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Reaction of Aluminum with Dilute Aqueous NaOH Solutions

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Abstract—Reaction of aluminum powder and foil with dilute aqueous NaOH solutions was studied. The kinetic characteristics of the process were determined, and its mechanism was discussed.

We have studied previously the reaction of aluminum with water glass of a high $SiO_2 : NaOH$ ratio. The reaction mechanism is complex, and, for its understanding, it is appropriate to examine specific features of reaction of Al with aqueous alkali. Available data [2–6] concern reaction of Al with concentrated aqueous alkalis. In this work we studied the reaction of Al foil and powder with dilute aqueous NaOH (C_0 0.003–0.1 N).

The reaction readily occurs even at room temperature, yielding hydrogen and sodium aluminate:

$$2Al + 2NaOH + 6H_2O = 2Na[Al(OH)_4] + 3H_2. \quad (1)$$

It should be noted that the structure and behavior of aluminate ions in alkaline solutions have been studied in detail [2]. In dilute solutions, the stable Al species are monomeric tetrahedral aluminate ions $[Al(OH)_4]^-$ and their dimers stabilized by cations present in solution.

Data on the hydrogen yield based on the reactant (Al or NaOH) that was taken in deficiency relative to the stoichiometry of Eq. (1) show that the reaction stoichiometry is strictly constant (Table 1). On the one hand, this fact shows that the reaction progress can be adequately monitored by the amount of the liberated hydrogen. On the other hand, it shows that side reactions such as, e.g., direct reaction of Al with water can be neglected under the conditions used.

The reaction of Al with aqueous NaOH is a typical topochemical reaction. With Al powder, the kinetic curves are S-shaped (Figs. 1a, 1b), and the reaction rate (W) is maximal at ~20 wt % conversion of Al (Fig. 2a). Here and hereinafter, W is calculated, using appropriate software, as the average rate from the positions of "adjacent" experimental points in the kinetic curves.

With Al foil (Figs. 1c, 1d, 2b), the multistage mechanism of the process is clearly manifested. The

Table 1. Data for calculating the stoichiometry of reaction (1) at 20°C

Reactants					Hydrogen yield		H_2/reactant ratio	
NaOH		Al		reactant in deficiency				
C_0, N	$\nu_1 \times 10^3$, mol	m, g	$\nu_2 \times 10^3$, g-atom		V, ml	$\nu_3 \times 10^3$, mol	ν_3/ν_1	ν_3/ν_2
0.0177	0.5	0.05	1.85	NaOH	16	0.7	1.42	
0.033	1.0	0.05	1.85	NaOH	32.5	1.45	1.45	
0.066	2.0	0.05	1.85	Al	60.5	2.7		1.46
0.1	3.0	0.05	1.85	Al	62.5	2.79		1.50
0.066	2.0	0.11	4.1	NaOH	69.0	3.08	1.50	
0.066	2.0	0.08	2.9	NaOH	69.0	3.08	1.50	
0.066	2.0	0.05	1.85	Al	59.0	2.63		1.42
0.066	2.0	0.02	0.74	Al	25.0	1.12		1.51
0.1	3.0		3.0	NaOH	102.5	4.58	1.52	

[a] Foil, S 100 cm^2.

