

Electrochemistry remote experiment - galvanic cell - II

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ABSTRACT — The paper is a free continuation of the paper presented at the REV 2009 conference, where we reported about remote experiment “Electrochemical cell characterization - is it a start of remote experiments in chemistry education? “. As a matter of fact it was meant as a small spur to the chemistry instructors to inspire them to build remote experiments, which are scarce in literature even now after five years. We want to present the continuation to the 2008 talk, showing what may be gained from a chemical remote experiment data, which wealth of information it may bring if properly used. We show how the experiment Electrochemical cell with controlled change of the electrolyte concentration and simultaneous measurement of electromotive force and electrolyte conductivity provides the possibility for the elucidation of the electrolyte conductivity, decision about strong/weak electrolytes, ions mobility and the study of Fermi level of various metals and reaction constant. In the paper we want to use the experience gained in the meantime with the experiment Electrochemical cell and show all the possibility it offers. Paper may serve for inspiration to build, using ISES system, similar experiments for chemistry education.

Index Terms— Computer oriented experiments, chemistry education, ICT in chemistry, remote experiments, Integrated Learning

I. INTRODUCTION

When we were starting the e-laboratory of remote experiments (Internet Natural Science Remote e-Laboratory - INRe-L [1]) in Trnava in 2004 as a continuation of a similar laboratory in Prague (see www.ises.info) and a constituent part of the Consortium INRe-L of three universities (Charles University in Prague, Tomas Bata University in Zlin and Trnava University in Trnava), we came across the crucial question which remote experiments to build. Then it was to our disposal the path breaking physical plug and play system hardware and software system - Internet School experimental System (ISES) [2] and as its part the controlling system for the building of remote experiments ISES WEB CONTROL kit [3] all of our own design. On top of this in Prague were then running 6 remote experiments from electricity and magnetism (see www.ises.info).

When we considered the first experiment for Trnava Department of Physics, we luckily met the fresh graduate from Chemistry Department, Lenka Valkova, MSc., who was then willing to undertake the “excursion“ to then unexplored chemistry field – remote experiment in electrochemistry. We then did not realize all the obstacles inherent in any chemical computerized experiment hands- on and remote, not even speaking about the resistance we encountered in part of chemistry instructors in chemistry laboratories. The only suspicious circumstance for us was the lack of chemistry remote experiments in literature (the only known for us an exception was the pioneering remote experiment on “Heat exchanger“ by Clark Colton from MIT, in operation from 2001[4].

Irrespective of all these facts we started and luckily enough we finished the remote experiment “Galvanic cell “ and defended the thesis and subsequently presented its results at the conference REV 2009 in Bridgeport. The contribution on remote experiment “Galvanic cell” [5] from the electrochemist point of view raised the substantial interest and was given the appreciation for “The best paper” of the conference.

After five years in 2012, the situation in chemistry remote experiments has hardly changed and papers on remote experiments in chemistry are still scarce. A very valuable initiative took place in 2006 in Cambridge where Cambridge, MIT and Leipzig chemistry departments organized “Weblabs in Chemical Engineering Education [6]. In 2007 they launched in Cambridge together with MIT the “Chemical reactor” remote experiment [7] and paper [8]. Also important is contribution on remote experimentation in analytical chemistry by D. Kennepohl [9] and that by A. Klein and G. Wozny on distillation column [10].

In the present paper we want to refer the experience gained in the meantime with this experiment and show all the possibility it offers for electrochemistry teaching. Paper may serve for inspiration to build, using ISES system, similar experiments for chemistry education.

