



pH OF AQUEOUS SOLUTIONS

INTRODUCTION

1. pH value of water and solutions

Water dissociates into hydrogen and hydroxide ions:



The equilibrium constant of this reaction, K_D is given by:

$$K_D = \frac{[H^+][OH^-]}{[H_2O]} \quad (2)$$

The value of the dissociation constant of water is very small, which means that the equilibrium is strongly shifted towards the substrates. This means that the vast majority of water molecules are undissociated. With a very good approximation, it can be assumed that the concentration of undissociated water molecules is constant and after multiplying both sides of equation (2) by $[H_2O]$ (concentration of water in water) we obtain a new constant parameter K_W , called the ionic product of water.

$$K_W[H_2O] = [H^+][OH^-] = 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \quad (T = 25^\circ\text{C}) \quad (3)$$

Taking into account the fact that one water molecule dissociates into one hydrogen ion and one hydroxide ion, one can come to the obvious conclusion that in "pure" water the concentration of these ions is equal, $[H^+] = [OH^-]$, which leads to the expression for the concentration of hydrogen ions:

$$\begin{aligned} [H^+]^2 &= 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \\ \text{so} \\ [H^+] &= 10^{-7} \text{ mol dm}^{-3} \end{aligned} \quad (4)$$

(for water and neutral solutions)

As you can see, the concentration of hydrogen ions in water, and therefore in neutral solutions (because $[H^+] = [OH^-]$), is $10^{-7} \text{ mol dm}^{-3}$. Instead of giving such small numbers, you can use orders of magnitude, or in other words, the concentration of hydrogen ions can be given on a logarithmic scale; the new unit is called pH:

$$\text{pH} = -\log[H^+] \quad (5)$$

The pH value of water and neutral solutions is therefore 7. The addition of acid will cause an increase in the concentration of hydrogen ions, i.e. a decrease in the pH value. Acidic solutions therefore have a pH lower than 7. The addition of alkali will increase the concentration of $[OH^-]$ ions. The product of the concentrations of hydrogen ions and hydroxide ions is constant, always equal to the K_W value, which leads to a decrease in the concentration of hydrogen ions. As a result, the pH of an alkaline solution is greater than 7.

2. The physical meaning of pH

In the equation defining pH, instead of concentration, there should be activity $a(H^+)$, which, in simple terms, expresses the concentration of free hydrogen ions "actively acting" in a given phenomenon:



$$\text{pH} = -\log a(\text{H}^+) \quad (6)$$

Two characteristics of the concept of pH should be noted here. First, the pH value defined by equations (5) and (6) is not dimensionless as it is supposed to be, but has a dimension that is the common logarithm of the concentration. Secondly, the measurement of the activity of one type of ion, and therefore the pH value, is impossible for thermodynamic reasons. So what exactly is the very useful concept of pH?

If we define the pH value as the logarithm of the ratio of two concentrations (or two activities), then we get a mathematically correct definition (the parameter becomes dimensionless) and a thermodynamic obstacle (the ratio of the two activities is measurable):

$$\text{pH} = -\log \frac{a_{\text{sample}}}{a_{\text{ref}}} \quad (7)$$

The pH value is therefore in fact the ratio of the activity of hydrogen ions of a given sample to the activity of these ions in an arbitrary frame of reference. Therefore, it is important when measuring pH to use legal standards, consistent with the generally (officially) accepted international standard. According to the existing tradition, pH is usually given as defined by the incorrect but simpler equations (5) or (6). However, it should be remembered that definition (7) is correct, as it also reflects the essence of the measured quantity.

3. pH measurement

One of the simpler methods of determining the pH of solutions is the use of acid-base indicators. These indicators are organic compounds that change color when the pH of solutions changes. Their common feature is the ability to undergo dissociation in solution, e.g. according to the reaction:



where:

HIn – undissociated indicator molecule,

In[−] – anion formed as a result of dissociation.