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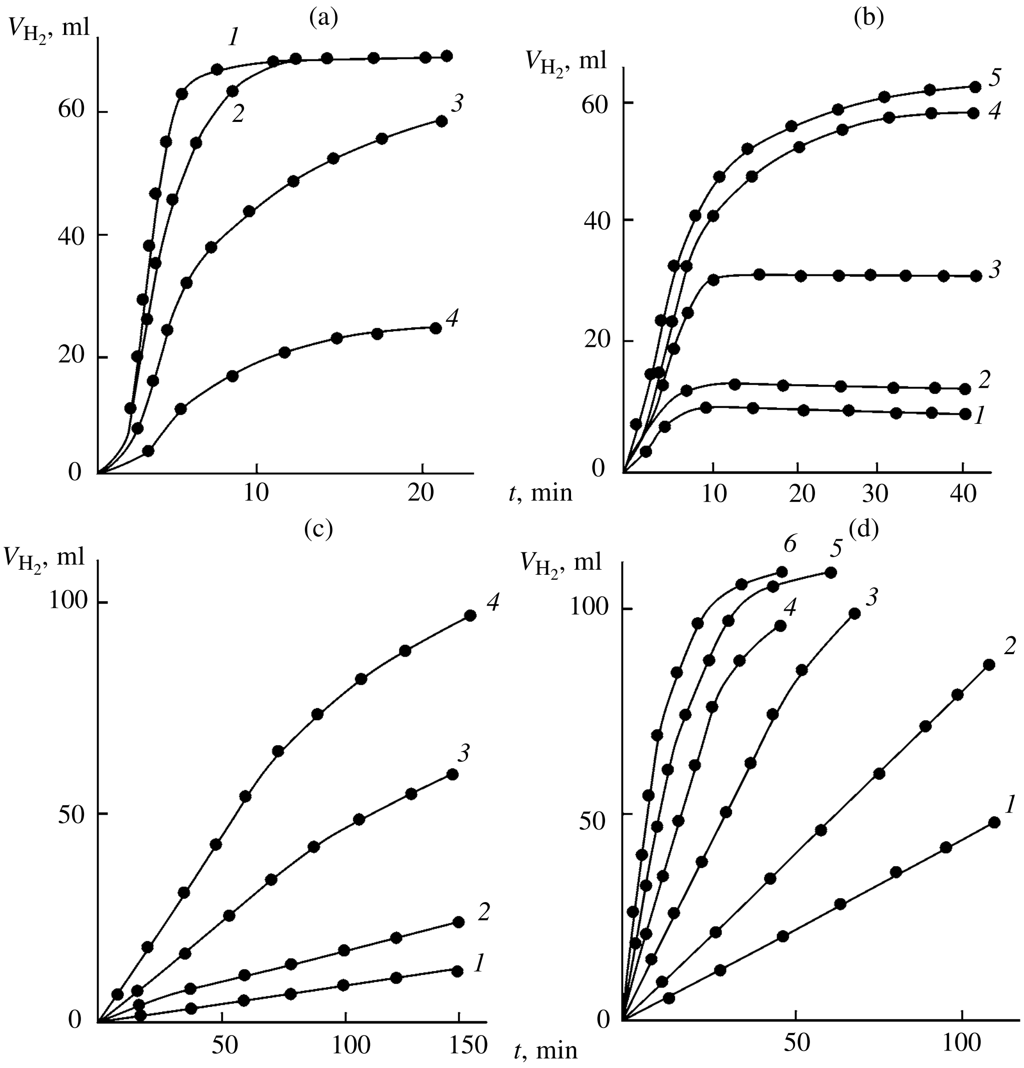


Fig. 1. Volume of liberated hydrogen as a function of time for (a, b) Al powder and (c, d) Al foil at varied (a) initial Al weight, (b) initial alkali concentration, (c) foil surface area, and (d) temperature. (a) m_0(Al), g: (*1*) 0.11, (*2*) 0.08, (*3*) 0.05, and (*4*) 0.02; 20°C, C_0(NaOH) 0.067 N. (b) C_0(NaOH), N: (*1*) 0.01, (*2*) 0.017, (*3*) 0.033, (*4*) 0.066, and (*5*) 0.1; 20°C, ν(Al) 1.85×10^{-3} mol. (c) S_{foil}, cm^2: (*1*) 8, (*2*) 18, (*3*) 50, and (*4*) 100; 30°C, C_0(NaOH) 0.1 N. (d) *T*, °C: (*1*) 30, (*2*) 40, (*3*) 50, (*4*) 60, (*5*) 70, and (*6*) 80; S_{foil} 50 cm^2, C_0(NaOH) 0.1 N.

reaction rate *W* first grows until ~0.02–0.2 wt % (depending on reaction conditions) conversion of Al is reached, after which the rate decreases to a steady-state level (rate of the developed process). The time required to attain this mode is conventionally termed the induction period.

These trends are apparently associated with the sample history and can be accounted for by removal of the protective oxide film [in the case of powder, impregnating agents added according to GOST (State Standard) 5494–71 are also removed] and by chemical "polishing" of the surface in the course of reaction with NaOH. Such "polishing" was observed during dissolution of Al in concentrated aqueous alkalis [3]. In line with this concept, mechanical polishing of Al foil somewhat shortens the induction period, whereas keeping Al foil in air at 240°C for 1 h, increasing the thickness of the oxide film, makes the induction period longer (Fig. 2c).

