

AALTO UNIVERSITY

School of Chemical Technology

Department of Chemistry and Material Science

CHEM-E4100 - Laboratory projects in chemistry

**DETERMINATION OF THE STANDARD POTENTIAL  
OF AN Ag/AgCl ELECTRODE AND THE MEAN  
ACTIVITY OF HCl**

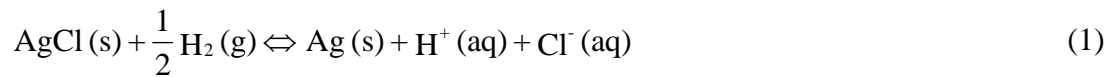


## 1 Introduction

The electrode potential is a measure of its oxidizing/reducing strength. Because the potential of an individual electrode cannot be measured, electrode potentials are expressed relative to some reference electrode. Thus, in order to compare different electrodes their potentials have to be measured with respect to the same reference such as the normal hydrogen electrode.

## 2 Theory

In a galvanic cell containing the Ag/AgCl and the normal hydrogen electrode with HCl acting as the electrolyte, the following reaction takes place:



In general, the reaction Gibbs energy  $\Delta G$  at constant temperature and pressure can be expressed in terms of the chemical potentials  $\mu_i$  as:

$$\Delta G = \sum_i \nu_i \mu_i \quad (2)$$

where  $\nu_i$  is the stoichiometric coefficient. The chemical potential is obtained from

$$\mu_i = \mu_i^0 + RT \ln(a_i) \quad (3)$$

where  $\mu_i^0$  is the standard chemical potential and  $a_i$  the activity of species  $i$ . By combining the standard chemical potentials under one term

$$\Delta G^0 = \sum \nu_i \mu_i^0 \quad (4)$$

eq. 2 can be written as

$$\begin{aligned}\Delta G &= \mu_{Ag}^0 + \mu_{H^+}^0 + \mu_{Cl^-}^0 + RT \ln (a_{H^+} a_{Cl^-}) - \left( \mu_{AgCl}^0 + \frac{1}{2} \mu_{H_2}^0 + \frac{1}{2} RT \ln (a_{H_2}) \right) \\ &= \Delta G^0 + RT \ln (a_{H^+} a_{Cl^-}) - \frac{RT}{2} \ln (a_{H_2})\end{aligned}\quad (5)$$

The activity of HCl ( $a_{HCl}$ ) is

$$a_{HCl}^2 = a_{H^+} a_{Cl^-} = \gamma_{H^+} \left( \frac{m_{H^+}}{m^0} \right) \gamma_{Cl^-} \left( \frac{m_{Cl^-}}{m^0} \right) = \gamma_{HCl}^2 \left( \frac{m_{HCl}}{m^0} \right)^2 \quad (6)$$

where  $\gamma_{HCl}$  is the mean activity coefficient and  $m_{HCl}$  is the molality ( $m^0 = 1 \text{ mol kg}^{-1}$ ) of HCl.

Assuming hydrogen to behave like an ideal gas we get

$$a_{H_2} = \frac{p(H_2)}{p^0} \quad (7)$$

where  $p(H_2)$  is the pressure of the hydrogen gas at the electrode surface and  $p^0 = 1 \text{ atm}$ . Taking into account the relation between the change in Gibbs energy and the electromotive force of the cell, given by  $\Delta G = -nFE$  (and  $\Delta G^0 = -nFE^0$ ) where  $n$  is the number of transferred electrons for the cell electrochemical reaction. With  $n = 1$ , we get the following from eq. 5 – 7:

$$E = E^0 - \frac{2RT}{F} \ln \left[ \gamma_{HCl} \left( \frac{m_{HCl}}{m^0} \right) \right] + \frac{RT}{2F} \ln \left[ \frac{p(H_2)}{p^0} \right] \quad (8)$$

where  $E^0$  is the standard cell potential. From Debye-Hückels limiting law we know that in very dilute water solutions ( $m < 0,01 \text{ mol kg}^{-1}$ ) at 25°C the log of the mean activity coefficient of the electrolyte is directly proportional to the square root of the ionic strength  $I$  of the solution ionic strength  $I = \frac{1}{2} \sum m_i z_i^2$ .

$$\ln \gamma_{\text{HCl}} = -A \sqrt{I} = -A \sqrt{\frac{1}{2} \left( \frac{m_{\text{H}^+}}{m^0} + \frac{m_{\text{Cl}^-}}{m^0} \right)} = -A \sqrt{\frac{m_{\text{HCl}}}{m^0}} \quad (9)$$

Substituting this formula into equation (8), let us define a new variable,  $E(m)$ , as

$$E(m) = E^0 + \frac{2ART}{F} \sqrt{\frac{m_{\text{HCl}}}{m^0}} = E + \frac{2RT}{F} \ln \left( \frac{m_{\text{HCl}}}{m^0} \right) - \frac{RT}{2F} \ln \left( \frac{p(\text{H}_2)}{p^0} \right). \quad (10)$$

By plotting  $E(m)$  as a function of the molality of HCl and extrapolating to  $m^{1/2} = 0$  we can find the standard cell potential  $E^0$ .  $E^0$  is the same as the potential difference between the cell's two electrodes

$$E^0 = E^0(\text{right}) - E^0(\text{left}) \quad (11)$$

so in this case

$$E^0 = E^0(\text{Ag(s)}, \text{AgCl(s)}, \text{Cl}^-(\text{aq})) - E^0(\text{H}_2(\text{g}), \text{H}^+(\text{aq})) \quad (12)$$

The standard potential of the normal hydrogen electrode (NHE) has been agreed to be equal to 0 ( $E^0(\text{H}_2(\text{g}) | \text{H}^+(\text{aq})) = 0$ ) so that the extrapolated value of  $E^0$  directly yields the standard potential for the Ag | AgCl electrode.

