**ENTHALPY OF NEUTRALIZATION**

## INTRODUCTION

According to the first law of thermodynamics, in any process, the change of internal energy, $\Delta U$ of the system, equals the sum of the heat exchanged with the environment, $\Delta Q$, and work, $\Delta W$, supplied to the system or made by the system during transformation:

$$\Delta U = \Delta Q + \Delta W \tag{1}$$

The internal energy of the system is a state function because its change in the duration of the transformation does not depend on the path of transformation but on the final and initial states. Heat and work are not state functions in every transformation. When the only work performed by the system during the transformation is volumetric, the first law of thermodynamics will take the form:

$$dU = \Delta Q - pdV \tag{2}$$

For an isobaric transformation (frequently considered in chemistry, $p$ = atmospheric pressure = const.), it is convenient to introduce a function called enthalpy, $H$, which is by definition a state function:

$$H = U + pV \tag{3}$$

The exact differential of $H$ equals:

$$dH = dU + pdV + Vdp \tag{4}$$

Taking into account the $dU$ value given by equation (2) in equation (4) we obtain:

$$dH = dQ + Vdp \tag{5}$$

For the isobaric transformation $Vdp = 0$:

$$dH = dQ \qquad \text{p = const} \tag{6}$$

Equation (6) expresses Hess's law, which says that in the isobaric transformation, the heat of reaction is equal to the change of enthalpy, and so it does not depend on the path of transformation. For the isochoric processes, the following expression is obtained from equation (2):

$$dU = dQ \qquad V = \text{const} \tag{7}$$

It follows from equation (7) that in the isochoric transformation, the heat of transformation does not depend on the path of transformation (**Hess's law**). It follows from equations (6) and (7) that the heat of conversion is equal to the change of the internal energy of the system for the isochoric transformation, while in the isobaric transformation, it is equal to the change of the enthalpy of the system. The difference between $\Delta H$ and $\Delta U$ for a given transformation depends on the change in volume occurring when the reaction occurs under constant pressure and on the value of this pressure. For gas reactions (ideal gas), there is a dependence:

$$\Delta H \cong \Delta U + \Delta n\, RT \quad \text{(gas phase)} \tag{8}$$

For reactions occurring in the solution, $\Delta U$ is practically equal to $\Delta H$ due to the negligibly small change in the volume of the system in the isobaric process.

**Heat of neutralization**

During the neutralization reaction of the acid with the base or vice versa, the heat is called heat of neutralization; for an isobaric process, it is equal to the enthalpy of neutralization:

$$H^+ + OH^- \rightarrow H_2O \qquad\qquad\qquad \text{heat} = \Delta H_1 \tag{9}$$

The value of $\Delta H_1$ for strong acids and bases is a constant value, independent of the type of acid and base, equal to about -65.6 kJ / mol. The thermal effect (enthalpy) of this reaction can be determined by measuring the thermal effects of the following processes:

- sulphuric acid dilution:

$$\frac{1}{2} H_2SO_4 + H_2O \rightarrow H^+ + \frac{1}{2} SO_4^{-2} + H_2O \qquad\qquad \text{heat} = \Delta H_2 \tag{10}$$

- neutralization of sodium base with sulfuric acid:

$$\frac{1}{2} H_2SO_4 + H_2O + Na^+ + OH^- \rightarrow Na^+ + \frac{1}{2} SO_4^{-2} + 2H_2O \qquad\qquad \text{heat} = \Delta H_3 \tag{11}$$
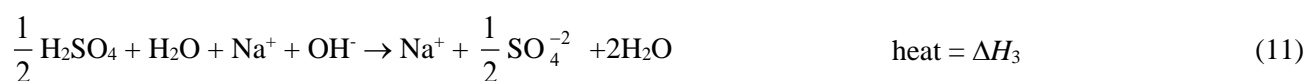
- dissolving glycerin in water (determining the heat capacity of a calorimeter):

$$C_3H_5(OH)_3 + H_2O \rightarrow C_3H_5(OH)_3(H_2O) \qquad\qquad \text{heat} = \Delta H_4 \tag{12}$$

