BUFFER CAPACITY IN HETEROGENEOUS MULTICOMPONENT SYSTEMS. REVIEW

Oxana Spinu*, Igor Povar

Institute of Chemistry of Academy of Sciences of Moldova, 3, Academiei str., Chisinau MD-2028, Republic of Moldova
*e-mail: oxana_spinu@yahoo.com; phone (+373 22) 73 97 36

Abstract. The quantitative basis of the theory of buffer properties for two-phase acid-base buffer systems and for multicomponent heterogeneous systems has been derived. The analytical equations for buffer action with respect to all components for diverse multicomponent systems were deduced. It was found a remarkable relation of proportionality between β_i quantities. It is shown, that the buffer properties in relation to the solid phase components are amplified with an increase of solubility due to protolytic or complex formation equilibria in saturated solutions. It has been established, that the buffer capacities of components are mutually proportional, whereas for heterogeneous systems these relationships depend on the stoichiometric composition of solid phases. The deduced equations can be applied to the assessment of buffer action of the systems "Natural mineral – soil solution", containing soluble and insoluble chemical species. A number of the important conclusions concerning the investigated buffer systems has been made. The obtained results can be used in various areas of chemical and biochemical researches, especially in soil science, ecological sciences, analytical chemistry, pharmacology, pharmaceutics, medical industry and synthetic organic chemistry

Introduction

Buffer capacity is an important concept in many areas of science: analytical and electroanalytical chemistry [1], geochemistry [2], biochemistry [3], medicine and pharmaceutical industry [4], water treatment [5], agriculture [6], environment [7], etc. The capacity of buffer systems to oppose (resist) to the variation of their composition (usually to *pH* changes) by influence of external fluxes of chemical compounds of natural or anthropogenic character, that shift chemical equilibria, is called buffer property, and its efficiency – buffer action. Despite of an abundance of the information on buffer systems, the quantitative theory of buffer action has been developed only for mono-phase systems [8,9]. The buffer action of mono-phase buffers is usually based on protolytic equilibria between water, a weak acid or base or ampholytic compound and their conjugate pairs [10,11]. The widespread use of buffers as well as the variety of chemical processes and phenomena associated with a certain acidity of solutions explains the constant interest in designing and studying new buffer systems.

Unlike the classical mono-phase buffer systems in which the buffer components are dissolved in a unique phase, in two-phase (heterogeneous) buffers they are distributed between two phases: in aqueous phase and solid (gaseous or liquid) phase. The aqueous (buffer) phase contains all the charged particles and a restricted quantity of electro-neutral species. The solid phase contains in significant quantities only electro-neutral particles and serves as their reservoir by means of which the equilibrium is adjusted and one of parameters of buffer system is maintained constantly [9-18]. The buffer action of two-phase systems is based on the shift of complex equilibria, both homogeneous and heterogeneous in the aqueous phase and between phases, respectively [19-21]. By increasing the acidity of solution the role of simultaneous proceeding protolytic reactions with participation of salt anions increases; with an increase of alkalinity the contribution of complex formation reactions occurring with participation of salt cations amplifies. Authors [15] have proved that the buffer capacity is a special case of the sensitivity analysis, as a more general theoretical approach, which studies the answer of system to various external perturbations (as for example, the variation of the certain component concentration). We believe that it is more correct to consider, as a potential reservoir of buffer heterogeneous systems, the complex chemical heterogeneous equilibria with participation of solid phases [16]. Unfortunately, so far there are a small number of studies dedicated to the systematic investigations and the development of theoretical aspects of the buffer action for two-phase systems [8,9,14-21]. Besides, in the majority of these studies only the *pH* – buffer properties of heterogeneous systems were investigated. The concept of "*buffer action*" helps to find out which reactions control the composition of natural waters, including soil solutions [22-32]. The parameters of buffer action are integrated functions of all the soil chemical components by virtue of their capacity, by means of chemical reactions and sorption-desorption processes, to extinguish or strengthen the effect of entered pollutants [33].

The aim of the present paper has been to develop the quantitative aspects of the buffer action of various components of heterogeneous systems and to establish their interrelation. In this paper, the quantitative aspects of the theory for two-phase buffers with partition equilibria of acid-base pairs between two liquids (aqueous and organic) are

considered in detail. It is proved that the heterogeneous multicomponent systems possess buffer action with respect to all components "i" of acid-base mixtures. Analytical equations for the buffer capacities of two-phase systems with respect to all the components of heterogeneous systems have been deduced. Moreover, it has been shown that the quantities in these systems are reciprocally proportional. In contrast to classical mono-phase buffers, in two-phase buffer systems the maximum buffer capacity β_H occurs when pH_{max} is equal to $pK_d + log(1 + P(HA))$, where K_d and $P(HA)$ are respectively the dissociation constant and the repartition constant of the acid between two phases.

Theoretical part
Buffer action of the systems "Mineral – saturated solution"

The buffer action of soil is one of its fundamental physicochemical characteristics. The soil buffer action composes of the buffer action of a set of mineral and organic components and presented by solid, liquid and gaseous compounds. The buffer capacity of soils in relation to chemical compounds is defined by the content of chemical elements in the soil solution (the parameter of intensity) and on the content of mobile compounds of these elements in solid phases (the parameter of capacity). The buffer capacity of soils can be discovered by the fact that the increase of amounts of toxic metals (*TM*) is not accompanied by an increase of their content in plants; the different buffer action of the soils in relation to one element is manifested in unequal toxic concentrations for plants [33]. The same soil can possess different buffer action in relation to different metals.

The complexity of the soil solution composition containing mineral phases and a large set of involved chemical compounds determine the possibility of simultaneous chemical reactions along with the capacity of solid phases of minerals to maintain relatively constant the aqueous solution composition [19-21,29-32,34-40]. Under real conditions the buffer action of natural heterogeneous aqueous systems is expressed so as the consumption of any element from solution causes the partial dissolution of solid phases and as a result the composition of the solution is restored.

Currently, extensive information on negative (harmful) transformations of soils, as a result of progressing acid and alkaline loads (in the form of mineral fertilizers, chemicals for protection of plants and industrial emissions dropping out with atmospheric precipitation) has been gathered. Thus, the quantitative assessment of the acid - base buffer action, revealing the degree of influence of the systematic use of fertilizers and technogenic pollution by substances of the acid and alkaline nature is an actual problem of the agrology. Besides, the buffer action of soils contains important information on the processes of soil formation (their orientation and intensity) which is used for the soil diagnostics and classification [33].

