1. Matter transport phenomena

1.a. Determination of diffusion coefficient of ammonia inside membrane

The mass transport through the membrane occurs when it is permeable to the substance. An example of selectively permeable membrane may be the cell wall for the metabolites but also the hydrophobic foil of the ion-selective electrode for ammonia.

The membrane separates the outer and inner ammonia solution (see **FIGURE 1**). Ammonia can be generated in the inner solution by release from NH_4Cl solution by the addition of $NaOH$. Ammonia diffuses into an outer solution where it can be neutralized to the NH_4^+ salt by acid. If the acid is weak (e.g. boric acid), the pH changes, which can be observed, for example, by changing the colour of the acid-base indicator.

The amount of ammonia dn that passes through the membrane for time dt (ie diffusion flux) is proportional to membrane area S and concentration gradient dc/dx. This is known as **1ST FICK'S LAW OF DIFFUSION**:

$$dn/dt = -D \cdot S \cdot (dc/dx) \qquad (1.1.)$$

where x is the distance coordinate and D is the diffusion coefficient of the migrating substance. Diffusion coefficient depends on the material of the membrane and on the temperature (to a lesser extent depends on the migrating substance concentration and pressure). The negative sign indicate that the substance flow goes in the direction of decreasing concentration.

FIGURE 1: Experimental scheme: S_i, S_o ... inner and outer solution. M...membrane, T...tube. M_1, M_2...rotary stirring elements. The meanings of the other symbols are in the text.

The diffusion of the substance can be non-stationary or stationary. In the event of the stationary diffusion, the concentration gradient across the membrane is a constant value that can be obtained as $\frac{dc}{dx} = (c_o - c_i)/l$ where c_o and c_i are, respectively, the substance concentrations in the outer and the inner solution at time t, l is the thickness of the membrane. The diffusion boundary conditions are in **TABLE I**.
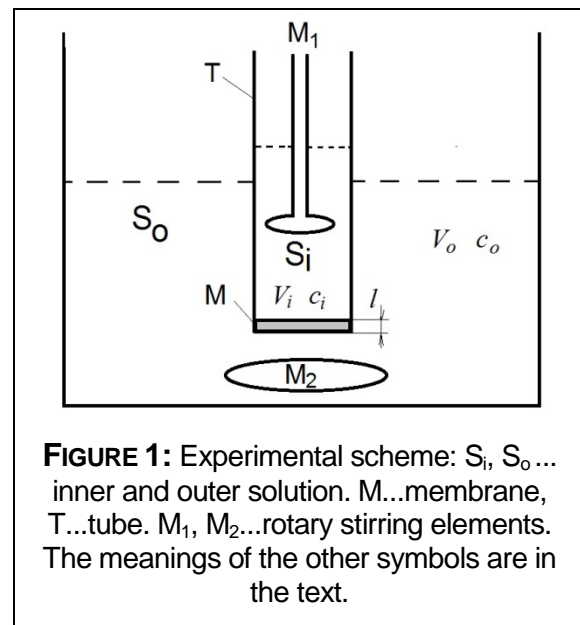
TABLE I: Concentration conditions of stationary diffusion over membrane. $\beta = V_o/V_i$ is the ratio between the volumes of the outer and inner solution. The stationary diffusion occurs immediately.

Time	Inner concentration	Outer concentration
$t = 0$	$c_i^{t=0}$	$c_o^{t=0} = 0$
$t > 0$	$c_i^{t=0} - \beta C$	$c_o^t = C$

Law of Conservation of Matter applied for the stationary diffusion of the substance from inner to outer solution yields the difference in concentrations on both sides of the membrane that is given by an expression $C - (c_i^{t=0} - \beta C) = -c_i^{t=0} + C(1 + \beta)$ which is valid at any experimental time t. The concentration of the substance in the outer solution C is given by expression $C = n/V_i$ where n is the amount of substance that has passed through the membrane. The adjustement provides differential change: $dn = V_i dC$. After inserting these relationships into the 1st Fick's Law (9.1.) we get:

$$V_i \left(\frac{dC}{dt}\right) = -DS \frac{-[c_i^{t=0} - C(1+\beta)]}{l} \tag{1.2.}$$

We separate the variables C, t and we choose the upper and lower bounds of the integrals according to the experimental conditions:

$$\int_0^C \frac{1}{[c_i^{t=0} - C(1+\beta)]} dC = \frac{DS}{l \cdot V_i} \int_0^t dt \tag{1.3.}$$

Integrating this equation provides:

$$-\frac{1}{(1+\beta)} ln \left[\frac{\left(c_i^{t=0} - C(1+\beta)\right)}{c_i^{t=0}}\right] = \frac{DS}{l \cdot V_i} \cdot t \tag{1.4.}$$

$$D = \frac{l \cdot V_i}{St \cdot (1+\beta)} ln \left[\frac{c_i^{t=0}}{c_i^{t=0} - C(1+\beta)}\right] = A \cdot ln \left[\frac{c_i^{t=0}}{c_i^{t=0} - C(1+\beta)}\right] \tag{1.5.}$$

The equation (1.5.) can be used to calculate the diffusion coefficient D of ammonia by data analysis from experiment in **FIGURE 1**.

? **TASK:** Determine the diffusion coefficient of ammonia through the ion selective membrane (producer: ORION co., dimensions: $S = 0.6\ cm^2$, $l = 0.032\ cm$).

✂ **LABORATORY AIDS AND CHEMICALS:** pH-meter with accuracy $\pm 0{,}001pH$, electromagnetic and mechanical stirrer, tube with ammonium permeable membrane, stopwatch, 2 beakers (*100-150 cm³*), 1 beaker (*50 cm³*), 2 volumetric glass pipettes (*25 cm³, 10 cm³*), burette (*10 cm³*), indicator (*0.1% bromocresol green (CAS No: 76-60-8) in ethanol*), stock solutions: *2% H₃BO₃, 0,01M NH₄OH, 0,1M NH₄Cl and 0.1M NaOH.*

📄 **INSTRUCTIONS:** Get acquainted with the use of the pH-meter with the combined glass ion selective electrode.

1. **CALIBRATION MEASUREMENT.** Prepare the base solution of boric acid by mixing *100 cm³* of *2%* boric acid stock solution with *1 cm³* stock solution of indicator. Prepare the base solution of ammonia by mixing *50 cm³* of *0.01mol dm⁻³ NH₄OH* with *0.5 cm³* stock solution of indicator. Pour the *50 cm³* of the base solution of boric acid with indicator into beaker and measure the initial pH. Add the volume *0.5 cm³* of the basic ammonium hydroxide solution to the measured solution and measure the pH. Repeat both the addition of the *0.5 cm³* of the basic ammonium hydroxide solution to the solution and the pH measuring. Make the ten additions in total and perform ten pH measurements.

2. **DIFFUSION COEFFICIENT MEASUREMENT.** Use the remaining basic boric acid solution with the indicator after removing 1ml (ie volume will be exactly 50ml). Put the magnetic stirrer element into solution. Pipette the volume *7 cm³* of *0.1 M NH₄Cl* and *1 cm³* of *0.1M NaOH* into the tube with membrane. Close the tube using the special stopper with mechanical stirrer S_i (see **FIGURE 1**). Switch the mechanical stirrer S_i on. Temporarily remove the unit of the electromagnetic stirrer and coat the beaker with

the basic boric acid solution on the tube from the bottom side. Switch the stopwatches on at this moment. Support the beaker with the basic boric acid solution by electromagnetic stirrer unit. Switch the stirrings on and choice the low rates. Adapt the rotary parts if need. Insert the pH sensor carefully into the outer solution and fasten it to the stand so that the sensor does not come into contact with stirring element. Measure the pH for *20-30* minutes at *30 sec* intervals.

REPORT: The calculated starting ammonia concentration $c_i^{t=0}$ in the tube. **CALIBRATION TABLE 1:** for all additions of ammonia base solution into base solution of boric acid: total volume of ammonia solution added, total volume, calculated ammonia concentration C in the solution, measured pH. **REVERSE CALIBRATION GRAPH 1:** dependence of ammonia concentration on pH. Make the nonlinear regression using the polynomial of grade 3 if need. **TABLE 2:** for all measuring times: *pH*, ammonia concentration C according to the calibration curve, values: factor A and argument of natural logarithm in relation (1.5.), diffusion coefficient. **NEXT:** statistical analysis of the experiment for diffusion coefficient *D* (ie remove the outlying values, consider the trend of *D*, calculate the *95%* Student`s or Normal confidence interval for *D*).