

Calorimetry

Introduction

The energy transitions accompanying the physical and chemical processes can manifest in different ways. Monitoring these processes is relatively simple in the case of where the largest energy transition is in the form of heat. The energy changes of the system in such cases may be two different types: release of heat (exothermic) or heat absorption (endothermic) is involved. The following processes are based on heat effect called calorimetry.

The purpose of calorimetric measurements may be different: one, the definition of heat capacity of pure substances (elements and compounds), mixtures and solutions, examination of phase transformation of these systems, on the other hand, the determination of reaction heat of the physical-chemical processes such as dissolution, dilution, miscibility, solvation, adsorption, etc... The heat effect of physical and chemical processes is measured directly by calorimeter.

The SI unit of the amount of heat is joule (J), previously the calories (CAL) was used as unit. The energy required for heating a body's temperature with 1 K is called **heat capacity**. As is known from thermodynamic considerations, defining the heat capacity we also have to grant that we are talking about heat capacity at constant pressure (c_p) or at constant volume (c_v). During the exercises the heat capacity at constant pressure (c_p) is used. Specific heat capacity is the heat needed to rise the temperature of 1 g substance with 1 K (J/K/g) **molar heat capacity** is the heat needed to rise the temperature of 1 mol substance with 1 K (J/K/mol).

The temperature measurement

On the basis of kinetic gas theory, the temperature is the rate of average kinetic energy of the molecules. Theoretically for measuring the temperature any temperature-dependent properties of material can be used, and any temperature scale can be prepared. In the practice the Celsius-made temperature scale spread, with the zero point of the measured freezing point of water at 101 325 Pa pressure. At the same pressure the one hundredth part of the difference between the detected boiling point of water and the zero point is 1 °C. (The thermodynamic temperature scale - the absolute or Kelvin scale – according to the second law of thermodynamics is independent from the quality of the substance, its zero point is -273.15 °C, and its scale is identical to the Celsius scale.) The thermometers used in practice divided into two groups: in the first group belong those which the material to be measured directly (mechanical) will not be contacted during the measurement. These include the infrared and visible radiation measuring instruments, measuring variations in the magnetic field devices, etc... The second category of devices are in direct contact measured on the sample and the temperature is changed by mechanical (liquid thermometers, bimetallic etc), electrical (thermistors, thermo-electric thermometers etc) or optical (e.g. liquid crystal) properties change. The operation of the thermometers based on the heat transfer. In the practices we use liquid thermometers working with thermal expansion. They consist of a liquid tank made of glass of low thermal expansion coefficient, a connecting even internal diameter measuring capillary and a scale located near the capillary. The tank is usually filled with mercury, because mercury coefficient of thermal expansion is independent of the greater range than other liquids from the temperature. Measuring range covers from the point of solidification to the point of boiling of the (-39 to 356 °C). Dividing the thermometers of mercury into groups: rod thermometer (the scale is scratched in the capillary) and disk thermometer (the scale on a disk located behind the capillary).

The calorimeter structure

The calorimeter serves to measure the changes of heat. The calorimeter used in practices consists of two parts (Figure 1): the lower 'B' part of the actual calorimeter, while the upper 'A' unit of measurement of materials used in high temperature environments for tempering. As it is shown on Figure 1., the measuring part of the calorimeter is isolated from its environment, in theory, adiabatic Dewar containers (thermos), in which a glass is a ground cork, into which the test sample is placed. In the sample there is a mercury thermometer and a stirrer with a thin mixer, which is moving up and down the promoting rapid mixing of reactants. As in practice a heat exchange has always created between the environment and the calorimeter, and this leads to error so the calorimeter is equipped with a well-sealed screw lid. To fill the various reactants and materials the rubber confine holes serve.

