

Do You Know What the Buffer Capacity of Your pH Buffer Is?

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Abstract This paper develops the item of buffer capacity of pH buffers and targets chemists, biologists, physiologists or anyone who may be interested to become familiar with and develop a quantitative perception of factors controlling buffer capacity of aqueous solutions (which can be complex mixtures of acids and/or bases and/or ionic salts, as are commercial pH buffers in use in a variety of applications which require control of pH, or most biological fluids, e.g., blood). The fundamental idea of representing a pH buffer or a buffered biological fluid with a matrix constitutes the leitmotif of the suggested approach through which the boring complexity of a quantitative mathematical treatment of buffer capacity has been overcome. It is shown how the matrix representing a given pH buffer or biological fluid (from which a quantitative evaluation of pH and buffer capacity can be performed) can be built in a matter of minutes (regardless of their complexity) in a MS Excel sheet by employing an Excel library of custom functions which is made available as associated material to this paper. Furthermore, from the matrix representing the pH buffer or biological fluid a plot can be derived which is used as a graphical support for enlightening the chemical significance of the matrix and to connect the buffer capacity to the Acid-Base chemistry which takes place in the represented pH buffer or biological fluid.

Keywords: *buffer capacity, pH buffers, biological fluids buffer capacity, Acid-Base equilibria*

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1. Introduction

pH buffers, and the associated term *buffer capacity*, are of widespread use in many fields of chemistry, biochemistry, biology, physiology, etc.

Nevertheless, as a consequence of the fact that the buffer capacity is not a property which can be directly measured and presented on the display of an instrument, as it is the case of pH, users may have a somewhat vague awareness about the actual buffering capacity of buffers they handle and about factors from which it depends.

In this paper we develop an approach to buffer capacity by which anyone interested may become familiar with its pH buffer and with factors which modulate buffer capacity.

Although, in the following, buffer capacity is developed by reference to synthetic pH buffers in use in the analytical and bioanalytical laboratory, the suggested approach is eminently suitable to be extended to the analysis of factors which modulate the buffer capacity of natural pH buffers as are most biological fluids (e.g., blood).

The suggested procedure is fundamentally based on the idea of representing a pH buffer (or a biological fluid) with a matrix which is built in a MS Excel sheet supported by a custom functions library which is made available as Visual Basic Application code text in the Appendix to this paper and as ready to use **myBuffers.xlsm** file in the Associated Content section.

For use of VB code, copy code from [Table 6](#) in Appendix at the end of this paper. Then, open MS Excel and in the **Developer** tab in the group **Code** click **VisualBasic** to open the **VisualBasic Editor**. Here, extend the **Insert** menu and select **Module** to insert a VB module. In the empty VB module past the copied code and, from the **File** menu exit the VB editor and return to Excel. Save your Excel file as **myBuffers.xlsm** for future use and for storing your elaborations.

After this, in the active Excel sheet are available a number of custom functions which are used much in the same way as embedded Excel functions and whose significance will be explained in the following.

For help on topics concerning use of VB and custom functions in MS Excel a readily available and best source of information is the Microsoft Office support (<https://support.office.com/en-nz/>).

2. Background Matters

2.1. Basic Acid-Base Chemistry Frame

Acids and/or bases and/or ionic salts are the matter from which pH buffers are made.

In the following, a group of chemical species which only differ in the number of bonded protons will be mentioned as an AB group (which is shorthand for Acid-Base group).

For instance, the group of species (H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}) constitutes an AB group which will be called phosphoric acid AB group.

Obviously, couples of species which belong to the same AB group may be conjugate if they differ for a single proton or non-conjugate if they differ by more than a single proton.

In an AB group there are as many conjugate couples as the number of species minus one. For instance the three conjugate pairs of the phosphoric acid (four species) AB group are: $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$, $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$.

For each conjugate couple in an AB group is defined an *acid dissociation constant* which connects species within the conjugate couple and which for convenience is usually expressed as a $\text{pK}_{a(i)}$.

By the way of example, three acid dissociation constants symbolized by pK_{a1} ($\text{H}_3\text{PO}_4 \rightarrow \text{H}_2\text{PO}_4^-$), pK_{a2} ($\text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-}$) and pK_{a3} ($\text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-}$) are associated to the phosphoric acid AB group

In abstract, AB groups may exist which contain from one to a large number of conjugate couples. However, for our purposes it will be sufficient to consider AB groups which contain up to four conjugate couples (or up to five chemical species).

An AB group may be introduced into a solution in a variety of ways. For instance, the laboratory operations of dissolving H_3PO_4 or NaH_2PO_4 or K_2HPO_4 or $(\text{NH}_4)_3\text{PO}_4$ in water, all transfer into the resulting solution the AB group of phosphoric acid.

A *group concentration*, C_g M, is associated to each AB group into a described solution.

An AB group concentration is an analytical datum which is deduced from the list and amounts of substances used to prepare a given solution (or from analysis of a biological fluid). For example, if 0.1 moles of Na_2HPO_4 are transferred to 1 litre of solution, the phosphoric acid AB group concentration will be $C_g = 0.1$ M. However, if 0.1 moles of Na_2HPO_4 and 0.1 moles of H_3PO_4 are concurrently dissolved in 1 litre of solution the phosphoric acid AB group concentration will be $C_g = 0.2$ M.

Regardless of the way an AB group is transferred to the solution, each species, S_i , belonging to the group will be present at equilibrium into the solution at a molar equilibrium concentration $[S_i]$.

By consequence, into a given solution, species within each AB group are related through a *mass balance relation*: $C_g = \sum_i [S_i]$ (which, for example, instantiate to $C_g = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$ for the phosphoric acid AB group).

It is useful to relate all real AB groups with the same number of conjugate couples to an abstract AB group which can be used as a representative surrogate for discussing general properties and relations which do not

depend on the particular chemical nature of species within the group.

In the following, we shall make reference to the four abstract AB groups presented in Table 1.

Symbols for abstract species in abstract AB groups have been selected, as far as possible, to be mnemonic. For instance letter <F> which appears in AB group (HHHFF, HHHF, HHF, HF, F) is the first letter in number <Four> which is the number of conjugate couples in this group.

In any of the abstract AB groups there is an acid species, which coincides with the most protonated species (e.g., HA, HHD, etc.) and a basic species which coincides with the least protonated species (e.g., A, D, etc.). Species which are both acid and basic are amphiprotic species which belong to two different conjugate couples (e.g., HD, HHT, HT, HHHF, etc.). Charges on species have been omitted for simplicity but, obviously, charge on each species in an AB group becomes more negative with decreasing bonded protons.

By assumption, a real Acid-Base group will always match one of the abstract groups in Table 1 and, furthermore, there is for each species in the real AB group a matching species in the corresponding abstract group.

By the way of example, the real carbonic acid AB group (H_2CO_3 , HCO_3^- , CO_3^{2-}) matches (HHD, HD, D) abstract group. Furthermore, H_2CO_3 matches HHD, HCO_3^- matches HD and CO_3^{2-} matches D. H_2CO_3 is an acid, CO_3^{2-} is a base and HCO_3^- is an amphiprotic species belonging to both couples $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$.

2.2. Buffer Capacity Basic Topics

The *buffer capacity* of a pH buffer is generally indicated with the Greek symbol *eta*, η , and carries the dimensions of a molar concentration.

Eta is, by purpose, defined in order to express quantitatively the capacity of the pH buffer to resist to chemical perturbations tending to change its native pH.

In fact, the buffer capacity, η , is defined operationally via a thought experiment in which a very small amount of a strong base (e.g., NaOH) is added to the buffer. The added NaOH will, obviously, increase the NaOH molar concentration, C_{NaOH} , into the buffer by a very small amount, δC_{NaOH} , and, concurrently, it will produce a very small increase, δpH , of its pH.

Assuming that δC_{NaOH} and δpH have been measured, the buffer capacity of the tested buffer is calculated by relation (1):

$$\eta = \frac{\delta C_{\text{NaOH}}}{\delta \text{pH}} \quad (1)$$

Table 1. Abstract Acid-Base groups with one to four conjugate species used as surrogates of real AB groups. Species within a given AB group differ in number of bonded protons and charge, although charges have been omitted for simplicity

Number of conjugate couples	Abstract AB Groups and Species (charges omitted)	Symbol for acid dissociation constants
1	(HA, A)	pK_a
2	(HHD, HD, D)	$\text{pK}_{a1}, \text{pK}_{a2}$
3	(HHHT, HHT, HT, T)	$\text{pK}_{a1}, \text{pK}_{a2}, \text{pK}_{a3}$
4	(HHHFF, HHHF, HHF, HF, F)	$\text{pK}_{a1}, \text{pK}_{a2}, \text{pK}_{a3}, \text{pK}_{a3}$

Relation (1) is usually interpreted to signify that *eta* coincides with the increase in the concentration of strong base necessary for increasing the pH of the tested buffer of one unity, although this interpretation is somewhat misleading. In fact, this is easily misunderstood to signify that if, for instance, we want to increase the pH of a given buffer of one unity, we should increase the NaOH concentration in the buffer of an amount, ΔC_{NaOH} , equal to *eta*.

Nevertheless, theoretical interpretation of the above thought experiment which defines the buffer capacity shows that *eta* is a function of the pH, $\eta(\text{pH})$, of the tested buffer.

It follows that in order to increase the pH of a given buffer of one unity it will be necessary to perform a change of C_{NaOH} , ΔC_{NaOH} , which is not simply equal to *eta* but is given by equation (2):

$$\Delta C_{\text{NaOH}} = \int_{\text{pH}}^{\text{pH}+1} \eta(\text{pH}) \delta \text{pH}. \quad (2)$$

By the way of example, a 0.1 M solution of a strong acid (e.g., HCl) has pH = 1 and buffer capacity equal to its concentration multiplied by 2.3, i.e., $\eta = 0.23$ M. Suppose that, by adding NaOH, we want to increase the pH of the 0.1 M HCl solution of one unity so that the final pH is two. A misinterpretation of definition (1) would convey the idea that we should add NaOH so that $\Delta C_{\text{NaOH}} = \eta = 0.23$ M. This prediction is clearly wrong since evidently we obtain an alkaline pH if, in the initial 0.1 M HCl solution, the NaOH concentration is increased up to 0.23 M.

In fact, according to (2), we have:

$$\begin{aligned} \Delta C_{\text{NaOH}} &= \int_{\text{pH}=1}^{\text{pH}=2} \eta(\text{pH}) \delta \text{pH} = \\ &= \int_{\text{pH}=1}^{\text{pH}=2} 2.3 \cdot 10^{-\text{pH}} \delta \text{pH} = 0.090 \text{ M} \end{aligned} \quad (3)$$

Please note that in equation (3) we have used the fact that $\eta(\text{pH}) = 2.3 \cdot 10^{-\text{pH}}$ for the solution of a strong acid.

Apart from that, the abstract function $\eta(\text{pH})$, which expresses the buffer capacity of a given buffer as a function of its pH, has a specific mathematical form for each buffer and it embodies as parameters the group concentrations and acid dissociation constants of all Acid-Base groups into the buffer. So much so that it does not exist a universal function $\eta(\text{pH})$ which can be applied to all buffers. Because of this, knowledge of the pH of a buffer will not be, in general, sufficient to calculate *eta* (unless one does know explicitly the mathematical function corresponding to $\eta(\text{pH})$ for the considered buffer).

It is for overcoming the difficulty of obtaining explicitly $\eta(\text{pH})$ for each buffer that we use a matrix representation of the buffer. Furthermore, we will also resort to a graphical presentation of this matrix to enlighten its significance and as a guide in our elaborations.

Nevertheless, for a number of reasons that will become apparent in the following, it is more convenient and simpler to evaluate a property which is proportional to *eta*, and which we shall call *signed buffer capacity* since we generally use the symbol η' (*eta-primed*) to indicate this property.

The relation between η and η' is very simple and is

formally expressed by equation (4):

$$\eta(\text{pH}) = 2.303 \times \eta'(\text{pH}). \quad (4)$$

Evidently, the capacity of calculating *eta-primed* is equivalent to the ability of calculating *eta*.

In most cases, in order to avoid repeated conversion of *eta'* to *eta*, it is possible to use throughout η' as a measure of the buffer capacity and to perform conversion only if the evaluation of the conventional buffer capacity (i.e., *eta*) of a buffer is explicitly required.

Using *eta'*, instead of *eta*, as a measure of the buffer capacity is analogous to using ml instead of litre as a measure of volume.

For instance, by substituting *eta* with *eta'* in equation (2) we obtain the equivalent relation (5):

$$\Delta C_{\text{NaOH}} = 2.3 \int_{\text{pH}}^{\text{pH}+1} \eta'(\text{pH}) \delta \text{pH}. \quad (5)$$

Analogously, as mentioned above, $\eta(\text{pH}) = 2.3 \cdot 10^{-\text{pH}}$, for the solution of a strong acid and this implies that $\eta'(\text{pH}) = 10^{-\text{pH}}$.

In practice, the merit of using η' instead of η consists in removing from the scenario the factor 2.303 which is the conversion factor from decimal to natural logarithm and which appears repeatedly in the mathematical development of the buffer capacity.

In the hypothetical case that the explicit form of function $\eta'(\text{pH})$ is known, all we should do to calculate the signed buffer capacity of a given buffer is to insert the pH value of the buffer, pH_b , into $\eta'(\text{pH})$ function in order to calculate the $\eta'(\text{pH}_b)$ value, which represents its signed buffer capacity. For instance, a $10^{-3.0}$ M solution of HCl has pH = 3.0 and a signed buffer capacity $\eta'(3.0) = 10^{-\text{pH}} = 10^{-3.0}$ M.

However, we can also calculate values of function $\eta'(\text{pH})$ at a number of arbitrary pH, so much so that, in the suggested approach, we shall calculate an array of values of $\eta'(\text{pH})$ on the whole range of pH from 0 to 14. The desired buffer capacity of the considered buffer is obtained selecting from the array of calculated values of $\eta'(\text{pH})$ point corresponding to the buffer pH.

