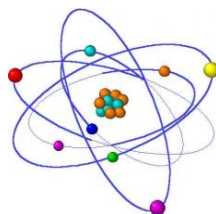## ZAPOROZHYE STATE MEDICAL UNIVERSITY

Kaplaushenko A.G., Pryakhin O.R., Varinskiy B.A., Iurchenko I.A.,

Shcherbak M.A., Samelyuk Yu.G., Kucheryavyi Yu.N., Hulina Yu.S.

ELECTROCHEMISTRY

Teaching and methodical manual

for foreign student

Zaporozhye, 2016

ЗАПОРІЗЬКИЙ ДЕРЖАВНИЙ МЕДИЧНИЙ УНІВЕРСИТЕТ

Каплаушенко А.Г., Пряхін О.Р., Варинський Б.О., Юрченко І.О., Щербак М.О., Самелюк Ю.Г., Кучерявий Ю.М., Гуліна Ю.С.

ЕЛЕКТРОХІМІЯ

Навчально-методичний посібник

для студентів англомовної форми навчання

Запоріжжя, 2016

Authors:
Kaplaushenko A.G., Pryakhin O.R., Varinskiy B.A., Iurchenko I.A., Shcherbak M.A., Samelyuk Yu.G., Kucheryavyi Yu.N., Hulina Yu.S.

Reviewers:
Parchenko V.V., Dr.hab., Professor of the Department of Toxicology and Inorganic Chemistry, Zaporozhye State Medical University;
Gladychev V.V., Dr.hab, Professor, Head of the Department of Medicinal Preparations Technology, Zaporozhye State Medical University.

Electrochemistry: teaching and methodical manual for foreign students / A.G. Kaplaushenko, O.R. Pryakhin, B.A. Varinskiy [et al.]. − 2nd ed., updated and suppl. − Zaporozhye, 2016. − 70 p.

Автори:
Каплаушенко А.Г., Пряхін О.Р., Варинський Б.О., Юрченко І.О., Щербак М.О., Самелюк Ю.Г., Кучерявий Ю.М., Гуліна Ю.С.

Рецензенти:
Парченко В.В., професор кафедри токсикологічної та неорганічної хімії Запорізького державного медичного університету, д. фарм. н..
Гладишев В.В., зав. кафедри технології ліків Запорізького державного медичного університету, д.фарм.н..

Електрохімія: навчально-методичний посібник / А.Г. Каплаушенко, О.Р. Пряхін, Б.О. Варинський [та ін.]. − 2ге вид., оновл. та доповн. − Запоріжжя, 2016. – 70 с.

Навчальний посібник розглянуто та затверджено:

Цикловою методичною комісією з фармацевтичних дисциплін
(протокол №__ від _____р.),
Центральною методичною радою ЗДМУ
(протокол №__ від _____р.)

CONTENTS

PREFACE

Medicinal Chemistry is one of the most rapidly developing areas within the discipline of Chemistry, both globally and locally. It is the study of the design, biochemical effects, regulatory and ethical aspects of drugs for the treatment of disease.

The aim of this discipline is to produce graduates with an appropriate background in biology and pharmacology, built upon a strong chemistry foundation.

Methodical recommendation of Medicinal Chemistry is designed to equip students with strong grounding in biological and chemical technique which is relevant to the pharmaceutical world.

The discipline gives an in-depth coverage of the chemical techniques required and relates these to the relevant pharmacology, anatomy, biochemistry and molecular biology.

The whole course of Medical chemistry which consists of ten topics is studied by students-physicians during the first year. Lecturer staff of department has prepared an educational and methodical recommendation in which the theoretical material is stated in the concise and available form.

The distribution of material on each of ten topics that are studied is set according to training program, the thematic plan of lectures and practical training.

The material of each topic is stated in such way that performance of practical work and the solution of situational tasks are preceded by theoretical part in which questions of medicine and biological value and also connection with other disciplines (biological chemistry, normal physiology, pathophysiology and others) are included.

Offered laboratory works and situational tasks will give students the chance to understand theoretical material fully and to use this knowledge in practice.

The experience of teaching medical chemistry shows that it is not always possible to coordinate an order of laboratory works realization with sequence of lecture course statement. That is why students usually have to prepare for practical work performance independently before the lesson. Therefore the theoretical part (in which the necessary volume of knowledge for conscious performance of experiment is given) precedes to each section of these Methodical recommendations.

Increasing of level of seminar and laboratory works is reached by use of such forms of occupations which open and consolidate theoretical knowledge, train scientific thinking, develop creative initiative and impart skills of handling devices and chemicals, chemical ware.

The structures, figures and schemes are clear and easy to follow and color is used well, highlighting main points without being distracting.

Chapters are helpfully signposted throughout, informing the reader how topics are related, which is especially important in such a multidisciplinary subject.

Topics are also presented clearly and with a logical progression culminating in the main points, questions and reading sections at the beginning of each chapter.

An assortment of case studies is provided and the authors work through each one in great detail, giving an overall perspective on the science.

Finally, very useful and informative appendices and a glossary are provided together with a comprehensive index that is good enough to rival any search engine!

There are many books that describe medicinal chemistry and its uses, but these methodological recommendations present medicinal chemistry and its related topics in a clear, informative and interesting way that really demonstrates the application and impact of this fundamental subject in society.

INTRODUCTION

Purpose: Study potentiometric method of for determining the concentration of ions in solutions. Learn basic theoretical laws of the method. Learn to determine the concentration of ions by potentiometric method and produce the appropriate calculations.

Targets:

- Draw diagrams representing electrochemical cell and write the cell notation;

- Know what reaction is taking place at the anode and cathode;

- Write equations for anode and cathode half-reactions, and for the overall cell reaction;

- Calculate standard cell potentials, E^o_{cell}, from half-cell potentials, E^o;

- Calculate nonstandard cell potentials, E_{cell}, using the Nernst equation;

- Calculate equilibrium constant (K_c) and standard free energy, ΔG^o, from E^o_{cell}.

- Know the different types of electrochemical cells and the difference between an electrochemical cells and an electrolytic cells;

- Know some important applications of electrochemical and electrolytic processes.

- Calculate amounts of products formed during electrolysis at anode and cathode.

- Know the concept of galvanic cell, and galvanic circuit.

- Know the mechanism of electrode potentials. Electric double layer. Standard electrode potentials.

- Know Nernst equation for electrode potential and EMF of the galvanic cell.

- Know classification: electrodes of the first and second kind, gas electrodes, ox/red electrodes and ion-selective electrodes.

- Know electrodes and circuits for measuring pH.

- Know potentiometric titration.

CONCISE THEORETICAL MATERIAL

1 Galvanic Cells

Electrochemistry is a branch of chemistry that deals with the exploitation of *spontaneous oxidation-reduction reactions* to obtain *electrical energy* and the *use of electrical energy to drive nonspontaneous reactions* important in industrial extraction of certain elements.

A galvanic cell (also called voltaic cell) is a device that uses a spontaneous oxidation-reduction reaction to produce electric current. The following are some examples of spontaneous oxidation-reduction reactions:

1. ME: $Zn(s) + CuSO_4(aq) \rightarrow Cu(s) + ZnSO_4(aq)$

    nie: $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$

2. ME: $Cr(s) + 3AgNO_3(aq) \rightarrow Cr(NO_3)_3(aq) + 3Ag(s)$

    nie: $Cr(s) + 3Ag^{+}(aq) \rightarrow Cr^{3+}(aq) + 3Ag(s)$

3. nie: $MnO_4^{-}(aq) + 5Fe^{2+}(aq) + 8H^{+}(aq) \rightarrow$

    $Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

4. ME: $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$

Spontaneous redox reactions are exothermic reactions. Heat produced in an exothermic reaction is normally lost as heat. However, it can be trapped and converted into electrical energy if the reactants involved are not in direct contact with each other. In galvanic cells redox reactions is split into two half-reactions, each occurring in two separate compartments, called ***half-cells***.

The chemical energy is used to drive electrons through the external circuit connecting the two half-cells, thus producing electric current.

For example, consider the following reaction:

$$Zn(s) + CuSO_4(aq) \rightarrow Cu(s) + ZnSO_4(aq)$$
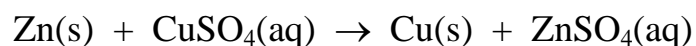
If zinc metal is placed in $CuSO_4$ solution, an exothermic reaction occurs, producing heat. In a galvanic cell set up, a zinc metal is placed in $ZnSO_4$ solution in one container, a copper metal in $CuSO_4$ solution in another container, the two metals are connected by a wire, and to complete the circuit,

the two solutions are connected by a "salt-bridge" containing strong electrolyte such as $KCl_{(aq)}$ or $K_2SO_{4(aq)}$ that allows ions to flow between the two half-cells. The reactants - zinc metal and copper ions are not allowed to come in direct contact. Because of the potential different between the two *half-cells*, electrons are force to flow from the zinc electrode (the *anode*) to the copper electrode (the *cathode*).

At the interface between the zinc electrode and $ZnSO_4$ solution Zn atoms are oxidized to Zn^{2+} ions; while at the interface between copper electrode and $CuSO_4$ solution Cu^{2+} ions combine with incoming electrons and is reduced to Cu atoms.

These oxidation and reduction processes are shown in the following half-reaction equations:

Anode-reaction (oxidation): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$;

Cathode-reaction (reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

The two half-cells are represented by notations $Zn|Zn^{2+}$ and $Cu^{2+}|Cu$. In a galvanic cell, the metal that is more readily oxidized serves as an anode and the other as cathode. Zinc is more easily oxidized than copper and it serves as the anode, while copper forms the cathode.

Oxidation half-reaction occurs at anode and reduction half-reaction at cathode. This galvanic or voltaic cell can be represented using the following cell notation:

$Zn|ZnSO_4(aq)||CuSO_4(aq)|Cu$

(A cell notation is always written with the anode on the left side and cathode on the right.)

At the anode half-cell, Zn^{2+} ions are continuously formed, creating an excess of positive ions. While in the cathode half-cell, Cu^{2+} ions are continuously reduced to Cu, causing a decrease in cation concentration.

To maintain electrically neutral solutions in both half-cells, anions flow into the anode half-cell and cations flows into the cathode half-cell. Thus, *electric current is the flow of charged particles – electrons flows from anode to*

cathode through wire; cations and anions flows in opposite direction through the salt-bridge.

Cell Potential

The driving force that enables electrons to flow from one electrode to the other is called ***electromotive force*** (emf), or ***cell potential*** (E_{cell}), which has the unit ***volt*** (V). A *volt* is *one Joule per Coulomb*, where Coulomb is the unit of charge.

2 Standard Reduction Potential

In a galvanic cell electrons flow from one electrode to the other because there is an electrical potential difference between the two half-cells, simply called the ***cell potential***. In the zinc-copper cell, electrons flow from $Zn|Zn^{2+}$ half-cell to $Cu|Cu^{2+}$ half-cell. The $Zn|Z^{2+}$ half-cell has a higher electrical potential than $Cu|Cu^{2+}$.
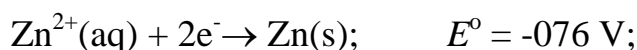
The magnitude of cell potential depends on the nature of the two half-cells, the concentration of the electrolyte in each half-cell, and temperature. The *standard cell potential*, E^{o}_{cell}, is the cell potential measured under standard conditions, (1 atm pressure for gas, 1 M of electrolytes, and at 25 ^{o}C).

The *standard half-cell potential* or *the reduction potential* of a substance is determined by connecting the half-cell of the substance (under standard conditions) to the *standard hydrogen electrode* (SHE) as reference half-cell.
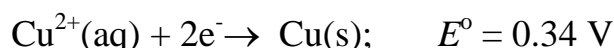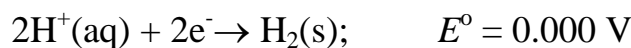
This reference half-cell consists of a Pt-electrode in a solution containing 1 M H^{+} into which H_2 gas is purged at a constant pressure of 1 atm. Because the reference half-cell is assigned zero potential, the cell potential measured under this conditions is the standard half-cell potential of the substance.

For example, when a $Zn|Zn^{2+}$(aq, 1 M) half-cell is connected to the reference half-cell (SHE), the voltage measured at 25 ^{o}C is found to be 0.763 V. However, in this set up, electron flows from $Zn|Zn^{2+}$ to "SHE", and relative to

SHE, the reduction potential for $Zn|Zn^{2+}$ half-cell will be the negative value of the measured voltage. That is,

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s); \qquad E^o = \text{-076 V};$$

(where E^o is the reduction potential)

$$2H^+(aq) + 2e^- \rightarrow H_2(s); \qquad E^o = 0.000 \text{ V}$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s); \qquad E^o = 0.34 \text{ V}$$

Since values are obtained against the standard hydrogen potential, species with positive reduction potentials are easier to reduce compared to H^+ ions; while those with negative reduction potentials are more difficult to reduce.

