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***Corresponding author:** Tadeusz Michałowski, Department of Analytical Chemistry, Technical University of Cracow, Cracow, Poland, E-mail: michalot@o2.pl

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Review Article

Dynamic buffer capacity versus alkalinity. Formulation in terms of Simms constants idea

Anna Maria Michałowska-Kaczmarczyk¹ and Tadeusz Michałowski^{2*}

¹Department of Oncology, The University Hospital in Cracow, Cracow, Poland

²Department of Analytical Chemistry, Technical University of Cracow, Cracow, Poland

Abstract

The Simms constants (g_i) concept is put in context with equations for some acid-base titration curves, formulated for D+T systems, with titrand D and titrant T prepared according to normal and isomolar mode. The relationships between g_i and successive dissociation constants (K_i) values for polyprotic acids are formulated. The mathematical formulation of dynamic buffer capacity concept is presented in general and elegant form, involving all soluble species formed in the system where only acid-base reactions are involved. The Simms constants are identified with protonation micro-constants related to specific basicity centers.

Abbreviations

C: Concentration [mol/L] of HB in T, D – titrand (solutions titrated), $\Delta = C_b - C_a$, g_i – Simms constant, $g_i^* = \gamma \cdot g_i$ – hybrid Simms constant, γ – activity coefficient of H^{+1} ions, $h = \gamma \cdot [H]$ – activity of H^{+1} ions, HB – strong acid, MOH – strong base, ST – sample tested as: s-ST = simple sample tested or c-ST = complex sample tested; T – titrant, V – volume [mL] of T, V_0 – volume [mL] of D, $W = V_0 + V$, $[X_i]$ – concentration [mol/L] of the species $X_i^{Z_i}$.

Introduction

The term ‘Simms constants’ is an eponym for virtual equilibrium constants (g_i) suggested by Simms [1,2] and presented elsewhere only as an alternative mathematical formalism applied to simple static acid-base systems. The Simms constants idea was extended [3,4], on modeling of acid-base titration realized according to isomolar mode [5-11]. Its further extension concerned the systems where total

alkalinity (TAL) was modelled [12,13], also in the systems with fulvic acids [14]. This idea can be extended on biological systems, such as the lymphatic system in living organisms. All the new possibilities offered by Simms constants idea were suggested by Michałowski [15].

The Simms constants idea resembles the mathematical problem known from integral calculus as partial fraction decomposition [16], related to some rational functions $R(x) = f(x)/g(x)$, where: a. the numerator $f(x)$ and the denominator $g(x)$ are both polynomials of variable x ; b. the degree of $f(x)$ is smaller than that of the $g(x)$; c. $g(x)$ is irreducible polynomial [17], i.e., it cannot be expressed as the product of two polynomials.

Application of the Simms constants g_i enables any q -protic acid H_nL (C_0 mol/L), characterized by successive dissociation constants K_i values, to be considered as a mixture of q monoprotic acids $HL_{(i)}$ ($i=1, \dots, q$) of the same concentration, i.e. C_0 mol/L; the g_i are ascribed to these acids as (virtual) dissociation



constants values. The relations between g_i and K_i values were formulated [14].

This idea will be presented below starting from equations for acid-base titration curves. In a titration $T(V) \rightleftharpoons D(V_0)$, V_0 mL of titrand (D) is titrated with V mL of titrant (T) and V_0+V mL of D+T mixture is obtained, if the additivity of V_0 and V is assumed. We apply here the abbreviated notation, where charges z_i of i -th species $X_i^{(z_i)}$ be omitted when written in terms of molar concentration, $[X_i]$.

Titration in normal and isomolar D+T systems will be formulated. In the normal mode, a sample tested (ST) as titrand D is titrated with HB (C) solution as titrant T. In isomolar systems, ST is a component of D and T, prepared as presented in Table 1. Simple (s-) and complex (c-) acid-base systems are considered herein.

Titration in simple D+T systems

The principle of the Simms constants formulation will be illustrated first for the $M_kH_{n-k}L$ (C_0) + HB (C_a) + MOH (C_b) mixture, considered here as the simple sample tested (s-ST) in the systems I and II.

Simple D+T system (I) – normal mode

Let V_0 mL of the s-ST, considered here as D, be titrated with V mL of a strong acid HB (C) as T. The charge and concentration balances are as follows :

$$\alpha + [M] - [B] + \sum_{i=1}^q (i-n)[H_iL] = 0 \quad (1)$$

$$[M] = (kC_0 + C_b)V_0/W, \quad [B] = (C_aV_0 + CV)/W, \quad \sum_{i=1}^q [H_iL] = C_0V_0/W \quad (2)$$

where: $W = V_0+V$ is the current volume of the D+T mixture,

$$\alpha = [H] - [OH] = [H] - K_w/[H] = h/\gamma - K_w \cdot \gamma/h \quad (3)$$