Although, at first sight, this may appear odd and analogous to lifting ants with a bulldozer, calculation of a full set of *eta'* values on the range $0 < \text{pH} < 14$ will allow us to incorporate curve $\eta'(\text{pH})$ into the graphical representation of the buffer matrix and this is very enlightening when, as in using *universal pH buffers*, a dynamic view of the buffer capacity is required.

3. Discussion and Results

3.1. MyBufferMatrix

In a MS Excel sheet (which we shall call **myBufferSheet**) a matrix representing the considered buffer (which we shall call **myBufferMatrix**) can be created in a matter of minutes using custom functions presented in Table 2, from which it can be seen that most custom functions are named according to formulas for abstract species in AB abstract groups of Table 1.

Table 2. List of custom functions employed for building myBufferMatrix. Each function matches one of the species of abstract Acid-Base groups in Table 1 and carries within round brackets arguments needed to calculate values of the function

#	FunctionName(argument1, argument2, ...)	Returned value
1	pH(StartCellRef, myStepValue, myEndValue)	Array of pH values
2	Acid_H(pH_Ref)	[H ⁺]
3	Base_OH(Acid_H_Ref, pKw)	[OH ⁻]
4	Acid_HA(Acid_H_Ref, C _g , pKa)	[HA] of couple HA/A
5	Base_A(Acid_H_Ref, C _g , pKa)	[A] of couple HA/A
6	Acid_HHD(Acid_H_Ref, C _g , pKa1, pKa2)	[H ₂ D] of couple HHD/HD
7	Amp_HD(Acid_H_Ref, C _g , pKa1, pKa2)	[HD] of couple HD/D
8	Base_D(Acid_H_Ref, C _g , pKa1, pKa2)	[D] of couple HD/D
9	Acid_HHHT(Acid_H_Ref, C _g , pKa1, pKa2, pKa3)	[H ₃ T] of couple HHHT/HHT
10	Amp_HHT(Acid_H_Ref, C _g , pKa1, pKa2, pKa3)	[H ₂ T] of couples HHHT/HHT&HHT/HT
11	Amp_HT(Acid_H_Ref, C _g , pKa1, pKa2, pKa3)	[HT] of couples HHT/HT&HT/T
12	Base_T(Acid_H_Ref, C _g , pKa1, pKa2, pKa3)	[T] of couple HT/T
13	Acid_HHHHF(Acid_H_Ref, C _g , pKa1, pKa2, pKa3, pKa4)	[H ₄ F] of couple HHHHF/HHHF
14	Amp_HHHF(Acid_H_Ref, C _g , pKa1, pKa2, pKa3, pKa4)	[H ₃ F] of couples HHHHF/HHHF&HHHF/HHF
15	Amp_HHF(Acid_H_Ref, C _g , pKa1, pKa2, pKa3, pKa4)	[H ₂ F] of couples HHHF/HHF&HHF/HF
16	Amp_HF(Acid_H_Ref, C _g , pKa1, pKa2, pKa3, pKa4)	[HF] of couples HHF/HF&HF/F
17	Base_F(Acid_H_Ref, C _g , pKa1, pKa2, pKa3, pKa4)	[F] of couple HF/F

A self-explicative name has been used for each function and its arguments which should make clear what the function is for and what data have to be provided in order to calculate values from the function.

Names start with one of the prefixes: <Acid_>, <Base_> or <Amp_> (which are related to the Acid-Base nature of the species for which the function must be used). The prefix is then followed by the formula which relates the function to one of abstract species in Table 1.

Although functions in Table 2 are related through their names to abstract species, in practice, each function is meant to be applied to any real chemical species which matches the abstract species appearing in its name (remembering that any real AB group matches a surrogate abstract group in Table 1, and for each species within the real AB group there is a matching species in the corresponding surrogate abstract group).

Application of the matching function from Table 2 to a chemical species, S_i, present in the considered buffer, returns its molar equilibrium concentration, i.e., [S_i] (as indicated in the third column of Table 2).

For this, to each function must be provided as arguments an arbitrary value for the proton concentration [H⁺], an arbitrary value for the group concentration, C_g, and from one to four pK_{a(i)} whose values depend on the specific chemical nature of the real AB group to which species S_i belongs.

For instance, function # 9 named <Acid_HHHT> is intended to be applied to the acid species of any AB group with three conjugate couples (e.g., to H₃PO₄) and returns [HHHT] (e.g., [H₃PO₄]). It takes as arguments a reference to a cell which contains an [H⁺] value, the actual group concentration C_g M of the real AB group into the buffer, and the actual values of pK_{a1}, pK_{a2} and pK_{a3} connecting conjugate species within the group.

For the matrix representation of a given buffer, for each species present into the buffer, a matching function from Table 2 is selected and applied to the species in order to calculate its equilibrium concentration at a number of preselected arbitrary pH values, which are initially entered in a column of myBufferSheet.

This arbitrary array of pH values is created in a column of myBufferSheet as the first step of the process of building myBufferMatrix applying function <pH> (#1 in Table 2). Function <pH> (whose use is explained in detail below) requires as arguments, to be specified by the user, a starting pH, an ending pH and the spacing between successive pH values. In the following we shall use an array of 281 pH values between 0 and 14 spaced 0.05 pH units.

Function <Acid_H> (#2 in Table 2) is used after function <pH> and creates in a second column of myBufferSheet, an array of [H⁺] values from the arbitrary array of pH. The elements of this array of [H⁺] values are passed by reference as the first argument (named <Acid_H_Ref>) to functions from #3 to #17 in Table 2.

Function <Base_OH> (#3 in Table 2) is simply employed to create in a third column of myBufferSheet an array of [OH⁻] values from the previously created [H⁺] array and from the value for the ionic product of water, pK_w, entered by the user.

Functions <pH>, <Acid_H> and <Base_OH> are used always in the same repetitive way for building the matrix representing any buffer and a typical procedure may be as described below.

Column A of myBufferSheet is left empty, to be used for annotations, and the array of pH values is created by default in column B of myBufferSheet.

Firstly, label B_pH is typed in cell B1. In order to create, in column B_pH, 281 pH values between pH = 0.00 and

pH = 14.00, spaced 0.05 pH units, type 0.00 in cell B2 and in cell B3 enter function <pH>. In the control box **Functions Arguments** enter as the first argument, named <StartCellRef>, a reference to cell B2 containing the starting pH value. Click OK and extend the function up to cell B282 so that column B_pH is filled with pH values (with pH = 14 in cell B282). By this process a definitive pH value is attributed to each row of myBufferSheet so much so that we can refer to a row by mentioning its pH.

In cells C1 and D1 type, respectively, labels [C_H⁺] and [D_OH] and in cells C2 and D2 insert functions <Acid_H> and <Base_OH>, respectively, and enter in the **Functions Arguments** control box required arguments (i.e., a reference to cell B2 for function <Acid_H> and a reference to cell C2 and a pK_w value (e.g., 14.00) for function <Base_OH>).

Now select both cells C2 and D2 and extend entered functions up to row 282.

Table 3. Data required for building myBufferMatrix for a 0.05 M ammonium phosphate dibasic ((NH₄)₂HPO₄) buffer. Letters before each species indicate column of row 1 of myBufferSheet in which the label of species must be transferred. Acid dissociation constants are at 25°C and zero ionic strength [5]

Acid-Base groups	Group Concentration	pK _{a(i)} (25°C)
(E_NH ₄ ⁺ , F_NH ₃)	0.1 M	pK _a = 9.25
(G_H ₃ PO ₄ , H_H ₂ PO ₄ ⁻ , I_HPO ₄ ²⁻ , J_PO ₄ ³⁻)	0.05 M	pK _{a1} = 2.15, pK _{a2} = 7.20, pK _{a3} = 12.15

A	B	C	D	E	F	G	H	I	J	K	L	M
1	B_pH	[C_H ⁺]	[D_OH]	[E_NH ₄ ⁺]	[F_NH ₃]	[G_H ₃ PO ₄]	[H_H ₂ PO ₄ ⁻]	[I_HPO ₄ ²⁻]	[J_PO ₄ ³⁻]	K_CB	L_eta'	M_jeta
2	0.00	1.00E+00	1.00E-14	1.00E-01	5.62E-11	4.96E-02	3.51E-04	2.22E-11	1.57E-23	1.10E+00	1.00E+00	0.000E+00
3	0.05	8.91E-01	1.12E-14	1.00E-01	6.31E-11	4.96E-02	3.94E-04	2.79E-11	2.22E-23	9.91E-01	8.92E-01	2.178E-01
4	0.10	7.94E-01	1.26E-14	1.00E-01	7.08E-11	4.96E-02	4.42E-04	3.51E-11	3.13E-23	8.94E-01	7.95E-01	3.093E-01
5	0.15	7.08E-01	1.41E-14	1.00E-01	7.94E-11	4.95E-02	4.95E-04	4.41E-11	4.41E-23	8.07E-01	7.08E-01	3.909E-01
41	1.95	1.12E-02	8.91E-13	1.00E-01	5.01E-09	3.07E-02	1.93E-02	1.09E-07	6.86E-18	9.19E-02	2.31E-02	1.068E+00
42	2.00	1.00E-02	1.00E-12	1.00E-01	5.62E-09	2.93E-02	2.07E-02	1.31E-07	9.26E-18	8.93E-02	2.21E-02	1.070E+00
43	2.05	8.91E-03	1.12E-12	1.00E-01	6.31E-09	2.79E-02	2.21E-02	1.57E-07	1.24E-17	8.68E-02	2.12E-02	1.073E+00
44	2.10	7.94E-03	1.26E-12	1.00E-01	7.08E-09	2.64E-02	2.36E-02	1.87E-07	1.67E-17	8.44E-02	2.04E-02	1.075E+00
45	2.15	7.08E-03	1.41E-12	1.00E-01	7.94E-09	2.50E-02	2.50E-02	2.23E-07	2.23E-17	8.21E-02	1.96E-02	1.077E+00
46	2.20	6.31E-03	1.58E-12	1.00E-01	8.91E-09	2.36E-02	2.64E-02	2.64E-07	2.97E-17	7.99E-02	1.88E-02	1.080E+00
47	2.25	5.62E-03	1.78E-12	1.00E-01	1.00E-08	2.21E-02	2.79E-02	3.13E-07	3.94E-17	7.78E-02	1.80E-02	1.082E+00
48	2.30	5.01E-03	2.00E-12	1.00E-01	1.12E-08	2.07E-02	2.93E-02	3.69E-07	5.21E-17	7.57E-02	1.71E-02	1.084E+00
141	6.95	1.12E-07	8.91E-08	9.95E-02	4.99E-04	5.07E-07	3.20E-02	1.80E-02	1.14E-07	3.15E-02	1.20E-02	1.128E+00
142	7.00	1.00E-07	1.00E-07	9.94E-02	5.59E-04	4.33E-07	3.07E-02	1.93E-02	1.37E-07	3.01E-02	1.24E-02	1.129E+00
143	7.05	8.91E-08	1.12E-07	9.94E-02	6.27E-04	3.69E-07	2.93E-02	2.07E-02	1.65E-07	2.86E-02	1.28E-02	1.130E+00
144	7.10	7.94E-08	1.26E-07	9.93E-02	7.03E-04	3.13E-07	2.79E-02	2.21E-02	1.97E-07	2.72E-02	1.30E-02	1.132E+00
145	7.15	7.08E-08	1.41E-07	9.92E-02	7.88E-04	2.64E-07	2.64E-02	2.36E-02	2.36E-07	2.56E-02	1.32E-02	1.133E+00
146	7.20	6.31E-08	1.58E-07	9.91E-02	8.83E-04	2.23E-07	2.50E-02	2.50E-02	2.81E-07	2.41E-02	1.34E-02	1.135E+00
147	7.25	5.62E-08	1.78E-07	9.90E-02	9.90E-04	1.87E-07	2.36E-02	2.64E-02	3.33E-07	2.26E-02	1.34E-02	1.137E+00
148	7.30	5.01E-08	2.00E-07	9.89E-02	1.11E-03	1.57E-07	2.21E-02	2.79E-02	3.94E-07	2.10E-02	1.34E-02	1.138E+00
149	7.35	4.47E-08	2.24E-07	9.88E-02	1.24E-03	1.31E-07	2.07E-02	2.93E-02	4.64E-07	1.95E-02	1.34E-02	1.140E+00
150	7.40	3.98E-08	2.51E-07	9.86E-02	1.39E-03	1.09E-07	1.93E-02	3.07E-02	5.45E-07	1.79E-02	1.32E-02	1.141E+00
151	7.45	3.55E-08	2.82E-07	9.84E-02	1.56E-03	9.02E-08	1.80E-02	3.20E-02	6.39E-07	1.64E-02	1.31E-02	1.143E+00
159	7.85	1.41E-08	7.08E-07	9.62E-02	3.83E-03	1.82E-08	9.15E-03	4.09E-02	2.05E-06	5.32E-03	1.12E-02	1.152E+00
160	7.90	1.26E-08	7.94E-07	9.57E-02	4.28E-03	1.48E-08	8.32E-03	4.17E-02	2.34E-06	4.04E-03	1.10E-02	1.155E+00
161	7.95	1.12E-08	8.91E-07	9.52E-02	4.77E-03	1.20E-08	7.55E-03	4.24E-02	2.68E-06	2.77E-03	1.10E-02	1.156E+00
162	8.00	1.00E-08	1.00E-06	9.47E-02	5.32E-03	9.66E-09	6.84E-03	4.32E-02	3.06E-06	1.51E-03	1.09E-02	1.157E+00
163	8.05	8.91E-09	1.12E-06	9.41E-02	5.94E-03	7.79E-09	6.19E-03	4.38E-02	3.48E-06	1.20E-03	1.10E-02	1.159E+00
164	8.10	7.94E-09	1.26E-06	9.34E-02	6.61E-03	6.27E-09	5.59E-03	4.44E-02	3.96E-06	-1.02E-03	1.11E-02	1.160E+00
165	8.15	7.08E-09	1.41E-06	9.26E-02	7.36E-03	5.04E-09	5.04E-03	4.50E-02	4.50E-06	-2.32E-03	1.14E-02	1.161E+00
166	8.20	6.31E-09	1.58E-06	9.18E-02	8.18E-03	4.05E-09	4.54E-03	4.54E-02	5.10E-06	-3.64E-03	1.17E-02	1.163E+00
167	8.25	5.62E-09	1.78E-06	9.09E-02	9.09E-03	3.25E-09	4.09E-03	4.59E-02	5.78E-06	-5.01E-03	1.20E-02	1.164E+00
181	8.95	1.12E-09	8.91E-06	6.66E-02	3.34E-02	1.38E-10	8.73E-04	4.91E-02	3.10E-05	-3.25E-02	2.31E-02	1.192E+00
182	9.00	1.00E-09	1.00E-05	6.40E-02	3.60E-02	1.10E-10	7.80E-04	4.92E-02	3.48E-05	-3.52E-02	2.39E-02	1.195E+00
183	9.05	8.91E-10	1.12E-05	6.13E-02	3.87E-02	8.76E-11	6.96E-04	4.93E-02	3.91E-05	-3.80E-02	2.45E-02	1.198E+00
184	9.10	7.94E-10	1.26E-05	5.85E-02	4.15E-02	6.97E-11	6.21E-04	4.93E-02	4.40E-05	-4.09E-02	2.49E-02	1.201E+00
185	9.15	7.08E-10	1.41E-05	5.57E-02	4.43E-02	5.54E-11	5.54E-04	4.94E-02	4.94E-05	-4.38E-02	2.53E-02	1.204E+00
186	9.20	6.31E-10	1.58E-05	5.29E-02	4.71E-02	4.41E-11	4.95E-04	4.95E-02	5.55E-05	-4.67E-02	2.55E-02	1.206E+00
187	9.25	5.62E-10	1.78E-05	5.00E-02	5.00E-02	3.50E-11	4.41E-04	4.95E-02	6.23E-05	-4.96E-02	2.55E-02	1.209E+00
188	9.30	5.01E-10	2.00E-05	4.71E-02	5.29E-02	2.79E-11	3.93E-04	4.95E-02	7.00E-05	-5.26E-02	2.54E-02	1.212E+00
189	9.35	4.47E-10	2.24E-05	4.43E-02	5.57E-02	2.21E-11	3.51E-04	4.96E-02	7.86E-05	-5.55E-02	2.51E-02	1.215E+00
190	9.40	3.98E-10	2.51E-05	4.15E-02	5.85E-02	1.76E-11	3.13E-04	4.96E-02	8.82E-05	-5.83E-02	2.47E-02	1.218E+00
191	9.45	3.55E-10	2.82E-05	3.87E-02	6.13E-02	1.40E-11	2.79E-04	4.96E-02	9.90E-05	-6.11E-02	2.41E-02	1.221E+00
192	9.50	3.16E-10	3.16E-05	3.60E-02	6.40E-02	1.11E-11	2.49E-04	4.96E-02	1.11E-04	-6.39E-02	2.34E-02	1.224E+00
193	9.55	2.82E-10	3.55E-05	3.34E-02	6.66E-02	8.83E-12	2.22E-04	4.97E-02	1.25E-04	-6.65E-02	2.26E-02	1.226E+00
242	12.00	1.00E-12	1.00E-02	1.78E-04	9.98E-02	6.55E-17	4.64E-07	2.93E-02	2.07E-02	-1.21E-01	2.23E-02	1.290E+00
243	12.05	8.91E-13	1.12E-02	1.58E-04	9.98E-02	4.96E-17	3.94E-07	2.79E-02	2.21E-02	-1.22E-01	2.37E-02	1.293E+00
244	12.10	7.94E-13	1.26E-02	1.41E-04	9.99E-02	3.73E-17	3.33E-07	2.64E-02	2.36E-02	-1.23E-01	2.52E-02	1.296E+00
245	12.15	7.08E-13	1.41E-02	1.26E-04	9.99E-02	2.81E-17	2.61E-07	2.50E-02	2.50E-02	-1.25E-01	2.68E-02	1.299E+00
246	12.20	6.31E-13	1.58E-02	1.12E-04	9.99E-02	2.10E-17	2.36E-07	2.36E-02	2.64E-02	-1.26E-01	2.84E-02	1.302E+00
247	12.25	5.62E-13	1.78E-02	9.99E-05	9.99E-02	1.57E-17	1.97E-07	2.21E-02	2.79E-02	-1.28E-01	3.02E-02	1.306E+00
248	12.30	5.01E-13	2.00E-02	8.90E-05	9.99E-02	1.17E-17	1.65E-07	2.07E-02	2.93E-02	-1.29E-01	3.22E-02	1.309E+00
278	13.80	1.58E-14	6.31E-01	2.82E-06	1.00E-01	6.16E-22	2.75E-10	1.09E-03	4.89E-02	-1.49E-01	6.32E-01	1.975E+00
279	13.85	1.41E-14	7.08E-01	2.51E-06	1.00E-01	4.37E-22	2.19E-10	9.78E-04	4.90E-02	-1.49E-01	7.09E-01	2.057E+00
280	13.90	1.26E-14	7.94E-01	2.24E-06	1.00E-01	3.10E-22	1.74E-10	8.74E-04	4.91E-02	-1.49E-01	7.95E-01	2.148E+00
281	13.95	1.12E-14	8.91E-01	2.00E-06	1.00E-01	2.20E-22	1.39E-10	7.80E-04	4.92E-02	-1.49E-01	8.92E-01	2.251E+00
282	14.00	1.00E-14	1.00E+00	1.78E-06	1.00E-01	1.56E-22	1.10E-10	6.96E-04	4.93E-02	-1.49E-01	1.00E+00	2.366E+00
1	B_pH	[C_H ⁺]	[D_OH]	[E_NH ₄ ⁺]	[F_NH ₃]	[G_H ₃ PO ₄]	[H_H ₂ PO ₄ ⁻]	[I_HPO ₄ ²⁻]	[J_PO ₄ ³⁻]	K_CB	L_eta'	M_jeta