The searched value is equal to:

$$\Delta H_1 = \Delta H_3 - \Delta H_2 \tag{13}$$

because in reaction (11), in addition to the heat of neutralization ($\Delta H_1$), there is dilution heat, needed to sulfuric acid introduced into the sodium hydroxide solution. The amount of the heat dissolving glycerin in water is determined by the heat capacity of the calorimeter, $c$, according to the equation:

$$c = \frac{\Delta H}{\Delta T} \tag{14}$$

The molar heat of dissolving glycerin in water is $\Delta H_4^M = -5.918$ kJ/mol.[1]

The molar value of the neutralization enthalpy $\Delta H_1^M$ can be calculated from the equation:

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[1] Physicochemial data, WNT, 1974

$$\Delta H_1^M = \frac{n_4}{2\,n_3}\Delta H_4^M \, \frac{\Delta T_3 - 0.2\,\Delta T_2}{\Delta T_4}$$

(15)

where:

| | | |
|---|---|---|
| $\Delta H_4^M$ | - | molar heat of dissolving glycerin in water |
| $\Delta H_1^M$ | - | molar heat of neutralization |
| $n_3$ | - | number of moles of $H_2SO_4$ used in the reaction (11) |
| $n_4$ | - | number of moles of glycerol used in the reaction (12) |
| $\Delta T_2$, $\Delta T_3$ i $\Delta T_4$ | - | temperature changes caused by the following reactions: (10), (11), and (12) |

**OBJECTIVE OF THE TASK**

The aim of the exercise is to determine the enthalpy of neutralization of the acid with a base.

**APPARATUS**

- Heat-insulating chamber
- Universal METEX multimeter
- Thermistor sensor.
- Mechanical stirrer

**INFO:** During this experiment instead of a thermometer, a thermistor sensor (c.a. 10 kOhm) is used to determine temperature changes of the processes. In this case, the resistivity of the sensor is measured and recorded.

**GLASSWARE AND SMALL EQUIPMENT**

- $100\ cm^3$ beaker (for measurements).
- $450\ cm^3$ beaker
- a $1.5\ cm^3$ automatic pipette
- electronic pipette Eppendorf Xplorer 50 – 1000 µl (0,05 $cm^3$ – 1 $cm^3$).
- a $25\ cm^3$ glass pipette
- a syringe.

**CHEMICALS**

- 3M solution of $H_2SO_4$
- 0.2M solution of NaOH
- Glycerin
- 3 $dm^3$ bottle with distilled water.

## EXPERIMENTAL PROCEDURES

1. Start the computer.
2. Run the METEX SCOPEVIEW program on the desktop and turn on the METEX multimeter.
3. In the METEX SCOPEVIEW program
   - press the POWER button to check communication with the multimeter (the program should start recording the meter's readings),
   - press the SCOPE button to start the system control panel,
   - set the appropriate resistance range (as indicated by the teacher),
   - give a name to the file before starting the measurement (by pressing the RECORD button),
   - press the SCOPE button to start the registration panel,
   - measurement recording starts after pressing the RUN button and ends after pressing the STOP button.
   - **Follow the instruction manual of the program located at the exercise and the teacher's instructions**
4. Pour 37.5 cm$^3$ of distilled water into the measuring vessel (beaker), place the beaker in the insulating chamber, and cover it with a built-in thermistor sensor.
5. Dip the stirrer, start it, and adjust its speed.
6. After a few minutes, start recording the resistance (temperature) by pressing the RUN button.
7. After about 1 minute, add 0.25 cm$^3$ of 3M $H_2SO_4$. Observe the resistance changes caused by the thermal effect ($\Delta T_2$) of diluting sulfuric acid.
8. After another minute, end the measurement by pressing the STOP button (at the end of the process, no significant fluctuations in the recorded resistance values should be considered).
9. Then turn off the agitator and remove the cover of the thermostat chamber with the stir bar and thermistor sensor. Place the lid on a beaker (450 cm$^3$) with distilled water. Wash the measuring cup. Set the system again.
10. Measurements should also be performed for thermal effects caused by the addition

   a) 0.05 cm$^3$ of 3M $H_2SO_4$ to a stabilised solution (36 cm$^3$ $H_2O$ distilled + 1.5 cm$^3$ 0.2M NaOH), effect ($\Delta T_3$),
   b) 0.25 cm$^3$ glycerine to 37.5 cm$^3$ $H_2O$ distilled, effect ($\Delta T_4$).

