MODERN ASPECTS OF ELECTROCHEMISTRY

No. 38

Modern Aspects of Electrochemistry

Modern Aspects of Electrochemistry, No. 37:

- The kinetics of electrochemical hydrogen entry into metals and alloys.
- The electrochemistry, corrosion, and hydrogen embrittlement of unalloyed titanium. This important chapter discusses pitting and galvanostatic corrosion followed by a review of hydrogen embrittlement emphasizing the formation of hydrides and their effect on titanium's mechanical properties.
- Oxidative electrochemical processes of organics, introduces an impressive model that distinguishes active (strong) and non-active (weak) anodes.
- Comprehensive discussions of fuel cells and Carnot engines; Nernst law; analytical fuel cell modeling; reversible losses and Nernst loss; and irreversible losses, multistage oxidation, and equipartition of driving forces. Includes new developments and applications of fuel cells in trigeneration systems; coal/biomass fuel cell systems; indirect carbon fuel cells; and direct carbon fuel cells.
- Exploration of the catalytic effect of trace anions in outer-sphere heterogeneous charge-transfer reactions.
- Results of the experimental and theoretical investigations on bridging electrolyte-water systems as to thermodynamic and transport properties of aqueous and organic systems. Revised version of chapter four in Number 35.

Modern Aspects of Electrochemistry, No. 36:

- The study of electrochemical nuclear magnetic resonance (EC-NMR); in situ both sides of the electrochemical interface via the simultaneous use of 13C and 193Pt NMR
- Recent impressive advances in the use of rigorous ab initio quantum chemical calculations in electrochemistry.
- Fundamentals of ab initio calculations, including density functional theory (DFT) methods, help to understand several key aspects of fuel cell electrocatalysis at the molecular level.
- The development of the most important macroscopic and statistical thermodynamic models that describe adsorption phenomena on electrodes
- Electrochemical promotion and recent advances of novel monolithic designs for practical utilization.
- New methods for CT analysis and an explanation for the existing discrepancy in Li diffusivity values obtained by the diffusion control CT analysis and other methods.

MODERN ASPECTS OF ELECTROCHEMISTRY

No. 38

Edited by

B. E. CONWAY
University of Ottawa
Ottawa, Ontario, Canada

C. G. VAYENAS
University of Patras
Patras, Greece

RALPH E. WHITE
University of South Carolina
Columbia, South Carolina

and

MARIA E. GAMBOA-ADELCO
Managing Editor
Superior, Colorado

KLUWER ACADEMIC PUBLISHERS
NEW YORK, BOSTON, DORDRECHT, LONDON, MOSCOW

eBook ISBN: 0-306-48704-7
Print ISBN: 0-306-48703-9

Created in the United States of America

LIST OF CONTRIBUTORS

A. J. APPLEBY
238 Wisenbaker Engineering
Research Center
Texas A&M University,
College Station, TX 77843-3402

ROLANDO GUIDELLI
Dept. of Chemistry,
Florence University,
Via della Lastruccia 3
50019 Sesto Fiorentino, Firenze,
Italy

ARJAN HOVESTAD
Faculty of Chemical Engineering,
Eindhoven University of
Technology,
Eindhoven, The Netherlands

LEONARD J. J. JANSSEN
Faculty of Chemical Engineering,
Eindhoven University of
Technology,
Eindhoven, The Netherlands

JOACHIM MAIER
Max-Planck-Institut für
Festkörperforschung,
Heisenbergstraße 1, 70569
Stuttgart, Germany

N. D. NIKOLIĆ
ICTM–Institute of
Electrochemistry,
Belgrade,
Serbia and Montenegro

K. I. POPOV
Faculty of Technology and
Metallurgy,
University of Belgrade,
Serbia and Montenegro

Z. RAKOČEVIĆ
Vinča Institute of Nuclear
Sciences,
Belgrade,
Serbia and Montenegro

WOLFGANG SCHMICKLER
Abteilung Elektrochemie,
Ulm University,
89069 Ulm, Germany

PAUL STONEHART
Stonehart Associates Inc.
17 Cottage Read,
Madison, Connecticut
06443-1220 U.S.A.

DOUGLAS WHEELER
UTC (United Technologies
Corporation) Fuel Cells,
195 Governor's Highway, South
Windsor, Connecticut
06074 U.S.A.

Preface

This volume comprises six chapters on aspects of fundamental and applied electrochemical science that will be of interest both to researchers in the basic areas of the subject and to those involved in aspects of electrochemical technologies.

Chapter 1 is the first part of a 2-part, major contribution by Joachim Maier on Solid State Electrochemistry: Thermodynamics and Kinetics of Charge Carriers in Solids. Part 2 will follow in volume 39 to be published in year 2005. This contribution reviews modern concepts of the equilibria involving charge carriers in solids in terms of concentrations of defects in solids and at grain-boundaries, including doping effects. Complementarily, kinetics of charge transfer and ion transfer are treated in some detail in relation to conductance, kinetics of surface processes and electrode-kinetics involving solid-state processes. This chapter will be of major interest to electrochemists and physicists in the semiconductor field and that involving ionic solids.

