

GENERAL CHEMISTRY LABORATORY 131

LABORATORY LECTURE

EXPERIMENT #7: ELECTROCHEMISTRY (2 PERIOD LABORATORY)

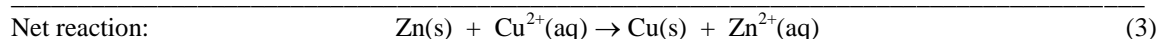
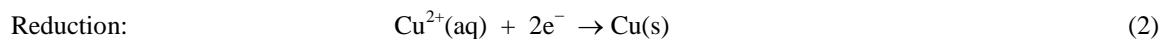
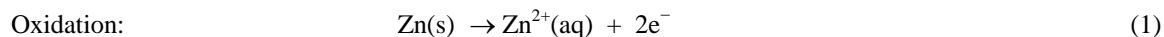
The goals of the experiment:

- to determine the order of reactivity for four metals (Zn(s), Cu(s), Ag(s) and Pb(s)) and their ionic solutions (Zn²⁺(aq), Cu²⁺(aq), Ag⁺(aq) and Pb²⁺(aq));
- to investigate voltaic cells in various combinations of these metals and their ionic solutions and to determine the voltaic cell with the highest cell voltage;
- to verify Nernst Law in measurements of cell voltage dependence on the concentration of the cell's ionic solution and its temperature;
- to analyze in an open project oxidation-reduction reactions in the concentration cell with silver electrodes and Ag⁺(aq) ionic solution.

I. REDOX REACTIONS AS THE BASE OF ELECTROCHEMICAL PROCESSES

Electrochemistry is an area of chemistry that deals with the relations between chemical changes and electrical energy. Because an electrical current is a flow of electrical charges, electrochemistry is primarily concerned with **electron transfer reactions**, which are based on **oxidation-reduction phenomena**. These oxidation-reduction chemical reactions can be used to produce electrical energy in so-called **voltaic**, or **galvanic**, cells. You will investigate properties of these cells in this laboratory experiment.

In oxidation-reduction reactions, electrons are transferred from one substance to another. Thus, if a zinc plate is immersed into a beaker with a solution containing copper (II) ions, [for example, a solution of Cu(NO₃)₂], zinc atoms will lose electrons in the process of oxidation by copper (II) ions, and copper ions will gain these electrons in the reduction process:



As you can see from eq.(1) and (2), electrons are transferred from the zinc atoms to Cu²⁺ ions. However, all these oxidation-reduction processes occur in one beaker on the surface of the zinc plate, at the spot of the contact between zinc atom and Cu²⁺ (aq) ion from the solution. Therefore, there is no actual pathway in electron transfer reaction (3). That is why we cannot register any electrical current during these electron transfer reactions. However, we can do a simple trick to generate electrical current in chemical reaction (3): we can separate oxidation and reduction processes between two different beakers.

Consider two beakers: one with Zn²⁺ (aq) solution (for example, Zn(NO₃)₂ solution), and the other beaker with Cu²⁺ (aq) solution (for example, Cu(NO₃)₂ solution). Assume that both ionic solutions have the same initial concentration. Let's immerse a Zn plate in the beaker with the zinc ionic solution and a copper plate in the beaker with the copper ionic solution. Obviously, after a short time each ionic solution will be at equilibrium with the immersed metal plate. Therefore, we can substitute forward reactions (1), and (2) with the appropriate equilibrium reactions:



During processes (4) and (5) each metal electrode releases some positive ions of the metal into the solution and, as a result, gains some electrons (see Fig.1). The question is which electrode, Zn or Cu, is more negatively charged as the result of reactions (4), and (5).

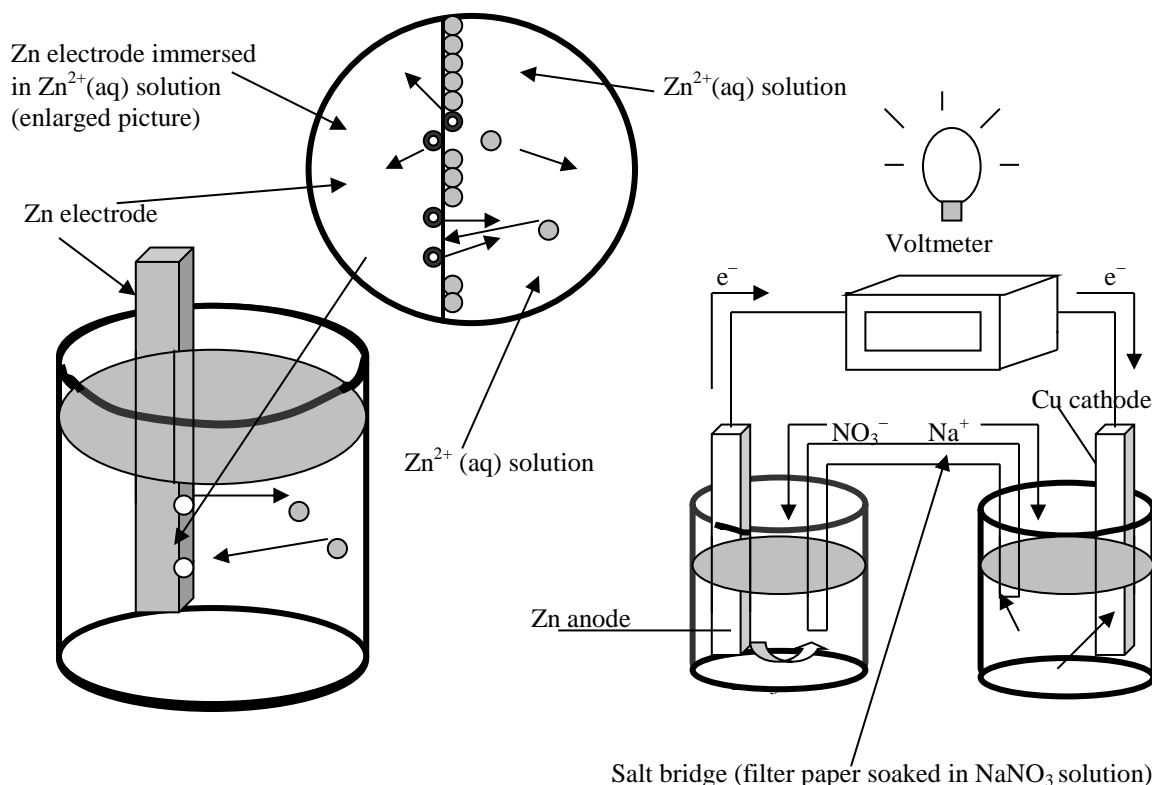


Fig. 1. Electrode equilibrium.
Oxidation and reduction occur on the Zn electrode until the condition (4) of equilibrium is reached.

Fig.2. Voltaic cell with a salt bridge.
To register an electrical current, an electrical bulb can be used instead of the voltmeter.

Assume that zinc tends to lose electrons more easily than copper. (You will check this statement at the very beginning of the lab experiment). In this case, at equilibrium in each beaker more solid zinc will be dissolved in reaction (4) than solid copper in reaction (5). Notice, that each act of metal dissolution charges the metal electrode with two electrons. Therefore, the zinc electrode will gain more electrons during process (4) than the copper electrode in process (5). Therefore, there will be nonzero voltage between the zinc and copper electrode because the zinc electrode will be charged more negatively compared to the copper electrode.

Let's connect the zinc and copper electrodes by an external metal wire. That provides a path for electrons between the Zn and Cu electrodes, but we still have an electrical gap between the solutions in our two beakers. To provide a "wire" for the metal ions in the solutions we will use a so-called **salt bridge**, which can conduct electricity using salt ions stored in it. As a simple and convenient salt bridge you will use a strip of filter paper soaked in saturated solution of NaNO₃ solution. Because filter paper has a fiber structure, Na⁺(aq) and NO₃⁻(aq) ions can move along the fibers and electrically connect the solutions in the beakers (see Fig .2). Now we have a closed electrical circuit with one point (Zn electrode) charged more negatively than the other one (Cu electrode). The difference in charges between zinc and copper electrodes creates an electrical field between them. Therefore, as soon as we connect Zn and Cu electrodes with a wire, the electrical field between them forces out the electrons from the zinc electrode to the copper electrode through the wire connection.

However, as soon as these electrons move from one beaker to another, the equilibrium in both beakers will be destroyed. There will be fewer electrons than there should be for equilibrium (4) in the beaker with the zinc electrode and more than there should be for equilibrium (5) in the beaker with the copper electrode. To reinstall the

equilibrium in the beaker with zinc, in accordance with Le Chatelier's principle, the additional amount of solid zinc will be dissolved from the Zn electrode in reaction (4). These zinc atoms will go into the solution in the form of positive $\text{Zn}^{2+}(\text{aq})$ ions releasing a new portion of electrons on the Zn electrode in reaction (1). To maintain the equilibrium in the beaker with the copper electrode, the electrons coming to the copper electrode from the zinc electrode will be consumed in reducing reaction (2) by $\text{Cu}^{2+}(\text{aq})$ ions from the CuNO_3 solution in the beaker. Reaction (2) between electrons and $\text{Cu}^{2+}(\text{aq})$ ions proceeds on the surface of the copper electrode, increasing its mass with a new portion of solid copper.

