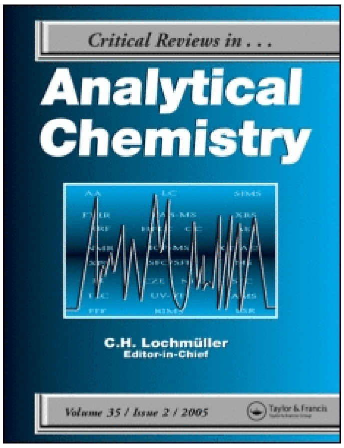

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The Generalized Approach to Electrolytic Systems: II. The Generalized Equivalent Mass (GEM) Concept

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The equivalent mass (EM, in terms established by IUPAC) and generalized equivalent mass (GEM, in terms suggested by Michałowski) concepts related to titrimetric methods of chemical analysis are considered from the viewpoint of the generalized approach to electrolytic systems (GATES). No chemical reaction notation is required for explanation of the GEM concept. The advantages of GEM over EM are discussed in details. The role of preliminary knowledge obtained from simulated titrations, realized according to principles offered by GATES, is emphasized.

Keywords Titration, equivalent mass

INTRODUCTION

The equivalent mass[1] concept is applied in all calculations referred to titrations, considered as a dynamic processes, in which a properly chosen titrant (T) is added in portions into the solution titrated (titrand, D). The obtained D+T mixture is homogenized thoroughly, after each addition of consecutive portion of T. The changes which occur during the titration are registered visually or with the use of instrumental (e.g., potentiometric, pH-metric) methods of analysis. In visual titrations, properly chosen indicators are used.

The simulated titrations considered in this paper refer to *quasistatic* processes realized in closed systems, under isothermal conditions. From the general requirements and assumptions for titrations it results that: (1) the equations for titration curves are formulated under assumption of validity of the related material balances and constancy of all equilibrium constants values; (2) the mixture is perfectly mixed (homogenized) and indications of a detecting device accurately and instantly follow the changes in the bulk solution, i.e., no delay in these indications occur; (3) all equilibrium constants in algorithms related to the system in question are taken into account; (4) the term "system" is referred to condensed (liquid or liquid+solid) phases, with diathermal walls preserving a transportation of gaseous species (e.g., H_2O, CO_2, O_2) between the system and its surroundings; and (5) the principle of additivity of D and T volumes is valid.

In this paper, the generalized equivalent mass (GEM) concept (1), based on firm algebraic foundations of the generalized approach to electrolytic systems (GATES) (2–4), is considered against the equivalent mass (EM) concept, based on a "fragile" chemical reaction notation, which is advocated by IUPAC. In this respect, the paper contradicts the viewpoints presented, for example, in the papers by West (5) and by Zhao and Lu (6).

FRACTION TITRATED

Let us consider the D+T system, obtained after addition of V mL of T containing the reagent B (C mol/L) into V_0 mL of D, i.e., the solution containing the analyte A (C_0 mol/L). The number of mmoles of A equals $n_A = C_0 \cdot V_0$ and the number of mmoles of B, added up to a given point of titration, equals $n_B = C \cdot V$. The value for $\Phi = n_B/n_A$ is named as the fraction titrated

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \quad [1]$$

If V_0 and V are expressed in mL, then (7)

$$C_0 \cdot V_0 = 10^3 \cdot m_A/M_A \quad [2]$$

where m_A [g] and M_A [g/mol] denote mass and molar mass of analyte (A), respectively.

From Eqs. [1] and [2] it follows

$$m_A = 10^{-3} \cdot C \cdot V \cdot M_A/\Phi \quad [3]$$

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[1] The embarrassing term "equivalent weight" (usually applied in literature) associates with force of gravity, expressed in force units (N).

The value of the fraction V/Φ in Eq. [3], obtained from Eq. [1],

$$V/\Phi = C_0 \cdot V_0/C \qquad [4]$$

is constant during the titration, particularly, at the end (e) and equivalence (eq) points

$$V/\Phi = V_e/\Phi_e = V_{eq}/\Phi_{eq} \qquad [5]$$

The V_e [mL] value is the volume of titrant (T) consumed up to the end point, where the titration is terminated (ended). The V_e value of titration is usually determined in visual titration, when a pre-assumed color change of D+T mixture is obtained. In acid-base pH-metric titrations, the pH_e value corresponds to the volume V_e [mL] of T added from the start of the titration and $\Phi_e = C \cdot V_e/(C_0 \cdot V_0)$ is the value of the mole fraction related to the end point.

The symbol Φ_{eq} is considered as the mole fraction at the hypothetical equivalence point, taken as an abstract notion, leaved without none reference to any chemical reaction notation. We will consider it simply as a "round" natural number. In further parts of this paper, some examples of the systems where Φ_{eq} is a ratio of some (small) natural numbers will also be considered.

To explain the GEM approach, let us, however, first consider a simple example, where the standard S is taken as an analyte A.

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

$$\Phi = \frac{C}{C_0} \cdot \frac{(1 - \bar{n}) \cdot C_0 - \alpha}{C + \alpha} \qquad [6]$$

is valid, where:

$$\alpha = 10^{-pH} - 10^{pH-14} \qquad [7]$$

$$\bar{n} = \frac{2 \cdot [H_2L] + [HL]}{[H_2L] + [HL] + [L]}$$

$$= \frac{2 \cdot 10^{7.68-2pH} + 10^{4.92-pH}}{10^{7.68-2pH} + 10^{4.92-pH} + 1} \qquad [8]$$

and $C_0 = 1/V_0$. The values of the corresponding equilibrium constants are involved in Eqs [7, 8], and hereafter. For simplicity of notation, charges of the species in Eq. [8] (and elsewhere) are omitted.

The Φ_e values in Table 1 are calculated from Eq. [6] at some particular pH_e values, which denote limiting pH-values of color change pH intervals for: phenol red (color 6.4 ÷ 8.0), phenolphthalein (8.0 ÷ 10.0), and thymolphthalein (9.3 ÷ 10.5). No acid-base indicator is involved in Eq. [6]; therefore, the $\Phi_e$values collected in Table 1 are principally referred to pH-metric titrations. In such instances, the pH_e values can be referred to the measuring system used for pH-metric titration.

Example 2. Some (Φ_j, E_j) values related to titration of C_0 = 0.01 mol/L solution of: (a) $FeSO_4$, (b) $H_2C_2O_4$, and (c) H_2O_2 in the presence of C_a = 1.0 mol/L H_2SO_4 with C = 0.02 mol/L $KMnO_4$ are collected in Table 2. The potentials $E = E_e$ [V] refer to normal hydrogen electrode; the details are presented in (8).

TABLE 1

The values for Φ_e for different $pH = pH_e$ values, calculated using Eq. [6], at C_0 and C values assumed in Example 1

	Φ_e		
pH_e	$V_0 = 50$ mL	$V_0 = 100$ mL	$V_0 = 200$ mL
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

Example 3. The solution containing KIO_3 (C_0 = 0.01 mol/L), HCl (C_a = 0.02 mol/L) + H_2SeO_3 (C_{Se} = 0.02 mol/L) (as the catalyst), and $HgCl_2$ (C_{Hg} mol/L) is titrated with C = 0.1 mol/L ascorbic acid ($C_6H_8O_6$). Some (Φ_e, E_e) points in the absence and in the presence of $HgCl_2$ in the system considered are presented in Table 3. This system was extensively discussed in references (8–10).

TABLE 2

The (Φ_e, E_e) values related to acidic (H_2SO_4) solutions of (a) $FeSO_4$, (b) $H_2C_2O_4$, and (c) H_2O_2 as D titrated with $KMnO_4$ solution as T.

a		b		c	
Φ_e	E_e	Φ_e	E_e	Φ_e	E_e
0.19800	0.701	0.39600	−0.374	0.39600	0.683
0.19900	0.719	0.39800	−0.365	0.39800	0.692
0.19980	0.761	0.39960	−0.345	0.39960	0.712
0.19990	0.778	0.39980	−0.336	0.39980	0.721
0.19998	0.820	0.39996	−0.315	0.39996	0.742
0.20000	1.034	0.40000	−0.207	0.40000	0.850
0.20002	1.323	0.40004	1.322	0.40004	1.320
0.20010	1.365	0.40020	1.363	0.40020	1.363
0.20020	1.382	0.40040	1.381	0.40040	1.385
0.20200	1.442	0.40400	1.442	0.40400	1.442

INDICATOR EFFECT

A properly chosen indicator is one of the material components of the D+T system in visual titrations. As such, it should be considered in the related balances (7, 8).

