DETERMINATION OF THE ENTROPY CHANGES

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Task 1

DETERMINATION OF THE ENTROPY CHANGES

I. Aim of the task

The aim of the task is determination of the entropy changes in the isolated system during melting of ice.

II. Introduction

1. The second law of thermodynamics.
2. The concept of entropy.
3. The changes of entropy in reversible and irreversible processes.
4. The methods of calculating the entropy changes in isothermal, isobaric and isochoric processes.
5. Entropy of mixing.

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III. Theory

III. 1. Spontaneous processes

The First Law of thermodynamics is expressed as follows: the internal energy, U, of an isolated system is constant, thus ΔU being the change in internal energy when a system changes from the initial to the final states, is equal to zero.

If we write W for the work done on a system, Q for the energy transferred as heat to a system, and ΔU for the resulting change in internal energy, then it follows that:

$$\Delta U = Q + W \tag{1}$$

This is the mathematical statement of the First Law of thermodynamics, for it summarizes the equivalence of heat and work and the fact that the internal energy is constant in an isolated system (for which $Q = 0$ and $W = 0$). The equation states that the change in internal energy of a closed system is equal to the energy that passes through its boundary as heat or work. It employs the 'acquisitive convention', in which $W > 0$ or $Q > 0$ if energy is transferred to the system as work or heat and $W < 0$ or $Q < 0$ if energy is lost from the system as work or heat.

The internal energy is a **state function** in the sense that its value depends only on the initial and final states of the system but is independent of the path between them. In other words, it is a function of the properties that determine the current state of the system.

The internal energy is a state function which determines whether the process is allowed or not. However, it does not specify whether the process occurs spontaneously and in which direction it will develop. For example, we assume that the considered system is gas enclosed in a container fitted with a moveable piston (see **Fig. 1**).

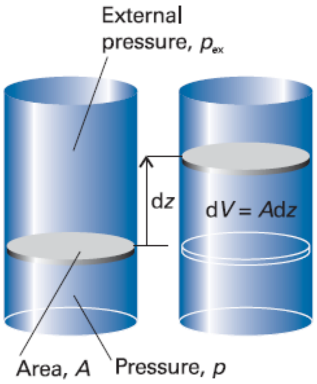

Fig. 1. System containing gas enclosed in a container fitted with a moveable piston [1].

Considering only a state of the system we cannot predict its behaviour. The First Law of thermodynamics allows both expansion and compression of the system. However, from experience we know that gas will spontaneously expand only in the case if a gas pressure inside is higher than atmospheric pressure. Generally, the spontaneity of the process is determined by the existence of appropriate incentives for a given process. In the above-mentioned example, such appropriate incentive was the differential pressure. For the heat conduction the temperature difference is required while diffusion processes are caused by the concentration difference.

All spontaneous processes of this type are also irreversible. **Thermodynamic irreversibility** means that a process cannot "spontaneously" run backwards. The return is only possible at the expense of surroundings. In an irreversible process a simultaneous return of a system and surroundings is impossible.

If the differences in values that cause appropriate transformations go to zero, processes will start to run infinitely slowly. Such processes are called **quasi-static processes**. A quasi-static process often ensures that the system will go through a sequence of states that are infinitesimally close to equilibrium (so the system remains in the quasi-static equilibrium), in which case the process is typically reversible. It is important to note that no real process is quasi-static. In practice, such processes can only be approximated by performing them infinitesimally slowly.

In summary: internal energy cannot be used to determine the directions of the processes. To determine the direction of the processes one should consider both the system and the surroundings.

III. 2. Entropy. The Second Law of thermodynamics

The First Law of thermodynamics led to the introduction of the internal energy, *U*. The internal energy is a state function that lets us assess whether a change is permissible: only those changes may occur for which the internal energy of an isolated system remains constant. The law that is used to identify the signpost of spontaneous change, **the Second Law of thermodynamics**, may also be expressed in terms of another state function, the **entropy**, *S*.