And what happens with the solutions in the beakers after the first portion of electrons arrived from the zinc to the copper electrode? Consider first the beaker with the zinc electrode. As we saw it above, some additional amount of solid zinc will be dissolved in this beaker and in the form of positive $\text{Zn}^{2+}(\text{aq})$ ions will go into the solution. **Therefore, the solution in the beaker with the zinc electrode will be charged positively.** Now, let's check the beaker with the copper electrode. Here, some amount of positive $\text{Cu}^{2+}(\text{aq})$ ions will be removed from the solution in reaction (2). Therefore, **the solution in the beaker with the copper electrode will be charged negatively.**

However, this is not the end of the story, because we should not forget about the salt bridge, which connects the ionic solutions in the beakers! The salt bridge is a filter paper soaked in a solution of NaNO_3 solution, so has positive ions of $\text{Na}^+(\text{aq})$ and negative ions of $\text{NO}_3^-(\text{aq})$ that can move from the salt bridge into the solutions in the beakers. So, the negative $\text{NO}_3^-(\text{aq})$ ions from the salt bridge will be attracted by the positively charged zinc solution to restore its charge back to neutral. The positive $\text{Na}^+(\text{aq})$ ions from the salt bridge will be attracted by the negatively charged copper ionic solution to restore its charge back from negative to neutral. After that, the equilibrium in each beaker will be restored, but once again, the zinc electrode will be charged more negatively than the copper electrode, because zinc loses electrons more readily than copper. Therefore, the same processes will go into the same repetitive cycle.

As you can see from the above analysis, the voltaic cell shown in Fig.2 provides a constant flow of electrons from the zinc to copper electrode, and the flow of positive and negative ions from the salt bridge to the solutions in the beakers. In other words, we will have an **electrical current** in our electrical circuit. (*Note that the current in the solutions and in the salt bridge is carried by the salt ions and not by electrons*).

To make all this charge flow visible we can install a voltmeter somewhere in the circuit and measure the voltage between two electrodes. We may even include an electrical bulb in the circuit and watch as it shines (see Fig. 2). We also can use a large chemical system of these "beakers" with metal plates (actually, you know the name of this system very well – it is a battery). In this case using the same process, we can start a car's engine or run an electrical car until... until what? Until the entire zinc electrode is dissolved in the first "beaker" and reaction (1) is completed.

II. CELL DIAGRAM AND THE NERNST EQUATION.

Electrochemical cells are often described by means of a **cell diagram**. For example, the cell diagram for the Zn|Cu cell discussed above is:



The single vertical bars indicate boundaries of phases that are in contact, and the double vertical bars indicate a salt bridge. The basic convention for obtaining the complete equation for a cell reaction from the cell diagram is **to write the equation for the half reaction of the left-hand electrode in the cell diagram as an oxidation half-reaction equation, and the equation for the half-reaction of the right-hand electrode as the reduction half-reaction occurs**. This convention enables us to write the equation for the complete cell reaction unambiguously. The electrode at which the reduction half-reaction occurs is called the **cathode**; the electrode at which the oxidation half reaction occurs is called the **anode**. Therefore, the left electrode in the cell diagrams is always the anode (it is Zn(s) in the case of diagram (6)) and the right one is always the cathode (it is Cu(s) for cell (6)).

Each electrochemical cell has its own **cell voltage**, which can be measured by a voltmeter. Walter Nernst, who received a Nobel Prize in 1920 for his work in electrochemistry, proposed in 1889 his famous equation, which

expresses the quantitative relationship between the cell voltage, E_{cell} , the concentration and temperature of the solutions used in the given voltaic cell:

$$E_{\text{cell}} = E_{\text{cell}}^0 - (RT/nF)\ln Q \quad (7)$$

The first term in (7), E_{cell}^0 , is the cell voltage at standard conditions (25°C, 1 atm, 1M concentration for all solutions). The second term, $(RT/nF)\ln Q$, describes the deviation of the cell voltage from its standard value because of concentration or temperature change. Here $R = 8.314 \text{ J/K}\cdot\text{mole}$ is the gas constant; T is the Kelvin temperature of the electrolyte solution; $F = 9.65 \times 10^4 \text{ C/mole}$ – Faraday’s constant, which represents the charge of 1 mole of electrons; “ n ” is the number of moles of electrons transferred from the reducing agent to the oxidizing agent in the balanced equation for the cell reaction, and Q is the reaction quotient for the overall redox reaction in the cell.

For the most common conditions of room temperature (25°C), and more convenient base 10 of logarithms, $(RT/F)\ln Q = 0.0592 \cdot \log Q$, so eq. (7) has the following form:

$$E_{\text{cell}} = E_{\text{cell}}^0 - (0.0592/n)\log Q \quad (\text{in Volts}) \quad (8)$$

III. HOW TO CALCULATE A STANDARD CELL VOLTAGE E_{CELL}^0

During the whole cycle of the electron transfer reactions at the standard conditions in the cell, each electron takes part in both half-reactions: a reduction half-reaction, when it gains a standard reduction voltage E_{red}^0 , and an oxidation half-reaction, which raises its potential by a standard oxidation voltage E_{ox}^0 . After the whole cycle of the electron transfer processes in the cell, each electron gains the total standard voltage E_{cell}^0 :

$$E_{\text{cell}}^0 = E_{\text{red}}^0 + E_{\text{ox}}^0 \quad (9)$$

The data for E_{red}^0 and E_{ox}^0 are tabulated in the tables of the standard reduction voltages, which are also called “standard reduction potentials.” Notice, that for a particular half-reaction, oxidation is the reverse of reduction, therefore

$$E_{\text{ox}}^0 = -E_{\text{red}}^0 \quad (\text{for the same half reaction}) \quad (10)$$

Keep in mind that (9) is an algebraic sum, because E_{red}^0 and E_{ox}^0 may have different signs for the cells where both electrodes are chosen from oxidizing or reducing agents.

Below in Table 1 you will find the standard reduction potentials at 25°C for the ionic reactions you will use in this laboratory experiment.

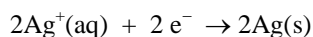
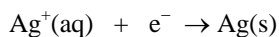
It is impossible to measure the absolute value of one single electrode’s potential, because only differences in the potentials can be recorded. Therefore, all the voltage values in Table 1 are measured using a so-called **standard hydrogen electrode (SHE)** as an **arbitrary zero reference**. All **metal ions** that are reduced with greater difficulty than H^+ (aq) have a negative reduction potential (*these metals are called reducing agents*). **Metal ions** that can be reduced more easily than **SHE** have the standard electrode potential with a positive sign (*these metal ions are called oxidizing agents*). The more powerful reducing agents are at the top of Table 1, the more powerful oxidizing agents – at the bottom.

Table 1. Standard reduction potentials for the aqueous solutions at 25°C

Reduction half-reaction at 25°C	Standard reduction potential, E_{red}^0 , Volts
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	- 0.76
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	- 0.13
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+ 0.34
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+ 0.80

Notice: a) the cell with a combination of stronger oxidizing and reducing agents has the larger standard cell potential E_{cell}^0 ; b) the cell voltage is an intensive property because it should be calculated as the standard potential per charge transferred in the reaction.

It means that the standard potentials E_{rxn}^0 for the reactions:

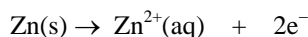


are the same: + 0.80V. Of course, the energy change in the second reaction is doubled in comparison with the first one. However, the charge is doubled also! Therefore, **the standard voltage value E_{cell}^0 (which is the energy per charge)** will be just the same. (Recall the mass and the density properties. You can double the mass of the same substance but its density will still be the same).

IV. EXAMPLE OF THE CELL VOLTAGE CALCULATION: EFFECT OF CONCENTRATION ON CELL VOLTAGE.

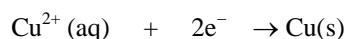
Let's calculate, for example, the cell voltage E_{cell} for *nonstandard conditions* with arbitrary concentrations of the reagents and products in the cell, using Nernst equation (8) and the data in Table 1 for the standard cell voltages.

