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Regular Kinetic Features of the Dissolution of Metal Oxides in Acidic Media

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A comparative analysis of experimental data and theories interpreting the regular kinetic features of the dissolution of metal oxides in acids has been carried out. Theories of the conjugated transfer of the cations and anions of the oxide to the electrolyte solution do not explain the results obtained. The regular kinetic features of the dissolution of oxide phases have been interpreted for the first time on the basis of the present-day theory of semiconductors, electrochemical concepts, and models of heterogeneous kinetics. The proposed electron-proton mechanism explains all the available data on the kinetics of the dissolution of oxides in mineral acids and complexones.
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I. INTRODUCTION

The intensification and optimisation of the processes involved in the etching of metals, the extraction and concentration of ores, and the removal of deposits from thermal power engineering equipment represent an important scientific and technical problem, requiring a knowledge of the mechanisms of these processes. In the present review, the complex character of the dissolution processes is demonstrated for the case of the reaction of metal oxides with aqueous solutions of various acids, for which the data on the kinetics and mechanism have not yet been adequately reviewed. A deeper analysis of the regular kinetic relationships obtained has been carried out using present-day electrochemical concepts, the zone theory of oxides, and heterogeneous models of the dissolution of oxide phases in acidic media.

The kinetics of the dissolution of metal oxides in electrolytes is influenced by the physicochemical properties of both the semiconducting oxides (the degree of covalent character of the bond, the presence of defects in the crystal lattice, the concentration of alloying additives, the crystallographic orientation of the active surface of the crystal, the nature of the active centres, the specific features of the surface states, which differ considerably from the states in the volume of the solid phase) and the solutions (concentration, pH, redox potential, presence of complex-forming reagents).

The existing reviews on this topic[1-16] do not cover the sources completely. An exhaustive analysis of data on the influence of ionising radiation on the kinetics of the dissolution of solids has been carried out.[5,17] The present review systematises the theoretical aspects of the kinetics of the dissolution of oxide phases. Electrochemical concepts have been used to explain many kinetic parameters (the order of the reaction with respect to different ions of the electrolyte), and the influence of oxidising agents, reducing agents, complex-forming reagents, and the adsorption of protons. For the quantitative calculation of the kinetic parameters of dissolution, the experimental data have been treated using present-day theories of the kinetics of heterogeneous processes. It has been shown that morphological models not only make it possible to take account of the change with time in the surface area of the dissolving oxide, but also help to explain the comparatively high activation energy of the dissolution of oxide phases in acids.

II. ANALYSIS OF THE KINETIC CURVES FOR THE DISSOLUTION OF METAL OXIDES IN ACIDIC MEDIA

1. Form of the kinetic curves. The typical form of the curves for the dissolution of powdered oxide specimens as the plots of the fraction of the dissolved substance α against the time t is shown in Fig.1. In the general case, the rate of dissolution $\partial\alpha/\partial t$ passes through a maximum (at $\alpha \cong 0.5$ to 0.7).[2,18-20] The section corresponding to the decrease in the rate of dissolution is difficult to analyse, since it depends to a marked extent on the characteristic features of the size distribution of the particles at this stage of the process.

2. Analysis of the curves for the dissolution of metal oxides in acids on the basis of affine transformations. The method of affine transformations[9,21,22] makes it possible to determine whether changes in the mechanism (stages) of a process are due to a particular factor influencing the rate of dissolution. If the kinetic curves corresponding to different values of any parameter are reduced to a single scale relative to the time $t/t_{0.5}$ (Fig.2), the sequence of stages in the dissolution process is assumed to be always the same from the start to the end of the reaction; the rate of the process is limited by a single stage, and not by several stages. This makes it possible to represent the rate of dissolution $(\partial\alpha/\partial t)$ in the form of a function with separable variables

$$\partial\alpha/\partial t = f(T, a_{H^+}, E) \cdot f(\alpha) \qquad (1)$$

where $f(T, a_{H^+}, E) = (\partial\alpha/\partial t)_{sp}$ is the specific rate of dissolution corresponding to unit surface area of the specimen; and $f(\alpha)$ is a function reflecting the nature of the change in

the surface area of the specimen in this process. Change in the variables, T, E, and a_{H^+} influences the time taken to reach a definite fraction (α) of dissolved oxide, whereas the morphology of the surface of the specimen remains unchanged for different successive values of α.[21]

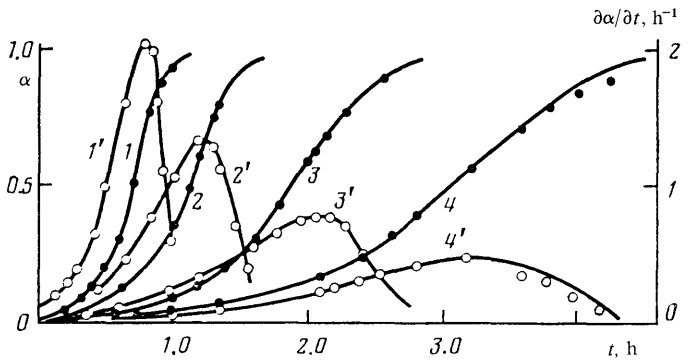


Figure 1. Time dependence of the fraction (α) of dissolved oxide CuO (*1*–*4*) and the specific rate $\partial\alpha/\partial t$ (*1'*–*4'*) of the dissolution of this oxide in aqueous H_2SO_4 solutions with different pH values at an electrolyte temperature of 25 °C; *1*) 0.43 (k_i = 7.37 h^{-1}); *2*) 0.65 (k_i = 3.65 h^{-1}); *3*) 0.85 (k_i = 2.14 h^{-1}); *4*) 1.05 (k_i = 1.34 h^{-1}). Points—experiment; lines—calculation using Eqn.(52), where $A = 0.022$.[166]

3. The theory of the specific rate of dissolution of oxide phases proposed by Nernst. In the literature up to the present, the specific rate of dissolution of crystals (1) has been calculated using the mathematical expression proposed by Nernst and Noyes.[23] The unsatisfactory features of the calculation of the specific rate of dissolution using Nernst's theory can be demonstrated. It follows from Nernst's theory[23] that the diffusion of the ions in the boundary layer of an electrolyte at the surface of separation with an oxide is the limiting stage of the dissolution of the solid

$$(\partial\alpha/\partial t)_{sp} = D(c_{sat} - c)/V \cdot \delta = k_1(1-\alpha) \qquad (2)$$

where D is the diffusion coefficient of the ions, c the concentration of the salt in the volume, c_{sat} the concentration of the salt in the saturated solution, V the volume of solution, and δ the thickness of the electrical double layer. Since Eqn.(2) does not make possible a complete description of all the regular kinetic features of dissolution, use is made of an expression of the form

$$(\partial\alpha/\partial t)_{sp} = k_2(c_{sat} - c)^n \qquad (3)$$

where n and k_2 are independent of the hydrodynamic conditions. According to Eqn.(3), the driving force of the dissolution is the difference between the salt concentrations ($c_{sat} - c$).

The unsatisfactory features of Eqns.(2) and (3) include the fact that they cannot explain the high value of the activation energy (65–85 kJ $mole^{-1}$). For a process taking place in the diffusion range, its value is 15–20 kJ $mole^{-1}$. In practice, Eqns.(2) and (3) are applicable in rare instances, since the values of k_1 and k_2 depend on the dissolution time and on the states of the volume and surface phases. Eqns. (2) and (3) describe the distribution of the concentration of the dissolved substance at a definite distance from the boundary of the solid phase, but they do not reflect the changes in concentration with time.[2] The data in Ref.24 were obtained with vigorous stirring of the electrolyte, when further increase in the rate of movement of the particles had no influence on their rate of dissolution; under these conditions, the equation of diffusion kinetics is not applicable. Kabai[24–27] modified Eqns.(1) and (3) and obtained the expression

$$\alpha = c/c_\infty = 1 - \exp[-(kt)^\gamma] \qquad (4)$$

where γ is a constant which depends on the nature of the system. Detailed verification of Eqn.(4) shows that it is inapplicable even for $\gamma = 1$.

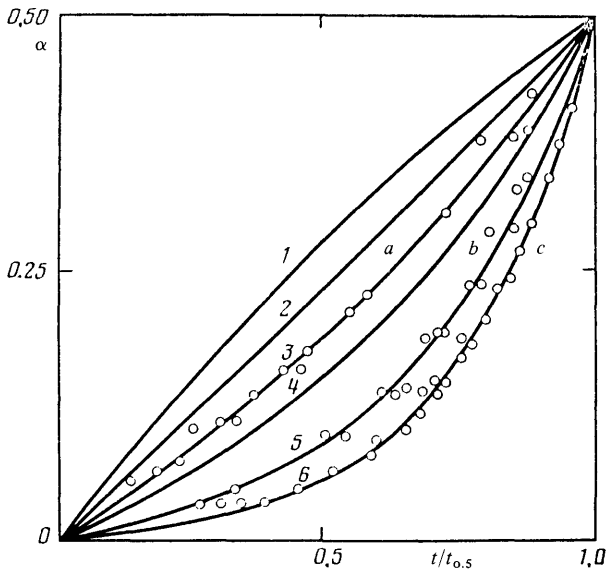


Figure 2. Dependence of the fraction of dissolved magnetite on the reduced time $t/t_{0.5}$ in aqueous solutions of H_3PO_4 (*a*), EDTA (*b*), and HEDP (*c*) under different experimental conditions (concentration, temperature, pH). Lines—calculation using Eqn.(52) for different values of A: *1*) $A = 10$; *2*) $A = 0.45$; *3*) $A = 0.20$; *4*) $A = 0.10$; *5*) $A = 0.025$; *6*) $A = 0.010$. Points—experimental data for different experimental conditions.

In the early nineteen-fifties, experimental data were obtained,[2] showing that these ideas cannot be used to describe the regular kinetic features of the dissolution of metal oxides, since analysis of the dependence of the specific rate of dissolution of oxide phases in acids on various factors established that it is determined by the concentration gradients of the protons and electrons (potential) and the stoichiometric composition of the solid phase, and this is not reflected in Eqns.(2) and (3). An explicit mathematical expression describing the specific rate of dissolution of oxides has not yet been found.

III. THE STRUCTURE OF THE ELECTRICAL DOUBLE LAYER AT THE OXIDE/ELECTROLYTE BOUNDARY AND THE DISTRIBUTION OF CHARGE AND POTENTIAL IN IT

In the dissolution of non-stoichiometric oxides (wustite, magnetite, uraninite, cobalt(II) oxide, pyrolusite, nickel(II) oxide, tenorite, and other oxides), the rate of the process depends on the potentil difference (Fig.3), since this process is determined by the rate of the transfer of ions through the electrical double layer.[2,3,28,29] It is possible to distinguish increases in the rate of dissolution due to the reduction (MnO, Mn_2O_3, MnO_2, Fe_2O_3, Fe_3O_4, FeO) and due to the oxidation (NiO, Cu_2O, UO_2) of the surface layers of the oxides.[2,3,30,31]

1. Nature of the Potential at the Oxide/Solution Boundary

When an oxide is brought into contact with a solution, an electrical double layer is produced at the oxide/electrolyte boundary (Fig.4). The total decrease in the potential (E) relative to the potential of the corresponding reference electrode (E^0) is given by

$$E=E_{sc}+E_H+E_{el}+E^0$$

where E_{SC} is the value of the potential in the volume zone of the oxide, and E_H and E_{el} the decrease in the potential in the Helmholtz layer and in the electrolyte respectively.[32] Regions of volume charge are produced on both sides of the boundary.[32] The equivalent scheme of the boundary is represented by three condensers connected in series.[33] The production of the volume charge in the oxide when it is brought into contact with the electrolyte is due to the insertion of protons (hydroxide groups) into the solid phase.[34] The charge density in this oxide is much lower than that in the metal.[33,35] Thus the potential jump between the phases[33] is concentrated almost entirely in the solid phase, and the contribution made to it by the Helmholtz layer is usually negligible.[35,36]

The magnitude and distribution of the charges and potentials are calculated using two fundamental relationships:

1) the Poisson equation

$$d^2E/dr^2=-\rho/\varepsilon\varepsilon_0 \qquad (5)$$

where ρ is the charge density (made up of both mobile charges, that is electrons $n(r)$ and holes $p(r)$, and stationary charges, that is ionised donors (N_D) and acceptors (N_A), that is $\rho(r) = e[-n(r) + p(r) - N_D + N_A]$); and ε and ε_0 are the dielectric constants of the specimen and a vacuum respectively;

2) the Gauss equation

$$dE/dr=-Q/\varepsilon\varepsilon_0 \qquad (6)$$

where Q is the density of the surface charges. It follows from Eqns.(5) and (6) that the value of the potential in the three regions will be given by the expression (see Fig.4)

$$E=\varepsilon_{sc}r_{sc}+\varepsilon_H r_H+\varepsilon_{el}\varkappa^{-1}$$

where ε_{SC}, ε_H, and ε_{el} are the electric field intensities in the region of the volume charge, the Helmholtz layer, and the electrolyte respectively; and r_{SC}, r_H, and $\varkappa^{-1}$ are the Debye length (characterising the extent of the layer occupied by the volume charge), the extent of the Helmholtz layer, and the thickness of the Gouy layer respectively. The analytical[37] and graphical[38] solution of Eqns.(5) and (6) makes it possible to calculate quantitatively a large number of parameters characterising the distribution of the potential jump. It should be noted that the calculated value $r_{SC} = (\varepsilon_{SC}kT/4\pi e^2 n_0)^{1/2}$ depends on the concentration of free charges (n_0) in the oxide. If $n_0 = 1 \times 10^{13}$ cm^{-3}, and the concentration of ions in a 0.01 M solution of the electrolyte

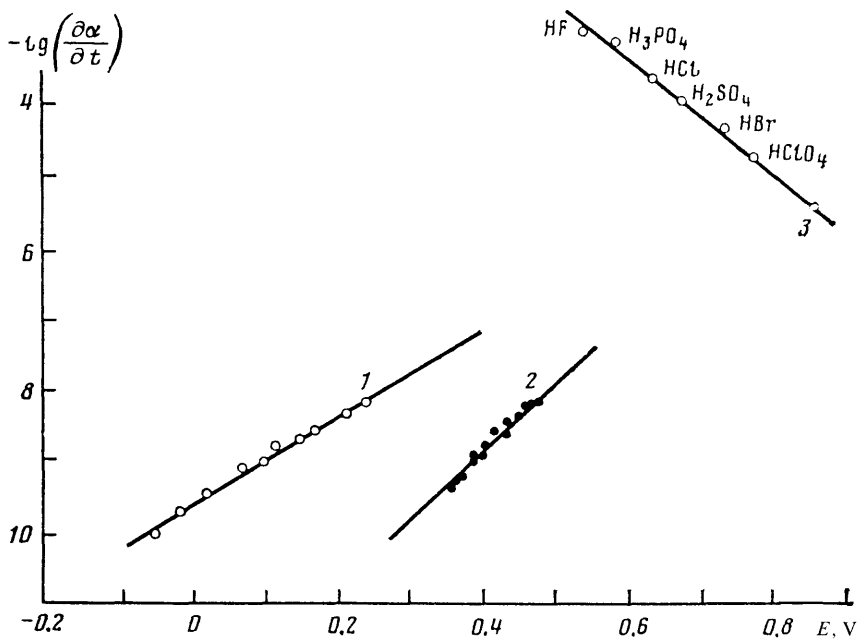


Figure 3. Dependence of the rate of dissolution on the potential for the following oxides: *1*) UO_2 (0.2 M Na_2CO_3 + 0.2 M $NaHCO_3$, 25 °C; $\partial E/\partial \lg \partial\alpha/\partial t$ = 150 mV); 2) UO_2 (1 M $HClO_4$, 25 °C; $\partial E/\partial \lg \partial\alpha/\partial t$ = 120 mV);[30] 3) Fe_2O_3 (1 M acid solutions, 50 °C; $\partial E/\partial \lg \partial\alpha/\partial t$ = 120 mV.[153]

is 10^{19} cm^{-3}, then the extent of the region occupied by the space charge ($r_{sc} \cong 10^{-4}$ cm) is 100 times the thickness of the diffuse layer. With increase in the concentration of free carriers (for example in the reduction of oxides showing n-conductivity), the quantity $r_{sc} \to 0$ as $n_0 \to \infty$. In this case all the space charge is "concentrated" on the electrode surface.

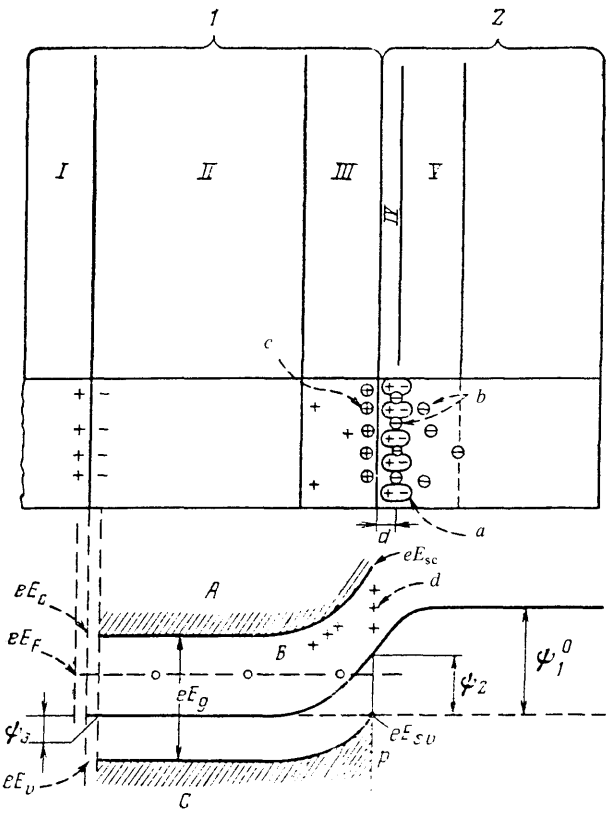


Figure 4. Structure of the electrical double layer at the oxide/electrolyte interface: *1*) solid phases: *I*) metal, *II*) oxide, *III*) region of space charge in the oxide; *2*) electrolyte: *IV*) Helmholtz layer, *V*) Gouy layer. Species creating the electrical double layer: *a*) oriented dipoles of water; *b*) excess ions of the solutions; *c*) adsorbed ions on the oxide, creating surface states; *d*) ionic states. Energy characteristics of the semiconductor (oxide): *A*) conductivity zone, *B*) non-compensated ions of the donors, *C*) valence zone; ψ_1, ψ_2, ψ_3 are the galvanic potentials of the solution, the surface states of the oxide phase, and the metal respectively.[73]

The rate of the dissolution of oxides is controlled chiefly by the magnitude of the potential in the Helmholtz layer. The magnitude of the potential in this case cannot be found experimentally. The values of the other components can be determined. For example, the magnitude of the potential E_{sc} is calculated from the dependence of the photopotential, the differential capacity, and the surface conductivity on the polarisation potential of an oxide electrode.[39-41] Usually, the value of the potential of the planar zones (E_{fb}), when $E_{sc} = 0$ and $E_{el} = 0$, was found. The values of E_{fb} are given in Table 1.

Table 1. Width of the band gap of metal oxides (eE_g) and the potentials of the planar zones of the electrodes [E_{fb}, V (normal electrode)] for different pH values.

Oxide	eE_g, eV	pH 2.0	pH 4.0	pH 6.0	pH 8.0	pH 10.0	pH 12.0	pH 14.0	Refs.
TiO_2	3.0	−0.14	−0.26	−0.38	−0.49	−0.61	−0.73	—	[42]
NiO*	from 1.72–1.90 to » 3.7	+0.97	+0.89	—	—	—	—	—	[43]
WO_3	2.4±0.1	+0.64	+0.51	+0.39	+0.27	+0.15	—	—	[44]
ZnO	3.2	+0.09	−0.02	−0.14	−0.24	−0.34	—	—	[45]
SnO_2	3.5±0.1	+0.36	+0.17	−0.12	−0.32	—	—	—	[46]
SnO_2**	3.5±0.1	—	+0.09	−0.10	−0.28	−0.48	—	—	[46]
Fe_2O_3	2.2	—	—	+0.14	−0.11	−0.23	−0.34	−0.45	[47]

*p-Type conductivity; n-type conductivity in the other cases.
**Studied in an acetate buffer containing $Fe(EDTA)^{2-}/Fe.(EDTA)^{-}$.

In the study of the kinetics of the dissolution of oxides, it has been assumed that the rate of the process is limited by the potential jump in the Helmholtz layer.[29,48] The factors influencing its magnitude can therefore be considered.

a) Factors influencing the magnitude of the potential in the Helmholtz layer. At $E_{sc} = 0$ (that is in the absence of a potential jump in the region of the space charge), the magnitude of the total E is determined by the potential jump in the Helmholtz layer. The study of the influence of various factors[32] on the potential of the planar zones is now not only a stimulus to study but also one of the methods for studying this layer. On oxides (ZnO, TiO_2, SnO_2, Fe_2O_3), the magnitude of E_H is a linear function of pH

$$E_H = E^0 - \left(\frac{2.3\,kT}{e}\right)(\mathrm{pH})$$

since the potential E_H is related to the concentration of adsorbed protons H^+ (the potential-determining ion). If it is assumed that the capacity C_H per unit surface area of the oxide electrode is independent of E_H, it follows that

$$e[H_s^+] = C_H E_H \qquad (7)$$

Here, the pH dependence is due to the reactions: $H_3O^+(aq) \to H^+(solid) + H_2O(aq)$

$$MO_{x_1} + (x_1 - x_2)e + (x_1 - x_2)H^+ \to MO_{x_2} + (x_1 - x_2)H_2O$$
$$\Delta G^0 = \Delta G^0(MO_{x_2}) - \Delta G^0(MO_{x_1}) + \Delta G^0(H_2O)$$
$$\frac{[H^+(solid)]}{[H_3O^+(aq)]} = \exp\left(-\frac{\Delta G^0}{kT}\right) = A\exp\left(-\frac{eE_H}{kT}\right) \qquad (8)$$

Comparison of Eqns.(7) and (8) shows that $eE_H = B - 2.3\,kT$ (pH). If adsorption of other ions of the electrolyte takes place, it leads to a change in the magnitude of E_H.

This potential jump is practically independent of the polarising potential, and its magnitude is not influenced by ions which have not been adsorbed on the electrode. The reason is that the extent of the Helmholtz layer is smaller than the thickness of the layer of the space charge. When charge is transferred from the volume to the surface of the semiconductor, only a small fraction of the consequent change in

the potential difference corresponds to E_H. The decrease in potential takes place chiefly in the region of the space charge, and not in the Helmholtz layer. The potential jump in the Helmholtz layer at the oxide/electrolyte boundary depends on the surface properties of the semiconductor, the ionic strength of the electrolyte, the pH of the solution, and the specific adsorption. The change in potential in the Helmholtz layer is due to the establishment of equlibrium between the solution and the oxide electrode.[49] When the oxides come into contact with the electrolyte solutions, a surface charge is produced as a result of the dissociation of acidic and basic groups; this process can be represented by the equations

$$HOMO^- + H^+ \overset{K_+}{\leftarrow} MO(solid) + H_2O \overset{K_-}{\rightarrow} MOH^+ + OH^-$$

where K_+ and K_- are the dissociation constants of the acidic and basic groups respectively.

Table 2. Electrocapillary zero at 25 °C and the isoelectric point of metal oxides.

Oxide	Coordination	Structure	$pH_{e.z.}$	$pH_{i.p.}$ (Ref.51)	
				hydrate	anhydrous
Cu_2O	2—4	oct.	>11.5	—	9.5±0.4
MgO	6—6	cub.	12.4	—	12.4±0.3
CdO	6—6	cub.	10.4	>10.5	10.4±0.2
NiO	6—6	cub.	9.85*	—	10.3±0.4
CuO	6—6	cub.	9.5	—	9.5±0.4
ZnO	4—4	hex.	9—10	10.3	9.3
α-Al_2O_3	6—4	hex.	6.5—9.5	9.2	6.7
α-Fe_2O_3	6—4	rhomb.	8.5	8.0±0.2	6.5
α-Cr_2O_3	6—4	rhomb.	7.0	7.29	6.49
UO_2	8—4	cub.	3.5—6.5	—	5.8±0.2
TiO_2	6—3	tetr.	4.7	6.0±0.3	3.5±0.2
SnO_2	6—3	tetr.	5.5	5.5	4.7
β-MnO_2	6—3	tetr.	7.0	—	4.0—4.5
WO_3	6—2	rhomb.	0.5	<0.3	—
Co_3O_4	—	cub.	10.35*	—	—
Fe_3O_4	—	cub.	6.4**	—	6.5±0.2

Note: oct. = octahedral, cub. = cubic, hex. = hexagonal, rhomb. = rhombohedral, tetr. = tetragonal symmetry. The pH values at the electrocapillary zero at 40, 60, and 80 °C for NiO are 9.58, 9.25, and 9.06 respectively, and those for Co_3O_4 are 10.04, 9.82, and 9.62.[52]

*Data from Ref.52; **data from Ref.2; for the other oxides—data from Ref.4.

For oxides, the potential-determining ions are usually hydrogen cations or hydroxide anions.[50] In the case of oxides, a change in pH has a significant influence on the sign of the surface charge. There exists a state of the solution (pH value) corresponding to the electrocapillary maxima, when the oxide surface has equal numbers of positive and negative groups. This point (the electrocapillary zero) is the most important parameter of the interface. The electrocapillary zero (e.z.) of an oxide (Table 2) is related to the change in the surface charge. Thus the surface charge (σ_0) is usually described using the specific adsorption of the potential-determining ions (H^+ or OH^-): $\sigma_0 = eF(\Gamma_{H^+} - \Gamma_{OH^-})$, where F is the Faraday number, and Γ_{H^+} and Γ_{OH^-} the quantities of adsorbed protons and hydroxide ions respectively. This charge leads to the production of a potential which changes with increase in the distance from the surface. The state of the solution corresponding to zero potential is called the isoelectric point (i.p.). In the absence of specific adsorption, that is in a solution of an indifferent electrolyte, the electrocapillary zero and the isoelectric point coincide (zero zeta-potential).

The value of the $pH_{i.p.}$ for oxides changes systematically with change in the properties of the cation. A study of 18 oxides[51] showed that the change is described by the equation

$$pH_{i.p.} = 18.6 - 11.5\ (z/r)$$

where z is the charge of the cation, and r the distance between the adsorbed proton and the cation (equal to the diameter of the oxygen ion plus the radius of the cation). It has been proved experimentally[53,54] that the position of the electrocapillary zero is related to the average electrostatic field in the oxide lattice.

It is of interest to try to find a correlation between the potential jump in the Helmholtz layer (E_H) and the magnitude of the surface charge. According to the ion–dipole model,[55,56] E is separated into the internal potential E_H and the psi-potential (ψ_1):

$$d\psi_1 = -59.2\ d\ (pH).$$

In the case of an oxide, the surface potential is given by more complicated equations.[57,58] Determination of the values of the electrocapillary zero and the isoelectric point on oxides has shown that their values depend on the structure of the surface and on the orientation of the atoms in the crystal (deviation from an ideal crystal usually displaces the isoelectric point towards the more acidic range), on the degree of surface hydration (with increase in the degree of hydration, the isoelectric point corresponds to a higher pH value[59]), and on the magnitude of the charge of the cation in the oxide,[59] the nature of the semiconducting properties of the oxide,[59] the presence of impurities, etc. The pH corresponding to the electrocapillary zero is also influenced by various factors,[59,60] some of which are indicated in Table 2.

A correlation exists between the position of the electrocapillary zero and the rate of dissolution of oxides. The lower the pH corresponding to the electrocapillary zero, the more difficult the dissolution of the oxide. Thus under identical conditions, ZnO and Cu_2O dissolve in acids much more rapidly than TiO_2, α-Cr_2O_3, and α-Fe_2O_3,[59] and the values of the pH at the electrocapillary zero are correspondingly much higher for zinc and copper(I) oxides. With increase in temperature, the electrocapillary zero for a number of specimens (oxides) studied is displaced into the acidic range.[52] The isoelectric point is displaced to higher pH values for hydrated specimens, compared with non-hydrated specimens, so that the former usually dissolves more readily.[51,59] At pH values above the electrocapillary zero, the oxide surface is negatively charged as a result of the strong adsorption of OH^- groups. The magnitude of the surface charge (q_-) decreases with decrease in pH. The magnitude of the positive charge (for example for haematite) depends chiefly on the activity a_{H^+}, and depends little on the anionic composition of the electrolyte.[59]

The surface charge is determined chiefly by the desorption of H^+ on the neutral surface. In some electrolytes (of the KCl type), q_+ depends not only on a_{H^+} but also on a_{Cl^-}. Under these conditions, the surface OH^- groups are displaced by Cl^- ions:

$$\left[\begin{matrix}\diagdown\\ -FeOH(OH)_2\\ \diagup\end{matrix}\right]^- \underset{OH^-}{\overset{2H^+,Cl^-}{\rightleftharpoons}} \left[\begin{matrix}\diagdown\\ -Fe(H_2O)_2^{2+}Cl^-\\ \diagup\end{matrix}\right]^+ + OH^-$$

There are two approaches to the solution of the problem of the nature of the potential jump. Quasi-equilibrium[34,35] and non-equilibrium (compromise)[49,61,62] potential jumps are distinguished. The reactions taking place at the oxide/electrolyte interface determine the magnitude of the potential jump and the rate of dissolution of the oxide in the acid.

b) Principal types of quasi-equilibrium reaction determining the magnitude of the potential jump in the Helmholtz layer. According to the theories of electrochemical kinetics, the magnitude of the potential jump at a phase boundary may be determined both by the exchange of hydrogen cations and metal ions between the oxide phase and the electrolyte solution and also by reactions of other types.[29,34,49,62,63] It is suggested that the potential-determining reactions in a multi-stage process of oxide dissolution are close to equilibrium (quasi-equilibrium), since the current due to the exchange of the potential-determining ions of the oxide phase[64] is greater than the current due to the dissolution of the oxides.[2]

Analysis of experimental data on the potential (E) for FeO_x and MnO_x electrodes shows that E is a complex function of pH, x, and $\ln a_{M^{2+}}$. In strongly acidic media, the magnitude of E is determined by the reaction

$$M^{3+}+e=M^{2+} \qquad (9)$$

and obeys the Nernst equation

$$E = E^0 + \frac{RT}{F} \ln \frac{[M^{3+}]}{[M^{2+}]}$$

In media close to neutral, the dependence of the potential on various factors (in the absence of M^{2+} ions) is determined by the parameters[49]

$$\partial E/\partial \ln[M^{2+}] \sim 0;\ \partial E/\partial(\mathrm{pH}) = 0.059;\ E^0 = f(x) \qquad (10)$$

and the value of E is determined by a reaction of the form:

$$MO_{x_1} + 2(x_1 - x_2)H^+ + 2(x_1 - x_2)e \rightarrow MO_{x_2} + (x_1 - x_2)H_2O$$

The potential may be linearly dependent on the stoichiometry of the oxide: $E^0 = a + bx$, or be determined by the expression:

$$E = E^0 + \frac{RT}{F} \ln \frac{[M^{2+}]}{[M^{(2-1)+}]} \qquad (11)$$

In the presence of M^{2+} ions (at the same pH values):[49]

$$\partial E/\partial \lg[M^{+2}] = -\frac{1}{x-1}0.029;\ \partial E/\partial(\mathrm{pH}) = -\frac{x}{x-1}0.059;\ E^0 = f(x) \qquad (12)$$

The change from Eqn.(10) to Eqns.(11) and (12) is determined by the magnitude of the pH and the ratio $[M^{3+}]/[M^{2+}]$.

To explain the dependence of the magnitude of the potential of the manganese oxide electrode on various factors, it has been suggested that use be made of reaction (9), which in weakly acidic media is complicated by the disproportionation of Mn^{3+}:

$$Mn^{3+} + \frac{x}{2(x-1)}H_2O \rightarrow \frac{2x-3}{2(x-1)}Mn^{2+} + \frac{1}{2(x-1)}MnO_x + \frac{x}{x-1}H^+ \qquad (13)$$

In this case the magnitude of the potential (11) is determined by the overall reaction

$$MnO_x + 2(x-1)e + 2xH^+ \rightarrow Mn^{2+} + xH_2O \qquad (14)$$

and obeys the equation:[95]

$$E = -1.196 + 0.687\frac{x^2 - 0.155x}{x-1} - \frac{0.059x}{x-1}\mathrm{pH} - \frac{0.029}{x-1}\lg[Mn^{2+}] \qquad (15)$$

Eqn.(15) corresponds to the theoretical relationship (14), which can be calculated using the expression:

$$E = -\frac{\Delta G^0}{2(x-1)F} = -\frac{x\Delta G^0(H_2O) + \Delta G^0(Mn^{2+}) - \Delta G^0(MnO_x)}{2(x-1)F} \qquad (16)$$

The relationship between the free energies of formation of the oxides of 3d elements $[\Delta G^0(MnO_x)]$ and x is given by the equation

$$\frac{\Delta G^0_x}{x} = \frac{\Delta G^0_i}{i} - \frac{\Delta G^0_i/i - \Delta G^0_j/j}{i-j}(i-x) \qquad (17)$$

where ΔG^0_i and ΔG^0_j are the free energies of formation of the oxides MO_i and MO_j from the elements.[65,66]

Substituting Eqn.(17) in Eqn.(16) gives†

$$E = E^0_{M/M^{2+}} + \frac{\Delta G^0_i/i - \Delta G^0_j/j}{2(i-j)F}\cdot\frac{x^2 - [\Delta G^0_i(i-j)/(\Delta G^0_i/i - \Delta G^0_j/j) + 1]x}{x-1} - \frac{xRT\cdot 2.303}{F(x-1)}(\mathrm{pH}) - \frac{RT\cdot 2.303}{2(x-1)F}\lg[M^{2+}] \qquad (18)$$

which corresponds to the empirical equation (15) found experimentally. It is also possible to verify the dependence of $\Delta G^0(MnO_x)$ on x:

$$\Delta G^0(MnO_x)/x,\ \mathrm{kJ\ mole^{-1}\ (g\text{-}atom\ O)^{-1}} = -496.733 + 132.773x \qquad (19)$$

The published[67] and calculated values of $\Delta G^0(MnO_x)/x$ are compared below:

x	1.00	1.33	1.50	2.00	2.50	3.00
Calculated from Eqn. (19)	363.96	320.15	297.57	231.19	164.80	98.41
Published data (Ref.67)	363.86	321.16	293.72	233.68	—	98.38

The data given confirm the results of the determination of the magnitude of the potential at the manganese oxide/electrolyte interface.

Other reactions may determine the magnitude of the potential in the Helmholtz layer, when E depends on the stoichiometric composition of the oxide phase:

$$MO_{x_1} + 2(x_1 - x_2)H^+ + 2(x_1 - x_2)e \rightarrow MO_{x_2} + (x_1 - x_2)H_2O$$
$$E = E^0_{O_x} + a + b(x_1 + x_2) + RT/F\ln[H^+]$$
$$x_2MO_{x_1} + 2(x_1 - x_2)e + (x_1 - x_2)M^{2+} \rightarrow x_2MO_{x_2}$$
$$E = E^0_{M/M^{2+}} + bx_1x_2 + \frac{RT}{F}\ln[M^{2+}]$$

$$MO_x(\mathrm{solid}) + H^+(\mathrm{aq}) + e \rightarrow MO_xH(\mathrm{solid});\ E = E^0 + RT/F\ln[H^+]$$

where $a = [\Delta G_j^0/j)i - (\Delta G_i^0/i)j]/(i-j)F,\ b = (\Delta G_i^0/i - \Delta G_j^0/j)/2(i-j)F.$

The nature of the observed dependence of the potential of the oxide electrode on pH and $\lg a_{M^{2+}}$ is used to establish the form of the equilibrium, and Eqn.(18) is used to determine the phase composition of the oxide being studied, to refine the value of E, and to find the thermodynamic characteristics of the phase MO_x.[61,65,66]

c) The theory of stationary (compromise) potentials. A compromise potential jump is produced if the oxide is not in equilibrium with the electrolyte solution. A theory of stationary potentials has been developed.[68] According to this theory, at the stationary potential the sum of the cathodic currents is equal to the sum of the anodic currents

$$\sum k_+[\mathrm{Ox}]\exp\left(\frac{\beta_i z_i FE}{RT}\right) = \sum k_-[\mathrm{Red}]\exp\left(\frac{\beta_i z_i FE}{RT}\right) \qquad (20)$$

† Here,

$$\Delta G_i^0 = \Delta G^0(M^{2+}) + \Delta G^0(H_2O) - \Delta G^0(MO).$$

where k_+ and k_- are the rate constants of the anodic and cathodic reactions; β_j and β_i the transfer coefficients; and E the electrode potential. In the general form, this equation cannot be solved for E.

The kinetic equations of stationary potentials have been studied in detail.[69-71] The case of the production of a compromise potential jump at an oxide/electrolyte phase boundary has been examined.[72] According to the ideas developed, in the dissolution of an oxide the magnitude of E is determined by the parallel transfer of OH^-(solid) and M^{z+}(solid) to the electrolyte:

$$OH^-(solid) + H^+(aq) \rightarrow H_2O(aq);\ M^{z+}(solid) \rightarrow M^{z+}(aq)$$

The rates of these reactions depend on the potential. The driving force of the dissolution process is the magnitude of the potential drop in the Helmholtz layer. For E^0_{SC} = const and $E_{el} = 0$, the rates of the transfer of the M^{z+} ions (i_M) and OH^- ions (i_{OH}) to the solution can be written in the form:

$$i_M = {}_+k_M \exp(\beta_+ z_+ FE/RT) \qquad (21)$$

$$i_{OH} = {}_-k_A a_{H^+} \exp(\beta_- z_- FE/RT) \qquad (22)$$

The magnitude of the stationary potential is calculated by solving the simultaneous equations (21) and (22):

$$E = \frac{RT}{(\beta_+ z_+ - \beta_- z_-)F} \ln\left(\frac{k_-}{k_+} a_{H^+}\right) = E^0 - \frac{RT \cdot 2{,}303}{F(\beta_+ z_+ - \beta_- z_-)}(pH) \ . \qquad (23)$$

The value of E obtained can be used to calculate the orders of the reaction with respect to H^+ and other ions.

Since there are two theories of the production of the potential jump (quasi-equilibrium and compromise), there are two approaches to the explanation of the reasons for the influence of E on the rate of the dissolution of oxides. A linear correlation is observed between E_{fb} and the value of E_{max} corresponding to the rate maximum.

2. Relationship Between the Semiconducting Properties of an Oxide and the Electrochemical Properties of the Electrolyte

A relationship exists between the semiconducting properties of an oxide and the electrochemical characteristics of the electrolyte solution–oxide system. The solution is characterised by the following electrochemical parameters: the standard oxidation (redox) potential for the redox couple (E^0), the average energy of the energy level of the molecule of the oxidising agent (unoccupied energy level) in the solution eE_{ox}, the average energy of the energy level of the molecule of the reducing agent (occupied energy level) in the solution eE_{red}, and the energy parameter of the solution eE_F, whose significance is analogous to that of the Fermi energy, since it is given by the relationship $eE_F = \frac{1}{2}(eE_{ox} + eE_{red}) = -E$.[36]

The properties of oxides as semiconductors are characterised by the following parameters: eE_v and eE_{vs} represent the energy of the top of the valence zone in the volume of the specimen and on the surface respectively, eE_F the Fermi energy, and eE_c and eE_{cs} the energies of the bottom of the conductivity zone in the volume and on the surface. The required relationship is established in explicit form by calculating and measuring the values of the potential of the planar zones (E_{fb}).

The comparison of the energy levels of the ions and the zone boundaries of an oxide on the same energy scale represents the most valuable contribution of the electrochemistry of semiconductors to the kinetics of the dissolution of oxides (see Fig.4). This comparison of the energy characteristics and electrochemical parameters is carried out as follows. The experimental relationship between the differential capacity of the oxide electrode (C_{SC}) and the polarisation potential of the oxide E (as $1/C^2_{SC} \rightarrow 0$) is used to determine the value of E_{fb} from the Mott-Schottky equation:

$$\frac{1}{C^2_{SC}} = \frac{2}{\varepsilon\varepsilon_0 e N_D}\left(eE_{SC} - \frac{kT}{e}\right) \qquad (24)$$

According to Eqn.(24), when oxides are polarised, a linear relationship is usually observed between C^{-2}_{SC} and the polarisation potential of the oxide electrode. In this case, if $E_{el} \rightarrow 0$ (concentrated solution), the potential of the planar zones is measured:

$$E_{fb} \approx E_H + E^0 \qquad (25)$$

In other words, the main potential jump corresponds to the Helmholtz layer. The linear relationships between C^{-2}_{SC} and E, obtained for oxides, indicate that the potential in the Helmholtz layer remains constant when the electrode is polarised; only the magnitude of the potential in the volume of the oxide phase is changed.[32] When E_{fb} has been determined, the electrochemical potential of the Fermi level of the oxide on the energy scale is found:

$$eE_{fb} = eE_F = -eE^0$$

For example, for ZnO, $eE_{fb} = -0.231$ eV (normal hydrogen electrode).[73] This result and Eqn.(25) give: $eE_F = -eE + eE^0 = +0.231 + (-4.5) = -4.269$ eV, where $eE^0 = 4.5$ eV [32] (see Fig.5). The values of eE_F and n and the known concentration N_c can then be used to determine the position of the bottom of the conductivity zone eE_c:

$$eE_F = eE_c - 2{,}3\ kT \lg(N_c/n) \ .$$

The width of the forbidden zone $eE_g = eE_c - eE_v$ can be used to find the positions of the zone boundaries.

The energy diagrams of the boundary of separation between the phases, constructed in this way, can be used to provide qualitative and semi-quantitative explanations for all the regular features of the dissolution of metal oxides in different media.

For example, the energy level diagram given in Fig.6 can be used to try to find which oxides can reduce hexacyanoferrate(III) ions by conductivity electrons, and which semiconductors by the injection of holes, that is by giving up electrons from the valence zone (see Fig.6, GaP and GaAs). These diagrams can be used only as the starting point for an analysis of the possible reactions between oxides and the ions of the liquid phase (solutions). To bring about the injection of electrons into an oxide, the energy of the levels eE_{red} should be equal to or greater than the energy of the unoccupied levels of the oxide, and for the capture of an electron by the ions, the energy of the level eE_{ox} should take values equal to or lower than the energy of the occupied levels. It has been found empirically[74] that injection of electrons is observed when the energy of the bottom of the conductivity zone of a semiconductor is higher than the energy $eE^0_{redox} = -eE^0$ by not more than 0.8 eV. Thus the ions Cr^{2+}, Eu^{2+}, V^{2+}, and Co^{2+} inject electrons into ZnO ($eE^0 \gg 0.1$ eV).[75]

Surface reactions (such as dissolution) involving the oxides, together with reactions involving the ions which complicate the picture (hydrolysis, complex formation, dimerisation, the production of unstable states), make the situation much more complex.

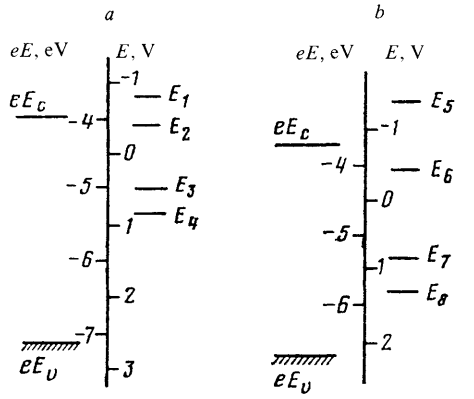


Figure 5. Positions of the energy zones of the oxide (*a*—ZnO, *b*—TiO_2) and the Fermi levels (potentials E_1–E_8) for various electrode reactions taking place at an oxide electrode in aqueous solution at pH 7: *1*) ZnO + $2H^+(aq)$ + $2e \rightarrow Zn + H_2O$ (E_1); *2*) $2H^+(aq) + 2e \rightleftharpoons H_2$ (E_2); *3*) ZnO + $2Cl^-(aq) + 2p \rightarrow ZnCl_2(aq) + \frac{1}{2}O_2$ (E_3); *4*) $H_2O + 2p \rightleftharpoons 2H^+(aq) + \frac{1}{2}O_2$ (E_4); *5*) $TiO_2 + 4H^+(aq) + 4e \rightarrow Ti + 2H_2O$ (E_5); *6*) $2H^+(aq) + 2e \rightleftharpoons H_2$ (E_6); *7*) $H_2O + 2p \rightleftharpoons 2H^+(aq) + \frac{1}{2}O_2$ (E_7); *8*) $TiO_2 + 4Cl^-(aq) + 4p \rightarrow TiCl_4(aq) + O_2$ (E_8).[85]

IV. FORMAL ELECTROCHEMICAL THEORIES OF THE DISSOLUTION OF METAL OXIDES

There are different versions of the theory of the influence of oxidising agents and reducing agents in an electrolyte on an oxide phase during its dissolution. The present-day physical theories of the reduction and oxidation of oxides as semiconductors, and classical electrochemical theories, explaining the mechanism of the influence of the potential on the dissolution of oxide materials, can be distinguished.

The dissolution of oxides is possible if the concentration of the ions in the electrolyte is lower than the saturation concentration. For a given deviation of the concentration from the limiting value, the rate of dissolution is related to the transfer reaction:

$$M^{z+}(solid) \rightarrow M^{z+}(aq);\ A^{z-}(solid) \rightarrow A^{z-}(aq)$$

For the dissolution of crystals in the absence of an external current, the densities of the transfer currents i_M and i_A are equal in magnitude, have different signs, and are conjugated. Volmer's equation[49] is used to describe the regular electrochemical features of the transfer of ions. The dependence of the rates of the transfer of the ions M^{z+} and A^{z-} to the solution on the potentials can be expressed by equations analogous to Eqns.(16) and (17):

$$i_M = {}_+k_M[M]\exp\left(\frac{\beta_+ z_+ F}{RT}E\right) - {}_-k_M a_{M^{z+}}\cdot\exp\left[-\frac{(1-\beta_+)z_+F}{RT}E\right] \quad (26)$$

$$i_A = {}_+k_A a_{A^{z-}}\exp\left(\frac{\beta_- z_- F}{RT}E\right) - {}_-k[A]\cdot\exp\left[-\frac{(1-\beta_-)z_-F}{RT}E\right] \quad (27)$$

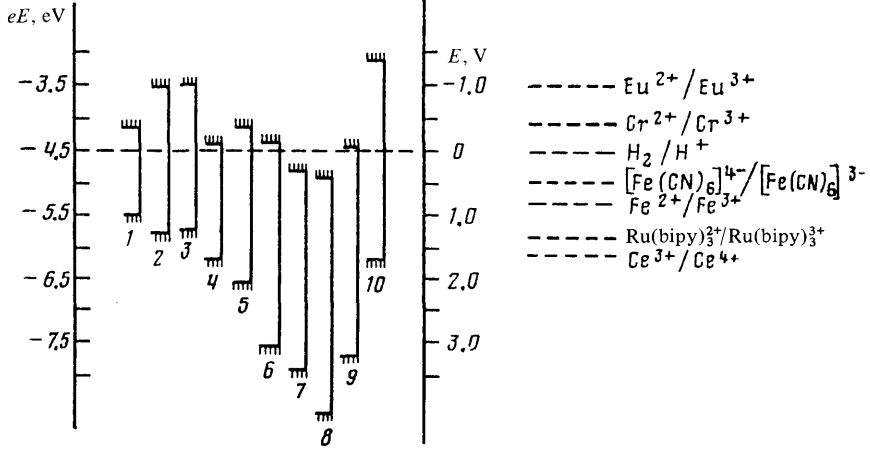


Figure 6. Relative positions of the energy levels of semiconductors and the Fermi levels for various redox reactions taking place at an electrode in aqueous solution: *1*) GaAs, pH 14; *2*) GaAsP, pH 14; *3*) GaP, pH 1; *4*) CdSe, pH 6; *5*) CdS, pH 6; *6*) ZnO, pH 2; *7*) SnO_2, pH 14; *8*) SnO_2, pH 1; *9*) TiO_2, pH 1; *10*) SiC, pH 1.[32]

1. Theory of the Conjugated Transfer of the Cations and Anions of an Oxide to an Electrolyte Solution

a) Jaenicke's theory of the dissolution of ionic crystals.[62,63] The transfer of cations is expressed by the anodic current (i_M), and the transfer of anions by the cathodic (i_A) current. The dissolution is associated with diffusion (through the electrical double layer of thickness δ) according to the equation:

$$i_d = i_M = -i_A = zFDc_M/\delta = zFDc_A/\delta$$

Jaenicke and Haase,[63] by combining Eqns.(26) and (27), and also taking account of the electrical neutrality condition ($a_{M^{z+}} = a_{A^{z-}}$), derived equations of the form:

$$i_d = \frac{\exp\left(\frac{zF\eta}{RT}\right) - \exp(-zF\eta/RT)}{\exp[(1-\beta_+)z_+F\eta/RT]/i_{e,M} - \exp[(-\beta_-z_-F\eta)/RT]/i_{e,A}} \quad (28)$$

where η is the overvoltage and $i_{e,M}$ and $i_{e,A}$ the exchange currents of the metal ions and the anions respectively;

$$c/c_{sat} = \exp\left(-\frac{zF\eta}{RT}\right)\left\{1 - \frac{i_{e,M}}{i_{e,A}}\exp\left[\frac{(1-\beta_-)+\beta_+}{RT}zF\eta\right]\right\}\Big/\left\{1 - \frac{i_{e,M}}{i_{e,A}}\exp\times\right.$$
$$\left.\times\left[-\frac{1-\beta_+ + \beta_-}{RT}zF\eta\right]\right\} \quad (29)$$

It follows from Eqn.(29) that as $c/c_{sat} \to 0$, the maximum overvoltage ($\eta = \eta_{max}$) is observed

$$\eta_{max} = \eta = \frac{RT}{(1-\beta_- + \beta_+)zF}\ln\frac{i_{e,A}}{i_{e,M}}$$

which corresponds to the maximum rate of dissolution:

$$i_{d,max} = i_{e,A}^{\beta_+/(1-\beta_-+\beta_+)} \cdot i_{e,M}^{\beta_+/(1-\beta_-+\beta_+)}$$

For $\beta_+ = \beta_- = 0.5$:

$$i_{d,max} = (i_{e,A} \cdot i_{e,M})^{1/2} \quad (30)$$

Analysis of Eqn.(30) shows that the rate of dissolution depends on the magnitude of the exchange currents ($i_{e,A}$ and $i_{e,M}$). At low values of the overvoltage ($\eta \ll RT/zF$):

$$(\partial\eta/\partial i_d)_{\eta=0} = \frac{RT}{2zF}\left(\frac{1}{i_{e,M}} - \frac{1}{i_{e,A}}\right) \quad (31)$$

The applicability of relationships (30) and (31) has not yet been confirmed experimentally.

b) Engell's theory of the dissolution of oxide phases.[29] In the derivation of the $E(i)$ relationship, Engell made the following assumptions: 1) the processes involved in the transfer of the ions [M^{z+}(solid) → M^{z+}(aq); A^{z-}(solid) → A^{z-}(aq)] are independent; 2) the total value of the chemical potential for the anions (μ_A) and cations (μ_M) is constant, that is $\mu_M + \mu_A = \mu_\pm$; 3) the dissolution is a non-equilibrium process, since the reverse reaction is suppressed; 4) the fact that the composition is constant is explained by the fact that the fluxes of the ions (the cations i_M and the anions i_A) through the electrical double layer are the same ($|i_M| = |i_A|$); 5) the rate of dissolution depends on the potential in the Helmholtz layer, in accordance with the Volmer equation; and 6) the surface concentrations of the cations and anions are given by the Boltzmann equation:

$$[A] = \exp[(\mu_A - \mu_A^0)/RT];\ [M] = \exp[(\mu_M - \mu_M^0)/RT]$$

where μ_M^0 and μ_A^0 are the chemical potentials of the ions at the surface at an ion concentration $c = 1$.

Allowance for the above assumptions, Eqns.(26) and (27), and

$$k_+\exp(-\mu_A^0/RT) = k_A^0;\ k_-\exp\left(-\frac{\mu_M^0}{RT}\right) = k_M^0;$$

$$\mu_M = \frac{1}{2}\{\mu_\pm RT\ln(k_A^0/k_M^0) + (\beta_A z_A - \beta_M z_M)FE\};$$

$$\mu_A = \frac{1}{2}\{\mu_\pm + RT\ln(k_M^0/k_A^0) + (\beta_A z_A - \beta_M z_M)FE\}$$

gives for $z_A = -z_A$

$$i_M = i_A = (k_A^0 k_M^0)^{1/2}\exp(\mu_\pm/2RT)\exp[\{\beta_M|z_M| - \beta_A|z_A|\}FE/2RT] \quad (32)$$

It follows from Eqn.(32) that the slope of the Tafel section is

$$\partial E/\partial\ln i = 2RT/F(\beta_M|z_M| - \beta_A|z_A|)$$

If $\beta_A z_A > \beta_M z_M$, an increase in the rate is observed with decrease in the potential. The values of the slope have been given[29] for cases where the dissolution is limited by the transfer of the anions

$$\partial E/\partial\ln i = (z_M - \beta_A|z_A|)F/RT$$

or the cations

$$\partial E/\partial\ln i = [\beta_M z_M - |z_M|]F/RT$$

Thus for FeO,[29] $\partial E/\partial\ln i = 0.080$ V. Since

$$z_{Fe^{2+}} = 2,\ z_{O^{2-}} = -2, \text{ it follows that } (\beta_{O^{2-}} - \beta_{Fe^{2+}}) = 0.32$$

Some aspects of Engell's theory have led to a number of comments:[2,48] 1) Engell regards oxides as purely ionic compounds, completely ignoring the influence of the important semiconducting properties of oxides (volume charge, electron and hole conductivity, energy of the levels); 2) according to Engell, the polarisation potential corresponds only to the region of the volume charge (the potential jump in the Helmholtz layer is not taken into account); and 3) some of the assumptions made by Engell exclude even slight deviation from stoichiometry.

c) Vermilyea's theory of the dissolution of oxide phases[72] makes it possible to explain the formal orders of the reaction with respect to hydrogen ions, the dependence of the rate of dissolution on the potential, and the influence of the anion composition of the electrolyte. According to Vermilyea,[72] the dissolution is an electrochemical process, and consists of two conjugated reactions, involving the transfer to the solution of the metal ions and oxygen ions.

Vermilyea established the dependence of the rate of dissolution on the potential by making use of the following assumptions: a) the dissolution process is irreversible; b) the concentration of ions on the surface is equal to $2n^0$:

$$[M] + [A] = 2n^0$$

where it follows from the last expression that deviations from stoichiometry are possible; and c) the rate of removal of the anions and cations are equal, that is $i_M = i_A$. From Eqns. (26) and (27) and assumptions (a)–(c), taking account of the fact that

$$_+k_M^0[M]\exp(\beta_+z_+FE/RT) = {}_+k_A[A]\exp(\beta_-z_-FE/RT)$$

it can be shown that the rate of dissolution is equal to

$$i_A = 2i_0[\exp(-\beta_-z_-F\eta/RT) + \exp(-\beta_+z_+F\eta/RT) \quad (33)$$

where the rate of free dissolution of the oxide (the magnitude of the potential is E_f) is:

$$i_0 = k_A^0\exp(\beta_-z_-FE_f/RT);\ \eta = E - E_f$$

If η is very small, it follows that

$$i_A = 2i_0[2 - (\beta_+z_+ + \beta_-z_-)\eta F/RT]^{-1} \quad (34)$$

The result obtained agrees with Engell's conclusion.[29] Eqn.(33) provides a fairly realistic explanation of the nature and existence of the maximum of the dependence of the rate of the dissolution of oxide phases on the potential.

In the case of cathodic polarisation, when the magnitude of the anodic current (i_A) can be neglected, Eqn.(33) becomes

$$i_A = kc^m_{H^+} \exp(\beta_- z_- F\eta/RT)$$

where $\eta \gg 0$. For $\beta_- = 0.5$ and $z_- = 1$, the calculation gives the value $\partial E/\partial \ln i = 120$ mV, which agrees with the experimental data.[76-78]

The above theories start from the assumption that the currents of the metal and oxygen ions are equal, that is that these transfer reactions are conjugated. Usually, the rate of removal of the ions is such that $i_M \gg i_A$ or $i_A \gg i_M$, so that the rate of dissolution is determined by the transfer of one particular ion. In this case the dissolution current is much smaller than the current of the exchange with respect to the metal ions and with respect to the anions.

2. Electron–Proton Theory of the Influence of the Potential

According to the electron–proton theory, the influence of the potential on the boundary of separation is revealed in the fact that the proton brings about mass transfer. Its first stage includes the electrochemical process of the transfer of protons through the oxide/solution interface and their adsorption on the surface of the oxide:

$$M^{z+}(solid) + O^{2-}(solid) + H^+(aq) + e \rightarrow OH^-(solid) + M^{(z-1)+}(solid)$$

where $M^{z+}(solid)$, $M^{(z-1)+}(solid)$, $O^{2-}(solid)$, and $OH^-(solid)$ are the species of the oxide phase. As a result of this reaction, the surface layer of the oxide is converted into a compound with variable (non-stoichiometric) composition. The concentration of protons present as OH groups, the electrical conductivity, and the stoichiometry of oxide are related to one another and depend on E. The second stage involves the "diffusion" of the atoms into the depth of the oxide phase with the simultaneous transfer of an electron from one metal ion to another, or dissociative diffusion. When the value of the potential is displaced into the cathodic range, the rate of the introduction of protons into the oxide increases. Their concentration in the oxide depends on the mobility of H^+ and on the magnitude of E.

The electron–proton theory is confirmed by a number of facts. Data obtained using hydrogen and oxygen isotopes indicate that hydrogen, and not oxygen, is transferred from the electrolyte solution into the oxide and in the opposite direction.[79,80] The fact that the cathodic and anodic charging curves show hysteresis, and also the slow changes in the current after the polarisation current is switched off, indicate that there is retarded diffusion of the protons.[34] The high rate of the electrochemical processes indicates that they involve fairly mobile species (the proton).

The participation of the protons in the electrochemical processes explains the differences in activity observed for hydrated and non-hydrated oxides. The introduction of protons into an oxide does not lead to a significant change in the crystal lattice parameters of the oxide.[34,81] It has been established that the rate of dissolution and the magnitude of the potential are directly proportional to the quantity of adsorbed protons [H^+(ads) ions[82]]:

$$i_d = (\partial\alpha/\partial t)_{sp} = K'[H^+(solid)] = K\theta_{H^+}$$

where θ_{H^+} is the degree of covering of the oxide surface by protons. It is known that the dependence of the degree of covering of a surface by adsorbed protons on the equilibrium concentration of the acid corresponds to the Freundlich equation[59,83]

$$\theta_{H^+} = Ba^n_{H^+}$$

where $n = 0.5$–0.6.

The above arguments have been used to derive# the dependence of the specific rate of dissolution of an oxide on the adsorption of H^+ ions on the oxide, the pH of the electrolyte, and E:

$$(\partial\alpha/\partial t)_{sp} = k \cdot a^m_{H^+} \exp[-(1-\beta_+)z_+FE/RT] \quad (35)$$

This expression makes it possible to explain all the regular kinetic features of the influence of H^+, E, and T on the specific rate of dissolution of oxide phases.

The order of the rate of dissolution of oxides with respect to hydrogen ions, $n_{H^+} = m$, should be 0.5. When E is displaced into the cathodic range, the rate of dissolution of the oxide should increase. The species taking part in the dissolution process is the proton.

For $\beta_+ = 0.5$ and $z_+ = 1$, the value of $\partial E/\partial \lg[(\partial\alpha/\partial t)_{sp}]$ should be 120 mV, which agrees with the experimental data.

V. THE SEMICONDUCTOR THEORY OF THE OXIDATION AND REDUCTION OF OXIDE PHASES

A different approach has been developed[35,36,84,86] for describing the regular kinetic features of the dissolution of oxides, which are semiconductors, in electrolytes containing added oxidising agents and reducing agents. According to this theory, when oxides are brought into contact with electrolyte solutions, transfer of electrons to the semiconductor from the ions of the solution, or in the opposite direction, this is due to the fact that the Fermi level (eE_F) in the oxide does not correspond to the Fermi level ($eE_{F,el}$) of the ions of the electrolyte.

When there is electrochemical polarisation of oxides in solutions of electrolytes having an oxidation potential E^0, an increase in their rate of dissolution in acidic media is possible. The thermodynamic conditions for the processes involved in the dissolution of oxide phases have been examined.[84] The thermodynamic data can be used to determine the standard potentials of the reactions involved in the cathodic and anodic decomposition of oxide materials. If $E < E^{decomp}$ or $eE_F > eE^{decomp}$, cathodic dissolution of the oxides, taking place with the participation of the electrons of the conductivity zone, is possible (see Fig.5). When $E > E^{decomp}_d$ or $eE < eE^{decomp}_d$, anodic dissolution of the oxides with the participation of the electrons of the conductivity zone is possible. For example, for the dissolution of zinc oxides with anodic polarisation of the electrode, these reactions can be represented in the form:

$$ZnO + p + H^+ \rightarrow Zn^{2+} + {}^1/_2H_2O_2$$

$$\Delta G^0_d = \Delta G^0(Zn^{2+}) + {}^1/_2\Delta G^0(H_2O_2) - \Delta G^0(ZnO) = -87.8 \text{ kJ mole}^{-1},$$

and the decomposition potential will be equal to:

$$E = -\Delta G^0_d/F = 0.91 \text{ V}.$$

The mechanism of the oxidation or reduction of oxides during dissolution with potentiostatic polarisation can also be explained with allowance for the semiconducting properties of the oxide phases. The transfer of electrons with polarisation, and the corresponding current, can be calculated

For a discussion of this topic see Refs.153, 166, and 209.

qualitatively using the diagram giving the distribution of the energy levels at the boundary of separation between the phases. The electrochemical reactions of oxide electrodes involve both electrons and holes. For an exchange reaction to take place on the surface of oxides, transfer must take place to levels situated close to the bottom of the conductivity zone or close to the top of the valence zone.[75] The positions of the characteristic energy levels in oxides (for example the bottom of the conductivity zone in a semiconductor) can be determined unambiguously, but in electrolyte solutions it is necessary to consider only the average values of the characteristic energies of the ions in the liquid (that is to take account of the fluctuation of the energy levels). These levels can be described by a Gaussian distribution function[32,88,89] (see Fig.7):

$$D(E) = W(E) = (4\pi kT\lambda_i)^{-1/2} \exp[-(eE - eE_{redox})^2/4kT\lambda_i]$$

where λ_i is the energy of the reorganisation of the environment which takes place as a result of the transfer of electrons from the electrode to the reagents in the solution as a result of the change in the charge of the particles. If it is necessary to determine, for example, the rate of transfer of an electron from the donor to the electrode, it can be expressed in terms of the rate of electron exchange between two isoenergetic levels in the electrode and in the solution, where the first of these levels is occupied, and the second is unoccupied. The rate of the redox reaction at the oxide surface is determined by the surface concentration of current carriers at the boundary of separation between the phases.[36] The expression for the exchange current of redox reactions at the boundary of separation should include the values of the standard redox potential E^0_{redox} and the concentrations of the reagents c_{red} and c_{ox}. It is possible to distinguish two cases (for *n*- and *p*-type semiconductors). The current of the electron transfer (i) from the valence zone of the semiconductor into the solution and on to the species being reduced, the acceptor (Ox), can be calculated. This reaction can be regarded as the transfer of a hole (p) from the acceptor into the valence zone:

$$Ox \rightarrow Ox^- + p$$

The rate of the process in this case will be directly proportional to the concentration of carriers in the valence zone and the density of acceptors (oxidising agent), which can capture an electron. Account must be taken of the fact that this exchange reaction can take place when the levels are situated close to the bottom of the conductivity zone or near the top of the valence zone. The transfer of an electron from the electrode to the acceptor is equivalent to the passage of an anodic current

$$i = c_{ox} \int_{-\infty}^{\infty} D(E)\, k(E)\, n(E)\, dE$$

where $D(E)$ is the probability of the distribution of the reagent particles with respect to energy, which can be described by a Gaussian distribution function; $n(E)$ the partial concentration of electrons (close to the surface of the semiconductor), whose energy is equal to eE; and $k(E)$ is the rate of the transfer of an electron with energy eE from the semiconductor to an ion in the solution having an energy eE'. Since the values of the functions $n(E)$ in the valence zone and $k(E)$ are practically constant for $eE \cong eE_S$, and the energy of the top of the valence zone close to the surface differs by an amount $-eE_{SC}$ from the energy of the top of the valence zone in the volume of the semiconductor (eE_V), it follows that the final expression for the current has the form:

$$i = kc_A \exp\{(eE^0 - eE_A)^2/4kT\lambda_i\} \qquad (36)$$

According to Eqn.(36), the rate of the process will be a maximum when the magnitude of the energy of the energy level of the acceptor eE_A is equal to the energy of the surface state. Eqn.(36) has been verified experimentally.[87] For ZnO, it was found that the value of the potential E^0 corresponding to the maximum of the exchange current is 0.8 V. Since $eE^0_{redox} = -eE^0$, it follows that $eE_{CS} = eE^0_{ox} = eE^0_{redox} + \lambda_i = -0.8 + \lambda_i$.

The current of the electron transfer from the species being oxidised, the donor (D_{red}), in the solution to an energy level of the surface states of the oxide can be found analogously. The corresponding reaction can be written in the form:

$$D = D^+ + e$$

For the calculation of the current it is possible to obtain a

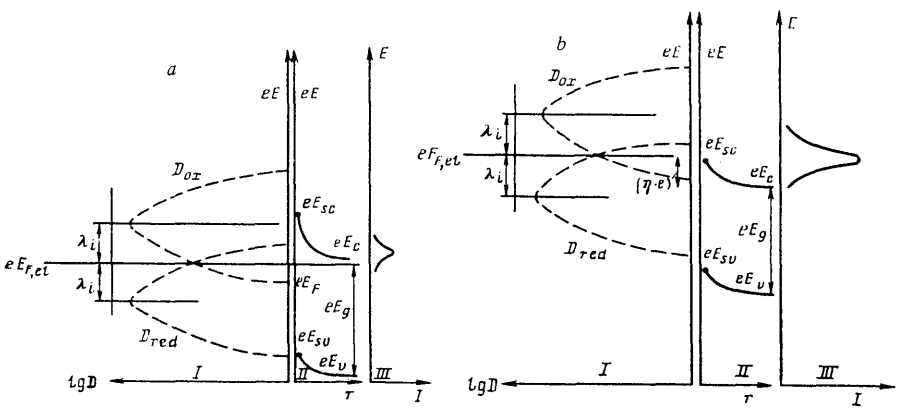


Figure 7. Positions of the energies at the semiconductor–solution interface for equilibrium (*a*) and for anodic polarisation of the semiconducting electrode (*b*): *I*) plot of the logarithm of the probability of the electrolyte redox species distribution against the magnitude of the energy, *II*) dependence of the position of the energy zones of the oxide on the distance from the interface, *III*) dependence of the current of the dissolution of the oxide phase on the magnitude of the applied voltage.[88]

relationship analogous to that proposed above:

$$i=kc_d\exp[(-eE-eE_d)^2/4kT\lambda_i] \quad (37)$$

Comparison of Eqns.(36) and (37) shows that the dependence of the current of the transfer of electrons on the potential passes through a maximum.[32] These regular features make it possible to explain the dependence of the rate of dissolution on the potential of the redox couples for oxides which are *p*- or *n*-type semiconductors.

Since the above theories are formal, it is of interest to examine the mechanism of the cathodic reduction or anodic oxidation of oxide phases and to discuss the question of why polarisation influences the rate of their dissolution.

VI. MECHANISM OF THE DISSOLUTION OF METAL OXIDES WITH CATHODIC AND ANODIC POLARISATION

The rates of these processes are limited by the magnitude of the potential of the redox reactions taking place on the surface of the oxide phase.[2] When the value of the stationary potential is displaced into the cathodic region, the rates of the dissolution of iron and manganese oxides increase.[2,90,91] The polarisation curves obtained for the polarisation of MnO_2 show two reduction waves, whose potentials depend on the concentration of metal ions and on pH. The peaks correspond to two processes:

$$MnO_2+H^++e\rightarrow MnOOH \quad (I)$$

$$MnOOH+H^++e\rightarrow Mn(OH)_2\rightarrow Mn^{2+} \quad (II)$$

The form of the polarisation curves ($E-i$) corresponds to the dependence of the rate of dissolution of the oxides Mn_2O_3, Fe_3O_4, and Fe_2O_3 on the potential.[90,91] There are two theories of the reduction of metal oxides. According to the first theory,[92–94] the reduction of an oxide phase is limited by the rate of removal of metal ions from it (Mn^{2+} for MnO_2 or Fe^{2+} for Fe_3O_4 and Fe_2O_3):

$$MO_x+2xH^++2(x-1)e\rightarrow M^{2+}+xH_2O$$

It is considered that MnO_2 (or Fe_3O_4) reacts as a reversible electrode, whose potential is determined by the concentration of metal ions M^{2+} and by the pH,[95,96] and $\partial E/\partial(pH) = 120$ mV/pH in the presence of both Mn^{2+} ions[95] and Fe^{2+} ions.[96] The quantity of electricity used up in this process[77] is twice that required for the reaction.[97] According to the theory being considered, the MnOOH formed is not the primary product, but is produced as a result of the reaction:[92,93,97–99]

$$MnO_2+Mn^{2+}+2H_2O\rightarrow\rightarrow 2MnOOH+2H^+$$

According to the second theory, the reduction of metal oxides is limited by the introduction of protons into the oxide phase. The reduction of the oxides takes place as a result of the transfer of protons through the electrolyte/oxide interface,[34,98–100] and is described by the equation:

$$MO_x(solid)+mH^+(aq)+me\rightarrow MO_{x-m}OH_m(solid)$$

There is no doubt that the last reaction takes place in alkaline media. The proton mechanism is confirmed by the ($E-i$, $i-t$) curves, which show the phenomena of concentration polarisation in the solid phase.[34] In the reduction of the oxides, the initial process is the adsorption of protons (to give OH groups); in the subsequent reduction, the hydrogen atoms diffuse into the oxide phase, leading to the reduction of deeper layers. The slow diffusion of hydrogen atoms brings about concentration polarisation in the solid phase.[34] X-Ray diffraction study of the products of the oxidation or disproportionation of magnetite has confirmed that under these conditions, a continuous series of solid solutions of Fe_3O_4 in γ-Fe_2O_3 is formed.[101] The yield of the cathodic process for the reaction for the most part never exceeds 100%; a solid solution of M_2O_3 in MO_2 or a solution of MOOH in MO_2 is formed.[102] The mechanism of the diffusion of protons has been examined quantitatively.[103,104] The presence of combined water in the oxides leads to an increase in the rate of diffusion of H^+.[34] The theory of the limiting stage of the diffusion of protons into the oxide does not explain the appearance in the electrolyte (in appreciable quantities) of Fe^{2+} and Mn^{2+} ions (at pH < 6) for the cathodic polarisation of Fe_2O_3 and MnO_2 respectively.

The theories can be combined by assuming that the chemical stage is complicated by a subsequent process. Using the last of the above equations for the reactions and taking account of the possible disproportionation of manganese(III) oxide gives:[76,105,106]

$$\begin{array}{l} 2(MnO_2+H^++e\rightarrow MnOOH) \\ 2\,MnOOH+2\,H^+\rightarrow MnO_2+Mn^{2+}+2\,H_2O \\ \hline MnO_2+4\,H^++2e\rightarrow Mn^{2+}+2\,H_2O \end{array}$$

Studies of the kinetics of the dissolution of the oxides NiO,[107] Cu_2O, CuO,[108,109] and UO_2[30] have shown that the rate of the process increases on anodic polarisation and when oxidising agents are introduced into the electrolyte solution.[30,109,110] The question of the stability of oxides on anodic polarisation is important not only in the study of their dissolution but also in practice, for the transformation of light energy into chemical energy. The question of the stability of oxides in acidic media has been studied.[36,84] It has been established experimentally that when holes are generated by anodic polarisation, illumination, or the addition of oxidising agents, there is an increase in the rate of dissolution, which (for example for ZnO) can be respresented in the form:

$$ZnO+2p\rightarrow Zn^{2+}+{}^1/_2O_2$$

In the dissolution of ZnO, oxygen is liberated, and Zn^{2+} ions are formed.[36,85,111–114] Similar results were obtained in the dissolution of copper oxides (Cu_2O, CuO),[85] which have hole conductivity and which decompose in acidic solutions with anodic polarisation to give Cu^{2+} and O_2. On the basis of potentiostatic measurements of the reduction and oxidation of a passivated nickel surface, a proton mechanism was proposed for the anodic polarisation of the oxides.[115–123]

1. Nature of the Active Centres and the Role of the Hydration of the Surface of Oxides in the Kinetics of Dissolution§

The dissolution of oxides begins on the active regions of their surface, as confirmed by etch figures. The introduction of the oxide TiO_2 into Fe_2O_3 (*n*-type semiconductor),[127] and also the addition of reducing agents to the acid solution, increases the rate of dissolution of iron(III) oxide, since there is an increase in the quantity of Fe^{2+} ions in the volume of the oxide phase.[2,128–130] The active centre for the dissolution in this case is Fe^{2+}. The rate of the dissolution of the oxides NiO and Cu_2O, which show *p*-type conductivity, increases when they are heated in an atmosphere with an increased oxygen pressure, and also when the value of the potential is displaced in the anodic direction. This is related to the fact that the active centres for the dissolution of NiO are Ni^{3+}.

§ For the bibliography on this topic, see Refs.53, 58, and 124–126.

The rate of the dissolution of oxides, and also their physical and chemical properties, are related to the degree of hydration of the surface.[4] A number of reviews[131–134] have been devoted to the study of the hydration and dehydration of oxide surfaces. Up to five types of isolated hydroxide group are usually distinguished on oxide surfaces. For example, the centre consisting of an OH group surrounded by four O^{2-} ions is the most basic, and a centre which has no neighbours (O^{2-} ions) is regarded as the most acidic. Acids react primarily with basic centres. The rate of the dissolution of ionic oxides is influenced considerably by change in the concentration of water in the acidic electrolyte. The rate of the dissolution of ZnO in alcoholic solutions of H_2SO_4 and HCl is slower by factors of 10^2–10^3 than that in aqueous solutions of the acids at the same concentrations.[135] A similar effect has been detected in the study of the kinetics of the dissolution of GeO_2 [10] and Al_2O_3 [136] in acids. The increase in the rate of dissolution of the oxides is directly proportional to the degree of hydration of the oxide phase.[10]

Another relationship was detected in studies of the influence of the concentration of acetone or ethylene glycol on the kinetics of the dissolution of Fe_3O_4 in HCl.[137,138] The rate of dissolution increases with increase in the concentrations of the acid, the iron(II) ions, and the non-aqueous solvents. The dependence of the time taken for 50% dissolution of Fe_3O_4 (0.5 g specimen) in 6 *N* HCl on the concentration (vol.%) of acetone and ethylene glycol is given below.

Acetone, vol. %	0	5	10	15	50	
$t_{0.5}$, min	47	41	23	15	1	
Ethylene glycol, vol.%	0	10	20	30	40	50
$t_{0.5}$, min	87	70	55	42	27	12

The rate of the dissolution is limited not by the reaction of magnetite with water molecules but by the process of proton transfer for the solution to the oxide phase. The increase in the rate of dissolution with increase in the concentration of non-aqueous solvents is related to the increase in the activity of the hydrogen ion (a_{H^+}) and the displacement of the potential (E_H) into the cathodic region.

2. Diffusion of Protons in the Oxide Phase During Its Dissolution

The study of the exchange equilibrium of ^2H and ^{18}O between a hydroxide and an electrolyte[34,139] has shown that the rate of the transfer of the hydrogen atoms is greater than that of the oxygen atoms. Linear scanning during the reduction of NiOOH gave the value of the proton diffusion coefficient ($D_{H^+} = 2 \times 10^{-9}$ cm^2 s^{-1}).[140] Higher values of the proton diffusion coefficient were observed during anodic polarisation, compared with the cathodic process. Other workers[141] have proposed a proton-diffusion process ($D_{H^+} = 2 \times 10^{-10}$ cm^2 s^{-1}) for the electrochemical formation of an NiOOH oxide film. Wyttenbach[142] gives the value $D_{H^+} = 4 \times 10^{-23}$ cm^2 s^{-1} (for the diffusion of H^+ at 25 °C) and $E_a = 96$ kJ mole^{-1}. The values of D_{H^+} for the other compounds are given below.

Compound	α-FeOOH	γ-AlOOH	NiOOH	δ-MnO_2
D_{H^+}, cm^{2}s^{-1}	$5.8 \cdot 10^{-17}$ [143, 144]	$5 \cdot 10^{-19}$ [145]	10^{-10}—10^{-11} [34]	10^{-18}—10^{-17} [139]

These values of the diffusion coefficients lie in a range between their values in electrolyte solutions and in the solid phase.

In electrochemical methods for determining the value of D_{H^+}, it is assumed that the rate of the redox processes is limited only by the diffusion of protons. The use of a potentiostatic method to study the formation of NiOOH during the anodic oxidation of Ni^{2+} ions[146,147] established, however, that the formation of $Ni(OH)_3$ is controlled by the change in the nature of the surface during the three-dimensional growth of the crystal. A noteworthy feature is the observed relationship between the diffusion of the protons and the semiconducting properties of the electrodes. In the opinion of Takehara and co-workers,[148] the surface concentration of the protonated regions and vacancies in oxides changes as a result of the reaction of charge transfer. The proton concentration gradient produced determines the rate of diffusion of H^+ between the surface and the volume of the oxide.

a) The specific features of the diffusion of protons.[12] Electrons move much more rapidly than protons, and lead to the appearance of a space charge, creating an electric field ($\partial E/\partial r$), which increases the velocity of the hydrogen ion flux (j_{H^+}).[149] The H^+ ion diffusion current will be:[150]

$$j_{H^+} = D_{H^+}\frac{\partial [H^+]}{\partial r} - \frac{D_{H^+}}{kT}[H^+]\frac{\partial E}{\partial r}. \qquad (38)$$

where $\partial[H^+]/\partial r$ is the proton concentration gradient in the oxide phase, j_{H^+} the velocity of the H^+ ion flux in the metal oxide, and D_{H^+} the proton diffusion coefficient in the oxide.

Eqn.(38) gave:

$$j_{H^+} = D_{H^+}\frac{\partial N_{H^+}}{\partial r}\{1 + N_{H^+}[N_D \exp(E_D - E_F)/kT + N_0 \exp(E_F - E_0)/kT]^{-1}\} \qquad (38a)$$

where N_D and N_{H^+} are the concentration densities of the donors and the protons respectively in the oxide.

Analysis of Eqn.(38a) shows that the effective proton diffusion coefficient (D_{eff}) in this case passed through a maximum as N_{H^+} increases with time and approaches N_D:

$$j_{H^+} = D_{H^+}\frac{\partial N_{H^+}}{\partial r}\left[1 + \frac{N_D}{N_{H^+} - N_D}\right] = \frac{\partial N_{H^+}}{\partial r} D_{eff} \qquad (39)$$

This result indicates that the rate of penetration of the protons into the oxide phase increases with time and passes through a maximum.

3. Dependence of the Specific Rate of Dissolution of Oxides on the Concentration of H^+ and Acids and on the Nature of the Electrolyte

The influence of the concentration of acids on the rate of dissolution of oxides has been the subject of a large number of studies.[2,4,12,13,17–20,151–166] The formal order of the reaction with respect to hydrogen ions (n_{H^+}) for the dissolution of oxide phases is ~0.5 (Table 3). When the dissolution is complicated by hydration, redox reactions, complex formation, and other factors, the formal order of the reaction with respect to acid takes different values. For the dissolution of iron(III) oxide in hydrochloric and hydrobromic acids, $n_{HA} \cong 2$,[18] and for the reaction of Fe_2O_3 with $HClO_4$, $n_{HA} = 0.9$.[18] The dependence of α on $t/t_{0.5}$ is invariant with respect to the acid concentration.[22] In most cases, the formal order of the reaction with respect to acids remains unchanged in the range of values of α 0.1–0.8.[22] This indicates that the morphology of the oxide phase/electrolyte interface remains unchanged for different values of α, and that the nature of the limiting stage of the process is independent of the acid concentration.

a) Interpretation of the order of the reaction according to Vermilyea's theory. According to Vermilyea's theory,[72] the mechanism of the dissolution of oxides is electrochemical, and

consists of two parallel reactions involving the transfer of H^+ and M^{z+} ions from the oxide to the solution. Substituting Eqn.(23) into Eqn.(21) shows that the rate of removal of the cations (M) will be:

$$i_M = a_{H^+}^{\beta_+ z_+/(\beta_+ z_+ - \beta_- z_-)} \cdot k_-^{\beta_+ z_+/(\beta_+ z_+ - \beta_- z_-)} / k_+^{\beta_- z_-/(\beta_+ z_+ - \beta_- z_-)} \quad (40)$$

Table 3. Formal order of the reaction for the dissolution of metal oxides with respect to hydrogen ions (n_{H^+}) and acid (n_{HA}).

Oxide	Electrolyte	n_{H^+}	Oxide	HA	n_{HA}
MgO	HCl	0.47 [167]	Fe_2O_3	HCl	1.94 [18]
Fe_2O_3	HCl	0.5÷0.6 [48]	Fe_2O_3	H_2SO_4	0.56 [18]
Fe_2O_3	H_2SO_4	0.5÷0.6 [48]	Fe_2O_3	HF	1.06 [18]
Fe_2O_3	HNO_3	0.5÷0.6 [48]	Fe_2O_3	H_3PO_4	0.59 [18]
Fe_2O_3	$HClO_4$	0.5÷0.6 [48]	Fe_3O_4	HCl	2 [18]
Fe_3O_4	HCl	0.5 [31]	BeO	HCl, H_2SO_4, $H_2C_2O_4$	1 [154]
BeO	HCl	0.47÷0.53 [154]	MnO	H_2SO_4	2 [160]
BeO	H_2SO_4	0.68÷0.70 [154]	Fe_2O_3	HCl	2 [161]
V_2O_5	$HClO_4$	0.5 [155]	Fe_3O_4	HCl	3 [161]
Cr_2O_3	$HClO_4$	0.46 [156]	Fe_2O_3	HCl	2.4 [162]
Mn_2O_3	H_2SO_4	−0.5 [157]	NiO	H_2SO_4, HNO_3	1.0±0.1 [163]
α-Fe_2O_3	HNO_3	0.65 [158]	Ni_2O_3	H_2SO_4, HNO_3	1.0±0.1 [163]
Ni_2O_3	H_2SO_4	0.5±0.2 [159]	NiO, Ni_2O_3	HCl	0.6±0.1 [163]
MnO	H_2SO_4	0.5 [160]	CuO	H_2SO_4	1.0±0.1 [163]

Note. Numbers in square brackets denote references (Ed. of Translation).

Table 4. Dependence of the formal orders of the reaction with respect to H^+ ions (n_{H^+}) on the nature of the stage limiting the dissolution of the metal oxide*.

Limiting stage	n	ν	z_-	$z_+ = 1$	$z_+ = 2$	$z_+ = 3$	$z_+ = 4$
$OH^- + H^+ \rightarrow HOH$	1	1	−1	1/2	2/3	3/4	4/5
$O^{2-} + H^+ \rightarrow OH^-$	1	1	−2	1/3	1/2	3/5	2/3
$O^{2-} + 2H^+ \rightarrow HOH$	2	1	−2	2/3	1	6/5	4/3

*The orders were calculated using the equations:[2]

$$i_{M^{z+}} = k_{H^+}^{n/\nu\left(\frac{\beta_+ z_+}{\beta_+ z_+ - \beta_- z_-}\right)} = i_{OH^-} = k_{H^+}^{n/\nu\left(\frac{\beta_- z_-}{\beta_+ z_+ - \beta_- z_-}\right)}$$

Table 4 gives the values of the formal orders of the reactions with respect to H^+ for different limiting stages. Eqn. (40) does not make it possible to explain the formal order of the reaction with respect to other ions (Fe^{2+}, Ni^{3+}, Cu^+, Mn^{2+}) influencing the rate of dissolution of the corresponding oxides. In the derivation of Eqn.(40) it was assumed that the quantity E is a compromise potential, and that reactions (21) and (22) are far from equilibrium. According to the experimental data, however, the potential jump should be regarded as quasi-equilibrium.

b) Determination of the formal order of a reaction with respect to the ions for the dissolution of metal oxides, on the basis of the proton theory. It is possible to find how the formal orders with respect to the ions change with change in the nature of the potential-determining reaction. If the magnitude of the potential

$$E = E^0 + \frac{RT}{F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} = \frac{RT}{F} \ln \left\{ \frac{[Fe^{3+}]}{[Fe^{2+}]} \exp\left(\frac{E^0 F}{RT}\right) \right\} \quad (41)$$

of iron oxides is determined by the reaction $Fe^{3+} + e \rightarrow Fe^{2+}$, the rate of dissolution can be found by substituting Eqn.(41) in Eqn.(35) for $\beta_+ = 0.5$, $z_+ = 1$, $m = 0.5$:

$$\left(\frac{\partial \alpha}{\partial t}\right)_{sp} = k a_{H^+}^m a_{Fe^{2+}}^{(1-\beta_+)z_+} a_{Fe^{3+}}^{-(1-\beta_+)z_+} = k a_{H^+}^{0.5} a_{Fe^{2+}}^{0.5} a_{Fe^{3+}}^{-0.5} \quad (42)$$

It follows from Eqn.(42) that the rate of dissolution of iron oxides increases with increase in the concentration of H^+ and Fe^{2+} ions (the formal order of the reaction with respect to Fe^{2+} is 0.5 ± 0.1, and that with respect to Fe^{3+} is −0.5 ± 0.1.[153] If the potential

$$E = E_x^0 + \frac{RT}{F} \ln (a_{H^+}^{x/(x-1)} / a_{Mn^{2+}}^{[2(x-1)]^{-1}})$$

is determined by the reaction

$$MnO_x + 2(x-1)e + 2xH^+ \rightarrow Mn^{2+} + xH_2O \quad (43)$$

reversible with respect to metal and hydrogen ions, it follows from Eqns.(25) and (43) that¶

$$k_i = k a_{H^+}^{m - x(1-\beta_+)z_+/(x-1)} \cdot a_{Mn^{2+}}^{(1-\beta_+)z_+/2(x-1)}$$

The formal order of the reaction with respect to H^+ and Mn^{2+} ions depends on the stoichiometric composition of the oxide. For $x = 1.5$ in MnO_x, the formal order of the reaction with respect to H^+ is −0.5, and that with respect to Mn^{2+} is +0.5. For $x = 2.0$, the formal orders of the reaction with respect to these ions are +0.1 and +0.25 respectively. The rate of dissolution of the oxide depends on x, and the reaction rate constant has a minimum value for $x \cong 2$. Expressions for determining the formal order with respect to the ions H^+ and M^{z+} for other versions of the potential-determining reactions are given below:

$$\frac{x_2}{x_1 - x_2} MO_{x_1} + M^{z+} + ze \rightarrow \frac{x_1}{x_1 - x_2} MO_{x_2} \quad (III)$$

$$MO_x + 2xH^+ + 2(x - z/2)e \rightarrow M^{z+} + xH_2O \quad (IV)$$

Reaction	n_{H^+}	$n_{M^{z+}}$
(III)	m	$-\frac{(1-\beta_+)z_+}{z}$
(IV)	$m - \frac{(1-\beta_+)z_+ x}{(x - z/2)}$	$\frac{(1-\beta_+)z_+}{2(x - z/2)}$

c) The influence of the anionic composition of the electrolyte and complex formation on the specific rate of dissolution of oxides in acidic media and complexones. The addition of anions to an electrolyte and the formation of stable complexes increases the rate of the dissolution of metal oxides. The extraction of cuprite into H_2SO_4 is more rapid than that into $HClO_4$,[168] since the sulphate complex of copper(II) is more stable than the perchlorate complex. A study of the dissolution of α-iron(III) oxide in mineral acids[19,48] showed that the formal orders with respect to the anions are 0.72 for Cl^-, 0.35 for SO_4^{2-}, 0.30 for NO_3^-, and 0.02 for ClO_4^-. The rate of dissolution can be represented in the form:[19]

$$d[Fe^{3+}]/dt = k[H^+]^{0.5}[A^{z-}]^m$$

A study of the influence of EDTA and hydroxyethylidenediphosphonic acid (HEDP) on the rate of dissolution of iron and manganese oxides established that complex formation leads to an increase in the intensity of the process. The logarithm of the rate constant for the dissolution of Fe_3O_4 or Fe_2O_3 increases linearly with increase in the logarithm of the

¶ At a constant potential, $n_{H^+} = m$, and the order of the reaction with respect to Mn^{2+} is equal to zero. 0.

stability constant of the complex of iron(III) with the anion of the electrolyte.[19] This agrees with data obtained by other workers.[153,154,168]

The more rapid extraction of BeO [154] and dissolution of titanium minerals[169] in H_2SO_4, compared with hydrochloric acid, indicates that the anions influence the kinetics of these processes, and is due to the ability of the SO_4^{2-} anions to form more stable complexes with beryllium and titanium ions. The influence of anions on the potential and the rate of the dissolution of UO_2 has been discussed.[30] The rate of dissolution of the oxides NiO, Ni_2O_3, and CuO in complexones, which form stable complexes with metal ions, however, decreases with increase in the ligand concentration.

There are two approaches to the explanation of the influence of anions on the dissolution of metal oxides.

The mechanism of the conjugated influence of cations and anions. According to the theory proposed by Vermilyea,[12,72] the increase in the rate of the dissolution of oxides under the influence of anions and complex formation is due to an increase in the ease of removal of cations from the crystal lattice of the oxide, in accordance with equations reflecting both the adsorption and reaction of ligands with the metal ion:

$$[M(OH)_n]^{(z_+-n)+}(\text{solid}) + p\,A^{q-}(\text{ads}) \rightleftarrows [M(OH)_n(A^{q-})_p]^{(z_+-n-qp)+}(\text{solid})$$

and to the subsequent transfer of the resulting complex to the solution

$$[M(OH)_n(A^{q-})_p]^{(z_+-n-qp)+}(\text{solid}) \rightarrow [M(OH)_n(A^{q-})_p]^{(z_+-n-qp)+}(\text{aq})$$

where A^{q-} is an anion with charge $q-$, A^{q-}(ads) represents anions adsorbed on the oxide phase, p is the coordination number of the metal ion, and n the number of OH^- ions coordinated to the M^{z+} ion.

The dependence of the rate of dissolution of the oxide on the concentration of protons and anions for the complex

$$[M(OH)_n(A^{q-})_p]^{(z_+-n-qp)+}$$

according to Vermilyea[72] will be:

$$i = k a_{H^+}^{\frac{\beta_+(z_+-n-qp)}{\beta_+(z_+-n-qp)-\beta_-z_-}} \cdot a_{A^{q-}}^{-\frac{\beta_-z_-qp}{\beta_+(z_+-n-qp)-\beta_-z_-}} \qquad (44)$$

Eqn.(44) gives the theoretical order of the reaction with respect to H^+ and A^{q-} ions. The available published data are given in Table 5.

Vermilyea's theory has made it possible only to establish the relationship between the stability constant of the complex formed by the metal cation with the ligand and the rate of dissolution of the oxide. This theory requires further development, since there are experimental data which it does not explain.

1) According to Vermilyea's ideas,[19,48] the limiting stage of the process reduces to the removal of a cation from the lattice (that is when the values of E are displaced into the positive range, the rate of the dissolution of the oxide should increase), whereas it has been established experimentally† that the rate of the process is limited by the removal of oxygen (OH group) or by the introduction of a proton into the oxide phase (since a displacement of the potential into the cathodic range increases the rate of dissolution of most oxides).

2. For the oxides Fe_2O_3, Fe_3O_4, MnO_2, MnO, and Mn_2O_3, the addition of the corresponding cations (strong reducing agents, Fe^{2+}, Mn^{2+}) to the acid increases the rate of dissolution of the oxide phase,[31,160,166] which is not consistent with the theory being discussed, since the species adsorbed is not the anion (in accordance with Vermilyea's ideas), but the cation.[48]

3. The theory does not explain the decrease in the rate of the dissolution of manganese and iron oxides in acidic media when MnO_4^-, $Cr_2O_7^{2-}$, and other anions which are oxidising agents with respect to Fe^{2+} and Mn^{2+} ions respectively are added to the electrolyte.

4. The theory does not explain the decrease in the rate of the dissolution of various oxides (CuO, Cu_2O, NiO, Ni_2O_3) with increase in the concentration of Complexones (EDTA, HEDP).

5. In Vermilyea's opinion, a strong complex-forming reagent such as 1,10-phenanthroline should increase the rate of the dissolution of the oxide phase, whereas experimentally, a decrease in the rate of the dissolution of iron oxide (Fe_3O_4, Fe_2O_3) is observed when this reagent is added to the solution.

The electron–proton mechanism of the influence of anions and complex formation. According to this mechanism, the influence of anions and complex formation reduces to a change in the value of E for the oxide electrode. Since at the surface of separation between the phases the value of the potential is determined by the reaction

$$M^{z+}A + e \rightarrow M^{(z-1)+}A$$

it follows that displacements of the potential into the cathodic region and into the anodic region are observed, depending on the nature of the ligand A.

Table 5. Theoretical values of the orders of the reaction with respect to hydrogen ions (n_{H^+}), anions (n_{Aq^-}), and the species whose transfer limits the rate of dissolution of metal oxides.[12]

Oxide	n_{H^+}	n_{Aq^-}			
		ClO_4^-	Cl^-	SO_4^{2-}	NO_3^-
$Fe_2O_3 \cdot nH_2O$	0.50	0.02; $Fe(OH)_2^+$	0.72; $FeCl_2^+$	0.35; $FeSO_4^+$	0.30; $Fe(OH)NO_3^+$, $Fe(NO_3)_2^+$
$Cr_2O \cdot 3.6H_2O$	0.46	~0; $Cr(OH)_2^+$	0.27; $Cr(OH)Cl^+$, $CrCl_2^+$	0.29; $CrSO_4^+$	—
$NiO \cdot nH_2O$	0.56	~0; $NiOH^+$	—	—	—

† There is other evidence that the limiting stage reduces to the transfer of a proton to the oxide phase (see p.1048).

In aqueous EDTA solutions, the magnitude of the standard redox potential of the reaction $Fe^{III}(EDTA) + e \rightarrow Fe^{II}(EDTA)$ is +0.14 V,[170] whereas for the systems containing 1,10-phenanthroline, the value of E is +1.2 V (at pH 0).[171] These ligands form stable complexes with iron ions. It is assumed that $pK_{Fe^{II}L} = 14.26$, $pK_{Fe^{III}L} = 25.1$, and $pK_{Fe(phen)_3^{2+}} = 21.3$.

Experimentally, different effects are observed (with increase in the ligand concentration, an increase in the rate of the dissolution of the oxide is observed for EDTA, and a decrease is observed for 1,10-phenanthroline), proving that the potential of the medium plays a decisive role in the kinetics of the dissolution of the oxide phase.

The increase in the rate of the dissolution of iron oxide with change in the anion composition of the electrolyte in the order: $HClO_4 < HNO_3 < HBr < H_2SO_4 < HCl < H_3PO_4 < HF$ [19,53] is due to the change in the magnitude of the potential[153]

$$E = E^0 + \frac{RT}{F}\ln\frac{[Fe^{III}]_{total}}{[Fe^{II}]_{total}} + \frac{RT}{F}\left(\ln\frac{1}{\gamma_{ox}} - \ln\frac{1}{\gamma_{red}}\right)$$

of the reaction $Fe^{III}A + e = Fe^{II}A$, which limits the transfer of protons from the acid solution to the oxide (Fe_2O_3).[174] Substituting Eqn.(44) in Eqn.(35) shows that the rate of the dissolution of iron(III) oxide is given by an expression of the form

$$k_i = k a_{H^+}^{n_i} a_{Fe(II)}^{(1-\beta_+)z_+} a_{Fe(III)}^{-(1-\beta_+)z_+}\left[\sum_{n=0}^{q}(K_{red})_n[A]^n \Big/ \sum_{i=0}^{q}(K_{ox})_i[A]^i\right]^{-(1-\beta_+)z_+} \quad (45)$$

$$\frac{1}{\gamma_{ox}} = \sum_{i=0}^{q}(K_{ox})_i[A]^i;\ (K_{ox})_0 = 1;\ \frac{1}{\gamma_{red}} = \sum_{n=0}^{q}(K_{red})_n[A]^n;\ (K_{red})_0 = 1$$

where γ_{ox} and γ_{red} are the fractions of the iron(II) and iron(III) ions not combined in the complex, and K_{ox} and K_{red} are the stability constants of the complexes formed by the Fe^{3+} and Fe^{2+} ions respectively.

It follows from Eqn.(45) that for $z_+ = 1$ and $\beta_+ = 0.5$, the rate constant (k_i) is linearly dependent on the difference between the stability constants of the complexes of Fe^{III} and Fe^{II} with the anion of the electrolyte. The calculated values of the orders of the reaction with respect to the ions Fe^{2+}, Fe^{3+}, and H^+ agree with the experimental values. The experimental data obtained are given in Table 6.[153]

Complexones, which displace the stationary value of E into the cathodic range, facilitate the dissolution of oxides (Mn_2O_3, MnO_2, Fe_3O_4, Fe_2O_3, etc.). The greater the difference ($pK_{Fe^{III}(EDTA)} - pK_{Fe^{II}(EDTA)} = 10.74$ [175]), the greater the rate of the dissolution of iron oxide. The reason for the decrease in the rate of the dissolution of copper and nickel oxides with increase in the concentration of Complexones in the solution is that these ligands displace the potentials of the oxide electrodes into the cathodic range. To increase the rate of the dissolution of these oxides, it is necessary to displace the potential into the anodic range. The electron–proton mechanism makes it possible to explain all the experimentally observed regular kinetic features of the dissolution of metal oxides.

4. The Influence of the Preparation of the Specimen and the Experimental Conditions

The kinetics of the dissolution of oxides are influenced by the method used to prepare the specimens,[176] the nature of the defects,[107] the state of the surface,[177] and the adsorption of ions from the solutions.[107] The dissolution of NiO in sulphuric acid shows an induction period,[107] the duration of which increases with increase in the time for which the specimen is kept in air, and this can be related to a change in both the quantity of defects and the electrical conductivity of the specimen. With increase in the oxygen pressure, the induction period for the dissolution of nickel(II) oxide decreases, due to an increase in the number of Ni^{3+} vacancies. In the dissolution of the oxides of copper, iron, and nickel, the addition of oxidising agents (MnO_4^-, $Cr_2O_7^{2-}$) and reducing agents (Fe^{2+}, I^-) to the electrolyte solution changes the duration of the induction period.[31,109,176] In the presence of these ions, which show oxidising properties in an acidic medium, the concentration of the defects (Ni^{3+}) in NiO decreases. The sites corresponding to the intersection of dislocations on the surface of the crystals represent the centres at which the dissolution process begins. The rate of the dissolution of NiO and Fe_2O_3 decreases with increase in the temperatures at which the specimens are heated from 700 °C to 1000 °C, since thermal treatment decreases the number of defects and leads to a decrease in the effective surface area of dissolution.[107,178,179]

The anisotropy of the dissolution of metal oxides. Polycrystalline specimens are characterised by orientational non-uniformity of the properties, so that a change in the nature of the kinetic curve with time is sometimes related to the non-uniformity of the dissolution of the surface of the specimen. This situation is observed in the dissolution in acid of TiO_2,[180] FeOOH,[181] Fe_2O_3,[182,183] and Al_2O_3.[184] Each plane of α-Al_2O_3 crystals is characterised by a definite form and orientation of the etch pits.[185]

The basal plane (0001) of α-Al_2O_3 and α-Fe_2O_3 is extracted into acids much more rapidly than the other planes.[4] The etch figures are determined by the crystal defects, depend on the anion composition of the solution and on the nature of

Table 6. Dependence of the kinetic parameters of the dissolution of iron(III) oxide on the nature of the acid (at 50 °C).

Acid	$t_{0.5}$, min	α_{max}	$E_{Fe(III)A/Fe(II)A}$, V (Ref.174)	Eqn. (46)	Eqn. (48)			
				$10^7 k_i$, cm min^{-1}	$10^7 k_i$, cm min^{-1}	$10^{-2} k_g$, cm^{-2}min^{-1}	$10^{-3} A$	$\tau_{0.5}$
HF	246	0.25	0.55	126	103.7	122.30	5.0	0.17
H_3PO_4	360	0.12	0.59	86	33.3	49.49	63.0	0.08
HCl	522	0.15	0.64	59.3	28.7	21.67	32.0	0.10
H_2SO_4	1 860	0.21	0.68	16.6	11.3	2.67	10.0	0.14
HBr	4 200	0.30	0.75	7.4	7.9	0.37	2.0	0.22
$HClO_4$	30 000	0.15	0.78	1.03	0.5	0.38	32.0	0.10

Note. $t_{0.5}$ is the time required for the dissolution of half of the oxide specimen; the rate constant (k_i) according to Eqn.(42) was calculated for 1 M acid solutions; $\tau_{0.5}$ is a quantity proportional to the time taken for the reaction to proceed to the extent $\alpha = 0.5$ ($\tau_{0.5} = k_i t_{0.5}$).

the acid, and show different geometries, depending on the orientation of the face.[4] The rate of the dissolution of a polycrystalline specimen depends on the relationship between its dimensions and the magnitude of the granules of which it is made up.[186] The chemical etching of crystals has established[187,188] that there is an increased reactivity at the dislocation sites. Studies carried out in this direction have been reviewed.[126]

5. Dependence of the Nature of the Dissolution on the Character of the Chemical Bond in Oxides and on the Presence of Additives

The processes associated with the dissolution of oxides (see Fig. 3) can be divided into three classes:[2]

1) non-oxidative dissolution (BeO, CdO, Al_2O_3);

2) the dissolution of oxides (CuO, NiO, UO_2) accelerated by oxidation processes[30,107–110] and anodic polarisation;[30, 107,110]

3) the dissolution of oxides (Fe_2O_3, MnO_2) accelerated by reduction processes[31] and cathodic polarisation.[152]

The dissolution of metal oxides in acids is a multi-stage process. The limiting stage may be a solid-phase process[189,190] or a reaction in the electrolyte solution (as shown for zinc oxide[191]). In an oxide with ionic bonds, the dissolution takes place by a solid-phase mechanism. The transfer of ions to the electrolyte solution in this case takes place without a change in the oxidation state of the cations and anions. The presence of additives and impurities in these oxides has little influence on the rate of their dissolution. The addition of the oxides Li_2O or Al_2O_3 to ZnO does not change the rate of their dissolution in HCl.[192]

In oxides with more covalent bonding, the presence of additives influences the rate of dissolution. The addition of Li^+ ions to NiO leads to an increase in the rate of the dissolution of the specimen, due to an increase in the electrical conductivity of this oxide.[107,149,193] The increase in electrical conductivity[193,194] leads to an increase in the exchange current of the potential-determining reaction and an increase in the rate of the diffusion of H^+ into the oxide. A similar effect is observed when Ti^{4+} ions are added to Fe_2O_3.[193]

For the dissolution of ionic crystals (BeO, ZnO) in H_2SO_4, the properties of the solution play a more important role than the properties of the solid phase. In the dissolution of covalent oxides, the structure of the solid phase (volume charge, different surface states, and also specific adsorption) determines the chemistry of the dissolution.

6. Influence of the Temperature of the Electrolyte on the Rate of the Dissolution of Oxides

The study of the influence of temperature on the dissolution of oxides in acids has established that the rate of the dissolution increases considerably with increase in the temperature of the electrolyte. The activation energy of the process reaches ~80–90 kJ mole^{-1} (see Table 7), which coincides with that obtained for the solid-phase reduction of iron oxides using H_2, CO, and other reagents as reducing agents.[206,207] The order of magnitude of these quantities is close to that of the activation energy of the diffusion of a proton into the oxide phase.[208] The high activation energy of the dissolution is due to heterogeneous processes whose limiting stage lies in the kinetic range.[20,31,153,209] The nature of the limiting stage remains unchanged with increase in the temperature of the electrolyte.

VII. MODELS DESCRIBING THE CHANGE IN THE SURFACE AREA OF THE DISSOLVING PARTICLE

The increase in the rate of the dissolution of oxides with time is attributed to a change in the magnitude of the surface area of the specimen as a result of etching. For the interpretation of the change in the kinetics of the process with time, it is possible to put forward a number of models which

Table 7. Effective activation energies (E_a, kJ mole^{-1}) of the dissolution of metal oxides in acid solutions.

Oxide	Acid	E_a	Oxide	Acid	E_a	Oxide	Acid	E_a	Oxide	Acid	E_a
Fe_2O_3	HCl	95.8 [4]	Fe_2O_3	H_2SO_4	91.6 [19]	Fe_2O_3	HNO_3	76.1 [19]	Fe_2O_3	$HClO_4$	80.3 [19]
NiO	HCl	72.0 [109]	Ni_2O_3	HCl	70.3 [109]	Fe_2O_3	HCl	113.0 [162]	Cu_2O	H_2SO_4	54.4 [163]
Cu_2O	H_2SO_4	96.2 [163]	CuO	H_2SO_4	54.4 [163]	CuO	H_2SO_4	96.2 [163]	Ni_2O_3	H_2SO_4	143.5 [176]
Fe_2O_3	HCl	90.4 [180]	Fe_2O_3	$HClO_4$	87.0 [180]	Fe_2O_3	HCl	41.8 [195]	Fe_2O_3	H_2SO_4	53.6 [195]
Fe_2O_3	HNO_3	44.4 [195]	Fe_2O_3	H_2SO_4	87.9 ± 4.2 [196]	Fe_2O_3	HF	51.5 [197]	TiO	H_2SO_4	62.8 [198]
Ti_2O_3	H_2SO_4	87.9 [198]	Ti_3O_5	H_2SO_4	75.3 [198]	Al_2O_3	HCl	47.3 [199]	Al_2O_3	HNO_3	47.7 [199]
Cr_2O_3	HF	43.1 [199]	Cr_2O_3	H_2SO_4	47.7 [200]	Cr_2O_3	8 *M* H_2SO_4 + + 40% acetone	35.1 [200]	ZnO	HCl	37.8 [201]
Mn_2O_3	H_2SO_4	78.7 [202]	NpO_2	$HClO_4$	77.0 [203]	UO_2	H_2SO_4	75.3 [204]	$TiO_{0.8}$	H_2SO_4	75.7 [205]
$TiO_{0.8}$	H_2SO_4	72.0 [205]	$TiO_{0.8}$	H_2SO_4	56.9 [205]	$TiO_{0.8}$	H_2SO_4	55.6 [205]	$TiO_{0.9}$	H_2SO_4	89.1 [205]
$TiO_{0.9}$	H_2SO_4	65.7 [205]	$TiO_{0.9}$	H_2SO_4	55.6 [205]	$TiO_{0.9}$	H_2SO_4	92.5 [205]	$TiO_{0.9}$	H_2SO_4	49.0 [205]
$TiO_{0.9}$	H_2SO_4	77.0 [205]	$TiO_{1.0}$	H_2SO_4	85.4 [205]	$TiO_{1.0}$	H_2SO_4	80.8 [205]	$TiO_{1.0}$	H_2SO_4	55.2 [205]
$TiO_{1.0}$	H_2SO_4	49.0 [205]	$TiO_{1.1}$	H_2SO_4	159.0 [205]	$TiO_{1.1}$	H_2SO_4	80.8 [205]	$TiO_{1.1}$	H_2SO_4	61.5 [205]
$TiO_{1.1}$	H_2SO_4	59.8 [205]	$TiO_{1.2}$	H_2SO_4	190.4 [205]	$TiO_{1.2}$	H_2SO_4	79.5 [205]	$TiO_{1.2}$	H_2SO_4	60.7 [205]
$TiO_{1.2}$	H_2SO_4	98.3 [205]	$TiO_{1.3}$	H_2SO_4	63.6 [205]	$TiO_{1.3}$	H_2SO_4	94.6 [205]	—	—	—

Note. Numbers in square brackets denote references (Ed. of Translation).

describe the development of the reaction front during the reaction of the specimen with the electrolyte and which make it possible to determine the explicit form of the function $f(\alpha)$ (1). It is of interest to discuss the general regular features of the dissolution of oxide particles when they are present continuously in the suspended state in the reaction vessel and are subjected to the action of the electrolyte. The change in the surface area during the dissolution of oxides is described by different relationships, depending on the original geometry of the specimens. If the original oxide can be represented in the form of a flat plate (electrode), and its dissolution takes place uniformly, the fraction of dissolved substance will change linearly with time: $\alpha = k_i t / r_0$.

The explicit form of this function has not yet been established for the case where the magnitude of the surface changes non-uniformly during the dissolution.

If the particle has a spherical shape, the time dependence of the fraction of the dissolved oxide will be described by the following equations:

$$1-(1-\alpha)^{1/3}=\frac{k_i t}{r_0}\,;\quad \frac{\partial\alpha}{\partial t}=(k_i/r_0)(1-\alpha)^{2/3} \qquad (46)$$

These equations were derived with the assumption that uniform dissolution of the particle takes place; usually, however, the dissolution of the particles of the oxide specimen is non-uniform. One of the formal heterogeneous models which shows the development of a non-uniform reaction front during the reaction of a particle with an acid is described below.

Kinetic theories of the dissolution of oxides taking account of the formation of active centres on the surface of spherical oxide phases are based on the applicability of the mathematical apparatus proposed by Delmon and Mampel.[210] According to this theory, the rate of dissolution is determined by two parameters: the rate constant for the production of nuclei, that is the active centres of the dissolution (k_g), and the rate constant for their dissolution (k_i). A relationship between α and t has been proposed.[210] The volume of a spherical particle with radius r_0 is equal to the sum of the volumes of layers which have a thickness dx and which are situated at a distance x from the surface. The volume of one dissolving layer is $\beta(x, t)$ and represents the sum of the dissolved volumes of each sphere, divided by the original volume $\frac{4}{3}\pi r_0^3$:

$$\alpha=\int_0^{r_0}\frac{3(r_0-x)^2}{r_0^3}\beta(x,t)\,\mathrm{d}x=\frac{3}{r_0}\int_0^{r_0}\left(1-\frac{x}{r_0}\right)^2\beta(x,t)\,\mathrm{d}x \qquad (47)$$

From the theory of heterogeneous kinetics, the value of $\beta(x, t)$ will be determined by the Poisson relationship[211]

$$\beta(x,t)=1-\exp(-S\gamma)$$

where $\gamma = r_0^2 k_g/(r_0 - x)^2 = N(\theta, x)$ is the number of dissolution centres produced on the surface of spheres with radius $(r_0 - x)$ at moment of time θ; and

$$S=\pi\left(\frac{r_0-x}{r_0}\right)[k_i^2(t-\theta)^2-x^2]$$

is the surface area of a dissolved segment with radius $(r_0 - x)$. Using the new parameters

$$A=4\pi r_0^3 k_g/k_i;\ \tau=k_i/r_0 t;\ \xi=x/r_0$$

Eqn.(47) can be reduced to the form:

$$\alpha=1-(1-\tau)^3-3\int_0^{\tau}(1-\xi)^2\exp\left(-\frac{A}{12}\,\frac{\tau^3-3\xi^2\tau+2\xi^3}{1-\xi}\,\mathrm{d}\xi\right) \qquad (48)$$

Eqn.(48) does not have an analytical solution. The kinetic parameters are calculated using the tabulated values of this function for different values of τ and A.[210] The calculation of the quantities k_i and k_g reduces to the determination of $\tau_{0.5}$, A, and $t_{0.5}$. The determination of A reduces to the superposition of the graph of the experimental data, constructed on coordinates $\alpha - (t - t_l)/(t_{0.5} - t_l)$, on the network of theoretical curves (on the same coordinates) for different values of A. The value of A (tabulated values[210]) is used to find $\tau_{0.5}$ for $\alpha = 0.5$.[210] The values of k_i and k_g are determined using the equations

$$k_i=r_0\frac{\tau_{0.5}}{t_{0.5}-t_l}\,;\quad k_g=Ak_i/4\pi r_0^3$$

Usually, k_i is much smaller than k_g, that is the process is limited by the rate of the dissolution of each active centre. As $A \to \infty$, the dependence of α on t is described by the expression used to analyse the kinetics of the dissolution of oxides:

$$1-(1-\alpha)^{1/3}=k_i t/r_0$$

The proton theory of dissolution, taking account of the formation of active nuclei in the volume of spherical oxide particles. To explain the anomalously rapid dissolution of oxides, there is another theory, according to which an increase in the number of active centres (nuclei) in the volume of an oxide takes place as a result of diffusion of H atoms.[166] During dissolution, filamentary branching of the nuclei is observed in a direction perpendicular to the surface of the specimen. Two stages of the process are distinguished: the production of the nuclei and their dissolution.[166,212] In front of the moving surface of the oxide/electrolyte interface there are nuclei (N_0) whose activation requires that they react with the adsorbed hydrogen diffusing from the surface of the oxide phase. The active centres are usually formed at dislocation sites. The hydrogen atoms can diffuse along the dislocations into neighbouring centres, forming new active centres (N).[212] These assumptions agree with data on the adsorption of protons and their subsequent diffusion into the volume of an oxide phase, and with the ideas developed by Lukovtsev and co-workers.[120]

The relationship between α and t was found from the following considerations:

a) the rate of formation of the nuclei $(\partial N/\partial t)_\theta$ is directly proportional to the product of the number of potential centres $(N_0 - N)$ existing at a given moment of time θ and the apparent degree of transformation, with allowance for their overlap and absorption (αf):[213]

$$\partial N/\partial t=k(N_0-N)\alpha_f=-k(N_0-N)\ln(1-\alpha) \qquad (49)$$

where αf is related to the actual degree of transformation α (in accordance with the Poisson equation) by the relationship

$$\alpha_f=-\ln(1-\alpha)=\int_0^t S(\theta,x)N(0,x)\,\mathrm{d}\theta$$

where $N(\theta, x)$ is the number of active centres on unit surface area of the sphere (at moment of time θ), observed at a depth x from the surface of the oxide; and $S(\theta, x)$ is the size of the segment cut out by the active centre in the sphere situated on the oxide surface;

b) the rate of dissolution of oxides is directly proportional to the product of the number of active centres and the unreacted fraction of the oxide $(1 - \alpha)$ (and not simply $\partial\alpha/\partial t = kN$, as given by Prout and Tomkins):[214]

$$\partial\alpha/\partial t = kN(1-\alpha) \quad \text{or} \quad \partial\alpha_f/\partial t = k_1 N \tag{50}$$

Assuming that the potential centres are in a large excess, Eqns.(49) and (50) can be used to find α_f:

$$\partial\alpha_f/\partial t = kN$$
$$\partial N/\partial t = k_1 N_0 \alpha_f \quad \text{or} \quad \partial^2\alpha_f/\partial t^2 - k_1 k N_0 \alpha_f = 0 \tag{51}$$

The solution of the differential equation (51) is the function

$$\alpha_f = A \operatorname{sh} k_i t$$

This gives an equation of the form:

$$-\ln(1-\alpha) = A \operatorname{sh}(k_i t); \quad \partial\alpha/\partial t = A k_i (1-\alpha)[A^2 + \ln^2(1-\alpha)]^{1/2} \tag{52}$$

where $k_i = (k_1 k N_0)^{1/2}$.

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The quantitative comparison, carried out in the present review, of the factors influencing the rate of the dissolution of metal oxides in acids has revealed the decisive role of the proton and electron concentration gradients (potential) on the kinetics of this process. The knowledge of the kinetics and mechanism of the dissolution of oxide phases has now reached a state in which future progress will depend on obtaining further details of the description of electrochemical processes at the oxide/solution interfaces.

The mechanism of the dissolution of a metal oxide and the nature of the limiting stage have still been insufficiently studied. The classical theories of the dissolution of ionic crystals require further development, since they do not yet make it possible to explain the influence of complexones on the kinetics of the dissolution of semiconducting oxides (CuO, NiO, Ni_2O_3, and other oxide specimens); moreover, for the great majority of metal oxides, the nature of the potential-determining reactions at the surface of separation between the solid and liquid phases has not yet been explained.

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