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EXERCISE 20a

THERMOCOUPLE CALIBRATION AND SOLIDIFICATION TEMPERATURE DETERMINING

Exercise Objective: Studying the structure and thermocouple operation principle. Thermocouple calibration and its thermoelectric coefficient determining. Studying the phenomenon of solidification and determining alloy (water) solidification temperature. Examples of applications of thermoelectric phenomena.

Topics: Seebeck phenomenon, contact potential difference, thermocouple, thermoelectric coefficient, water solidification, solidification temperature, heat of phase transition.

1. Introduction

Thermocouple Construction and Operation Principle

A thermocouple is a simple device used to measure temperature. The thermocouple operation principle can be explained by referring to the **Seebeck phenomenon**, This phenomenon consists of the appearance of a thermoelectric force in a circuit containing two different connected metals or semiconductors if the junctions between them are at different temperatures.

To explain this, suppose we have a single metal A. The characteristic of metal is that it has so-called **free electrons** with a certain concentration (i.e., the number of electrons per unit volume) similar to the concentration of the atoms of which the metal is composed. Where did these free electrons come from? It was established that metal is formed from neutral atoms of a particular element. These atoms form a regular crystal lattice and from each atom, one (or more) of the weakly bonded valence electrons are "stripped off". These electrons called free electrons are not bound to a particular atom, but can move throughout crystal lattice, which consists of positively charged ionized atoms. A metal is electrically neutral because the negative charge of free electrons is balanced by the positive charge of the ionized atoms.

If a neutral metal A with a certain electron concentration is brought into contact with a neutral metal B that has a lower concentration of free electrons, then at the point of contact, electrons from metal A will flow (diffuse) into the area where there are fewer electrons, i.e., into metal B. As a result, in the area of the junction, the previously neutral metals will become charged: metal A positively and metal B negatively (Fig. 1a). The influx of electrons into metal B forms a negative electric potential in it, which begins to prevent further flow of electrons from metal A. Eventually, a certain potential difference U_{BA}, determined by the junction temperature, will be established between the two metals.

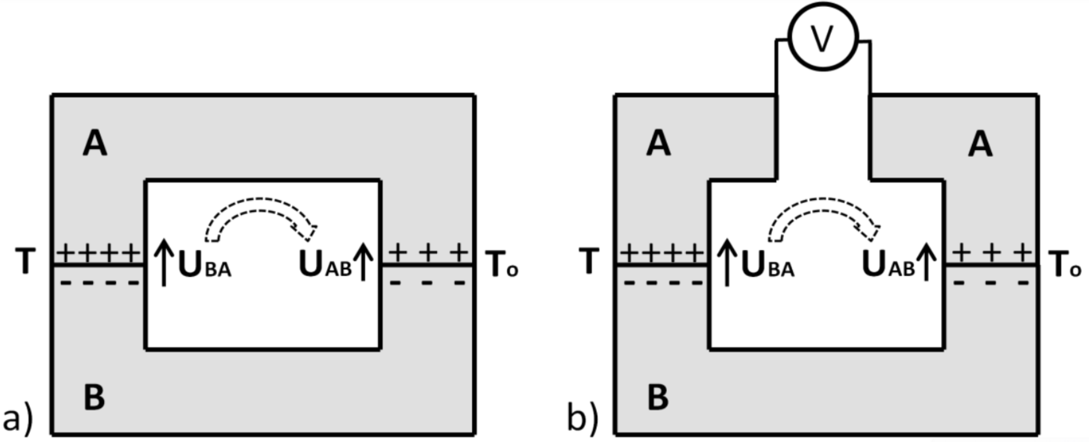

Fig. 1. a) Closed circuit composed of metal A with a higher concentration of free electrons and metal B with a lower concentration of free electrons. b) The same circuit with a voltmeter connected to measure the thermoelectric voltage.

This is the so-called **contact potential difference**, which depends on the temperature **T** of both metals at the point of contact.

