Second Edition

Physical Chemistry of Ionic Materials

Ions and Electrons in Solids

JOACHIM MAIER

WILEY

Physical Chemistry of Ionic Materials

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Ions and Electrons in Solids

Joachim Maier Max Planck Institute for Solid State Research, Stuttgart, Germany

Second Edition

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Preface to the Second Edition

This second edition is a substantially reworked version of the first. First of all, textual defects in the presentation have been removed. Although it would be easy to justify their presence in a book in which the defects are the major players*, it is advisable to refrain from using such cheap argument. Fortunately, most of the defects have been local and easily identifiable as imperfections. The justification for leaving major parts unchanged is based on Dyson's dictum, which the reader finds** in footnote 31 in Chapter 8 and hence because of the fact that the conceptual parts do not lose their validity. Consequentially, the major new additions refer to applied aspects. In particular, the field of batteries has experienced a boost and many new materials surfaced. In fact, the chapter about solid-state electrochemistry now turned into two, the first on fundamentals and the second on applications. Moreover, sections on photo- and bio-electrochemistry have been included, as well as a small paragraph on atomistic modeling. Last but not least, a chapter on nanoionics has been added, not only because it is a favorite subject of the author but also because it wonderfully criss-crosses all the various topics, ranging from bonding properties to electrochemistry via thermodynamics and kinetics, and forms an (almost) perfect ending. It equally affects the fundamentals and applications and beyond that may foster synergies between various disciplines. In addition to the persons that I had acknowledged in the first edition, let me thank Eugene Kotomin, Bettina Lotsch, Jochen Mannhart, Davide Moia, and Rob Usiskin for scientific discussions; Madeleine Burkhardt for her great help in getting the new text written; and finally Angelika simply for being around. Annette Fuchs, Maximilian Hödl, Markus Joos, Rotraut Merkle, Davide Moia, Chuanlian Xiao, and Yue Zhu have kindly read the new sections.

Stuttgart, November 2022

Joachim Maier

** A brief statement on the extensive use of footnotes (like this one) shall be added. In spite of a certain loss of elegancy, I consider them extremely helpful as they provide in-depth information such as proofs or advanced information without disrupting the reading flow. They are highly recommended to be visited if the reader wants to dive into a special topic, but they are not necessary for the understanding of the major text. The alternative, to put such information in an isolated appendix, might be aesthetically preferable but is – as experience shows – not really helpful.

^{*} There is a crack in everything, that's how the light gets in. (Leonard Cohen)

Preface to the First Edition

The book that you are about to read is, in a broad sense, concerned with the physical chemistry of solids. More specifically, it deals with the ionic and electronic charge carriers in ionic solids. The latter species are the major players in the game when one attempts a detailed understanding or deliberate tuning of kinetic properties. The charge carriers that we refer to are not necessarily identical with the charged particles that constitute the solid but rather with the effective particles that transport charge, i.e. in the case of ionic crystals the ionic point defects, in addition to excess electrons and holes. These ionic and electronic charge carriers constitute the redox and acid-base chemistry in the same way as is the case for aqueous solutions; they permit charge and matter transport to occur and are also reactive centers in the sense of chemical kinetics. This explains the central role of defect chemistry in this book. The more classical introductory chapters on chemical bonding, phonons, and thermodynamics of the perfect solid may, on the one hand, be considered as preparation for the key chapters that deal with thermodynamics of the real solid, as well as with kinetics and electrochemistry - both being unthinkable without the existence of defects; on the other hand, they provide the complement necessary for the book to serve as a textbook of physical chemistry of solids. (In fact, the different chapters correspond to classical fields of physical chemistry but referred to the solid state.) The structure of the book is expected to be helpful in view of the heterogeneity of the potential readership: This addresses chemists who traditionally consider solids from a static, structural point of view and often ignore the "internal life" enabled by defect chemistry, physicists who traditionally do not take pertinent account of composition as a state parameter, and materials scientists who traditionally concentrate on materials properties and may not adequately appreciate the basic role of electrochemistry. Of course, the book cannot fully cover the materials space or the world of properties. If the reader is a chemist, he or she may miss special chapters on covalent and disordered solids (e.g. polymers); the physicist will certainly find electronic properties under-represented (e.g. metals), and the materials scientist may have expected a detailed consideration of mechanical and thermal properties. Nonetheless the author is convinced - and this is based on the lectures on Physical Chemistry and Materials Science given to very different audiences in Cambridge (USA), Tübingen and Stuttgart (Germany) and Graz (Austria) - that he made a germane selection to highlight the physical chemistry of charge carriers in solids. A certain preference for examples stemming from the working group of the author is not the result of slothfulness or vanity; rather, it is based on the endeavor to concentrate on a few model materials. The many cross-references are meant to facilitate reading; proofs or remarks that would disturb the flow of reading and belong to a different level are put into footnotes, and they should be considered when reading the text a second time. Compared to the German version, which appeared earlier (Festkörper – Fehler und Funktion, Prinzipien der Physikalischen Festkörperchemie; B. G. Teubner Stuttgart,

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2000), the English text is – apart from a few modifications and hopefully a smaller concentration of "defects" – essentially a 1 : 1 translation. I am indebted to D. Bonnell, W. B. Eberhardt, K. Funke, O. Kienzle, M. Martin, M. Rühle, E. Schönherr, and A. Simon for the discussions and the courtesy of providing valuable figures. I would like to thank my co-workers and colleagues for critical remarks. In particular, I appreciate helpful discussion with Jürgen Fleig, Janez Jamnik, Klaus–Dieter Kreuer, Rotraut Merkle, and Roger de Souza. I am also indebted to Dr de Souza for his great help in the process of translating the German version into English. I would like to thank Barbara Reichert for the unremitting editorial assistance. Sofia Weiglein and M. Trieloff deserve thanks for their help as regards many tiny things (infinity times zero might be a very significant number). Harry Tuller (MIT Cambridge) and Werner Sitte (TU Graz) provided the hospitality and my wife Eva the additional free time, without which this book would have never been completed. Many thanks to them.

