Buffer Index and Buffer Capacity for a Simple Buffer Solution

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The quantitative expression of the buffering effects of electrolyte solutions has been a subject of study for many researchers. In 1922, Van Slyke (*1*) proposed the *buffer value* as a quantitative unit for measuring buffering effects It is defined as:

$$\beta = \frac{dB}{dpH} \qquad \text{or} \qquad \beta = -\frac{dA}{dpH} \tag{1}$$

where B is the number of moles of strong base and A, the number of moles of strong acid.

Developing the differential eq 1, Van Slyke obtained the following expression for the buffer value in the particular case of a simple buffer:

$$\beta = 2.3\,\frac{K'\left[H^+\right]}{\left(K' + \left[H^+\right]\right)^2}\,C \tag{2}$$

where C is the total concentration of the buffer and K', the dissociation constant of the conjugate acido-basic species.

In 1937, Kolthoff (*2*) introduced the term of *buffer capacity* or *buffer index* as a name for the differential ratio dB/dpH. Later studies related to the same problem (*3–5, 7, 8*) used as starting point both the Van Slyke's concept and Kolthoff's naming. However, the relationships obtained differ in the method of deriving the differential ratio.

In this paper, we clearly demonstrate that there is a difference between the buffer index (β) and the buffer capacity (BC) of a simple buffer solution.

Discussion

In our opinion, the electrolyte solution's buffer index, β, can be defined as the differential ratio of the increase in the amount of strong acid or strong base added to the pH variation. The necessary condition is that the amount of strong acid or strong base added must be far less than the electrolyte concentration. For example, if 10^{-4} mol of HCl is added to a 0.1 M solution of HCl, the variation of pH will be

$$dpH = (pH_f - pH_i) = (0.999566 - 1) = -4.34 \times 10^{-4}$$

The ratio between the amount of strong acid added and the variation of pH, which means the buffer index of the solution, is

$$\beta_a = -\frac{dA}{dpH} = -\frac{10^{-4}}{-4.34 \times 10^{-4}} = 0.23 \tag{3}$$

If NaOH is added to the same solution mentioned above, in such a way that the amount of the strong base added is 10^{-4} mol, the pH variation is

$$dpH = (pH_f - pH_i) = (1.000434 - 1) = 4.34 \times 10^{-4}$$

As a result, the buffer index will be

$$\beta_b = \frac{dB}{dpH} = \frac{10^{-4}}{4.34 \times 10^{-4}} = 0.23 \tag{4}$$

so

$$\beta_a = \beta_b = \beta = 0.23 = 2.3\,C \tag{5}$$

where C is the initial concentration of electrolyte solution.

According to IUPAC (*6*), the definition of buffer index *or* buffer capacity is as follows: "The capacity of a solution to resist changes in pH on the addition of strong acid or strong base which may be expressed numerically as the number of moles of strong acid or strong base required to change the pH by one unit when added to one liter of the specified buffer solution". We are able to demonstrate that, if the definition of buffer capacity given by IUPAC is respected, this quantitative unit is quite different from the buffer index because the pH variation stated in it is large ($\Delta pH = \pm 1$).

Let us now calculate the amount of a strong acid or a strong base that, when added to a 0.1 M solution of HCl, modifies the pH value by one unit. In the case of the addition of a strong acid,

$$\Delta pH = -1 \Rightarrow pH_f = 0 \Rightarrow C_a = 0.9 \text{ mol}$$

where C_a is the amount of strong acid added. This is, according to the IUPAC definition, the buffer capacity of the electrolyte solution in the case of addition of a strong acid:

$$BC_a = -\frac{C_a}{\Delta pH} = -\frac{0.9}{-1} = 0.9 \text{ mol} \tag{6}$$

Correspondingly, in the case of the addition of a strong base:

$$\Delta pH = +1 \Rightarrow pH_f = 2 \Rightarrow C_b = 0.09 \text{ mol}$$

where C_b is the amount of strong base. This value represents the buffer capacity of the electrolyte solution in the case of addition of a strong base:

$$BC_b = \frac{C_b}{\Delta pH} = \frac{0.09}{1} = 0.09 \text{ mol} \tag{7}$$

It is obvious that if the IUPAC definition is followed, the buffer capacity is not equivalent to the buffer index for an electrolyte solution:

$$\beta_a = \beta_b = \beta \neq BC_a \neq BC_b \tag{8}$$

Plainly a difference exists between the two quantitative units, because

$$\beta = \left(\frac{\Delta B}{\Delta pH}\right)_{\Delta pH \to 0} = \left(-\frac{\Delta A}{\Delta pH}\right)_{\Delta pH \to 0} = \frac{dB}{dpH} = -\frac{dA}{dpH} \tag{9}$$

and

$$BC_a = \left(-\frac{\Delta A}{\Delta pH}\right)_{\Delta pH = -1} \tag{10a}$$

$$BC_b = \left(\frac{\Delta B}{\Delta pH}\right)_{\Delta pH = +1} \tag{10b}$$

Applying Rubinson's relation (*8*) for the case of a simple buffer and considering the concentration of the conjugate species comparable and large enough to neglect the terms $[H^+]$ and $[OH^-]$ from the following sum

$$\frac{dB}{d\mathrm{pH}} = 2.303\left(\frac{K_a[H^+]}{\left(K_a+[H^+]\right)^2}C+[H^+]+[OH^-]\right) \qquad (11)$$

it is possible to obtain

$$\beta_a = \beta_b = \beta = 2.303\alpha(1-\alpha)C \qquad (12)$$

where C is the analytical concentration of the buffer ($C = [HA] + [A^-]$) and α, the molar fraction of one of the conjugate acido-basic species (e.g., $\alpha_{A^-} = [A^-]/C$).

