JOURNAL OF MATERIALS SCIENCE 15 (1980) 237–246

Mechanism of dissolution of MgO crystals in acids

K. SANGWAL
Department of Physics, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat State, India

A simple model of dissolution of MgO crystals in acids involving chemical reactions and adsorption process on the crystal surface is used to derive expressions connecting rates of surface dissolution and selective etching with concentration, temperature and nature of an acid and with surface orientation. The experimental data of the dependence of etch rates of MgO on various etching parameters are then compared with the theory. The effect of acid viscosity and concentration are also briefly analysed and compared with the experimental observations. It is argued that the experimental results can be understood on the basis of the proposed mechanism if adsorption of the reactants and the complexes formed during dissolution on a perfect surface and at dislocation sites is taken into consideration. It is concluded that the adsorption processes play an important role in the formation of good, contrasting dislocation etch pits.

1. Introduction

The dissolution rate of MgO crystals depends on the nature, temperature and concentration of an acid and on the surface orientation [1–4]. The values of the activation energy and the pre-exponential factor of the dissolution process are frequently found to be dependent on the nature and concentration of an acid [1–3]. The activation energy remains constant while the pre-exponential factor of dissolution changes markedly from one surface to another [4]. Strong (HNO_3, HCl and H_2SO_4) and weak (CH_3COOH, C_2H_5COOH and $C_6H_8O_7$) acids produce etch pits at fresh and old dislocations, but only dilute solutions of moderately weak acids (H_3PO_4 and HCOOH) form etch pits at old dislocations [1–4].

According to the theory of two-dimensional dissolution [5], the dissolution rate is given by

$$v_s = d\nu_s \exp\left[-\Delta G_s^*/kT\right] \qquad (1)$$

where d is the depth of a unit pit, ν_s the frequency factor of the order of the Debye frequency and ΔG_s^* the free energy change associated with the formation of a unit pit in a perfect surface of the crystal. Taking the depth of the unit pit as a, $1.3a$ and $1.15a$ (where $a = 4.2 \times 10^{-8}$ cm) on $\{1\,0\,0\}$, $\{1\,1\,0\}$ and $\{1\,1\,1\}$ faces, $\nu_s = 10^{13}\ \text{sec}^{-1}$, and multiplying by the product of the density of MgO and (60×60), we have the values of the pre-exponential factor of the surface dissolution as $5.8 \times 10^9\ \text{g cm}^{-2}\,\text{h}^{-1}$, $7.3 \times 10^9\ \text{g cm}^{-2}\,\text{h}^{-1}$ and $6.7 \times 10^9\ \text{g cm}^{-2}\,\text{h}^{-1}$ for $\{1\,0\,0\}$, $\{1\,1\,0\}$ and $\{1\,1\,1\}$ faces of MgO, respectively.

The free energy change $\Delta G_s^* = \pi\gamma' d r_s^*$ [6], where γ' is the specific free energy of a molecule going from the solid to the solution and r_s^* the radius of the critical nucleus. Taking the typical values of $r_s^* = d/2$ and $\gamma' = \gamma/2$ as in the case of LiF [6], we have

$$\Delta G_s^* = \pi\gamma d^2/4. \qquad (2)$$

Here γ is the specific surface free energy of the crystal in vacuum. Substituting the reported values [7] of γ, one obtains a value for ΔG_s^* of 1.0 and 3.8 eV for $\{1\,0\,0\}$ and $\{1\,1\,0\}$ faces of MgO, respectively.

The theory of two-dimensional nucleation therefore yields values of the pre-exponential factor and the activation energy which are very much higher than the experimental values [1–3]. The theory also does not give a satisfactory explanation for the concentration dependence of

0022–2461/80/010237–10$03.00/0

the pre-exponential factor, or for the constancy of the activation energy for different planes.

Recently a treatment of the dissolution process from a consideration of chemical reactions has been advanced to explain the anisotropy of the dissolution of quartz [8]. Though this treatment explains several features of the etching of quartz, it neither gives an estimate of the activation energy nor considers adsorption processes taking place on the crystal surface during dissolution.

In this paper a theory of dissolution of MgO crystals in acids is formulated and the experimental data reported so far analysed.

2. Model for dissolution

The dissociation of monobasic acids, for example HCl, HNO_3, HCOOH, CH_3COOH, etc., into a hydrogen ion, H^+, and an anion, An^-, is complete in only one step which corresponds to only one value of the dissociation constant, k_c. A polybasic acid, such as H_2SO_4, H_3PO_4, $(COOH)_2$, etc., dissociates in steps and a different and lower dissociation constant corresponds to the detachment of each H^+ ion. Invariably the first step dissociation constant is far greater than the following steps dissociation constants [9]. Consequently a polybasic acid may be considered as HAn. If n_H, n_{An} and n_a are the concentrations (number of molecules/ions cm^{-3}) of H^+, An^- and HAn, respectively, and α is the degree of dissociation of HAn, then $n_H = n_{An} = \alpha n_a$.

We assume that dissolution of MgO on the crystal–etchant interface involves the following consecutive steps:

(1) Availability of H^+ and An^- ions on the surface.

(2) Capture and migration of H^+ and An^- ions on the surface.

(3) Formation of a complex.

(4) Adsorption of the complex onto the surface.

(5) Formation of an activated complex on the surface.

(6) Adsorption of the activated complex.

(7) Dissociation of the activated complex into reaction products.

(8) Adsorption of the reaction products on the surface.

(9) Transport of the reaction products into the etchant.

Steps 1 and 9 of the transport of the reacting and reacted species are determined by the diffusion kinetics, while the other steps may be regarded to be limited by the reaction rate between the acid and the solid. Denoted Mg by M, the sequence of the etching process may be written as:

$$2\text{MO} + 2\text{H}^+ + 2\text{An}^- \rightarrow \text{MO}\colon\begin{matrix}\cdot\text{H}^+\\ \cdot\text{H}^+\end{matrix} + \begin{matrix}\text{An}^-\cdot\\ \text{An}^-\cdot\end{matrix}\colon\text{MO} \tag{3}$$

$$\text{MO}\colon\begin{matrix}\cdot\text{H}^+\\ \cdot\text{H}^+\end{matrix} + \begin{matrix}\text{An}^-\cdot\\ \text{An}^-\cdot\end{matrix}\colon\text{MO} \rightarrow \underset{\text{(unadsorbed)}}{\text{MO}\colon\begin{matrix}\cdot\text{H}...\text{An}\cdot\\ \cdot\text{H}...\text{An}\cdot\end{matrix}\colon\text{MO}} \tag{4}$$

$$\underset{\text{(unadsorbed)}}{\text{MO}\colon\begin{matrix}\cdot\text{H}...\text{An}\cdot\\ \cdot\text{H}...\text{An}\cdot\end{matrix}\colon\text{MO}} \rightarrow \underset{\text{(adsorbed)}}{\text{MO}\colon\begin{matrix}\cdot\text{H}...\text{An}\cdot\\ \cdot\text{H}...\text{An}\cdot\end{matrix}\colon\text{MO}} \tag{5}$$

$$\underset{\text{(adsorbed)}}{2\text{MO}\colon\begin{matrix}\cdot\text{H}...\text{An}\cdot\\ \cdot\text{H}...\text{An}\cdot\end{matrix}\colon\text{MO}} \rightarrow \underset{\text{(activated)}}{2\text{MO}\colon\begin{matrix}\cdot\text{H}...\text{An}\cdot\\ \cdot\text{H}...\text{An}\cdot\end{matrix}\colon\text{MO}^*} \tag{6}$$

$$\underset{\text{(activated)}}{2\text{MO}\colon\begin{matrix}\cdot\text{H}...\text{An}\cdot\\ \cdot\text{H}...\text{An}\cdot\end{matrix}\colon\text{MO}^*} \rightarrow 2\text{MAn}_2 + 2(\text{MO}\cdot\text{H}_2\text{O}) \tag{7}$$

3. Rate of surface dissolution

Let m_H and m_{An} be the masses of H^+ and An^- ions, respectively. Assuming that the velocity of the ions in dilute and concentrated solutions changes with T as in ideal gases, the numbers n_1 and n_2 of H^+ and An^- ions striking the surface ($cm^{-2}\,sec^{-1}$) are

$$n_1 = n_H\left(\frac{3kT}{m_H}\right)^{1/2}$$

$$n_2 = n_{An}\left(\frac{3kT}{m_{An}}\right)^{1/2} \tag{8}$$

If the number of captured pairs of H^+ ions on the surface is n_3, E_1 the energy required for the capture and migration of a pair of H^+ ions, then the change in the Helmholtz free energy is given by

$$\begin{aligned} F &= E - TS \\ &= n_3E_1 - kT\ln\left[\left(\frac{n_1!}{(n_1-n_3)!\,n_3!}\right)^2\right]. \end{aligned} \tag{9}$$

Using Stirling's formula $\ln x! = x\ln x - x$, the logarithmic term can be written as

$$\ln\left[\frac{n_1!}{(n_1-n_3)!\,n_3!}\right] \simeq n_1 \ln n_1 - (n_1-n_3) \times \ln(n_1-n_3) - n_3 \ln n_3 .$$

When equilibrium is attained, the Helmholtz free energy is constant. Therefore

$$\left(\frac{\partial F}{\partial n_3}\right) = 0 = E_1 - 2kT[\ln(n_1-n_3) - \ln n_3] = E_1 - 2kT \ln[(n_1-n_3)/n_3] .$$

Assuming $n_1 \gg n_3$, the above equation can be written as

$$n_3 = n_1 \exp[-E_1/(2kT)] \qquad (10)$$

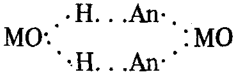
If ϕ_1 is a function which allows for the adsorption of a pair of H^+ ions onto the surface and Z the number of free pairs of bonds on the surface, then the number n_3 of the adsorbed pairs of H^+ ions on the surface may be written as†

$$n_3 = \frac{\phi_1}{Z} n_1 \exp[-E_1/(2kT)] = \frac{\phi_1 n_{\mathrm{H}}}{Z} (3kT/m_{\mathrm{H}})^{1/2} \exp[-E_1/(2kT)] . \qquad (11)$$

Similarly if ϕ_2 is another adsorption function and E_2 is the energy required for the capture and migration of a pair of An^- ions, then the number n_4 of the captured pairs of An^- ions is

$$n_4 = \frac{\phi_2 n_{\mathrm{An}}}{Z} (3kT/m_{\mathrm{An}})^{1/2} \exp[-E_2/(2kT)] . \qquad (12)$$

If E_3 is the energy required for the formation of a complex



$$\mathrm{MO}\!:\!\begin{array}{c}\cdot\mathrm{H}\ldots\mathrm{An}\cdot\\ \\ \cdot\mathrm{H}\ldots\mathrm{An}\cdot\end{array}\!:\!\mathrm{MO}$$

the change in the Helmholtz free energy produced by the formation of n_5 complex molecules is

$$F = n_5 E_3 - kT \ln \frac{n_3!}{(n_3-n_5)!\,n_5!} \cdot \frac{n_4!}{(n_4-n_5)!\,n_5!} .$$

Substituting the solution of the factorial terms, obtained as before by using Stirling's formula, and differentiating with respect to n_5, at equilibrium from the above equation we get

$$\left(\frac{\partial F}{\partial n_5}\right) = 0 = E_3 - kT \ln \frac{(n_3-n_5)(n_4-n_5)}{n_5^2} .$$

For $n_3 \gg n_5$ and $n_4 \gg n_5$, this equation may be rearranged in the form

$$n_5 = n_3^{1/2} n_4^{1/2} \exp[-E_3/(2kT)] = \frac{(\phi_1 \phi_2 n_{\mathrm{H}} n_{\mathrm{An}} 3kT)^{1/2}}{Z m_{\mathrm{H}}^{1/4} m_{\mathrm{An}}^{1/4}} \times \exp\{-[\tfrac{1}{4}(E_1+E_2) + (E_3/2)]/kT\} . \qquad (13)$$