Now, let us assume that metals A and B are wires connected at both ends. One of the junctions is at temperature T, which causes a contact potential difference $U_{BA}(T)$ to arise at this junction (see Figure 1a). Let us also assume that the other ends of the wires are in contact at temperature T_0, resulting in a contact potential difference $U_{AB}(T_0)$ at this junction. If we now "trace" the circuit formed by the two wires, for example, in the direction indicated by the dashed double arrow, we see that these potentials are oppositely directed. Thus, they are subtracted one from another, resulting in a net thermoelectric force in the thermocouple system. This force can be measured without current flow by connecting a voltmeter with infinitely high internal resistance, as shown in Figure 1b.

In practice, high-quality voltmeters have a very high but still finite internal resistance. Therefore, instead of measuring the thermoelectric force directly, such voltmeters measure its approximate value, referred to as the thermoelectric voltage. Moreover, due to the high internal resistance of the voltmeter and the virtually current-free measurement, we can neglect other thermoelectric effects associated with current flow, such as the Peltier or Thomson effects. If the temperatures of both junctions are equal ($T = T_0$), the contact potential differences will also be equal, and the voltmeter will show zero voltage. It is worth noting that connecting the voltmeter to the circuit using additional wires made of a different metal than metal A introduces additional junctions into the system. However, if these additional junctions are at the same temperature T_1 (which may differ from T and T_0), for example, at ambient temperature, the contact potential differences generated at these additional junctions cancel each other out and do not affect the net voltage measured by the voltmeter. This is known as the **law of the third metal**.

The principal advantages of thermocouples include small size, low thermal capacity, minimal time inertia, high sensitivity, a wide measurement range, and the ability to directly convert a non-electric quantity – temperature – into an electric quantity – voltage. This allows for transmitting signals over long distances, processing and storing data on the temperature of the studied object, as well as controlling various processes. Other benefits of thermocouples are reliability, simplicity, and low production costs.

It should also be noted that if, in the system shown in Fig. 1b, the voltmeter is replaced with an electric load, the thermoelectric voltage will cause an electric current to flow through the device, allowing it to operate without an additional power source. It is sufficient to ensure a proper temperature difference between the two junctions so that such a system, known as a thermoelectric cell, functions as a low-power current generator. This is an example of the direct conversion of thermal energy (used to heat one of the junctions) into electrical energy.

In the last example of the thermoelectric cell, we observed the direct conversion of thermal energy into electrical energy. To achieve this conversion, we had to ensure a temperature difference between the two junctions in the cell, which resulted in a current flow in the system. However, the opposite effect can also be achieved. If, in the system with two junctions at the same temperature shown in Fig.1b, we replace the voltmeter with a power supply forcing a current flow, this current will cause one junction to heat up and the other to cool down, resulting in a temperature difference between the two junctions. If we reverse the direction of the current flow, the roles of the junctions will switch: the first will cool, and the second will heat. The effect of heating or cooling a junction due to an electric current passing through it is called the **Peltier effect**. It is mainly used in refrigerators but also in heaters, though less frequently due to cost considerations. If an electric current of intensity **I** flows through a junction, the heat energy generated or absorbed per unit of time (power) P_P is defined by the equation:

$$P_p = \pi_p \cdot I \tag{1}$$

where: π_p is the Peltier constant, which depends on the types of metals (or semiconductors) forming the junction and the temperature of the junction. Semiconductor p-n junctions have higher thermal efficiency. Currently, multi-stage Peltier modules are available on the market, offering a maximum temperature difference between the cooled and heated sections exceeding even 100°C.

