MARITIME UNIVERSITY OF SZCZECIN

Institute of Mathematics, Physics and Chemistry
Department of Chemistry

EXERCISE INSTRUCTION

Laboratory Exercise 7

Corrosion – causes and prevention

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EXERCISE SHEET

<table>
<tr><td>1</td><td colspan="3">Relation to subjects: ESO/25, 27 DiRMiUO/25, 27 EOUNiE/25, 27</td></tr>
<tr><td></td><td>Specialty/Subject</td><td>Learning outcomes for the subject</td><td>Detailed learning outcomes for the subject</td></tr>
<tr><td></td><td>ESO/26 Chemistry of water, fuels and lubricants</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP3 – Water quality indicators;
SEKP6 – Determination of selected indicators of technical water quality;</td></tr>
<tr><td></td><td>DiRMiUO/26 Chemistry of water, fuels and lubricants</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP3 – Water quality indicators;
SEKP6 – Determination of selected indicators of technical water quality;</td></tr>
<tr><td></td><td>EOUNiE/26 Chemistry of water, fuels and lubricants</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP3 – Water quality indicators;
SEKP6 – Determination of selected indicators of technical water quality;</td></tr>
<tr><td>2.</td><td colspan="3">Purpose of the exercise:
mastering the basic chemical concepts of corrosion and acquiring practical knowledge in the field:
– galvanic cells and processes taking place in the cell,
– a series of (voltage) activities of metals,
– mechanism of electrochemical corrosion,
– anodic protection,
– processes taking place in the cell.</td></tr>
<tr><td>3.</td><td colspan="3">Prerequisites:
general knowledge of oxidation and reduction processes, properties and corrosion of metals, knowledge of the principles of work in a chemical laboratory.</td></tr>
<tr><td>4.</td><td colspan="3">Description of the laboratory workplace:
laboratory glassware kit, multimedia projector, metal sample kit, electrochemical corrosion reagent kit, phenolphthalein, ferroxide indicator.</td></tr>
<tr><td>5.</td><td colspan="3">Risk assessment:
the likelihood of chemical burns from exposure to 0.2 M sulphuric acid is very small, and the effects are minimal.
Final assessment – VERY SMALL THREAT
Safety measures required:
1. Lab coats, gloves and safety glasses.
2. Health and safety cleaning products, paper towels.</td></tr>
<tr><td>6.</td><td colspan="3">The course of the exercise:
1. Getting to know the workplace manual (appendix 1) and familiarizing with the kit for testing electrochemical corrosion,
2. Carrying out chemical reactions.</td></tr>
<tr><td>7.</td><td colspan="3">Exercise report:
1. Develop an exercise in accordance with the instructions contained in the workplace manual.
2. Solve the given tasks and/or answer the questions included in the set of tasks and questions to be completed by the student.</td></tr>
<tr><td>8.</td><td colspan="3">Archiving of research results:
a report on exercises, prepared in accordance with the rules in force in the lab, should be submitted in writing to the academic teacher during the next classes.</td></tr>
<tr><td>9.</td><td colspan="3">Assessment method and criteria:
a) EKP1, EKP2 – checking the knowledge of basic chemical concepts of corrosion in class,</td></tr>
</table>

