Experiment Nr. 17

DETERMINATION OF THE HEAT CAPACITY OF MIXED LIQUID

Theoretical part

Heat capacity or thermal capacity is a physical quantity equal to the ratio of the heat added to (or removed from) an object resulting in its temperature change:

$$C = \frac{dQ}{dT}$$

The unit of heat capacity is joule per kelvin ($J.K^{-1}$). Heat capacity is an extensive property of matter, meaning it to be proportional to the size of the system. When expressing the same phenomenon as an intensive property, the heat capacity is divided by the amount of substance, mass, or volume, thus the quantity is independent of the size or extent of the sample. The **molar heat capacity** is the heat capacity per mole of a pure substance and the **specific heat capacity**, often called simply as specific heat, is the heat capacity per unit mass of a material.

$$c = \frac{1}{m}\frac{dQ}{dT}$$

The unit of specific heat capacity is joule per kilogram and kelvin ($J.kg^{-1}.K^{-1}$). Nonetheless some authors use the term specific heat to refer to the ratio of the specific heat capacity of a substance at any given temperature, to the specific heat capacity of another substance at a reference temperature, much in the fashion of specific gravity. In some engineering contexts, the volumetric heat capacity is used.

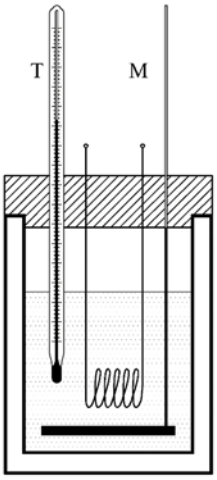
Specific heat and other thermodynamic parameters describing the heat interchange are usually studied by **calorimetry**. Calorimetry is the science or act of measuring changes in state variables of a body for the purpose of deriving the heat transfer associated with changes of its state due, for example, to chemical reactions, physical changes, or phase transitions under specified constraints. Calorimetry is performed with a calorimeter. A **calorimeter** is an object used for calorimetry, or the process of measuring the heat of chemical reactions or physical changes as well as heat capacity. Differential scanning calorimeters, isothermal micro-calorimeters, titration calorimeters and accelerated rate calorimeters are among the most common types. A simple calorimeter just consists of a thermometer attached to a metal container filled with water. An **adiabatic calorimeter** is a calorimeter used to examine a runaway thermodynamic reaction. Since the calorimeter runs in an adiabatic environment, any heat generated by the material sample under test causes the sample to increase in temperature, thus fuelling the reaction. No adiabatic calorimeter is fully adiabatic - some heat will be lost by the sample to the sample holder. A mathematical correction factor, known as the phi-factor, can be used to adjust the calorimetric result to account for these heat losses. The phi-factor is the ratio of the thermal mass of the sample and sample holder to the thermal mass of the sample alone.

Determination of the specific heat capacity of the liquid

For our measurement, an electric calorimeter will be used. It is a thermally insulated vessel equipped with an electrical heating system. Heat generated by an electrical heater could be defined as follows:

$$Q = P \cdot \tau,$$

where P is electrical power and τ is the time of heating.
The heat transferred to the system by a heater increases the temperature of the calorimeter (with heat capacity K_K) that is filled with measured liquid of mass m by ΔT (or Δt).



Considering that the heat losses are minimized by the calorimeter design, the heat supplied by the electrical heater is equivalent to the heat absorbed by the calorimeter approximately:

$$Q = P \cdot \tau = (K_K + mc)\Delta t$$

Specific heat capacity c of the liquid can be thus determined by following formula:

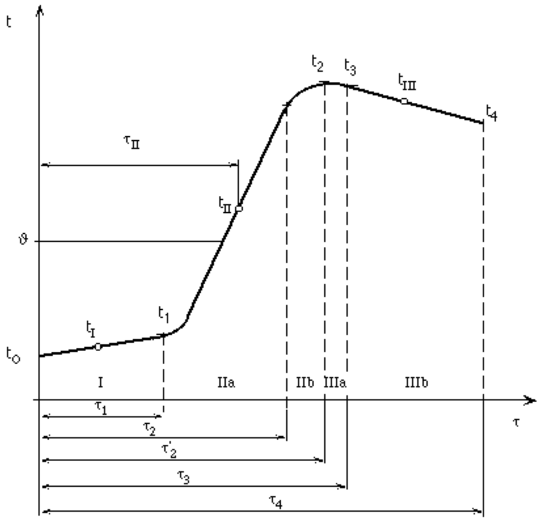
$$c = \frac{P\tau}{m(t_2 - t_1)} - \frac{K_K}{m}$$

Measurement objective

1. Determine the specific heat capacity of selected liquid (water, glycerine and alcohol mixture with ratio 2:1:1).
2. Determine the uncertainty of the obtained specific heat capacity. Compare the result with the value calculated from the liquid mixture ratio.