As an example, we will consider below the $\text{Zn}(\text{s})|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s})$ cell. First, let us calculate the standard cell voltage E_{cell}^0 using the same convention rule: the left-hand electrode in the cell diagram is oxidized, the right-hand electrode is reduced. The oxidation half-reaction in this cell will be:



Because $E_{\text{ox}}^0 = -E_{\text{red}}^0$, we can find the value of E_{ox}^0 from data Table 1 as $(-E_{\text{red}}^0)$ for the reduction reaction $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$: $E_{\text{ox}}^0 = -E_{\text{red}}^0 = -(-0.76\text{V}) = 0.76\text{V}$

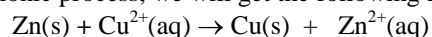
The reduction half-reaction in the cell will be:



with the reduction standard potential $E_{\text{red}}^0 = +0.34\text{V}$ (see Table 1). Therefore, for the overall standard cell voltage E_{cell}^0 we will get the following value:

$$E_{\text{cell}}^0 = E_{\text{ox}}^0 + E_{\text{red}}^0 = 0.76\text{V} + 0.34\text{V} = 1.1\text{V}$$

Now, to write the complete Nernst equation (8) for the cell, we have to construct the overall chemical reaction in the cell, and use it to calculate the reaction quotient Q for the whole cell. Combining the oxidation and reduction half-reactions in the cell in the net ionic process, we will get the following net ionic equation for the cell:



As you can see from this equation, the number of moles of electrons transferred from the reducing agent (Zn) to the oxidizing agent ($\text{Cu}^{2+}(\text{aq})$) is 2 for each mole of Zn and $\text{Cu}^{2+}(\text{aq})$. Therefore, $n = 2$ in eq. (8) and $0.0592/n \approx 0.030$. Using the above ionic equation as the overall chemical reaction in the cell, we can write the reaction quotient Q in the form of

$$Q = [\text{Zn}^{2+}(\text{aq})] / [\text{Cu}^{2+}(\text{aq})]$$

(Notice, that Q doesn't depend on the concentration of solids). Therefore, the final form of the Nernst equation for the Zn|Cu voltaic cell will be:

$$E_{\text{cell}} = 1.1\text{V} - (0.030\text{ V}) \log Q \quad (11)$$

As you can see from (11), the cell voltage E_{cell} has relatively weak logarithmic dependence on Q . Therefore, an increase in Q from $Q=10^{-4}$ to $Q=10^4$ (which corresponds to the change in the ratio of concentrations $[\text{Zn}^{2+}(\text{aq})]/[\text{Cu}^{2+}(\text{aq})]$ by eight orders of magnitude !), changes the cell voltage by only about 0.30 Volts. You can also see the linear dependence of the cell voltage on $\log Q$. The plot of eq.(11) for E_{cell} versus $\log Q$ shown in Fig.3 below.

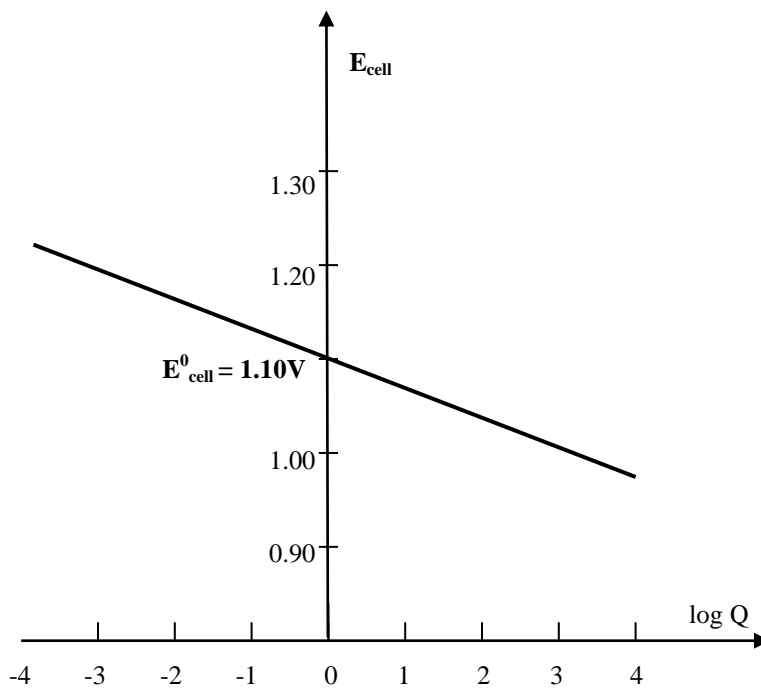


Fig. 3. Plot of E_{cell} versus $\log Q$ for Zn|Cu cell [eq. (11)]. $Q = [\text{Zn}^{2+}(\text{aq})] / [\text{Cu}^{2+}(\text{aq})]$

V. RELATIONSHIP BETWEEN THE STANDARD CELL VOLTAGE E_{CELL}^0 AND THE SPONTANEITY OF THE OVERALL CELL REACTION

To determine the direction of the redox process and eventually the direction of the current in the voltaic cell, we need to calculate the free energy change, ΔG , associated with the chemical reaction in the cell. The value of ΔG is a measure of the driving force (or spontaneity) of the process. **If the free energy change of the redox reaction in the cell (ΔG) is negative, the reaction will occur spontaneously in the direction indicated by the chemical equation. If ΔG is positive, the reaction will proceed in the direction opposite to the one indicated by the equation.**

The cell potential of a redox process, E_{cell} , is related to the free-energy change in the cell, ΔG , as:

$$\Delta G = -nFE_{\text{cell}} \quad (12)$$

and for the case when both reactants and products are in their standard states:

$$\Delta G^0 = -nFE_{\text{cell}}^0 \quad (12a)$$

From the last formula, we can see that **if the value of E_{cell}^0 is positive** for the net cell reaction, **ΔG^0 is negative and the reaction proceeds spontaneously** in the direction indicated by the cell diagram: electrons will flow from the left electrode in the cell diagram to the right one. **If E_{cell}^0 is negative, ΔG^0 is positive, and the actual spontaneous reaction will go in the opposite direction** than indicated by the cell diagram.

VI. TEMPERATURE DEPENDENCE OF THE CELL VOLTAGE

As everybody knows, after some time of usage any voltaic cell (or battery) will be “dead”. In chemical language, it means that the chemical cell (or battery of cells) reaches the equilibrium state when $Q=K$ and $E_{\text{cell}}=0$. Therefore, the Nernst equation (7) can be rewritten at equilibrium as:

$$0 = E_{\text{cell}}^0 - (RT/nF) \ln K$$

This formula immediately leads to

$$E_{\text{cell}}^0 = (RT/nF) \ln K \quad (13)$$

Therefore, the larger equilibrium constant K corresponds to the higher standard cell potential E_{cell}^0 . Now, let's substitute equation (13) into (7), to rewrite Nernst equation (7) in the form that allows us to investigate the temperature dependence of the cell voltage E_{cell} in the laboratory:

$$E_{\text{cell}} = (RT/nF) \ln K - (RT/nF) \ln Q \quad (14)$$

Using the logarithm property

$$\ln A - \ln B = \ln A/B$$

we can simplify equation (14) to the form:

$$E_{\text{cell}} = (RT/nF) \ln K/Q \quad (15)$$

As you can see from equation (15), the cell voltage E_{cell} is **almost proportional** to the absolute temperature T . Why is it only **almost** proportional? Recall that the equilibrium constant K depends on temperature. Therefore, $\ln K$, also depends on temperature. To find the precise temperature dependence for E_{cell} , we should find the temperature function of $\ln K$. The easiest way to find it is to substitute equation (13) into (12):

$$\Delta G^0 = -nFE_{\text{cell}}^0 = -nF(RT/nF) \ln K = -RT \ln K \quad (16)$$

As we know from thermodynamics:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (17)$$

Here ΔH° and ΔS° are the standard enthalpy and entropy changes for the net ionic reaction in the cell. Combining equations (16) and (17) together, we can derive the following equation for the temperature dependence of the equilibrium constant K:

$$RT \ln K = -\Delta H^{\circ} + T\Delta S^{\circ} \quad (18)$$

Now we can substitute equation (18) into (13) and get the final expression:

$$E_{\text{cell}}^{\circ} = - (1/nF) [\Delta H^{\circ} - T\Delta S^{\circ}] \quad (19)$$

This is the cell temperature dependence, which will be investigated experimentally in the lab. As you can see from (19), there are two sources of temperature dependence in this equation: the explicit factor T and the implicit temperature dependence of the enthalpy and entropy changes ΔH° and ΔS° . As known from thermodynamics, ΔH° and ΔS° do change with the temperature T. However, these changes are small comparison to the explicit factor T. Therefore, for the sake of simplicity, we assume that ΔH and ΔS can be approximated in (19) by their standard values ΔH° and ΔS° at room temperature. **Within these assumptions, equation (19) shows that E_{cell} is proportional to the absolute temperature value T of the ionic solutions in the cell.**

In the lab you will investigate the temperature dependence of the Pb(s)|Pb²⁺(aq)||Cu²⁺(aq)|Cu(s) cell with the equal concentrations of the Pb²⁺(aq) and Cu²⁺(aq) solutions. Therefore,

$$Q = [\text{Pb}^{2+}(\text{aq})]/[\text{Cu}^{2+}(\text{aq})]=1$$

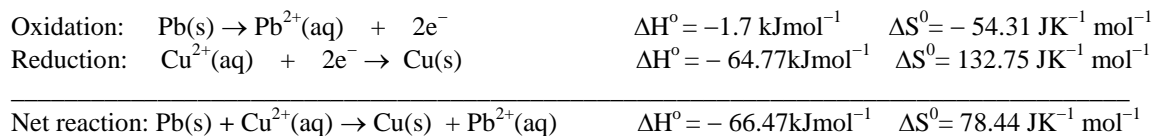
$$\ln Q = 0$$

and equation (15) for E_{cell} has the form:

$$E_{\text{cell}} = (RT/nF) \ln K/Q = (RT/nF) \ln K = E_{\text{cell}}^{\circ} \quad (15a)$$

To understand this laboratory experiment better, let us calculate the theoretical values of E_{cell}° for the Pb(s)|Pb²⁺(aq)||Cu²⁺(aq)|Cu(s) cell at different temperatures.