Example 4. 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

TABLE 3
Some (Φ_e, E_e) points for the system containing KIO_3 (C_0 = 0.01 mol/L), HCl (C_a = 0.02 mol/L) + H_2SeO_3 (C_{Se} = 0.02 mol/L) titrated with C = 0.1 mol/L ascorbic acid in the absence and in the presence of $HgCl_2$ (C_{Hg} mol/L); potentials E_e [V] refer against normal hydrogen electrode

$C_{Hg} = 0$				$C_{Hg} = 0.07$	
Φ_e	E_e	Φ_e	E_e	Φ_e	E_e
2.450	1.004	2.950	0.632	2.950	0.970
2.475	1.000	2.975	0.620	2.975	0.960
2.490	0.995	2.990	0.607	2.990	0.947
2.492	0.994	2.992	0.604	2.992	0.944
2.494	0.992	2.994	0.600	2.994	0.940
2.496	0.989	2.996	0.595	2.996	0.935
2.498	0.983	2.998	0.586	2.998	0.926
2.500	0.903	3.000	0.414	3.000	0.652
2.502	0.809	3.002	0.380	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
2.510	0.768	3.010	0.359	3.010	0.359
2.525	0.744	3.030	0.345	3.030	0.345
2.550	0.727	3.060	0.336	3.060	0.336

C = 0.1 mol/L HCl as T, is as follows

$$\Phi = \frac{C}{C_0} \cdot \frac{(4\bar{n} - 10) \cdot C_0 + (1 - \bar{m}) \cdot C_{0In} + \alpha}{C - \alpha} \qquad [9]$$

where α is given by Eq. [7], $C_0 = 1/V_0$, and

$$\bar{n} = \frac{3 \cdot [H_3BO_3] + 2 \cdot [H_2BO_3] + [HBO_3]}{[H_3BO_3] + [H_2BO_3] + [HBO_3] + [BO_3]}$$

$$= \frac{3 \cdot 10^{35.78-3pH} + 2 \cdot 10^{26.54-2pH} + 10^{13.80-pH}}{10^{35.78-3pH} + 10^{26.54-2pH} + 10^{13.80-pH} + 1} \qquad [10]$$

$$\bar{m} = \frac{[HIn]}{[HIn] + [In]} = \frac{1}{1 + 10^{pH-5.3}} \qquad [11]$$

The Φ_{eq}-values obtained in the presence of the indicator in D can be compared with those obtained at $C_{0In} = 0$ (Table 4). 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.

Example 5. The solution of $ZnCl_2$ (C_0 = 0.01 mol/L) buffered with NH_4Cl (C_1 mol/L) and NH_3 (C_2 mol/L), $C_1 + C_2 = C_N$, r = C_2/C_1, is titrated with C = 0.02 mol/L EDTA in presence of Eriochrome black T ($C_{0In} = p \cdot 10^{-5}$ mol/L, p = 2, 4, 6, 8, 10) as the indicator from wine red to blue color. The curves of logy vs. Φ relationships, where $y = x_2/x_1$ and:

$$x_1 = \sum_{i=0}^{3} [H_iIn]$$

$$x_2 = [ZnIn] + 2[ZnIn_2]$$

are plotted in Fig. 1, where (A) refers to r = 1, (B) refers to r = 4. It is stated that at C_N = 0.1 mol/L, the solution becomes violet (red + blue) in the nearest vicinity of $\Phi_{eq} = 1$. At C_N = 1 mol/L, the mixed color of the solution is assumed from the very beginning of the titration (Fig. 2). At C_N > 1 mol/L, the solution is blue from the start of the titration.

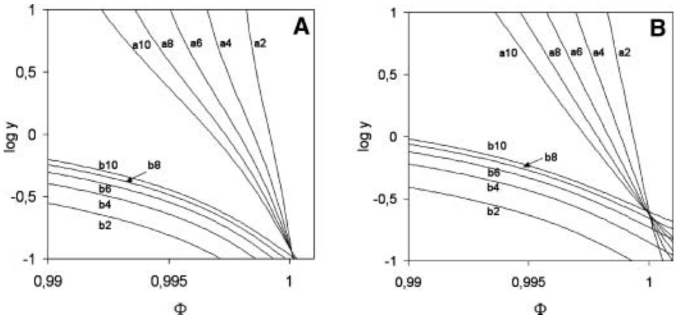

FIG. 1. The log y vs. Φ relationships in close vicinity of Φ_{eq} = 1, for $C_{In} = p \cdot 10^{-5}$ mol/L (p = 2, 4, 6, 8, 10); curves ap correspond to C_N = 0.1 mol/L, curves bp correspond to C_N = 1 mol/L; (A) refers to r = 1, (B) refers to r = 4.

SOME REMARKS

The amount of analyte in titrimetric analysis is determined from the amount of a standard reagent required to react with the analyte completely. Titrations are based on standardization and determination steps. During the standardization step, the titrant T with unknown C of the species B is added into titrand D, containing the standard S (e.g., potassium hydrogen phthalate, borax), with mass m_S [g] accurately known. However, the C_0 of S in D is known only approximately, as the total volume of water applied for dissolution and dilution of the standard sample is practically not known before titration. Such an approach results from the fact that the Φ_e does not change distinctly with dilution of the sample, although this effect may appear

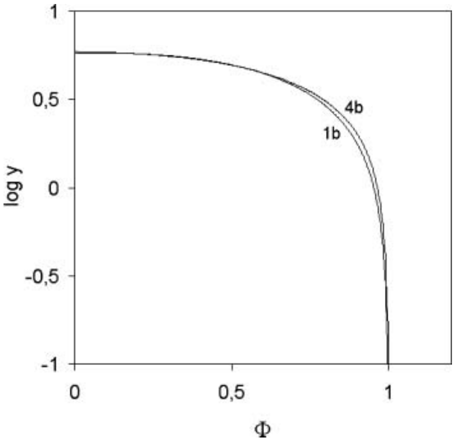

FIG. 2. The log y vs. Φ relationships plotted at C_N = 1 mol/L, and r = 1 (curve 1b) and r = 4 (curve 4b).

TABLE 4
The values for Φ_e calculated from Eq. [9] for different pH = pH$_e$, C_{0In} and V_0 [mL] values assumed in Example 4. The pH$_e$ values are related to the pH-interval $< 4.4 \div 6.2 >$ corresponding to the color change of methyl red (HIn)

		Φ_e		
pH$_e$	C_{0In}	$V_0 = 50$ mL	$V_0 = 100$ mL	$V_0 = 200$ mL
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

to be significant in some instances (see Tables 1 and 4). For example, the dilution practically does not affect the results of NaOH standardization against potassium hydrogen phthalate, if pH titration is applied and titration terminated at pH$_e \approx 8.0$ (Table 1). The dilution effect acts undesirably on the results of the analysis of HCl standardization against borax (see Table 4) in the presence of Methyl red as an indicator; the Φ_e value becomes more distant from $\Phi_{eq} = 2$ for higher V_0 values. Nevertheless, higher concentrations C_{0In} of the indicator are undesirable, while too small C_{0In} causes difficulties in registration of the V_e value. If the concentration C of the reagent B in T is known accurately, the titrant T can be applied for determination of the unknown mass m_A of the analyte A in the sample analyzed.