Experiments on revealing the effect of reaction products on the hydrogen liberation rate (Fig. 2d) showed that aluminate ions at low initial concentration (3.3×10^{-3} M) do not affect *W* and at higher concentration (8.3×10^{-2} M) decrease the maximal rate by a factor of 1.3. Thus, aluminate ions accumulated in solution inhibit hydrogen liberation, which explains the kinetic features at high conversions (Fig. 2a).

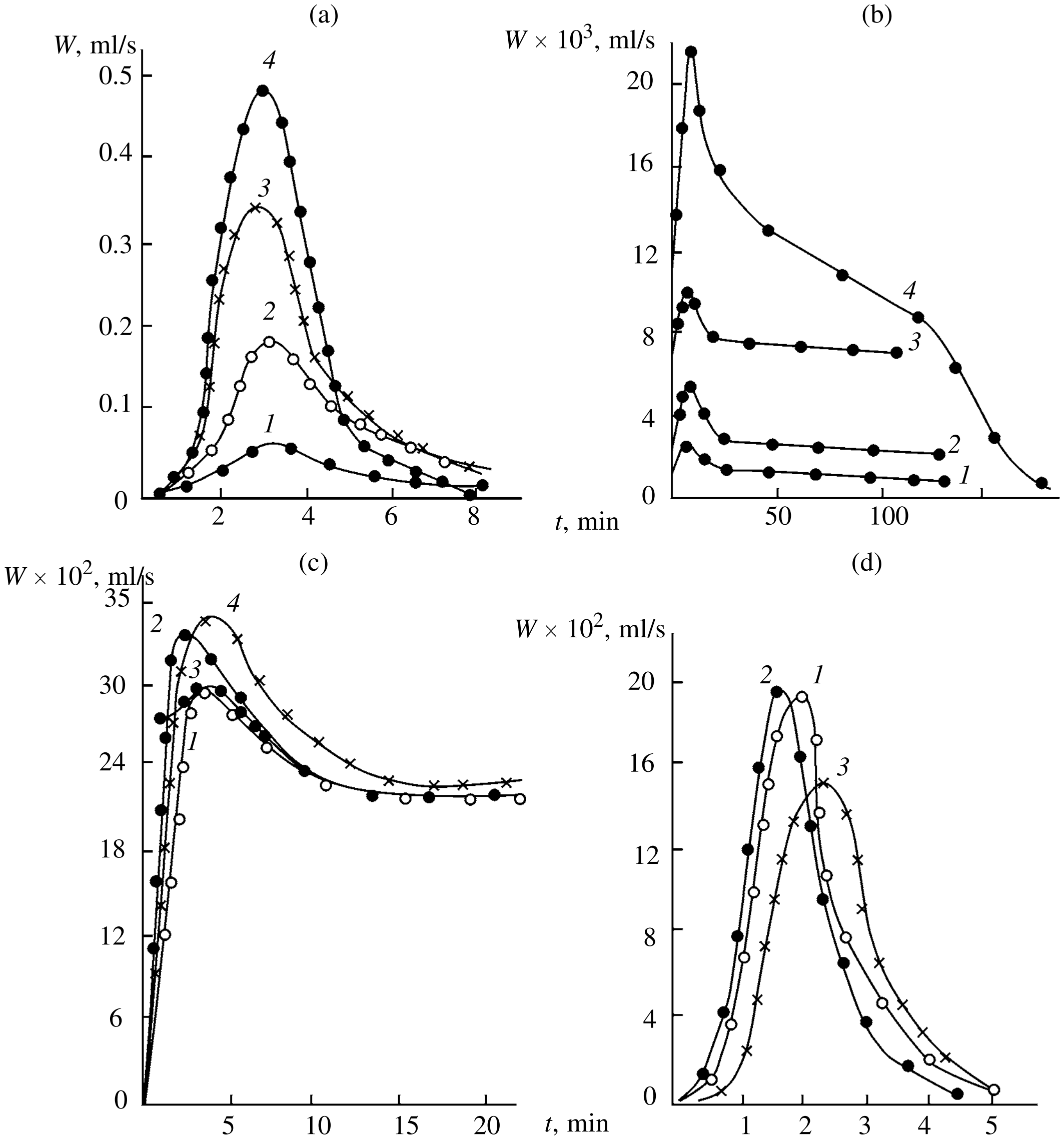


Fig. 2. Rate of hydrogen liberation as a function of time. (a) Al powder; initial Al weight (m_0, g): (*1*) 0.02, (*2*) 0.05, (*3*) 0.08, and (*4*) 0.11; 20°C, C_0(NaOH) 0.1 N. (b) Al foil; surface area (S, cm^2): (*1*) 8, (*2*) 18, (*3*) 50, and (*4*) 100; 30°C, C_0(NaOH) 0.1 N. (c) Al foil after various surface pretreatments: (*1*) no pretreatment, (*2*) heated in air for 1 h at 240°C, (*3*) mechanically polished, and (*4*) mechanically polished and then heated for 1 h at 240°C; S_{foil} 50 cm^2, 30°C, C_0(NaOH) 0.1 N. (d) Al powder, dissolution in the presence of reaction products, C_0(Na[Al(OH)$_4$]), M: (*1*) 0, (*2*) 3.3×10^{-3}, and (*3*) 8.3×10^{-3}; 30°C, ν(Al) 0.001 mol, C_0(NaOH) 0.017 N.

With Al powder, the maximal reaction rate ($W_{\max}$, ml s^{-1}) is a linear function of the initial Al weight (m, g), $W_{\max} = (4.65 \pm 0.14)m$, which is an indirect evidence of the first reaction order with respect to Al.