Therefore, relative to H^+, Cu^{2+} is easier to reduce, whereas Zn^{2+} is more difficult to reduce. When $Zn|Zn^{2+}$ is connected to $Cu|Cu^{2+}$ half-cells, the spontaneous process will be the flow of electrons from $Zn|Zn^{2+}$ to $Cu|Cu^{2+}$ half-cell.

In galvanic cells, species with more positive reduction potential serves as cathode and one with less positive or more negative reduction potential serves as the anode half-cell.
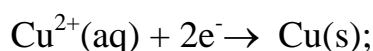
The *net cell potential* is the sum of the two half-cell potential. For the Zn-copper cell,
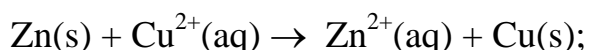
Anode half-cell reaction:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-;$$
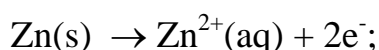
$$E^o_{Zn \longrightarrow Zn2+} = 0.76 \text{ V}$$

Cathode half-cell reaction:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s);$$

$$E^o_{Cu2+ \longrightarrow Cu} = 0.34 \text{ V}$$

Overall cell reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s);$$

$$E^o_{cell} = E^o_{Zn \longrightarrow Zn2+} + E^o_{Cu2+ \longrightarrow Cu} = 0.76 \text{ V} + 0.34 \text{ V} = 1.10 \text{ V}$$

For a cell consisting of $Cr|Cr^{3+}$ and $Ag|Ag^+$ half-cells, the cell notation and cell potential are:

$Cr|Cr^{3+}(aq, 1\ M)||Ag^{+}(aq, 1\ M)|Ag$
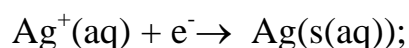
(anode)   (cathode)

Anode half-cell reaction:

$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^{-}$;
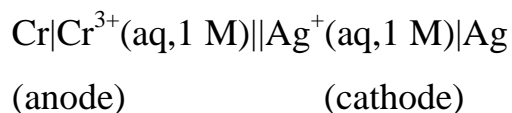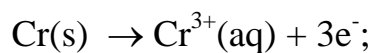
$E^{o}_{Cr \longrightarrow Cr3+} = 0.73$ V

Cathode half-cell reaction:

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s(aq))$;

$E^{o}_{Ag+ \longrightarrow Ag} = 0.80$ V

Overall cell reaction:

$Cr(s) + 3Ag^{+}(aq) \rightarrow Cr^{3+}(aq) + 3Ag(s)$;
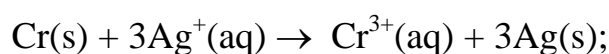
$E^{o}_{cell} = E^{o}_{Cr \pm Cr3+} + E^{o}_{Ag+ \pm Ag} = 0.73$ V $+ 0.80$ V $= 1.53$ V

$E^{o}_{cell} = 0.73$ V $+ 0.80$ V $= 1.53$ V

3. Cell Potential and Free Energy

The cell potential measures the potential difference between the two half-cells. A potential difference of 1 V is equivalent to 1 Joule of work done per Coulomb of charge that flows between two points in the circuit.

Maximum work produced = charge x maximum potential

$W_{max} = -qE_{max} = \Delta G$

Electrical charge, $q = nF$; ➔ $\Delta G = -nFE_{cell}$; or $\Delta G^{o} = -nFE^{o}_{cell}$

where n = mole of electrons transferred or that flow through circuit,

and F = 96,485 C/mol e^{-} is called Faraday's constant

For example, the reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ has $E^{o}_{cell} = 1.10$ V

The standard free energy is, $\Delta G^{o} = -2$ mol e^{-} x $\dfrac{96,485\ C}{1\ mol\ e^{-}}$ x 1.10 V = -2.12 x 10^{5} J

2.12 x 10^{2} kJ is the maximum work that can be derived per mole of Zn reacted by Cu^{2+}.

4. Dependence of Cell Potential on Concentration

The quantitative relationship between electrolyte concentration and cell potential is given by the following **Nernst Equation**:

$E_{cell} = E^o{}_{cell} - (RT/nF) \, lnQ$;

E_{cell} is cell potential under non-standard conditions, while $E^o{}_{cell}$ is cell potential under standard conditions (calculated from standard reduction potentials), R = 8.314 J/(mol.K), F = 96,485 C/mol, is the Faraday's constant; Q is the reaction quotient, such that, for the reaction:

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$, $Q = [Zn^{2+}]/[Cu^{2+}]$.
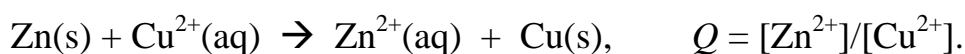
At 25 °C, $\dfrac{RT}{F} = \dfrac{(8.314 \, J/mol.K)(298 \, K)}{96,485 \, C/mol} = 0.0257 \, J/C = 0.0257 \, V$

The expression for the *Nernst equation* becomes,

$E_{cell} = E^o{}_{cell} - \dfrac{(0.0257 \, V)}{n} \, lnQ$;

For example, the non-standard cell potential for

$Zn|Zn^{2+}(aq, 0.010 \, M)||Cu^{2+}(aq, 1.0 \, M)|Cu$ can be calculated as follows:

$E_{cell} = (E^o{}_{Cu2+|Cu} + E^o{}_{Zn|Zn2+}) - \dfrac{(0.0591 \, V)}{n} \, log([Zn^{2+}]/[Cu^{2+}])$;

$= (0.34 \, V + 0.76 \, V) - \dfrac{(0.0591 \, V)}{n} \, log(0.010 \, M/1.0 \, M)$

$= 1.10 \, V + 0.060 \, V = 1.16 \, V$

For the voltaic cell, $Cu|Cu^{2+}(aq)||Ag^{+}(aq)|Ag$, the Nernst equation is expressed as:

$E_{cell} = (E^o{}_{Ag+|Ag} + E^o{}_{Cu|Cu2+}) - (0.0591 \, V/2) \, log \, ([Cu^{2+}]/[Ag^{+}]^2)$

If $[Ag^{+}] = 0.010 \, M$, $[Cu^{2+}] = 1.0 \, M$, and $E^o{}_{cell} = 0.80 \, V - 0.34 \, V = 0.46 \, V$,

$E_{cell} = 0.46 \, V - \dfrac{(0.0591 \, V)}{2} \, log\{1.0/(0.010)^2\}$

$= 0.46 \, V - \dfrac{(0.0591 \, V)}{2} (4.0) = 0.46 \, V - 0.12 \, V = \underline{0.34 \, V}$

The cell potential calculated from Nernst equation is the maximum potential at the instant the cell circuit is connected. As the cell discharges and

current flows, the electrolyte concentrations will change, Q increases and E_{cell} deceases.

The cell reaction will occur spontaneously until it reaches equilibrium, at which point $Q = K$ (the equilibrium constant) and

$E_{cell} = E^o_{cell} - (RT/nF) \, ln(K) = 0$;

$ln(K) = nFE^o_{cell}/RT$; $K = \exp(nFE^o_{cell}/RT)$

Note also that at equilibrium, $\Delta G = \Delta G^o - RT \, ln(K) = 0$ (no current flows through the circuit)

Concentration Cells

A *concentration cell* is an electrochemical cell in which both half-cells are of the same type, but with different electrolyte concentrations. The following cell notations are examples of concentration cells:

$Cu|Cu^{2+}$ (aq, 0.0010 M)$||Cu^{2+}$(aq, 1.0 M)$|Cu$

$Ag|Ag^{+}$ (aq, 0.0010 M) $||Ag^{+}$(aq, 0.10 M)$|Ag$
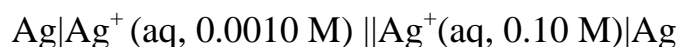
In concentration cells, the half-cell with the lower electrolyte concentration serves as an anode half-cell and one with the higher electrolyte concentration is the cathode half-cell. At the anode half-cell, oxidation reaction occurs to increase the electrolyte concentration and at the cathode half-cell, a reduction reaction occurs to decrease its electrolyte concentration. Oxidation-reduction reaction will continue until the electrolyte concentrations in both half-cells become equal.

At anode half-cell:

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$; (in 0.0010 M Cu^{2+})
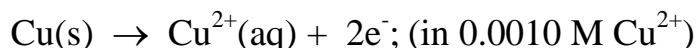
At cathode half-cell:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$; (in 0.50 M Cu^{2+})
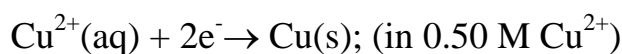
5 Batteries

Batteries are galvanic cells or a group of galvanic cells connected in series, where the total battery potential is equal to the sum of the potentials of the individual cells. There are three types of batteries – *primary* batteries, *secondary* batteries, and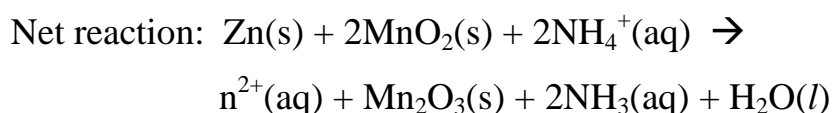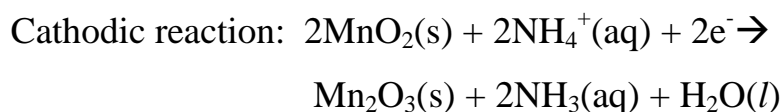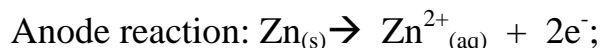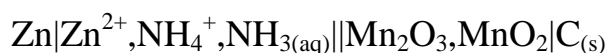 the *fuel cell*. Primary batteries are not re-chargeable, where as secondary batteries are re-chargeable. Fuel cell will last as long as there is an ample supply of fuel to provide the energy.
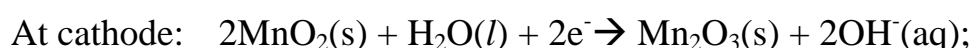
Dry Cells: The normal (acidic) dry batteries, alkaline batteries, and the mercury batteries are example of *primary batteries*. The "acidic" dry battery consists of Zinc casing as container, anode and as the reducing agent; graphite rod as (inert) cathode; aqueous NH_4Cl paste as electrolyte, and MnO_2 powder as the oxidizing agent.

$$Zn|Zn^{2+},NH_4^+,NH_{3(aq)}||Mn_2O_3,MnO_2|C_{(s)}$$

Anode reaction: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$;

Cathodic reaction: $2MnO_2(s) + 2NH_4^+(aq) + 2e^- \rightarrow$

$$Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$$

Net reaction: $Zn(s) + 2MnO_2(s) + 2NH_4^+(aq) \rightarrow$

$$n^{2+}(aq) + Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$$

The reverse reaction is prevented by the formation of $[Zn(NH_3)_4]^{2+}$ ions.

A new dry cell battery has a potential of about 1.5 V regardless of the size, but the amount of energy that a battery can deliver depends on its size. For example, a D-size battery can deliver more current (greater amperes) than an AAA-size battery. Normal dry batteries use aqueous NH_4Cl paste as electrolyte and are referred to as acidic batteries due to the following ionization: $NH_4^+(aq)$ $\rightarrow NH_3(aq) + H^+(aq)$
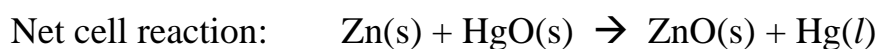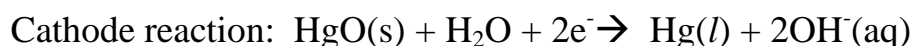
Alkaline batteries also use zinc (as the reducing agent) and MnO_2 (as oxidizing agent), but aqueous paste containing KOH, instead of NH_4Cl, is used as the electrolyte. The anode and cathode reactions are as follows:

At anode: $Zn(s) + 2OH^-_{(aq)} \rightarrow ZnO(s) + H_2O_{(l)} + 2e^-$;

At cathode: $2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$;

Net reaction: $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$

Since all reactants involved are in the solid form, alkaline batteries can deliver a fairly constant voltage until the limiting reactant is completely used up. They also last longer because zinc metal corrodes more slowly under basic conditions.

