BUFFERS AND BUFFER CAPACITY

1 THEORY

1.1 Principle:

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 (free base)   + TrisHCl (the salt, conjugated acid)
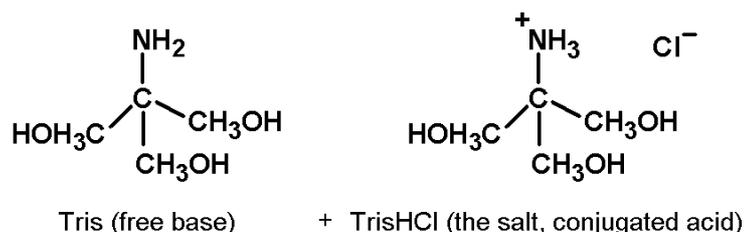
(Tris: **Tris [2-amino-2-(hydroxymethyl)-propan-1,3-diol)]**, an organic base)

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:

$$pH \ = \ pK_a \ + \ log\frac{c_s}{c_{ac}}$$

pK_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 pK_a.

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 smallest at the acid : base ratio 1:1, the buffer capacity is maximal at the same point.

Titration curve of sodium phosphate buffer
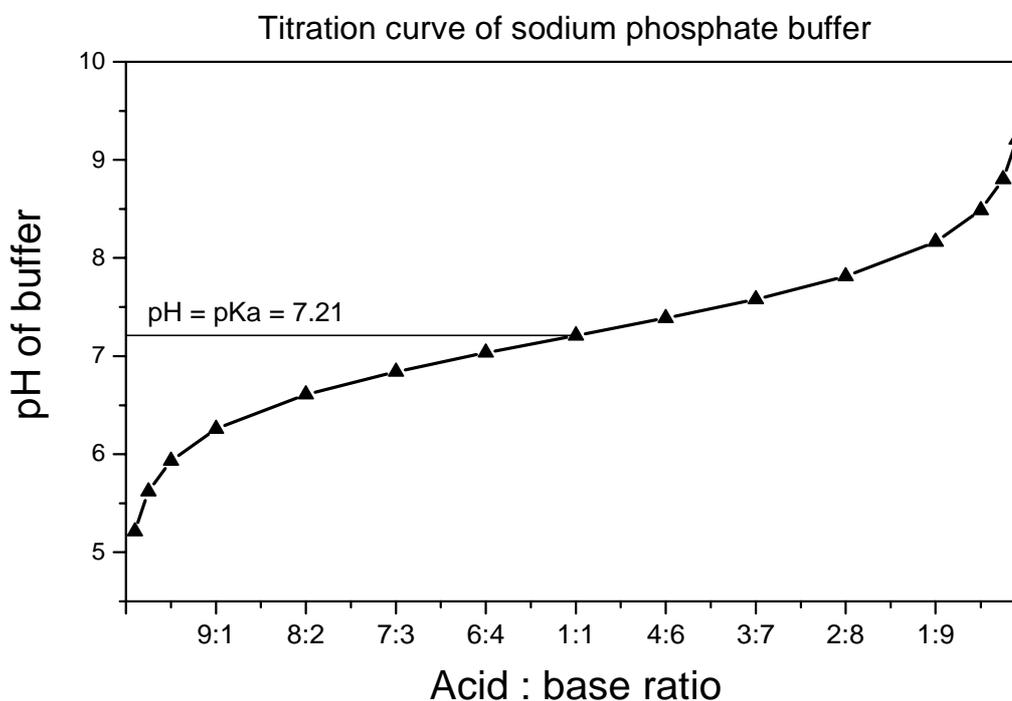
1.2   Calculation of pH of buffer after addition of strong acid or base

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 3/2 = 7.21 + log 1.5 = 7.21 + 0.17609 = 7.386.

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:

$$HCl \ + \ Na_2HPO_4 \ \rightarrow \ NaH_2PO_4 \ + \ NaCl$$

before addition of HCl:

Number of moles for	total phosphate:	(0.6 x 0.25) = 0.15 mol
	NaH$_2$PO$_4$:	0.15 /5 x 2 = 0.06 mol
	Na$_2$HPO$_4$:	0.15 /5 x 3 = 0.09 mol

after addition of HCl 0.15 x 0.2 = 0.03 mol:

Number of moles for	total phosphate:	(0.6 x 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 2/3 = 7.21 + log 0.6667 = 7.21 − 0.17609 = 7.034.

The pH change (effect of addition): ΔpH = 7.386 − 7.034 = − 0.352

2 PRACTICE

Consider following experiment: three sodium phosphate buffers were made of acid:base ratios 1:1, 9:1 and 1:9 by mixing primary and secondary phosphate solutions as indicated in the table; the NaCl was included as a negative control (no buffering). pH of all these solutions were measured using the pH meter. Then, NaOH was added to all solutions and pH was measured again. All the data were collected into the following table:

Tube No		1	2	3	4
Na_2HPO_4 0.1 mol/l	ml	5	1	9	-
NaH_2PO_4 0.1 mol/l	ml	5	9	1	-
NaCl 0.1 mol/l	ml	-	-	-	10
acid/conjugate base ratio	ml	1 : 1	9 : 1	1 : 9	-
pH measured	ml	*6.63*	*7.61*	*5.71*	*6.47*
pH expected/calculated	ml				
Added to all tubes					
NaOH 0.1 mol/l		2.0	2.0	2.0	2.0
pH measured		*7.06*	*10.83*	*6.51*	*11.76*
pH expected/calculated					

Using the Henderson-Hasselbalch equation, calculate the pH values of all three prepared phosphate buffers ($pK_a = 7.21$) both before and after the NaOH addition. Fill into the table and compare with the measured values.

Considering both the measured as well as the theoretical (calculated) values, look at the pH changes after the NaOH additions, and conclude which of the prepared solutions show(s) the highest buffer capacity. Do all the solutions behave as buffer ?