

## 5. Specific heat

### 5.1 Introduction

There are many examples for phenomena from daily life in which one kind of energy is converted into another kind. Examples include:

- The conversion from potential to kinetic energy and back during motion in a gravitational field.
- Generation of electric energy from mechanical energy.
- Conversion of electric energy into heat in many devices like a pressing iron or a stove.
- Energy chemically stored in food is used for the production of heat and muscle work.
- Deceleration of a body by friction produces heat.

The law of energy conservation of mechanics only describes the conversion between potential and kinetic energy. In thermodynamics this conservation law is generalized including heat and internal energy of a body into the total energy. The **First Law of Thermodynamics** reads:

$$\delta Q = dU + \delta W,$$

where  $\delta Q$  denotes the heat supplied to the system ( $\delta Q > 0$ ) or released by the system ( $\delta Q < 0$ ),  $dU$  the change in internal energy of the system, and  $\delta W$  the work provided by the system ( $\delta W > 0$ ) or done on the system by an external force ( $\delta W < 0$ ).

The internal energy may have various contribution like *e.g.* the kinetic and potential energies of all molecules of the system. In thermodynamics the absolute amount of energy is less of interest than the change in energy during a process. The process can be a change in temperature (= change in kinetic energy) or a change in thermodynamic state or phase (like crystal structure) of the system.

In this experiment we use the first law of thermodynamics in order to describe the energy content of solids as function of temperature. Keywords are:

- Energy conservation and the first law of thermodynamics,
- specific heat, in particular of condensed matter.

## 5.2 Theory

### 5.2.1 Specific heat

Supplying heat to a body leads to an increase in temperature. The temperature rise depends on the material and the mass of the body. The specific heat is a measure of the energy required to heat up 1 kg or 1 mol of a material by 1 K:

$$\delta Q = n \cdot C \cdot dT \quad \text{or} \quad (5.1)$$

$$\delta Q = m \cdot c \cdot dT. \quad (5.2)$$

Here:  $\delta Q$  = heat provided to or released from the system,  
 $dT$  = change in temperature,  
 $n$  = number of moles,  
 $m$  = mass,  
 $C$  = (specific) heat capacity per mole, and  
 $c$  = (specific) heat capacity per kg.

In general, and in particular in gaseous state, the boundary conditions are important, *i.e.*

$C_V$ : specific heat at constant **volume**,  
 $C_p$ : specific heat at constant **pressure**.

If the volume is constant during a energy (heat) exchange, no work is done ( $\delta W = 0$ ) and the first law leads to the following relation:

$$C_V = \left( \frac{\delta Q}{dT} \right)_{V=const} = \frac{dU}{dT}. \quad (5.3)$$

If we supply heat to a gas kept at constant pressure, the volume of the gas increases and a part of the heat is used for the work done by the expanding gas. Therefore the specific heat of a gas at constant pressure is significantly higher than that at constant volume. In contrast to that, a solid hardly changes its volume, so

$$C_p \approx C_V = \frac{dU}{dT} \quad \text{for a solid.} \quad (5.4)$$

If the internal energy of a body  $U$  is known as function of temperature  $T$ , the specific heat of this body can be calculated using Eq. 5.4.

### 5.2.2 Equipartition theorem for solid bodies

The internal energy of a body is the sum of all energies of all atoms and molecules contained therein. The energy of a atom is the sum of its potential and kinetic energy. Since the atom can move in three directions of space, the kinetic energy is given by

$$E_{\text{kin}} = \frac{m}{2} (v_x^2 + v_y^2 + v_z^2). \quad (5.5)$$

If we assume the atoms being bound by springs to their equilibrium positions, any displacement from this position leads to an increase in potential energy. Since the displacement is possible in three directions of space, the potential energy becomes

$$E_{\text{pot}} = \frac{1}{2} (k_x x^2 + k_y y^2 + k_z z^2), \quad k_x, k_y, k_z = \text{spring constants.} \quad (5.6)$$

The total energy  $E_{\text{tot}} = E_{\text{kin}} + E_{\text{pot}}$  of an atom quadratically depends on  $f = 6$  independent variables  $(x, y, z, v_x, v_y, v_z)$ . According to the equipartition theorem, the average energy in each of these degrees of freedom amounts to  $k_B T/2$  where  $T$  is the absolute temperature and  $k_B = 1.3806 \cdot 10^{-23}$  J/K the Boltzmann constant.

Thus, the average energy of an atom becomes

$$\bar{E} = \frac{6}{2} k_B T = 3k_B T \quad (5.7)$$

and the internal energy of one mole of atoms ( $N_A$  atoms or molecules) is:

$$U = 3N_A k_B T = 3RT, \quad (5.8)$$

where

$$\begin{aligned} N_A &= 6.022 \cdot 10^{23} \text{ mol}^{-1} &&= \text{Avogadro's number} \\ R &= k_B \cdot N_A = 8.314 \text{ J/(K mol)} &&= \text{universal gas constant.} \end{aligned}$$

Together with Eqn. (5.4) we obtain the law of Dulong-Petit:

$$C = \frac{dU}{dT} = 3R \quad (5.9)$$

for the specific heat per mole. The specific heat for crystalline solids does not depend on the material. In the present experiment we will verify this hypothesis using copper and aluminum samples.