Entropy is a state function which is used to determine the direction of spontaneous changes. Entropy lets us assess whether one state is accessible from another by a spontaneous change. **The First Law** uses the internal energy to identify **permissible changes**, **the Second Law** uses the entropy to identify the **spontaneous changes** among those permissible changes.

For the reversible processes, the total value of the entropy of a system and surroundings before a change is equal to the value after the change:

$$(S_{sys} + S_{sur})_a = (S_{sys} + S_{sur})_b \tag{2}$$

where *a* and *b* mark the initial and final state, respectively.
For irreversible processes:

$$(S_{sys} + S_{sur})_a > (S_{sys} + S_{sur})_b \tag{2a}$$

Equations (2) and (2a) can be written in a different way. For the reversible process:

$$\Delta S_{sys} + \Delta S_{sur} = 0 \tag{3}$$

where ΔS_{sys} is the entropy change of the system, ΔS_{sur} is the entropy change of the surroundings.

For the irreversible process:

$$\Delta S_{sys} + \Delta S_{sur} > 0 \tag{4}$$

Denoting ΔS_{sys} + ΔS_{sur} as ΔS, equations (3) and (4) can be written in short form. For the reversible process:

$$\Delta S = 0 \tag{5}$$

For the irreversible process:

$$\Delta S > 0 \tag{6}$$

In reversible processes the change of the entropy of the system and surroundings ($\Delta S = 0$) is equal to zero. In the case of irreversible processes ΔS is greater than zero ($\Delta S > 0$), that is, the sum of the entropy of the system and surroundings increases.

Therefore, **the Second Law of thermodynamics** can be expressed in terms of the entropy as:

$$\Delta S \geq 0 \tag{7}$$

III. 3. The thermodynamic definition of entropy

The thermodynamic definition of entropy concentrates on the change in entropy, dS, that occurs as a result of a physical or chemical change (in general, as a result of a ‘process’). The definition is motivated by the idea that a change in the extent to which energy is dispersed depends on how much energy is transferred as heat which stimulates random motion in the surroundings. On the other hand, work stimulates uniform motion of atoms in the surroundings and so does not change their entropy.

Entropy is a state function which determines the degree of disorder of the system as well as its surroundings. The higher entropy of the system is, the more chaotic structure the system has and vice versa.

The thermodynamic definition of entropy is based on the expression:

$$dS = \frac{dQel.rev}{T} \tag{8}$$

where dQ_{rev} is the elementary process heat conducted in the reversible way.

For a measurable change between two states *i* and *f*, this expression integrates to:

$$\Delta S = \int_i^f \frac{dQel.rev}{T} \tag{9}$$

That is, to calculate the difference in entropy between any two states of a system, we find a *reversible* path between them, and integrate the energy supplied as heat at each stage of the path divided by the temperature at which heating occurs.

If the reversible process occurs at a constant temperature (T = const), then:

$$\Delta S = \frac{1}{T}\int_i^f Q_{el.rev} = \frac{Q_{rev}}{T} \tag{10}$$

For the reversible process at a constant temperature, the ch ange of the entropy is the relationship between heat and temperature at which this process occurs.

If the heat of the irreversible process is added to Eq. (8), then:

$$dS > \frac{Q_{el.}}{T} \tag{11}$$

Equations (8) and (10) are frequently written together as:

$$dS \geq \frac{Q_{el.}}{T} \tag{12}$$

III. 4. Entropy of phase transition

The change of the physical state is related to the change of entropy because the change of the physical state implies the change in the degree of the system order. In a phase transition, heat is absorbed, but the temperature remains constant. This temperature is called the **temperature of phase transition**, T_{pt}. Moreover, the phase transition occurs in a state of equilibrium, thus the process must be reversible.