As a criterion for quantitative assessment of the intensity of buffer action of the studied multicomponent heterogeneous systems, one can use the value of the buffer capacity β_i^S (the superscript index "S" specifies the presence of solid phases), which can be defined as a partial derivative:

$$\beta_i^S = \left(\frac{\partial C_i^0}{\partial \ln[i]} \right)_{C_j^0 (j \neq i)}$$

where C_i^0 and $[i]$ denote the initial (analytical) concentration in mixture and equilibrium concentration of the component "i" of solid phase, correspondingly, the subscript index shows that the initial concentrations of other components of the mixture are maintained constant.

We will examine the process of formation of the sparingly soluble salt of arbitrary stoichiometric composition $M_m A_{n(S)}$ (M - metal ion, A - anion of salt):

$$M_m A_{n(S)} = mM + nA, \qquad K_S = [M]^m [A]^n. \tag{1}$$

The following set of possible simultaneous reactions in the saturated solution is taken into account:

$$M + iH_2O = M(OH)_i + iH, \qquad K_i = [M(OH)_i][H]^i /[M] \tag{2}$$

$$A + jH = H_j A, \qquad K_j = [H_j A]/\left([A][H]^j\right) \tag{3}$$

$$M + qA + rH = MH_r A_q, \qquad K_q = [MH_r A_q]/\left([M][H]^r [A]^q\right) \tag{4}$$

$$H_2O = H + OH, \qquad K_w = [H][OH]. \tag{5}$$

For the sake of simplicity, the charges of species are omitted. Near to the reaction equations, the corresponding equilibrium constants are specified. The mass balance (*MB*) conditions in this system can be formulated by the following equations:

$$C_M^0 = \Delta C_M + C_M^r = \Delta C_M + \sum_{i=1}\sum_{j=0} i[M_i(OH)_j] + \sum_{q=1}\sum_{r=0}[MH_rA_q] \tag{6}$$

$$C_A^0 = \Delta C_A + C_A^r = \Delta C_A + \sum_{l=0}[H_lA] + \sum_{q=1}\sum_{r=0} q[MH_rA_q] \tag{7}$$

$$C_H^0 = [H] - [OH] + \sum_{l=1} l[H_lA] - \sum_{i=1}\sum_{j=1} j[M_i(OH)_j] + \sum_{q=1}\sum_{r=1} r[MH_rA_q] \tag{8}$$

The quantity C_i^r represents the residual concentration in solution of the ion "i", e.g. the total concentration of all the species, containing a given ion, while ΔC_i is its molar quantity in the solid phase in 1 L of solution [14-17,41-42]. In the Eq.(8) C_H^0 denotes the excess of H^+ ions in relation to hydroxyl ions in two-phase mixtures ($C_H^0 = -C_{OH}^0$). The square brackets designate the equilibrium concentrations of species in solution.

From the stoichiometric composition of the solid phase, the following ratio is obtained:

$$\frac{\Delta C_M}{m} = \frac{\Delta C_A}{n} \text{ or } \Delta C_A = \frac{n}{m}\Delta C_M \tag{9}$$

On the basis of the written equations it is possible to deduce the formulas for calculating the buffer capacity in relation to any component of the mixture. After a series of transformation, one can finally get:

$$\beta_M^S = -\frac{\left(\sum_{i=1}\sum_{j=0} ij[M_i(OH)_j] + \frac{m}{n}\sum_{l=1} l[H_lA] - \sum_{q=1}\sum_{r=1} r[MH_rA_q] + \frac{m}{n}\sum_{q=1}\sum_{r=1} rq[MH_rA_q]\right)^2}{[H] + [OH] + \sum_{l=1} l^2[H_lA] + \sum_{i=1}\sum_{j=0} j^2[M_i(OH)_j] + \sum_{q=1}\sum_{r=1} r^2[MH_rA_q]} +$$

$$+ \frac{m^2}{n^2}\sum_{l=0}[H_lA] + \sum_{q=1}\left(\frac{m^2q^2}{n^2} - 2\frac{mq}{n} + 1\right)\sum_{q=1}\sum_{r=0}[MH_rA_q] + \sum_{i=1}\sum_{j=0} i^2[M_i(OH)_j] \tag{10}$$

or

$$\beta_M^S = \varphi_3 - \frac{\varphi_1^2}{\varphi_2}, \tag{11}$$

where φ_1, φ_2 and φ_3 denote the following concentration functions:

$$\varphi_1 = \sum_{i=1}\sum_{j=0} ij[M_i(OH)_j] + \frac{m}{n}\sum_{l=1} l[H_lA] - \sum_{q=1}\sum_{r=1} r[MH_rA_q] + \frac{m}{n}\sum_{q=1}\sum_{r=1} rq[MH_rA_q] \tag{?}$$

$$\varphi_2 = [H] + [OH] + \sum_{l=1} l^2[H_lA] + \sum_{i=1}\sum_{j=0} j^2[M_i(OH)_j] + \sum_{q=1}\sum_{r=1} r^2[MH_rA_q] \tag{12}$$

$$\varphi_3 = \frac{m^2}{n^2}\sum_{l=0}[H_lA] + \sum_{q=1}\left(\frac{m^2q^2}{n^2} - 2\frac{mq}{n} + 1\right)\sum_{q=1}\sum_{r=0}[MH_rA_q] + \sum_{i=1}\sum_{j=0} i^2[M_i(OH)_j] \tag{?}$$

Similarly, it is possible to prove that, for the buffer capacity towards proton, the following expression is valid:

$$\left(\frac{\partial C_H^0}{\partial \ln[H]}\right)_{C_M^0, C_A^0} \equiv \beta_H^S = \varphi_2 - \frac{\varphi_1^2}{\varphi_3} \tag{13}$$

For the buffer capacity towards the anion of the solid phase one can deduce:

$$\beta_A^S = \frac{n^2}{m^2}\varphi_3 - \frac{n^2}{m^2}\frac{\varphi_1^2}{\varphi_2} = \frac{n^2}{m^2}\left(\varphi_3 - \frac{\varphi_1^2}{\varphi_2}\right) = \frac{n^2}{m^2}\beta_M^S \tag{14}$$

On the basis of obtained Eq.(11), Eq.(13) and Eq.(14) the following remarkable conclusion follows: the buffer capacities towards different components are reciprocally proportional, while the buffer capacities in relation to the ions of the solid phase are interconnected through its stoichiometric coefficients:

$$\frac{\beta_A^S}{n^2} = \frac{\beta_M^S}{m^2} \tag{15}$$

It is worthy to mention that the obtained relations are only valid in the presence of the mineral (solid phase) $M_m A_{n(S)}$. The thermodynamic stability area of the latter is determined by the value of the Gibbs energy of the overall process (1)-(5) [14,43,44]:

$$\Delta G_{S,tot} = -mRT \ln \frac{C_M^r}{C_M^0} - nRT \ln \frac{C_A^r}{C_A^0} \tag{16}$$

The solid-phase is stable if $\Delta G_{S,tot} > 0$. The condition $\Delta G_{S,tot} = 0$ corresponds to the beginning of its dissolution and (or) sedimentation.