II. PHILOSOPHY OF THE REMOTE EXPERIMENT

„ELECTROCHEMICAL CELL“

All substantial information concerning remote experiment were given in a previous paper [5] here we give only the facts for reader's orientation. We choose in 2007 the "Galvanic cell" as a typical electrochemical energy source as we consider the energy topics to be of utmost importance. In Fig. 1 is the arrangement and in Fig. 2 the photo of the remote experiment, composed of two vessels made from a transparent material provided with two metallic electrodes connected via a membrane and filled with two ionic electrolytes. The collected data is the voltage on the cell and the conductivity of the electrolyte. The remote experiment apparatus should be computer oriented in the sense that it should enable to control the preselected steps, i.e. the preparation of the initial starting conditions, the time realization of the titration process and the corresponding data collection and their visualization, storing and transport for the subsequent processing. We realized this experiment by ISES (Internet School Experimental System - see www.ises.info) as a physical hardware. The system ISES is presented elsewhere [2], here it is sufficient to mention that it is an universal experimental computer oriented system for schools based on the hardware (mainly modules covering the common quantities encountered in natural sciences subjects) and software (enabling the data collection, their plotting and processing). It is friendly in use hardware and software for easy building of chemistry, physics and biology experiments with a plenty modules: voltmeter, ammeter, conductivity meter, pH meter and more others. All these modules are fully programmable. The data are depicted in analogue and digital form on variable number of panels. For the envisaged experiment electrochemical cell it was necessary to build several additional modules (titration pump, electromagnetic valve and stirrer), described in detail in [5]. The controlling program of the remote experiment "Galvanic cell" was built using the ISES WEB CONTROL kit [3]. This is the environment for designing the controlling programs for experiments built on ISES hw. It is basically the universal controlling unit for the whole set of remote experiments, delivered on the CD as a ready-to-use unit, whose unique function for the specific remote experiment is provided by the additional unit (.psc unit) that is compiled for the specific functioning of the remote experiment expressed by the flowchart (Fig. 3). This unit approach enormously simplifies the building of any remote experiment and, at present, we are concerned with the symbolic construction of the .psc unit together with the controlling webpage [11] to remove programming at all.

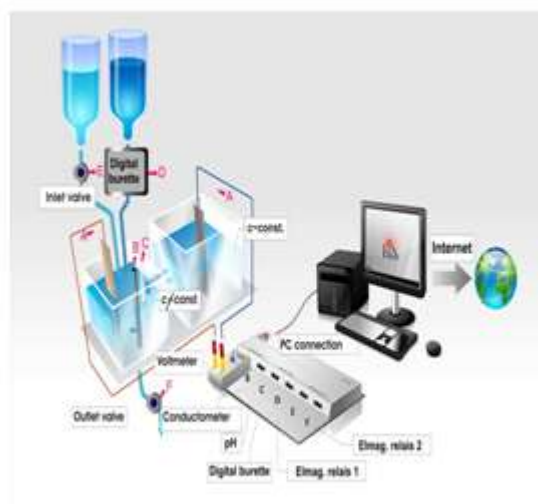


Figure 1. Schematic diagram of the remote interactive real experiment across Internet – Electrochemical cell (with two vessels and two metallic electrodes connected via a membrane, the measured data is the voltage and the conductivity of the electrolyte)



Figure 2. The photograph of the remote experiment „Galvanic cell“. Visible is the reaction chamber formed by two half cells, dividend by polymer membrane , titration pump , containers for solutions of $\text{Cu}_2(\text{NO}_3)_2$, $\text{C}_2(\text{NO}_3)_2$ and HNO_3 acid , and for concentrated $\text{Cu}_2(\text{NO}_3)_2$, and valves for letting in and letting out the solutions and acid [5]

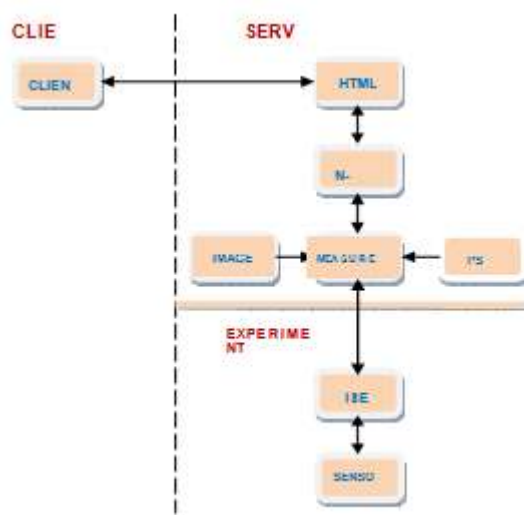


Figure 3. General scheme of the controlling server from WEB ISES CONTROL KIT, with controlling server unit (with N-GINX server, Image server, Measure server), PSC unit and Experiment server (ISES panel and sensors) [11]

