Investigation of buffer capacity

Theoretical background: P.W. Atkins: *General Chemistry,*, Chapter 15.2 (The pH of mixed solutions).
Type of the practice: Individual.
Aim of the practice: Understanding the concept of buffer capacity and determining buffer capacity experimentally or by calculations.

1 Introduction

Buffers can moderate the effect of addition of acids or bases on the change of *p*H (on the change of acidity) of an aqueous solution. According to the Brønsted–Lowry acid–base concept, a buffer is a solution that contains a conjugate acid base pair, which can be either a weak acid (*e.g.*, acetic acid) and its conjugate base pair (acetate) or a weak base (*e.g.*, ammonia) and its conjugate acid (ammonium ion). In common practice, those conjugate acid–base pairs are measured in from separated sources, *i.e.*, a weak acid or base and its salt together.

The two most important properties of buffer systems are the *p*H of the buffer and the buffer capacity available at a given *p*H. Buffer capacity is essentially a measure of how much the buffer can moderate the pH change. Both of these properties depends on the composition of the buffer as described below. Let suppose we have a weak acid, HA and its salt with a strong base, MA. If we dissolve the salt, $\mathrm{MA} \rightarrow \mathrm{A^-} + \mathrm{M^+}$ electrolytic dissociation occurs, producing the conjugate (weak) base pair of the HA acid. It can hydrolyze (react with water), *i.e.*, $\mathrm{A^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{HA} + \mathrm{OH^-}$ reaction can occur. It can be characterized by the hydrolization constant, $\mathrm{K_h}$. If the weak acid is added to this solution, it can dissociate to some extent according to the $\mathrm{HA} \rightleftharpoons \mathrm{A^-} + \mathrm{H^+}$ equation. This equilibrium can be characterized by the dissociation constant, $\mathrm{K_a}$. The two systems (equilibria) are not independent because of the common components. They are connected by a third equilibrium process, the dissociation (self-ionization) of water $\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-}$, which can be characterized by the ionic product of water $\mathrm{K_w}$. Obviously $\mathrm{K_h} \times \mathrm{K_a} = \mathrm{K_w}$. If a strong acid is added to this system, some of the $\mathrm{A^-}$ ions will be protonated, the weak acid dissociation equilibrium shifts towards the HA formation. Only small part of the protons from the strong acid remains in free $\mathrm{H^+}$ form, so the change in the hydrogen ion concentration ($[\mathrm{H^+}]$) (and thus in *p*H) of the solution is smaller compared to when the acid would be added to pure water. Similarly, when a strong base is added to the buffer solution, the deprotonation of the weak acid HA will moderate the increase in $[\mathrm{OH^-}]$. It follows that the buffer solution can moderate equally the *p*H change after addition of acid or base, if $[\mathrm{A^-}] = [\mathrm{HA}]$.

The *p*H of the buffer solution can be estimated as follows. (Estimated, because we should use activities of the components in a given solution, but we simplify to use concentrations, assuming that the activity coefficients are close to 1.) The dissociation constant of the weak acid is $\mathrm{K_a} = \dfrac{[\mathrm{A^-}] \cdot [\mathrm{H^+}]}{[\mathrm{HA}] \cdot \mathrm{c^0}}$, where the equilibrium concentrations of the substances are denoted with the square brackets and $\mathrm{c^0}$ is the standard concentration. From the previous expression $[\mathrm{H^+}] = \mathrm{K_a} \cdot \dfrac{[\mathrm{HA}] \cdot \mathrm{c^0}}{[\mathrm{A^-}]}$. At a given temperature and ionic strength $\mathrm{K_a}$ is constant, so the *p*H of the prepared buffer solution is a function of $[\mathrm{A^-}]$ and $[\mathrm{HA}]$. Approximately true that $[\mathrm{A^-}]$ is the concentration of the MA salt ([salt]) and [HA] is approximately equal to the measured-in concentration of the weak acid ([acid]). Logarithmizing the expression we get the Henderson – Hasselbalch equation:

$$p\mathrm{H} = p\mathrm{K_a} + \lg\left(\frac{[\mathrm{salt}]}{[\mathrm{acid}]}\right),$$

where $p\mathrm{K_a} = -\lg \mathrm{K_a}$. So, it can be seen that at identical weak acid and salt (conjugate base) concentrations, the dissociation constant of the acid determines the *p*H of the buffer and that can be varied over a wide range by varying the ratio of the two concentrations. The logic presented above is true not only for a buffer prepared from a weak acid and the corresponding salt, but also from a weak base and the corresponding salt. Only the conjugate acid–base pairs should be exchanged.

In practice, the concentration ratio of the conjugate acid–base pair can be changed not only by dissolving a salt and a weak acid (or a salt and a weak base) in a common solvent. The ratio $\frac{[A^-]}{[HA]}$ can also be modified by adding a strong acid to the weak acid solution. The dissociation of the weak acid is then reduced and practically [HA] corresponding to the measured-in concentration will be present. Titration of this solution with a strong base shifts the equilibrium towards the deprotonation of the weak acid and different ratio of $\frac{[A^-]}{[HA]}$ is obtained at each titration point (incuding the point, where $[HA] = [A^-]$). With proper titration, the weak acid will eventually be present as $[A^-]$. Such a titration shall be performed in the practice to map in which range the buffer system (under study) has significant buffer capacity and what is its numerical value.

There are various definitions of buffer capacity. The weakest definition states that the buffer capacity is the amount of strong acid or strong base that can be added to the buffer that does not cause a *significant change* in the pH of the buffer solution. Since the expression, *significant change* is very much ill-defined (could be $2-3$ pH unit, or in biological systems only $0.1-0.3$ unit), mostly we use the definition: buffer capacity (B_C) is the amount of substance of a strong acid or strong base that is added to a solution of 1 dm^3 to change the pH by one unit. If $[HA] \neq [A^-]$, the value of the buffer capacity will vary depending on whether acid or base is added. That is,

$$B_C = \frac{dn}{dpH} \quad \left(= \frac{d\left(c_b \cdot \left(1dm^3\right)\right)}{dpH} = \frac{-d\left(c_a \cdot \left(1dm^3\right)\right)}{dpH} \right) \tag{1}$$

where n is the amount of substance of a strong base added to 1 dm^3 buffer solution. Since the addition of strong acid is equivalent to the subtraction of strong base, therefore the amount of strong acid added corresponds to $-n$. The numerical value of this amount of substance is equal to the molar concentration of the strong base added (c_b) or to the negative molar concentration of the strong acid added (c_a) -1 as shown by Eq. (1). This consideration and giving the definition of B_C in differential form provides that *(1)* the numerical value is the same in case of adding either acid or base, as well as *(2)* the value of the buffer capacity is always positive with the unit of the amount of substance. In the followings, concentrations are used in all formulas and (for the sake of simplicity) the unit volume is not always indicated, but it is always implied though not plainly expressed.

2 Determining buffer capacity by calculation

This section gives the formulas necessary to calculate buffer capacity. The deductions require the knowledge of the following notations and definitions (most of them are already known from analytical chemistry):

- The *total concentration* (T) of a component means the overall concentration of that unit independently from its forms. For example, if a solution contains the AB, AB_2 and AB_3 substances composed from the A and B particles then the total concentration of B can be given by the equation:

  $$T_B = [B] + [AB] + 2 \cdot [AB_2] + 3 \cdot [AB_3]$$

  using the equilibrium concentrations. Analytical methods, like weighting or volumetric analysis, usually provide the total concentration as experimental data.
- The *protonation constant* (K_p) is the equilibrium constant of a protonation process.[1] The process and its equilibrium constant for the anion of a monoprotic acid can be given by following equation:[2]

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[1] The equilibrium constant of the dissociation process is more frequently used in analytical chemistry but the formulas to be deduced are simpler by using the protonation constants.