$$h = \gamma \cdot [H], \quad ph = -\log h \quad (4)$$

h is the activity and γ – the activity coefficient of H^{+1} ions with concentration [mol/L] denoted as $[H]$. Let

$$\bar{n}(q) = \frac{\sum_{i=1}^q i \cdot [H_iL]}{\sum_{i=0}^q [H_iL]} = \frac{\sum_{i=1}^q i \cdot K_i^H [H]^i}{\sum_{i=0}^q K_i^H [H]^i} \quad (5)$$

be the mean number of protons attached to the basic form L^{-n} , and

$$K_i^H = \frac{[H_iL]}{[H]^i [L]} \text{ for } iH^{+1} + L^{-n} = H_iL^{+i-n}$$

$$(i = 1, \dots, q); \quad q = \max\{i\}; \quad K_0^H \equiv 1$$

The K_j^H are interrelated with the dissociation constants K_j ($j = 1, \dots, q$) values

$$K_j = \frac{[H][H_{q-j}L]}{[H_{q-j+1}L]} \text{ for } H_{q-j+1}L^{+q-j-n} = H_{q-j}L^{+q-j-1-n} + H^{+1}$$

in the relationships

$$K_i^H = \frac{1}{\prod_{j=q-i+1}^q K_j} \quad (i = 1, \dots, q)$$

From Equations 1, 2 and 5 we have, by turns,

$$\sum_{i=1}^q i[H_iL] = \bar{n}^{(q)} \cdot C_0V_0/W$$

$$\alpha + (kC_0 + C_b)V_0/W - (C_aV_0 + CV)/W +$$

$$(n - \bar{n}^{(q)})C_0V_0/W = 0$$

$$CV/W = \alpha + ((\bar{n}^{(q)} + k - n)C_0 + \Delta)V_0/W \quad (6)$$

where $\Delta = C_b - C_a$. We apply the identity

$$\bar{n}^{(q)} + k - n \equiv (q - n + k) - (q - \bar{n}^{(q)}) \quad (7)$$

and notations:

$$A = (q - n + k) \cdot C_0 + \Delta \quad (8)$$

$$G^{(q)} = q - \bar{n}^{(q)} = \frac{\sum_{i=1}^q (q-i) \cdot [H_iL]}{\sum_{i=0}^q [H_iL]} \\ = \sum_{i=1}^q \frac{g_i}{[H] + g_i} = \sum_{i=1}^q \frac{g_i^*}{h + g_i^*} \quad (9)$$

where the Simms constants (g_i) and hybrid Simms constants (g_i^*) [3]

$$g_i^* = \gamma \cdot g_i, \quad pg_i^* = -\log g_i^* \quad (i = 1, \dots, q) \quad (10)$$

are involved (see notation in Eq. 4). The A value (Eq. 8) is termed as alkalinity, perceived here as a simple case of total alkalinity, TAL [12-15]. Then from Eq. 6 we get, by turns,

$$CV/V_0 = A + \alpha \cdot (1 + V/V_0) - G^{(q)} \cdot C_0$$

$$(C - \alpha) \cdot V/V_0 = A - G^{(q)} \cdot C_0 + \alpha$$

$$V = V_0 \cdot \frac{A - G^{(q)} \cdot C_0 + \alpha}{C - \alpha}, \quad W = V_0 \cdot \frac{A - G^{(q)} \cdot C_0 + C}{C - \alpha}$$



Current concentration of HB from T in D+T mixture is [18-20]

$$c = C \cdot \frac{V}{W} = C \cdot \frac{A - G^{(q)} \cdot C_0 + \alpha}{A - G^{(q)} \cdot C_0 + C}$$

$$= C \cdot \left(\frac{A - G^{(q)} \cdot C_0 + C - (C - \alpha)}{A - G^{(q)} \cdot C_0 + C} \right) = C \cdot \left(1 - \frac{C - \alpha}{A + C - G^{(q)} \cdot C_0} \right) \quad (11)$$

Simple D+T system (II) – isomolar mode

The condition for (approximately) constant ionic strength is fulfilled in isomolar D+T system [3,4], where D and T are prepared in identical flasks (V_f mL) according to the scheme illustrated in Table 1. The isomolarity condition for the D+T mixture during the pH titration is expressed by relation

$$C_1 V_{MB} = C_1 V_{MB}^* + C V_B \quad (12)$$

for the D+T system with HB (C) in T. From ionic strength viewpoint, the presence of HB (C) in T is compensated by a surplus $V_{MB} - V_{MB}^* = C V_B / C_1$ of MB (C_1) in the second flask, where D is prepared. Both flasks are filled up to the marks (V_f) with water. It is assumed that $C_1 V_{MB} \gg C V_B$; then the isomolarity condition ensures also constancy of dielectric permittivity and improves the additivity of volumes V_0 and V .

