Journal of Thermal Analysis, Vol. 5 (1973) 363—377

THERMAL REACTIONS OF INORGANIC HYDROXY-COMPOUNDS UNDER APPLIED ELECTRIC FIELDS, III

EFFECT OF EXTERNAL D. C. FIELDS ON PROTON TUNNELLING AND MASS TRANSPORT

K. J. D. MacKenzie*

Department of Ceramics, University of Sheffield, U.K.

(Received November 9, 1971; in revised form April 17, 1972)

The energy level separation in symmetrical and unsymmetrical double minimum potentials in the presence of electric fields is calculated by first-order perturbation theory, from which the tunnelling probability of protons is obtained for both perturbed and unperturbed potentials. Tunnelling probability is slightly increased by fields of about 10^5 V/m, but a greater increase in tunnelling probability occurs when a symmetric potential becomes unsymmetric. The tunnelling process is too rapid to account for observed differences in dehydroxylation behaviour of $Al(OH)_3$, $Mg(OH)_2$ and kaolinite under electrolysis. Estimates, from indirect evidence, of the rates of anion defect generation and annihilation support the theory that the rate-determining field-dependent process is the surmounting of anionic lattice vacancies by oxygen-containing species.

In parts I and II [1, 2] it was shown that the dehydroxylation behaviour of the three related hydroxy-compounds kaolinite [$Al_2Si_2O_5(OH)_4$], brucite [$Mg(OH)_2$] and gibbsite [$Al(OH)_3$] differed considerably when carried out under an electric field; appreciable enhancement of the reaction was observed in kaolinite but the beneficial effect of the field was much less marked in brucite. Electric fields slightly retarded the reaction in gibbsite. A qualitative explanation of these observations, based on a "transport complex" theory of Rouxhet et al. [3] was proposed in part II [2] but calculations of the relative effect of the field on the various possible transport processes are needed to test the feasibility of these suggestions.

The two processes of dehydroxylation which are most likely to be affected by applied electric fields are proton elimination (by tunnelling out of the P.E. wells of the lattice) and the removal or crystallochemical rearrangement of other charged species (impurity ions or oxide ions). The removal of water from the lattice will not be directly influenced by the field unless it diffuses as H^+ and OH^-; diffusion of molecular water through the lattice may however be indirectly enhanced by an increase in the number of lattice vacancies resulting from the electrolytic removal of other ions.

The primary aim of the present calculations is to examine the effect of electric fields on proton tunnelling in hydroxy-solids. In an attempt to determine which of the field-dependent processes is responsible for the observed differences in dehydroxylation behaviour under electrolysis, the effect of fields on the other

---

* Present address: Chemistry Division, D.S.I.R., Gracefield, Wellington, New Zealand.

transport phenomena must also be examined. Although conclusions regarding the latter are likely to be less reliable, having had to be inferred from data which is incomplete and sometimes contradictory, they help to construct an overall picture of the electrolysis mechanism in the three contrasting hydroxides.

1. Effect of electric fields on proton tunnelling

This calculation falls naturally into three sections; in the first it is necessary to establish an analytic form of the double minimum potential energy well and calculate the energy levels therein, secondly this potential is perturbed by the application of an electric field and the new energy levels calculated, and thirdly the tunnelling probability from each level in the perturbed and unperturbed systems is calculated, from which is derived the total tunnelling probability for both cases.

(*a*) *The unperturbed system.* The present treatment is based on a dimensionless form of the Schrädinger wave equation [4]:

$$[d^2\psi(\xi)/d\xi^2] + \tfrac{1}{2}(E' - V')\psi(\xi) = 0 \qquad (1)$$

where $E' = E/\frac{1}{4}\hbar\beta$, $V' = V/\frac{1}{4}\hbar\beta$, E is the total energy of the hydrogen-bonded system and V is the potential energy, $\xi = (\mu\beta/h)^{\frac{1}{2}}x$, μ is the reduced mass of the hydrogen-bonded atoms, x is the proton coordinate measured from the energy maximum separating the two wells of the double minimum potential and β is an arbitrary frequency [4].

The eigenfunctions, approximated as a linear combination of the first N eigenfunctions $U_n(\xi)$ of a harmonic oscillator are given by [4]

$$\Phi_i(\xi) = \sum_{n=0}^{N-1} C_{i,n}\, U_n(\xi) \qquad (2)$$

where $U_n(\xi)$ is the nth eigenfunction of the simple harmonic oscillator, with even or odd parity according to n even or odd.

Following Heilbronner et al. [5a] the double minimum potential can be expressed in terms of a polynomial in ξ:

$$V(\xi) = \tfrac{1}{2}\hbar\beta(v_2\xi^2 + v_3\xi^3 + v_4\xi^4) \qquad (3)$$

the coefficients of which are chosen [4] to give the function of the required barrier height (E^*), separation of minima ($\Delta\xi$) and asymmetry factor (V^*) (see Fig. 1), where $v_3 = 0$, $V^* = 0$ and the potential is symmetric. In the unreacted hydroxide lattice the degree of asymmetry is likely to be much less than at the onset of dehydroxylation when the probability of proton transfer through the barrier is increased; both symmetric and unsymmetric potentials are therefore investigated.

