

## 1. Matter transport phenomena



Matter transport occurs most commonly by mechanical and convection movements over long distances or diffusion and migration to smaller distances.

The driving forces of diffusion of molecules, atoms and ions are the gradients of the chemical potentials that can be approximated at ideal conditions by the concentration gradients of the transporting components for uncharged particles. The driving force depends also on external electric field that is important if the migrating component has electric charge.

Diffusion of uncharged component is described by 1<sup>st</sup> and 2<sup>nd</sup> Fick's law if behaviour of component is close to ideal. Important are bound conditions of diffusion. The diffusion problem can be treated numerical or analytical way from mathematical point of view.

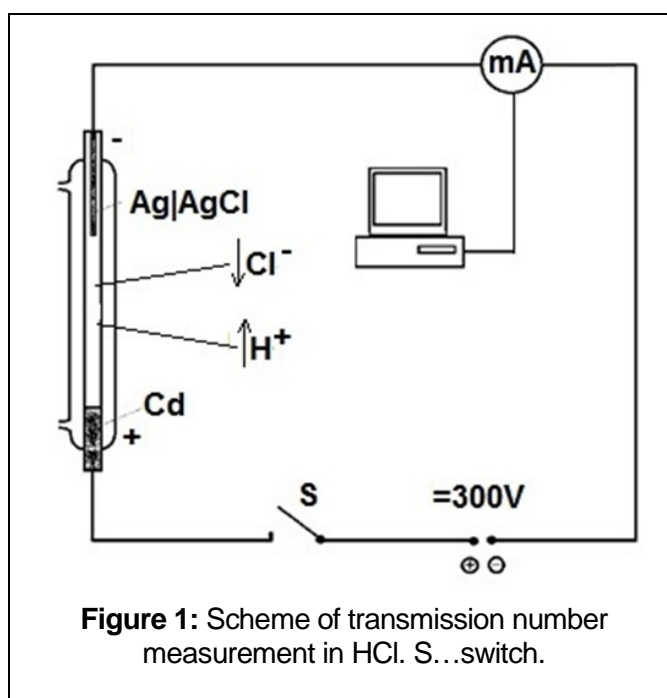
In open systems (e.g., living cells), a stationary diffusion and migration occur frequently. The constant concentration gradients are stabilised within matter transport through the system at stationary state.

### 1.a. Determination of transference number from rate of interface motion



In the same electric field, different ions move with different speeds. That results in special migrating effect. The mixture of two electrolytes, having a common anion (eg  $Cl^-$ ) and different cations, create an interface with a change in cation concentration. The interface moves to the cathode. The solution involving a faster cation (eg  $H^+$ ) is called the leading electrolyte, the solution with slower cation (eg  $Cd^{2+}$ ) is called the indicator electrolyte. Monitoring of this phenomenon is the basis of today's electromigration analytical methods, such as isotachopheresis or capillary electrophoresis.

The monitoring of the interface between electrolytes can be done with a simple experiment (see **Figure 1**). The leading electrolyte is a solution of hydrochloric acid (coloured by crystal violet). The indicator electrolyte is a solution of  $CdCl_2$  which is formed in the anode space by electrochemical oxidation of the cadmium electrode after application of external voltage. Crystal violet dissociates weakly, migrates therefore at a negligible rate, and its colour is  $pH$ -dependent (purple at neutral  $pH$ , blue at acidic  $pH$ ). The colour change of the solution visualizes the interface between the leading and the indicator electrolyte.



The displacement  $\Delta l$  of the interface means that the hydrogen ions have given, within time interval  $(t_2 - t_1)$ , to the cathode the charge:

$$q^+ = S \cdot \Delta l \cdot c = \Delta V \cdot c_{H^+} \quad (1.1.)$$

where  $S$  is the interface area and  $c$  is the concentration of hydrogen ions. Contemporarily, the chloride ions transferred the charge  $q^-$  in the opposite direction to anode. In total, the charge  $|q| = |q^+| + |q^-|$  was transferred. The absolute values of the charges  $|q^+|$ ,  $|q^-|$  are not equal because in the same electric field the ions  $H^+$  and  $Cl^-$  move by different absolute velocities and in the opposite directions.

The part that the ion contributes to the absolute value of the total transmitted charge is the so-called transference number. For hydrogen cation in **Figure 1**:

$$t_+ = \frac{|q^+|}{|q|} = \frac{c_{H^+} \cdot \Delta V \cdot F}{|q|} \quad (1.2.)$$

where  $F$  is Faraday's constant ( $96\,484\text{ C}\cdot\text{mol}^{-1}$ ).

The total passed electric charge  $|q|$  can be determined by the integration of the electric current  $I$  flowing over time:

$$|q| = \int_{t_1}^{t_2} I \cdot dt \quad (1.3.)$$

The upper and lower bounds of the integral are selected according to experiment conditions (usually two passes through two significant positions on volume-calibrated tubes). The transference number of hydrogen ions in  $HCl$  at  $25\text{ }^\circ\text{C}$  is  $t_+ = 0,8209$ . The sum of the transference numbers of all moving ions is equal to 1.



**TASK:** Determine the transference number of hydrogen cation and chloride anion by the interface motion method in  $0.01\text{M HCl}$ . Use the digital ammeter to transfer data to PC for automatic recording of electric current over time.



**LABORATORY AIDS AND CHEMICALS:** Glass volume scale tube with water jacket ending with cadmium electrode, argent chloride electrode,  $0.1\text{M KCl}$  for electrode preservation, syringe ( $5\text{ cm}^3$ ) with polyethylene hose, thermostat (if higher measurement accuracy is required), DC power supply ( $300\text{ V}$ ), switch and connection wires, digital ammeter connected to a PC, beaker ( $50\text{ cm}^3$ ),  $0.01\text{M HCl}$  coloured with  $1 \cdot 10^{-4}\text{M}$  crystal violet (CAS No 548-62-9).



The voltage used on the electrodes will be up to  $300\text{ V}$ , therefore caution should be exercised when working with the apparatus under electrical voltage.



**INSTRUCTIONS:** Suck the solution of  $0.01\text{M HCl}$  coloured with crystal violet in the syringe with a thin hose and push it into volume scale tube (see **Figure 1**). There must be no bubble at the bottom near  $Cd$  electrode (anode). Insert the argent chloride electrode (cathode) into the top of the tube. Remove the excess solution with cotton tampon. Switch the thermostat on and wait for the temperature stabilisation if you want to achieve higher measurement accuracy.

Check the electrical circuit, familiarize yourself with the operation manual of the ammeter, turn the computer on, set up the data collection to one times per (3-5) seconds. Ask the supervisor for supervision and turn on the power supply. After

stabilizing the instrument, set the power source to  $\approx 300\text{ V}$ . Turn the switch  $S$  on and start the data collection.

Observe the colour interface and record the time and the current when the interface passes through the first mark ( $0\text{ cm}^3$ ) on the scale tube (when the interface crosses the mark, you can turn off and immediately turn on the circuit by switch  $S$ ). Record the passes through next marks ( $0.3$ ,  $0.6$ ,  $0.9$  and  $1.2\text{ cm}^3$ ) in the same way.

After the measurement, replace the solution in the scale tube with a new  $HCl$  solution and repeat the entire measurement 2 times. Leave the distilled water inside the scale tube after you finish the work.



Use the trapezoidal method to numerically calculate the integral value in eqn (1.3.) (for example, apply MS EXCEL). Substitute the limits  $a$ ,  $b$  of the integral by the times when interface passes through selected volume marks. You can get four charges  $|q|$  from each experiment (ie 8-12 in total). Perform a statistical evaluation of the acquired transmission number values.



**REPORT: GRAPH 1:** One selected record of electric current dependence on time with volume values near time marks. **TABLE 1-3:** for each electric current dependence: marked times  $t_i$  and  $t_{i+1}$ , currents  $I_{t_i}$  and  $I_{t_{i+1}}$ , volumes:  $V_{t_i}$ ,  $V_{t_{i+1}}$  and  $\Delta V = V_{t_{i+1}} - V_{t_i}$ , passed electric charge  $|q|$ , transference number of hydrogen cation  $t_+$  and chloride anion  $t_-$ . **NEXT:** Average of  $t_+$  and  $t_-$ , confidence interval of  $t_+$  and  $t_-$ , comparison with tabulated transference numbers.