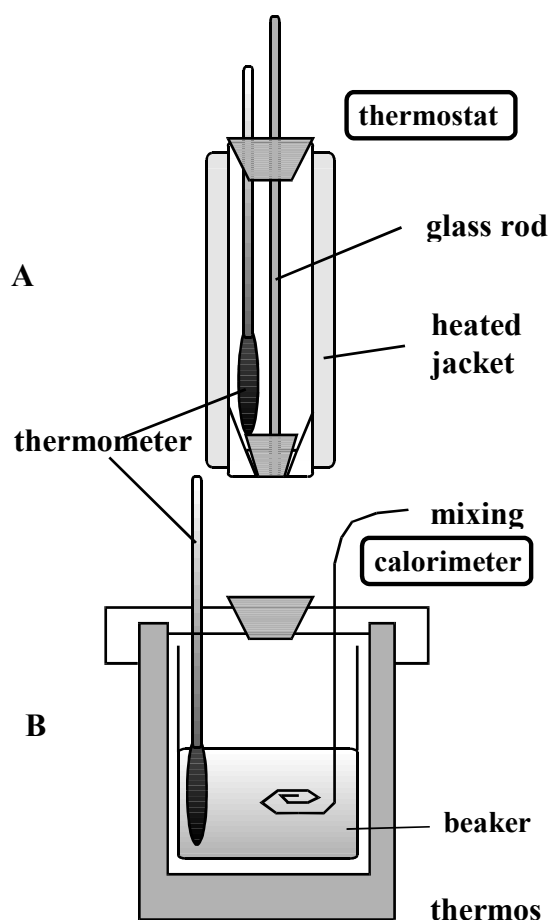


Fig. 1 The construction sketch of the calorimeter used in the laboratory practice

The warming parts of the calorimeter - such as mixing, internal glass, etc., the test system heat to take. This material, in parts by weight, and also different, so the calorimeter heat capacity is generally not the sum of heat capacities of components, but usually determined experimentally. (Combined heat capacity of the calorimeter parts of the past calorimeter is called water-value). The calorimeter heat capacity of course, the pilot assessment results should factor correction made, since the amount of heat that would not be calculated otherwise. The calorimeter used in practice is detailed in a supplementary electrically heated thermostat.

The thermostat is a narrowing-down, surrounded by insulating material and a glass heating interline consists of a thermometer, and outlet openings in the lower shut-off glass rod located attached to rubber. The thermostat liquid or solid samples higher than room temperature, about 60-70 °C temperature-controlled, and the outlet hole through located the bottom of calorimeter is advantage. The use of certain practices will be described.

Determination of the heat capacity of the calorimeter

Since the heat capacity is the most important feature of the calorimeter in the beginning of the exercises following should be taken into account: the different calorimeters should not be confused with the accessories, since this gauge heat capacity changes entail. The tests, if provided otherwise, do a clean dry bowl. This mixture should be corrosion protected by law in any case, it is washed with distilled water, and it should be dried. The determination of the calorimeter's heat capacity is that the body of a calorimeter an equal amount of heat given off by the calorimeter, and it contains other objects amount of heat absorbed by. Be the calorimeter with weight of water m_1 at temperature t_1 . If water with m_2 weight and t_2 temperature is added, the calorimeter and the temperature of the material contained in it, after equalization, a common t_c temperatures ($t_2 > t_c > t_1$) will be. The given off heat by the water with m_2 weight is:

$$Q = c_w m_2 (t_2 - t_c)$$

where c_w specific heat capacity of water. The amount of heat absorbed by the system, it should be agree:

$$Q = c_w m_1 (t_c - t_1) + c_{cal} m_{cal} (t_c - t_1)$$

where c_{cal} - specific heat capacity of the calorimeter,
 m_{cal} - the calorimeter mass.

$$C_{cal} = c_{cal} \cdot m_{cal} = \frac{c_w m_2 (t_2 - t_c) - c_w m_1 (t_c - t_1)}{t_c - t_1} \quad (1)$$

After rearranging the context, the following conclusions:(1) C_{cal} where the calorimeter of heat capacity at constant pressure.

