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An Unified Quantitative Approach to Electrolytic Systems

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Balancing of electrolytic systems is applied both for equilibrium analysis and for kinetic purposes. The advantages of such approach were compared with one based on the reaction notation. The equilibrium analysis was the basis to introduce the unified equivalence mass concept and to evaluate the relative systematic error in a titrimetric analysis; it enables the best *a priori* conditions for appropriate titrations to be chosen. Balancing of kinetic systems provides a formulation adaptable, among others, to oscillating systems of the Belousov–Zhabotinsky type.

Bilansowanie układów elektrolitycznych zastosowano w analizie równowagowej i kinetyce. Korzyści wynikające z takiego podejścia porównano z opartym na notacji reakcji. Analiza równowagowa jest podstawą do wprowadzenia zunifikowanego pojęcia równoważnika chemicznego i oszacowania błędu systematycznego w analizie miareczkowej; daje to możliwość wyboru najlepszych *a priori* warunków miareczkowania. Bilansowanie układów kinetycznych wprowadza formalizm możliwy do zastosowania m.in. w układach oscylacyjnych typu Biełousowa-Żabotyńskiego.

Diversity in notation of reactions, that occur during titration made in defined system, disqualifies the equivalent mass concept advocated by IUPAC [1–4]. On the contrary, the approach based on balances and the term of fraction titrated [5], provides a reasonable tool for resolution of the problem in question. The new approach was subsequently proposed for resolution and elucidation of kinetic systems, *e.g.* oscillating systems of the Belousov–Zhabotinsky type [6]; it seems to be superior and more comprehensible than other ones known hitherto, *i.e.* based on a reaction notation.

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Reaction notation

The criteria of correctness of a reaction notation are not specific: the equalities in number of atoms of particular elements on both sides and in total charges are only required. In this respect, the equilibrium constant related to a reaction and one related to the reaction with inversed sides are of equal rights [7]; *e.g.* the two opposing reactions: $Pb^{2+} + S^{2-} = PbS$ and

$$PbS = Pb^{2+} + S^{2-} \tag{1}$$

are written correctly though (1) proceeds only to a slight degree. The reaction (1) is the basis to formulate solubility product for PbS. What is more, some equilibrium data refer to reactions that do not practically proceed or even cannot proceed in a system, *e.g.* solubility products for HgS or PtS. In such instances, it is even impossible to formulate equilibrium constants from its definition viewpoint. For example, the ionic product $[Hg^{2+}][S^{2-}]$ calculated for 1 l of aqueous solution containing 1 ion Hg^{2+} and 1 ion S^{2-} is greater than the solubility product for HgS ($pK_{so} = 52.4$) and the solution should be considered as a supersaturated one.

Any discretion in a choice of a reaction notation disqualifies it, at any rate, as one well-suited for quantitative conclusions. An option was the notation involving the species predominating in a system in question; notation of the predominant reaction is not required for correct formulation, however. For example, partial dissolution of PbS after addition of HCl can be expressed by reaction

$$PbS + 2H^+ = Pb^{2+} + H_2S$$

and the solubility product

$$K'_{so} = \beta_2^H K_{so} = 10^{-7.5}$$

where $[H_2S] = \beta_2^H[H^+]^2[S^{2-}]$, $\log\beta_2^H = 20.0$. Similarly, a partial dissolution of HgS in HCl can be expressed by equation

$$HgS + 2H^+ + 4Cl^- = HgCl_4^{2-} + H_2S \tag{2}$$

and the solubility product

$$K'_{so} = \beta_4 \beta_2^H K_{so} = 10^{-17.33} \tag{3}$$

where $[HgCl_4^{2-}]=\beta_4 [Hg^{2+}][Cl^-]^4$, $\log\beta_4=15.07$; then $K'_{so} \approx 2.8\times10^{-48}$, *i.e.* the reaction (2) does not provide the troubles in formulation of solubility product for HgS. In this context, K_{so} for HgS can be considered only as a quantity which may be calculated from the formula (3). It should be noted that the equilibrium constants (*e.g.* solubility products, stability constants) are related to a large number of interacting components. Other explanations, *e.g.*, one based on an assumption of a great divergency between activity and concentration in very diluted solutions, are not significant.

The set of balances

According to the approach applied in previous papers [8–17], the reaction considered as a defined sequence of marks, is only a "carrier" of the related equilibrium constant and a basis for an algebraic equation involving defined components of the system with the equilibrium constant, according to the law of mass action.

The components that form the system are introduced by a set of linearly independent reactions. It enables some ambiguities (affected *e.g.*, by incoherencies or roundings of physicochemical data) to be avoided.

The relations for equilibrium constants complete the set of r equations written in a general form

$$\sum_{j=1}^{p} \alpha_{ij} [X_j] = \gamma_i \qquad (i = 1,...,r) \tag{4}$$

The set of equations related to a redox system consists of electron, charge and z concentration balances (together $r = 2+z$ balances) whereas electron (pre)balance is omitted in non-redox systems ($r = 1+z$); α_{ij} is the coefficient related to j-th species X_j ($j = 1,...,p$), of molar concentration $[X_j]$, in i-th balance, $i = 1,...,r$; γ_i – expressions involving analytical concentrations and volumes of titrand and titrant (for concentration balances and electron (pre)balance [11–13]) or equal zero (for charge balance). If k-th species, X_k ($k \in \langle 1,p \rangle$), does not enter (as concentration) into the i-th balance, then $\alpha_{ik}=0$.

Equivalent mass

The crude definition of equivalent mass [1–4] implies separate formulations for different kinds of titrimetric analyses. Particularly, the equivalent mass of a component X in acid–base (or redox) reaction is defined through the number of protons (or electrons) combined or released in reaction with 1 mole of X. In all instances, this concept is based on a notation of the main reaction as distinguished from other reactions proceeding in a system considered. Such a superficial approach is justifiable if the efficiencies of accompanying, miscellaneous reactions can be neglected; this assumption is usually not valid, however. As the mole concept required some elucidation [18,19], the equivalence mass concept needs the reinterpretation.