In the second chapter, Appleby presents a detailed discussion and review in modern terms of a central aspect of electrochemistry: Electron Transfer Reactions With and Without Ion Transfer. Electron transfer is the most fundamental aspect of most processes at electrode interfaces and is also involved intimately with the homogeneous chemistry of redox reactions in solutions. The subject has experienced controversial discussions of the role of solvational interactions in the processes of electron transfer at electrodes and in solution, especially in relation to the role of "Inner-sphere" versus "Outer-sphere" activation effects in the act of electron transfer. The author distils out the essential features of electron transfer processes in a *tour de force* treatment of all aspects of this important field in terms of models of the solvent (continuum and molecular), and of the activation process in the kinetics of electron transfer reactions, especially with respect to the applicability of the Franck-Condon principle to the time-scales of electron transfer and solvational excitation. Sections specially devoted to hydration of the proton and its heterogeneous transfer, coupled with electron transfer in cathodic H deposition and H_2 evolution, are important in this chapter.

Chapter 3, by Rolando Guidelli, deals with another aspect of major fundamental interest, the process of electrosorption at electrodes, a topic central to electrochemical surface science: Electrosorption Valency and Partial Charge Transfer. Thermodynamic examination of electrochemical adsorption of anions and atomic species, e.g. as in underpotential deposition of H and metal adatoms at noble metals, enables details of the state of polarity of electrosorbed species at metal interfaces to be deduced. The bases and results of studies in this field are treated in depth in this chapter and important relations to surface - potential changes at metals, studied in the gas-phase under high-vacuum conditions, will be recognized. Results obtained in this field of research have significant relevance to behavior of species involved in electrocatalysis, e.g. in fuel-cells, as treated in chapter 4, and in electrodeposition of metals.

In chapter 4, Stonehart (a major authority in the field of H_2 fuel-cell technology and its fundamental aspects) writes, with co-author Wheeler, on the topic of : Phosphoric Acid Fuel-Cells (PAFCs) for Utilities: Electrocatalyst Crystallite Design, Carbon Support, and Matrix Materials Challenges. This contribution reviews, in detail, recent information on the behavior of very small Pt and other alloy electrocatalyst crystallites used as the electrode materials for phosphoric acid electrolyte fuel-cells.

A materials - science aspect of metal electrodes is treated in chapter 5, by Nicolić and Radočević: Nanostructural Analysis of Bright Metal Surfaces in Relation to Their Reflectivity. This is an area of practical importance in electrochemistry applied, e.g., to metal finishing. Details of how reflectivity and electron microscopy can be usefully applied in this field are given with reference to many examples.

Finally, in chapter 6, another direction of applied electrochemistry is treated by Hovestad and Janssen; Electroplating of Metal Matrix Composites by Codeposition of Suspended Particles. This is another area of metals materials-science where electroplating of a given metal is conducted in the presence of suspended particles, e.g. of Al_2O_3, BN, WC, SiC or TiC, which become electrodeposited as firmly bound occlusions. Such composite deposits have improved physical and electrochemical properties. Process parameters, and mechanisms and models of the codeposition processes are described in relation to bath compositions, particle compositions, micrographs and dispersion hardening conditions.

B. E. Conway

University of Ottawa
Ottawa, Ontario, Canada

R. E. White

University of South Carolina
Columbia, South Carolina

C. Vayenas,

University of Patras
Patras, Greece

Contents

Chapter 1

SOLID STATE ELECTROCHEMISTRY I: THERMODYNAMICS AND KINETICS OF CHARGE CARRIERS IN SOLIDS

Joachim Maier

Chapter 2

ELECTRON TRANSFER REACTIONS WITH AND WITHOUT ION TRANSFER

A. J. Appleby

Chapter 3

ELECTROSORPTION VALENCY AND PARTIAL CHARGE TRANSFER

Rolando Guidelli and Wolfgang Schmickler

Chapter 4

PHOSPHORIC ACID FUEL-CELLS (PAFCs) FOR UTILITIES: ELECTROCATALYST CRYSTALLITE DESIGN, CARBON SUPPORT, AND MATRIX MATERIALS CHALLENGES

Paul Stonehart and Douglas Wheeler

Chapter 5

NANOSTRUCTURAL ANALYSIS OF BRIGHT METAL SURFACES IN RELATION TO THEIR REFLECTIVITY

N. D. Nicolić, Z. Radočević and K. I. Popov

Chapter 6

ELECTROPLATING OF METAL MATRIX COMPOSITES BY CODEPOSITION OF SUSPENDED PARTICLES

Arjan Hovestad and Leonard J. J. Janssen

MODERN ASPECTS OF ELECTROCHEMISTRY

No. 38

1

Solid State Electrochemistry I: Thermodynamics and Kinetics of Charge Carriers in Solids

