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A – 6

Calorimetry

1, 2, 3: ΔU, Δn, ΔV were wrong

Objective

The neutralization enthalpy of said acid as well as the solvation enthalpy for water free Na_2CO_3 and $Na_2CO_3 \cdot 10\,H_2O$ should be determined. From these results the hydration enthalpy of Na_2CO_3 is calculated.

Basics

A calorimeter is used to determine the amount of heat. Therefore the temperature change is measured.

$Q = (C_k + c_W m_W) \cdot \Delta T$

Q : released reaction heat
C_k : heat capacity of the calorimeter
c_W : specific heat capacity of water
m_W : mass of water in the calorimeter
ΔT : temperature change.

For the heat capacity of the calorimeter a calibration with an immersion heater is carried out. The following formula is used. $Q = UIt = (C_k + c_W m_W) \cdot \Delta T_{cal}$; U : voltage
I : current
t : time duration

If an acid reacts with a base, neutralization enthalpy becomes free. When measured at a constant pressure, it corresponds to the neutralization heat, and, in our case, also the formation enthalpy of H_2O. This is because we have a strong base react with a strong acid ($H^+ + OH^- \rightarrow H_2O$). This only applies to diluted solutions, because here we can ignore other factors such as the dilution enthalpy.

$Q = n \cdot \Delta H_N^* = (C_k + c_W m_W)\,\Delta T$ n : mole number
ΔH_N^* : neutralization enthalpy without to include dilution enthalpy

$\rightarrow |\Delta H_N^*| = \frac{1}{n} UIt \frac{\Delta T}{\Delta T_{cal}}$; $\Delta H_N = \Delta H_N^* - \Delta H_d$ ΔH_d : dilution enthalpy
ΔH_N : neutralization enthalpy

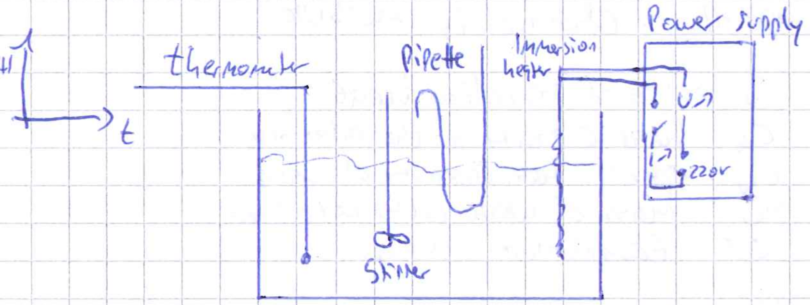
In order to determine the solution enthalpy, the corresponding substance is dissolved in e.g. water and the enthalpy change is measured. If $\Delta H_L > 0$, heat must be supplied from the outside in order to keep the temperature constant. The hydration enthalpy ΔH_{hydr} can also be determined with this method. $\Delta H_{hydr} = \Delta H_L^{salt} - \Delta H_L^{hydr}$

$\rightarrow Q = n \Delta H_L^{salt} = (c_K + c_W m_W) \Delta T^{salt} \rightarrow \Delta T^{salt} > 0$

$Q = n \Delta H_L^{hydr} = (c_K + c_W m_W) \Delta T^{hydr} \rightarrow \Delta T^{hydr} < 0$

$\rightarrow |\Delta H_L^{salt}| = \frac{R I^2 t}{n} \frac{\Delta T^{salt}}{\Delta T_{cal}}$ $\quad |\Delta H_L^{hydr}| = \frac{\Delta T^{hydr}}{\Delta T^{salt}} \Delta H_L^{salt}$

Setup and test execution



The calorimeter is filled with 600g of distilled water and the pipette is filled with 50g of distilled water. For calibration, the immersion heater (0,8A for 120 seconds) is heated. The temperature is recorded every second, a T(t) curve is obtained.

For the neutralization enthalpy, 6g of NaOH are dissolved in the 600g H_2O and 50ml of 2M HCl are introduced with the pipette. A T(t) curve is again determined.

The same setup without the pipette is used to determine the solution heat: The calorimeter is filled with 600g of H_2O and calibrated as before. 10g Na_2CO_3 and 26,98g $Na_2CO_3 \cdot 10H_2O$ are respectively dissolved therein. You get a T(t) curve again.