If the phase transition occurs under a constant pressure, then a heat of a given phase transition Q_{rev} is equal to the change of the enthalpy (so-called enthalpy of phase transition, $\mathit{\Delta} H_{pt}$):

$$Q_{rev} = \mathit{\Delta} H_{pt} \tag{13}$$

Because T_{pt} = const, using Eq. 10, we can write:

$$\Delta S = \frac{\Delta H_{pt}}{T_{pt}} \tag{14}$$

If phase transition is exothermic ($\mathit{\Delta} H<0$) e.g. in a solidification or condensation process, the entropy of the system decreases ($\mathit{\Delta} S<0$). The system undergoes arrangement indeed.

If phase transition is endothermic ($\mathit{\Delta} H>0$) e.g. in a melting or boiling process, the entropy of the system increases ($\mathit{\Delta} S>0$).

III. 5. Relationship between entropy and temperature of a system

We can use Eq. 9 to calculate the entropy of a system at a temperature T_f, knowing its entropy at a temperature T_i and the heat supplied to change its temperature from one value to another. We shall be particularly interested in the entropy change when the system is subjected to a constant pressure (such as from the atmosphere) during the heating.

If temperature change takes place at a constant pressure, the heating effect of such a process corresponds to a change of the enthalpy of the system, unless the work is only of a volume. The change of enthalpy caused by isobaric heating or cooling concerns a reversible process thus it corresponds to the reversible thermal effect:

$$dH = Q_{el.rev} \tag{15}$$

Then from the definition of constant-pressure heat capacity:

$$dH = C_p dT \tag{16}$$

so when used in Eq. 9 it gives:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p \; dT}{T} \tag{17}$$

If we assume that C_p does not depend on temperature, then Eq. 17 can be written as:

$$\Delta S = C_p \int_{T_1}^{T_2} \frac{dT}{T} = C_p \, ln \frac{T_2}{T_1} \tag{18}$$

The same expression can be applied at a constant volume, but with C_p replaced by C_V.

IV. Experimental

A. Devices and materials

1. Devices:

- calorimetric setup,
- electric stirrer,
- calorimeter heat capacity determination setup (power adapter, voltmeter, ammeter, heater installed in the calorimeter lid, PC system, AR-Soft software).

2. Materials:

- distilled water,
- ice.

B. Program

Thermal effects that accompany all kinds of chemical reactions or physicochemical processes are usually measured with devices known as calorimeters. Different calorimeter designs are in use depending on the intended application, e.g. measurements of thermal effects at low or high temperatures, under high or low pressures, etc.

The main part of the calorimeter used in this experiment is a Dewar vessel (see **Fig. 2**) with a lid equipped with a glass stirrer propelled by an electric motor, a temperature sensor connected to a computer device and a resistance wire heating element to determine the heat capacity of the calorimeter by the electric method.

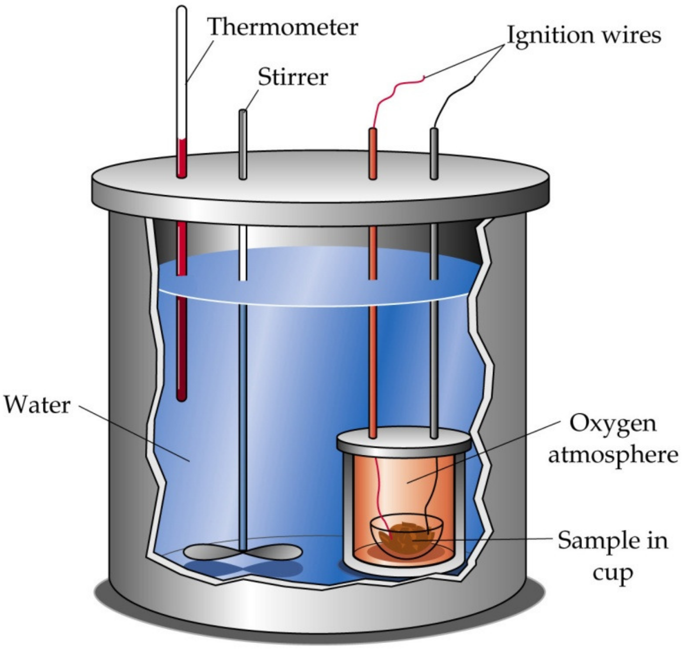

Fig. 2. Dewar vessel scheme [7].

