**AL-FARABI KAZAKH NATIONAL UNIVERSITY**

**FACULTY OF CHEMISTRY AND CHEMICAL TECHNOLOGY**

**DEPARTMENT OF PHYSICAL CHEMISTRY, CATALYSIS AND PETROCHEMISTRY**

**MEASUREMENT OF THE GALVANIC ELEMENTS' EMF**

Instructions to the laboratory work on «Chemistry» discipline

for the students of 6B05301

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1. PURPOSE OF WORK.

The aim of the work is to study the possibility of converting chemical energy into electrical energy during the work of galvanic cell. To investigate the influence of various factors on the value of EMF cells.

2. THEORETICAL STATEMENTS

**1. Electrode potentials**

**Occurrence of a potential jump at the metal-solution electrolyte boundary**

If any metal plate is placed in the metal salt solution of the plate, the transition of metal atoms from the plate, which we will hereafter call the electrode, into the solution will begin and the reverse transition of metal ions will be higher in one direction compared to the other, i.e., either the transition of metal ions from the solution to the electrode will predominate. The predominant transition of metal ions in one direction will occur until the values of the corresponding thermodynamic potentials are equal [1]. In this case, the rates of forward and reverse transitions of ions will be equal. The process of transition of the metal atoms of the electrode into the solution with the loss of electrons by the atoms and the formation of positively charged ions corresponds to the oxidation process:

Ме→Меz++Ze

where z is the number of electrons lost, e is the charge of the electron.

The reverse process – reduction

Меz++Ze→ Ме.

When the forward and reverse process speeds are equal, = the states of the electrode and solution do not change, and the electrode is in equilibrium state.

In a state of equilibrium, the following cases may occur.

Metal ions have partially transferred from the solution to the electrode, and since they have a positive charge, the electrode will be positively charged with respect to the solution and will attract negatively charged acid residue ions to its surface as a result of such transfer. Thus, when a copper plate is dipped into a solution of copper sulfate at a certain concentration of the solution, some of the positively charged copper ions from the solution will transfer to the copper plate, which will also be positively charged and th At the surface of the positively charged electrode there is a rim of negatively charged ions and, accordingly, a jump of electric potential (Fig. 1,2).

Part of the negative charged ions will be attracted to the surface of the electrode at a minimum distance , equal to their radius. At a distance greater than , there will be both positive and negative ions, the latter in some excess, decreasing with distance from the electrode; at some distance from the electrode, the concentrations of positive and negative ions will equalize and the solution will become electrically neutral ions i.e., uncharged, from the solution will be electrically attracted to it.

–

##### Металл

Раствор

+

+

+

+

+

+

+

+

+

–

–

–

–

–

–

–

–

–

–

φ

δ0

φ1

φа

|  |  |
| --- | --- |
| **Figure 1 - Distribution of negatively charged ions on the positively charged electrode** | **Figure 2 - Distribution of the potential jump on the positively charged electrode** |

The charged surface of the electrode together with the oppositely charged layer of solution adjacent to the electrode is called the double electric layer. The part of the electrical double layer formed by the ions directly adjacent to the electrode (at a distance ) is called the dense part of the electrical double layer. In this part, there is a linear change in potential between the electrode and the plane passing through the centers of the adjacent ions. The potential jump in the dense part of the double layer is denoted by the letter. The part of the double electric layer located behind the dense part is called the diffuse part.

The potential change behind the dense part of the double electric layer in it is nonlinear and is denoted by .

The total potential jump, at the electrode-solution boundary consists of the sum of the potential jumps in the dense and diffuse parts of the double electric layer:

=𝝍+ (1)

and is called the absolute potential jump*.*

2. In the case when some of the metal atoms transfer as positive ions into the solution, excess electrons remain on the electrode, the electrode is negatively charged with respect to the solution and attracts positive ions of the solution to its surface, which form a positively charged ionic cover of the electrode (Fig. 3, 4). This phenomenon occurs when a zinc electrode is immersed in a zinc salt solution.

3. Potential jumps can also occur at the electrode-solution interface when the electrode material ions are absent in the solution, i.e., when the electrode is inert in the given medium [2].

For example, if the platinized plate electrode is placed in a dilute solution of hydrochloric acid and hydrogen is blown through the solution, the latter will be adsorbed by the plate and an equilibrium will be established between the adsorbed hydrogen and the solution:

H22H+,

and an electric charge appears on the plate, a double electric layer is formed at the electrode surface, and an electric potential surge occurs between the plate and the solution. The role of the platinum or other inert material in generating the jump in electric potential is limited to accepting or giving up the electrons involved in the electrode reaction.

|  |  |
| --- | --- |
| **Figure 3 - Diffusion of positively charged ions on a negatively charged electrode** | **Figure 4 - Distribution of the potential jump on the negatively charged electrode** |

**Equilibrium potential**

The jump in electric potential between the electrode where the redox reaction takes place and the solution, which is established when the rates of the forward and reverse reactions are equal, is called the equilibrium potential of the electrode in a given solution.