Source: description of experiment.

data analysis neutralization enthalpy

$n(NaOH) = 0{,}15\,mol$ $n(HCl) = 0{,}1\,mol$ → $0{,}1\,mol$ water

$|\Delta H_N^*| = \frac{1}{n} U \cdot I \cdot t \cdot \frac{\Delta T}{\Delta T_{eich}} = \frac{1}{0{,}1\,mol} \cdot 35V \cdot 0{,}8A \cdot 120s \cdot \frac{1{,}85K}{1{,}2K}$
$= 51800 \frac{J}{mol} = 51{,}8 \frac{kJ}{mol}$

with ΔT and ΔT_{eich} of the graphs neutralization and calibration 1

$\Delta H_N^* = -51{,}8 \frac{kJ}{mol}$ since heat is submitted, ΔH_N^* must be < 0

$\Delta H_N = \Delta H_N^* - \Delta H_d = -51{,}8 \frac{kJ}{mol} - 1{,}883 \frac{kJ}{mol} = -53{,}683 \frac{kJ}{mol}$

Dissolution enthalpy

$NaCO_3$ $\Delta T_{eich} = 1{,}25K$ (graph calibration 2) $\Delta T(Na_2CO_3) = 0{,}75K$ (graph Na_2CO_3)

$n(NaCO_3) = \frac{m}{M} = \frac{10{,}24g}{106} = 0{,}0966\,mol$

$|\Delta H_L^{salt}| = \frac{U \cdot I \cdot t}{n} \cdot \frac{\Delta T_{salt}}{\Delta T_{eich}} = 20869{,}57 \frac{J}{mol} = 20{,}87 \frac{kJ}{mol}$

$\Delta H_L^{salt} = -20{,}87 \frac{kJ}{mol}$

$NaCO_3 \cdot 10H_2O$ $\Delta T_{eich} = 1{,}2K$ $\Delta T(NaCO_3 \cdot 10H_2O) = 2{,}2K$ graph calibration 3 and $Na_2CO_3 \cdot 10H_2O$

$n(NaCO_3 \cdot 10H_2O) = \frac{m}{M} = \frac{27{,}63g}{286g/mol} = 0{,}0966$

$|\Delta H_L^{hydr}| = \frac{UIt}{n} \cdot \frac{\Delta T_{hydr}}{\Delta T_{eich}} = 63{,}768 \frac{kJ}{mol} = \Delta H_L^{hydr}$

$\Delta H_{hydr} = \Delta H_L^{salt} - \Delta H_L^{hydr} = -84{,}638 \frac{kJ}{mol}$

error analysis

- The multimeter measured the temperature with an error of $\Delta T = 0{,}1K$
- The measurement uncertainty of the voltage, ~~and~~ electric current and weight were given by the manufacturer information: $\Delta U = 5V$ (1), $\Delta I = 0{,}05A$, $\Delta n = \frac{\Delta m}{M} = \frac{0{,}1g}{M}$ (2)

⇒ error of neutralization enthalpy:

$\Delta n(HCl) = |2 \frac{mol}{l} \cdot \Delta V| = 2 \cdot 10^{-3} mol$, $\Delta V = 1ml$ (3)
$= \Delta n(water)$

$\frac{\Delta(\Delta H_n^*)}{\Delta H_n^*} = |\frac{\Delta n}{n}| + |\frac{\Delta U}{U}| + |\frac{\Delta I}{I}| + |\frac{\Delta(\Delta T)}{\Delta T}| + |\frac{\Delta(\Delta T^{cal})}{\Delta T^{cal}}|$

$= \frac{0{,}002\,mol}{0{,}1\,mol} + \frac{5V}{35V} + \frac{0{,}05A}{0{,}8A} + \frac{0{,}1K}{1{,}85K} + \frac{0{,}1K}{1{,}2K} = 0{,}363$

$\Rightarrow \Delta(\Delta H_n^*) = 0{,}363 \cdot |\Delta H_n^*| = 0{,}363 \cdot 51{,}8 \frac{kJ}{mol} = 18{,}79 \frac{kJ}{mol}$