III. EXPERIMENTAL RESULTS OF REMOTE EXPERIMENTS

The typical time-dependent data given by the remote experiment “Galvanic cell” of the composition $\text{Zn(s)}|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$ for starting volumes of copper nitrate $\text{Cu}(\text{NO}_3)_2 V_0 = 4 \text{ ml}$ in the oxidation half cell obtained during the titration are in Fig. 4a (the electrolyte conductivity σ and in Fig. 4b (the standard redox potential E equal? the electromotive voltage ε .

student is the apparent strong nonlinearity of the conductivity σ with the respect to the time of titration t (in

Fig. 4a). After reconsidering more closely the concentration -time dependence due not only to the increase of the mass of the salt $m(t)$, but also to the volume of its solvent $V(t)$ (herewater),

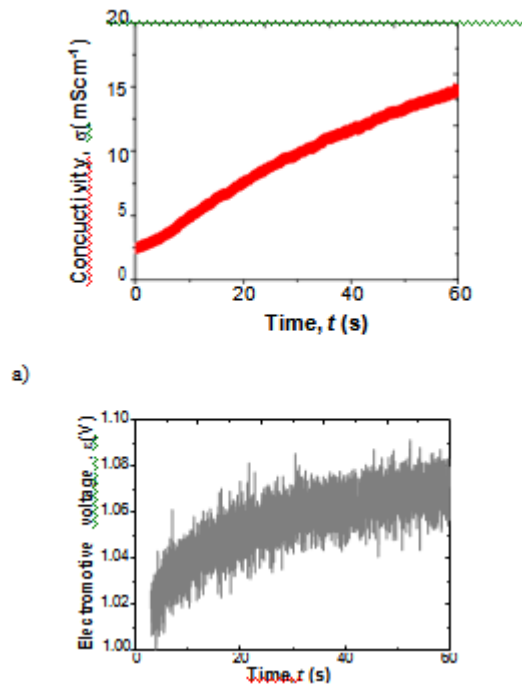


Figure 4. Data obtained from remote experiment: Electrolyte conductivity $\sigma(t)$ time dependence during the titration cycle in the half cell $\text{Cu}(\text{NO}_3)_2$; starting volume is $V_0 = 4 \text{ ml}$

Electromotive force $\varepsilon(t)$ time dependence during the where m is the mass of the copper nitrate $\text{Cu}(\text{NO}_3)_2$, $M = 139 \text{ g mol}^{-1}$ is its molecular weight and $m_0 = 1,39 \text{ kg}$ is the starting mass of the copper nitrate at $t = 0 \text{ s}$, V_0 is the starting volume of the electrolyte, $V_0 = 4 \text{ ml}$ at $t = 0 \text{ s}$ and a and b are the titration rates ($a = 6.6 \cdot 10^{-6} \text{ kg s}^{-1}$, $b = 2.5 \cdot 10^{-8} \text{ m}^3 \text{ s}^{-1}$) of the salt mass and the electrolyte volume, respectively.

After recalculation of the data in Fig. 4a using eq. (1) we obtain the corresponding concentration dependences i.e. concentration dependence of the conductivity of the copper nitrate $\text{Cu}(\text{NO}_3)_2$, $\sigma(c)$ given in Fig. 5a which is quite linear function of the salt concentration.