Stuttgart, January 2004

Joachim Maier

1

Introduction

1.1 Motivation

It may seem odd to ask the reader in the first sentence of the book he or she has just opened to put it down for a moment (naturally with the intention of picking it up and reading it again with greater motivation). Consider, however, your environment objectively for a moment. The bulk of it is (as we ourselves are to a large degree) made up of solid matter. This does not just apply to the materials, from which the house in which you live is built or the chair in which you may be seated is made, it also applies to the many technical products which make your life easier, and in particular to the key components that are hidden from your eyes, such as the silicon chip in the television set, the electrodes in lithium-based batteries powering mobile phones or enabling electrotraction and the oxide ceramics in the oxygen sensors of automobiles. It is the rigidity of solids which endows them with characteristic, advantageous properties: The enduring structure of our world is inconceivable without solid matter, with its low diffusion coefficients at least for one component (the reader may like to consider for a moment his or her surroundings being in spatial equilibrium, i.e. with all diffusion barriers having been removed). In addition and beyond the mere mechanical functionality, solids offer the possibility of subtly and reproducibly tailoring chemical, electric, magnetic and thermal functions.

The proportion of functional materials and, in particular, electrical ceramics in daily life is going to increase enormously in the future: Chemical, optical or acoustic sensors will analyse the environment for us, actuators will help us influence it. More or less autonomous systems perceiving the environment by sensors and influencing it by actuators, controlled by computers and powered by an autarchic energy supply (battery) or by an 'electrochemical metabolism' (fuel cell) are by no means visions for the distant future. Wherever it is possible, attempts are being made to replace fluid systems by solid ones, for instance, liquid electrolytes by solid ion conductors. In short: The importance of (inorganic or organic) solids can hardly be overestimated (even if we ignore the crowning functionality of biopolymers, as (almost)¹ done in this book). Furthermore, solid state reactions were not only of importance for and during the creation of our planet, but also constitute a large portion of processes taking place, nowadays, in nature and in the laboratory.

Perhaps you are a chemistry student in the midst of your degree course or a chemistry graduate already with a complete overview of the syllabus. You will then certainly agree that the greater part of a chemist's education is concerned with liquids and, in particular, with water and aqueous solutions. Solids, when they are considered, are almost always considered from a naive 'outer' point

1 See Sections 6.11 and 8.3 of Chapter 6 for systems far from equilibrium.

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2 1 Introduction

of view, i.e. as chemically invariant entities: Interest is chiefly concerned with the perfect structure and chemical bonding; in aqueous solutions it either precipitates or dissolves. Only the surface is considered as a site of chemical reactions. The concept of a solid having an 'internal chemical life', which makes it possible for us to tailor the properties of a solid, in the same manner that we can those properties of aqueous solutions, sounds – even now – somewhat adventurous.

On the other hand, solid state physicists have influenced the properties of semiconductors such as silicon, germanium or gallium arsenide by defined doping in a very subtle way. If the reader is a physicist, I believe he or she would agree that the role of composition as a parameter is not sufficiently appreciated in physics. Even though internal chemical equilibria are sometimes considered and doping effects are generally taken into account, concentration is still too strongly focused on singular compositions and electronic carriers. In fact, a large number of functional materials are based on binary or multinary compounds, for which stoichiometric effects play an enormous role.

Lastly this text is addressed to materials scientists for whom the mechanical properties frequently and traditionally are of prime interest. Electrochemical aspects are generally not sufficiently considered with respect to their importance for the preparation and durability of the material and optimization of its function. Thus, the fields of electroceramics and more generally of solids for energy applications are addressed.

The chemistry and physics of defects play a key role in the following text [1, 2]. After all, in the classical examples of water in chemistry and silicon in physics, it is not so much the knowledge of the structure or of the chemical bonding that has made it possible to carry out subtle and controllable tuning of properties, but rather the phenomenological knowledge of the nature of relevant particles, such as H_3O^+ ions, OH^- ions or foreign ions in water that determine its acid-base and redox chemistry. In the case of silicon the relevant particles are conduction electrons and electron holes, which, on account of their properties, determine the (redox) chemistry and the electronic properties.

Focusing on such relevant particles leads to the generalized concept of defect chemistry that permits the treatment of internal chemical processes within the solid state (in this context Figure 1.1 is illustrative). In processes, in which the structure of the phase does not alter, the perfect state can be regarded as invariant and all the chemical occurrences can then be reduced to the behaviour of the defects, that is, the deviations from the perfect state. The foundation stone of defect chemistry was laid by Frenkel, Schottky and Wagner [1, 2] as early as the 1930s; there is an extensive technical literature covering the field [3–14], but in chemistry and physics it has not yet become an adequate and generally accepted component of our training. In this sense this text is intended to motivate the chemist to deal with the internal chemistry of solid bodies. I hope that the effort will



Figure 1.1 In the same way as the treatment of ideal gases is simple – since the particles are dilute and uncorrelated (l.h.s.) –, the treatment of the solid state becomes equally simple from the viewpoint of the (dilute) defects (r.h.s.). (The portion of matter increases from the left to the right, while the portion of vacancies correspondingly decreases.)

be rewarded with a density of 'aha experiences' that will be adequate to compensate for the trouble caused by the physical language which is sometimes necessary. The physicist should be stimulated by the text to examine the internal equilibria of solid materials, changes in their composition and, in particular, the properties of more complex materials. The motivation here ought to be the fact that the formalism of defect chemistry is largely material independent, at least as long as the defect concentrations are sufficiently low, and that it offers a universal phenomenological description in such cases. Finally the text is intended to help the materials scientist to optimize the functional properties of materials, but also to understand the preparation and degradation of structural materials.

If this attempt at motivation is an 'attack on open doors', then the sentences I have written may at least act as a guide for the path ahead.

The text concentrates on ionic materials and on electrical and electrochemical properties in order to keep the contents within bounds. On the whole, we will refer to a 'mixed conductor', for which ion and electron transport are both important and with regard to which the pure electronic conductor and the pure ionic conductor represent special cases. We will specifically address material transport with respect to its significance for electrochemistry and reaction kinetics. Whenever necessary, indications of the generality of the concepts are interspersed. In order to make the treatment reasonably complete, references are given whenever a detailed consideration is beyond the scope of the book.

