

MATERIALS SCIENCE FORUM

Editor-in-Chief: G. E. Murch
Central Research Laboratories
I.C.I.-Australia

KINETICS AND MASS TRANSPORT IN SILICATE AND OXIDE SYSTEMS

Proceedings of a Meeting held in London in September 1984

Guest Editors: R. Freer and P. F. Dennis

Trans Tech Publications
Switzerland - Germany - UK - USA



MATERIALS SCIENCE FORUM

Editor-in-Chief: G. E. Murch

Associate Editor: N. L. Peterson (Argonne)

Editorial Board: F. Benière (Rennes)
C. R. A. Catlow (London)
L. T. Chadderton (Melbourne)
M. Doyama (Tokyo)
P. Kofstad (Oslo)
R. Krishnan (Trombay)
C. Moynihan (Troy)
J. Nowotny (Krakow)
W. Schilling (Jülich)
J. Bruce Wagner, Jr. (Tempe)
H. Wollenberger (Berlin)

TRANS TECH PUBLICATIONS
Switzerland - Germany - UK - USA

Copyright© 1986 Trans Tech Publications Ltd., Switzerland
ISBN-087849-539-8

Distributed in North America by

Trans Tech Publications c/o
Karl Distributors
16 Bear Skin Neck
Rockport, MA 01966
USA

and worldwide by

Trans Tech Publications Ltd.
Trans Tech House
4711 Aedermannsdorf
Switzerland

Printed in the Netherlands

PREFACE

Mass transport and related kinetic processes in silicate and oxide systems (including minerals, glasses, composites, melts and liquids) are of considerable interest and importance to fields as diverse as Ceramics, Chemistry, the Earth Sciences, Engineering, Materials Science and Physics. With significant advances in instrumentation, experimental methods, and computer modelling techniques during the last twenty years rapid progress has been made in our understanding of these systems. However, it is becoming increasingly clear that, whilst there has been a regular contact and interchange of ideas between workers in selected subject groups, many problems are fundamental to all disciplines and would benefit from a common approach.

To try and breach the artificial subject boundaries and provide a forum for all workers interested in silicates and oxides a conference was held on KINETICS AND MASS TRANSPORT IN SILICATE AND OXIDE SYSTEM in London in September, 1984. The meeting was sponsored by the Mineralogical Society of Great Britain, the British Ceramic Society (now Institute), the Institute of Physics, and the Polar Solids Discussion Group of the Royal Society of Chemistry. Additional support was provided by I.C.I. plc, the British Ceramic Research Association, Morganite Refractories Ltd., and W. & C. Spicers Ltd. of Cheltenham.

As well as providing a focus for silicate and oxide research, the meeting sought: (i) to review some of the recent developments and achievements in experimental and theoretical techniques for characterising the defect and transport properties; (ii) to illustrate the wide range of problems encountered in the various disciplines in both academic and industrial environments; and (iii) to identify problems of an interdisciplinary nature. A total of 37 papers were presented in oral and poster sessions and most are included in this volume. The contributions represent a wide range of interests, but they are linked by a number of common themes. The overall framework for the volume is provided by the 6 invited review papers which introduced the individual sessions.

Most of the delegates agreed that the conference had demonstrated the potential value of interdisciplinary meetings in this important area of materials science. As conference convenors we were encouraged by the enthusiastic support for the meeting and we hope that the proceedings accurately reflect the current activities and that they stimulate further interest in this exciting and rewarding field.

Finally, we would like to mention that, at the request of the authors, all the papers in this volume have been subject to independent refereeing.

R. FREER
Dept. Metallurgy and Materials Science
University of Manchester/UMIST
Manchester M1 7HS, U.K.

P. F. DENNIS
Dept. Geology
University College London
London WC1E 6BT, U.K.

CONTENTS

Preface

Mass Transport in Oxides - An Overview

J. B. Goodenough

1

CHARACTERISATION

Some Recent Advances in the Characterisation of Silicates

M. A. Carpenter

19

Neutron Activation Induced Beta Autoradiography as a Technique for Locating Minor Phases in Thin Section: Emulsion Response

Characteristics

P. J. Potts

35

High Resolution Powder Neutron Diffraction

A. N. Fitch

45

Neutron Scattering Investigation of the Defect Structure of Y_2O_3 , Stabilised ZrO_2 and its Dynamical Behaviour at High Temperatures