Batteries used in calculators and watches are *mercury batteries*. The following reactions occur at the anode and cathode sections of the cell:

Anode reaction: $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O + 2e^-$;

Cathode reaction: $HgO(s) + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-(aq)$

Net cell reaction: $Zn(s) + HgO(s) \rightarrow ZnO(s) + Hg(l)$
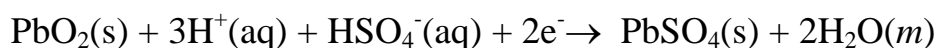

Lead Storage Batteries

These are batteries used in all types of automobiles. The lead storage batteries contain sulfuric acid as electrolyte. Each cell contains a number of grids of lead alloy. One set of alternating grids is packed with lead metal and the other with lead(IV) oxide, PbO_2. Each set of grids, which are the electrodes, are connected in a parallel arrangement, which enables the cell to deliver more current - the amount of current delivered depends on the surface area of the electrode. Each cell in a lead storage battery produces a potential of about 2.01 V. A standard 12-V battery used in most cars contains six cells connected in series.

Spontaneous Reactions that occur in the lead storage battery are:

Anode reaction:

$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$

Cathode reaction:

$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(m)$

Net reaction:

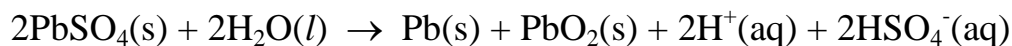$Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
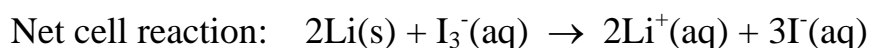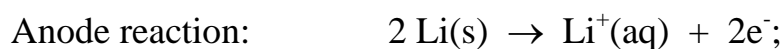
The greatest advantage of lead storage batteries is that they are re-chargeable. When you start the engine the discharge reaction occurs, but while

the car is being driven, the battery obtains energy from the motor through the alternator and the following re-charging reaction occurs:

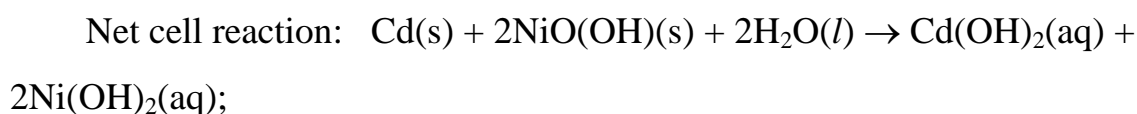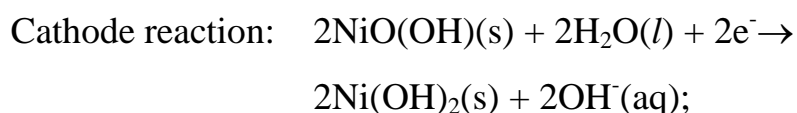$$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq)$$

Lead storage batteries also have a longer lifetime and can deliver a relatively large amount of current and electrical energy within a short time. The major disadvantages are: (1) they are very heavy and bulky - non-portable; (2) lead is a toxic metal and the disposal creates environmental problems; (3) the battery must be kept upright and H_2SO_4 is very corrosive.

Lithium batteries: these are batteries used in cameras and computers.

Anode reaction: $\quad\quad 2\,Li(s) \rightarrow Li^+(aq) + 2e^-$;

Cathode reaction: $\quad I_3^-(aq) + 2e^- \rightarrow 3I^-_{(aq)}$

Net cell reaction: $\quad 2Li(s) + I_3^-(aq) \rightarrow 2Li^+(aq) + 3I^-(aq)$

The **nickel-cadmium** batteries are rechargeable batteries used in cordless phones. They contain cadmium as the anode and hydrated nickel oxide as the cathode. The electrolyte is made up of aqueous KOH paste.

Anode reaction: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$;

Cathode reaction: $\quad 2NiO(OH)(s) + 2H_2O(l) + 2e^- \rightarrow$
$$2Ni(OH)_2(s) + 2OH^-(aq);$$

Net cell reaction: $\quad Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(aq) +$
$2Ni(OH)_2(aq)$;

Fuel Cells:

A *fuel cell* is a galvanic cell that uses hydrogen (as fuel), which reacts with oxygen, and a large amount of energy from the reaction is available to produce electricity. The fuel is supplied continuously from an external tank. The hydrogen-oxygen fuel cells are used in the space shuttle modules.

Anode reaction: $\quad 2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$;

Cathode reaction: $2H_2O(l) + O_2(g) + 4e^- \rightarrow 4OH^-(aq)$

Net cell reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + Energy$
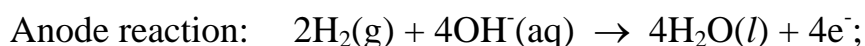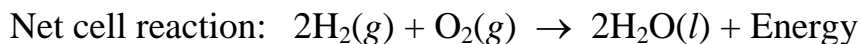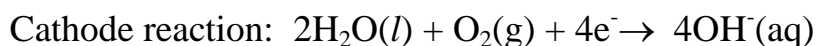
6 Corrosion Control

Corrosion is a spontaneous oxidation of metals by atmospheric oxygen – a process that has great economic impact. Consider the rusting process of a steel pipe. The process is accelerated by the presence of water droplets on the metal surface. At the edge of the droplet, the part of iron exposed to the air acts as the cathode for the electrochemical reaction. At the center of the droplet, the metal acts as anode and get oxidized (corroded).

O_2 OH^- Fe^{2+} OH^- O_2

Cathode   Anode   Cathode

At the edge of the droplet, molecular oxygen is reduced to OH^-:
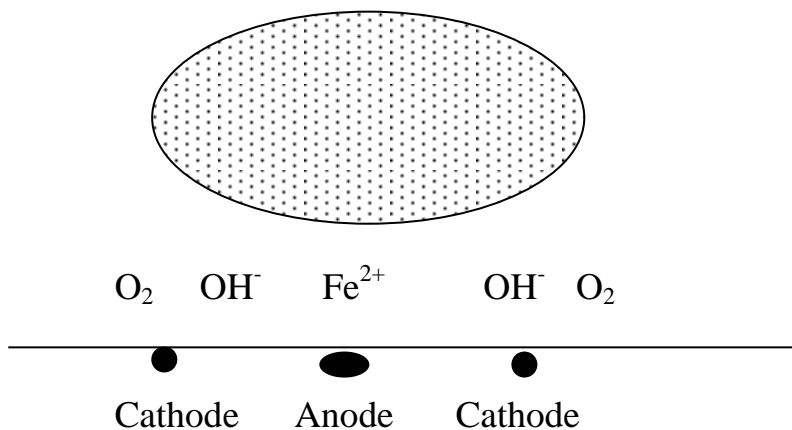
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
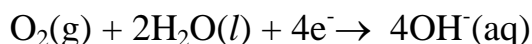
and at the center of the droplet, metallic iron is oxidized to Fe^{2+}:

$2Fe(s) \rightarrow 2Fe^{2+}(aq) + 4e^-$

Inside the droplets, Fe^{2+} combines with OH^- to form iron(II) hydroxide, $Fe(OH)_2$, which is then further oxidized to iron(III) oxide, $Fe_2O_3.H_2O$.

$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$

$4Fe(OH)_2(s) + O_2(g) \rightarrow 2Fe_2O_3.H_2O(s) + 2H_2O$
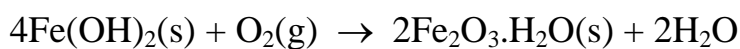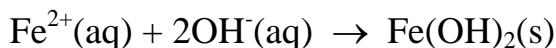
"rust"

Corrosion prevention can be done by *passive* method, such as by painting the metal surface, thus prevents contact of the metal surface with oxygen and moisture.

The active method of corrosion prevention involves electrochemical process, which is the method employed in the control of corrosion of underground steel pipes and tanks. If the pipe is wrapped or tied with a metal that is more electropositive than iron, such as magnesium, aluminum, or zinc, then in electrochemical reactions these metals will act as the anodes and the iron (pipe) as the cathode, while the wet soil acts as the electrolyte. The sacrificial metals will be oxidized before the pipe.

For example, if magnesium is used as sacrificial anode, the following reactions will occur:

$$2Mg(s) \rightarrow 2Mg^{2+}(aq) + 4e^-; \qquad \text{(at anode)}$$

and, $\qquad O_2(g) + 2H_2O(l) + 4 e^- \rightarrow 4OH^-(aq) \qquad$ (at cathode)

Net reaction: $2Mg(s) + O_2(g) + 2H_2O \rightarrow 2Mg(OH)_2(s)$;

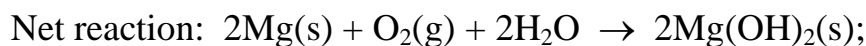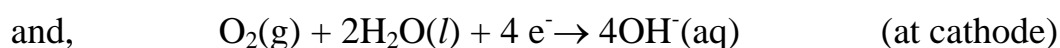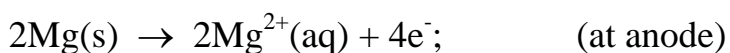This method of corrosion prevention using active metals such as magnesium as sacrificial anode is called a ***cathodic protection***, because as a cathode the pipe will not oxidized.

7. Electrolysis

A galvanic cell produces current from a spontaneous oxidation-reaction. An ***electrolytic cell*** uses electrical energy to drive nonspontaneous oxidation-reduction reactions.

Electrolysis involves forcing a current through a cell to produce a chemical change, which has a negative cell potential. For example, a lead storage or car battery is a galvanic cell during the discharge process, that is when you starts the car or when the headlight is on without the engine running. When the car is driven the re-charging reaction occurs and the battery acts as an electrolytic cell.

For example, the following spontaneous reaction occurs in a galvanic cell that consists of $Zn|Zn^{2+}_{(aq)}$ and $Cu|Cu^{2+}_{(aq)}$ half-cells:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s); E^o_{cell} = 1.10 \text{ V}$$
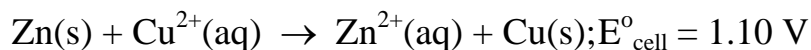
In an electrolytic cell, the reverse reaction occurs if a voltage greater than 1.10 V is applied. A higher voltage than E^o is needed to cause the reverse reaction; the excess voltage is referred to as **overpotential** or *overvoltage*.

Three types of reactions are possible in electrolytic cells when a sufficient voltage is applied:

• Solute ions or molecules may be oxidized or reduced;

• The solvent can be oxidized or reduced;

• Metal electrode that forms the anode can be oxidized.

Which of these reactions will actually take place depends both on the thermodynamic and kinetic properties of each reaction. In general, the half-reactions with the most positive (or the least negative) reduction potential will occur before others. If the difference in the standard reduction potentials between two half-cell reactions is small, concentration may determine the outcome of electrolysis. This is a kinetic factor.

For example, the following reactions are possible during the electrolysis of 1 M $NaCl_{(aq)}$:

At anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$; $E^o = -1.36$ V

$2H_2O \rightarrow O_2(g) + 4H^+(aq) + 4e^-$; $E^o = -1.23$ V

At cathode: $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^o = -0.83$ V

$Na^+(aq) + e^- \rightarrow Na(s)$; $E^o = -2.71$ V
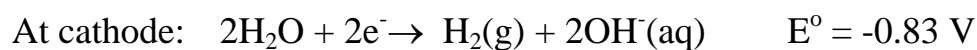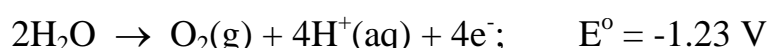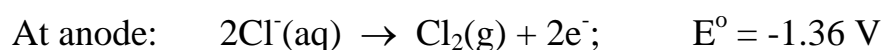
In an actual electrolysis of aqueous sodium chloride, Cl_2 is formed at the anode instead of O_2 although E^o for the formation of O_2 from H_2O is less negative than for the formation of Cl_2 from Cl^-. This is because the formation of O_2 involves a higher activation energy (overvoltage), thus kinetically less

favorable. At the cathode, H_2 is formed since it requires less voltage than the reduction of $Na^+_{(aq)}$.

If a solution containing metal cations that require lower potential or one that has a positive reduction potential is electrolyzed, the metal will be deposited on the cathode and no hydrogen will be produced.

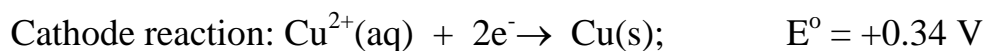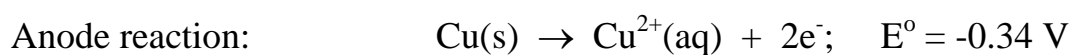For example, the electrolysis of aqueous copper(II) chloride solution will yield Cl_2 gas at the anode and copper metal deposits at the cathode. If the anode is made of copper, it will also be oxidized because of the lower voltage requirement relative to water.