If E_4 is the energy of adsorption of a complex molecule on the surface, the number n_6 of the adsorbed molecules on the surface is

$$n_6 = n_5 \exp[-E_4/(kT)] \qquad (14)$$

If n_{Mg} is the density of Mg^{2+} and O^{2-} ions on a surface, the number density n_7 of the adsorbed complex molecules on the surface is

$$n_7 = n_6/n_{\mathrm{Mg}} = \frac{(\phi_1 \phi_2 n_{\mathrm{H}} n_{\mathrm{An}} 3kT)^{1/2}}{Z n_{\mathrm{Mg}} m_{\mathrm{H}}^{1/4} m_{\mathrm{An}}^{1/4}} \times \exp\{-[\tfrac{1}{4}(E_1+E_2) + \tfrac{1}{2}E_3 + E_4]/kT\} . \qquad (15)$$

If E_5 is the energy required for the formation of an activated complex, the number density n_8 of the activated complex on the surface is

$$n_8 = n_7 \exp[-E_5/(2kT)] = \frac{(\phi_1 \phi_2 n_{\mathrm{H}} n_{\mathrm{An}} 3kT)^{1/2}}{Z n_{\mathrm{Mg}} m_{\mathrm{H}}^{1/4} m_{\mathrm{An}}^{1/4}} \times \exp\{-[\tfrac{1}{4}(E_1+E_2) + \tfrac{1}{2}E_3 + E_4 + \tfrac{1}{2}E_5]/kT\} . \qquad (16)$$

If δ is the interval along the potential barrier over which the activated complex passes before dissociating with a frequency [9]

$$\nu = \frac{1}{\delta}\left(\frac{kT}{2\pi\mu}\right)^{1/2}$$

into reaction products, the number n_9 of the activated complex molecules that can dissociate is

$$n_9 = n_8 \nu = \frac{n_8}{\delta}\left(\frac{kT}{2\pi\mu}\right)^{1/2} .$$

---

†Corresponding to a high value of Z, adsorption of acid ions is expected to be more. But once equilibrium is attained the number of adsorbing ions decreases with increasing Z as a result of the repulsion of like charges accumulated on the surface. However, the dependence need not be simple as has been assumed.

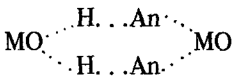
If E_6 is the energy of dissociation of an activated complex molecule into products, the number n_{10} of the formation of a pair of MAn_2 molecules is

$$n_{10} = n_9 \exp[-E_6/(2kT)]$$
$$= \frac{n_8}{\delta}\left(\frac{kT}{2\pi\mu}\right)^{1/2} \exp[-E_6/(2kT)]. \quad (17)$$

In the above equations μ is the reduced mass of the activated complex, given by [9]

$$\mu = m_1/2 \quad (18)$$

where m_1 is the mass of the complex



$$\begin{array}{ccc} & \mathrm{H}\ldots\mathrm{An} & \\ \mathrm{MO} & & \mathrm{MO} \\ & \mathrm{H}\ldots\mathrm{An} & \end{array}$$

of which the activated complex is composed.

If d is the height of a dissolution step, the surface dissolution rate is

$$v = dn_{10} = \frac{dn_8}{\delta}\left(\frac{kT}{2\pi\mu}\right)^{1/2} \exp[-E_6/(2kT)]$$
$$= \frac{d(\phi_1\phi_2 n_{\mathrm{H}} n_{\mathrm{An}} 3kT)^{1/2}}{Z\delta n_{\mathrm{Mg}} m_{\mathrm{H}}^{1/4} m_{\mathrm{An}}^{1/4}}\left(\frac{kT}{2\pi\mu}\right)^{1/2} \times$$
$$\exp\{-[\tfrac{1}{4}(E_1+E_2)+\tfrac{1}{2}E_3+E_4$$
$$+\tfrac{1}{2}(E_5+E_6)]/(kT)\} \quad (19)$$

Taking $\phi_1\phi_2 = \phi^2$, $n_a = N_A c$, where N_A is the Avogadro number, c the acid concentration as a molarity and $m_{\mathrm{An}}/m_{\mathrm{H}} = r_{\mathrm{m}}$, we may write the dissolution rate as

$$v = \frac{d\phi N_A \alpha c}{Z\delta n_{\mathrm{Mg}} r_{\mathrm{m}}^{1/4}}\left(\frac{3kT}{m_{\mathrm{H}}}\frac{kT}{2\pi\mu}\right)^{1/2} \times$$
$$\exp\{-[\tfrac{1}{4}(E_1+E_2)+\tfrac{1}{2}E_3+E_4$$
$$+\tfrac{1}{2}(E_5+E_6)]/(kT)\}. \quad (20)$$

If ΔE_s is the heat of adsorption of the activated complex on a perfect surface, the dissolution rate is

$$v_s = v \exp[\Delta E_s/(kT)]$$
$$= \frac{d\phi N_A \alpha c}{Z\delta n_{\mathrm{Mg}} r_{\mathrm{m}}^{1/4}}\left(\frac{3kT}{m_{\mathrm{H}}}\frac{kT}{2\pi\mu}\right)^{1/2} \exp[\Delta E_s/(kT)]$$
$$\times \exp\{-[\tfrac{1}{4}(E_1+E_2)+\tfrac{1}{2}E_3+E_4$$
$$+\tfrac{1}{2}(E_5+E_6)]/(kT)\}. \quad (21)$$

