

INFLUENCE OF CRYSTALLOGRAPHIC ORIENTATION ON THE KINETICS OF COPPER DISSOLUTION IN SODIUM HYDROXIDE

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The kinetics and mechanism of copper dissolution in sodium hydroxide were studied on different crystal planes. Differences in the reactivity on the planes (100), (110), and (111) were observed. The differences in the kinetics and mechanism depend on the reaction regime and can be related under certain conditions to the work function.

The reaction kinetics on monocrystalline materials has been increasingly more studied during the last two decades¹⁻⁸. Such studies enable to elucidate the kinetic behaviour of heterogeneous systems with regard to the specific role of the surface due, *e.g.*, to the density of atoms on the individual crystal planes, number of interrupted chemical bonds and their orientation in the case of nonmetals, or electronic structure of their atoms.

The reactivity of different crystallographic planes of copper monocrystals in acidic medium was systematically studied by Mayanna and Setty⁴⁻⁸. They attributed the observed differences to differences in the density of dislocations on the studied surfaces. A similar study in an alkaline medium has not been reported in the literature. The present work deals with the kinetics and mechanism of reactions of copper single crystals on three basic crystallographic planes, (100), (110), and (111), in sodium hydroxide as a continuation of our work about kinetic behaviour of polycrystalline copper^{9,10}. Our aim was to find differences in the kinetic behaviour of the mentioned planes assuming that the process is governed by a phase step. Therefore and with respect to our earlier findings^{9,10} we chose suitable reaction conditions, especially temperature and concentration of the corroding medium.

EXPERIMENTAL

The reaction kinetics was studied by following the increase of Cu^{2+} ions in the course of time in a tempered glass reaction vessel of 1.5 dm³ holding capacity. The temperature was 10–50°C maintained to within $\pm 0.1^\circ\text{C}$, the partial pressure of oxygen 0.02–0.1 MPa, concentration of NaOH 0.1–4.0 mol/dm³, rate of stirring 1 300 r.p. min (the process rate was independent of the rate of stirring above 1 000 r.p. min).

Oriented sections of a copper single crystal were used. The latter was grown from polycrystalline copper of spectral purity by the method of secondary recrystallization. The accuracy of the plane orientation was $\pm 2^\circ$ and the density of dissociations about 10^6 cm^{-2} . An area of about 4 cm^2 was treated chemically, the remaining portion of the sample being covered with a layer of epoxy resin. The sample was treated prior to the measurement as follows: It was degreased by means of a surfactant, rinsed thoroughly with distilled water, etched for 3 min in 1 : 1 nitric acid under intense stirring, and the last traces of oxides were removed in 1 : 1 hydrochloric acid in the absence of air. The sample was then provided with an electrical contact and fastened with the aid of a glass rod in the reaction apparatus so that the active plane was located about 2–3 cm above the blades of the stirrer.

Cu(II) ions in solution were determined quantitatively by the spectrophotometric carbamate method¹¹. The formed copper diethyldithiocarbamate was extracted with chloroform and determined on a Specord UV VIS spectrophotometer (Zeiss, Jena). The thickness of the cuvette was 1 cm. Chloroform served as a comparative solution.

Solid reaction products on the surface were analysed qualitatively by coulometry, galvanostatic reduction, and by the Debye–Scherrer diffractometric method.

Chemicals were of reagent grade; a carbonate-free solution of NaOH was prepared⁹. Every measurement was repeated 3–5 times and mean values were plotted. The mean relative error was 5–10%. The rate of dissolution was expressed in $\text{kg m}^{-2} \text{ h}^{-1}$.

The open circuit potential of copper in NaOH solution was measured with a pH meter 26 (Radiometer, Copenhagen) against a saturated calomel electrode separated by salt bridge filled with saturated KCl. The open circuit potentials were expressed against hydrogen electrode. The measured solutions were in oxygen atmosphere at atmospheric pressure. To study the pressure dependence, oxygen was mixed with nitrogen and their ratio was controlled by flow meters UPLS-3.

RESULTS AND DISCUSSION

Time Course of Dissolution

The time course of the dissolution was followed by measuring the concentration of Cu(II) ions in solution at 30 min intervals for 5–6 h at various conditions; the open circuit potential of copper was followed at the same time. The dissolution was influenced by crystallographic orientation of the studied plane, oxygen pressure, concentration of NaOH, and temperature.

