

FUNDAMENTAL CONCEPTS IN SURFACE INTERACTIONS

J. A. DUMESIC
*University of Wisconsin
Madison, Wisconsin 53706*

AN IMPORTANT PART of chemical reaction engineering is the "design" of heterogeneous catalysts; and, in general, this design process rests both on (1) experience (e.g. correlations of catalytic activity and selectivity with the catalyst's solid state and surface properties) and (2) a fundamental understanding of the interaction of surfaces with adsorbed species. While the former aspect of catalyst design is already well established in ChE graduate training, the concepts contained in the latter are not usually encountered in ChE graduate curricula. Instead, the student must combine several courses—for example, in quantum chemistry, statistical mechanics and solid state physics—in order to cover the essential features of surface interactions. Yet, this approach does not provide the continuity that is necessary for effective application of these concepts to catalytic phenomena.

One possible solution to this problem is to develop a one-semester introductory course to the fundamentals of surface interactions and their applications to adsorption and catalysis; by stressing the physical, chemical and catalytic breadth that is necessary for the understanding of surface phenomena, the course can be given to first-year graduate students without prerequisites. Subsequent to this course, a student with special interest in surface phenomena can take an interdisciplinary program to develop depth in various areas. The advantage of this approach is that the interrelation between the physical, chemical and catalytic concepts is made at the outset, thereby providing the necessary continuity. Furthermore, this course would give a catalysis-related point of view into surface interactions for students from

such areas as solid state physics, chemistry and material science. What follows is a suggestion for the scope and organization of such a course (based on a new course in development at the University of Wisconsin). In addition, the relationship of this course to the University of Wisconsin curriculum in chemical reaction engineering is shown in Figure 1. As limiting cases, reaction engineering is divided into (1) reactor engineering and design, and (2) catalysis and catalyst design, since these are the two major areas of specialization within this field.

COURSE SCOPE

IN CONTEMPORARY SURFACE science and catalysis research, there appears to be a gap between developments in fundamental theories of adsorption for simple species (e.g. H, CO), and

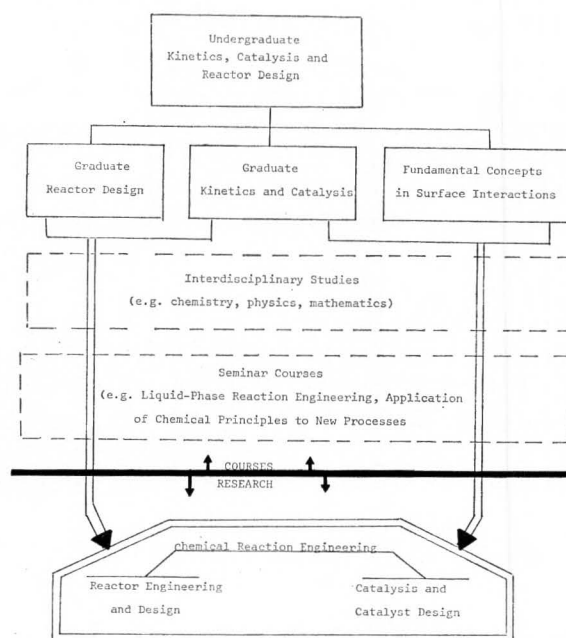


FIGURE 1. Curriculum in Chemical Reaction Engineering.

interpretations of reaction kinetics and adsorption behavior for catalytically interesting species (e.g. hydrocarbons). This gap arises primarily from the difficulty (computational, not fundamental) in treating "complex" adsorbed species rigorously in the framework of the adsorption theories. Yet, it seems reasonable (from both a research and educational point of view) to develop and use the concepts of the theories qualitatively (for now) to aid in the understanding of these "complex" adsorption and reaction phenomena. This is, in fact, a major objective of the suggested course.

The least that one must expect of a qualitative theory of adsorption phenomena is that it be consistent with the symmetry of the (adsorbed species—surface) system. Furthermore, it seems reasonable to exhaust those concepts derivable from symmetry alone (since this can be done rigorously) before construction of a qualitative theory. Therefore, the first part of the course deals with group theory, and its application to surface and chemical phenomena.

Before considering detailed calculations of the electronic structure of the (adsorbed species—surface) system, it is convenient to treat the adsorbed species and the solid at infinite relative separation. That is, the next phase of the course introduces molecular orbital theory and solid state physics, respectively. Subsequently, the adsorbed species is allowed to interact with the surface, leading to chemisorption.

In the final part of the course, the theoretical concepts are applied to various topics in adsorption and catalysis. This demonstrates how the general theory can be simplified to obtain meaningful results for different types of catalysts and reactions.

COURSE STRUCTURE

THE OVERALL STRUCTURE of the course is schematically shown in Figure 2, and it is seen therein that there are four major divisions: symmetry, solid state, surface interactions, and applications to adsorption and catalysis. These are discussed in greater detail below.

1. Symmetry

One begins with the concept of symmetry operations (e.g. proper rotations, mirrors), and the classification of molecular structure in terms of point group symmetries. For a given point group, representations for the group and the bases

for these representations are then considered. Through appropriate manipulation, each representation can be decomposed into a set of irreducible representations; this leads to the character table for the group. With a minimum of abstract derivation, group theory can be applied to chemical phenomena; indeed, the different applications result primarily from different choices of basis. These applications include: (1) infrared and Raman spectroscopies, (2) crystal field theory, (3) hybridization, (4) ligand field theory, (6) the Woodward-Hoffmann rules, and importantly (7) molecular orbital theory.