R. Osborn, N. H. Andersen, K. Clausen, M. A. Hackett, W. Hayes, M. T. Hutchings, and J. E. MacDonald

55

KINETICS

The Kinetics of Al, Si Ordering in Minerals

A. Putnis

63

Time-Temperature - Transformation Curves for Kaolinite

F. Onike, G. D. Martin, and A. C. Dunham

73

Calcined Natural Magnesite - Influence of Time and Temperature on the Transformation and Resulting Industrial Properties

N. Kimyongur and P. W. Scott

83

Kinetics of the Quartz-Cristobalite Transformation in Refractory-Grade Silica Materials

H. Schneider, A. Majdic and R. Vasudevan

91

Mechanism and Kinetics of Na, K. Unmixing in Al(Si, Ge) Alkali Feldspars

B. Deckers, H. Kroll, and H. Penteringhaus

103

Rate Studies on Hydration and Dehydration of Synthetic Mg-Cordierite

P. W. Mirwald, C. Jochum, and W. V. Maresch

113

Some Observations Concerning the Growth Kinetics of Biotite During the Thermally-Induced Transformation of White Mica (Phengite) in the Contact Aureole of the Traversella Intrusion (N. Italy)	
<i>R. Wirth</i>	123
A Mechanism for the Reaction Between Magnesium Oxide and a Natural Chromite at 1530°C	
<i>S. C. Kohn</i>	133
An Application of Kinetic Crystal Growth Models to Trace Element Zoning in Alkali Basaltic Clinopyroxenes	
<i>A. Duda and N. Shimizu</i>	139
Closure Profiles in Cooling Systems	
<i>M. H. Dodson</i>	145
Application of Experimental Kinetic Data to some Petrological Problems	
<i>D. C. Rubie and A. B. Thompson</i>	155
MODELLING STUDIES	
Computer Simulation Studies of Silicates	
<i>C. R. A. Catlow, M. Doherty, G. D. Price, M. J. Sanders, and S. C. Parker</i>	163
Mass Transport in Anion Deficient Fluorite Oxides	
<i>A. N. Cormack</i>	177
Diffusion Controlled Growth and Dissolution of Spheres of Finite Initial Size	
<i>M. Cable and J. R. Frade</i>	187
Model Intercalation Studies	
<i>H. D. B. Jenkins</i>	195
MASS TRANSPORT	
New Techniques for Studying Mass Transport in Oxides	
<i>J. A. Kilner</i>	205
On the Behaviour of Fayalite and Olivine in Oxygen Potential Gradients	
<i>R. Weghöft and H. Schmalzried</i>	223
Oxygen Diffusion Studies in Minerals: The Effect of Surface Reaction Processes in Hydrothermal Exchange Experiments	
<i>S. C. Elphick, P. F. Dennis, and C. M. Graham</i>	235

Tracer Diffusion of Cobalt and Silicon in Cobaltous Oxide – Silica Liquid Mixtures <i>J. Kieffer, G. Borchardt, S. Scherrer, and S. Weber</i>	243
Cation Diffusion in Natural Silicate Melts <i>P. Henderson, J. Nolan, and R. K. Lowry</i>	257
Mineral Dissolution Rates in a Superheated Basalt Melt <i>C. H. Donaldson</i>	267
Electrophoretic Mobility Variations During Feldspar Dissolution <i>M. Tranter and R. Raiswell</i>	275
INDUSTRIAL TOPICS	
Application of Mass Transport Studies to Industrial Problems <i>A. Atkinson</i>	287
Model Study of SiF ₄ Volatilisation from an Oxide Glass Melt <i>J. M. Parker and G. F. West</i>	297
Mass Transport Processes in the Oxidation of Calcium Doped β' – SIALON <i>F. N. Chukukere and F. L. Riley</i>	307
Thermoelectric Power Studies of Oxides with the Fluorite Structure <i>A. V. Chadwick, E-S. Hammam, B. Zeqiri, and F. Beech</i>	317
SUBJECT INDEX	327

MASS TRANSPORT IN OXIDES - AN OVERVIEW

John B. Goodenough
Inorganic Chemistry Laboratory,
South Parks Road, Oxford OX1 3QR

ABSTRACT

Mass transport in solids may occur via molecular, atomic, or ionic motion. Molecular motion occurs via insertion/extraction reactions that do not involve reduction or oxidation of the host. Solid electrolytes represent ionic conductors. Insertion/extraction reactions that do reduce or oxidize the host give rise to a mixed ionic/electronic conduction. These different types of mass transport are reviewed briefly with an emphasis on the factors that determine the mobilities of the mobile species within a host structure.