The Φ_e values presented in Tables 1–4 at the pH = pH$_e$ or E = E$_e$ assumed are very close to the "rounded" Φ_{eq} values: 1 (= 1/1) in Table 1; 0.2 (=1/5) in Table 2 (column a), 0.4 (=2/5) in Table 2 (columns b, c); 2.5 (=5/2) and 3 (=3/1) in Table 3 (at $C_{Hg} = 0$); 3 (=3/1) in Table 3 (at $C_{Hg} = 0.07$); and 2 (=2/1) in Table 4. The effect of preliminary sample dilution can also be considered (Tables 1 and 4). The numerical values for Φ_e in the systems considered above are close to Φ_{eq} values expressed by a ratio of small natural numbers: 1/1, 1/5, 2/5, 5/2, 3/1, and 2/1 in the examples specified above, or 1/2 in the example presented later (see Section 8.2.2).

From [3] and [5] one obtains:

$$m_A = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_e} \quad [12]$$

$$m_A = 10^{-3} \cdot C \cdot V_{eq} \cdot \frac{M_A}{\Phi_{eq}} \quad [13]$$

However, Eq. [12] cannot be applied for the evaluation of m_A value (V_e known, Φ_e unknown). Also, Eq. [13] is useless (the "rounded" Φ_{eq} value is known exactly, but V_{eq} is unknown) as V_e (not V_{eq}) in visual titrations is determined experimentally.

Because Eqs. [12] and [13] appear not to be applicable, the third, approximate formula for m_A has to be applied, namely:

$$m_A' = 10^{-3} \cdot C \cdot V_e \cdot M_A/\Phi_{eq} = 10^{-3} \cdot C \cdot V_e \cdot R_A{}^{eq} \quad [14]$$

where Φ_{eq} is put for Φ_e in Eq. [12] and

$$R_A{}^{eq} = M_A/\Phi_{eq} \quad [15]$$

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

$$\begin{aligned} \theta &= (m_A' - m_A)/m_A = m_A'/m_A - 1 \\ &= V_e/V_{eq} - 1 = \Phi_e/\Phi_{eq} - 1 \end{aligned} \quad [16]$$

For $\Phi_e = \Phi_{eq}$ one gets $\theta = 0$ 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 its color change during the titration is possible on the basis of analysis of the related titration curve.

From eqs [12], [14], and [16] we get

$$m_A = m_A'/(1 + \theta) = m_A' \cdot (1 - \theta + \theta^2 - \cdots) \quad [17]$$

ONE–DROP ERROR

For consideration of the one-drop error, let us assume that the end point was not attained after addition of V' mL of titrant. An additional drop with volume ΔV is then added. If the end point is attained this time, i.e., $V_e = V' + \Delta V$, the uncertainty in titrant volume equals to ΔV. 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

$$\begin{aligned} \Delta\Phi &= \Phi_e - \Phi' = C \cdot V_e/(C_0 \cdot V_0) - C \cdot V'/(C_0 \cdot V_0) \\ &= C \cdot \Delta V/(C_0 \cdot V_0). \end{aligned}$$

At $V_0 = 100$ mL, $C_0 = 0.01$ mol/L, $C = 0.1$ mol/L, and $\Delta V = 0.03$ mL we have

$$\Delta\Phi = C \cdot \Delta V/(C_0 \cdot V_0) = 0.003 \quad [18]$$

The difference between Φ_e and Φ_{eq} when compared with the indefinity $\Delta\Phi$ in Φ value, is acceptable from the one-drop error viewpoint when $|\Phi_e - \Phi_{eq}| < 0.003$. Taking the value $\Phi_e = 2.0048$ 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 $\Delta\Phi = 0.003$; 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 $V_0 = 100$ mL, $C_0 = 0.01$ mol/L, $C = 0.1$ mol/L, and pH$_e = 4.4$ equals, in Φ-units: $|2.0048 - 2.0047| = 0.0001$ at $C_{0In} = 10^{-5}$ mol/L or $|2.0058 - 2.0047| = 0.0011$, i.e., it appears to be insignificant in comparison to $\Delta\Phi = 0.003$ and can be therefore neglected.

As a rule, in the pH-region where Φ_e is close to Φ_{eq} value, we have $\alpha/C \ll 1$ and then Eq. [9] can be rewritten as

$$\Phi = 4\bar{n} - 10 + \delta\Phi \qquad [19]$$

where

$$\delta\Phi \cong (4\bar{n} - 10) \cdot \alpha/C + (1 + \alpha/C) \cdot ((1 - \bar{m}) \cdot C_{0In} + \alpha)/C_0 \qquad [20]$$

Similarly, the equation for titration of D with potassium hydrogen phthalate (KHL, C_0)+ phenolphthalein (HIn, C_{0In}) with C mol/L NaOH has the form

$$\Phi = \frac{C}{C_0} \cdot \frac{(1 - \bar{n}) \cdot C_0 + (1 - \bar{m}) \cdot C_{0In} - \alpha}{C + \alpha} \qquad [21]$$

(compare with Eq. [6]) and can be transformed into the form

$$\Phi = 1 - \bar{n} - \delta\Phi \qquad [22]$$

where:

$$\begin{aligned}\delta\Phi &\cong (1 - \bar{n}) \cdot \alpha/C - (1 - \alpha/C)\\ &\quad \times ((1 - \bar{m}) \cdot C_{0In} - \alpha)/C_0 \qquad [23]\\ \bar{m} &= \frac{1}{10^{9.7-pH} + 1} \qquad [24]\end{aligned}$$

The inequality $\delta\Phi < \Delta\Phi = 0.003$ is valid in Eqs. [20] and [23] within the pH color ranges assumed for methyl red in Example 4 and for phenolphthalein in Example 1. The $\delta\Phi$ values are less significant for smaller C_{0In} and more concentrated standard solutions (i.e., lower V_0 values). However, the solubility (C_{sol}) of the standard (e.g., borax) used, is a limitation in this respect, $C_0 < C_{sol}$.

EFFECT OF BUFFER CAPACITY

As a rule, the pH_e value is not exactly equal to the pre–assumed pH value corresponding to the limiting pH value where color change of the indicator applied in titration occurs. The matter is whether greater pH changes are affected by small volumes of titrant added, i.e., the problem of buffer capacity arises.

For this purpose, let us introduce the "dynamic" buffer capacity (β_V) concept, defined by formula (1, 7)

$$\beta_V = |dc/dpH| \qquad [25]$$

where

$$c = CV/(V_0 + V) = \Phi C_0 C/(C + \Phi C_0) \qquad [26]$$

First, the relationship between β_V and the slope (η) of titration curve

$$\eta = |dpH/d\Phi| \qquad [27]$$

is applied. The value for η assumes the greatest value (η_{max}) at the close vicinity of the equivalence (stoichiometric) point, then we have

$$\beta_V = |dc/dpH| = (dc/d\Phi)/|dpH/dF| = p/\eta \qquad [28]$$

where

$$p = dc/d\Phi = C_0 \cdot C^2/(C + \Phi \cdot C_0)^2 \qquad [29]$$

The change in p appears to be small in the vicinity of equivalence point (eq) and can be neglected. Indeed, one can define $p_{eq} = C_0 \cdot C^2/(C + \phi_{eq} \cdot C_0)^2$. Applying the identity

$$\begin{aligned}&(C/C_0 + \Phi_{eq})/(C/C_0 + \Phi) \equiv ((C/C_0 + \Phi)/(C/C_0 + \Phi_{eq}))^{-1}\\ &\equiv ((C/C_0 + \Phi_{eq} - (\Phi_{eq} - \Phi))/(C/C_0 + \Phi_{eq}))^{-1} = (1 - x)^{-1}\end{aligned}$$

and the expansion in series $(1 - x)^{-2} = 1 + 2 \cdot x + 3 \cdot x^2 + \ldots$, valid for $|x| < 1$, we calculate

$$\begin{aligned}\Delta_p &= (p - p_{eq})/p_{eq} = p / p_{eq} - 1\\ &= [(C/C_0 + \Phi_{eq})/(C/C_0 + \Phi)]^2 - 1\\ &= [1 - (\Phi_{eq} - \Phi)/(C + \Phi_{eq} C_0)]^{-2} - 1 \qquad [30]\\ &= 2 \cdot (\Phi_{eq} - \Phi)/(C/C_0 + \Phi_{eq})\\ &\quad + 3 \cdot [(\Phi_{eq} - \Phi)/(C/C_0 + \Phi_{eq})]^2 + \ldots\end{aligned}$$