In the system II, the charge balance (Eq. 1) and the relations:

$$\sum_{i=1}^q [H_i L] = d \cdot C_0 \quad (13)$$

$$\sum_{i=1}^q i [H_i L] = \bar{n}^{(q)} \cdot d \cdot C_0 \quad (14)$$

are valid, where $d = \frac{V_{ST}}{V_f}$. From Equations 1, 12 – 14 we have

$$\alpha + [M] - [B] + (\bar{n}^{(q)} - n) \cdot d \cdot C_0 = 0 \quad (15)$$

where:

$$[M] = d \cdot (k \cdot C_0 + C_b) + \frac{C_1 V_{MB}}{V_f} - \frac{C V_B}{V_f} \cdot \frac{V}{W};$$

$$[B] = d \cdot C_a + \frac{C_1 V_{MB}}{V_f} \quad (16)$$

Table 1: Composition of titrand (D) and titrant (T) for an isomolar D+T system (II, IV); ST-sample tested (as s-ST or c-ST); HB-strong acid; MOH-strong base; $d = V_{ST}/V_f$.

Component	D	T
ST	V_{ST}	V_{ST}
HB (C)	–	V_B
MB (C_1)	V_{MB}	V_{MB}^*
H ₂ O	$V_f - V_{ST} - V_{MB}$	$V_f - V_{ST} - V_B - V_{MB}^*$

Putting Equations 7 and 16 in Eq. 15 gives

$$\alpha + d \cdot (k \cdot C_0 + C_b) - \frac{C V_B}{V_f} \cdot \frac{V}{W} - d \cdot C_a +$$

$$(\bar{n}^{(q)} - n) \cdot d \cdot C_0 = 0 \quad \Leftrightarrow$$

$$\frac{C V_B}{V_f} \cdot \frac{V}{W} = ((q - n + k) \cdot C_0 + \Delta) \cdot d + \alpha -$$

$$(q - \bar{n}^{(q)}) \cdot d \cdot C_0 \quad \Leftrightarrow$$

$$c = \frac{C V_B}{V_f} \cdot \frac{V}{W} = d \cdot A + \alpha - d \cdot G^{(q)} \cdot C_0 \quad (17)$$

where A is expressed by Eq. 8. Note that $C V_B / V_f = C_B$ is the concentration of HB in T, prepared as indicated in Table 1, i.e. $c = C_B V / W$ is the current concentration of HB from T in the D+T mixture (compare with a remark at Eq. 11).

Titrations in complex D+T systems

In further parts of the paper, we consider a mixture

$K_{m_k} H_{n_k - m_k} L_{(k)} (C_{0k}; m_k = 0, \dots, n_k; k = 1, \dots, P) + H_{n_k + m_k} L_{(k)} B_{m_k} (C_{0k}; m_k = 0, \dots, q_k - n_k; k = P+1, \dots, Q) + HB (C_a) + MOH (C_b)$ as the complex sample tested (c-ST).

Complex D+T system (III) – normal mode

V_0 mL of the c-ST as D is titrated with V mL of HB (C) as T. We have the balances:

$$\alpha + [K] + [M] - [B] + \sum_{k=1}^Q \sum_{j=0}^{q_k} (j - n_k) [H_j L_{(k)}] = 0 \quad (18)$$

$$\sum_{j=0}^{q_k} [H_j L_{(k)}] = C_{0k} \cdot \frac{V_0}{W}$$

$$[K] = \sum_{k=1}^P m_k C_{0k} \cdot \frac{V_0}{W};$$

$$[M] = C_b \cdot \frac{V_0}{W};$$

$$[B] = (\sum_{k=P+1}^Q m_k C_{0k} + C_a) \cdot \frac{V_0}{W} + C \cdot \frac{V}{W} \quad (19)$$



Applying Equations 19 and

$$\sum_{j=0}^{q_k} j \cdot [H_j L_{(k)}] = \bar{n}_k^{(q_k)} \cdot C_{0k} \cdot \frac{V_0}{W}$$

$$(k = 1, \dots, P, P+1, \dots, Q) \tag{20}$$

we rewrite Eq. 18 as follows:

$$\alpha + \sum_{k=1}^P m_k C_{0k} \cdot \frac{V_0}{W} + C_b \cdot \frac{V_0}{W} - (\sum_{k=P+1}^Q m_k C_{0k} + C_a) \cdot \frac{V_0}{W}$$

$$- C \cdot \frac{V}{W} + \sum_{k=1}^P \sum_{j=0}^{q_k} (j - n_k) [H_j L_{(k)}] + \sum_{k=P+1}^Q \sum_{j=0}^{q_k} (j - n_k) [H_j L_{(k)}] = 0 \Rightarrow$$

$$\alpha + \sum_{k=1}^P m_k C_{0k} \cdot \frac{V_0}{W} + C_b \cdot \frac{V_0}{W} - (\sum_{k=P+1}^Q m_k C_{0k} + C_a) \cdot \frac{V_0}{W}$$

