7 - GAS LAWS

Instruction manual for virtual exercises at Laboratorium Fizyki I teren południowy

The exercise aims to figure out the universal gas constant and verify the validity of equations describing the basic gas processes.

1. BACKGROUND

1.1 Ideal gas and real gas

Ideal gas describes an idealized substance consisting of a very large number of non-interacting molecules – material points in a volume limited by perfectly rigid walls. These particles are in constant motion, constantly colliding with each other. All directions of this movement are completely equal.

From a high school course, we know an equation **called the Clapeyron** equation that binds macroscopic physical volumes (state parameters) that characterize the state of **gas: pressure p, volume V and** temperature on the absolute scale **T**:

$$pV = nRT\ ,$$

where **n is the number of moles** of the considered Ideal gas and R = 8,31 $Jmol^{-1}K^{-1}$ **so-called gas constant**.

As you know, unlike the ideal gas that is subject to the Clapeyron equation, the behavior **of actual gas** describes **the van der Waals equation:**

$$\left(p + \frac{a}{V^2}\right)(V - b) = nRT\ \ ,$$

that takes into account the interaction between gas molecules and finite particle sizes themselves (a and b – are the experimentally assigned constants). This equation can be rewritten as:

$$V^3 - \left(b + \frac{nRT}{p}\right)V^2 + \frac{a}{p}V - \frac{ab}{p} = 0\ .$$

For the fixed values T and p, this equation is a third-degree polynomial of V. It, therefore, has one or three rational zeros. That is, for a given pressure value (at a specific temperature), the gas can occupy one or three specific volumes. **The theoretical graphs** of this equation for different temperatures are shown in Figure 1. From this figure, you can see that the curves (called **isotherms)** plotted for different temperatures are significantly different from each other. Curves obtained at temperatures below a certain characteristic temperature T_k intersect a straight line p=const. at three points. For temperatures higher than $T_{k,}$ we get only one intersection. The higher the temperature, the more close the isotherm is to the isotherm of perfect gas. The isotherm separating all monotonous isotherms from "wavy" **isotherm** is called critical isotherm, and the corresponding temperature T_k is the **critical temperature.** The dotted curve in Fig. 1 separates the area under the curve in which the substance can exist in two phases from the homogeneous state area. The K point in the graph – called critical, defines the so-called critical state of the substance, strictly determined by the corresponding pressure – p_k , temperature – $T_{k,}$ and volume – V_k. At this point, the difference between liquid, gas, and saturated steam disappears. **A substance that exists above critical temperature is contractually called "gas".** In the area of pressures and temperatures distant from critical pressure and temperature, actual gases also meet the Clapeyron equation with sufficient accuracy.