Figure 1. myBufferMatrix for 0.05 M ammonium phosphate dibasic buffer (pH = 8.05) at 25 °C

Amongst many others, we take as leading example a 0.05 M ammonium phosphate dibasic buffer made up by transferring 6.6 g of $(\text{NH}_4)_2\text{HPO}_4$ to 1 litre of solution. For this buffer Table 3 synthesizes the relevant data.

Please note that, for reference, we have added to the formula of each species a letter indicating column of myBufferSheet in which the symbol is transferred as a label.

The symbol of each species is transferred to row 1 in the indicated column and enclosed within square brackets denoting molar concentrations.

In the case of the ammonium phosphate dibasic buffer, labels in cells E1, F1, G1, H1, I1, J1 of myBufferSheet will be, respectively, $[\text{E_NH}_4^+]$, $[\text{F_NH}_3]$, $[\text{G_H}_3\text{PO}_4]$, $[\text{H_H}_2\text{PO}_4^-]$, $[\text{I_HPO}_4^{2-}]$, $[\text{J_PO}_4^{3-}]$.

Now, insert in myBufferSheet in cell of row 2 under labels $[\text{E_NH}_4^+]$, $[\text{F_NH}_3]$, $[\text{G_H}_3\text{PO}_4]$, $[\text{H_H}_2\text{PO}_4^-]$, $[\text{I_HPO}_4^{2-}]$, $[\text{J_PO}_4^{3-}]$ the matching function selected from custom functions library using data in Table 3 to specify required arguments. Finally, select simultaneously cells from E2 to J2 and extend the entered functions up to row 282.

This operation will fill myBufferSheet with numbers and expose a matrix whose elements coincide with myBufferSheet cells and which will be the basis of all successive elaborations.

A number of selected rows of myBufferMatrix for the 0.05 M $(\text{NH}_4)_2\text{HPO}_4$ buffer are presented for reference in Figure 1.

The content of each cell of myBufferMatrix, which by construction belongs to a row of specified pH, is interpreted as the equilibrium molar concentration of species indicated in the column label calculated, with entered group concentration and $\text{pK}_{a(i)}$, at the pH of its row. For instance, in Figure 1 there are 281 equilibrium concentrations calculated for each of the eight species in the ammonium phosphate dibasic buffer at pH values exposed in column B_pH.

Now, to begin, if you do not know what it is the native pH of your buffer you can easily calculate it by entering suitable but simple code in the first empty column of myBufferMatrix (column K of myBufferMatrix in Figure 1).

Firstly, type label K_CB (shorthand for Charge Balance) in cell K1 and in cell K2 type the following code:

$$\text{K_CB} \rightarrow \text{Cell K2:} = \text{C2} + \text{E2} - \text{H2} - 2 * \text{I2} - 3 * \text{J2}$$

Finally, extend code in cell K2 up to cell K282 so that column K_CB is filled with numbers which ranges from positive to negative (see Figure 1). Explore values in column K_CB and select row which contains the value closest to zero (either positive or negative). The selected row (row 163) corresponds to the native pH of the buffer (pH = 8.05) and each cell of row 163 corresponds to the equilibrium molar concentration into the buffer of the species indicated by the column label.

In Figure 1 a yellow background has been applied to row 163 which exposes the equilibrium composition of the native 0.05 M $(\text{NH}_4)_2\text{HPO}_4$ buffer.

To see what has been calculated in column K_CB, consider that the charge balance in the solution imposes the following relation (6) between concentrations of charged species into the solution:

$$[\text{E_NH}_4^+] + [\text{C_H}^+] = [\text{D_OH}^-] + [\text{H_H}_2\text{PO}_4^-] + 2[\text{I_HPO}_4^{2-}] + 3[\text{J_PO}_4^{3-}] \quad (6)$$

It is quite apparent that code entered in column K_CB simply calculates the difference between the left side and right side members of charge balance (6) at each of the 281 pH values in column B_pH. Row 163 has been extracted simply because it is the row in which the charge balance equation is best verified because in cell K163 we see that the difference between the two members of equation (6) is only $2.5 \cdot 10^{-4}$ M.

3.2. From myBufferMatrix to myBufferPlot

Assume that in myBufferSheet we have created myBufferMatrix and found, on the basis of the charge balance relation, row corresponding to the native pH of the buffer and which exposes equilibrium concentrations of all specie in the buffer.

The procedure for creating a useful graphical representation of myBufferMatrix is exactly the same, regardless of the complexity of the buffer at hand (and, then, on the size of myBufferMatrix) and it is best explained by using matrix representing 0.05 M ammonium phosphate dibasic buffer in Figure 1.

In myBufferSheet exposing matrix in Figure 1, click with the mouse to select column B_pH and drag selection up to column J_PO4³⁻ for selecting simultaneously all columns containing species.

On the **Insert** tab of Excel ribbon in the **Charts** group, select **Scatter** as type of graph and insert a dispersion graph without markers. In the very blink of an eye, one obtains plot in Figure 2A.

This plot is the most direct representation of the matrix, but it is not very useful since it is very difficult to interpret because the represented concentrations extend over a range of several orders of magnitude.

A most useful and suggestive representation is readily obtained by converting the y-axis in Figure 2A to a logarithmic scale.

For this, click anywhere in the chart for displaying the **Design**, **Layout**, and **Format** tabs in Excel ribbon. On the **Layout** tab, in the **Axes** group extend menu **Principal Vertical Axis** and select **Show with logarithmic scale**. This will produce myBufferPlot shown in Figure 2B which will be our support for calculating and interpreting the buffer capacity of the represented buffer.

By construction, each column of myBufferMatrix is converted to a curve in Figure 2B (except column B_pH which is used as the abscissa).

An obvious corollary of this is that each species into the buffer corresponds to a curve in myBufferPlot.

A fundamental step, for the intelligibility of myBufferPlot, is to attach to each curve a label which specifies the species represented by the curve.

Labels as those in Figure 2B, which coincide with columns' labels in myBufferMatrix, are hooked to curves with a few mouse clicks with the following procedure.

First select with the mouse a curve in myBufferPlot so that markers for data points appear on the curve. Then click again on the curve to select a single point of the data series. Finally, on the **Layout** tab in the group **Data**

Labels click **More Data Label Options** to open the control box **Format Data Labels** and add a label to the selected data point choosing as label type the name of the data series. Leave the control box open and select in turn a data point on each curve and add the name of each series as a data label to the corresponding curve.

Curves in myBufferPlot of Figure 2B are drawn in a (pH, log[...]) plane.

Symbol [...] represents the equilibrium concentration of any species in the represented buffer. In fact, the log[...] axis is a multi-tasking axis representing the y-coordinate of any of the curves drawn in the plot.

Labels of the y-axis, have the scientific format <1.E-##>. Figures after the exponential <E> symbol represent log[...]. For instance, label 1.E-4 indicates a value of -4 for log[...] on the y-logarithmic-axis.

Figure 2B is the visual version of the matrix representing 0.05 M ammonium phosphate dibasic buffer in Figure 1, from which one can see immediately the distribution, at any pH, of species in the solution.

In fact, since log[...] increases as the argument, [...], increases, we see that, at a given pH, the concentration of a species whose curve lies up in myBufferPlot is larger than the concentration of a species whose curve lies down.

For instance, at pH = 8.05 (which is the native pH of the 0.05 M $(\text{NH}_4)_2\text{HPO}_4$ buffer) NH_4^+ is the prevailing species and HPO_4^{2-} has a lower concentration because its curve lies under curve of NH_4^+ . Furthermore, at pH ≈ 8 , we see that $[\text{H}_2\text{PO}_4^-] \approx [\text{NH}_3] > [\text{PO}_4^{3-}] > [\text{H}_3\text{PO}_4] \approx [\text{OH}^-] > [\text{H}^+]$.

As a matter of fact exact values of the concentrations, if required, could be readily read from myBufferPlot by moving the mouse pointer to any selected point of any curve.

For our purposes, a very important aspect of myBufferPlot is the shape and slope of curves representing species into the solution.

MyBufferPlot of any buffer will always expose lines representing H^+ and OH^- which are invariant (since they derive from the invariant columns $C_{[\text{H}^+]}$ and $D_{[\text{OH}^-]}$ of myBufferMatrix) and have, respectively, slopes -1 and +1.