Influence of crystallographic orientation. Fig. 1 shows the time course of the dissolution for the planes (100), (110), and (111) in 0.5M NaOH at 15°C and 0.1 MPa oxygen pressure. Whereas the (100) plane dissolves at a constant rate from the beginning of the reaction, *i.e.*,

$$m \sim \tau, \quad (1)$$

the dissolution of the (110) and (111) planes from the beginning of the measurement, $\tau = 0.5 \text{ h}$, till the attainment of the stationary state (about 3 h) obeys the equations

$$m \sim e^{k\tau} \quad \text{or} \quad m \sim \tau^n, \quad (2), (3)$$

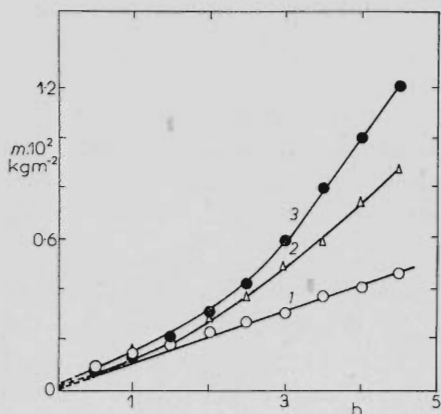


FIG. 1

Influence of crystallographic orientation on dissolution rate of Cu. Electrolyte 0.5M NaOH at 15°C, $P_{O_2} = 0.1$ MPa. 1 (100), 2 (110), 3 (111)

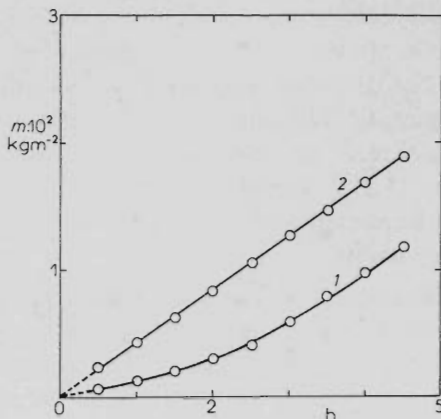


FIG. 2

Time course of reaction on the (111) plane of Cu crystal in 0.5M-NaOH at 15°C and 0.1 MPa oxygen pressure. 1 as in Fig. 1, 2 change of the solution or of the sample (see text)

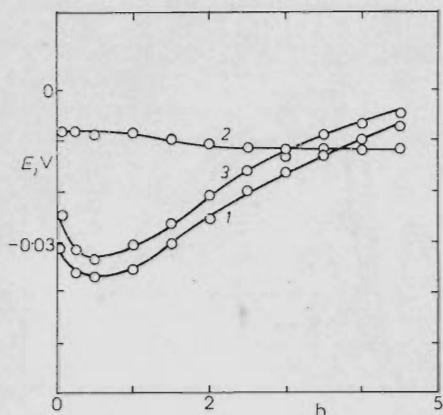


FIG. 3

Time course of potential on the (111) plane of Cu crystal. Reaction in 0.5M NaOH at 15°C, $P_{O_2} = 0.1$ MPa; curves 1, 2 after change of solution, 3 after change of sample

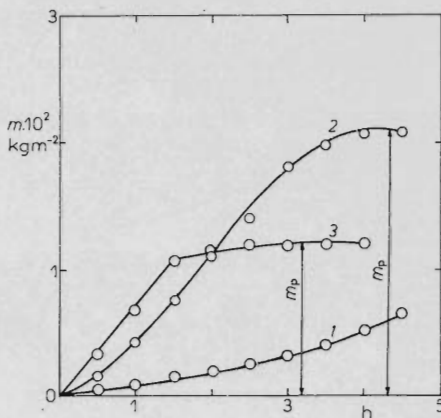


FIG. 4

Influence of temperature on time course of reaction on (111) plane of Cu crystal. Electrolyte 0.5M-NaOH, $P_{O_2} = 0.1$ MPa; 1 $t = 10^\circ\text{C}$, 2 $t = 25^\circ\text{C}$, 3 $t = 40^\circ\text{C}$

where k and n are constants at the given conditions, $n \neq 1$. After about three hours a stationary state is attained also on these planes and the rate of dissolution becomes constant (in further dependences, these stationary rates are given). If a solution of NaOH containing Cu(II) ions is used, the rate of dissolution is constant from the beginning. The same effect is observed, *e.g.*, if the (111) plane is left intact after 4 h of reaction and is placed into a new NaOH solution that does not contain Cu(II) ions (Fig. 2, curve *b*). It follows that these ions act catalytically in the initial stage of the reaction, whereas in the stationary state, when the surface is covered with Cu_2O , they have no effect.

