1. Activity of constituents and ions

1.a. Determination of temperature dependence of oxygen solubility in water

When the liquid phase is in contact with the gas phase at a constant temperature and pressure, the components of the solution are evaporated to the gas phase and the gaseous components are simultaneously absorbed by the liquid phase. Dynamic equilibrium exists. The thermodynamic equilibrium state will occur after a certain period of time if the system is closed (ie, there is no mass exchange between the system and surrounding). The activities of the components in the solution and in the gas phase are equal in thermodynamic equilibrium. In this way, the components of the Earth's atmosphere and the hydrosphere behave as well.

The pressure of the standard Earth's atmosphere at sea level is $p_0 = 101325 Pa$. The standard Earth's atmosphere had the following composition in 1962: *78.084% vol of N₂; 20.9476% O₂; 0.934% Ar; 0.0314% CO₂; 0.001818% Ne; 0.000524% He; 0.0002% CH₄* . The composition of the hydrosphere is different, in particular, it vary in content of *NaCl* on land and in the seas.

There is an exchange of components between the water and the atmosphere. The water evaporates and the gases are dissolved in the water. We are talking about 100% oxygen saturation when the equilibrium concentration of oxygen in water is reached at a given temperature and pressure. Actual saturation may vary from 100% because it is influenced by other effects in water and in the atmosphere. Other components such as CO_2 or N_2 behave similarly. As the gas pressure in the Earth's atmosphere is low and the water content in the fresh water is high, it is possible to simplify the behaviour of the components in land water as the *H2O-pure gas* thermodynamic system.

The dissolution of oxygen in the water can be treated as a thermodynamic equilibrium:

$$O_2(g) + H_2O(l) \leftrightarrow O_2(aq) \tag{1.1.}$$

which can be described by the thermodynamic equilibrium constant

$$K_{eq} = \frac{a_{O2}^{aq}}{a_{O2}^{g} a_{H2O}^{l}} \doteq \frac{x_{O2}^{aq}}{p_{O2}^{g}} = \frac{1}{H^{px}} \tag{1.2.}$$

Here some following approximations were done in the eqn (1.2.). The relationship $a_{O2}^{aq} = \gamma . x_{O2}^{aq}$ applies to oxygen activity in water. The activity coefficient γ is near to 1, so the activity can be replaced by a molar fraction of oxygen in water x_{O2}^{aq}. The oxygen activity in the gas phase is given by the relationship $a_{O2}^{g} = f_{O2}^{g}/p_0 = \phi p_{O2}^{g}/p_0 \doteq p_i$, where f_{O2}^{g} is oxygen fugacity and ϕ is fugacity coefficient, which is equal to *1* for low pressure of Earth's atmosphere. It means that the oxygen activity a_{O2}^{g} can be replaced by partial pressure of oxygen p_i in *Atm* unit. Despite a certain amount of dissolved oxygen, water is a virtually pure substance (solvent), its activity is $a_{H2O}^{l} = x_{H2O}^{l} \doteq 1$. The value of H^{px} in equation (1.2.) is so called Henry constant, which depends mainly on the temperature and salt content in water (i.e. salinity).

Considering the accepted activity approximations in eqn (1.2.), the simple relation between the oxygen concentration x_{O2}^{aq} in pure water and its partial pressure p_{O2}^{g} above the level has form:

$$p_{O2}^{g} = x_{O2}^{aq} . H^{px} \tag{1.3.}$$

which is known as Henry's law. The "px" index at Henry's constant indicates that the Henry's equation involve the oxygen partial pressure p_{O2}^{g} above water and oxygen molar fraction in the water x_{O2}^{aq}. The Henry's law can be also written by other formulas that use different concentration units.

The experimental dependence of the Henry's constant on temperature use to be frequently approximated by the function:

$$H^{px} = H_0^{px} \ exp\left[-\frac{\Delta_{sol}H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{1.4.}$$

where $\Delta_{sol}H$ has the meaning of the dilution enthalpy of the oxygen in water. The constants $C_H = -\Delta_{sol}H/R$ and H_0^{px} are given in the tables (see table in **Figure 1**).

The solubility of O_2 (or other gases) decrease with temperature and increases with pressure. The removals of the dissolved gases from the water is carried out chemically (e.g., by sodium thiosulphate in the case of oxygen) or by bubbling with an inert gas (e.g., replacement of oxygen with nitrogen).

