

Electrochemistry (potentiometry)

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http://tera.chem.ut.ee/~koit/arstpr/pot_en.pdf

1 Electrochemical cell

Potentiometry is one type of electrochemical analysis methods. Electrochemistry is a part of chemistry, which determines electrochemical properties of substances. An electrical circuit is required for measuring current (unit: ampere, A) and potential (also voltage, unit: volt (V)) created by movement of charged particles. Galvanic cell (electrochemical cell, Fig. 1) serves as an example of such system.

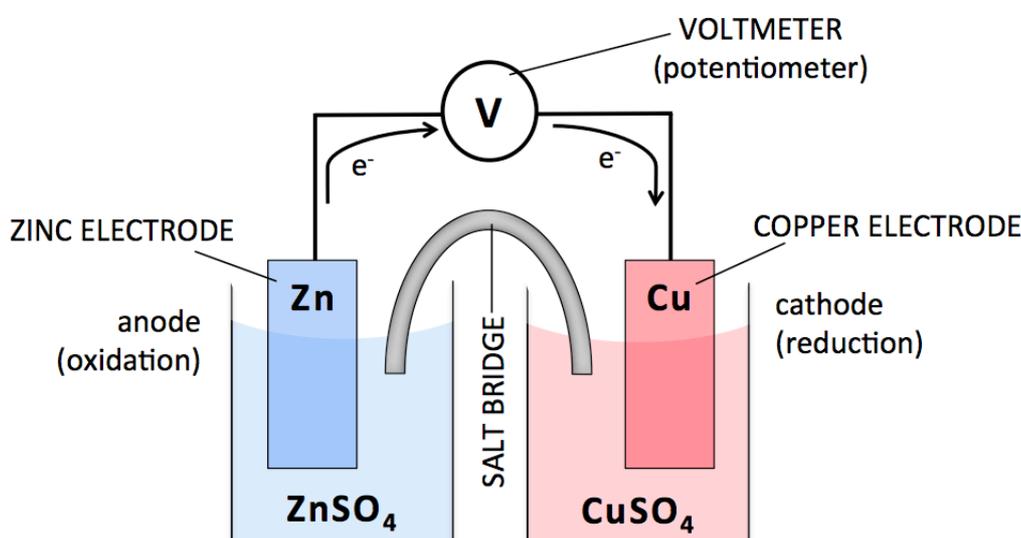


Figure 1. A galvanic electrochemical cell.

Electrochemical cell consists of two solutions connected by a salt bridge and electrodes to form electrical circuit. Sample cell on figure 1 consists of solutions of $ZnSO_4$ and $CuSO_4$. Metallic Zn and Cu electrodes are immersed in respective solutions. Electrodes have contacts firstly through wires connected to the voltmeter and secondly through solutions and a salt bridge, forming an electric circuit. Salt bridge consists of a tube filled with saturated salt solution (e.g. KCl solution). The ends of the tube are capped with porous frits that prevent solutions from mixing, but permit movement of ions.

Three distinct charge transfer processes are described for the system in Fig 1:

1. Electrons move in electrodes and wires from zinc electrode to copper electrode.
2. Ions move in solutions:
 - a. In solution on the left, zinc ions move away from the electrode and sulfate ions move towards it.
 - b. In solution on the right, copper ions move towards the electrode and negatively charged ions (sulfate) away from it.
 - c. In salt bridge positive ions move right and negative ions left.
3. On the surfaces of electrodes electrons are transferred to ions or vice versa:
 - a. Zinc electrode dissolves: $Zn \rightarrow Zn^{2+} + 2e^-$
 - b. Metallic copper is deposited on the electrode surface: $Cu^{2+} + 2e^- \rightarrow Cu \downarrow$

Three processes mentioned above are important parts of a closed electrical circuit making the flow of electrical current possible.

Potential on an electrode depends on the ions present in the solution and their concentration. This way electrochemical cells can be used to determine ions and their concentration in solution. The dependence of potential between electrodes from concentration of ions is expressed by Nernst equation (Eq. 1).

$$E = E_0 - \frac{RT}{nF} \ln a \quad (1)$$

E – electrode potential,

E_0 – standard potential of the electrode,

R – universal gas constant (8.314 J/(K•mol)),

F – Faraday constant (96485 C/mol),

T – temperature in kelvins,

n – charge of the ion or number of electrons participating in the reaction,

a – activity of the ions. Activity of the ions is a function of concentration. For solutions with concentrations lower than about 0.1 mol/l, activity can be approximated to concentration. Thus a logarithmic dependence exists between potential and the activity (concentration) of ions in solution.

2 Potentiometry

Potentiometry is based on the measurement of the potential of an electrode system (e.g. electrochemical cell).

Potentiometric measurement system consists of two electrodes called reference and indicator electrode, potentiometer and a solution of analyte (figure 2).

Reference electrode is an electrode with potential which is a) independent of concentration of analyte (or other) ions in solution; b) independent of temperature.

Potential of an **indicator electrode** depends mainly on the concentration of the analyte ions (in this case hydrogen ions).

Potentiometric measurements enable selective detection of ions in presence of multitude of other substances.

In case of figure 2, the potential of the indicator electrode is sensitive to hydrogen ions. In a system like this, the potential is measured in reference to a calomel electrode, e.g. calomel electrode functions as the reference electrode.