11. Each thermal effect should be measured twice.


## CALCULATIONS

1. From the obtained measurements, make graphs of resistance dependence (thermistor) from the duration of the reaction.

2. Temperature change values (thermistor resistance), occurring in equation (15), can be replaced with section heights (calculated from differences between max and min values), proportional to the size of temperature changes.

3. Using equation (15), calculate the enthalpy of neutralization. To calculate the number of moles of glycerol contained in 1 cm$^3$, take the value of the density of glycerine equal to d = 1.2613 g/cm$^3$

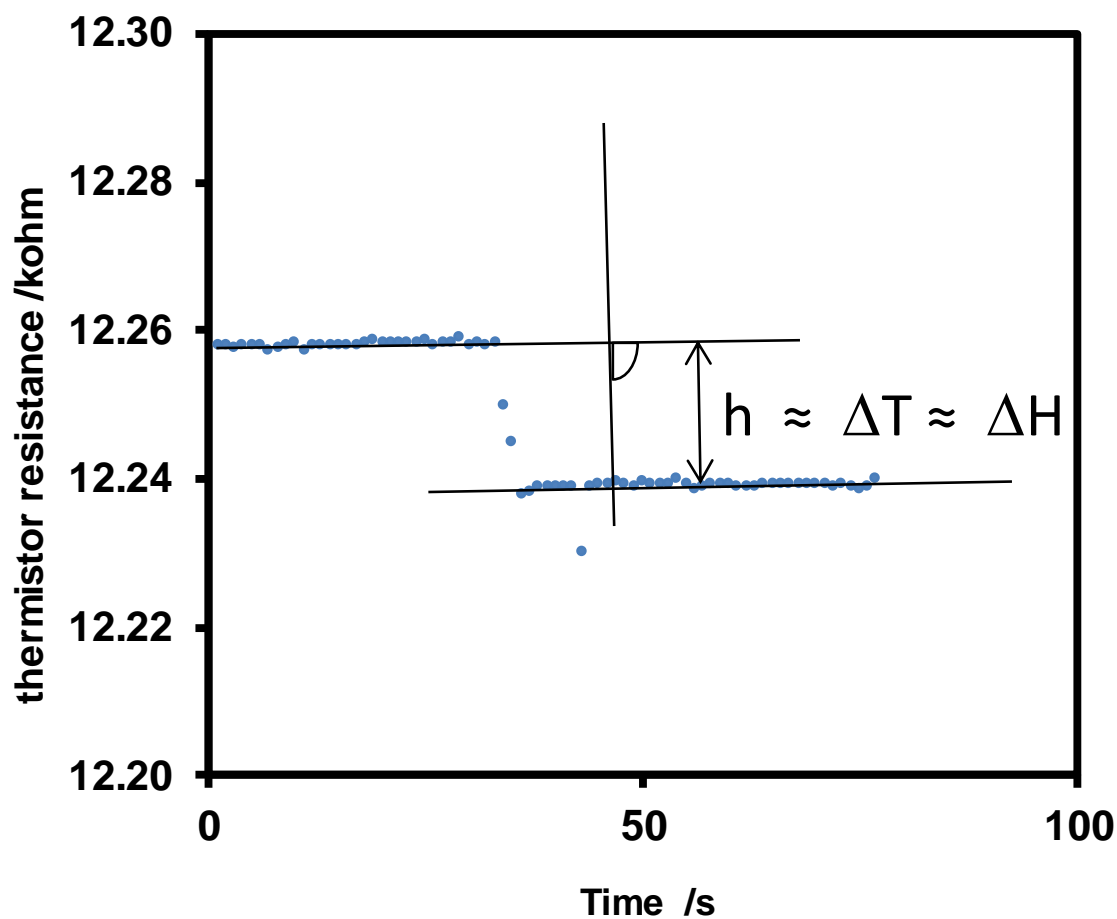Figure 1. The example of the temperature changes determination.

Template of the table and draft of the study

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|---|---|---|
| ……………………………..<br>*Faculty*<br><br>…………………………………..<br>*Field of study*<br>*Full-time/ part-time studies* | ………………………………………………<br>*Name and surname* | …………………………………………...<br>*Date:* |
| Group no.: …………………<br><br>Team no.: ………………… | ………..………………<br>*Exercise no.:* | ………………………………………..<br>*Instructor:* |

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

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: