Experiment No. 53

Measurement of calorific quantities (specific heat)

Keywords:
Heat, internal energy and enthalpy as state functions, heat capacity, specific heat, molar heat, Dulong-Petit rule, 1st law of thermodynamics, calorimeter, water value, evaluation of calorimetric measurements, heat of chemical reactions

Literature:
Gerthsen, Kneser, Vogel "Physics"
Kohlrausch "Practical Physics", Volume 1

Basics:
Heat is a form of energy and as such an extensive quantity that can be divided and distributed as desired. Depending on the external conditions, the internal energy U (v = const.) or the enthalpy H (p = const.) are used as suitable state functions for describing the heat content of thermodynamic systems. The heat is caused by the disordered, irregular movement of the particles (kinetic theory of heat). The heat energy contained in a body is equal to the sum of the kinetic energies of this thermal motion.

In contrast, temperature is an intensive quantity that has the same value in all parts of a system in thermal equilibrium. The amount of heat contained in bodies of the same temperature can vary greatly because it depends on the ability of the respective bodies to store heat. Since heat cannot be weighed directly, a quantity of heat can only be measured via the effect that its supply or discharge causes and which is expressed in a measurable temperature difference. It is therefore obvious to set the amount of heat transported ΔQ as a product:

(1) $\Delta Q = C \bullet \Delta T$

where the factor C contains all information about the special properties of the material.

It is called the heat capacity of the substance. It indicates the amount of heat required to increase the temperature of the substance by one degree. C is proportional to the mass of the substance:

(2) $C = c \bullet m$ where m = mass

The proportionality factor c is called specific heat [J grd^{-1} g^{-1}].
Based on one mole, the molar heat is obtained from C:

(3) $c_m = C / n$ [J grd^{-1} mol^{-1}]

Molar heats are important quantities in physical chemistry. They are needed, among other things, for calculating energy conversions in chemical reactions. The temperature dependence of the molar heats of solids at low temperatures was explained by M. Planck, A. Einstein and P. Debye, among others. At sufficiently high temperatures, the molar heat of solid elements tends towards the limit value 3 R (≈25 J K^{-1} mol^{-1}) regardless of the type of substance (Dulong-Petit rule).

In principle, a distinction must be made as to whether the amount of heat is supplied at constant pressure or at constant volume. At constant pressure, a body generally expands when the temperature increases, so that volume work must be carried out against the external pressure. Therefore is $C_p > C_v$. This difference is particularly important for gases (for ideal gases, $C_p - C_v = R$).

Specific heats (or molar heats) can be measured easily by calorimetry, using the specific heat (molar heat) of any substance as a comparison. This could be water, for example, where a heat supply of 4.184 J to 1 g of water causes a temperature increase of 1 degree (from 14.5 to 15.5 °C at p = 1 atm). This amount of heat is also referred to as 1 calorie (cal) (not an SI unit!). Calorimetry can be used to measure the heat given off by substance x (mass m_x) by placing it in a water bath at a lower temperature T_w and a specific heat c_W known by definition. After the temperature has been equalized, the mixture temperature T_M is determined. Since the heat given off in this process must be equal to the heat absorbed (conservation of energy, first law of thermodynamics), the following balance applies:

(4) heat given off = heat absorbed or:

$$- c_X \bullet m_X. \bullet (T_M - T_X) = + c_W \bullet m_W \bullet (T_M - T_W) + W_K \bullet (T_M - T_W)$$

The second term on the right-hand side of equation (4) takes into account the absorption of heat by the calorimeter. W_K is the heat capacity of the calorimeter and is also called the "water value" of the calorimeter because of its reference to water.

Because the specific heat is temperature dependent, the method described can only provide an average value depending on the temperature difference.