	b) SEKP4 – the detailed effect of the student's learning will be assessed on the basis of the observations, conclusions and solutions to tasks and problems presented in the report, given for independent solution/development: – **mark 2,0** – the student does not have basic knowledge of metals and their corrosion, or is unable to use it in practice to solve the problems of protecting structures and devices against corrosion; – **mark 3,0** – has basic chemical knowledge of the activity of metals, the mechanism of electrochemical corrosion and protection against corrosion, and can use it to a small extent to solve potential problems in his specialty; – **mark 3,5 – 4,0** – has extensive chemical knowledge of corrosion and its mechanisms, methods of protection against corrosion, operation of electrochemical cells and is able to use it in a wide range in his profession; – **mark 4,5 – 5,0** – has complete chemical knowledge of corrosion and electrochemical cells, their mechanisms and is able to use complex chemical knowledge to identify the mechanism of electrochemical corrosion and select the best protection method in complex corrosion cases.
10.	**References:** 1. https://assets.openstax.org/oscms-prodcms/media/documents/Chemistry2e-WEB.pdf (accessed 15.07.22). 2. A. Kozłowski, A. Kalbarczyk-Jedynak, M. Ślączka-Wilk, K. Ćwirko, C. Wiznerowicz, G. Gorzycka, Instrukcje stanowiskowe do ćwiczeń laboratoryjnych: Korozja i ochrona przed korozją, AM Szczecin 2022 (in Polish). 3. J. E. McMurry, R. C. Fay, J. K. Robinson, Chemistry, 7th edition, global edition, publisher: Pearson, 2016. 4. A. Blackman, S. Bottle, S. Schmid, M. Mocerino, U. Wille, Chemistry, 2nd edition, publisher: John Wiley&Sons, 2012. 5. G. Curran, Chemistry, publisher: The Career Press, 2011. 6. J. T. Moore, Chemistry for Dummies, publisher: Wiley Publishing, 2015. 7. D. Kealy, P.J. Haines, Analytical Chemistry, publisher: BIOS Scientific Publishers Limited, 2002. 8. Sparkcharts Chemistry, 2002 Spark Publishing, A Division of Barnes & Noble, Canada 2014. 9. M. D. Jackson, Chemistry, 2015 BarCharts, Inc. (Quickstudy.com). 10. M. Charmas, English for Students of Chemistry, Maria Curie-Skłodowska University Press, Lublin 2012. 11. Stundis H., Trześniowski W., Żmijewska S.: Ćwiczenia laboratoryjne z chemii nieorganicznej. WSM, Szczecin 1995 (in Polish). 12. M. Wesołowski, K. Szefer, D. Zimna, Zbiór zadań z analizy chemicznej, Wydawnictwa Naukowo – Techniczne, Warszawa 1997 (in Polish).
11.	Notes

1. THEORY

KEYWORDS:

- the electrochemical series,
- corrosion – definition and prevention.

The electrochemical series

The electrochemical series (the activity series) is built up by arranging chemical elements in order of their increasing standard electrode potentials (Fig. 1).

Standard Electrode Potentials E^0 established by measuring the potentials of various electrodes versus standard hydrogen electrode at 25°C

Electrode	Electrode Reaction					E^0 [Volts] at 25°C
Li^+/Li	Li^+	+	e^-	⇄	Li	– 3,000
K^+/K	K^+	+	e^-	⇄	K	– 2,922
Ba^{2+}/Ba	Ba^{2+}	+	$2e^-$	⇄	Ba	– 2,920
Ca^{2+}/Ca	Ca^{2+}	+	$2e^-$	⇄	Ca	– 2,840
Na^+/Na	Na^+	+	e^-	⇄	Na	– 2,713
Mg^{2+}/Mg	Mg^{2+}	+	$2e^-$	⇄	Mg	– 2,370
Al^{3+}/Al	Al^{3+}	+	$3e^-$	⇄	Al	– 1,660
Mn^{2+}/Mn	Mn^{2+}	+	$2e^-$	⇄	Mn	– 1,180
Zn^{2+}/Zn	Zn^{2+}	+	$2e^-$	⇄	Zn	– 0,763
Cr^{3+}/Cr	Cr^{3+}	+	$3e^-$	⇄	Cr	– 0,710
Fe^{2+}/Fe	Fe^{2+}	+	$2e^-$	⇄	Fe	– 0,441
Cd^{2+}/Cd	Cd^{2+}	+	$2e^-$	⇄	Cd	– 0,402
Co^{2+}/Co	Co^{2+}	+	$2e^-$	⇄	Co	– 0,277
Ni^{2+}/Ni	Ni^{2+}	+	$2e^-$	⇄	Ni	– 0,236
Sn^{2+}/Sn	Sn^{2+}	+	$2e^-$	⇄	Sn	– 0,136
Pb^{2+}/Pb	Pb^{2+}	+	$2e^-$	⇄	Pb	– 0,126
Fe^{3+}/Fe	Fe^{3+}	+	$3e^-$	⇄	Fe	– 0,040
$2H_3O^+/H_2+2H_2O$	$2H_3O^+$	+	$2e^-$	⇄	H_2+2H_2O	0,000
Cu^{2+}/Cu	Cu^{2+}	+	$2e^-$	⇄	Cu	+ 0,368
Cu^+/Cu	Cu^+	+	e^-	⇄	Cu	+ 0,522
$I_2/2I^-$	I_2	+	$2e^-$	⇄	$2I^-$	+ 0,536
$Hg_2^{2+}/2Hg$	Hg_2^{2+}	+	$2e^-$	⇄	$2H$	+ 0,798
Ag^+/Ag	Ag^+	+	e^-	⇄	Ag	+ 0,799
Hg^{2+}/Hg	Hg^{2+}	+	$2e^-$	⇄	Hg	+ 0,854
$Br_2/2Br^-$	Br_2	+	$2e^-$	⇄	$2Br^-$	+ 1,066
Pt^{2+}/Pt	Pt^{2+}	+	$2e^-$	⇄	Pt	+ 1,200
$Cl_2/2Cl^-$	Cl_2	+	$2e^-$	⇄	$2Cl^-$	+ 1,359
Au^{3+}/Au	Au^{3+}	+	$3e^-$	⇄	Au	+ 1,420
Au^+/Au	Au^+	+	e^-	⇄	Au	+ 1,680
$F_2/2F^-$	F_2	+	$2e^-$	⇄	$2F^-$	+ 2,850

