ENTHALPY OF A NEUTRALIZATION REACTION

1. PURPOSE OF THE WORK

Determination of the enthalpy of reaction at the neutralization of some acids.

2. THEORETICAL NOTIONS

The work aims to determine the heat of neutralization in three distinct cases: a) strong acid + strong base; b) weak acid (base) + strong base (acid); c) strong dibasic acid + strong base.

Acid: the substance that loses a proton, turning into its conjugate base.

Base: the substance that tends to accept a proton by turning into conjugated acid. Schematically, the acid-base equilibrium is represented by the equation:

$$A \Leftrightarrow B + H \tag{1}$$

Equation (1) is a process that cannot take place in reality. Combining two equations of type (1) we obtain an equation valid for any reactions of acids and bases:

$$\begin{aligned} &\text{Acid 1} \Leftrightarrow \text{Base 1} + H^+ \\ &\text{Base 2} + H^+ \Leftrightarrow \text{Acid 2} \\ &\text{Acid 1} + \text{Base 2} \Leftrightarrow \text{Base 1} + \text{Acid 2} \end{aligned} \tag{2}$$

Depending on their strength, acids and bases, respectively, can be divided into:

- strong acids: HCl, H_2SO_4, HNO_3.
- weak acids: HNO_2, HCOOH, CH_3COOH.
- base tari: NaOH, KOH.
- weak bases: NH_3, amines.

The reaction between an acid and a base is called a neutralization reaction.

The following cases will be studied ***experimentally***:

a) strong monobasic acid + strong base (HCl + NaOH)

Since the strong acids and bases, as well as the resulting salt are completely dissociated into ions, the neutralization reaction can be written:

$$H^+ + Cl^- + Na^+ + HO^- \Leftrightarrow Na^+ + Cl^- + H_2O \qquad \Delta^r H_1 \tag{3}$$

where $\Delta^r H_1$ is the enthalpy of reaction (heat of neutralization)

By reducing the equal terms results:

$$H^+ + HO^- \Leftrightarrow H_2O \qquad \Delta^r H_1 \tag{3'}$$

It follows that the thermal effect of the neutralization reaction corresponds to the enthalpy of formation of one mole of water from its ions.

b) strong dibasic acid + strong base (H_2SO_4 + NaOH)

The neutralization reaction can be written as:

$$2H^+ + SO_4^{2-} + 2Na^+ + 2HO^- \Leftrightarrow 2Na^+ + SO_4^{2-} + 2H_2O \qquad \Delta^r H_2 \qquad (4)$$

where $\Delta^r H_2$ is the enthalpy of reaction (heat of neutralization)

or: $$2H^+ + 2HO^- \Leftrightarrow 2H_2O \qquad \Delta^r H_2 \qquad (4')$$

It can be seen that, in this case, the heat of neutralization is given by the heat of formation of two moles of water, so that: $\Delta^r H_2 = 2\Delta^r H_1$.

c) weak acid + strong base (CH_3COOH + NaOH)

Weak acids, like weak bases, exist in solution only partially dissociated. The value of the neutralizing heat, denoted by $\Delta^r H_3$, will depend on the dissociation constant (notation K_d) of the acid or the weak base. The scheme of the dissociation equilibrium of a weak acid can be written in the form:

$$AH \Leftrightarrow \alpha A^- + \alpha H^+ + (1-\alpha)AH \qquad (5)$$

$$K_d = \frac{\left[H^+\right]\left[A^-\right]}{\left[AH\right]} = \frac{\alpha^2}{1-\alpha}\cdot c \qquad (6)$$

where:

α = degree of dissociation, defined according to the relation: $\alpha = \frac{no.\,dissociated\ molecules}{no.\,initial\ of\ molecules}$

c = solution concentration

In this case a neutralizing heat is expected to be $\Delta^r H_3 < \Delta^r H_1$.

3. EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- Dewar vessel, electric stirrer, thermometer, digital direct current source with voltage and current display, 500 mL cylinder, 1000 mL Berzelius glass, two 25 mL pipettes, funnel, stopwatch.

3.2. PROCEDURE

The experimental determinations comprise two distinct parts:

a) determination of the calorimeter constant;

b) determination of the heat (enthalpy) of neutralization for each of the 3 cases above.

1) ***Determining the calorimeter constant***. The constant of the calorimeter is given by the total caloric capacity of the calorimeter and its accessories.

This constant can be determined either by performing a chemical process whose thermal effect is known, or by passing through the calorimeter a known amount of electricity and observing the temperature variation.

Experimentally, to determine the calorimeter constant, proceed as follows:

Fill the calorimeter with 900 mL of water and place the lid of the calorimeter through which the agitator and the ends of the calorimeter heating element pass. Place the thermometer through the lid so that it measures the temperature in the calorimeter. Start the stirrer so that its rotational speed is moderate. The stirring speed will be kept constant throughout the determinations. Start a stopwatch and read the temperature for 5 minutes every minute, noting the values in the results table. Note the constant temperature with θ_i (initial temperature).