Curves of other species are, in general, constituted of two or more segments connected with a short curve.

One of the segments always approaches the horizontal direction and has slope close to zero. Either a segment of slope +1 or a segment of slope -1 is always present. Curves representing amphiprotic species have always all types of segments (i.e., segments approaching slopes +1, 0 and -1).

For instance, in Figure 2B the segment with non-zero slope of curve representing $[\text{NH}_4^+]$ has slope approaching -1 (as can be judged from the fact that it is parallel to the line of H^+).

On the contrary, the non-zero slope segment of curve representing $[\text{NH}_3]$ has slope approaching +1 (since it is parallel to the line of OH^-).

Curves representing two conjugated species always meet in a point which is very important and which will be called a *system point* [1,2,3].

A system point is by definition a point in which the equilibrium concentrations of the two conjugate species have equal concentrations and, by construction, it always fall at a x-axis coordinate which coincides with $\text{pK}_{a(i)}$ which connects the two conjugate species. In other words, a system point always fall at $\text{pH} = \text{pK}_{a(i)}$.

Vice versa, in myBufferPlot there are always as many system points as $\text{pK}_{a(i)}$ which connect species within Acid-Base groups present in the solution.

For instance, in Figure 2B there are four system points. The first system point falls at $\text{pH} = \text{pK}_{a1} = 2.15$, which is the first acid dissociation constant of phosphoric acid. System points at $\text{pH} = (7.20, 12.15, 9.25)$ coincide respectively with pK_{a2} and pK_{a3} of phosphoric acid and pK_a of ammonium ion.

Through a system point a segment of a curve (of slope ± 1) is connected to a segment of slope zero, so that the slope of the curve in a system point is ± 0.5 .

Rows corresponding to system points have been evidenced with a red background in Figure 1.

This dissection of curves in myBufferPlot is very important for the following discussion.

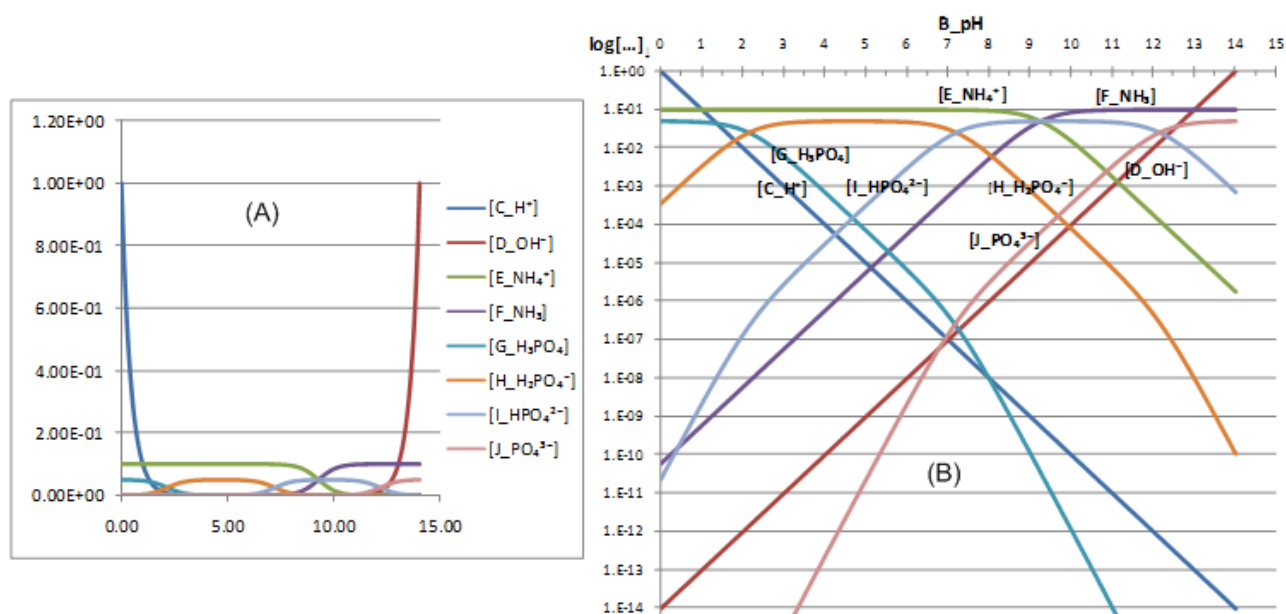


Figure 2. (A) myBufferPlot presented by MS Excel using data from myBufferMatrix in Figure 1. (B) Same as (A) after changing y-axis to a logarithm scale and adding labels for axes and curves

3.3. Evolution of myBufferMatrix and myBufferPlot

All the work for calculating the buffer capacity of a given buffer consists in constructing and entering in a column of myBufferMatrix (labelled<..._eta'>) a suitable formula which, on the basis of data in myBufferMatrix, will fill the column with values of the function η' (pH) appropriate for the solution at hand.

For brevity this formula will be mentioned as BC-Formula (*Buffer Capacity Formula*). The calculated content of the <..._eta'> column of myBufferMatrix can then be added as a curve to myBufferPlot so that by visual inspection of the η' (pH) curve we can judge if the correct BC-Formula has been entered and get a dynamic view of the buffer capacity.

In order to build in the formula bar of myBufferSheet exposing myBufferMatrix the BC-Formula, it is of the outmost importance to understand that the η' (pH) function is constituted of a number of additive terms [4].

For real AB groups employed in formulations of pH buffers, it is in general a very good approximation to assume that each conjugate AB couple into the buffer contributes an addend to the summation which expresses η' (pH).

An obvious corollary of this is that η' (pH) is made up of as many additive terms as are the number of conjugate Acid-Base couples into the buffer.

In an aqueous buffer there are always at least two conjugate Acid-Base pairs (i.e., H^+/H_2O and H_2O/OH^-). It follows that η' (pH) contains at least two terms which represent the contribution of water to the buffer capacity. The contribution of water to η' (pH), η' (pH)_w, is very simple and invariant.

We have the basic expression (7₁):

$$\eta'(\text{pH})_w = [C_H^+] + [D_OH^-]. \quad (7_1)$$

Then, firstly, to myBufferMatrix in Figure 1 we add a column labelled <L_eta'> and in a cell of row 2 under label <L_eta'> we enter code which calculates the contribution of water to the buffer capacity.

Equation (7₁) is readily converted to the following Excel code:

BC-Formula₁→Cell L2: = C2 + D2

Code in Cell L2 is then extended up to cell L282 so that column L_eta' is filled with numbers representing values of η' (pH)_w at each of the 271 pH values in column B_pH.

In order to follow graphically the evolution of the entered BC-Formula, we add to myBufferPlot, as a new data series named <L_eta'>, the calculated values of η' (pH)_w.

In the blink of an eye, myBufferPlot evolves from plot in Figure 2B to plot in Figure 3A.

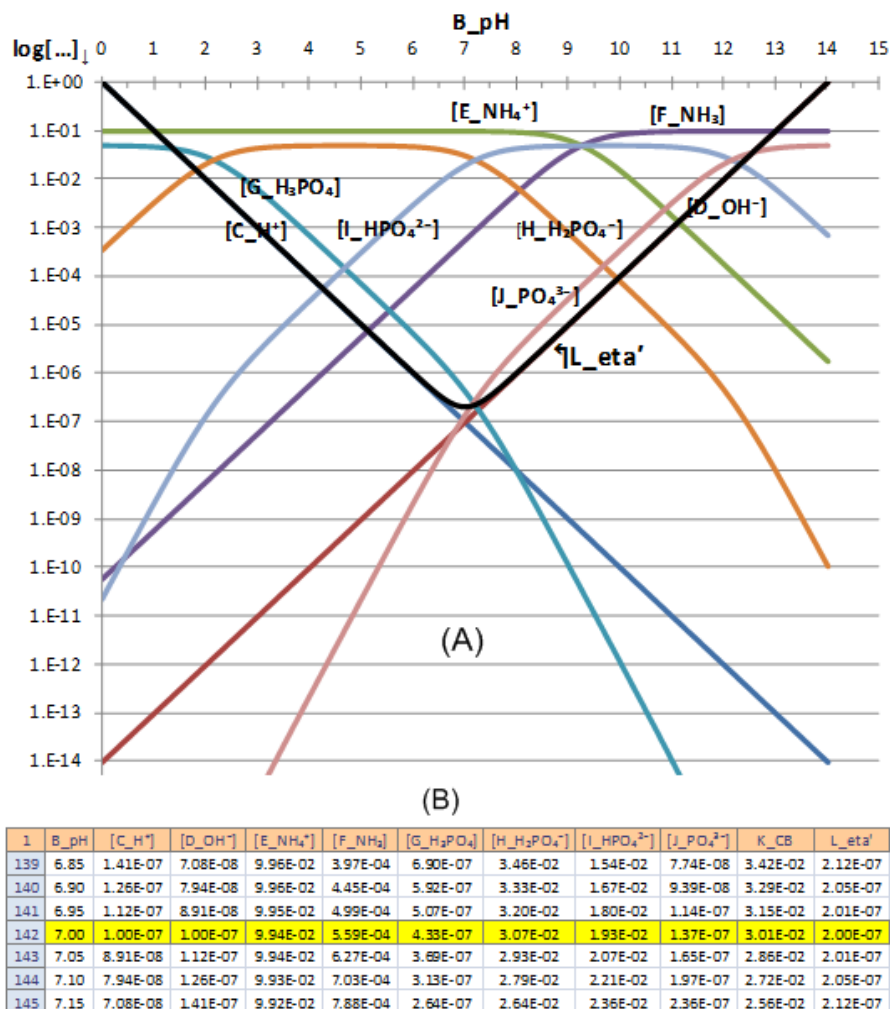


Figure 3. MyBufferPlot, (A), and, (B), extract of the current content of myBufferMatrix (rows 139-145) after entering (in cell L_eta') BC-Formula with the invariant contribution of water to signed buffer capacity.

Actually, the solid black curve labelled <L_eta'> in Figure 3A represents the buffer capacity that the solution would have if no dibasic ammonium phosphate was present. But, obviously, if no dibasic ammonium phosphate was present the pH of the solution would be that of pure water, i.e., 7.00 (at 25°C). Then, if we hover with the mouse on curve <L_eta'> and read the value corresponding to pH = 7.00, we obtain $2.00 \cdot 10^{-7}$ M which is the signed buffer capacity of pure water (at 25°C). This value is the same (see Figure 3B) as the current value in column L_eta' of myBufferMatrix in row corresponding to pH = 7.00 (row 142).

This value of the signed buffer capacity for pure water converts to $\eta = 2.3 \cdot 2.00 \cdot 10^{-7} = 4.6 \cdot 10^{-7}$ M.

Values of $\eta_{\text{signed}} = 2.0 \cdot 10^{-7}$ M and $\eta = 4.6 \cdot 10^{-7}$ M, calculated for signed and conventional buffer capacity of pure water, have a special significance: they represent the minimum value for the buffer capacity of an aqueous solution at 25°C. In fact, addition to pure water of any substance with Acid-Base properties invariably increases the buffer capacity, although, obviously, it may either increase or decrease its pH.

In the dibasic ammonium phosphate solution there are four additional conjugate pairs, so that, according to the rule declared above there are four additional terms to be added to the BC-Formula.

One of these terms, $\eta'(\text{pH})_{\text{NH}_4^+/\text{NH}_3}$, will represent the contribution to $\eta'(\text{pH})$ of the couple $\text{NH}_4^+/\text{NH}_3$.

The contribution of a given conjugate couple HX/X^- can be expressed either through the concentration of the acid species of the couple, $[\text{HX}]$ (e.g., $[\text{NH}_4^+]$) or through the concentration of the basic species, $[\text{X}^-]$ (e.g., $[\text{NH}_3]$).

As a general rule, only the concentration of one of the two species of a given conjugate pair must appear in the BC-Formula (never both!).

Suppose that we decide to add the contribution of the HX/X^- couple via $[\text{HX}]$. Then, the term to be added to the basic equation (7₁) is:

$$\eta'(\text{pH})_{\text{HX}/\text{X}^-} = \frac{K_a}{K_a + [\text{H}^+]} [\text{HX}]. \quad (8)$$

Alternatively, to add the contribution of the HX/X^- couple via $[\text{X}^-]$, the term to be added to equation (7₁) is:

$$\eta'(\text{pH})_{\text{HX}/\text{X}^-} = \frac{[\text{H}^+]}{K_a + [\text{H}^+]} [\text{X}^-]. \quad (9)$$

Factor multiplying the concentration of acid form, HX , and factor multiplying the concentration of basic form, X^- , of a conjugated couple are functions of $[\text{H}^+]$ which embody as parameter the acid dissociation constant which connects the two species in the pair. These factors have always the same form (and, with use, it is very easy to remember them), although, obviously, the value of K_a depends on the conjugate pair considered.

Please note that whatever may be the Acid-Base pair considered, relation (10) holds between these two factors:

$$\frac{K_a}{K_a + [\text{H}^+]} + \frac{[\text{H}^+]}{K_a + [\text{H}^+]} = 1. \quad (10)$$

Please remember that either a term corresponding to the right side member of equation (8) or a term corresponding to the right side member of equation (9) must be used in the BC-Formula (never both!).

Suppose that in the case of the ammonium phosphate dibasic buffer we want to add the contribution of the $\text{NH}_4^+/\text{NH}_3$ couple via $[\text{E}_{\text{NH}_4^+}]$.