If $\Phi_{eq} - \Phi = 0.003$, $\Phi_{eq} = 1$, and $C/C_0 = 10$, $\Delta_p = 2 \cdot 0.003/(10+1) = 0.055\%$. Then one can assume that η_{max} corresponds to the minimal buffer capacity (β_{Vmin})

$$\beta_{V\,min} = p_{eq}/\eta_{max} \qquad [31]$$

see Eq. [27]. Particularly, from for the equation

$$\Phi = \frac{C}{C_0} \cdot \frac{C_0 - \alpha}{C + \alpha} \qquad [32]$$

referred to the titration of a strong monoprotic acid (e.g., HCl, C_0 mol/L) with a strong base (e.g., KOH, C mol/L) and Eq. [7], we get

$$\begin{aligned}1/\eta &= d\Phi/dpH = \ln 10 \cdot C \cdot (C/C_0 + 1) \cdot ([H^{+1}]\\ &\quad + [OH^{-1}]) \cdot (C + [H^{+1}] - [OH^{-1}])^{-2} \qquad [33]\end{aligned}$$

In acid–base titrations, the functions $\Phi = \Phi$ (pH) are monotonic over the entire pH range admissible for Φ values, i.e., $\Phi \geq 0$; then one can write $d\Phi/dpH = 1/(dpH/d\Phi)$. At $C = 0.1$ mol/L, $C_0 = 0.01$ mol/L, $pK_w = 14.0$, and $pH = 4.4$, we have

$$\begin{aligned}1/\eta &= 2.303 \cdot 0.1 \cdot (0.1/0.01 + 1) \cdot (10^{-4.4} + 10^{-9.6})\\ &\quad \cdot (0.1 + 10^{-4.4} - 10^{-9.6}) = 0.010125\end{aligned}$$

and then $\eta = 98.8 \cong 10^2$. Applying the approximation $d\Phi/dpH = \Delta\Phi/\Delta pH$, we get $\Delta\Phi = 0.01 \cdot \Delta pH$; for $\Delta pH = 0.1$, i.e., the Φ value calculated at $pH_e = 4.5$ or 4.3 differs from one calculated at $pH_e = 4.4$ by a value $\Delta\Phi = 0.001$, i.e., lower than one–drop error. The approximation is acceptable for small ΔpH values in a vicinity of equivalence point.

EQUIVALENCE AND INFLECTION POINTS

A relatively simple relationship between V_{eq} and the volume $V = V_{inf}$ related to inflection point (inf) on the titration curve, where $d^2V/dpH^2 = 0$, can be obtained from Eq. [32]. In this case we have (7, 11)

$$V_{eq} - V_{inf} = (V_0 + V_{eq}) \cdot x_{inf}/(1 + x_{inf}) = V_0 \cdot (C_0/C + 1) \cdot x_{inf}/(1 + x_{inf}) \quad [34]$$

where

$$x_{inf} = [1 - (1 - 32 \cdot K_w/C^2)^{1/2}]/2 = 8 \cdot K_w/C^2 + (8 \cdot K_w/C^2)^2 + \cdots \quad [35]$$

Similar relationships were found for titration of KOH with HCl and for titration of NaCl with $AgNO_3$ (11) (or *vice versa*); in the latter case, K_{sp} (for AgCl) is taken instead of K_w.

Some pH-metric and potentiometric methods of analysis are based on the determination of V_{inf} value, related to inflection point, where the greatest change ("jump") in pH or potential E occurs. However, in automatic titrations, indications of the variable measured (pH or E) are distorted in comparison with ones obtained under equilibrium conditions and the inflection point provides biased results for V_{eq} value. The issue is that the concentration of analyte at the indicator electrode should be the same, at any stage of the titration, as one in the bulk solution at the moment of pH or E readout. This distortion becomes excessively high in the jump region of the titration curve, pH = pH(V) or E = E(V), where the buffer capacity of the D+T mixture is low. This makes some other methods of V_{eq} evaluation more valuable, particularly (1°) extrapolative Gran methods and (2°) indicative method represented by pH-static titration.

METHODS OF V_{eq} EVALUATION

The Gran Methods

The original Gran (I and II) methods (12–14) were perceived as a manner of linearization of S–shaped curves, obtained in potentiometric or pH–metric titrations. In the papers issued later, numerous modifications of these methods were proposed and applied for exact determination of V_{eq}values, particularly in redox D+T systems (2, 3, 7, 15, 16). Some of these modifications were also applied for calibration of redox indicator electrodes (2, 3).

The original Gran I method is based on the approximation

$$\ln(1 + x) \cong x \quad [36]$$

which is valid only for$|x| \ll 1$. The approximation

$$\ln(1 + x) \cong 1/(1/x + 1/2) \quad [37]$$

proposed by Michałowski (7), appears to provide better results than the extension of ln(1+x) into Maclaurin series up to the 18th term, at $|x| \leq 1$ (15). The re-activated Gran I method, based on the formula [37], has been applied, among others, for iron (II, III) speciation (16), on the basis of the single titration curve E = E(V).

Further modifications of the Gran methods were, in principle, based on Eq. [37] and the function (2)

$$E = \omega - a \cdot (\alpha + \beta \cdot V) + a \cdot \ln \frac{V}{V_{eq}} - a \cdot \ln \left(1 - \frac{V}{V_{eq}}\right) \quad [38]$$

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

pH-Static Titration

pH-static titration is a relatively new method (15, 17 – 20) of V_e registration, applicable to the systems where at least two types of reactions occur; one of them has to be an acid–base reaction. The proton consumption or generation occurs in redox, complexation, or precipitation reactions, for example:

- titration of (buffered) solution of arsenite(III) with I_2+ KI solution (redox reaction);
- titration of (buffered) solution of zinc salt with EDTA (complexation reaction);
- addition of dimethylglyoxime into (buffered) solution of nickel salt (precipitation reaction).

Principle of the Method

The principle of pH-static titration is based on alternating addition of primary (PT) and auxiliary (AT) titrants into $V_0 + \Delta V_{AD}$ mL of D+AD solution with pH = pH_0 value established by addition (according to titrimetric mode) of ΔV_{AD} mL of an acid or base, as the adjusting (AD) solution, into V_0 mL of titrand (D), containing the analyte X and a buffer (or the species able to form the buffering mixture) and some other reagent(s), if necessary; $\Delta V_{AD} = 0$ if this adjustment (regulation) seems to be unnecessary (not advisable) from analytical viewpoint.

PT and AT are added alternately in portions ΔV_{Pi} and ΔV_{Ai}, respectively. First the D+AD solution is treated with a portion ΔV_{P1} mL of PT and then the pH_0 value is returned with an increment ΔV_{A1} mL of AT added according to titrimetric mode. The procedure of alternating addition of ΔV_{Pi} of PT and ΔV_{Ai} of AT is conducted N times (i = 1, . . . ,N); the volumes ΔV_{Ai} aimed, every time, to get the pre–assumed pH_0 value. Total volumes of PT and AT added after j–th operation are $V_{Pj} = \sum_{i=1}^{j} \Delta V_{Pi}$ and $V_{Aj} = \sum_{i=1}^{j} \Delta V_{Ai}$, respectively. As a rule, $\Delta V_{Pi} = \Delta V_{P1}$ = const and then $V_{Pj} = j \cdot \Delta V_{P1}$ (j =1, 2,. . .). The set of points $(V_{Pj}, V_{Aj})|j = 1, \ldots, N$ is then drawn on the plane with orthogonal co–ordinates (x, y) = (V_P, V_A). The pH–static titration curve is thus obtained in the form of a broken line consisting of line segments (or partly rectilinear segments) intersecting at the point R. Perpendicular projection of the point R on the abscissa (V_P) gives the value $V_P = V_{inter}$. If $V_{inter} \cong V_{eq}$, the method provides the correct information on the content of the analyte X in the sample tested. Some further details on the method are given in (15, 20).

