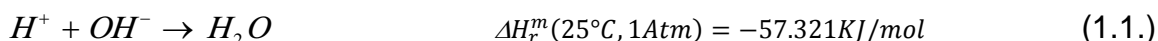# 3. Thermochemical measurements

3.a. Determination of neutralization and dilution heats

When neutralizing aqueous solutions of acids with alkaline solutions, an elementary reaction of dissociated ions occurs:

$$H^+ + OH^- \rightarrow H_2O \qquad\qquad \Delta H_r^m(25°C, 1Atm) = -57.321 KJ/mol \qquad (1.1.)$$

However, the actual heat released during the neutralization (ie, total enthalpy change ΔH_{nt}) of strong acids with strong bases is also affected by other effects, such as heat of dilution ΔH_{hd}. In addition, when neutralizing weak acids or weak bases, a certain amount of energy is consumed to dissociate ΔH_{dis} to release ions *[H⁺]* or *[OH⁻]*. Therefore, the resulting neutralizing heat effect is moreover affected by the dilution and dissociation heats of weak acid or base:

$$\Delta H = \Delta H_{nt} = \Delta H_r + \Delta H_{hd} + \Delta H_{dis} \qquad (3.2.)$$

The total amount of the released heat *Q* during neutralization in the calorimeter is determined by the temperature rise in the calorimeter according to the formula:

$$Q = C \cdot \Delta T = -\Delta H \qquad\qquad (3.3.)$$

where ΔT is the temperature rise during neutralization, *C* is the heat capacity of the calorimeter, which indicates the amount of heat required to heat the calorimetric vessel with its content of $1°C$. In the case of an aqueous solution experiment, the *C* constant depends mainly on the amount of water ($c_{H_2O}^p(25°C, 1Atm)$ =4.1796 J K⁻¹ kg⁻¹).

We calibrate the heat capacity of the calorimeter *C* by measuring the temperature rise $\Delta T'$ in the calorimeter after releasing heat Q_E, which is produced by the passage of the current *I* through the electrical resistor immersed in the calorimeter filling. The heat capacity is given by eqn

$$C = \frac{Q_E}{\Delta T'} = \frac{E \cdot I \cdot t}{\Delta T'} \qquad\qquad (3.4.)$$

where *E* is the voltage at the resistance heater terminals and *t* is the flow time of the electric current *I*.

? TASK: Determine the neutralization ΔH_{nt} and dilution ΔH_{hd} heats of both strong (*HCl*) and weak acid (*acetic acid*) when reacting with a strong base (*NaOH*). Determine the heat of reaction ΔH_r when neutralizing strong acid with a strong base. Estimate the dissociation heat ΔH_{dis} of the weak acid.

LABORATORY AIDS AND CHEMICALS: Dewar vessel, digital thermometer equipped by external sensor, operator PC, rotary el. stirrer, heating element in a glass case, automatic dispenser(*10 cm³*), ammeter, voltmeter, rheostat, manual switch, pipettes (*10* and *50 cm³*), *2M HCl, 2M CH3COOH (HAc), 0,1M NaOH, 2M CH3COOH (HAc), 0.1M NaOH*, phenolphthalein indicator.

ASSEMBLING OF CALORIMETER. The main part of simple calorimeter according **FIGURE 1** is the Dewar vessel of about *500 cm³*. Fill the vessel with *0,1M NaOH* or water. The choice depends on the thermal effect that will be measured. The tube goes from the dispenser with *2M HCl* or *HAc* acid to the Dewar vessel. Check electric

connection between temperature sensor, digital thermometer, and operator PC. Switch on thermometer and PC. Test the software for collection of data before experiment.

📄 **INSTRUCTIONS:**

1. **Preparation of acid dispenser.** Because the dispenser tube has a considerable volume, there is always a certain amount of air or liquid in it before calorimetric measurement. Thus a multiple dose ($10\,cm^3$) of the selected acid has to be eliminated to the waste. The exact amount of the acid solution should be determined by titrating the dose volume with the *NaOH* solution of known concentration.

