

Handout

Base electrochemistry (exp. BE)

Introduction

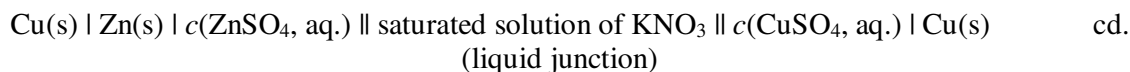
This measurement makes you familiar with setting up a galvanic cell, reveal its current – voltage characteristics, applying the zero current approximation in determining electromotive force, E_{MF} of a galvanic cell.

Measuring tasks

Experimental determination of E_{MF} and cell voltage of a galvanic cell, studying the concentration dependence of E_{MF}

Background

Cell diagram to be studied:



A quantity proportional to the maximum work done by the system can be measured when system does not do any work: w_{\max} , $dw = 0$. This quantity is the *electromotive force*. A battery in operation produces a current flowing in an expense of its energy has been stored during the latest charging process. As the battery is working the circuit consumes energy as heat evolving in a resistance in the circuit. The longer the time the circuit is allowed to work the higher the energy expenditure of battery or galvanic cell. In such conditions the battery's working capability can not be determined.

When current is zero or minimized to several nA (nano Amperes) the voltage measured by a voltmeter is proportional to the maximum work actually done by the galvanic cell.

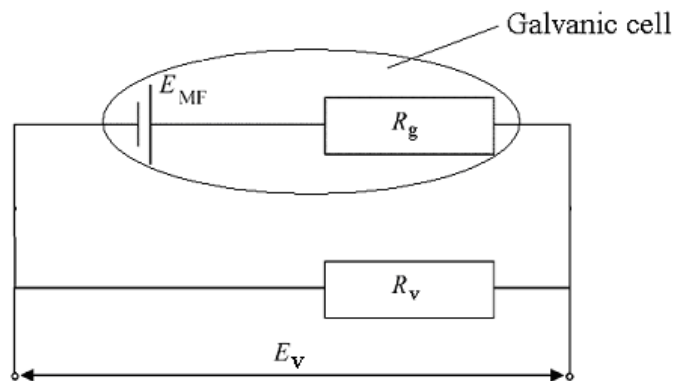


Fig. 1. Electric circuit including a galvanic cell and a voltmeter. R_g and R_v represent the solution resistance in the galvanic cell and the solid internal resistance of voltmeter respectively.

The sum of potential differences in a circuit containing a galvanic cell (voltage source) and two resistances can be given,

$$E_{MF} - E_g - E_v = 0 \quad 1.$$

where E_g and E_v are potential drops at the galvanic cell resistance, R_g and voltmeter resistance, R_v respectively. Introducing resistances:

$$E_{MF} = I(R_g + R_v) \quad \text{or} \quad E_{MF} = I \cdot R_g + E_v \quad 2.$$

In the limit to $I \rightarrow 0$, $E_v \rightarrow E_{MF}$. This is the condition at which electromotive force is measured. It concludes from Eq. 2. that the cell voltage E_v is always smaller than E_{MF} .

The measurement of E_{MF} by using high input resistance voltmeter

High input resistance voltmeters are capable to measure the E_{MF} of galvanic cells. The magnitude of input resistance depends on the exchange current of component electrodes. When resistance is high enough (e.g. $\approx 10^{10} \Omega$) the current flowing in the galvanic cell can be neglected to the exchange current.

The determination of E_{MF} by extrapolation

There is a method for determining E_{MF} without a high input resistance voltmeter. The galvanic cell is loaded with resistances of different magnitude. The resistance R_v in Fig. 1. is substituted and the corresponding cell voltage is measured. The function of cell voltage vs. current is plotted and a straight line is fitted to the points. The E_{MF} is found from extrapolating the straight line to zero current. The difference between the E_{MF} and cell voltage is the value of voltage drop on internal resistance, R_g

From Eq. 2 we get

$$E_v = E_{MF} - I \cdot R_g$$

Eliminating current, by substituting $I = \frac{E_v}{R_v}$

$$E_v = E_{MF} - \frac{E_v}{R_v} \cdot R_g \quad 3.$$

It is a good approximation for this equation that the internal resistance of galvanic cell is independent of current, therefore the value of R_g is constant. In this case the equation can be

plotted in a linearized form. In a linearized form E_v is a linear function of $\frac{E_v}{R_v}$, and the

intercept and slope are E_{MF} and R_g respectively.