With Al foil, the rate of the developed process linearly grows with increasing surface are S of the foil (Fig. 3a), and the calculated specific rate W/S is a linear function of the initial NaOH concentration: $W/S = k_{\text{app}}C_0$ (Fig. 3b). It should be noted that the process is kinetically controlled, since, under similar conditions, the rate of the more active reaction of Al powder with NaOH does not change at an almost 20-fold change in the stirring rate. For example, at 30°C and stirring rate varied within 60–1000 rpm, the maximal rate is 6.3 ml s^{-1} g^{-1}.

Data on the influence of temperature on the rate of hydrogen liberation in reactions with Al powder and foil are listed in Table 2.

The time dependences of the rate of hydrogen liberation in the reaction with Al powder at 6–32°C have the shape similar to that of the curves in Fig. 2a.

Table 2. Influence of temperature on the rate of hydrogen liberation in reactions with Al powder [m_0(Al) 0.03 g; C_0(NaOH) 0.017 N] and foil [S 50 cm^3; C_0(NaOH) 0.1 N]

Foil			Powder		
T, °C	W_{max}/S, ml s^{-1} cm^{-2}	W/S, ml s^{-1} cm^{-2}	T, °C	W_{max}/m_0, ml s^{-1} g^{-1}	C_{prod}, M
30	2.5	1.8	14	1.2	–
40	4.5	2.5	20	2.75	–
50	7.5	5.1	26	4.4	–
60	14.5	10	32	5.6	–
70	25	17.5	30[a]	6.0	–
80	40	27.5	30[a]	6.3	3.3×10^{-2}
			30[a]	5.0	3.3×10^{-2}

[a] At C_0(NaOH) 0.022 N.

The temperature dependence of the maximal specific rate of hydrogen liberation ($W^{sp}_{max} = W_{max}/m_0$) is described by the equation

$$\ln W^{sp}_{max} = (22.0 \pm 3.0) - (51.5 \pm 6.6) \times 10^3/RT, \text{ ml s}^{-1}\text{ g}^{-1}.$$