The conventional theory draws the dividing line between electrolytes with those completely dissociated – strong electrolytes, and those where reverse recombination results in only partial dissociation of electrolyte molecules – weak electrolytes, which is the function of the electrolyte concentration, formulated in Debye-Hückel theory [12]. For this purpose the molar conductivity Λ ($\Omega \text{ cm}^2 \text{ mol}^{-1}$) defined,

□

titration cycle in $\text{Zn}(\text{s})|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s})$; the starting volume is $V_0 = 4 \text{ ml}$

□ □ ,

c

(3)

IV. EVALUATION OF REMOTE EXPERIMENT

DATA

Next we will show information available from the measurements in Fig. 4a and 4b.

Electrolyte conductivity

The standard model for the electrolyte conductivity takes into account both the concentration of the ions (here denoted by the activity a^+ and a^-), their charge state (z^+ is introduced). Taking into consideration the definition of the conductivity (1) and supposing constant mobility, we should obtain the proof of strong/weak electrolyte by the constant/not constant molar conductivity Λ .

For strong electrolytes $\Lambda = \text{const.}$, which is our case, as obvious from Fig. 6 whereas for weak electrolytes $\Lambda < 1$ and decreasing with the concentration c .

In Fig. 6, where the molar conductivity Λ is plotted on the concentration of electrolyte c , the molar conductivity is basically independent on the concentration (giving molecular conductivity $\Lambda \sim 30\text{-}40 \text{ S cm}^2 \text{ mol}^{-1}$) and thus we may decide for the completely dissociated copper nitride $\text{Cu}(\text{NO}_3)_2$. When we accept the concept of constant mobility and taking into consideration the charge state and numbers of ions, we obtain from eq. (1) the average and

plausible value of the average mobility of the Cu^{2+} and

and z^- and their mobility (b^+ and b^-)

$$\sigma = e z^+ b^+ a^+ + e z^- b^- a^- \quad (1)$$

Electromotive force

Electromotive force of the cell

where e is the elemental charge $e = 1.6 \cdot 10^{-19}$ C and the activities are defined as the dissociated part of the salt $a = \kappa c$, where $\kappa \ll 1$.

Evaluating the conductivity σ of the electrolyte in Fig. 4a the student has to decide first about the basic property of the electrolyte, here copper nitrate $\text{H}_2\text{O}/\text{Cu}(\text{NO}_3)_2$ in the whole range of used concentrations. Surprising for the $\text{Zn}(\text{s})|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s})$ is expressed by standard electrochemical potentials E^0 of both half cells, corresponding to the redox reactions $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2e^-$ as oxidation reaction with $E_{\text{O,Cu}} = 0.34$ V and $\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu}(\text{s})$ as reduction reaction with $E_{\text{b,Zn}} = -0.76$ V.

The electromotive voltage of the cell is then given, expresses very similar behaviour of the Fermi levels in the

$$\varepsilon = E^0 = E_{\text{Zn}}^0$$

P-N junctions due to their doping concentration [13].

If we take the results depicted in Fig. 4b and use the changing concentration of ions (c_{ion}) for the Cu half cell, we may obtain the concentration (action) dependences of the electromotive force ε for starting volumes of $V_0 = 4$ ml, corresponding to the equation (4) depicted in Fig. 5b. The test of the correctness of our measuring and evaluation procedures is the result of the fitting to the Nernst eq. (4) which compares well with the theoretical values giving $E^0 = 1.08$ V and the pre exponential factor $kT/ez = 0.015$ V. It is also interesting that a direct plotting of the measured electromotive force ε on the measured conductivity σ (given in Fig. 7) gives quite identical

results as to standard electrode potential $E^0 = 1.02$ V and the preexponential factor $kT/ez = 0.017$ V, which compares well both with theoretical values and those, obtained from more detailed evaluation procedure described in connection with Fig. 5b. The reason is quite obvious as the conductivity is directly proportional to concentration with some proportionality constant.