[2] In cases of polyprotic acids (where m is the number of the potential protons to be donated), the protonic equilibrium of their

$$\mathrm{H^+ + A^- \rightleftharpoons HA}, \qquad \mathrm{K_p} = \frac{[\mathrm{HA}]\cdot \mathrm{c}^0}{[\mathrm{H^+}]\cdot[\mathrm{A^-}]} \tag{2}$$

At first, B_C is formulated for the simplest case when the anion of a monoprotic acid is partially protonated in a solution of the volume of 1 dm^3, and the amount of the strong base added into the solution is n. Before adding the base, the total concentrations of the hydrogen ion ($\mathrm{T_H}$) and the anion of the acid ($\mathrm{T_A}$) can be given by the

$$\begin{aligned} \mathrm{T_H} &= [\mathrm{HA}] + [\mathrm{H^+}] - [\mathrm{OH^-}] = \mathrm{K_p}\cdot[\mathrm{H^+}]\cdot[\mathrm{A^-}] + [\mathrm{H^+}] - \frac{\mathrm{K_w}}{[\mathrm{H^+}]} && (3)\\ \mathrm{T_A} &= [\mathrm{HA}] + [\mathrm{A^-}] = \mathrm{K_p}\cdot[\mathrm{H^+}]\cdot[\mathrm{A^-}] + [\mathrm{A^-}] && (4) \end{aligned}$$

equations if [HA] and $[\mathrm{OH^-}]$ are expressed and substituted from equation (2) and from the definition of the ionic product of water ($\mathrm{K_w} = ([\mathrm{H^+}]\cdot[\mathrm{OH^-}])/(\mathrm{c}^0)^2$), respectively. (In the above equations, standard concentrations are not shown, for the sake of simplicity, but it simply means we always use concentrations in mol/dm^3 unit.) The validity of equation (4) is obvious from the definition of the total concentration; however, equation (3) requires some explanation. There are two sources of free $\mathrm{H^+}$: *(1)* the partial dissociation of the weak acid and *(2)* the self-ionization of water. The latter one is not included in the total concentration of the hydrogen ion since it is not added into the solution. The self-ionization of water produces the same amount of H+ and OH- therefore the $([\mathrm{H^+}] - [\mathrm{OH^-}])$ difference gives the concentration of hydrogen ion derived from the dissociation of the weak acid.

If $[\mathrm{A^-}]$ is expressed from Eq.(4) $\left([\mathrm{A^-}] = \frac{\mathrm{T_A}}{1+\mathrm{K_p}\cdot[\mathrm{H^+}]}\right)$, and it is substituted into equation (3) then

$$-\mathrm{T_H} = \frac{\mathrm{K_w}}{[\mathrm{H^+}]} - [\mathrm{H^+}] - \mathrm{T_A}\cdot\frac{\mathrm{K_p}\cdot[\mathrm{H^+}]}{1+\mathrm{K_p}\cdot[\mathrm{H^+}]} \tag{5}$$

the equation is reached after some rearrangements from which the $[\mathrm{H^+}]$ (and also the pH) can be calculated knowing the total concentrations and the protonation constant.

If n amount of base is added into 1dm^3 buffer solution, then the value of $\mathrm{T_H}$ is decreased by this number since adding base into a solution is equivalent to taking acid from it:

$$\Delta\mathrm{n} = \Delta(-\mathrm{T_H}), \qquad \text{illetve} \qquad \mathrm{dn} = \mathrm{d}(-\mathrm{T_H})\,.$$

Based on some simplifications, the buffer capacity can be given with the following equation:[3]

$$\mathrm{B_C} = \ln(10)\cdot\left(\frac{\mathrm{K_w}}{[\mathrm{H^+}]} + [\mathrm{H^+}] + \frac{\mathrm{T_A}\cdot\mathrm{K_p}\cdot[\mathrm{H^+}]}{(1+\mathrm{K_p}\cdot[\mathrm{H^+}])^2}\right).$$

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anion can be described by m processes and m equilibrium constants:

$$\mathrm{H + H_{i-1}A \rightleftharpoons H_iA}, \qquad \mathrm{K_{p,i}} = \frac{[\mathrm{H_iA}]\cdot\mathrm{c}^0}{[\mathrm{H}]\cdot[\mathrm{H_{i-1}A}]} \qquad (\mathrm{i} = 1\ldots\mathrm{m})$$

The charge numbers are not indicated for the sake of clarity.