Taking $\delta = 10^{-9}$ cm, $d = fa = f \times 4.2 \times 10^{-8}$ cm, $N_A = 6 \times 10^{23}$, $\mu^{1/2} = 10$ (Table I), $r_{\mathrm{m}}^{1/4} = 3$ (Table II), $n_{\mathrm{Mg}} = r_f n_{\mathrm{Mg}}(1\,0\,0) = r_f \times 1.1322 \times 10^{15}\ \mathrm{cm}^{-2}$, $\Delta E_s = 4\ \mathrm{kcal\,mol}^{-1}$ (equal to the heat of adsorption of a complex [10]), we obtain

$$v_s = \frac{28.4 f\phi\alpha c}{Z r_f} \exp\{-[\tfrac{1}{4}(E_1+E_2)+\tfrac{1}{2}E_3+E_4$$
$$+\tfrac{1}{2}(E_5+E_6)]/(kT)\} \quad (22)$$

in cm sec^{-1}. Here r_f is the ratio of the concentration of Mg^{2+} ions on a face to that on the $\{1\,0\,0\}$ face, and f the ratio of the depth of a unit pit on a face under consideration to the depth of the pit on the $\{1\,0\,0\}$ face. Multiplying Equation 22 by the density of MgO and (60 × 60), we have the dissolution rate, in g cm^{-2} h^{-1}, as

$$v_s = A_s \exp[-E_s/(kT)] \quad (23)$$

where

$$A_s = 3.66 \times 10^5 \frac{f\phi\alpha c}{Z r_f} \quad (24)$$

and

$$E_s = [\tfrac{1}{4}(E_1+E_2)+\tfrac{1}{2}E_3+E_4+\tfrac{1}{2}(E_5+E_6)].$$

Since $E_5 + E_6 = \Delta H^0$ the heat of formation of the reactants (i.e. the heat of the reaction) is given by

$$E_s = [\tfrac{1}{4}(E_1+E_2)+\tfrac{1}{2}E_3+E_4+\tfrac{1}{2}\Delta H^0]. \quad (25)$$

TABLE I Reduced mass of some adsorbed complexes (mass of MgO = 40.3)

Complex	m_1	$\mu = m_1/2$	$\mu^{1/2}$
2MgO HCl	153.6	76.8	8.76
2MgO $\mathrm{HNO_3}$	206.6	103.3	10.16
2MgO $\mathrm{HSO_4}$	276.6	138.3	11.76
2MgO $\mathrm{H_2PO_4}$	276.6	138.3	11.76
2MgO $\mathrm{HCO_2}$	172.6	86.3	9.29
2MgO $\mathrm{CH_3CO_2}$	200.6	100.3	10.01
2MgO $\mathrm{C_2H_5CO_2}$	228.6	114.3	10.69
2MgO $\mathrm{H(CO_2)_2}$	260.6	130.3	11.41
2MgO $\mathrm{HCO_2(CHOH)_2CO_2}$	380.6	190.3	13.79
2MgO $\mathrm{(CO_2H)_2CH_2C(OH)CH_2CO_2}$	464.6	232.3	15.24

TABLE II Values of $r_m^{1/4}$ of some ions

Ion	$r_m^{1/4}$	Ion	$r_m^{1/4}$
Cl^-	2.45	$CH_3CO_2^-$	2.75
NO_3^-	2.80	$C_2H_5CO_2^-$	2.90
HSO_4^-	3.12	$H(CO_2)_2^-$	3.08
$H_2PO_4^-$	3.12	$HCO_2(CHOH)_2CO_2^-$	6.20
HCO_2^-	2.60	$CO_2HCH_2C(OH)CH_2CO_2^-$	6.63

4. Etch rates at dislocation

Lattice defects act as adsorption-active centres by virtue of their different adsorption potential [9]. If the energies involved at a dislocation site are denoted by E', from Equation 22 the dissolution rate at a defect site can be given as

$$v_d = 3.66 \times 10^5 \frac{f\phi\alpha c}{Zr_f} \times \exp\{-[\tfrac{1}{4}(E_1' + E_2') + \tfrac{1}{2}E_3' + E_4' + \tfrac{1}{2}(E_5' + E_6')]/(kT)\}.$$

Since $E_5 + E_6 = \Delta H^0 = E_5' + E_6' + \Delta H_d^0$ for a heterogeneous catalytic process [9],

$$v_d = 3.66 \times 10^5 \frac{f\phi\alpha c}{Zr_f} \exp[\Delta H_d^0/(2kT)] \times \exp\{-[\tfrac{1}{4}(E_1' + E_2') + \tfrac{1}{2}E_3' + E_4' + \tfrac{1}{2}\Delta H^0]/(kT)\}.$$

Taking a typical value of the heat of desorption, ΔH_d^0, of the complex at a dislocation site equal to the heat, E_4, of adsorption of the complex, the above expression may be written as

$$v_d = A_d \exp[-E_d/(kT)] \tag{26}$$

with

$$A_d = 2.0 \times 10^7 \frac{f\phi\alpha c}{Zr_f} \tag{27}$$

and

$$E_d = [\tfrac{1}{4}(E_1' + E_2') + \tfrac{1}{2}E_3' + E_4' + \tfrac{1}{2}\Delta H^0] \tag{28}$$

5. Diffusion-controlled dissolution

When a crystal is placed in a reactant, a diffusion layer of thickness, δ_f, develops at the solid–liquid interface. If v_1 and v_2 are the true and apparent dissolution rates on the surface, c_1 and c the concentrations of the acid on the surface and in the bulk, and β the diffusion rate constant, the apparent dissolution rate is expressed by [9]:

$$\frac{1}{v_2} = \frac{[(v_1/\beta)c_1^m + c_1]^n}{c_1^m v_1}. \tag{29}$$

Here n and m are the true and apparent orders of the reaction on the surface. The concentrations c and c_1 are related by the expression

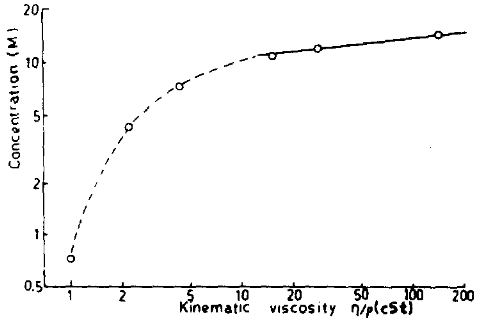


Figure 1 Graph showing the relationship between kinematic viscosity, η/ρ (cSt), and concentration c (M) of H_3PO_4 [11].

