

IIW4

Modul Thermodynamics

Heat as a Form of Energy

The aim of the first part of this experiment is to evaluate the specific heat capacity of copper, aluminium and lead. In the second part the conversion between mechanical energy and heat shall be investigated. Moreover the conversion factor between the old measuring unit *Calorie* and the modern unit *Joule* shall be found by using the specific heat of copper calculated before.

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1.1 Preliminary Questions

- What is the specific heat capacity of a material? What is the difference between the specific and the molar heat capacity?
- What does *Dulong-Petit's* law mean?
- What is the meaning of the equipartition principle?
- Which ideas lead to the equipartition principle and why is it only accurate for solids?
- With these ideas in mind - how could one calculate the specific heat capacity of a monoatomic gas? How could one do this for a diatomic gas or for a solid?

1.2 Theoretical Background

1.2.1 Fundamentals of the Calorimetry: Energy, Heat and Work

Today it seems obvious that heat is a form of energy. Therefore it might astonish that J. R. MAYER was the first to treat heat as a form of energy in 1840. He extended the principle of conservation of energy, which only contained mechanical systems at that time, by the concept of heat. This means that the energy of a solid is the sum of its kinetic energy and the heat stored inside - it is called the *internal energy*. If heat is applied to a physical body the internal energy increases. On the other hand side its internal energy decreases when heat is extracted from an object. Furthermore the internal energy of a body can be changed by doing physical work. The whole calorimetry is based on the principle of energy conservation: "The increase of internal energy dE of a physical body is equal to the supplied heat δQ and the work δA done on the system":

$$dE = \delta Q + \delta A \quad (1.1)$$

J. P. JOULE tried to explain the relationship between mechanical work and heat with the following experiment. A paddle wheel in the water is set in motion by a slowly falling weight. The mechanical energy that is released by the weight travelled a certain distance parallel to the Earth's gravitational field is released into the water by means of friction of the paddle wheel. JOULE then measured the increasing temperature of the water. He was able to show that the resulting rise of the heat is proportional to the work generated by friction.

In this experiment mechanical energy will be converted to thermal energy using friction. For the historical reasons mentioned above, it can also be explained that heat was originally assigned to have another unit than energy, the *calorie*. It was defined as the amount of heat required to heat one gram of water at atmospheric pressure from 14.5°C to 15.5°C. Today heat energy is measured in Joule as all other forms of energy. The conversion factor is given by $1\text{J}=1\text{mKg}/\text{s}^2$, $1\text{cal}=4.1868\text{J}$ respectively.

Heat Capacity and Specific Heat

If heat is added to a physical body, its temperature rises, provided that it does not change its state of aggregation. The relationship between the supplied heat δQ and the increase of temperature δT is given by

$$\delta Q = \Gamma \cdot \delta T \quad (1.2)$$

The quantity $\Gamma = \delta Q / \delta T$ is called *heat capacity* of the respective object. It is proportional to the mass m of the object

$$\Gamma = m \cdot c \quad (1.3)$$

The unit of the heat capacity is J/K. If the body is chemically and physically homogeneous, it makes sense to express the heat capacity as a function of material-dependent quantities.

- In case of a heat capacity related to the mass m one calls it the *specific heat capacity* given by $c = C/m$ with the unit $[c]=\text{J/K/kg}$;
- If the heat capacity is related to the amount of substance n it is called *molar heat capacity* $C_m = C/n$ with the physical unit $[C_m]=\text{J/K/mol}$;
- If the heat capacity is related to the volume V it is called the *volumetric heat capacity* $s = C/V$ with the unit $[s]=\text{J/K/m}^3$.

Generally Γ and c are temperature dependent, but for many solids and liquids Γ and c are nearly constant around room temperature.

The Law of Dulong-Petit

The law of Dulong-Petit was empirically found and named after P. L. DULONG and A. T. PETIT . It states that for solids at low temperatures, the molar specific heat capacity C_m is independent of the material and can be approximated by

$$C_m = 3R = 24.924 \frac{\text{J}}{\text{mol} \cdot \text{K}} \quad (1.4)$$

Hereby R is the universal gas constant. Today, this law can be established with the help of statistical mechanics for a specific class of "simple" solid bodies. However, most solid bodies show significant deviations from the law of Dulong-Petit. Moreover, experiments show that the specific heat of each solid decreases sharply at low temperatures and disappears at $T = 0\text{K}$. This drastic deviation from the law of Dulong-Petit could be explained qualitatively for the first time by A. EINSTEIN, and later more quantitatively by P. DEBYE.

