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BOOK REVIEW

Principles of Adsorption and Reaction on Solid Surfaces. Richard I. Masel Wiley–Interscience, New York, 1996

Principles of Adsorption and Reaction on Solid Surfaces is a review of fundamental concepts in adsorption and catalysis on solid, single-crystal surfaces. As its title denotes, this book has three major themes: solid surfaces, adsorption, and chemical reaction on solid surfaces. What may not be evident from the title is that most of the text deals with the surface science of catalysis on metal surfaces—other applications receive much less attention. Another characteristic feature of this text is its focus on models. By assuming a historical approach, which tracks the evolution of models for surface phenomena, Masel reviews numerous factors which govern adsorption and chemical reaction on solid surfaces. His in-depth coverage of modern theories and their associated numerical methods is the best and most novel feature of this text. This text fills a void that has grown in the years that have passed since the publication of *The Theory of Adsorption and Catalysis* (Clark, Academic Press, San Diego, 1970) and is complementary to more recent texts by Zangwill (*Physics at Surfaces*, Cambridge Univ. Press, Cambridge, UK, 1988) and Somorjai (*Introduction to Surface Chemistry and Catalysis*, Wiley–Interscience, New York, 1994). *Principles of Adsorption and Reaction on Solid Surfaces* could be adopted as a textbook for a senior undergraduate or graduate-level course. Serious researchers in surface science and catalysis should also purchase this text.

After a brief introduction in Chapter 1, which provides a historical context for studying reactions on surfaces as well as an overview of experimental methods in surface science, Masel jumps right into the meat of the text in Chapter 2. Chapter 2 presents a comprehensive review of the major concepts associated with quantifying surface structure. Concepts such as Bravais lattices, space groups, Miller indices, stereographic triangles, and Wood's notation for overlayer structure are introduced and applied to a variety of different solids. Although Masel's text is certainly not the only place where these topics can be found, his extensive and pedagogical elaboration on them is unique. Many examples are shown for structures of both low Miller index surfaces and difficult-to-visualize stepped surfaces. In addition, source code is included (in both FORTRAN and C) for a computer program that calculates surface structures of fcc solids. After a thorough study of this chapter, one emerges with a good foundation for understanding surface structure and appreciating its role in adsorption and reaction on surfaces.

Chapters 3, 4, and 5 focus on adsorption and, individually, they deal with adsorbate bonding at surfaces, adsorption isotherms, and adsorption kinetics. Following the trend that is common for most chapters in this book, Chapter 3 begins with a historical overview that introduces general features of adsorption. Subsequently, the discussion shifts to models for adsorbate–surface binding. Here, it is assumed that the reader has some knowledge of quantum chemistry and the electronic structure of solids. If this is not the case, appendices are available to provide some of the requisite background. After briefly discussing physical adsorption, Masel moves on to chemical adsorption, which comprises the bulk of the chapter. His approach is to outline the evolution of models for chemical bonding at metal surfaces and to evaluate the feasibility of their assumptions. The initial discussion focuses on older, empirical models and provides a context for understanding the evolution of the surface science literature. More practical is the subsequent discussion of quantum models, which begins with molecular orbital calculations and evolves to modern methods, which accurately represent surface electronic structure. By the end of the chapter, one is left with an appreciation of the key physical phenomena involved in adsorbate–surface bonding.

Adsorption isotherms are the main subject of Chapter 4. After a brief description of the different types of isotherms that are observed experimentally, Masel moves on to models for adsorption isotherms. Although some attention is given to older and (mostly) empirical models for adsorption isotherms, the bulk of the chapter is focused on lattice–gas models for adsorbates that interact laterally with one another. Here, some knowledge of statistical mechanics is required and can be found in the appendix. Various methods for obtaining isotherms are reviewed and include analytical approximations as well as Monte Carlo simulations. These topics are presented in sufficient detail to enable a dedicated student to implement them. As in the case of surface structure, much of the material in this chapter can be found in other (older) textbooks on surface science—for example, *The Theory of Adsorption and Catalysis* comes to mind. However, by including recent advances in Monte Carlo modeling of adsorption, this text assumes a more modern perspective reflecting advances made possible by rapidly growing computing capabilities over the past 10 to 15 years.

How does a molecule in the gas phase become adsorbed onto a solid surface? Chapter 5 is dedicated to this topic. Here, the concepts of trapping, sticking, and scattering are introduced. Models are presented to describe these phenomena on both bare and adsorbate-covered surfaces. In line with the modern, computer emphasis of this text, source code is included for computer programs that calculate trapping probabilities. Researchers could also benefit from Masel's efforts to integrate lattice-based theories for immobile adsorption into the mainstream of surface science.

