

# Calorimetry

In the engineering practice, one of the decisive factors in sizing refrigeration and heating equipment and thermal behaviour of boundary structures is the specific heat of the materials used. In material science, some changes in the structure of the material (e.g. phase transitions) can be traced by measuring the specific heat. In this measurement two methods are to be used to determine experimentally the specific heat of solid and liquid materials. Also, specific latent heat of fusion and molar heat of solution are to be measured in the exercise.

## I. THEORETICAL BACKGROUND

### A. Specific heat and heat capacity

The internal energy  $U$  of a body can be changed by macroscopic work  $W$  done on the substance or by molecular level energy exchange  $Q$  (called heat) in course of direct contact of another body. This experience is summarized in the first law of thermodynamics:

$$\Delta U = Q + W, \quad (1)$$

where  $\Delta U$  is the change in internal energy.

If we transfer heat to a body (e.g. heat the body with electric radiator), its internal energy (may) also change. Experience has shown that – in case of transferring only a moderate amount of heat –, the temperature change  $\Delta T$  is directly proportional to the heat transmitted, and is inversely proportional to the mass  $m$  of the test substance and also depends on the quality of the test substance:

$$Q = cm\Delta T, \quad (2)$$

where  $c$  is the specific heat (capacity). The numerical value of the specific heat of a material shows how much heat is needed to change the temperature of 1 mass unit of the substance by 1 K. Its unit is J/(kg·K).

From (1) and (2) it is seen that the specific heat depends on the circumstances of the heating process since the work depends on it (the internal energy change does not depend on the process, it depends only on the final and the initial state). However, for solid and liquid materials the specific heat (with good approximation) does not depend on the process as the thermal expansion of these materials is very small. So the work is negligibly small. This means that the heat exchange is equal to the change of the internal energy of the body. Moreover, the specific heat also does not depend on the temperature if the temperature is not too low. During the exercise we utilize these facts. The specific heat for materials can be found in standard tables.

In practice many times the connection between the amount of heat absorbed or rejected by the sample and

the temperature change of the body is needed. In this case a sample specified quantity is useful, namely the heat capacity  $C = cm$  instead of the specific heat. It shows how much heat is needed for the given sample to change its temperature by 1 K. Its unit is J/K.

### B. Latent heat and heat of solution

In many thermodynamical processes one can find phase transition when for example the solid phase goes into liquid phase (melting): Well known fact that the ice melts after putting it into a warm beverage. The opposite process is freezing. When the liquid turns into vapour (gas) phase, it is called evaporation. During the phase transition the temperature of the substance does not change, however heat (called latent heat) is gained or rejected. According to experiences this amount of heat is proportional to the mass of the substance:

$$Q = Lm. \quad (3)$$

The coefficient  $L$  is the specific latent heat, which shows how much heat is needed for the complete phase change of a unit mass material. In case of melting or freezing it is called specific latent heat of fusion, in case of vaporization it is called specific latent heat of vaporization. The unit of specific latent heat is J/kg.

There are many materials in the construction industries that releases or absorbs heat when solved in water. Examples are the solution of calcium oxide (burnt lime), calcium sulphate (gypsum) and cement (for making concrete). In planning the individual operations, the evolving heat should be taken into account or even should be utilised.

The determination of heat of solution is illustrated by the determination of the heat of solution of a common compound, calcium chloride ( $\text{CaCl}_2$ ). Calcium chloride intensively releases heat when solved, therefore can also be used to melt ice. When spilled on roads it efficiently melts the ice, and is less harmful to the plants than sodium chloride and can also be used at lower temperatures. In concrete mixtures it accelerates the solidification process (however, being corrosive, it cannot be used in reinforced concrete). It is also used in some highways to reduce the flying dust: sprayed on the road it absorbs water from air, and water layer develops on the road surface that binds the dust.

The molar heat of solution  $L_{\text{sol}}$  provides the amount of heat which is released or gained by the substance of 1 mol when it dissolves in a solvent:

$$Q = nL_{\text{sol}} = \frac{m}{M}L_{\text{sol}}, \quad (4)$$

where  $n = m/M$  is the number of moles,  $m$  is the mass of the substance, and  $M$  is the molar mass of the substance. The unit of molar heat of solution is J/mol.

## II. MEASUREMENT METHODS

### A. Measuring specific heat by mixing

The sample material characterized by known weight  $m_s$ , initial temperature  $T_s$  and unknown specific heat  $c_s$  is mixed (blended) with a material with known specific heat  $c$ , mass  $m$ , and initial temperature  $T$  – mostly with a liquid usually not chemically reacting with the sample material to be measured (usually water). We measure the final equilibrium temperature  $T_f$  of the mixed system.

