

Carbon Dioxide Solubility in Water

Recommendations Regarding the Experiment

There are two long exercises in the proposed experiment. Exercise 1.5 and exercise 2.1 in total may take more than three hours to complete. Consider this fact when allocating time and responsibilities to the participants during the experiment.

Part 1: Reference Points

Exercise 1.1: Gas compressibility measurement

Use a sticky tape to attach the long straightened PVC tube to the table. Attach the measuring tape next to the tube (see Fig. 1).

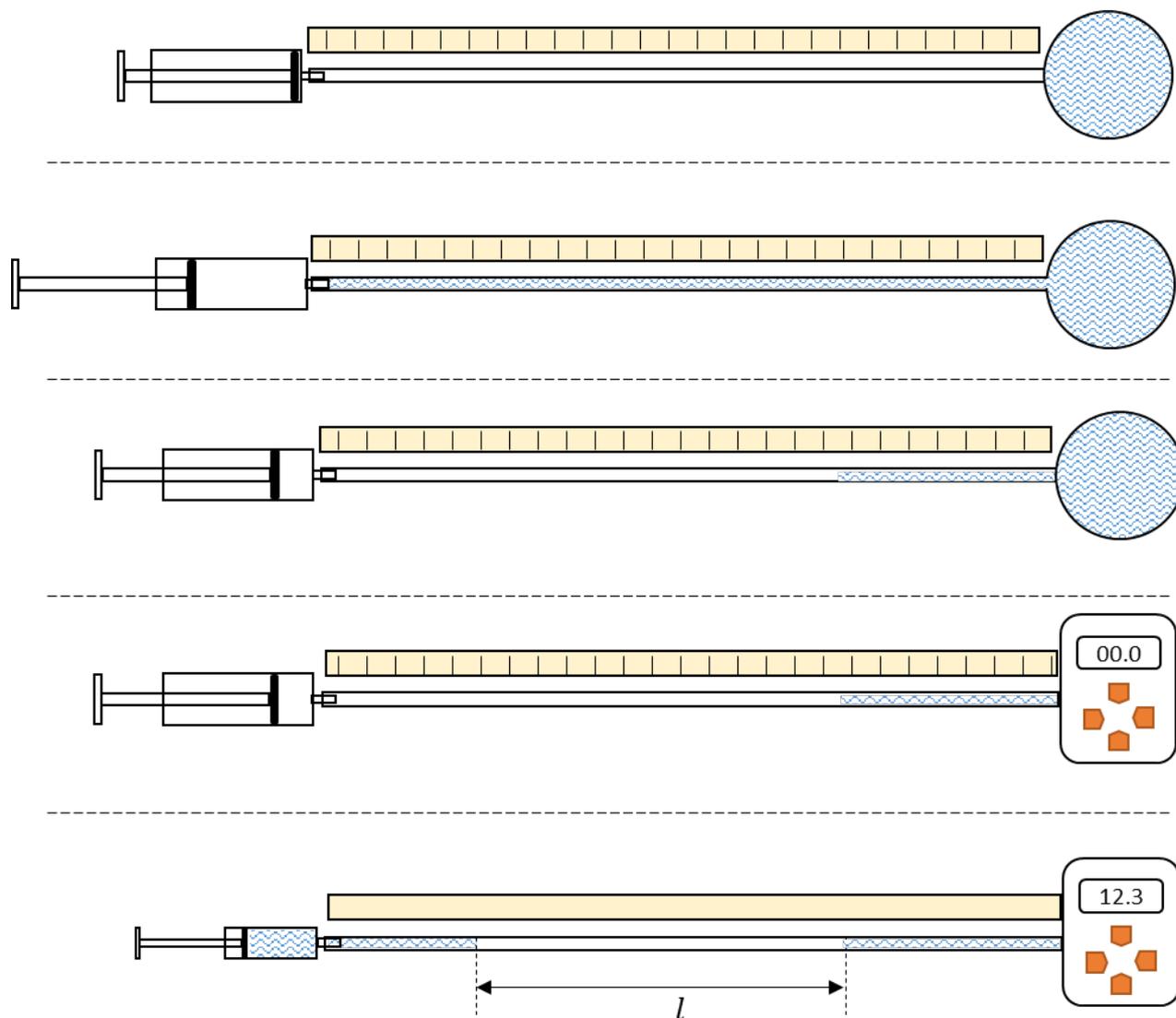


Fig. 1. Preparation for measuring the dependence of length l of air column in the tube versus additional pressure