We should start with the elementary oxidation and reduction half-reactions in the cell. For each of these reactions we can use the textbook data for ΔH° and ΔS° . Then we will sum them up into the net ionic reaction in the cell, and find the resultant values for ΔH° and ΔS° for the net reaction. Finally, we will use these resultant values of ΔH° and ΔS° in equation (19), to calculate the value of the cell potential at different temperatures:



As you can see from the above calculations, for the net ionic reaction in the cell: $\Delta H^{\circ} = -66.47 \text{ kJmol}^{-1}$, $\Delta S^{\circ} = 78.44 \text{ JK}^{-1} \text{ mol}^{-1}$, n=2 (the number of moles of electrons for each mole of the Pb or Cu metals). Let's substitute now all these data in equation (19):

$$E_{\text{cell}} = (1/nF) [-\Delta H^{\circ} + T\Delta S^{\circ}] = \{1/(2 \cdot 96,500 \text{ C mol}^{-1})\} [-(-66.47 \text{ kJ} \cdot \text{mol}^{-1}) + T \cdot 78.44 \text{ JK}^{-1} \text{ mol}^{-1}] =$$

$$= [1/(2 \cdot 96,500)] [66,470 + T \text{ K}^{-1} \cdot 78.44] \text{ V} = [0.346 + 0.408 \cdot 10^{-3} T \text{ K}^{-1}] \text{ V} \quad (20)$$

The temperature value T in (20) should be in Kelvin. We also used for the Faraday constant value the conversion factor $1\text{JC}^{-1} = 1\text{V}$

In the lab you will measure the cell voltage for several different values of temperature: $0\text{ }^{\circ}\text{C}$, room temperature (about $25\text{ }^{\circ}\text{C}$), and $65\text{ }^{\circ}\text{C}$. Let's use equation (20) to calculate the theoretical values of E_{cell} at these temperatures:

$$0\text{ }^{\circ}\text{C}: T = 273\text{ K}, E_{\text{cell}} = [0.346 + 0.408 \cdot 10^{-3} \cdot 273]\text{ V} = 0.457\text{V}$$

$$25\text{ }^{\circ}\text{C}: T = 298\text{ K}, E_{\text{cell}} = [0.346 + 0.408 \cdot 10^{-3} \cdot 298]\text{ V} = 0.467\text{V}$$

$$65\text{ }^{\circ}\text{C}: T = 338\text{ K}, E_{\text{cell}} = [0.346 + 0.408 \cdot 10^{-3} \cdot 338]\text{ V} = 0.484\text{V}$$

As you can see from the above calculations, the cell potential E_{cell} only slightly increases when the temperature changes from $0\text{ }^{\circ}\text{C}$ to $65\text{ }^{\circ}\text{C}$. In part, that is because E_{cell} in formula (19) is proportional to the **absolute temperature** of the solutions in the cell, which changes relatively small in the range between 273K and 338 K. To visualize the linear temperature dependence of the cell potential E_{cell} , a plot of equation (20) for E_{cell} versus T has been constructed below.

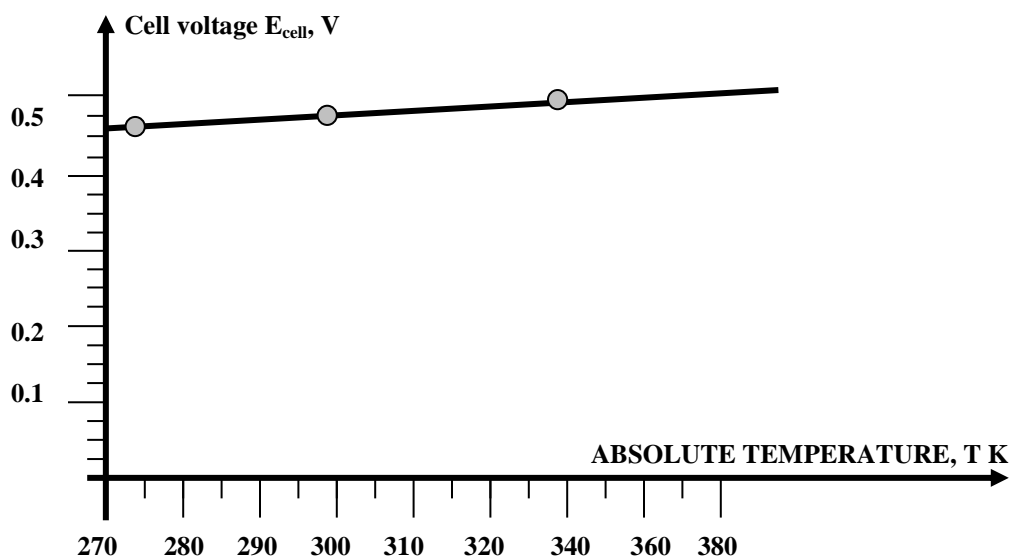


Fig.4. The graph of E_{cell} versus absolute temperature T for the $\text{Pb(s)}|\text{Pb}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$ cell. The calculations are based on the Nernst equation (20).

○ --calculated values of E_{cell} at $T = 273\text{K}, 298\text{K},$ and 338K .

VII. CONCENTRATION CELLS

Let's consider the Nernst equation for the voltaic cell, when two **identical electrodes are immersed in two identical ionic solutions at the same concentrations**. For example, consider the voltaic cell with two silver electrodes and two solutions of AgNO_3 at $25\text{ }^{\circ}\text{C}$ with the concentration 0.200M. The cell diagram for this voltaic cell can be written symbolically as:

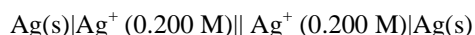


In this case for the standard cell potential E_{cell}^0 (which should be calculated at the standard conditions: $[\text{Ag}^+(\text{aq})] = 1.0\text{M}$, 1.0 atm , 25°C) we can write the following equations (see Table 1):

Cathode (reduction)	$\text{Ag}^+(1.0\text{M}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	$E_{\text{red}}^0 = 0.80\text{ V}$
Anode (oxidation)	$\text{Ag}(\text{s}) \rightarrow \text{Ag}(1.0\text{M}) + \text{e}^-$	$E_{\text{ox}}^0 = -E_{\text{red}}^0 = -0.80\text{ V}$
Net reaction in the cell	$\text{Ag}^+(1.0\text{M}) \rightarrow \text{Ag}^+(1.0\text{M})$	$E_{\text{cell}}^0 = E_{\text{red}}^0 + E_{\text{ox}}^0 = 0.00\text{ V}$

Therefore, the standard voltage E_{cell}^0 for the cell is zero. The result is quite understandable, because at the standard conditions the cell has two identical $1.0\text{M Ag}^+(\text{aq})$ solutions with two identical $\text{Ag}(\text{s})$ electrodes in them. Therefore, the cell is at the equilibrium when $\Delta G = 0$. That is why, according to eq.(12a), the cell voltage E_{cell}^0 is zero.

What is the value of the second term in Nernst equation (7), $RT/nF\ln Q$, which describes the voltage produced in the cell due to concentration or temperature deviation from the standard conditions? Consider the similar voltaic cell **but with non-standard 1.0M concentrations of silver nitrate** solution in each cell compartment. For example, it can be the cell:



As you can see from the net equation for the cell, it has the nonstandard **but the identical silver nitrate concentrations** of 0.200M in both cell compartments. Therefore, the reaction quotient for the cell will be $Q = 0.200\text{M}/0.200\text{M} = 1$. But in this case: $\ln Q = \ln 1 = 0$ and the additional term in Nernst equation is also zero at these conditions. Therefore, **the cell with the identical ionic solutions and the same metal electrodes in both compartments has zero cell voltage because it is at equilibrium.**

Now let's consider the same voltaic cell but under conditions, when the concentration of the AgNO_3 solutions are different in two cell compartments. For example, $[\text{Ag}^+(\text{aq})] = 0.2000\text{M}$ at the silver cathode and $[\text{Ag}^+(\text{aq})] = 0.0002\text{M}$ at the silver anode. In this case, the cell is out of equilibrium. Therefore, $\Delta G < 0$ for the net redox reaction in the cell and according to general formula (12) it should generate some cell voltage that can be measured in the experiment.