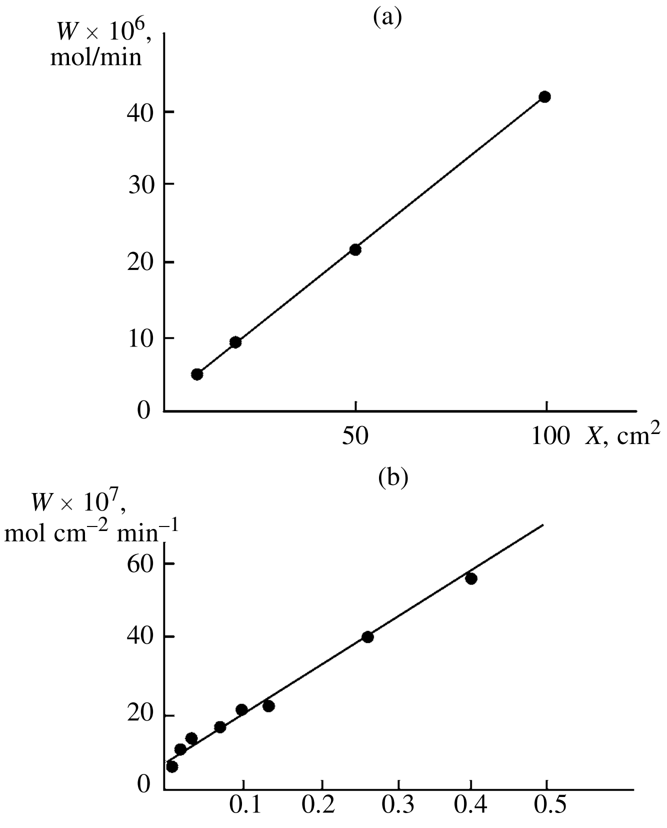


Fig. 3. (a) Rate of the developed process of hydrogen liberation as a function of the Al foil surface area and (b) specific reaction rate as a function of the initial NaOH concentration. (a) 30°C, C_0(NaOH) 0.1 N; (b) 50°C, S_{foil} 18 cm^2.

Figure 4 shows how the specific rate of hydrogen liberation ($W^{sp} = W/S$, where S is the foil surface area) in the reaction with Al foil at various temperatures depends on the calculated thickness L of the dissolved foil, characterizing the extent of the reaction. The procedure for calculating L is given below. The steady-state specific rate is attained at the calculated thickness of the dissolved layer of 0.1 μm (at the total foil thickness of 0.1 mm).

The temperature dependence of the maximal specific rate has the form

$$\ln W^{sp}_{max} = (16.4 \pm 0.4) - (52.6 \pm 1.4) \times 10^3/RT, \text{ ml s}^{-1}\text{ m}^{-2}.$$

For the developed process, this dependence is described by

$$\ln W^{sp} = (21.6 \pm 0.4) - (53.3 \pm 1.0) \times 10^3/\text{RT}, \text{ ml s}^{-1}\text{ m}^{-2}.$$

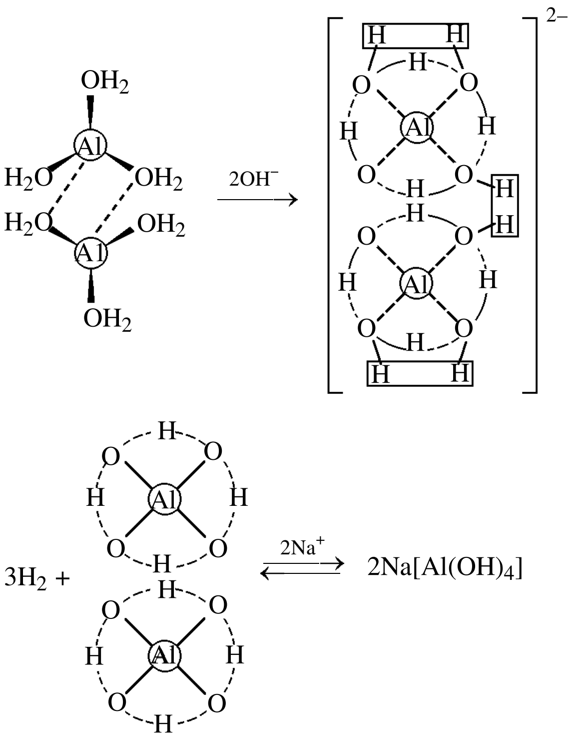
The temperature dependence of the first-order rate constant for the foil has the form

$$\ln k = (12.26 \pm 0.5) - (51.7 \pm 1.3) \times 10^3/\text{RT}, \text{ mol s}^{-1}\text{ m}^{-2}.$$

Thus, the activation energy of the reaction of dilute NaOH with Al powder and foil is 51.5–53.5 kJ mol^{-1}, which is comparable with the energy of a hydrogen bond. This may be associated with the fast proton exchange between proton-containing species in solution, i.e., with the relay mechanism of diffusion of hydroxide ions to the aluminum surface [7].

The reaction of aluminum with aqueous alkalis is a topochemical redox reaction in which tetrahedral aluminate ions $[Al(OH)_4]^-$ or their dimers pass into solution. It is reasonable to assume that the starting aluminum species in the developed process are hydrated Al atoms on the surface.