Note

The voltage – current characteristics of electrodes are usually not linear, they can be regarded as linear in the vicinity of equilibrium potential. That is why R_g is taken approximately independent of current only at small currents flowing through the cell. If electrode processes have no influence on the resistance of the cell, and cell resistance is controlled only by ohmic

components like the thickness of solution, stoppers and so on, this approximation can also be applied.

Procedure: measurement of electromotive force of a galvanic cell

Tools, chemicals

3 piece of glass cell with stopper (stoppers must not be greased)
1 copper rod
1 zinc rod
1 calomel electrode saturated in KCl
Emery-paper (for Cu and Zn separately)
25 ml beaker
5 piece of 50 ml beaker for different concentration CuSO₄ solutions
0,1 M CuSO₄ solution
CuSO₄ solutions of 0.03, 0.01, 0,003, 0,001 M, which prepared from 0,1 M CuSO₄ solution by dilution with 0.1 M MgSO₄ solution (ionic strength)
0,1 M ZnSO₄ solution
Saturated solution of KNO₃ (for liquid junction)
2 clips for glass cells
Voltmeter at least with 10¹⁰ ohms input resistance
6 pieces of test-lead

Experimental steps

1. Get up a Daniell cell using two glass cells separated by liquid junction. The glass tube joints should be bubble free. Glass-joints should be wetted by the electrolyte filled into the cell. Do not use grease for stoppers!

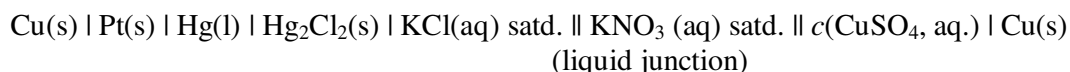
2. E_{MF} and cell voltage determination.

The E_{MF} of assembled cell is measured by the high input resistance voltmeter and note the result in LR page. We attach to the cell known resistances, R_v and measure cell voltage, E_v with high input resistance voltmeter. Carry out measurement from high to low resistances, one series with both of stoppers open and one series with both of stoppers closed. The data are noted in a table. As it is awaited, the cell resistance will be smaller at stoppers open position. Do not alter the stopper position (open or closed) when measuring the series. Close stoppers at the end.

Studying the concentration dependence of E_{MF}

This measurement is done in a different place in the lab in groups.

The CuSO₄ solutions prepared beforehand is filled into the cell one another starting with the most diluted one. (The constant ionic strength is set, therefore the mean activity coefficient, γ_{\pm} for all the solutions is also constant.) With every solution, the following galvanic cell is set:



and E_{MF} of cells is measured by the high input resistance voltmeter. We will have 5 data pair.

We start with 0,001 M CuSO₄ solution. The freshly polished Cu-plate is rinsed with the solution is also filled in the cell, and Cu-plate is immersed. After a waiting time of 3 – 4 minutes the E_{MF} of cell is noted. We advance in measurements from dilute to more concentrated solutions. When changing solutions a distilled water rinsing is not necessary. A rinse with more concentrated solution is enough.

Table proposed for data handling.

$c_{Cu^{2+}} / \text{mol dm}^{-3}$	$\lg(c_{Cu^{2+}} / \text{mol dm}^{-3})$	E_{MF} / V

Calculations

1. Evaluation for data of cell voltage.

The function E_v vs $\frac{E_v}{R_v}$ given in Eq. 3. is plotted. The least squares fit to the data will give us

E_{MF} as the intercept, and R_g from the slope.

This evaluation is carried out for data collected at open and closed stopper status.

2. Evaluation for data of concentration dependence of cell E_{MF} .

The data of cell E_{MF} is plotted against $\lg(c_{Cu^{2+}} / \text{mol dm}^{-3})$ see Nernst equation. A straight line is fitted to the points, and the two fitting parameters of the straight line can be taken proportional to the constants in Nernst equation.

3. The maximum work of galvanic cell.

The Gibbs free energy of the cell reaction is calculated from the following reaction:

$$\Delta_r G = -zFE_{cell} \quad 4.$$

We take the value of E_{MF} to be identical with E_{cell}

For the Daniell cell both the data measured with high input resistance voltmeter and the data extrapolated should be substituted in Eq. 4.

Data form to be given

- E_v / V - R_v / Ω or $k\Omega$ data pairs (at closed and open stopper position)

- $E_v - \frac{E_v}{R_v}$ plot with line fit (data measured at closed and open stopper position)

- E_{MF} data in Volts or mV measured with high input resistance voltmeter, and two extrapolated data

- internal resistance (at closed and open stopper position) determined from the slope of

$E_v - \frac{E_v}{R_v}$ function in $k\Omega$.