We start with an extensive introduction to the perfect solid, its bonding and its vibrational properties, knowledge of which is necessary for understanding the physical chemistry of the processes involved. In order not to lose sight of the purpose of the book these sections have been kept as simple as possible (but as precise as necessary). The same applies to the general thermodynamic and kinetic sections, which also serve to introduce the formal aspects. Nevertheless, in view of the heterogeneity of the potential readership, this detailed mode of presentation has been chosen deliberately in order to be able to assume a uniform degree of knowledge when discussing defect chemistry. Some material may be repeated later in the text and this is intended to ensure that some chapters can be omitted by the advanced readers without loss of internal consistency.

The text will have fulfilled its purpose in an ideal manner, if it not only conveys to the reader the elegance and power of the defect concept, when it not only puts him or her in the position of being able to recognize the common aspects of different properties and processes such as doping and neighbouring phase effects, ionic and electronic conductivity, passivation and corrosion of metals, diffusion and reaction processes, synthesis kinetics and sintering kinetics in solids, electrode reactions and catalysis, sensor processes and battery processes; but also puts the reader in the position to optimize the solid state 'strategically' at the 'writing desk' in those situations in which the desired parameters are already known.

1.2 The Defect Concept: Point Defects as the Main Actors

As already mentioned, phenomenological understanding of condensed phases with regard to the tunability of chemical and electrical properties implies knowledge of the defects as the relevant particles and their interactions, rather than (or at least in addition to) knowledge of the structure of the perfect state. This is known to be the key to phenomenological understanding of the aqueous phase and to control its chemical and electrical properties. In pure water these defects or 'chemical excitations' are H_3O^+ and OH^- ions. Let us consider the first row in Figure 1.2. As shown, it is



Figure 1.2 (a) If the basic compositionally unperturbed structure (chemical ground structure) is subtracted 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 neighbourhood. In the case of fluid phases (see previous text) 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) The third row shows the case of purely electronic disorder whereby localized charge carriers are assumed for the sake of clarity. Source: Adapted from Ref. [14].

advantageous, in a purely phenomenological sense, to subtract from the real structure the instantaneous perfect water structure. We are left with an excess proton and a missing proton, i.e. a 'proton vacancy'. This is also the result of subtracting the H_2O molecule completely (Eq. (1.1c)) from the autoprotolysis reaction² according to

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad |-H_2O \tag{1.1a}$$

instead of

$$Nil \rightleftharpoons |Cl|^+ + Cl^-$$
$$SOCl_2 \rightleftharpoons SOCl^+ + Cl^-$$

Conversely, these considerations emphasize that internal acid-base chemistry of solids involves point defects [15]. In Chapter 5 we will see that such acid-base reactions, together with redox-reactions, constitute defect chemistry.

² It is naturally possible to formulate the whole of aqueous acid-base chemistry in water in this minimal notation. Equation (1.1c) would also formally describe autoprotolysis in liquid ammonia. An analogous Cl^- disorder reaction would be suitable for describing the dissociation of $SOCl_2$:

$$\begin{aligned} H_2 O &\rightleftharpoons H^+ + OH^- \quad \left| -H_2 O \right. \eqno(1.1b) \\ Nil &\rightleftharpoons H^+ + \left| H \right|^- \end{aligned} \tag{1.1c}$$

Here |H|⁻ denotes a proton vacancy.³

Let us now consider disorder in a crystalline phase, to be specific, in solid AgCl. In this case some silver ions have left their regular sites,⁴ and hence, left vacancies behind. As one can see (Figure 1.2b), there is a very close analogy to Eq. (1.1). Even the nature of the driving force for the internal dissociation, namely the gain in entropy of configuration, is identical. The 'subtraction' of the perfect structure as an invariant yields an excess cation (Ag⁻) and a cation vacancy (|Ag|') as the relevant particles. Just as in Eq. (1.1c) we can write

$$\operatorname{Nil} \rightleftharpoons \operatorname{Ag'} + |\operatorname{Ag}|' \tag{1.2a}$$

The old-fashioned charge designations (dot and dash) denote the relative charges: The crystal segments containing the defects such as

$$\begin{bmatrix} Ag^+ & Cl^- \\ Ag^+ \\ Cl^- & Ag^+ \end{bmatrix}^+ \quad \text{and} \quad \begin{bmatrix} Ag^+ & Cl^- \\ & \\ Cl^- \end{bmatrix}$$

are positively or negatively charged in an absolute sense, but the local positive or negative charge at the proper defect-site – interstitial or vacant site – represents a charge relative to the perfect situation. This differentiation between absolute and relative charge was naturally not necessary for H_2O .

The disorder in the electron shells is to be comprehended in an analogous manner. Here the bonding electrons, more precisely the valence electrons, have left their 'regular' positions and have been excited into the conduction band. This also creates excess particles and missing particles, which are conduction electrons (e') and electron holes (h'). Let us take a (main group) metal oxide with the (perfect) composition MO as our model compound and for the purpose of better visualization assume that, to a good approximation, the valence band is composed of the oxygen p-orbitals, while the conduction band is composed of the outer metal orbitals. Hence, the reaction can also be formulated as an internal redox reaction

$$O^{2-} + M^{2+} \rightleftharpoons O^{-} + M^{+} \tag{1.3a}$$

The minimal notation (subtraction of the perfect phase MO on both sides of the equation, see Figure 1.2c) then becomes

$$Nil \rightleftharpoons h' + e' \tag{1.3b}$$

In silver chloride this corresponds to the charge transfer from Cl^- to Ag^+ . The advantage of the notation used in Eq. (1.3b) is that it is independent of such detailed bonding considerations. The building element formulation of Eqs. (1.2a), (1.3b) and also of Eq. (1.1c) is an adequate notation for the thermodynamic, i.e. phenomenological treatment and emphasizes the superposition of perfect and defect components in energetic questions.