When equilibrium is established, for example, at a metal electrode immersed in a solution of the electrode metal salt, the chemical potentials of metal ions at the electrode and in the solution must be equal.

=

The chemical potential of charged particles, usually called the electrochemical potential, also includes an electrical energy reserve and is written in the form:

(2)

where zF𝝋 is the stock of electric energy of the substance's gram-ion; 𝝋 is the electric potential of charged particles of a given phase with respect to an infinitely distant point or simply any point [3].

At equilibrium on the electrode

(3)

where is the electric potential of charged particles (metal ions) on the electrode; is the electric potential of discharged particles in the solution.

**Dependence of electrode potential on solution composition and temperature**

From expression (3) we find:

(4)

or

(5)

Equations (4) and (5) establish the dependence of the equilibrium potential of the electrode relative to the solution in which the electrode is immersed on the temperature and concentration (activity) of metal ions in solution (), which are in oxidized form, and concentration (activity) of metal ions in metal ().

If the electrode is made of any one metal rather than an alloy, the ion activity and instead of equation (5) can be written:

(6)

where is the activity of metal ions in solution.

**Hydrogen potential scale**

The values of the standard chemical potentials included in equations (4) - (6) are unknown and therefore φ^0' and the absolute potential jump cannot be calculated. There are also no experimental methods for measuring the absolute potential jump at the electrode-solution interface. Therefore, in order to be able to compare the values of the equilibrium potentials of the various electrodes, it was agreed to measure them with respect to the potential of the equilibrium hydrogen electrode under standard conditions, the potential of which was assumed to be zero at all temperatures.

The standard conditions were taken to be the conditions when the activity of hydrogen ions in the solution was equal to one at the hydrogen pressure equal to the normal atmospheric pressure [4].

The potential of the electrode in the hydrogen potential scale is the difference between the potential of this electrode and the hydrogen electrode under standard conditions.

Thus, the equilibrium potential of the metallic electrode on the hydrogen potential scale will be the difference:

𝝋= (7)

where is the absolute potential of the hydrogen electrode under standard conditions, which is a function of temperature.

The difference is denoted by and is called the standard electrode potential:

(8)

It follows from equation (8) that the electrode potential is standard when the activity potential of the forming ions in the solution is equal to one, i.e. =1.

In the general case, the dependence of any electrode potential on solution composition and temperature is given by the Nernst equation:

𝝋= (9)

Where is the standard potential of the reaction occurring on the electrode; is the activity of potential-determining ions (atoms, molecules) that are in the oxidized form; is the activity of potential-determining ions (atoms, molecules) that are in the reduced form.

**2. Galvanic cell E.M.F.**

**Galvanic cell**

A system consisting of two electrodes placed in an electrolyte solution, which creates an electric current in an external circuit when the electrodes are connected outside the electrolyte by some metallic conductor, is called a galvanic cell [1-4].

To describe galvanic elements, a conventional notation is used, according to which the material of one of the electrodes is given first, then the solution in which this electrode is placed, then the solution in which the second electrode is immersed, and finally the material of the other electrode. The electrodes are separated from the solution by a solid vertical line, and the solutions are separated either by two vertical lines, when it is believed that there is no jump in potential at the border of the solutions, or by a dotted line, when such a jump cannot be neglected. Thus the copper-zinc element can be written as follows:

*(-)Zn|ZnS|CuS|Cu(+)*

where + and - signs indicate the polarity of the electrodes;and - concentrations of the solutions.

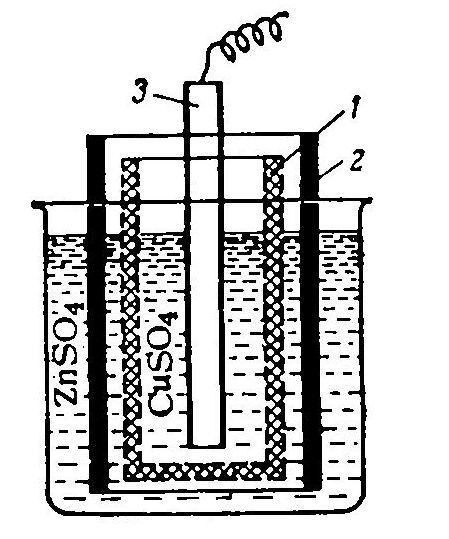
If there is a large difference between and , when the potential jump at the boundary of the two solutions cannot be neglected, this element is written in another form:

*(-)Zn|ZnS:CuS|Cu(+)*

In those cases where one wants to indicate only the ions involved in electrode reactions, the record is simplified:

*(-)Zn|||Cu(+)*

The design of the copper-zinc galvanic cell (Daniel cell) is shown in Fig. 5.



