

## **M10. Determination of changes of the thermodynamic functions of state. Determination of the entropy of thermodynamic system.**

### **Goal:**

Determine an ice's heat of fusion and changes in entropy during melting process of the ice. Develop understanding of a thermodynamical description of heat related phenomena. Build ability to describe these phenomena in a quantitative way, making use of the laws of thermodynamics and associated physical quantities.

### **Topics:**

- The basics of thermodynamics [1] – Chap. 18; temperature – Chaps. 18-2 through 18-5, heat – Chaps. 18-7 through 18-9
- Thermodynamic system. The state of thermodynamic system.
- Laws of thermodynamics; the zeroth, the first and the second [1] - Chaps. 18-3, 18-10 and 20-4 respectively.
- Entropy [1] – Chap. 20; irreversible processes – Chap. 20-2; a statistical view – Chap. 20-8
- Internal energy, enthalpy and entropy as thermodynamic functions of state.
- Heat balance. The concepts of heat and temperature [1] – Chap. 18-7
- Melting process. The heat of melting process.
- Process of dissolution. Heat of dissolution.

### **Theory:**

Thermodynamics is a branch of physics which investigates phenomena related to a heat transfer between material bodies. It describes a thermodynamical system by means of so called intensive thermodynamic quantities such as temperature, volume and pressure. Statistical mechanics deals with the same phenomena but from a microscopic point of view, regarding positions and motions of particles constituting the macroscopic body by means of statistical averaging.

A very important concept in thermodynamics is to divide an investigated part of the universe into two parts: system and its surrounding. This should be done in a way which allows us to easily describe interaction between the system and the surrounding, so it is a matter of our purpose or convenience.

In thermodynamics there are only two ways in which the surrounding may interact with the system: the heat transfer and the mechanical work.

The principles of thermodynamics are gathered into four laws, each one introduces some quantity necessary to describe the heat phenomenon. The zeroth law states that if two systems (or parts of a system) in thermal equilibrium with a third system, they are also in thermal equilibrium with each other. Conceptually, this law allows constructing the thermometer, a device which is able to check out whether two, possibly distant, objects are in thermal equilibrium. The zeroth law introduces a physical quantity called temperature. Bodies at the same temperature are in thermal equilibrium with each other. On the other hand objects at different temperatures, when brought into thermal contact, equal their temperatures.

The zeroth law does not explain in what way the thermal equilibrium of two bodies in thermal contact is achieved. This is the goal of the first law of thermodynamics. It says, that change of the state of the system may be caused by work or by the heat transfer (or any combination of these two). Moreover it gives a quantitative meaning to 'change of the state', introducing an internal energy of the system. The internal energy is the sum of all kinds of energy enclosed in the system. It includes kinetic energy of the chaotic motion of atoms or molecules, potential energy of their interactions, energies of motion and interaction of constituent part of the molecules and atoms. On the contrary, the kinetic energy of the motion of the body as whole does not add up to the internal energy, the same holds for the potential energy of some external interaction (e. g. gravitational). Using the internal energy, the first law is given as follows:

$$\Delta U = Q - W,$$

where  $\Delta U$  is the change in the internal energy caused by an amount  $Q$  of heat and work  $W$ . There is a sign convention for  $W$  and  $Q$ : work done by the system is positive (it decreases the system's internal energy), while work done on the system is negative (it increases the system's internal energy); heat flow into the system is positive, while heat flow out of the system is negative.

One should note, that heat is nothing else but a kind of the energy transfer which takes place when different bodies (or parts of the same body) are at different temperatures. One also should notice, that from the thermodynamics points of view heat and work are equivalent in their ability to change the internal energy. Moreover, work may be turned into heat (as when the friction force acts) and heat may be converted into the mechanical work (by means of so called heat engines, as a steam engine for example). This is emphasised by equipping both these quantities by the unit – 1 J.

Let us take a look at a thermodynamical system from the microscopic point of view, as statistical mechanics do. Any material body, gas, liquid or solid contains is made up of a very large number of particles (molecules or atom). These particles undergo chaotic motions – translational, rotational and vibrational. A velocity of a particular molecule changes very often in an unpredictable way. It is impossible to describe motions of all particles by means of Newton's equations, but the average values of microscopical quantities describing the particles may be found and related to the macroscopical ones. In this way, the temperature is solely related to the mean kinetic energy of the particles, while the pressure is given as the mean change in momenta of particles during their collisions with walls of the container.

