

Study of the Behavior of Gallium in Aqueous Solutions of Electrolytes

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Abstract – Numerical values of the reaction rate constants and activation energies were obtained for the system gallium – aqueous solutions of electrolytes with respect to the nature of the electrolyte and aggregation state of metal. It is shown that dissolution in sulfuric acid media is characterized by low velocity constants, which increase in transition to hydrochloric acid media. Under conditions close to the potential conditions for a dropping gallium electrode, interactions occur in the transition region. The stage of chemical interaction for crystalline gallium under similar conditions determines the total rate. The average activation energy upon dissolution of crystalline gallium under considered conditions is 2–3 times higher than the values obtained upon dissolving molten gallium, and it varies from 30 to 90 kJ/mol.

Keywords – gallium; electrolyte; liquid metal dropping electrode; dissolution; reaction rate constant; activation energy.

I. INTRODUCTION

Despite the absence of an ore base, gallium belongs to smart metals crucial for knowledge-intensive industries actively developing throughout the world [1–3]. Gallium belongs to the group of rare metals, and its content in the earth's crust is $15 \cdot 10^{-4}$ % wt. Gallium is found in ores containing aluminum and silicon oxides, and zinc, copper, arsenic and germanium sulphides. Coal deposits contain considerable amounts of gallium. Waste of the electronics industry is the secondary raw material used for *Ga* production [4]. The presence of metal in various types of natural and technogenic raw materials affects the choice of the technology for its extraction [5, 6]. The scale of aluminum production (gallium is mined from aluminate solutions during production of alumina from bauxite or nepheline ores [7, 8], and from technogenic solid waste of the Bayer process [9, 10]) and coal processing [11] allows production of a significant amount of *Ga* for world market (Fig. 1).

Gallium is widely used in the industry (alloys, opto- and microelectronics, medical devices, solar cells) due to unique combination of its properties, since the *Ga* crystal lattice consists of diatomic molecules, which is not typical of metals. This chemical characteristic features a large temperature range of the liquid state (up to 2230 °C), the ability to supercool and a number of other characteristics.

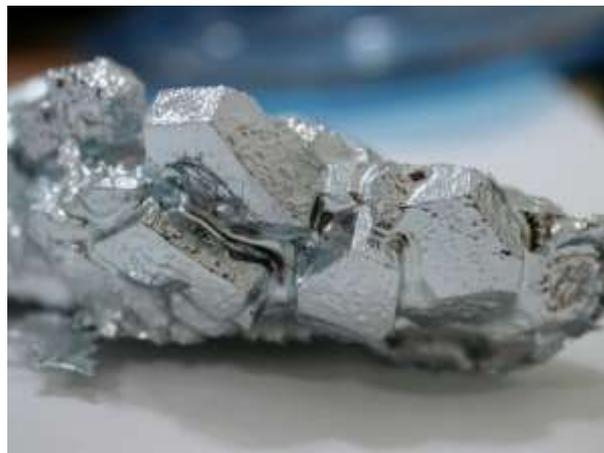


Fig. 1. Gallium crystals (<https://ru.wikipedia.org/wiki>).

Gallium in the liquid state can be used as a dropping or flowing liquid metal electrode [12]. The specificity of widely used liquid electrodes from mercury, gallium and their amalgam in electrochemistry is related to their ideal surface, its energy homogeneity and isotropy of properties.

An electrochemical reaction is known to be a heterogeneous reaction: first, the reacting substance approaches the electrode, after that, the electrochemical reaction proceeds, when electrons are transferred across the phase boundary, and, finally, the resulting products are removed from the electrode surface. Most electrode processes are accompanied by chemical interactions, which (along with phase overvoltage) cause concentration polarization. Processes on liquid metal electrodes occur typically without activation polarization and make the used electrochemical systems highly efficient. Only stages of chemical interaction or mass transfer can be limiting. The stages of mass transfer obey the laws of molecular or convective diffusion, and the stages of chemical interaction obey the laws of chemical kinetics. However, the issues related to dissolution, passivation, and film growth on the metal surface, which determine the mechanism of interaction of *Ga* with electrolytes, are poorly studied.