**Figure 5 - Copper-zinc element (Daniel-Jacobi element):**

1 - porous diaphragm; 2 - zinc cylindrical electrode; 3 - copper electrode.

When the electrodes are short-circuited through an external circuit, the copper electrode will undergo a copper reduction process:

and on the zinc electrode - zinc oxidation process:

*Zn=*

The electrons remaining on the electrode during the oxidation reaction will flow in an external circuit from zinc to copper, where they will participate in the copper reduction process. In solution, the current in the galvanic cell will be carried by copper and zinc ions moving to the zinc electrode and sulfate ions moving to the copper electrode.

The equilibrium potentials of the copper and zinc electrodes are related to the activity of the copper and zinc ions in solution by the Nernst equation:

The difference in the equilibrium potential of the electrodes of a galvanic cell is equal to the electromotive force of that cell (abbreviated as e.m.f.):

*E=* (10)

or

*E* (11)

In equation (11) is the standard efficiency of a galvanic cell, i.e. a galvanic cell in which the activities of the potential-determining ions are equal to one. The standard e.m.f. of a galvanic cell is equal to the difference of the standard potentials of the individual electrodes of the galvanic cell.

Galvanic cells are divided into chemical cells (Daniel-Jacobi cell) and concentration cells, the theoretical basis of which is presented in ( ).

**3.Relationship between galvanic element's e.m.f. and the maximum work of the process**

Galvanic cells can be reversible and irreversible. A galvanic cell is reversible if the current-forming reaction in the cell can be reversed by applying an infinitesimal amount of the element's emf to it from the outside. An example of reversible galvanic cells is the mentioned Daniel cell (if we neglect the transition of ions across solution boundaries):

*(-)Zn|ZnS*

In this element, when it works, there will be a reaction:

*Zn+CuS*

If an external e.m.f. is applied to the element, oppositely directed relative to the element's e.m.f., it will react:

*Cu+ZnS*

That is, unlike the current-forming reaction in the element, copper will begin to dissolve and zinc will begin to be released from solution.

An example of an irreversible element would be a chain:

*(-)Zn|CuS*

There will be a process going on in this element when it works:

*Zn+CuS*

If an external oppositely directed e.m.f. is applied to it, it will dissolve copper on the copper electrode and release it on the zinc electrode, i.e. this process will not be reversed by the work of the galvanic cell.

The work of any reversible process under certain restrictions imposed on the conditions of the process, for example, at constant temperature and pressure, will be the maximum useful work, so the thermodynamic calculation of e.m.f. is possible only in the case of reversible galvanic cells. The dependence of the maximum useful work of a chemical reaction on temperature is given by the Gibbs-Helmholtz equation (12) and (13):

∆G=∆H+T(δ∆G/∆T)p (12)

∆F=∆U+T(δ∆F/∆T)v (13)

where G and F are isobaric-isothermal and isochoric-isothermal potentials.

The maximum useful work of the electrochemical reaction is

(14)

(15)

where E is the e.m.f. of the galvanic cell; z is the number of electrons involved in the total electrochemical reaction; F is Faraday's number.

Substituting ∆G and ∆F into the Gibbs-Helmholtz equations instead of ∆G and ∆F, expressing their values through e.g., we obtain these equations in a form that relates the e.m.f. to the thermal effect of the reaction and the temperature effect:

(16)

(17)

where is the temperature coefficient.

Or, considering that *-∆Н=*- the heat effect of reaction at constant pressure and *-∆U=* – the heat effect of reaction at constant volume, we obtain:

(18)

(19)

When the galvanic cell's e.m.f. is independent of temperature, i.e., , equations (18) and (19) turn into Thomson equations, which are a special case of Gibbs-Helmholtz equations:

(20)

(21)

For condensed systems, which include aqueous solutions, , since the volume of the solution depends little on pressure, and only equations (16), (18), and (20) can be used to calculate e.m.f.

The entropy of the electrochemical reaction is determined by the formula:

(22)

also, enthalpy

*∆H=-nFE+nFT(δE/δT)* (23)

The relationship between the equilibrium constant of a chemical reaction and standard electrode potentials is expressed by the relation:

(24)

*lgK=()/0.059, Т=298К*

Heat capacity:

∆ (25)

**Types of electrodes**

The electrodes that make up a galvanic cell are divided into certain groups [1-4].