The main reaction proceeding in a chemical system is usually influenced by some accompanying, coupled reactions. Particularly, redox reactions are coupled with acid–base and complexation reactions. For example, the results of ascorbinometric titration of iodate in presence of $HgCl_2$ are quite different than ones obtained in its absence [14]. Three (electron, proton and ligand) kinds of exchange phenomena occur there and, moreover, solid iodine is precipitated. Generally, if two or more kinds of exchange phenomena occur, the serious difficulties arise in the 'old-fashioned' meaning of the equivalent mass concept. Moreover, the main reactions occurring at various stages of titration may appear to be quite different [13].

All the diversities in the meaning of the equivalence concept touched above are quite avoided when the unified equivalent mass [8,20], based on the concept of the fraction titrated, ϕ, is employed. This concept refers to systems of any degree of complexity, *e.g.*, multicomponent and multiphase (precipitation and extraction) systems.

In contrary to the definitions obligatory till now, none of the reactions proceeding there is favourized and only the reactions providing the related equilibrium constants are taken into account. The usefulness of unconventional definition is comprehensively outlined and illustrated by some examples concerning acid–base, complexometric and redox titrations. The unification enables one to define a relative systematic error resulting from the choice of the end point in potentiometric or visual titration.

Unified equivalent mass concept

The fraction titrated, ϕ, when applied to the titrand–titrant system where V ml of C mol l^{-1} of reagent A is added into V_0 ml of C_0 mol l^{-1} of analyte B, is defined by equation [5]

$$\phi = CV/(C_0V_0) \tag{5}$$

The fraction titrated is closely related to the equivalent mass R_B of component B. If m_B and M_B denote mass [g] and molar mass [g mol^{-1}], respectively, of the determined substance B, we get [8]

$$m_B = 10^{-3}\, CV_eM_B/\phi_e \tag{6}$$

$$m_B = 10^{-3}CV_{eq}M_B/\phi_{eq} \tag{7}$$

where subscripts e and eq refer to the end and equivalence points, respectively. Equations (6) and (7) provide two different definitions of equivalent mass: 1) $R_B^e = M_B/\phi_e$ if V_e is obtained and 2) $R_B = M_B/\phi_{eq}$ if equivalence volume V_{eq} is determined.

The V_e value is obtained in titrations terminated at the moment where the corresponding indicator acts, *e.g.* the change of colour of visual indicator or current in titration with amperometric end-point detection. Nevertheless, the results of titrations are usually calculated from the approximate formula

$$m'_B = 10^{-3}CV_eM_B/\phi_{eq} \tag{8}$$

The right side of (8) is obtained by setting ϕ_{eq} for ϕ_e in eq.(6). The relative systematic error in m_B determination, committed by this approximation, equals [8]

$$\delta = (m'_B - m_B)/m_B = \phi_e/\phi_{eq} - 1 = V_e/V_{eq} - 1 \tag{9}$$

Equation (6) could be applied if all parameters involved in expression for ϕ are known beforehand.

The new concept of equivalent mass enables to minimize the error caused by setting ϕ_{eq} for ϕ_e in the related formula (8) if the end point is obtained. Results of the evaluation depend on reliability of equilibrium constants applied for this purpose.

Despite the fact that the equivalence mass depends on the composition of titrand+titrant system considered, the approach and general definition are the same, *i.e.* the equivalent mass is defined through the value of fraction titrated.

The formulation of expressions for ϕ and calculation of δ [eq. (9)], related to defined conditions of analysis, will be illustrated with some examples concerning titrimetric analysis. The related data are obtained on the basis of concentration and charge balances (for non-redox systems) or charge, concentration and electron balances (for redox systems), with a set of equilibrium data involved.

A. Acid–base titration

Example A1. C_0=0.01 mol l^{-1} H_3PO_4 is titrated with C = 0.1 mol l^{-1} NaOH. The fraction titrated is expressed by equation [8]

$$\phi = \frac{C}{C_0} \times \frac{(3 - \bar{n})C_0 - [H] + K_w/[H]}{C + [H] - K_w/[H]} \tag{10}$$

where pK_w=14,

$$\bar{n} = (3\beta_3^H[H]^3 + 2\beta_2^H[H]^2 + \beta_1^H[H])/(\beta_3^H[H]^3 + \beta_2^H[H]^2 + \beta_1^H[H] + 1) \tag{11}$$

and $\log\beta_1^H$ =12.3, $\log\beta_2^H$ =19.5, $\log\beta_3^H$=21.6. The relative systematic error (δ) in B = H_3PO_4 determination depends on the kind of visual indicator used. Then one obtains, for example:

Methyl orange:

a) pH_e=3.8, ϕ_{eq}=1, ϕ_e=0.9635, δ=-3.65%

b) pH_e=4.4, ϕ_{eq}=1, ϕ_e=0.9922, δ=-0.78%

"5.1" indicator

pH_e=5.1, ϕ_{eq}=1, ϕ_e=1.0060, δ= 0.60%

Phenolphthalein

pH_e=10.0, ϕ_{eq}=2, ϕ_e=2.0154, δ= 0.77%

The pH_e values, related to the first and second equivalence (stoichiometric) points, are as follows:

$pH(1) = 0.5\log\{\beta_3^H/\beta_1^H + (\beta_2^H/\beta_1^H)(C+C_0)/(C_0C)\} = 4.79$

$pH(2) = -0.5\log\{(\beta_1^H K_w/\beta_2^H)(C+2C_0)/(C_0C)+1/\beta_2^H\} = 9.49$

Example A2. Standardisation of HCl against borax preparation. A weighed amount m=0.38137 g of borax ($Na_2B_4O_7 \cdot 10H_2O$, molar mass 381.37 g mol^{-1}), contained in V_0 ml of aqueous solution, is titrated with C = 0.1 mol l^{-1} HCl solution against methyl red (change of colour in pH interval 4.4–6.2).

Dissolution of 1 mmole of borax in water leads to formation of 2 mmoles of NaH_2BO_3 and 2 mmoles of H_3BO_3:

$$Na_2B_4O_7 + 7\,H_2O = 2NaOH + 4H_3BO_3 = 2NaH_2BO_3 + 2H_3BO_3 \tag{12}$$

Analytical concentration of borax in the titrand is C_0=1/V_0 mol l^{-1}. Concentrations of the components originating from the hydrolysis (12) are: $2C_0$=2/V_0 mol l^{-1} for

NaH_2BO_3 and $2C_0=2/V_0$ mol l^{-1} for H_3BO_3. The related titration curve is expressed by equation

$$\phi = \frac{C}{C_0} \times \frac{(4\bar{n} - 10)C_0 + [H] - K_w/[H]}{C - [H] + K_w/[H]} \tag{13}$$

where $\bar{n}$ is defined by eq.(11), and β_i^H are involved in relations:

$$[H_iBO_3] = \beta_i^H[H]^i[BO_3] \qquad (i = 1, 2, 3; \beta_i^H = 13.80, 26.54, 35.78)$$

The ϕ_e values, obtained from eq.(13), are collected in Table 1. It can be seen that the best conditions for HCl determination take place in the vicinity of the middle point of the pH interval, where orange colour of methyl red is observed; the assumption $\phi_{eq} = 2$ leads to the smallest systematic error there [(eq.9)].

