Practical Lesson No 2

BUFFERS AND BUFFER CAPACITY

Reagents:
1. NaH_2PO_4 0.1 mol/l
2. Na_2HPO_4 0.1 mol/l
3. NaCl   0.1 mol/l
4. HCl   0.1 mol/l
5. NaOH standard solution   0.1 mol/l

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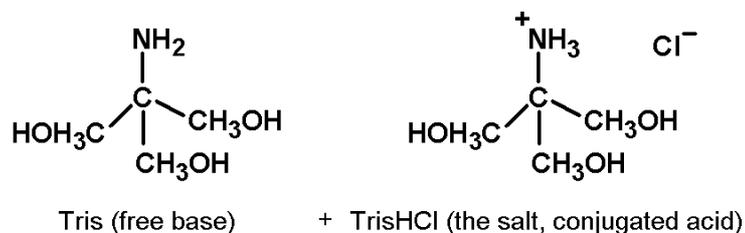
(Tris: **Tris [2-amino-2-(hydroxymethyl)-propan-1,3-diol)**], an organic base)

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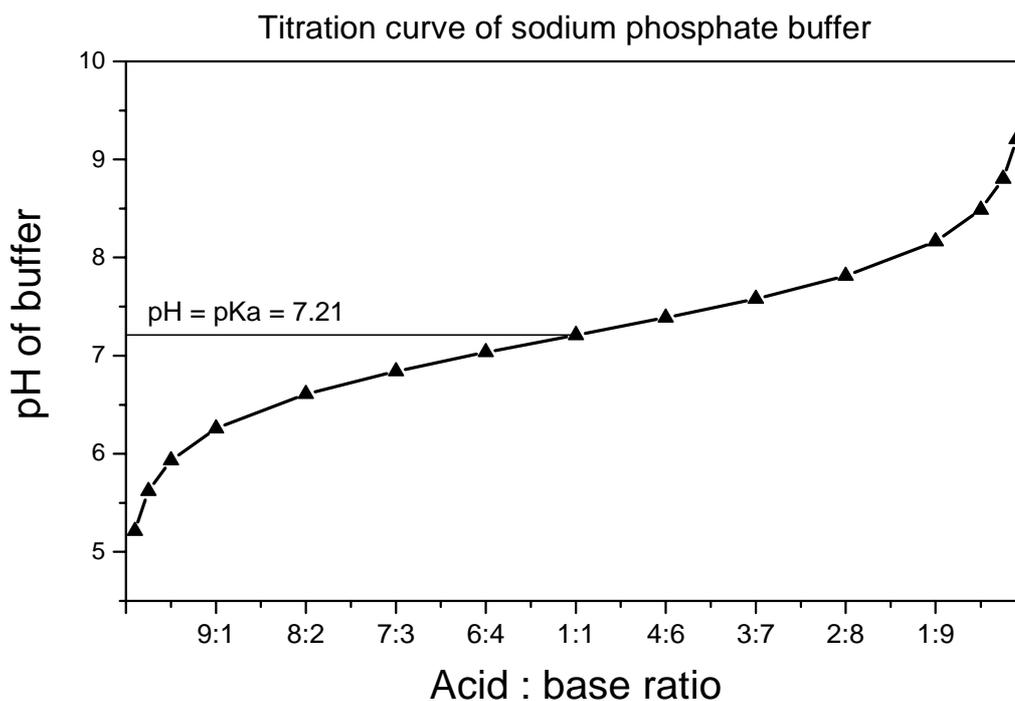
1.2 Calculation of pH of buffer after addition of strong acid or base

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:

$$pH = pK_a + \log 3/2 = 7.21 + \log 1.5 = 7.21 + 0.17609 = \underline{7.386}.$$

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:

$$pH = pK_a + \log 2/3 = 7.21 + \log 0.6667 = 7.21 − 0.17609 = \underline{7.034}.$$

The pH change (effect of addition): $\Delta pH = 7.386 − 7.034 = \underline{− 0.352}$

2 EXPERIMENTAL

2.1 Directions for use of the pH meter EIM

The pH meter has been already switched on, checked and calibrated by technicians using standard buffer solutions pH 7.0 and 4.0. **Do not change any settings!**

pH measurement:
a. The electrode is resting in buffer of pH 7.00 (the green solution). For measurement of pH pull the electrode out from the buffer pH 7.0, rinse it with distilled water, wipe gently with a piece of tissue paper (just touch, avoid rubbing the glass bulb that would charge it with static electricity), and place it into the sample solution in plastic container.
b. Wait until stable reading is achieved (the usual response time of glass electrode is about one minute). Write down the value.
c. Pull the electrode out, rinse again with distilled water, wipe with a piece of tissue paper, and place it into another sample, or, when the experiment is complete, into the buffer pH 7.0.

NOTE: In the meantime in case of repetitive measurements and when the work is finished, always leave the electrode immersed in the standard buffer pH 7.00. **The electrode can be irreversibly damaged when it is allowed to get dry, it must never happen!**

2.2 Evaluation of titration curves for strong and weak acid

Titration curve means a plot of pH against amount of alkali added to sample of acid (see also figure in the Practical Lesson 1). Comparison and analysis of titration curves for a strong and weak acid is useful for understanding of concept of buffering.
From technical reasons, you will not obtain your own data here, but rather, the task is to evaluate previous data that we provide.

Description of experimental procedure:

20 ml of either HCl (c = 0.1 mol/l), or CH_3COOH (c = 0.1 mol/l) was measured into titration flask. The initial pH was measured. Then, NaOH (c = 0.1 mol/l) was added step by step in amounts as indicated, and pH was measured after each addition.

Tasks for evaluation:

a. For both acids, plot measured pH values against volume (ml) of added base (as in figure in Pract. Lesson 1).

b. Calculate pH of hydrochloric acid (activity coefficient f = 0.796) and compare with the initial measured value.

c. Calculate pH of acetic acid 0.1 mol/l (pK_a = 4.75) and compare with the initial measured value.

d. Compare the shapes of both curves – which of the mixtures used could work as a buffer and for what pH range ?

e. From the inflection point of your titration curve, determine pK_a of acetic acid.

2.3 Buffer capacity

Procedure:

a. Number the test tubes and prepare the initial mixtures 1-4 as shown in 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					
pH measured ml					
pH calculated ml					
Add to all tubes					
acid or base 0.1 mol/l		1.0	1.0	1.0	1.0
pH measured					
pH calculated[1]					

b. Using the Henderson-Hasselbalch equation, calculate the pH values of prepared phosphate buffers (pK_a = 7.21) before as well as after addition of 1 ml of HCl 0.1 mol/l.

c. Measure pH of the initial mixtures and compare these values with the calculated ones.

d. Then add to each of the four tubes 1 ml of HCl 0.1 mol/l, mix and measure pH again. Compare the obtained values with calculated ones.

e. Conclude which of the prepared solutions shows the highest buffer capacity. Do all the examined solutions behave as buffers?

f. Alternatively, you can test the buffer capacity of the prepared solutions by adding 1 ml of NaOH 0.1 mol/l instead of HCl.

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[1] Only in cases when the buffering capacity has not been exceeded (over-titrated)