To determine the value of this cell voltage we need to calculate the value of the reaction quotient Q for the redox reaction in the cell. Therefore, we have to figure out in what direction the reaction in the cell will go. Actually, we have only two options: either the concentration gap between $\text{Ag}^+(\text{aq})$ solutions in the cell compartments increases or decreases in the process of the redox reaction in the cell.

It is easy to understand that the concentration gap between cell compartments cannot be increased spontaneously, because in this case the cell will go spontaneously further and further out of equilibrium, generating spontaneously higher and higher cell voltage which, of course, cannot be true. As we know from thermodynamics (and from the everyday life experience), any system, which is initially out of equilibrium finally reaches the equilibrium state when $\Delta G = 0$. But the only way to reach the equilibrium in our voltaic cell is to decrease the concentration gap in $[\text{Ag}^+(\text{aq})]$ between the solutions in the cell compartments. Therefore, the redox reaction in the cell should increase the lower concentration of silver ions $\text{Ag}^+(\text{aq})$ at the cathode and decrease its higher concentration at the anode's compartment:

Cathode (reduction):	$\text{Ag}^+(0.2000\text{M}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	(concentration of the Ag^+ ions is decreased)
Anode (oxidation)	$\text{Ag}(\text{s}) \rightarrow \text{Ag}^+(0.0002\text{M}) + \text{e}^-$	(concentration of the Ag^+ ions is increased)
Net reaction:	$\text{Ag}^+(0.2000\text{M}) \rightarrow \text{Ag}^+(0.0002\text{M})$	

To calculate the value of the cell voltage for this kind of cell we must use Nernst equation (8):

$$E_{\text{cell}} = E_{\text{cell}}^0 - (0.0592/n) \cdot \log Q$$

with $E_{\text{cell}}^0 = 0$ and $n=1$. So:

$$E_{\text{cell}} = -0.0592 \text{ V} \cdot \log Q \quad (22)$$

and because

$$\log Q = \log (0.0002/0.2000) = \log 10^{-3} = -3$$

$$E_{\text{cell}} = -0.0592 \text{ V}(-3) \approx 0.18 \text{ V}$$

This is a so-called **concentration cell**. The redox reaction proceeds to equalize the concentration of $\text{Ag}^+(\text{aq})$ ions in cell compartments. Notice, that this is exactly what would happen if we simply mixed two $\text{Ag}^+(\text{aq})$ solutions of different concentration in one beaker: we would get the resultant solution with the averaged concentration of $\text{Ag}^+(\text{aq})$ ions. The electrochemical cell does absolutely the same with only one important difference: it mixes these solutions **with electron transfers between two different beakers** instead of mixing solutions themselves.

Notice also that concentration cells have much smaller cell voltage E_{cell} than usual voltaic cells, because the standard cell voltage is zero for these particular cells. However, you can see from the above analysis that the process of “mixing solutions with electrons” can be used in experiment to generate cell voltage.

GENERAL CHEMISTRY LABORATORY

CH131

LABORATORY EXPERIMENT #7: ELECTROCHEMISTRY

(2 PERIOD LAB)

Name: _____

ID#: _____

TF: _____

SECTION/Day/ Time: _____

BOSTON UNIVERSITY

VIII. DETAILED PROTOCOL OF THE EXPERIMENT

PART ONE: FIRST LABORATORY PERIOD

WORK IN PAIRS BUT WRITE YOUR REPORTS INDIVIDUALLY

SAFETY

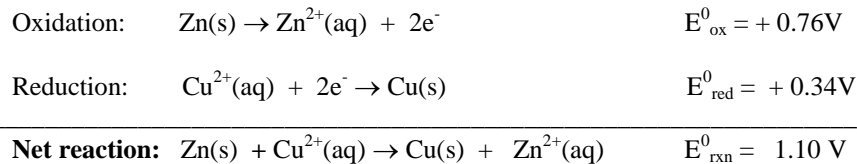
Some of the metal salts you will use in this experiment are toxic, especially those of lead (II). **BE SURE TO RINSE OFF ANY REAGENTS THAT COME IN CONTACT WITH YOUR SKIN.** Be sure to wash your hands before touching your face and before you leave the lab. Be aware that solution of silver nitrate can develop the coloration of the skin (or nails) at the place of contact. This coloration will wear off by itself in a couple of weeks. It can be very bad, however, in the eye, since the stain will take years to fade. Therefore, for the sake of safety we strongly recommend: a) **WEAR SAFETY GOGGLES and VINYL DISPOSABLE GLOVES;** b) **HANDLE METAL STRIPS IN THE SOLUTIONS ONLY BY TWEEZERS.**

VIII.1. Interaction of metal and metal ions

- A. Prepare a clean well plate. Rinse it with distilled water and dry with a paper towel. Fill four wells 3/4 full of 0.2M $\text{Zn}(\text{NO}_3)_2$ stock solutions. **Wearing vinyl gloves** clean the obtained strips of Zn, Cu, Pb and Ag with steel wool. Place each clean metal strip into the separate $\text{Zn}(\text{NO}_3)_2$ solution in the wells for about 1 min and record the appearance of a chemical reaction between the metal and the ionic solution in Data Table 2 below.
- B. Prepare a clean beaker with distilled water. **Using tweezers** take each metal strip out of the ionic solution in the well plate, rinse it in the beaker with distilled water and put them on a piece of a paper towel on the bench. **Wearing vinyl gloves** clean the strips with steel wool to prepare them for the next experiment. Pour the solutions of $\text{Zn}(\text{NO}_3)_2$ from the well plate into the designated waste beaker and later from the waste beaker - into the waste container in the lab. Rinse the well plate with distilled water and dry it with a paper towel. Now your experimental set up is ready for the next experiment.
- C. Repeat the whole experiment with three other stock solutions: 0.2M $\text{Cu}(\text{NO}_3)_2$, 0.2M AgNO_3 and 0.2M $\text{Pb}(\text{NO}_3)_2$. Record the appearance of a chemical reaction between each metal and the ionic solution in Data Tables 3-5. **Write "NR" in Data Tables if you don't observe any reaction in the well plate approximately for 1 min.**
- D. In Data Table 6 write the balanced net ionic equations for each metal/solution combination tested in the experiment. Use the data from Table 1 (see the lab lecture above) to calculate the values of the standard voltage for each net reaction. Calculate the value of E^0_{rxn} and the sign of ΔG^0 for each reaction. Compare the calculated sign of ΔG^0 value with the presence or absence of the reaction in the well. **Write "NR" in Data Table 6 if you observe no reaction in the well plate approximately for 1 min.**

Example #1: Zn(s)/Cu²⁺ (aq) system

In this case, you will see a black substance on the surface of the zinc plate. It is the layer of Cu(s), which is deposited on the zinc surface as the product of the following reactions:



As you can see from the simple calculations above, there is a very important conclusion: a standard voltage E_{rxn}^0 of this net reaction is positive! Because the standard free energy change ΔG^0 of the reaction is

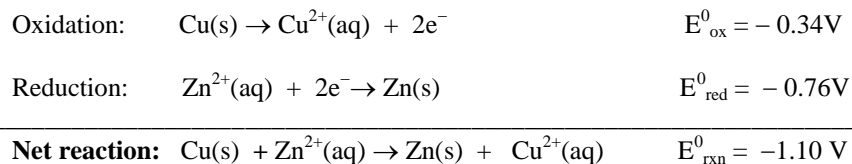
$$\Delta G^0 = -nFE_{\text{rxn}}^0$$

and n and F are positive constants, $\Delta G^0 < 0$ for the overall net ionic reaction in the well. That is why the net reaction between Zn(s) and Cu²⁺ (aq) is spontaneous and manifests itself by plating out Cu(s) on the surface of the Zn plate.

Actually, you can predict the sign of ΔG^0 for this net reaction even without calculations: **you observe the spontaneous reaction, so ΔG^0 should be negative!**

Example #2: Cu(s)/ Zn²⁺ (aq) system.

In that case:



As you can see from the above analysis, $E_{\text{rxn}}^0 < 0$ for the Zn(s)/Cu²⁺(aq) system. It leads to $\Delta G^0 > 0$ for the net reaction. Do you expect to see a solid plating of copper on the Zn plate in a Cu²⁺ (aq) solution?

Finally, for the system with the same metal and metal ion (for example, Zn(s)/Zn²⁺(aq) system), you can easily calculate that $E_{\text{rxn}}^0 = 0$. So, $\Delta G^0 = 0$ for the net reaction in the well. It means the chemical system is in the state of the dynamic equilibrium: the rates of oxidation and reduction reactions are the same. Do you expect to see any visible evidence of the equilibrium state in the system?