The potential-time curve typical for the (111) plane is shown in Fig. 3 (curve *a*). If the solution contains Cu(II) ions already at the beginning of the reaction, this curve is only slightly shifted towards positive potentials (curve *c*). A substantial change occurs if the sample from the preceding measurement is left intact and the solution of NaOH is renewed. In this case the reaction proceeds at a constant rate from the beginning, the quantity of Cu_2O does not change and accordingly the open circuit potential remains constant. It follows that at constant activity of NaOH, oxygen pressure, temperature, and rate of stirring the open circuit potential depends formally only on the quantity of solid oxidation products on the surface (this phenomenon will be dealt with in a later work).

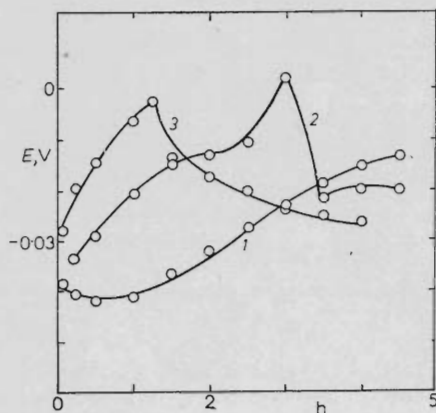


FIG. 5

Influence of temperature on time course of potential of (111) Cu crystal plane. Electrolyte 0.5M-NaOH, $P_{\text{O}_2} = 0.1$ MPa; 1 $t = 10^\circ\text{C}$, 2 $t = 25^\circ\text{C}$, 3 $t = 30^\circ\text{C}$

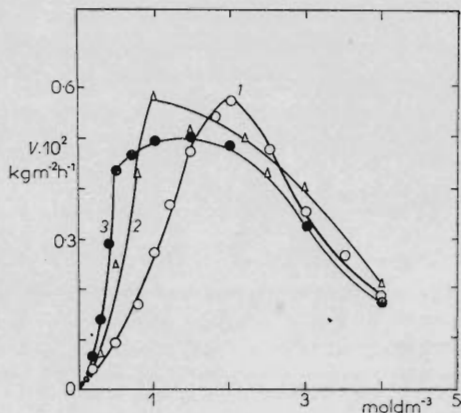


FIG. 6

Dependence of dissolution rate of Cu crystal on concentration of NaOH. $t = 25^\circ\text{C}$, $P_{\text{O}_2} = 0.1$ MPa; 1 (100), 2 (110), 3 (111)

Influence of oxygen pressure. With all three planes, the rate of copper dissolution increases with the pressure of oxygen. For example, at 0.02 MPa and 15°C in 0.5M-NaOH, $1.8 \cdot 10^{-3}$ kg/m² copper dissolves from the (111) plane during 4 h, but when the oxygen pressure increases to 0.1 MPa, $9.9 \cdot 10^{-3}$ kg/m² copper dissolves during the same time interval, representing an almost 6 fold increase. The time course of the reaction is at lower oxygen pressures than 0.05 MPa equal for all three planes and corresponds to Eq. (1); at higher pressures the reaction course on the (110) and (111) planes is different from that on (100) and obeys Eqs (2) or (3).

Reaction course at different temperatures. A temperature increase above 20°C has the same effect on the reaction on all three planes. This is illustrated by the time course on the (111) plane in Fig. (4). At temperatures $t \geq 25^\circ\text{C}$, the reaction rate is constant from the beginning. After a certain time, which becomes shorter with increasing temperature, the process stops and a layer of CuO can be detected on the surface, which was not observed at lower temperatures within the limits of the considered time interval. Hence, the stopping of the reaction can be attributed to the CuO layer. The quantity of copper dissolved before the reaction is stopped, m_p , depends strongly on the temperature and obeys the equation

$$m_p = A \cdot e^{-B/T}, \quad (4)$$

where A and B are constants whose values are given in Table I. Negative values of B are due to the fact that the value of m_p decreases with increasing temperature as a result of a shortening of the time after which the reaction becomes stopped by the formed CuO layer. The absolute values of B can therefore be considered as a relative measure of the activation energy of formation of the passivating layer.