Table 1. ϕ_e values found for different V_0 and pH_e for borax solution titrated with $C = 0.1$ mol l^{-1} HCl solution

V_0	ϕ_e		
	pH_e 6.2	5.3	4.4
50	1.9964	1.9999	2.0027
100	1.9964	2.0001	2.0047
200	1.9965	2.0009	2.0107

Example A3. V_0 ml of the solution containing 1 mmole of potassium hydrogen phthalate was prepared for titration with C = 0.1 mol l^{-1} NaOH solution.

Four different indicators were taken into account: phenol red (6.4–8.0), cresol red (7.2–8.8), phenolphthalein (8.3–10.0), tymolphthalein (9.3–10.5). The ϕ_e values obtained on the basis of equation

$$\phi = \frac{C}{C_0} \times \frac{(1 - \bar{n})C_0 - [H] + K_w/[H]}{C + [H] - K_w/[H]} \tag{14}$$

where $C_0=1/V_0$ and

$$\bar{n} = \{2\beta_2^H[H]^2 + \beta_1^H[H]\}/\beta_2^H[H]^2 + \beta_1^H[H]+1\}$$

$$[H_iL] = \beta_i^H[H]^i[L] \ (i = 1, 2; \log\beta_i^H = 4.92, 7.68)$$

are collected in Table 2.

Acid–base properties of an indicator itself and its effect on ϕ_e value were not taken into account in the equations for titration curves given above. Such simplification is usualy justified by small concentration of indicator (C_{0I}) in a sample. The equations for titration curves involving indicators of $K_lH_{m-l}I$ (C_{0I}, $l = 0,...,m$) type are presented in ref. [8].

Table 2. ϕ_e found for different V_0 and pH_e values due to the potassium hydrogen phthalate solution titrated with C = 0.1 mol l^{-1} NaOH solution

	ϕ_e		
pH_e	V_0 50	100	200
6.4	0.9679	0.9679	0.9678
7.2	0.9948	0.9948	0.9948
8.0	0.9992	0.9993	0.9994
8.3	0.9997	0.9998	1.0001
8.8	1.0002	1.0006	1.0015
9.2	1.0009	1.0017	1.0041
9.3	1.0012	1.0022	1.0051
9.9	1.0048	1.0087	1.0207
10.0	1.0060	1.0110	1.0260
10.5	1.0190	1.0349	1.0825

B. Complexometric titration

Example B1. C_0 = 0.01 mol l^{-1} KCN is titrated with C = 0.1 mol l^{-1} $AgNO_3$ (Liebig's method). At the end point, where the solubility product (K_{so}) for AgCN is reached (pK_{so}=15.9), one obtains

$$\phi_e = 0.5 - 0.25\{(2C+C_0)(\beta_1^H [H]_e+1)/(C_0C)+\beta_3/\beta_2\}[CN]_e \qquad (15)$$

where $\log\beta_i$=19.85, 20.55, 19.42 for $Ag(CN)_i^{+1-i}$ (i= 2, 3, 4), $\log\beta_1^H$ = 9.2 for HCN, and

$$[CN]_e=C_0C/(2C+C_0)/(\beta_2K_{so}), \qquad [H]_e=\{K_w/\beta_1^H[CN]_e+1)\}^{1/2}$$

From eq.(15) we get ϕ_e=0.49982, *i.e.* the theoretical error resulting from substitution ϕ_{eq}=0.5 in eq.(6) is δ= -0.036%.

Example B2. V_0 = 25 ml of C_0 = 0.01 mol l^{-1} $ZnCl_2$ solution buffered with NH_4Cl (C_1 mol l^{-1}) and NH_3 (C_2 mol l^{-1}), $C_1 + C_2 = C_N$, C_2/C_1 = 4, is titrated with C = 0.02 mol l^{-1}EDTA in the presence of Erio T ($C_I=p\times10^{-5}$; p = 2, 4, 6, 8, 10) as the indicator. The related curves of log[Zn*] *vs.* ϕ and log y *vs.* ϕ relationships are plotted in Figs. 1–3, where:

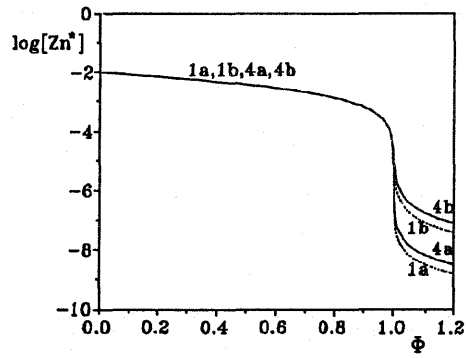

Figure 1. The log[Zn*] *vs.* ϕ relationships plotted for C_N = 0.1, r=1 (curve 1a), C_N=0.1, r=4 (curve 4a), C_N=1, r=1 (curve 1b) and C_N=1, r=4 (curve 4b); $\log\beta_i^{OH}$= 4.4, 11.3, 13.14, 14.64 for $Zn(OH)_i$ (i=1,2,3,4); $\log\beta_j^N$ = 2.18, 4.43, 6.74, 9.4 for $Zn(NH_3)_j$ (j= 1, 2, 3, 4)

$$[Zn^*] = [Zn] + \Sigma [Zn(OH)_i] + \Sigma [Zn(NH_3)_j]$$

$x_1 = \Sigma [H_iI]$, $x_2 = [ZnI] + 2[ZnI_2]$ and $y = x_2/x_1$.

