Mathematical Description Development of Reactions of Metallic Gallium Using Kinetic Block Diagram

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Abstract. A kinetic block diagram based on a logical sequence of actions in the mathematical processing of a kinetic data is used. A type of reactions of metallic gallium in hydrochloric acid solutions is determined. It has been established that the reactions of the formation of gallium oxide and its salts proceed independently and in the absence of the diffusion resistance. Kinetic models connecting the constants of the reaction rate with the activation energy and describing the evolution of the process are obtained.

1. Introduction
Gallium is attractive when it is used as a dripping or flowing liquid metal electrode. The specific nature of liquid electrodes from mercury, gallium, their amalgams and galls is associated with an ideal, energetically homogeneous surface. All the processes on the liquid metal electrodes, as a rule, move without activation polarization and ensure high efficiency of the electrochemical systems used. Only chemical reaction or mass transfer stages can be limiting and this is the stage of any heterogeneous reaction [2]. Study of peculiarities of these stages is possible in the systems where no current and constant mixing takes place. The response of the system under study to mixing is considered as a good sign that the reaction takes place and is limited by mass transfer. The analysis of experimental results is usually carried out from the point of view of formal chemical kinetics, which is based on the principle of material balance. The problems to be solved are often typical so it is not surprising that the chemists began to apply mathematical modeling and computer analysis in the section of chemical kinetics. This was facilitated by the universality of mathematical models, allowing the results of laboratory research to be transferred to real objects [3]. Simple software application (Excel program) allows for a small set of kinetic data to make a conclusion about the mechanism of a chemical reaction.

The aim of this work is to determine the type of gallium reactions using the kinetic block diagram, to create a mathematical model to describe a process evolution.

2. Materials and methods
To create conditions that allow treating the chemical interaction as a limiting stage of a heterogeneous process, a technique is chosen when the medium and the sample are mobile. Stirring of gallium samples in solutions of electrolytes was carried out on a magnetic stirrer. Parallel experiments were conducted and classical methods of statistical processing of results as well as standard Excel program were used [4]. 25 samples were dissolved at different stages of the experiments: the root-mean-square
error of the arithmetic mean was 8.2·10⁻³ for the liquid and 9.9·10⁻³ for the solid samples of gallium. Aqueous solutions of hydrochloric acid were used as electrolytes. The accuracy of the temperature measurement during the thermostating of the working space did not exceed ± 2 K, the standard deviation of the activation energy determination was ± 1.5 kJ/mol. In Fig. 1, for example, a series of metal gallium dissolution isotherms in 0.1 M hydrochloric acid solutions is given, the remaining series have similar curves.

The control for the dissolution process was carried out by loss of sample mass [5]. The quantitative characteristic of gallium dissolution is determined by a relative change in the sample mass: \( a = (m_0 - m)/m_0 \) (here \( m_0 \) is the initial mass; \( m \) is the mass after the experiment).

The rate of dissolution of metal can be expressed by the following equation:

\[
\frac{da}{d\tau} = k \cdot (1 - a)^n,
\]

where \( k \) is the rate constant of the chemical reaction; \( n \) is the reaction order.

Taking into account the temperature dependence, the equation includes the activation energy:

\[
\frac{da}{d\tau} = k_0 \exp \left(-\frac{E}{RT}\right) (1 - a)^n.
\]

In the equations, the velocity is expressed not in a traditional way, which means not through a concentration, but through a relative change in the mass of the sample; however, this is not an obstacle for obtaining quantitative characteristics of the process [6].

To use the kinetic block diagram, molar concentrations of chloride and gallium oxide were calculated (according to known stoichiometric ratios for a known solution volume).

3. Results and clarifications

The chemical interaction of gallium with hydrochloric acid can be shown by the following reaction:

\[
Ga + 3HCl \rightarrow GaCl_3 + \frac{3}{2}H_2.
\]

As a result, gallium chloride readily soluble in water is obtained. The process can be represented by final ionization reaction \( Ga \rightarrow Ga^{3+} + 3e \) with Gibbs energy equal to -153.1 kJ/mol.

Gibbs free energy of oxidation reaction:
is -998.24 kJ/mol and is accompanied by the formation of insoluble gallium oxide (III).

To break the bonds between diatomic gallium molecules provided by van der Waals forces, not much energy is required. However, when searching for the answer to the question of where this energy originates, the following questions arise: which particles provide the release of gallium atoms and their ionization - acid anions, ions or dipoles of water, atomic oxygen or its anions? What is the true mechanism of this stage?

In this analysis, it will be assumed that the alternative reaction is the formation of gallium oxide. After this, the problem is reduced to the question of the relationship between two reactions - the formation of chloride and gallium oxide.

In the kinetic analysis, it should be enough to know a set of concentrations when the reagent A \((c_A)\) is consumed and a product B \((c_B)\) is run in time. However this situation is rather unusual as both gallium chloride and gallium oxide are interaction products. Let us now introduce the notions and assume that \(c_A\) is the concentration of gallium chloride; \(c_B\) is the concentration of gallium oxide.

The kinetic type of a complex chemical reaction is finally determined by its characteristic features in a block diagram [7].

In the course of analysis, the independence of the change in concentrations of oxide and gallium chloride, the inequality of the rates of these reactions is revealed. These relationships lead to the conclusion that there are no links between the reactions. This is possible in the conditions of excessive amount of the reacting substances, therefore, both reactions are considered simple (Fig. 2).
In formal kinetics, a simple reaction is an algorithm of the following type: \( aA \rightarrow bB \). In the case, described in this article, the algorithms would be as follows: \( Ga \rightarrow aA \) and \( Ga \rightarrow bB \). A more detailed description of the mechanism of the process is possible only with the involvement of quantum and chemical theories.

The evolution (development in time) of the reaction of dissolution describes the following equations:
- for molten gallium - \( \frac{d\alpha}{dt} = 1.14\exp(-17360/RT) \);
- for crystalline gallium - \( \frac{d\alpha}{dt} = 2.67 \cdot 10^{-2} \exp(-62140/RT) \).

The obtained mathematical models refer to the gallium system, i.e. hydrochloric acid in a wide range of concentrations.

4. Conclusion

When using the kinetic block diagram, the assumption of possible parallel or sequential reactions accompanying the dissolution of metallic gallium in the solution of hydrochloric acid was refuted. The sequence of mathematical processing and the kinetic block diagram used, allowed one to shorten the time of analysis of experimental data, to determine the type of the considered reactions and to find their mathematical description.

References

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