

BUFFERS AND BUFFER CAPACITY

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Principle of buffering

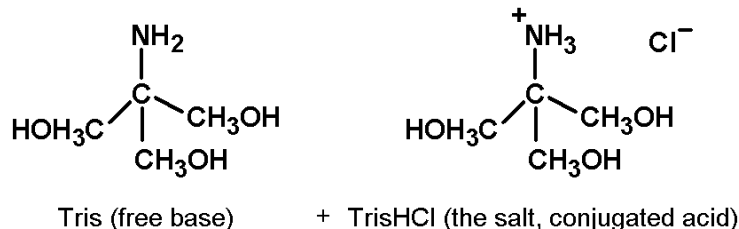
A *buffer* solution is a solution that resists changes in pH either when diluted or when limited amounts of acid or base are added to it. Such a solution can be prepared by combining a weak acid and its salt with a strong base (conjugated base) or, analogously, a weak base and its salt with a strong acid (conjugated acid).

For example:

Acetate buffer: CH_3COOH (the weak acid) + CH_3COONa (the salt, conjugated base)

Phosphate buffer: NaH_2PO_4 (the weak acid) + Na_2HPO_4 (the salt, conjugated base)

Tris buffer:



(Tris: **Tris [2-amino-2-(hydroxymethyl)-propan-1,3-diol]**, an organic base)

The *Henderson-Hasselbalch equation* describes the behaviour of such a buffer and for the mixture of a weak acid and its salt with a strong base (conjugated base) it has the form:

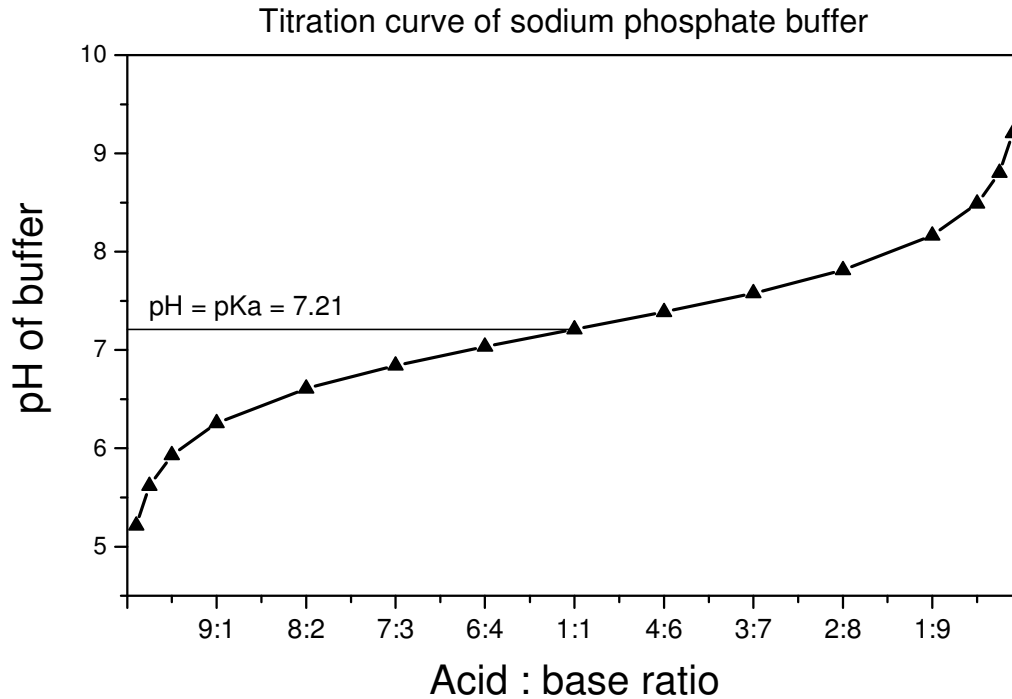
$$\text{pH} = \text{p}K_a + \log \frac{c_s}{c_{ac}}$$

$\text{p}K_a$ negative logarithm of the dissociation constant for the weak acid,

c_s substance concentration of the salt (conjugated base),

c_{ac} substance concentration of the weak acid (conjugated acid).