If the system is heat insulating, heat exchange takes place only between the sample and the material with known parameters. However, the experiment cannot be performed without some heat loss to the environment. Primarily on two basic reasons: even the temperature of the vessel, in which the sample and the other material is mixed, changes during the measurement, and there is always some heat loss to the environment. These two cause errors. But these errors can be compensated (or at least reduced) by taking into account the heat loss caused by the heat capacity of the vessel and by using well heat isolated containers called calorimeters (thermos or vacuum flasks).

If we knew the mass and the specific heat of the different parts of the vessel and their temperature rise, the energy used to heat them during the measurement could be calculated. However, this condition is practically not feasible. Instead, we measure directly the heat capacity  $C_{\text{flask}}$  of the calorimeter. If we put the sample into the calorimeter containing the known material, heat transfer occurs amongst the sample, the known material and the calorimeter. Change in the internal energy of the sample is equal to that of the known material and the vessel:

$$c_s m_s (T_s - T_f) = cm(T_f - T) + C_{\text{flask}}(T_f - T). \quad (5)$$

From this equation the specific heat of the sample can be determined.

### B. Measuring specific heat by electric heating

In this method the temperature of the test sample characterized by specific heat  $c_s$  and mass  $m_s$ , is elevated using an electric heating for time  $\Delta t$ . The energy provided by the heater increases the internal energy of the sample and flask:

$$VI\Delta t = c_s m_s \Delta T + C_{\text{flask}} \Delta T, \quad (6)$$

where  $V$  is the voltage of the heater,  $I$  is the current flowing through the heater, and  $\Delta T$  is the temperature

change during the operation of the heater. This equation can also be used to determine the specific heat of the sample.

### C. Measuring specific latent heat of fusion

Mixing method can be used for measuring the specific latent heat of fusion of a material. For example for ice: If the initial temperature of known amount of ice ( $m_i$ ) is the melting point (for ice the melting point is  $T_i = 0^\circ\text{C}$ ), and it is put into water of known mass  $m$ , temperature  $T$  and specific heat  $c$ , the ice melts (if its amount is not too large) and warms up to the final equilibrium temperature  $T_f$ . Again heat exchange can be observed only in the water-ice-flask system:

$$Lm_i + cm_i(T_f - T_i) = cm(T - T_f) + C_{\text{flask}}(T - T_f). \quad (7)$$

This equation can be used for determining the specific latent heat of fusion.

### D. Measuring molar heat of solution

If known amount of salt ( $m_s$ ) is dissolved in water of mass  $m$ , specific heat  $c$ , and its temperature changes by  $\Delta T$ , the energy balance:

$$cm\Delta T = \frac{m_s}{M}L_{\text{sol}}. \quad (8)$$

From this equation the molar heat of solution can be calculated. The molar heat of solution can be positive (endothermic; heat is gained from the environment) or negative (exothermic; heat is released to the environment).

## III. MEASUREMENT TOOLS

In the exercise temperature is measured by platinum 1000 standard thin layer resistive thermometer. Its resistance is 1000  $\Omega$  at  $0^\circ\text{C}$ , and linearly changes by changing the temperature. At given temperature the resistance can be calculated by using the following formula:

$$R(T) = 1000 \Omega \left[ 1 + 3.92 \cdot 10^{-3} \frac{1}{^\circ\text{C}} (T - 0^\circ\text{C}) \right]. \quad (9)$$

Of course with this formula one can calculate the corresponding temperature for given resistance.

- 2 pcs.  $\sim$ 1 litre stainless steel vacuum flasks with platinum resistive thermometers;
- caps for minimizing the heat loss of the vacuum flasks;
- fixing for the hot water flask;
- electric kettle for warming water;

- resistive heater with 10  $\Omega$  resistance and 50 W maximal power;
- Multimeter HAMEG, power supply for the resistive heater;
- 1 pc. aluminium and 1 pc. plastic test-piece;
- stirrer;
- water from tap;
- ice;
- measuring cylinder;
- ruler, caliper;
- scale;
- calibrated mercury thermometer.

#### IV. MEASUREMENT TASKS

**Boiling water may cause burning injuries, pay attention not to overspill the boiling water, and not to touch the hot metal test-piece! Utmost care and attention should be paid to these dangers during the measurements.**

##### 1. Calibration of the platinum thermometer

Temperature is measured by platinum thermometer. However, because of the finite resistance of the wires, and banana plugs, there is a constant (temperature independent) serial resistance, temperature correction is needed. The thermometers of both vacuum flasks should be calibrated using mercury thermometers in cold tap water. Determine the serial resistance and the temperature correction. (The equilibrium temperature should be reached before the final reading. To facilitate this use the stirrer.)

For practical reasons at this stage decide which flask is for hot, which flask is for cold water and use the corresponding temperature correction. In which of the following tasks is it necessary and in which is it not necessary to apply the temperature correction?