³ According to Eq. (1.1c) we could also refer to the OH^- ion (more precisely to the difference of OH^- and H_2O) as a proton hole or an anti-excess-proton. The following joke may be instructive in this context: A mathematics teacher notices that 10 pupils left the class-room even though only 9 have been in. His comment: If one pupil enters the room, the occupation is zero and the world is in order again.

⁴ Perfect AgCl is dissociated in the sense that it consists of ions; but it is not dissociated into free particles since Ag^+ and Cl^- are trapped in their deep Coulomb potentials. The latter, 'superionic' dissociation is described by Eq. (1.2).

6 1 Introduction

Unfortunately the formulation suffers from a lack of vividness precisely on account of the high degree of abstractness. From a descriptive point of view, structure element formulation is to be preferred. Nonetheless, descriptions utilizing very detailed structural elements, as in Eqs. (1.1a) or (1.1b), are not employed in the case of ionic solids, although the disorder in AgCl (Eq. (1.2a)) could certainly be analogously formulated as the 'dissociation reaction of the lattice molecule' according to

$$2\text{AgCl}_{(\text{AgCl})} \rightleftharpoons \text{Ag}_2\text{Cl}_{(\text{AgCl})}^+ + \text{Cl}_{(\text{AgCl})}^- \tag{1.2b}$$

(the lower index refers to the perfect state), or even – by analogy to $H_9O_4^+$ – by inclusion of further regular neighbours (see Chapter 5). The author has resisted, for two reasons, the temptation to select such a 'molecular' notation: Firstly, the field of the 'internal chemistry' of solids is already conceptually overloaded, and secondly, such a chemical notation would be clumsy for complicated solids or in kinetic considerations. Instead the conventional Kröger–Vink notation [3] is used: It also considers structural elements, in that it refers to absolute structures, but 'boiled down' to only the 'atomic' particles actually reacting. That means in the case of our silver chloride example that the anion-sublattice is completely omitted from the description, while, on the other hand, vacancies (here in the cation-sublattice) are explicitly taken into account as structural elements using the symbol \lor . So instead of Eqs. (1.2a) or (1.2b) we write

$$(Ag_{Ag^{+}}^{+}) + (V_{i}^{0}) \rightleftharpoons (Ag_{i}^{+})^{\cdot} + (V_{Ag^{+}}^{0})'$$
(1.2c)

or abbreviated by the omission of all absolute charges

$$Ag_{Ag} + v_i \rightleftharpoons Ag_i + v'_{Ag}$$
(1.2d)

The superscript in Eq. (1.2d) again represents the relative charge, i.e. the difference between the charge in the real case and that in the perfect case $(' = -1, \cdot = +1)$. An effective charge of zero is not indicated or is sometimes indicated by means of a cross ('×'). The subscript denotes the crystallographic position in the perfect structure (i: interstitial site). Specifically Eq. (1.2d) indicates that a silver ion (Ag⁺) has moved from a regular silver ion position (subscript Ag) to a vacant (\lor stands for vacancy) interstitial site (subscript i) where it becomes an interstitial silver ion Ag⁻ and leaves a vacancy (\lor'_{Ag}) in the silver ion lattice. The regular components such as Ag_{Ag}, \lor_i or Cl_{Cl} do not carry an effective charge, while the interstitial silver ion bears the relative charge +1 (= +1 - 0) and the silver vacancy the relative charge -1 (= 0 - (+1)). Structure element notation is not used in the case of electronic defects, rather the building element notation of Eq. (1.3b). This has the advantage that, firstly, the formulation is independent of the nuances of the bonding and that, secondly, a possible double counting of electronic states⁵ is avoided. Since an ionic crystal is a rigid body with well-defined sites and the picture is only slightly complicated by vibrations (or rotations) about the equilibrium state, it is possible (and necessary) to distinguish in contrast to the fluid phase water, between several defect types, as will be discussed in Section 5.5.

In addition to defects intrinsically formed in pure substances by thermal disorder, defects are also generated by the incorporation of foreign materials. Hence, the (substitutional) incorporation of a D^{2+} cation in place of an M^+ cation leads to a point defect $(D_{M^+}^{2+})^- \equiv D_M^-$, while the (additive) interstitial incorporation of a cation of higher valence leads to a defect with a higher effective charge, namely D_i^- . Although dissolved foreign substances are similarly important in liquids, it is necessary to point out another basic difference between liquid and solid phases: The simultaneous dissolution of cations and anions does not normally constitute a difficulty in the case of deformable fluids, and

⁵ The electronic shell is included in the symbol for the element.

Figure 1.3 Doping AgCl with $CdCl_2$ (only Cd^{2+} dissolves) leads to the formation of silver vacancies. The arrow indicates that silver conductivity is produced in this manner (migration of the vacancies in the opposite direction). This doping process generates electronic effects too, although to a small degree (see Section 5.6).



electroneutrality is automatically guaranteed. The normal case in the solid state is that either only the anion or the cation (here D²⁺) is soluble. The dissolution of D²⁺ then takes place either by substitution of M⁺ or by taking up an unoccupied interstitial position.⁶ The change in charge must be compensated by creation of another defect. Thus, the introduction of D²⁺ (by substituting⁷ for an M⁺ or by occupation of a free interstitial position) is associated with the formation of negatively charged ionic and electronic defects such as cation vacancies (V'_M) and conduction electrons. Such electronic (redox) and ionic (acid-base) effects are not independent of each other but appear simultaneously in a coupled way. Figure 1.3 shows cation vacancies created by substitution of a monovalent silver ion by a divalent cadmium ion. A further example is the creation of a high concentration of oxygen vacancies, and thus a high ionic conductivity in ZrO₂ by doping with CaO or Y₂O₃. This important ceramic material is used in automobile exhaust gas sensors and in high temperature fuel cells. The oxygen vacancies (V'_O) compensate for the charges of the Ca^{''}_{Zr} or Y'_{Zr} defects. Electronic effects play a very minor role in this oxide. In defect notation the incorporation can be written as

$$CaO + Zr_{Zr} + O_O \rightarrow ZrO_2 + Ca_{Zr}'' + \vee_O^{\circ}$$

$$\tag{1.4}$$

A third example is the partial replacement of La^{3+} in La_2CuO_4 by Sr^{2+} (forming the defect Sr'_{La}). As in the previous example oxygen vacancies and electron holes are also produced here; but unlike in the previous case the electronic effects are significant. Hence, the substitution brings about marked oxidation of the crystal. Such oxidation is necessary for the occurrence of 'high temperature superconduction' in this oxide.