$$- C \cdot \frac{V}{W} + \sum_{k=1}^P (\bar{n}_k^{(q_k)} - n_k) C_{0k} \cdot \frac{V_0}{W}$$

$$+ \sum_{k=P+1}^Q (\bar{n}_k^{(q_k)} - n_k) C_{0k} \cdot \frac{V_0}{W} = 0 \Rightarrow$$

$$\alpha + \Delta \cdot \frac{V_0}{W} - C \cdot \frac{V}{W} + \sum_{k=1}^P (\bar{n}_k^{(q_k)} + m_k - n_k) C_{0k} \cdot \frac{V_0}{W}$$

$$+ \sum_{k=P+1}^Q (\bar{n}_k^{(q_k)} - m_k - n_k) C_{0k} \cdot \frac{V_0}{W} = 0 \tag{21}$$

Applying the identities:

$$\bar{n}_k^{(q_k)} + m_k - n_k \equiv (q_k + m_k - n_k) - (q_k - \bar{n}_k^{(q_k)})$$

$$\bar{n}_k^{(q_k)} - m_k - n_k \equiv (q_k - m_k - n_k) - (q_k - \bar{n}_k^{(q_k)})$$

from Eq. 21 we have, by turns,

$$\alpha + \Delta \cdot \frac{V_0}{W} - C \cdot \frac{V}{W} +$$

$$+ \sum_{k=1}^P (q_k + m_k - n_k) C_{0k} \cdot \frac{V_0}{W}$$

$$- \sum_{k=1}^P (q_k - \bar{n}_k^{(q_k)}) C_{0k} \cdot \frac{V_0}{W} +$$

$$\sum_{k=P+1}^Q (q_k - m_k - n_k) C_{0k} \cdot \frac{V_0}{W}$$

$$- \sum_{k=P+1}^Q (q_k - \bar{n}_k^{(q_k)}) C_{0k} \cdot \frac{V_0}{W} = 0 \Rightarrow$$

$$C \cdot \frac{V}{W} = A \cdot \frac{V_0}{W} + \alpha - \sum_{k=1}^P G^{(q_k)} \cdot C_{0k} \cdot \frac{V_0}{W} = 0 \quad / \cdot \frac{W}{V_0} \Rightarrow \tag{22}$$

$$C \cdot \frac{V}{V_0} = A + \left(1 + \frac{V}{V_0}\right) \cdot \alpha - \sum_{k=1}^P G^{(q_k)} \cdot C_{0k} = 0 \Rightarrow \tag{23}$$

where

$$G^{(q_k)} = q_k - \bar{n}_k^{(q_k)} = \sum_{i=1}^{q_k} \frac{g_{ki}}{[H] + g_{ki}} = \sum_{i=1}^{q_k} \frac{g_{ki}^*}{h + g_{ki}^*} \tag{24}$$

and alkalinity A is expressed as follows

$$A = \sum_{k=1}^P (q_k + m_k - n_k) \cdot C_{0k} + \sum_{k=1}^Q (q_k - m_k - n_k) \cdot C_{0k} + \Delta \tag{25}$$

The g_{ki} and g_{ki}^* in Eq. 24 denote i-th Simms constant and hybrid Simms constant related to k-th component. From Eq. 23 we get, by turns,

$$(C - \alpha) \cdot \frac{V}{V_0} = A - \sum_{k=1}^Q G^{(q_k)} \cdot C_{0k} + \alpha$$

$$\frac{V}{V_0} = \frac{A - \sum_{k=1}^Q \sum_{i=1}^{q_k} G^{(q_k)} \cdot C_{0k} + \alpha}{C - \alpha} \Rightarrow$$

$$\frac{W}{V_0} = \frac{A - \sum_{k=1}^Q G^{(q_k)} \cdot C_{0k} + C}{C - \alpha}$$

Current concentration of HB from T in D+T mixture, is

$$c = C \cdot \frac{V}{W} = C \cdot \frac{A - \sum_{k=1}^Q G^{(q_k)} \cdot C_{0k} + \alpha}{A - \sum_{k=1}^Q G^{(q_k)} \cdot C_{0k} + C} \Rightarrow$$

$$c = C \cdot \frac{V}{W} = C \cdot \left(1 - \frac{C - \alpha}{A + C - \sum_{k=1}^Q G^{(q_k)} \cdot C_{0k}}\right) \tag{26}$$

