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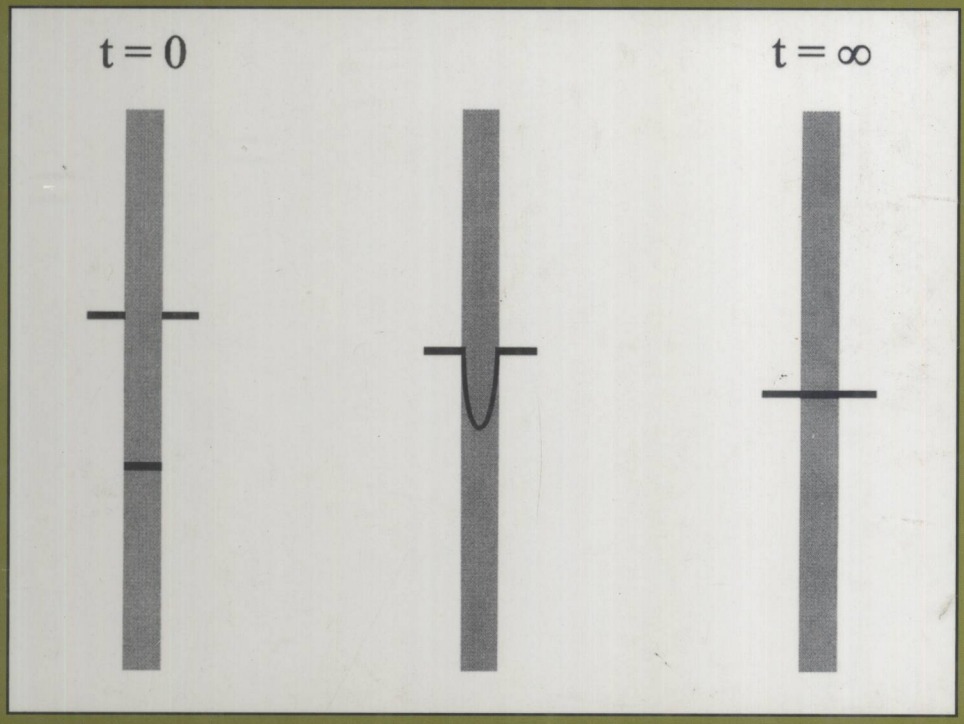
CHEMICAL PROPERTIES OF MATERIAL SURFACES



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CHEMICAL PROPERTIES OF MATERIAL SURFACES

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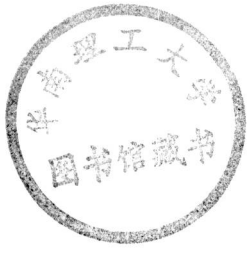

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To the memory of my father
Zdzislaw Kosmulski
1922–1998

Preface

Adsorption phenomena at solid–electrolyte solution interfaces at room temperature and at atmospheric pressure are reviewed in this book with a special emphasis on the mutual relationship between adsorption and surface charging. This relationship is particularly significant for adsorption of inorganic ions on silica, metal oxides and hydroxides, certain salts, e.g. silicates, and clay minerals. The models of surface ionization and complexation originally developed in colloid chemistry are widely used in different fields, including catalysis, ceramics, corrosion science, environmental sciences, geology, mineral processing, nuclear waste management, and soil science. Association with one of the traditional branches of science (and thus preference for particular journals or conferences) is only one of many factors that have split the scientists interested in adsorption at solid–solution interfaces into many insulated groups. For example, Western papers have rarely been cited in former Soviet Union papers and vice versa even though English translations of the leading Russian scientific journals are readily available. Each group has its own goals and methods, and specific systems of interest, and often ignore other systems and methods. The generalizations formulated by different groups are frequently based on a selective approach. They are not necessarily applicable in other systems and sometimes contradict each other. The aim of this book is to systematize the existing knowledge and to facilitate the exchange of ideas between different parts of the scientific community.

The point of zero charge (PZC) is a central concept in adsorption of charged species. This well-known term has been given very different meanings. The relationship between the zero points obtained by different methods and at different conditions is discussed in this book. An up-to-date compilation of values of the points of zero charge of various materials obtained by different methods is presented. These materials range from simple to very complex and from well- to ill-defined. Collections of zero points compiled by different authors are compared, and the correlation between these zero points and other physical quantities is analyzed.

Methods used in studies of adsorption of ions, their advantages and limitations, the meaning of results, and possibilities to combine results obtained by different methods are discussed. A large compilation of adsorption data is presented. The results obtained in simple adsorption systems (with one specifically adsorbed species) are sorted by the adsorbent and then by the adsorbate. Then, more complex systems are discussed with many specifically adsorbing species.

