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.
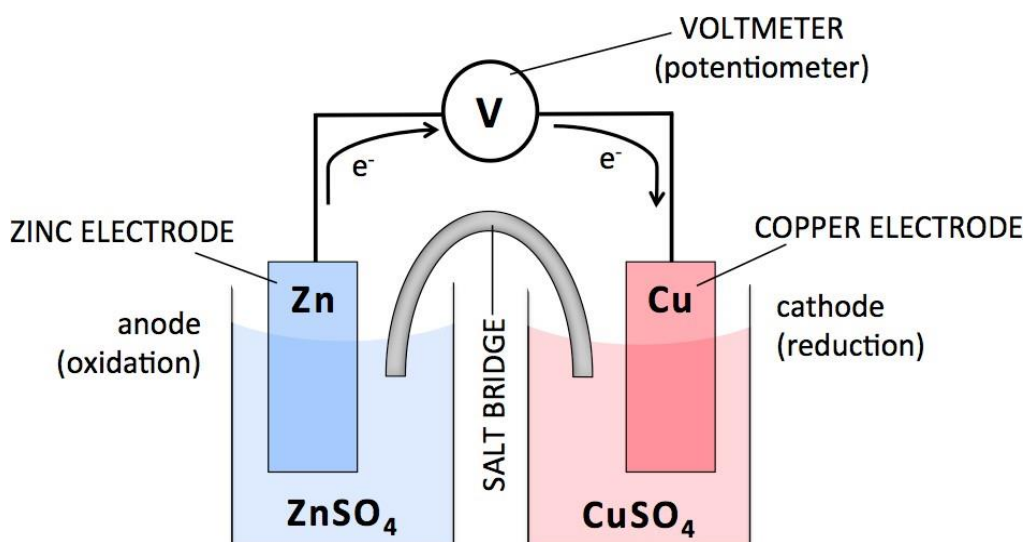

Figure 1. A galvanic electrochemical cell.

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).

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

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.

Potentiometry electrodes

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