ACTIVE

NOBLE

Fig. 1. The Electrochemical Series of Elements

The Hydrogen has an electrode potential of 0V and it is treated as a reference electrode. It means that other electrode potentials are measured against this value (laboratory used). The most reactive metal in the electrochemical series is lithium and the least reactive is gold. The electrochemical series (the activity series) can be used to predict reactions between acids and metals or reactions between metals and metal salts. Also, the electrochemical series can be a guide to a relative corrosion behavior – the more electronegative (active) metal shows a stronger tendency to ionize and go to the solution which means that this metal forms anode when combined with more electropositive (noble) metal and is corroded preferentially.
Metals with negative values of standard electrode potentials (active metals) can react with acids (hydracids and oxoacids) and these metals can displace hydrogen from acid solution:

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2\uparrow$$
$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + H_2\uparrow$$

Metals with positive values of standard electrode potentials (noble metals) do not displace hydrogen from acid solution and do not react with hydracids. Some of the metals with positive standard electrode potentials, for example copper, can react with selected oxoacids like concentrated and diluted nitric acid, concentrated sulfuric acid:

$$Cu + \text{concentrated } 2H_2SO_4 \longrightarrow CuSO_4 + SO_2\uparrow + 2H_2O$$
$$Cu + \text{concentrated } 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$
$$Cu + HCl \longrightarrow \text{no reaction occurs}$$

Metal with a lower value of standard potential can displace a metal with a higher value of standard potential from the salt solution. In other words a more reactive metal will displace a less reactive metal ion from a compound:

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$
$$Cu + ZnSO_4 \longrightarrow \text{no reaction occurs}$$

Corrosion

Corrosion can be simply defined as the reaction between a material – usually a metal and its environment (environment can be solid, liquid or gas). The process of corrosion converts a metal to a more chemically stable form like oxide, hydroxide, sulfide. The corrosion is a chemical or electrochemical (or chemical and electrochemical) reaction between a metal and its environment leading to a gradual destruction of a metal/metals.

In other words corrosion occurs when a metal is exposed to air, water, electrolyte – it occurs because of the great tendency of certain metals to react electrochemically with oxygen, water and other substances within the atmosphere. When metal for example iron corrodes it forms oxides ($Fe_2O_3 \cdot H_2O$ – rust) and hydrated oxides, see the reactions below:

$$Fe \longrightarrow Fe^{2+} + 2e^- \text{ (anodic reaction)}$$
$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

(reduction of oxygen – a typical cathodic reaction in aerated and neutral environments; in acidic environments there is a reduction of hydrogen: $2H^+ + 2e^- \longrightarrow H_2$)

$$2\,Fe + O_2 + 2H_2O \longrightarrow 2\,Fe(OH)_2\downarrow$$
$$4\,Fe(OH)_2 + O_2 \longrightarrow 2\,Fe_2O_3 \cdot H_2O + 2\,H_2O$$

Selected types of aqueous corrosion:

- uniform attack (the most common type of corrosion, caused by chemical or electrochemical reactions),
- galvanic corrosion (occurs when two different metals are located together in an electrolyte – metals must be exposed to an electrolyte),
- crevice corrosion (an example of localized corrosion that targets one area of the metal structure),
- pitting corrosion (an example of localized corrosion that targets one area of the metal structure).