Precise determination of dissolved oxygen (DO) concentration in water is possible by titration according to Winkler, but the use of membrane oxygen sensor completed by amperometric signal is much easier. The oxygen sensor contains, in the simplest case, a working electrode (cathode) and an anode. Both electrodes (*Pb* or *Cd*) are immersed in *KOH* electrolyte that is separated from the sample by a selective oxygen-permeable membrane. On the working electrode under given potential, the oxygen molecules are reduced to hydroxide anions. The electrochemical reaction is a source of electrical current between the anode and the cathode. The higher the oxygen concentration in the measured sample, the higher the current signal. For accurate measurements, the instrument should be calibrated to solutions of known concentration of dissolved oxygen.

? **TASK:** Determine the saturation curve of oxygen when bubbling with air and the desaturation curve of oxygen when bubbling with nitrogen. Determine the dependence of oxygen solubility in distilled water on temperature in the range of about *1-35 °C* and compare the experiment with table values for oxygen and other gases.

✂ **LABORATORY AIDS AND CHEMICALS:** distilled water and ice. Instrument for measuring temperature, pH and dissolved oxygen content (eg Orion 4 Star pH / DO). Aeration (aquarium compressor equipped by porous stone). Stopwatch. Electromagnetic stirrer with heating. Beaker (*500ml*). Heat-insulating pad. Liquid nitrogen in thermos flask or other inert gas source.

📄 **INSTRUCTIONS:** Get to know with instrument manual for measuring temperature *t*, dissolved oxygen (DO) and pH in water.

1. **Monitoring oxygen saturation curve at room temperature:**
   a) Pour about *200 ml* of distilled water into a clean beaker. Measure the water temperature. Place the beaker with water on the electromagnetic stirrer. Insert the heat-insulating pad between the beaker and top of electromagnetic stirrer. Make sure the heating is off.
   b) Immerse the sensors (DO, pH) and the aerating stone below the water level. Measure the initial signals: *t* (temperature), *pH*, *DO* (dissolved oxygen in *mg/l*).
   c) Switch the aeration on and start the stopwatch at the same time. Measure the dissolved oxygen content (DO) for *15* minutes at *1 min* intervals.

**d)** Note the temperature and pH at the end.

2. Monitoring oxygen desaturation curve:

a) Use the water from the previous measurement. Make ready the source of nitrogen.

b) Switch the nitrogen bubbling on and follow the instructions in the previous points **1b** to **1d**.

3. Dependence of oxygen solubility on temperature.

a) Prepare the experiment according to the instructions in **1a** to **1b**.

b) Add ice (about *150 ml*) to the beaker.

c) Switch the mixing and aeration on. Wait until the temperature of the water-ice mixture approaches about 1ºC and the oxygen content is stabilized.

d) Replenish (if needed) the ice so that approximately 1 cm layer of ice still floats on the level.

e) At the lowest temperature, perform several measurements (temperature, pH and DO) until the ice is completely melted.

f) Continue the measuring of all signals at higher temperatures while the water is heated by ambient heat. Apply the temperature step about 1C.

g) Remove the heat-insulating pad if the temperature rises slowly between the measurements. Start the heating on of the electromagnetic stirrer if you need to increase the heating rate.

h) Measure until the temperature reaches 35ºC.

DATA ANALYSIS: Calculate the Henry's constants H^{px} for oxygen and at least two other selected gases according to the relationship (1.4.) for 10 temperatures in the range *0-35 °C* (use table in **Figure 1**). Calculate the molar fraction of oxygen and two other gases in water according to Henry's Law (1.3.). Use the laboratory temperature and the partial pressure of gases in the standard Earth atmosphere in calculation. In the same way, calculate the molar fraction of dissolved gases in water for other 10 temperatures ranging from 0-35 °C. Find the water density at 10 different temperatures, the relative mass of water, oxygen and selected gases from the tables. Use the obtained values to calculate the oxygen solubility in water in units of *mg O_2 /dm^{-3}*.