The analysis of the derived equations shows that the buffer capacities grow with the increase of the precipitate solubility, e.g. by rising the residual concentration of the component of minerals.

Buffer properties for liquid two-phase acid-base buffer systems

The concept of buffering is closely related to the problem of controlling the chemical composition of multicomponent systems. For analytical chemists it is essential to preserve as a constant not only the pH value (e.g., the proton concentration), but the concentrations of other components in the system. In the examined extraction systems, the organic phase serves as the buffer reservoir [31,45-47]. At present, for these systems there is no rigorous theoretical base allowing a priori estimation of their buffer effectiveness as well as a systematic search for new heterogeneous mixtures with high buffer action. Janjić et al. [45] have investigated the buffer action with respect to the hydrogen ion (proton) for the multicomponent two-phase systems containing both separate organic acids and bases, and their mixtures. These authors made an attempt to deduce an equation for an assessment of buffer capacity of such systems. However, the obtained expressions are bulky and in some cases neglect a number of side equilibria, occurring in the organic phase.

For two-phase buffers with polyprotic acids, the following process of formation in aqueous solution of the polyprotic acid of stoichiometric composition $H_n A$ takes place:

$$nH + A \leftrightarrow H_n A, \quad K_n = [H_n A]/\big([H]^n [A]\big) \tag{17}$$

The following set of concomitantly reactions proceeding in two-phase systems "Aqueous solution (*aq*) – organic solvent (*o*)" proceeds:

$$H_k A_{(aq)} \leftrightarrow H_k A_{(o)}, \quad P(H_k A) = [H_k A]_o / [H_k A]_{aq} \tag{18}$$

$$H_2 O \leftrightarrow H + OH, \quad K_w = [H][OH] \tag{19}$$

Here and below, for sake of convenience, the charges of species are omitted, the subscript (*aq*) is also neglected in the case of equilibria taking place only in aqueous solution. Near to equations the associated equilibrium constants are specified: K_n is the protonation constant of polyprotic acid $H_n A$ and $P(H_k A)$ is the constant of distribution of the molecular acid $H_k A$ between two non-mixing liquids. For simplicity, it has been assumed that the system obeys ideal behavior of the studied systems where the ionic strength is zero. Consequently, the ion activities are equal to their concentrations, while the activity of pure species is equal to unity (or included in the equilibrium constants) [24,25,48,49]. The conditions of mass balance in the given heterogeneous system can be formulated as follows:

$$C_A^0 \equiv \tilde{a} = \sum_{n=0} [H_n A]_{aq} + [H_k A]_o = [A]\left(1 + \sum_{n=1} K_n [H]^n\right) + P(H_k A) K_k [H]^k [A] \tag{20}$$

$$C_H^0 = [H] - [OH] + \sum_{n=1} n[H_n A] + k[H_k A]_o = [H] - K_W [H]^{-1} + [A] \sum_{n=1} n K_n [H]^n + kP(H_k A) K_k [H]^k [A] \tag{21}$$

The C_A^0 value in the Eq.(20) represents the analytical concentration of the anion A^{n-1} of acid in considered heterogeneous system. In the Eq.(21) C_H^0 denotes the excess of H^+ ions towards to hydroxyl - ions in the two-phase mixture ($C_H^0 = -C_{OH}^0$) [12]. When deducing Eq.(20) and Eq.(21) it was assumed that the volume of water phase V_{aq} is equal to the volume of organic phase V_o:

$$V_{aq} = V_o \tag{22}$$

We present here only final results, omitting the intermediate deduction of the equations through the equilibrium constants Eqs.(17) - (19) as it has been done in the Eqs.(20) and (21):

$$\beta_A = \left(\frac{\partial C_A^0}{\partial \ln[A]}\right)_{C_H^0} = \sum_{n=0}[H_nA]_{aq} + [H_kA]_o + \left(\frac{\partial \ln[H]}{\partial \ln[A]}\right)_{C_H^0}\left(\sum_{n=1}n[H_nA] + k[H_kA]_o\right) \equiv \tilde{a} + \tilde{n}\left(\frac{\partial \ln[H]}{\partial \ln[A]}\right)_{C_H^0} \tag{23}$$

where through $\tilde{n}$ is designated the sum that the third member of the Eq.(23) contains. Considering that $C_H^0 = const$:

$$\left(\frac{\partial C_H^0}{\partial \ln[A]}\right)_{C_H^0} = 0 = \tilde{n} + \left([H] + [OH] + \sum_{n=1}n^2[H_nA] + k^2[H_kA]_o\right)\left(\frac{\partial \ln[H]}{\partial \ln[A]}\right)_{C_H^0} \equiv \tilde{n} + \tilde{h}\left(\frac{\partial \ln[H]}{\partial \ln[A]}\right)_{C_H^0} \tag{24}$$

Whence

$$\left(\frac{\partial \ln[H]}{\partial \ln[A]}\right)_{C_H^0} = -\frac{\tilde{n}}{\tilde{h}} \tag{25}$$

Substituting the obtained expression for the partial derivative Eq.(24) in the Eq.(23), it is finally received:

$$\beta_A = \tilde{a} - \frac{\tilde{n}^2}{h} = C_A^0 - \frac{\left(\sum_{n=1}n[H_nA] + k[H_kA]_o\right)^2}{[H] + [OH] + \sum_{n=1}n^2[H_nA] + k^2[H_kA]_o} \tag{26}$$

In the case of monoprotic acid HA, $n = 1$, within the range of pH values, where the concentrations of $[H^+]$ and $[OH^-]$ can be neglected, the Eq.(26) becomes significantly simpler, $\beta_A \cong [A]$, e.g. the buffer capacity is equal to the equilibrium concentration of the anion of acid.

