

Kinetics and mechanism of the reaction of aluminium in aqueous solution of sodium hydroxide

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The kinetics of the reaction of spectrally pure aluminium in aqueous solution of sodium hydroxide is governed in the investigated reaction regime by the experimental kinetic equation $v = kc_{\text{OH}^-}c_{\text{O}_2}^{0.5}$. The rate-determining step and depolarization processes involving the reduction of protons and oxygen have been ascertained on the basis of the postulated mechanism.

Кинетика реакции спектрально чистого Al в водном растворе гидроксида натрия при исследуемом режиме реакции подчиняется экспериментальному кинетическому уравнению $v = kc_{\text{OH}^-}c_{\text{O}_2}^{0.5}$. На основании постулируемого механизма была определена скорость определяющая стадия и деполаризационные процессы, которыми являются реакции восстановления протонов и кислорода.

The kinetic behaviour of aluminium, which is an important construction material, has been given great attention since long ago [1—11]. However, it is worth noticing that most papers deal with the reaction of aluminium in alkaline medium more from the view-point of corrosion as a practical problem than from the view-point of the laws of heterogeneous reaction. In addition, pure metal was used only in few studies. As the specificity of this material manifests itself more just in this case, the presented paper is concerned with the kinetic behaviour of pure aluminium in sodium hydroxide and elucidation of the mechanism of this reaction.

Experimental

The kinetic measurements were carried out in an apparatus described in paper [12] which enabled us to choose the regime in the temperature range $(10—50 \pm 0.1)^\circ\text{C}$ and ensured

constant hydrodynamic conditions and oxygen atmosphere with possible choice of partial pressure up to 0.1 MPa.

Spectrally pure aluminium (Johnson Matthey Ltd., London) was used in the form of rod (diameter 6 mm) as experimental material. Precisely known area was exposed to aggressive medium and the remaining surface was masked with epoxide. The standard treatment of the surface consisted in mechanical grinding with metallographic paper of granularity 320; 400; 4/0; 6/0; in this order. The rubbed surface was polished with the paste Neoxid and subsequently it was chemically activated in 20 % NaOH for 5—7 min. The variable pressure of oxygen was obtained by mixing oxygen with nitrogen in flow meters of the type ULTS 3.

The amount of dissolved aluminium was determined spectrophotometrically (Specord UV VIS, Zeiss, Jena). A solution of aluminone was used as reagent according to procedure [13]. The width of the cells used was 1 cm. Water served as reference standard.

The presented results are means of three independent measurements the reproducibility of which corresponds to 3—5 %.

Results and discussion

Time course of aluminium dissolution in NaOH

The quantity of metal which passed into solution is given in Fig. 1 as a function of time. It is obvious that the course is linear in the time interval 0—2 h, which indicates that the situation in the interface metal—electrolyte does not change during the reaction and the products which are soluble are transported into the solution. The rate of dissolution [$\text{kg m}^{-2} \text{h}^{-1}$] given by the slope of the straight line expressing the time dependence of aluminium loss is dependent on aggressivity of the medium, oxygen concentration, temperature, and different admixtures in the solution.

Influence of sodium hydroxide concentration on the rate of dissolution

The influence of the OH^- ions was investigated in the concentration range $c(\text{NaOH}) = 0.10\text{—}5.85 \text{ mol dm}^{-3}$ at 25 °C and oxygen pressure of 0.1 MPa (Fig. 2). In agreement with the data published in literature, the concentration dependence exhibits a maximum even for spectrally pure metal, namely at $c(\text{NaOH}) = 5 \text{ mol dm}^{-3}$. The dissolution of metal in that wide concentration interval is affected by the change in conductivity and viscosity of the medium as well as the change in oxygen solubility due to increasing concentration of hydroxide. *Balezin* [8] correlates the dependence of reaction rate on hydroxide concentration with the change in conductivity of the solution and shows that the maximum of conductivity corresponds to the maximum of the rate of reaction. Other factor which may have influence on the decrease in reaction rate beyond the