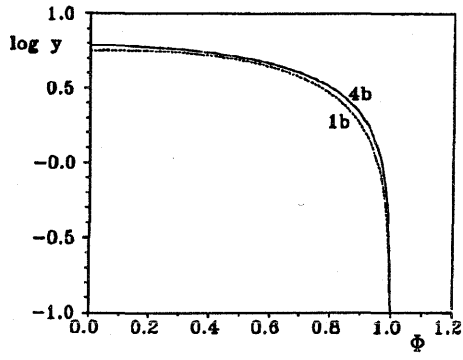

Figure 2. Graphs of log$y$ *vs.* ϕ relationships at $C_I = 2\times10^{-5}$ (p = 2), C_N = 1 and: r = 1 (curve 1b), r = 4 (curve 4b)

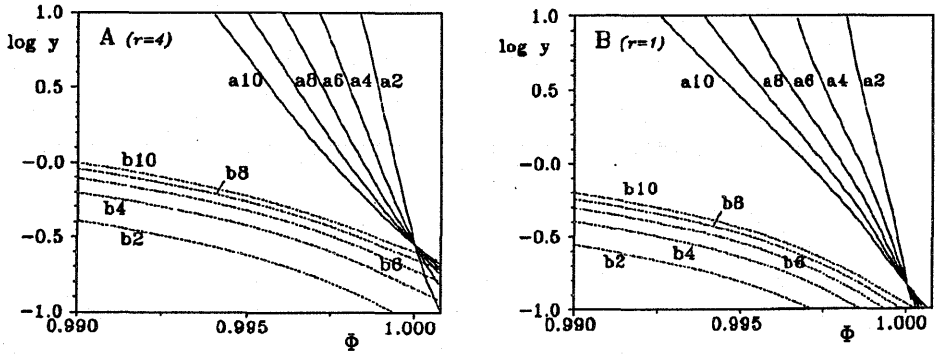

Figure 3. The log$y$ *vs.* ϕ relationships, $y = x_2/x_1$; Erio T (H_3I; $\log\beta_{1i}^{H}$ = 11.55, 17.8, 21.7 for H_iI, i=1, 2, 3) forms red complexes: ZnI ($\log\beta_1^1$ =12.9) and ZnI_2 ($\log\beta_1$ = 20.0); $C_I = p\times10^{-5}$ (p = 2, 4, 6, 8, 10); curves $ap = a2,...,a10$ are related to C_N = 0.1 mol l^{-1}, curves $bp = b2,...,b10$ are related to C_N = 1 mol l^{-1}; r = 4 (A) and r = 1 (B)

C. Redox titration

Example C1. V_0=100 ml of acidified (H_2SO_4, C_a=1 mol l^{-1}) solution containing C_0=0.01 mol l^{-1}: a) $FeSO_4$, b) $H_2C_2O_4$, c) H_2O_2 is titrated with V ml of C=0.02 mol l^{-1} $KMnO_4$. The related titration curves are plotted in Fig. 4 for stability constants taken from refs [3,21–24].

Some $(\phi,E)=(\phi_e,E_e)$ pairs related to the corresponding curves are collected in Table 3. It enables the best *a priori* conditions for titration of the related analytes to be chosen.

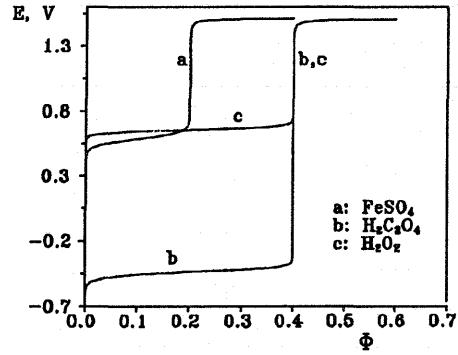

Figure 4. Graphs of E *vs.* ϕ dependences due to titration of C_0=0.01 mol l^{-1} solution of: a) $FeSO_4$, b) $H_2C_2O_4$, c) H_2O_2 with C=0.02 mol l^{-1} $KMnO_4$; $p(O_2)$=1013 hPa in the case *c* [12]

Table 3. (ϕ_e,E_e) values related to the systems with a) $FeSO_4$, b) $H_2C_2O_4$, c) H_2O_2 as analytes (C_0=0.01 mol l^{-1}) titrated with C=0.02 mol l^{-1} $KMnO_4$

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

Example C2. V_0=100 ml of C_0=0.01 mol l^{-1} Br_2 is titrated with C=0.1 mol l^{-1} NaOH. Some points (ϕ_e, pH_e, E_e), obtained on the basis of physicochemical data quoted in ref.[12], are collected in Table 4.

Example C3. V_0=100 ml of Na_3AsO_3 (C_0=0.002 mol l^{-1}) alkaline solution obtained after dissolution of As_2O_3 in NaOH was treated with H_2SO_4 and $NaHCO_3$ and then titrated with 0.01 mol l^{-1} I_2 in 0.1 mol l^{-1} KI. The pH *vs.* ϕ relationship is given in Fig. 5 where the curve consisting of two segments intersecting at ϕ=2, can be also applied for localization of the equivalence point (Fig. 6).

Example C4. According to the procedure established in iodometric determination of cupric ions, the (acidified) solution of cupric salt is pretreated with ammonia until the blue colour of the solution is acquired and then a due excess of acetic acid is added. The mixture is treated with an excess of potassium iodide and then titrated with standardised sodium thiosulfate solution.

Table 4. (ϕ_e, pH_e, E_e) points for Br_2 (0.01 mol l^{-1}) + NaOH (0.1 mol l^{-1}) system

ϕ_e	pH_e	E_e
1.9900	6.479	1.060
1.9950	6.660	1.050
1.9998	7.618	0.993
1.9999	7.766	0.984
2.0000	7.950	0.973
2.0001	8.143	0.962
2.0002	8.310	0.952
2.0010	8.925	0.916
2.0210	10.242	0.838

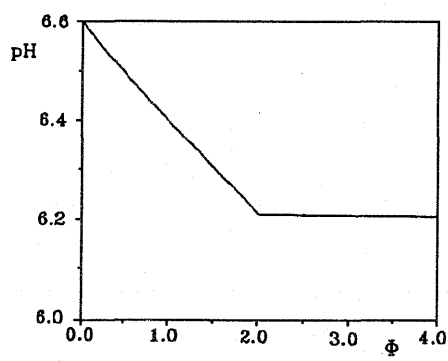

Figure 5. The pH *vs.* ϕ relationships; V_0=100 ml of titrand (0.002 mol l^{-1} H_3AsO_3, 0.01 mol l^{-1} NaOH, 0.01 mol l^{-1} H_2SO_4, 0.03 mol l^{-1} $NaHCO_3$) is titrated with I_2 (0.01 mol l^{-1}) in KI (0.1 mol l^{-1})