Now it is possible to consider the change in temperature during a thermodynamical process. Both heat and work change the internal energy of the system. In the case of dilute gases, this energy only consists of kinetic energy of the chaotic motion of the particles. Hence, any change in the internal energy results in the change in the temperature. The case of liquids and solids is a bit different, because their particles are so close to each other that they interact and there is a potential energy related to these interactions. During a phase transition, for example a melting process, the heat provided to a substance changes only this potential part of the internal energy. The mean kinetic energy of the chaotic motion of particles remains constant and the temperature does not change.

The zeroth and the first law of thermodynamics are not sufficient to determine a direction of a spontaneous thermodynamical process. A very unlikely process such freezing water in a pool during a hot summer, without external interference, is not disallowed by either the zeroth or the first law of thermodynamics. Discerning between 'natural' and 'unnatural' processes is governed by the second law of thermodynamics. It introduces entropy, whose change is given in a following way:

$$\Delta S = \frac{\Delta Q}{T},$$

where  $\Delta Q$  is a small amount of heat provided to or taken away from the system at temperature  $T$  during a reversible thermodynamical process. The unit of entropy is  $\frac{1J}{1K}$ . The change in entropy may be either positive or negative. The second law of thermodynamics states that the natural processes take place in a way, which causes an increase in entropy of the system and its environment. In the case of an isolated system, there is not heat transfer between the system and the environment, so  $\Delta Q = 0$ . However, if the process occurring in such a system is irreversible (e.g. melting of ice), the change in

entropy is still positive. Only reversible processes in the isolated systems are accompanied with constant entropy and its zero change. Let us examine the heat transfer, i.e. the heat flow between a body at a higher temperature  $T_1$  and a body at a lower temperature  $T_2$ . This is an example of the natural process, which occurs everyday around us. Denoting a small amount of heat transferred between these bodies as  $\Delta Q$  (positive), the change in entropy for the first body is equal to  $-\Delta Q/T_1$  - heat flows out of this body, while for the second body is equal to  $\Delta Q/T_2$ , so the total change in entropy equals:

$$\Delta Q/T_2 - \Delta Q/T_1.$$

This is a positive quantity, since  $T_1 > T_2$ . An opposite example is mentioned above hypothetical spontaneous freezing of the water during a hot day. In such a process the heat would be transferred from a colder to warmer body. The formula for the change in entropy is the same as above, but now  $T_1 < T_2$ , and the total change would be negative. The second law of thermodynamic ruled out occurring of this process in a natural, spontaneous way. Of course, we may freeze this water, but using for example a refrigerator and supplying external power.

In this exercise, melting of ice takes place in the isolated container called calorimeter, so there is no heat transfer between the system and the environment,  $Q = 0$ . However, regarding different parts of the system, i.e. the block of ice at its melting point, water originating from the ice, at the same temperature, an inner container of the calorimeter with water inside, initially at ambient temperature, heat transfers can be observed between above mentioned parts due to their different temperatures. But because the overall heat transfer equals zero,  $Q = 0$ , particular heat transfers should be balanced, i.e. the amount of heat given by hotter parts of the system have to equal the amount of heat taken by the colder ones, which can be summarized as follows:

$$Q_1 + Q_2 = Q_3 + Q_4,$$

where  $Q_1$  is the amount of heat added to the ice in the melting process,  $Q_2$  is the amount of heat taken by the water originating from the ice and raising its temperature,  $Q_3$  is the amount of heat given by the water filling the calorimeter and  $Q_4$  is the amount of heat given by the inner container. All these amounts of heat may be expressed as follows:

$$\lambda m_i + c_w (T_2 - T_0) m_i = c_w (T_1 - T_2) m_w + c_c (T_1 - T_2) m_c,$$

where  $\lambda$  is the heat of fusion of ice,  $c_w$  is the specific heat of water,  $c_c$  is the specific heat of a material