A plot of open circuit potential against temperature is shown in Fig. 5. At a lower temperature, at which Cu₂O is formed, the potential is shifted with the time toward

TABLE I
Values of constants A and B in eq. (4)

Cryst. plane	$A, \text{kg m}^{-2}$	B, K
(100)	$1.97 \cdot 10^{-7}$	-3 600
(110)	$17.80 \cdot 10^{-7}$	-2 800
(111)	$1.24 \cdot 10^{-7}$	-3 600

more positive values. A similar shift is observed at higher temperatures as long as Cu_2O is formed. As soon as the formation of CuO begins, the potential drops to more negative values.

Concentration Dependence

The influence of the concentration of NaOH on the rate of dissolution of copper was studied in the range $0.1-4.0 \text{ mol/dm}^3$ at 15°C and 0.1 MPa oxygen pressure for three planes (Fig. 6). The rate of dissolution increases with NaOH concentration to a maximum and then diminishes. This course is qualitatively the same for all studied planes and also for polycrystalline copper^{9,10}. The maximum rate and the corresponding concentration are different on different planes.

The reaction rate on the (100) plane depends on the concentration of NaOH in the ascending portion of this dependence according to

$$v \sim c^{1.5} . \quad (5)$$

The rate of dissolution of the (110) plane in the interval $c = 0.1-0.8 \text{ mol/dm}^3$ and that of the (111) plane in the interval $c = 0.1-0.5 \text{ mol/dm}^3$ obeys the relation

$$v \sim e^{kc} , \quad (6)$$

suggesting that this case is more complicated and a more detailed knowledge of the mechanism would be necessary for a mathematical treatment. The planes (110) and (111) were covered with a thin Cu_2O layer after the reaction had been finished, whereas no solid products were observed on the (100) plane.

In the descending portion of the mentioned dependence, the differences in the reactivity become small, so that the curves for all the three planes can be considered practically identical. The time dependences suggest a constant rate of dissolution from the beginning of the reaction and the copper surface was covered with an oxide layer.

The influence of the concentration was measured also with respect to the reaction temperature. It was expressed by the ratio of the reaction rates, v_{25}/v_{15} , at temperatures of 25 and 15°C for the (100) plane (Fig. 7). This ratio represents a temperature coefficient which enables to distinguish the rate-determining step for different concentration intervals.

Influence of Oxygen Pressure

The time course of the copper dissolution at various pressures suggests that the reaction is sensitive against oxygen pressure. Its effect is shown in Fig. 8 for all three planes in the range $0.02-0.1 \text{ MPa}$ at 15°C in 0.5M-NaOH . It is apparent that the

effect of the oxygen concentration is largest on the (111) plane and smallest on (100), where the following relation holds:

$$v \sim \sqrt{P}. \quad (7)$$

For the (110) and (111) planes in the mentioned pressure range we have

$$v \sim e^{kP}. \quad (8)$$

Influence of Temperature

The influence of the temperature in the range from 10 to 50°C at a pressure of 0.1 MPa in 0.5M-NaOH is shown in Fig. 9, where $\ln v$ is plotted against $1/T$. This dependence is in accord with the Arrhenius equation and is typical for reactions in which the rate-determining step changes. Calculated values of the apparent activation energy for the individual planes are in Table II. According to our experiments, the rate is independent of the temperature above 20°C (for the (100) plane above 30°C). This can be attributed to the fact that the rate of oxygen diffusion to the copper surface increases with the temperature whereas its concentration in the solution drops.

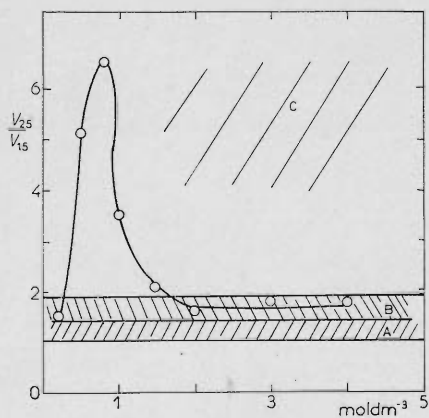


FIG. 7

Influence of NaOH concentration on the ratio of dissolution rates on (100) Cu crystal plane at 15 and 25°C. $P_{\text{O}_2} = 0.1$ MPa; A process controlled by diffusion in solution, B intermediate region, C process controlled by chemical reaction

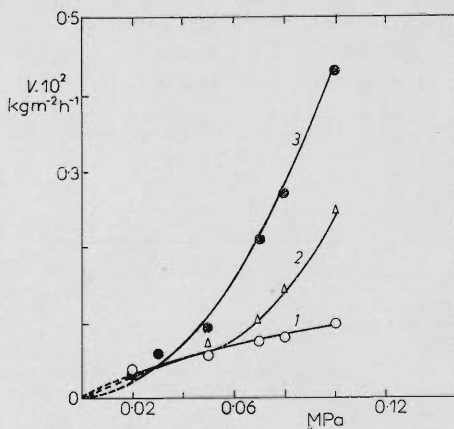


FIG. 8

Influence of oxygen pressure on dissolution rate of Cu. Electrolyte 0.5M-NaOH at 15°C; 1 (100), 2 (110), 3 (111)

Thus, the effect of temperature is cancelled and the apparent activation energy approaches zero.