In a similar way, for the buffer capacity in relation to proton, it is possible to obtain the following expression:

$$\beta_H \equiv \left(\frac{\partial C_H^0}{\partial \ln[H]}\right)_{C_A^0} = [H] + [OH] + \sum_{n=1}n^2[H]^n + k^2[H_kA]_o^k - \frac{\left(\sum_{n=1}n[H_nA] + k[H_kA]\right)^2}{C_A^0} \equiv \tilde{h} - \tilde{n}^2/\tilde{a} \tag{27}$$

It is important to notice, that for monoprotic acid the Eq.(27) simplifies significantly:

$$\beta_H \equiv \left(\frac{\partial C_H^0}{\partial \ln[H]}\right)_{C_A^0} = [H] + [OH] + [HA] + [HA]_o - \frac{([HA] + [HA]_o)^2}{C_A^0} \tag{28}$$

The maximum buffer capacity for a given C_A^0 occurs when $(\partial\beta_H/\partial \ln[H])_{C_A^0} = 0$, i.e. when:

$$pH_{max} = pK_d + \log(1 + P(HA)) \qquad, \tag{29}$$

where $K_d = 1/K_I$ is the dissociation constant of weak acid HA. It is well-known that for the mono-phase buffer system $pH_{max} = pK_d$. Consequently, in comparison with classical aqueous buffers, the pH_{max} value in the case of two-phase systems is shifted by $log(1 + P(HA))$, which depends mainly on the nature of organic solvent. From the Eqs.(26) and (27) a remarkable identity follows:

$$\beta_A\tilde{h} = \beta_H\tilde{a} \tag{30}$$

Therefore, the investigated heterogeneous system shows buffer properties with respect to both ions of the polyprotic acid, and the values of buffer capacity β_A and β_H are reciprocally proportional. For monoprotic acids, since $h = [H] + [OH] + [HA] + [HA]_o$ and $\tilde{a} = C_A^0$, the identity Eq.(30) becomes:

$$\beta_A = (H) + [OH] + [HA] + [HA]_o) = \beta_H ([A] + [HA] + [HA]_o).$$

Similarly, it is possible to obtain the expressions for calculating the buffer capacities in the case of the polyprotic base BH_m as well.

Results and discussion
Buffer action of heterogeneous system "Mineral - saturated solutions"

The buffer action of heterogeneous system "*Mineral - saturated solutions*" depends on the chemical composition of the water solutions, as well as on the composition and properties of the mineral phases. We will examine a concrete real system "*Iron (III) minerals - saturated solution*", although the approach developed here can be applied for any other. As iron occurs in many minerals and materials, it is mostly present in all superficial waters. The average concentration of iron in river waters is 0.7 mg/L [50]. With an increase of the acidity of waters (up to a critical threshold of water biota survival; for example, for mollusks this threshold is *pH* 6.0 and for perches it is *pH* 4.5), the content of iron (III) increases rapidly because of the interaction of iron (III) hydroxide of natural materials with acid:

$$\tfrac{1}{2} Fe_2O_{3(S)} + 3H^+ \Leftrightarrow Fe^{3+} + \tfrac{3}{2} H_2O, K_{S1} = [Fe^{3+}][H^+]^{-3}$$

$$FeOOH_{3(S)} + 3H^+ \Leftrightarrow Fe^{3+} + 2H_2O, K_{S2} = [Fe^{3+}][H^+]^{-3}$$

$$Fe(OH)_{3(S)} + 3H^+ \Leftrightarrow Fe^{3+} + 3H_2O, K_{S3} = [Fe^{3+}][H^+]^{-3}$$

We find the following important relation of proportionality between the buffer capacities of heterogeneous systems, "*Fe(OH)$_{3(S)}$ - saturated aqueous solution* ":

$$\beta_H^S = 3^2 \beta_{Fe}^S \tag{31}$$

In the case of formation of poorly soluble oxy-hydroxides of the stoichiometric composition $M(OH)_{n(S)}$, $MOOH_{(S)}$ or $1/2 M_2O_{n(S)}$, the relation (31) can be generalized [14,16,51]:

$$\frac{\beta_H^S}{n^2} = \frac{\beta_M^S}{1^2} \tag{32}$$

Besides the process of dissolution of the mineral of iron, a set of possible equilibria in the system "*Mineral phase – soil solution*" (see Table 1) is considered [52]. For the calculations the following composition heterogeneous mixture was used (mol L^{-1}): $C_{Fe}^0 = 1 \cdot 10^{-6} \div 1 \cdot 10^{-4}$, $C_F^0 = 5 \cdot 10^{-6}$, $C_{Org}^0 = C_{PO_4}^0 = C_{SO_4}^0 = 1 \cdot 10^{-4}$, $C_{CO_3}^0 = 1 \cdot 10^{-3}$.

Table 1
The equilibrium constants of the analyzed reactions.

The equations of reactions	logK
$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	-2.187
$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+$	-4.59
$Fe^{3+} + 3H_2O = Fe(OH)_3^0 + 2H^+$	-12.56
$Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H^+$	-21.59
$1/2 \; \alpha - Fe_2O_{3(S)hematite} + 3H^+ = Fe^{3+} + 3/2H_2O$	-0.85
$1/2 \; \gamma - Fe_2O_{3(S)maghemite} + 3H^+ = Fe^{3+} + 3/2H_2O$	+1.75
$1/2 \; \varepsilon - Fe_2O_{3(S)} + 3H^+ = Fe^{3+} + 3/2H_2O$	+2.35
$\alpha - FeOOH_{(S)goethite} + 3H^+ = Fe^{3+} + 3H_2O$	+0.40
$\gamma - FeOOH_{(S)lepidocrocite} + 3H^+ = Fe^{3+} + 3H_2O$	+3.70

Equations of reactions	logK
$2-line-Fe(OH)_{3(S)}+3H^+ = Fe^{3+}+3H_2O$	+3.00
$6-line-Fe(OH)_{3(S)}+3H^+ = Fe^{3+}+3H_2O$	+3.40
$Fe^{3+}+F^- = FeF^{2+}$	6.04
$Fe^{3+}+2F^- = FeF_2^+$	10.47
$Fe^{3+}+SO_4^{2-} = Fe(SO_4)^+$	4.05
$Fe^{3+}+2SO_4^{2-} = Fe(SO_4)_2^-$	5.38
$Fe^{3+}+H^+ +2SO_4^{2-} = FeH(SO_4)_2$	8.10
$Fe^{3+}+Org^{3-} = FeOrg$	8.00
$Org^{3-}+H^+ = HOrg^{2-}$	4.30
$2Fe^{3+}+2H_2O = Fe_2(OH)_2^{4+}+2H^+$	-2.85
$3Fe^{3+}+4H_2O = Fe_3(OH)_4^{5+}+4H^+$	-6.29
$Fe^{3+}+H^+ +PO_4^{3-} = FeHPO_4^+$	19.87
$Fe^{3+}+2H^+ +PO_4^{3-} = FeH_2PO_4^{2+}$	21.70
$Fe^{3+}+3H^+ +PO_4^{3-} = FeH_3PO_4^{3+}$	26.61
$CO_3^{2-}+H^+ = HCO_3^-$	10.329
$CO_3^{2-}+2H^+ = H_2CO_3$	16.681
$H^+ +PO_4^{3-} = HPO_4^{2+}$	12.38
$2H^+ +PO_4^{3-} = H_2PO_4^+$	19.57
$3H^+ +PO_4^{3-} = H_3PO_4$	21.72
$H^+ +F^- = HF$	3.17