$\Rightarrow \Delta H_n^* = (-53{,}683 \pm 18{,}79) \frac{kJ}{mol}$

⇨ error of solvation ethalpy: $\Delta n(Na_2CO_3) = \left|\frac{\Delta M}{M}\right| = \frac{0{,}1\,g}{106\,g/mol} = 0{,}00094\,mol$

$$\frac{\Delta(\Delta H_L^{salt})}{\Delta H_L^{salt}} = \left|\frac{\Delta n}{n}\right| + \left|\frac{\Delta U}{U}\right| + \left|\frac{\Delta I}{I}\right| + \left|\frac{\Delta(\Delta T)}{\Delta T}\right| + \left|\frac{\Delta(\Delta T^{cal})}{\Delta T^{cal}}\right|$$

$$= \frac{0{,}00094\,mol}{0{,}0966\,mol} + \frac{5\,V}{35\,V} + \frac{0{,}05\,A}{0{,}8\,A} + \frac{0{,}1\,K}{0{,}75\,K} + \frac{0{,}1\,K}{1{,}25\,K} = 0{,}4284$$

$\Rightarrow \Delta(\Delta H_L^{salt}) = 0{,}4284 \cdot 20{,}87\,\frac{kJ}{mol} = 8{,}94\,\frac{kJ}{mol}$ $\Rightarrow \Delta H_L^{salt} = (20{,}87 \pm 8{,}94)\,\frac{kJ}{mol}$

⇨ error of solvation ethalpy of $Na_2CO_3 \cdot 10H_2O$: $\Delta n = \left|\frac{\Delta M}{M}\right| = \frac{0{,}1\,g}{286\,g/mol} = 3{,}5 \cdot 10^{-4}\,mol$

$$\frac{\Delta(\Delta H_L^{Hydr})}{\Delta H_L^{Hydr}} = \frac{0{,}00035\,mol}{0{,}0966\,mol} + \frac{5\,V}{35\,V} + \frac{0{,}05\,A}{0{,}8\,A} + \frac{0{,}1\,K}{2{,}2\,K} + \frac{0{,}1\,K}{1{,}2\,K} = 0{,}3378$$

$$\Rightarrow \Delta(\Delta H_L^{Hydr}) = 0{,}3378 \cdot 63{,}768\,\frac{kJ}{mol} = 21{,}539\,\frac{kJ}{mol}$$

$\Rightarrow \Delta H_L^{Hydr} = (63{,}768 \pm 21{,}539)\,\frac{kJ}{mol}$

⇨ error of hydration enthalpy: $\Delta(\Delta H^{Hydr}) = |\Delta(\Delta H_L^{salt})| + |\Delta(\Delta H_L^{Hydr})| = 30{,}48\,\frac{kJ}{mol}$

$\Rightarrow \Delta H_{Hydr} = (-84{,}638 \pm 30{,}48)\,\frac{kJ}{mol}$

discussion

We couldn't find any results in the literature to compare with the experimental results. We found a blog entry on the internet, so we used this to compare the neutralization enthalpy of HCl with NaOH.

experimental result: $-53{,}683\,\frac{kJ}{mol} \pm 18{,}79\,\frac{kJ}{mol}$, result for comparison: $-55{,}94\,\frac{kJ}{mol}$

As you can see the measurement worked very well because the deviation is only 4%.

For the other enthalpy results, it would be better to minimize the errors, because they are very ~~...~~ large. For example you could use digital equipment which is more accurate than the analog variable ratio transformer.

Sources:

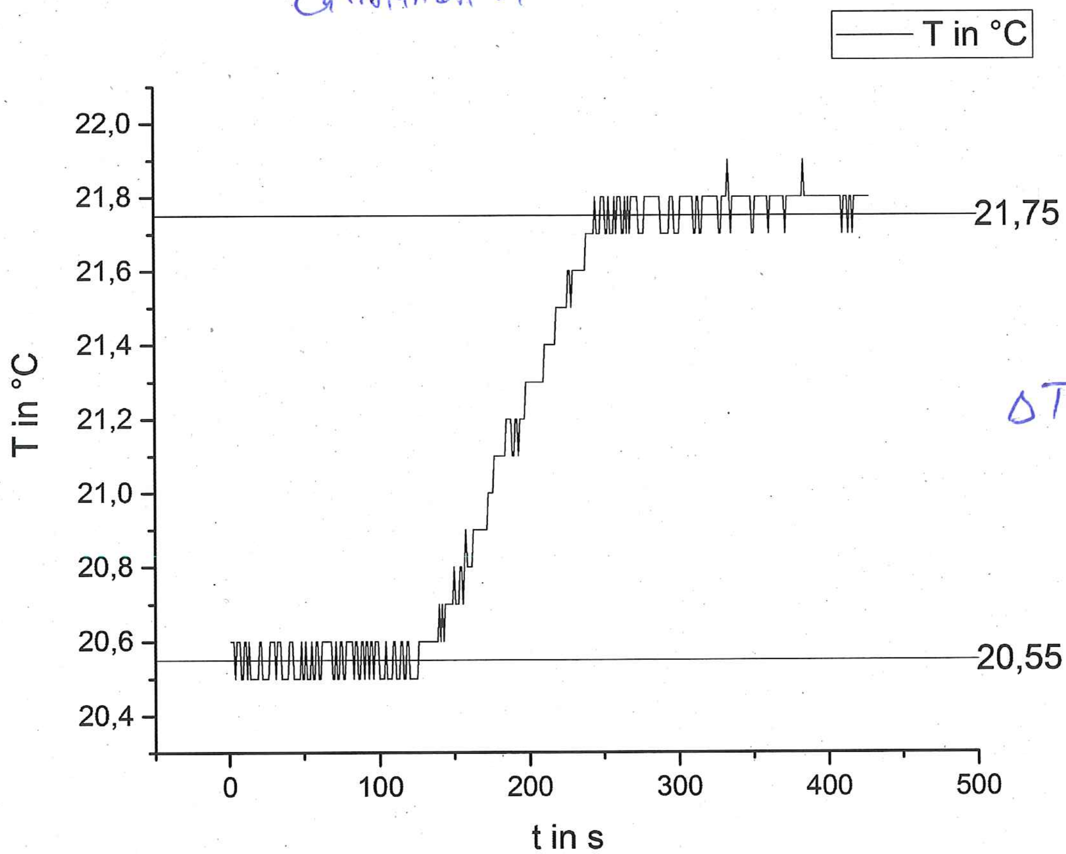
- http://www.chemieonline.de/forum/archive/index.php/t-170860.html
- description of experiment

Additional Questions

1. Since water is a polar ~~xx~~ molecule, it forms a dipole. These can accumulate on the charged ions and form a hydration sphere. A repeated crystallization is thereby prevented

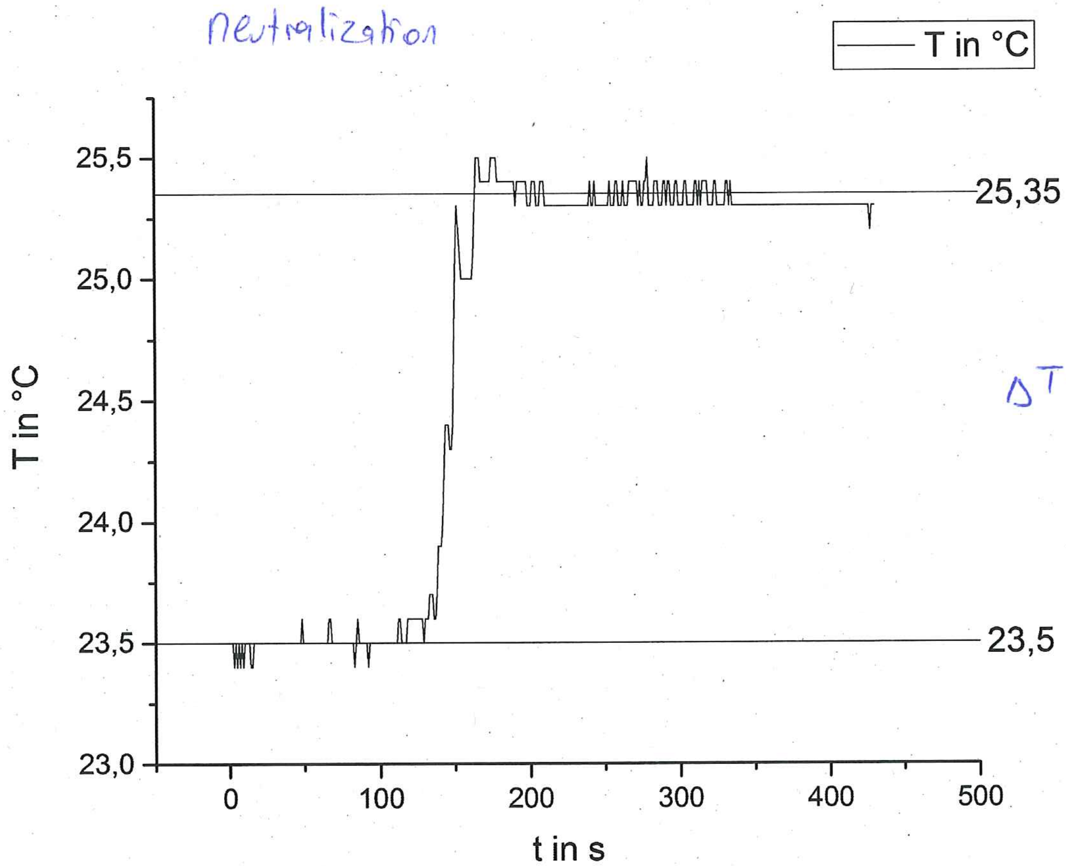
2. Two energies must be considered. One the one hand the lattice energy and the solution energy. The lattice energy shows you how much ~~xxxx~~ you have to spend to remove the ions out of the ion crystal. The solution energy is released when the hydration sphere is formed.
If the solution energy is bigger then the lattice energy (Na_2CO_3) then the water is warming.
If the solution energy is smaler then the lattice energy ($Na_2CO_3 \cdot 10H_2O$) then the watr is cooling down.

