

A6 Calorimetry

Duty:

Three main purposes in this experiment are obligatory:

- (1) the neutralization enthalpy of salt acid should be determined
- (2) the solvation enthalpy for water-free Na_2CO_3 and $\text{Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O}$ should be measured
- (3) Basing on (1) and (2) the hydration enthalpy of Na_2CO_3 has to be calculated.

Theoretical Backgrounds

Calorimeter: A container thermally isolated from surroundings, filled with reactants dissolved in liquid medium and equipped with a precise thermometer, enables to measure the reaction heat Q . The heat Q generated by a chemical reaction as proceeding in a liquid medium within a time interval Δt can be measured simply by monitoring the corresponding temperature jump, $\Delta T = T_f - T_i$. The dissipation of the reaction heat proceeds via warming of both the liquid medium (water in this case) and the calorimeter itself (the walls predominantly). Thus, the following relation applies:

$$Q = (C_K + c_W m_W) \Delta T \quad (1)$$

Q [J] : released reaction heat

C_K [J K^{-1}]: heat capacity of the calorimeter

c_W [$\text{J g}^{-1} \text{K}^{-1}$] specific heat capacity of water

m_W [g] : the mass of water in the calorimeter

ΔT [K]: the reaction conditioned temperature jump

The C_K value in Eq. 1 represents all contributions to the calorimeter-conditioned heat losses and consequently is not known (depends on the construction and isolation of the calorimeter). It has to be determined experimentally by performing precisely a calibration procedure. When supplying a well-defined heat quantity, (Joule's heat by an immersion heater, $Q = UIt$) to whole system water/calorimeter one can determine the heat capacity of the calorimeter C_K simply by measuring the related temperature increase, ΔT_{cal} . When the heater operating under voltage U consumes an electric current I within a time interval t then a well-defined heat amount $Q = UIt$ is supplied:

$$Q = U I t = (C_K + c_W m_W) \Delta T_{cal} \quad (2)$$

U [V]: voltage supplied to the immersion heater

I [A]: resulting current flowing through the resistance of the heater

t [s]: the operation time required to generate the heat quantity Q

Note: the mechanical heat equivalent: $1 \text{ cal} = 4,185 \text{ J}$ and $1 \text{ VAs} = 1 \text{ Ws} = 1 \text{ J}$.

Fig. 1 illustrates the typical time evolution of the temperature as recorded in a whole detection range. Due to the fact that the thermal isolation of a calorimeter is never perfect one observes a spontaneous long-term temperature drift (exchange with the surroundings). Thus, the determination of the real reaction-conditioned temperature jump, ΔT , proceeds via measuring the time evolution $T(t)$ over a longer time period and determining the mean T values for *Vorperiode* and *Nachperiode*, T_A and T_B , respectively,