REPORT: Common graph 1: Temperature dependence of Henry's constants H^{px} for oxygen and at least two other selected gases. **Table 1:** under aeration: time, measured values (*t, pH, DO*), degree of saturation (use graph construction in **Figure 1**). **Tabule 2:** under nitrogen bubbling: measured values (*t, pH, DO*), degree of oxygen saturation. **Common graph 2:** Time dependence of oxygen saturation degree when bubbling by air and nitrogen. **Table 2:** time, *t, pH* and *DO* while heating. **Common graph 3:** both measured and subtracted (use **Figure 1**, suppose saturation 100%) dependence of oxygen content in water on temperature. The same calculated temperature dependence for two selected gases (details in "Data analysis" section).
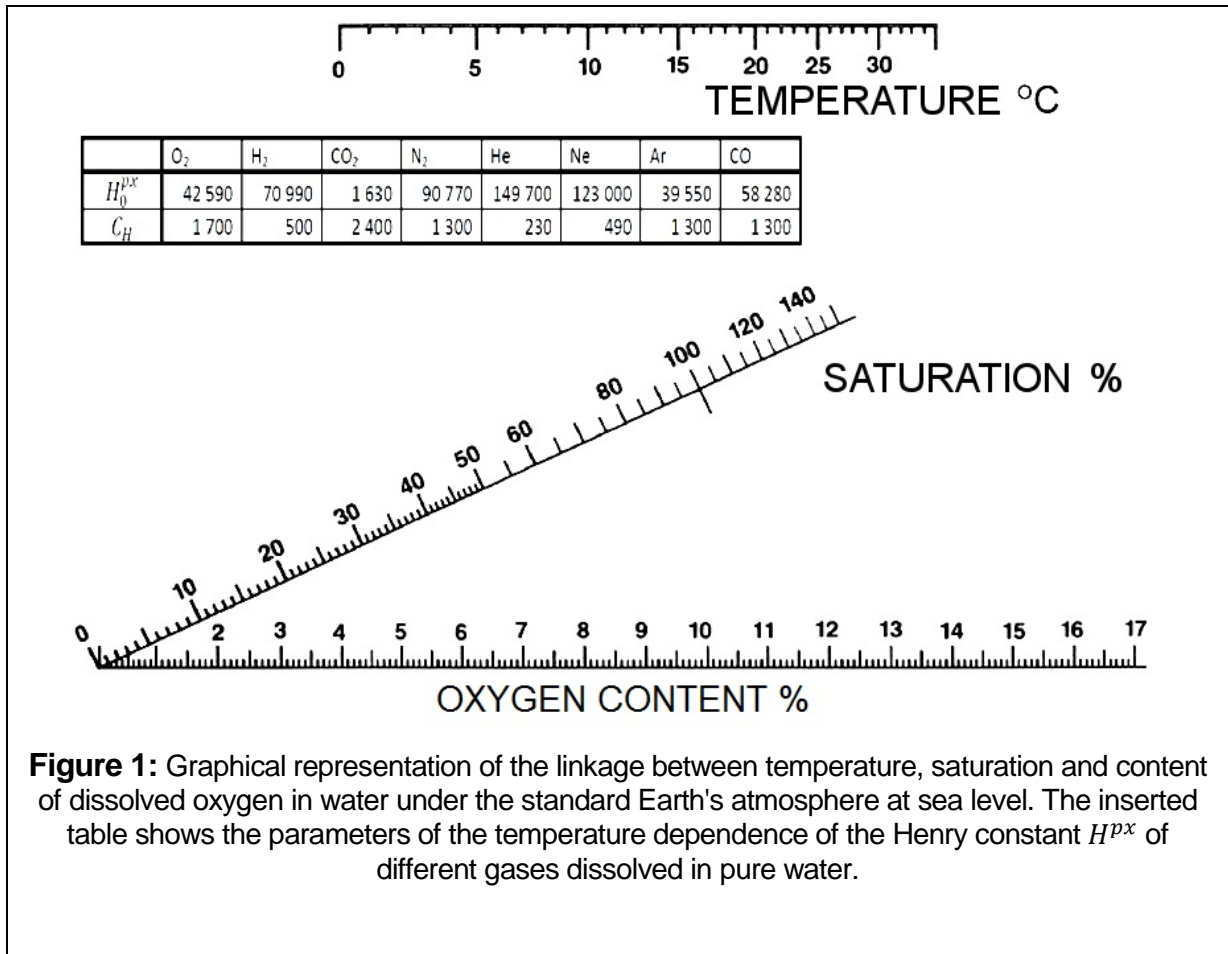
Figure 1: Graphical representation of the linkage between temperature, saturation and content of dissolved oxygen in water under the standard Earth's atmosphere at sea level. The inserted table shows the parameters of the temperature dependence of the Henry constant H^{px} of different gases dissolved in pure water.