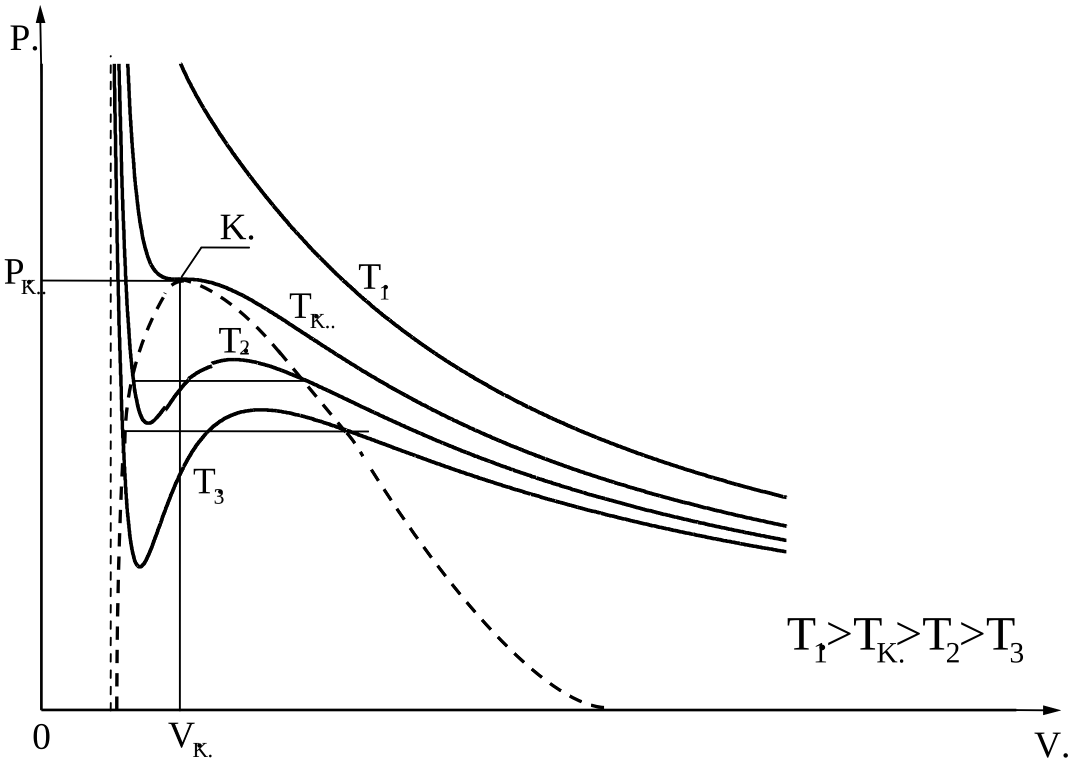


Fig. 1 Van der Waals gas isotherms for different temperatures. K - critical point, T_K - critical temperature, V_K - critical volume, p_K - critical pressure.

The experimental curves look slightly different. At high temperatures (T>T_k), they are similar to theoretical curves. At temperatures below T_k, horizontal parts appear on them, indicating that the pressure remains constant despite the volume change. What physical processes correspond to the different parts of these isotherms?

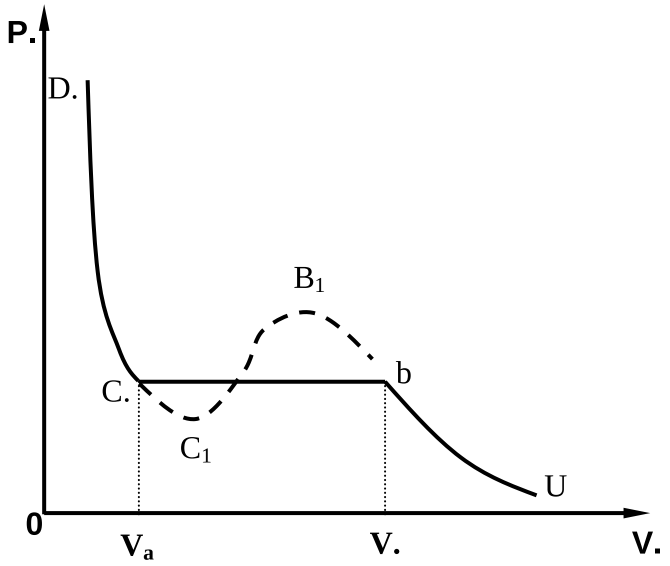


Fig. 2 Isoterma of a real gas (the continuous line is indicated by experimental isotherm and the dotted line is a theoretical isotherm).

During isothermal compression on section AB (Fig. 2), the gas (unsaturated steam) behaves similarly to the perfect gas – reducing the volume causes an increase in pressure. Further compression leads to the appearance of saturated steam and liquid in the vessel – condensation occurs. The pressure in this process remains constant. Condensation occurs throughout the BC section and at point C we are already dealing only with liquid. The BC section corresponds to the balance between the liquid and its saturated steam. Further compression causes a sharp increase in the pressure in the liquid with slight changes in its volume (low compressibility of the liquid).

Sections AB and CD of theoretical isotherm correspond to states that can always be realized experimentally. Section BB_1 of this isotherm corresponds to the state of matter, which we call **saturated steam** (steam with a pressure higher than the pressure of saturated steam at a given temperature). It can occur only if there are no so-called condensation centers (ions, pollen, etc.) in the volume occupied by the steam, the existence of which causes instant condensing of saturated steam on them, which corresponds to a section of the BC level.

Similarly, under conditions that hinder the boiling process (absence of gas bubbles on the walls of the vessel and inside the liquid, which could be followed by "internal" evaporation), a liquid can be obtained at a pressure lower than the pressure of saturated steam at a given temperature (section CC_1). The states of the substance corresponding to section C_1B_1 cannot be permanently realized in nature.