Task:
Measure the following specific heats:

a) of aluminum, lead and copper (relative to water)
b) of ethanol (relative to copper)

On the experimental setup:
A Dewar vessel is used as a calorimeter. It has a double-walled glass jacket that is evacuated to prevent heat loss and silver-plated on the inside. The temperatures are measured with a mercury thermometer; the temperature equalization is accelerated with a stirrer.

Note: Only use fully demineralized (VE) water for the entire measurement!

Procedure:

1) To determine the water value, fill approx. 50 g of water (weigh to the nearest 0.1 g) into the calorimeter. Measure 2 min every 15 s. Then carefully but quickly add the same amount of water heated to approx. 40 °C. Measure the temperature again for 2 min every 15 s while stirring constantly.

2) To determine the specific heat of aluminum, first weigh the aluminum cube. Then heat it in a beaker in boiling water for 10 min.

3) Fill 100 g of water into the calorimeter. Measure the temperature every 15 s for 2 minutes. Then quickly place the heated aluminum cube into the calorimeter and measure the temperature again every 15 s for 2 minutes.

4) Repeat 2) and 3) for the lead cube.

5) Repeat 2) and 3) for the copper cube.

6) Repeat 3) for the copper cube and ethanol as the calorimeter liquid.

Evaluation:

1) Draw your measurement points in a temperature/time diagram (see Fig. 1).

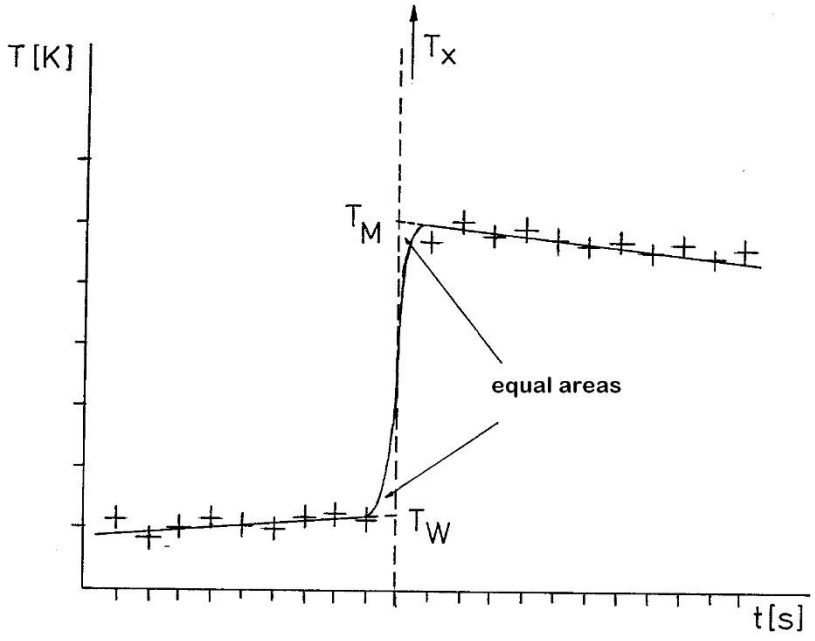

Fig. 1: Evaluation of calorimetric measurements

2) Determine the respective T_M and T_W values by graphic extrapolation!

3) Set up the respective balance equations and calculate:
a) the water value W_K of the calorimeter
b) the specific heats and the molar heats for copper, aluminum, lead and ethanol

4) Discuss the accuracy of your measurement:
a) How accurate are the individual measured values?
b) Compare your results with literature data (e.g. from the "Handbook of Chemistry and Physics")
c) Is the deviation from the literature value within the error limits of your measurement?
d) How large is the error in the specific heats (molar heats) if the water value of the calorimeter is not taken into account?
5) Compare the molar heats of aluminum, lead and copper that you determined with the statement of the Dulong-Petit rule!

Accessories:
Aluminium, lead, copper cubes, 2 thermometers (0-100 °C, 0-50 °C), Dewar flask as calorimeter, beaker (150 cm^3), measuring cylinder (150 cm^3), stop watch, hot plate, tweezers, ethanol