Heat Balance

Calorimetry experiments deal with the measurement of the amount of heat in a system. It is common to determine the amount of heat by measuring the temperature change of a known amount of a reference substance. Water is suitable as such a reference substance because it has a well-known specific heat, is easily and cheaply available in a sufficient purity, causes rapid heat transfer and is harmless. The heat can come from any source: chemical reaction, cooling of a material above a certain temperature difference or change in the state of aggregation of a material (e.g. freezing), but it could also be mechanical or electrical energy. However, it can also be mechanical or electrical energy. It is only important to know that the amount of heat produced in this way is the same as that which is absorbed by the water:

$$|Q_{\text{Subst.}}^{\nearrow}| = |Q_{\text{Wasser}}^{\searrow}| \quad (1.5)$$

The specific heat capacity c of a substance can be defined as the amount of heat that 1kg of this substance emits or absorbs when its temperature changes by 1K:

$$\Delta Q = m \cdot c \cdot \Delta T \quad (1.6)$$

For example, suppose we heated up a block of material M to a temperature T_1 and now bring it into an amount of m_W of water at temperature T_3 . At contact, the block and the water exchange heat until both have reached the same temperature T_2 , the mixing temperature. The heat balance now looks like this:

$$|Q_M^{\nearrow}| = c_M \cdot m_M \cdot (T_1 - T_2) = |Q_W^{\searrow}| = c_W \cdot m_W \cdot (T_2 - T_3) \quad (1.7)$$

The balance equation for latent heat looks similar (analogously for evaporation heat and melting heat):

$$|\Delta W_S^{\nearrow}| = \Lambda_S \cdot m_S = |Q_W^{\searrow}| = c_W \cdot m_W \cdot (\Delta T_W) \quad (1.8)$$

1.3 Experiment

1.3.1 Material

Component	Number
Metal plate	1
Tripod with wire mesh	1
Sample holder	1
Thermometer 50°C	1
Thermometer 250°C	1
Gas burner with lighter	1
Sample body	3
Dewar calorimeter vessel	1
Beaker	1
Copper calorimeter	1
Crank handle	1
Teflon plate	1
Thermometer	1
Table clamp	1
Nylon cord	1
Weighing stick with hook	1

1.4 Procedure of Measurement

1.4.1 Specific Heat Capacities of the Dewar Calorimeter Vessel

Take the measurement to determine the heat capacity of the dewar calorimeter vessel by mixing water of different, well-known temperature. For a detailed description please see the appendix (A.1).

1.4.2 Specific Heat Capacities of Solids

- Determine the mass of the three different cylindric, metallic sample bodies. That fore use the weighing machine next to the experiment "IM1 Volumen- und Dichtebestimmung".
- Estimate the systematic error of the measurement of the mass.
- Do the following procedure for all three different metallic sample bodies:

1. Weigh the same amount of water you used to determine the heat capacity of the dewar calorimeter vessel before and put it into the empty calorimeter.
2. Measure the temperature inside the calorimeter continuously every 30 seconds. While doing this put a metallic sample body into the sample holder above the gas burner and heat it to approximately 90°C. During the process of heating insert the thermometer into the aperture of the sample at the top.
Caution: *Please do not exceed 100°C to protect the thermometer.*
3. Extinguish the flame of the gas burner and wait for the temperature of the sample body not to climb any more - it should be stable around 90°C. Write down this temperature.
4. Take the thermometer out of the sample body.
5. Now bring the metallic sample body (without thermometer) rapidly into the dewar calorimeter vessel.
Caution: *Hot! Use the wire with hook and be careful not to burn your fingers.*
6. Observe the temperature of the water inside the dewar calorimeter vessel for approximately five more minutes and write down your values after every 30 seconds.
7. Repeat this procedure two more times beginning at point 1.

At the end, you need to have three series of measurement for every metallic sample body.