### Remarks

- The law of Dulong-Petit is only valid at high temperature. For most materials this condition is fulfilled at room temperature already.
- For crystalline compounds, the equipartition theorem holds if the compound assumes a regular crystal structure. A molecule containing  $Z$  atoms has then a specific heat capacity per mole of  $3ZR$ . For instance:
  - NaCl, NaBr, and LiCl have  $C = 6R$ ,
  - $\text{ZnCl}_2$  has  $C = 9R$ .
- In an ideal gas the molecules do not interact. Therefore the potential energy is zero and the total energy equals the kinetic energy:

$$E = E_{\text{kin}} = \frac{m}{2} (v_x^2 + v_y^2 + v_z^2) \Rightarrow f = 3.$$

A diatomic gas possesses three translational degrees of freedom and two rotational energy:

$$E = E_{\text{kin}} + E_{\text{rot}} = \frac{m}{2} (v_x^2 + v_y^2 + v_z^2) + \frac{\theta}{2} (\omega_y^2 + \omega_z^2) \Rightarrow f = 5.$$

**Problem:** What is the average energy of one particle at temperature  $T$  of a

- monatomic gas?
- diatomic gas?
- Calculate  $C_V$  and  $C_p$  for the two cases.

## 5.3 Experimental

### 5.3.1 Goal of the experiment

In this experiment the specific heat of aluminum and copper is to be determined by means of a calorimeter: a known quantity of heat  $\delta Q$  is supplied to a given quantity  $n$  of the material. The resulting temperature rise  $dT$  is measured allowing us to calculate the specific heat by using  $C = \delta Q / (n dT)$ .

### 5.3.2 Method

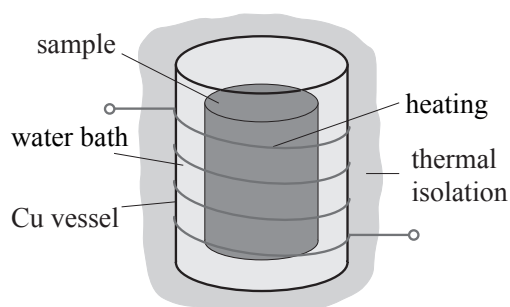


Figure 5.1: The calorimeter.

The calorimeter is a thin-walled vessel made out of copper, which can be heated by means of a filament wrapped around the vessel. The vessel is filled with water and contains the sample to be investigated. The water serves as thermal contact between the vessel, the thermometer, and the sample. The whole setup is thermally isolated ensuring that only very little power is lost.

Hence, the energy supplied to the calorimeter by the electric heating is given by Joule's power :

$$\delta Q = E_{\text{el}} = V \cdot I \cdot t \quad (5.10)$$

where  $V$  denotes the voltage,  $I$  the heating current, and  $t$  the time duration. Since the whole calorimeter is assumed to be in thermal equilibrium, the heat is related to the temperature rise by

$$\delta Q = (T_2 - T_1) \cdot (nC + n_{\text{W}}C_{\text{W}} + W_{\text{calo}}), \quad (5.11)$$

where:

- $n$  = number of moles of the material,
- $C$  = specific heat (per mole) of the sample,
- $T_1$  = initial temperature,
- $T_2$  = final temperature,
- $C_{\text{W}}$  = specific heat of water = 75.33 J/(mol K),
- $n_{\text{W}}$  = number of moles of water,
- $W_{\text{calo}}$  = heat capacity of the vessel  
= heta required to heat the vessel by 1 K.

In order to calculate the specific heat  $C$  of the sample by using Eq. 5.11, the heat capacity  $W_{\text{calo}}$  of the calorimeter has to be determined. des calorimeters bestimmt werden. This can be done by filling the calorimeter with water and measuring the temperature rise as function of time during

heating. We obtain:

$$\begin{aligned}\delta Q &= V' \cdot I' \cdot t = (T'_2 - T'_1) (W_{\text{calo}} + C_W n'_W) \\ W_{\text{calo}} &= \frac{V' \cdot I' \cdot t}{T'_2 - T'_1} - C_W n'_W\end{aligned}\quad (5.12)$$

where:  $n'_W$  = number of moles of water,  
 $T'_1$  = initial temperature,  
 $T'_2$  = final temperature.

Once  $W$  is known, we obtain the specific heat  $C$  of the sample:

$$C = \frac{1}{n} \cdot \left( \frac{V \cdot I \cdot t}{T_2 - T_1} - C_W n_W - W_{\text{calo}} \right).\quad (5.13)$$

### 5.3.3 Realization of the experiment

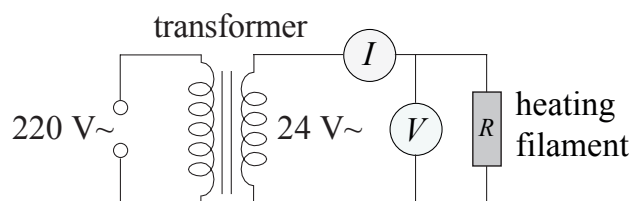


Figure 5.2: Electric circuitry.