Figure 1 shows the calculation results of the buffer capacity β_{Fe}^S as a function of *pH* for the various iron (III) minerals. The analysis of the derived equations for the heterogeneous system showed that the increase in the total concentration C_{Fe}^0 for the *pH* values above 4.5, as well as the nature of the mineral have an insignificant effect on the area of the buffer action of studied system due to the very low solubility of iron oxy - hydroxides minerals. The appearance of maxima on the curves β_H^S (*pH*) and β_{Fe}^S (*pH*) (Figures 1-3) is due to the dissociation process of carbonic acid with formation of HCO_3^- ions (*pH* = 6.36) and CO_3^{2-} (*pH* = 10.34).
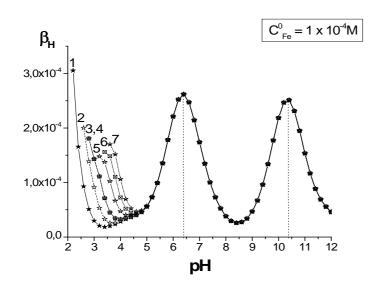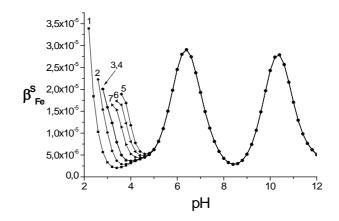

Figure 1. The curves of dependence of the buffer capacity β_H on *pH* for the system "*Iron (III) mineral - saturated aqueous solution*". The used concentrations (mol L^{-1}):

$C_{Fe}^0 = 1 \cdot 10^{-4}$, $C_F^0 = 5 \cdot 10^{-6}$,

$C_{Org}^0 = C_{PO_4}^0 = C_{SO_4}^0 = 1 \cdot 10^{-4}$,

$C_{CO_3}^0 = 1 \cdot 10^{-3}$

1 - α-Fe$_2$O$_3$ (hematite),
2 - γ-Fe$_2$O$_3$ (maghemite),
3 – ε-Fe$_2$O$_3$,
4 – α-FeOOH (goethite),
5 - γ-FeOOH (lepidocrocite),
6 – Fe(OH)$_3$ (2-line ferrihydrite),
7 – Fe(OH)$_3$ (6-line ferrihydrite).

Figure 2. The curves of dependence of the buffer capacity β_{Fe}^{S} **on *pH* for the system**
"*Iron (III) mineral - saturated aqueous solution*". The used concentrations (mol L⁻¹):
$C_{Fe}^{0} = 1 \cdot 10^{-4}$, $C_{F}^{0} = 5 \cdot 10^{-6}$, $C_{Org}^{0} = C_{PO_4}^{0} = C_{SO_4}^{0} = 1 \cdot 10^{-4}$, $C_{CO_3}^{0} = 1 \cdot 10^{-3}$.

1 - α-Fe₂O₃ (hematite), 2 - γ-Fe₂O₃ (maghemite), 3 – ε-Fe₂O₃, 4 - α-FeOOH (goethite), 5 - γ-FeOOH (lepidocrocite), 6 – Fe(OH)₃ (2-line ferrihydrite), 7 - Fe(OH)₃ (6-line ferrihydrite).
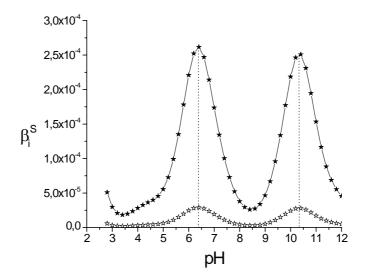

Figure 3. Buffer capacities β_{H}^{S} **(1) and** β_{Fe}^{S} **(2) versus *pH* for the system**
"*Hematite - saturated aqueous solution*".

The used concentrations (mol L⁻¹): $C_{Fe}^{0} = 1 \cdot 10^{-5}$, $C_{F}^{0} = 5 \cdot 10^{-6}$, $C_{Org}^{0} = C_{PO_4}^{0} = C_{SO_4}^{0} = 1 \cdot 10^{-4}$, $C_{CO_3}^{0} = 1 \cdot 10^{-3}$.

The iron (III) ions and its complexes have a significant contribution only in very acidic solutions up to *pH* 4.5. The analysis of the data presented in Figures 2 and 3 allows us to conclude that the studied heterogeneous system has a buffer capacity in relation to ions of hydrogen and iron (III). We will note down that these relations are valid only in the presence of solid phases.

Another example of real natural system that we examined is "*Gibbsite – saturated aqueous solution*". By increasing the acidity in aqueous solutions the content of aluminium grows quickly due to the interaction of the gibbsit with an acid:

$$Al(OH)_{3(S)} + 3H^{+} = Al^{3+} + 3H_2O, K_S = [Al^{3+}][H^{+}]^{-3}$$

An important interrelation between the buffer capacities of the heterogeneous system "*Gibbsite Al(OH)₃₍s₎ - saturated aqueous solution*" system can be identified [53,54]:

$$\beta_{H}^{S} = 9\beta_{Al}^{S} \tag{33}$$

Besides the process of gibbsite dissolution, a set of possible equilibria in the system "*Mineral phase – natural water*", listed in Table 2 has been taken into account [52]. The following composition of the heterogeneous system has been used for the calculations: $C_{Al}^0 = 1 \cdot 10^{-4}$ mol L^{-1}, $C_F^0 = 5 \cdot 10^{-6}$ mol L^{-1}, $C_{Org}^0 = 1 \cdot 10^{-4}$ mol L^{-1}, $C_{PO_4}^0 = 1 \cdot 10^{-4}$ mol L^{-1}, $C_{SO_4}^0 = 1 \cdot 10^{-4}$ mol L^{-1} and $C_{CO_3}^0 = 1 \cdot 10^{-3}$ mol L^{-1}. One can state that the influence of H^+ in the studied *pH* interval may be neglected, and the OH^- ions exercise influence on β_H^S only at *pH* > 8.5. The aluminium ions and their hydroxocomplexes make a significant contribution in acid solutions up to *pH* 5.5 and at pH > 8 because of the predominance of the stable anionic hydroxocomplex $Al(OH)_4^-$. The results of the calculations of the buffer capacities β_H^S as a function of *pH* for different compositions of the heterogeneous mixture are shown in Figures 4–5. Obviously, an increase of the total concentration C_{Al}^0 (Figure 4) augments the area of the buffer action because of the extension of the *pH* interval of the thermodynamic stability of the solid phase. At concentrations of fluoride $C_F^0 = 5 \cdot 10^{-4}$ mol L^{-1}, the β_H^S value increases sharply in the range of *pH* values of the gibbsite dissolution – formation with a simultaneous narrowing of the total *pH* range of the buffer action (Figure 5).

Table 2

Equilibrium constants and values of enthalpies (ΔH).

Equations of reactions	log K	ΔH (cal mol^{-1})
$Al^{3+} + H_2O = AlOH^{2+} + H^+$	-4.99	11900
$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$	-10.00	22000
$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	-23.00	44060
$Al(OH)_{3(S)} + 3H^+ = Al^{3+} + 3H_2O$	9.35	−22800
$Al^{3+} + F^- = AlF^{2+}$	7.02	1100
$Al^{3+} + 2F^- = AlF_2^+$	12.76	2000
$Al^{3+} + 3F^- = AlF_3$	17.03	2500
$Al^{3+} + 4F^- = AlF_4^-$	19.73	2200
$Al^{3+} + 5F^- = AlF_5^{2-}$	20.92	1800
$Al^{3+} + SO_4^{2-} = AlSO_4^+$	3.01	2150
$Al^{3+} + 2SO_4^{2-} = Al(SO_4)_2^-$	4.90	2840
$Al^{3+} + Org^{3-} = AlOrg$	8.39	—
$Al^{3+} + H^+ + Org^{3-} = AlHOrg^+$	13.09	—
$Org^{3-} + H^+ = HOrg^{2-}$	6.83	—
$Org^{3-} + 2H^+ = H_2Org^-$	12.73	—
$Org^{3-} + 3H^+ = H_3Org$	14.49	—
$H^+ + F^- = HF$	3.17	3460
$H_2O = H^+ + OH^-$	-14.00	13340
$2Al^{3+} + 2H_2O = Al_2(OH)_2^{4+} + 2H^+$	-6.3	—
$3Al^{3+} + 4H_2O = Al_3(OH)_4^{5+} + 4H^+$	-12.1	—
$Al^{3+} + H_2PO_4^- = AlH_2PO_4^{2+}$	3.1	—
$PO_4^{3-} + H^+ = HPO_4^{2-}$	12.0	—
$PO_4^{3-} + 2H^+ = H_2PO_4^-$	19.21	—
$PO_4^{3-} + 3H^+ = H_3PO_4$	21.36	—

Note: 1 cal = 4.184 J, Org - organic ligand, the „—" specifies the absence of experimental data.

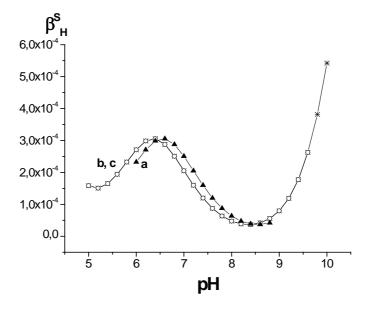**Figure 4.** Buffer capacity β_H^S versus *pH* for the "*Gibbsite - saturated aqueous solution*" system.
Concentrations (mol L^{-1}):
$C_{Al}^0 : a - 1 \cdot 10^{-3}, \ b - 1 \cdot 10^{-4}, \ c - 1 \cdot 10^{-5}, \ C_F^0 = 5 \cdot 10^{-6}, \ C_{Org}^0 = C_{PO_4}^0 = C_{SO_4}^0 = 1 \cdot 10^{-4}, \ C_{CO_3}^0 = 1 \cdot 10^{-3}.$

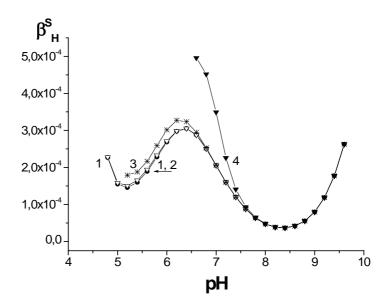**Figure 5.** Buffer capacity β_H^S versus *pH* for the "*Gibbsite - saturated aqueous solution*" system.
Concentrations (mol L^{-1}):
$C_F^0 : 1 - 5 \cdot 10^{-7}, \ 2 - 5 \cdot 10^{-6}, \ 3 - 5 \cdot 10^{-5}, \ 4 - 5 \cdot 10^{-4}, \ C_{Al}^0 = C_{Org}^0 = C_{PO_4}^0 = C_{SO_4}^0 = 1 \cdot 10^{-4}, \ C_{CO_3}^0 = 1 \cdot 10^{-3}.$

The dependences of β_H^S (pH) for different concentrations of carbonate ion are presented in Figure 6. By taking into account the contribution of equilibria including carbonate ion in the total buffer capacity β_H^S, the $\beta_{CO_3}^H$ value was calculated separately. A comparison of the calculated curves shows that equilibria with CO_3^{2-} participation have a substantial contribution to β_H^S at a $C_{CO_3}^0 > 1 \cdot 10^{-4}$ mol L^{-1} (Figures 7a and 7b). The analysis of the obtained data

presented in Figures 4–7, taking into account Eq.(33) allows us to conclude that the investigated heterogeneous system has a considerable buffer capacity towards to aluminium as well.
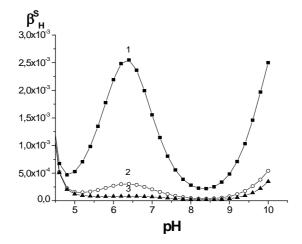

Figure 6. Buffer capacity β_H^S **versus** *pH* **for the "***Gibbsite - saturated aqueous solution***" system.**
Concentrations (mol L^{-1}):
$$C_{CO_3}^0 : 1 - 1 \cdot 10^{-2}, \ 2 - 1 \cdot 10^{-3}, \ 3 - 1 \cdot 10^{-4}, \ C_{Al}^0 = C_{PO_4}^0 = C_{SO_4}^0 = 1 \cdot 10^{-4}, \ C_F^0 = 5 \cdot 10^{-6}.$$