Then the term to be added to equation (7₁) is:

$$\eta'(\text{pH})_{\text{NH}_4^+/\text{NH}_3} = \frac{10^{-9.25}}{10^{-9.25} + [\text{C}_{\text{H}^+}]} [\text{E}_{\text{NH}_4^+}]. \quad (11)$$

On the contrary, to add the contribution of the $\text{NH}_4^+/\text{NH}_3$ couple via $[\text{F}_{\text{NH}_3}]$, the term to be added to equation (7₁) is:

$$\eta'(\text{pH})_{\text{NH}_4^+/\text{NH}_3} = \frac{[\text{C}_{\text{H}^+}]}{10^{-9.25} + [\text{C}_{\text{H}^+}]} [\text{F}_{\text{NH}_3}]. \quad (12)$$

By using equation (12) for the contribution of ammonium ion/ammonia couple, equation (7₁) evolves to equation (7₂):

$$\eta'(\text{pH}) = [\text{C}_{\text{H}^+}] + [\text{D}_{\text{OH}^-}] + \frac{[\text{C}_{\text{H}^+}]}{10^{-9.25} + [\text{C}_{\text{H}^+}]} [\text{F}_{\text{NH}_3}] \quad (7_2)$$

and BC-Formula, in Cell L2 of myBufferSheet becomes:

$$\text{BC-Formula}_2 \rightarrow \text{Cell L2:} = \text{C2} + \text{D2} + (\text{C2}/(\text{C2} + 10^{-9.25})) * \text{F2}$$

As usual, code entered in Cell L2 is extended up to cell L282. After this, myBufferPlot in Figure 3A evolves into plot in Figure 4A.

Solid black curve labeled <L_eta'> in Figure 4A represents now the signed buffer capacity that the ammonium phosphate dibasic buffer would have if it did not contain the phosphoric acid AB group. In other words, curve labeled <L_eta'> in Figure 4A represents the signed buffer capacity of a solution containing only the ammonium ion AB group at a group concentration of 0.1 M.

In order to understand what exactly the previous statement signifies, it is necessary to remember that stating that a given solution contains the ammonium ion AB group at a group concentration of 0.1 M only signifies that in this solution the mass balance (13) is verified:

$$[\text{E}_{\text{NH}_4^+}] + [\text{F}_{\text{NH}_3}] = 0.1 \text{ M}. \quad (13)$$

Then, the sentence: "a solution in which the group concentration of the ammonium ion AB group is 0.1 M" does not specify a single solution since it can be referred to a variety of solutions containing the Acid-Base couple $\text{NH}_4^+/\text{NH}_3$.

For instance, amongst others, solutions *a*, *b* and *c* below are a sample of solutions in which the group concentration of ammonium ion AB group is 0.1 M:

- a → 0.1 M NH_4Cl ; pH = 5.10;
- b → 0.1 M NH_3 ; pH = 11.10.
- c → 0.05 M NH_4Cl + 0.05 M NH_3 ; pH = 9.25.

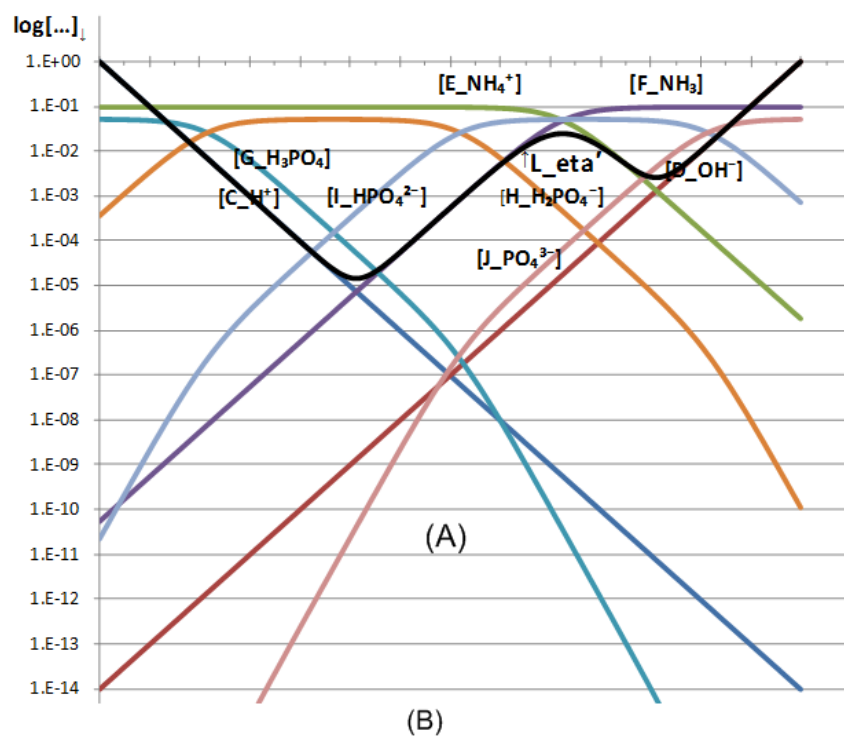


Figure 4. MyBufferPlot (A) and extract of the current content of myBufferMatrix (B) after entering (in cell L) BC-Formula with contribution of water and $\text{NH}_4^+/\text{NH}_3$ couple to signed buffer capacity

We now can very well see that curve labelled $L_{\text{eta}'}$ in Figure 4A and the current content of column $L_{\text{eta}'}$ of myBufferMatrix expose the signed buffer capacity of a variety of solutions containing only the $\text{NH}_4^+/\text{NH}_3$ couple.

As can be easily determined, solutions *a*, *b*, and *c* above have respectively pH = (5.10, 11.10, 9.25) and their signed buffer capacity is immediately determined by reading myBufferPlot in Figure 4A or from cells of myBufferMatrix in column $L_{\text{eta}'}$ (corresponding to pH of the considered solution).

From Figure 4B we see that the signed buffer capacity of solutions *a*, *b*, and *c* above are respectively $\text{eta}' = (1.50\text{E-}05 \text{ M}, 2.63\text{E-}03 \text{ M}, 2.50 \text{E-}02 \text{ M})$ which convert to $\text{eta} = (0.000035 \text{ M}, 0.0060, 0.0575 \text{ M})$.

If we now look again at Figure 4A with this interpretation in mind, we can see a very general characteristic of system points: system points, in general, correspond to maxima of the buffer capacity. This is to say that if we keep the group concentration of the ammonium ion AB group to 0.1 M, we can realize a solution with the maximum buffer capacity when we prepare solution *c* above. On the contrary we obtain the lowest buffer capacity when we dissolve only ammonium chloride (solution *a* above) while a 0.1 M ammonia solution (solution *b* above) has a buffer capacity in-between.

Any mixture of ammonia and ammonium chloride, with a 0.1 M group concentration, has pH between 5.10 and 11.10 and a signed buffer capacity between 0.025 M and 0.000015 M. The buffer capacity of any of these mixtures can be read in column $L_{\text{eta}'}$ of myBufferMatrix of Figure 4B (once the corresponding pH has been evaluated).

Finally, the three contributions to eta' of conjugate acid base couples $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$, $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ have to be added to the BC-Formula for calculating the buffer capacity of the 0.05 M ammonium phosphate dibasic buffer.

Strictly, the contribution of the phosphoric acid AB group to the buffer capacity is mathematically complex [4].

However, as we have mentioned above, for real AB groups employed in buffer formulations it is a very good approximation to treat Acid-Base conjugate couples in the same AB group as separate HX/X^- couples belonging to different AB groups. If this approximation is implemented we need, for calculating the phosphoric acid contribution to the buffer capacity, only to iterate application of equation (8) or (9) for each of the three couples $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$, $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$.

For common real AB groups with two or more conjugate couples the best approximation is usually obtained by expressing the contribution of each couple via the amphiprotic species of each couple. If this strategy is

adopted the following terms must be added to the right side member of equation (7₂)

$$\eta'(\text{pH})_{\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-} = \frac{[\text{C_H}^+]}{10^{-2.15} + [\text{C_H}^+]} [\text{H_H}_2\text{PO}_4^-]$$

$$\eta'(\text{pH})_{\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}} = \frac{[\text{C_H}^+]}{10^{-7.20} + [\text{C_H}^+]} [\text{I_HPO}_4^{2-}]$$

$$\eta'(\text{pH})_{\text{HPO}_4^{2-}/\text{PO}_4^{3-}} = \frac{10^{-12.15}}{10^{-12.15} + [\text{C_H}^+]} [\text{I_HPO}_4^{2-}]$$

Finally, equation (7₃) is obtained for the buffer capacity of 0.05 M (NH₄)₂HPO₄ buffer:

$$\begin{aligned} \eta'(\text{pH}) = & [\text{C_H}^+] + [\text{D_OH}^-] \\ & + \frac{[\text{C_H}^+]}{10^{-9.25} + [\text{C_H}^+]} [\text{F_NH}_3] \\ & + \frac{[\text{C_H}^+]}{10^{-2.15} + [\text{C_H}^+]} [\text{H_H}_2\text{PO}_4^-] \\ & + \frac{[\text{C_H}^+]}{10^{-7.20} + [\text{C_H}^+]} [\text{I_HPO}_4^{2-}] \\ & + \frac{10^{-12.13}}{10^{-12.15} + [\text{C_H}^+]} [\text{I_HPO}_4^{2-}] \end{aligned} \quad (7_3)$$

Equation (7₃) is readily converted to the following final BC-Formula₃:

$$\text{BC-Formula}_3 \rightarrow \text{Cell L2:} = \text{C2} + \text{D2} + (\text{C2} / (\text{C2} + 10^{-9.25})) * \text{F2} + (\text{C2} / (\text{C2} + 10^{-2.15})) * \text{H2} + (\text{C2} / (\text{C2} + 10^{-7.20})) * \text{I2} + (10^{-12.15} / (\text{C2} + 10^{-12.15})) * \text{I2}$$

When BC-Formula₃ is entered in cell L2 end extended up to cell L282, column L_eta' of myBufferSheet is filled with values of eta' calculated at each of the pH values in column B_pH and myBufferMatrix takes its final form shown in Figure 1. Concurrently myBufferPlot evolves to its final form in Figure 5.

Either hovering with the mouse on myBufferPlot in Figure 5 or reading value in column L_eta' of myBufferMatrix in Figure 1 at pH = 8.05, we find that the native signed buffer capacity (η') of a 0.05 M (NH₄)₂HPO₄ buffer is 0.011 M which converts to a conventional buffer capacity (η) of 0.025M.

Apart from that, inspection of Figure 5 shows now an η'(pH) curve very suggestive which traverse myBufferPlot as a wave with maxima and minima.

One can easily check that maxima of this wave, in general, correspond to system points. In system points curve representing η'(pH) goes generally through a point which lies 0.3 log unity under the system point.

One can also extract from Figure 5 the strict correlation between the η'(pH) wave and curves representing species in myBufferPlot. This correlation can be spelled as follows. η'(pH) wave traverse myBufferPlot always starting (at low pH) on line representing H⁺ and ending (at high pH) on

line representing OH⁻. In between start and end, η'(pH) wave is guided by segments of curves representing species into the solutions which either have slope approaching +1 or slope approaching -1 (η'(pH) wave disregards horizontal segments). When, at a given pH there are several segments with non-zero slope, η'(pH) adheres to the one highest in myBufferPlot. When, during its route through myBufferPlot, η'(pH) wave reaches a crossing points between two curves, it always continues by following the segment with non-zero slope highest in myBufferPlot.

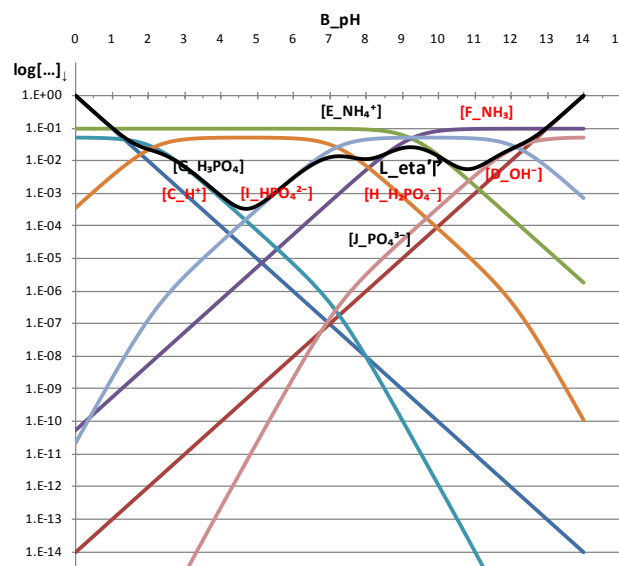


Figure 5. MyBufferPlot derived from myBufferMatrix in Figure 1. The contribution of the various Acid-Base conjugate couples into the solution to the signed buffer capacity (black solid curve) has been expressed through species indicated with red labels

By following these rules, it is possible to imagine the general shape of the η'(pH) wave by the mere inspection of myBufferPlot. For this, even a brute version of myBufferPlot, without labels, can be used.

This ability is very useful when only a qualitative description of the η'(pH) function is required or in cases in which an approximate value of the buffer capacity, as can be read from the bare myBufferPlot, is sufficient.

Although many words have been spent to obtain the buffer capacity of the 0.05 M ammonium phosphate dibasic buffer, the actual calculation procedure is very fast and the complete myBufferMatrix in Figure 1 and the supporting myBufferPlot in Figure 5 can be obtained in a time much shorter than expended to read this section.

3.4. The special Case of Strong Acids and Strong Bases

If we develop, within the frame presented above, the buffer capacity of solutions of strong acids and strong bases we find a very peculiar and far-reaching result.

Common strong acids and strong bases have by definition, acid dissociation constants, K_a , which are, respectively, either much larger than one (e.g., HI/I⁻ → pK_a ≈ -10, HCl/Cl⁻ → pK_a ≈ -7, HClO₄ → pK_a ≈ -4, etc.) or lower than the ionic product of water (e.g., Na⁺/NaOH → pK_a ≈ 14.2; K⁺/KOH → pK_a ≈ 14.5, etc.) [5].