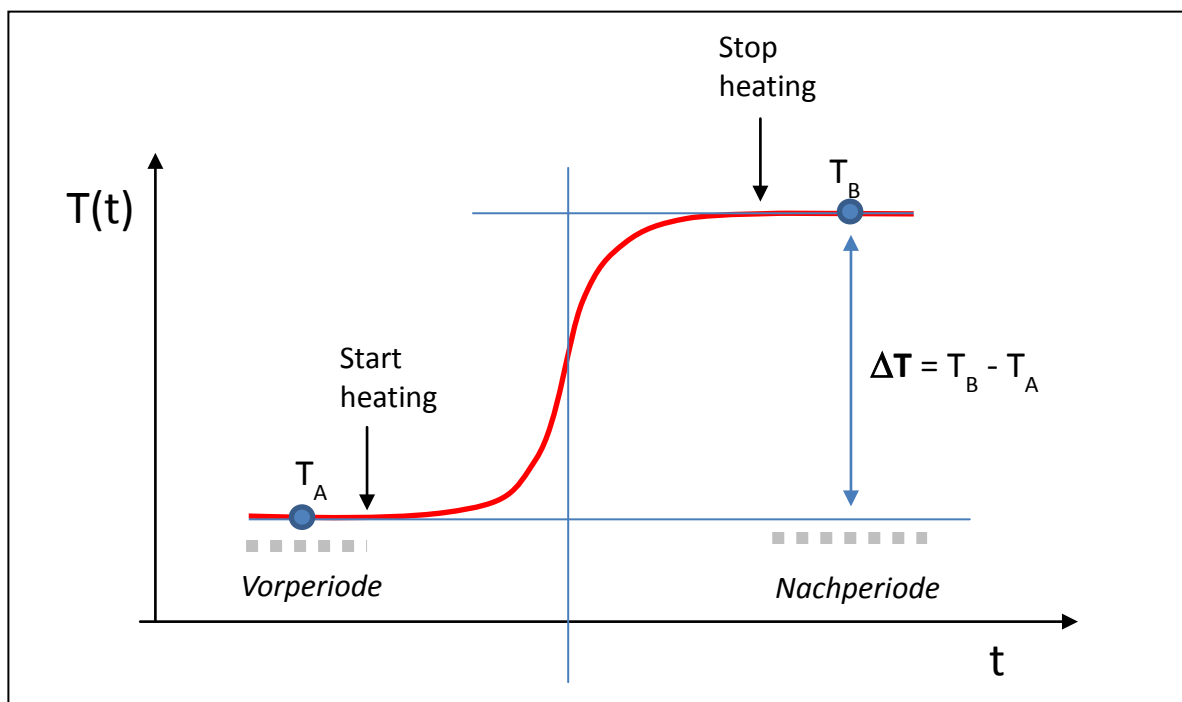


Fig. 1 The temperature jump ΔT is defined as the difference between the mean temperature T_B in the *Nachperiode* and the mean temperature T_A in the *Vorperiode*, $\Delta T = T_B - T_A$.

Neutralization Enthalpy of HCl

When a strong base reacts with an acid the neutralization enthalpy will be released. When the ambient pressure in the system is kept constant during the reaction then the enthalpy is identical to the neutralization heat. The base-acid neutralization process in water is accompanied by a reaction of the H^+ and OH^- ions which ends with the formation of water molecules, i.e. the neutralization enthalpy equals the formation enthalpy of H_2O from ionic educts. Consequently, one can expect to get the same value of the neutralization enthalpy for different bases and acids. However, this applies only for diluted solutions, at highly concentrated solutions one has to consider other contributions, e.g. dilution enthalpy. Thus, at the aforementioned requirements the neutralization enthalpy ΔH_N can be determined by measuring the corresponding neutralization heat:

$$Q = n \Delta H_N^* = (C_K + c_W m_W) \Delta T \quad (3)$$

n [mol] : mole number of water formed (g-mol)

ΔH_N^* [J mol⁻¹]: neutralization enthalpy without to include the dilution enthalpy

The following relation follows from the equation (2) and (3):

$$|\Delta H_N^*| = \frac{1}{n} U I t \frac{\Delta T}{\Delta T_{cal}} \quad (4)$$

Therefore, after including the dilution enthalpy ΔH_d the formula (4) becomes modified as follows:

$$\Delta H_N = \Delta H_N^* - \Delta H_d \quad (5)$$

Hydration and Dissolution Enthalpy

Dissolution of n moles of a substance in a solvent is accompanied by an enthalpy change of ΔH_L per mole of dissolved substance. According to the prefix nomenclature the related enthalpy change is positive, $\Delta H_L > 0$, when surplus heat has to be supplied from outside to the system in order to keep the temperature constant. The hydration enthalpy ΔH_{hydr} corresponds to the formation of solid hydrates from one mole of a solid water-free salt and water. The ΔH_{hydr} can be determined as a sum of two components: (1) ΔH_L^{salt} : the molar solution enthalpy of the solid water-free salt, and (2) ΔH_L^{hydr} : the molar solution enthalpy of the crystalline hydrated salt:

$$\Delta H_{hydr} = \Delta H_L^{salt} - \Delta H_L^{hydr} \quad (6)$$

ΔH_L^{salt} and ΔH_L^{hydr} , both will be determined by calorimetrically.