Joachim Maier

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany. E-mail: s.weiglein@fkf.mpg.de

I. INTRODUCTION

This contribution deals with thermodynamics and kinetics of charge carriers in solids in the case of zero or non-zero electrical or chemical driving forces. It does not intend to repeat well-known electrochemical principles, however, it intends to underline the special situation in solids by, on one hand, emphasizing characteristic aspects due to the solid nature, but on the other hand, stressing the common and generalizing aspects of the picture whenever it appears necessary. This also implies that specific solid state aspects (such as structural details, anisotropies or strain effects) are neglected whenever their influence is not indispensable for the understanding.

The present contribution does not include solid state techniques to measure electrochemical parameters, nor does it consider applications of solid state electrochemistry. Such topics will be dealt with in a second part which will appear separately.[1]

Modern Aspects of Electrochemistry, Number 38, edited by B. E. Conway *et al.* Kluwer Academic/Plenum Publishers, New York, 2005.

In the traditional electrochemical community solids have a long tradition, however, almost exclusively from the stand-point of electronic processes. Careful studies have been performed in order to understand the behavior of metallic or semi-conductive electrodes in contact to liquid electrolytes in great detail. Ionic processes are mostly considered to occur “outside” the solid, i.e., on its surfaces or in the fluid phases adjacent. More recently, in particular in conjunction with applications such as lithium batteries or fuel cells the ionic conductivity and the appearance of mixed ionic electronic conductivity within the solid state is more and more appreciated, but even in “modern” electrochemical textbooks one hardly finds any specific mention of the ionic charge carriers in solids, which are the ionic point defects. On the other hand, such considerations are in the focus of entire solid state communities which, however, vastly concentrated on solid electrolytes. Recently and again triggered by electrochemical applications such as batteries, fuel cells, sensors or chemical filters, interfacial processes are more and more getting to the fore in the field of solid state ionics. Hence, treatments that try to combine and generalize relevant aspects and concepts are desired. The contribution does not aim to be exhaustive, it concentrates on issues being particularly relevant in this context. It can partly rely on and refer to a variety of excellent existing reviews[2-22] and in particular on a comprehensive monograph that appeared recently.[23,24]

II. SOLIDS VS. LIQUIDS

If a liquid is reversibly cooled below the melting point, the solid, i.e., a three-dimensional giant molecule (“3D polymer”) forms, characterized by a long range order. So-formed crystals exhibit strict periodicity. While, in the case of liquids, structural configurations fluctuate in space and time, glasses as “frozen liquids” or other amorphous solids show also fluctuations but essentially only with respect to the position coordinate.

There is neither a sharp demarcation in the treatment of solids compared to molecular units, nor is there a strict demarcation in the treatment of different bonding types. It is Schrödinger’s (or Dirac’s) equation that describes the bonding situation in all cases. Nonetheless, it proves meaningful to use “ad hoc” classifications.

In some cases the bond strength between the "monomers" (intermolecular forces) is weak and molecular crystals are formed, in others the intermolecular forces are not at all saturated within the monomer and no real distinction between inter- and intramolecular forces can be made, as is the case in typical ionic crystals, covalent crystals or metal crystals. In the latter two cases the orbitals of the bonding partners severely overlap forming comparatively wide bands in which the electrons are delocalised. In the case of metals (e.g. Na) the topmost non-empty band is only partially filled also in the thermal ground state, and the outer electrons are nearly freely mobile. In the case of typical covalent crystals (such as Si), at $T = 0$ K the topmost non-empty band is completely filled, the electrons therein immobile, and the bands of higher lying unoccupied levels separated by a substantial gap (which corresponds to the energy distance between the bonding and anti-bonding level in the two-atom problem). Those electrons can also be thought to be situated between the bonding partners. In the case of ionic crystals (e.g. NaCl) the bonding electrons are affiliated with orbitals of the electronegative partners only. Hence orbitals of the anionic partner usually form the highest occupied band while orbitals of the cationic partner form the lowest unoccupied band. (This is at least so in the case of main group elements. In a variety of transition metal oxides, e.g., both valence and conduction bands refer to the cationic states.) Owing to poor interaction of the atoms of the same kind the bands are quite narrow. (In this context it is also worthy of mention that — according to Mott — too large a distance between atoms prevents sufficient orbital overlap and delocalization.[25,26])

As well known from semiconductor physics, in non-metals electrons are, at finite temperatures, excited from the highest occupied band to the lowest unoccupied band to form excess electrons in the conduction band and electron holes in the valence band. Owing to long-range order each crystal possesses a certain amount of "free" electronic carriers. The mixed conductor which exhibits both ionic and electronic conductivity, will play an important role in this text, since it represents the general case, and pure ionic and electronic (semiconductors) conductors follow as special cases.