1.4.3 Determination of the Conversion Factor between Calorie and Joule

- Determine the mass of the empty copper calorimeter. Use again the weighing machine next to the experiment "IM1 Volumen- und Dichtebestimmung".
- Measure the diameter of the copper calorimeter with a calliper gauge. Then estimate the systematic error of the calliper gauge.
- Remove the screw plug and the seal at the top of the copper calorimeter.
- Hold the copper calorimeter with the hole to the top and fill in distilled water.
- Measure the mass of the copper calorimeter with the distilled water inside and calculate the mass of the water.
- Insert the seal and fix it with the screw plug again.
- Put the copper calorimeter into the basic device with the crank handle. To do this, insert the rivet pin on the bottom of the calorimeter into the slots in the holder and turn it so that it clicks into place and the calorimeter body is fixed.
- Insert the thermometer very carefully and as far as possible into the calorimeter hole and tighten the screw plug of the calorimeter.
Caution: *Use the thermometer which is the most exact for a temperature range between 20°C and 30°C and make sure it does not break.*
- Read the initial temperature.
- Put the 5kg weight on the floor just underneath the copper calorimeter.
- Wind the nylon cord about four times (not more than six times) around the copper calorimeter and fix it to the 5kg weight on the floor. The cord should hang down at the front side of the handle.

- Operate the crank handle and check whether the 5kg weight is raised by a few cm and is kept at a constant height when the handle is turned further. If it is lifted too far, reduce the number of turns of the nylon cord. In case that it does not lift off the ground, increase the number of turns.

Caution: *Do not put your feet underneath the 5kg weight in case it drops down.*

- Follow this procedure four times in total:
 1. Read the initial temperature of the thermometer and write it down.
 2. Turn the crank handle between 100 and 200 times and try to keep the 5kg weight on a constant height while turning the handle.
 3. Write down the number of turns you turned the crank handle.
 4. Read the final temperature of the thermometer and write it down.
 5. Wait for ten minutes to cool down the copper calorimeter.
 6. Repeat this measurement for three more times beginning at point 1.

You need to have four series of measurement at the end.

1.4.4 After the experiment

- Make sure that the gas burner is switched off.
- Put the thermometers back into their protective covers.
- Empty the dewar calorimeter, the copper calorimeter and glass vessels and wash them carefully.
- Clean up the workspace.

1.5 Tasks for the Analysis

1.5.1 Heat Capacity of the Calorimeter

- Plot the temperature-time diagram of your measurement data of the water inside the calorimeter analogously to Figure A.1. Compare to the theoretical expectations.
- Determine the heat capacity Γ of the dewar calorimeter vessel.
- Do an error calculation.

1.5.2 Specific Heat of Solids

- Use the heat capacity Γ of the dewar calorimeter vessel to calculate the specific heat capacity of copper, aluminium and lead. Compare to the literature values.
- Determine the molar heat capacity of copper, aluminium and lead and check with the law of Dulong-Petit.
- Do a full error calculation.

1.5.3 Determination of the Conversion Factor between Joule and Calorie

- Find the conversion factor between Joule and Calorie with the specific heat capacity determined before and compare it to the literature value.
- Do a complete error calculation.

1.6 Literatur

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- Wolfgang Demtröder, Experimentalphysik I - Mechanik und Wärme, Springer Verlag, 2008
- Horst Kuchling, Taschenbuch der Physik, Verlag Harri Deutsch, 1991

A.1 Heat Capacity of the Calorimeter Vessel

Since the heat capacity of the dewar calorimeter vessel is not negligible it has to be determined in a preliminary experiment. One has to try to find the heat capacity Γ , which is given by the following equation:

$$\Gamma_{\text{Cal}} = c_{\text{glass}} \cdot m_{\text{glass}} \quad (\text{A.9})$$

It is hard to find the exact mass of the glass of the calorimeter, and even if this would be known one had to find the heat capacity of this material. However it is a lot easier to use a substance with well-known heat capacity for the preliminary experiment. Since the mass of the glass m_{glass} corresponds to the filling level of the water, the heat capacity Γ of the calorimeter depends on the amount of water inside. For a successful outcome of the experiment one has to use the same amount of water for the later on experiment than it was used for this preliminary experiment.

1. The dewar calorimeter has to be filled with cold water of temperature T_1 , e.g. *melted* ice cube-water mixture of total mass m_1 . Make sure it is totally liquid, so there is no solid ice in the water.
2. Observe the development of the temperature of the water inside the dewar calorimeter for a few minutes and write down the values.
3. Meanwhile use the gas burner to heat up water of the mass m_2 to a temperature around $T_2 \approx 50^\circ\text{C}$. Observe the temperature of the water with mass m_2 and write down the values.
4. Put the hot water into the dewar calorimeter, mix m_1 and m_2 and observe the temperature for a couple of minutes - write down the temperature every 30 seconds.