$$c = \frac{v_1}{\beta} c_1^m + c_1 \tag{30}$$

The dependence of viscosity on concentration at high values of the latter is of the form $c = k_1(\eta/\rho)^{n'}$ (Fig. 1) and $\beta = \eta/\rho\delta_f$, assuming that $\delta_f = k_2 c^{n''}$. Here k_1, k_2, n' and n'' are constants and η and ρ the viscosity and density of the etchant. In terms of c and η/ρ, Equation 29, using Equation 30, may be written in the form

$$\log v_2 = (1 - n - n'' - 1/n)\log c + (1/n)\log k_1 + \log k_2$$

$$\log v_2 = (n' - n'n'' - 1)\log(\eta/\rho) + (1 - n + n'')\log k_1 + \log k_2. \tag{31}$$

6. Comparison with experimental data

Equations 24 and 27 show that A_s and A_d grow with f, α and c and decrease with Z and r_f. Equations 25 and 28 show that the values of E_s and E_d depend on the energies of adsorption of H^+ and An^- ions and of the complexes on the surface and at dislocations. Consequently, we can treat A's and E's separately.

6.1. Pre-exponential factor

For the {100} face of MgO crystals, $f = 1$, $Z = 1$ and $r_f = 1$. Thus Equations 24 and 27 reduce to

$$A_s = 3.66 \times 10^5 \phi\alpha c$$

$$A_d = 2.0 \times 10^7 \phi\alpha c. \tag{32}$$

The dependence of pre-exponential factors of dissolution for HCl, HNO_3, H_2SO_4, H_3PO_4 and HCOOH is similar (Fig. 2) following the relation

$$A = A_0(\alpha c^2)^{0.1} \tag{33}$$

where A denotes the pre-exponential factor for

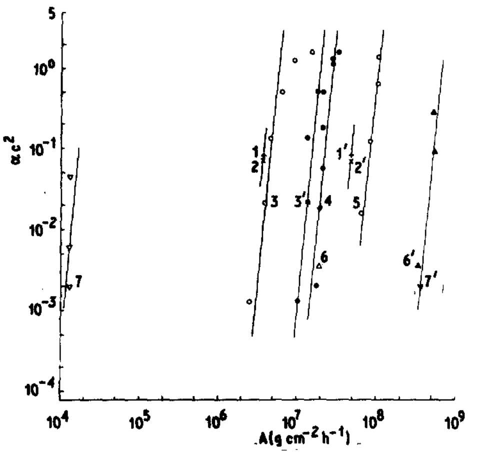


Figure 2 Plots of αc^2 versus pre-exponential factors A_s and A_d ($g\,cm^{-2}\,h^{-1}$) of surface dissolution (curves 1 to 7) and selective etching along the surface (curves 1'–7'). 1 and 1', HNO_3; 2 and 2', HCl; 3 and 3', H_2SO_4; 4, H_3PO_4; 5 and 5', HCOOH; 6 and 6', CH_3COOH and 7 and 7', C_2H_5COOH.

dissolution of the surface as well as at dislocation sites, and A_0 a constant corresponding to the value of the pre-exponential factor at $\log(\alpha c^2) = 1$. A_0 is related to the degree of dissociation, α, of an acid (Fig. 3) by the equations

$$A_{0s} = 3.0 \times 10^6 \alpha^{-1}$$

$$A_{0d} = 1.0 \times 10^7 \alpha^{-1} \qquad (34)$$

for surface dissolution and selective etching, respectively. Thus

$$A_s = 3.0 \times 10^6 \alpha^{-0.9} c^{0.2}$$

$$A_d = 1.0 \times 10^7 \alpha^{-0.9} c^{0.2} \qquad (35)$$

Equations 32 and 35 are fairly well in agreement if

$$\phi = 1/(\alpha^{1.9} c^{0.8}) \qquad (36)$$

According to the Freundlich isotherm [9], the surface coverage of the adsorbate

$$\theta = \frac{\alpha'}{m'} \exp(\Delta S_a m' T) \cdot c^{m'RT} \qquad (37)$$

where α' is the surface concentration of the occupied sites on the surface, m' is a constant and ΔS_a the increase in the entropy of adsorption; obviously $\phi = 1/\theta$. Since the Freundlich isotherm is applicable for adsorption up to one monomolecular thickness and in our case $m'RT = 0.8$, it follows that the adsorption involved in the dissolution of MgO in dilute HCl and HNO_3 and at all concentrations of H_2SO_4, H_3PO_4 and HCOOH is of less than monomolecular thickness.

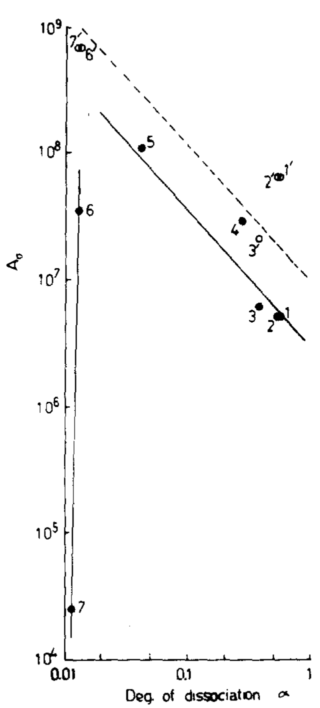


Figure 3 Dependence of A_0 (see text) on degree of dissociation α: 1 and 1', HNO_3; 2 and 2', HCl; 3 and 3', H_2SO_4; 4, H_3PO_4; 5 and 5', HCOOH; 6 and 6', CH_3COOH; 7 and 7', C_2H_5COOH. Points 1 to 7, lower curve, for surface dissolution and 1' to 7', upper curve, for selective etching.