Using a 20-ml syringe, fill the tube fully with water by lowering the open end of the tube into a cold water box. After that, squeeze out a part of water from the tube so

that completely filled is only a part of the tube, which is close to a tube end. Connect this end of the tube to the manometer. Disconnect the 20-ml syringe from the tube. Fill with water the 5-ml syringe and attach it to the other end of the tube, where the larger syringe was attached and where there is no water. Press the syringe piston to create additional pressure in the tube. Experimentally obtain the relationship between the air column length l inside the tube and additional pressure Δp in it. Enter the measurement results in the table. Get at least 7 experimental points in the whole range of possible pressures.

In a few words in English (or Russian), or by means of symbolic drawings, explain the main reason why the edge of the water column that is closer to the manometer moves when the pressure changes. In this connection note the description of the manometer.

Exercise 1.2: Measuring the expansion coefficient of plastic tube

Use a 20-ml syringe to measure the inner volume v_0 of the tube. Also measure the length L of the tube. Calculate the cross-section area s_0 of the tube channel.

If additional pressure is created inside the plastic tube then the cross-section area of the tube channel changes. Suggest a method to reliably measure the relative change in cross-section area $\Delta s / s_0$ as a function of additional pressure Δp in the tube. Explain the proposed method with the help of drawings similar to those shown in Fig. 1; make annotations to all the elements in your drawings. Measure the above relationship by obtaining at least 7 experimental points in the whole possible range of positive additional pressures in the tube. Draw a graph of the relationship obtained. Determine the slope of the graph.

Exercise 1.3: Boyle-Mariotte's Law

According to the Boyle-Mariotte law, additional pressure Δp inside the tube is related to the volume V of air in it:

$$p_0 V_0 = (p_0 + \Delta p) V, \quad (1)$$

where V_0 is the initial volume of gas inside the tube, p_0 is a certain constant.

Using the results of previous measurements, calculate the relationship between Δp and V_0/V and plot it. Determine the slope of the graph and its intercept. Find p_0 from the obtained data. Do not forget to take into account the initial additional pressure inside the tube, which appears when the 5-ml syringe is inserted into it.

Exercise 1.4: Comparison with atmospheric pressure

Compare the value of p_0 obtained in exercise 1.3 with the atmospheric pressure p_a written on the blackboard in the classroom. Do these values coincide? Should the precisely measured value of p_0 coincide with the atmospheric pressure? If you believe there should be a discrepancy, explain the reason behind it in a few words in English or Russian.

Exercise 1.5: Deviation from Boyle-Marriotte's law

Sparkling water is the water in which carbon dioxide (CO_2) is dissolved. If a sealed bottle is partially filled with such water then there is a CO_2 gas above the water surface. This gas can be mixed with air and/or with saturated water vapor. In the stationary state, the rate of carbon dioxide release from water will be equal to the rate of carbon dioxide return from the gas phase into the water. In this case, the concentration of carbon dioxide both in water and in the gas phase will not change, and the partial pressure of carbon dioxide in the gas phase also will not change.

The amount of gas dissolved in water in stationary conditions is proportional to the partial pressure of carbon dioxide above water and to the volume of water. The number of moles of gas dissolved in water under stationary conditions can be expressed as

$$v_w = \frac{\alpha p V_w}{RT_0} \quad (2)$$

where p is the equilibrium partial pressure of carbon dioxide above water, V_w is the volume of water, R is the molar gas constant, $T_0 = 273,15 \text{ K}$ is the temperature corresponding to zero degrees Celsius. The quantity α is the solubility of carbon dioxide in water.

If, for some reason, the amount of gas dissolved in water is larger than the equilibrium value given by formula (2), then the rate of gas release from water will exceed the rate of gas dissolution in water. Therefore, the amount of gas dissolved in water will decrease while the partial pressure of carbon dioxide above water will increase. This process will continue until the carbon dioxide partial pressure above water and the amount of gas dissolved in water are related by equation (2), which means that the equilibrium state has been established.