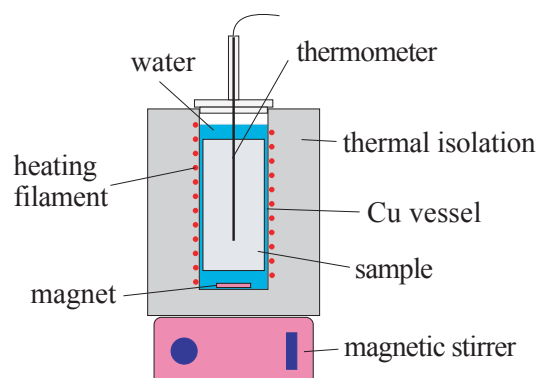


Figure 5.3: Experimental setup.

The setup is shown in Fig. 5.3. The magnetic stirrer insures that the temperature gradient between the wall of the vessel and the (colder) part in the center of the vessel be minimized.

#### Preparation

- Mount the electric circuit following Fig. 5.2. Please, ask the assistant to check the circuitry *before* switching on!
- The assistant will explain the use of the magnetic stirrer.

#### Determination of the heat capacity of the calorimeter

- The calorimeter is to be filled with water until the level is lower by 1-2 cm than the border of the calorimeter. The quantity of water used must be measured either by means of a graduated cylinder or by weighing. Place the calorimeter on the stirrer.

- Connect the thermometer and switch on the stirrer.
- **Without** electric heating record the temperature every 30 sec over 5 mins. Verify that the calorimeter reaches thermal equilibrium.
- Switch on the heating and note the time! Read the temperature during heating every 30 sec over 10 mins. The difference between initial and final temperature should be greater than 25°. Note the heating current and voltage.
- Switch off the heating..
- Read the temperature every 30 sec over 10 mins. If the temperature remains changes little, measurements every minute are sufficient.
- Compile all data in a clearly arranged table.

#### Determination of the specific heat of either Al or Cu

- Determine the weight of the sample and introduce it into the calorimeter carefully using the threaded bar. Do not damage the calorimeter!
- Fill the calorimeter with water until the sample is completely immersed. Measure the quantity of water!
- Connect the thermometer and switch on the stirrer.
- Again wait for thermal equilibrium: measure the temperature every 30 sec during 5 mins without heating.
- Switch on the heating and note the time! Read the temperature during heating every 30 sec during 10 mins. The difference between initial and final temperature should be greater than 40°. Note the heating current and voltage.
- Switch off the heating..
- Read the temperature every 30 sec (or 60 sec) during 10 mins. .
- Compile all data in a clearly arranged table.

#### 5.3.4 Analysis and report

- Answer the question in the theory part.
- Sketch and describe the experimental setup.

### Calculation of the heat capacity $W$

- Plot the data on graph paper (provided by us).
- Determine the initial and final temperature  $T_1$  and  $T_2$  as shown in Fig. 5.3.4 by extrapolation of the curves before and after heating to  $t_1$  and  $t_2$ , when the heating was switched on and off, respectively.
- Calculate the heat capacity  $W_{\text{calo}}$  of the calorimeter using Eqn. (5.12).

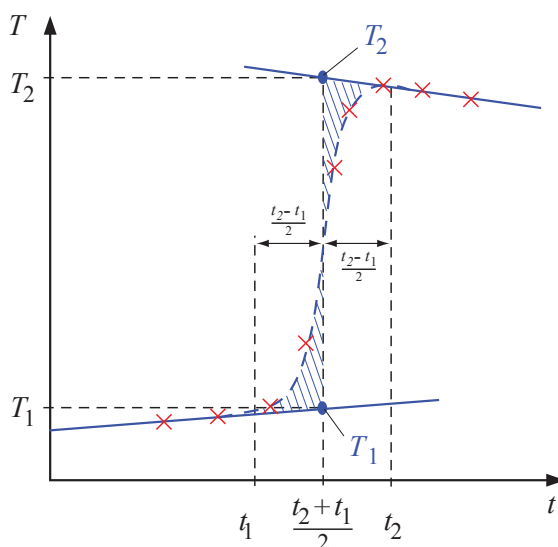


Fig. 5.3.4 Extrapolation of the temperature.

### Calculation of the specific heat

- Plot the data on graph paper (provided by us).
- Determine the initial and final temperature  $T_1$  and  $T_2$  as shown in Fig. 5.3.4 by extrapolation of the curves before and after heating to  $t_1$  and  $t_2$ , when the heating was switched on and off, respectively.
- Calculate the specific heat using Eqn. (5.13).
- Compare your results with the values obtained from the law of Dulong-Petit.

### Estimation of the measurement error

- Estimate the uncertainties (fluctuations and error due to reading) on current, voltage, time, and mass.
- Estimate the uncertainty of  $T_1$  and  $T_2$  from the graphs.

Note: Since the heat capacity and specific heat is calculated using differences and fractions, the total error resulting from these uncertainties can become quite large.