Thus, in analogy to eq. (3) the following relations obey:

$$Q = n \Delta H_L^{salt} = (C_k + c_w m_w) \Delta T^{salt} \quad \rightarrow \quad \Delta T^{salt} > 0 \quad (7)$$

$$Q = n \Delta H_L^{hydr} = (C_k + c_w m_w) \Delta T^{hydr} \quad \rightarrow \quad \Delta T^{hydr} < 0 \quad (8)$$

Whereby, the same mole number n of Na_2CO_3 and $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ has to be dissolved.

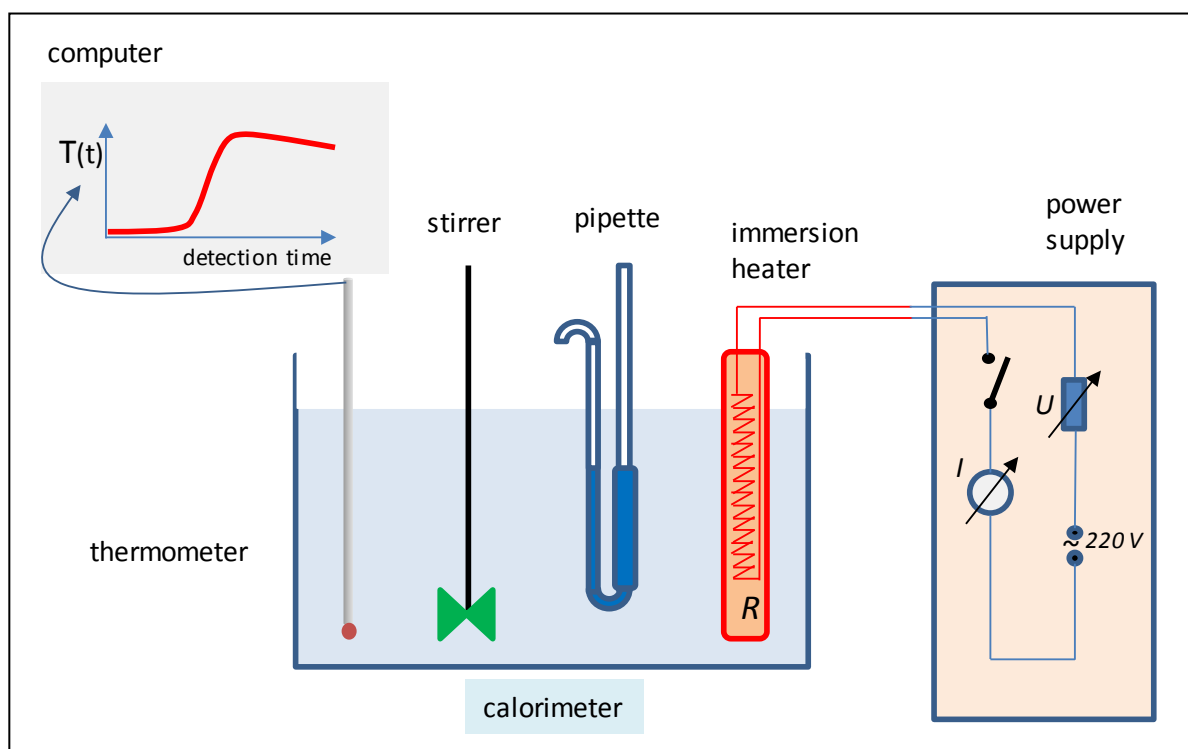
The calibration C_K value will be determined by means of the well-defined Joule heat supplied by an immersion heater. (see Eq. (2)) Finally, the following equations summarize the experimental procedure which enables to determine the ΔH_L^{salt} and ΔH_L^{hydr} :

$$\left| \Delta H_L^{salt} \right| = \frac{RI^2 t}{n} \frac{\Delta T^{salt}}{\Delta T_{cal}} \quad \text{and} \quad \Delta H_L^{salt} < 0 \quad (9)$$

$$\left| \Delta H_L^{hydr} \right| = \frac{\Delta T^{hydr}}{\Delta T^{salt}} \Delta H_L^{salt} \quad \rightarrow \quad \Delta H_L^{hydr} > 0 \quad (10)$$