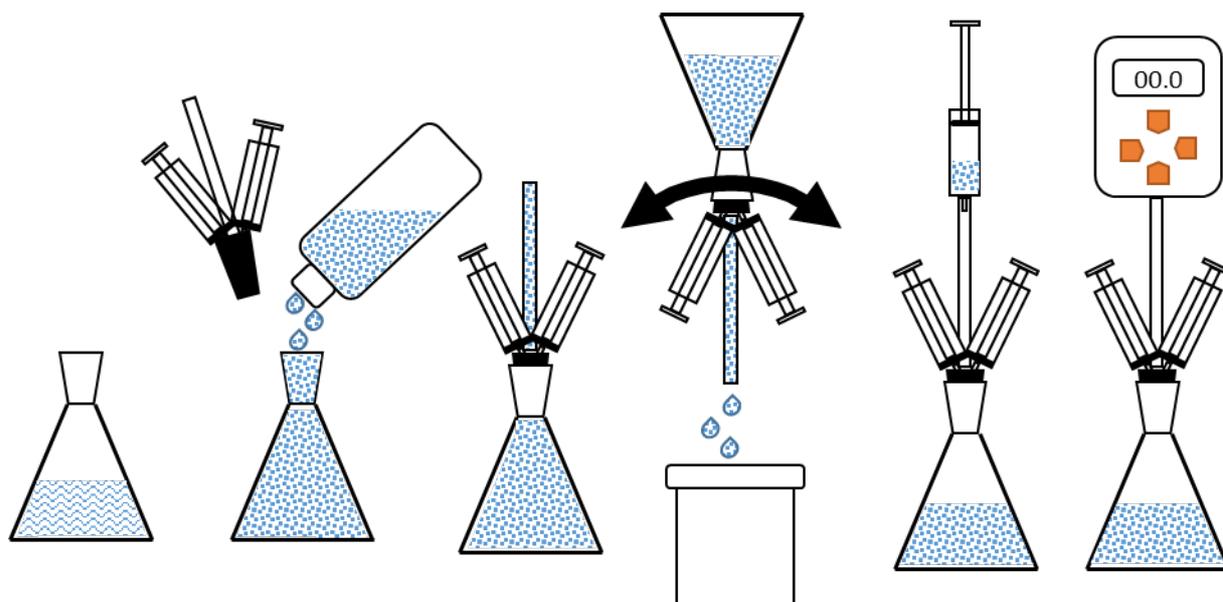


Fig. 2. Preparation for measuring the solubility of carbon dioxide in water

Measure the volume of one of the flasks closed with a plug. Measure the volume of the tube used to connect the flask with the manometer. The internal volume of the manometer inlet is approximately 0.5 ml.

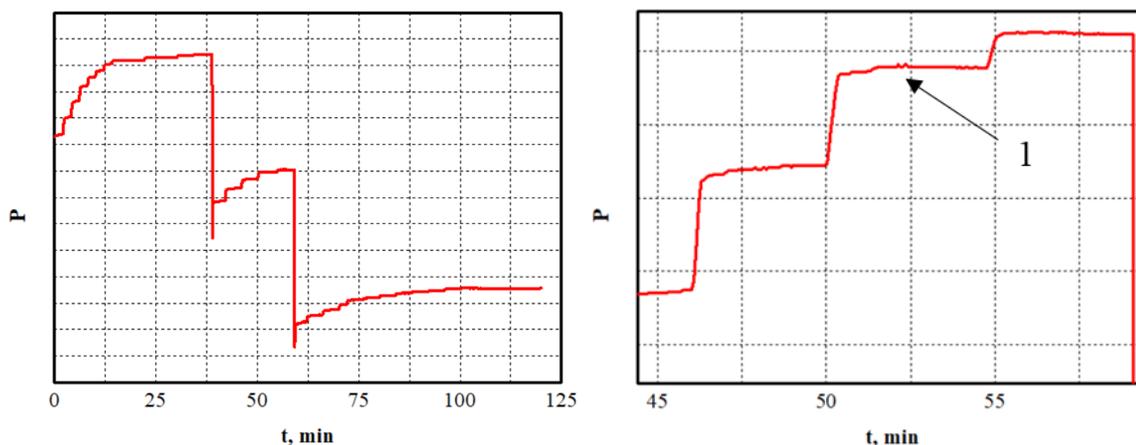
Pour 10 ml of water into this flask (Fig. 2). Add sparkling water from the bottle to the flask so that no air remains in it. Close the flask using the plug with syringes and tube inserted in it to connect it to the manometer. Turn the flask over and shake it while pointing the tube into the water box. The water will begin to flow out through the tube. If water starts flowing into the syringes inserted in the plug, press down on their pistons to return the water back to the flask. In this way, pour so much sparkling water and regular water out of the flask that there is approximately 40-50 ml of liquid left in the flask. Pinch the tube with a plastic clip. Then connect another 20-ml syringe to the tube and open the clip. Pull the piston of the syringe connected to the flask via the tube to the "10-ml" mark, thus sucking out of the tube the remaining water and small amount of carbon dioxide from the flask. Pinch the connecting tube again with the plastic clip, disconnect the syringe and connect the tube to the manometer. Return the clip to the open position. Now you have a flask with carbonated water containing practically no air above the surface.