Under the conditions we will refer to here (the yield strength is not reached), a potentially applied stress does not change the form (no plastic deformation) during the electrochemical performance or measurements, rather is elastically supported. (The viscosity is virtually infinite; only at very high temperatures and/or extreme driving forces a creep of the solid becomes possible.) There is no convective flow, and diffusive transport is the decisive mechanism of mass transport. Owing to this, solid-solid contacts frequently exhibit a low degree of perfection.

Under usual conditions at least one sublattice is very rigid and—in the case of interest (in particular when dealing with solid ion conductors)—one sublattice exhibits a significant atomic mobility. The selectivity of the conductivity (cf. also the selective solubility of foreign species) is indeed a characteristic feature of solids.

A paramount role is played by point defects;[1,2] the configurational entropy gained by their presence allows them to be present even in thermodynamical equilibrium; they have their counterpart in liquids and will be considered explicitly in the next chapter.

Further characteristic solid state properties following from the high bond strength compared to kT, are the anisotropies of structure and properties (transport coefficients e.g. are tensors) as well as the occurrence of higher-dimensional defects such as dislocations and internal boundaries.

Grain boundaries are a specific feature of the solid state and are typical non-equilibrium defects. Their metastability, however, is often so high and their influence can be so great that it is very necessary to consider them explicitly. In the following text we will refer to them as frozen-in structure elements with zero mobility. Dislocations are usually more mobile and can often be healed out (if they are not constituting grain boundaries); we will neglect them in the following.

While external boundaries are in principle necessary because of mass conservation, their amount, nature and arrangement, and hence the shape, are usually not in equilibrium. (As long as we can ignore the energetic influence of intersections of surfaces, the Wulff-shape represents the equilibrium shape of crystals.[27,28] The Wulff-shape is characterized by a ratio of surface tension and orthogonal distance from the center that is common to every surface plane; as it is only rarely established, we will also consider the shape as frozen-in.) The occurrence of internal interfaces leads to the fact that upon the (usually strictly periodic) atomic structure we have to superimpose the micro-structure which is of rather fuzzy periodicity – if we may use this term at all. Lastly let us come back to the point that sluggish kinetics prevent many materials from adopting the ordered state: In inorganic glasses or many polymers the atomic structure is amorphous. Then, as already stated, structural fluctuations occur in space but under usual conditions not in time. Let us start with the atomic structure and the ionic charge carriers therein.

III. POINT DEFECTS AS CHARGE CARRIERS

The ionic charge carriers in ionic crystals are the point defects.[1,2,23,24] They represent the ionic excitations in the same way as H_3O^+ and OH^- ions are the ionic excitations in water (see Fig. 1). They represent the chemical excitation upon the perfect crystallographic structure in the same way as conduction electrons and holes represent electronic excitations upon the perfect valence situation. The fact that the perfect structure, i.e., ground structure, of ionic solids is composed of charged ions, does not mean that it is ionically conductive. In AgCl regular silver and chloride ions sit in deep Coulomb wells and are hence immobile. The occurrence of ionic conductivity requires ions in interstitial sites, which are mobile, or vacant sites in which neighbors can hop. Hence a “superionic” dissociation is necessary, as, e.g. established by the Frenkel reaction:

$$Ag_nCl_n + Ag_{n'}Cl_{n'} \rightleftarrows (Ag_{n+1}Cl_n)^+ + (Ag_{n'-1}Cl_{n'})^- \qquad (1)$$

or more concisely in a “molecular notation”

$$2\,AgCl \rightleftarrows Ag_2Cl^+ + \square Cl^- \qquad (2)$$

where it is indicated that a vacancy is formed within the cluster from which Ag^+ is removed.

A major difference of the crystalline state compared with the liquid state, is that the sites are crystallographically defined and need to be conserved in such reactions. In defect nomenclature this crystallographic site is usually given as a lower index, where i denotes the interstitial site which is occupied in $(Ag_{n+1}Cl_n)^+$, or referring to Eq. (2) in the Ag_2Cl^+ unit. In the rock-salt structured AgCl where the Ag^+ ions regularly occupy all octahedral interstices of the close-packed