The last result of the Galvanic cell study is the reaction constant k . At equilibrium is $E = 0$ V and realizing that then $\frac{c_{\text{Red}}}{c_{\text{Ox}}} = k$ we have using eq. (4)

Concentration, c (mol dm⁻³)

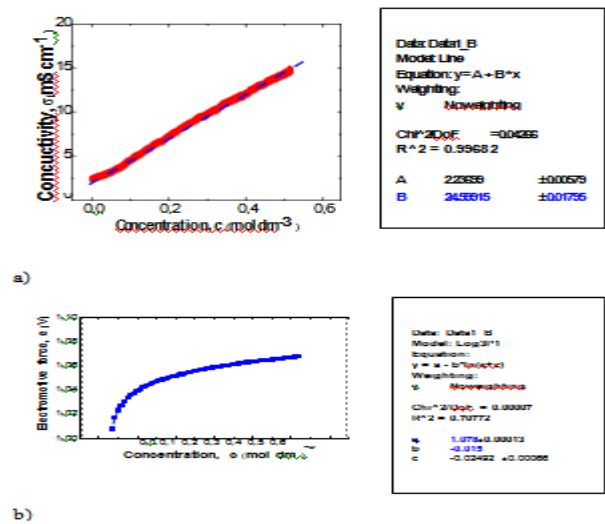


Figure 5. Recalculated data from Fig. 3: Electrolyte conductivity $\sigma(c)$

concentration dependence in half cell on copper nitrate $\text{Cu}(\text{NO}_3)_2$;
 starting volume is $V_s = 4\text{ml}$) or

Electromotive force $\epsilon(c)$ concentration dependence in
 ez c_{Ox}

$\text{Zn}(\text{s})|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s})$; the starting volume is $V_0 = 4\text{ ml}$. b); for recalculation $c = c(t)$ the eq. (1) is used;
 Fitting of the electromotive force ϵ of the $\text{Zn}(\text{s})|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s})$ galvanic cell by the Nernst equation
 (4) yielding the standard potential of the cell $E^0 = 1.08\text{ V}$ and preexponential factor $kT/ez = 1.05\text{ Vb}$)

This result would be valid for equal concentrations c of oxidation (in $\text{H}_2\text{O}/\text{Zn}_2(\text{NO}_3)_2$) and reduction (in
 $\text{H}_2\text{O}/\text{Cu}_2(\text{NO}_3)_2$) species (or their activities a) for both half cells. If the concentration in both half cells differs,
 the Nernst equation is valid, giving the additional difference of the chemical potentials in both half cells with the
 concentration quotient of both ionic species in both half cells
 $E^0 = 0.025/2 \ln(K)$, $K = 7.8 \cdot 10^{34}$ for the Zn/Cu cell.

This means that the reaction $\text{Cu} + \text{Zn}^{2+} \rightleftharpoons \text{Zn} + \text{Cu}^{2+}$
 strongly favours products, as do many redox reactions
 meaning also the high spontaneity of the redox reaction [15].

$$\epsilon = E^0 - \frac{kT}{ez} \ln \left(\frac{c_{\text{Red}}}{c_{\text{Ox}}} \right),$$

(4)

Cell electrical properties

It may be interesting for some students to evaluate the electrical properties of the home - made source of
 electrical energy, i.e. electromotive force ϵ and internal resistance R_i . Parameters are obvious from equivalent
 circuit in inset of Fig. 8, the loading characteristics, using

where k is the Boltzmann constant, $k = 1,38 \cdot 10^{-23}\text{ J K}$, T is the temperature, z charged state of the redox ions
 (here $z=2$) and c_{Red} and c_{Ox} are the concentration of active reduction (Cu^{2+}) and oxidation (Zn^{2+})
 ions in the respective half cells. It is interesting to notice that the Nernst eq.(4), the dependence of the voltage of
 the cell on the current through the cell is in Fig. 8 (interesting enough the remote experiment
<http://remotlab6.truni.sk> from the Trnava e- laboratory was used for the purpose). The electromotive force was
 determined as $\epsilon = 1.03\text{ V}$, the internal resistance $R_i = 16,4\text{ k}\Omega$ and the maximum applicable power $P_{\text{max}} = 3,36$
 mW.