The procedure is similar for covalently bonded materials, such as silicon or organic polymers, although sites in the latter are not always sharply defined. If pentavalent phosphorus is introduced into silicon, this leads to the formation of some P_{Si}^{\cdot} defects (that is P⁺ on Si), since the fifth valence electron in the sp³ hybridized basic silicon structure can be readily delocalized as a quasi-free electron. In the same manner trivalent aluminium takes electrons from silicon, that is from the valence band (Figure 1.4). This defect (Al'_{Si}) bears the formal charge (-1) ((Al⁻_{Si})'). The electronic counterdefect is a delocalized electron hole (h'):

$$Al + Si_{Si} \rightarrow Si + Al'_{Si} + h^{\circ}$$
(1.5)

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3(s) + 3HCl(aq)$$

⁶ As in organic chemistry, it is possible to distinguish between addition, substitution and elimination reactions (in and on the 'giant molecule solid'). Rearrangement reactions also occur (cf. phase transitions).
7 Such substitution reactions also play a role in aqueous solution: The precipitation reaction,

e.g. corresponds to the substitution of hydroxide groups by chloride in the aqueous substrate. This process too is associated with considerable changes in chemical (cf. acidity) and electrical (cf. proton conduction) properties.



M^{⊕ X} O²

 O^{2}

Figure 1.4 Al doping of silicon effects the formation of a 'vacancy' in the electronic shell (see arrow tip). The arrow indicates that this results in electronic (hole) conductivity. The electron hole migrates in the opposite direction.

Figure 1.5 Oxygen incorporation resulting from the jump of an adsorbed oxygen particle into a vacant oxygen site with the uptake of two electrons. In the example, the excess electron states correspond to monovalent metal ions. It is assumed, for the sake of the example, that the absorbed oxygen before passing into the vacancy, is in the neutral state, but this is generally not the case mechanistically.

Ionic and electronic defects can also be created by an excess or deficit of a native component⁸ instead of by the introduction of foreign species. This takes place, for instance, in an oxide by interaction with the oxygen of the neighbouring phase (see Figure 1.5). At sufficiently high temperatures, varying the oxygen content of the gas phase makes possible a continuous tuning of the precise position in the phase diagram. Such phase widths are often tiny and the changes obtained often negligible with respect to total mass or to the energy of the phase, but the change in defect density and all the properties specifically associated with it can be immense. Thus, in n-conducting SnO_2 an increase of the oxygen partial pressure of the surroundings leads to a drastic reduction in conductivity, according to:

$$\frac{1}{2}O_2 + \bigvee_0^{\cdot} + 2e' \rightleftharpoons O_0 \tag{1.6}$$

In this case the oxygen introduced occupies oxygen vacancies in the lattice. It is incorporated in the form of O^{2-} , and electrons are required for this; these are available in SnO_2 in the form of conduction electrons. In more chemically oriented terms we may state that reduced Sn states $(Sn^{m+}, m<4)$ are oxidized and, thus, annihilated. If, as in La₂CuO₄, there are (almost) no excess electrons in the material, the incorporation of oxygen is associated with the consumption of bonding electrons. Holes are then created in the valence band and the p-type conductivity increases. Chemically⁹ speaking this corresponds to the oxidation of Cu²⁺ or O²⁻ to Cu³⁺ or O⁻. The hole density in La₂CuO₄ is increased in this manner and induces superconductivity at low temperatures.

For simplicity of presentation individual mechanisms have been emphasized until now. However, in practice, various different defect states occur simultaneously. Their distribution, i.e. their concentration, can be obtained from solution of the overall reaction scheme. This will be treated systematically in Chapter 5. Here we just mention that oxygen vacancies cannot only be destroyed by redox reactions but also by pure acid-base reactions. Thus, H₂O can be dissolved in many oxides

⁸ Native components are understood as components occurring in the pure material (i.e. M and X in MX). In binary compounds the phase width corresponds to the toleration of redox effects.

⁹ This simple chemical notation in terms of defined valence changes only provides a correct picture in those cases in which valence or conduction bands can be overwhelmingly assigned to the cation or anion (see Section 5.3). However, in general, there is a hybridization, as for the Cu and O orbitals in the case of cuprates.



with the formation of internal OH groups (OH⁻ on O²⁻ positions). According to

$$H_2 O + V_0^{"} + O_0 \rightleftharpoons 2OH_0^{"} \tag{1.7}$$

the 'OH⁻ part' of the water molecule occupies the vacancy, while the 'H⁺ part' is added to a regular O^{2-} (i.e. O_O).

In this manner defects do not just constitute the 'internal chemical life' but also the (chemical) 'communication with the environment'. Naturally, the detailed kinetics must also be based on the defect concept. The related overall chemical or electrochemical process is made up of an interfacial reaction (more precisely a coupled scheme of individual elementary reactions at an interface) and the 'transport reaction', that is a site exchange process within the bulk of the solid. This is also valid for true solid state reactions involving the formation of a new phase. The necessary internal mobility is made possible by the presence of defects, as shown in Figures 1.3, 1.4 and also 1.5. The arrows indicate that an atomic vacancy or an electronic hole migrates by neighbouring atoms or electrons occupying the vacant sites. Hence, in this case defect transport and mass transport are in opposite directions. When excess ions or excess electrons migrate, the direction of defect transport and mass transport is identical. Diffusion processes, as described in this manner, frequently constitute the rate-determining step in solid state chemical kinetics. However, elementary reactions at interfaces, which are defect reactions, too, may also dominate the kinetics in many cases.¹⁰

Since the defects involved carry charges, they play a prominent role in the conversion of chemical signals to electrical signals (and vice versa). The example given in Figure 1.6 can serve as leitmotif for this. As already explained, varying the oxygen content alters the internal chemistry (i.e. defect concentrations) of oxides, with immense effects on the electrical conductivity. The measurement of the electrical signal 'conductivity' can be used for elegant and accurate detection or even for control of the oxygen content of the environment. Such a chemical sensor is only one of many highly interesting electrochemical applications.