II. METHODS AND MATERIALS

Interaction of metals with aqueous electrolyte solutions involves dissolution processes followed by adsorption, corrosion and other disintegrations of the surface layer. Research methods typically used imply a different combination of medium and sample interaction. The medium can be mobile or stationary relative to the fixed sample, the sample can be placed in the flow, etc. [13, 14]. We have chosen the technique when the medium and the sample are mobile, since this ensures the most characteristic physical and energy state of gallium for these conditions [15].

Gallium samples were mixed in electrolyte solutions using a magnetic stirrer, metal surface-renewal was provided, and diffusion caused by porous surface films formation was enhanced.

Metallic gallium used was preliminarily purified to 99.99% in accordance with the method of F. Sebba, which implies repeated washing of the metal in concentrated and then in dilute acids, and final washing in distilled water. After purification, gallium was transferred in small droplets onto a polyethylene surface for solidification and sample formation. In most cases, solidification was accompanied by partial crystallization, the sample surface was inhomogeneous, and the faces of different configurations were adjacent to rounded sections.

The dissolution process was controlled with regard to the weight loss of the metal sample. Samples weighing up to 0.1 g were used, and the losses were of the order of $n \cdot 10^{-3}$ g. Aqueous H_2SO_4 and HCl solutions and corresponding aluminum salts were used as electrolytes. A dry, pre-weighed sample was placed in a 100 ml beaker filled with solution, which was placed on a magnetic stirrer. After the experiment, the sample was removed from the solution, rinsed with distilled water, dried and weighed.

The quantitative characteristic of gallium dissolution α is determined by the relative change in sample mass:

$$\alpha = (m_0 - m) / m_0, \times 100\%,$$

where m_0 is the initial sample mass; m is the sample mass after the experiment.

Classical methods of statistical processing and standard Microsoft Excel widely applied in metallurgy were used to process experimental data [16].

The reproducibility of the results obtained in metal dissolution studies is usually high; however, unique gallium properties include low melting point (melting point 29.77 °C) and tendency to overcooling, and in the experiment gallium showed effects difficult to control. Therefore, up to 25 samples were dissolved in various series of experiments: the mean square error of the arithmetic mean was $8.2 \cdot 10^{-3}$ for liquid and $9.9 \cdot 10^{-3}$ for solid gallium samples.

The concentration ranges of the salt systems up to saturated solutions are considered. Saturated salt solutions are of interest from a methodological point of view since they show a dynamic equilibrium between the metallic and ionic modification of gallium in one of the types $(Ga(OH)_3 \rightarrow Ga^{3+} + 3OH^-$ or

$H_3GaO_3(OH)_3 \rightarrow 3H^+ + GaO_3^{3-}$) that does not distort redox pattern [12].

Some experiments were performed at room temperature, and at points above room temperature, the beakers were placed in water bath with an external heating from the UTU-4 thermostat.

It was experimentally shown that metal dissolution is active, and it is enhanced in acid-salt systems at concentrations close to saturated ones. Fig. 2.3 shows an example of a series of isotherms for metallic gallium dissolved in various solutions.

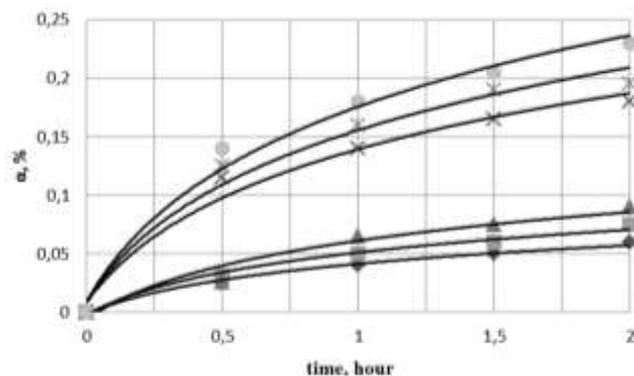


Fig. 2. Dissolution of gallium in 1M HCl solution at temperatures, K: 1 – 288; 2 – 293; 3 – 299; 4 – 304; 5 – 313; 6 – 323.