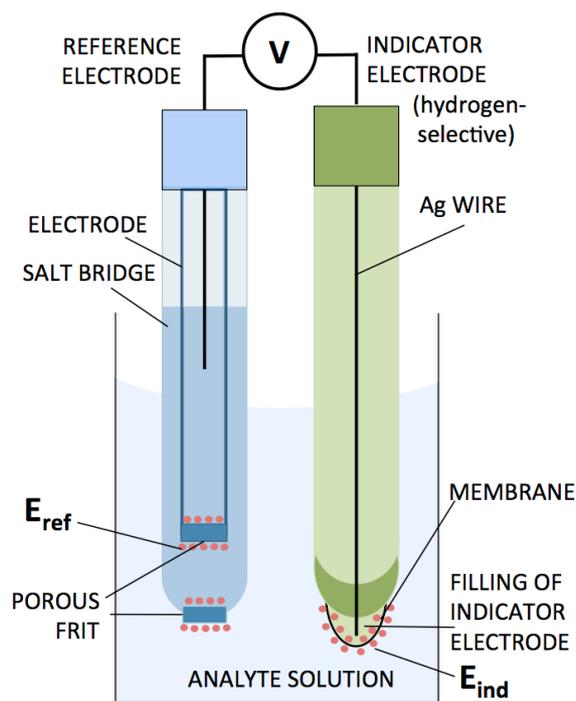


Figure 2. Potentiometric measurement system (for pH measurement)

3 Nernst equation in practice

Due to the complex nature of overall potential, Nernst equation is often used in form of equation 2 (compare to equation 1):

$$E_{cell} = K \pm \frac{0.059}{n} \log c \quad (2)$$

E_{cell} - overall potential,

c - concentration of analyte ions, which can be used instead of activity (a) only in case of dilute solutions
 K - includes all remaining potentials in the system (including junction potential and potential of reference electrode).

Constant 0,059 V includes constant terms from equation 1 and temperature $T = 298$ K. Sign in equation 2 depends on the ions determined: in case of cations it is “+” and in case of anions it is “-”.

4 Acidity of solutions and pH

4.1 Acidity

Acidity of a solution characterizes the concentration of hydrogen ions in it: the more hydrogen ions in the solution, the more acidic it is. Addition of acid to a solution increases the concentration of hydrogen ions, hence also its acidity. Addition of base (e.g. a hydroxide) to a solution decreases the concentration of hydrogen ions. We will now look closer to the acidity of aqueous solutions.

Water undergoes autoprotolysis (self-ionization) forming both hydrogen and hydroxide ions. This process can be understood considering equation 3.



Reaction in equation 3 is an equilibrium reaction. This means that if acid is added, the concentration of hydrogen ions increases and part of the hydroxide ions reacts with hydrogen ions yielding water. This way the concentration of hydroxide ions decreases and the acidity of the solution increases.

On the other hand, when base is added, the concentration of hydroxide ions increases and concentration of hydrogen ions decreases, hence acidity also decreases.

The equilibrium state of reaction (eq 3) can be expressed in terms of water autoprotolysis constant (eq. 4).

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \quad (4)$$

Equation 4 is valid for dilute solutions at room temperature. This relationship also demonstrates that concentration of hydroxide ions decreases upon increase in hydrogen ion concentration, and vice versa.

4.2 pH scale

In order to characterize the acidity of solutions, the unitless value of pH is used. The pH is defined as the negative logarithm of hydrogen ion concentration (activity) in a solution (equation 5). The equation 5 shows that the higher the concentration of hydrogen ions, the lower the pH of a solution.

$$\text{pH} = -\log[\text{H}^+] \quad (5)$$

If case of distilled water all the hydrogen ions originate from autoprotolysis of water (equation 3). As no other source of hydrogen or hydroxide ions is present, then their concentrations are equal, $[\text{H}^+] = [\text{OH}^-]$. Now the concentration of hydrogen ions in pure water can be calculated from equation 4:

$$[\text{H}^+] = \sqrt{[\text{H}^+]^2} = \sqrt{10^{-14}} = 10^{-7} \quad (6)$$

Knowing the concentration of hydrogen ions, the pH of pure water can be found using equation 5.

$$pH = -\log 10^{-7} = 7 \quad (7)$$

Hence, the pH of pure water is 7 (equation 7). However, if some acid is dissolved in water, for example 0,01 M hydrochloric acid (HCl) then its pH is:

$$pH = -\log 0,01 = 2 \quad (8)$$

pH of base solution can be calculated from equations 4 and 5. For example for 0.01 M NaOH solution the hydrogen ion concentration is found first (equation 9) and then the pH is calculated (equation 10):

$$[H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{0,01} = 10^{-12} \quad (9)$$

$$pH = -\log 10^{-12} = 12 \quad (10)$$

Potentiometric determination of pH is introduced by practical exercise: "Influence of antacid and some food on acidity of gastric juice. Potentiometric determination of pH."

5 Problems and exercises

1. Compare the indicator and reference electrodes. What do they have in common and what are the differences?
2. Calculate the concentration of hydroxide and hydrogen ions in a solution with pH=3.
3. pH of a solution of HCl is 1.2. Calculate the concentration of chloride ions.
4. Using the calibration curve below find the concentration of analyte in a sample for which potential 375 mV was measured.