Anode reaction: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$; $E^o = -0.34$ V

Cathode reaction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$; $E^o = +0.34$ V

Electrolysis of Water

The decomposition of water is a nonspontaneous process, which an amount of energy of about 400 kJ/mol of water. However, the decomposition of water can be effected by electrolysis, in which oxygen is formed at the anode and hydrogen at the cathode:

Anode reaction: $2H_2O \rightarrow O_2 + 4H^+_{(aq)} + 4e^-$; $E^o = -1.23$ V

Cathode reaction: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-_{(aq)}$; $E^o = -0.83$ V

Net reaction: $6H_2O \rightarrow 2H_2 + O_2 + 4(H^+ + OH^-)$; $E^o = -2.06$ V

$2H_2O \rightarrow 2H_2 + O_2$;
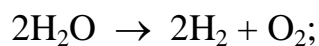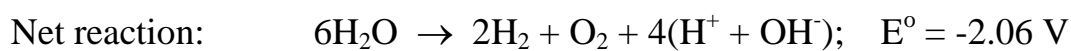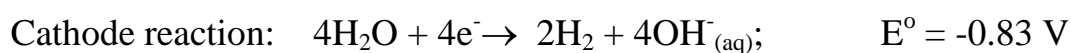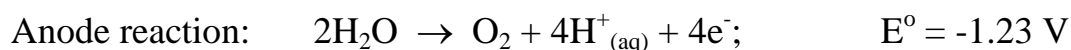
This potential assumes an electrolytic cell with $[H^+] = [OH^-] = 1$ M and $P_{H2} = P_{O2} = 1$ atm. In the electrolysis of pure water, where $[H^+] = [OH^-] = 10^{-7}$ M, the potential for the overall process is -1.23 V. However, applying a voltage of 1.23 V will not be sufficient to affect the electrolysis of water. An extra voltage of about 1 V (as *overpotential* or *overvoltage*) is needed to make the electrolysis takes effect.

Electrolysis of Solution Containing Mixtures of Ions

Consider a solution containing Cu^{2+}, Zn^{2+}, and Ag^+ is electrolyzed using a current with sufficient voltage to reduce all three cations. In such electrolysis, the metal having the smallest potential will be the first to be formed. The reduction potentials of these elements are as follows:

$Ag^+(aq) + e^- \rightarrow Ag(s)$; $E^o = 0.80$ V

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$; $E^o = 0.34$ V

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$; $E^o = -0.76$ V
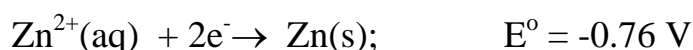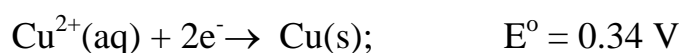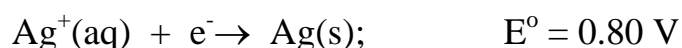
Since the reduction of Ag^+ to Ag has the most positive potential, silver will be deposited at the cathode before the other metals, which is then followed by Cu and Zn, respectively. If the voltage supply is properly controlled, starting with the lowest voltage possible, it is possible to separate the three metals using electrolysis.

The Stoichiometry of Electrolysis – Total Charge and Theoretical Yield

An electric current that flows through a cell is measured in **ampere** (**A**), which is the amount of charge, in **Coulomb** (**C**), that flows through the circuit per second. That is,

Ampere = Coulomb/second (1 **A** = 1 **C/s**)

Coulomb = Ampere x time in second (1 **C** = 1 **A.s**) = total charge

Joule = Coulomb x Volt (1 **J** = 1 **C.V**)

The amount of substances formed at the anode or cathode can be calculated from the magnitude of current (in amperes) and time (in seconds) of electrolysis.

For example, if a current of 1.50 A flows through an aqueous solution of $CuSO_4$ for 25.0 minutes, the amount of charge passing through the solution is

(1.50 C/s)(25.0 minutes)(60 seconds/minutes) = 2250 C

The number of moles of electrons passing through the solution 0.0233 mol

Since the reduction of Cu^{2+} requires 2 mol e^- per mole of Cu:

$Cu^{2+} + 2e^- \rightarrow Cu$,
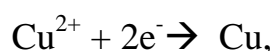
the amount of copper formed at the cathode is:

(0.0233 mol e⁻) x (1 mol Cu) x (63.55 g Cu) = 0.741 g Cu

               2 mol e⁻   1 mol Cu

If the above process uses a cell with a voltage of 3.0 V, the energy consumed is:

3.0 V x 225^0 C = 6750 C.V = 6800 J = 6.8 kJ

8 Commercial Electrolytic Processes

The production of active metals such as sodium, magnesium, and aluminum from their compounds can only be accomplished by electrolysis, which is carried out by passing current in the order of $10^4 - 10^5$ Amperes. The most common examples of this method of production are those of sodium, magnesium, and aluminum. Sodium and magnesium are produced by electrolysis of molten sodium chloride and magnesium chloride, respectively.

The Production of Aluminum

Aluminum is produced by electrolysis of molten Al_2O_3 in cryolite (Na_3AlF_6) in a process called the **Hall-Heroult process**, named after the founders. The electrolytic cells for aluminum production use graphite for both anode and cathode. The following reactions are thought to take place during the electrolysis which occurs at temperature above 1000 °C:

At temperature above 1000 °C alumina reacts with molten cryolite ion:

$$Al_2O_3 + 4AlF_6^{3-} \rightarrow 3Al_2OF_6^{2-} + 6F^-;$$
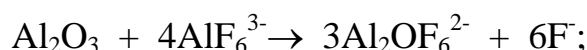
Then the anode and cathode reactions are thought to occur as follows:

Anode reaction: $2Al_2OF_6^{2-} + 12F^- + C \rightarrow 4AlF_6^{3-} + CO_2 + 4e^-;$

Cathode reaction: $AlF_6^{3+} + 3e^- \rightarrow Al + 6F^-;$

The overall cell reaction is: $Al_2O_3 + 3C \rightarrow 4Al + 3CO_{2(g)}$

The anode, which is made of graphite, is consumed in the process and must be replaced from time to time. Since aluminum is denser than aluminum

oxide and cryolite, the molten aluminum sinks to the bottom of the cell and can be removed quite easily. The aluminum produced in this process is about 99.5% pure. Aluminum forms strong but light construction materials when alloyed with zinc or magnesium, which are often used for making aircraft and aircraft engine.

Electrolysis of Molten Salt to Produce Sodium

The electrolysis of molten salt to produce sodium metal is commercially carried out in the **Downs cells** at temperature around 600 ^{o}C. Chlorine is a by-product in this process.

At the anode: $2\ Cl^- \rightarrow Cl_2(g) + 2e^-$

At the cathode: $2Na^+ + 2e^- \rightarrow 2Na(l)$

Net reaction: $2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$
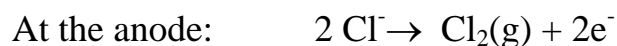
In the Downs cells the anode and cathode chambers are separated by a steel screen to prevent contact between molten sodium metal and chlorine gas to prevent an explosive reaction between the two reactive elements. The molten sodium metal forms a layer above the molten NaCl and can be siphoned off. To obtain sodium metal, the electrolysis must use molten NaCl, to which $BaCl_2$ is added to lower the melting point. If aqueous NaCl is used, water will be reduced at the cathode and hydrogen gas, instead of sodium, is produced.

Electrolysis of Brine Solutionfor Commercial Production of Sodium Hydroxide

Sodium hydroxide is commercially produced by electrolysis of brine solution (saturated salt solution in the *chlor-alkali process*.

Anode reaction: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$;

Cathode reaction: $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$;

Net reaction: $2NaCl(aq) + 2H_2O \rightarrow 2NaOH(aq) + H_2(g) + Cl_2(g)$
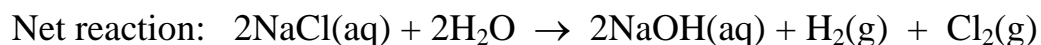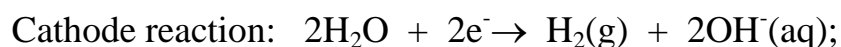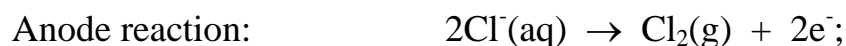
The voltage requirement for the reduction of Na^+ is higher than that required for reducing water. Thus, hydrogen gas is produced instead of sodium metal. Oxygen gas is not formed at the anode because it involves a high overvoltage compared to that for chlorine gas. As a result, the overall voltage requirement to oxidize water (which will produce oxygen gas) is greater than the overall potential needed to produce chlorine gas.

Electro-refining of Copper

Electrolysis is also an important process in the purification of some metals. For example, impure copper from the chemical reduction of copper ore is cast into large slabs that serve as the anodes for electrolytic cells. The cells also use thin sheets of ultra pure copper as cathodes and aqueous copper(II) sulfate as the electrolyte. Assuming zinc and iron as the major impurities in the copper slabs, the following reactions occur at the anode:

$$Zn \rightarrow Zn^{2+}(aq) + 2e^-; \qquad E^o = 0.76 \text{ V}$$

$$Fe \rightarrow Fe^{2+}(aq) + 2e^-; \qquad E^o = 0.44 \text{ V}$$

$$Cu \rightarrow Cu^{2+}(aq) + 2e^-; \qquad E^o = -0.34 \text{ V}$$
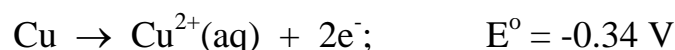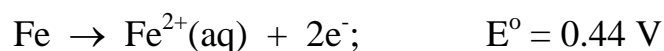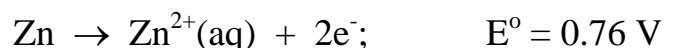
By maintaining a low voltage supply, only copper is deposited at the cathode, which is made of pure copper metal sheet; ionic impurities remain in solution.

Electroplating

Plating a thin coating of a metal that resist corrosion can protect other metals that readily corrode. The process is called ***electroplating***, in which the corrosion resistant metal is used as the anode where it is oxidized and goes into solution. The ions formed from this metal are then reduced at the cathode, which consists of utensils to be electroplated. The electrolyte usually contains a low ion concentration of electroplating metal. For example, in *silver plating*, silver metal is used as the anode and the utensil to be silver-plated as the

cathode; the electrolyte consists of $AgNO_3$ in KCN(aq). In solution Ag^+ forms complex with CN^-

$$Ag^+(aq) \; + \; 2CN^-(aq) \; \rightarrow \; Ag(CN)_2^-(aq);$$
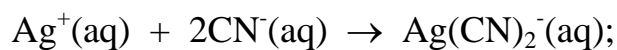
This reaction maintains a very low concentration of free Ag^+ ion in solution and yields a very thin and uniform silver coating.

Anode reaction: $\quad Ag \; + 2CN^-(aq) \; \rightarrow \; Ag(CN)_2^-(aq) \; + e^-;$

Cathode reaction: $\quad Ag(CN)_2^-(aq) \; + e^- \rightarrow \; Ag(s) \; + \; 2CN^-(aq);$
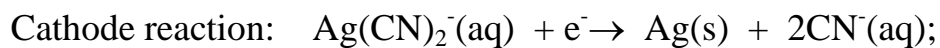
QUESTIONS FOR SELF-TRAINING

1. The concept of galvanic cell, and galvanic circuit.

2. The mechanism of electrode potentials. Electric double layer. Standard electrode potentials.

3. Nernst equation for electrode potential and EMF of the galvanic cell.

4. Classification: electrodes of the first and second kind, gas electrodes, ox/red electrodes and ion-selective electrodes.

5. Electrodes and circuits for measuring pH.

6. Potentiometric titration.

7. For each of the following compounds, identify the oxidation state for each element.

a) $CaBr_2$

b) Na_3P

c) H_2S

d) $Ca(NO_2)_2$

e) H_2SO_4

f) NaH_2PO_4

g) CO_3^{-2}

h) BaS_2O_3

i) N_2F_4

j) $HOCl$

k) CH_3Cl

l) $LiNH_2$

8. Identify the oxidation state for each atom, tell which substance is oxidized and which is reduced, and identify the oxidizing and reducing agents:

a) I_2O_5 (s) + 5 CO (g)→ 5 CO_2 (g) + I_2 (s)

b) $NaNO_3$ (aq) + Pb (s) → $NaNO_2$ (aq) + PbO (s)

c) 4 NaOH (aq) +$Ca(OH)_2$ (aq) + C (s) + 4 ClO_2 (aq) →

→ 4 $NaClO_2$ (aq) + $CaCO_3$ (s) + H_2O

d) $8 H_3O^+ (aq) + MnO_4^- (aq) + 5 Fe^{+2} (aq) \rightarrow$

$\rightarrow Mn^{+2} (aq) + 5Fe^{+3} (aq) + 12 H_2O (l)$
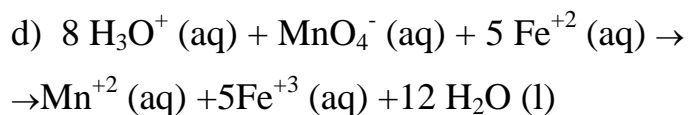
9. What is the connection between oxygen gas (O_2) and oxidation?