Measurement procedure

The calorimeter is filled with a mixed liquid. Because we have to know the mass of the liquid itself, we have to determine the mass of the empty calorimetry and of the liquid-filled calorimeter and subtract these values. For the weighing, use the digital scale. The initial temperature should be lower than the room temperature (temperature of the liquid should be 7 - 15 °C).
While stirring the liquid, record the temperature data every 10 seconds by a thermocouple using the computer. Note that the calorimeter temperature change can be divided into three separate intervals:



I - the temperature of the liquid is below room temperature. A moderate increase of the temperature could be observed due to the heat transferred from the ambient environment to the calorimeter. Record the data for about 5 minutes in this phase.
II - the liquid is heated until the moment when the calorimeter reaches the maximum temperature above the room temperature. Note that the temperature change below and above the room temperature should be approximately the same due to the heat losses compensation.
III - The liquid reached the maximum temperature that is above the room temperature. A moderate decrease of the temperature could be observed due to the heat transferred from the calorimeter to the ambient environment. Record the data for about 5 minutes in this phase.

The heating of the liquid is performed due to the spiral heating wire. The electrical power should be calculated from the voltage and current that are observed in the wiring diagram.

Important constants

The water specific heat capacity as a function of temperature:

t [°C]	**c [J·kg^{-1}·K^{-1}]**	**t [°C]**	**c [J·kg^{-1}·K^{-1}]**	**t [°C]**	**c [J·kg^{-1}·K^{-1}]**
0	4217,8	35	4178,1	70	4189,7
5	4201,3	40	4178,4	75	4192,9
10	4192,2	45	4179,3	80	4196,4
15	4186,3	50	4180,5	85	4200,5
20	4181,8	55	4182,2	90	4205,2
25	4179,5	60	4184,3	95	4210,4
30	4178,4	65	4186,7	100	4216,0

Specific heat capacity values of selected liquids

Liquid	**c [J·kg^{-1}·K^{-1}]**
Ethyl alcohol	2430
Glycerine	2390
petroleum	2090
mercury	139

The heat capacity of the calorimeter K_K = (100 ± 10) J.K^{-1}.
The electrical power should be about 30 - 40 W.

Uncertainty calculation notes

The uncertainty of the specific heat capacity is the Type B evaluation only. The uncertainty sources are: mass of the liquid, heating time, electric power, starting temperature point t_1, end temperature point t_2 and the heat capacity of the calorimeter. The uncertainty of the specific heat capacity of the liquid is

$$u_{cB}=\sqrt{\left(\frac{\partial c}{\partial m}\right)^2 u_{mB}^2+\left(\frac{\partial c}{\partial P}\right)^2 u_{PB}^2+\left(\frac{\partial c}{\partial \tau}\right)^2 u_{\tau B}^2+\left(\frac{\partial c}{\partial K_K}\right)^2 u_{K_K B}^2+\left(\frac{\partial c}{\partial t_1}\right)^2 u_{t_1 B}^2+\left(\frac{\partial c}{\partial t_2}\right)^2 u_{t_2 B}^2}\ ,$$

where

$$\frac{\partial c}{\partial m}=-\frac{1}{m^2}\left(\frac{P\tau}{(t_2-t_1)}-K_K\right)$$

$$\frac{\partial c}{\partial P}=\frac{\tau}{m(t_2-t_1)}$$

$$\frac{\partial c}{\partial \tau}=\frac{P}{m(t_2-t_1)}$$

$$\frac{\partial c}{\partial K_K}=-\frac{1}{m}$$

$$\frac{\partial c}{\partial t_1}=\frac{P\tau}{m(t_2-t_1)^2}$$

$$\frac{\partial c}{\partial t_2}=-\frac{P\tau}{m(t_2-t_1)^2}$$

The sub uncertainty of the electrical power u_{PB} should be calculated from the voltage U and current I uncertainties. The relative uncertainty of the electrical power is

$$u_{rPB}=\sqrt{u_{rUB}^2+u_{rIB}^2},$$

where the sub uncertainties u_{rUB} and u_{rIB} should be determined according to the measuring instrument used. In our case, we use the digital instruments. The user's manual show the direct current standard error according to the selected range as follows:

Quantity	Range	standard error
Direct Current	2 mA	0.3 % rdg + 3 digits
	20 mA	
	200 mA	
	20 A	0.5 % rdg + 3 digits
Direct Voltage	200 mV	0.05 % rdg + 3 digits
	2 V	
	20 V	
	200 V	