INTRODUCTION

Mass transport in solids is of three distinguishable types: (1) molecular insertion/extraction reactions, (2) ionic conduction in solid electrolytes, and (3) mixed electronic/ionic conduction.

Molecular insertion/extraction reactions occur in layered compounds and in framework structures. The layered compounds consist of strongly bonded sheets with weak Van der Waals or cation bonding between the sheets. Van der Waals bonding is common in the dichalcogenides; in oxides it is only found where cation displacements within a strongly bonded layer form local dipoles. For example, MoO_3 and V_2O_5 contain the oxocations $(\text{MoO})^{4+}$ and $(\text{VO})^{3+}$ oriented normal to the layers. Intercalation of water to form hydrated species introduces hydrogen bonding between the layers, as is illustrated in Fig. 1 for $\text{MoO}_3 \cdot n\text{H}_2\text{O}$, $n=0, 1, 2$. Note that no hydrogen is associated with the $(\text{MoO})^{4+}$ cation; two with the opposite oxide ion.

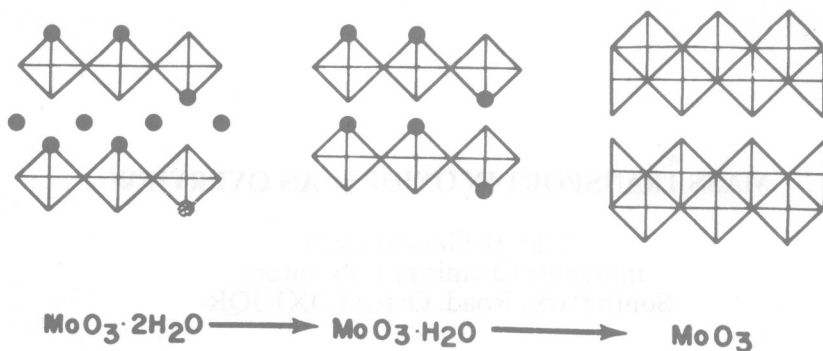


Figure 1. Structural relationships between (a) $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, (b) $\text{MoO}_3 \cdot \text{H}_2\text{O}$, and (c) MoO_3 . Black circles are OH_2 ; crossed squares represent MoO_6 octahedra. The Mo(VI) ions are displaced from center of octahedron towards the terminal O^{2-} ion in all structures.

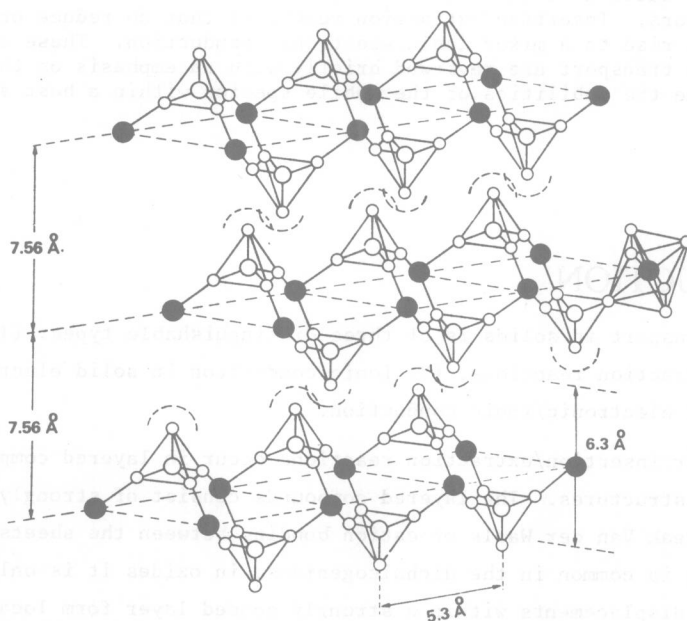


Figure 2. Arrangement of octahedrally coordinated Zr(IV) layers and phosphate groups in $\alpha\text{-[Zr(PO}_4)_2\text{]H}_2 \cdot \text{H}_2\text{O}$. Dashed semicircles represent approximate size of the $\text{O}^{(-)}$, after Ref. [1].

The sheet silicates have their strongly bonded layers held together by hydrogen bonds, as in the kandites, or by interlayer alkali ions such as K^+ that charge-compensate for Al^{3+} substitution of Si^{4+} ions in the tetrahedral-site layers of the anhydrous smectites, vermiculites, and micas.

Molecular insertion/extraction reactions in the layered oxides is possible because the interlayer bonding is sufficiently weak that the layers may be prized apart. They freely incorporate interlamellar water or organic species of many different kinds. Hydrated species readily exchange any interlamellar cations that are present; the mobilities of the interlamellar cations, particularly of the protons, increases with the water content.

The acid salts of tetravalent metals, which have the general formula $M^{IV}(HPO_4)_2 \cdot nH_2O$, may form as α or γ layered structures [1]. Fig. 2 illustrates the arrangement of three adjacent macroanions in α - $[Zr(PO_4)_2]H_2 \cdot H_2O$. The interlayer water and protons are not shown. Like the sheet silicates, these salts are good cation exchangers, can contain variable amounts of water, and freely incorporate ammonia, amines, and alcohols.

Framework structures contain an internal space of fixed volume; intercalation is therefore more selective whether one, two, or three dimensional. The zeolites have the most open three-dimensional frameworks, and they have been extensively studied and exploited as molecular sieves and catalysts [2].

Solid electrolytes are, ideally, conductors of a single ionic specie and electronic insulators. Framework structures have been shown to provide fast Na^+ -ion and K^+ -ion conduction [3], but the sizes of the internal channels within which the mobile ions move need to be tailored to match the mobile-ion size.

The fact that Li^+ ions are mobile at room temperature in close-packed oxide-ion arrays provides an important synthetic route to compounds of unusual cation ordering and oxidation state. This situation provides particular synthetic flexibility for mixed electronic/ionic conductors, as is illustrated below.

Types of Conduction

Electrons

Two types of d.c. electronic conduction are encountered, tunnelling and diffusion. Itinerant electrons in partially filled conduction bands tunnel from one equivalent atom to another in a crystalline array. The mobility of an itinerant electron is given by

$$\mu_e = e\tau_s/m^* \quad (1)$$

where e/m^* is the ratio of the charge to the effective mass of the electron and τ_s is the mean-free-time between scattering events caused by aperiodicities in the periodic potential within which it moves. These aperiodicities may be introduced by thermal motions of the atoms (phonons), native crystal-line defects, or chemical impurities.

Where the time for an electron to tunnel between energetically equivalent sites is longer than a trapping optical-mode lattice vibration, the mobile electrons of a partially filled conduction band may become trapped by a local lattice deformation. The trapped (localized) electron with its local deformation is called a small polaron. Small polarons move diffusively through the lattice; thermal energy must be supplied to make equal the donor and acceptor energies on neighboring equivalent ions so that tunnelling can occur, and the local deformation is transferred with the mobile electron after tunnelling has taken place. Diffusive motion gives rise to an Einstein mobility.

$$\mu_p = eD_p/kT \quad (2)$$

where D_p is the polaron diffusion coefficient. Small polarons contribute to the configurational entropy similarly to diffusing ions.

Protons

Among the ions, the proton is unique in the character of its bonding and hence in the variety of movements available to it. As the smallest cation, the proton coordinates only two nearest oxide-ion neighbors; and if the O-H-O separation is greater than about 2.4 \AA , the proton is shifted toward one anion and away from the other to form a double-well potential and an asymmetric hydrogen bond. If the two coordinated anions are inequivalent, the proton is shifted toward the more polarizable anion. If the two neighboring anions are equivalent, one potential well is made deeper than the other only by the motion of the proton from the center of the bond. Although displacement toward one anion is energetically equivalent to a displacement toward the other, proton transfer from one well to the other requires a thermal excitation over a barrier enthalpy ΔH_w . This enthalpy decreases sharply with anion separation, and the jump frequency $\nu_h = \nu_o \exp(-\Delta H_w/kT)$ increases.

Where a small π -bond repulsion between filled oxide-ion p orbitals permits a closer O-H-O separation, a proton may bond equally strongly to both anions. Such a symmetric hydrogen bond tends to occur where two equivalent

oxide ions are strongly polarized to opposite sides by neighboring cations. The O_2H_5^+ dioxonium ion, for example, consists of two water molecules bonded by a symmetric hydrogen bond; the O_3H_7^+ molecule contains two slightly bent, symmetric O-H-O bonds between a central OH unit and two terminal OH_2 groups.

Cooperative displacements of protons within a network of asymmetric hydrogen bonds, as is illustrated in Fig. 3 for KH_2PO_4 , may give rise to a spontaneous polarization P_s of the solid. In such ferroelectric materials, long-range ordering of the displacements occurs below a critical temperature, the Curie temperature T_c . Reversal of P_s to $-P_s$ in a d.c. electric field produces a transient current; it is a giant displacement current.

Because the proton tends to form a single strong bond with one anion neighbor, its association with the second neighbor in an asymmetric bond may be easily broken. Therefore, the axis of the short O-H bond librates at low temperatures and may be reoriented from one bond direction to another by either an external electric field or, randomly, by thermal energy. At higher temperatures, the molecule may tumble, thus freely rotating its attached proton. At still higher temperatures, the anion to which the proton is attached may diffuse through the solid (or structured liquid between particles or sheets, or within a framework) to translate the proton and its carrier over a long range.

Translation of a proton riding "piggy back" on an anion is commonly referred to as "vehicular" motion. In such vehicular motion, the mobile molecule may carry a positive charge (e.g. NH_4^+ , OH_3^+ , O_2H_5^+ , O_3H_7^+), a negative charge (e.g. NH_2^- , OH^-), or be neutral (e.g. NH_3 or OH_2). Translation of a charged molecule over a long distance gives rise to a d.c. current, provided appropriate sources and sinks of the mobile species are at the electrodes. Translation of neutral species only produces a flux of mass. Neutral species are generally volatile at modest temperatures.

A bare proton may also diffuse through a hydrogen-bond system to give a d.c. current. It does so by the Grotthuss mechanism, which consists of a combination of piggy-back reorientations and proton displacements. Each of these two steps carries an activation energy. The greater the concentration of water present, the lower the activation energy for piggy-back reorientation.

Other Cations

In an aqueous solution, a mobile cation carries a hydration sphere; in an anhydrous solid the mobile cations are bare. Where the space available to the mobile cation is large enough, smaller cations may enter a solid with an

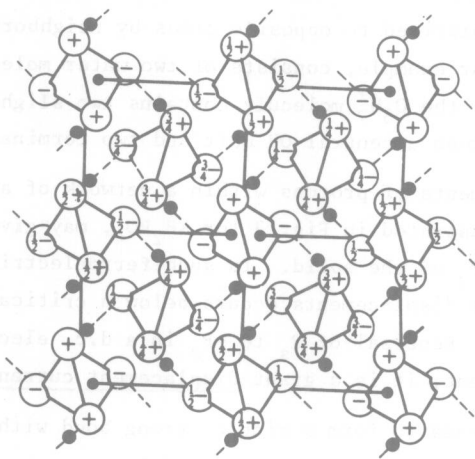


Figure 3. A view on the a - b plane of KH_2PO_4 in the ferroelectric phase. Not shown are P in centers of tetrahedra and K^+ ions. Full dark circles represent protons. After C.N.R. Rao and K.J. Rao, Phase Transitions in Solids, (McGraw-Hill, 1978) p. 315.

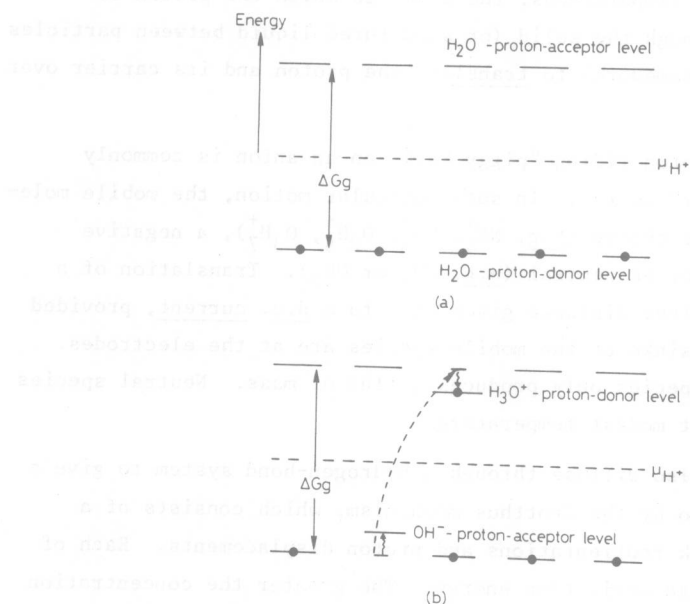


Figure 4. Proton energy levels for pure water (a) without and (b) with excitation of an H_3O^+ - OH^- pair.

associated water molecule. In an octahedral interstice, for example, a Li^+ or Na^+ ion may coordinate with three host oxide ions on one side and an associated, mobile water on the other, the water hydrogen-bonding to the oxide ions on the opposite side of the host interstice [4]. The mobility of such a hydrated cation must be distinguished from that of the bare cation.

Mobile bare cations generally coordinate several anions and move diffusively through a crystalline array by hopping over an activation-energy barrier separating energetically equivalent sites. The sites are considered energetically equivalent as long as the configurations $\text{M} + \square$ and $\square + \text{M}$ have the same energy even though a local lattice reorganization accompanies the mobile ion, as in the case of a small polaron. However, ionic mobility requires only a partial occupancy of the energetically equivalent sites; if this condition is not fulfilled, thermal energy is required to create such a condition [5].

Oxide Ions

Oxide ions carry a relatively large negative charge and therefore interact strongly with the crystalline electric field. Moreover, a strong coulomb interaction between oxide-ion vacancies or between an oxide-ion vacancy and the impurity that creates it tends to produce vacancy ordering and/or traps that inhibit oxide-ion motion. Consequently the search for fast oxide-ion conduction at lower temperatures in a solid electrolyte has met with frustration. Nevertheless, mixed electron/oxide-ion conductors having good conductivities at lower temperatures are known; in these materials the oxide-ion vacancies are charge-compensated by mobile electrons that screen the coulomb interactions.

Ionic Conductivity

In the case of long-range diffusion, the ionic conductivity along a principal crystallographic axis is

$$\sigma_q = n_q q \mu_q \quad (3)$$

where n_q is the mobile-particle density, q is its charge, and

$$\mu_q = qD/kT \quad (4)$$

is its mobility along the crystallographic axis.

If the mobile particles move independently of one another, the single-particle jumps from occupied sites to energetically equivalent unoccupied sites may be described by random-walk theory; to first order the diffusion

coefficient is given by

$$D_q = (z/2d)\ell^2(1-c)v_h \quad (5)$$

where $d=1, 2$, or 3 for one-, two- or three-dimensional motion, $c \equiv n_q/N$ is the concentration of mobile ions on the array of N energetically equivalent lattice positions per unit volume accessible to the mobile ions, and z is the number of like nearest neighbors in this array. The factor $z(1-c)$ is thus the probability that a mobile ion has a like neighboring site that is empty. The jump frequency

$$v_h = v_o \exp(-\Delta G_m/kT) \quad (6)$$

contains the attempt frequency v_o , which is the optical-mode vibrational frequency for an ion displacement toward a neighboring equivalent site, and a mean migrational free energy

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (7)$$

for a charge-carrier hop between energetically equivalent sites separated a mean distance ℓ . Substitution of equations (4) - (7) into (3) gives

$$\sigma_q = \gamma(Nq^2/kT)c(1-c)\ell^2v_o \exp(-\Delta H_m/kT) \quad (8)$$

$$\gamma = f(z/2d)\exp(\Delta S_m/k) \quad (9)$$

where the factor f , of order unity, is introduced to account for any correlations between ionic jumps of neighboring mobile ions. An $N \sim \ell^{-3}$ makes $\sigma_q \sim \ell^{-1}$ increase with decreasing jump distance ℓ .

The fundamental determinants of the ionic conductivity are the factors $c(1-c)$ and v_h . Although v_o softens with decreasing ΔH_m , the exponential term determines the magnitude of v_h . For fast ionic conduction at room temperature, a small ΔH_m and a $c(1-c) \neq 0$ are required.

Empirically, long-range d.c. ionic conductivity is described by an equation of the form

$$\sigma_q = (A/T)\exp(-E_A/kT) \quad (10)$$

and comparison of equations (8) and (10) to deduce an $E_A = \Delta H_m$ is only valid where there is a partial occupancy of energetically equivalent mobile-ion sites such that the factor $c(1-c)$ is a temperature-independent fraction.