10. Nitrogen can have oxidation states varying from +5 to –3. Give an example of nine different real-life compounds or ions, EACH of which has a different oxidation state for N. Remember molecules probably exist in "real life" if you can draw a valid Lewis structure for them!

11. Write balanced chemical half-reactions describing each of the following:

a) Reduction of iron (III) ions to metallic iron

b) Elemental zinc corroding to give Zn^{+2}

c) Sn^{+4} ions converting to Sn^{+2} ions

d) Oxidation of cadmium to cadmium (II) ions

e) H_3O^+ ions reacting to form H_2 and water

f) Give the potential for each of the reactions given above in parts a-e.

12. Scan the periodic table for elements which are easily oxidized and easily reduced.

a) Where on the periodic table would you find elements that are good oxidizing agents?

b) Where would you find elements that are good reducing agents?

c) Why does this pattern (described in parts a and b above) make sense in terms of our understanding of periodicity and atomic structure?

13. Balance the following redox reactions:

a) $Ag^+ (aq) + Fe (s) \rightarrow Ag (s) + Fe^{+2} (aq)$

b) $H^+ (aq) + H_2O_2 (aq) + Co (s) \rightarrow H_2O + Co^{+3} (aq)$

c) $H_2CO (aq) + O_2 (aq) \rightarrow CO_2 (g) + H_2O (l)$

14. Consider a tin-lead galvanic cell (all *ions* are in their +2 state; there no +4 ions present).

a) Sketch a diagram of the cell, indicating the flow of electrons. Label the anode, cathode, wire, salt bridge, ions in solution (specific what they are), and electrodes.

b) Under each electrode, write the appropriate oxidative or reductive half reactions.

c) Write the shorthand cell diagram.

d) Calculate the cell potential. Is this an effective combination for a galvanic cell? Explain why or why not.

e) How could you use a tin-lead galvanic cell to create a 9.0 Volt battery?

15. Why is it necessary to use a salt bridge in a galvanic cell?

16. What two elements do you think were used in the old "Nicad" batteries?

a) Write 2 half reactions and an overall balanced equation for this reaction.

b) Which element was in the anode?

c) What is the voltage for this battery?

d) The Nicad battery runs for a while, and then goes "dead." Explain what happened in the cell that caused it to stop working. If there's more than one possibility, give them all.

17. A quick glance around the chem lab reveals the following chemicals: Au, Al, K^+, Cl^-, I_2, and Zn^{+2}.

a) Choose TWO which would make the highest voltage battery.

b) Which one (from part a) is the reducing agent?

c) Calculate the cell potential for this battery.

d) What's happening at the cathode of this battery?

18. Predict whether the following reactions will happen, and justify your answers with half reactions and a calculation of E_{cell}.

a) Will a solution of silver ions and chlorine gas react to produce chloride ions and solid silver metal? Why or why not?

b) Will iodide ions react with zinc (II) ions? Why or why not?

c) Will iodide ions react with silver (I) ions? Why or why not?

19. Is E for the following reactions the same or different? Explain your answer.

$Cu^{+2} + 2e^- \rightarrow Cu$

$2Cu^{+2} + 4e^- \rightarrow 2Cu$
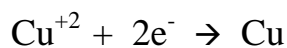
20. You spilled $PbCl_2$ solution on your grandma's solid copper bust of Elvis Presley. Are you in electrochemical danger? Explain and justify your answer.

21. Grandma pours an aqueous solution of FeI_3 into your tin golfing trophy. Are you in electrochemical danger? Explain and justify your answer.

22. What is the relationship between the table of standard reduction potentials and the single replacement activity series that we discussed last fall for single replacement reactions? Explain.

23. Molten aluminum oxide can be converted to aluminum metal and oxygen gas.

a) Is this process spontaneous (galvanic) or non-spontaneous (electrolytic)? How do you know?

b) What voltage is involved?

c) Running at 5.00 amps, how long does it take to make enough aluminum for a roll of aluminum foil? A typical large roll is about 0.850 kg of foil.

d) How much does it cost in electricity alone to make enough aluminum for a roll of aluminum foil? Power costs about $0.080 per kilowatt-hour. A watt

is a volt*amp. Assume minimum voltage is applied (no overpotential needed). Where are most aluminum plants located?

TASKS

Exercise #1

For each of the following galvanic cell, write the anode and cathode half-cell reactions, the overall cell reaction, and calculate the standard cell potential. Use the standard reduction half-cell potentials given in Table-17.1 (page 833)

(a) $Zn|Zn^{2+}(aq, 1\ M)||Fe^{3+},Fe^{2+}(aq, 1\ M)|Pt$;

(b) $Zn|Zn^{2+}(aq, 1\ M)||Br_2,Br^-(aq, 1\ M)|Pt$;

Exercise #2

Write the cell notation and calculate the standard cell potential for galvanic cells in which the following reactions occur:

(a) $Pb(s)\ +\ 2\ Fe^{3+}(aq)\ \rightarrow\ Pb^{2+}(aq)\ +\ 2Fe^{2+}(aq)$

(b) $2Li(s)\ +\ I_3^-(aq)\ \rightarrow\ 2Li^+(aq)\ +\ 3I^-(aq)$
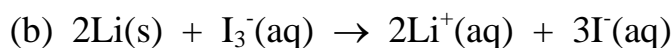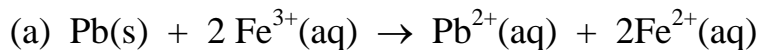
Exercise #3

In the following reaction: $Zn(s) + CuSO_4(aq)\ \rightarrow\ ZnSO_4(aq) + Cu(s)$,

What is the maximum energy produced when 15.0 g of Zn is completely reacted in a Zn-Cu electrochemical cell that has an average cell potential of 1.05 V?

Exercise #4

The following reaction has an average cell potential of 3.00 V: $2\ Li(s)\ +\ LiI_3 \rightarrow 3\ LiI(aq)$

How much energy can be derived from a reaction in which 5.00 g of Li is oxidized?

Exercise #5

Write an overall net ionic equation and calculate the cell potential at 25 °C for:

$Zn|Zn^{2+}(aq, 0.0050\ M)||Cu^{2+}(aq,1.0\ M)|Cu$

Exercise #6

Write an overall net ionic equation and calculate the cell potential at 25 °C for:

$Cu|Cu^{2+}(aq, 0.0050 \text{ M})||Ag^{+}(aq, 0.50 \text{ M})|Ag$

Exercise #7

The standard cell potential (E^{o}_{cell}) for the following galvanic cell is 1.10 V

$Zn|Zn^{2+}(aq, 1M)||Cu^{2+}(aq, 1M)|Cu$

What is the K value for the reaction: $Zn(s) + Cu^{2+}(aq) \rightleftarrows Zn^{2+}(aq) + Cu(s)$?

Exercise #8

Determine the cell potentials of the following concentration cells:

(a) $Cu|Cu^{2+}(aq, 0.0010 \text{ M})||Cu^{2+}(aq, 1.0 \text{ M})|Cu$

(b) $Ag|Ag^{+}(aq, 0.0010 \text{ M})||Ag+(aq, 0.10 \text{ M})|Ag$

Exercise #9

A concentration cell is set up by connecting a half-cell containing a zinc electrode in 0.10 M $ZnSO_{4 \, (aq)}$ and another half-cell containing zinc electrode in a saturated solution of ZnS. If the K_{sp} of ZnS is 2.5×10^{-22}, what is the expected cell potential at $25°C$?

Exercise #10

What products are formed at the anode and cathode, respectively, when each of the following solutions is electrolyzed?

(a) LiCl(aq)　(b) $CuSO_4$(aq)

(c) NaCl(l)　(d) H_2SO_4(aq),
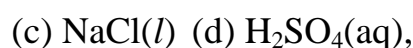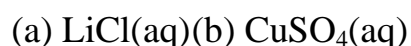
using platinum as electrodes.

Exercise #11

In an electrolysis of a solution contains a mixture of Fe^{2+}, Cu^{2+}, and Pb^{2+} ions, in what order will the metals be deposited on the cathode? If the anode is a mixture of Fe, Cu, and Pb, in what order will they be oxidized?

Exercise #12

How many grams of silver will be produced if a current of 1.50 A passes through a solution of $AgNO_3$ for 30.0 minutes?

Exercise #13

How long (in minutes) would it take to deposit 0.67 g of copper from a solution containing Cu^{2+} using a cell that operates at 6.0 V and produces a current of 1.3 A? How much energy (in kJ) is consumed to produce this amount of copper?

Exercise #14

How many grams of Na and Cl_2, respectively, can be produced in 1.00 hr by the electrolysis of molten NaCl in a Downs cell that operates at 5.0 V and 7.5×10^4 amperes? How many kilowatt-hours (kWh) of energy are consumed to produce this amount of sodium and chlorine? (Faraday's constant = 96,485 C/mol e⁻; 1 kWh = 3.6×10^6 J)

Exercise #15

The electrolysis of Al_2O_3 in molten cryolite to produce aluminum metal uses a cells that operate at 4.5 V and 2.0×10^5 A. How long does it take to produce 908 kg (~ 1 ton) of aluminum? How much kWh of energy is consumed to produce this much aluminum? (Faraday's constant = 96,485 C/mol e⁻; 1 kWh = 3.6×10^6 J)

Exercise #16

Molten magnesium chloride is electrolyzed in a cell that operates at 4.5 V and 1.5×10^5 A. How many kilograms of magnesium are produced in an 8.0-hour shift? What other product is also formed and on which electrode? (Faraday's constant = 96,485 C/mol e⁻; 1 kWh = 3.6×10^6 J)

THE STANDARD ANSWERS

Redox reactions can be broken into two half-reactions:

Example-1:

Oxidation half-reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e-$

Reduction half-reaction: $Cu^{2+}(aq) + 2 \, e- \rightarrow Cu(s)$

Overall reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$

Example-2

Oxidation half-reaction: $5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e-$

Reduction half-reaction: $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow$

$Mn^{2+}(aq) + 4H_2O(l)$

Overall reaction: $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow$

$Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$
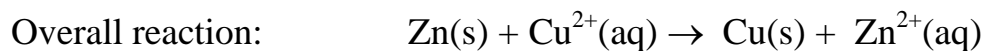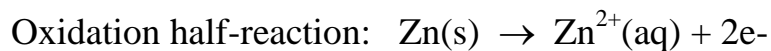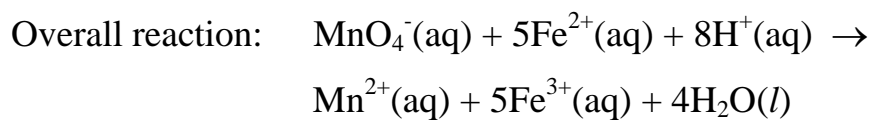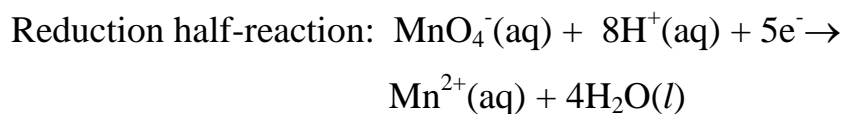
EXPERIMENTAL PART

Laboratory work: Electrochemistry

Part A. Redox Reactions:

1. Fill four cells in each of four columns of a 24-well microcell plate about three-fourths full with 1.0 M $Cu(NO_3)_2$, 1.0 M $FeSO_4$, 1.0 M $Pb(NO_3)_2$, and 1.0 M $Zn(NO_3)_2$ as shown in the diagram below.

2. Polish small strips (4 each) of Cu, Fe, Pb and Zn with steel wool or sand paper and place them on a paper towel with written labels to insure that the metals are not mixed up with each other. Partially submerge the strips into the cell rows as shown below.

Place only part of the metal into the solution so that any sign of a reaction (such as deposit of a metal on the submerged part of the strip) can be determined by comparison with the unsubmerged portion of the metal strip.

	$Cu(NO_3)_2$	$FeSO_4$	$Pb(NO_3)_2$	$Zn(NO_3)_2$
Cu(s)				
Fe(s)				
Pb(s)				
Zn(s)				

3. After 5 minutes examine each cell carefully to see if any metal displacement redox reaction has occurred.

Record your observations in a table as shown above in your laboratory notebook.

Then repolish and rinse the strips and return them to labeled paper towels located at the rear of the lab. If you are unsure about the identity of any strips, give them to your lab instructor.