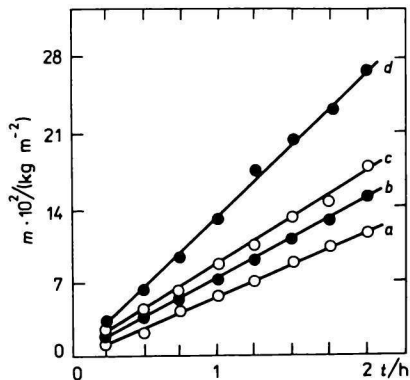


Fig. 1. Time course of Al dissolution in NaOH.
 a) 1.0 M-NaOH, $P_{O_2} = 0.03$ MPa, $\theta = 25$ °C;
 b) 1.0 M-NaOH, $P_{O_2} = 0.1$ MPa, $\theta = 25$ °C;
 c) 2.0 M-NaOH, $P_{O_2} = 0.1$ MPa, $\theta = 25$ °C;
 d) 1.0 M-NaOH, $P_{O_2} = 0.1$ MPa, $\theta = 35$ °C.

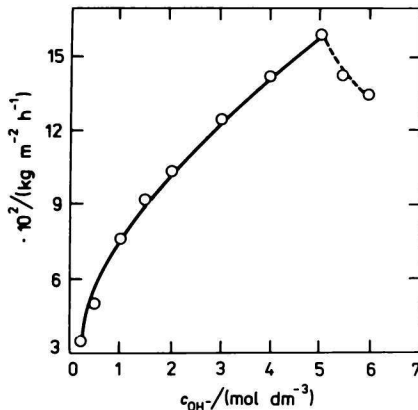


Fig. 2. Influence of NaOH concentration on the rate of Al dissolution.
 $\theta = 25$ °C, $P_{O_2} = 0.1$ MPa.

maximum is the increasing viscosity. Because of the temperature dependence on the basis of which it was disclosed that the process takes place in kinetic region, the viscosity as a factor reducing the reaction rate is not effective in our case. It results from the determined relationship between the rate of dissolution and oxygen pressure over the solution (see later) that we must respect the influence of concentration of the dissolved oxygen which decreases with increasing concentration of NaOH. For this reason, the concentration dependence of the rate of dissolution has been corrected (Fig. 3) by the relationship

$$v_{\text{cor}} = v_{\text{exp}}[\alpha_0/\alpha_c]^{0.5}$$

where v_{cor} , v_{exp} , α_0 , and α_c stand for corrected rate, measured rate, solubility of oxygen in water, and solubility of oxygen at a given concentration of NaOH [14]. This expression has been used for calculating the reaction order with respect to OH^- by using the differential method (Fig. 4). Its value is equal to 0.5 for the noncorrected reaction rate and 1 for the corrected reaction rate in a solution of 0.5–4.0 M-NaOH.

Influence of oxygen pressure on the reaction rate

The dependence of the reaction rate on oxygen pressure in the chosen reaction regime (25 °C, $c(\text{NaOH}) = 1$ mol dm^{-3}) was investigated in the partial pressure

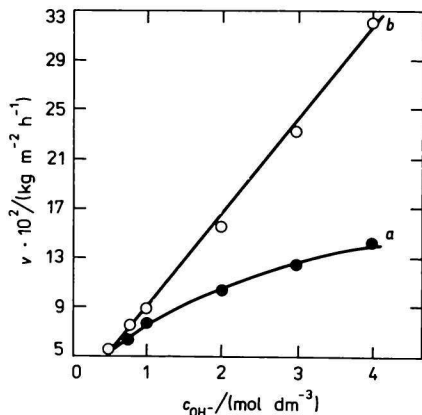


Fig. 3. Concentration dependence in the range 0.5—4.0 M-NaOH at $\theta = 25^\circ\text{C}$, $P_{\text{O}_2} = 0.1$ MPa.
a) Noncorrected; b) corrected.