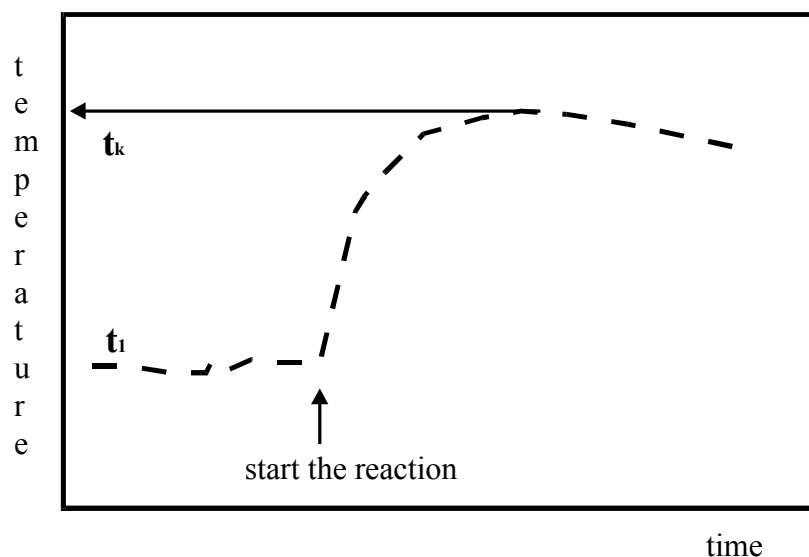


Fig. 2 The measured temperature change vs. time in the calorimeter during determination of heat capacity. The starting temperature of the calorimeter is t_1 and the maximal common temperature is t_k indicated.

During the experiment, the calorimeter temperature changes over time, as shown in Fig. 2. After equilibration, the common temperatures start to cool slowly to the temperature of the environment of the system as the adiabatic condition is not completely fulfilled. Therefore, the evaluation of the graph is needed to determine the highest common temperature.

Experiment design

Load 70-75 cm³ of distilled water the upper thermostat and switch it on 40V-power supply voltage reduction. Heat the water around 65 °C for about 20 minutes. The mass the glass of the calorimeter weigh, and then load into approx. 80g of accurately known mass of water (m_1). Place the cup in the calorimeter, close the calorimeter, the thermostat then place under the spout. In every two minutes read the temperature of both the calorimeter and the thermostat. When the temperature does not change more, the calorimeter holding the opening in pulling the plug and slowly raise the thermostat obstructed plug ended glass rod is - then the heated water reaches the calorimeter. Close the calorimeter with the plug, and mix the fluid in the calorimeter. In every thirty second read and record the temperature, for about ten minutes.

Plot of the calorimeter temperature as a function of time, then using the highest temperatures of the calorimeter, calculate the heat capacity. The mass of water in the thermostat m_2 received if the experiment is complete, the re-weighed to within glass, obtained by subtracting from the crowd of mass m_1 and the glass. The heat capacity determination is measured three times enter the following results into the table:

Table to calculate the heat capacity of the calorimeter

	m_1 [g]	m_2 [g]	t_1 [K]	T_2 [K]	T_c [K]	C_{cal} [J/K]
1	75					
2	80					
3						
Average±deviation						

Calculate the average heat capacity of three measurements and the error. Attach the temperature-time diagrams. Devote sufficient time and attention to the specific heat capacity determination, as this is more strongly influenced by the results of calorimetric measurements.

Determination of ice's melting heat

Using the calorimeter besides the heat capacity, also define the quantity of heat related to the different phase transitions of materials. The phase transitions in most material at a given temperature (or narrow temperature range) are performed. The sharp change and temperature is also indicates the homogeneity of the material: think of the melting point, which can infer the material purity. With our calorimeter the simplest phase transitions of ice at room temperature, i.e., melting studied. (Of course, suitable modifications can be made of other materials melting heat, or, for example determination of energy relations of orthorhombic and monoclinic sulfur transformation). The crystalline structure is a bundle of mol heat transition required quantity of heat is called the molar melting heat (J / mol).