Figure A.1 shows schematically the development of the temperature: From *A* to *B* the cold water with temperature T_1 slowly approaches towards room temperature. At point *B* the hot water of temperature T_2 is mixed into the cold water. There the temperature increases rapidly. Between *E* and *F* the temperature falls slowly and approaches towards room temperature T_f . The reason for that is that the calorimeter is not completely adiabatic. The temperature

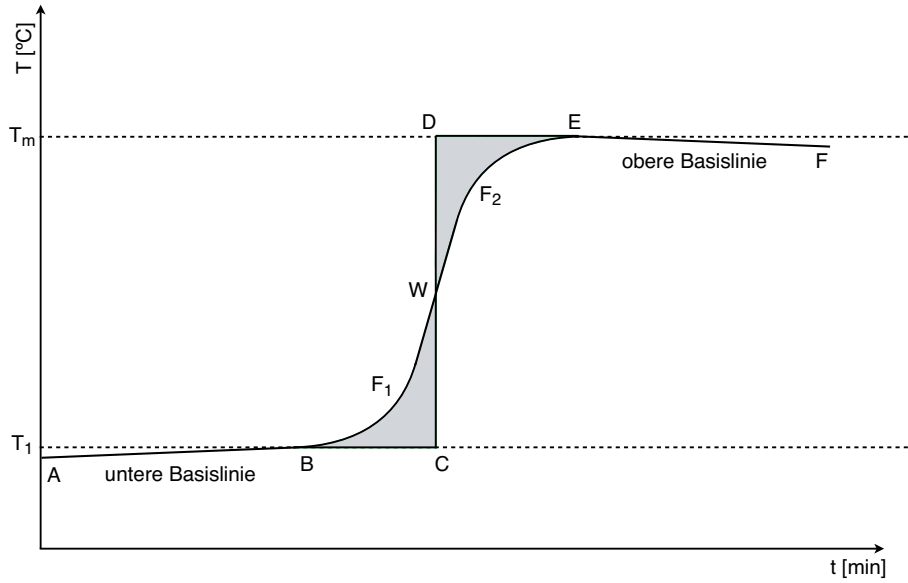


Figure A.1: A temperature-time diagram to determine the mixed temperature T_m in a calorimeter.

inside the calorimeter tends to adjust room temperature. The heat flow is proportional to the difference of the temperature T inside and T_f outside the calorimeter. For constant T_f this leads to the conclusion that:

$$dT/dt \propto T \quad (\text{A.10})$$

This equation can be integrated:

$$T = (T_m - T_1) \cdot e^{(-t/\tau)} + T_f, \quad \text{für } T_m > T_f, \quad (\text{A.11})$$

$$T = (T_1 - T_f) \cdot e^{(-t/\tau)} + T_f, \quad \text{für } T_1 < T_f \quad (\text{A.12})$$

One can see that the state of equilibrium takes form exponentially. In our case τ is huge compared to the time of measurement so the base lines between A and B , E and F respectively, can be approximated with straight lines. Because of the heat flow, the difference in temperature $E - B$ is not equal to the theoretically ideal temperature difference $D - C$, as it can be seen in Figure A.1.

The second effect is the differentiable course of the curve from B to E . If the added water would immediately distribute its heat the temperature curve would be a step function. But the system needs some time until a new equilibrium can be established. It behaves as if it were smeared over a time interval. So it is important to find the end time of the heat supply. It lies at the turning point W of the temperature curve, because there the direction of curvature changes, that is, heat input transforms to loss.

But because one can hardly measure the temperature curve in the range B to E (the temperature change cannot be read quickly enough on the thermometer), the turning point cannot be identified. Therefore one draws a perpendicular line the way that it lies exactly in the middle between B and E . The difference $D - C$ then gives the true difference in temperature. With the measurement accuracy that can be achieved in this experiment, $E - B$ usually corresponds to $D - C$.

Then Γ_{Cal} can finally be obtained by using

$$Q_{\text{emit}} = m_2 \cdot c_{\text{H}_2\text{O}} \cdot (T_2 - T_m) \quad (\text{A.13})$$

and

$$Q_{\text{absorb}} = (m_1 \cdot c_{\text{H}_2\text{O}} + \Gamma_{\text{Cal}})(T_m - T_1) \quad (\text{A.14})$$

It follows the heat capacity of the dewar calorimeter

$$\Gamma_{\text{Cal}} = \frac{m_2 \cdot c_{\text{H}_2\text{O}} \cdot (T_2 - T_m) - m_1 \cdot c_{\text{H}_2\text{O}}(T_m - T_1)}{T_m - T_1} \quad (\text{A.15})$$