Chapters 6 through 10 focus on chemical reactions at surfaces, which are the final topic of the text. Chapter 6 provides an introduction to the subsequent chapters by developing qualitative ideas about how and why a catalyst works. Here, Masel also establishes one of the major themes of the final chapters, which is to develop strong analogies between reactions on surfaces and fluid-phase reactions. The substantive discussion begins in Chapter 7, which reviews kinetic models for surface reactions. Langmuir–Hougen–Watson models are discussed along with related, semiempirical models. An extensive discussion is included of models for temperature-programmed desorption (TPD). Here most of the discussion focuses on lattice–gas models and many of the methods that were introduced in the discussion of adsorption isotherms in Chapter 5 are revisited. These models are subsequently extended from TPD to surface reactions, in what appear to be original derivations by Masel. The utility of the section on surface reactions would have been enhanced by incorporation of original results from the surface science literature.

A review of reaction-rate theories and model potential-energy surfaces for chemical reaction is presented in Chapters 8 and 9. Collision theory and transition-state theory are reviewed along with linear free-energy relationships and rules (e.g., the configurational mixing model, symmetry considerations) that govern whether a chemical reaction can occur. Although these concepts are important in understanding surface reactions, most of the material in Chapters 8 and 9 is focused on fluid-phase reactions. Here, Masel could have better served his readers by discussing examples from the surface science literature. For example, a significant amount of

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research has been dedicated to surface diffusion over the past 10 to 15 years. These studies would provide an excellent means by which to introduce and demonstrate transition-state theory. Similarly, it would have been useful to draw on experimental molecular-beam studies of surface-chemical reactions, to introduce reaction-rate theories in the context of surface science.

Masel does return to the surface in Chapter 10, where he revisits the material from Chapters 6–9 to concoct a summary of the characteristic attributes of a successful catalyst. The roles of factors such as bond energetics, bond orientation and symmetry, steric effects, surface geometry, surface electronic structure, and reactant charging are reviewed. Examples from the surface science literature are included to demonstrate these phenomena. This chapter reflects, to a greater extent than the other chapters, Masel's synthesis and organization of ideas from the surface science literature. Researchers in the surface science community can feel fortunate that such an attempt has been made. As knowledge in this area continues to develop, we can anticipate that Masel's efforts to quantify our understanding of catalysis will provide a foundation for future texts.

A review of Masel's text would not be complete without mentioning the supporting material. One factor that enhances the attractiveness of this text for use in advanced undergraduate or graduate courses is that it contains over 400 homework problems, many with their origins in the surface science literature. In addition, Masel includes many derivations as well as solved example problems at the end of the substantive chapters. As discussed above, source code is included for computer programs that model surface phenomena using modern methods. These programs could be useful in research. Another bonus that comes with this text is the appendix (available upon request), which reviews statistical mechanics, quantum theories of interatomic forces, and band structure of solids. Whether one is a student, an instructor, or a researcher, benefits can be reaped from Masel's extensive efforts to synthesize, organize, and clarify this tremendous amount of material.

Finally, to put into perspective the contributions in Masel's text, I have chosen two modern and related texts: *Physics at Surfaces* (by Zangwill) and *Introduction to Surface Chemistry and Catalysis* (by Somorjai). While all three texts have the aim of reviewing fundamental concepts in surface science, each text accomplishes this objective via a different approach. It appears that Masel has chosen the majority of topics in his text because of their relevance to catalysis. However, this is not the case with Zangwill, who reserves only one short chapter for catalysis, and Somorjai, whose scope extends significantly beyond catalysis. Another notable difference between the texts is that Zangwill and Somorjai emphasize experimental methods to a greater extent than Masel. In terms of style, Zangwill's text assumes a physical orientation, while Masel and Somorjai tend to adopt a chemical perspective. Within that perspective, however, Somorjai tends to summarize experimental data from the surface science literature, whereas Masel emphasizes the interpretation of experimental data. By applying Masel's theories to Somorjai's data, an instructor could formulate a nearly endless number of homework problems and perhaps some interesting research topics.

A final hallmark of Masel's text is his casual, pedagogical style. Masel creates the impression that he is conversing with the reader. His numerous derivations reveal insight into the way he thinks. This could be valuable for students who have not formed a coherent approach to problem solving. Masel also identifies gray areas in the surface science literature and honestly states his own opinions. I imagine that certain researchers may not agree with all of his opinions. However, hypotheses and differences of opinion are the driving force for research, which will ultimately lead to a complete understanding of adsorption and chemical reaction on solid surfaces.

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