Pour some hot water from the water bath into the water box so that the water temperature in the box is close to room temperature. Immerse the flask into the water box and fix the flask with a support stand so that it touches the bottom of the box and is almost completely immersed in water. Leave the flask in water for 5 minutes to establish a thermodynamic equilibrium between the contents of the flask and the water box.

In this experiment you will be required to measure the equilibrium pressure of carbon dioxide above water. It may take dozens of hours for the equilibrium state to establish. To speed up the equilibration process, you may slightly shake the water flask. The rate of carbon dioxide escape from water will increase and the partial pressure during the shaking will increase much quicker than it would have been if the flask had been left at rest. However, due to shaking, the carbon dioxide partial pressure may increase too much, exceeding the equilibrium pressure. Therefore, shake the water flask for 15 seconds so that the pressure does not become higher than the equilibrium pressure. After shaking, the water in the flask will keep moving for 2-3 minutes, i.e. it will not be in a stationary state. Therefore, after shaking wait for more than 3 minutes so that after water has stopped moving in the flask you can observe whether the pressure in the flask will rise or fall. It is suggested that the waiting time be 4 minutes and 45 seconds, so that the full cycle of shaking and waiting is 5 minutes. If pressure in the flask increases in the last minutes of waiting, it means that the gas pressure is still lower than the equilibrium pressure. Then the flask must be shaken again. If pressure in the flask does not change during the last minutes of waiting, it means that the pressure is close to equilibrium. If pressure in the flask drops in the last minutes of waiting, it means that the pressure is higher than the equilibrium pressure and we missed the equilibrium pressure.

Disconnect the flask from the support stand. Gently stir water in the flask for 15 seconds with rotating movements, so that most part of the flask remains submerged in water. Place the flask back on the bottom of the box and secure it again in the submerged position with a support stand. Wait 4 minutes 45 seconds, and then repeat all the operations again. Observe the pressure in the last 2 minutes of waiting. If the pressure in the flask increases, stir water in the flask again and wait for 4 minutes 45 seconds again. Continue this cyclic experiment until you see that the pressure has stopped changing in the last 2 minutes of waiting. Then stir water in the flask once more to make sure that the pressure starts dropping during the last two minutes of waiting. **Write down the manometer reading corresponding to the equilibrium pressure in the flask (see Fig. 3).**

Pull the piston of the first syringe out to the "20-ml" mark and fix it with a lock-pin (see equipment description); repeat the experiment with stirring water in the flask. **Write down the new equilibrium pressure.** Pull the piston of the second syringe out to the "20-ml" mark and repeat the experiment.



**Fig. 3. Typical view of the graph of pressure in the flask versus time.
1-equilibrium pressure**

Please note that due to diffusion, the amount of carbon dioxide in the flask is slowly reducing. That is, in the resulting state of equilibrium, the actual gas escape rate from the liquid will balance the sum of two rates: the rate of gas dissolution in liquid and the rate of diffusion flow of molecules from the flask. However, we will assume that the obtained pressure satisfies equation (2).