Complex D+T system (IV) - isomolar mode

In the system IV, the charge balance (Eq. 18) and the relations:

$$\sum_{j=0}^{q_k} [H_j L_{(k)}] = d \cdot C_{0k},$$

$$\sum_{j=0}^{q_k} j [H_j L_{(k)}] = \bar{n}_k^{(q_k)} \cdot d \cdot C_{0k} \quad (k = 1, \dots, P, P+1, \dots, Q);$$

$$[K] = \sum_{k=1}^P m_k \cdot d \cdot C_{0k};$$

$$[M] = d \cdot C_b + \frac{C_1 V_{MB}}{V_f} - \frac{C V_B}{V_f} \cdot \frac{V}{W};$$

$$[B] = d \cdot (\sum_{k=P+1}^Q m_k \cdot C_{0k} + C_a) + \frac{C_1 V_{MB}}{V_f} \tag{27}$$

are valid, see Eq. 12. Putting Equations 27 in Eq. 18 gives

$$\alpha + d \cdot \sum_{k=1}^P m_k \cdot C_{0k} + d \cdot C_b - \frac{C V_B}{V_f} \cdot \frac{V}{W} -$$

$$d \cdot (\sum_{k=P+1}^Q m_k \cdot C_{0k} + C_a) +$$

$$d \cdot \sum_{k=1}^Q (\bar{n}_k^{(q_k)} - n_k) \cdot C_{0k} = 0 \Rightarrow$$

$$\alpha + d \cdot \Delta - \frac{C V_B}{V_f} \cdot \frac{V}{W}$$

$$+ d \cdot \sum_{k=1}^P (\bar{n}_k^{(q_k)} - n_k + m_k) \cdot C_{0k} +$$



$$d \cdot \sum_{k=P+1}^Q (\bar{n}_k^{(qk)} - n_k - m_k) \cdot C_{0k} = 0 \Leftrightarrow$$

$$\frac{CV_B}{V_f} \cdot \frac{V}{W} = \alpha + d \cdot \Delta + d \cdot \sum_{k=1}^P (\bar{n}_k^{(qk)} - n_k + m_k) \cdot C_{0k}$$

$$+ d \cdot \sum_{k=P+1}^Q (\bar{n}_k^{(qk)} - n_k - m_k) \cdot C_{0k} \Leftrightarrow$$

$$c = \frac{CV_B}{V_f} \cdot \frac{V}{W} = d \cdot A + \alpha - d \cdot \sum_{k=1}^Q G^{(qk)} \cdot C_{0k} \quad (28)$$

where A is identical with Eq. 25; see also the remark at Eq. 25, as a particular case of Eq. 28.

Dynamic buffer capacity

The c values (Equations 11, 17, 26, 28), expressing current concentration of HB (C) from T in D+T mixture, are the basis to formulate the dynamic buffer capacity

$$\beta_V = \left| \frac{dc}{dph} \right| \quad (29)$$

Recapitulating, for normal mode (systems I and III), we have $c = CV/W$, and for isomolar mode (systems II and IV) we have $c = C_B \cdot \frac{V}{W}$, where $C_B = \frac{CV_B}{V_f}$.

Applying the general relation

$$\frac{dz}{dph} = \frac{dz}{dh} \cdot \frac{dh}{dph} = -\ln 10 \cdot h \cdot \frac{dz}{dh} \quad (30)$$

- to $z = \alpha$ (Eq. 3), we have

$$\frac{d\alpha}{dh} = \frac{1}{\gamma} + K_W \gamma / h^2$$

$$h \cdot \frac{d\alpha}{dh} = \frac{h}{\gamma} + K_W \gamma / h = [H] + [OH]$$

$$\frac{d\alpha}{dph} = -\ln 10 \cdot ([H] + [OH]) \quad (31)$$

- to $z = G^{(q)}$ (Eq. 9), we have

$$h \cdot \frac{dG^{(q)}}{dh} = - \sum_{i=1}^q \frac{h \cdot g_i^*}{(h+g_i^*)^2} = - \sum_{i=1}^q \frac{[H] \cdot g_i}{([H]+g_i)^2} \quad (32)$$

we obtain the formulas for β_V related to particular systems (I) – (IV). Note that $[H] + [OH] = (\alpha^2 + 4K_W)^{1/2}$, $K_W = [H][OH]$, see Equations 3 and 31.

The β_V for the system (I)

From Eq. 11 we obtain

$$h \cdot \frac{dc}{dh} = C \cdot \frac{h \cdot \frac{d\alpha}{dh} (A + C - G^{(q)} \cdot C_0) - (C - \alpha) \cdot C_0 \cdot h \cdot \frac{dG^{(q)}}{dh}}{(A + C - C_0 \cdot G^{(q)})^2} \Leftrightarrow$$

$$\beta_V = \left| \frac{dc}{dph} \right| = \ln 10 \cdot C \cdot \frac{([H] + [OH]) \cdot (A + C - C_0 \cdot \sum_{i=1}^q \frac{g_i}{[H]+g_i}) + (C - \alpha) \cdot C_0 \cdot \sum_{i=1}^q \frac{[H] \cdot g_i}{([H]+g_i)^2}}{(A + C - C_0 \cdot \sum_{i=1}^q \frac{g_i}{[H]+g_i})^2} \quad (33)$$

As we see, the β_V is expressed in terms of [H] and g_i .

The β_V for the system (III)

From Eq. 26 we have

$$\beta_V = \left| \frac{dc}{dph} \right| = \ln 10 \cdot C \cdot \frac{([H] + [OH]) \cdot (A + C - \sum_{k=1}^Q \sum_{i=1}^{qk} \frac{g_{ki}}{[H]+g_{ki}} \cdot C_{0k}) + (C - \alpha) \cdot \sum_{i=1}^q \frac{[H] \cdot g_{ki}}{([H]+g_{ki})^2} \cdot C_{0k}}{(A + C - \sum_{k=1}^Q \sum_{i=1}^{qk} \frac{g_{ki}}{[H]+g_{ki}} \cdot C_{0k})^2} \quad (34)$$

The β_V for the system (II)

From Eq. 17 we have

$$h \cdot \frac{dc}{dh} = h \cdot \frac{d\alpha}{dh} - d \cdot h \cdot \frac{dG^{(q)}}{dh} \cdot C_0$$

$$\beta_V = \left| \frac{dc}{dph} \right| = \ln 10 \cdot \left(([H] + [OH]) + d \cdot C_0 \cdot \sum_{i=1}^q \frac{[H] \cdot g_i}{([H]+g_i)^2} \right) \quad (35)$$

The β_V for the system (IV)

From Eq. 28 we have

$$\beta_V = \left| \frac{dc}{dph} \right| = \ln 10 \cdot \left(([H] + [OH]) + d \cdot \sum_{k=1}^Q \sum_{i=1}^{qk} \frac{[H] \cdot g_{ki}}{([H]+g_{ki})^2} \cdot C_{0k} \right) \quad (36)$$

From Equations (35) and (36) it results that β_V does not depend on alkalinity A when the titration is realized according to isomolar mode. The β_V depends on A when the titration is performed according to normal mode, see Equations 33 and 34.

Simms constants in a system with hydroxo-complexes

The Simms constants can be also related to the system of hydroxo-complexes, $Me(OH)_i^{+n-i}$ ($i = 1, \dots, p$) formed by hydrolysable cations. Assuming $p=2$, we define



$$\bar{n}^{(2)} = \frac{[\text{MeOH}] + 2[\text{Me}(\text{OH})_2]}{[\text{Me}] + [\text{MeOH}] + [\text{Me}(\text{OH})_2]} \quad (37)$$

Applying the stability constants K_i^{OH} of hydroxo-complexes

$$\text{Me}^{+u} + i\text{OH}^{-1} = \text{Me}(\text{OH})_i^{+u-i} \Leftrightarrow K_i^{\text{OH}} = \frac{[\text{Me}(\text{OH})_i]}{[\text{Me}][\text{OH}]^i} \quad (38)$$

we have, in particular,

$$\bar{n}^{(2)} = \frac{K_1^{\text{OH}}[\text{OH}] + 2K_1^{\text{OH}}[\text{OH}]^2}{1 + K_1^{\text{OH}}[\text{OH}] + K_1^{\text{OH}}[\text{OH}]^2} = \frac{K_1^{\text{OH}}K_W[\text{H}] + 2K_1^{\text{OH}}K_W^2}{[\text{H}]^2 + K_1^{\text{OH}}K_W[\text{H}] + K_1^{\text{OH}}K_W^2} \quad (39)$$

where $K_W = [\text{H}][\text{OH}]$. The right side of Eq. 39 can be presented as the sum of two partial fractions

$$\bar{n}^{(2)} = \frac{g_1}{[\text{H}] + g_1} + \frac{g_2}{[\text{H}] + g_2} = \frac{(g_1 + g_2)[\text{H}] + 2g_1g_2}{[\text{H}]^2 + (g_1 + g_2)[\text{H}] + g_1g_2} \quad (40)$$

Comparing the right sides of Equations 39 and 40, we get

$$g_1 + g_2 = K_1^{\text{OH}}K_W \text{ and } g_1 \cdot g_2 = K_2^{\text{OH}}K_W^2 \quad (41)$$

Comparing the Equations 41 and Equation 9 obtained for $q=2$, we see obvious similarities between $2 - \bar{n}^{(2)}$ for proto-complexes and $\bar{n}^{(2)}$ for hydroxo-complexes ($p=2$). Analogous regularities are valid also for other $p=q$ values.

Calculation of g_i values

The g_i values can be calculated under assumption that K_i^{H} or K_i values are known beforehand. Such calculations can be made with use of the iterative computer program, exemplified in [14] for $q = 4$. In particular, for DCTA = H_4L ($q = 4$) we have [21]: $\log K_1^{\text{H}} = 11.78$, $\log K_2^{\text{H}} = 17.98$, $\log K_3^{\text{H}} = 21.58$, $\log K_4^{\text{H}} = 24.09$, i.e., $\text{p}K_1 = 2.51$, $\text{p}K_2 = 3.60$, $\text{p}K_3 = 6.20$, $\text{p}K_4 = 11.78$, and then we get: $\text{p}g_1 = 2.550589$, $\text{p}g_2 = 3.560505$, $\text{p}g_3 = 6.198906$, $\text{p}g_4 = 11.779999$. As we see, the $\text{p}g_i$ values are not distant from $\text{p}K_i$ values and then $\text{p}K_i$ values can be taken as starting values for $\text{p}g_i$, when calculations are made according to an iterative procedure, e.g. one offered by MATLAB [22]. When the successive $\text{p}K_i$ values are more distant, the $\text{p}g_i$ values are very close to the $\text{p}K_i$ values, $\text{p}g_i \approx \text{p}K_i$. Such a case occurs e.g. for H_2CO_3 ($q = 2$): $\text{p}K_1 = 6.3$, $\text{p}K_2 = 10.1$, where $\text{p}g_1 = 10.099931$, $\text{p}g_2 = 6.300069$. Generally, the differences $|\text{p}K_i - \text{p}g_i|$ are more distinct when the successive $\text{p}K_i$ values for an acid are closer to each other.

Interrelations between K_i and g_i values for a q -protic acid H_nL

Generalizing and applying the summation notations, we get [14]

$$K_1 = \sum_{i=1}^q g_i, K_1 \cdot K_2 = \sum_{i=1}^{q-1} \sum_{j=i+1}^q g_i \cdot g_j,$$

$$K_1 \cdot K_2 \cdot K_3 = \sum_{i=1}^{q-2} \sum_{j=i+1}^{q-1} \sum_{k=j+1}^q g_i \cdot g_j \cdot g_k,$$

$$\dots, K_1 \cdot K_2 \cdot \dots \cdot K_q = g_1 \cdot g_2 \cdot \dots \cdot g_q \quad (42)$$

The expression for $\prod_{i=1}^k K_i$ (Eq, 22), formulated for q -protic acid, is a sum involving

$$\binom{q}{k} = \frac{q!}{k!(q-k)!} \quad (43)$$

components formed from k different g_i values. In combinatorics, the binomial coefficient $\binom{q}{k}$ [23] expresses the number of distinct k -element subsets (combinations) formed from a set containing q different elements [24], as in the Pascal's triangle [25]. For further details see [14,26].

Calculation of alkalinity (A) from equation for titration curve

Example. V_0 mL of NaHCO_3 (C_{01}) + Na_2CO_3 (C_{02}) solution as D is titrated with V mL of HCl (C) as T. The desired form of equation for titration curve is derived as follows:

$$\alpha + (C_{01} + 2C_{02}) \cdot \frac{V_0}{W} - C \cdot \frac{V}{W} = (2 - \bar{n}^{(2)}) \cdot (C_{01} + C_{02})$$

$$C \cdot \frac{V}{W} = (C_{01} + 2C_{02}) \cdot \frac{V_0}{W} + \alpha - (2 - \bar{n}^{(2)}) \cdot (C_{01} + C_{02}) \cdot \frac{V_0}{W}$$

$$C \cdot \frac{V}{V_0} = (C_{01} + 2C_{02}) + (1 + \frac{V}{V_0}) \cdot \alpha - \left(\sum_{k=1}^2 \frac{g_k}{[\text{H}] + g_k} \right) \cdot (C_{01} + C_{02})$$

where $A = C_{01} + 2C_{02}$, see Eq. 23.

Acid-Base Microequilibria as a Stochastic Process

On the basis of formulation with the Simms constants involved one can state that the dissociation of H^{+1} from different protonation sites/centers proceeds independently, and the proton uptake/dissociation from/to these sites (basicity centers) can be perceived as a stochastic process, categorized in terms of a success/failure. The degree of dissociation $\text{HL}_{(i)} = \text{H}^{+1} + \text{L}_{(i)}^{-1}$ from the i -th site is



$$\alpha_i = \alpha_i(\text{pH}) = \frac{1}{10^{\text{p}g_i - \text{pH}} + 1} = \frac{1}{e^{\beta \cdot (\text{p}g_i - \text{pH})} + 1} \quad (44)$$

where $\beta = \ln 10$. The $\alpha_i = \alpha_i(\text{pH})$ fulfills the properties of cumulative distribution function

$$\lim_{\text{pH} \rightarrow -\infty} \alpha_i(\text{pH}) = 0$$

$$\lim_{\text{pH} \rightarrow \infty} \alpha_i(\text{pH}) = 1$$

$$\alpha_i(\text{pH}) = \int_{-\infty}^{\text{pH}} f_i(x) \cdot dx \quad (45)$$

where $y = f_i(\text{pH})$ is the probability density function

$$f_i(\text{pH}) = \frac{d\alpha_i(\text{pH})}{d\text{pH}} \quad (46)$$

It implies that

$$f_i(\text{pH}) = \beta \cdot \frac{10^{\text{p}g_i - \text{pH}}}{(10^{\text{p}g_i - \text{pH}} + 1)^2} = \beta \cdot \alpha_i(\text{pH}) \cdot (1 - \alpha_i(\text{pH})) \quad (47)$$

The function plotted in Figure 1 appears some similarities with the Fermi-Dirac distribution function [27].