The Dewar vessel is filled with calorimetric liquid (in this case, water) and the lid is screwed on. The lid prevents the liquid from evaporation or heat loss. The calorimeter used in this experiment is not fully protected from exchanging the heat with the environment, and therefore the temperature within the Dewar vessel does not reach a constant value even after a long time. Initially, temperature fluctuations are significant, with the so-called temperature run being established several minutes after calorimeter setup and characterized in slight or nearly identical changes in temperature per unit time. Depending on ambient temperature, the temperature inside the Dewar vessel is either increasing or increasing slowly and continuously.

Once settled, temperature changes can be measured to calculate the temperature correction factor for the overall heat exchange between the calorimeter and its environment. Thus, each calorimetric measurement consists in reading out the temperature values at specific time intervals, determination of the temperature correction factor, determination of the heat capacity of the calorimeter and finally calculation of the thermal effect of the process being studied. The temperature inside the calorimeter is measured at the accuracy of 0.01 K at constant, usually half-minute intervals.

The figure below presents the temperature changes in three periods: the initial period, the main period and the final period.

A graphical method can be used to easily determine the temperature change due to the process being studied adjusted for the exchange of heat between the calorimeter and the environment (ΔT_{adj}) (see **Fig. 3**).

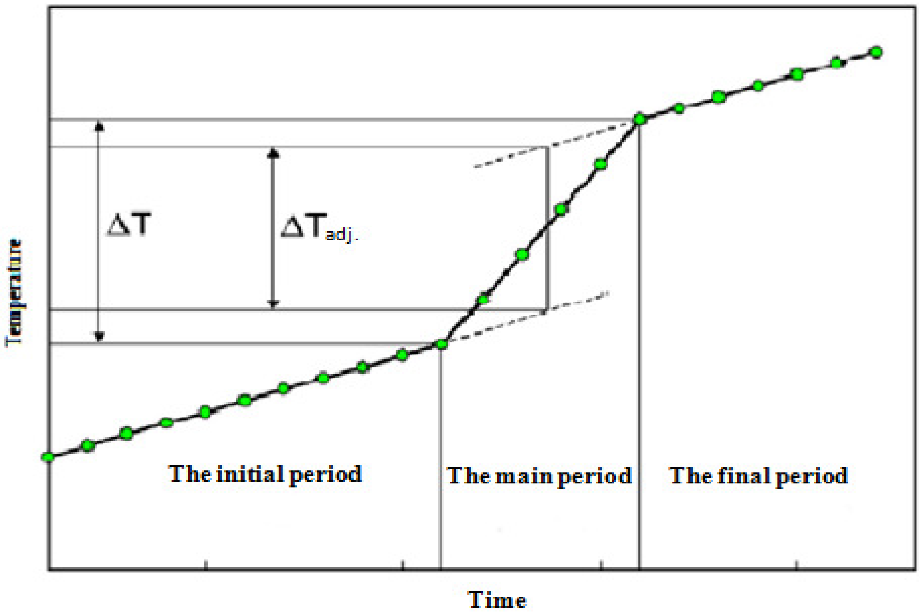

Fig. 3. A chart of calorimeter temperature as a function of time.

The thermal effect of the process is calculated from the following equation:

$$Q_p = \Delta H = C_k \, \Delta T_{adj} \tag{19}$$

where C_k is the heat capacity of the calorimeter.

The heat capacity of the calorimeter is determined precisely by delivering a known amount of heat to the calorimeter using a heating element (resistance wire) connected with a current of known voltage (U) and intensity (I). The heat emission (Q) is given by:

$$Q = U\,I\,t \;\; [J] \tag{20}$$

where t is the time of current flow in seconds.