The barrier height E^* can be estimated from the hydrogen bond energy in AlOOH, given by Lippincott and Schroeder [6] as 4.5 kcal.mole^{-1}; although hydrogen bonding does not occur in brucite or kaolinite, the hydrogen–oxygen bond dissociation energies of these compounds have been calculated to be very similar to that of the hydrogen-bonded gibbsite [7]. The separation of minima $\Delta\xi$ is estimated by subtracting twice the length of the O–H bond from the O–O distance and was set at 0.7 Å for all three hydroxides. The asymmetry factor was taken as 1.4 kcal.mole^{-1} in the present calculations; although the exact value is unknown, the object of the calculations is not invalidated by the assumption of an arbitrary unperturbed potential function. It may be noted that these barrier dimensions are in reasonable agreement with those tabulated by Caldin [8] for reactions in solution in which tunnelling is known to occur.

The data for the symmetric and unsymmetric unperturbed potential functions are given in Table 1 which also includes the eigenvalues (in units of $\frac{1}{4}\beta\hbar$), obtained by diagonalization of a 30 × 30 secular determinant using an Elliott 503 computer.

Table 1

Data for unperturbed symmetric and unsymmetric double minimum potential functions. Energies are in units of $\frac{1}{4}\beta\hbar$ ($\frac{1}{4}\beta\hbar = 288$ cm^{-1})

	Symmetric	Asymmetric
$E^*/\frac{1}{4}\beta\hbar$	5.06	5.08
$V^*/\frac{1}{4}\beta\hbar$	0	1.68
$\Delta\xi$	4.00	4.10
v_2	−1.264	−1.00
v_3	0	0.05
v_4	0.158	0.12
Energy levels		
i = 1	−2.0036	−1.9494
i = 2	−0.4171	0.3078
i = 3	4.2898	4.1131

(*b*) *The perturbed system.* The wavefunctions thus calculated are now perturbed by a perturbation operator H' representing the electric field F:

$$H' = Fe\xi/(\mu\beta/\hbar)^{\frac{1}{2}} \tag{4*}$$

where e is the electronic (or protonic) charge. The resulting energy difference ΔE_i is given by

$$\Delta E_i = \int_{-\infty}^{\infty} \Phi_i(\xi) H' \Phi_i(\xi) \, d\xi = Q'_{i,i} \tag{5}$$

where Φ_i is as defined in equation (2).

To evaluate equation (5), use is made of the fact that the integral $Q'_{i,i}$ can be written [5b]

$$Q'_{i,i} = \sum_{n=0}^{N-2} \sqrt{\frac{n+1}{2}}\, C_{i,n} C_{i,n+1} + \sum_{n=1}^{N-1} \sqrt{\frac{n}{2}}\, C_{i,n} C_{i,n-1} \tag{6}$$

---

[*] Equation (4) follows from fundamental laws of electrostatics, see e.g. Fleming, Trans. Farad. Soc., **66** (1970) 3090.

For $Q'_{i,i}$ to be non-zero, the wavefunction $\Phi_i(\xi)$ must have non-zero coefficients of both odd and even parity; since this condition can never be satisfied in the case of the symmetric potential, it follows that ΔE_i must always be zero for the symmetric potential.

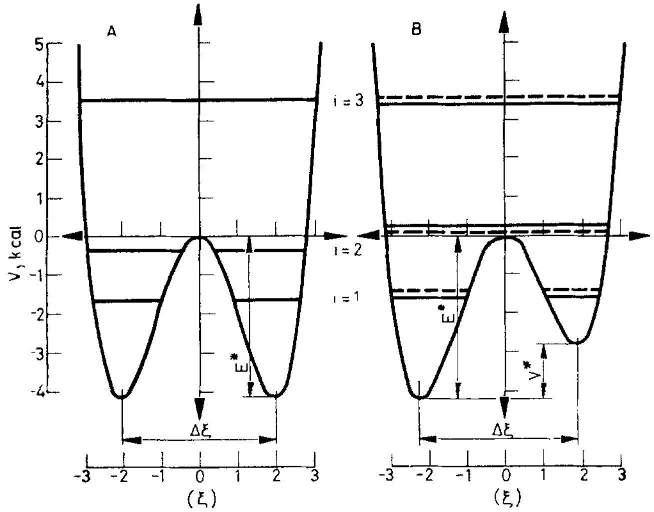

Fig. 1. Double minimum potential functions corresponding to the data of Table 1. A. Symmetric function, showing the first three energy levels, the position of which are unaltered by the field. B. Unsymmetric function showing the first three energy levels in the absence of a field (solid lines) and perturbed by a field of 10^5 V/m (dashed lines)

The values of ΔE_i were evaluated by computer for the asymmetric potential by substituting into equation (6) the eigenfunction coefficients previously obtained for the unperturbed potential. The resulting energy contributions to the first three energy levels are shown as a function of the perturbing field strength F in Fig. 2, from which it is seen that the contributions to the first and third levels are negative in sign, by contrast with the contribution to level 2. In terms of the sign convention used to define the original potential function, this means that levels 1 and 3 are raised and level 2 lowered with respect to the unperturbed system, as is shown in Fig. 1B.