- E_{MF} data from concentration dependence in tabulated form

- The $E_{MF} - \lg(c_{Cu^{2+}}/\text{mol dm}^{-3})$ function plotted together with the equation of fitted line.

Minimum level tests (MLT).

Base electrochemistry

Electrode, the electrochemical cell, cell reaction, half cell reaction, the Nernst-equation, redox electrodes (e.g.: Pt/Fe²⁺/Fe³⁺), gas electrodes (e.g.: platinized Pt/H₂ gas/H⁺ (aq)), definition of pH, electromotive force (E_{MF}), cell reaction potential (E_{cell}), the relation between E_{cell} and $\Delta_r G$, mean activity of electrolytes, mean activity coefficient of electrolytes.

MLT Q.and A:

Q1. Electrochemical definition: electrode.

A1. Electrode is referred to a half cell including electrode metal and the surrounding electrolyte. The border of an electrode (half cell) is the liquid junction of the cell, where it is contacted to the other half cell.

Q2. Definition: cell diagram.

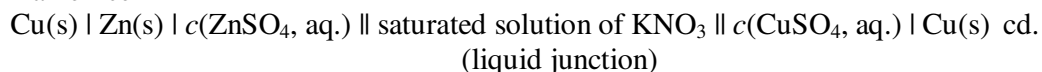
A2. The way of giving of a cell diagram is an instruction for setting the cell, and it should be in conform with the sign convention of electromotive force, E_{MF} .



On the right, you can find the calomel reference electrode, which is the positive electrode. The hydrogen electrode on the left is negative. The electromotive force should be positive: $E_{MF} > 0$, therefore

$$E_{MF} = \varepsilon_{right} - \varepsilon_{left} \geq 0$$

Daniell cell



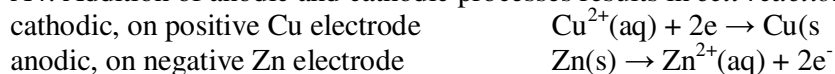
As discharging positive ions (Cu²⁺) cause in the interface an electron deficiency copper electrode is at positive potential. The writing of cell diagram is correct.

Q3. Definition: anode, cathode.

A3. **Anode:** we may use either a galvanic cell or electrolysis cell, the anode is that electrode where the half cell reaction is **oxidation**. **Cathode:** the cathode is that electrode where the half cell reaction is **reduction**.

Q4. Definition: cell reaction

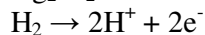
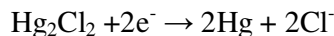
A4. Addition of anodic and cathodic processes results in *cell reaction*. For Daniell cell:



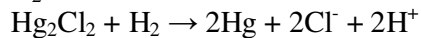
The potential difference:

$$\phi_{Cu} - \phi_{Zn} = E_{cell} \text{ and } E_{cell} \geq 0$$

In the case of pH measurement:



Cell reaction:



Q5. What is the electrochemical process in hydrogen electrode?



Q6. What is the role of platinised Pt surface in establishing the electrode process in hydrogen electrode?

A6. The high real surface area of platinised platinum is a catalyst for process $H_2 \rightarrow 2H.$ in electron transfer step atomic hydrogen is the reactant.

Q7. What is the main difference between a redox and, e.g. metal/metal ion electrode?

A7. In an electrode like $Cu|Cu^{2+}(aq)$, the reduced and oxidized components are found in different phases, i.e. the reduced in the solid phase (copper sheet) and oxidized in aqueous liquid phase ($CuSO_4$ solution). In a redox electrode like $Pt|Fe^{2+}/Fe^{3+}$, both oxidized and reduced components are in liquid phase.

Q8. Why do you use high input resistance voltmeter for electromotive force measurement?

A8. In the measuring conditions of *electromotive force* (E_{MF}), it is stated that the current flowing in the circuit should be zero or approximately zero, in order not to load the galvanic cell.

If galvanic cell is not loaded the measured potential difference $\Delta\phi = E_{MF}$, but if an appreciable current I flows in the measuring circuit of resistance R than $\Delta\phi = IR - E_{MF}$.

A high input resistance of voltmeter makes sure the measurement is carried out at a condition. $I \rightarrow 0.$

Q9. Write the potential difference in a circuit containing a galvanic cell and a voltmeter!

A9. The sum of potential differences in a circuit containing a galvanic cell (voltage source) and two resistances can be given,

$$E_{MF} - E_g - E_v = 0 \quad 1.$$

One of the resistances is in the voltmeter, the other is the internal resistance of galvanic cell.