

## PRACTICAL 6

### DETERMINATION OF $C_p/C_v$ OF AIR BY THE CLÉMENT-DESORMES METHOD AND CALCULATION OF THE CHANGE OF THE ENTROPY IN DIFFERENT PROCESSES

**Objective:** experimental determination of the heat capacity ratio  $C_p/C_v$  for air and the calculation of the change of entropy of an ideal gas in different processes.

**Equipment & accessories:** a glass vessel with a valve, a hand pump, a manometer.

#### INTRODUCTION

To describe the behavior of thermodynamic systems, Clausius introduced the state function, which he called an entropy. If the system receives the heat  $dQ$  from surrounding bodies (or gives it back), then the change of the entropy is determined as

$$dS = \frac{dQ}{T}. \quad (1)$$

Equation (1) is valid for equilibrium processes. For non-equilibrium processes

$$dS > \frac{dQ}{T}. \quad (2)$$

In case of an equilibrium adiabatic ( $dQ = 0$ ) process, according to Eq. (1),  $dS = 0$ , i.e., the entropy is not changed. Therefore, this process is also called *isentropic*. In case of a non-equilibrium adiabatic process, the entropy is increased, according to Eq. (2).

The entropy is a function of the state, i.e., its change does not depend on the type of process, but it is uniquely determined by the values of macroparameters in the initial state 1 and the final state 2:

$$\Delta S = \int_1^2 \frac{dQ}{T}.$$

The integral can be taken along any equilibrium “path”. The entropy of the system can be expressed in terms of a pair of macroparameters:  $(p, V)$ ,  $(p, T)$  or  $(V, T)$ .

For an ideal gas, described in the variables  $(p, V)$  and  $(p, T)$ , the entropy is determined by the equations:

$$S(p, V) = \nu(C_V \ln p + C_p \ln V) + \text{const}, \quad (3)$$

$$S(p, T) = \nu(C_p \ln T - R \ln p) + \text{const}', \quad (4)$$

it is defined up to an additive constant. Here  $\nu$  is the number of moles of a gas,  $R$  is the universal gas constant, and  $C_V$  and  $C_p$  are the molar heat capacities at constant volume and at constant pressure, respectively.

In contrast to the entropy, the heat capacity of gases substantially depends on the type of process, i.e., it is a function of the process, not a state. Hence, depending on the process, the heat capacity can be positive, negative, infinitely large, or even equal to zero.

If during the whole process the heat capacity of the gas is unchanged, then such a process is referred to as *polytropic*. For an ideal gas, the equation of a polytropic process is:

$$pV^n = \text{const}, \quad (5)$$

where  $n$  is a real number that is called the polytropic index. The molar heat capacity of a gas  $C$  in the polytropic process is associated with the value of  $n$  by the equation:

$$C = \frac{nC_V - C_p}{n-1}. \quad (6)$$

In case of the equilibrium adiabatic process,  $C = 0$ , and, as it can be seen from (6), the polytropic index is equal to the ratio  $C_p/C_V$  referred to as the *adiabatic constant*  $\gamma$ :  $\gamma = C_p/C_V$ . The equilibrium adiabatic equation for an ideal gas (Poisson's equation):

$$pV^\gamma = \text{const}. \quad (7)$$

The adiabatic constant  $\gamma$  is uniquely determined by the heat capacity  $C_V$  and  $C_p$  of an ideal gas, because they are related by the Meier equation  $C_p - C_V = R$ . Therefore, the heat capacities are

$$C_V = \frac{R}{\gamma-1}, \quad C_p = \frac{\gamma R}{\gamma-1} \quad (8)$$

According to the conclusions of the classical molecular-kinetic theory of ideal gases,  $C_V$ ,  $C_p$  and  $\gamma$  are determined by the number of degrees of freedom  $i$  of gas molecules:

$$C_V = \frac{i}{2}R, \quad C_p = \frac{i+2}{2}R, \quad \gamma = \frac{i+2}{i} \quad (9)$$

In this Practical, you will experimentally determine the adiabatic constant of the air and the entropy change of a some air mass in different processes, and you will also calculate the air molar heat capacity in some processes.

One of the simplest methods for definition  $\gamma$  for gases is the method of adiabatic expansion (the method of Clément-Desormes). The method is as follows. In a vessel with a water-pipe manometer for measuring the pressure in this vessel and a valve for connecting the air in the vessel with the atmosphere, a little amount of the air is pumped when the valve is closed. In some time, the air temperature in the vessel will become equal the room temperature  $T_1$ , the pressure  $p_1$  will be slightly higher than atmospheric pressure (the first state of the gas).