In the paper we wanted to show the wealth of information the remote chemical experiment may bring. We
 realize the obstacles on the way: Though we have mastered the software and hardware of remote experiments in
 physics crossing borders to chemistry is not the straightforward for many reasons, first in principle
 „static“ character of chemical processes, where any changes, visible by the web camera are missing, second was
 the lack of some ISES components, which we had to construct at home and which are not available to the
 chemical teaching audience. The third ill-quality of the chemical experiments is their time scale, which
 sometimes prohibits their on line execution within reasonable time. Also the strict condition of the necessity

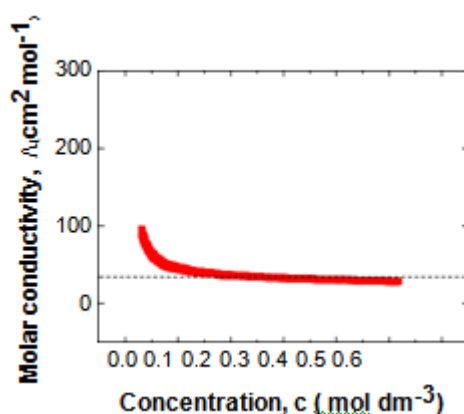


Figure 6. The molar conductivity on electrolyte concentration $\Lambda(c)$ of the strong electrolyte $\text{H}_2\text{O}/\text{Cu}(\text{NO}_3)_2$

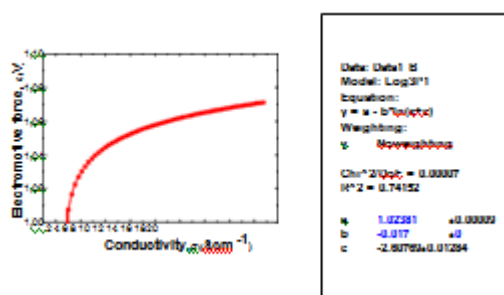


Figure 7. Evaluation of electromotive force ε from remote experiment data of $\sigma(t)$ and $\varepsilon(t)$; the fitting results are very close to those of Fig. 4b

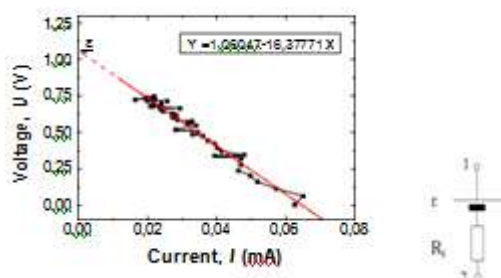


Figure 8. The loading characteristics of the galvanic cell, i.e. the dependence of the cell voltage U on the cell current I ; inset: the equivalent circuit of the galvanic cell.

V. DISCUSSION AND CONCLUSIONS

Let us start our conclusions by the sentence from the preface of the very recent book on remote experimentation [15] by prof. dr. Susan M. Zvacek: “In the meantime, however, innovations such as remote and virtual labs will continue to act as catalysts for improving engineering education worldwide”. The same goes for the chemistry education. To bring the system into starting condition in short time poses a very severe restriction. The conclusions may be summarized as follows:

- The measuring available software and especially hardware ISES [www.ises.info] are very suitable for the wide range of hands on and remote experiments in chemistry,
- The new modules for ISES – burette, valve and electromagnetic stirrer open many new applications in chemistry, hitherto not possible,
- A wealth of information may be gained from remote experiment “Galvanic cell” providing the possibility for the elucidation of the electrolyte conductivity, decision about strong/weak electrolytes, ions mobility and the study of Electrochemical potentials of various metals and even electrolytes and the corresponding reaction constant. The details concerning the evaluation of weak electrolytes and the experiment on analysis of unknown electrolytes by titration will be published elsewhere [16]

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