In the case of dissolution in dilute CH_3COOH and C_2H_5COOH

$$A_s = 7.0 \times 10^{101} \alpha^{50.1} c^{0.2}.$$

Comparing this with Equation 32, one gets

$$\phi = 1.9 \times 10^{96} \alpha^{49.1} c^{-0.8} \qquad (38)$$

whence

$$\theta = c^{0.8}/(1.9 \times 10^{96} \alpha^{49.1}) \qquad (39)$$

This indicates that though here also $m'RT = 0.8$, θ is a complicated function of α unlike in other acids.

6.2. Activation energy of dissolution

From Equations 25 and 28 it follows that knowing the values of $[\frac{1}{4}(E_1 + E_2) + \frac{1}{2}E_3 + E_4]$, $[\frac{1}{4}(E_1' + E_2') + \frac{1}{2}E_3' + E_4']$ and ΔH^0, E_s and E_d may be estimated. At somewhat higher HCl concentrations, the values of $[\frac{1}{4}(E_1' + E_2') + \frac{1}{2}E_3']$ and E_4' for MgO have been computed to be 0.17 eV and 0.15 eV [10]. Although $[\frac{1}{4}(E_1 + E_2) + \frac{1}{2}E_3]$ may be taken to be equal to $[\frac{1}{4}(E_1' + E_2') + \frac{1}{2}E_3']$, E_4 remains unknown. Therefore E_s cannot be

TABLE III Heat of formation and activation energies of surface dissolution and selective etching of MgO in some acid solutions

Acid	ΔH^0 (kcal mol^{-1})	E_d (eV) Estimated	E_d (eV) Observed	E_s (eV)
HCl	34.90	1.07	0.68	0.59 0.55
HNO_3	34.89	1.07	0.68	0.59
H_2SO_4	34.89	1.07	0.65	0.59
H_3PO_4	122.54	2.96	–	0.62

estimated. Substituting the typical values of $[\frac{1}{4}(E_1'+E_2')+\frac{1}{2}E_3']$ and E_4', and the values of ΔH^0 from the literature [12], the calculated E_d for some acids is given in Table III. The experimentally observed values of E_d and E_s in dilute solutions of the acids are also listed in the table.

It may be noted that the observed E_d values for HCl, HNO_3 and H_2SO_4 are about two-thirds of the calculated values. It also appears that the expected experimental E_d in the case of H_3PO_4 should be far smaller than the calculated value. This disagreement indicates the formation of still heavier activated complexes. Further, the heat of formation of phosphates changes in the sequence:

ortho- > monortho- > diortho-phosphate.

Since in our calculations we have used the heat of formation of $Mg_3(PO_4)_2$ in place of $Mg(H_2PO_4)_2$, the observed greater discrepancy is natural.

The values of activation energy of dissolution at low and high concentrations of some acids are observed [3] to be comparatively high. Since the heat of adsorption, $[\frac{1}{4}(E_1+E_2)+\frac{1}{2}E_3]$, of H_2O is higher than that of HCl and HNO_3, a higher activation energy at low concentrations is expected (cf. Equations 25 and 28). The heat of adsorption at monomolecular thicknesses is larger than that involved in polymolecular adsorption [13], therefore the increased activation energy at very high acid concentrations could be due to the setting-in of only monolayer adsorption.

Since the change in the energy of physical adsorption on different faces is negligible, Equations 25 and 28 also indicate that the activation energy does not change appreciably from one surface to another. Experimental results on the selective etching of different faces of MgO corroborate this inference.

6.3. Energy of a dislocation and adsorption

From Equations 25 and 28

$$[\tfrac{1}{4}(E_1'+E_2')+\tfrac{1}{2}E_3'-\tfrac{1}{4}(E_1+E_2)-\tfrac{1}{2}E_3] -(E_4'-E_4) = E_d-E_s.$$

Since for physical adsorption

$$[\tfrac{1}{4}(E_1'+E_2')+\tfrac{1}{2}E_3'] \simeq [\tfrac{1}{4}(E_1+E_2)+\tfrac{1}{2}E_3]$$

the difference in the energies of dissolution may be attributed mainly to the difference in the energy of adsorption of the complex on the surface and at a dislocation site. Therefore

$$(E_4'-E_4) = (E_d-E_s) = \frac{1}{p}E_c \qquad (40)$$

where $1/p$ is a proportionality constant which signifies the extent of adsorption at a dislocation site, and E_c dislocation energy. The experimentally obtained values of (E_d-E_s) and the corresponding $1/p$ using $E_c = 1.3$ eV [14] are given in Table IV.

The energy of adsorption of a complex non-polar molecule is the sum of the adsorption energy of the groups constituting it [13]. Therefore the energy of adsorption of the molecules of acetic, propionic and citric acids at dislocation sites may be supposed to be relatively high. Consequently, these acids produce good etch pits on the {100} face of MgO crystals [3, 15]. The significance of $1/p$ is therefore clear: the higher the value of $1/p$, the better is the revelation of etch pits (Table IV).

6.4. Surface orientation effects

Assume that the adsorption factor ϕ follows the same relationship, expressed by Equations 36 and 38 on different crystallographic planes. Then two cases arise, namely, when the effects of free bonds are either significant or insignificant. Using Equations 24 and 27 the expected anisotropy in the two cases may be obtained (Table V). Thus the pre-exponential factor changes in the sequence {100} > {111} > {110} and {100} > {110} > {111} in the cases when the effects of free bends are insignificant and significant, respectively.

The observed relative rates of dissolution [4] in H_2SO_4 and H_3PO_4 are given in Table VI. From Tables V and VI, the effect of the number of free bonds on dissolution in 4N H_2SO_4 and in 2.21 and 44.1 N H_3PO_4 is obvious. In concentrated H_2SO_4 the free bond effect is negligible.

