Physical chemistry

Thermochemistry

Calorimetry

LD Chemistry Leaflets

C4.3.3.3

Determination of the enthalpy of neutralisation of acids and alkali solutions

Aims of the experiment

- To learn about neutralisation as a reaction.
- To observe the large amounts of energy released during neutralisation.
- To determine the heat of neutralisation.
- To observe that when the number of moles is equivalent, the heat of neutralisation of a reaction is always the same amount.

Principles

Neutralisation is a reaction between acids and bases. In a narrow sense, acids are substances that are able to supply protons (H^+). In aqueous environments, protons form so-called oxonium ions (H_3O^+) with water. In a narrow sense, bases are substances that are able to supply hydroxide ions (OH^-). In neutralisation, oxonium ions react with hydroxide ions to form water.

$$H_3O^+ + OH^- \rightleftharpoons 2\ H_2O$$

In the case of neutralisation, energy in the form of heat – the heat of neutralisation – is released to the environment due to the reaction between the oxonium ions and the hydroxide ions. Since acids and bases, particularly when they are concentrated, consist of very many oxonium and hydroxide ions, many reactions take place at the same time. Because of the many simultaneously occurring reactions, a large amount of heat is released in a very short time even though each individual reaction gives off very little heat.

The molar enthalpy of neutralisation ΔH_r^θ is equal to the quotient of the heat Q given off and the volume V and the concentration c of the acids and bases that react together.

$$\Delta H_r^\theta = -\frac{\Delta Q}{V \cdot c}$$

The heat Q is determined using the formula

$$\Delta Q = C_p \cdot \Delta T$$

with the heat capacity C_p of the equipment and chemicals and the temperature change ΔT.

In this experiment, neutralisation reactions for various acids with soda lye are compared.

Risk assessment

In the experiment, and in working with concentrated acids and bases, always wear protective aprons, goggles and gloves.

Fig. 1: Set-up of the experiment.

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Soda lye, 1 mol/l	
Signal word: **Hazard**	**Hazard statements** H314 Causes severe skin burns and severe eye damage. H290 May be corrosive to metals. **Safety statements** P280 Wear protective gloves/protective clothing/eye protection/face protection. P301+P330+P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting. P305+P351+P338 IF IN EYES: Rinse carefully with water for several minutes. Remove contact lenses if present and easy to do so. Continue rinsing. P310+P310 If exposed or if you feel ill, call a POISON CENTRE or a physician immediately.

Soda lye, dilute, approx. 2 mol/l	
Signal word: **Hazard**	**Hazard statements** H314 Causes severe skin burns and severe eye damage. H290 May be corrosive to metals. **Safety statements** P280 Wear protective gloves/protective clothing/eye protection/face protection. P303+P361+P353 IF ON SKIN (or hair): Remove/take off all contaminated clothing immediately. Rinse skin with water/shower. P305+P351+P338 IF IN EYES: Rinse carefully with water for several minutes. Remove contact lenses if present and easy to do so. Continue rinsing. P310 Call a POISON CENTER or doctor/physician immediately. P301+P330+P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.

Hydrochloric acid, 1 mol/l and approx. 2 mol/l	
Signal word: **Caution**	**Hazard statements** H290 May be corrosive to metals. **Safety statements** P234 Keep only in original container. P390 Absorb spillage to prevent material damage.

Acetic acid, dilute, approx. 2 mol/l	
Signal word: **Caution**	**Hazard statements** H315 Causes skin irritation. H319 Causes serious eye irritation. H290 May be corrosive to metals. **Safety statements** P280 Wear protective gloves/protective clothing/eye protection/face protection. P305+P351+P338 IF IN EYES: Rinse carefully with water for several minutes. Remove contact lenses if present and easy to do so. Continue rinsing. P332+P313 In case of skin irritation: Get medical advice/attention. P337+P313 If eye irritation persists: Get medical advice/attention. P302+P352 IF ON SKIN: Wash with plenty of water and soap.