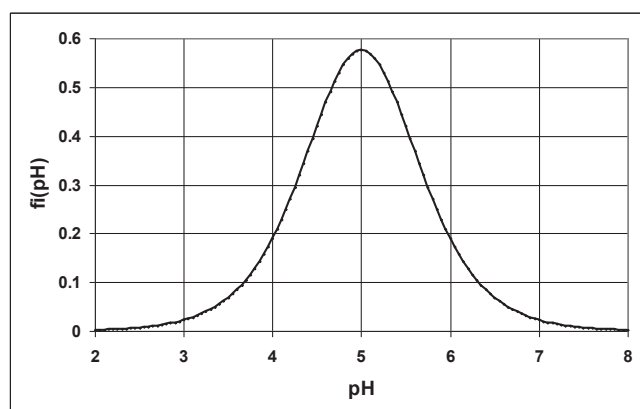


Figure 1: The function $y = f_i(\text{pH})$ (Eq. 20) plotted for $\text{p}g_i = 5.0$.

A link between the species of defined and undefined composition

In order to assume a "common basis" between species of defined composition and ones of undefined composition, such as fulvic acids [14], a formal procedure of their "shredding" into virtual monoprotic acids can be used. Each proton-generating or proton-accepting place of the resulting monoprotic acids or their bases will be considered as the center of acidity or basicity. The approach based on application of Simms constants meets these aspirations. Generally, any of the monoprotic acids ascribed to the polyprotic acid of a defined composition, will be an acid with undefined composition (and thus an undefined molecular mass),

like a monoprotic acid, resulting from similar, mental operation applied to fulvic acid molecules. The difference is that, in the first case, the concentrations of the virtual monoprotic acids are known, and equal to the concentration of the generic, polyprotic acid.

Most bio- and drug molecules contain two or more basic sites. Their properties, in particular, charge and charge distribution within their structure are characterized by various acid-base parameters, e.g. protonation constant (pK). In ^1H NMR method, pH can be calculated from chemical shifts of indicator molecules throughout the pH-scale (0–14). A subsequent aim was to accurately determine the microscopic protonation constants of the most basic natural amino acid, arginine, by ^1H NMR-pH titrations. Developing a ^{15}N NMR method for the determination of group-specific basicities of individual amino groups. The basicity centers can be also referred to micro-constants [28], related to bioanalysis, drug metabolism and pharmacokinetic analysis of small molecules, macromolecules, tested with use of LC/MS/MS, HPLC/UV, and immunoassay techniques [29].

The fate of ionizable drug molecules in the body depends on external parameters, especially pH in extramolecular environment. Binding of drug molecules to the target is highly affected by the protonation state of ionizable groups. Site-specific basicities can be quantified by the microscopic protonation constants, which provide information on their submolecular basicity. Regardless of a concrete dissociation scheme, the assumption about independent dissociation for each ionogenic group leads to a one-to-one correspondence between the sets of intrinsic (microscopic) and apparent (macroscopic) constants. The assumption of independent dissociation enormously simplifies the theoretical treatment.

To interrelate microscopic acidity constants (pK values) of polyprotic acids or bases with their macroscopic pK values, the Ising models [30], which have received much attention in statistical mechanics, were used in [31].

Consideration of molar concentration of some macromolecules, such as HAs and FAs is impossible, owing to undefined molecular and then molar masses of these acids. One can only define approximate molar concentrations of acidity/basicity centers (mainly carboxylic acids and primary amine groups) in these acids and then recalculate them on the total mass or volume of the sample tested.



The equilibrium constant values at high ionic strengths may differ significantly from those obtained in more diluted solutions. It should be noted that the equilibrium constants cited e.g. in [21], come from the papers published over many decades. Earlier equilibrium constants were determined using models adapted to contemporary computing capabilities.

Normal mode of acid-base titration in the D+T system presented above is usually associated with a significant change in ionic strength of the solution, which changes the activity coefficient (γ), and consequently the equilibrium constants (K_i) values [13]. It was the main leitmotif of application of titration according to isomolar instead of normal mode, as indicated above.

Final comments

The novel approach to acid-base equilibria, based on application of Simms constants idea, is derived on the basis of charge and concentration balances, and applied – for illustrative purposes – to titrations in D+T systems of different complexity. This approach was suggested as one applicable to formulation of total alkalinity (TAL) in natural waters [12,13], also with fulvic acids [14], and their complexes with different metal ions. This idea can be extended on biological systems, such as lymphatic systems in living organisms, as well. The models are perceived as the challenge/counterproposal put towards the approaches known hitherto in the literature.

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