Exercise 1.6: Calculation of carbon dioxide solubility at room temperature

Write down a formula for the total number of carbon dioxide moles in the flask as the sum of the number of moles in the gas phase and in the dissolved state. For this purpose use the following notations: V_w as the volume of water in the flask, V as the volume of gas phase, p as the equilibrium partial pressure of carbon dioxide above water, T as the temperature of water and gas in the flask, $T_0 = 273.15$ K, R as the universal gas constant, and α as the solubility of carbon dioxide in water.

Let's assume that during the experiment the total number of carbon dioxide moles in the flask is constant.

When the negative inlet of manometer is open, the pressure measured by the manometer is the difference between the pressure in the flask and the atmospheric pressure p_a . Write down a formula for the carbon dioxide partial pressure in the flask as a function of the manometer reading Δp . When deriving the formula, remember what the gas phase consists of. Calculate the product pV (equilibrium pressure of carbon dioxide in the flask by the volume of its gas phase) versus the equilibrium pressure of carbon dioxide.

Draw a graph of the obtained relationship $pV(p)$. Calculate its slope.

Write down the water temperature in the box during the measurements. Remove the plug from the flask. Measure the volume of water in the flask using an electronic scale (take the water density as 1 g/cm^3). Calculate the carbon dioxide solubility on the basis of the graph slope and the obtained values of the box water temperature and the volume of water in the flask. Estimate the error of your measurements.

Part 2: Solubility-Temperature Relationship

Exercise 2.1: Measuring the temperature dependence of pressure in humid flask

Pour 30 ml of plain water into one of the flasks. Close the flask with a thermometer plug. Place the flask in water at room temperature. Wait a few minutes and connect a manometer to the flask. Wait until pressure in the flask stops changing. Write down the manometer reading and the water temperature in the box. Transfer the flask to the water bath. Completely immerse the flask in hot water by placing it inside a metal cylinder with holes, and secure it with the support stand. Wait until a thermal equilibrium is established; record the pressure in the flask and the water temperature in the water bath.

Exercise 2.2: Temperature dependence of water vapor pressure

Based on the data obtained and the results of previous experiments, calculate the change in vapor pressure in the flask Δp_w due to its transfer from the box to the water bath. Write down basic formulas that should be used for this calculation.

Exercise 2.3: Measuring the temperature dependence of pressure in the flask with sparkling water

If you are going to use in this exercise a flask other than the one used in exercise 1.5, then measure its volume. If you are going to use your old flask then just write down its volume again in the answer sheet.

In this exercise use a new bottle of sparkling water that has not yet been opened.

Fill the flask with a mix of plain water and sparkling water using a thermometer plug. Use the method described in exercise 1.5 but with the following slight difference. When removing water from the tube, move the syringe piston to a 20-ml mark to lower the initial pressure in the flask more than you did in exercise 1.5.

Place the flask in a water box at room temperature. Stir and wait several times to achieve equilibrium between gas and water in the flask. Write down the manometer reading corresponding to the equilibrium pressure at room temperature.

Put the flask in the water bath by placing it inside a metal cylinder with holes (this cylinder will prevent water spilling out of the bath while stirring the flask). Carry out an experiment similar to the previous experiment conducted at room temperature. The equilibrium pressure at high temperature cannot be measured accurately because the bath heater is switched on and off periodically. Try to make the best possible estimate of the equilibrium pressure, i.e. the manometer reading corresponding to the equilibrium pressure. After completing the measurement of pressure in the flask placed in the water bath, measure the volume of sparkling water inside the flask.

Exercise 2.4: Carbon dioxide pressure as a function of temperature

Calculate the carbon dioxide partial pressure at room temperature and at water bath temperature based on the data obtained in previous exercises. Write down basic formulas used in this calculation.

Exercise 2.5: Solubility-temperature dependence

Using the carbon dioxide solubility at room temperature as the reference point, calculate the carbon dioxide solubility at the water bath temperature from the data obtained. Write down basic formulas used for such calculation. Does the solubility of carbon dioxide increase or decrease with increasing temperature?