This example also indicates the arrangement of this book. The thermodynamics of defects (Chapter 5) will enable us to specify the concentrations of the individual ionic and electronic defects and, thus, the ionic and electronic conductivities as a function of the relevant thermodynamic parameters (such as temperature and composition of neighbouring phase). In this way the (thermochemical¹¹) equilibrium state of the solid is precisely defined. In the defect chemical

¹⁰ In the spirit of Chapter 5 the interface represents a (higher-dimensional) defect itself. Point defects within the interface are centres of enhanced reactivity (excitations within the higher-dimensional defect).

¹¹ The external shape, i.e. the surface, also belongs to the detailed description. Like the precise macrostructure (bulk plus surfaces) the 'microstructure' (inclusion of internal interfaces, dislocations etc.) is almost without exception a nonequilibrium structure but highly relevant on account of its metastability (see Section 5.4).

10 1 Introduction

kinetics chapter (Chapter 6) we then consider mechanistically how and how rapidly changed state parameters bring about compositional changes. It is of particular importance for our example to elucidate how rapidly the defect concentrations and the conductivities change as the oxygen content changes. The charge of the defects makes electrochemistry a relevant subject per se. Since the thermodynamic and kinetic considerations already involve electrochemical equilibrium and nonequilibrium effects, the special electrochemical chapters (Chapters 7, 8) at the end of the book are devoted to electrochemical systems that are of scientific importance – for the measurement, interpretation and control of interesting properties – or of technological importance for energy utilization or information conversion. The concluding chapter (Chapter 9) on nanoionics revisits most of these aspects but from the viewpoint of size effects.

This main part of the book (Chapters 5–9) is obviously related to Materials Science; it is almost a triviality to conclude that, at least for ionic solids, now defect chemistry is fundamental to and, to a large extent, the substance of this interdisciplinary area.¹² Materials research is synonymous with the strategic exploitation of structure-property relationships, with a view to the optimization of properties. If the question posed by material research is, say, the optimization of electrical properties via selection of materials and control parameters, then this question immediately refers back to the thermodynamics and kinetics of defect chemistry. As far as materials are concerned, we concentrate on inorganic ionic materials that are electrochemically of relevance (electroceramics). Although implicitly discussed, classical semiconductor materials as well as polymers are only touched on in order to emphasize the generality of the concepts.

The first four chapters dealing with the perfect state are more introductory. According to Figure 1.2 we formally construct our real solids by superposition of the perfect solid ('chemical groundstate') and the defects ('chemical excitations'). Both ensembles are not independent of each other but strictly coupled in equilibrium. For this reason we start with a concise treatment of the chemically perfect solid. Firstly, there is a discussion (Chapter 2) of the chemical bonding and then of the formation of the solid state, followed by a discussion of lattice vibrations (Chapter 3).

The purpose of the chapter dealing with equilibrium thermodynamics of the perfect solid (Chapter 4) is to elaborate, on the one hand, simple expressions for the thermodynamic functions of the 'chemical ground state' and, on the other hand, to make the reader familiar with questions of internal and external equilibria, not least with the intention to provide the equipment to deal with the thermodynamics of defect formation. (The major portion of the free enthalpy at absolute zero consists of bonding energy, while the temperature dependence is largely determined by the vibration properties.)

Evidently, the structure of this book refers to the classical areas of Physical Chemistry (bonding theory, thermodynamics, kinetics, electrochemistry) related, however, to the solid state. In this sense, the monograph may partly serve as a textbook of physical chemistry of solids. In order not to lose track of our subject we will confine ourselves to the simplest cases. Nonetheless the introductory chapters are rather comprehensive in order to take account of the heterogeneity of potential readers. This, however, should not distract from the actual topic of the book. Those, who are familiar with these aspects or who are only interested operatively in the application of

¹² Materials research implies structure optimization on all relevant scales. The most important step is the selection of the solid ground state, i.e. synthesis of the chemical compound that is able to provide the optimizable 'property world'. Within this framework tuning the defects allows fine-adjustment, but this is frequently accompanied by enormous variation in properties. The adjustment of the supra-atomic architecture in the form of nano-, micro- and macrostructure (external shape) completes the procedure. The appropriate combination of different materials then leads to the design of relevant systems.

the defect-chemical formalism can skip these introductory chapters with an acceptable loss of continuity or they can refer to them later if relevant problems arise in understanding.

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Bonding Aspects: From Atoms to Solid State

2

Strictly speaking, a knowledge of the independent state variables (such as temperature, pressure, numbers of the different particles involved) is all that is required to calculate the equilibrium composition, structure and even the external equilibrium form (i.e. the shape of the solid body) using the Schrödinger equation (or more precisely its relativistic generalization, i.e. Dirac's equation). However, in view of the many-body problem such a statement is almost without exception purely academic. This is even more true in the case of nonequilibrium, and particularly for instationary systems. Calculations of this type are limited to the simplest of examples even if we separate the electronic from the nuclear motion and treat the systems in the time-independent single-electron approximation neglecting relativistic effects. Even then the uncertainties of the numerical solution are frequently of the order of magnitude of the differences of interest, when, for example, the stability of a given crystallographic structure is considered. For this reason the procedure generally employed involves a combination of a priori chemical knowledge with respect to atomic and molecular properties and a posteriori knowledge with respect to the crystallographic structure.

Since a solid body represents a giant three-dimensional molecule ('3-D polymer') with possible anisotropy in the chemical bonding and with terminal groups constituting its surfaces, the description according to bonding theory is a many-body problem – in terms of both nucleons and electrons. It is appropriate to start out from the simplest type of chemical bond, namely, the two-atom problem in the single-electron approximation. This is not only didactically appropriate, but also useful in so far as the energetics of the whole solid state is frequently largely represented by the short range interactions.