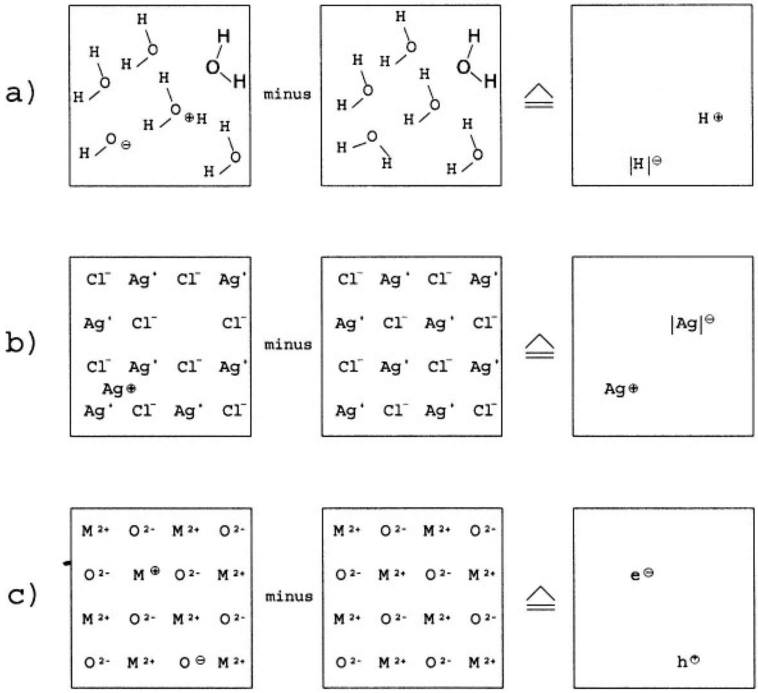

Figure 1. a) If the compositionally unperturbed structure (chemical ground structure) is substracted from the real structure, the point defects shown on the right remain. Naturally each is surrounded by a distorted region (effective radius of the point defect) which affects at least the immediate neighborhood. In the case of fluid phases (see above) this procedure can only be regarded as an instantaneous picture. Owing to the absence of defined sites no distinction is made between various types of defect reactions as is done in the solid state. b) Frenkel disorder is sketched in the second row. c) Third row shows the case of purely electronic disorder. Here the charge carriers are assumed to be localized for the sake of clarity.[20]

chlorine lattice $(n' = 6)$, the interstitial site is the tetrahedral interstice $(n = 4)$. Instead of writing □ it is customary to use the symbol V (for vacancy).[2]

Since the above disorder reaction is restricted to the silver sublattice we can condense Eq. (2) to the even more concise form:

$$\mathrm{Ag}^{+}_{\mathrm{Ag}^{+}} + \mathrm{v}^{0}_{\mathrm{i}} \rightleftarrows \mathrm{Ag}^{+}_{\mathrm{i}} + \mathrm{v}^{0}_{\mathrm{Ag}^{+}} \qquad (3)$$

As already considered, the absolute charges do not really matter, the regular Ag-ion, $\mathrm{Ag}^{+}_{\mathrm{Ag}^{+}}$, is not mobile in contrast to the silver vacancy $\mathrm{v}^{0}_{\mathrm{Ag}^{+}}$. Hence it is advantageous to refer to relative charges (the structure element $\mathrm{M}^{z^{*}}_{\mathrm{S}z^{r}}$ has the relative charge $z^{*}- z^{r}$). Omitting the absolute charges leads to the Kröger-Vink formulation[29]

$$\mathrm{Ag}^{x}_{\mathrm{Ag}} + \mathrm{v}^{x}_{\mathrm{i}} \rightleftarrows \mathrm{Ag}^{\bullet}_{\mathrm{i}} + \mathrm{v}'_{\mathrm{Ag}} \qquad (4)$$

Here the cross denotes the relative charge zero, the prime ' the relative charge -1 and the dot · the relative charge +1. Even though it is the special notation that creates quite an activation barrier to deal with point defect chemistry, it proves extremely helpful, once being familiar with it. Equation (4) denotes the so-called Frenkel reaction in structural element formulation, i.e., in terms of particles that actually constitute the real crystal. Unfortunately, thermodynamics demand strictly speaking the treatment of so-called building elements, elements that you can add to the perfect crystal.[30] The chemical potential of a vacant site, e.g. measures the increase in Gibbs energy on adding a vacancy. However, adding the structure element vacancy $(\mathrm{v}'_{\mathrm{Ag}})$ requires the removal of a lattice constituent $(\mathrm{Ag}^{x}_{\mathrm{Ag}})$. This leads to a complete relative description in which the Frenkel reaction is described by

$$\mathbf{Nil} \rightleftarrows \textbf{(excess silver ion)}^{\bullet} + \textbf{(lacking silver ion)}' \equiv \mathrm{Ag}^{\bullet} + |\mathrm{Ag}|' \qquad (5)$$

(On the r.h.s. the defects are written in Schottky's building element notation,[30] also used in Fig. 1.) Equation (5) is obtained by subtracting 2AgCl from Eq. (2) or bringing the regular constituents in Eq. (4) to the right hand side: Obviously $\textbf{(excess silver ion)}^{\bullet} \equiv (\mathrm{Ag}^{\bullet}_{\mathrm{i}} - \mathrm{Ag}^{x}_{\mathrm{Ag}})$ and (lacking silver ion)' $\equiv \mathrm{V}'_{\mathrm{Ag}} - \mathrm{Ag}^{\mathrm{x}}_{\mathrm{Ag}}$ are the entities for which chemical potentials can be rigorously defined.

