Chemical Bonds Outside Metal Surfaces

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Preface

The problem of molecules interacting with metal surfaces has for a very long time been recognized to be of considerable technological as well as fundamental importance. Thus in the former category, a substantial number of important synthetic reactions for industrial purposes make use of metal surfaces as catalysts. Or again, problems of corrosion of metals are of great practical importance, such as in nuclear-reactor technology [see, for instance, my earlier articles, in: *Physics Bulletin*, Volume 25, p. 582, Institute of Physics, UK (1974); and in: *Physics and Contemporary Needs* (Riazuddin, ed.), Vol. 1, p. 53, Plenum Press, New York (1977)]. It is therefore of significance to strive to gain a more fundamental understanding of the atomic, and ultimately the electronic, processes that occur when a molecule is brought into the proximity of a metal surface.

The present volume focuses mainly on the theory and concepts involved; however, it is intended for readers in chemistry, physics, and materials science who are not specialists in theory but nevertheless wish to learn more about this truly interdisciplinary area of theoretical science. The aim of the book is to present the way in which valence theory can be synthesized with the understanding of metals that has been gained over the last half century or so. While advanced theory has at times been necessary, the detail is largely presented in an extensive set of Appendixes. Very occasionally, when such theory appears in the main text, the reader has usually been advised what to omit if he is merely interested in the main predictions of the theoretical arguments.

My indebtedness to many other workers will rapidly become evident to the readers of this book. Special thanks are due to my former research students: Drs. Richard C. Brown [see, for instance, *Phys. Rep.* **24C**, 77 (1976)], the late Ian D. Moore, Ilana Gabbay, John S. McCaskill, and Kathie R. Painter, as well as to Messrs. Peter J. Hiett and Kevin Joyce, who were Part II students in Theoretical Chemistry at Oxford. Invaluable help and advice in the general area covered by this book were provided by my friends and colleagues: Drs. Peter Grout, Don Richardson, and Gaetano Senatore, and also Professors Fernando Flores, "Jay" Mahanty, and Mario Tosi. Regular visits to the Theoretical Physics Division at AERE Harwell over many years have kept me in touch with the materials-science problems related to nuclear technology and thanks are due to Dr. A. B. Lidiard and his colleagues for the stimulation and motivation provided by these visits.

While I must, of course, accept sole responsibility for the contents of this book, and indeed no other person has read more than an individual chapter, it is a pleasure to thank Mr. Richard G. Chapman in Oxford, Dr. C. J. Wright (Harwell, UK), and Professor Z. W. Gortel at the University of Alberta, Edmonton, for helpful comments on parts of the manuscript. Should any readers find my book sufficiently interesting and be willing to trouble themselves, I would be most grateful to be told where I might improve the presentation, or where, I trust only very occasionally, I have misunderstood or erred in emphasis or judgment.

It is also a pleasure to thank all the authors who have generously allowed the reproduction of figures from their papers (the references are cited in the caption in each such case), and especially Dr. R. M. Lambert, Cambridge, UK, for supplying the original of Figure 6.3. Last, but by no means least, Professor H. Suhl very kindly acted as host for my visit to the University of California, San Diego, La Jolla, during a sabbatical leave granted by the University of Oxford. To him, his group of research students, and his colleague Dr. R. Kariotis, go my warm thanks for the opportunity to complete this book in an ideally quiet and scholarly atmosphere.

N. H. March

Contents

1. Background, Phenomenology, and Motivation . . . 1

2. Diatomic Molecules 23

3. Conformation and Electronic Structure of Polyatomic Molecules . . . 57

4. Dynamics of Adparticles and Neutron Inelastic Scattering

5. Molecular Desorption

6. Catalysis . . . 171

Chapter 1

Background, Phenomenology, and Motivation

The description of a chemical bond in interaction with a metal surface has long been a matter of concern for both fundamental theory and technology. Ideally, of course, such a description should take account of both the detailed electronic structure of the metal, including its surface, and the valence theory of the molecule involved. There has been a good deal of progress in implementing this program, but so far it has proved possible to carry out this task only by very lengthy numerical procedures.

Therefore, it is plainly of interest to seek simpler methods, starting from the most basic approximations of valence theory, and then incorporating the proximity of the metal surface by means of approximate concepts, such as image theory applied to a perfect electric conductor. Such a procedure, as discussed in Chapter 2 for diatoms, makes sense when the molecule is well outside the electron cloud spilling out from the metal surface, i.e., in the physisorbed regime, but needs refinement and extension in the face of chemical interaction between molecule and metal (e.g., the case of H_2O on ruthenium metal, treated at some length in Chapter 3).

However, even if such a program, combining the electronic band theory (allowing for Coulomb interactions between electrons) of the metal surface with the finest available wave functions for the molecular electrons, were tractable eventually by largely analytical theory, it would still not make very close contact with many of the important questions for chemical physics and materials science. This is because dynamics, rather than static conformational theory, is a major ingredient in any attempt to answer many salient questions in this area, such as desorption rates from metal surfaces and the way the rates of chemical reactions can be dramatically changed in the presence of catalytic metal surfaces.

To emphasize this perspective, we shall first discuss the background to the kinetics of adsorption and desorption after an elementary introduction to the problem of chemisorption in two limiting cases. In addition to their intrinsic interest, such investigations of kinetics frequently lead to valuable information concerning the nature of bonding in the adsorbed phase. A short introduction to reaction mechanisms outside surfaces follows.