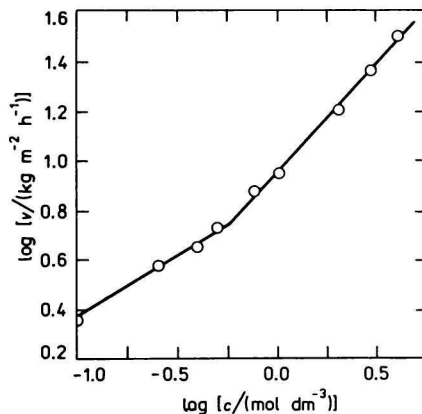


Fig. 4. Determination of reaction order with respect to the OH^- ions.

range of oxygen 0—0.1 MPa (Fig. 5). The linearization of the curve in the coordinates v vs. $P^{0.5}$ shows that the reaction rate is proportional to the squared root of partial pressure of oxygen and the progress of reaction with respect to oxygen pressure may be expressed by the following equation

$$v = a + bP^{0.5} \quad (1)$$

where a is the reaction rate in the absence of oxygen ($P_{\text{O}_2} = 0$). Thus the reaction order with respect to oxygen is equal to 0.5.

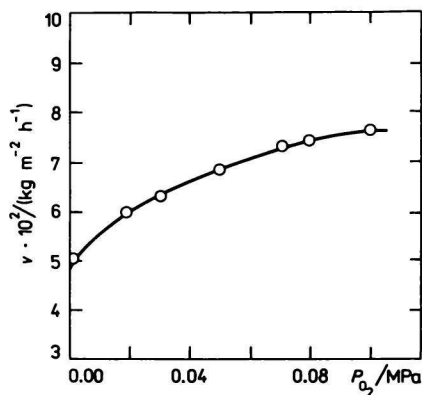


Fig. 5. Influence of oxygen pressure on the solubility of Al in 1.0 M-NaOH; $\theta = 25^\circ\text{C}$.

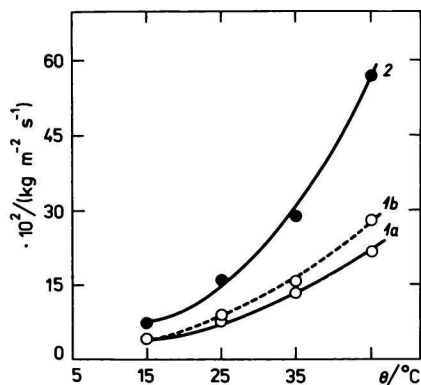


Fig. 6. Influence of temperature on the rate of Al dissolution in the solution.
1a. 1.0 M-NaOH; 1b. corrected, 1.0 M-NaOH; 2. 5.0 M-NaOH.

Influence of temperature

The temperature regime of the reaction varied from 15 °C to 45 °C for 1.0 M-NaOH and 5 M-NaOH at the partial pressure of oxygen of 0.1 MPa. The individual courses corresponded to the Arrhenius' law (Fig. 6). The apparent activation energy was evaluated from the linearized relations.

As the reaction order with respect to oxygen was equal to one half, it was necessary to make corrections by the use of the dependence of absorption coefficients of oxygen on temperature in pure water [14] and 1 M-NaOH. The corrected relationships were used for graphic evaluation of activation energy. The values of the noncorrected and corrected activation energy as well as the temperature coefficient are given in Table 1.