Part B: Reduction Potentials:

1. Before constructing the galvanic cells, set up the Vernier system in DATAMATE with the voltage probe connected to channel 1 of the LabPro interface.

2. Hit CLEAR on the main screen of DATAMATE and the program will check for sensors. Once the voltage probe has been identified, and a reading near 0 volts is shown, you are ready to record data from the main screen.

Obtain a 1.5 V battery from the instructor's desk and connect the red lead of the voltage probe to the (+) end of the battery (the cathode) and the black lead to the (−) end (the anode). If the voltage reading is not 1.5 V +/− 0.2 V, inform you instructor.

3. Wet a 2–3 inch long strip of filter paper with KNO3 solution. Remove excess liquid gently (the paper easily rips when wet!) by blotting it on a paper towel and fold the paper into a U-shape; this will serve as your salt bridge. Place the salt bridge so that it will be immersed into each of two solutions in adjacent wells of a 12-well microcell plate (see Figure 3 below).

4. Construct a galvanic cell by adding solutions of 1.0 M $Cu(NO_3)_2$ as the aqueous Cu^{2+} and 1.0 M $Zn(NO_3)_2$ as the aqueous Zn^{2+} to the two adjacent wells. Do not immerse the copper and zinc at this time.

Connect the leads from the voltage probe to the zinc and copper electrodes.

Recall that the red lead must be connected to the cathode and the black to the anode to obtain a positive cell voltage.

5. Immerse the electrodes in the solutions and remove them in 5-10 seconds while avoiding contact with the salt bridge. If the voltage reading on the Vernier calculator is positive, the electrodes are connected correctly; if not, repolish and rinse the electrodes and reverse the connections.

To Vernier

(+)   (-)

Filter paper salt bridge

Microcell plate
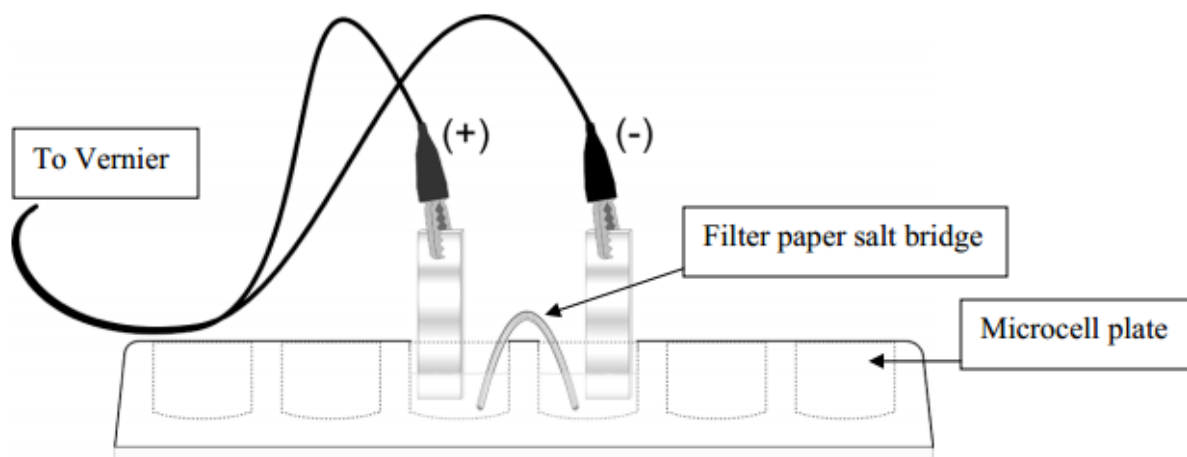
6. Record the positive cell potential, in volts, in your laboratory notebook. You will find that the voltage recorded is less than what you would expect based on standard reduction potentials. For example the Zn/Cu cell may be less than the 1.10 V calculated in the Introduction section. This is partly due to the presence of an oxide formed on one of the electrodes, a process which occurs very rapidly for easily oxidized metals and which changes the half-cell potential.

7. Repeat steps 3-6 for galvanic cells of Fe (in 1.0 M $FeSO_4$) - Zn and Pb(in 1.0 M $Pb(NO_3)_2$) - Zn. Use a freshly prepared filter paper strip for the salt bridge of each cell.

Part C: Nernst Equation for varying Cu2+ concentrations:

1. Prepare three dilute solutions of $CuSO_4$ by serial dilution from a 1.0 M $CuSO_4$ stock solution as follows: Transfer1.0 mL of 1.0 M $CuSO_4$ stock solution into a labeled (with tape) 100.00 mL volumetric flask and dilute to the mark with de-ionized water to form a 0.01 M solution.

Rinse the pipet with a small volume of the solution to be transferred prior to use. Next take the 0.01 M solution just formed and transfer 1.0 mL of it into a labeled 100.00 mL volumetric flask.

Dilute to the mark with de-ionized water to form the 0.0001 M solution. Repeat one more time so that you have the following set of solutions in labeled flasks:

Solution A – 1 M $CuSO_4$ (stock solution) Solution B – 0.01 M $CuSO_4$

Solution C – 0.0001 M $CuSO_4$ Solution D – 0.000001 M $CuSO_4$

2. Prepare a half-cell of Cu2+ by placing the copper solution D into a 12-microcell well.

3. Remove the copper and zinc electrodes from the half-cells used previously and clean and re-polish them.

4. Place 1.0 M $Zn(NO_3)_2$ in a cell next to the Cu^{2+} half-cell. Connect the two half-cells with a freshly prepared salt bridge. Connect the copper and zinc electrodes to the correct voltage probe leads. Measure and record the cell potential in your laboratory notebook using the same technique (5-10 second immersion) with the voltage probe as in Part B.

5. Remove the $CuSO_4$ solution with a disposable pipet and repeat the measurement of E cell (steps 3-4) for the remaining three copper solutions in order of increasing concentration. Then, in the same way, measure the Ecell for the unknown Cu^{2+} solution. Record the measured values in a table as shown below in your notebook.

Solution	D	C	B	A	Unknown
$[Cu^{2+}]$	0.000001 M	0.0001 M	0.01 M	1.0 M	
Volts					

Part D: Determine the E° for a voltaic cell using Cu and unknown metal:1

1. Obtain a small amount of the unknown electrolyte solution labeled "1.0 M X ion" and the corresponding metal strip, "X". This metal is one of the metals in the table of Standard Reduction Potentials at the end of the In-Lab section.

2. Use a disposable pipet to transfer a small amount of 1.0 M X ion solution to a well adjacent to the 1.0 M CuSO4 solution in a 12-microcell-test plate.

3. Make a new salt bridge by soaking a short length of filter paper in the KNO3 solution.

4. Connect the X and Cu half-cells with the filter paper. Measure the positive potential of the X-Cu voltaic cell using the same technique as in Part B (Red lead to the Cu, which is the cathode).

5. After recording the potential once (5-10 seconds), remove both electrodes from the solutions and clean and polish each electrode. Set up the galvanic cell again. Connect the voltage probe as before.

6. Record the potential again. If the two measured potentials do not agree within .1 volts, test the galvanic cell a third time and record the potential immediately after making the connection with the voltage probe. Calculate the average of the measured potentials to use in the Post-Lab calculation.

Laboratory work: Potentiometric titration of acids

Put 10,0 ml of acid of an unknown concentration using pipette into a glass. Immersed an electrode into solution, and start adding 0.5 ml portions of 0.1 M NaOH solution from the burette. After addition of each portion the solution mix it and fix the pH on the scale of the device.

At the beginning of the titration pH change is small, then adding a certain amount of titrant will lead to a sharp rise and again slight pH change.

Stop the titration and write the data to following table:

№	V_{NaOH}, ml	pH	№	V_{NaOH}, ml	pH
1			11		
2			12		
3			13		
4			14		

5			15		
6			16		
7			17		
8			18		
9			19		
10			20		

Determine the equivalent amount of alkali according to the graph (V_{eq})
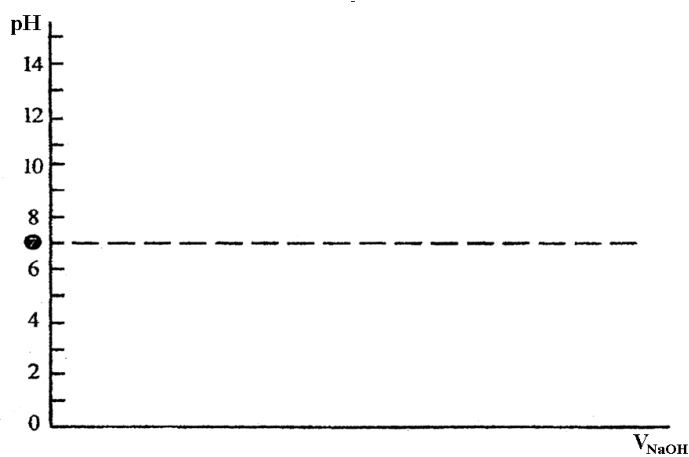
Calculate the concentration of the acid:

$$N_{HCl} = \frac{N_{NaOH} \cdot V_{eq}}{V_{HCl}} ;$$

$N_{HCl} =$

TESTS

Please indicate, how the equivalent admittance of weak electrolyte is changed at given temperature with dissolution:

a) *Fast grows and reaches a maxima;

b) Slowly grows, and then drops;

c) Slowly increases;

d) Is not changed;

e) Decreases;

What electrode is used most frequently as indicator at titrating the basis:

a) *Glass

b) Chlorine-argentine

c) Calomel

d) Quinhydrone

e) Standard hydrogenous

On what from the following formulas it is possible to calculate ionic strength of electrolyte?

a) *0,5 c^2z^2

b) 0,5 cz^2

c) 0,5cz

d) 0,5 az^2

e) 0,5cz^2

For what galvanic cell value of electromotive force does not depend from Ai:

a) *Ag/AgNO$_3$/AgNO$_3$/Ag

b) Pt/H$_2$/HCl/AgCl/Ag

c) Ag/AgCl/KNO$_3$/K

d) Pt/Fe^{2+}Fe^{3+} // Sn^{2+}Sn$^{4+/}$Pt

e) Pt/H$_2$/C$_6$H$_5$OH // CH$_3$COOH/H$_2$/Pt

The glass electrode is widely applied to measuring ?I in biological environments, in the liquid medicinal forms etc. Please indicate, to what type of electrodes the glass electrode belongs?

a) *Ion-selective
b) Electrode of II kind
c) Electrode of I kind
d) Redox electrode
e) Gaseous electrode

One of yardsticks of an estimation of quality of some medicinal preparations is the pH value. Please indicate, what galvanic cell is suitable for determination of pH:

a) *Ag,AgCl|HCl|glass. membrane|H+||KCl|AgCl,Ag
b) Cd, Hg|CdSO$_4$ || HgSO$_4$, Hg
c) Zn|ZnSO$_4$ || CuSO$_4$|Cu
d) Pb|PbSO$_4$ || PbI$_2$|Pb
e) Ag|AgNO$_3$|NH$_4$NO$_3$|AgNO$_3$|Ag

For quantitative determination of potassium hydroxide the method of potentiometric titrating is selected. A point of equivalence in this method is determined on leap of:

a) *Electromotive force;
b) Diffuse current;
c) Voltage;
d) Current intensity;
e) Intensity of a fluorescence

Concentration of sodium of bromide has been determined by a method of potentiometric titrating. Titrant - standard solution of silver nitrate. Please select an indicator electrode:

a) *Argentine
b) Hydrogenous
c) Platinum
d) Chlorine-argentine
e) Antimony

The diffusion potential arises on border between:

a) *Two solutions;
b) Two metals;
c) Metal and solution

What from the following circuits is more preferential to use for determination of concentration of medicinal matter having acid-base properties:

a) *Ag/AgCl/HCl/glass membrane / explor. sol./KCl/AgCl/Ag
b) Pt/H$_2$/explor. sol./KCl/AgCl/Ag
c) Pt/H$_2$/explor. sol./KCl/Hg$_2$Cl$_2$/Hg
d) Pt/C$_6$H$_4$(OH)$_2$, C$_6$H$_4$O$_2$/explor. sol./KCl/AgCl/Ag
e) Ag/AgCl/KCl/explor. sol./KCl/AgCl/Ag

What is the nature of a biopotential?

a) *It is a membrane potential;
b) It is a electrode potential;
c) It is an contact potential

What potential from the listed electrodes does not depend from pH?

a) *Calomel
b) Hydrogenous

c) Glass

d) Quinhydrone

What from the following electrodes most frequently uses for determination of pH?

a) *Glass

b) Quinhydrone

c) Zinc

d) Chlorine-argentine

The degree of dissociation using conductometric method is determined: (degree of dissociation of solutions - a; electrical conductivity L):

a) *a =- L (v) / L(max)

b) a = - L(max) / L (v)

c) a=x/c* L(max)

The greatest significance of equivalent conductivity has the electrolyte solution, if:

a) *An indefinitely weak solution;

b) If the concentration of solution is max;

c) Speeds of cation and anion are equal

What pH in a point of equivalence in a method of potentiometric titrating, i.a. when all acid has been titrated by alkali at pH will be equal to:

a) *pH = 7

b) pH< 7

c) pH> 7

Equation of Nernst for a galvanic cell of Daniel-Jacobi:

a) *$E=E0 - RT/nF \ln a\ Zn^{2+}/a\ Cu^{2+}$

b) $E = E_0 - RT/nF \lg a\ Zn^{2+}/a\ Cu^{2+}$

c) $E = E_0 - RT/nF \ln [a\ Zn^{2+} - a\ Cu^{2+}]$

The magnitude of a potential of an electrode of a II kind is described by an equation:

a) *$E = E_0 - RT/nF \ln a\ C^{l-}$

b) $E = E_0 - RT/2F \lg C\ Cl^-$

c) $E = E_0 + 0.059 \lg C\ Ag\ Cl/C\ KCl$

Nernst Equation for determination or indicator electrodes:

a) *$E = E_0 + 0.059 \lg a\ H^+$

b) $E = E_0 + 0.059 \ln pH$

c) $E = E_0 - RT/nF \ln C\ H+/pH$

Please record an equation of Nernst for a membrane glass electrode in an alcaline environment:

a) *$E = E_0 + RT/nF \ln a\ Na^+$

b) $E = E_0 - RT/nF \lg [OH^-]$

c) $E = E_0 - 0.059 \lg C$ of a glass / C solut.