2.1 Chemical Bonding in Simple Molecules

2.1.1 Ideal Covalent Bonding

Let us first consider an arrangement of two (a, b) atoms of the same nature (X_a, X_b) produced according to

Reaction
$$B = 2X \rightleftharpoons X_2$$
 (2.1)

in which it is only necessary to take account of one electron, a condition that is only strictly met in the H_2^+ molecule; hence, there are two relevant wave functions $|\tilde{ab}\rangle$ and $|\tilde{ab}\rangle$, which

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correspond to bonding and antibonding states and which are, to an approximation (according to the LCAO method), composed of the wave functions of the single atom problems $|a\rangle$ and $|b\rangle$ as follows^{1,2}:

$$|ab\rangle \propto |a\rangle + |b\rangle$$
 (2.2a)

$$|\tilde{ab}\rangle \propto |a\rangle - |b\rangle$$
 (2.2b)

The probability density of finding the electron is determined by the square of the absolute value of the overall wave function. Squaring Eqs. (2.2a) and (2.2b) obviously results in an increased electron density between the nuclei in the case of Eq (2.2a) and a decreased value in the case of Eq. (2.2b) when compared with the pure atomic orbitals (non-bonding state). The first case refers to the bonding situation, while the second case refers to an anti-bonding state. It would be, however, wrong to make the increased potential energy due to the increased electron density between the nuclei solely responsible for the bonding. The potential energy balance is not so favourable since the accumulation or removal of electrons from the centre takes place at the cost of the density at the atoms. (Attention must therefore be paid to the conservation of charge and thus to the normalization (cf. proportionality factor in Eq. (2.2)).) It is the kinetic energy due to the 'larger available space' is particularly obvious in extended systems such as conjugated polymers or metals. The modified energy states $\hat{\epsilon}$ and $\bar{\epsilon}$ of the two-atom one-electron problem which are approximately⁴ altered by $\pm\beta$ with respect to the initial energy $\epsilon_a = \epsilon_b$:

$$\hat{\epsilon} = \epsilon_a - |\beta| \quad \text{and} \quad \breve{\epsilon} = \epsilon_a + |\beta|$$
(2.3)

2 In agreement with literature the Dirac bra/ket notation is used here to represent functions as vectors that are formed from the infinite set of the function values (or in a more operational representation as vectors in Hilbertian space spanned by the countable infinite set of basis-functions in which the function under regard is developed): $\langle c|$ designates the complex conjugate of $|c\rangle$, the scalar product $\langle c|d\rangle$ is then the sum over the products of the individual function values that is the integral over the corresponding product of the functions. The scalar product $\langle c|c\rangle$ is a measure of the integrated electron density referring to c and may be normalized to unity. The assumed linear combination is naturally an approximation. That linear combination, which corresponds to the lowest energy, is, hence, not necessarily identical to the 'true function', but, nevertheless, the readily proved variation theorem shows that it is the nearest of all possible alternative linear combinations to this. A variation calculation leads, in the case of such a linear combination, to a normal minimax problem in the coefficients and to the solutions given earlier, as described in all quantum chemical textbooks (e.g. [4–7]). There is a clear treatment of the physical basis in Ref. [8]. 3 With respect to the complex interaction between kinetic and potential energy as a function of the nuclear distance and the importance for chemical bonding, cf. Ref. [9].

4 Strictly speaking the aforementioned model yields

$$\widehat{\epsilon} = \frac{H_{aa} + H_{ab}}{1 + S} = (H_{aa} + H_{ab})(1 - S_{ab} + S_{ab}^2 - S_{ab}^3 + \cdots)$$
$$\overline{\epsilon} = \frac{H_{aa} - H_{ab}}{1 - S} = (H_{aa} - H_{ab})(1 + S_{ab} + S_{ab}^2 + S_{ab}^3 + \cdots).$$

Obviously the distance of $\hat{\epsilon}$ to H_{aa} is less than that of H_{aa} to $\bar{\epsilon}$. If $S_{ab} \ll 1$, β in Eqs. (2.3) and (2.6) might be identified with the resonance integral; this assumption is generally unjustified (see [5]), but is frequently employed. The better approximation (Eqs. (2.3) and (2.4)) does not completely agree with the second approximation of this presentation, but is a favourable approximation for the present problem since the missing term ($S_{ab}H_{ab}$) and the second order terms partially compensate (see sign).

¹ The procedure mentioned here is that of L. Pauling [1] and corresponds to a linear combination of atomic orbitals (LCAO) [2] which is extensively employed in the molecular orbital theory. In terms of a more general approach one has to use different prefactors C_1 and C_2 in front of the individual atomic orbital functions in Eqs. (2.2a) and (2.2b). The minimization of energy (see footnote 2), i.e. of $\langle ab|\mathcal{H}|ab \rangle/\langle ab|ab \rangle$, delivers $C_1 = \pm C_2$ as expected from the symmetry of the problem [3].

If we now adopt for the two-electron problem (one bonding electron per X) the energy levels from this single-electron model⁵ and compare with the initial states, the bonding energy of the two atoms X_a and X_b in the molecule X_2 formed, i.e. the reaction energy in Eq. (2.1), is obtained as $\Delta_B \epsilon = 2\hat{\epsilon} - 2\epsilon_a \cong -2|\beta|$. The (negative) quantity β here represents the reduced resonance integral⁴

$$\beta = \langle \mathbf{a}|\mathcal{H}|\mathbf{b}\rangle - \langle \mathbf{a}|\mathcal{H}|\mathbf{a}\rangle\langle \mathbf{a}|\mathbf{b}\rangle \tag{2.4}$$