The buffer capacity of a solution of a strong acid, for instance HCl, is given by equation (7₄)

$$\eta'(pH) = [H^+] + [OH^-] + \eta'(pH)_{HCl/Cl^-} \quad (7_4)$$

On the other side, for a solution of a strong base, for instance NaOH, we have:

$$\eta'(pH) = [H^+] + [OH^-] + \eta'(pH)_{Na^+/NaOH} \quad (7_5)$$

If the term $\eta'(pH)_{HCl/Cl^-}$ in equation (7₄) is expressed through an instance of equation (8), and the term $\eta'(pH)_{Na^+/NaOH}$ through an instance of equation (9), we have, in the range $0 < pH < 14$:

$$\eta'(pH)_{HCl/Cl^-} = \frac{10^7}{10^7 + [H^+]} [HCl] \cong [HCl] \quad (14)$$

$$\eta'(pH)_{Na^+/NaOH} = \frac{[H^+]}{10^{-14.2} + [H^+]} [NaOH] \cong [NaOH] \quad (15)$$

Since in a solution of hydrochloric acid [HCl] is vanishingly low and, correspondingly, in a solution of NaOH the concentration of the basic form, [NaOH], is always very low we deduce from relations (14) and (15) that, in the usual range of pH, both equations (7₄) and (7₅) converge to relation (7₁) which expresses the buffer capacity of pure water as a function of pH:

$$\eta'(pH)_w = [H^+] + [OH^-] \quad (7_1)$$

In other words, we find that water, solutions of strong acids, strong bases and, eventually, mixtures of strong acids and bases share a common $\eta'(pH)$ function which is that of pure water.

In practice, this signifies that addition of strong acids and/or bases to water do not modify the $\eta'(pH)$ function.

These facts are demonstrated in Figure 6 and Figure 7 which show that both the *eta'*(pH) function of a 0.1 M solution of HCl ($pK_a = -7$) and of 0.1 M NaOH ($pK_a = 14.2$) coincide with that of pure water.

The chemical reason for this state of affairs is the fact that the segment of slope -1 of curve representing [HCl] lies very low in myBufferPlot of Figure 6 in the range $0 < pH < 14$ and then it becomes irrelevant for the buffer capacity; symmetrically, the segment with slope +1 of curve representing [NaOH], in myBufferPlot of Figure 7, falls under line representing [OH⁻] in the range $0 < pH < 14$ and because of this it is irrelevant for the buffer capacity.

However, it is easily seen that this is only a particular case of the very general fact that addition of a strong acid and/or of a strong base to any buffer does not modify its $\eta'(pH)$ function.

Please note that the above statement is far from signifying that addition of strong acid and/or base to a given buffer or solution does not modify its buffer capacity. In fact, addition of strong acid and/or base to whatever buffer or solution will always change its pH and then, in general, its buffer capacity.

By the way of example, from Figure 6 and Figure 7 one can easily see that both a 0.1 M HCl solution (pH = 1.00) and a 0.1 M NaOH solution (pH = 13.00) have a signed buffer capacity of 0.1 M which is orders of magnitudes higher than the signed buffer capacity of pure water, despite that the 0.1 M HCl, 0.1 M NaOH solutions and pure water share a common *eta'*(pH) function (black solid curve in Figure 6 and Figure 7).

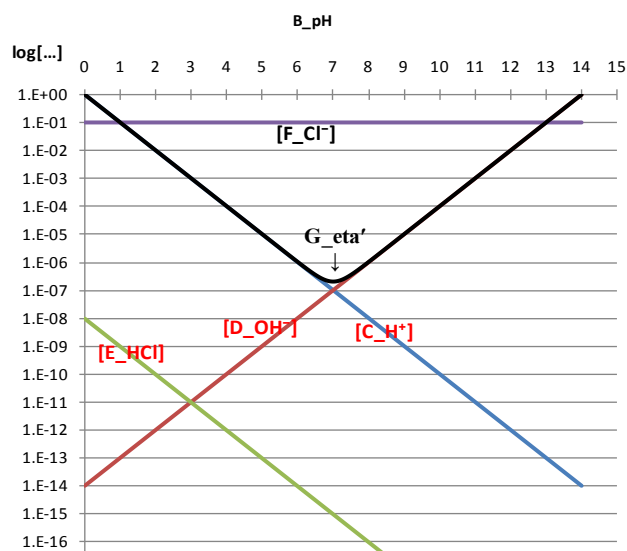


Figure 6. MyBufferPlot for 0.1 M HCl ($pK_a = -7$) showing that the BC-Formula is not affected by the presence of strong acid. Red labels indicate species used to develop the BC-Formula.

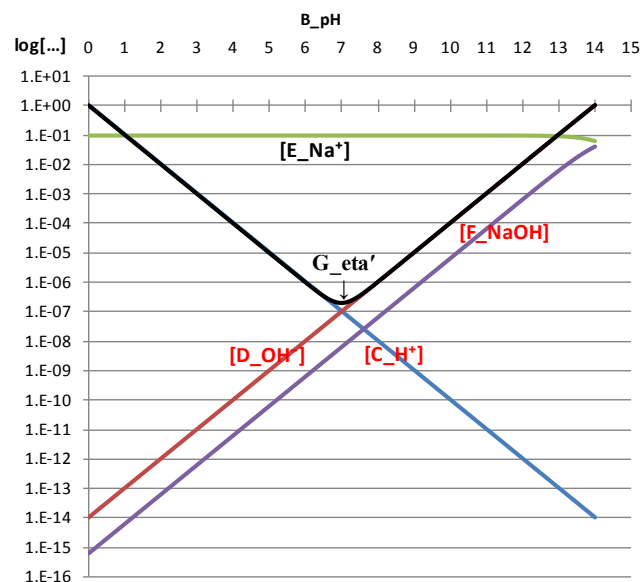


Figure 7. MyBufferPlot for 0.1 M NaOH ($pK_a = 14.2$) showing that the BC-Formula is not affected by the presence of strong base. Red labels indicate species used to develop the BC-Formula.

In practice, what we have deduced above is a sort of conservation principle for the BC-Formula: the BC-Formula for a given buffer is not modified by the addition of strong acid and/or base.

This fact shed a new light on the chemical significance of the abstract *eta'*(pH) function associated to a given buffer according to the above procedure: *eta'*(pH) describes the evolution of the signed buffer capacity of the buffer while its pH is modified by addition of strong acid and/or strong base.

This is strictly true if, in abstract, a solid strong acid or a solid strong base is added to the native buffer because, in effect, the operation of transferring to the buffer any amount of solid strong acid or strong base does not appreciably modify the group concentration of Acid-Base groups into the buffer.

However, in practice, we can extend this idea to the case in which a solution of strong acid or strong base is

added to a given buffer, provided that the volume of the buffer is not increased dramatically (which would result in a decrease of group concentrations of all AB groups into the buffer and, consequently, in a change of η' (pH)).

If addition of NaOH or HCl solution to the native buffer, performed because the native buffer pH does not coincide with the desired pH, produces a not negligible dilution of the buffer components, then in the above procedure a suitably lower group concentration of AB groups into the buffer must be used to evaluate the η' (pH) function.

Please also notice that dilution of a pH buffer with sample is supposed not to change the buffer pH (since the job of a pH buffer is that of imparting to the sample its own pH) but, because of the decreased concentration of AB groups into the buffer, will always lower its buffer capacity. As in the previous case, the effective buffer capacity of a pH buffer must be evaluated using for the AB groups concentrations the values after dilution.

3.5. Integrated Buffer Capacity, $\int\eta$ (pH)

For reasons that will become soon apparent, it is practically useful to derive from function η (pH) a new function which will be called *integrated buffer capacity* and which will be indicated with the self-explaining symbol $\int\eta$ (pH).

The integrated buffer capacity carries dimension of a molar concentration (as η (pH)).

The value of $\int\eta$ (pH) at $\text{pH} = \text{pH}_x$ is calculated from relation (16):

$$\int\eta(\text{pH}_x) = \int_{\text{pH}=0}^{\text{pH}=\text{pH}_x} \eta(\text{pH}) \quad (16)$$

In other words, $\int\eta(\text{pH}_x)$ represents the integral of the conventional buffer capacity extended from $\text{pH} = 0$ to a running $\text{pH} = \text{pH}_x$.

$\int\eta(\text{pH}_x)$ represents the change in the concentration of strong base (e.g., ΔC_{NaOH}) to be performed into the buffer for changing its pH from 0.00 to the current pH_x .

Integral in equation (16) can be approximated by a summation which can easily be calculated, from values of the signed buffer capacity in column $\langle \dots \eta' \rangle$, in an empty column of myBufferMatrix according to equation (17):

$$\begin{aligned} \int\eta(\text{pH}_x) &= \int_{\text{pH}=0}^{\text{pH}=\text{pH}_x} \eta(\text{pH}) \\ &\approx 2.303 \cdot \Delta\text{pH} \cdot \sum_{\text{pH}=0}^{\text{pH}=\text{pH}_x} \eta'(\text{pH}_i) \end{aligned} \quad (17)$$

In equation (17), ΔpH represents the spacing between successive pH values in column B_pH of myBufferMatrix (which is entered as an argument of function $\langle \text{pH} \rangle$ of Table 2) and $\eta'(\text{pH}_i)$ are the calculated values of $\eta'(\text{pH})$ (in column $\langle \dots \eta' \rangle$ of myBufferMatrix).

In the above discussed example of 0.05 M $(\text{NH}_4)_2\text{HPO}_4$ buffer $\Delta\text{pH} = 0.05$ and $\eta'(\text{pH}_i)$ values are in column L_eta' (see Figure 1).

In order to calculate values of the function $\int\eta$ (pH) at each of the 281 pH_x values in column B_pH of myBufferMatrix in Figure 1, enter label M_∫eta in cell M1, 0.00 in cell M2 and the following code in cell M3:

M_∫eta → **cell M3:** =2.3026*0.05*SUM(\$L\$2:L3)

Finally extend code in cell M3 up to cell M282 so that column M_∫eta is filled with values of $\int\eta$ (pH) function at each of the 281 pH values in column B_pH.

A plot of the integrated buffer capacity as a function of pH can be produced with a few mouse clicks in myBufferSheet exposing myBufferMatrix.

For instance, plot in Figure 8 has been derived from myBufferMatrix in Figure 1.

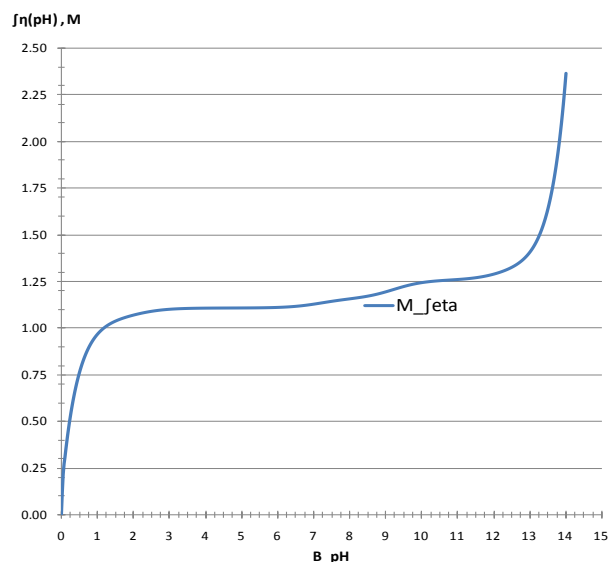


Figure 8. Integrated buffer capacity, $\int\eta$ (pH), of 0.05 M ammonium phosphate dibasic buffer calculated from myBufferMatrix in Figure 1

On the basis of demonstrations in the previous paragraph, namely that addition of solid strong base and/or strong acid do not modify the η' curve of the buffer, the difference, $\int\eta(\text{pH}_y) - \int\eta(\text{pH}_x)$, between values of the integrated buffer capacity at two pH can strictly be interpreted as the number of moles of strong base (if $\int\eta(\text{pH}_y) - \int\eta(\text{pH}_x) > 0$) or strong acid (if $\int\eta(\text{pH}_y) - \int\eta(\text{pH}_x) < 0$) to be transferred into 1 litre of the buffer in order to change its pH from pH_x to pH_y .

For instance the pH of 1 litre of 0.05 M $(\text{NH}_4)_2\text{HPO}_4$ ammonium phosphate changes from 8.05 to 7.00 by addition of 0.03 moles of a strong acid since $\int\eta(7.00) - \int\eta(8.05) = 1.129 - 1.159 = -0.03$ M (see Figure 1). This is approximately equivalent to 3 ml of HCl 1 M per 100 ml of buffer.

Obviously, a better approximation of the integral in equation (17) is obtained by decreasing the step ΔpH .

$\Delta\text{pH} = 0.05$ gives a good approximation when initial and final pH are on a flat region of the η' curve but, if judged necessary, ΔpH can be decreased at will by zooming into the matrix with function $\langle \text{pH} \rangle$.

3.6. Basic Example: The Britton-Robinson Universal pH Buffer

A universal pH buffer is a buffer in which several Acid-Base groups are consciously introduced with the aim of obtaining a buffer which keeps, comparatively speaking, a high buffer capacity extending over a large range of pH.

During use, the desired pH is imparted to the buffer by addition of a strong base or a strong acid and the universal buffer acquires a buffer capacity at the imparted pH which

depends from its composition (and, eventually, from other secondary factors, e.g., temperature).

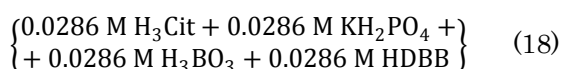
Ideally, this buffer capacity should be high and, possibly, not much dependent on the particular pH imposed to the buffer in the pH range for which its use is intended.

We can translate the above constraints simply stating that the η' (pH) function of an ideal universal buffer must traverse myBufferPlot of the buffer as a straight horizontal line which lies as high as possible in the plot.

One of the most popular universal pH buffers is the Britton-Robinson buffer [6] (although a search of the literature shows that a plethora of universal pH buffers have been formulated and proposed and many are in common use and commercially available [4]).

In its original formulation the Britton-Robinson buffer is prepared by transferring to 1 litre volumetric flask 6.008 g of citric acid (H₃Cit), 3.983 g of KH₂PO₄, 1.769 g of boric acid (H₃BO₃) and 5.266 g of 5,5'-diethylbarbituric acid (HDBA) and filling to the mark with distilled water.