For H_2SO_4 and $AlCl_3$ solutions, the pattern of the dissolution curves of gallium is similar.

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

$$da/d\tau = k \cdot f(\alpha),$$

where k is the reaction rate constant.

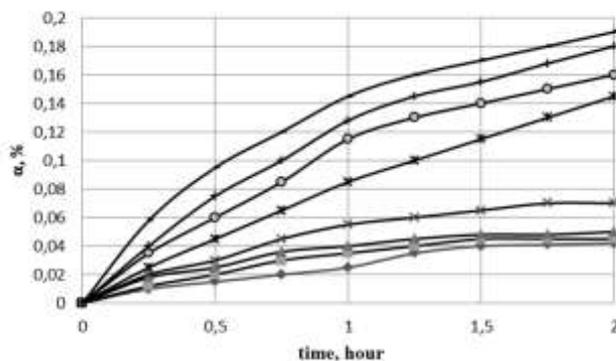


Fig. 3. Dissolution of gallium in saturated solution of $Al_2(SO_4)_3$ at temperatures, K: 1 – 287; 2 – 291; 3 – 299; 4 – 301; 5 – 305; 6 – 316; 7 – 325; 8 – 341.

The Arrhenius equation for the rate constant is $k = k_0 \cdot \exp(-E/RT)$, where k_0 is a pre-exponential factor. Hence, the kinetic equation can be represented as follows:

$$da/d\tau = k_0 \cdot \exp(-E/RT) f(\alpha).$$

The parameter $f(\alpha)$ depends on the reaction mechanism; it can be generally expressed as $f(\alpha) = (1-\alpha)^n$, where n is the reaction order. In this case, the kinetic equation takes the form:

$$d\alpha/d\tau = k_0 \cdot \exp(-E/RT) (1-\alpha)^n.$$

To determine the activation energy of the reaction E , we selected the postulate of the first order of reaction since there is no need to select the n values [17, 18]. We used plots in the $\ln k = f(T^{-1})$ coordinates, where data should be plotted as a straight line with an inclination angle proportional to the activation energy. A standard deviation of the procedure was ± 1.5 kJ/mol. The straight pattern of the dependencies obtained confirmed the correctness of the chosen postulate.

In the experiments, the changes in the surface of the metal and its energy state are difficult to consider, and therefore it is difficult to estimate the actual process rate. Experimentally determined activation energy that depends on experimental conditions and is included in the above equations is usually referred to as apparent E^* [19]. In all kinetic studies, the apparent values rather than the true characteristics are typically determined since the latter require quantum-chemical approaches.

III. RESULTS

The kinetic curves in Fig. 2.3 shows numerous characteristic differences in gallium behavior in the considered conditions. In all the cases, the process is active at the initial stage with subsequent stabilization. The initial segment of the kinetic curve can be used to calculate the numerical values of the dissolution rate constants k^* . Similar to activation energies, they refer to the apparent experimentally determined values (Table 1).

TABLE I. EXPERIMENTAL VALUES OF GALLIUM DISSOLUTION RATE CONSTANTS

Electrolyte	k^* , hour ⁻¹	
	Gallium solid	Gallium liquid
Sulfuric acid	$2.86 \cdot 10^{-4}$	$3.76 \cdot 10^{-2}$
Aluminium sulphate	$8.50 \cdot 10^{-4}$	$4.16 \cdot 10^{-2}$
Hydrochloric acid	$2.67 \cdot 10^{-2}$	1.14
Aluminum chloride	$6.07 \cdot 10^{-2}$	1.21

Experimentally determined k^* and E^* values give an insight into the mechanism of heterogeneous interaction, help determine the region of the process and its limiting stage. The E^* values for gallium dissolution in 1M solutions are presented in Table 2.

Very few data on the activation energy of dissolution and oxidation of gallium are available in the literature, but the order of the values found corresponds to E^* values of Ga leaching [20].