Then the valve is opened and it is closed again at the moment when the pressure  $p_2$  in the vessel becomes equal to the atmospheric pressure (and this should be done as quickly as possible so that the heat exchange occurring during this time through the vessel walls can be neglected). As a result of adiabatic expansion, the air temperature in the vessel will drop to  $T_2$  (the second state of the gas).

In time, the air temperature in the vessel will rise and reach the room temperature  $T_1$ , the pressure will rise to the value of  $p_3$  (third state).

The transition of the gas from the first state to the second occurs adiabatically and obeys the Poisson equation (7), which in this case it is convenient to write in the variables ( $p$ ,  $T$ ):

$$\frac{p_1^{\gamma-1}}{T_1^\gamma} = \frac{p_2^{\gamma-1}}{T_2^\gamma}. \quad (10)$$

The isochoric transition from the second state to the third can be described by the Gay-Lussac equation:

$$\frac{p_3}{T_1} = \frac{p_2}{T_2}. \quad (11)$$

Excluding temperature from equations (10) and (11), we find:

$$\left(\frac{p_1}{p_2}\right)^{\gamma-1} = \left(\frac{p_3}{p_2}\right)^{\gamma}.$$

Substituting into this equation the values of the pressures  $p_1$  and  $p_3$ , expressed through the atmospheric pressure  $p_2$  and the difference of the columns of water in the manometer:

$$p_1 = p_2 + \rho gh_1, \quad p_3 = p_2 + \rho gh_2 \quad (\rho - \text{density of water}),$$

we get:

$$\left(1 + \frac{\rho gh_1}{p_2}\right)^{\gamma-1} = \left(1 + \frac{\rho gh_2}{p_2}\right)^{\gamma}.$$

The components  $\frac{\rho gh_1}{p_2}$  и  $\frac{\rho gh_2}{p_2}$  are significantly less than one, so with sufficient accuracy, the parts can be limited to only the first two members of the binomials, which gives:

$$1 + \frac{\rho gh_1}{p_2}(\gamma-1) \approx 1 + \frac{\rho gh_2}{p_2}\gamma.$$

Hence it is easy to obtain a formula for the calculation  $\gamma$ :

$$\gamma \approx \frac{h_1}{h_1 - h_2}. \quad (12)$$

If the gas expands from the first state to the second more slowly, then due to the flux of heat from the environment, the process will not be longer adiabatic, but it can be considered as polytropic, since the relative change in state parameters is very small (about  $10^{-2}$ ). In this case, instead of the Poisson equation (7), one should use the polytropic equation (5), which differs from (7) only by replacing  $\gamma$  with  $n$ . Therefore, using the values of  $h_1$  and  $h_2$ , we can calculate the polytropic index  $n$  using a formula similar to (12):

$$n \approx \frac{h_1}{h_1 - h_2}.$$

## DESCRIPTION OF EXPERIMENTAL SETUP

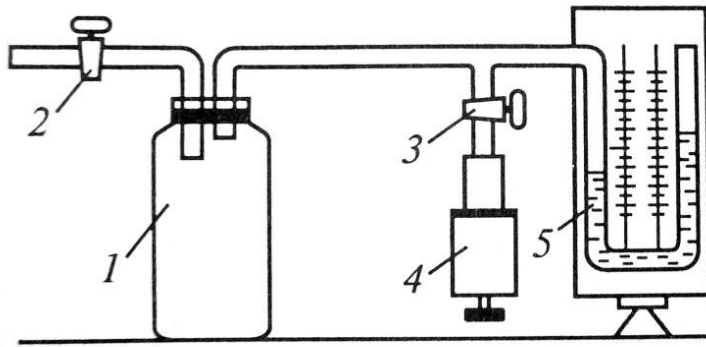


Fig. 1. Experimental setup

The scheme of the experimental setup for determining the ratio of the heat capacities of air by the Clément-Desormes method is presented in Fig. 1.

The thin-walled vessel *1* of a capacity of 25 liters is connected to a water-pipe manometer *5* and a hand pump *4*. It also can be connected to the atmosphere with the help of a valve *2*. The valve *3* allows isolating the pump *4* from the vessel *1*. The excess air pressure in the vessel *1* in comparison with the atmospheric pressure is measured by the manometer *2*.

## MEASUREMENTS AND PROCESSING RESULTS

### Task 1. Determination of the adiabatic constant $\gamma$ of the air

1. With the closed valve *2*, using the hand pump, fill the balloon with air up to pressure  $p_0$  above atmospheric that corresponds to  $h_0 = 20 - 30$  cm, difference in levels of the water-pipe manometer. Then, shut the valve *3*. Write down the value of  $h_0$  in the protocol.

During the pumping, the temperature in the vessel is increased slightly. Wait until the temperature in the vessel, due to the isochoric cooling, returns to the room value  $T_1$ .

