(12):2741–2742

[96] Michałowska-Kaczmarczyk AM, Michałowski T. Solution to Ostwald's dilution law challenge. Analytical and Bioanalytical Chemistry. 2014;**406**(22):5251–5251

[97] Michałowski T, Toporek M, Rymanowski M. pH-Static titration: A quasistatic approach. Journal of Chemcal Education. 2007;**84**(1):142–150

[98] Michałowski T. On the precision of the method of titration to a preset pH value. Talanta. 1989;**36**(8):875–878

[99] Michałowski T, Parczewski A. A new definition of buffer capacity. Chemia Analityczna. 1978;**23**:959–964

[100] Michałowska-Kaczmarczyk AM, Michałowski T, Asuero AG. Formulation of dynamic buffer capacity for phytic acid. American Journal of Chemistry and Applications 2015;**2**(1): 5–9

[101] Kościelniak P, Michałowski T. An error of mercurimetric titration of chloride in presence od sodium nitroprusside as indicator. Chemia Analityczna. 1986;**31**:665–668

[102] Michałowski T. An error of Liebig-Deniges method of determination of the cyanide. Chemia Analityczna. 1983;**28**:313–315

[103] Michałowski T, Asuero AG, Ponikvar-Svet M, Toporek M, Pietrzyk A, Rymanowski M. Principles of computer programming applied to simulated pH–static titration of cyanide according to a modified Liebig-Denigès method. Journal of Solution Chemistry. 2012;**41**(7): 1224–1239

[104] Michałowski T., Wybraniec S., Ponikvar M. The modified method of spectro-pehametric determination of dissociation constants. Chemia Analityczna (Warsaw). 2008;**53**:737–742

[105] Sáez-Plaza P, Michałowski T, Navas MJ, Asuero AG, Wybraniec S. An overview of the Kjeldahl method of nitrogen determination. Part I. early history, chemistry of the procedure, and titrimetric finish. Critical Reviews in Analytical Chemistry. 2013;**43**(4):178–223

[106] Sáez-Plaza P, Navas MJ, Wybraniec S, Michalowski T, Asuero AG. An overview of Kjeldahl method of nitrogen determination. Part II. sample preparation, working scale, instrumental finish and quality control. Critical Reviews in Analytical Chemistry. 2013;**43**(4):224–272

[107] Michałowski T, Asuero AG, Wybraniec S. The titration in the Kjeldahl method of nitrogen determination: Base or acid as titrant?. Journal of Chemical Education. 2013;**90**(2):191–197