2. **Determination of both neutralization heat ΔH_{nt} of strong acid and calorimeter constant** *C.* Fill the Dewar vessel with *0,1M NaOH* solution of the volume that will be needed to neutralize the later dosed acid.
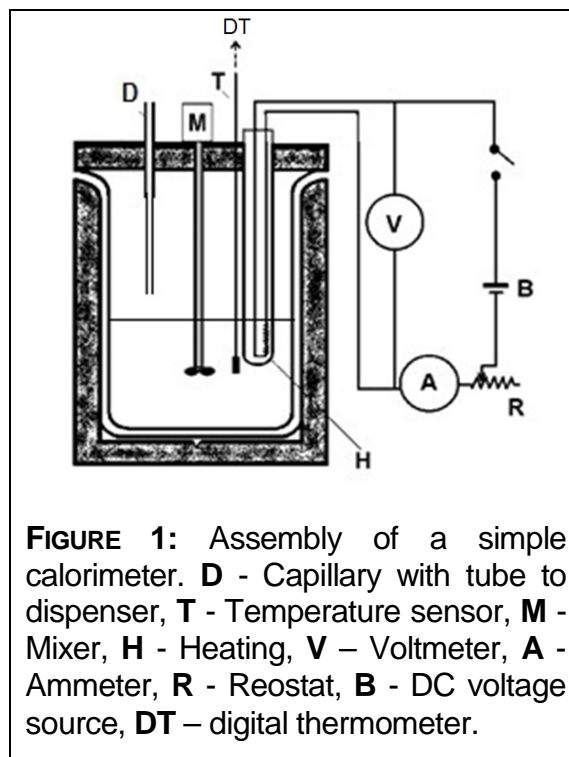

FIGURE 1: Assembly of a simple calorimeter. **D** - Capillary with tube to dispenser, **T** - Temperature sensor, **M** - Mixer, **H** - Heating, **V** – Voltmeter, **A** - Ammeter, **R** - Reostat, **B** - DC voltage source, **DT** – digital thermometer.

(ie. exact amount *10 ml 2M HCl* needs *200ml 0.1M NaOH*). Put the stirrer, the acid dispenser capillary, the heating element, and the temperature sensor into the

calorimeter stopper. Turn on the rotary stirrer. During the shortest period of time between switching on and off, set the current intensity through the heating element to the value (*0.5 A*) using the rheostat. Start data collection using PC. Record the temperature in the calorimeter at its initial relaxation (approx. *5-7 min*) as well as after adding the *10 ml* dose of *2M HCl* (approx. *4 min*). Then switch on the heating and write down immediately the start time ($\pm 1\,sec$) from the PC monitor and the electric current. After the temperature rises by approx. *0,7°C*, turn off the heating and write down the exact time again from the PC monitor. Leave the temperature in the calorimeter relaxing for another *10 minutes* and then stop the measurement. This all will give you a temperature record similar to the **FIGURE 2**. After the measurement, empty and rinse the calorimeter by water.

3. **Determination of both diluting heat ΔH_{hd} of strong acid and calorimeter constant**
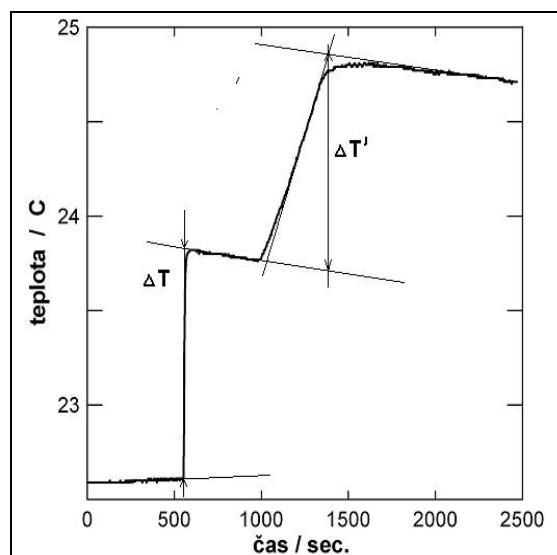

FIGURE 2: Dependence of temperature on time when the strong acid is neutralized with a strong hydroxide, including a further course of determination of the heat capacity *C* of the calorimeter.

C. Measure and put into the Dewar vessel as much water as used of *0,1M NaOH* solution in the previous neutralization experiment. Check the dispenser of *2M HCl* solution and follow the same procedure as done during the neutralization experiment using water instead of *0,1M NaOH* solution.

4. **Determination of neutralisation and diluting heats of weak acid (HAc).** Work exactly in the same way as it was done before when working with strong acid, including determining the calorimeter heat capacity and dilution heat.

DATA ANALYSIS: For all experiments: fit the lines on the linear regions of the temperature – time dependence according to **FIGURE 2**. Evaluate the values ΔT and $\Delta T'$ as accurately as possible. You should perform linear interleaving and evaluation using a computer if a suitable SW is available.

REPORT: For both strong and weak acids: **Graph 1-4:** Dependence of temperature on time obtained during measuring of neutralization and dilution heats. **Table 1:** for all experiments: *NaOH* or water wolume, molar masses of *NaOH* and acid used at neutralization, temperature increase of neutralization ΔT and of dilution $\Delta T'$, the voltage, current, and time values used in the eqn (3.4.), heat capacity of the calorimeter *C*, molar neutralization enthalpy ΔH_{nt}^m or molar diluting enthalpy ΔH_{hd}^m. **NEXT:** comparison of measured molar reaction enthalpy for strong acid (*HCl*) with its tabulated value ΔH_r^m. Estimation of molar dissociation enthalpy of weak acid (*HAc*).