When two different metals are located together in a corrosive electrolyte the Galvanic cell (Fig. 2) is formed and that leads to a galvanic corrosion and also it might lead to a uniform attack and localized corrosion.

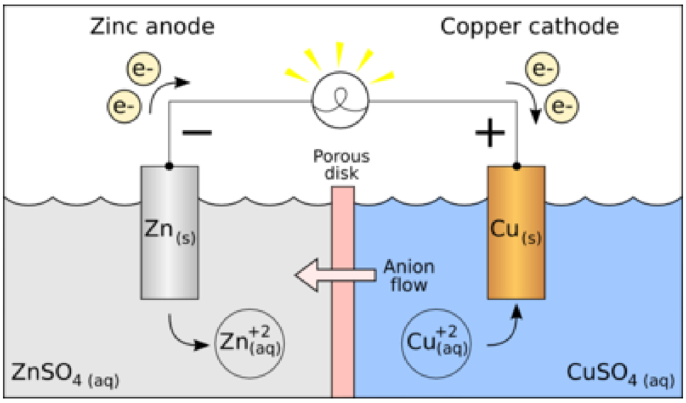

Fig. 2. The example of the Galvanic cell
(source: https://en.wikipedia.org/wiki/Galvanic_cell, accessed February, 1, 2022)

The electrochemical cell is an external circuit that connects two electrodes the anode and the cathode to facilitate the reaction. At the anode (–) an oxidation reaction occurs (oxidation = loss of electrons – formation of ions in solution), at the cathode (+) a reduction reaction occurs (reduction = gain of electrons). In any of the corrosion process, the anode (the anode reactions = corrosion) and the cathode reactions must both occur at the same time and at equal rates. The electrons are released at the anode and then are gained in the corresponding cathodic reaction – a small corrosion current flows from anode to cathode. The presence of electrolyte is essential in aqueous corrosion.

$Zn \longrightarrow Zn^{2+} + 2e^-$ the anode reaction in Daniell’s Cell; The Anode = Oxidation
$Cu^{2+} + 2e^- \longrightarrow Cu$ the cathode reaction in Daniell’s Cell. The Cathode = Reduction

Selected examples of prevention of corrosion:

- painting,
- adding oil or grease,
- noble and sacrificial metal coatings (example: zinc is more reactive than iron and iron can be coated with zinc),
- passivation.

Additional tasks and questions to be performed by the student:

1. On the basis of electrochemical series, complete the reactions that will take place:

   a) $Cu + HBr \longrightarrow$
   b) $Ag + HCl \longrightarrow$
   c) Cu + concentrated $HNO_3 \longrightarrow$
   d) $Ca + H_2SO_4 \longrightarrow$
   e) Fe + diluted $H_2SO_4 \longrightarrow$
   f) $Zn + CuSO_4 \longrightarrow$
   g) $Zn + FeSO_4 \longrightarrow$
   h) $Mg + CuSO_4 \longrightarrow$
   i) $Al\ (NO_3)_3 + Ag \longrightarrow$
   j) $Zn + HBr \longrightarrow$

2. Describe in few sentences the prevention of corrosion on ships.

2. INSTRUCTION 7 – LABORATORY EXERCISE 7

Materials and reagents (Experiments: 1 – 4):

Glass test tube set, micro spatula, polyethylene plastic pipettes, measuring cylinder, steel plate, sandpaper, copper, lead and aluminum foil, solutions of: hydrochloric acid (2M HCl), concentrated hydrochloric acid (HCl), nitric acid solution (2M HNO_3), concentrated nitric acid (HNO_3), zinc, iron, copper, iron (II) sulfate (5% $FeSO_4$), copper (II) sulfate (1% $CuSO_4$), silver nitrate ($AgNO_3$), sulfuric acid (VI) (H_2SO_4 1 : 3), ferroxyl indicator solution (1% solution of potassium hexacyanoferrate (III) $K_3[Fe(CN)_6]$, 1% solution of phenolphthalein, 3% solution of sodium chloride), potassium hexacyanoferrate (III) (1% $K_3[Fe(CN)_6]$).