The treatment in terms of excess and lacking particles is the key to defect chemistry. The similarity with "aqueous chemistry" is obvious: We end up with an analogous "disorder" equation (as a snap-shot at a given time) with H_3O^+ and OH^- as "defects" when removing all H_2O from the autoprotolysis reaction:

$$2\,H_2O \rightleftarrows H_3O^+ + OH^- \tag{6}$$

$$H_2O \rightleftarrows H^+ + OH^- \tag{7}$$

$$\mathrm{Nil} \rightleftarrows (\text{excess proton})^+ + (\text{lacking proton})^- \equiv H^+ + |H|^- \tag{8}$$

(compare Eq. 6 with Eq. 2; Eq. 7 with Eqs. 3 and 4; and Eq. 8 with Eq. 5). Here we still can use absolute charges since the ground state is uncharged.

The analogous situation is met if we excite an electron from the ground state (electron in the valence band, VB) to an energetically higher position (in the conduction band, CB), e.g. in silicon, according to

$$\mathrm{Si}_{\mathrm{Si}} + \mathrm{Si}_{\mathrm{Si}} \rightleftarrows \mathrm{Si}^{+}_{\mathrm{Si}} + \mathrm{Si}^{-}_{\mathrm{Si}} \tag{9}$$

$$\mathrm{e}^{-}_{\mathrm{VB}} + \mathrm{v}_{\mathrm{CB}} \rightleftarrows \mathrm{v}_{\mathrm{VB}} + \mathrm{e}^{-}_{\mathrm{CB}} \tag{10}$$

the symbol V denotes here the electronic vacancy (hole). Equation (10) reads in relative charges

$$\mathrm{e}^{\mathrm{x}}_{\mathrm{VB}} + \mathrm{v}^{\mathrm{x}}_{\mathrm{CB}} \rightleftarrows \mathrm{e}'_{\mathrm{CB}} + \mathrm{v}^{\bullet}_{\mathrm{VB}} \tag{11}$$

or simpler in building element notation $(e' \equiv e'_{CB} - v^{x}_{CB}$, $h^{\bullet} \equiv v^{\bullet}_{VB} - e^{x}_{VB} \equiv |e|^{\bullet})$

$$\text{Nil} \rightleftarrows (\text{excess electron})' + (\text{lacking electron})^{\bullet} \equiv e' + h^{\bullet} \qquad (12)$$

Equation (12) is independent of any detailed knowledge of the band structure. In AgCl where the valence band is formed by the Cl-p orbitals and the conduction band by the Ag-d orbitals, the detailed formulation of Eq. (12) would read

$$Ag^{+} + Cl^{-} \rightleftarrows Ag^{0} + Cl^{0} \qquad (13)$$

while in PbO, to mention a main group metal oxide (see Fig. 1c), we would have to write

$$Pb^{2+} + O^{2} \rightleftarrows Pb^{+} + O^{-} \qquad (14)$$

In the case of transition metal compounds such as $LaMnO_3$ d-level splitting can be so pronounced that both valence and conduction band are derived from d-orbitals. For $LaMnO_3$, e.g. Eq. (12) has to be interpreted as a redox disproportionation

$$Mn^{3+} + Mn^{3+} \rightleftarrows Mn^{4+} + Mn^{2+} \qquad (15)$$

Note that generally bands correspond to hybrids, and attributing bands to certain elements is an approximation. Unlike the electronic "energy" level distribution, the distribution of ionic "energy" levels in crystals (the meaning of which we will consider in the next section) is discrete. In the electronic case we face bands comprising a manifold of narrowly neighbored levels, so that we better speak of a continuous density of states.

In a fluid system such as water the energy levels can be conceived as smeared out on spatial and time average, while in amorphous solids the structure fluctuations occur in space but (approximately) not in time (see e.g. Refs.[31-34]).

IV. EQUILIBRIUM CONCENTRATION OF CHARGE CARRIERS IN THE BULK

1. Defect Reactions

A major difference between crystals and fluids refers to the necessity of distinguishing between different sites. So the autoprotolysis in water could, just from a mass balance point of view, also be considered e.g. as a formation of a OH^- vacancy and a H^+ vacancy. In solids such a disorder is called Schottky disorder (S) and has to be well discerned from the Frenkel disorder (F). In the densely packed alkali metal halides in which the cations are not as polarizable as the Ag^+, the formation of interstitial defects requires an unrealistically high energy and the dominating disorder is thus the Schottky reaction

$$\mathrm{Na_{Na}} + \mathrm{Cl_{Na}} \rightleftarrows \mathrm{NaCl} + \vee'_{\mathrm{Na}} + \vee^{\bullet}_{\mathrm{Cl}} \tag{16}$$

which reads in building element notation

$$\text{Nil} \rightleftarrows \text{NaCl} + (\text{lacking sodium ion})' + (\text{lacking chlorine ion})^{\bullet} \tag{17}$$