Table 1

Values of activation energy and temperature coefficients for the reaction of Al in NaOH

c(NaOH) mol dm ⁻³	E/(kJ mol ⁻¹)		$\alpha = v(\theta + 10 \text{ }^\circ\text{C})/v(\theta)$			
	Noncorrected	Corrected	$\theta/^\circ\text{C}$:	25—15	35—25	45—35
1.0	44.7	46.2		1.8	1.7	1.7
5.0	51.0	—		2.1	1.8	1.9

On the basis of the discussed experimental results as well as the data published in literature, we may postulate the mechanism of the investigated reaction which obeys the experimental rate equation of the form

$$v = kc_{\text{OH}^-} \cdot c_{\text{O}_2}^{0.5} \quad (2)$$

as follows:

Oxygen present in the reaction medium is adsorbed on the surface of aluminium, which may be depicted by the equation



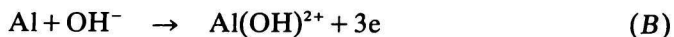
The adsorption equilibrium is to be expressed by the following equation

$$K = \frac{a_{\text{Al}\dots\text{O}}}{a_{\text{Al}} a_{\text{O}_2}^{1/2}} \quad (3)$$

The aggressivity of alkaline medium, as known, is dependent on the possibility of origination of the soluble $[\text{M}(\text{OH})_x]^{y-}$ complex ions. Aluminium forms such soluble

complexes and the anodic process (dissolution) may be broken down into the following steps.

By the effect of the OH^- ions, the anodic process proceeds and three electrons are liberated



The adsorbed oxygen has depolarization effect and draws two electrons



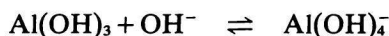
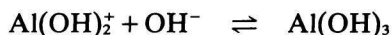
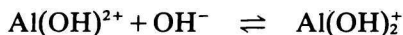
Summary equation expressing these steps is



It is known that the reaction proceeds and sets free hydrogen even in the absence of oxygen, which means that simultaneous depolarization of hydrogen takes place



The $\text{Al}(\text{OH})^{2+}$ intermediate is involved in a number of complex-forming equilibria which lead to the formation of soluble aluminate. That may be described by the following equations



Summarily, the complex-forming equilibria may be expressed as follows



while the equilibrium in alkaline medium is shifted to the right side.

In order to reveal the rate-determining step, we can assume that the adsorption equilibrium is established rapidly. Then the time courses indicate stationary states in the interface. On the basis of these facts, we may come to the conclusion that reaction (D) is a slow process and the oxygen bound in the adsorption complex functions as a depolarizer. If this process were more rapid than others, a deposit of $\text{Al}(\text{OH})_3$ would be formed on the surface and its existence would manifest itself by influencing the time course, which was not observed in any case. Other mentioned steps take place in the solution and may be considered rapid.

If we take reaction (D) for the slowest step, the reaction rate depends on activity of the OH^- ions and $\text{Al}\dots\text{O}$ complex

$$v = k' a_{\text{OH}^-} a_{\text{Al}\dots\text{O}} \quad (4)$$

With respect to equilibrium (A), we can express $a_{\text{Al}\dots\text{O}}$ by means of eqn (3) and insert into eqn (4). Thus we obtain

$$v = k' a_{\text{OH}^-} K a_{\text{O}_2}^{1/2} = k a_{\text{OH}^-} a_{\text{O}_2}^{1/2} \quad (5)$$

which is the relationship corresponding to the experimental rate equation (1) where $k = k' K$.

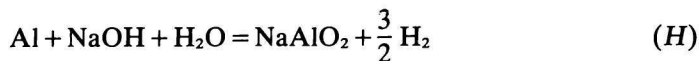
Summarily, the investigated reaction may be described by this equation



It results from the proposed mechanism that the reaction involves the mixed hydrogen and oxygen depolarization.

The discussed mechanism refers to the ascending section of the concentration curve and does not fully describe the situation in the region of low hydroxide concentrations $c < 0.5 \text{ M-NaOH}$. We have found that the reaction order with respect to OH^- in this region changes from one to one half, which is in agreement with literature [2, 9].

If the reaction proceeds in the absence of oxygen, the depolarization reaction is represented only by the reduction of protons. In this case, the reaction may be described by the scheme presented in literature [1]



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