Particle *HIn* and anion *In*[−] they differ in color. A quantitative measure of the equilibrium state of this process is the dissociation constant of the indicator *K*_{*In*}:

$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \quad (9)$$

Which after transformation can be represented as:

$$\text{pH} = \text{p}K_{\text{In}} + \log \frac{[\text{In}^-]}{[\text{HIn}]} \quad (10)$$

A noticeable change in the color of the solution containing the indicator occurs at $\text{pH} = \text{p}K_{\text{In}}$. Therefore, different indicators show a color change at different pH values.

It is also possible to measure the pH quantitatively using indicators, by spectrophotometric determination of the concentration ratio $[\text{In}^-]/[\text{HIn}]$.



The most common method of pH measurement consists in measuring the electromotive force of a cell containing an electrode whose potential depends on the concentration of hydrogen ions. The most convenient indicator electrode used to measure the concentration of hydrogen ions is the **glass electrode**.

4. Buffer solutions

Diluting or adding an acid (or base) to a base (or acid) solution changes the pH of the solution. The property of buffer solutions is to maintain a constant pH value despite dilution or the addition of small amounts of acids or bases. This property is the reason for the high utility of **buffer solutions**. Buffering properties have mixtures of weak acids and their salts with strong bases, or weak bases in mixtures of their salts with strong acids. An example of this type of buffer is a mixture of acetic acid (a weak acid) with sodium acetate (a salt of a weak acid and a strong base). The weak acid HA (e.g. acetic) present in this solution dissociates according to the equation:



The acid dissociation constant, K_{kw} , is given by the equation:

$$K_{kw} = \frac{[H^+][A^-]}{[HA]} \quad (12)$$

Equation (12) leads to relation (13):

$$\text{pH} = \text{p}K_{kw} + \log \frac{[\textit{salt}]}{[\textit{acid}]} \quad (13)$$

Because the concentration of ions A^- is determined by the salt concentration (a weak acid dissociates poorly, a salt dissociates well).

As can be seen from equation (13), the pH value of such a solution depends on the value of the dissociation constant of a weak acid (or base) and the concentration ratio of the acid (base) and its salt.

OBJECTIVE OF THE EXERCISE

Observation of changes in pH caused by the addition of a strong base solution to acid solutions (weak and strong) and buffer solutions with a similar initial pH value.

LABORATORY EQUIPMENT, LABORATORY GLASSWARE

- pH-meter
- magnetic stirrer
- Burette
- Funnel
- Pipettes 50 cm³, 20 cm³, 1 cm³
- Measuring flasks. 100 cm³ – 3 pieces
- Narrow beaker 75 cm³
- Beakers 3 pieces



- Erlenmayer flasks 200 cm³ – 2 pieces

CHEMICALS

1 mol·dm⁻³ NaOH solution
1 mol·dm⁻³ HCl solution
1 mol·dm⁻³ CH₃COOH solution
Phenolphthalein solution
Buffer pH = 7

EXPERIMENT PROCEDURES

1. Please prepare in two 100 cm³ flasks HCl and CH₃COOH solutions with concentrations of 0.01 mol·dm⁻³ as shown in table 1. Pipette 50 cm³ of the obtained HCl solution into a beaker (75 cm³) and add a few drops of phenolphthalein. Measure the pH of this solution with a pH meter. After the measurement, add 0.2 cm³ of 0.1 mol·dm⁻³ NaOH solution from the burette to the solution with the stirring on. Read the pH with the stir bar turned off. In this way, add 1 cm³ of NaOH solution 0.1 mol·dm⁻³ (in 0.2 cm³ portions) reading the pH each time. Then add further portions of 0.1 mol dm⁻³ NaOH, 0.5 cm³ each, also reading the pH, until pH = 10. Repeat the measurements for the acetic acid solutions. Discard the acid solutions remaining in the flasks and wash the flasks.
2. Please prepare in a flask (100 cm³) an acetate buffer solution (indicated by the instructor) as shown in Table 1. Measure the initial pH for 50 cm³ of the solution and after adding further portions of the NaOH 0.1 mol dm⁻³ solution in the manner given for solutions acids (reaching about 8 cm³ of the titration solution).