Many materials show a certain degree of chemical dissolution. The present survey is limited to materials whose solubility is low. This does not imply that the solubility is always negligible in the systems of interest.

Kinetics of adsorption and adsorption of surfactants and macromolecular species are broad fields, with their own methodologies, theories, and literature. Only selected topics directly related to the main subject of the present book are briefly treated.

Many recently published review articles, book chapters, and even entire books are devoted to adsorption of ionic species. Usually they cover one adsorbent (or a group of related adsorbents) or specific method(s). Some of these publications were very helpful during the preparation of this book, but current original papers were the main source of information.

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Marek Kosmulski

Contents

Preface v

1. INTRODUCTION 1
   References 10

2. PHYSICAL PROPERTIES OF ADSORBENTS 12
   I. Crystallographic Data 12
   II. Thermochemical Data 49
   References 63

3. SURFACE CHARGING IN ABSENCE OF STRONGLY ADSORBING SPECIES 65
   I. Zero Charge Conditions 65
   II. Correlations Between Zero Points and Other Physical Quantities 206
   III. Surface Charging in Inert Electrolytes 223
   IV. Temperature Effects 266
   V. Nonaqueous Media 282
   References 293

4. STRONGLY ADSORBING SPECIES 310
   I. Experimental Methods 326
   II. Small Ions 355
   III. Organic Compounds and their Mixtures 475

IV. Surfactants 491
V. Polymers 503
VI. Competition 510
VII. Kinetics 512
References 555

5. ADSORPTION MODELING 577
I. Surface Sites 579
II. Surface Reactions and Speciation 585
III. Primary Surface Charging 589
IV. Specific Adsorption 666
V. Surface Heterogeneity 700
References 704

6. SORPTION PROPERTIES OF SELECTED ORGANIC MATERIALS 709
I. Activated Carbons 710
II. Latexes 714
III. Other Materials 715
References 715

Appendix A1: Abbreviations *717*
Appendix A2: Trade Names and Trademarks *725*
Appendix A3: Points of Zero Charge *731*
Index *745*

1

Introduction

Properties of numerous adsorbents have been reported in the literature. This presentation is confined to materials

- Having the same bulk and surface chemical composition.
- Sparingly soluble in water.
- Showing pH dependent surface charging.

The above terms are relative, for example, some changes in surface composition due to solvation or selective leaching are unavoidable, but this is a part of the adsorption process. Adsorbents prepared by grafting or by adsorption of thin films (one or a few molecular layers) of substances whose properties are completely different from those of the support constitute an example of essential difference between the surface and bulk properties. Such materials combine high mechanical resistance, high surface area, and low cost of the support and desired sorption properties of the film and they are widely applied in different fields, but they are out of scope of this book. On the other hand, the surface properties of composite materials with external layer at least 10 nm thick are closely related to bulk properties of the coating, and a few examples of such materials will be discussed.

Solubility is another issue that requires some explanation. Materials more soluble than silica, i.e. about 10^{-3} mol dm^{-3} (this is an arbitrary choice) will not be discussed here. There is no sharp border between "soluble" and "insoluble", e.g. dissolution of relatively soluble materials is often sufficiently slow to allow

completion of sorption process before significant amount of the adsorbent is dissolved, moreover, the presence of certain adsorbates can substantially depress the dissolution rate and/or the equilibrium solubility. On the other hand, the solubility of materials reputed insoluble, can be significantly enhanced in the presence of certain complexing and/or redox agents. Kinetics of dissolution of silica is related to surface charging and depends on pH and ionic strength [1], and so is the solubility of many other materials. Chemical dissolution of oxides has been reviewed by Blesa et al. [2, 3] It should be emphasized that points of zero charge of relatively soluble materials, e.g. BaO and SrO have been reported in the literature.

Gel like materials containing sufficient amount of water are much more penetrable to ions than crystalline materials. Materials penetrable to ions are often characterized using the methods and terminology of ion-exchange, i.e. by their exchange capacities and diffusion coefficients of particular ions, and the affinity of particular ions to such materials is expressed in terms of selectivity coefficients. Misak [4] reviewed sorption properties of hydrous oxides from such a perspective, but in some other publications the uptake of ions by gel like materials is treated as adsorption. It is rather difficult to compare results interpreted in terms of the "ion exchange" approach on the one hand and adsorption approach on the other. Finally, in some publications dealing with materials not penetrable to ions a terminology borrowed from ion exchange is used: the adsorbents are "in hydrogen form", "in sodium form", etc. This can be translated into the language used in adsorption, e.g. "adsorbent in calcium form" is considered as adsorbent with pre-adsorbed calcium. Specific approach is required to describe surface charging of and adsorption on clay minerals on the one hand and zeolites on the other.