One of the long-term aims of any theory of chemical bonds outside metal surfaces must be a comprehensive first-principles theory of catalytic reactions, as already implied above. Though no such complete theory exists at the time of writing, it is important for motivating and furthering work in the area covered by the present book to recognize both the types of problem that will be encountered, as well as the salient features that any useful theory must eventually embrace. Therefore, we felt it important in this introductory chapter, and following the lead given by Spencer and Somorjai in their important review on catalysis, to present the "case history" of one important catalytic process: the hydrogenation of carbon monoxide. This is then complemented in the final chapter by, first, an introduction to definitions and concepts of importance in catalysis, and second, a discussion of some selected topics in the modern theory of catalysis, chosen to throw light on basic principles (such as orbital symmetry conservation), which may perhaps, eventually, be taken over successfully from free-space chemical-reaction theory (e.g., Woodward–Hoffmann rules) into reaction theory outside metal surfaces. We have in this way endeavored to include in this book enough exemplary material for scientists in the boundary regions between physics, chemistry, and materials science to recognize just what factors one may eventually be forced to incorporate into the theory in order to understand fully the rich variety of phenomena encountered in the processes of catalysis.

With this general introduction, we shall next briefly review a little of the relevant historical background to the quantitative study of molecules outside metal surfaces, to be treated in detail in Chapters 2 and 3.

1.1. CHEMISORPTION IN IONIC AND COVALENT LIMITS

As a prelude to the more quantitative studies of diatoms and polyatomic molecules adsorbed on metal surfaces, to be discussed in Chapters 2 and 3, it is natural that the early work focused on the limiting cases of purely ionic and purely covalent bonding.(1)

1.1.1. Ionic Bond Formation

The formation of an ionic bond was thought to comprise two stages:

1. An electron transfer from the gas molecule to the surface.
2. The gas ion approaches the surface until the equilibrium separation is attained.

The transfer of an electron from the gas molecule to the surface involves an energy gain of $W - I$, where W is the work function and I the ionization potential. For a pure ionic bond, the heat of adsorption, Q_0 say, is given approximately by

$$Q_0 = N_A(W - I + e^2/4r_0) \tag{1.1.1}$$

where N_A denotes Avogadro's number. The final term in equation (1.1.1) already invokes image theory (also utilized in some detail in the next two chapters) to write the energy of attraction needed to bring the ion within the ionic radius r_0 of the surface. In Table 1.1, the values calculated in this way are compared with the experimental values for alkali-metal atoms on tungsten. There is fair agreement, and the same is found for molybdenum, etc., such systems having been treated, for example, by Moesta.(2)

1.1.2. Covalently Bonded Cases

When one turns to the adsorption of gases such as hydrogen or oxygen on metallic surfaces, an equation such as (1.1.1) is no longer of any use. Here one must consider the other limiting case, namely that of purely covalent bonding.

Early work, summarized for instance by Wedler,(3) expressed the heat

TABLE 1.1. Calculated and Experimental Heats of Chemisorption for Alkali Metal Atoms on Tungsten[a]

System	$N_A W$	$N_A I$	$N_A e^2/4r_0$	Q_0^{calc}	Q_0^{exp}
Na on W	104	118	45	31	32
K on W	104	100	36	40	—
Cs on W	104	89	31	46	64

[a] The model for calculation is the purely ionic limit, based on equation (1.1.1), and units are kcal mol^{-1}.

of adsorption for, say, the case of hydrogen as

$$Q_0 = 2E_{\text{Me-H}} - E_{\text{H-H}} \tag{1.1.2}$$

where $E_{\text{Me-H}}$ and $E_{\text{H-H}}$ are the bond energies for the adsorbed phase and for hydrogen, respectively. Then $E_{\text{Me-H}}$ can be evaluated following Pauling$^{(4)}$ in the form

$$E_{\text{Me-H}} = \tfrac{1}{2}(E_{\text{Me-Me}} + E_{\text{H-H}}) + 23.06(x_{\text{Me}} - x_{\text{H}})^2 \tag{1.1.3}$$

where the last term involving the electronegativity difference allows for the ionic contribution of the bond. The quantity $E_{\text{Me-Me}}$ is obtained from the heat of sublimation H_s, say, by setting

$$E_{\text{Me-Me}} = \tfrac{2}{12}H_s \tag{1.1.4}$$

in the case of a face-centered-cubic metal with twelve nearest neighbors. The heat of adsorption is then derived by combining equations (1.1.2) and (1.1.3) to yield

$$Q_0 = E_{\text{Me-Me}} + 46.1(x_{\text{Me}} - x_{\text{H}})^2 \tag{1.1.5}$$

The difference of electronegativities will be discussed further in Chapter 2. For the moment it will be noted that earlier work by Eley$^{(5)}$ took the difference of electronegativity from the dipole moment M of the Me–H bond. In turn, M was estimated from measurements of the surface potential. As an alternative approach, Stevenson$^{(6)}$ estimated the electronegativity of the metal from the work function, using Pauling's value of 2.1 for the electronegativity x_{H}. The results of this approach along the two routes of Eley and of Stevenson are compared with experiment in Table 1.2. This work will be developed in Chapter 2 by appealing to results from band-structure calculations of the various transition-metal series.

TABLE 1.2. Measured and Calculated Heats of Chemisorption (units are kcal mol^{-1})

System	Q_0, exp	Q_0, Eley	Q_0, Stevenson
H_2 on Ta	45	34	50
H_2 on W	45	37	46
H_2 on Cr	45	16	24
H_2 on Ni	18.4	19	29
H_2 on Fe	32	19	32