Equipment and chemicals

1	Pocket-CASSY 2 Bluetooth	524 018
1	CASSY Lab 2	542 220
1	NiCr-Ni adapter S, type K	524 0673
1	Temperature probe, NiCr-Ni, 1.5 mm, type K	529 676
1	Electronic balance 200 g : 0.01 g	667 7977
1	Mini magnetic stirrer	607 105
3	Stirring magnets 15 mm x 5 mm diam.	666 850
3	Beakers, Boro 3.3, 150 ml, squat	602 023
2	Measuring cylinder 50 ml, with plastic base	665 753
1	Saddle base	300 11
1	Stand rod 25 cm, 10 mm diam.	301 26
1	Bosshead S	301 09
1	Soda lye, diluted, approx. 2M, 500 ml	673 8400
1	Soda lye, 1 mol/l, 500 ml	673 8420
1	Hydrochloric acid, approx. 2 mol/l, 500 ml	674 6920
1	Hydrochloric acid 1 mol/l, 500 ml	674 6900
1	Acetic acid, dilute (approx. 2 mol/l), 500 ml	671 9550
Also necessary for wireless measurement:		
1	Rechargeable battery for Pocket-CASSY 2 BT	524 019
1	Bluetooth dongle	524 0031
Additionally required:		
PC with Windows XP/…/10		

Set-up and preparation of the experiment

Preparation

1. Insert the stand rods into the saddle base (for set-up, see Figure 1.).

2. Fasten the bosshead to the stand rod.

3. Connect the Pocket CASSY 2 to the PC with a USB cable.

Note: The Pocket CASSY 2 can also be connected to the PC via Bluetooth. To do so, connect the Pocket CASSY 2 Bluetooth to the rechargeable battery for the Pocket CASSY 2. Plug the Bluetooth dongle into a USB port on the PC.

4. Connect the NiCr-Ni temperature probe to the Pocket CASSY 2 Bluetooth via the NiCr-Ni adapter S.

5. Set up a magnetic stirrer next to the stand and place a beaker on it.

6. Fasten the temperature probe to the bosshead and place in the beaker.

Performing the experiment

1. Load the settings in CASSY Lab 2.

2. For the measurement, the weights of the empty beaker and of the stirring magnets (magnetic stir bars) are determined and recorded.

3. In a measuring cylinder, 50 ml of acid are measured out. In a second measuring cylinder, 50 ml of base are measured out.

4. The neutralisation of multiple combinations of acid and base will be examined. All measurements are listed in Table 1.

Tab. 1: Acid/base combinations.

Measure-ment	Acid	Base
1	Hydrochloric acid 1 mol/l	Soda lye, 1 mol/l
2	Hydrochloric acid, approx. 2 mol/l	Soda lye, approx. 2 mol/l
3	Acetic acid, approx. 2 mol/l	Soda lye, approx. 2 mol/l

5. Place the stirring magnet in the beaker and turn on the magnetic stirrer.

6. Now transfer the acid from the measuring cylinder to the beaker.

Note: It is important to start with either the acid or the base in every measurement! The acid is used from this point on.

7. Check to see that the temperature probe is immersed in the acid. If not, the probe must be immersed in the acid.

8. Start recording in CASSY Lab 2 and allow the plotting a few minutes. The measured temperature should not change much, in other words stay linear.