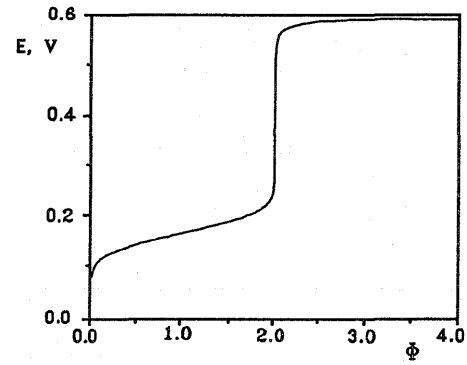

Figure 6. *E vs.* ϕ relationship for the system specified in Figure 5

V_0 = 25 ml of the solution containing $CuSO_4$ (C_0 = 0.01 mol l^{-1}), H_2SO_4 (0.1 mol l^{-1}), NH_3 (0.25 mol l^{-1}) and CH_3COOH (0.75 mol l^{-1}) was treated with 5.8 ml of 2.0 mol l^{-1} KI and then titrated with C = 0.1 mol l^{-1} $Na_2S_2O_3$. Fragments of the calculated titration curve related to the nearest vicinity of equivalence point are depicted in Fig. 7 for two different pK_{so} values for CuI and other data found in the literature.

Example C5. V_0=10 ml of the solution containing KIO_3 (0.05 mol l^{-1}), KI (C_I=0.1 mol l^{-1}) and H_2SO_4 (0.01 mol l^{-1}) is titrated with $Na_2S_2O_3$ (0.1 mol l^{-1}). The calculated titration curve depicted in Fig. 8 provide a statement (rather unexpected, at first sight) that $Na_2S_2O_3$ acts there as strong base; this reaction, known *e.g.* in qualitative analysis, can be expressed by the equation (see Fig. 9)

$$IO_3^- + 6S_2O_3^{2-} + 3H_2O = I^- + 3S_4O_6^{2-} + 6OH^-$$

Both E (Fig. 10) and pH can be chosen as the quantity measured during the titration.

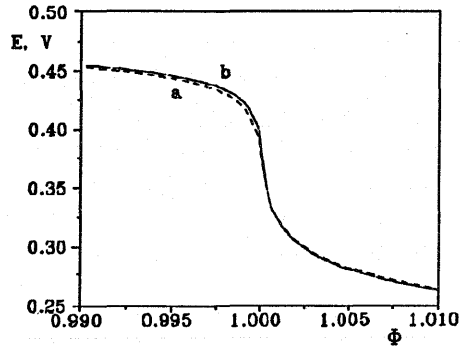

Figure 7. Fragments of theoretical titration curves related to addition of 0.1 mol l^{-1} $Na_2S_2O_3$ as titrant to V_0=30.8 ml of solution composed of 25 ml of $CuSO_4$ (0.01 mol l^{-1}), NH_3 (0.25 mol l^{-1}), CH_3COOH (0.75 mol l^{-1}) and 5.8 ml of 2.0 mol l^{-1} KI found for pK_{so}: 11.96 (curve a) and 12.6 (curve b)

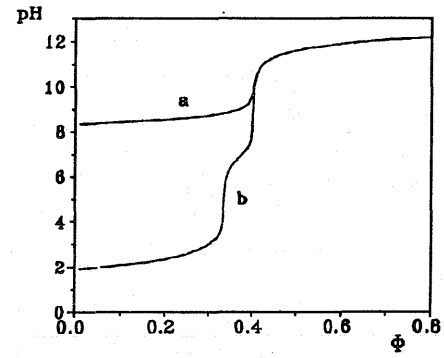

Figure 8. The curves of pH *vs.* ϕ relationships plotted for C_I=0.1 (curve a) and C_I=0 (curve b)

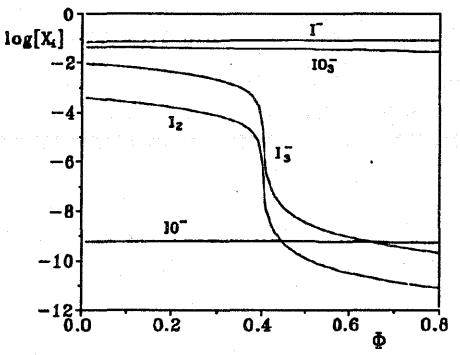

Figure 9. The log[X_i] *vs.* ϕ relationships for different iodide species X_i

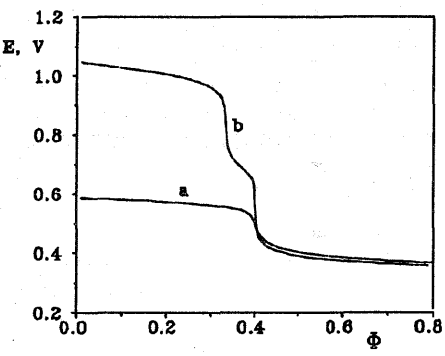

Figure 10. The curves of *E vs.* ϕ relationships plotted for C_I=0.1 (curve a) and C_I=0 (curve b)

D. Precipitation titration

Example. V_0= 50 ml of C_0=0.04 mol l^{-1} KSCN solution was treated successively with 25 ml of 0.1 mol l^{-1} $AgNO_3$ (an excess), 75 ml of 0.5 mol l^{-1} HNO_3 and 0.003 mol l^{-1} $Fe(NO_3)_3$ (Volhard's method). The excess of silver ions was titrated with V ml of C=0.1 mol l^{-1} NH_4SCN. The systematic error involved with perception of pink color of $FeSCN^{2+}$ depends linearly on its concentration in the close vicinity of equivalence point.

Remarks on equivalent mass

The equivalent mass concept was abolished by ISO, although it is of pivotal importance in titrimetric analysis. Its obligatory formulation is not generally acceptable because it does not provide any quantitive data involving an influence of

complexing agents, choice of indicator, a dilution effect, *etc.* Moreover, the prior knowledge of products formed in the reaction is required there. Such information is obtainable from equilibrium analysis applied to defined titrand–titrant system; one should note, however, that kinetics is not involved there, see *e.g.* ref. [12].

The malevolent attitude towards this concept has been strengthened recently [25]. It was stated there, neither more nor less, that the equivalence mass concept is adaptable only for acid–base and redox titrations. This unfounded statement may evoke a surprise, especially when considered in aspect of the unified equivalent mass concept.

The unified, unconventional definition (UD) of equivalent mass retains its validity regardless of the kind of processes that occur during titration; its superiority over definition recommended (RD) by IUPAC is inherent in several aspects.

a) Stoichiometry. RD is founded on stoichiometric notation of the main reaction during titration. In reality, the main reaction is usually accompanied by side reactions; *e.g.*, $Hg^{2+} + Cl^- = HgCl^+$ is the most important side reaction in relation to the main reaction $Hg^{2+} + 2Cl^- = HgCl_2$ at the vicinity of equivalence point [17]. In UD, none of the reactions is favoured in this respect.

In some systems, one kind of product predominates distinctly over residual ones at equivalence point(s); this circumstance is not obligatory, however. An example is the system where KBr (0.1 mol l^{-1}) acidified with H_2SO_4 (0.5 mol l^{-1}) is titrated with 0.1 mol l^{-1} $KMnO_4$. Four species: Br_2, HBrO, $HBrO_3$ and BrO_3^- are formed in comparable quantities there (Fig. 11); nevertheless, the resulting reaction is stoichiometric and inflection point on the related titration curve (Fig. 12) coincides with the stoichiometric point.

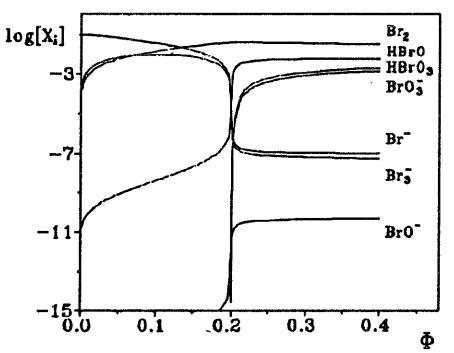

Figure 11. The log[X_i] *vs.* ϕ relationships for different bromine species X_i in the (Br^- + MnO_4^-) system

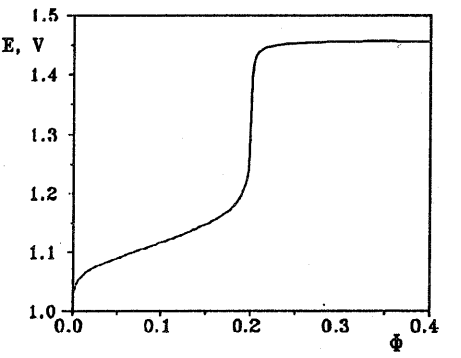

Figure 12. The *E vs.* ϕ relationship for the (Br^- + MnO_4^-) system

Stoichiometry of a reaction sometimes varies during titration [13]. An example is the system where KI (0.1 mol l^{-1}) is titrated with chlorine water (Cl_2, 0.5 mol l^{-1}), see Fig. 14. At first stage, the main reactions proceeding there are:

$$3I^- + Cl_2 = I_3^- + 2Cl^-$$

$$2I^- + Cl_2 = I_{2(s)} + 2Cl^- \qquad (s - solid)$$

$$2I^- + Cl_2 = I_2 + 2Cl^-$$

An excess of Cl_2 added oxidizes the iodine species into HIO_3 or IO_3^-, *e.g.*

$$I_3^- + 8Cl_2 + 9H_2O = 3HIO_3 + 16Cl^- + 15H^+$$

The related titration curves are presented in Fig. 14.

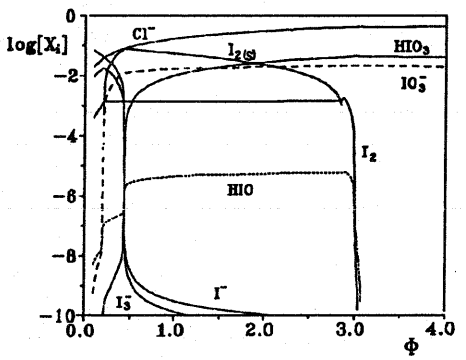

Figure 13. The $\log[X_i]$ *vs.* ϕ relationships for different species X_i related to the system where V_0 = 10 ml of 0.1 mol l^{-1} KI is titrated with 0.5 mol l^{-1} Cl_2

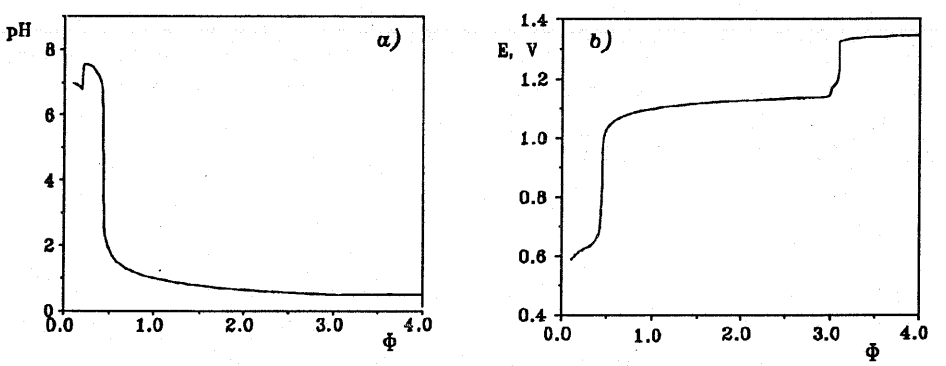

Figure 14. (a) pH *vs.* ϕ (b) *E vs.* ϕ and relationships for the (KI + Cl_2) system

b) Systematic error. In contrary to RD, UD enables the best *a priori* conditions of analysis to be chosen. Although the equivalent mass is a redundant term only, its applicability is indispensable for correct calculation of mass m'_B of a species B determined. For example, mass m'_B of iodate (B = IO_3^-) titrated with ascorbic acid in the titrand–titrant system described in [14] can be found from the formula

$$m'_B = 10^{-3} C V_e \times \frac{M_B}{2.5} \qquad (16)$$

at first inflection point, ϕ_{eq}=5/2, or

$$m'_B = 10^{-3} C V_e \times \frac{M_B}{3} \tag{17}$$

at second inflection point if $HgCl_2$ does not enter the titrand composition, $C_{Hg} = 0$, $\phi_{eq} = 3$. If a due excess of $HgCl_2$ is present there, eq. (17) is valid (Fig. 15).