TABLE IV Relationship between the estimated values of dislocation core energy E_c, $(E_d - E_s)$, $1/p$ and pit formation at dislocation sites

Acid	Reference	E_s (eV)	E_d (eV)	$(E_d - E_s)$ (eV)	$1/p$	Remarks on pit dimensions at dislocations	Nature of etching
HCl	[3]	0.55	0.68	0.13	0.10	s†	Deep etch pits at fresh, shallow pits at old dislocations
	[2]	0.59	0.68	0.09	0.07	s + e	
HNO_3	[2]	0.59	0.68	0.09	0.07	s + e	Deep etch pits at fresh, shallow pits at old dislocations
H_2SO_4	[2]	0.59	0.65	0.06	0.05	s + e	Deep etch pits at fresh, shallow pits at old dislocations
HCOOH	[3]	0.65	0.70	0.05	0.04	o	Shallow pits at old dislocations
CH_3COOH	[3]	0.66	0.81	0.15	0.12	s	Deep pits at old and fresh dislocations
C_2H_5COOH	[3]	0.47	0.76	0.29	0.22	s	Deep pits at old and fresh dislocations

†s = screw, e = edge and o = old dislocations.

TABLE V Calculated relative pre-exponential factors of different faces

Face	{100}	{110}	{111}
n_{Mg}	1.1322×10^{15}	0.8006×10^{15}	0.8716×10^{15}
f	1	1.3	1.15
Relative A_s for $Z = 1$	1	1.8	1.5
Relative A_s for $Z = 1, 2, 3$	1	0.9	0.5

TABLE VI Relative etch rates and pre-exponential factors of dissolution in some acids

Etchant	Temperature °C	{100}	{110}	{111}
Polishing				
4 N H_2SO_4	23	1	0.77	0.75
36 N H_2SO_4	23	1	1.38	1.38
2.21 N H_3PO_4	23	1	0.91	1.36
	65	1	0.68	0.68
44.1 N H_3PO_4	65	1	0.57	0.75
Selective etching				
4 N H_2SO_4	†	1	0.54	0.75
36 N H_2SO_4	†	1	1.54	2.46

†Ratio of pre-exponential factors of dissolution between 20 and 80° C.

6.5. Effect of acid concentration and viscosity on dissolution rate

Equation 31 shows that the dissolution rate of a diffusion-controlled process is independent of the reaction rate at the surface, and that it depends only on c and η/ρ. Since $n < 1$ [1, 2] and $n' < 1$ (Fig. 1), for a simple case when $n'' = 1$, we have

$$\log v_2 = -K_1 \log c + \log K_2$$

$$\log v_2 = -K_1' \log (\eta/\rho) + \log K_2' \qquad (41)$$

where K's are constants. This equation shows that dissolution rate decreases with an increase in c and η/ρ. Experiments [2, 4] bear out this inference.

The temperature dependence of η/ρ follows an

TABLE VII Etch pits and pyramids on $\{100\}$ MgO surfaces and the corresponding concentrations, degree of dissociation and entropy of adsorption in different acids

Acid	Concentration (M)	Degree of dissociation α	ΔS_a (kcal mol^{-1} K^{-1})	Observed etching behaviour
HNO_3	0.1	5.66×10^{-1}	− 8.10	⟨110⟩ pits
	8.0	9.00×10^{-2}	− 11.60	⟨100⟩ pits and also pyramids
HCl	0.1	5.22×10^{-1}	− 8.26	⟨110⟩ pits
	8.0	6.70×10^{-2}	− 12.16	⟨100⟩ pits and also pyramids
H_2SO_4	0.1	3.58×10^{-1}	− 8.97	⟨110⟩ pits
	4.5	6.45×10^{-2}	− 12.23	⟨100⟩ pits and pyramids
	9.0	4.60×10^{-2}	− 12.87	⟨100⟩ pits and pyramids
	18.0	3.28×10^{-2}	− 13.51	⟨100⟩ pits and hillocks
H_3PO_4	0.1	2.81×10^{-1}	− 9.43	⟨100⟩ pits
	3.0	6.00×10^{-2}	− 12.37	⟨100⟩ pits and pyramids
	13.2	2.85×10^{-2}	− 13.78	pyramids
HCOOH	0.1	4.11×10^{-2}	− 13.08	⟨100⟩ pits
	3.0	7.95×10^{-3}	− 16.21	pyramids
	22.0	2.24×10^{-3}	− 18.6	pyramids
CH_3COOH	0.1	1.31×10^{-2}	− 15.85	⟨100⟩ pits and also pyramids
	9.0	1.39×10^{-3}	94.29	⟨100⟩ pits
C_2H_5COOH	0.1	1.15×10^{-2}	− 9.46	⟨100⟩ pits
	9.0	1.22×10^{-3}	100.69	⟨100⟩ pits

Arrhenius-type equation. Therefore if the plots of $v_{s,d}$ versus $1/T$ and of η/ρ versus $1/T$ give identical values of activation energy, dissolution may be taken as diffusion-controlled.

From a study of overall (surface) dissolution of MgO in concentrated H_2SO_4 the activation energy of dissolution was observed to be approximately equal to that of viscosity decrease, but that corresponding to selective etching was relatively high [4]. This indicates that though the dissolution process at the surface is diffusion-controlled, the local reactivity at dislocations may still render it partly or fully chemically-controlled. Hence while inferring the nature of rate-limiting kinetics from the dependence of selective etch rate on $1/T$ one should be cautious.

6.6. Etch pits and pyramids

The etching behaviour [1–3, 16] of the acids used in our analysis is summarized in Table VII. Clearly etch pits are formed in many acid solutions, while etch pyramids are formed in concentrated HCl, HNO_3, moderately concentrated H_2SO_4 and in H_3PO_4 and HCOOH in a wide concentration range.

Using Equations 36 and 37, we have

$$m'RT = 0.8 \qquad (42)$$

$$\alpha^{1.9} = \frac{\alpha'}{m'} \exp\left(\Delta S_a m' T\right) \qquad (43)$$

at $T = 300\,\mathrm{K}$, $m' = 1.33 \times 10^{-3}$. Substituting the values of T and m', and arbitrarily taking $\alpha' = 1$, Equation 43 reduces to

$$\alpha^{1.9} = 1.12 \times 10^{3}\, e^{\Delta S_a} \qquad (44)$$

Obviously ΔS_a is a function of α. Substituting the values of α corresponding to the concentrations given in Table VII, ΔS_a may be estimated (Table VII).