[3] Eq.(1) can be transformed with the help of $\Delta\mathrm{n} = \Delta(-\mathrm{T_H})$ and $\mathrm{dn} = \mathrm{d}(-\mathrm{T_H})$ considerations together with the differentiation rules of complex functions $\left(\frac{df(g(x))}{dx} = \frac{df(g)}{dg}\cdot\frac{dg(x)}{dx}\right)$:

$$\mathrm{B_C} = \frac{\mathrm{dn}}{\mathrm{d}p\mathrm{H}} = \frac{\mathrm{dn}}{\mathrm{d}[\mathrm{H^+}]}\cdot\frac{\mathrm{d}[\mathrm{H^+}]}{\mathrm{d}p\mathrm{H}} = \frac{\mathrm{d}(-\mathrm{T_H})}{\mathrm{d}[\mathrm{H^+}]}\cdot\frac{\mathrm{d}[\mathrm{H^+}]}{\mathrm{d}p\mathrm{H}}\,. \tag{6}$$

According to Eq.(5) and the differentiation rule of quotients $\left(\frac{\mathrm{d}\left(\frac{\mathrm{f(x)}}{\mathrm{g(x)}}\right)}{\mathrm{dx}} = \frac{\frac{\mathrm{df(x)}}{\mathrm{dx}}\cdot\mathrm{g(x)} - \mathrm{f(x)}\cdot\frac{\mathrm{dg(x)}}{\mathrm{dx}}}{\mathrm{g^2(x)}}\right)$:

According to this equation, buffer capacity is the function of the hydrogen ion concentration at a given buffer concentration. Since $[\mathrm{H}^+]$ can change orders of magnitude, the buffer capacity is more frequently expressed as the function of pH:

$$\mathrm{B_C} = \mathrm{B_C}(p\mathrm{H}) = \ln(10)\cdot\left(\frac{\mathrm{K_w}}{10^{-\mathrm{pH}}} + 10^{-\mathrm{pH}} + \frac{\mathrm{T_A}\cdot\mathrm{K_p}\cdot 10^{-\mathrm{pH}}}{(1+\mathrm{K_p}\cdot 10^{-\mathrm{pH}})^2}\right), \tag{9}$$

In the followings, $\mathrm{B_C}$ is always regarded as a function of pH, but it is not indicated for the sake of simplicity.

It can be seen from equation (9) that the buffer capacity is proportional to the sum of three terms. The value of any quantity in these three terms can only be a non-negative number providing positive sign for the buffer capacity. Inside the large parentheses, the first and the second terms have large numerical values in basic and acidic solutions, respectively. It shows that buffer capacity is intrinsically large in in either strong base or strong acid solution, so the added acid or base does not change the pH of the solution significantly, independently of the quality of the buffer. The third term characterizes the buffer itself, and it has large numerical value in different pH ranges, depending on the values of $\mathrm{T_A}$ and $\mathrm{K_p}$.

If the buffer may consist of various protonated forms of a divalent anion $\left(\mathrm{A}^{2-}\right)$ then the expression of $\mathrm{B_C}$ changes [4]:

$$\mathrm{B_C} = \ln(10)\cdot\left(\frac{\mathrm{K_w}}{10^{-\mathrm{pH}}} + 10^{-\mathrm{pH}} + \mathrm{T_A}\cdot\mathrm{K_{p,1}}\cdot 10^{-\mathrm{pH}}\cdot\frac{(1+4\cdot\mathrm{K_{p,2}}\cdot 10^{-\mathrm{pH}} + \mathrm{K_{p,1}}\cdot\mathrm{K_{p,2}}\cdot 10^{-2\cdot\mathrm{pH}})}{(1+\mathrm{K_{p,1}}\cdot 10^{-\mathrm{pH}} + \mathrm{K_{p,1}}\cdot\mathrm{K_{p,2}}\cdot 10^{-2\cdot\mathrm{pH}})^2}\right). \tag{10}$$