In particular if the anions are as small as F^-, e.g. in CaF_2, we can have Frenkel disorder in the anion sublattice, which is also referred to as anti-Frenkel-disorder ($\overline{\mathrm{F}}$),

$$\mathrm{F_F} + \vee_{\mathrm{i}} \rightleftarrows \mathrm{F}'_{\mathrm{i}} + \vee^{\bullet}_{\mathrm{F}} \tag{18}$$

Equation (18) reads in building element notation

$$\text{Nil} \rightleftarrows (\text{excess fluorine ion})' + (\text{lacking fluorine ion})^{\bullet} \tag{19}$$

In addition, there should also be the possibility of having the so-called anti-Schottky reaction $(\overline{\mathrm{S}})$ in materials with comparatively loose structures, such as orthorhombic PbO

$$\mathrm{PbO} + \mathrm{v}_{\mathrm{i(Pb)}} + \mathrm{v}_{\mathrm{i(O)}} \rightleftarrows \mathrm{Pb}_{\mathrm{i}}^{\bullet\bullet} + \mathrm{O}_{\mathrm{i}}'' \qquad (20)$$

or in terms of building elements

$$\mathrm{PbO} \rightleftarrows (\text{excess lead ion})^{\bullet\bullet} + (\text{excess oxygen ion})'' \qquad (21)$$

More complex internal defect reactions involve association reactions or doping effects; they will be considered later. (For more extensive treatments of defect chemistry see Ref.[2])

All these reactions leave the 1:1 composition, the “Dalton composition”[23], unchanged. However, according to the phase rule, stoichiometric variations are possible by tuning the chemical potential of one component, e.g. the chlorine partial pressure over AgCl or the oxygen partial pressure over PbO, (or generally n-1 component partial pressures in a n-component multinary, e.g. the O_2 and SrO partial pressures over $SrTiO_3$). The interaction with oxygen may be formulated as:

$$\frac{1}{2}\mathrm{O}_2 + \mathrm{v}_{\mathrm{O}}^{\bullet\bullet} + 2\mathrm{e}' \rightleftarrows \mathrm{O}_{\mathrm{O}} \qquad (22)$$

meaning that the oxygen is incorporated on a vacant site as O^{2-} which requires the annihilation of two conduction electrons. Equally the interaction could have been formulated by assuming that two regular electrons are annihilated (and $2h^{\bullet}$ would be formed), or we could have incorporated oxygen ions into interstitial sites. In equilibrium one formulation suffices, since the others follow by reaction combinations. It is advisable to use a formulation in terms of majority carriers. Evidently, Eq. (22) involves the ionic and electronic defects, changes the oxide $MO_{1+\delta}$ into $MO_{1+\delta+\Delta\delta}$ and implies a variation of the mean oxidation numbers. (In ternary systems such stoichiometric changes can occur without involving the electronic budget, e.g. the incorporation of H_2O in NaOH.)

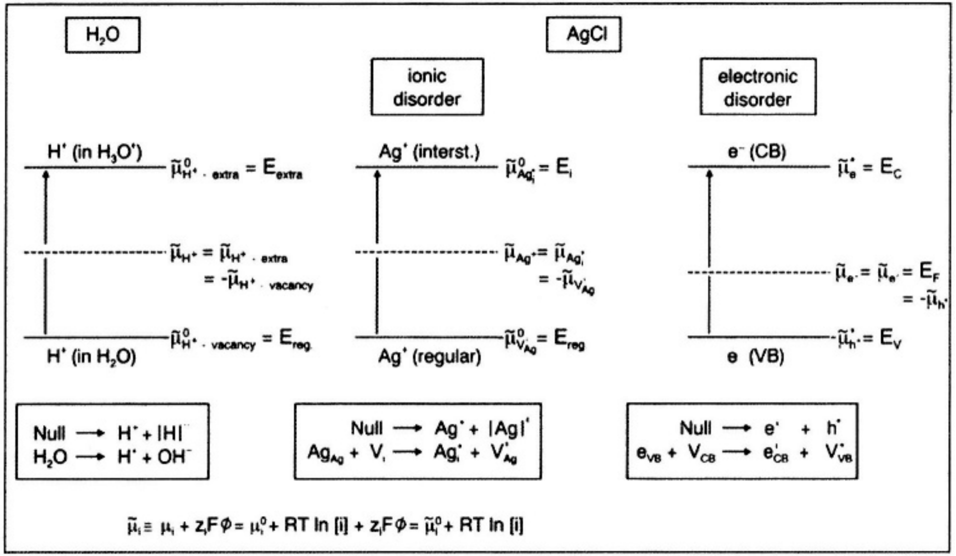

Figure 2. Electronic and ionic disorder in ionic solids and in water in "physical" (top) and "chemical" language (*bottom*).[20] The coupling of the ionic and electronic Fermi levels takes place via the chemical potential of the neutral components (here: $\tilde{\mu}_{\mathrm{Ag}^+} + \tilde{\mu}_{\mathrm{e}^-} = \mu_{\mathrm{Ag}}$) (see Fig. 3). A further relevant example could be the breaking-up of an ion pair in a polymer.