## 3 Experimental

### 3.1 Preparation of Ag/AgCl electrode

Grind the surface of a silver wire clean using sandpaper. Clean the surface with water and measure its diameter. Use a two electrode system for electro-oxidation of Ag to AgCl: Ag as the working electrode (WE) and platinum as the counter electrode (CE), 1 M HCl as the electrolyte. Place the silver wire so that 3 cm of it is below the liquid surface. Use a chronopotentiometric measurement to oxidize silver with a constant current density of  $5 \text{ mA cm}^{-2}$  (calculate the area based on its diameter) for 10 min or until the voltage rises over 1 V. Store the oxidized part of the electrode in  $\sim 3 \text{ M KCl}$ .

### 3.2 Measuring the Ag/AgCl electrode

Prepare a series of solutions (total weight 250 g each) with HCl molalities of 0.001, 0.002, 0.004, 0.006, 0.008, 0.01, 0.02 and  $0.05 \text{ mol kg}^{-1}$ . Molality of the stock solution is  $0.5 \text{ mol kg}^{-1}$ . Place the solutions into a thermostat at  $25 \text{ }^\circ\text{C}$ . Pour the most diluted solution into the cell, insert the hydrogen and Ag|AgCl electrodes and turn the thermostat on at  $25 \text{ }^\circ\text{C}$ . Start measuring voltage and switch the hydrogen gas flow on. Once the voltage has stabilized, write it down and change the electrolyte by first rinsing the cell with the next electrolyte. Make a table of the voltage at the respective HCl molalities. Hydrogen gas flows to the hydrogen electrode through a water bottle. Read the air pressure and determine the height of the water column exerting a force on the hydrogen electrode.

**CARE !!! TREAT THE HYDROGEN ELECTRODE CAREFULLY AS IT BREAKS EASILY!**

## 4 Results

All the equations used in the report must be presented in the theory part and complete example substitutions (with units) are shown in results part. Also, show all the values you have used for calculating the results either in a table or in text.

Calculate  $E(m)$  for each measurement. The effective pressure  $p(\text{H}_2)$  at the hydrogen electrode depends on the air pressure  $p_a$ , the hydrostatic pressure  $p_h$  and the vapour pressure  $p(\text{H}_2\text{O})$  of water in the following way:

$$p(\text{H}_2) = p_a + p_h - p(\text{H}_2\text{O}) \quad (13)$$

Plot  $E(m)$  as a function of  $m^{1/2}$  and determine the standard potential of the  $\text{Ag} | \text{AgCl}$  electrode. Determine the standard deviation of  $E^0$  using regression analysis (confidence level of 95 %). Calculate the mean activity coefficient of HCl from equation (8) and put the values into a table. Do not use equation (9)! Plot your mean activity coefficients versus literature values (CRC).

### About the report

- Introduction: Write something general about Ag/AgCl electrodes or reference electrodes.
- Theory: You don't have to derive all the equations as long as you present all the equations you are going to use.
- Experimental: Describe what you have done, as if you were writing a scientific article.
- Results: Three plots are required: electrode preparation, fitting of  $E(m)$  and mean activity coefficient vs. molality. Remember to show full example substitutions of each calculation!

Also, answer the following questions:

- 1) Why is the electrode preparation measurement stopped at 1 V?
- 2) Calculate the thickness of the formed AgCl layer by assuming that the density of AgCl is  $5.56 \text{ g cm}^{-3}$ .
- 3) What is meant by standard potential?
- 4) Give the cell notation and the electrode reactions (in the second part of the work).
- 5) Describe the structure of the electrodes used (in the second part of the work).
- 6) Why is the voltage measured in a zero current cell?
- 7) Why is it preferable to prepare solutions by weighing as opposed to using volumetrics?
- 8) Explain why the cell voltage decreases as the molality of HCl increases.

### **Submission**

Submit the report as a single pdf file named:

Firstname\_Lastname\_Ag\_AgCl\_day\_month\_year.pdf

day\_month\_year according to the date of the second part of the lab work. For corrected versions add c1, c2,... to the end.



## 5 Literature

1. Mortimer, R.G., *Physical Chemistry*, The Benjamin/Cummings Publishing Company, Inc., California 1993, p. 298-305.
2. Atkins, P.W., *Physical Chemistry*, 6<sup>th</sup> edition, Oxford University Press, Oxford 1998, p. 263-265.
3. Kalliorinne, K., Kankaanperä, A., Kivinen, A., Liukkonen, S., *Fysikaalinen kemia 2, Termodynamiikka*, Kirjayhtymä, Rauma 1990, p. 185-187.