Figure 7. Total buffer capacity β_H^S **versus** *pH*, **carbonate buffer capacity** $\beta_{CO_3}^H$ **vs.** *pH* **and their difference**

$\beta_H^S - \beta_{CO_3}^H$ **for the "***Gibbsite - saturated aqueous solution***" system.**

Concentrations (mol L^{-1}): $C_{CO_3}^0 : a - 1 \cdot 10^{-3}, \ b - 1 \cdot 10^{-4}, \ C_{Al}^0 = C_{PO_4}^0 = C_{SO_4}^0 = 1 \cdot 10^{-4}, \ C_F^0 = 5 \cdot 10^{-6}.$

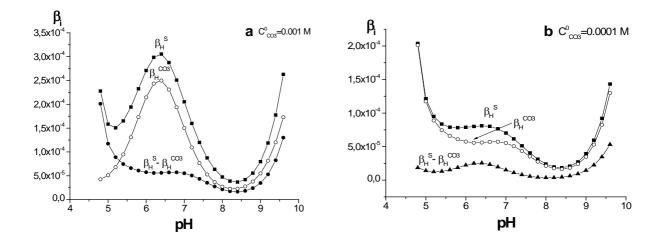The influence of temperature on the value of the buffer capacity was also studied [55]. The results of the calculations are presented in Figure 8. The equilibrium constants for different temperatures have been estimated by the Van't Hoff equation.

$$logK_2 = logK_1 + (1/T_1 - 1/T_2) \ \Delta H/2.303R$$

The necessary values of enthalpies (ΔH) are listed in Table 2. T_1 was set to 298 K = 25 °C. It was assumed that the temperature insignificantly influences the ΔH values inside the investigated temperature range. An analysis of the curves in Figure 8 shows that the buffer capacity increases with a temperature decrease, whereas the *pH* interval of 5.5 – 7.0 of the maximum values of the buffer capacity displaces slightly.
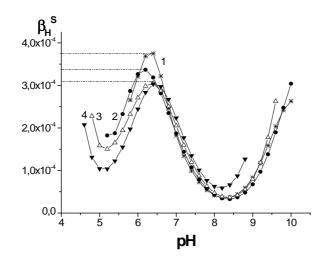
Figure 8. Buffer capacity β_H^S **versus *pH* for the "*Gibbsite - saturated aqueous solution*" system at different temperatures (t, °C): (1) –5, (2) +10, (3) +25 and (4) +40.**
Concentrations (mol L⁻¹): $C_{CO_3}^0 = 1 \cdot 10^{-3}, C_{Al}^0 = C_{PO_4}^0 = C_{Org}^0 = C_{SO_4}^0 = 1 \cdot 10^{-4}, \ C_F^0 = 5 \cdot 10^{-6}$.

Buffer properties for liquid two-phase acid-base buffer systems
Buffer with mono- and diprotic acids

The theoretically calculated and experimentally measured dependences of the buffer capacity on *pH* in the case of two-phase system 1-octanol – water for monoprotic *n*-hexanoic acid and diprotic 1,2-benzenedicarboxylic acid are shown in Figure 9 and Figure 10, respectively. Experimental data [45,56] were obtained at 25 °C and constant ionic strength. For both systems, the experimental data correlate well with the theoretical curves, calculated by Eqs.(27 – 28) that confirms their correctness. The values in Figures 9 and 10 testify the validity of Eq.(29). (The necessary equilibrium constants were taken from [45,56].)
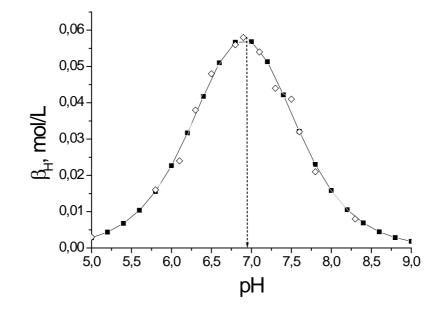

Figure 9. Buffer capacity versus *pH* for two-phase system containing n-hexanoic acid *HA* and 1-octanol:
(■) the calculated values; (◊) experimental data [56];
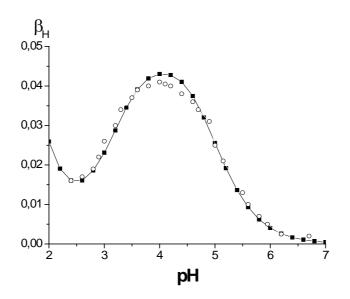**1-octanol : water = 1:1; C_A^0 = 0.1 mol L⁻¹, I = 0, t = 25 °C.**

Figure 10. Dependence of buffer capacity on *pH* for two-phase system containing 1,2-benzenedicarboxylic acid and 1-octanol: (■) calculated values; (○) experimental data [45];
1-octanol : water=1:1; C_A^0 = 0.0488 mol L^{-1}, I = 1 (NaCl), t = 25 ^{0}C.

Two-phase buffers with monoprotic acids in which dimerization occurs

Mono-component systems: propanoic acid – water – benzene (I) and decanoic acid – water – benzene (II): The numerical values of the equilibrium constants used for calculating the theoretical buffer curves as well as the experimental data were taken from [56]. The theoretical and experimental data are presented in Figure 11 (a,b). It can be seen that the theoretical curves are in good agreement with experimental values.
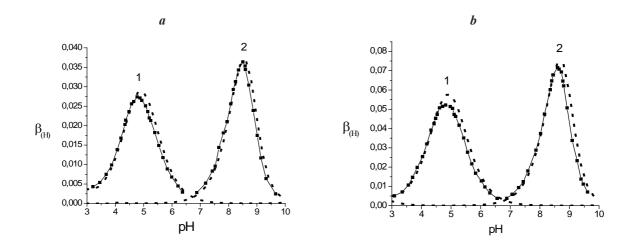

Figure 11. Buffer capacity β_H versus *pH* for mono-component two-phase systems with propanoic (a) and decanoic (b) acids, C_A^0 =0.05 mol L^{-1} (a) and C_A^0 =0.1 mol L^{-1} (b) and α = 1;
(■) – experimental values, dotted lines – experimental curves, I = 0.1, t = 25 ^{0}C.