pH-Static Titration of Cyanide According to the Modified Liebig-Denigès Method

Let the pH of V_0 = 50 mL of the solution (titrand, D) containing KCN (C_0 = 0.002 mol/L) + diethanolamine (DEA, C_{DEA} = 0.02 mol/L) + KI (C_{KI} = 0.002 mol/L) be adjusted with C_{AD} =

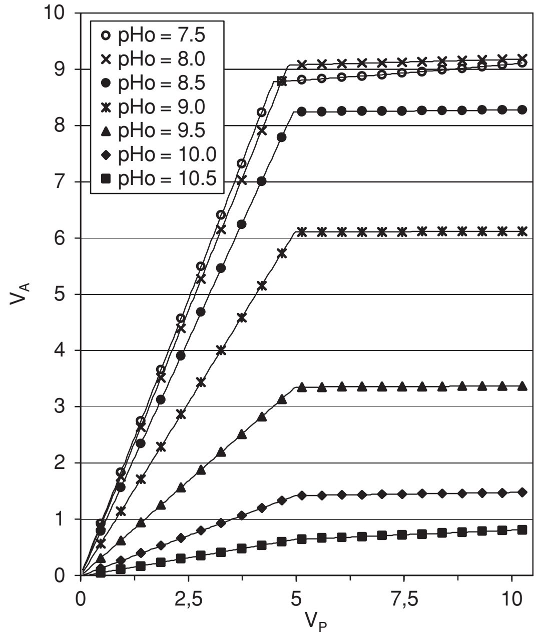

FIG. 3. The curves of V_A vs. V_P relationships plotted for pH-static titration at different pre-assumed pH_0 values.

0.1 mol/L H_2SO_4 to the pre-assumed pH_0 value. The resulting D+AD solution is then titrated, repeatedly and alternately, with $AgNO_3$ ($C_{PT} = 0.01$ mol/L) and NaOH ($C_{AT} = 0.01$ mol/L).

The volumes V_{int} corresponding to the point of intersection (*int*) of lines on the (V_P, V_A) plane (Fig. 3), related to different pH_0 values, are presented in Table 5 (column A).

The values for Φ_{int} obtained in pH-static titration and Φ_e values obtained in classical, pH-metric titration of D+AD solution with 0.01 mol/L $AgNO_3$ [Fig. 4, Table 3 (column B)] correspond to the first appearance of the precipitate AgI in the system. The values of Φ_{int} are close to $\Phi_{eq} = 1/2$ at higher pH_0 values pre-assumed in the titration (Table 2, column A). At lower pH_0 values of the starting D+AD solution, we have $\Phi_{int}(pH_0) > \Phi_e(pH_0)$. At higher pH_0 values, $\Phi_e(pH_0) \cong \Phi_{int}(pH_0)$ (Table 2, column B). For $pH_0 = 10.5$, the theoretical error equals $\theta = -0.2\%$ (Eq. [16]) for the pH-static titration.

TABLE 5

The pH_0 and the related Φ_{int} values related to pH-static titration (column A) and conventional titration (column B) of cyanide according to the modified Liebig-Denigès method.

	Φ_{int}	
pH_0	A	B
7.5	0.4473	0.1641
8.0	0.4820	0.4212
8.5	0.4936	0.4903
9.0	0.4973	0.4968
9.5	0.4985	0.4983
10.0	0.4988	0.4988
10.5	0.4990	0.4989

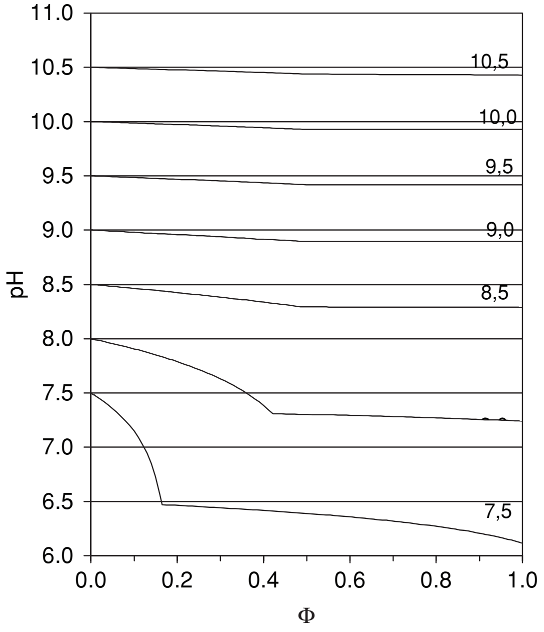

FIG. 4. The pH vs. Φ relationships plotted for conventional pH-metric titration at different starting pH_0 values assumed.

The example of a simulated pH-static titration procedure indicates some "traps" of this method. First, it indicates the pre-assumed pH_0 value where the results with acceptable error of analysis are obtained. However, at relatively high pH_0 values the curve plotted in (V_P, V_A) coordinates has a flattened shape (Fig. 4), disadvantageous from analytical viewpoint. A compromized resolution of the problem is required, also from the viewpoint of the volatility of HCN (one of the analyte species), $[HCN]/[CN^-] = 10^{9.2-pH}$. The volatility of buffering species should also be taken into account. For this purpose, DEA is proposed for NH_3 (applied in the original method). Another parameter tested this way is the concentration of buffering species, discussed in (20). Conventional pH-metric titration of the D+AD with $AgNO_3$ solution indicate the breaking point that disappears (Fig. 4) at higher pH_0 values assumed at the start of the titration.

ON THE CHEMICAL REACTION NOTATION AND THE ROLE OF STOICHIOMETRY

In context with EM, one can refer to the place and the role of a chemical reaction notation that plays hitherto a central role in simple calculations based on stoichiometry. One should necessarily distinguish between (a) the informative aspect of this notation and (b) the requirements for the reaction notation involved with formulation of the related equilibrium constant. Particularly, the informative aspect is a kind of "code" designed to express briefly some chemical (also analytical) activities. In some instances, some "mixed" notations, understandable for chemists, are commonly applied. For example, the notation

$$NO_2^* = NO_2 + h\nu \qquad [39]$$

involves, in formal reaction notation, the "incompatible" components: NO_2^* and NO_2, expressed in "symbol units" and $h\nu$, expressed in energy units. This notation, unacceptable in common algebra, can be interpreted as a "code", where the signs "+" and "=" have similar meaning as "+" and "=" in the statement: child + matchbox = fire.

Any chemical reaction notation, applied as the "carrier" to formulate the related equilibrium constant on the basis of mass action law, should be written correctly from formal viewpoint. This notation should involve only the real species in the system.

It is obvious that any ambiguities in a reaction notation disqualify it as a potential source of quantitative inferences, when taking into account that:

1. The number of possible linear combinations generated from two or more chemical reactions is infinite;
2. A particular reaction notation involves only a part of species of the system considered;
3. The obligatory definition of EM requires a choice of a particular reaction as one "responsible" for all phenomena occurred in the system, irrespectively on the degree of complexity of the system.

According to EM approach, one stoichiometric reaction is ascribed, for quantitative purposes, to the system obtained after addition of NaOH solution into HCl solution, where one equilibrium constant is involved, and to the system KIO_3+ HCl + H_2SeO_3+ $HgCl_2$ titrated with ascorbic acid (Example 3), where ca. 40 independent equilibrium constants are involved in the related balances (8–10).

The concept of stoichiometry, presented in historical review by Szabadvary (21) and considered lately by Sherman and Kuselman (22), "refers to compounds, reactions and systems, and expresses an ideal state where a fixed, usually rational numerical relationship between the quantities of substances in a reaction or compound, exists" (23). This concept was extensively applied in different areas of analytical chemistry, especially in gravimetry and titrimetry, spectrophotometry, coulometry, and isotope dilution (24). The stoichiometric notation also plays a central role in the systems where (normal) kinetic (25) and oscillating (26) reactions occur. In all instances, the central role is ascribed to a correct chemical reaction notation (27).