Chemical interaction of gallium with acids occurs by the reactions:

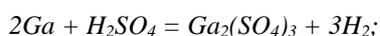


TABLE II. EXPERIMENTAL VALUES OF THE APPARENT ACTIVATION ENERGY FOR GALLIUM DISSOLUTION

Electrolyte	E^* , kJ/mol	
	Gallium solid	Gallium liquid
Sulfuric acid	83.10 ± 0.19	25.38 ± 0.04
Aluminium sulphate	54.88 ± 0.13	24.39 ± 0.05
Hydrochloric acid	62.10 ± 0.14	27.26 ± 0.05
Aluminum chloride	38.12 ± 0.71	17.36 ± 0.04

The interaction leads to the formation of gallium salts highly soluble in water, hence, the process can be represented by the final ionization reaction:



The Gibbs energy equal to 153.1 kJ/mol indicates its spontaneity regardless of the solvent temperature and nature.

Gallium ionization is accompanied by the destruction of the solid gallium crystal lattice and by the breakage of bonds in the molten metal. Apparently, the processes are very similar, which is due to the interaction of diatomic molecules on the surface with particles in the solution. Moreover, these molecules, both in the solid and in the molten states, are bound only by van der Waals forces, the destruction of which requires little energy.

When analyzing the significance of a particular reaction in gallium dissolution, the stage of oxygen adsorption on chemically active surface centers with a subsequent formation of the chemisorbed oxygen layer should be considered most important. The layer, which consists of atoms forming chemical bonds with metal cations, is a precursor of the oxide film. Its occurrence is facilitated by different energies of different crystallographic faces of the solid metal surface. Chemical bonds are formed more easily and are more stable in case of crystal-chemical compatibility between the metal and oxide lattices [20]. This is evident for a pair of diatomic oxygen and gallium molecules. The stability of a new phase in the form of oxide on the gallium surface is ensured by favorable mutual arrangement of oxygen anions and metal cations, which is close to their arrangement in the normal crystal lattice of oxide. Calculation of the Gibbs free energy by the reaction



gives the change of Gibbs energy equal to 998.24 kJ/mol and indicates that gallium oxidation is accompanied by the formation of insoluble gallium oxide (III). Passivation and formation of the protective layer on the Ga surface are associated with this thermodynamically favorable reaction.

The mechanism of the formation of gallium oxide by the reaction formally recorded as an oxidation reaction is complex. It was previously assumed that the Ga passivation in acidic and alkaline solutions leads to the formation of insoluble gallium oxide (III). Later, passivating oxides were established to have a more complex structure. It is obvious that the formation of other compounds is associated with the structure of the gallium atom (its electron configuration with free sublevels and the presence of three electrons in the outer orbit). Lower valence oxides and

amphoteric hydroxides that ensure the presence of Ga^{3+} and GaO_3^{3-} can be observed among them.

The obtained k^* values show that the process of gallium dissolution depends on the electrolyte nature. Fig. 4 shows the dependence of α in different 1 M solutions.

Some authors believe that the interaction of gallium with sulfuric acid is accompanied by the reaction



elemental sulfur coats the metal surface with white powder and ceases further dissolution. The obtained minimal values of relative changes of the sample masses in H_2SO_4 solutions can be due to with this.

It was experimentally established that after 1–2 hours the dissolution ceases, *Ga* samples lose the metallic luster, and their surface is covered with a protective film. However, issues related to the growth of films on the metal surface (not only gallium) or its removal have been poorly studied. The adsorbed oxygen anions are likely to penetrate into the metal surface, since the mobility of metal atoms and oxide ions in crystal lattices is insignificant. Metal atoms become even less mobile when they come into contact with chemisorbed oxygen and rearrange into a chemically inert oxide lattice.

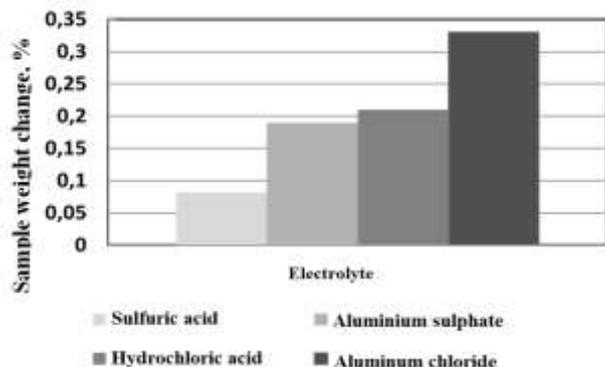


Fig. 4. Tendencies of *Ga* dissolution.