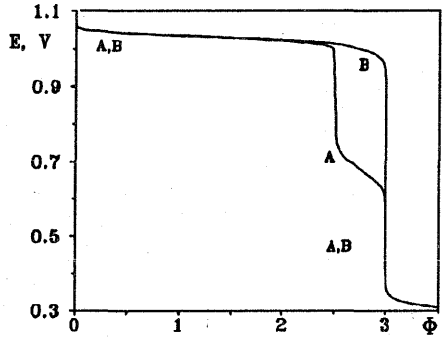

Figure 15. The *E vs.* ϕ relationships for (IO_3^- + ascorbic acid) system at the data quoted in [10]; C_{Hg}=0 for curve A, C_{Hg}= 0.07 mol l^{-1} for curve B

c) Indicator. An influence of the indicator (kind and concentration) on accuracy of determination can be taken into account in UD. Particularly, concentration of sodium nitroprusside affecting the systematic error of mercurimetric titration of chloride [17] or concentration of K_2CrO_4 affecting an error of determination of chloride in Mohr's method [16] were considered. An influence of concentrations: C_I (Erio T) and C_N (ammonia buffer) on ϕ value within color change of the indicator is given in Figs. 2 and 3. At pH≈9.8

$$[HI] \gg [H_3I] + [H_2I] + [I]$$

and only the colour due to HI (blue) is visible after crossing the equivalence point; before the equivalence point, the red color due to complexes ZnI and ZnI_2 is observed. The solution becomes violet (red + blue) at the nearest vicinity of equivalence point provided that ammonia concentration is not too high. At higher concentrations of ammonia, the mixed colour of the solution is assumed from the very beginning of the titration (Fig. 2).

d) pH of the solution affects the direction of a reaction. The well-known example is the (H_3AsO_4 + KI) system where the reaction involved with formation of $I_{2(s)}$, I_3^- and I_2 takes place, *e.g.*

$$H_3AsO_4 + 2I^- + 2H^+ = H_3AsO_3 + I_{2(s)} + H_2O$$

(see Fig. 1b). Concentrations of the arsenate species (mainly H_3AsO_4) depend on H_2SO_4 concentration (Fig. 17). No inflection points on the related titration curves are observed (Fig. 18).

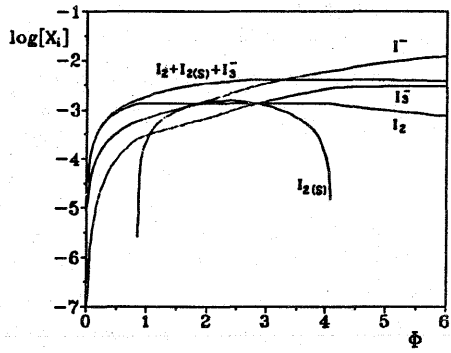

Figure 16. Changes in concentration of the main iodine species: I^-, $I_{2(s)}$, I_3^-, I_2 during addition of 0.1 mol l^{-1} KI into 100 ml of 0.005 mol l^{-1} H_3AsO_4 acidified with H_2SO_4 (10 mol l^{-1})

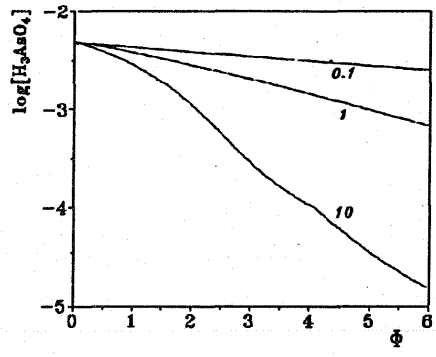

Figure 17. Changes in concentration of H_3AsO_4 at different molar concentrations of H_2SO_4 indicated at the corresponding curves; the curves are plotted for the data specified at Fig. 16

Referring to example C4 we state that CuI and iodine(0) species are not formed with 100% efficiencies at the stage of addition of KI solution (Fig. 19). Formation of these components tends to be completed during the titration, see Fig. 7.

The equilibrium analysis enables optimal *a priori* conditions of titrimetric analysis to be reached, as well; *e.g.* concentration of a proper indicator can be found this way [16,17]. Analytical procedures can be reconstructed and amounts of reagents added in quantitative analysis are defined.

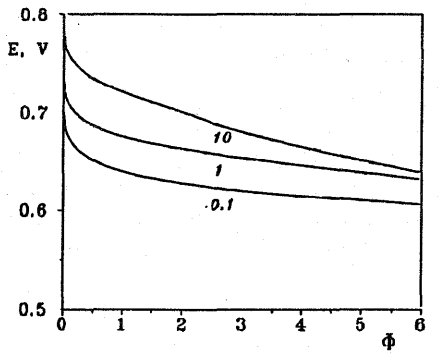

Figure 18. The *E vs.* ϕ relationships plotted for different concentrations of H_2SO_4 (indicated at the corresponding curves) and other data specified at Fig. 16

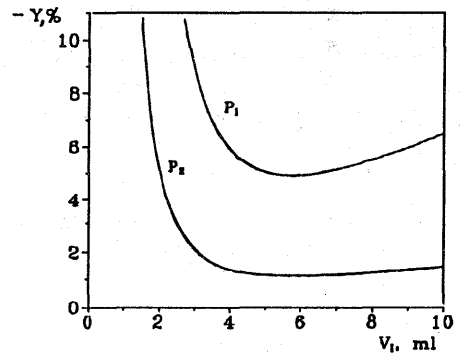

Figure 19. The relationships between negative errors (-*Y*, %) of iodometric determination of Cu^{+2} and volume V_I of KI added; $Y = (m'_B/m_B - 1)\times 100\%$ for B = Cu^{2+} : P_1 – curve found for pK_{so}= 11.96; P_2 – curve found for pK_{so}= 12.6; further data are given in Fig. 7

The UD thus formulated provides the chemists-analysts a precisely defined quantity; it is not an alternative but solely correct definition providing the possibility to choose *a priori* the best conditions for determination, in multicomponent titrand, as well. A deep inspection in the system tested which enables the theory of a process

to be known exhaustively is another, very important aspect of the matter. The controversial equivalent mass definition recommended by IUPAC is really unpleadable and untenable in juxtaposition with the definition based on balances related to a system although the reluctance to implement changes is great, until now.