One should first consider, what the term "correct notation" means. In the common meaning, practiced extensively in scientific literature and didactics, the correctly written chemical reaction notation should fulfil two basic requirements: (1) equal number of atoms of particular elements and (2) equal charges on both sides of the reaction notation. According to such requirements, the reaction $Mn^{2+} + MnO_4^- = 2MnO_2$ is written incorrectly whereas the reactions: $Mn^{2+} + MnO_4^- + e^- = 2MnO_2$ or $2MnO_4^- + 3Mn^{2+} + 2H_2O = 5MnO_2 + 4H^+$ can be considered to be written correctly. From the EM viewpoint, the reactions:

$$HCl + NaOH = NaCl + H_2O \qquad [40]$$

$$H^+ + OH^- = H_2O \qquad [41]$$

are written correctly, although HCl, NaOH, and NaCl do not exist as the species in aqueous media; their concentrations in aqueous solution are in principle equal to zero.

An attempt to formulate the equilibrium constant of reaction [40] provides the indeterminate expression of 0/0 type. The equilibrium constant for $NaCl = Na^+ + Cl^-$ equals infinity whereas one referred to $Na^+ + Cl^- = NaCl$ equals zero.

Equilibrium constants K are related to correctly written chemical reaction notations, where only the species (i.e., forms really existing in the system) are involved. In such cases, the inequality $0 < K < \infty$ is fulfilled. Then any reaction not designated to formulate the expression for an equilibrium constant obtained on the basis of mass action law should be omitted in considerations. However, the equilibrium constant values, found in equilibrium data tables, should be pre-selected carefully.

Formal correctness does not also mean that the reaction really proceeds in the system—the reasons are, however, different.

The correctly written reaction notation $Mg^{2+} + 2H_2O = Mg(OH)_2 + 2H^+$ involves the entities that can exist as species, but it does not mean that $Mg(OH)_2$ precipitate is formed when magnesium salt (e.g., $MgCl_2$) is introduced into water. From charge and concentration balances related to this system it results that $[H^+] – [OH^-] = [MgOH^+]$, i.e., $[H^+] > [OH^-]$; in acidic media, $Mg(OH)_2$ does not precipitate.

The correctly written reaction notation $4MnO_4^- + 2H_2O = 4MnO_2 + 3O_2 + 4OH^-$ does not correspond to the reaction occurred when potassium permanganate is introduced into water, although it is possible from thermodynamic viewpoint. Simply, the overvoltage supplied by MnO_4^- ions in aqueous media is not sufficient to provide the energy required to volumetric work required to form bubbles of gaseous oxygen (O_2) in it. Consequently, $KMnO_4$ and H_2O form, also at elevated temperatures, a metastable system. Further examples testifying about limited informative contents of a chemical reaction notation can be found in (7).

In this context, it is difficult to accept some statements met in contemporary literature. Some of them, taken from (22), are cited below, *in extenso*.

(1) The stoichiometric reaction is considered as a linear combination of molecular equations describing the mechanism of a complex chemical transformation. The basic problem in this case is to determine the combination coefficients (stoichiometric numbers) (27).

(2) The intermediates, which are specified in the molecular equation and disappeared during the combination, and a number of physicochemical conditions based on conservation principles and the theory of linear equations should be taken into account for this determination (28).

(3) Stoichiometry of complex chemical systems with two or more reactions between the same components is being developed using linear algebra and other mathematical methods.

In principle, all the statements resemble the procedure realized in the combination of equations for calculation of enthalpies or equilibrium data according to the Hess rule.

Another problem, involved with stoichiometry, has been raised in (29). From the EM viewpoint, it is no matter which of the reactions:

$$I_2 + 2OH^- = IO^- + I^- + H_2O \qquad [42]$$

$$3I_2 + 6OH^- = IO_3^- + 5I^- + 3H_2O \qquad [43]$$

referred to titration of iodine with strong base, is considered in stoichiometric calculations; stoichiometries of both reactions are the same: 3:6 = 1:2. However, as stated in (29), the efficiency of reaction [43] is ca. $2.5 \cdot 10^9$ times greater than the efficiency of reaction [42]; $2.5 \cdot 10^9 \approx$ (80 y)/(1 s). Nonetheless, in all handbooks and monographs, the reaction [42] is taken for stoichiometric calculations.

Any particular reaction proceeding in a chemical system is stoichiometric in its notation. It concerns partial chemical equations designed to formulate the algebraic equations for the corresponding equilibrium constants, completing the set of material balances from the GEM viewpoint. In EM, none of the partial equations can play the role of the reaction "responsible" for the stoichiometry of the resultant reaction — with one exception: the reaction $H^+ + OH^- = H_2O$, referred to the simplest acid-base system, where NaOH and HCl solutions are mixed.

However, some reactions do not proceed according to the expected, resultant stoichiometry. For example, the "resultant" reaction between H_3AsO_4 in acidic (H_2SO_4) media with KI solution (8) proceeds only partially and the titration curve E = E(V) thus obtained does not reflect the desired (from analytical viewpoint) S-shape, with a distinct change of potential at the vicinity of the equivalent point. Briefly, the resultant effect of all stoichiometric reactions may not reflect the (expected) stoichiometric properties.

It does not mean, however, that only S-shaped titration curve is the *conditio sine qua non*, required to evaluate V_{eq} in titrimetry. For example, in the extrapolative Gran methods, V_{eq} is evaluated by extrapolation (see Section 8.1). Another resolution is the curve-fitting method [see e.g., (30–37)] where V_{eq} or concentration of analyte in the sample can be evaluated as one of parameters of the system with the use of iterative computer programs or, in some instances, according to least squares method.

Finally, one should refer again to the problem raised in connection with notation of Eq. [39] and with the "*quasi*-algebraic" properties exhibited by the principle of chemical reaction notation. In physical calculations, based on "truly-algebraic" principles, it is not admissible to compare, e.g., energy or work (scalars) with moment of a force (vector), although all physical quantities can be expressed in the same physical units [Joules]. Zero-vector (**0**) is different from zero-scalar. Assuming that all components of a chemical reaction are expressed in the same units (symbols), it is not acceptable to consider the following notations:

$$Fe^{2+} = Fe^{3+} + e^-,\ Fe^{2+} - e^- = Fe^{3+},\ Fe^{2+} - e^- - Fe^{3+} = 0$$

equivalently; the term on the right side of the last notation should be considered rather as a lack of symbol, not zero (scalar) or . . . the symbol of oxygen atom (*reductio ad absurdum*). Nonetheless, the manner represented by the last notation is applied in chemical thermodynamics and even the concept of matrix algebra related to chemical reactions is introduced. The first two notations can be "put in words" (removal of an electron from Fe^{2+} ion).

It is not easy, however, to put in words even a simple reaction occurred during titration of C_0 mol/L H_3PO_4 with C mol/L NaOH. At $C_0 \approx 10^{-2}$, the titrand contains comparable concentrations of H_3PO_4, $H_2PO_4{}^-$, and H^+. The $[H^+]$ value for C_0 mol/L H_3PO_4 is calculated from the equation $[H^+]^2 + k_1[H^+] - C_0k_1 = 0$ and then the mean number of protons bound to PO_4^{3-} in C_0 mol/L H_3PO_4 equals

$$\begin{aligned}\bar{n} &\cong (3[H_3PO_4] + 2[H_2PO_4{}^-])/([H_3PO_4] + [H_2PO_4{}^-]) \\ &= (3x + 1)/(x + 1)\end{aligned}$$

where $x = (1 + 4C_0/k_1)^{1/2}$. At $C_0 = 0.01$ mol/L, $pk_1 = 2.04$, we have: $x = 2.32$ and $\bar{n} \cong 2.4$. In this case, the statement that one proton in each molecule of H_3PO_4 is neutralized when titration is ended at $pH_e = pH(\Phi = 1) = 0.5 \cdot \log\{K_3{}^H/K_1{}^H + (K_2{}^H/K_1{}^H) \cdot (1/C_0 + 1/C)\}$ (8), where $\bar{n} = 2.0$, is not correct; the change in the number of protons bound as the result of the titration is different from 1, $\Delta\bar{n} = 2.4 - 2.0 = 0.4$. In this system, two main reactions can be indicated:

$$H_3PO_4 + OH^- = H_2PO_4^- + H_2O \qquad [44]$$

and [41], occurring in the system in question. Application of Eq. [44] is the only inadmissible simplification; Eqs. [44] can be considered as a kind of dummy that possess only informative character, i.e., it may be considered only in terms of a "code" applied against a more extensive (verbal) description of (analytical) activities.