On Figure 12 the functional dependence $\beta_H = f(pH)$ for (2.4-dichlorophenoxy)acetic acid for aqueous solution and two-phase mixture by means of different organic solvents is graphically illustrated. One can see that high β_H values within a large *pH* range (3.75÷5.75) can be assured by using different organic solvents [57]. The necessary equilibrium data were taken from [58].
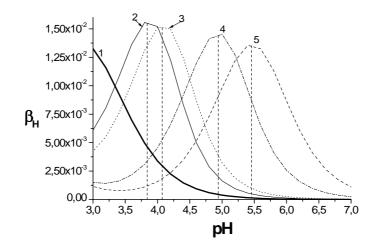
Figure 12. Buffer capacity β_H versus *pH* for mono-component two-phase systems with (2.4-dichlorophenoxy) acetic acid, $C_A^0 = 0.05$ mol L⁻¹, α = 1, t = 25 ⁰C for different organic solvents: 1 – no solvent; 2 – ethylbenzene; 3 – 1-octanol; 4 – chlorbenzene; 5 – nitrobenzene.

pH and pA buffer properties of two-component system in which mixed dimmer occurs

The authors [56] found that the rule of additivity for calculating the total buffer capacity as a sum of separate contributions for this system is not valid. As a result, there are some substantial deviations of the theoretical curves from experimental data within the interval of *pH* from 4 to 7. The experimental data for this system, along with the calculated theoretical curve are presented in Figure 13. As one can see, the experimental values $\beta_H = f(pH)$ are in good agreement with those calculated, contrasting to the results received by authors [56]. Thus, the experiment confirms the validity of our developed theoretical approach.
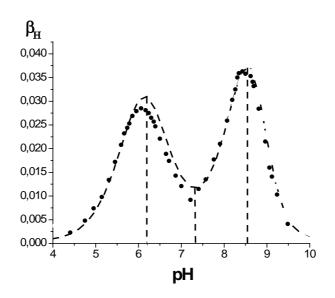

Figure 13. Experimental data [56] (●) and calculated values (---) for β_H *(pH)* as a sum of the contributions of separate acids for the two-component two-phase buffer system containing hexanoic and decanoic acids. $V(C_6H_6) \div V(H_2O) = 1 \div 1$, $C_A^0 = C_B^0 = 0.05$ mol L⁻¹, I = 0.1, t = 25 ⁰C.

In Figure 14 the curves of dependences $\beta_H = f(pH)$, $\beta_A = f(pH)$ and $\beta_B = f(pH)$ are presented. From here it is possible to conclude, that the buffer capacity of two-phase mixtures containing an acid capable to form homogeneous and mixed dimers in the organic solvent, is much higher with respect to anions, than to proton, i.e. $\beta_A (\beta_B) > \beta_H$. At the same time, the maximum value of both functions is registered in the conditions of predominance of the un-bonded anion in aqueous phase.
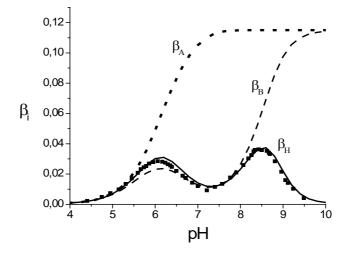
Figure 14. Curves $\beta_H = f(pH)$, $\beta_A = f(pH)$ **and** $\beta_B = f(pH)$ **for the two-component two-phase buffer system, containing hexanoic and decanoic acids.** $V(C_6H_6) \div V(H_2O) = 1 \div 1$, $C_A^0 = C_B^0 = 0.05$ **mol L⁻¹, I = 0.1, t = 25 ⁰C.**

On Figure15 the functional dependence $\beta_A = f(pA)$ for (2.4-dichlorophenoxy)acetic acid for aqueous solution and water-1-octanol mixture is depicted. One can notice that the presence of organic solvent amplifies significantly (approximately by 70 times) the β_A value at $pA = 5.4$. Therefore, two-phase mixtures can be successfully used for designing new buffers with respect to any component for investigated systems. The developed approach can be expanded to other, more complicated systems, containing metal-ligand complexes.
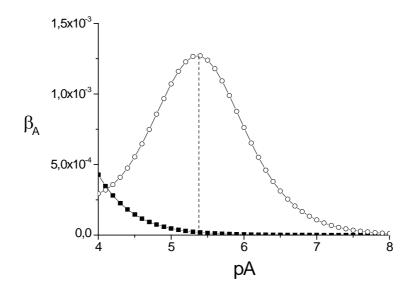

Figure 15. Buffer capacity β_A **versus** *pA* **for the mono-component system with (2.4-dichlorophenoxy) acetic acid in water (curve 1) and water-1-octanol mixture (curve 2),** $C_H^0 = 0.005$ **mol L⁻¹, α = 1; t = 25 ⁰C.**

Conclusions

The analyzed heterogeneous systems manifest buffer actions towards protons, cations or anions of weak bases or acids. The deduced analytical expressions for buffer capacities in respect to all ions of distributed species between two immiscible liquids are reported. For all investigated systems a relation of proportionality between buffer capacities is found. On the basis of the analysis of found identities it can be concluded that it is sufficient to measure only the β_H value, while the quantity β_A can be calculated from a set of expressions identities derived in this work. This conclusion is especially valuable since for the β_H measurement it is necessary to determine potentiometrically the *pH* values while for the β_A determination it is required to measure the $pA = - log[A]$ values. It is known, that the pH-metric method is

much more precisely and does not require special ion-selective electrodes as for *pA* measurement, which have been developed so far only for a few number of anions. The experimental evidence completely confirms the validity of the derived equations. The relation of proportionality between the buffer capacities in respect to all ions of the species distributed between phases has been also found for the heterogeneous systems of the type "*Solid phase-saturated aqueous solution*", which serves as a proof of the generality of this phenomenon. It is demonstrated that the pH_{max} value of the maximal buffer capacity shifts for two-phase system in comparison with classical aqueous buffer mixtures by *log(1 + P(HA))* which depends mainly on the nature of organic solvent. Also, it has been explained the nature of synergic effect of the total buffer action of heterogeneous mixtures. Generally, the mixture of acids and bases shows a cumulative effect, but in the case of interaction of distributed species in the organic phase, it manifests a synergic effect, e.g. the buffer action amplifies It is finally worth noting that heterogeneous buffer systems can be created on the basis of well-known species and do not require any special installations. The deduced relations may be used for search and design of new ion-molecular two-phase buffers with required properties. Owing to the described properties, the considered heterogeneous systems can find widespread use in various areas of chemical and biochemical researches, especially in analytical chemistry, pharmacology, pharmaceutics, medical industry and synthetic organic chemistry.

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