With regard to the kinetics of the overall process, it is obvious that the oxidation stage precedes or occurs along with the processes of growth or removal of the protective layer from the metal surface.

In dissolution of solid and molten gallium, E^* values are different – in molten gallium they are low and much smaller than those in solid gallium. This is obviously due to the fact that the interphase boundary "liquid metal–electrolyte" is subject to turbulization of the boundary layers caused by the Marangoni effect and constant updates, which reduces energy barriers and intensifies mass exchange processes.

Most of the values of the experimentally determined activation energies for liquid gallium dissolution (Table 2) do not exceed 30 kJ/mol (this value is taken when estimating the limiting stage to separate the kinetic and transition regions). The dissolution of liquid gallium occurs in the transition region if chemical and diffusion resistances are commensurable (rates of transport stages and chemical interaction). Chemical

interactions on the surface of molten gallium occur intensively and have little effect on the overall rate of the process.

Dissolution of crystals is energy-consuming compared to that of the liquid metal state. In dissolution of crystalline gallium, experimentally obtained E^* values are characteristic of the processes which occur in the kinetic region, when the rates of chemical interactions are low. This is partly due to the metal surface passivation, however, mixing facilitates destruction of the surface film, which does not prevent the approach of reagents to the surface. The results show that chemical interaction is likely to occur at low rates on the inner surface of the film adjacent to the metal surface.

E^* values significantly vary in media with the same anion but they are found to be lower in saline. Obviously, this is due to the presence of aluminum ions in the system, which are almost similar in nature and affect the characteristics of chemical interactions. In particular, aluminum ions can participate in the formation of surface films.

IV. CONCLUSION

Analysis of the results obtained revealed the effect of the electrolyte composition on the mechanism of *Ga* dissolution. In addition, it was proved that dissolution in sulfuric acid media is characterized by low rate constants; in the transition to hydrochloric acid media, the rates are found to increase by almost two orders of magnitude. Similar changes occur during aggregative transformation of gallium.

The experimentally determined rate constants for the dissolution of solid gallium in sulfate media are $2.86 \cdot 10^{-4} h^{-1}$ in acidic solution and $8.50 \cdot 10^{-4} h^{-1}$ in $Al_2(SO_4)_3$ solution. For liquid gallium, the constants show a 2-fold increase, and they amount to $3.76 \cdot 10^{-2} h^{-1}$ in acidic and $4.16 \cdot 10^{-2} h^{-1}$ in saline solutions. In chloride media, the considered constants are higher and equal to $2.67 \cdot 10^{-2}$ in acidic solution and $6.07 \cdot 10^{-2}$ in aluminum salt solution in dissolution of gallium crystals. In dissolution of molten metal, the constants amount to 1.14 in acidic solution and to $1.21 h^{-1}$ in saline solution.

The activation energy values are in good conformity with the data provided. In the given conditions, the activation energy in the dissolution of crystalline gallium is about 2–3 fold higher than that observed in dissolution of molten gallium and ranges from 30 to 90 kJ/mol.

In the conditions close to the implementation of a liquid metal dropping electrode, the interactions in the gallium–aqueous solutions system of electrolytes are observed to occur in the currentless mode mainly in the transition region. They depend on the commensurability of the rates of chemical interaction and transfer of reagents participating in the process.

Cooling at 5–10 degrees and crystallization of gallium lead to dramatic changes in the mechanisms of dissolution of the metal. For crystalline gallium, the presence of the surface film and the presence of the geometric and energetic inhomogeneity of the surface relief are characteristic. At the same time, an important fact is low rates of dissolution and chemical interaction. Despite the presence of protective films, the total

rate of the process is determined by the stage of chemical interaction.

The results of the study are required for the development and creation of systems that employ liquid metal electrodes, and for the use of gallium film effects to develop optical and electronic devices.

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