To what type of electrodes a chlorine-argentine electrode belongs:

a) *II kind;

b) I kind;

c) Ion – selective;

d) Gaseous

Whether the membrane glass electrode in acidic environment will work as a hydrogenous electrode?

a) *Yes

b) No

The diffusion potential arises on border:

a) *Of two solutions;

b) Of metal and membrane of a cell

The verbiage of a Kohlrausch law:

a) *At infinite dissolution the electrical conductivity is equal to the sum of movabilities of cations and anions;

b) At infinite cultivation the electrical conductivity depends on an ion concentration of electrolyte;

c) Electrical conductivity does not depend on absolute speeds of cation and anion

Between specific and equivalent conductivity (L) there is a relation:

a) *L(v) =x v

b) L (v) =1/x*10

c) L (v) =L (max) c

Physical sense of equivalent conductivity:

a) *It is conductivity of a strata of electrolyte by thickness 1m, placed between electrodes of such thickness, that volume of solution between them conta

b) It is value, reciprocal to electrical conductivity referred to 1 kmole/m^3;

c) It is conductivity of electrolyte solution equivalent to conductivity of standard electrolyte

What is specific conductivity?

a) *It's a value, reciprocal to resistance of one cubic meter of solution with an rib of length of 1 m;

b) It is value, equivalent to resistance of one cubic meter of solution with an rib of length of 1 m;

c) It is a electrical conductivity of electrolyte solution at a unit surface charge

To what the ionic strength of solution is equal?

a) *To half-sum of products of molarity of each ion on quadrate of its charge;

b) To a half-sum of products of concentration of each ion on magnitude of activity ratio;

c) To quadrate of a charge on a half-sum of activities of all ions.

Measure of active acidity of environment - pH it is:

a) *A negative decimal logarithm of an ion concentration of hydrogen;

b) Total acidity of solution;

c) Hydrogen ion exponent of amphoteric electrolyte.

The ionization constant of weak electrolyte expressed by: (degree of dissociation of solutions - a)

a) *$Cd=ca^2/1-a$;

b) $Cd=ca/1-a$;

c) $Cd=a(1-c)/c(1-a)$.

How it is possible to calculate activity ratio?

a) *On an equation of Debye-Hukkel;

b) On an equation of Ostwald;

c) On an equation of ionic strength of solution.

How the concentration magnitude of a degree of dissociation influences?

a) *The degree of dissociation is moderated a degree of dissociation grows;

b) Remains to a constant.

To what degree of dissociation of solutions (a) of weak electrolytes is equal?

a) *0 < and < 1

b) a=1

c) a=0

What is a degree of dissociation?

a) *This is a relation of dissociated molecules to a total number of particles of electrolyte in solution;

b) This is a relation of source molecules of electrolyte solution to an amount of dissociated molecules

c) This is a relation of dissociated molecules to number of non-dissociated molecules of solution.

To what degree of dissociation of solutions (a) of non-electrolytes is equal?

a) *a=0

b) a=1

c) 0 < a < 1

It is impossible to measure the actual voltage of any half cell by itself because

a) of resistance of wire

b) electrical neutrality is maintained

c) a reaction does not take place of its own

d) *both half-cell reactions occur simultaneously

An electrochemical cell can be changed into an electrolytic cell by

a) changing the electrolytes in two half cells

b) changing the conc. of the electrolytes

c) *providing higher potential from outside

d) reversing the electrodes

In electrolysis, one mole of aluminium atoms is deposited by

    a) five moles of electrons

    b) *three moles of electrons

    c) two moles of electrons

    d) one mole of electrons

During discharge in the case of lead storage batteries density of sulphuric acid

    a) increases

    b) *decreases

    c) may decrease or increase

    d) remains constant

For reducing 1 mole of ferrous ions to iron the number of faradays of electricity required will be

    a) 4

    b) 1.5

    c) 0.5

    d) *1

One mole of electrons is same as

    a) faraday

    b) *coulomb

    c) ampere

    d) none of these

The decomposition of an electrolyte by passing electric current depends upon

    a) energy of electrolysis

    b) *quantity of current which is passed

    c) shape of the electrode

d) size of the container

Which of the following is the best reducing agent in aqueous solution?

a) *Li

b) Cs

c) Rb

d) K

If mercury is used at cathode during the electrolysis of aqueous NaCl the ions discharged at the cathode are

a) hydroxide

b) chloride

c) *sodium

d) none of these

Salt Bridge is used because it

a) forms insoluble precipitates with the electrolytes in the two half cells

b) enhances the flow of electrons by overcoming liquid junction potential

c) *maintains the electrical neutrality of the two half cells

d) provides the extra ions

On passing one faraday of electricity through molten lead (II) bromide, amount of bromine obtained is

a) 5 gm mole

b) 3 mole

c) 1 mole gm atom

d) *1 gm equivalent

During the electrolysis of fused sodium chloride, the anodic reaction is

a) reduction of chloride ions

b) oxidation of sodium ions

c) *oxidation of chloride ions

d) None of the above

More electropositive elements have more

a) *negative reduction potential

b) positive oxidation potential

c) tendency to loose electrons

d) positive reduction potential

In the concentration cells the electrical energy is due to

a) *transfer of a substance from one solution to another solution

b) temperature

c) reduction of fuel

d) chemical action

The most important condition for a galvanic cell is

a) *the two half cells should be connected internally by some device

b) the electrolytes should taken in a separate container

c) the electrolytes should not have physical contact

d) the electrodes should be inert

Passing 96.5 coulombs of charge through molten NaOH will deposit

a) 0.046 g

b) *0.023 g

c) 230 g

d) 46 g

Which of the following metals when coupled will give maximum e.m.f. for a voltaic cell.

a) Pb and Sn

b) Cu and Ag

c) *Ca and Cu

d) Fe and Cu

Art of electroplating was enunciated by

a) Einstein

b) *Brugantally

c) Ampere

d) Kohlorausch

Electrochemical equivalent is the mass of the element liberated during electrolysis when

a) 2 faraday electricity is passed

b) 1 amp. current for 1 hrs is passed

c) *1 coulomb electricity is passed

d) 3 amp current is passed

In the process of electroplating an object with nickel

a) *the object is made cathode and pure nickel as anode

b) the object is made anode and pure nickel as cathode

c) pure nickel is made the anode

d) the object is made the cathode

Which of the following is not a good conductor?

a) Silver

b) *Solid NaCl

c) Fused NaCl

d) Aqueous solution of NaCl

Aqueous solution of HCl conducts electricity because it

    a) dissociates

    b) dimerises

    c) *ionises

    d) forms hydrogen bond

At infinite dilution of an electrolyte, the equivalent conductance of cations and anions are

    a) dependent on the nature of solvent

    b) *independent of nature of ions

    c) independent of each other

    d) dependent on each other

The quantity of an ion discharged during electrolysis is directly proportional to

    a) chemical equivalent of the ion

    b) time of flow of current

    c) current strength

    d) *All the above

Substances that dissociate and conduct electricity in aqueous solutions are

    a) emulsios

    b) colloidal solution

    c) electrolytes

    d) *conductors

The electrode by which electrons enter the electrolyte may be

    a) *cathode

    b) conductor

    c) anode

d) anode or cathode

Voltaic cell stops functioning after sometimes because there is

    a) the decrease in oxidation potential outweigh the increase in reduction potential

    b) *the decrease in oxidation potential value equalises the increase in reduction potential value

    c) decrease in oxidation potential value

    d) increase in oxidation potential and decrease in reduction potential

On passing electricity through dil sulphuric acid the amounts of substance liberated at the cathode and anode are in the ratio

    a) 2:3

    b) 3:2

    c) *1:8

    d) 8:1

A Galvanic cell:

    a) Has a spontaneous chemical reaction

    b) Has a positive cell potential

    c) Has a negatively charge anode

    d) None of the above

    e) *All of the above

An electrolytic cell:

    a) Has a non-spontaneous chemical reaction

    b) Requires application of a negative potential to make the reaction occur

    c) Has a positively charged anode

    d) *All of the above

    e) None of the above

In a galvanic cell:

a) Electrons flow from the cathode to the anode via the external circuit

b) *Electrons lose some of their energy in the external circuit

c) Electrons travel through the salt bridge, or electrolyte

d) The chemical reaction has a positive free energy change

e) None of these

Fluorine is above chlorine in the table of standard reduction potentials. This implies:

a) Chlorine is more easily reduced

b) Chloride ions can reduce fluorine

c) *Fluoride ions can reduce chlorine

d) Can't tell from this information

In the cell represented by the shorthand notation: Cd(s) | Cd+2(aq) || F-(aq), F2(g) | Pt(s),

a) The platinum is being oxidized by the fluorine gas

b) The Cd+2 ions are being reduced

c) The F- is being oxidized to fluorine gas

d) *The oxidation compartment is on the left

e) None of the above

In an electrolytic cell containing aqueous Na2SO4 and two platinum electrodes, what is produced at the cathode?

a) Sodium metal

b) SO2(g)

c) Oxygen gas

d) Nothing

e) *Hydrogen gas

Which of the metals Zn, Cu, Al, and Ni can cathodically protect a sample of iron from corrosion?

    a) All of them

    b) None of them

    c) *Only Zn and Al

    d) Only Cu and Ni

    e) Only Zn

If we pass a current of 10.0 Amperes through a solution for 1 hour, how many moles of electrons are used?

    a) *10 x 1

    b) 10 x 1 x 3600

    c) 10 x 1 x 3600 x 96487

    d) 10 x 1 x 3600 / 96487

    e) none of the above

The REDOX reaction $Zn(s) + Cu+2(aq) = Zn+2(aq) + Cu(s)$ has Eo = +1.10 V. The standard free energy for this reaction can be calculated as:

    a) DGo = 96487 (1.10) J/mol

    b) *DGo = 2 (96487) (1.10) J/mol

    c) DGo = - 96487 (1.10) J/mol

    d) DGo = - 2 (96487) (1.10) J/mol

    e) DGo = - 3 (96487) (1.10) J/mol

Secondary batteries can be recharged because:

    a) The products are in physical contact with the electrodes

    b) The anode is not destroyed during use

    c) *Both of the above

    d) Neither of the above

What is the oxidation state of H_2?

    a) 1

    b) *0

    c) -1

    d) 1/2

What is the oxidation state of gold in $Au(CN)_4^-$?

    a) *3

    b) -1

    c) 0

    d) 4

What is the oxidation state of Xe in $XeOF_4$?

    a) 2

    b) -2

    c) *6

    d) -6

In which of the following compounds does O have an oxidation state not equal to -2?

    a) H_2O

    b) *HOF

    c) ClO_4^-

    d) H_2SO_4

Which of the following reactions is **NOT** a redox reaction?

    a) $Na + Cl \text{ ---> } NaCl$

    b) $*H_2O_2 \text{ ---> } HO_2^- + H^+$

    c) $Ni^{2+} + Fe \text{ ---> } Fe^{2+} + Ni$

    d) $NaOH + HCl \text{ ---> } NaCl + H_2O$

Give the line notation for a cell that reduces $CuSO_4$ to Cu and oxidizes Zn to Zn^{2+}.