C. Method

1. Calibration of the calorimeter

- fill the Dewar vessel with 500 g of room-temperature water,
- after tightening the calorimeter lid, start up the stirrer and turn on the temperature sensor,
- open the AR-Soft application to record the temperature changes using the computer device,
- after opening, click the "Channels and Transmission Config" icon. In the "Channel Config" tab click the "monitoring and recording” option and confirm the changes,
- temperature changes are monitored by clicking the "data view" icon,
- after several minutes, when the temperature changes become small, turn the heater on.
- read the voltage in volts and the current in amps,
- when the temperature of water increases by ca. 1°C, turn off the heater and continue to monitor temperature changes for another 3-5 minutes.
- having completed the measurements, disconnect the setup and discard the water from the calorimeter.

2. Main measurement

- notice: About half an hour before main measurement (melting) crush some ice. Weigh 500 g of ice at the temperature of ca. 35°C and carefully pour it into the Dewar vessel,
- after tightening the calorimeter lid, start up the stirrer and turn on the temperature sensor,
- open the AR-Soft application to record the temperature changes using the computer device,
- after opening, click the "Channels and Transmission Config" icon. In the "Channel Config" tab click the "monitoring and recording” option and confirm the changes,
- temperature changes are monitored by clicking the "data view" icon,
- After several minutes, when the temperature changes become small, charge the calorimeter with a pre-weighed 100 g sample of ice,
- read the temperature drops due to melting ice every thirty seconds,
- continue the measurements for 5 minutes after the ice has melted completely, as evidenced by slow, slight changes in temperature (the final section of the chart),

- having completed the measurements, disconnect the setup and discard the water from the calorimeter.

NOTICE! If the ice was not transferred into the calorimeter in a quantitative manner (e.g. some ice had been spilled), weigh the water after completing the experiment and calculate the mass of ice from the difference of water weights before and after the measurement.

Repeat the measurement for a new portion of ice.

D. Results and conclusions

Use the temperature readings to plot out dependence of the temperature versus time for the calorimeter calibration and the main measurement. Draw separate graphs for both correlations. Next, determine the adjusted temperature change (ΔT_{adj}) for both processes using the graphical procedure described above.

The overall change in entropy due to ice melting is the sum of the changes in the entropy of the system (ice) and the environment (the calorimeter and the calorimetric liquid). The change in the entropy of ice is in turn related to two separate processes including:

- the phase transition (ice melting). The change in entropy due to this process (ΔS_1), according to equation (14), equals:

$$\Delta S_1 = \frac{\Delta H_{mel}}{T_{mel}} = \frac{mL_{mel}}{T_{mel}} \tag{21}$$

  where: ΔH_{mel} – the change in enthalpy due to melting, T_{mel} – the ice melting temperature, m – the ice mass, $L_{mel} = 3.352 \cdot 10^5$ J/kg (latent heat of melting for ice);

- heating of water formed by melting the ice from the melting temperature to the final temperature (T_f). The change in entropy due to this process (ΔS_2) equals:

$$\Delta S_2 = C_p ln\frac{T_f}{T_{mel}} = mc_p ln\frac{T_f}{T_{mel}} \tag{22}$$

  where: C_p – the heat capacity of water formed by melting the ice under constant pressure; c_p – the specific heat capacity of water; T_f – the final measurement temperature: $T_f = T_1 + \Delta T_{adj}$; T_1 – the initial measurement temperature; ΔT_{adj} – the change in temperature due to ice melting adjusted for heat exchange.

The change in the entropy of the environment (calorimetric setup) associated with calorimeter being cooled down from the temperature T_1 to the final temperature T_f is provided by the following equation:

$$\Delta S_3 = C_k ln\frac{T_f}{T_1} \tag{23}$$

where C_k is the heat capacity of the calorimeter given by the equation:

$$C_k = \frac{Q}{\Delta T_{adj}} \tag{24}$$

In the above formula, Q is provided by equation (20) and ΔT_{adj} is the adjusted change in temperature determined in the calorimeter calibration.

The overall change in the entropy of the system and the environment is the sum of the entropy changes calculated above.

Use the calculated overall change in entropy to determine whether the process is reversible or irreversible.