From the experimentally found time course of the reaction, influence of electrolyte concentration, oxygen pressure, and temperature, and with regard to the findings of other authors⁹⁻²¹ the mechanism of oxidation and subsequent dissolution can be discussed as follows. The dissolved oxygen is transported to the interface where an adsorption and dissociation equilibrium is formed according to

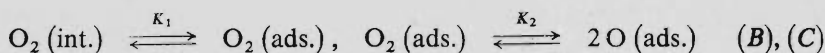
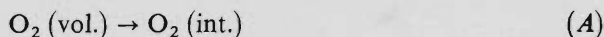


TABLE II

Apparent activation energy for reaction of Cu single crystal in 0.5 M-NaOH ($P_{\text{O}_2} = 0.1 \text{ MPa}$)

Temp. int. °C	E^* , kJ mol ⁻¹		
	(100)	(110)	(111)
10–20°	66.5	143.0	81.5
20–30°	161.0	—	—
20–40°	—	—	0
20–50°	0	0	—
30–50°	0	—	—

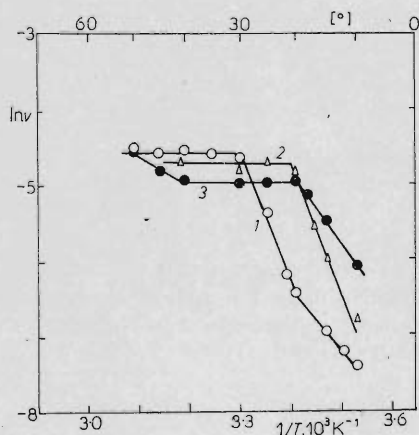
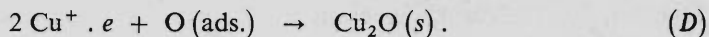


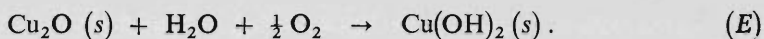
FIG. 9
Influence of temperature of dissolution rate of Cu in 0.5M-NaOH. $P_{\text{O}_2} = 0.1 \text{ MPa}$; 1 (100), 2 (110), 3 (111)

Although the adsorption takes place in the presence of OH^- and Na^+ ions and an excess of H_2O molecules, it can be assumed that the equilibrium (B) is shifted to the right side¹². The equilibrium constant of the dissociation (C) is, on the contrary, small¹³.

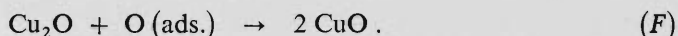
The formation of Cu_2O can be written as



This equation does not represent the elementary step of the formation of Cu_2O , whose detailed mechanism at 25°C was described by Boggio¹³. The formed copper(I) oxide passes at lower temperatures (up to about 20°C) into the solution through the following intermediate step:

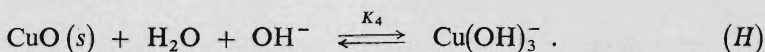
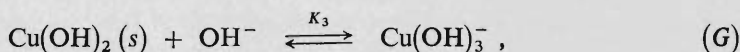


At higher temperatures, besides Cu_2O also CuO is found on the surface. This is formed by a reaction between adsorbed atomic oxygen and Cu_2O according to



It is little soluble in 0.5M NaOH and hinders the dissolution of copper. The latter equation is simplified; in reality oxygen is at the laboratory temperature chemisorbed on the surface of the *p*-type oxide prevailing in the form O^- (ref.^{14,15}) (in the case of NiO up to 97% ¹⁶), which reacts with Cu^+ in the Cu_2O lattice under formation of CuO .

Copper(II) hydroxide and (in solutions more concentrated than 0.5 mol/dm^3) copper(II) oxide dissolve according to



At concentrations above 1 mol/dm^3 the tetrahydroxocopper(II) complex is formed¹⁷. Besides reaction (F), CuO can be formed also by dehydration of the hydroxide, especially at higher temperatures. The kinetics and mechanism of this reaction were already studied^{18,19}.