Calibration 1

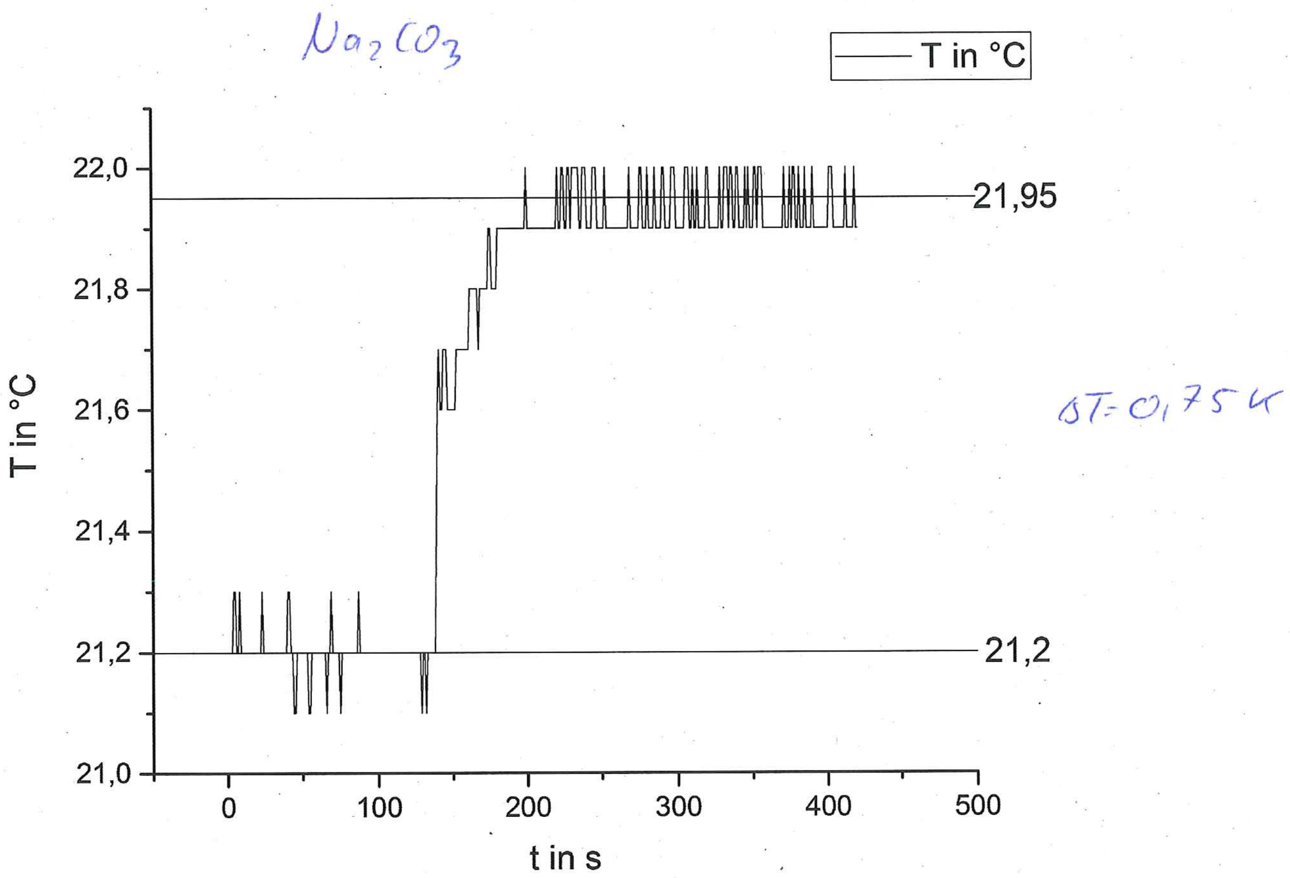


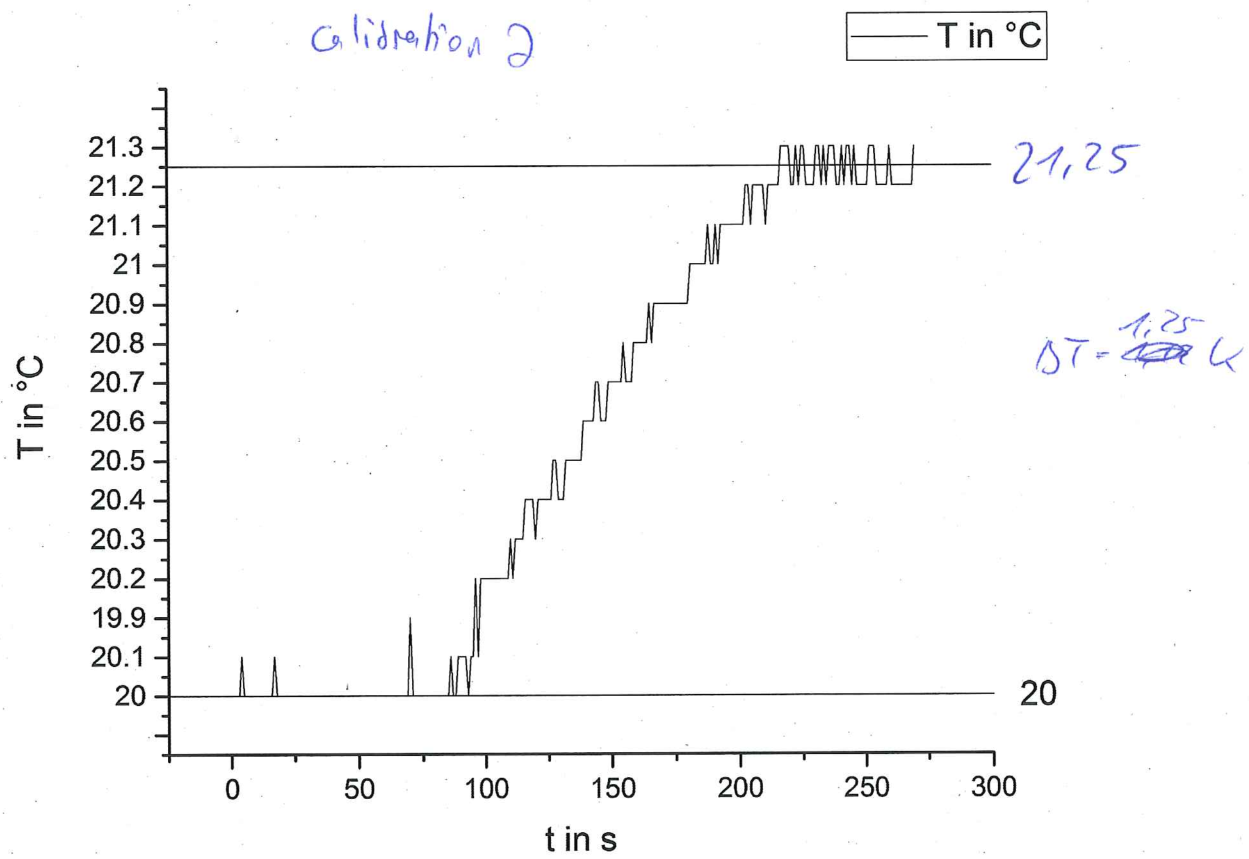
ΔT = 1,2 K

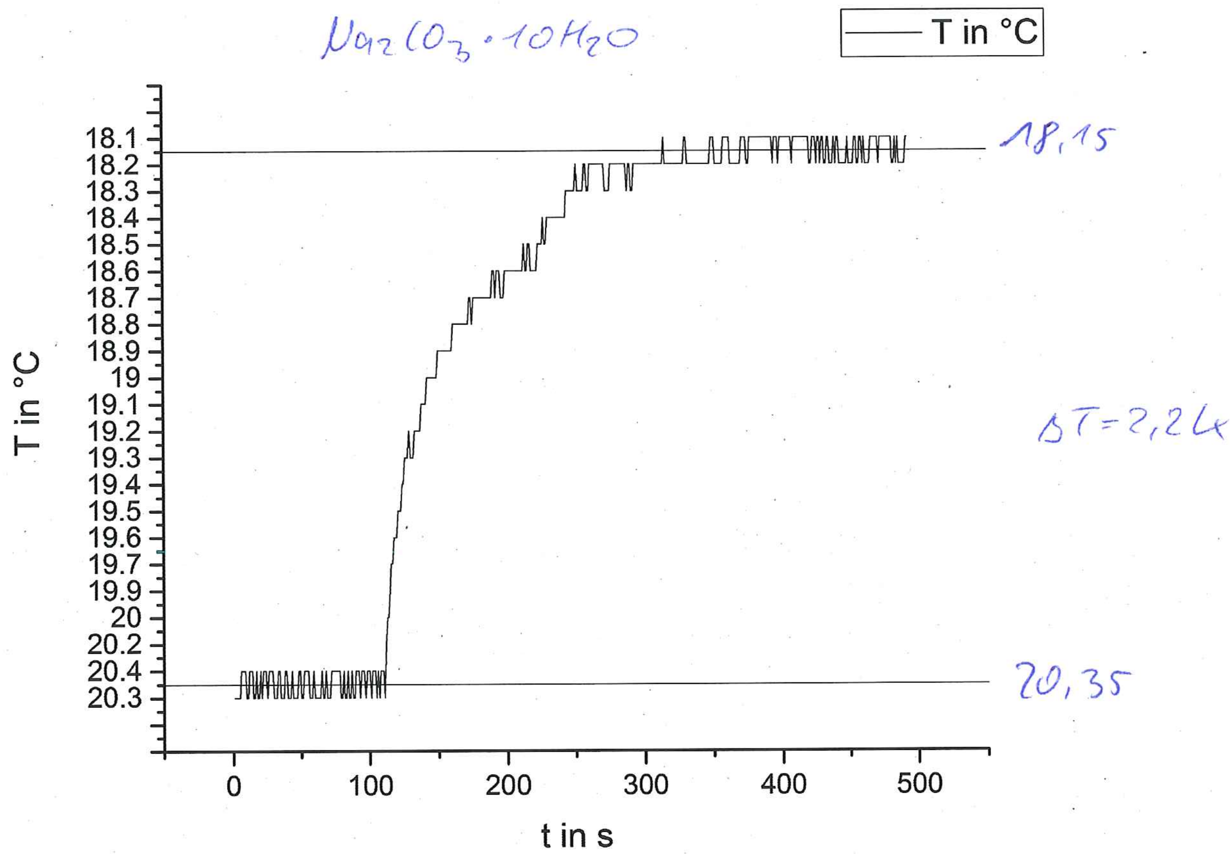
neutralization



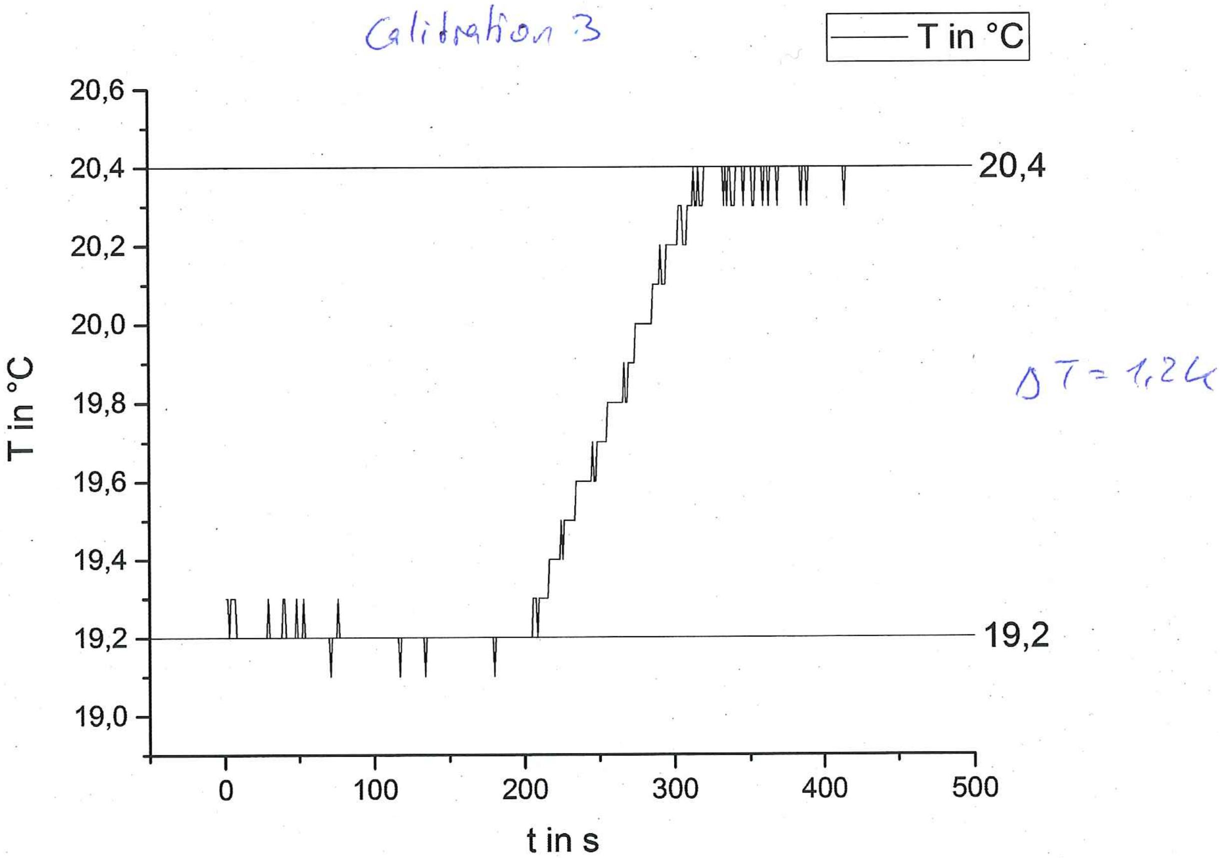
ΔT = 1,85 K


Na2CO3
T in °C
22,0
21,8
21,6
21,4
21,2
21,0
T in °C
0
100
200
300
400
500
t in s
21,95
21,2
ΔT=0,75 K


calibration 2
T in °C
21.3
21.2
21.1
21
20.9
20.8
20.7
20.6
20.5
20.4
20.3
20.2
19.9
20.1
20
T in °C
0
50
100
150
200
250
300
t in s
21,25
20
ΔT=1,25 K



Na2CO3·10H2O
T in °C
18.1
18.2
18.3
18.4
18.5
18.6
18.7
18.8
18.9
19
19.1
19.2
19.3
19.4
19.5
19.6
19.7
19.9
20
20.2
20.4
20.3
0
100
200
300
400
500
t in s
18,15
ΔT=2,2K
20,35



Calibration 3
T in °C
20,6
20,4
20,2
20,0
19,8
19,6
19,4
19,2
19,0
0
100
200
300
400
500
t in s
20,4
19,2
ΔT=1,2K