The significance of the factor $c(1-c)$ is illustrated in Fig. 4 for the

hydrogen-bond system in pure ice. The protonic energy level on a water molecule is represented by a bar; if it is occupied, the bar contains a circle. The proton-transfer reaction



requires an energy ΔG_g , so the density of mobile charge carriers is

$$[\text{OH}^-] = [\text{OH}_3^+] \sim \exp(-\Delta G_g/2kT) \quad (12)$$

which makes the measured activation energy of equation (10)

$$E_A = \Delta H_m + (\Delta H_g/2) \quad (13)$$

The H_2O -proton donor and acceptor levels correspond to the valence and conduction bands of a semiconductor. Mobile extrinsic charge carriers are introduced into a semiconductor by chemical doping; similarly mobile protons are introduced into an aqueous electrolyte by alteration of the pH. A $\text{pH} > 7$ means an $[\text{OH}^-] \gg [\text{OH}_3^+]$, which lowers the protonic electrochemical potential toward the H_2O -proton donor level, and proton Grotthus diffusion of the type



is the negative analog of hole conduction in a p-type semiconductor. A $\text{pH} < 7$ means an $[\text{OH}^-] \ll [\text{OH}_3^+]$, and Grotthus diffusion of the type



is the positive analog of electron conduction in an n-type semiconductor. The concentration of mobile proton vacancies or protons, and hence the value of $c(1-c)$, depends upon pH.

Examples

Particle and Layered Hydrates

Particle hydrates and layered hydrates consist of small particles or layers, commonly oxides, separated by a hydrogen-bonded aqueous matrix. Because hydrogen bonds can be broken by the application of pressure, these composite materials can be prepared into dense sheets at room temperature by cold-pressing. This fact has technological significance because a solid protonic electrolyte is used as a large-area electronic insulator separating the two electrodes of an electrochemical cell as well as the two reactants of the cell. Fast protonic conduction is found in the presence of neutral species, such as water or ammonia, that are volatile at temperatures too low for normal sintering.

Because the hydrogen-bonding, aqueous matrix is confined to small dimensions between particles, the matrix remains solid above the melting point of water. However, proton motion within this matrix is similar to that in the liquid state; it may occur via either Grotthuss or vehicular diffusion.

Particle size (or layer width) and composition influence the mobile-proton concentration as follows [6]. Metal ions at the surface of an oxide particle bind water in order to complete their normal coordination. A fraction of the protons associated with this water distribute themselves over the surface of the oxide to create surface hydroxyl anions. In a hydrate, the surface proton concentration comes into equilibrium with that of the matrix. If protons are pushed off the surface, the particles (or layers) become negatively charged; if protons are attracted to the surface, the particles (layers) become positively charged. The particles change sign at a critical pH, the point of zero zeta potential (pzzp). An oxide is said to be acidic if its pzzp is $< \text{pH } 7$ so that protons are pushed off the surface into a neutral (pH) aqueous matrix; it is basic if its pzzp is $> \text{pH } 7$. Colloidal particles and layers have a large surface-to-volume ratio, so they are more effective than large particles at changing the pH of the aqueous matrix. The mobilities of the protons or proton vacancies are greater the less structured the water in which they move, and the structure of the aqueous matrix decreases with distance from the surface of the particle or layer. Therefore the conductivity of a particle or layered hydrate drops off with increasing temperature more rapidly than predicted by equation (10) if the higher temperatures cause a loss of water. Technical applications at elevated temperatures require operation under a high pressure of water vapor.

The protonic conductivities vs reciprocal temperature for several particle and layered hydrates are compared in Fig. 5 with that of a strong acid, 1M HCl. The high protonic conductivity of solid $\text{H}_3\text{Mo}_{12}\text{P}_{40}\cdot 29\text{H}_2\text{O}$ is due to the small size and strongly acidic (pzzp $< \text{pH } 7$) character of the elementary particles as well as the large fraction of water. In this compound, the elementary particles are uniform $\text{Mo}_{12}\text{P}_{40}$ polyanions, called Keggin units, that consist of a central PO_4 group corner-sharing with four triangular units of three edge-shared Mo(VI) octahedra. The Mo(VI) ions form short $\text{M}=\text{O}$ bonds with the terminal oxide ions, and no short $\text{O}-\text{H}$ bond is formed at a terminal oxygen to compete with the $\text{M}=\text{O}$ bond. The other surface oxide ions of the Keggin unit bridge two Mo(VI) ions, and their interaction with two Mo(VI) ions is stronger than that of a water oxide ion to its two protons. Consequently the equilibrium