Practice Description

Weigh the mass of the calorimeter's glass, and then load into it approx. 75 g of correctly known mass of water (m_w). Place the cup in the calorimeter, close to the calorimeter. In every two minutes read thermometer showing the temperature of the water. When in the temperature is not further changing, the calorimeter holding slot and slide it gently pulling the plug the dish, about 10-15 g of small pieces of ice, which bears a drunk carefully with paper wool. Close the calorimeter with the plug, and with slow motion stir the calorimeter water-ice mixture. Thirty per second read and record the temperature, for about ten minutes. Plot of the calorimeter temperature is a function of time, and then the lowest temperatures used to calculate the ice melting heat. The system where the mass of ice, if the experiment is complete once again weighed to within the glass, which is deducted from the m_v and glass in the mass.

The ice melting heat determination two more times, carry out the following results enter the table:

Table for the calculation of melting heat of ice

	m_w [g]	m_i	t_w [K]	t_i [K]	t_c [K]	$\Delta H_{ice,melt}$ [J mol ⁻¹]
1				0		
2				0		
3				0		
Average±deviation						

Calculate the average of three measurements on heat of fusion, considering the followings:

From the calorimeter (t_1) and from the m_w weight of water the m_i weight of ice draws $m_i q_{melt}$ amount of heat during the melting and additional amount $c_w m_i (t_c - 0)$ heat until reaching the common t_c

temperature. During these processes the calorimeter and the water is cooling down to t_c . In terms of looking q_{melt} quantity of the previous considerations, conservation of energy can be written equations expressing the following relationship are obtained:

$$\Delta H = q_{melt} = \frac{(c_w m_w + C_{cal})(t_1 - t_c) - c_w m_i (t_c - 0)}{m_i} \quad (2)$$

Attach the temperature - time diagrams.

Neutralization of heat defined

Practice Description

Prepare 40 cm³ of 1 M acid and 40 cm³ of 1 M alkali solution in practical teacher designated by the solutions; they weigh the mass (ms, ml). The alkaline should be directly measurements made prior to performing the same temperature and the temperature of the acid value set! The calorimeter vessel was first pour 40 cm³ 1 M acid solution. If the different concentrations of acid, it weighed so much, which contains many acid, than 40 cm³ of 1 M acid solution. Check the temperature of two solutions, such as the average count the initial temperature (T_1). Then, alkaline calorimeter to be sent and quickly sealed as often as possible (5-10 sec) measured the temperature in 10-15 minutes. The measured values are presented graphically. The maximum value is used to calculate the molar neutralization heat, the following considerations:

Counteraction is released in the first heat of the calorimeter accessories, on the other hand, resulting in the reaction of brine heats up. The brine mass ms ml, specific heat capacity cp, salt, which is practical value for the sheet at the end of the table values determined by extrapolation. The saline concentration of acid and base solution calculates the concentration of light. The former, taking into account the following deduced from the molar heat of neutralization:

$$\Delta H_s = \frac{[(m_s + m_1)c_{p,salt} + C_{cal}](t_c - t_1)}{c_{salt} * V_{alt}} \quad (3)$$

The protocols define the date and the value of the molar heat of neutralization compare with data from literature! Attach the temperature-time graph as well.

	c M	C _p kJ kg ⁻¹ K ⁻¹	c M	C _p kJ kg ⁻¹ K ⁻¹	c M	C _p kJ kg ⁻¹ K ⁻¹
HCl	2.63	3.521				
NaOH	0.28	4.123	0.56	4.045	2.77	3.701
KOH	0.19	4.094	0.28	4.077	2.70	3.396
HNO ₃	0.16	4.130	0.81	3.920	2.58	3.550
NaCl	0.18	4.113	0.55	4.020	1.35	3.822
KCl	0.20	4.095	0.55	3.958	1.08	3.772
NaNO ₃	0.12	4.138	0.20	4.103	0.99	3.890
KNO ₃	0.20	4.086	0.41	4.002	0.83	3.845

$$c_v = 4.184 \text{ kJ kg}^{-1} \text{ K}^{-1}$$