Fill out data Table 7 below, using Table 1 for the standard reduction potential values (see the example of Zn(s)/Cu²⁺(aq) and Cu(s)/Zn²⁺(aq) systems provided in Table 7). **Notice:** In your calculations made for E_{rxn}^0 , the sign of ΔG^0 for each investigated system, and the conclusion made in the last column of Table 7 should support your observation data recorded in Table 2-5.

Data Table 2. Reaction of Zn, Cu, Pb and Ag metals in $\text{Zn}^{2+}(\text{aq})$ ionic solution

Ionic solution used in the experiment	Metal strip used in the experiment			
	Zn(s)	Cu(s)	Pb(s)	Ag(s)
$\text{Zn}^{2+}(\text{aq})$				

Data Table 3. Reaction of Zn, Cu, Pb and Ag metals in $\text{Cu}^{2+}(\text{aq})$ ionic solution

Ionic solution used in the experiment	Metal strip used in the experiment			
	Zn(s)	Cu(s)	Pb(s)	Ag(s)
$\text{Cu}^{2+}(\text{aq})$				

Data Table 4. Reaction of Zn, Cu, Pb and Ag metals in $\text{Ag}^+(\text{aq})$ ionic solution

Ionic solution used in the experiment	Metal strip used in the experiment			
	Zn(s)	Cu(s)	Pb(s)	Ag(s)
$\text{Ag}^+(\text{aq})$				

Data Table 5. Reaction of Zn, Cu, Pb and Ag metals in $\text{Pb}^{2+}(\text{aq})$ ionic solution

Ionic solution used in the experiment	Metal strip used in the experiment			
	Zn(s)	Cu(s)	Pb(s)	Ag(s)
$\text{Pb}^{2+}(\text{aq})$				

Data Table 6. Spontaneity of the oxidation/reduction reactions

System	Net ionic reaction for the system in the well	E^0_{rxn} , Volts	Sign of ΔG^0 ($<$, $=$ or $>$ 0)	Type of reaction ("Spontaneous" or "no reaction")
Zn(s)/ Cu ²⁺ (aq)	Zn(s) + Cu ²⁺ (aq) → Cu(s) + Zn ²⁺ (aq)	1.1	< 0	Spontaneous
Cu(s)/Zn ²⁺ (aq)	Cu(s) + Zn ²⁺ (aq) → Cu ²⁺ (aq) + Zn(s)	- 1.1	> 0	NR
Zn(s)/Zn ²⁺ (aq)	Zn(s) + Zn ²⁺ (aq) → Zn ²⁺ (aq) + Zn(s)	0	= 0	Equilibrium, No appearance of rxn
Zn(s)/Ag ⁺ (aq)				
Zn(s)/Pb ²⁺ (aq)				
Cu(s)/Cu ²⁺ (aq)				
Cu(s)/Ag ⁺ (aq)				
Cu(s)/Pb ²⁺ (aq)				
Pb(s)/Zn ²⁺ (aq)				
Pb(s)/Cu ²⁺ (aq)				
Pb(s)/Ag ⁺ (aq)				
Pb(s)/Pb ²⁺ (aq)				
Ag(s)/Zn ²⁺ (aq)				
Ag(s)/Cu ²⁺ (aq)				
Ag(s)/Ag ⁺ (aq)				
Ag(s)/Pb ²⁺ (aq)				

E. Compare the metals in this experiment (Zn, Cu, Pb and Ag) by their relative reactivity as reducing (or oxidizing) agents and arrange them in the rows of oxidizing and reducing reactivity in Table 7 using the observation data from Table 2-5. **Note:** a) **the highest oxidizing reactivity** should be assigned to **the metal, that has an ionic solution which reacts with solid samples of all other metals** (oxidizing them to their metal ions); b) **the metal which reacts with ionic solutions of all other metals** (reducing the metal ions in the solution to the neutral metal atoms) has the highest reducing reactivity.

Table 7. Relative reactivity of four metals and their ions. (Put the most reactive metal (or ion) at the left side of the row)

Oxidizing relative reactivity row for Zn^{2+} , Cu^{2+} , Pb^{2+} and Ag^+	
Reducing relative reactivity row for Zn , Cu , Pb and Ag	

VIII.2. Voltaic cells

A. Fill a 100-ml beaker 1/3 full of 1M $NaNO_3$ solution and obtain strips of filter paper. In the next several experiments you will use a strip of filter paper soaked in the $NaNO_3$ solution as a salt bridge for the voltaic cells.

B. Prepare a clean well plate. Rinse it with distilled water and dry it with a paper towel. Label four wells as “Zn”, “Cu”, “Pb” and “Ag”. Fill the wells 3/4 full of $Zn(NO_3)_2$, $Pb(NO_3)_2$, $Cu(NO_3)_2$ and $AgNO_3$ stock solutions respectively.

C. Connect the solutions of $Zn(NO_3)_2$ and $Pb(NO_3)_2$ in the wells by a strip of filter paper soaked in $NaNO_3$ solution. One side of this “bridge” should be immersed in the $Zn^{2+}(aq)$ solution, the other one – in the $Pb^{2+}(aq)$ solution. $Na^+(aq)$ and $NO_3^-(aq)$ ions can move along the fiber structure of the filter paper and connect the solutions in the wells exactly as a regular salt bridge does in all classical electrochemistry experiments. **Don't make the paper bridge too long- it will affect your measurement data.**

D. Assemble a $Zn(s)|Zn^{2+}(aq)||Pb^{2+}(aq)|Pb(s)$ cell (see Fig. 5 below). Clip a strip of Zn metal in the negative clamp of the voltmeter (it has black wire) and submerge it into the $Zn(NO_3)_2$ solution. (It will be your Zn half-cell, which is usually denoted as $Zn(s)|Zn^{2+}(aq)||$). Clip a strip of clean Pb metal by the other voltmeter's clamp and submerge it into the $Pb(NO_3)_2$ solution. (It will be the Pb half-cell denoted as $||Pb^{2+}(aq)|Pb(s)$). Switch the voltmeter “ON” (to the position DC V) just long enough to take a stable reading. Then turn it off (or disconnect it). Repeat this measurement two more times and record the absolute value of each voltage and its average value in Data Table 8.

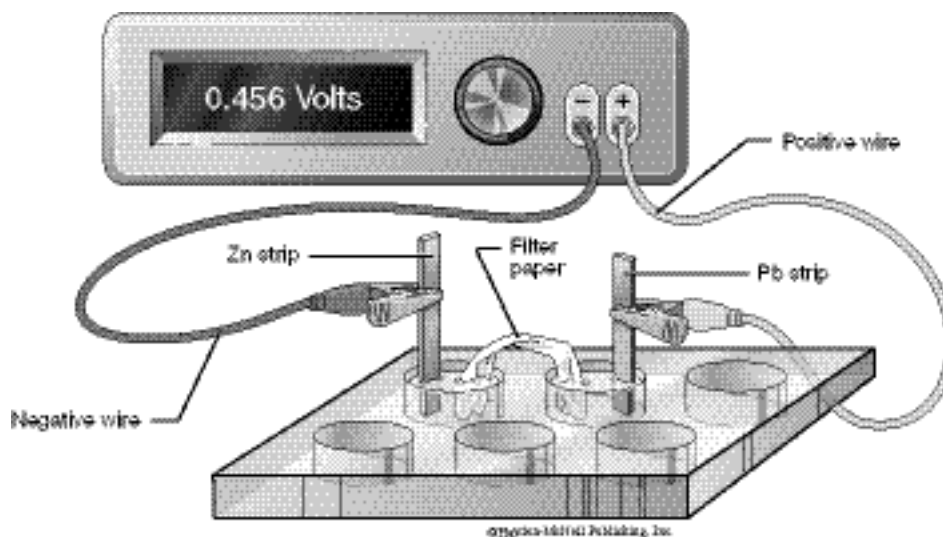


Fig.5. Experimental set up for the voltaic cell measurements. Be aware that metal clamps of the voltmeter are not immersed in the solutions. Otherwise, you can get the wrong measurements (Why?)

E. Assemble all the possible cells combining different metals and wells. **Record the positive voltage** and cell symbol for each cell. (**Note:** switch the wires in case you measure a negative voltage value). To avoid cross contamination of the solutions in different wells for **each new cell use a new strip of filter paper**.

F. Repeat each voltage measurement three times and compute an absolute value of the average voltage for each cell. Record your data in Table 8. The goal of this experiment is to discover the voltaic cell with the highest absolute voltage value and find the relationship between the absolute value of the cell voltage and the level of the metal's reactivity recorded in Table 7.