If $[A^-]/[HA] = r$, the buffer index of the simple buffer is expressed by eq 13:

$$\beta = 2.3\frac{r}{(r+1)^2}C \qquad (13)$$

The buffer index, which is the same for addition of either a strong base or a strong acid, depends on *r* and C. It reaches its maximum value (β = 0.57C) when *r* = 1 (Van Slyke, *1*).

Let us now determine the expressions for the buffer capacity of a simple buffer according to IUPAC definition when either a strong acid or a strong base is added. When adding a strong acid, HA_1, to the buffer solution which contains HA and A^- species, the following reaction occurs:

$$A^- + HA_1 \rightarrow HA + A_1^-$$

In the initial system, the analytical concentration of the electrolyte, C, is

$$C = [A^-]_i + [HA]_i$$

and the concentration of H_3O^+ ions is

$$[H_3O^+]_i = K_a\frac{[HA]_i}{[A^-]_i} = \frac{K_a}{r} \qquad (14)$$

where K_a is the dissociation constant of the weak acid HA.

After adding an amount C_a of a strong acid, the concentrations, become, respectively,

$$C = [A^-]_f + [HA]_f$$

$$[A^-]_f = [A^-]_i - C_a$$

$$[HA]_f = [HA]_i + C_a$$

$$[H_3O^+]_f = 10[H_3O^+]_i$$

$$[H_3O^+]_f = K_a\frac{[HA]_f}{[A^-]_f} = K_a\frac{[HA]_i + C_a}{[A^-]_i - C_a} \qquad (15)$$

As a result,

$$\frac{10}{r} = \frac{[HA]_i + C_a}{[A^-]_i - C_a} \qquad (16)$$

Considering

$$[A^-]_i = \frac{r}{r+1}C \quad \text{and} \quad [HA]_i = \frac{1}{r+1}C$$

the following equation is obtained for the buffer capacity, BC_a:

$$BC_a = -\frac{C_a}{\Delta\mathrm{pH}} = C_a = \frac{9r}{r^2+11r+10}C \qquad (17)$$

After adding an amount C_b of a strong base, the following reaction occurs:

$$HA + B \rightarrow BH^+ + A^-$$

In the final stage, the pH variation is ΔpH = +1, and it can be stated,

$$C = [A^-]_f + [HA]_f$$

$$[A^-]_f = [A^-]_i + C_b$$

$$[HA]_f = [HA]_i - C_b$$

$$[H_3O^+]_f = [H_3O^+]_i/10$$

Making the same substitutions as in the previous case, the buffer capacity BC_b is given by:

$$BC_b = \frac{C_b}{\Delta\mathrm{pH}} = C_b = \frac{9r}{10r^2+11r+1}C \qquad (18)$$

Analysis of the BC_a and BC_b expressions reveals that

when $r = 1$, $BC_a = BC_b = (9/22)C = 0.41C$

when $r > 1$, $BC_a > BC_b$

when $r < 1$, $BC_a < BC_b$

Both functions $BC_a = f(r)$ and $BC_b = f(r)$ present a maximum. The coordinates of these maximum points obtained from the zero derivative conditions are

$$\frac{d(BC_a)}{dr} = 0 \Rightarrow r = \sqrt{10} \quad \text{and} \quad (BC_a)_{max} = 0.52C$$

$$\frac{d(BC_b)}{dr} = 0 \Rightarrow r = \frac{1}{\sqrt{10}} \quad \text{and} \quad (BC_b)_{max} = 0.52C$$

Figure 1 shows the diagram obtained representing β, BC_a, and BC_b as functions of −log *r* = *pr* (for C = 1 M). From the diagram it is possible to deduce that, if the buffer capacity is expressed the minimum concentration of strong

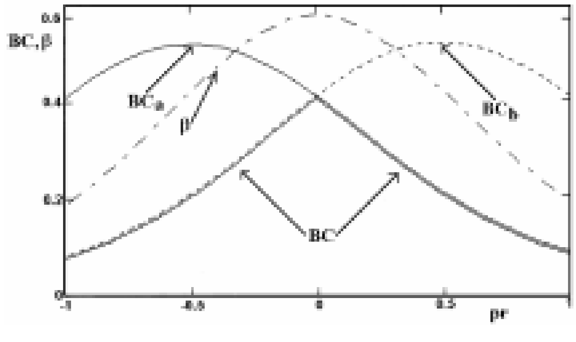

Figure 1. Variation of BC_a, BC_b, and β with *pr* (*pr* = −log *r*) for C = 1 M.

acid or strong base that causes a variation of 1 unit in the buffer's pH, then

for $r = 1$, $(BC)_{max} = BC_a = BC_b = 0.41C < \beta_{max} = 0.57C$

for $r > 1$, $BC = BC_a$

for $r < 1$, $BC = BC_b$

The buffer capacity *defined in this way* is always smaller than the buffer index of the electrolyte solution. However, the maximum point is obtained for both quantitative units at the same value of r ($r = 1$).

Conclusion

From the significance of both quantitative units, β and $BC_{a,b}$, it is obvious that the buffer index is the one that has maximum utility in systems where the addendum's concentration is very small (e.g., biological systems). On the other hand, in the case of quantitative chemical analysis, where the way pH is modified during the determination is known, the quantitative unit that better describes the buffering effect must be the acid buffering capacity or the base buffering capacity. For example, if an ammonium buffer is used in an EDTA titration (process that generates H_3O^+ ions) to bring the pH value to pH = 10 so its buffer capacity has the value 0.1 mole/liter, the calculation of the total buffer concentration must be based on eq 19

$$BC_a = 0.1 \tag{19}$$

and not on eqs 20 and 21

$$BC = BC_b = 0.1 \tag{20}$$

$$\beta = 0.1 \tag{21}$$

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