Performing the measurements

Fig. 2 shows a representative scheme of the experimental setup used here for calorimetric measurements:



The calorimeter (Dewar container) has to be filled with 600 g of distilled water. The disposable pipette has to be filled with 50 g distilled water and together with the immersion heater, thermometer and stirrer set into the Dewar. For the calibration procedure the immersion heater has to operate in water for exactly $t_0=120$ sec (stopwatch) at constant current of exactly 0.8 A. If necessary the current I can be corrected by means of the resistor at the power supply. The water temperature has to be measured continuously before, during and after heating with a constant sampling rate of 1 measurement per second at constant stirring power. In this way one gets the $T(t)$ curve (*Vorperiode*: the time interval foregoing the reaction ignition is about $t_i \sim 1$ minute, the same time interval should be used for equilibration after completing the heating, *Nachperiode*: $t_f \sim 1$ minute).

For the measurement of the neutralization enthalpy exactly 6 g NaOH will be dissolved in 600 g H₂O. In the next step the content of the pipette, 50 ml 2m HCl, has to be injected into the water at permanent stirring. The T(t) function has to be recorded within the whole detection time: $t = (\text{Vorperiode} / \text{Reaction} / \text{Nachperiode})$. The immersion heater remains in the Dewar all the time. The solution heat will be determined by means of the setup shown in Fig. 2., but without to exploit the disposable pipette. One has to fill the calorimeter with 600 g distilled water and subsequently the same calibration procedure described above can be performed.

One weigh 10 g water-free Na₂CO₃ and the same mole number of hydrates

Na₂CO₃ · 10 H₂O (= 26,98 g). The T(t) function has to be recorded for both dissolved water-free and for dissolved water-containing salts.

Data Analysis

All T(t) curves together with the calibration curve should be plotted and by exploiting the compensation procedure the related temperature jumps have to be determined. The neutralization enthalpy should be presented according to eq. 5, whereby the value of the dilution enthalpy $H_d = 1,883 \text{ kJmol}^{-1}$ should be used for calculations (adhere to the prefix please). The experimental results have to be compared to the corresponding values from the related literature.

Molecular weights:	Na ₂ CO ₃	106 g/mol
	Na ₂ CO ₃ · 10 H ₂ O	286 g/mol

Knowledge required

Topics: first and second law the thermodynamics, internal energy, enthalpy, ideal solutions, standard states, lattice energy (cohesion energy), solubility of solid substances in water.

Additional Questions

Why is water a good solvent for ionic compounds? You should answer the following question:

Why the dissolution of Na₂CO₃ in water is accompanied by a warming and in contrast the dissolution of Na₂CO₃ · 10 H₂O is associated with cooling-down of the system.

Estimation of the error bars

Which kind of error estimations should be performed here: The maximal errors or Gauss's error propagation? In all the experiments performed here the enthalpy has been measured only once.

Consequently the statistic information is missed and the possible error calculation has to be reduced to the maximal values.

All single values directly measured here, U , I , t , n , ΔT are defective loaded with some uncertainties. The absolute errors ΔU and ΔI can be found as the transformer settings $\Delta(\Delta T)$ can be derived from the manual of the voltmeter used. Δt and Δn should be roughly estimated (Δn is governed by random mass losses of the polycrystalline material on the glass walls). ΔH represents a product of different variables x_i . In such a case the formula for estimation of the maximal errors becomes simplified.

$$\Delta f(x_1, x_2, x_3, \dots, x_n) = \sum_{i=1}^n \left| \frac{\partial f}{\partial x_i} \Delta x_i \right| = |f| \sum_{i=1}^n \left| \frac{\Delta x_i}{x_i} \right|$$

Δx_i are the absolute values of the errors; $\frac{\Delta x_i}{x_i}$ are the relative errors of the variables measured directly;

As a simple example one could estimate the errors for a function $f = \frac{xy}{z}$ assuming certain values for directly measured variables x , y and z as well as for their absolute errors Δx , Δy and Δz . The experimental report should contain all $T(t)$ plots with graphical determination of the temperature jumps ΔT .