The reaction notation seems to be a kind of the "last resort" used when a lack of sufficient physicochemical knowledge on the system is extremely painful. A striking example is the Karl–Fischer method of water determination. The existence of possible intermediates formed in the system is based only on speculations; particularly, the equilibrium constants and rate constants in this system are unknown (38).

The role of a chemical reaction notation may (or rather should) be limited only to one purpose—namely to formulate the expression for the related equilibrium constant value. Such a procedure can be named as an "escape into algebra." Indeed, the expression for equilibrium constant, formulated on the basis of mass action law, is an algebraic expression, whereas a chemical reaction notation appears only "*quasi*-algebraic" properties, involved, e.g., with the formulation of linear combinations of particular reactions, practiced on an elementary level of chemical education.

GEM VERSUS EM

The equivalence mass (EM) concept (5, 6) is still recommended and advocated by IUPAC. Its principle is to formulate the reaction and to apply then the method of finding the fourth term of the mathematical proportion when three terms are given (the rule of three):

$$\begin{array}{l} n_AA + n_BB + (\ldots) = (\ldots) \\ \qquad n_A \qquad\qquad n_B \\ 10^3 \cdot m_A/M_A \quad C \cdot V_{eq} \end{array} \qquad [45]$$

where n_A and n_B refer to the number of milimoles. The following expression is obtained

$$m_A = 10^{-3} \cdot C \cdot V_{eq} \cdot \frac{M_A}{n_B/n_A} \qquad [46]$$

Comparing the eqs. [46] and [13], one can state that the identity occurs at $\Phi_{eq} = n_B/n_A$; e.g., for the reaction

$$5Fe^{2+} + MnO_4{}^- + 8H^+ = 5Fe^{3+} + Mn^{2+} + 4H_2O \qquad [47]$$

we have: $n_A = 5$, $n_B = 1$, and then $\Phi_{eq} = 1/5 = 0.2$.

In the light of discussion concerning Eq. [13] one can state that Eq. [46] is not valid if V_{eq} (not V_e) is determined by visual titration. The volume V_e does not correspond to the equivalence point but to an excessive amount of $KMnO_4$ solution, where $[MnO_4{}^-] \approx 10^{-5}$ mol/L and pink color appears; one drop ($\Delta V = 0.03$ mL) of 0.02 mol/L $KMnO_4$ introduced into 100 mL of the water (or colorless non-reducing solution) makes $[MnO_4^-] \approx 0.02 \cdot 0.03/110 \approx 0.5 \cdot 10^{-5}$ mol/L. In other instances, e.g.,in presence of yellow background color of solution resulting from iron(III) species formed as the result of the titration, the pink color is masked. Similarly, the pink color of $FeSCN^{2+}$ appears at the end of argentometric titration of thiocyanate ions according to the Volhard method (1). Concentrations of MnO_4^- or $FeSCN^{2+}$ (and other species in the related methods of analysis) can be found according to GATES, at any stage of the titration.

The choice of the reactions in EM depends on the stoichiometry derived from experimental data. It is usually involved with speculations done when searching different intermediates (22). One can notice that under experimental conditions (presence of H_2SO_4 in D), strong sulphate complexes $Fe(SO_4)_i^{(3-2i)+}$ ($i = 1, 2$) are formed and concentrations of complex species: $FeSO_4$ and $MnSO_4$ are comparable with $[Fe^{2+}]$ and $[Mn^{2+}]$, respectively. By considering Eq. [47] in terms of the predominating species, one can write:

$$\begin{array}{l} 5FeSO_4 + MnO_4{}^- + 6HSO_4{}^- + 2H^+ \\ \quad = 5Fe(SO_4)_2{}^- + MnSO_4 + 4H_2O \end{array} \qquad [48]$$

The stoichiometries in Eqs. [47] and [48] (where electrons are cancelled) are identical, of course.

It could be noticed that EM applies the "proportion principle" to "fragile" chemical reaction notation, whose symbols are referred to letters, not numbers. The 'fragility' can be discussed on the basis of examples considered above.

Returning to the reaction [40], one should remember that the symbols: HCl, NaOH, and NaCl are not related to species existing in aqueous solutions. One could ask: can the EM definition be based on fictitious entities?

Reaction [40] can be also considered as a kind of chemical "code." It can be interpreted as the information that NaOH (solution) has been added into HCl (solution) and (. . .). One could ask again: can the EM definition be based on a code?

Referring to the notations given in [42] and [47], one could ask: can the EM definition be referred to minor species (reagents, products)?

In all the questions above, "yes" can be the answer. One could argue that the mnemonic approach based on the EM concept works satisfactorily in titrimetric analyses, and that the indicators are ascribed properly to particular analytes. Similar argumentation could be referred to many branches of analysis.

This argumentation is not satisfactory, however, to the ones considering analytical chemistry as a science, not as an art (craft). Any science can be defined as the systematic and coordinated knowledge based upon the accurate observations of facts and on which general principles and laws rely. Analytical chemistry is perceived by some scientists as a fundamental discipline and the most important part of chemistry, providing theoretical foundations of analysis (39) and the interface between metrology and problem solving (40). Particularly, GATES concerns the physicochemical approach based on balances and equations for equilibrium constants, resolved with use of iterative computer programs (MATLAB, MINUIT, DELPHI, etc.). GATES provides the tool that enables one to foresee the course of processes and resolves many problems of analytical and physicochemical nature. It is compatible with models formed for analytical purposes, exemplified by algorithms derived for the Gran I method (Section 8.1). None of the balances is based only on the components of the related reaction equation. Simply, the reaction notation does not involve all components of the system considered.

By comparing EM and GEM one can summarize that:

(1a) EM is formulated for a defined system *a posteriori*, with the use of a stoichiometric reaction (Eq. [45]), formulated on the basis of experiments, realized under defined conditions of analysis.
(1b) GEM is formulated *a priori*, on the basis of GATES, with no relevance to a stoichiometry.
(2a) In EM, formulation of a (dummy) chemical reaction notation for stoichiometric calculations is admitted.
(2b) When referring to GEM, see (1b).
(3a) In EM, molar mass M_A is divided by the number n_B/n_A (Eq. [46]) resulting from the stoichiometry of Eq. [45].

(3b) In GEM, molar mass M_A is divided by the Φ_{eq} value (Eq. [14]) resulting from GATES.

(4a) EM is defined separately for particular types of elementary (acid–base, redox, complexation, and precipitation) reactions.

(4b) GEM is formulated in unified manner, with no relevance to particular types of reactions, occurred simultaneously and/or sequentially, and referred to systems of any degree of complexity (1).

(5a) Formulation of EM does not involve any physicochemical knowledge on the system considered.

(5b) GEM is formulated on the basis of all attainable (and pre-selected) physicochemical knowledge on the system in question.

(6a) EM does not provide any possibilities to evaluate an effect of pH and accompanying substances.

(6b) GATES provides the basis explaining possible changes in GEM, affected by presence of some accompanying substances (see Table 3).

(7a) Formulation of EM enables only to "target" (mark) only the equivalent points, i.e., information from the vicinity of the equivalence points is inadmissible.

(7b) In the GATES referred to GEM concept it is possible to calculate coordinates of the end points, taken from the vicinity of equivalence point where the (properly or improperly) chosen indicator acts (see Sections 2, 3). This way, one can choose a proper indicator and the most appropriate (from analytical viewpoint) color change of the indicator. Also the coordinates of the equivalence point can be determined more accurately than hitherto.

(8a) Any speciation in the system within EM is not possible.