1.2 Gas processes

The equation of ideal gas, for a given amount of gas, can be rewritten in another form:

$$\frac{pV}{T} = nR = const.$$

From the above equation, it seems that a certain amount of gas must not exist at any combination of pressure, volume, and temperature. Changing state parameters is limited by the above condition. Special cases of state parameter changes are gaseous processes in which one of the state parameters is immutable. We may have three gas processes:

1. **Isothermal process** - the temperature is constant, the equation of transition takes the form of pV = const **(Boyle-Mariotte's law).** The internal energy of the gas is unchanged in this transformation.
2. **Isobaric process** – the pressure remains unchanged; the equation of transition takes the form of V/T = const **(Gay-Lussac's law).**
3. **Isochoric process** - volume is constant, the equation of transition takes the form of p/T = const **(Charles's** law). In this transformation, you cannot perform any work on gas, nor can the gas perform any work.
4. In addition to three processes where one of the state parameters remains, another transformation called **adiabatic process is** defined. This process evolves in such a way that the gas does not exchange heat with the environment. If the gas is performing the work, then its internal energy decreases, while if the work is performed on the gas, it leads to the growth of internal energy of the gas and to the increase in its temperature. There are dependencies between p, V, and T (note that all three parameters change):

$pV^{\kappa} = const.$ (in other variables $TV^{\kappa-1} = const.$ or $T^{\kappa}V^{\kappa-1} = const.$)

A power exponent (kappa) $\kappa = \frac{c_p}{c_v}$ is a physical parameter dependent on the molecular structure of the gas under consideration. $\mathbf{c_p}$ is the specific heat of the gas measured at constant **pressure,** $\mathbf{c_V}$ is the **specific** heat of the **gas** at a constant volume (the specific heat is the amount of heat to be supplied to the unit of mass of the substance so that its temperature rises by 1 K).

In practice, adiabatic process occurs when the phenomenon occurs quickly enough that the heat does not manage to be carried out outside the system (or brought to it). This is the case, for example, in internal combustion engines (therefore, the efficiency of internal combustion engines depends, among others, on the value *of* κ*).*

The specific heat capacity, measured at constant pressure, shall be greater than the specific heat measured at a constant volume. This difference is related to the fact that when a gas mass occupies a constant volume, the entire amount of heat supplied increases its internal energy, and if the gas is under constant pressure, part of the heat is used to perform the $\Delta L=p\Delta V$ work associated with the change in gas volume. It can be shown that for one mole of Ideal gas:

$\mu c_p - \mu c_v = R$ or $C_p - C_v = R$,

where C_p and C_v are molar **heats at constant pressure and volume, respectively.**

1.3 Kinetic molecular theory of gas

The first law of thermodynamics is a fundamental **dependency in the field of heat science:**

$$\Delta U = \Delta Q + \Delta L\,,$$

which states that the change in internal energy U of the thermodynamic system under consideration may occur as a result of the heat exchange ΔQ with the environment or as a result of ΔL -work by the system or over the system. For Ideal gas, the internal energy is the sum of the kinetic energy of all gas molecules, and as we show below, it depends only on the temperature. It can be shown that in a mixture of gases, for each molecule, regardless of its type, there is on average the same kinetic energy of the progressive movement. The concept of the number of degrees of freedom **of** a molecule is introduced: this is the number of independent parameters needed to clearly determine the position of a molecule in space. If the gas is monoatomic, the position of each molecule can be determined by specifying three *spatial coordinates x, y, and z* of its center of mass – that is, the single-atom molecule has three degrees of freedom. For a two-atom molecule, the values of the two angles describing its orientation in space must be given in addition; five parameters together or five degrees of freedom. The first three degrees of freedom correspond to the possibility of the molecule moving in three directions of space, the other two being able to spin around two axes perpendicular and perpendicular to the section connecting the atoms.

If the gas is monoatomic, then due to the equality of all directions of the insular movement of molecules, you can write:

$$\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2\,,$$

where the mean values of the speed component squares along the x, y and z axes.$\bar{v}_x^2, \bar{v}_y^2, \bar{v}_z^2$,
The element in the sum of these values is called the square mean speed $v_{sq.\,m.}$ Thus:

$$\bar{v}_{kw}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2 = 3\bar{v}_x^2\,.$$