G. Empty and rinse your well plate to prepare it for the next experiment.

VIII.3. Effect of concentration on the cell voltage

In this experiment, you will investigate the effect of the solution concentration on the cell voltage. The experiment will be done with several $\text{Cu(s)}|\text{Cu}^{2+}(\text{aq})||\text{Ag}^+(\text{aq})|\text{Ag(s)}$ cells with a constant concentration of $\text{Cu}^{2+}(\text{aq})$ solution in the $|\text{Cu}^{2+}(\text{aq})|\text{Cu}$ half-cell and a variable concentration of $\text{Ag}^+(\text{aq})$ solution in the $\text{Ag(s)}|\text{Ag}^+(\text{aq})|$ half-cell.

A. Using 0.20M $\text{Ag}^+(\text{aq})$ stock solution, distilled water and the serial dilution technique prepare 10.0ml of each: 0.02M $\text{Ag}^+(\text{aq})$, 0.002M $\text{Ag}^+(\text{aq})$ and 0.0002M $\text{Ag}^+(\text{aq})$ solution. Before you start the preparation of the diluted $\text{Ag}^+(\text{aq})$ solutions check your dilution calculations with your lab TF.

B. Label four clean wells in the well plate and place a few ml of each of the four $\text{Ag}^+(\text{aq})$ solutions (the stock one and the three others prepared by the serial dilution) in separate clean wells. The fifth well should be filled with the 0.20M $\text{Cu}^{2+}(\text{aq})$ stock solution.

C. Connect $\text{Cu}^{2+}(\text{aq})$ solution with 0.0002M $\text{Ag}^+(\text{aq})$ solution in the well plate by the salt bridge made of the strip of filter paper soaked in the NaNO_3 solution. Clip the clean strip of Cu in the voltmeter's clamp and submerge it into the $\text{Cu}^{2+}(\text{aq})$ solution. Place a clean Ag strip into the second voltmeter's clamp and immerse in 0.0002M $\text{Ag}^+(\text{aq})$ solution. Measure the cell voltage as you did in the previous experiment and record the data in Table 9 below.

D. Obtain two more readings of the cell voltage and calculate its average value.

E. Rinse and dry the Ag strip. Repeat this experiment, constructing a similar cell with 0.002M $\text{Ag}^+(\text{aq})$ solution. **Note:** use a new strip of filter paper for each following experiment!

F. Repeat this experiment using the same $\text{Cu(s)}|\text{Cu}^{2+}(\text{aq})|$ half-cell and 0.0002M, 0.002M, 0.020M and 0.200M $\text{Ag}^+(\text{aq})$ solutions for $|\text{Ag}^+(\text{aq})|\text{Ag(s)}$ half-cell.

G. Write the net ionic equation for the reaction in the above $\text{Cu(s)}|\text{Cu}^{2+}(\text{aq})||\text{Ag}^+(\text{aq})|\text{Ag(s)}$ cell. Using the standard voltage data from Table 1, check the signs of E_{cell}^0 and ΔG^0 for the cell, and the direction of its net ionic reaction. This analysis will help you write the correct formula for the reaction quotient Q. Then use Nernst equation (8) (see the lab lecture above) to analyze the character of the dependence between the cell voltage E_{cell}^0 and the reaction quotient Q. Compare the difference in the $\text{Ag}^+(\text{aq})$ concentrations [it is several orders of magnitude between 0.200M and 0.0002M $\text{Ag}^+(\text{aq})$] and the voltage difference between the cells in the above experiment. Explain your results. For full credit, attach the sample of these calculations to your lab report.

H. For the voltaic cell under the investigation, make a plot of theoretical values for E_{cell} versus $\log Q$ (where Q is the reaction quotient for the cell reaction) and the similar plot for the experimental data of E_{cell} versus $\log Q$ using your measurement from data Table 9. Compare the theoretical and experimental plots in your lab report.

Data Table 8: Looking for the most powerful voltaic cell

Cell #	Cell symbol	Cell voltage, V			Average Cell voltage, V
		1-st Run	2-nd Run	3-rd Run	
1	$\text{Zn(s)} \text{Zn}^{2+}(\text{aq}) \text{Ag}^+(\text{aq}) \text{Ag(s)}$				
2	$\text{Zn(s)} \text{Zn}^{2+}(\text{aq}) \text{Cu}^{2+}(\text{aq}) \text{Cu(s)}$				
3	$\text{Zn(s)} \text{Zn}^{2+}(\text{aq}) \text{Pb}^{2+}(\text{aq}) \text{Pb(s)}$				
4	$\text{Pb(s)} \text{Pb}^{2+}(\text{aq}) \text{Ag}^+(\text{aq}) \text{Ag(s)}$				
5	$\text{Pb(s)} \text{Pb}^{2+}(\text{aq}) \text{Cu}^{2+}(\text{aq}) \text{Cu(s)}$				
6	$\text{Cu(s)} \text{Cu}^{2+}(\text{aq}) \text{Ag}^+(\text{aq}) \text{Ag(s)}$				

Data Table 9. Effect of concentration on the cell voltage value

Cell #	Cell	Cell Voltage (E_{cell}), V			
		1-st Run	2-nd Run	3-rd Run	Average
1	$\text{Cu(s)} \text{Cu}^{2+}(\text{aq}) 0.00020\text{M Ag}^+(\text{aq}) \text{Ag(s)}$				
2	$\text{Cu(s)} \text{Cu}^{2+}(\text{aq}) 0.0020\text{M Ag}^+(\text{aq}) \text{Ag(s)}$				
3	$\text{Cu(s)} \text{Cu}^{2+}(\text{aq}) 0.020\text{M Ag}^+(\text{aq}) \text{Ag(s)}$				
4	$\text{Cu(s)} \text{Cu}^{2+}(\text{aq}) 0.20\text{M Ag}^+(\text{aq}) \text{Ag(s)}$				

VIII. 4. Temperature dependence of the $\text{Pb(s)}|\text{Pb}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$ cell voltage

A. Room temperature measurements. Assemble the $\text{Pb(s)}|\text{Pb}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$ cell in the **small** test tubes (see Fig. 6 below). Fill two small test tubes 3/4 full with Pb^{2+} and Cu^{2+} stock solutions (first fill one test tube with 0.20M $\text{Pb}(\text{NO}_3)_2$ solution and then the other one with 0.20M $\text{Cu}(\text{NO}_3)_2$ solution). Place them inside a 150 ml beaker. Connect the $\text{Pb}^{2+}(\text{aq})$ and $\text{Cu}^{2+}(\text{aq})$ solutions in the test tubes by a strip of filter paper soaked in NaNO_3 solution. Clip the clean Pb strip in the negative voltmeter clamp and immerse it in the test tube with $\text{Pb}^{2+}(\text{aq})$ solution. Clip the clean Cu strip in the positive voltmeter clamp and immerse it in the second test tube with the $\text{Cu}^{2+}(\text{aq})$ solution. Measure the value of the cell voltage three times at room temperature and calculate its average value. (**See Fig. 6 below for the experimental set up**). Record the data and room temperature at the time of measurement in data Table 10 below. Discard the used salt bridge.

B. Low temperature measurements. Fill the beaker 3/4 full with a mixture of ice and water. Immerse your test tubes in the cold bath prepared in the beaker. Wait about 10 minutes for the solutions in the test tubes to cool and then connect the solutions with the **fresh** strip of filter paper soaked in NaNO_3 . Measure the value of the cell voltage for the $\text{Pb(s)}|\text{Pb}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$ cell at the cold temperature three times and calculate its average value. Record the temperature of the cell solutions (it should be in the range of 0 ± 3 °C). (It will be enough to measure the temperature of one solution: the temperature of the other one will be just the same. Don't contaminate one solution with the other in the process of temperature measurement). Record your data in data Table 10 and discard the iced water and the used strips of filter paper after the experiment.

C. High temperature measurements. For this experiment, you should use a special water bath with an automatically fixed hot water temperature. Place the same experimental test tubes with $\text{Pb}^{2+}(\text{aq})$ and $\text{Cu}^{2+}(\text{aq})$ stock solutions in the rack immersed in a hot water bath and check the water temperature (it should be about $65 - 70$ °C). Prepare two clean glass rods. Wait about 10 minutes for the solutions in the test tubes to heat up and then mix each solution with a separate glass rod (you need two glass rods to avoid cross contamination of the solutions). Using a clean digital thermometer check the temperature of the solution in one of the test tubes: it should be close to the water bath temperature. After that, connect the solutions in the test tube with a **fresh** strip of filter paper soaked in NaNO_3 solution. Keeping the test tubes in the water bath, assemble the $\text{Pb(s)}|\text{Pb}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$ cell in the same manner you did in **Sec. A and B** for the cell voltage measurement at room and low temperature. Measure the value of the cell voltage at the recorded elevated temperature three times, and calculate its average value. Record the data of your measurements according Data Table 10. (**See Fig. 7 below for experimental set up**).

D. Use the experimental data from Table 10 to make a plot of the Voltage versus Temperature for the $\text{Pb(s)}|\text{Pb}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$ cell voltage. Compare your results with the theoretical graph in Fig.4 and the Nernst equation in the form of eq. (20) (see the lab lecture above).