(8b) The GATES referred to GEM concept offers dynamic speciation in the titration process (1, 2, 4, 8). It enables one to formulate main and accompanying reactions, together with their efficiencies, on any stage of this process and follow all what is invisible in real experiments.

(9a) In EM, calculation of errors at the end points is impossible.

(9b) Using GATES, one can evaluate the errors involved with registration of V_e value. It frequently happens that pH of color change of an indicator does not involve $pH = pH_{eq}$ corresponding to the equivalence point.

(10a) Formulation of EM does not involve the range of color change of an indicator effects. All necessary information is provided experimentally.

(10b) Procedure of GEM formulation realized with use of GATES enables to explain and measure quantitatively the effects specified in (9a). It enables to choose a proper indicator and its best color change, where V_e is close to V_{eq} within the one drop error (Section 5).

(11a) Formulation of EM does not provide any prerequisites for optimization of an analytical method.

(11b) The GATES realized for GEM purposes provides the basis for optimization *a priori* (see Fig. 3 and Table 5).

(12a) The manner of EM formulation does not provide a basis for searching new methods of analysis.

(12b) The GATES procedure realized for GEM purposes enables to foresee and optimise new analytical methods, modify, improve and optimise old analytical methods.

(13a) The manner of EM formulation does not provide any prerequisities about characteristic changes of some variables measured.

(13b) The GATES procedure provides some information that can be (potentially)] used for GEM purposes.

(14a) Formulation of EM does not provide any chemical knowledge on the system tested.

(14b) The manner of GEM formulation provides a deep knowledge on the electrolytic – mono- and poly-phase systems. It enables to distinguish between equilibrium and metastable systems and indicate the effects resulting from transportation phenomena occurred at indicating electrode.

In a common approach referred to redox systems, the titration curve is divided into two parts, referred to separately as $V < V_{eq}$ and $V > V_{eq}$, i.e., the most interesting (from analytical viewpoint) region of the vicinity of the equivalence point (V_{eq}, E_{eq}) is omitted in the formulation. The E_{eq} value is calculated from the incorrect equation based on the stoichiometry of the related equation. In GATES, based on the GEB concept (2, 29, 41) the titration curve is expressed by one function, involving the equivalence point (see e.g., Table 1).

Referring to (12b), one can indicate a new, interesting method of As(III) determination by titration with $I_2 + KI$ solution (4). In this case, pH-metric titration is performed in buffered(!) solution and the titration curve thus obtained consists of two rectilinear parts, intersecting at the point close to the equivalence point. As concerns (13b), application of GATES enabled us to state (for the first time) the maxima on pH vs. Φ curves occurred at the equivalence points for some D+T systems (1, 8, 10).

One can also refer to the matter involved with completing the physicochemical data related to a system considered. Particularly, the stability constants (K_{3i}) of (possible *a priori*) sulphate complexes $Mn(SO_4)_i^{(3-2i)+}$ formed by Me^{3+} ions are unattainable in literature, $[Mn(SO_4)_i^{(3-2i)+}] = K_{3i} \cdot [Mn^{3+}][SO_4^{2-}]^i$. For this purpose, different "virtual" values for K_{3i} (i = 1 or i = 1, 2) were assumed in calculations. The fragments of the related parts of titration curves, plotted for $\Phi \in (0.2, 0.3)$, are presented in Fig. 5a and compared with the one obtained experimentally (Fig. 5b). This comparison leads to the conclusion that at most weak complexes are formed. The K_{3i}-values for the curve 1 in Fig. 5a are comparable with ones ($\log K_{31} = 4.18$, $\log K_{32} = 7.4$) ascribed to complexes $Fe(SO_4)_i^{(3-2i)+}$ (i = 1, 2).

FINAL COMMENTS

Formulation of a stoichiometric reaction notation is a consequence of interpretation of the data obtained from simulated

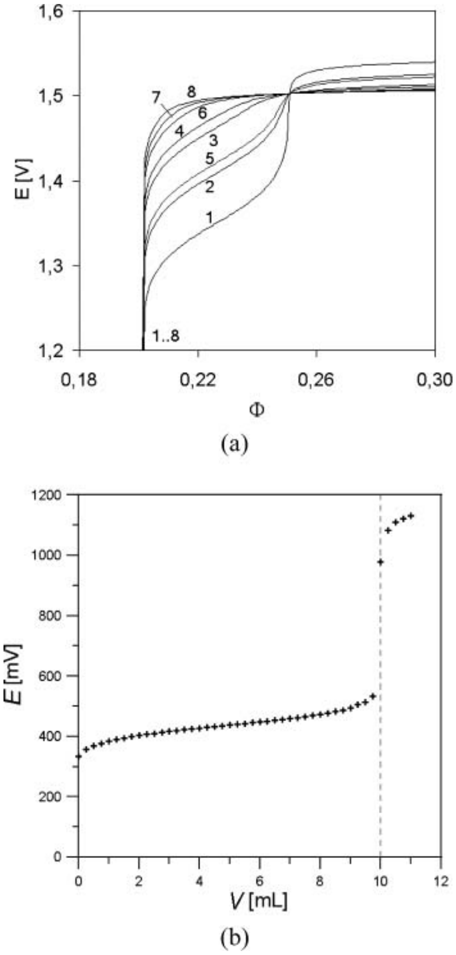

FIG. 5. (a) Fragments of hypothetical titration curves plotted for different pairs of stability constants (K_{31}, K_{32}) of the sulphate complexes $Mn(SO_4)_i^{+3-2i}$: 1 – (10^4, 10^7), 2 – (10^3, 10^6), 3 – ($10^{2.5}$, 10^5), 4 – (10^2, 10^4), 5 – (10^4, 0), 6 – (10^3, 0), 7 – (10^2, 0), and 8 – (0, 0); (b) the titration curve obtained experimentally.

speciation curves (4) obtained on the basis of physical laws of conservation (i.e., charge, electron, and concentration balances) and physicochemical data (equations for the related equilibrium constants). It particularly refers to complex analytical systems.

The difficulties associated with the complex nature of the system and algebraic equations involved disappear, however, when GATES is applied. This way, some complex processes, such as the pH–static titration in a two–phase system, are realized (12). The computer program that enables one to follow the simulated procedure (pH–static titration of cyanide, according to a modified Liebig–Denigès method) to be effected automatically has also been prepared (42).

The principle of the GEM concept enables one to select consciously the best *a priori* conditions of analysis and indicates some effects involved with an insufficient physicochemical knowledge of the system (4, 10), particularly involved with activation barriers for some reactions (1) or transportation phenomena at electrode surface and kinetics of reactions in the bulk solution; the latter problems are particularly involved with automated titrations. The generalized approach to electrolytic systems, applied for GEM purposes, also enables one to choose the best a priori conditions of analysis.

In calculations done according to GATES, all equilibrium constants assume constant values during the titration, where a change in ionic strength (I) occurs, as a rule. It is well-known that any equilibrium constant (K) value depends on the temperature (T), ionic strength, and dielectric permeability (ε) values, $K = K(T,I,\varepsilon)$ and $\varepsilon = \varepsilon(T,I)$; the same remark concerns standard redox potentials. Within GATES, it would be possible to assume all the changes considered, provided that the relationships $K_i = K_i(T,I,\varepsilon)$ are known beforehand for all equilibrium constants (K_i) considered in the system; however, they are unknown. On the other hand, the change in K_i value affected by ionic strength in isothermic ($T = const$) processes are frequently smaller than the indefinity resulting from experimental errors, the model applied, and the instrumental technique applied for K_i determination.

ABBREVIATIONS

A	analyte (substance determined) in D
B	reagent in T, reacts with A
C	concentration [mol/L] of B in T
C_0	concentration [mol/L] of A in D
D	titrand (solution titrated)
e	refers to the end point
EM	equivalent mass, according to IUPAC
eq	refers to the equivalence point
GATES	generalized approach to electrolytic systems
GEB	generalized electron balance
GEM	generalized equivalent mass
HIn	protonated form of indidator
K_{In}	dissociation constant of HIn, $pK_{In} = -\log K_{In}$
T	titrant
V	volume [mL] of T added
V_0	volume [mL] of D

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