It follows from the mentioned mechanism that differences in the reactivity will be apparent at such conditions at which the interaction of oxygen with the metal surface (C, D) will participate in the rate-determining step in a decisive manner. The largest differences in the reactivity of individual crystallographic planes are manifested

in the ascending portion of the concentration dependence (Fig. 6). The rates in 0.5M NaOH are in the ratio $v_{100} : v_{110} : v_{111} = 1 : 2.6 : 4.5$. Of physical factors that can influence the surface reactivity, atomic density and work function should be considered in the first place. The atomic density is known to increase in the order $(110) < (100) < (111)$ and the work function in the order^{20,21} $(111) < (110) < (100)$. It is seen that the mentioned reaction rates increase with decreasing work function. The following equation was found experimentally for the (100) plane

$$v = kc^{1.5}P^{1/2} \quad (9)$$

The order of 1.5 with respect to NaOH is only apparent since NaOH not only dissolves the copper oxides but also lowers the activity of water in the interface by hydration of Na^+ and OH^- ions, thereby facilitating adsorption of oxygen. The reaction on the (100) plane is limited by interaction of adsorbed oxygen atoms with electrons (*D*).

Since the work function is lower on the (110) and (111) planes, it can be assumed that the reaction (*D*) proceeds more rapidly; and this is indeed the case (Fig. 1). Copper(I) oxide is formed on the surface up to a certain thickness. In a stationary state, the rates of oxidation (*D*, *E*) and dissolution (*G*, *H*) are approximately equal. The film formation on the copper surface and subsequent steps with parallel reactions complicate the mathematic analysis so that the orders with respect to NaOH and O_2 cannot be evaluated in the common way.

The oxidation of copper is at higher temperatures accelerated so that oxygen diffusion in solution becomes rate determining and the chemical anisotropy of the crystal becomes indistinguishable. The reactivity is similarly influenced by lowering the oxygen pressure (e.g., to 0.03 MPa in 0.5M-NaOH) or by lowering its solubility, i.e., by using more concentrated solutions than 2.5M-NaOH.

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REFERENCES

1. Gatos H. C.: *Science* 137, 311 (1962).
2. Piontelli R.: *Electrochim. Metal.* 1, 5 (1966).
3. Bertocci V.: *J. Electrochem. Soc.* 113, 604 (1966).
4. Mayanna S. M., Setty T. H. V.: *Indian J. Chem.* 10, 295 (1972).
5. Mayanna S. M., Setty T. H. V.: *Corros. Sci.* 14, 691 (1974).
6. Mayanna S. M., Setty T. H. V.: *Indian J. Chem.* 12, 1083 (1974).
7. Mayanna S. M., Setty T. H. V.: *Corros. Sci.* 15, 627 (1975).
8. Mayanna S. M., Setty T. H. V.: *Indian J. Technol.* 14, 193 (1976).
9. Miadoková M., Sušínska P.: *This Journal* 42, 412 (1977).
10. Miadoková M., Sušínska P.: *Acta F. R. Univ. Comen. Chimia* 23, 15 (1980).

11. Malát M.: *Absorpční anorganická fotometrie*. Academia, Prague 1973.
12. Garner W. E., Stone F. S., Tiley P. F.: Proc. Roy. Soc. A 211, 472 (1952).
13. Boggio J. E.: J. Chem. Phys. 57, 4738 (1972).
14. Szabó Z. G., Kalló D.: *Contact Catalysis*. Akadémiai Kiadó, Budapest 1976.
15. Bielański A., Haber J.: Catal. Rev.-Sci. Eng. 19, 1 (1979).
16. Bielański A., Najbar M.: J. Catal. 25, 398 (1972).
17. Ugorec M. Z., Buketov E. A., Akhmetov K. M.: Zh. Neorg. Khim. 13, 1526 (1968).
18. Buketov E. A., Ugorec M. Z., Akhmetov K. M.: *Degidratsia Gidrookisei Metallov v Schelochnykh Rastvorakh*. Nauka, Alma-Ata 1971.
19. Ugorec M. Z., Sharipov M., Arginbaev D. K., Akhmetov K. M., Ashikhmina T. P.: Trudy Khim.-Met. Inst. AN Kaz. SSR 24, 21 (1974).
20. Blevis E. A., Crowell C. R.: Phys. Rev. 133, A 580 (1964).
21. Underwood N.: Phys. Rev. 47, 502 (1935).

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