Graphically the Henderson-Hasselbalch equation plotted as the acid : conjugated base ratio vs. pH of buffer actually constitutes the titration curve of the weak acid (see figure on the next page). Note also that for the acid : base ratio 1:1 the pH of buffer just equals the $\text{p}K_a$ (this is valid for uni-univalent systems, e.g., $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$, $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$).



The equation for a weak base and its salt with a strong acid (conjugated acid) has the form:

$$pH = pK_w - pK_b + \log \frac{c_b}{c_s}$$

pK_b negative logarithm of the dissociation constant for the weak base,

c_b substance concentration of the base,

c_s substance concentration of the salt (conjugated acid),

$pK_w = 14 = -\log 10^{-14}$ (ionic product of water).

Buffer capacity (β) is defined as the amount of a strong acid or a strong base that has to be added to 1 litre of a buffer to cause pH change of 1.0 pH unit:

$$\beta = \frac{\Delta c_b}{\Delta pH} = -\frac{\Delta c_{ac}}{\Delta pH}$$

The buffer capacity depends on the amounts of substance of the weak acid and its conjugated base in the buffer. It is in fact directly related to the first derivative of the buffer titration curve, or, in other words, the slope of the titration curve. As the slope of the titration curve is the smallest at the acid : base ratio 1:1, the buffer capacity is maximal at the same point (the second derivative of the titration curve is equal to zero at the same point).

Calculation of pH of buffer after addition of strong acid or base

Example:

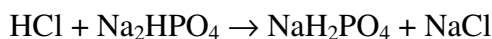
Let's have 600 ml of a sodium phosphate buffer of concentration $c = 0.25$ mol/l and the ratio acid : base is 2:3. Next, we add 150 ml of HCl, $c = 0.2$ mol/l. How much the pH changes after this addition? (pK_a of sodium dihydrogen phosphate is 7.21)

Solution:

In order to calculate the pH of this buffer before and after addition of HCl, we need to know the ratio of acid : base for both conditions. The ratio is given for the original buffer as 2:3, so we can easily use the Henderson-Hasselbalch equation to calculate the original pH:

$$pH = pK_a + \log \frac{3}{2} = 7.21 + \log 1.5 = 7.21 + 0.17609 = \underline{7.39}.$$

Next, we need to consider how the ratio acid : base changes following addition of HCl. The strong acid actually titrates the basic component of the buffer, converting it into the acidic component:



Before addition of HCl:

| | | |
|---------------------|------------------------------------|--------------------------------------|
| Number of moles for | total phosphate: | $0.6 \times 0.25 = 0.15$ mol |
| | NaH ₂ PO ₄ : | $0.15 \times \frac{2}{5} = 0.06$ mol |
| | Na ₂ HPO ₄ : | $0.15 \times \frac{3}{5} = 0.09$ mol |

After addition of HCl $0.15 \times 0.2 = 0.03$ mol:

| | | |
|---------------------|------------------------------------|--------------------------------------|
| Number of moles for | total phosphate: | $0.6 \times 0.25 = 0.15$ mol |
| | NaH ₂ PO ₄ : | 0.06 mol + 0.03 mol = 0.09 mol |
| | Na ₂ HPO ₄ : | 0.09 mol - 0.03 mol = 0.06 mol |

The new ratio of acid : base is 0.09 : 0.06, i.e. 3 : 2.

And the resulting pH is:

$$pH = pK_a + \log \frac{2}{3} = 7.21 + \log 0.6667 = 7.21 - 0.17609 = \underline{7.03}.$$

The pH change (effect of addition): $\Delta pH = 7.39 - 7.03 = \underline{-0.36}$