Make sure that the water in the manometer stops moving, and write down the difference between the levels  $h_1$  in the protocol.

Quickly open the valve 2, and as soon as the water in the columns of the manometer will be at the same level, close it (this alignment takes place almost instantly).

Again, wait for the establishment of thermodynamic equilibrium with the environment and determine the manometer pressure  $h_2$ .

Calculate the value of  $n$ .

Repeat the experiment 5-6 times. Present the results of measurements and calculations in the form of a table.

Find the theoretical values of the adiabatic constant of the air, considering that the air is almost entirely composed of diatomic molecules. The values of  $n$  obtained in the experiment usually correspond to the range (1.30 - 1.35), which indicates that the expansion process is not close to an adiabatic type. The larger the obtained value of  $n$ , the closer the process to the adiabatic.

Choose from a series of 1.1 the measurement with the largest value of  $n$ . This number can be considered as the experimental value of the adiabatic constant  $\gamma$ .

2. Repeat the experiment 2-3 times, slowly turning the valve 2 (so that the expansion lasts a few seconds until the atmospheric pressure is established).

For each experiment, calculate the value of the polytropic index  $n$  and make sure that the values obtained are smaller than in the series of experiments 1.1.

3. Select from series 1.1 and 1.2 the largest and smallest values of  $n$ , respectively. Calculate the molar heat capacities  $C$  in the fast and slow expansion processes (use the theoretical values for air as  $C_V$  and  $C_p$ ). Is  $C$  positive or negative in these processes? In which process it is more non-zero – in a fast one or a slow one? Explain the result.

## Task 2. Calculation of the change of entropy of the air mass in different processes

1. Using the equation (3) for entropy with the parameters ( $p$ ,  $V$ ), calculate the entropy change of air in the vessel  $\Delta S_1$  during its isochoric cooling after the end of pumping to room temperature. To calculate, use the results of the experiments of the first series.

Predetermine with the Mendeleev-Clapeyron law the number of moles of air  $\nu_1$  in the vessel after pumping (use laboratory devices values to determine the room temperature and the atmospheric pressure.).

Calculating  $\Delta S$ , it should be noted that the relative changes in the parameters are small, so you can use the equations for approximate calculations:

$$\ln(1+x) \approx x, \quad \frac{1}{1+x} \approx 1-x, \quad x \ll 1.$$

2. Calculate the change in entropy  $\Delta S_2$  of the initial amount of gas  $\nu_1$  during its rapid expansion. To calculate, use the results of the same experiment as in the previous step. In this case, it is more convenient to use the expression (4) for entropy through the coordinates ( $p$ ,  $T$ ).

Pre-calculate the temperature  $T_2$  in the vessel after the end of the rapid expansion (it is easily calculated using the data of the subsequent isochoric heating).

Compare the obtained value  $\Delta S_2$  with the expected theoretical value. Would we get  $\Delta S_2$  exactly zero if we could expand arbitrarily fast?

3. Calculate  $\Delta S_2$  at a slower expansion based on the results of one-two experiments of the second series.

Has the entropy increased or decreased during this process? Explain this. How are the speed of the expansion process and the change of entropy related?

## QUESTIONS AND EXERCISES

1. Using the data from one of the experiments, calculate: the mass of air that is pumped into the balloon; the temperature of the air that is heated up as a result of pumping; the mass of air released from the vessel when you open the valve.
2. Calculate  $\gamma$  air at 100% humidity, normal pressure and room temperature. In which case the influence of water vapor and the heat capacity of air can be significant?
3. Based on the first law of thermodynamics, obtain the equation of the polytropic process (5).
4. Based on the Poisson equation, obtain the adiabatic process equation in the coordinates  $(V, T)$  and  $(p, T)$ .
5. At what values of the polytropic index the gas is heated during the compression? Cooled during the compression? Is its heat capacity negative?
6. The process of expansion of an ideal gas is described by the equation:  
a)  $pV^2 = \text{const}$ ; b)  $p^2V = \text{const}$ . Is the gas heated or cooled in this process? Receives or gives the heat back? Is its heat capacity positive or negative?
7. Calculate  $\gamma$  for a mixture containing:  
a) 16 g of oxygen and 11 g of carbon dioxide;  
b) 2 moles of helium and 0.5 moles of oxygen;  
c) 30% (by mass)  $O_2$  and 70%  $N_2$ .
8. Does the entropy of gas increase or decrease in processes: isobaric expansion, isothermal expansion, isochoric cooling, adiabatic expansion into the void?
9. How does the heat capacity of  $C_V$  gases depend on temperature? How is this dependence explained by quantum theory?