Oscillating reactions

The subject of oscillating reactions proceeding in aqueous solutions (monophase systems) has been extensively exploited, particularly within the last two decades. The Belousov–Zhabotinsky (BZ) and the Bray–Liebhafsky (BL) systems, where temporal oscillations take place in continuously stirred batch reactors, are well-known examples there [26,27] (the oscillation reactions proceed also in continuous flow systems where electrolyte solutions are pumped to the cell at a constant rate); their oscillating behaviour is not sufficiently known till now, however. The assumption of a perfect, vigorous stirring (with a stirrer or inert gas) under isothermal conditions enables the transport (diffusion) phenomena to be omitted in mathematical description of the process in question. One of the BZ oscillating systems is based on oxidation of organic components containing active methylene ($-CH_2-$) group (*e.g.* malonic or citric acid) with BrO_3^- ions, in presence of *e.g.* cerium Ce^{4+}/Ce^{3+} catalyzing pair.

To elucidate the kinetics of oscillation, exhibited by changes in potential and/or absorbance of the system, some mathematical models were applied. For example, the model known as Oregonator [28,29] was usually applied for description of BZ reaction in homogeneous, perfectly mixed batch systems. Although a number of papers appear each year in chemical periodicals, an expected turning-point in generalizing approach has not set in, however [26].

The oscillating reactions can proceed at constant volume and constant analytical concentrations of all components existing in the solution. It enables the related balances involved in the system to be applied.

All oscillating reactions known hitherto are based on electron-transfer phenomena. As a particular case, a system containing a constant, defined number of reagents mixed together is considered. In this case, the expressions for γ_i assume constant values. Thus $r = 2 + z$ balances [eq.(4)] and their time (t) derivatives, written in general form

$$\sum_{j=1}^{p_i'} \alpha_{ij} \times d[X_j]/dt = 0 \tag{18}$$

(where $p_i' \leq p$) are valid. Equations (4) and (18) form a set of $2r = 2(2 + z)$ linearly independent equations, completed by linearly independent relations between some concentrations; a due set of parameters, of both thermodynamic (*e.g.* standard potentials, stability constants of complexes) and kinetic (rate constants) nature, are involved in there. Equations (4) and (18) are then considered as (independent of time) constraints put on concentrations and rates of reactions in the system.

The time-derivatives in eq.(18) can be expressed as follows

$$d[X_j]/dt = \sum_u k_{ju} f_u(\mathbf{X}) - \sum_v k_{jv} f_v(\mathbf{X}) \tag{19}$$

where k_{jw} – rate constants, $w = u,v$, $k_{jw} \geq 0$, $f_u(\mathbf{X})$, $f_v(\mathbf{X})$ – functions involving rationally selected concentrations $[X_l]$, $l \in <1,p>$. Some species entering the balances (4), *e.g.* Na^+ ions introduced by sodium bromate in BZ system, do not participate in the oscillation reactions and their concentration remains unchanged, *i.e.* $d[Na^+]/dt = 0$.

The set of independent variables should be then formulated. For example, bromine species can be expressed by relations involving concentration of bromide ions, E and pH, obtained according to mass action law. The choice of independent variables is conditioned by appropriate measuring devices applied; *e.g.* $[Br^-]$ is measured with ion-selective bromide electrode, potential E – with platinum electrode, pH – with glass electrode, all inserted (together with a reference electrode in perfectly mixed measuring cell – reactor).

Concentrations of some components cannot be directly measured with a specific electrode. In such instances, other analytical techniques must be put in work; *e.g.* Ce(IV) species absorb light and this property can be exploited for analytical purposes. Absorbance A, measured at the wavelength λ, can be expressed by equation

$$A = \sum_{j=1}^{p''} \omega_j [X_j] \tag{20}$$

where p'' ($p'' \leq p$) is the number of species absorbing light at the wavelength λ, ω_j – coefficients defined *e.g.* as products of molar absorptivities (ε_j) and length of the light path (l) in a cuvette, $\omega_j = \varepsilon_j l$. It enables any system of this kind to be resolved.

As results from the sketchy approach presented above, the kinetic balances can be easily derived from the related balances [eq. (4)] involving concentrations of the components considered. Among others, all primary, intermediate and final components of organic substance (*e.g.* malonic acid) can be involved there, also as complexes with other ions.

The measuring cell applied for the determination of thermodynamic (equilibrium constants) and kinetic (rate constants) parameters involved in eqs.(4), (18)–(20) should provide the possibility of simultaneous measurement of different variables *in situ*, at defined moments of time; its construction is then much more advanced than one considered *e.g.* in ref. [30]. The parameters considered can be found through iterative manner, *i.e.* through fitting the above equations to experimental data registered at defined points (moments) $t = t_n$, $n = 1,...,N$; N must exceed the number of the parameters defined this way. A great number of possible models can be then limited to the best one(s). Resolution of the equations and discrimination of the model provides the temporal (t) relationships, $y_i = y_i(t)$, namely:

$$[X_j] = f_j(t) \tag{21}$$

$$E = E(t) \tag{22}$$

$$A = A(t) \tag{23}$$

The relationships $y_i=y_i(t)$ can be presented graphically on the plane, $y_i = y(y_j)$, or in three-dimensional phase space $y_i = y(y_j,y_k)$; y_i values related to concentrations can be presented in logarithmic scale. It enables the periodic or chaotic nature of oscillations to be elucidated [6,27,31,32].

The rudimentary formulation of balances (4), (18) requires, among others, a deep knowledge of intermediate species formed during gradual oxidation of organic substance (*e.g.* malonic acid) into CO_2 and H_2O. On the other hand, there is a great number of potential possibilities in formulation of the equations for $f_w(\mathbf{X})$ in eq.(19) if intuition and experience is employed. The experience is also needed to distinguish between the processes of thermodynamic nature (*i.e.* proceeding instantly, where only equilibrium constants are involved) and ones of kinetic nature (where rate constants are also applied). The approach suggested enables the kinetic equation for any of the components in the system to be formulated.

Some limitations are caused by nature of the species formed. Particularly, a limited solubility of CO_2 in BZ or O_2 in BL [31] has to be taken into account.

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