Heat is also generated or absorbed when an electric current flows through a homogeneous conductor (or semiconductor) along which a temperature gradient occurs. This thermoelectric phenomenon is called the **Thomson effect**, and the heat generated or absorbed in this phenomenon is referred to as **Thomson heat**. This means, for example, that in metal B shown in Fig. 1, heat is either generated or absorbed depending on the direction of the current flow and whether the temperature increases or decreases along the direction of the current. For small temperature differences at the ends of the conductor, the Thomson heat exchanged with the surroundings per unit of time (i.e., power) P_T can be calculated using the approximate equation:

$$P_T \approx \sigma \cdot I \cdot (T - T_0) \tag{2}$$

where: σ is the Thomson coefficient, which depends on the type of material and temperature, I is the current intensity, and T and T_0 are the temperatures at the ends of the conductor where Thomson heat is generated or absorbed. The coefficient σ is considered positive if the flow of current from a point with a higher temperature to a point with a lower temperature causes heat generation. It is important to note that Thomson heat differs from Joule-Lenz heat, which is always generated when current flows through a conductor, regardless of the current's direction or whether there is a temperature gradient along the conductor.

In a thermocouple system where current flows, all the thermal phenomena described above occur simultaneously. In this experiment, as already mentioned, we measure the voltage in the system shown in Fig.1b using a voltmeter with very high internal resistance. As a result, virtually no current flows in the system, and only the **Seebeck effect** is responsible for the thermoelectric voltage generation.

2. Measuring Principle and Measuring System

Thermocouple Calibration

The idea of using the circuit shown in Fig. 1, called a thermocouple, for measuring temperature, is change the thermoelectric voltage U when the temperature difference between the junctions changes. To do this, one of the junction should be at a constant reference temperature T_o, for example in a mixture of water and ice (Fig. 2), the temperature of which is 0°C at normal pressure. The second junction is placed at the location whose temperature T we want to measure. Under these conditions, any changes in the measured temperature T will affect the change in the contact potential difference $U_{BA}(T)$, and hence the thermoelectric voltage U measured by the voltmeter. The thermocouple must be pre-calibrated to use for temperature measurement, i.e., using a reference thermometer to determine the dependence of the voltage measured by the voltmeter on variation using a heater of temperature T – the junction, placed in the same vessel as the reference thermometer.

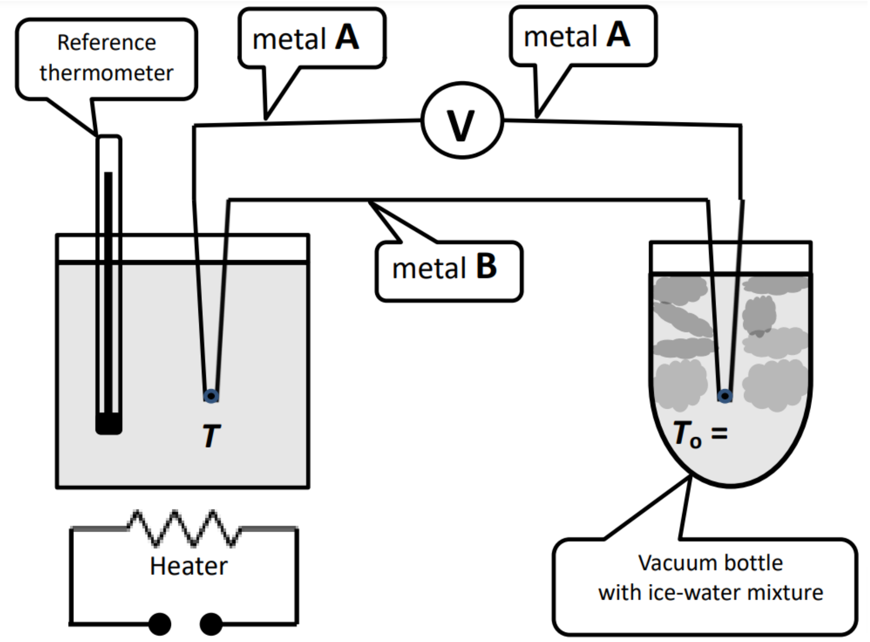

Fig. 2. Schematic of the measuring system used to thermocouple calibration or to measure the temperature T when the thermocouple is already calibrated (then the reference thermometer is unnecessary).