The kinetic molecular theory establishes a relationship between microscopic and macroscopic gas sizes. Thus, the average kinetic energy of gas molecules is related to its temperature of dependence:

$$E_k = \frac{m v_{kw}^2}{2} = \frac{3}{2}kT\,,$$

where k is a physical constant called Boltzmann constant ($k=R/N_A= 1{,}38\ 10^{-23}\ JK^{-1}$, N_A is the number of gas molecules in 1 mole called the Avogadro number equal to6 10^{-23} mol^{-1}). It leads to the conclusion that:

$$\frac{3m\bar{v}_x^2}{2} = \frac{3m\bar{v}_y^2}{2} = \frac{3m\bar{v}_z^2}{2} = \frac{3}{2}kT\,, \qquad \text{whence} \qquad \frac{m\bar{v}_x^2}{2} = \frac{m\bar{v}_y^2}{2} = \frac{m\bar{v}_z^2}{2} = \frac{1}{2}kT\,.$$

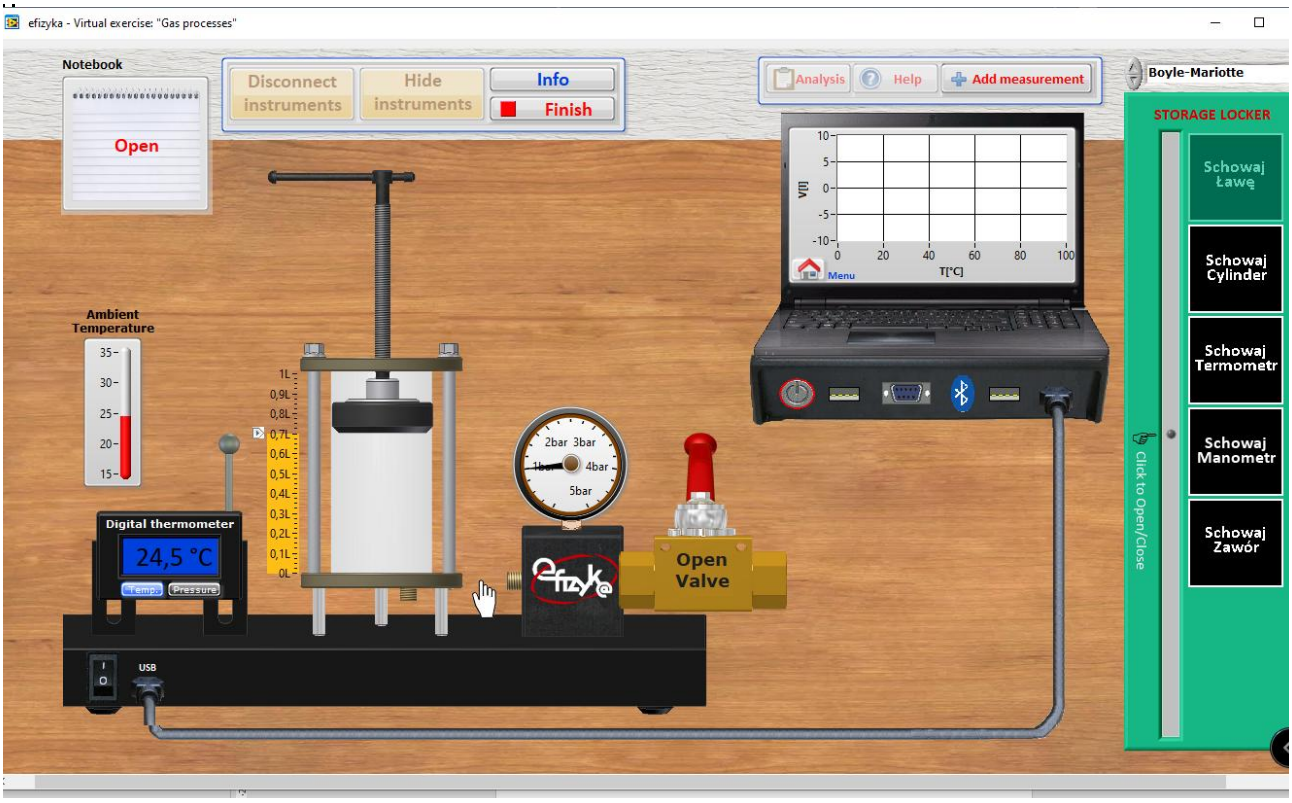
We can therefore see that for each degree of freedom of a monoatomic gas molecule, and there is on **average the same kinetic energy** of 1/2kT. The same is true if the molecule has more degrees of freedom. In general, therefore, **the so-called principle of energy equilibrium** (i.e., equal energy distribution) can be formulated: in a state of thermodynamic equilibrium for each degree of freedom of the molecule, there is on average the same kinetic energy equal to 1/2kT, regardless of how many degrees of freedom the molecules of a given gas have. For gas whose molecules have n degrees of freedom, we therefore have:

$$E_{k\acute{s}} = \frac{nkT}{2}\,.$$

2. CONSTRUCTION OF THE EXPERIMENTAL SETUPS

The "Gas Laws" application simulates gas processes.