The relation between ΔE_i and the perturbing field strength is broadly similar to that calculated by a variation method by Wiedemann and Zundel [9]; their conclusion that small energy level shifts occur in symmetrical double minimum potentials (which is a consequence of neglecting the fact that in the presence of electric fields symmetric potentials cannot exist as such but become weakly unsymmetric) is at variance with the present calculations more in a matter of terminology than of substance.

It should also be noted from Fig. 1 that the changes in the energy levels caused by fields of the strength used in the electrolysis experiments [1, 2] are rather smaller than the changes which occur when a symmetric potential becomes unsymmetric, i.e. when the proton transfer reaction has been initiated.

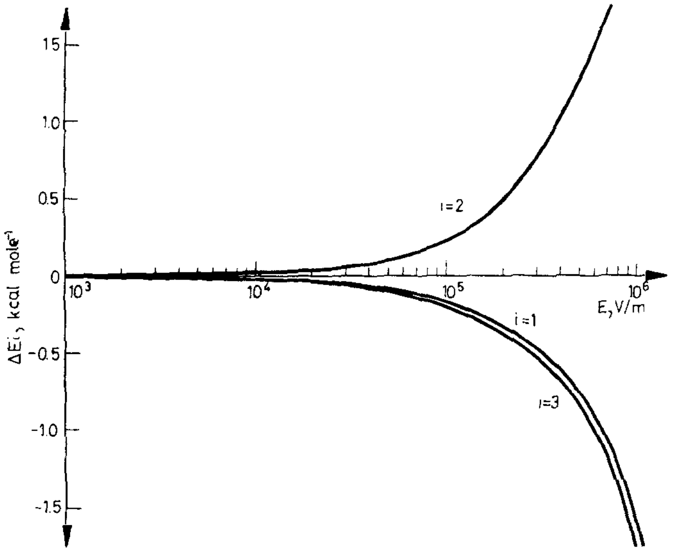

Fig. 2. Change in the energy of the first three levels as a function of perturbing field strength for the unsymmetrical potential

(*c*) *Tunnelling probability in the perturbed and unperturbed systems.* The permeability of a potential barrier can be calculated by a quantum-mechanical method, or by the so-called "quasi-classical" approach. In both cases the object is to calculate the tunnelling frequency ν_t which is then related to the transfer reaction rate by an expression of the type:

$$\frac{d\alpha}{dt} = (2\pi mkT)^{\frac{1}{2}}/h\delta\nu_t N_0 \exp(-G_f/2kT) \tag{7}$$

where α is the fraction reacted, m is the protonic mass and δ the effective transfer distance. The term in G_f represents the number of rate determining barriers (specifically the number of Schottky defects of formation energy G_f) and corresponds to the concentration of activated complexes in gas phase transition state theory.

In the "quasi-classical" approach adopted here the average tunnelling probability $\bar{P}_i$ must be evaluated; this is then related to the tunnelling frequency by:

$$\nu_t = \nu\bar{P}_i \tag{8}$$

where ν is the classical vibration frequency of the system. In the quantum-mechanical approach, the tunnelling frequency is given approximately by [10]

$$\nu_t = \frac{8\,(\epsilon_k - \epsilon_i) \int_{(a)} \mathrm{d}r\, \phi_i^2 \int_{(b)} \mathrm{d}r\, \phi_i^2}{h} \tag{9}$$

where ϵ and ϕ are respectively the eigenvalues and eigenfunctions of a double minimum potential in which the two well regions are labelled a and b; i and k refer to the a and b regions respectively. The results of the present "quasi-classical" calculations will later be compared with published results obtained by the quantummechanical approximation [10].

Two types of analytic solution of the barrier penetration problem are available; the first, due to Bell [11], approximates the barrier to a parabola of base width $2a$, and leads to the approximate expression:

$$P_i \approx \exp\,\{-2\pi^2 a(2mE^*)^{\frac{1}{2}}/h[1-(w^*/E^*)]\} \tag{10}$$

A more recent treatment by Bell [12] gives an exact solution for a symmetrical potential barrier:

$$P_i = 1 + \exp\,\{[2\pi^2 a(2mE^*)^{\frac{1}{2}}/h]\;[1-(w^*/E^*)]\}^{-1} \tag{11}$$

where m and w^* are the mass and energy of the tunnelling species and E^* and a the height and half base width of the barrier.

The second type of solution, due to Eckart [13], results in the expression for P_i:

$$P_i = \frac{\cosh\,\{[4\pi l(2mw^*)^{\frac{1}{2}}h] - 1\}}{\cosh\,[4\pi l(2mw^*)^{\frac{1}{2}}h] + \cosh\pi[(32E^*\;ml^2/h^2) - 1]^{\frac{1}{2}}} \tag{12}$$

where l is the tunnelling width of the barrier. The Eckart solution was used in this calculation since it better describes tunnelling behaviour at lower energies [14].

The tunnelling probabilities P_i at each energy level are evaluated and combined with a Boltzmann energy distribution D_i:

$$D_i = \exp - (ih\nu/4\pi kT) \tag{13}$$

to give the average tunnelling probability $\bar{P}_i$:

$$\bar{P}_i = \frac{\sum\limits_{i=1}^{N} P_i\, D_i}{\sum\limits_{i=1}^{N} D_i} \tag{14}$$

The tunnelling frequency and hence the tunnelling rate can then be calculated for the various energy levels of the perturbed and unperturbed double minimum potentials.

In calculating the average tunnelling probability $\bar{P}_i$ from equation (14), the summation was taken over the first three energy levels since the tunnelling probability approaches unity at about the third energy level. Strictly, P_i should approach unity at the top of the barrier; the present anomaly arises from differences between the assumed Eckart barrier shape and the true barrier shape. For self-consistency the bound state energy levels are defined here in terms of P_i (i.e. where $P_i < 1$), rather than in terms of barrier height (i.e. where $E_i < E^*$).

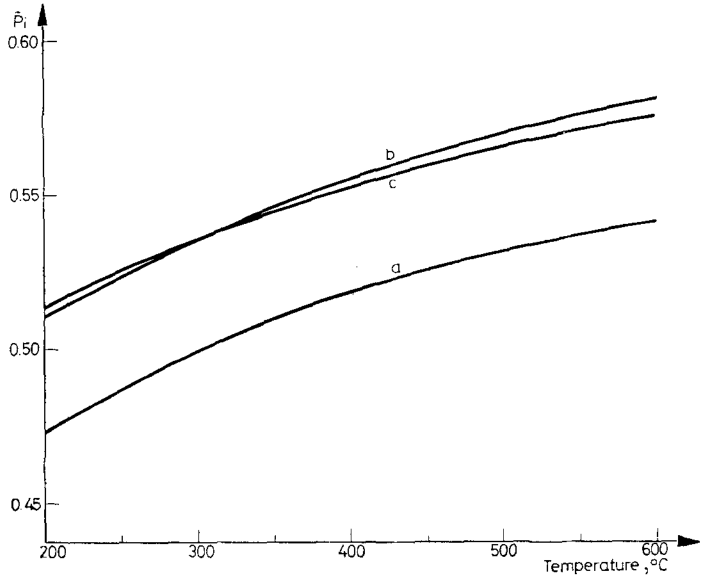

Fig. 3. Mean tunnelling probabilities as a function of temperature. Curve a: Symmetric potential. Curve b: Unsymmetric potential in absence of field. Curve c: Unsymmetric potential perturbed by field of 10^5 V/m

The results of the calculations of average tunnelling probability $\bar{P}_i$ are shown as a function of temperature in Fig. 3, from which it is seen that the tunnelling probability from an asymmetric well is always greater than from a symmetric well. For an asymmetric well in the presence of a field, the average tunnelling probability (and hence the rate) is slightly greater at lower temperatures but crosses over and becomes smaller than the unperturbed rate at increasing temperature. It is interesting to note that similar rate behaviour is displayed by brucite when dehydroxylated in the presence of a field [2]. However, calculations of tunnelling frequency ν_t and reaction rate (Table 2) show that these differences are very small compared with the rate of tunnelling, which is itself very rapid. In computing the tunnelling rate from equation (7) the effective transfer distance δ was taken as the barrier width at the first tunnelling level, and the formation energies for Schottky defects G_f were estimated as in the following section. The

Table 2

Tunnelling frequencies ν_t and log reaction rates log $d\alpha/dt$ for unperturbed and electrically perturbed potentials in $Al(OH)_3$, $Mg(OH)_2$ and kaolinite. Perturbing field strength $F = 10^5$V/m

Compound	Temperature, °C	Symmetric potential (unperturbed)		Asymmetric potential (unperturbed)		Asymmetric potential (perturbed)	
		$\nu_t \times 10^{13}$, s^{-1}	log $d\alpha/dt$ (t in sec)	$\nu_t \times 10^{13}$, s^{-1}	log $d\alpha/dt$ (t in sec)	$\nu_t \times 10^{13}$ s^{-1}	log $d\alpha/dt$ (t in sec)
$Al(OH)_3$	200	5.29	25.56	5.67	25.59	5.70	25.59
	300	5.55	27.53	5.95	27.56	5.95	27.56
	400	5.75	28.87	6.15	28.90	6.13	28.90
$Mg(OH)_2$	300	5.55	29.12	5.95	29.15	5.95	29.15
	400	5.75	29.87	6.15	29.90	6.13	29.90
	500	5.90	30.82	6.32	30.85	6.27	30.84
Kaolinite	400	5.75	27.78	6.15	27.81	6.13	27.80
	500	5.90	28.91	6.32	28.94	6.27	28.94
	600	6.02	29.75	6.44	29.78	6.39	29.78

conclusion that the tunnelling process is very rapid is unaffected by even large errors in these assumed values.

The computed values of the tunnelling frequency for the unperturbed systems, obtained by the "quasi-classical" method (Table 2), are in excellent agreement with those derived by Brickmann and Zimmermann [10] by a quantum-mechanical method (equation 9); the agreement with the "quasi-classical" results of Brickmann and Zimmermann [10] is less good, probably because of the use by those authors of a different approximation to the barrier shape.

The present calculations suggest that although electric fields do exert finite effects on the proton tunnelling behaviour of the hydroxy-compounds under study, the effects are too small and the tunnelling process too rapid to account for the observed differences in behaviour, which differences must therefore be attributed to some other electrolysis phenomenon.

2. Effect of electric fields on mass transport phenomena

In terms of the theory of Rouxhet et al. [3] involving a rate-determining "transport complex", the foregoing calculations show proton tunnelling to be a relatively rapid and field-insensitive means of generating large energy barriers (vacancies) in the crystal, which barriers must be overcome by the movement of "transport complexes" containing oxygen. If, as the theory suggests, this movement is the rate-determining step, the total process must be the resultant of two competing processes, namely defect generation and elimination. It is therefore desirable to know more about the rates of these two processes.

Since the anionic defects are generated in the first instance by dehydroxylation, a reasonable approximation to the rate of the generation process can be obtained from the known dehydroxylation kinetics of the respective hydroxides. On the other hand, the annihilation of defects involves migration of oxide ions, anionic vacancies and impurity ions and can be estimated only indirectly from data for the pure oxides. Since this is more speculative, it must be regarded as the least satisfactory part of the theoretical treatment, giving results which are more qualitative than quantitative.

(*a*) *Reaction rate due to defect generation.* The rate of reaction due to defect formation is taken to be proportional to the number of Schottky defects present at a given temperature; since the creation of anion vacancies is viewed as a rate-retarding step, the reaction rate of interest here is taken as being inversely proportional to the number of vacancies both in and out of the electric field. The rate of defect generation is only slightly changed by the presence of the field, which influences the proton tunnelling process by the amount calculated in the previous section. The reaction rate due to defect generation is then given by

$$\mathrm{d}N/\mathrm{d}t = k[N_0 \exp\left(-G_f/2RT\right)]^{-1} \tag{15}$$

where N_0 is the total possible number of Schottky defects of formation energy G_f and k is a constant, taken here as unity. The values of G_f for hydroxides are lower than those tabulated for the pure oxides; an estimate can be made from the activation energy for the dehydroxylation process (bearing in mind however that this energy also includes the transport of water from the reactant). The value of N_0 can be identified with the total number of hydroxyl groups (potential defects) per unit volume and is obtained from the unit cell parameters for each hydroxide. The values of G_f were approximated to the respective dehydroxylation energies (32 kcal.mole^{-1} for $Mg(OH)_2$ [15], 46 kcal.mole^{-1} for gibbsite [16] and 50 kcal.mole^{-1} for kaolinite [17]). The values of N_0 computed from the unit cell parameters are respectively 6.0×10^{21}, 6.0×10^{22} and 2.5×10^{22} cc^{-1}.

(*b*) *Rate of defect elimination.* Once formed, the anionic defects are removed from the system by thermal diffusion of impurity ions to the defect sites or by thermal self-annealing processes. Both processes are field dependent since they involve the movement of charged species, but because of a scarcity of unambiguous experimental data, meaningful estimates of the order of magnitude of the effects are difficult to make. Diffusion measurements contain information about the thermal movement of both charged and uncharged species, but the process to which the measurements refer is not always unique and identifiable. Similar difficulties apply to the interpretation of electrical mobility data from conductance measurements. Since however diffusion and conductance measurements provide the chief means of estimating ease of defect removal in the presence and absence of a field, the most recent data available has been used here in an attempt to determine the importance of the elimination process to the overall reaction rate.

The diffusion coefficient D of a species is related to its total jump frequency ν, the jump distance a and the number of like neighbouring sites Z by [18]:

$$D = a^2\nu/Z \tag{16}$$

Since the jump velocity in the x-direction (say) is given by $a\nu/Z$, the number of species of concentration N_0 removed from a zone of cross-sectional area A and thickness D/a in t seconds is given by:

$$N = ADN_0t/a \tag{17}$$

whence

$$dN/dt = ADN_0/a \tag{18}$$

Although the process is random in all directions, we here concern ourselves only with the progress in (say) the x-direction since we will later be comparing this with the situation in which an electric field is assumed to be acting in the x-direction.

To make use of equation (18) it is necessary to assess values for the diffusion coefficient of oxygen in the *oxides* under consideration since it is the defect structure of the dehydroxylated regions of the crystal which is assumed to control the rate of further dehydroxylation.

Several values for the diffusion coefficient of oxygen in Al_2O_3 have been reported [19], corresponding to the high and low temperature processes in both single crystal and polycrystalline samples. The expression $D = 6.3 \times 10^{-8} \exp(-57{,}600/RT)$, which is thought [19] to refer to oxide ion mobility, was used here.

The diffusion coefficient of oxygen in MgO, given by Oishi and Kingery [20] as $D = 2.56 \times 10^{-6} \exp(-62{,}400/RT)$ was used here; this value is thought to refer to impurity controlled oxide ion mobility but is apparently the only value available.

Since no direct measurement of anion defect mobility has been reported for kaolinite, metakaolinite or mullite, a value had to be inferred from diffusion measurements of deutroxide in micas [21]; this process is considered by Rouxhet to be dominated by the diffusion of an oxygen-containing "transport complex" and therefore reflects the movement of this oxygen species rather than the movement of bare deuterons [21]. The formal similarity between the micas and kaolinite makes it likely that the derived diffusion coefficient $D = 3.5 \times 10^3 \exp(-47{,}000/RT)$ is a reasonable approximation to the required coefficient for kaolinite.

The possibility that anion vacancies are plugged by impurity ions must also be considered. The brucite and gibbsite samples used in this study were pure synthetic materials; the role of impurities is therefore only likely to be significant in the case of kaolinite. The diffusion measurements from which the behaviour of kaolinite was inferred were on natural micas containing impurities, the effect of which is therefore included in the measured coefficient and cannot be separated from it.

In the calculations of dN/dt from equation (18) a value of $a = 3$ Å was used, following Rouxhet et al. [3]. The sample cross-sectional area A was 0.95 cm^2 for brucite and gibbsite and 0.44 cm^2 for kaolinite.

To calculate the effect of a field on the process of defect removal, use is made of the fact that in a semiconductor in which the charge is carried predominantly by one species of mobility μ, the conductance σ is given by:

$$\sigma = eN_0\mu \tag{19}$$

where e is the electronic charge and N_0 the number of charge carriers. The drift velocity Ω of the charge carriers in a field F is then:

$$\Omega = \mu F = \sigma F/N_0 e \tag{20}$$

From similar considerations to those used to derive the diffusional flux in the x-direction,

$$\mathrm{d}N/\mathrm{d}t = \Omega A N_0 = A\sigma E/e \tag{21}$$

The conductance to be substituted in equation (21) must refer uniquely to the species in question, namely the oxide ion. In practice it is difficult to obtain such data, as measured conductances always represent the sum of several contributions. By selecting the appropriate physical conditions of measurement it is however sometimes possible to record conductances which are almost entirely due to one component.

The conductance expression of Pappis and Kingery [22] for single crystal Al_2O_3 at low oxygen pressure [$\sigma = 1.03 \times 10^3 \exp(-65{,}462/RT)$ ohms^{-1}cm^{-1}], thought by these authors to refer to the movement of oxide ion vacancies was used here. The alternative possibility that this conductance might be caused by the movement of interstitial Al^{3+} was also considered by Pappis and Kingery who did not however reach a definite conclusion; the following treatment is strictly valid only if their former interpretation is correct. The similarity between the activation energies of this process and that of other processes identified with oxide ion migration [26] suggests that this value might reasonably be ascribed to oxide ion migration.

Of the several conductance measurements reported for MgO those of Mitoff [23], Weigelt and Haase [24] and Lempicki [25] are considered by Davies [26] to refer to oxide ion vacancy migration because of their correspondence with the oxide ion diffusion data for MgO [20]. The conductance expression $\sigma = 1.6 \times 10^{-1} \exp(-55{,}000/RT)$ ohms^{-1}cm^{-1}, derived from the combined results of all these workers was used here for MgO.

The conductance expression used here for kaolinite, derived from the data of Fripiat and Toussaint at 400 – 500° [27] was $\sigma = 1 \times 10^{-3} \exp(-15{,}000/RT)$ ohms^{-1}cm^{-1}. The conductance at these temperatures is said by these authors to be due to lattice defects in the metakaolinite rather than to the movement of protons although the known retention of residual protons in kaolinite up to at least 1100° [28] suggests that a small part of the conductance is protonic.

3. Results and discussion

The results of all the foregoing calculations for gibbsite, brucite and kaolinite are combined in Fig. 4. The overall reaction rates both in the presence and absence of a field (lines *e* and *f*) are here represented as a combination of the defect generation and elimination reactions both in the presence of the field (lines *b* and *d*) and in the absence of the field (lines *a* and *c*). It will be noted that on the scale of Fig. 4 the difference in the rates of defect generation due to the effect of the field on proton tunnelling cannot be distinguished for any of the three compounds over their temperature range of dehydroxylation. On the other hand, appreciable differences are imposed by the field on the rates of processes involving anion rearrangement, and even although the calculations are based in some cases on doubtful interpretation of data, the composite rate curves show very similar

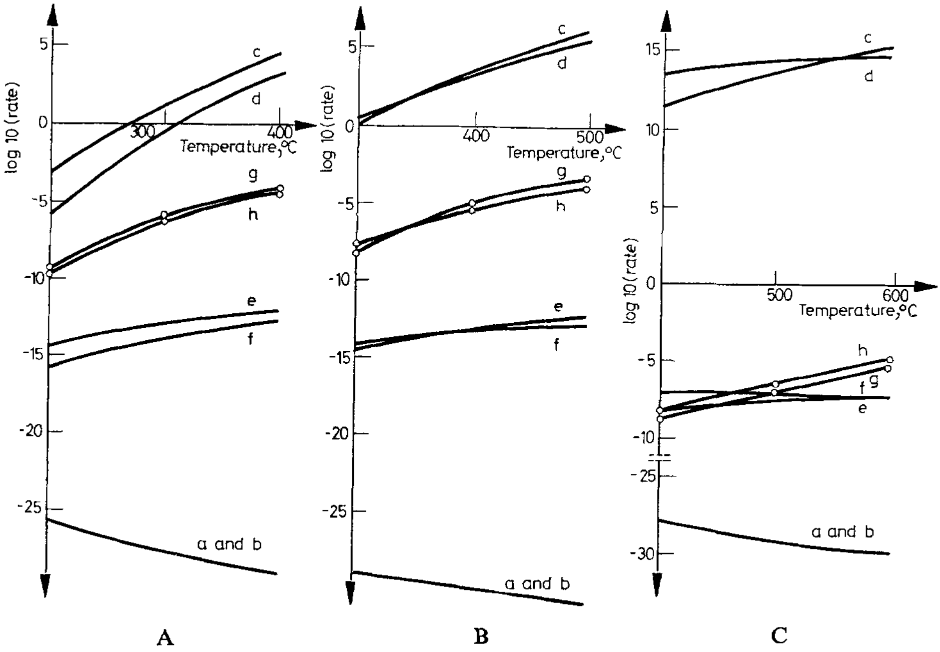

Fig. 4. Rates of the various competing processes as a function of temperature
A. gibbsite. B. brucite. C. kaolinite.

Curves a.	Defect generation in absence of field	(equation 7)
Curves b.	Defect generation in presence of field	(equation 7)
Curves c.	Defect elimination in absence of field	(equation 18)
Curves d.	Defect elimination in presence of field	(equation 21)
Curves e.	Resultant rate in absence of field	
Curves f.	Resultant rate in presence of field	
Curves g.	Experimental rate in absence of field	
Curves h.	Experimental rate in presence of field	

trends to those observed experimentally (lines *g* and *h*). Superposition of the experimental and calculated rate curves would not be expected since the experimental values are merely the rate constants arising from arbitrarily chosen kinetic models [1, 2] (the close superposition of experimental and calculated curves for kaolinite must be regarded as fortuitous). Fig. 4 shows, however, that the assumption of a "transport complex" as the rate limiting step in the reaction qualitatively explains the differences in electrolysis behaviour between gibbsite, brucite and kaolinite at different temperatures in terms of differences in the temperature dependence of the competing processes. Thus, although defect elimination is the rate limiting process in all three hydroxides, the effect of the field on this process varies from compound to compound. In the case of kaolinite, the beneficial effect of the field on defect elimination is probably due to two causes – the higher temperature range over which the reaction proceeds, and the impurity content, which provides a field-sensitive mechanism for the rearrangement of the anion structure. By contrast, gibbsite loses its anion defects only slowly (as evidenced by the number of transition aluminas which occur as intermediates during dehydroxylation). Brucite represents an intermediate case in which the temperature coefficients of the field-dependent and field-independent defect elimination processes cross over in the temperature range of the reaction, leading to different electrolysis behaviour at high and low temperatures.

4. Conclusions

1. Electric fields slightly enhance the proton tunnelling behaviour of hydroxides by changing the spacing of the energy levels in the double minimum potential. The effect is much smaller than the differences in tunnelling behaviour between symmetric and unsymmetric potentials; however the former probably do not occur in hydroxides at dehydroxylation temperatures.
2. Tunnelling, whether in the presence or absence of electric fields is too fast to account for the observed differences in the electrolysis behaviour of gibbsite, brucite and kaolinite.
3. Speculative deduction of the rates of other transport processes from diffusion and conductance data provides an explanation of the observed dehydroxylation behaviour in terms of competing processes of defect generation and removal. Where the presence of a field increases the rate of anion defect removal more than the rate of defect generation (as in kaolinite) the overall reaction rate is increased; the reverse case may also occur (as in gibbsite). Brucite behaves in a manner intermediate between these two extremes.

*

Part of this work was carried out under an S.R.C. research grant. The author is indebted to Dr. J.P.M. Bailey for advice on the quantum-mechanical calculations, Dr. W.T. Raines and Dr. P.G. Rouxhet for helpful discussion. and to Mrs. F. Jackson for the computing.