At exactly 5 minutes, the DC power source starts. During heating, the temperature, current intensity and voltage at the terminals are read and noted in the table from minute to minute. The heating is switched off after exactly 5 minutes by switching off the power supply. The temperature is observed for another 5 minutes after the heating is switched off. Note the constant final temperature with θ_f.

The values obtained for the temperature difference $\Delta\theta = \theta_f - \theta_i$ in the time interval *t*, the average of the values read for the intensity *I* and the voltage *U* are entered in relation (8) and the constant of the calorimeter denoted by *W* is calculated.

According to Joule's law, the amount of heat needed to heat the calorimeter is:

$$Q = W \cdot \Delta\theta = U \cdot I \cdot t \quad (7)$$

$$W = \frac{U \cdot I \cdot t}{\Delta\theta}, \text{ J/grad} \quad (8)$$

where:

W - **calorimeter constant**: the amount of heat required to raise its temperature by one degree

U - average values for voltage, V

I - average values for intensity, A

t - time, s

$\Delta\theta = \theta_f - \theta_i$

2) ***Determination of the heat of neutralization***

Calculate the required volume of 1 N acid solution to obtain 850 mL of 0.05 N solution by dilution.

a) The following reagents are used: 1N NaOH and 0.05N HCl.

For the experimental determination, the following work steps are performed:

- the calorimeter is emptied
- 0.05 N HCl solution is introduced into the calorimeter;
- insert the thermometer and record the temperature every 30 seconds for 2.5 minutes, the constant value of the temperature is $\theta_i^{,}$;
- at exactly 2.5 minutes, 42.5 mL of 1N NaOH solution is introduced into the calorimeter;
- the temperature is continued until the 5th minute, the constant value of the temperature is $\theta_f^{,}$;
- the neutralization heat is calculated according to the relation:

$$Q_{HCl} = W \frac{M_{HCl}}{m_{HCl}} \left(\theta'_f - \theta'_i \right), \text{ J/mol} \qquad (9)$$

Thus, the value of the neutralization enthalpy for hydrochloric acid results ($\Delta^r H^0_{HCl}$):

$$\Delta^r H^0_{HCl} = -Q_{HCl} \qquad (10)$$

b) The following reagents are used: 1N NaOH and 0.05N H2SO4.

The experimental determination involves the same steps as in the determination in point a), with the mention that 850 mL of 0.05N H_2SO_4 solution and 42.5 mL of 1N NaOH solution are used.

With the experimental data obtained it is calculated $\Delta^r H_{H_2SO_4}$.

c) The following reagents are used: 1N NaOH and 0.05N CH_3COOH.

Proceed analogously to the previous cases, using 850 mL of 0.05N CH_3COOH solution and 42.5 mL of 1 N NaOH.

It is calculated $\Delta^r H^0_{CH_3COOH}$.

4. EXPERIMENTAL DATA PROCESSING

4.1. The data are entered in tables of the form:

I. Determination of the calorimeter constant:

Time, min	0	1	2	3	4	**5**	6	7	8	9	**10**	11	12	13	14	15
Temperature, °C																
Voltage, V	-	-	-	-	-							-	-	-	-	-
Intensity, A	-	-	-	-	-							-	-	-	-	-

II. Determination of the thermal effect of the neutralization reaction:

Time, min	0	0,5	1	1,5	2	**2,5**	3	3,5	4	4,5	5
Temperature sol. HCl, °C											
Temperature sol. H_2SO_4, °C											
Temperature sol. CH_3COOH, °C											

4.2. Calculate the calorimeter constant according to equation (8).

4.3. Calculate the heat of neutralization, respectively the enthalpy of neutralization, for each case, using equations (9) and (10).

4.4. Based on the comparison of the determined results, the necessary conclusions will be drawn.

Data from the literature

$M_{H_2O} = 18,03$ g/mol ; $\rho_{H_2O} = 998,2$ g/L

$M_{HCl} = 36,49$ g/mol

$M_{H_2SO_4} = 98,08$ g/mol

$M_{CH_3COOH} = 60,05$ g/mol

5. QUESTIONS

5.1. Can the reaction between hydrochloric acid and Ca hydroxide (or Mg hydroxide) be considered similar to case b)? But in the case of the reaction between hydrochloric acid and Al hydroxide?

5.2. The comparison between the enthalpies of neutralization remains valid: $\Delta^r H_3 < \Delta^r H_1$ - point c) of the paper - in case of reaction between a strong acid and a weak base? Exemplified for: HCl (strong acid) and NH_4OH (weak base).