9. Now add the base all at once to the acid in the beaker and record the temperature for a few more minutes.

10. Repeat the experiment with the next acid/base combination.

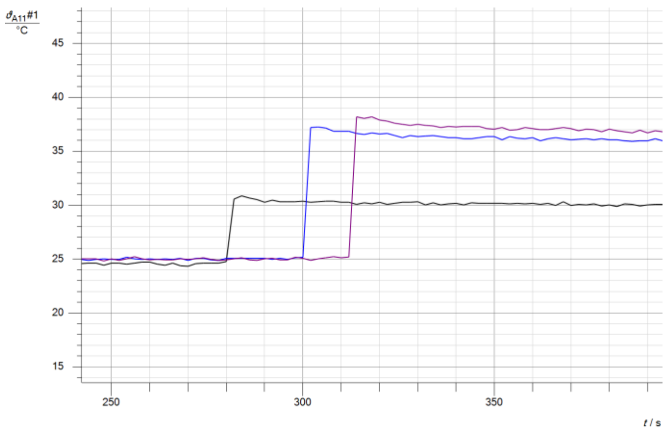

Fig. 2: Temperature plot of the neutralisation reactions. Here, black is: measurement 1 1 mol/l HCl/NaOH, violet: measurement 2 2 mol/l CH_3COOH/NaOH, blue: measurement 3 2 mol/l HCl/NaOH.

Observation

As can be seen in Figure 2, the temperature in the beaker suddenly jumps after the base is added. In the 2-molar acids and bases, the jump is about twice as much as in the 1-molar hydrochloric acid/soda lye. The temperature increase in the hydrochloric acid/soda lye and the acetic acid/soda lye are approximately the same.

Evaluation

Determine the temperature difference

The molar heat of neutralisation can be calculated from the temperature difference. To do so, first the molar heat of neutralisation *Q* must be derived from the individual heated components and their individual specific heat capacities C_p.

Tab. 2: Heat capacities of the material and equipment used.

Material	C_p
Water	$4.2\,\frac{J}{g \cdot K}$
Beaker	$0.8\,\frac{J}{g \cdot K}$

The common heat capacity C_p of the equipment is calculated as follows:

$$C_p = 100\ g \cdot 4.2\,\frac{J}{g \cdot K} + m(beaker) \cdot 0.8\,\frac{J}{g \cdot K}.$$

Note: The 100 g result from the 50 ml of acid and the 50 ml of base. As a simplification, it is assumed that together they total 100 ml and that only water results from the neutralisation. The resultant salt is ignored. Since 100 ml corresponds to about 100 g, it is entered into the formula here.

The heat of reaction ΔQ can now be calculated using the

$$\Delta Q = C_p \cdot \Delta T$$

formula.

The temperature difference ΔT is determined using CASSY Lab 2. To this end, a horizontal line is made at the maximum of the neutralisation curve and at the starting temperature. The line can be added through the **Set mark → Horizontal line** menu (right click on the display field) or using Alt + W.

After determining the temperature difference ΔT, the molar enthalpy of neutralisation ΔH_r^θ is calculated using the heat of neutralisation *Q* and the moles *n* of the respective acid.

$$\Delta H_r^\theta = -\frac{\Delta Q}{n}$$

In this case, the moles *n* are calculated through the volume of the acid V_{acid} and the concentration c_{acid} using the formula $n = V_{acid} \cdot c_{acid}$. The following new formula results:

$$\Delta H_r^\theta = -\frac{\Delta Q}{V \cdot c}$$

Tab. 3: Values determined during the experiments. In the process, measurement 1: 1 mol/l HCl/NaOH, measurement 2: 2 mol/l CH_3COOH/NaOH, measurement 3: 2 mol/l HCl/NaOH.

Measured quantities determined	Measurement		
	1	2	3
m(beaker)	73.3 g	71.6 g	73.5 g
T_{max}	30.8°C	37.2°C	38.2°C
T_{min}	24.6°C	25.0°C	24.8°C
$\Delta T = T_{max} - T_{min}$	6.2 K	12.2 K	13.4 K

Note: Since the temperature difference of 1 °C corresponds to a temperature difference of 1 K, the °C can be replaced by K after the subtraction.

Calculation of the heat amount and the molar enthalpy of neutralisation

With the two formulas

$C_p = 100\ \text{g} \cdot 4.2\ \frac{\text{J}}{\text{g·K}} + m(beaker) \cdot 0.8\ \frac{\text{J}}{\text{g·K}}$,

and

$\Delta Q = C_p \cdot \Delta T$

results for the heat quantity as an overall formula

$$\Delta Q = 100\ \text{g} \cdot 4{,}2\ \frac{\text{J}}{\text{g·K}} + m(beaker) \cdot 0{,}8\ \frac{\text{J}}{\text{g·K}} \cdot \Delta T\,.$$

Then, the molar enthalpy of neutralisation $\Delta_R H_m$ is

$$\Delta H_r^{\theta} = -\frac{\Delta Q}{V \cdot c}$$

calculated.