References

1. K. J. D. MacKenzie, J. Thermal Anal., 5 (1973) 5.
2. K. J. D. MacKenzie, J. Thermal Anal., 5 (1973) 19.
3. P. G. Rouxhet, R. Touilleaux, M. Mesdagh and J. J. Fripiat, Proc. Int. Clay Conf., Tokyo, 1 (1969), 109.
4. R. L. Somorjai and D. F. Hornig, J. Chem. Phys., 36 (1962) 1980.
5. a. E. Heilbronner, H. H. Gunthard and R. Gerdil, Helv. Chim. Acta, 39 (1956), 1171.
   b. E. Heilbronner, H. Rutishauser and F. Gerson, Ibid., 42 (1959) 2285.
6. E. R. Lippincott and R. Schroeder, J. Phys. Chem. 61, (1957) 921.
7. J. J. Fripiat, H. Bosmans and P. G. Rouxhet, J. Phys. Chem., 71 (1967) 1097.
8. E. F. Caldin, Chem. Revs., 69 (1969) 135.
9. E. G. Wiedemann and G. Zundel, Z. Naturforsch., 25a (1970) 627.
10. J. Brickmann and H. Zimmermann, J. Chem. Phys., 50 (1969) 1608.
11. a. R. P. Bell, The Proton in Chemistry, Cornell University Press, Ithaca, New York, 1959, p. 205.
    b. R. P. Bell, Proc. Roy. Soc., A148 (1935) 241.
12. R. P. Bell, Trans. Farad. Soc., 54 (1959) 1.
13. C. Eckart, Phys. Rev., 35 (1930) 1303.
14. R. J. LeRoy, K. A. Quickert and D. J. LeRoy, Trans. Farad. Soc., 66 (1970) 2997.
15. R. S. Gordon and W. D. Kingery, J. Amer. Ceram. Soc., 50 (1967) 8.
16. G. W. Brindley and M. Nakahira, Z. Krist., 112 (1959) 136.
17. G. W. Brindley, J. H. Sharp, J. H. Patterson and B. N. N. Achar, Amer. Min., 52 (1967) 201.
18. J. M. Pollock, Quart. Revs., 24 (1970) 601.
19. Y. Oishi and W. D. Kingery, J. Chem. Phys., 33 (1960) 480.
20. Y. Oishi and W. D. Kingery, J. Chem. Phys., 33 (1960) 905.
21. P. G. Rouxhet, Amer. Min., 55 (1970) 841.
22. J. Pappis and W. D. Kingery, J. Amer. Ceram. Soc., 44 (1961) 459.
23. S. P. Mitoff, J. Chem. Phys., 31 (1959) 1261.
24. W. Weigelt and G. Haase, Ber. Deut. Keram. Ges., 31 (1954) 45.
25. A. Lempicki, Proc. Phys. Soc. Lond., B66 (1953) 281.
26. M. O. Davies, J. Chem. Phys., 38 (1963) 2047.
27. J. J. Fripiat and F. Toussaint, J. Phys. Chem., 67 (1963) 67.
28. K. J. D. MacKenzie, J. Inorg. Nucl. Chem., 32 (1970) 3731.

Résumé — La séparation des niveaux d'énergie des potentiels à minimum double, symétrique et asymétrique, se calcule à l'aide de la théorie des perturbations du premier ordre, à partir de quoi la probabilité de l'effet tunnel des protons s'obtient aussi bien pour les potentiels perturbés que pour les non perturbés. La probabilité de l'effet tunnel augmente quelque peu sous l'influence de champs d'environ 10^5 V/m, mais une augmentation plus notable de cette probabilité apparaît quand un potentiel symétrique devient asymétrique. Le processus de l'effet tunnel est trop rapide pour rendre compte des différences de comportement observées pour $Al(OH)_3$, $Mg(OH)_2$ et la kaolinite lors de l'électrolyse déshydroxylante. Des estimations faites à partir de données indirectes pour connaître les vitesses d'apparition des défauts anioniques et celles de leur disparition, viennent à l'appui de la théorie suivant laquelle le processus dépendant du champ et déterminant la vitesse est celui de l'occultation des lacunes du réseau anionique par des espèces contenant de l'oxygène.

Zusammenfassung — Die Trennung des Energieniveaus in symmetrischen und unsymmetrischen doppelten Minimumpotentialen in Gegenwart von elektrischen Feldern wird mittels einer Störungstheorie erster Ordnung berechnet, aus welcher die Wahrscheinlichkeit der Tunnelbildung von Protonen für gestörte sowie ungestörte Potentiale erhalten wird. Felder von 10^5 V/m erhöhen die Wahrscheinlichkeit der Tunnelbildung in geringem Maße, eine bedeutendere Zunahme der Wahrscheinlichkeit der Tunnelbildung tritt jedoch auf, wenn ein symmetrisches Potential unsymmetrisch wird. Der Vorgang der Tunnelbildung ist zu schnell um die Unterschiede des Verhaltens von $Al(OH)_3$, $Mg(OH)_2$ und Kaolinit bei der elektrolytischen Dehydroxylierung zu erklären. Schätzungen der Geschwindigkeiten der Anionen-Defektbildung und -Vernichtung aus indirekten Angaben unterstützen die Theorie, daß der geschwindigkeitsbestimmende, feldbedingte Vorgang die Überdeckung der Lücken im Anionengitter durch sauerstoffhaltige Arten ist.

Резюме — Разделение энергетического уровня в симметричных и несимметричных потенциалах с двойным минимумом в присутствии электрических полей рассчитано по теории возмущения первого порядка. Из этой теории получена туннельная вероятность протонов как для возмущенного, так и для невозмущенного потенциалов. Туннельная вероятность слабо увеличивается электрическими полями около 10^5V/м; значительное ее увеличение происходит, если симметричный потенциал становится несимметричным. Туннельный процесс является слишком быстрым, чтобы объяснить наблюдаемые различия в ходе дегидроксилирования $Al(OH)_3$, $Mg(OH)_2$ и каолинита при электролизе. Оценки скоростей образования и уничтожения анионного дефекта, полученные из косвенных доказательств, подтверждают теорию.