Comparing this formula to equation (9) clearly shows that the calculation of buffer capacity can be done with a much more complicated expression. Although multivalent anions also have practical importance as buffers (e.g., phosphate ions), these ones are not studied at the practice because of the complexity of the expression of $\mathrm{B_C}$.

If a buffer solution consists of more substances, then the third term of them must be summarized. For example, if a buffer solution includes two (conjugate base) anions (A_1^- és A_2^-) with the total concentrations of $\mathrm{T_{A_1}}$ and $\mathrm{T_{A_2}}$ and with the protonation constants of $\mathrm{K_{p1}}$ és $\mathrm{K_{p2}}$ then the buffer capacity can be given by the:

$$\mathrm{B_C} = \ln(10)\cdot\left(\frac{\mathrm{K_w}}{10^{-\mathrm{pH}}} + 10^{-\mathrm{pH}} + \sum_{\mathrm{j}=1}^{2}\frac{\mathrm{T_{Aj}}\cdot\mathrm{K_{pj}}\cdot 10^{-\mathrm{pH}}}{(1+\mathrm{K_{pj}}\cdot 10^{-\mathrm{pH}})^2}\right) \tag{11}$$

equation. The same formula can be used if both the anion and the cation of the buffer take part of protonation processes. In this case, the total concentration should be calculated from the stoichiometric composition of the buffer salt.

$$\frac{\mathrm{d}(-\mathrm{T_H})}{\mathrm{d}[\mathrm{H}^+]} = -\frac{\mathrm{K_w}}{[\mathrm{H}^+]^2} - 1 - \frac{\mathrm{T_A}\cdot\mathrm{K_p}}{(1+\mathrm{K_p}\cdot[\mathrm{H}^+])^2}, \tag{7}$$

while using the definition of pH:

$$\frac{[\mathrm{H}^+]}{\mathrm{c}^0} = 10^{-p\mathrm{H}} = \mathrm{e}^{-p\mathrm{H}\cdot\ln(10)}, \frac{\mathrm{d}[\mathrm{H}^+]}{\mathrm{d}p\mathrm{H}} = -\ln(10)\cdot\mathrm{c}^0\cdot\mathrm{e}^{-p\mathrm{H}\cdot\ln(10)} = -\ln(10)\cdot[\mathrm{H}^+]. \tag{8}$$

If we substitute the derivatives given by Eq. (7) and (8) to Eq. (6) we obtained the definition of the buffer capacity.

[4] In this case, instead of Eq.(3) and (4), we use

$$\begin{aligned}\mathrm{T_H} &= 2\cdot[\mathrm{H_2A}] + [\mathrm{HA}^-] + [\mathrm{H}^+] - [\mathrm{OH}^-] = 2\cdot\mathrm{K_{p,1}}\cdot\mathrm{K_{p,2}}\cdot[\mathrm{H}^+]^2\cdot[\mathrm{A}^{2-}] + \mathrm{K_{p,1}}\cdot[\mathrm{H}^+]\cdot[\mathrm{A}^{2-}] + [\mathrm{H}^+] - \frac{\mathrm{K_w}}{[\mathrm{H}^+]}\\ \mathrm{T_A} &= [\mathrm{H_2A}] + [\mathrm{HA}^-] + [\mathrm{A}^{2-}] = \mathrm{K_{p,1}}\cdot\mathrm{K_{p,2}}\cdot[\mathrm{H}^+]^2\cdot[\mathrm{A}^{2-}] + \mathrm{K_{p,1}}\cdot[\mathrm{H}^+]\cdot[\mathrm{A}^{2-}] + [\mathrm{A}^{2-}]\end{aligned}$$

equations to express $-\mathrm{T_H}$-t. We differentiate the received expression according to $[\mathrm{H}^+]$, then express $\mathrm{B_C}$ with Eq.(6) and (8).

Table 1: Data for solution preparation and calculations.

Substances	c_p (M)	$V_{0.1\,\mathrm{M\,HCl}}$ (cm^3)	$\lg K_{p,1}$	$\lg K_{p,2}$	V_{titrant} (cm^3)
boric acid	0.035 – 0.050	5.00	9.1	-	0; 0.3; 0.6;...;2.7; 3; 4; 5;...;25;
sodium acetate	0.035 – 0.050	55.00	4.6	-	
ammonium chloride	0.035 – 0.050	5.00	9.3	-	
oxalic acid	0.020 – 0.025	5.00	4.0	1.3	0; 1; 2;...;15; 15.5; 16; 16.5;...;25;
malonic acid	0.020 – 0.025	5.00	5.3	2.6	
succinic acid	0.020 – 0.025	5.00	5.3	4.0	
ammonium acetate	0.020 – 0.025	30.00	9.3 és 4.6	-	0; 0.5; 1.0;...; 25

3 Experimental determination of buffer capacity

If the protonation constants are unknown in a buffer solution, or the calculation seems to be more difficult (e.g., in cases of multivalent anions) then buffer capacity can be determined experimentally by *p*H metric titration. This method is based on the differential form of the definition of buffer capacity given in equation (1).

Let V_0 is the initial volume of the solution to be titrated and let c_b is the concentration of the titrant which is a strong base solution. Let V_j and V_{j+1} are the consumptions in two subsequent titration points and let pH_j and pH_{j+1} are their corresponding measured *p*H. Accordingly, the change of the added amount of the base between these two titration points is $c_b\left(V_{j+1}-V_j\right)$. By definition given in equation (1), the change of the amount of the base (Δn) applies to $1\,\mathrm{dm}^3$ buffer solution which can be approximated by the:

$$\Delta n \cong c_b(V_{j+1}-V_j)\cdot\frac{1\,\mathrm{dm}^3}{V_0+\dfrac{V_{j+1}+V_j}{2}} \tag{12}$$

formula in the above case, if the $(V_{j+1}-V_j) \ll (V_0+V_j)$ inequality is valid and the volumes are given in dm^3. From similar considerations:

$$\Delta pH = pH_{j+1} - pH_j. \tag{13}$$

The differences given in expressions (12) and (13) should be substituted into equation (1) to get the formula for calculating the buffer capacity between two successive titration points:[5]

$$B_c^{\mathrm{measured}} = \frac{dn}{dpH} \approx \frac{\Delta n}{\Delta pH} = \frac{c_b(V_{j+1}-V_j)}{pH_{j+1}-pH_j}\cdot\frac{1\,\mathrm{dm}^3}{V_0+\dfrac{V_{j+1}+V_j}{2}}\,. \tag{14}$$

The task at the practice is to determine the buffer capacity of a buffer solution given by the instructor. It shall be carried out by both calculation and experiments by *p*H metric titrations.

4 Measurements

From Table 1, the instructor assigns *(1)* the substance to be used, *(2)* the concentration of the solution to be titrated within the given ranges and *(3)* the initial volume of this solution between 30 – 40 cm^3. In case of no specific instruction, these data are boric acid, 0.05 M and 35 cm^3, respectively. The next tasks are to be carried out:

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[5] Since this number is essentially an approximation of a differential, the same value is valid for the whole range determined by the two points.