This composition converts to the analytical array (18):



from which it is clear that the citric acid (H₃Cit, H₂Cit⁻, HCit²⁻, Cit³⁻), the phosphoric acid (H₃PO₄, H₂PO₄⁻, HPO₄²⁻, PO₄³⁻), the boric acid (H₃BO₃, H₂BO₃⁻, HBO₃²⁻, BO₃³⁻), the diethylbarbituric acid (HDBA, DBA⁻) and the potassium hydroxide (K⁺/KOH) Acid-Base groups are simultaneously transferred to the buffer which, at equilibrium, contains 18 different chemical species:

In order to build myBufferMatrix representing the Britton-Robinson buffer the group concentrations in analytical array (18) and acid dissociation constants at 25°C in Table 4 will be assumed [5,7].

Table 4. Acid dissociation constants of components of Britton-Robinson buffer at 25°C

Acid-Base group	pK _{a1}	pK _{a2}	pK _{a3}
Citric acid	3.15	4.75	6.40
Phosphoric acid	2.15	7.20	12.15
Boric acid	9.25	12.75	13.80
Diethylbarbituric acid	8.00		
Potassium ion	14.5		

Although myBufferMatrix for Britton-Robinson buffer is very large occupying 19 columns (from B_pH to [T_BO₃³⁻]) of myBufferSheet, it can be built in a matter of minutes by extending the procedure demonstrated above.

However, because of its huge size, only a few rows of this matrix are presented for reference in Figure 9B with the derived myBufferPlot in Figure 9A.

In myBufferPlot of Figure 9A no attempt has been made to apply labels to curves for which the default colours applied by MS Excel have been retained and may serve to identify species according to the plot legend.

In order to obtain the native pH of Britton-Robinson buffer, Excel code which calculates the difference between the left side and right side members of charge balance (19) is entered in cell U under label U_CB:

$$\left\{ \begin{array}{l} [C_H^+] + [E_K^+] = [D_OH^-] + [H_DBA^-] + \\ + [J_H_2PO_4^-] + 2[K_HPO_4^{2-}] + 3[L_PO_4^{3-}] + \\ + [N_H_2Cit^-] + 2[O_HCit^{2-}] + 3[P_Cit^{3-}] + \\ + [R_H_2BO_3^-] + 2[S_HBO_3^{2-}] + 3[T_BO_3^{3-}] \end{array} \right\} \quad (19)$$

Code to be entered in cell U2, and then extended up to cell U282, is the following:

U_CB→Cell U2: =C2+E2-D2-H2-J2-2*K2-3*L2-N2-2*O2-3*P2-R2-2*S2-3*T2

The value closest to zero in the U_CB column (= 4.16·10⁻⁴) is found in cell U56 which identify row corresponding to pH = 2.70 which is the calculated native pH of the Britton-Robinson buffer (see Figure 9B).

We now must build the BC-Formula in order to evaluate the buffer capacity of the Britton-Robinson buffer.

Table 4 exposes eleven pK_a, and, by consequence, it will be necessary to add eleven additional terms to the basic equation (7₁).

Table 5. Species selected to express the contribution of each conjugate Acid-Base couple to the buffer capacity of Britton-Robinson buffer and corresponding expressions to be added to the basic equation (7₁)

Conjugate couple	Selected species	Expression
K ⁺ /KOH	KOH	[H ⁺]/([H ⁺] + 10 ^{-14.5})[DBA ⁻]
HDBA/DBA ⁻	DBA ⁻	[H ⁺]/([H ⁺] + 10 ⁻⁸)[DBA ⁻]
H ₃ Cit/H ₂ Cit ⁻	H ₂ Cit ⁻	[H ⁺]/([H ⁺] + 10 ^{-3.15})[H ₂ Cit ⁻]
H ₂ Cit ⁻ /HCit ²⁻	H ₂ Cit ⁻	10 ^{-4.75} /([H ⁺] + 10 ^{-4.75})[H ₂ Cit ⁻]
HCit ²⁻ /Cit ³⁻	HCit ²⁻	10 ^{-6.4} /([H ⁺] + 10 ^{-6.4})[HCit ²⁻]
H ₃ PO ₄ /H ₂ PO ₄ ⁻	H ₂ PO ₄ ⁻	[H ⁺]/([H ⁺] + 10 ^{-2.15})[H ₂ PO ₄ ⁻]
H ₂ PO ₄ ⁻ /HPO ₄ ²⁻	H ₂ PO ₄ ⁻	10 ^{-7.20} /([H ⁺] + 10 ^{-7.20})[H ₂ PO ₄ ⁻]
HPO ₄ ²⁻ /PO ₄ ³⁻	HPO ₄ ²⁻	10 ^{-12.15} /([H ⁺] + 10 ^{-12.15})[HPO ₄ ²⁻]
H ₃ BO ₃ /H ₂ BO ₃ ⁻	H ₂ BO ₃ ⁻	[H ⁺]/([H ⁺] + 10 ^{-9.25})[H ₂ BO ₃ ⁻]
H ₂ BO ₃ ⁻ /HBO ₃ ²⁻	H ₂ BO ₃ ⁻	10 ^{-12.75} /([H ⁺] + 10 ^{-12.75})[H ₂ BO ₃ ⁻]
HBO ₃ ²⁻ /BO ₃ ³⁻	HBO ₃ ²⁻	10 ^{-13.80} /([H ⁺] + 10 ^{-13.80})[HBO ₃ ²⁻]

To express the contribution of the eleven conjugate Acid-Base couples, exposed in the first column of Table 5, we have selected, on the basis of myBufferPlot in Figure 9A, amongst a number of alternatives, species indicated in the second column of Table 5.

In the third column of Table 5, it is given, for each conjugate couple, the term to be added to the right side member of equation (7₁) in order to derive an explicit expression for the η' (pH) function.

The derived expression for η' (pH) function is implemented in myBufferSheet via the following code to be entered in cell V2 under label <V_eta'>:

BC-Formula→Cell V2: =C2+D2+(C2/(C2+10^{-14.2}))*F2+(C2/(C2+10⁻⁸))*H2+(C2/(C2+10^{-3.15}))*N2+(10^{-4.75}/(C2+10^{-4.75}))*N2+(10^{-6.4}/(C2+10^{-6.4}))*O2+(C2/(C2+10^{-2.15}))*J2+(10^{-7.2}/(C2+10^{-7.2}))*J2+(10^{-12.15}/(C2+10^{-12.15}))*K2+(C2/(C2+10^{-9.25}))*R2+(10^{-12.75}/(C2+10^{-12.75}))*R2+(10^{-13.80}/(C2+10^{-13.80}))*S2

Code in Cell V2 is extended up to Cell V282 and column V_eta' of myBufferSheet is filled with values of eta'(pH) at each of the 281 pH values in column B_pH (see Figure 9B).

The signed buffer capacity, $\eta'(2.70) = 1.27 \cdot 10^{-2}$ M, of the native Britton-Robinson buffer can now be read in Cell V56 (in row corresponding to pH = 2.70; see

Figure 9B). This value is converted to $\eta = 2.3 \cdot 1.27 \cdot 10^{-2} = 0.0292$ M.

However, most importantly, myBufferPlot in Figure 9A evolves to myBufferPlot in Figure 10, when a curve corresponding to the content of column V_eta' of myBufferMatrix is added to the plot (black solid curve).

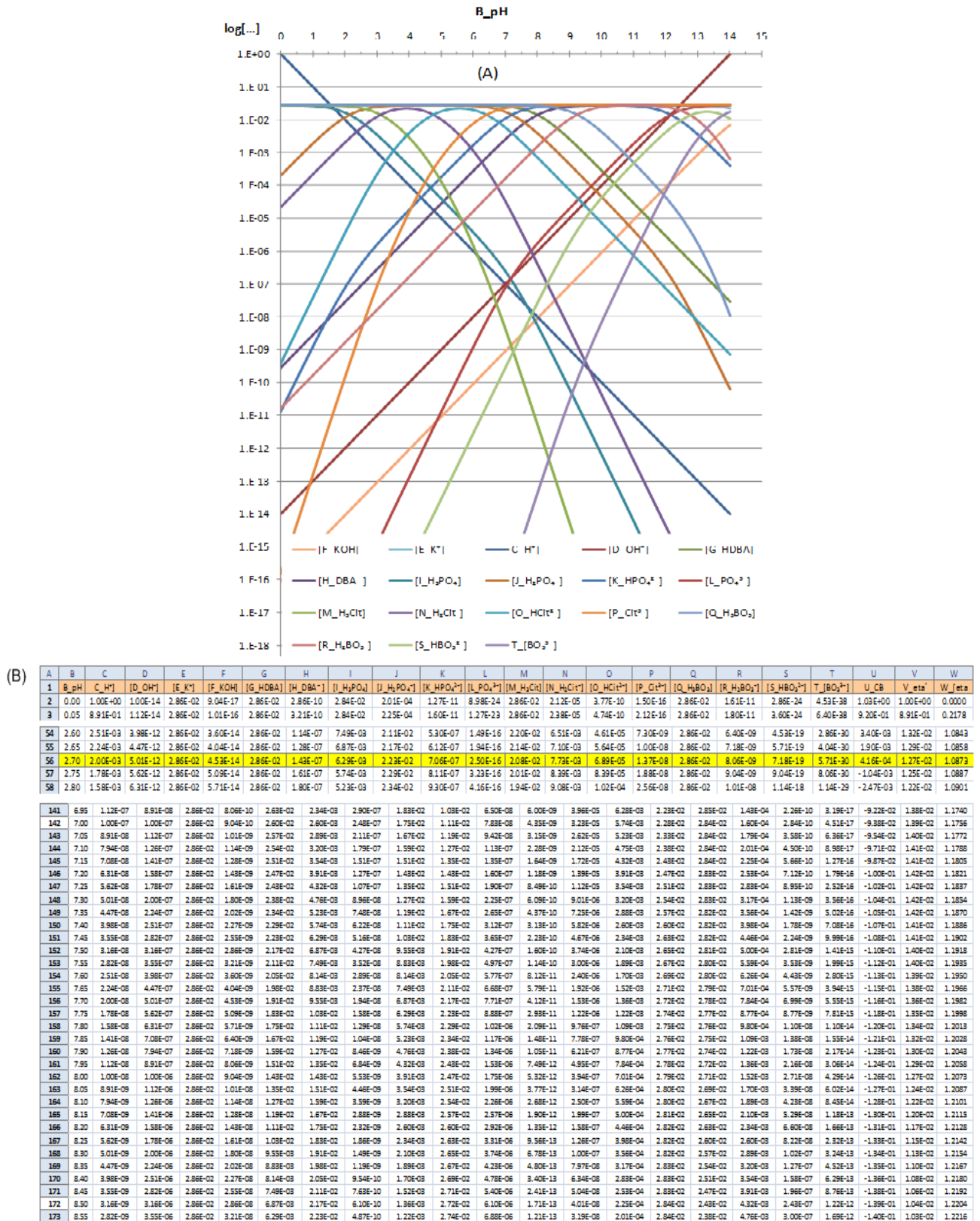


Figure 9. (A) MyBufferPlot for Britton-Robinson buffer described by analytical array (18); letter before symbol of each species indicates column of myBufferMatrix allotted to the species.(B) Sample of myBufferMatrix for Britton-Robinson buffer; row corresponding to the native composition of the buffer has been given a yellow background

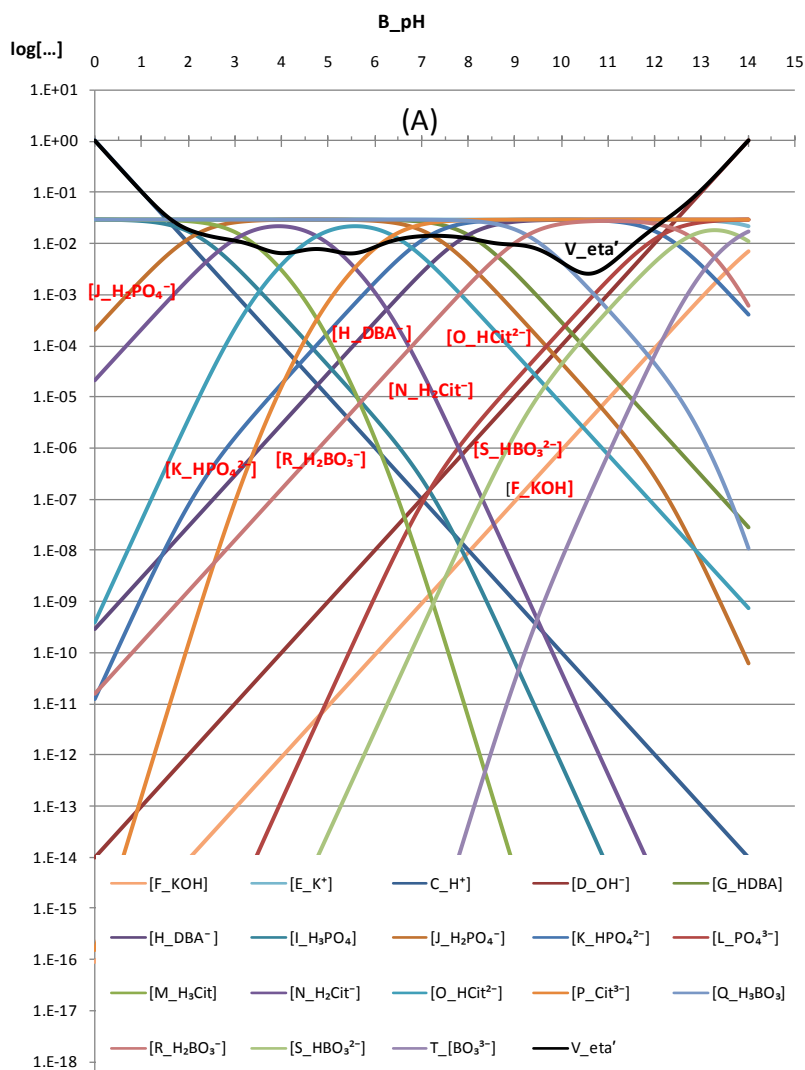


Figure 10. MyBufferPlot for Britton-Robinson buffer described by analytical array (18) (same as in Figure 9A) but with added η' (pH) curve (black solid curve with label $V_{\eta'}$) and red labels indicating species employed to develop the BC-Formula