of calorimeter;  $m_i$ ,  $m_w$  and  $m_c$  are the mass of ice, the mass of water initially in the calorimeter and the mass of the inner container, respectively;  $T_0$ ,  $T_1$  and  $T_2$  are the ice's melting point, the initial temperature of a content of the calorimeter and the final temperature of the content, respectively. Hence the heat of fusion of ice is in the following form:

$$\lambda = \frac{(c_w m_w + c_c m_c)(T_1 - T_2) - c_w m_i (T_2 - T_0)}{m_i}.$$

Calculating formulae for the change in entropy in described processes demands integrating, so only final formulae are listed below:

$$\Delta S_1 = \lambda \frac{m_i}{T_0} \text{ the change in entropy of the melting ice ,}$$

$$\Delta S_2 = c_w m_i \ln \frac{T_2}{T_0} \text{ - the change in entropy of heated water originated from the ice and}$$

$$\Delta S_3 = (c_w m_w + c_c m_c) \ln \frac{T_2}{T_1} \text{ - the change due to cooling the water inside the calorimeter and its inner}$$

container .

A total change in entropy during the melting process of the ice block inside isolated container is as follows:

$$\Delta S_3 = \Delta S_1 + \Delta S_2 + \Delta S_3.$$

### Helpful quantities and definitions:

- specific heat – the amount of heat necessary to raise 1 kg of a substance by one  $1^\circ \text{C}$  or 1 K

$$c = \frac{q}{m\Delta T}, [c] = \frac{1\text{J}}{1\text{kg}1\text{K}}$$

- heat of transformation – the amount of heat taken from or given to 1 kg of a substance which experiences a phase transition. The heat of fusion:

$$\lambda = \frac{Q}{m}, [\lambda] = \frac{1\text{J}}{1\text{kg}}$$

- state function – the property of a system, which depends only on the current state of the system not on the way the current state has been achieved, so it is independent of the path. Internal energy U and entropy S are examples (amongst many others) of the state function

**Instruction:**

1. Determine the mass of inner container of calorimeter. Remember that it should be dry.
2. Fill half of the inner container of calorimeter with distilled water and determine its mass  $m_{cw}$ .
3. Calculate mass of water  $m_w$ .
4. Put the water-filled inner container into the thermal screen of calorimeter and measure the initial temperature  $T_1$ .
5. Take a piece of ice from the refrigerator, wait until it became wet, dry it out and drop it into the water-filled calorimeter. Observe temperature changes, but do not look inside calorimeter. Assign the lowest temperature from your observation as the final one -  $T_2$  (the ice completely melted)
6. Measure the mass of calorimeter filled with water and melted ice  $m_{cwi}$  and calculate mass of melted ice.
7. Calculate the ice heat of fusion using the equation derived from heat balance:

$$\lambda = \frac{(c_w m_w + c_c m_c)(T_1 - T_2) - c_w m_i (T_2 - T_0)}{m_i}$$

where:  $T_0$  – the melting point of ice.

8. Calculate the entropy change for the ice melting process:

$$\Delta S_1 = \lambda \frac{m_i}{T_0}$$

9. Calculate the entropy change of water aroused from melted ice:

$$\Delta S_2 = c_w m_i \ln \frac{T_2}{T_0}$$

10. Calculate the entropy change of the water-filled calorimeter:

$$\Delta S_3 = (c_w m_w + c_c m_c) \ln \frac{T_2}{T_1}$$

11. Calculate total entropy change of the system:

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

12. Enter the results into the table.

$m_c$	$m_w$	$m_i$	$T_1$	$T_2$	$\lambda$	$\Delta S_1$	$\Delta S_2$	$\Delta S_3$	$\Delta S$
[kg]	[kg]	[kg]	[K]	[K]	[J/kg]	[J/K]	[J/K]	[J/K]	[J/K]
					..... □	..... $\Delta S_1$	..... $\Delta S_2$	..... $\Delta S_3$	..... $\Delta S$

$$c_c = 891,2 \text{ J/kgK}; c_w = 4185 \text{ J/kgK}$$

[1] Walker J., Halliday and Resnick, *Principles of physics : international student version*, 9 th ed., extended, Hoboken : John Wiley & Sons, Inc., 2011. , ISBN 978-0-470-56158-4