Meditsiiniline keemia/Medical chemistry LOKT.00.009

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 circle is required for measuring current and potential (voltage) created by movement of charged particles. Galvanic cell (Fig. 1) serves as a sample of such system.

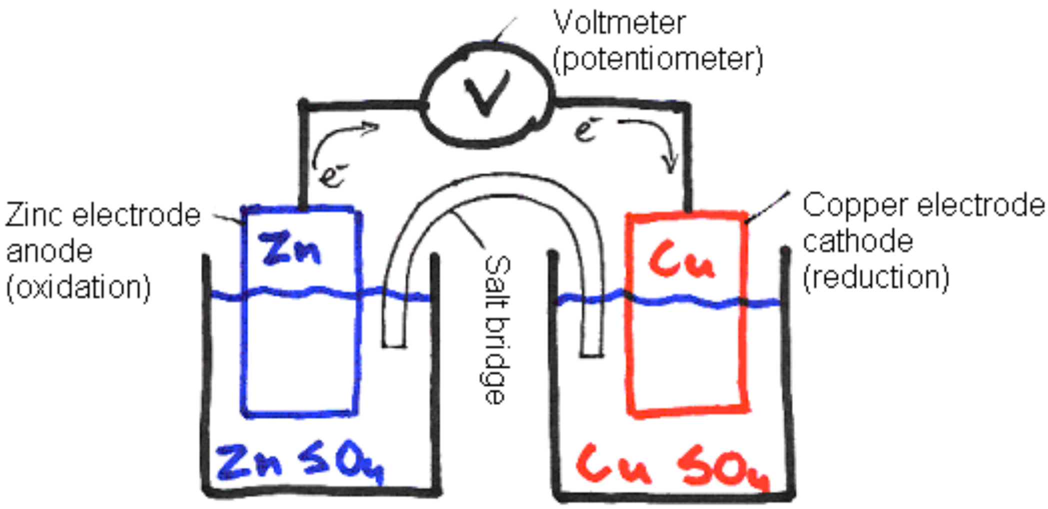

Figure 1. A galvanic electrochemical cell.

Electrochemical cell consists of two solutions connected by salt bridge and electrodes to form electrical circle. 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 two contacts: a) through wires connected to voltmeter; b) through solutions and salt bridge. 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 form a closed electrical circle 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).

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

where 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 an electroanalytical method which is based on measurement of potential of anelectrode system. Potentiometric measurements enable selective detection of ions in presence of multitude of other substances.
Potentiometric measurement system consists of two electrodes, potentiometer and a solution of analyte (Fig 2). In system like one depicted on figure 2, the potential is measured in reference to calomel electrode e.g. calomel electrode functions as reference electrode. **Reference electrode** is an electrode with potential which is a) independent of analyte (or other) ions in solution; b) independent of temperature.
In case of figure 2, the electrode sensitive to hydrogen ions is an indicator electrode. Potential of an **indicator electrode** depends mainly on the concentration of the analyte ions (in this case hydrogen ions).

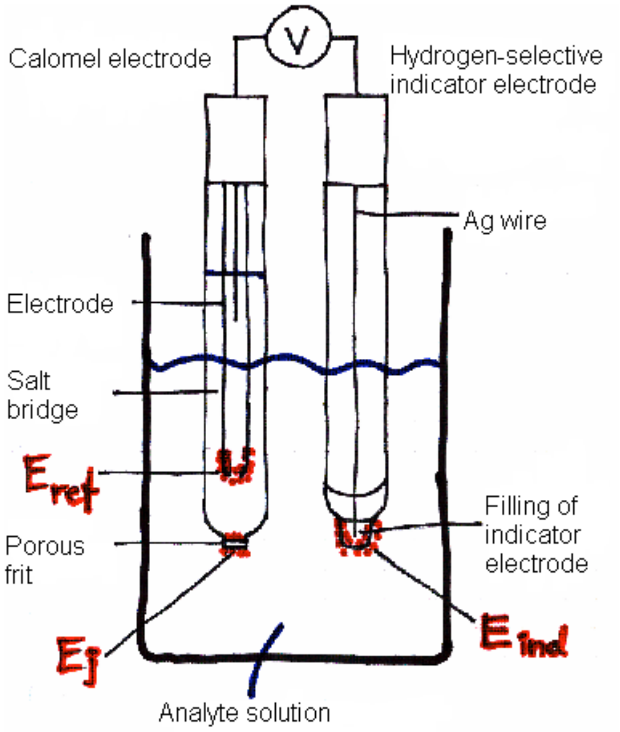

Figure 2. Potentiometric measurement system (for pH measurement).

3 Nernst equation in practice

Due to the complex nature of overall potential Nernst equation is often used in form of equation 2

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

where E_{cell} is overall potential, a activity (concentration) of analyte ions and 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.

4 Acidity of solutions and pH

4.1 Acidity

Acidity of a solution characterizes the concentration of hydrogen ions in it. Addition of acid to a solution increases the concentration of hydrogen ions, hence also its acidity. Addition of bases to a solution decreases the concentration of hydrogen ions. These relationships can be understood considering equation 3.

$$H_2O \rightleftarrows H^+ + OH^- \qquad (3)$$

Reaction 3 is an equilibrium reaction. This means that if acid is added (concentration of hydrogen ions increases) part of hydroxide ions reacts with hydrogen ions yielding water. This way the concentration of hydroxide ions decreases. On the other hand, when base is added the concentration of hydroxide ions increases and concentration of hydrogen ions decreases, hence acidity decreases.
The equilibrium state of reaction 3 can be expressed in terms of water autoprotolysis constant (eq. 4).

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

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

pH is defined as negative logarithm of hydrogen ion concentration (activity) (equation 5).

$$pH = -\log[H^+] \qquad (5)$$

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

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

Hence pH of pure water is 7 (equation 7).

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

If some acid is dissolved in water, for example 0,01 M hydrochloric acid (HCl) then its pH is:

$$pH = -\log 0{,}01 = 2 \qquad (8)$$

pH of base solution can be calculated from equations 4 and 5. For example 0.01 M NaOH solution:

$$[H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{0{,}01} = 10^{-12} \text{ ja } pH = -\log 10^{-12} = 12 \qquad (7)$$

Potentiometric determination of pH is introduced by practical exercise: “Influence of antacid and some foodstuffs on acidity of gastric juice. Potentiometric determination of pH.”.

5 Problems and exercises

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