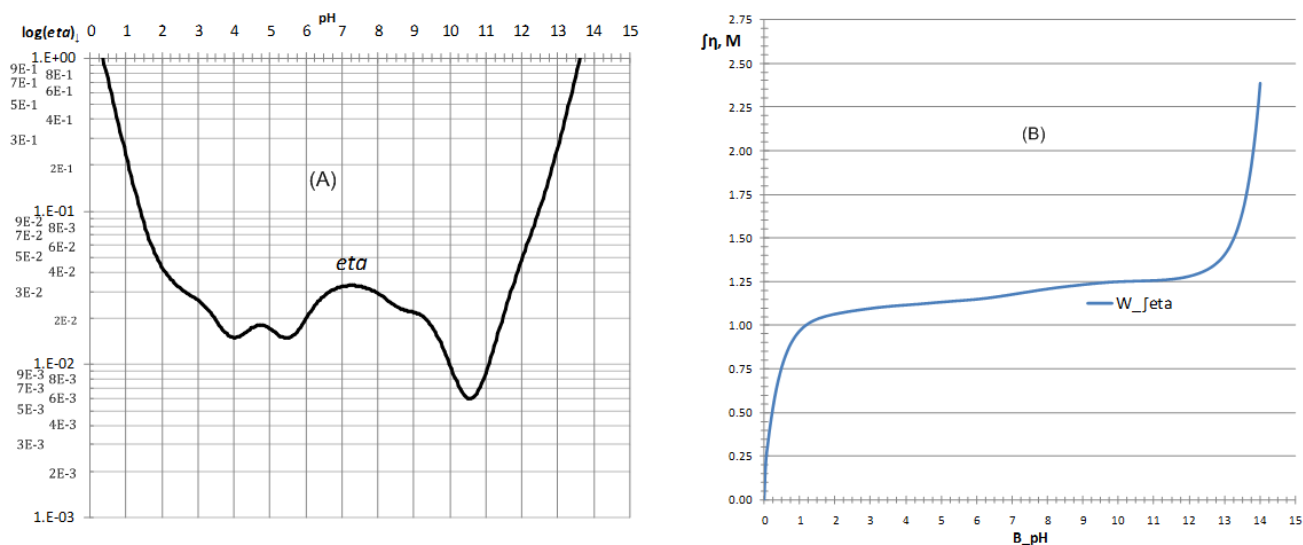


Figure 11. η (pH) and W_{η} (pH) curves, respectively (A) and (B), for Britton-Robinson buffer calculated from myBufferMatrix in Figure 9B

In Figure 11A the curve of η' (pH) of Figure 10 has been isolated, converted to η (pH) and enlarged so that details can be seen.

As can be seen from Figure 11A, in the range $2.7 < \text{pH} < 9$, the Britton-Robinson buffer goes very close to target

of obtaining a flat buffer capacity curve since the conventional buffer capacity changes only roughly between 0.032 M (at pH around 7) and 0.021 M (at pH around 9).

However a fall of the buffer capacity takes place at $\text{pH} > 9$, with a minimum of about 0.006 M at $\text{pH} \approx 10.5$.

In Figure 11B it is exposed the integrated buffer capacity of Britton-Robinson buffer. From this and myBufferMatrix in Figure 9B it can be evaluated that in order to raise the native pH of Britton-Robinson buffer up to 7.0 a change in η from 1.087 M to 1.176 M must be performed which corresponds to the addition of ~ 0.089 moles of NaOH per litre of buffer (or about 4.5 ml NaOH 2 M per 100 ml of buffer). Further increase from pH = 7, up to pH = 8.5, will require in addition $1.22 - 1.176 = 0.044$ mol of NaOH per litre (or only about 2.2 ml more of NaOH 2 M per 100 ml buffer).

As we have mentioned above, if more precise evaluations are desired the ΔpH value appearing in equation (17) can be decreased very easily under the default value of 0.05 we have adopted in this paper, either by using from the beginning a smaller step when the function $\langle\text{pH}\rangle$ is applied or, *a posteriori*, by using the $\langle\text{pH}\rangle$ function with a smaller step on a range of cells of myBufferMatrix of interest.

4. Associated Content

Ready to use **MyBuffers.xlsm** Excel file with custom functions library presented in [Table 2](#).

5. Conclusion

The presented approach to the buffer capacity allows calculation of an array of values of the buffer capacity in an arbitrary range of pH to be performed from the matrix representing a given solution, pH buffer or biological fluid.

There is no limit to the complexity of solutions which

can be treated and results and graphical representations are obtained in a matter of minutes by appropriate use of data in the matrix.

Whatever it may be solution, pH buffer or biological fluid the matrix representing it can be obtained in a matter of minutes in a MS Excel sheet by employing the custom functions library made available in this paper.

The approach to buffer capacity discussed in this paper is directed toward a wide audience and it is also suitable to be used in an educational environment, because basic quantitative concepts concerning the buffer capacity and the Acid-Base chemistry from which it depends can easily be developed and presented graphically.

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Appendix: Table 6 Copy and paste code in a VB Module of MS Excel; see annotations in code for information.

```

Public Function pH(StartCellRef, myStepValue, myEndValue)
'Creates an array of pH values! Arguments: StartCellRef -> Reference to a cell (usually B2) which
'contains the starting pH (usually 0.00). myStepValue->spacings between pHs in pH array;
'myEndValue-> end value in pH array (usually 14)
pH = StartCellRef + myStepValue
If pH >myEndValue Then
pH = myEndValue
End If
End Function
Public Function Acid_H(pH_Ref)
'Converts pH in [H+]; Argument-> Reference to cell on same row containing a pH value
Acid_H = 10 ^ -pH_Ref
End Function
Public Function Base_OH(Acid_H_Ref, pKw)
'Creates an array of pOH values from the array of [H+]! Arguments: Acid_H_Ref -> Reference to a cell (usually C2)
'which contains [H+]; pKw-> a value for ionic product of water (usually 1.00E+14)
Base_OH = 10 ^ -pKw / Acid_H_Ref
End Function
'HA/A Acid-Base group
Public Function Acid_HA(Acid_H_Ref, Cg, pKa)
' Calculates values of [HA];Arguments: Acid_H_Ref->Reference to cell on the same row containing [H+];
' Cg-> group concentration as value; pKa->pKa value connecting species in HA/A couple;
Acid_HA = Cg * (Acid_H_Ref / (Acid_H_Ref + 10 ^ -pKa))
End Function
Public Function Base_A(Acid_H_Ref, Cg, pKa)
' Calculates values of [A]; Arguments: same as Acid_HA
Base_A = Cg * (10 ^ -pKa / (Acid_H_Ref + 10 ^ -pKa))
End Function
'HHD/HD/D Acid-Base group
Public Function Acid_HHD(Acid_H_Ref, Cg, pKa1, pKa2)
'Calculates values of [HHD];Arguments:Acid_H_Ref->Reference to cell on the same row containing [H+];Cg-> group
' conc as value; pKa1->pKa value connecting species in HHD/HD couple; pKa2->pKa value connecting species HD/D.
Acid_HHD = Cg * ((Acid_H_Ref ^ 2) / (Acid_H_Ref ^ 2 + Acid_H_Ref * 10 ^ -pKa1 + 10 ^ -pKa1 * 10 ^ -pKa2))
End Function
Public Function Amp_HD(Acid_H_Ref, Cg, pKa1, pKa2)
' Calculates values of amphiprotic species [HD];Arguments:same as for Acid_HHD
Amp_HD = Cg * ((Acid_H_Ref * 10 ^ -pKa1) / (Acid_H_Ref ^ 2 + Acid_H_Ref * 10 ^ -pKa1 + 10 ^ -pKa1 * 10 ^ -pKa2))
End Function
Public Function Base_D(Acid_H_Ref, Cg, pKa1, pKa2)
' Calculates values of basic species [D]; Arguments:same as for Acid_HHD
Base_D = Cg * ((10 ^ -pKa1 * 10 ^ -pKa2) / (Acid_H_Ref ^ 2 + Acid_H_Ref * 10 ^ -pKa1 + 10 ^ -pKa1 * 10 ^ -pKa2))
End Function
'HHHT/HHT/HT/T Acid-Base group
Public Function Acid_HHHT(Acid_H_Ref, Cg, pKa1, pKa2, pKa3)
' Calculates values of acid species [H3T]; Arguments: Acid_H_Ref->Reference to cell on the same row containing [H+];
' Cg-> group concentration as value; pKa1->pKa value connecting species in H3T/H2T couple
'pKa2->pKa value connecting species in H2T/HT couple; pKa3->pKa value connecting species in HT/T couple.
Acid_HHHT = Cg * ((Acid_H_Ref ^ 3) / (Acid_H_Ref ^ 3 + Acid_H_Ref ^ 2 * 10 ^ -pKa1 + _
Acid_H_Ref * 10 ^ -pKa1 * 10 ^ -pKa2 + 10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3))
End Function
Public Function Amp_HHT(Acid_H_Ref, Cg, pKa1, pKa2, pKa3)
' Calculates values of amphiprotic species [H2T]; Arguments: same as for Acid_HHHT
Amp_HHT = Cg * ((Acid_H_Ref ^ 2 * 10 ^ -pKa1) / (Acid_H_Ref ^ 3 + Acid_H_Ref ^ 2 * 10 ^ -pKa1 + _
Acid_H_Ref * 10 ^ -pKa1 * 10 ^ -pKa2 + 10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3))
End Function
Public Function Amp_HT(Acid_H_Ref, Cg, pKa1, pKa2, pKa3)
' Calculates values of amphiprotic species [HT];Arguments: same as for Acid_HHHT
Amp_HT = Cg * ((Acid_H_Ref * 10 ^ -pKa1 * 10 ^ -pKa2) / (Acid_H_Ref ^ 3 + Acid_H_Ref ^ 2 * 10 ^ -pKa1 + _
Acid_H_Ref * 10 ^ -pKa1 * 10 ^ -pKa2 + 10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3))
End Function
Public Function Base_T(Acid_H_Ref, Cg, pKa1, pKa2, pKa3)
' Calculates values of basic species [T];Arguments: same as for Acid_HHHT
Base_T = Cg * ((10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3) / (Acid_H_Ref ^ 3 + Acid_H_Ref ^ 2 * 10 ^ -pKa1 + _
Acid_H_Ref * 10 ^ -pKa1 * 10 ^ -pKa2 + 10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3))
End Function
'HHHHF/HHHF/HHF/HF/F Acid-Base group
Public Function Acid_HHHHF(Acid_H_Ref, Cg, pKa1, pKa2, pKa3, pKa4)
' Calculates values of acid species [H4F];
'Arguments: Acid_H_Ref->Reference to cell on the same row containing [H+];Cg-> group concentration as value.
'pKa1->pKa value connecting species in H4F/H3F couple; pKa2->pKa value connecting species in H3F/H2F couple
'pKa3->pKa value connecting species in H2F/HF couple; pKa4->pKa value connecting species in HF/F couple
Acid_HHHHF = Cg * ((Acid_H_Ref ^ 4) / (Acid_H_Ref ^ 4 + Acid_H_Ref ^ 3 * 10 ^ -pKa1 + Acid_H_Ref ^ 2 * 10 ^ -
-pKa1 * 10 ^ -pKa2 + Acid_H_Ref * 10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3 + _
10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3 * 10 ^ -pKa4))
End Function
Public Function Amp_HHHF(Acid_H_Ref, Cg, pKa1, pKa2, pKa3, pKa4)
' Calculates values of amphiprotic species [H3F];
'Arguments: Acid_H_Ref->Reference to cell on the same row containing [H+]; Arguments: same as for Acid_HHHHF
Amp_HHHF = Cg * ((Acid_H_Ref ^ 3 * 10 ^ -pKa1) / (Acid_H_Ref ^ 4 + Acid_H_Ref ^ 3 * 10 ^ -pKa1 + _
Acid_H_Ref ^ 2 * 10 ^ -pKa1 * 10 ^ -pKa2 + Acid_H_Ref * 10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3 + _
10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3 * 10 ^ -pKa4))
End Function
Public Function Amp_HHF(Acid_H_Ref, Cg, pKa1, pKa2, pKa3, pKa4)
' Calculates values of amphiprotic species [H2F]; Arguments: same as for Acid_HHHHF
Amp_HHF = Cg * ((Acid_H_Ref ^ 2 * 10 ^ -pKa1 * 10 ^ -pKa2) / (Acid_H_Ref ^ 4 + _
Acid_H_Ref ^ 3 * 10 ^ -pKa1 + Acid_H_Ref ^ 2 * 10 ^ -pKa1 * 10 ^ -pKa2 + _
Acid_H_Ref * 10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3 + 10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3 * 10 ^ -pKa4))
End Function
Public Function Amp_HF(Acid_H_Ref, Cg, pKa1, pKa2, pKa3, pKa4)
' Calculates values of amphiprotic species [HF]; Arguments: same as for Acid_HHHHF
Amp_HF = Cg * ((Acid_H_Ref * 10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3) / (Acid_H_Ref ^ 4 + _
Acid_H_Ref ^ 3 * 10 ^ -pKa1 + Acid_H_Ref ^ 2 * 10 ^ -pKa1 * 10 ^ -pKa2 + _
Acid_H_Ref * 10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3 + 10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3 * 10 ^ -pKa4))
End Function
Public Function Base_F(Acid_H_Ref, Cg, pKa1, pKa2, pKa3, pKa4)
' Calculates values of basic species [F]; Arguments: same as for Acid_HHHHF
Base_F = Cg * ((10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3 * 10 ^ -pKa4) / (Acid_H_Ref ^ 4 + Acid_H_Ref ^ 3 * _
10 ^ -pKa1 + Acid_H_Ref ^ 2 * 10 ^ -pKa1 * 10 ^ -pKa2 + Acid_H_Ref * 10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3 + _
10 ^ -pKa1 * 10 ^ -pKa2 * 10 ^ -pKa3 * 10 ^ -pKa4))
End Function

```