DESCRIPTION OF RESULTS

1. Based on the measured pH values of individual solutions, plot graphs for all tested solutions in the following system: pH = $f(V)$, where V is the volume of added solution in cm³.
2. Describe the results of your research.

Optional: calculate the pH values of the prepared solutions, using the formulas in the course of the exercise.



Table 1. Method of preparing solutions.

Nr	Solution	Method for preparing
1 2	0,01 mol·dm ⁻³ HCl 0,01 mol·dm ⁻³ CH ₃ COOH	Transfer 10 cm³ of acid with a concentration of 1 mol·dm ⁻³ to a volumetric flask (100 cm ³) and fill it up to the mark with water. Take 10 cm ³ from the solution obtained, transfer it to the next volumetric flask (100 cm ³), and fill it up to the mark with water.
3	0,1 mol·dm ⁻³ CH ₃ COONa + 0,01 mol·dm ⁻³ CH ₃ COOH	11 cm³ 1 mol·dm ⁻³ CH ₃ COOH and 10 cm ³ 1 mol·dm ⁻³ NaOH dilute to the mark with water in a flask (100 cm ³)
4	0,1 mol·dm ⁻³ CH ₃ COONa + 0,1 mol·dm ⁻³ CH ₃ COOH	20 cm³ 1 mol·dm ⁻³ CH ₃ COOH and 10 cm³ 1 mol·dm ⁻³ NaOH dilute to the mark with water in a flask (100 cm ³)
5	0,01 mol·dm ⁻³ CH ₃ COONa + 0,1 mol·dm ⁻³ CH ₃ COOH	11 cm³ 1 mol·dm ⁻³ CH ₃ COOH and 1 cm³ 1 mol·dm ⁻³ NaOH dilute with water to the mark in the flask (100 cm ³).
6	0,1 mol·dm ⁻³ NaOH	Transfer 10 cm³ 1 mol·dm ⁻³ NaOH to a volumetric flask (100 cm ³) and fill up to the mark with water
7	0,1 mol·dm ⁻³ HCl	Transfer 10 cm³ 1 mol dm ⁻³ HCl to a volumetric flask containing approximately 70 cm ³ of distilled water and top up to the mark with distilled water

$$pK_a(\text{CH}_3\text{COOH}) = 4,76$$



Template of the table and draft of the study

<p>..... <i>Faculty</i></p> <p>..... <i>Field of study</i> <i>Full-time/ part-time studies</i></p>	<p>..... <i>Name and surname</i></p>	<p>..... <i>Date:</i></p>
<p><i>Group no.:</i></p> <p><i>Team no.:</i></p>	<p>..... <i>Exercise no.:</i></p>	<p>..... <i>Instructor:</i></p>

<p>..... <i>Wydział</i></p> <p>..... <i>Kierunek</i> <i>Studia stacjonarne/niestacjonarne</i></p>	<p>..... <i>Imię i Nazwisko studenta</i></p>	<p>..... <i>Data wykonywania ćwiczenia:</i></p>
<p><i>Nr grupy:</i></p> <p><i>Nr zespołu:</i></p>	<p>..... <i>Nr ćwiczenia:</i></p>	<p>..... <i>Nazwisko Prowadzącego:</i></p>

1. Temat ćwiczenia
2. Cel ćwiczenia:
3. Wstęp teoretyczny:
4. Pomiary:
5. Obliczenia:
6. Wykresy:
7. Wnioski

1. Exercise title:
2. The aim of the exercise:
3. Theoretical introduction:
4. Results:
5. Calculations:
6. Graphs:
7. Conclusions: