

Related topics

Nernst equation, activity, concentration, electrode potential, membrane potential, concentration cells, transference numbers, semi-permeable membrane, selectively permeable membrane.

Principle and task

On the interface between two solutions with different ion concentrations an electrochemical potential establishes itself. Its magnitude is determined by the concentration ratio and the transference numbers of the ions involved.

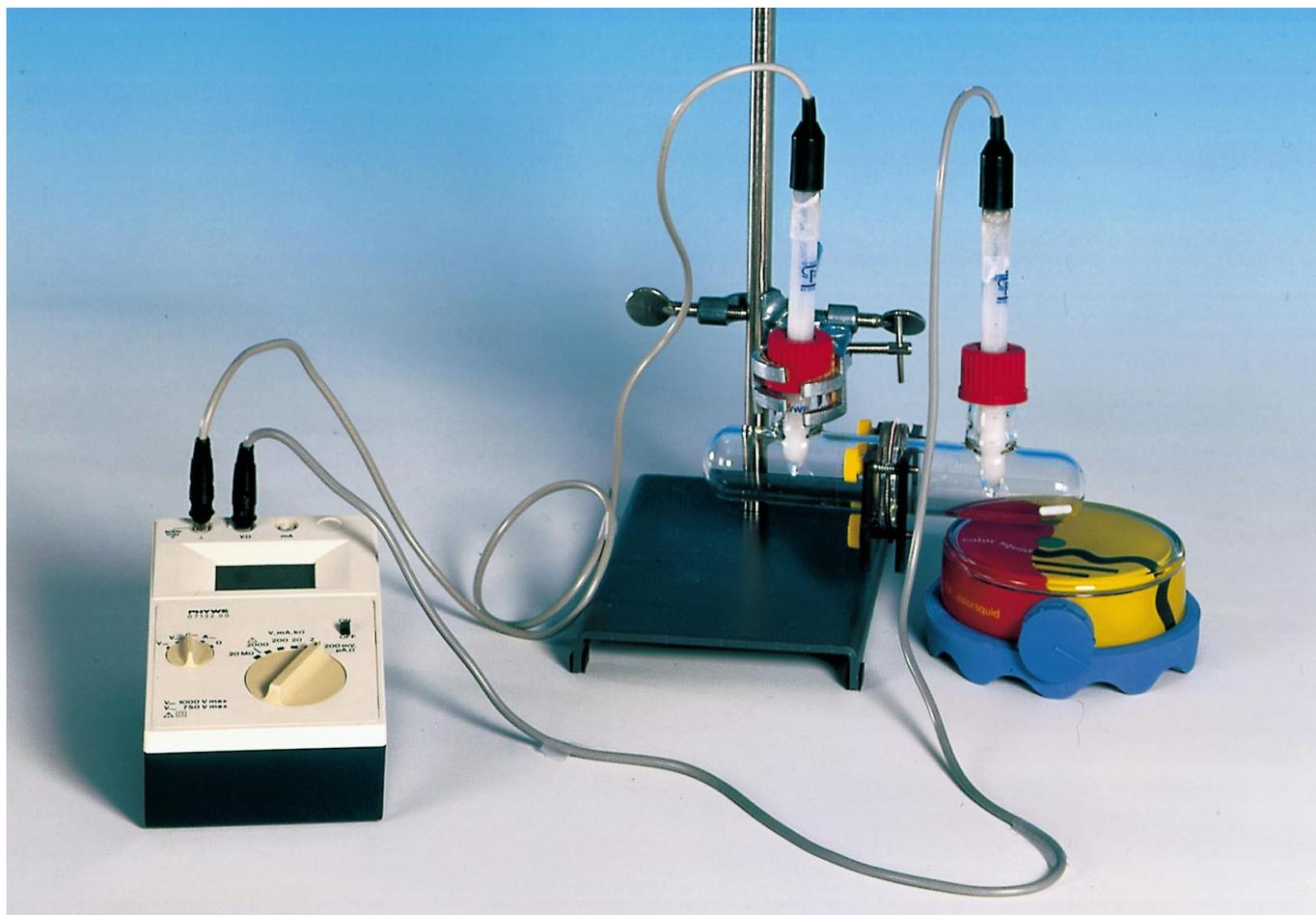
This potential difference can be measured as a function of the concentration at semi-permeable and ion-selective membranes.

Equipment

Osmosis/electrochemistry chamber	35821.00	1
Reference electrode, AgCl	18475.00	2
Magn. stirrer, mini, controlable	35712.93	1
Magn.stirring bar 15 mm, cyl.	46299.01	1
Digital multimeter	07134.00	1
Stopwatch, digital, 1/100 sec.	03071.01	1
Retort stand, h 750 mm	37694.00	1
Reference electrode, AgCl	18475.00	2
Immersion probe NiCr-Ni, -50/1000C	13615.03	1
Laboratory balance, data outp. 620 g	45023.93	1

Right angle clamp	37697.00	1
Universal clamp	37715.00	1
Volumetric flask 1000 ml, IGJ24/29	36552.00	7
Volumetric flask 100 ml, IGJ12/21	36548.00	6
Volumetric pipette, 1 ml	36575.00	2
Volumetric pipette, 5 ml	36577.00	1
Volumetric pipette, 10 ml	36578.00	1
Volumetric pipette, 20 ml	36579.00	3
Volumetric pipette, 50 ml	36581.00	2
Pipettor	36592.00	1
Pipette dish	36589.00	1
Glass beaker, tall, 100 ml	36002.00	4
Glass beaker, tall, 250 ml	36004.00	1
Syringe 1 ml, Luer, 10 pcs	02593.03	1
Cannula 0.6×60 mm, Luer, 20 pcs	02599.04	1
Funnel, glass, top dia. 80 mm	34459.00	2
Wash bottle, plastic, 500 ml	33931.00	1
Pasteur pipettes, 250 pcs	36590.00	1
Rubber caps, 10 pcs	39275.03	1
Spoon, special steel	33398.00	1
Scissors, straight, pointed, l 110 mm	64623.00	1
Membrane, permeable f. cations, 5 pcs	31504.02	1
Cellophane, 200×200 mm, 10 sheets	32987.00	1
Potassium chloride 250 g	30098.25	1
Sodium chloride 500 g	30155.50	1
Hydrochloric acid, 0.1 m, 1000 ml	48452.70	1
Water, distilled 5 l	31246.81	2

Fig. 1: Experimental set-up: Diffusion potentials / Nernst equation.



Problems

1. Measurement of the diffusion potential as a function of the concentration gradient at a cellophane membrane.
2. Measurement of the diffusion potential as a function of the concentration gradient at a cation-selective membrane.
3. Determination of the transference numbers of the ions in HCl, NaCl and KCl.

Set-up and procedure

Perform the experimental set-up according to Fig. 1. Prepare the solutions required for the experiment as follows:

- 0.1 molar HCl solution: Pour the contents of the ampoule (for 1 l of 0.1 M hydrochloric acid solution) into a 1000 ml volumetric flask and top the volumetric flask off with distilled water up to the calibration mark.
- 0.05 molar HCl solution: Pipette 50 ml of 0.1 M hydrochloric acid solution into a 100 ml volumetric flask and top off the flask with distilled water up to the calibration mark.
- 0.02 molar HCl solution: Pipette 20 ml of 0.1 M hydrochloric acid solution into a 100 ml volumetric flask and top off the flask with distilled water up to the calibration mark.
- 0.01 molar HCl solution: Pipette 100 ml of 0.1 M hydrochloric acid solution into a 1000 ml volumetric flask and top off the flask with distilled water up to the calibration mark.
- 0.005 molar HCl solution: Pipette 50 ml of 0.01 M hydrochloric acid solution into a 100 ml volumetric flask and top off the flask with distilled water up to the calibration mark.
- 0.002 molar HCl solution: Pipette 20 ml of 0.01 M hydrochloric acid solution into a 100 ml volumetric flask and top off the flask with distilled water up to the calibration mark.
- 0.001 molar HCl solution: Pipette 100 ml of 0.01 M hydrochloric acid solution into a 1000 ml volumetric flask and top off the flask with distilled water up to the calibration mark.
- 1 molar NaCl solution: Weigh 58.45 g of sodium chloride into a 1000 ml volumetric flask, dissolve the salt in distilled water and fill the volumetric flask up to the calibration mark with distilled water.
- 0.001 molar NaCl solution: Pipette 1 ml of 1 M sodium chloride solution into a 1000 ml volumetric flask and top off the flask with distilled water up to the calibration mark.
- 1 molar KCl solution: Weigh 74.55 g of potassium chloride into a 1000 ml volumetric flask, dissolve the salt in distilled water and fill the volumetric flask up to the calibration mark with distilled water.
- 0.1 molar KCl solution: Pipette 10 ml of 1 M potassium chloride solution into a 100 ml volumetric flask and top off the flask with distilled water up to the calibration mark.
- 0.01 molar KCl solution: Pipette 1 ml of 1 M potassium chloride solution into a 100 ml volumetric flask and top off the flask with distilled water up to the calibration mark.
- 0.001 molar KCl Solution: Pipette 1 ml of 1 M potassium chloride solution into a 1000 ml volumetric flask and top off the flask with distilled water up to the calibration mark.

1. Measurements on the cellophane membrane

When not in use, the silver chloride reference electrodes are to be rinsed with distilled water and stored in a 250 ml beaker in a 0.1 KCl solution.

To obtain a piece of cellophane in the proper size, place the membrane between two sealing rings from the delivery package of the osmosis/electrochemistry chamber, and cut around them with a pair of scissors leaving a margin of approximately 1 cm outside the sealing rings. Subsequently, moisten the cellophane with distilled water; place it between two sealing rings and the flanges of the two halves of the osmosis/electrochemistry chamber; screw it into the flange holder.

Using two 100 ml beakers, fill the two halves of the osmosis/electrochemistry chamber as nearly simultaneously as possible with approximately 50 ml each of the respective solution. The asymmetry potential between the two silver chloride reference electrodes is measured in the 0.1 M KCl solution and is to be considered by the calculations if it exceeds a value of ± 0.1 mV.

Rinse and dry the electrodes before each measuring procedure. For the measurements, fix them for 15 seconds in the opening of the chamber halves and determine the diffusion potential. Connect the electrode immersed in the respectively less concentrated solution with the ground (earth) connection of the multimeter. Repeat the measurements at intervals of 2 minutes and average the measured values. Check the asymmetry potential after each measurement. Measure and record the temperature of the solutions.

When changing the concentrations, rinse the Osmosis/electrochemistry chamber thoroughly with distilled water. When the type of ion, e.g. from HCl to NaCl, is changed, the membrane must be replaced. Measure the following concentration relationships:

0.001 M HCl against 0.1 M; 0.05 M; 0.02 M; 0.01 M;
0.005 M and 0.002 M HCl;

0.001 M NaCl against 1 M NaCl;

0.001 M KCl against 1 M KCl.

2. Measurements on the cation-permeable membrane

The cation permeable membrane is supplied in pieces of the correct size. If necessary, cut the corners slightly. The membrane should not dry out and must therefore be stored in distilled water.

Fill one half of the osmosis/electrochemistry chamber with 50 ml of 0.01 M KCl solution. In the other half put in a small magnetic stirring bar and fill in exactly 45 ml of 0.001 M KCl solution. Once again, check the electrode's asymmetry potential before each new measurement. Connect the electrode in the 0.01 M solution to the ground port of the multimeter. Increase the concentration in the chamber half which initially contained the 0.001 solution by adding small volumes of 1 M KCl solution. To do so it is appropriate to use an injection syringe. Read the volumes to be added and the resulting concentration from Table 1. The establishment of the membrane potential requires several minutes after each alteration in concentration.

Table 1: Volumes of KCl solution and resulting concentrations

Measurement number	Added 1 M KCl / ml	Sum 1 M KCl / ml	Concentration KCl / mol/l
1	0	0	0.001
2	0.05	0.05	0.00211
3	0.05	0.1	0.00322
4	0.05	0.15	0.00432
5	0.05	0.2	0.00542
6	0.05	0.25	0.00652
7	0.1	0.35	0.00871
8	0.1	0.45	0.01089
9	0.1	0.55	0.01306
10	0.05	0.6	0.01414
11	0.05	0.65	0.01522
12	0.05	0.7	0.0163
13	0.05	0.75	0.01738
14	0.05	0.8	0.01845

Table 2: Activity coefficients f

Concentration [mol/l]	HCl	NaCl	KCl
0.001	0.9656	0.9659	0.9652
0.002	0.9521	0.9531	0.9520
0.005	0.9285	0.9296	0.9274
0.01	0.9043	0.9059	0.9022
0.02	0.8755	0.8767	0.8706
0.05	0.8304	0.8285	0.8182
0.1	0.7964	0.7858	0.7707
0.2	0.7667	0.7414	0.7200
0.5	0.7571	0.6885	0.6552
1.0	0.8090	0.6644	0.6110

Table 3: Transference numbers t_+ and t_- at 18°C and $c = 1 \text{ mol/l}$

	HCl	NaCl	KCl
t_+	0.828	0.383	0.492
t_-	0.172	0.617	0.508

Theory and evaluation

Potential differences occur between metal electrodes and solutions as well as between different solutions. If there is no phase boundary between the solutions, diffusion potentials are formed. If a membrane separates the solutions, diffusion or Donnan potentials are formed depending on the properties of the membrane.

In accordance with the Nernst equation, the cell voltage of a cell consisting of two similar electrodes which only differ in the activity of their ions (concentration cell) the cell voltage is

$$E = \frac{RT}{zF} \cdot \ln \frac{a_2}{a_1} \quad (1)$$

where

a_1, a_2 = the activities of the ions in the half-cells.

Such a cell results at a semi-permeable membrane. The cell voltage, i.e. the potential difference on the two sides of the membrane, can be measured with reference electrodes.

Since a semi-permeable membrane, e.g. cellophane, allows both cations and anions to pass, the cell voltage will change to the extent that a charge separation resulting from different diffusion velocities of the ions becomes established. In the process, the more rapidly diffusing ions will ultimately be slowed by their charge, whereas the slower ones will be accelerated.

The transference numbers t_{\pm} of the ions are calculated from the cation and anion velocities (v_+, v_-):

$$t_{\pm} = \frac{v_{\pm}}{v_+ - v_-} \quad (2)$$

They provide a measure of the proportion of cations and anions on the current flow through the electrolytes.

The following is valid for their sum:

$$t_+ + t_- = 1 \quad (3)$$

The diffusion potential $\Delta\varphi_D$ on the membrane can be calculated analogously to equation (1) under consideration of the transference numbers:

$$\Delta\varphi_D = (t_- - t_+) \frac{RT}{zF} \ln \frac{a_2}{a_1} \quad (4)$$

The sign of the diffusion potential depends on which type of ion has the higher velocity.

On a cation-permeable membrane there can be no charge transfer due to anions ($t_- = 0$). Thus, for the diffusion potential it follows from equations (3) and (4) that:

$$\Delta\varphi_D = \frac{RT}{zF} \ln \frac{a_2}{a_1} \quad (5)$$

In contrast, if both types of ion have transference numbers of approximately equal magnitude (e.g. KCl), only small diffusion potentials are formed at the semi-permeable membrane. Solutions of this type are preferably used in reference electrodes to avoid potential jumps. The saturated AgCl solution in which the chloridized silver wire of a silver/silver chloride electrode is also immersed in a 3 molar KCl solution for this reason.

When solutions of differing concentration are separated by a cellophane membrane, which is permeable for both cations and anions, the concentration ratio and thus also the diffusion potential changes with time. When the potential is to be correlated to the initial concentrations, one must measure immediately after the chambers have been filled. In contrast to this,

the diffusion potential at an ion-selective membrane is formed by only diffusion of one type of ion and remains stable for longer periods as further diffusion is suppressed by charge separation.

The current flow during measurement also exerts a strong effect on the measured diffusions potential. Although the measuring device has a very high input impedance, a noticeable potential drop can occur for a measurement period of 15 seconds and repeated measurements. If a value deviates by more than 5 mV from the initial value, that measurement should not be considered in the evaluation.

Figure 2 shows the diffusion potential at the cellophane membrane as a function of the logarithm of the activity and/or the concentration ratios. The activities are calculated with the aid of the activity coefficients from Table 2 ($a = f \cdot c$). The slope m of the straight line $y = mx + y_0$ is determined by linear regression. It corresponds $(t_+ - t_-) RT/zF$ (eqn. (4)). The absolute member y_0 of the regression equation contains the asymmetry potential of the reference electrodes and the dilution error. From equations (3) and (4) the transference numbers can be calculated using the slope m :

$$t_{\pm} = \frac{1}{2} \left(1 \pm m \cdot \frac{zF}{RT} \right) \quad (6)$$

Analogously to Figure 2, the diffusion potential at a cation permeable membrane is presented in Figure 3 as a function of the logarithm of the concentration ratio. As not all of the required activity coefficients have been compiled, the calculations were performed only with the concentration data. Up to a concentration of 0.02 mol/l, the coefficients are sufficiently large

to allow this. If it is necessary to work with higher concentrations and/or concentration ratios, the missing activity coefficients must be interpolated. In this experiment, the potential changes its sign as the chamber half which initially contained 0.001 M solution ultimately has a higher concentration as the other chamber half with the 0.01 M KCl solution, because portions of 1 M KCl solution are added to this 0.001 M solution. The slope m of the regression line corresponds to $-RT/zF$ (eqn. (5)).

Data and results

1. Cellophane membrane

From the slope m of the regression lines, the following transference numbers were obtained for HCl in agreement with equation (6): $t_+ = 0.83$ and $t_- = 0.17$ at 298 K and using the activity coefficients from Table 2.

For 298 K and using the activity coefficients from Table 2, the following transference numbers were calculated for NaCl and KCl from the given diffusion potentials according to equation (4):

NaCl: $\Delta\varphi_D = 27.1 \text{ mV}$, $t_+ = 0.42$, $t_- = 0.58$

KCl: $\Delta\varphi_D = 0.8 \text{ mV}$, $t_+ = 0.50$, $t_- = 0.50$

2. Cation-permeable membrane

The slope m of the regression lines were compared with the theoretical value. At 296 K a value of -25.1 mV was obtained by exclusively plotting concentration ratios. The theoretical value $(-RT/F, T = 296 \text{ K})$ is -25.5 mV and is valid for all 1-1 electrolytes at cation-permeable membranes.

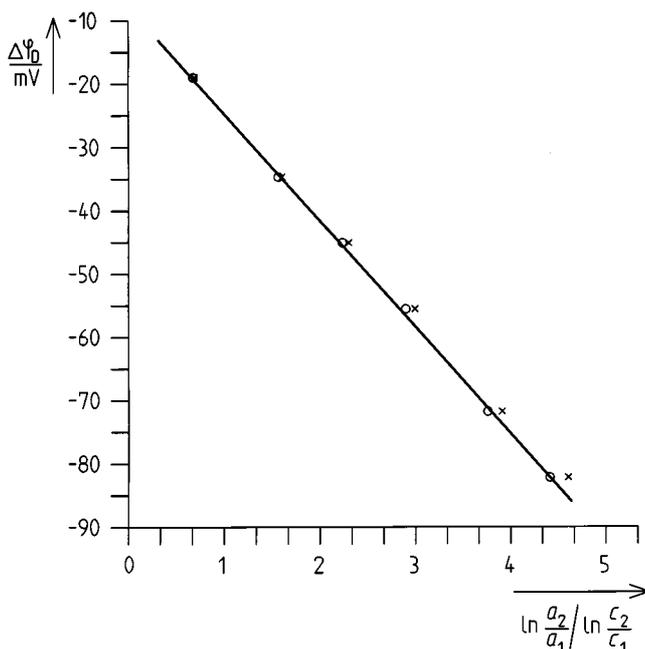


Fig. 2: Diffusion potential $\Delta\varphi_D$ for HCl as a function of $\ln a_2/a_1$ (o) and $\ln c_2/c_1$ (x) (for cellophane).

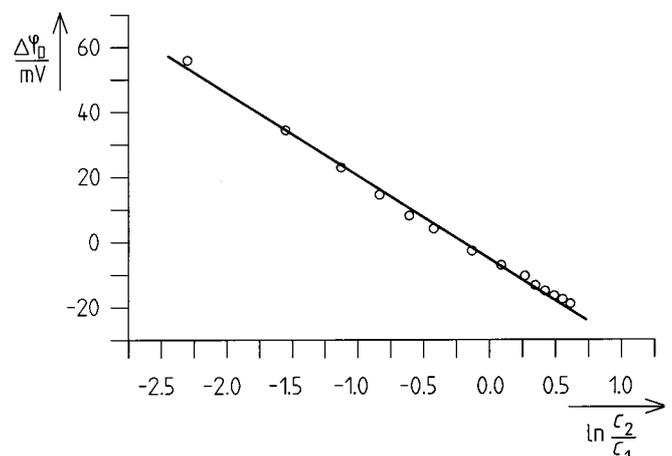


Fig. 3: Diffusion potential $\Delta\varphi_D$ for KCl as a function of $\ln c_2/c_1$ (cation membrane).