2.1 Isothermal transformation



The appearance of measuring apparatus for the Boyle-Mariotte law

The measurement setup for the analysis of Boyle-Mariotte law is shown in the diagram above and consists of the following parts:

1. the hermetic air vessel with the piston,
2. pressure gauge
3. thermometer
4. pressure valve.

The principle of operation of the measuring system is based on the possibility of compressing the gas in a closed vessel by changing the volume occupied by it. We make a change in volume with a movable piston. As a result of the movement of the piston, there is a change in pressure inside the vessel. The temperature of the gas in the vessel during the experiment is constant and equal to the ambient temperature, and therefore the basic assumption when examining Boyle-Mariotte's law is fulfilled. During the experiment, one measures the volume, the pressure, and the temperature. The volume is read from the scale placed next to the vessel with the gas. A pressure gauge is used to measure the pressure. A digital thermometer with a display that measures temperature with an application thermocouple is used to measure the temperature. A thermocouple is an element that quickly adopts the ambient temperature with which it comes into contact. In the figure above, it is a gray element connected to the thermometer. In the exercise, the ambient temperature is measured, which is equal to the temperature of the gas in the vessel.

2.2 Isobaric process

The appearance of the measurement setup for analysis of the Gay-Lussac's law

The Gay-Lussac law analysis system that is shown in the diagram above consists of the following parts:

1. hermetic air vessel with piston,
2. pressure gauge
3. thermometer
4. pressure valve,
5. water tank with thermostat.

The principle of operation of the measurement system is based on the possibility of controlling of the volume of gas in a closed vessel by changing the temperature. For this purpose, a vessel with a movable piston placed in a water tank attached to the heating system (electric heater) was used. The water in the tank is the heat reservoir for the gas vessel. This means that the gas temperature in the vessel tends to be the temperature value of the surrounding water. The change in water temperature occurs as a result of the operation of the electric heater, which can be started by means of a thermostat control knob. A thermostat is a device that controls the operation and power of an electric heater, the value of which is selected so as to obtain and then maintain the temperature at the set level. The thermostat knob is used to set the water temperature in the tank; the red LED indicates that the heater is on (that is, the changing temperature), while the green indicates that the set temperature has been reached. The user also has the possibility to adjust the heating and cooling speed of the water in the thermostat. As a result of the temperature change, there is a change in the pressure inside the vessel, which then pushes on (or sucks in) the moving piston, thereby moving it. Changing the position of the piston and thus the volume of gas in the vessel changes the pressure value, which tends to the ambient pressure value, which balances the push force of the piston. As a result, the gas pressure during the experiment is constant. During the experiment, the volume, pressure and temperature are measured. The volume and the pressure measurements are performed identically in Boyle-Mariotte's experiment. Temperature measurements are also the same as in the Boyle-Mariotte law experiment, except that the thermocouple is placed in water whose temperature is equal to the temperature of the gas in the vessel.

2.3 Isochoric process

The appearance of the measurement setup for analysis of Charles's law

The measurement setup for the analysis of Charles's law is shown in the diagram above and consists of the following parts:

1. hermetic air vessel,
2. pressure gauge
3. thermometer
4. pressure valve,
5. water tank with thermostat.

The principle of operation of the measurement system is based on the possibility of changing the gas pressure in a closed vessel by changing the gas temperature. The change in gas temperature is achieved by placing the gas vessel in a water tank attached to the heating system (electric heater). The water in the tank is the heat reservoir for the gas vessel. This means that the gas temperature in the vessel tends to be the temperature value of the surrounding water. The change in water temperature occurs as a result of the start of the electric heater, which can be started by means of a thermostat control knob. A thermostat is a device that controls the operation and power of an electric heater, the value of which is selected so as to obtain and then maintain the temperature at the set level. The thermostat knob is used to set the water temperature in the tank, the red LED indicates that the heater is on (that is, the changing temperature), while the green indicates that the set temperature has been reached. The user also has the ability to adjust the heating and cooling speed of the water in the thermostat. As a result of the temperature change, the pressure inside the vessel changes, except that the gas cannot change its pressure as a result of the change in volume, as it is constant. The experiment measures volume, pressure and temperature.