The calculation of the heat quantity Q and the molar enthalpy of neutralisation $\Delta_R H_m$ is done once as an example for the mixture HCl/NaOH (measurement 1). The calculation for the two other mixtures is done similarly and is indicated in Table 4.

Measurement 1: HCl/NaOH

$C_p = 100\ \text{g} \cdot 4.2\ \frac{\text{J}}{\text{g·K}} + 73.35\ \text{g} \cdot 0.8\ \frac{\text{J}}{\text{g·K}}$

$C_p = 478.7\ \frac{\text{J}}{\text{K}}$

$\Delta Q = 478.7\ \frac{\text{J}}{\text{K}} \cdot 6.2\ \text{K} = 2967\ \text{J} = 2.97\ \text{kJ}$

$$\Delta H_r^{\theta} = -\frac{2{,}97\ \text{kJ}}{0.05\ \text{l} \cdot 1\ \frac{\text{mol}}{\text{l}}} = -59.4\ \text{kJ/mol}$$

Tab. 4: Calculated values for heat capacity C_p, the heat quantity Q and the molar enthalpy of neutralisation ΔH_r^{θ} Here, measurement 1 is: 1 mol/l HCl/NaOH, measurement 2: 2 mol/l CH_3COOH/NaOH, measurement 3: 2 mol/l HCl/NaOH.

Measured quantities determined	Measurement		
	1	2	3
C_p	478.7 $\frac{\text{J}}{\text{K}}$	477.3 $\frac{\text{J}}{\text{K}}$	478.9 $\frac{\text{J}}{\text{K}}$
ΔQ	2.97 kJ	5.82 kJ	6.42 kJ
ΔH_r^{θ}	$-59.4\ \frac{\text{kJ}}{\text{mol}}$	$-58.2\ \frac{\text{kJ}}{\text{mol}}$	$-64.2\ \frac{\text{kJ}}{\text{mol}}$

Thus, for the molar enthalpy of neutralisation ΔH_r^{θ} for 1 mol/l HCl/NaOH, a value of −59.4 kJ/mol results, for 2 mol/l CH_3COOH/NaOH a value of −58.2 kJ/mol results and for 2 mol/l HCl/NaOH a value of −64.2 kJ/mol results.

Results

The molar enthalpy of neutralisation ΔH_r^{θ} of the two hydrochloric acid/soda lye mixtures are very near one another even though the concentrations of the hydrochloric acid and the soda lye are different. So the molar enthalpy of neutralisation does not depend on what the concentration of the hydrochloric acid and the soda lye are. In Figure 2, it is very clear that when the concentration is doubled, the temperature doubles as well.

The results of the molar heat of neutralisation ΔH_r^{θ} of mixtures of 2 mol/l CH_3COOH/NaOH and 2 mol/l HCl/NaOH are also right next to one another even though these are different acids. Thus, the molar enthalpy of neutralisation is not dependent on the type of acid either.

This means that the heat of neutralisation is always the same in equivalent mole amounts and that the heat of neutralisation only depends on the number of oxonium ions and hydroxide ions that react with one another according to the reaction equation. Water is formed in the process. The resultant salt formed by the acid and the base plays no role here.

Since in the neutralisation heat is given off, this is an exothermic reaction. The result is that the molar enthalpy of neutralisation has a negative sign and thus goes through a negative enthalpy change.

In comparison with the literature value of −57.4 kJ/mol, it is shown that the molar enthalpy of neutralisation can be determined very well in this experiment.

Note: The calculation actually only applies to infinitely dilute mixtures. Therefore, dilution effects would have to be taken into account. This also explains the slightly different results.

Cleaning and disposal

The neutralised mixtures can be poured down the drain under flowing water.