We assume that both diffusion of hydroxide ions to the surface and their subsequent chemisorption occur by the relay mechanism. A particular role is presumably played by pairs of surface aluminum atoms hydrated in the conjugated fashion; successive chemisorption of two hydroxide ions on these atoms results in occurrence of the following reaction:



(2)

The presumed mechanism formally corresponds to a topochemical reaction in which the limiting step is chemisorption of the second hydroxide ion; in terms of the transition state theory for topochemical reactions [8], provided that the fraction of the Al surface occupied by adsorbed aluminate and hydroxide ions is insignificant, we thus obtain an expression for W which is in agreement with the experiment:

$$W = k_{\mathrm{app}}S[\mathrm{OH}^-]e^{-E_{\mathrm{app}}/RT}.$$

EXPERIMENTAL

Aluminum foil was of food grade; according to atomic absorption analysis, it contained ≤0.3% foreign metals (Mg, Fe, Cu, Mn, etc.) and Si. Aluminum powder was of technical grade (PAP-1 brand), specific surface area 7000 $\mathrm{cm}^2\,\mathrm{g}^{-1}$, GOST 5494–71, total content of Mg, Si, Fe, Cu, and Mn 2.5–3%.

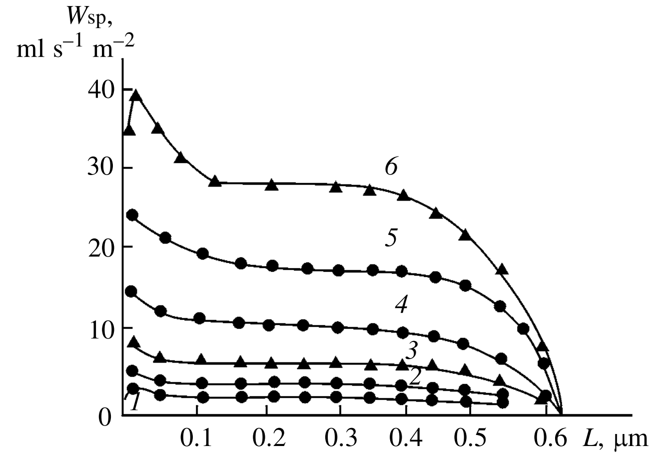


Fig. 4. Specific rate of hydrogen liberation as a function of the calculated thickness L of the dissolved Al foil layer at various temperatures. T, °C: (*1*) 30, (*2*) 40, (*3*) 50, (*4*) 60, (*5*) 70, and (*6*) 80; S_{foil} 50 cm^2, C_0(NaOH) 0.1 N.

Metallographic analysis of aluminum powder, performed on an MIM-8M microscope at 500× magnification with sections of particles etched in 4% $\mathrm{HNO_3}$, showed that the particles had irregular shape with the mean grain diameter of 30–50 μm. To remove paraffin coating applied to aluminum particles during fabrication, the powder was heated for 1 h at 200°C on an oil bath with continuous stirring.

Sodium hydroxide was of analytically pure grade.

The kinetics of the reaction of Al with alkali was monitored volumetrically, by liberation of hydrogen. The installation was described in [1].

The starting components were mixed at room temperature and placed in a glass vessel with a temperature-controlled water jacket. The temperature was measured with a Chromel–Copel thermocouple. The liberated hydrogen was collected in a gas buret. The mixture was stirred with a magnetic stirrer at a controllable rate.

The effect of the reaction products was studied as follows. Aluminum foil was placed in a definite volume of 0.1 N NaOH, and the reaction completion was judged from the completion of hydrogen liberation. Then the remaining foil was removed, 0.03 g of Al powder and 5 ml of 0.01 N NaOH solution were added (to attain the alkali concentration of 0.01 N), and the reaction progress was monitored.

In experiments with Al powder, its conversion was calculated as follows:

$$\alpha = \Delta m/m_0 \times 100\% = V_{\mathrm{H_2}}/1.224m_0 \times 100\%,$$

where m_0 is the initial Al weight, g; Δm, weight loss of the powder upon treatment with NaOH, g; V_{H_2}, volume of hydrogen liberated in the process, l; and 1.224 l, volume of hydrogen liberated in the reaction of 1 g of Al with alkali according to the stoichiometry of reaction (1). The specific rate of hydrogen liberation W^{sp} was calculated as follows. For powder, $W^{sp} = W/m_0$, where W is the rate of hydrogen liberation, ml s^{-1}; for foil, $W^{sp} = W/S$, where S is the geometric surface area of the foil.

In kinetic experiments with the foil, it was weighed before and after the reaction. The thickness of the dissolved Al layer was calculated as follows:

$$L = V/S = 1/S\Delta m/\rho = V_{H_2}/S\,1.244\,\rho,$$

where V is the volume of dissolved Al; ρ, Al density; and V_{H_2}, volume of liberated hydrogen.

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