Electrodes of the first kind, reversible by cation, and the Nernst equation for them is written as:

(26)

Electrodes of the second kind, reversible by both anion and cation. They represent a metal coated with a hard-soluble salt of that metal immersed in a salt solution containing an anion of the same name as the anion of the hard-soluble salt.

Schematically, the second kind of electrode can be represented by .

The Nernst equation:

(27)

Prove for yourself the reversibility of the second kind of electrode on the activity of the cation.

Redox electrodes are inert material dipped into a solution containing oxidized and reduced forms. The Nernst equation for these electrodes is as follows:

(28)

where is the activity of the oxidized form;

- activity of the reduced form.

For a complex redoxy electrode, the scheme is written as Red, Ox, e.g:

Mn

n=5;

*E=+*

For detailed information on all types of electrodes, see the textbooks [2-6].

In this paper, we will consider the redox electrodes in more detail.

For the redox electrode, equation (28) can be written in general terms:

(29)

At the same time

(30)

Where ∆G is the change in Gibbs free energy and K is the equilibrium constant of the electrochemical reaction of the redox couple, for example: Fe(3+)+e=Fe(2+).

If we add to the solution of the reduced form of the first redox couple the solution of the oxidized form of the second one, the oxidation potential of the resulting mixture will be expressed by equation (31). For example, to a solution of the reducing agent KJ (J/J pair) add a solution of the oxidizing agent Cu(2+) pair Cu(2+)/Cu(J+)/

(31)

(32)

If , the reaction equation between the components of the redox couple can be written in the form *Re*

Let's move from activities to concentrations:

(33)

If we carry out not one addition of the reagent, but a potentiometric titration of the reduced form of one oxidation form pair to another, we obtain the following curve (Fig. 6):

Let the solution contain m-eq. *Re* before the titration, after adding m-eq. *Re*и *Y-()/*. The oxidative potential of the solution will be equal to:

(34)

At the moment when half of the contained in the solution , will be equal to and E i.e. oxidizing potential of the solution will be equal to the standard potential of the first (titrated) redox couple.

At the equivalence point, where the number of m-eq of added is ,

Finally, when an amount of equal to 2is added to the solution, we have E=. Thus, from the titration curve it is possible to calculate the standard potentials of the redox couple and the equilibrium constant of the redox reaction at a given temperature.

In the case of unequal stoichiometric coefficients in the equation of the redox reaction

can thus be obtained for the equivalence point

=

The described method of determining , does not take into account the errors due to the neglect of activity coefficients and the diffusion potential, i.e. the values found are apparent rather than thermodynamic. The influence of the pH of the medium is also not taken into account, so the values may be very different from the tabulated ones.

3. DESCRIPTION OF EQUIPMENT

**Instrumentation:** High-ohmic potentiometer, zero-galvanometer (sensitivity 1А/del), vessels for Daniel-Jacobi element electrodes, electrolyte bridges, copper, zinc, platinum electrodes, chlorosilver reference electrode EVL-IMZ, electrode for measuring oxidative potential EPV-01.

For the measuring procedure on the potentiometer see. «Practical work on physical chemistry», ed. by S.V.Gorbachev [7], pp. 298-301.

4. OPERATING PROCEDURE

**Task 1.** Measuring the EMF of Daniel-Jacobi element

**Purpose of the work:** To determine the EMF a galvanic cell depending on the activities of the solutions used; compare the obtained results with the theoretical ones calculated by the Nernst equation.

**Procedure:** prepare the electrodes, clean their surface with filter paper, rinse with water, dip the copper electrode in nitric acid (1:5) for a few seconds, and the zinc electrode in hydrochloric acid of the same concentration, rinse the electrodes thoroughly with water again. Having prepared solutions of CuSO4and ZnSO4(concentrations as instructed by the teacher), various versions of the Daniel-Jacobi element are made, the EMF is measured. In one of the cases, the value of the diffusion potential is estimated by first measuring with direct contact of the solutions, and then using an electrolyte bridge with a saturated KCl solution.

Calculate the values ​​of the EMF from the Nernst equation, using activity values of the coefficients and the standard potentials of the «Handbook of Electrochemistry» [8 ](eds. A.M.Suhotin) or D.Dobosh «Electrochemical constants» [9 ]. Build a graph of dependence of E on  determine the slope coefficient of the electrode function.

**Task 2.** Determination of appearing standard redox-pair potentials and redox equilibrium constants by potentiometric curve.