    a) Cu (s) | Cu^{2+} (aq) || Zn^{2+} (aq) | Zn (s)

    b) *Zn (s) | Zn^{2+} (aq) || Cu^{2+} (aq) | Cu (s)

    c) Zn (s) | Zn^{2+} (aq), SO_4^{2-} (aq) || Cu^{2+} (aq), SO_4^{2-} (aq) | Cu (s)

    d) Cu (s) | Cu^{2+} (aq), SO_4^{2-} (aq) || Zn^{2+} (aq), SO_4^{2-} (aq) | Zn (s)

In the following galvanic cell, identify the direction of electron flow: Pt (s) | MnO_4^- (aq), Mn^{2+} (aq), H^+ (aq) || Fe^{2+} (aq), Fe^{3+}(aq) | Pt (s)

    a) From anode to cathode: right half-cell to left half-cell

    b) From cathode to anode: right half-cell to left half-cell

    c) From cathode to anode: left half-cell to right half-cell

    d) *From anode to cathode: left half-cell to right half-cell

What is the direction of ion flow through a porous disk in a galvanic cell?

    a) There is no ion flow through the disk whose purpose is to separate the two half-cells

    b) Negative ions flow from the oxidation half-cell to the reduction half-cell

    c) *Positive ions flow from the anode half-cell to the cathode half-cell

    d) Negative ions flow from the oxidation half-cell to the reduction half-cell

What is the sign of ΔG for a galvanic cell?

    a) Positive

    b) *Negative

    c) Either negative or positive

    d) Zero

What is the sign of E for a galvanic cell?

    a) *Positive

b) Negative

c) Either positive or negative

d) Zero

Which half-reaction takes place at the anode?

a) The one with the greater reduction potential

b) The one that transfers the most number of electrons

c) The reduction

d) *The oxidation

Which of the following is an equation for ΔG?

a) $\Delta G = \Delta G^o - (RT/nF) \ln Q$

b) $\Delta G = nFE$

c) *$\Delta G = \Delta G^o + RT \ln Q$

d) $\Delta G = \Delta H + T\Delta S$

What is the free energy of formation for water, given its E^o for decomposition into hydrogen and oxygen is -1.23 V?

a) -475 kJ / mol

b) *-237 kJ / mol

c) 237 kJ / mol

d) 475 kJ / mol

e) 455 kJ / mol

Using your chemical intuition, which of the following species is the strongest oxidizing agent?

a) *F_2

b) H_2

c) Br_2

d) Ca

What species must copper be oxidized to if the cell potential for one of its redox reactions is 1.0 V and the free energy of the reaction is -289.5 kJ / mol?

a) Cu^-

b) Cu^{2+}

c) Cu^+

d) *Cu^{3+}

What is a faraday?

a) A unit of current

b) A unit of energy

c) *A unit of charge

d) A mole of electrons

What happens to the cell potential of a non-standard state reaction when the temperature increases?

a) *Decreases

b) Increases

c) Stays the same

d) Not enough information to solve the problem

Which of the following statements about concentration cells are true?

a) The electrons flow from the cathode to the anode

b) Their potentials are constant in time

c) Useful voltages cannot be harnessed from such cells

d) *Reduced material can plate at the cathode

What is the potential of the following cell at 45°C? Ag (s) | Ag^+(aq) || Ag^+ (aq) [0.1 M] | Ag (s)

a) 0.126 V

b) 0.63 V

c) *0.063 V

d) -0.063 V

e) 0.0063 V

What is the direction of ion flow through the porous disk in a concentration cell?

a) Negative ions flow from the anode compartment to the cathode compartment

b) *Positive ions flow from the oxidation half-cell to the reduction half-cell

c) There is no ion flow in a concentration cell because it is not a real reaction

d) Positive ions flow from the reduction half-cell to the oxidation half-cell

Why do most ships with iron hulls hang from those hulls a piece of magnesium?

a) *The magnesium has a greater oxidation potential than the iron and therefore acts as an anode, being dissolved into the ocean, while the ship's hull acts as a cathode and is this protected against corrosion.

b) The magnesium has a greater reduction potential than the iron and therefore acts as an anode, being dissolved into the ocean, while the ship's hull acts as a cathode and is thus protected against corrosion.

c) The magnesium has a greater reduction potential than the iron and therefore acts as a cathode, being dissolved into the ocean, while the ship's hull acts as an anode and is thus protected against corrosion.

d) The magnesium has a greater oxidation potential than the iron and therefore acts as a cathode, being dissolved into the ocean, while the ship's hull acts as an anode and is thus protected against corrosion.

Even though redox reactions are reversible by applying an outside source emf, why aren't all batteries rechargeable?

a) Redox reactions are not all reversible, and those used in batteries are good examples of non-reversible redox reactions.

b) All batteries are, in fact, rechargeable but big business doesn't want you to know that.

c) Because batteries are usually dry-cells, due to the lack of mixing of reagents it is unlikely that most of the reagents will come into contact with the electrodes and hence, can only react once and not be recharged.

d) *Redox reactions are not 100% efficient, that is to say that the yield on a redox reaction is generally not quantitative so multiple charges and discharges would make the battery's potential decrease dramatically due to the decrease in available reagents (Nernst Equation).

Which of the following redox reactions is primarily responsible for producing most of what you eat?

a) $CH_4 + O_2$ ---> CH_3OH

b) $C_2H_6 + O_2$ ---> C_2H_5OH

c) *$CO_2 + H_2O$ ---> $C_6H_{12}O_6$

d) $CO_2 + CH_4$ ---> $C_2H_4O_2$

What is the potential of the following reaction that has a ΔG of -264 kJ / mol?

$Na^+ + Cl^-$ ---> $NaCl$
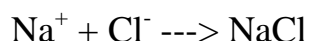
a) 2.74 V

b) *0

c) 1.37 V

d) -2.74 V

e) 2.74 V

Aluminum, in the 18th century, was more valuable than gold. Explain why that was so, and why now the opposite is true.

a) *Al has a greater oxidation potential than Au, so Au was more abundant in its elemental form. After the discovery of electrolysis, it became a simple task to design a process to refine Al from its ore. Almost all the gold on earth, however, is in its elemental form so the discovery of electrolysis did not have such a profound effect on the price of Au as it did for Al.

b) Al has a greater oxidation potential than Au, so Al was more abundant in its elemental form. After the discovery of electrolysis, it became a simple task to design a process to refine Au from its ore. Almost all the aluminum on earth, however, is in its elemental form so the discovery of electrolysis did not have such a profound effect on the price of Au as it did for Al.

c) Al has a greater reduction potential than Au, so Au was more abundant in its elemental form. After the discovery of electrolysis, it became a simple task to design a process to refine Al from its ore. Almost all the gold on earth, however, is in its elemental form so the discovery of electrolysis did not have such a profound effect on the price of Au as it did for Al.

d) Al has a greater reduction potential than Au, so Al was more abundant in its elemental form. After the discovery of electrolysis, it became a simple task to design a process to refine Au from its ore. Almost all the aluminum on earth, however, is in its elemental form so the discovery of electrolysis did not have such a profound effect on the price of Au as it did for Al.

At which electrode is H_2 in the electrolysis of water?
   a) The anode
   b) The electrode connected to the negative side of the battery
   c) *The cathode
   d) Cannot be determined with the given information

Why is it necessary to add some salts to water for the electrolysis of water to proceed?

a) Due to the production of acid during the electrolysis, a buffer is needed to maintain a constant pH.

b) *Water, as a poor electrical conductor needs some electrolyte solution to give the necessary conduction for the electrolysis to proceed.

c) Salts are necessary to prevent the explosion of the dangerous gasses hydrogen and oxygen.

d) Salts are not needed for the reaction to proceed.

Which of the following is **NOT** produced during the electrolysis of water?

a) Electricity

b) Acid

c) Hydrogen

d) Oxygen

Relative to the amount of oxygen produced, how much hydrogen gas is evolved during the electrolysis of water?

a) L

b) Half as much

c) The same amount

d) *Twice as much

If you added a drop of phenolphthalein during the electrolysis of water, at which electrode would you see the color change and why?

a) The anode because phenolphthalein tests for the production of base

b) The anode because phenolphthalein tests for the production of acid

c) *The cathode because phenolphthalein tests for the production of base

d) The cathode because phenolphthalein tests for the production of acid

How long will it take 1.0 kg of Au to late from a solution of Au^{3+} with a current of 150 A?

a) 54.4 minutes

b) *2 hours 43 minutes

c) 136 hours

d) 2 days

How many grams of Pu (from Pu^{2+}) will be plated onto a cathode in ten minutes with a current of 10 A?

a) *7.6 g

b) 15.2 g

c) 3.8 g

d) 0.76 g

A metal plates 1.41 g onto a cathode from a species in solution in 70 minutes with a current of 2.5 A. Identify the species.

a) Na^+

b) Au^{3+}

c) Fe^{3+}

d) *Cr^{4+}

How long will it take to completely dissolve a silver anode whose mass is 3 g if a 2.0 A current is passed through it.

a) 11.2 minutes

b) 44.8 minutes

c) *22.4 minutes

d) 5.6 minutes

At STP, what volume of hydrogen gas is produced in the electrolysis of water is a current of 50 A is passes through a solution of pure water for 10 minutes?

a) 3.48 L

b) *0 L.

c) 6.96 L

d) 1.74 L

At STP, what volume of hydrogen gas is produced in the electrolysis of water is a current of 50 A is passes through a solution of salt water for 10 minutes?

a) *3.48 L

b) 0 L

c) 6.96 L

d) 1.74 L

What is the molar mass of a substance that plates 5 g of itself in 10 minutes with a current of 10 A and requires 2 electrons per mole of that substance?

a) 80.4 g / mol

b) 321.6 g / mol

c) 32.2 g / mol

d) *160.8 g / mol

Given a solution with equal concentrations of the following species, using your chemical intuition, which one should plate first if the external potential is slowly increased from zero to larger values?

a) Na

b) Li

c) *Al

d) Mg

Using your chemical intuition, what combination of elements would make a very powerful battery?

a) F and Cl

b) *F and Li

c) I and Fe

d) Cd and Fe

Would a table of standard oxidation tables be just as valid as a table of standard reduction potentials and why?

a) Yes, because they are the same.

b) *Yes, because the choice of writing reactions as reductions is purely arbitrary.

c) No, because there is a physical basis for writing reactions as reductions.

d) No, because the Nernst Equation tells us that equations should only be written as reductions.

BASIC REFERENCES

1. Medical chemistry: educational and methodical recommendations / A.G. Kaplaushenko, I.A. Iurchenko, B.A. Varinskiy, M.A. Shcherbak, Yu.N Kucheryavyi. − Zaporozhye, 2014. − 263 p.

2. Medical chemistry: textbook for students of higher medical educational institutions of the III-IV accreditation levels / V.A. Kalibabchuk, V.I. Halynska, V.I., Hryshchenko [et al.]. − Kyiv : Medicine Publishing, 2010. - 223 p.

3. Fundamentals of Medicinal Chemistry / Gareth Thomas, John Wiley & Sons − First Edition. − December, 2003. − 285 p.

4. An Introduction to Medicinal Chemistry / Graham L. Patrick. − Oxford University Press − 4th Edition. − October, 2009. − 776 p.

SUPPORTING REFERENCES

1. Principles of Bioinorganic Chemistry/ Stephen J. Lippard, Jeremy M. Berg, University Science book, 2005, 411 p.

2. Biological Inorganic Chemistry: Structure and Reactivity 1st Edition. Harry B. Gray, Edward I. Stiefel, Joan Selverstone Valentine, Ivano Bertini. University Science book, 2007, 731 p.

3. Biological Inorganic Chemistry, Second Edition: A New Introduction to Molecular Structure and Function 2nd Edition. Robert R. Crichton . Elsevier. 2012, 447 p.

4. Foye's Principles of Medicinal Chemistry 7th Edition. David A. Williams. Lippincott Williams & Wilkins, 2013. 1500 p.

5. Principles of Colloid and Surface Chemistry, Third Edition, Revised and Expanded (Undergraduate Chemistry: A Series of Textbooks) 3rd Edition. Paul C. Hiemenz, Raj Rajagopalan. Taylor & Francis. 1997, 650 p.

6. Physical Chemistry, 9th Edition 9th Edition. Peter Atkins , Julio de Paula. Oxford University Press. 2010. 959 p.

7. Handbook of Surface and Colloid Chemistry, Fourth Edition. K. S. Birdi. CRC Press. 2015. 708 p.