##### 2. Measuring the heat loss of the vacuum flask

Fill up the vacuum flask with boiling water, and wait until the system becomes thermalized. Thereafter, because of the imperfect heat isolation, the vacuum flask releases some heat to the environment, causing slow temperature decrease. Read and record the temperature of the water in every 30 s for 5 minutes. Plot the temperature as a function of time, and determine the rate of temperature change ( $\Delta T/\Delta t$ ) by fitting straight line. Is the system thermally insulated well?

##### 3. Estimation of the heat capacity of the vacuum flasks

Measure the mass of both of the stainless steel flasks. The specific heat of the stainless steel is 500 J/(kg $^{\circ}$ C), the thickness of the inner and outer wall of the vacuum flask are identical. Estimate the heat capacity of the vacuum flask. (Only the inner part is in contact with the water inside the flask.)

##### 4. Measuring the specific heat of water by electric heating

Fill the vacuum flask with cold water. Measure the mass of the water. Immerse the resistive heater into the flask and read the temperature after reaching the equilibrium. Record the voltage and the current of the heater adjusted by the instructor and the temperature by 6 and 12 minutes after the start of the heating. Use timer for measuring the time. During the measurement it is worth sometimes to move the flask in order to observe the same temperature inside the water everywhere (instead of the stirrer). Determine the specific heat by using both of the time data. Compare it with the data found in standard tables. For the heat capacity of the flask consider the estimated value (Task 3).

**After finishing the measurement with the resistive heater, first remove the plug of the heater from the supply and then raise out the heater from the water and not inversely. If the heater is operating in air, the heater can explode since the heater can barely give heat to the air.**

##### 5. Measuring the heat capacity of the vacuum flask by mixing

Fill the cold water flask with  $\sim 0.4$  litre cold water, and the other flask with  $\sim 0.4$  litre boiling water. Measure the mass of the cold and the hot water. After reaching the thermal equilibrium read the initial temperatures for the cold and the hot water. Pour the cold water into the flask containing the hot water applying continuous stirring. Wait until the thermal equilibrium is reached, and then record the final temperature. Determine the heat capacity of the flask. Compare this result with that in Task 3. Use the specific heat of the water measured in Task 4 or the data found in tables.

The hot water vacuum flask should always be fixed to prevent any accidental tilt.

##### 6. Measuring the specific heat of aluminium

Measure the volume of the aluminium cylinder by using caliper or ruler. Knowing the density of aluminium, calculate the mass of the aluminium cylinder. Compare it with the value measured by the scale (exclude the mass of the thread and the cap connected to the cylinder). Pour as much hot water into the other flask that after putting the cylinder

in the water, the water does not spill out. Immerse the aluminium cylinder totally into cold water and measure the temperature upon reaching the thermal equilibrium. Measure the mass of the hot water and its initial temperature after reaching the equilibrium. Then put the cold aluminium cylinder into the hot water and record the equilibrium temperature. Determine the specific heat of aluminium. Compare the result with value found in tables. For specific heat of water use the result of Task 4 or the data found in tables. Do not forget about the heat capacity of the flask.

7. *Measuring the specific heat of the plastic test-piece*

Repeat Task 6 using the plastic test-piece. This PVC plastic cylinder contains gaps with which the thermal equilibrium can be reached faster since the surface through which the thermal process takes place, is larger. When calculating the mass of the PVC cylinder subtract the contribution of the gaps in the volume.

8. *Measuring the specific latent heat of ice by mixing*

Pour  $\sim 0.7$  litre hot water into the hot water flask. Measure its mass, and wait until the thermal equilibrium is reached, then measure the initial temperature. Fill up the flask with melting ice and wait until the ice is completely melted and the equilibrium temperature develops (use the stirrer). Then measure the equilibrium temperature and the to-

tal mass of water inside the flask for obtaining the mass of the ice. Determine the specific latent heat of ice. Compare the result with value found in tables. For specific heat of water use the result of Task 4 or the data found in tables. Do not forget about the heat capacity of the flask.

9. *Measuring the molar heat of solution of calcium chloride*

Pour  $\sim 100$  g distilled water into the white thermo cup with cap. Immerse the digital thermometer into the water and wait until the temperature stabilizes (use the cap and the plastic stirrer). Record this temperature. Pour  $\sim 2$  g of  $\text{CaCl}_2$  salt into the black coffee cup. Then pour this amount of salt into the distilled water and applying the stirrer wait until the temperature stabilizes. Read this temperature. Determine the molar heat of solution for  $\text{CaCl}_2$ . Compare it with the value found in standard tables. For specific heat of distilled water use the value found in tables. Is the process exothermic or endothermic?

*Repeat the measurements 4-8 if possible. If substantial differences occur between measurements, or if the results substantially differ from the reference values found in tables, try to find the reason and make the necessary measures to eliminate the measurement errors.*