3. MEASUREMENTS

In all the experiments, at least 15 measurement points shall be collected over the entire acceptable range of the variable parameter.

3.1 Isothermal process

1. Remove the laptop from the locker and choose Boyle-Mariotte process from the menu above the locker.
2. Remove from the magazine all instruments needed to perform these measurements (remember to select the appropriate process from the menu above the locker).
3. Connect and turn all devices on.
4. Set the ambient **temperature different from** the default.
5. Close the valve.
6. Move the piston.
7. Save the result of the new thermodynamic conditions by clicking Add Measurement.
8. Perform steps 6 to 7 until a minimum volume is reached or until critical pressure is reached, which will be indicated by a warning message.

3. 2 Isobaric transformation

1. Remove the laptop from the locker and choose the Gay-Lussac process from the menu above the locker.
2. Remove from the locker all the instruments needed to perform the measurements (remember to select the appropriate process from the menu above the locker).
3. Connect and turn all devices on.
4. Close the valve.
5. Set the temperature of the thermostat and wait until the green LED lights up.
6. Save the result of the new thermodynamic conditions by clicking Add Measurement.
7. Perform steps 5-6 until the maximum temperature is reached or until critical pressure is reached, which will be indicated by a warning message.

3. 3 Isochoric process

1. Remove the laptop from the locker and choose the Charles's process from the menu above the locker.
2. Remove from the magazine all instruments needed to perform the measurements remember to select the appropriate process from the menu above the locker).
3. Connect and turn on all devices.
4. Close the valve.
5. Set the temperature of the thermostat and wait until the green LED lights up.
6. Save the result of the new thermodynamic conditions by clicking Add Measurement.
7. Perform steps 5-6 until the maximum temperature is reached or until critical pressure is reached, which will be indicated by a warning message.

4. RESULTS

Distribution of tasks:
The exercise consists of three independent **parts. Each of the team members performs ONLY one of them.** The breakdown is as follows (order of people according to the students' list):

1, 4, 7,... a person from the group performs the experiment: "Boyle-Mariotte's Law - constant temperature.
2, 5, 8,... a person from the team performs the experiment: "Gay-Lussac Law" - constant pressure.
3, 6, 9,... a person from the team performs the experiment: "Charles's Law" - a constant volume.

4.1. Results analysis

1. The measurement results are displayed on the virtual laptop screen, and the graph and the table with measurement data are created in a separate notepad window. The results of the measurements can be exported to excel or a text file by right-clicking on the laptop screen with the result displayed.
2. The results of the measurements are always affected by uncertainty (according to the general theory of the measurement), at least equal to the smallest scale on the measurement gauge or higher for one order of magnitude (please ask the tutor for details).
3. Be sure to convert the measurement results to basic units of the SI system (pascals, kelvins, cubic meters) **BEFORE** calculations.
4. Determine the values to be found on the X and Y axes and their uncertainties $u(x_i)$ and $u(y_i)$ for each measurement point. Note that the dependency y(x) is to be linear, and the slope coefficient must be equal to the searched value R. The optimal choice of y(x) dependencies is the selection of variables on the X and Y axes so that the slope coefficient of the straight line is directly equal to the value of the gas constant R.
5. Show the measured values in the graph on which this relationship will be linear. Draw the graph with the uncertainty of each measurement point. The graph should occupy at least half of page A4, and preferably the entire page so that you can see measurement points, uncertainty sections, pasted fitting results, axis labels, etc.
6. Make linear fitting ax+b. Each fitting software provides, in addition to coefficients a and b, their uncertainties u(a) and u(b). **These are type A uncertainties.** Based on the fitting results, determine the most likely value for R and u(R). This will be type A uncertainty for R.
7. Calculate u(R) for one **selected measurement** point, i.e. type B **uncertainty.**
8. Combine both uncertainties.
9. Calculate extended uncertainty.
10. Save the final result and compare it with the reference value.
11. During the fitting, one should also get the value of chi ^2. If the program does not calculate **it, calculate it yourself** (based on the definition).
12. Write conclusions based on the result of the chi^2 test and the calculated R value.