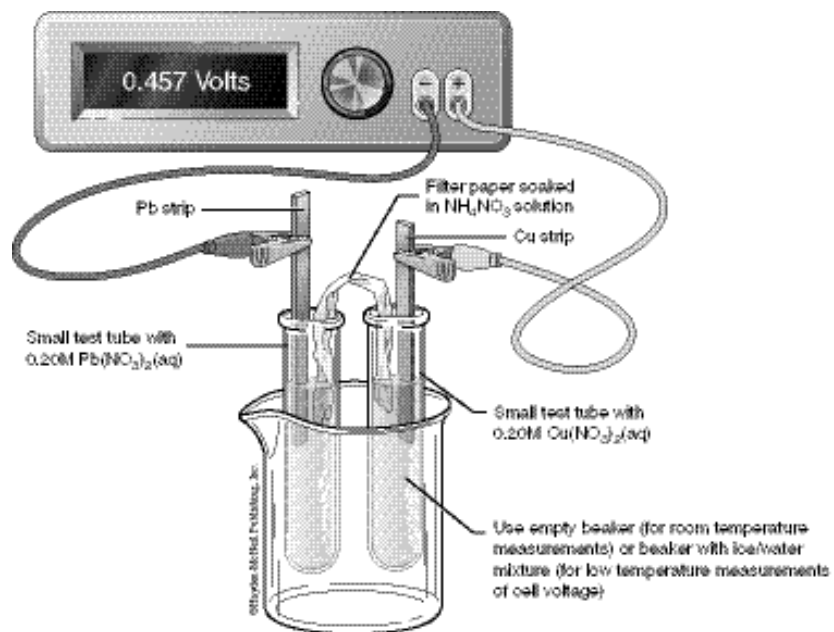


Fig.6 Experimental set up for cell voltage measurements in cold-water bath and at room temperature.

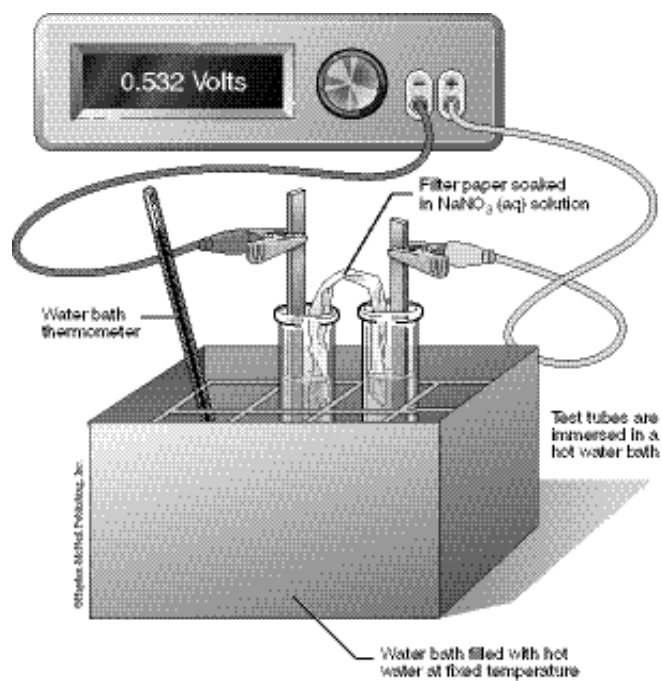


Fig. 7 Experimental set up for high temperature cell voltage measurements.
 Note: Water bath temperature should be kept at about of 65-70 $^{\circ}\text{C}$.

Data Table 10. Temperature dependence of the cell voltage for the $\text{Pb(s)}|\text{Pb}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$ cell

		Cell voltage, V			
Exp. #	Temperature, °C	1-st Run	2-nd Run	3-rd Run	Average
Cell voltage at room temperature					
1					
Cell voltage in cooled solutions					
2					
Cell voltage in heated solutions					
3					

IX. PART II. OPEN PROJECT ON CONCENTRATION CELL

The goal of the second lab period of the Electrochemistry lab is to use the experimental experience gained in Part I of the laboratory to investigate the concentration cell made of silver electrodes and the solution of silver nitrate, AgNO_3 . The main challenge of this project is to increase the voltage of this cell to at least 0.18V by changing its concentration and/or temperature of the ionic solutions.

IX.1 The concentration cell experimental set up. Fill and label two clean wells on the well plate with the stock solution of 0.20M $\text{Ag}^+(\text{aq})$. Using two clean strips of Ag metal as electrodes and a strip of filter paper soaked in NaNO_3 solution as a salt bridge, construct the concentration cell shown in Fig.8 below and measure its cell voltage. Explain the observed result.

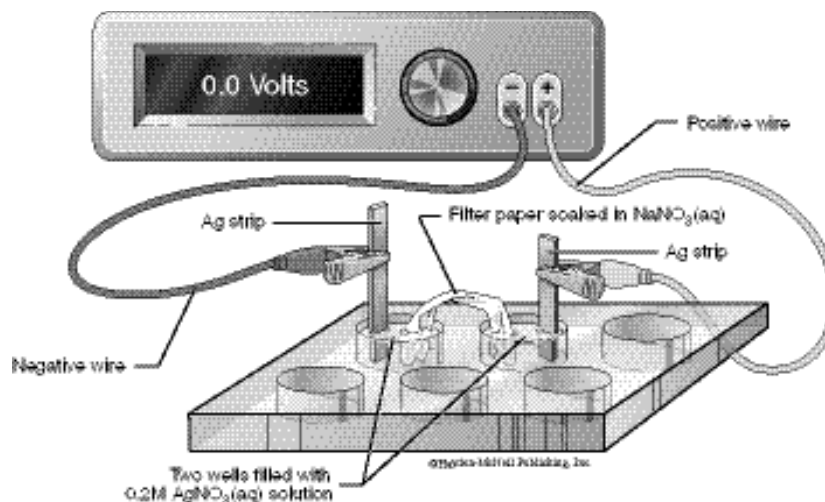


Fig.8. Experimental set up for the investigation of the concentration voltaic cell.

IX.2. Investigate in the experiment the cell voltage dependence on $(-\log Q)$ for the assembled concentration cell. Record your experimental data according to Data table 11 and construct the experimental graph for E_{cell} versus $(-\log Q)$ based on table 11 data. Write the net ionic equation and Nernst equation for this concentration cell and make the theoretical graph for E_{cell} versus $(-\log Q)$ for the same dilutions and $(-\log Q)$ values that have been used for the experiment recorded in Data table 11. Compare the theoretical and experimental graphs for E_{cell} -vs- $(-\log Q)$ and explain their deviation for large $|\log Q|$ values.

X. Results summary.

Attach to your lab report the following lab materials:

1. Data table 1-10.

2. For the voltaic cell $\text{Cu}(\text{s})|\text{Cu}^{2+}(\text{aq})||\text{Ag}^+(\text{aq})|\text{Ag}(\text{s})$ make: a) a theoretical plot based on Nernst equation for E_{cell} versus $\log Q$; b) on the same graph make the plot for E_{cell} versus $\log Q$ based on your experimental data in Table 9 (see VIII.3.A-H for details).

3. For the voltaic cell $\text{Pb}(\text{s})|\text{Pb}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s})$: a) copy on the graph paper the theoretical plot in Fig.4 for E_{cell} versus temperature; b) on the same graph construct the plot for E_{cell} versus temperature based on your experimental data in table 10 (see VIII.4.A-D for details).

4. For the open project on the concentration cell $\text{Ag}(\text{s})|\text{Ag}^+(\text{aq})||0.20\text{M Ag}^+(\text{aq})|\text{Ag}(\text{s})$: a) construct a theoretical plot based on Nernst equation for E_{cell} versus $(-\log Q)$; b) on the same graph make the plot for E_{cell} versus $(-\log Q)$ based on your experimental data in Table 11. Explain the difference for the increased dilution.

5. Separate pages with all calculations needed for data tables 1-11 and all the graphs.

Data Table 11. Open project on the concentration cell: Cell voltage versus dilution

Cell #	Cell	Cell Voltage (E_{cell}), V			
		1-st Run	2-nd Run	3-rd Run	Average
1	$\text{Ag(s)} 0.20\text{M Ag}^+(\text{aq}) 0.20\text{M Ag}^+(\text{aq}) \text{Ag(s)}$				
2	$\text{Ag(s)} 0.02\text{M Ag}^+(\text{aq}) 0.20\text{M Ag}^+(\text{aq}) \text{Ag(s)}$				
3	$\text{Ag(s)} 0.002\text{M Ag}^+(\text{aq}) 0.20\text{M Ag}^+(\text{aq}) \text{Ag(s)}$				
4	$\text{Ag(s)} 0.0002\text{M Ag}^+(\text{aq}) 0.20\text{M Ag}^+(\text{aq}) \text{Ag(s)}$				
5					
6					