Therein, \mathcal{H} represents the Hamiltonian operator that is the energy operator in the Schrödinger equation

$$\mathcal{H}|ab\rangle = \epsilon|ab\rangle \tag{2.5}$$

and is obtained from the operators for the potential energy and the kinetic energy.⁶ For conciseness the individual integrals in Eq. (2.4) are written in the common Dirac-notation.² While the functional details are not of relevance here, it is important, though, that the situation is characterized by three integrals (see rhs of Eq. (2.4)): The integrals $\langle a|\mathcal{H}|b\rangle$ (resonance integral $\equiv H_{ab} =$ $H_{ba}^* = H_{ba}$) and $\langle a|b\rangle$ (overlap integral $\equiv S_{ab} = S_{ba}^* = S_{ba}$) are measures of the overlap of the atomic orbitals, for they only have contributions differing from zero at those positions, for which both $|a\rangle$ and $|b\rangle$ differ from zero. The contribution of the third integral, the Coulomb integral $\langle a|\mathcal{H}|a\rangle$ (\equiv $H_{aa} = H_{bb} \equiv \langle b|\mathcal{H}|b\rangle$, also known as α , is – for a given internuclear distance – only appreciably different from zero in the region of the nucleus. However, there the interaction with the neighbouring nucleus may be neglected and \mathcal{H} be set as equal to the Hamiltonian operator of the single atom problem; in consequence α characterizes the non-bonding situation and can be represented by $\epsilon_a(=\epsilon_b)$, as already used in Eq. (2.3). Nevertheless, the presentation of the energy states by

$$\tilde{e}_{ab} = \alpha - |\beta| \quad \text{and} \quad \tilde{e}_{ab} = \alpha + |\beta|$$

$$(2.6)$$

is more generally valid than Eq. (2.3). Figure 2.1 illustrates the integrals and energy functions discussed as functions of the internuclear distance of H_2^+ . The centring or symmetrical 'sharing' of two bonding electrons can be generalized to cover the bonding of homonuclear atoms and, in the concrete case of the bonding of say a Cl₂ molecule, corresponds formally to the creation of two noble gas configurations (Ar-configuration=/Ar/):

$$|\underline{Cl}^{x} + {}^{x}\underline{Cl}| \Rightarrow |\underline{Cl} - \underline{Cl}|$$

$$KL3s^{2}3p^{5} \quad KL3s^{2}3p^{5} \quad \underbrace{KL3s^{2}3p_{y,z}^{4}}_{/Ar/} \underbrace{\left(3p_{x}3p_{x}\right)^{2}}_{/Ar/} 3p_{y,z}^{4}3s^{2}LK.$$

$$(2.7)$$

This is naturally a very approximate description in which not even all the outer electrons are included in bond formation. A more precise procedure creates eight orbitals from the outer s and

⁵ We obviously ignore electron–electron interactions. Later on, some situations in which such interactions will be important, will be briefly considered (see in particular Mott–Hubbard criterion). In these cases the ratio of the interaction energy and β is decisive for the strength of the effect.

⁶ While the first is derived from classical momentum (**p**) considerations via the transformation $\mathbf{p} \rightarrow \frac{h}{2\pi i} \nabla$, the classical expression is retained in the case of the potential energy that only depends on the local coordinate. \mathcal{H} is, thus, given in the end by the space functions and the second space derivatives (kinetic energy \propto (momentum)²). It can be shown that \mathcal{H} is a Hermitian operator, i.e. $\langle a|\mathcal{H}|b\rangle = \langle b|\mathcal{H}|a\rangle^*$. The star denotes the complex conjugate. Such Hermitian operators have, as they must, real eigenvalues: Because $\langle a|\mathcal{H}|a\rangle = \epsilon \langle a|a\rangle$ and $\langle a|\mathcal{H}|a\rangle^* = \epsilon^* \langle a|a\rangle^* = \epsilon^* \langle a|a\rangle$, it follows that $\epsilon = \epsilon^*$.



Figure 2.1 The matrix elements $S_{ab} \equiv S, H_{ab}, H_{aa}$, the reduced resonance integral β and energy eigenvalues of H_2^+ as functions of nuclear distance. The equilibrium value corresponds to the minimum of \hat{e} in the LCAO approximation used (a_0 = Bohr unit of length = 0.529 Å; E_0 = Hartree energy unit = 27.21 eV). Source: From Ref. [5].

p electrons (which are referred to as σ and π orbitals depending on symmetry: $\sigma(s)$, $\sigma^*(s)$, $\sigma(p)$, $\sigma^*(p)$ and two $\pi(p)$ and $\pi^*(p)$ orbitals⁷). The number of 'real bonds' in the case of the example given earlier, e.g. in the case of the Cl₂ molecule is 1, since the corresponding antibonding orbitals are also filled for all orbitals apart from $\sigma(p)$ (14 outer electrons) and, thus, energetically nullify the effect of filling the respective bonding states approximately (Eq. (2.3)) (cf. 'bond order' [6]). Figure 2.2 applies to the atomic dimers of the first octet in the periodic table. The energetic order of the levels shown comes from the fact that the s-orbitals are energetically lower than the p-orbitals and that the degree of overlap of the π orbitals is less than that of the σ orbitals and so, to an approximation, the corresponding $|\beta|$ values are smaller and the size of the splitting too. When orbital interactions are taken into account, these energy levels are altered; the changes are perceptible, at least for the



Figure 2.2 The approximate position of the energy levels of the molecular orbitals in the homonuclear molecule X_2 formed from the atomic levels in X. Consider N_2 as an example. Since every nitrogen contributes 5 outer shell electrons, the lowest 5 MOs are doubly occupied. It is the occupation of the $\sigma(p)$ and of the two $\pi(p)$ orbitals that contribute to bonding, the s interaction is nonbonding: $|N \equiv N|$. In the same manner a double bond is formed for O_2 from the p orbitals. However, here the $\pi^*(p)$ orbitals are singly occupied and the ground state is a triplet state. This explains the paramagnetism of the O_2 molecule.

⁷ The overlap of s-orbitals and of p-orbitals lying in the direction of the bonding axis (p_x see previous text) leads to σ orbitals, which are rotationally symmetrical about their bonding axis, while the p_y , p_z orbitals perpendicular to the axis form π bonds. For every MO orbital type there is a bonding ($\hat{\sigma}$, $\hat{\pi}$ or simply σ , π) and an antibonding ($\hat{\sigma}$, π or σ^* , π^*) level.