Thermocouples made of specific metals have repeatable, precisely defined characteristics that make the voltage measured in the thermocouple system dependent on the temperature of one junction, when the other is maintained at a constant reference temperature. These characteristics can be found in the appropriate tables. The selection of different metals or metal alloys makes it possible the creation of thermocouples with high sensitivity operating in various temperature ranges, while maintaining appropriate mechanical (e.g., the thermocouple does not melt) and chemical properties.

The most commonly used thermocouples are made of:

- Copper and constantan (40% Ni and 60% Cu) – measurement range: 70 K to 800 K,
- Platinum and platinum-rhodium (90% Pt and 10% Rh) – measurement range: up to 1300 K,
- Iridium and iridium-rhodium alloy – measurement range: up to 2300 K.

Determining the Solidification Temperature of a Metal Alloy

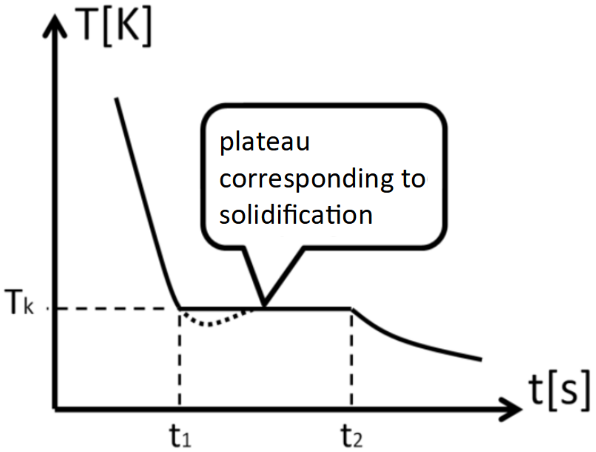

Fig. 3. Dependence of the temperature of a cooling substance on time for a substance undergoing a first-order phase

Let us consider a first-order phase transition. During such a transition, heat is released or absorbed, while the temperature of the substance remains constant. First-order phase transitions include changes in the state of matter, such as solidification, melting, evaporation, condensation, sublimation, and resublimation. In the exercise, the process of solidification is studied. During this process, the cooling curve, i.e. the dependence of the substance temperature on time, will look like in Fig. 3. Initially, when the substance is in the liquid phase, the release of heat to the environment is accompanied by a decrease in temperature. When the substance begins to solidify (moment t_1 on the graph), heat continues to be released to the environment, but the temperature remains a constant value corresponding to the solidification temperature T_k — on the graph, we observe the so-called plateau (read: plato) represented by a horizontal continuous line. When the entire substance solidifies (t_2), the release of heat to the environment will again be accompanied by a further decrease in the substance's temperature. The heat released during solidification between moments t_1 and t_2 results from the fact that the internal energy of the substance in the liquid phase at the solidification temperature is higher than the internal energy of the substance at this temperature in the solid phase. Therefore, when the body solidifies, energy is released in the form of heat, the amount of which is equal to the difference in the internal energies of the substance in both phases.

The heat released or absorbed by a **unit mass** of a substance (kg) during a first-order phase transition at constant temperature is called the **latent heat of phase transition**. The values of this heat are characteristic of the substance type and can be found in physical reference tables.

On the graph corresponding to the solidification of the liquid substance tested in the exercise, in the time interval in which the plateau occurs, the measured temperature may initially decrease and then increase. The reason for this may be the supercooling of the liquid, i.e. the lowering of the liquid temperature below the solidification temperature T_k (dashed line on the graph). Such a state can be obtained either by slow cooling of a very pure liquid (i.e. without crystallization nuclei on which the crystallization process could begin), or as a result of very rapid cooling even of a contaminated liquid. Another reason for deviations from the plateau may be the fact that due to the rapid release of heat to the environment, the liquid does not cool uniformly throughout its volume (it begins to solidify from the surface where the temperature is the lowest), and the temperature is measured at one point. Another reason for small changes in body temperature during solidification may be the fact that the liquid substance being tested is multi-component and as a result of solidification, partial segregation of components occurs, and therefore the composition of the liquid that has not yet solidified may change slightly, which entails a small change in the solidification temperature. In this case, in order to determine the solidification temperature of the metal alloy, the instructions contained in the manufacturing instructions should be followed.