For a given material all the defect reactions considered so far occur to a greater or lesser extent. It is the problem of the next section to show how the equilibrium concentrations of all defects (including electronic carriers) can be calculated.

2. Equilibrium Defect Concentrations in Pure Compounds

Figure 2 translates the charge carrier formation reaction into an "energy level" diagram for various systems. In fact these levels refer to standard chemical potentials or (in the case of the "Fermi-levels") to full chemical potentials (see e.g. Refs.[3,35]). As long as —in pure materials— the gap remains large compared to RT, the Boltzmann-form of the chemical potential of the respective charge carrier (defect) is valid,

$$\mu_j = \mu_j^\circ + RT \ln (c_j / c_j^\circ) \tag{23}$$

independent of the charge carrier situation and also independent of the form of the energy level distributions. If there is a smearing out of the levels or even a band of levels, μ_j° refers to an effective level, such as the band edges when dealing with the electronic picture. Equation (23) results from a simple combinatorial analysis by assuming a random configurational entropy, and it is the configurational entropy which is the reason why defective states of atomic dimensions (such as vacancies, interstitial sites, excess electrons, holes, H_3O^+, OH^- etc.) are important in thermal equilibrium, i.e., exhibiting non-zero concentrations. Figure 3 shows the coupling of the ionic level picture and the electronic level picture for AgCl via the thermodynamic relation $\mu_{Ag^+} + \mu_{e^-} = \mu_{Ag}$ and hence via the precise position in the phase diagram.

Let us consider an elemental crystal first (with defect d). If N_d identical defects are formed in such a crystal of N identical elements, a local free enthalpy of Δg_d^0 is required to form a single defect, and if interactions can be neglected, the Gibbs energy of the defective crystal (G_p refers to the perfect crystal) is

$$G = G_p + N_d \Delta g_d^\circ - k_B T \ln \binom{N}{N_d} \tag{24}$$

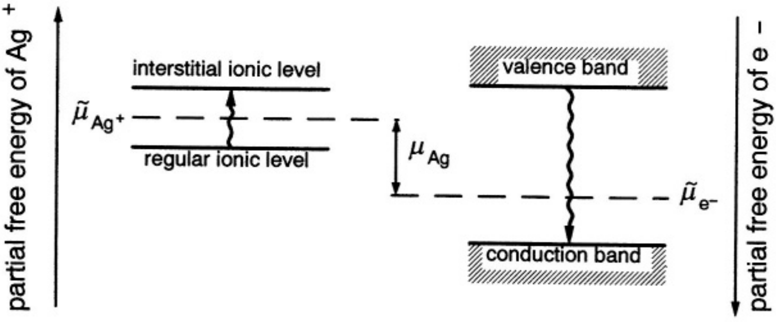

Figure 3. Coupling of ionic and electronic levels in AgCl.[36,37] (Reprinted from J. Maier, "Defect chemistry and ion transport in nanostructured materials. Part II. Aspects of nanoionics." *Solid State Ionics,* **157,** 327-334. Copyright © 2003 with permission from Elsevier.)

(For a description of how $\mathbf{\Delta g^0}$ can be atomistically computed, the reader is referred to the literature.[18,38-40]) Owing to the infinitely steep decrease of the configurational entropy term (cf. last term in Eq. 24) there is a minimum in G (see Fig. 4) that occurs in our elemental crystal if the

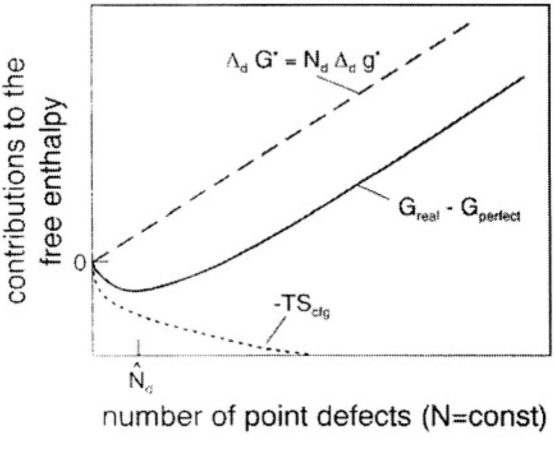

Figure 4. Contributions to the free enthalpy of the solid by defect formation with a constant total number of sites.