1. If they are not ready then 0.1 M HCl solution and 0.1 M NaOH solution must be prepared (with the minimum volume of 100 cm^3).
2. 100 cm^3 solution with the concentration of c_P should be prepared in a volumetric flask by weighting the necessary amount from the assigned material. The solution should also contain the necessary volume of 0.1 M HCl solution which is given in the third column of Table 1.
3. The burette should be cleaned and filled with the 0.1 M NaOH solution.
4. The pH meter should be calibrated before the titration by using two buffer solutions with known pH values. If more buffers are available then the pH∼4 and pH∼10 are to be used, or the buffers having the closest pH values. *Do not calibrate with cold solutions, please wait while their temperatures reach room temperature.*
5. During the pH metric titration, the previously given volume of the solution should be titrated with the 0.1 M base solution. The added volumes of the base must be close to the planned ones which are given in the last column of Table 1. The exactly added volume and the measured pH should be written into the report at the titration points. If the measured volume slightly deviates from the planned one, then the measured one should be written and should be used during the calculations. Two parallel titrations should be done. For the titrations, use a suitable sized beaker; both the sensor part of the pH electrode (glass bulb and the ceramic plug) should be in the solution.

5 Evaluation of the measured data

The experimental conditions, as well as the measured and calculated data should be summarized in the following table:

Compound: ...... c_p= .... M, V_0= .... cm^3 t_{lab} .... °C

V (cm^3)	$pH^{measured}$	$\frac{pH_j + pH_{j+1}}{2}$	$B_c^{measured}$ (mol)	T_A (M)	$B_c^{calculated}$ (mol)

1. The first two columns of the table contain the data of the measured titration curve. The third column is the average of two consecutive measured pH values. These averages will be the independent variables during the further calculations and on the graphs.
2. The fourth column is the buffer capacity calculated from the experimental data by equation (14).
3. The fifth column of the table is the total concentration of the anion of the buffer investigated along the titration points. In the rows of the table, this value can be calculated by the help of the T_A expression.

$$T_A = c_P \cdot \frac{V_0}{V_0 + \frac{V_j + V_{j+1}}{2}}$$

4. The calculated values of the buffer capacity should be given in the last column of the table. Depending on the substance investigated, you should decide if formula (9), (10) or (11) should be used to calculate this column. The T_A values is used from the fifth column. The ionic product of water is to be calculated by equation (found in the appendix) supposing that the values of the ionic strength can be approximated by the value of c_p. The independent variables for the calculations come from the third column.
5. After the above table is completed, a graph should be created, including both the experimental buffer capacity and the calculated one as the function of the third column of the table. Finally, the similarities and the occasional deviations between the two plotted curves must be interpreted and/or explained. It concerns all the three ranges of the curve determined by the strong acid, the base and the weak acid.

Control questions

1. Give the definitions of buffers!
2. What is buffer capacity?
3. Define buffer capacity!
4. Define the total concentration!
5. What are the formulas of the total concentrations in the solution of a monoprotic weak acid, expressed with the equilibrium concentrations, the ionic product of water and the protonation constant?
6. What is the expression of the buffer capacity in the solution of a monoprotic weak acid?
7. How the buffer capacity can be calculated at a given pH from the measured data of a pH metric titration curve?
8. 100 cm^3 0.1 M NaH_2PO_4 solution is mixed with 150 cm^3 0.2 M H_3PO_4 solution. What are the total concentrations of Na^+, H^+ and PO_4^{3-} in the mixed solution?
9. Calculate the values of the buffer capacity at $p\mathrm{H} = 7$ and $p\mathrm{H} = 9$ in 0.08 M ammonium chloride solution!
   $K_w = 1{,}2 \times 10^{-14}$ and $K_p = 2 \times 10^9$.
10. 50 cm^3 of 0.05 M weak acid solution is titrated with 0.1 M NaOH solution. The measured pH values are 7.345 and 7.497 at the consumptions of 6.0 and 6.1 cm^3, respectively. What value of the buffer capacity can be calculated in the solution at $p\mathrm{H} = 7.421$?
11. Based on the data given in question 10, what is the total concentration of the anion of the weak acid at the given point?

Remark: The change of the ionic strength is neglected during this experiment. Its effect on the shape of the $B_C(p\mathrm{H})$ curves are small so it would be unnecessary to keep the ionic strength at constant value in a more complicated experiment.