Please note that if in the graph shown in Fig. 3 the temperature T is replaced by the thermoelectric voltage U measured in the thermocouple system (such a graph should be made in the exercise report), the graph shape will not change because in the tested temperature range the thermoelectric voltage is a linear function of temperature.

3. Tasks to be performed

3.1. Measurements and their Processing – Thermocouple Calibration

In the exercise being performed, the first task is to calibrate the thermocouple by plotting the dependence $U = f(T)$, i.e., the thermoelectric voltage U measured in the thermocouple system as a function of the varying temperature T of one of the thermocouple junctions, while the other junction is maintained at a constant reference temperature T_o = 0°C. The calibration should be carried out in the temperature range from 20°C to 90°C (to ensure safety, do not exceed the upper limit). In the studied range, the dependence $U(T)$ can be described with very good approximation by a linear relationship:

$$U = \alpha\,(T-T_o) \tag{3}$$

where α is the thermoelectric coefficient of the thermocouple. The value of this coefficient equals the thermoelectric force in the thermocouple system when the temperature difference between the junctions is one degree Celsius (or one Kelvin), indicating the sensitivity of the thermocouple.

The thermoelectric coefficient should be determined using the linear regression method, which identifies the equation of the line that best fits the measured points on the calibration graph $U = f(T)$. The slope of the determined line corresponds to the thermoelectric coefficient of the thermocouple. Therefore, the uncertainty in determining the slope of the line, also calculated using the linear regression method, represents the uncertainty in the determined thermoelectric coefficient.

A detailed description of the steps performed during the thermocouple calibration can be found in the execution instructions for this exercise.

3.2. Measurements and their Processing – Determining of the Alloy Solidification Temperature

In order to the solidification temperature determine of the tested metal alloy, we use the measurement system shown schematically in Fig. 2. The joint, which was in a vessel with water at temperature T, is transferred to the crucible containing the tested alloy. The crucible is placed on the heater and heated to a temperature of about 85°C (the system should not be overheated). Then, the heater is turned off and the crucible is placed on a suitable metal base that accelerates the removal of heat to the environment. During the cooling of the alloy, we note the time t and the thermoelectric voltage U, and then draw a graph of the alloy cooling $U=f(t)$. From the graph, we determine the voltage U_k corresponding to solidification (plateau). Then, using equation (3) and the thermoelectric coefficient α determined during the thermocouple calibration, we calculate the solidification temperature T_k of the alloy. A detailed description of the activities performed to determine the solidification temperature and the analysis of measurement uncertainty can be found in the implementation instructions for this exercise.

Determining the solidification temperature of the alloy can be replaced by determining the solidification (freezing) temperature of water. This part of the exercise is described in detail in the exercise instructions.

4. Questions:

1. Thermocouple structure and its application. Advantages of a thermocouple.
2. Explain the formation of a contact potential difference at the contact of two metals.
3. Present the mechanism of thermoelectric force formation.
4. Explain thermocouple calibration.

5. State the dependence of thermoelectric force on the temperature of one thermocouple junction while the other junction is maintained at a constant reference temperature.
6. Define the thermoelectric coefficient and state its unit. How can it be determined?
7. What are the Peltier and Thomson phenomena?
8. Sketch and explain the solidification curve.
9. State the method of the solidification temperature determining.
10. State the calculating method of the determined alloy solidification temperature uncertainty.
11. What is the first-order phase change heat?

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