**Purpose of the work:** To calculate the standard potentials of the used redox pairs and the equilibrium constant of the reaction between them.

**Procedure:** A platinum electrode for measuring the oxidation potential EPV-01 is placed before measurements for 10 minutes in a hot chromium mixture, after cooling, the electrode is washed several times with distilled water. A certain volume of 0.1 mol/L of the reducing agent specified by the teacher is placed in a 50-100 ml beaker. The beaker is placed on a magnetic stirrer, the electrolyte bridge, the platinum electrode are immersed in the solution and titrated with the oxidizing agent specified by the teacher. If necessary, acid and alkali are added to the reducing agent solution. The titration is repeated two times: for the first time it is titrated approximately by adding 0.5-1.0 ml of titrant to determine the area of ​​a sharp change in potential. When the titration is repeated, this part of the curve should be obtained by adding the titrant in 0.1 ml portions.

A titration curve is plotted in the E coordinates (relative to the silver chloride electrode) - the amount of meq of the oxidizer. Determine the position of the equivalent point (value y0). Accordingly, the potentials are values corresponding to y0/2 and 2y0; find E01and E02. In cases where n 1≠n2, use equations (39-41) and calculate the equilibrium constant. The found experimental values ​​E01and E02 arerecalculated into the hydrogen scale. The recalculation is carried out as follows: to the calculated value of E 0(with its sign), add + 0.222V (potential of the saturated silver chloride electrode at room temperature). It should be noted that the values ​​of the standard potentials determined by this method can differ greatly from the reference ones due to the differences in the acidity of the medium and the neglect of the diffusion potential.

**Task 3.** Determination of the standard potential of the redox electrode.

**Purpose of the work:** Calculate the slope of the electrode function and the standard potential of the redox pair from the Nernst equation.

**Procedure:** Platinum electrode as prepared as in task 2. At the direction instructor constitute 5-7 solutions redox system (). Measurement of oxidation potentials with a silver chloride reference electrode. The measured values ​​are converted to the hydrogen scale. The values ​​of the activities are calculated using the values ​​of the activity coefficients from the same reference books as in task 1. The values ​​of the standard potential of the redox pair and the slope of the electrode function are calculated by the method of least squares.

5. RESULTS MANAGEMENT

Record the results obtained in Table 1 according to the sample.

Table 1 - Table for recording experimental data

|  |  |  |  |
| --- | --- | --- | --- |
| № | Used solutions | Е10, mV | Е20, mV |
| 1 |  |  |  |
| 2 |  |  |  |
| 3 |  |  |  |
| 4 |  |  |  |
| 5 |  |  |  |

Based on the information you receive, do the following:

a) Construct a titration curve in the coordinates E (relative to the silver chloride electrode) - the amount of m-eq of the oxidizing agent.

b) Find the potential values corresponding to and ; .

c) Calculate the equilibrium constant.

Compare results and draw conclusions.

6. SAFETY RULES

In the course of laboratory work it is forbidden:

1. Switching the unit on and off without the permission of the teacher or laboratory assistant.

2.Leaving the unit energized without supervision.

3.Work with ungrounded equipment.

When performing laboratory work, the student must:

- work in a gown, use personal protective equipment if necessary;

- work neatly, keep clean;

- pour out the used solutions into the drain tanks designed for this purpose;

- handle chemical tableware, reagents, equipment with care;

- perform the work in the described sequence.

7. REPORT REQUIREMENTS

The report must contain the following sections:

1. Purpose of the work.

2. Schematic diagram of the experimental setup with a brief description.

3. Intermediate and final results of the experiments.

4. Calculations on processing the results of the experiment.

5. Conclusion based on the results of experiments and calculations.

6. The work should be signed by the student and the instructor.

8. CONTROL QUESTIONS

1. What is called an electrical double layer?

2. What is electrode potential?

3. What does the term standard potential of a given electrode mean?

4. What is called a galvanic cell?

5. How to determine the EMF of a galvanic cell? (calculate EMF for any element).

6. How is the EMF of a reversibly working galvanic cell related to the Gibbs energy, the equilibrium constant of the reaction proceeding in this cell?

7. What is the physical meaning of the temperature coefficient of the EMF and with what thermodynamic quantity is it directly related?

8. How to calculate the entropy and enthalpy of an electrochemical reaction occurring in a reversibly operating element?

9. What are the 1st and 2nd kind electrodes? How to calculate their electrode potentials?

10. What is a redox electrode? Using any redox electrode as an example, calculate its electrode potential and the equilibrium constant of the reaction taking place on this electrode.

9. LIST OF RECOMMENDED LITERATURE

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