**Laboratory work**

**DETERMINATION OF THE pH OF HYDRATE FORMATION and THE PRODUCT OF THE SOLUBILITY (PoS) of METAL HYDROXIDE**

**1.** **The** **purpose of the work:** to determine the pH of hydrate formation by potentiometric titration and to calculate the PoS of metal hydroxide by analytical and graphical methods.

**2. Theoretical part**

The formation of metal hydroxide, which precipitates as a solid phase from a salt solution of this metal, occurs after the pH of the solution reaches a certain value, which is called the pH of hydrate formation.

To experimentally determine the pH of hydrate formation, the method of potentiometric titration of a salt solution with alkali is used. With this titration, after each addition of alkali from the burette, the pH of the solution is measured by means of a glass electrode. Initially, there is usually a gradual increase in pH, which, however, stops as soon as the pH value corresponding to the precipitation of solid metal hydroxide is reached, and a horizontal section appears on the titration curve (Fig.1). Throughout this section, the added alkali is consumed to precipitate new portions of metal hydroxide. Therefore, this section can be traversed only after all metal ions are bound by hydroxyl ions.

If we assume that metal hydroxide Ме(ОН)n in solution is in equilibrium with ions according to the scheme:

Ме(ОН)n⇔Меn++n[ОН-] (1)

then

PoS =[Ме n+][ОН-]=[Ме n+](Кw/[Н+])n (2)

where Кw is the ionic product of water.



Fig.1. pH measurement during titration of salt solution

Moving from concentration to activities and logarithming equation (2) we get:

 (3)

or

 (4)

For n=2 from (4) we get:

 (5)

or

 (6)

Equation (5) shows the linear dependence of the pH of hydrate formation on the activity of the metal ion in solution; the higher the activity of the metal, the lower the pH value, the precipitation of metal hydroxide should begin.

Knowing the pH of hydrate formation and the volume of the added alkali solution (in order to determine the concentration of metal ions at the point of the titration curve corresponding to the beginning of precipitation of hydroxide), an approximate value of the solubility product of metal hydroxide can be calculated. A more accurate calculation of the solubility product of hydroxide can be achieved if the activity coefficient of metal ions is taken into account.

**3. Working procedure**

Appliances and utensils: installation pH meter (EV-74 ionometer), magnetic stirrer, burette, glass, pipette, 50ml flask.

Reagents: solutions of 0.1 n CuSO4, ZnSO4, NiSO4, CdSO4, Pb(NO3)2, 0.1 n NaOH.

Prepare four solutions of the following concentrations from divalent metal salt (as directed by the teacher) 50 ml each: 0.001; 0.005; 0.01; 0.02 n (to do this, take 0.5; 2.5; 5; 10 ml from the initial 0.1 n solution, respectively, and dilute each of them with water to 50 ml). Pour one of the prepared solutions into a glass and immerse the glass electrode and the electrolytic key of the silver chloride electrode (reference electrode) of the pH meter into it. The ball of the glass electrode must be completely immersed in the test liquid. From the burette, with continuous stirring, add 0.1-0.2 ml of 0.1 n alkali solution to the glass and measure the pH of the solution after each portion of the reagent.

Based on the data obtained, plot the pH – volume of the added alkali, which is a titration curve (see Fig. 2) and find the break point followed by the horizontal section of this curve. The pH value at this point corresponds to the pH of hydrate formation. From the break point, lower the perpendicular to the abciss axis, find the volume of alkali that went to titration and calculate the concentration (normality) of metal ions in equilibrium with undissociated hydroxide molecules.



Figure 2. Determination of the pH of metal hydroxide

Do the same with the other three salt solutions. The results obtained should be entered in the table:

|  |  |  |  |
| --- | --- | --- | --- |
| Initial concentration of titrated salt solutions | pH value of hydrate formation | Activity of metal ions | PoS |
| 0,001 |  |  |  |
| 0,005 |  |  |  |
| 0,01 |  |  |  |
| 0,02 |  |  |  |

**4. Processing the results**

To calculate the PoS according to equation (6), it is necessary to move from concentration to activity. The average ionic activity of the electrolyte solution (а±) is found by the equation:

*а±=γ± . m*±

where γ*±* is the average ionic activity coefficient

 m± is the average ionic molality of the solution is defined as

, from here 

In dilute solutions, the molarity (c) is approximately equal to the molarity (m). For example, for divalent metal salts:

M=c = normality (H)/2

The value of γ± is not always known, so you can use the data presented in the table for calculation. (Short Reference of physico-chemical quantities, edited by K.P. Mishchenko and A.A. Ravdel, ed. "Chemistry", L., 1974., p. 128)

or calculate it using the Debye-Guckel equation:



where A = 0.517 (for aqueous solutions);

 Z+, Z- - valences of the cation and anion of this salt;

 J is the ionic strength of the salt solution, which is calculated by the formula:



**Based on the results of the experiment, it is necessary to perform the following tasks:**

1. Construct the dependence of pH = f(VNaOH), (for each concentration separately);

2. Find the pH of hydrate formation from the graph.

3. Find the PoS of metal hydroxide from Equation 6.

4. From the obtained pH values of hydrate formation and activity of metal ions to draw graphics of pH = f(aMen+ ).

5. The found pH values of hydrate formation and PoS are compared with the literature data and the relative measurement error is calculated.

**5. Safety precautions**

In the process of performing laboratory work, it is prohibited:

1. Turn on and off the installation without the permission of the teacher or laboratory assistant;

2. Leave the energized installation unattended.

3. Work with ungrounded equipment.

When performing laboratory work , the student must:

* work in a bathrobe, use personal protective equipment if necessary;
* work carefully, keep clean;
* drain the waste solutions into specially designed drains for this purpose;
* carefully handle chemical utensils, reagents, equipment;
* perform the work in the described sequence.

**6.Report Requirements**

The report should contain the following sections:

* the purpose of the work;
* schematic diagram of the experimental setup with its brief description;
* intermediate and final results of experiments;
* calculations for processing the results of the experiment;
* the output of the results of experiments and calculations on the equipment.

**7. Security questions**

1. What is the pH of hydrate formation?

2. What is the relationship between the pH of hydrate formation and the activity of metal ions in solution?

3. How is the pH of hydrate formation determined experimentally?

4. How is the PoS of hydroxide calculated by the pH of hydrate formation?

**8. Recommended literature:**

1. Eremin V.V., Kargov S.I., Uspenskaya I.A., Kuzmenko N.E., Lunin V.V. Fundamentals of physical chemistry. Theory and problems. – M.: Exam, 2005. - 480 p.

2. Smetanina E.I., Kolpakov V.A. Laboratory workshop on physical chemistry: textbook/Tomsk Polytechnic University. − Tomsk: Publishing House of Tomsk Polytechnic University, 2012. – 272 p

3. Klebanova N.A., Klebanov A.V., Sleptsova N.N. Electrochemical methods of analysis: laboratory workshop / - Mogilev: UO "Kuleshov Moscow State University", 2010. - 76 p.: ill.

4. Ospanova A.K., Seilkhanova G.A. Selected chapters of physical chemistry // Textbook. – Almaty. - 2011, 146 p.

5. Ospanova A.K., Seilkhanova G.A., Murzagalieva M.G. Laboratory workshop on electrochemistry//Study guide. - Almaty: Kazak University, 2008, 72 p

6. <https://pnu.edu.ru/media/filer_public/2013/04/08/fiz-chem_lab8.pdf>

DRAWINGS for the English version