Most materials discussed in this book are electrical insulators, and their surface charge is regulated by sorption processes. However, a few oxides show sufficient degree of electronic conductivity that makes it possible to polarize the surface using an external battery. For example, the charging curves of IrO_2 can be plotted as a function of pH (when the oxide is polarized to constant potential) or as a function of polarizing potential at constant pH [5]. Properties and preparation of oxide electrodes (often termed DSA, dimensionally stable anodes) were reviewed by Trasatti [6]. Also adsorption properties of some sulfides, e.g. natural chalcocite [7] can be modified by polarization by external electric potentials.

The "dry" surface chemistry, i.e. chemistry of solid-gas interfaces has its own methodology and language. A substantial difference between wet and dry surface chemistry is that adsorption from solution is always an exchange, the "empty" surface is in fact occupied by solvent. In spite of an obvious relationship between dry and wet surfaces, only wet surface chemistry will be discussed here, although some quantities (e.g. the BET surface area) and relationships involve results obtained for dry surfaces. In particular, certain adsorbates considered show substantial vapor pressure at room temperature, and sorption of their vapors has been studied. Such results, albeit related to sorption of the same species from aqueous solution are beyond the scope of the book.

With a huge amount of information, that has been published on sorption properties of materials of interest, and in view of broad spectrum of goals and viewpoints of the authors of the cited publications and of potential readers of this book, it is not easy to organize the entire material. The grouping of data

is based on concepts of colloid chemistry. Many results are compiled in tabular form. They are sorted by the formal chemical formula of the adsorbent and then by the adsorbate.

Chapter 2, which is not directly related to surface properties presents physical and chemical properties of the materials of interest. Not all materials described in Chapter 2 are then directly referred to in subsequent chapters. For example mixed oxides are not only adsorbents, but also potential products of surface reactions involving simple oxides: crystallographic data are helpful in identifying such products, and thermochemical data in predicting the direction of the reaction. Chapter 2 also shows how many well-defined and potentially interesting materials have not been studied as adsorbents and may stimulate further research. The present author has once submitted a manuscript "Let us measure points of zero charge of exotic oxides", but a reviewer was against such an intriguing title and finally the title was changed it into a more usual one. Now there is a chance to broadcast and extend this idea: there are so many important and well-defined materials whose points of zero charge are unknown. On the other hand for some materials that have been extensively used as adsorbents crystallographic or thermochemical data are incomplete. Availability of physical data for oxides, aluminates and silicates is illustrated in Figs. 1.1–1.3, respectively. Symbols of elements whose simple or mixed oxides are considered as adsorbents in this book are printed in boldface; black background: crystallographic and thermochemical data available, gray background: only crystallographic data available.

The organization scheme of the crystallographic and thermochemical tables presented below is also used in the next chapters. Simple oxides, hydroxides and oxohydroxides are listed first, in alphabetical order of the symbol of the electropositive element and then from low to high oxidation state, and then from low to high degree of hydration. Then results for mixed oxides (all component oxides are insoluble with one exception of CO_2) are listed according to the symbol of the most acidic element, and then according to the symbols of less acidic elements. Aluminosilicates are listed after aluminates as a separate group, followed by clay minerals (listed alphabetically by name). A few basic carbonates are also included in spite of solubility of CO_2 in water. Namely, basic carbonates are potential products of reaction of certain (hydr)oxides with atmospheric CO_2. Also other sparingly soluble basic salts of water soluble acids can be formed from (hydr)oxides at sufficiently high concentrations of certain anions, so the example of carbonates is not unique, but physical properties of the other basic salts are not reported in Chapter 2. For derivatives of less common oxides the crystallographic data are not given explicitly, only formulae of salts for which such data exist are reported.

The presentation of adsorption data follows the rule "from the simplest to the most complicated". This was achieved by organizing the adsorbates into the following categories (listed from the simplest to the most complicated)

- H^+/OH^-
- Inert electrolytes
- Small ions and neutral organic molecules that tend to be specifically adsorbed
- Surfactants
- Polymers

H																	He
Li	**Be**											B	C	N	O	F	Ne
Na	**Mg**											**Al**	**Si**	P	S	Cl	Ar
K	Ca	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	Ge	As	Se	Br	Kr
Rb	Sr	**Y**	**Zr**	**Nb**	Mo	Tc	**Ru**	Rh	Pd	**Ag**	**Cd**	**In**	**Sn**	**Sb**	Te	I	Xe
Cs	Ba	**La**	**Hf**	**Ta**	**W**	Re	Os	**Ir**	Pt	Au	**Hg**	Tl	**Pb**	**Bi**	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt									

Ce	**Pr**	**Nd**	Pm	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Th	Pa	**U**	Np	**Pu**	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

FIG. 1.1 Availability of physical data for oxides; black background: crystallographic and thermochemical data available.