Similarly, using Equations 37 and 39, one obtains

$$\alpha^{-49.1} = 2.13 \times 10^{99}\, e^{\Delta S_a}. \qquad (45)$$

Substituting the values of α for CH_3COOH and C_2H_5COOH, the ΔS_a values here may also be obtained (Table VII).

Since we are dealing with adsorption where the heat of adsorption is always positive. Consequently, ΔS_a should also be positive. This is contrary to our expectation. Even in a very dilute solution, ΔS_a turns out to be negative. The reason

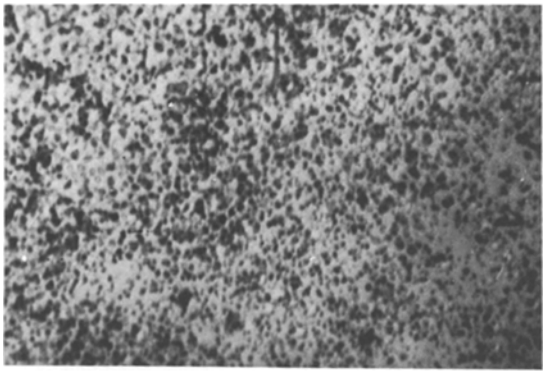


Figure 4 Etch pyramids formed by 0.87 N CH_3COOH at 27.5° C after $5\frac{1}{2}$ h (× 150).

for this is associated with the assumption that $\alpha' = 1$. In an ideal acid solution where the degree of dissociation $\alpha \approx 1$ it can be shown (cf. Equation 44) that for $\Delta S_a = 0$, the concentration of the occupied sites $\alpha' \approx 0.1\%$. For smaller values of α which is usually the case, α' should still be smaller in the case of acids other than CH_3COOH and C_2H_5COOH. Without investigating further this aspect of α', some interesting features of the etching process can, nevertheless, be noted on the basis of the trend of the change of entropy of adsorption alone.

With an increase in the concentration of HNO_3, HCl, H_2SO_4, H_3PO_4 and HCOOH, pyramids, ⟨100⟩ pits, circular pits and ⟨110⟩ pits are formed in that order. In CH_3COOH at very low concentrations ill-defined rounded ⟨100⟩ pits are formed, but on prolonged etching pyramids are produced (Fig. 4). At high concentrations of CH_3COOH and in C_2H_5COOH, ⟨100⟩ pits are produced. Table VII shows these results in terms of the increase in entropy of adsorption. With increasing entropy of adsorption in an acid, pyramids, ⟨100⟩ pits, circular pits and ⟨110⟩ pits are formed in that order. A relatively large change in the adsorption entropy in the case of CH_3COOH and C_2H_5COOH in the same concentration range can also be the cause of the formation of contrasting etch pits in concentrated solutions of these acids.

7. Conclusions

(1) The application of activated complex theory in conjunction with the adsorption of reacting species and complexes on MgO surfaces provides a fairly satisfactory explanation of the dependence of dissolution rates at surface and at dislocation sites on the temperature, concentration and nature of an acid and on the surface orientation of MgO crystals.

(2) The dissolution process is accompanied by physical adsorption of the reactants and the complexes (also activated complex). In dilute solutions of acids the adsorption corresponds to a layer of less than monomolecular thickness. The formation of pits and pyramids is associated with the adsorption process.

Acknowledgements

The author is pleased to thank his colleagues, particularly Professor R. C. Bhandari, Professor A. R. Patel, Dr S. K. Arora and Dr T. C. Patel, for their criticism of an earlier version of the manuscript and for several suggestions, which have significantly contributed to the shaping of the paper in its present form. He is also grateful to Shri P. G. Salvi for typing the manuscript.

References

1. K. SANGWAL and T. C. PATEL, *Kristall und Technik* 13 (1978) 281.
2. K. SANGWAL and S. K. ARORA, *J. Mater. Sci.* 13 (1978) 1977.
3. K. SANGWAL, T. C. PATEL and M. D. KOTAK, *Kristall und Technik* 14 (1979) 949.
4. *Idem, J. Mater. Sci.* 14 (1979) 1869.
5. N. CABRERA, *J. Chem. Phys.* 53 (1956) 675.
6. W. H. ROBINSON, in "Techniques of Metals Research" Vol. 2, Part 1 (Interscience, New York, 1968) p. 291.
7. J. E. LENNARD-JONES and P. A. TAYLOR, *Proc. Roy. Soc. London A* 109 (1925) 476.
8. V. V. SOROKA, E. I. LAZORINA and V. N. STEPANCHUK, *Kristallogr.* 22 (1977) 619.
9. Ya. GERASIMOV, V. DREVING, E. EREMIN, A. KISELEV, V. LEBEDEV, G. PANCHENKOV and A. SHLYGIN, "Physical Chemistry" Vol. 2 (Mir, Moscow, 1974).
10. K. SANGWAL, *J. Mater. Sci.* (in press).
11. R. E. KIRK and D. F. OTHMER, (editors) "Encyclopedia of Chemical Technology" (Interscience Encyclopedia, Inc., New York, 1953) p. 406.
12. R. C. WEAST, (editor) "Handbook of Chemistry and Physics" 53rd edition (Chemical Rubber Co., Cleveland, Ohio, 1972–73).
13. Ya. GERASIMOV, V. DREVING, E. EREMIN, A. KISELEV, V. LEBEDEV, G. PANCHENKOV and A. SHLYGIN, "Physical Chemistry" Vol. 1 (Mir, Moscow, 1974).
14. K. SANGWAL, *Kristall und Technik* 14 (1979) 965.
15. K. SANGWAL, T. C. PATEL and M. D. KOTAK, *J. Mater. Sci.* 14 (1979) 1509.
16. K. SANGWAL and J. N. SUTARIA, *ibid.* 11 (1976) 2271.

Received 24 May and accepted 28 June 1979.