Experiment 1 – Reactions of acids with metals

Experimental procedure:

Pour 3 cm^3 of hydrochloric acid solution (2M HCl) to each of two test tubes. Add zinc into the first test tube and copper into the second test tube.

Pour 3 cm^3 of nitric acid solution (2M HNO_3) to each of two test tubes. Add zinc into the first test tube and copper into the second test tube. Pour 1 cm^3 of concentrated nitric acid (HNO_3) into a test tube and add copper.

Fill in the table below:

Test tube	Acid	Metal	Reaction of acid with metal (balanced chemical equation)
1.	2M HCl	Zn	
2.	2M HCl	Cu	
3.	2M HNO_3	Zn	
4.	2M HNO_3	Cu	
5.	CONCENTRATED HNO_3	Cu	

Data analysis (after the experiment):

1. Fill in the table.

Experiment 2 – Reaction of metal with metal salt solution (displacement reactions between metals and their salts)

Experimental procedure:

To each of seven test tubes pour 3 cm^3 of solution listed in the given table and add the corresponding metal (also listed in the table):

Test tube	Solution	Metal	Reaction (metal + salt)	Conclusion
1.	1% $CuSO_4$	Zn		
2.	0.1M $AgNO_3$	Zn		
3.	5% $FeSO_4$	Zn		
4.	1% $CuSO_4$	Fe		
5.	0.1M $AgNO_3$	Fe		
6.	5% $FeSO_4$	Cu		
7.	0.1M $AgNO_3$	Cu		

Data analysis (after the experiment):

1. Fill in the table.

Experiment 3 – Corrosion cell

Experimental procedure:

Take a steel plate and clean it using sandpaper and acetone. Place a large drop of ferroxyl indicator solution on a clean surface. Leave it for 30 minutes.

Data analysis (after the experiment):

1. Write reactions from the experiment.
2. Explain the mechanism of electrochemical corrosion of iron, write the anode and cathode reactions (corrosion in acidic and neutral environment).

Experiment 4 – Prevention of iron corrosion

Experimental procedure:

Pour distilled water (half of the test tube) to each of three test tubes then add 2 – 3 drops of sulfuric acid solution (H_2SO_4 1 : 3) to each of three test tubes and a few drops of potassium hexacyanoferrate (III) (1% $K_3[Fe(CN)_6]$) – this salt is a very sensitive reagent indicating the presence of ferrous iron (Fe^{2+}) with which it produces an intense blur color (Turnbull's blue). Stir it. Clean three steel nails with sandpaper, wrap the first nail as closely as possible with aluminum foil – put it into the first test tube, the second with copper foil – put it into the second test tube and the third with lead foil – put it into the third test tube. Leave it for 60 minutes. After 60 minutes remove wrapped steel nails, rinse with running water and unwrap it. Fill in the table below:

Test tube	Iron/metal	The colour of solution	Anode reaction
1.	Fe/Al		
2.	Fe/Cu		
3.	Fe/Pb		

Data analysis (after the experiment):

1. Explain the mechanism of prevention of iron corrosion based on the Experiment 4: write the anode reactions. Clarify why not every analyzed metal can protect iron against corrosion?
2. Explain where and why metal or alloy blocks are used to protect the ship against corrosion?

3. GUIDELINES FOR WRITING THE FINAL LABORATORY REPORT

1. First page of the report – The Laboratory Report Cover Sheet found on our website: https://www.am.szczecin.pl/en/facilities/institute-of-mathematics-physics-and-chemistry/department-of-chemistry/chemistry-lab-manuals/
2. Second page of the report – „The Theoretical Part” – on a maximum of one page including brief description of keywords.
3. Third page of the report – „The Experimental Part” – including all performed experiments with titles, raw data, reactions, calculations, tables, graphs, etc. It should be written in accordance with „Data analysis (after the experiment)”.
4. Additional task/tasks given by the academic teacher.
5. References.

4. IN ORDER TO PASS THE LABORATORY EXERCISE STUDENTS MUST PASS „THE ENTRY TEST” AND SUBMIT THE FINAL LABORATORY REPORT AT THE NEXT LABORATORY MEETING. THE LAB REPORT MUST BE ACCEPTED BY THE ACADEMIC TEACHER.