Along with the above applications, one must introduce the concept of matrix elements of operators, since symmetry can be used to deduce

There appears to be a gap between developments in fundamental theories of adsorption for simple species (e.g. H, CO), and interpretations of reaction kinetics and adsorption behavior for catalytically interesting species (e.g., hydrocarbons).

when various matrix elements must be identically zero. Then it is shown that two states may "interact" with each other when matrix elements between them are nonzero; depending on the symmetry of the interaction operator (e.g. the Hamiltonian) this imposes restrictions on the symmetry of interacting states.

When translation is added to the point group symmetry operations, then the two- and three-dimensional space groups are generated. Special sites in the unit cell are classified according to their point group symmetries; for the two-dimensional space groups, these sites become adsorption sites on surfaces. However, the most striking consequence of the translational symmetry is diffraction. As examples, x-ray diffraction (three-dimensional) and/or low energy electron diffraction can be discussed. This leads naturally into the reciprocal lattice. When "external diffraction" is replaced by "internal electron diffraction," solid state electronic structure is introduced.

2. Solid State

After a brief review of the Schrödinger equation and its implications in atomic structure (i.e.

s-, p- and d-orbitals), the free electron gas model for simple metals is derived. In so doing, k-space (wavevector space) can be introduced, followed by the computation of the density of states from constant energy contours in k-space. The occupation of these states by the electrons is in accord with Fermi-Dirac statistics. Next, the effect of the periodic placement of the metal atoms is "turned on," leading to "internal electron diffraction." As discussed in the symmetry part of the course, diffraction can be described by the reciprocal lattice, and in this way k-space becomes divided into the Brillouin zones. Furthermore, the translational symmetry of the lattice requires that the electron wavefunctions be written as Bloch functions, and all Brillouin zones can then be diffracted (translated in k-space) back into one zone. This is the reduced zone scheme for display of band structure.

Through the free electron gas model the basic concepts of solid state physics have now been introduced. Next, these concepts are used to discuss qualitatively the electronic structure of semiconductors. Of particular importance are (1) doping of semiconductors (p- and n-type), (2) conduction electrons and valence holes, and (3) the bending of bands due to electron transfer.

Of special importance are transition metals and the associated d-band. Because the d-orbitals are not as diffuse as the outer valence s- and p-orbitals (e.g. 3d orbitals are less diffuse than 4s and 4p), the tight-binding approximation can be used to describe the d-band; on the other hand, the (nearly) free electron gas model seems adequate to describe the broader (in energy) s- and p-bands resulting from the valence s- and p-orbitals. Qualitatively, at least, the electronic structure of transition metals can now be simply represented.

Finally, the solid state portion of the course can be supplemented by a discussion of defects and defect reactions. An appropriate defect symbolism should be introduced (e.g. Kröger symbolism), allowing defect reactions to be written consistent with the material balance, charge balance and lattice site balance. Then problems in for example non-stoichiometry, disorder type, and controlled (through doping) valence and defect concentration can be addressed.

3. Surface Interactions

One is now ready to consider the interaction of adsorbed species with surfaces. To parallel the solid state section, one may begin with adsorption

I. SYMMETRY	II. SOLID STATE	III. SURFACE INTERACTIONS
<u>Point Group Symmetry</u>	<u>Free Electron Gas</u>	<u>Semiconductors</u>
Representations/Bases Character Tables	Density of States Fermi-Dirac Statistics Brillouin Zones Bloch Functions	Boundary Layer Theory Cumulative Adsorption Depletive Adsorption Photocatalytic Effects
<u>Applications</u>	<u>Semiconductors</u>	<u>"One-Dimensional Metal"</u>
IR/Raman Spectroscopies Crystal/Ligand Fields Woodward-Hoffmann rules Hybridization	Conduction Electrons Valence Holes Doping (p and n)	Surface States Adatom Density of States Bonding/Antibonding States Surface Molecule
<u>Molecular Orbital Theory</u>	<u>Transition Metals</u>	<u>Real Metals</u>
Matrix Elements Orbital "Interactions"	s, p, and d-bands Tight-Binding	Green's Functions Level Width Function Level Shift Function Surface bands Symmetry of Adsorption
<u>Space Group Symmetry</u>	<u>Defects</u>	
Translation Diffraction Reciprocal Lattice	Symbolism Balances	

IV. APPLICATIONS TO ADSORPTION AND CATALYSIS

FIGURE 2. Structure of the Course: Fundamental Concepts in Surface Interactions.

on semiconductors. Starting with boundary layer theory one again encounters bending of the electron bands due to charge transfer at the surface. This leads to the cases of cumulative and depletive adsorption. As a more advanced example, one may discuss photoadsorptive and photocatalytic effects in semiconductor catalysis.

For adsorption on metals, a one-dimensional model can be used to illustrate many of the physical principles pertinent to adsorption on real surfaces. Specifically, a semi-infinite chain of atoms is modelled in the tight-binding approximation to form a one-dimensional d-band. Of significance, is the density of states on the surface atom, and in certain cases a localized surface state is formed (i.e., the electron density of this state decays exponentially from the surface into the bulk). Then, an adatom is allowed to "adsorb" on the surface end of the chain, and one calculates the adatom density of states. For a sufficiently strong interaction between the adatom and the surface, localized bonding and antibonding states are formed, leading to the concept of a surface molecule.

The treatment of adsorption on two-dimensional surfaces is facilitated by introduction of the Green's function. It then follows that the metal and adatom density of states (for the interacting system of adatom plus metal) are readily derivable from the Green's function. In particular, the adatom density of states can be written in terms of a level width function and a level shift function. Then, in order to bring together all aspects of the course: (1) a surface d-band is

constructed in the tight-binding approximation (solid state), (2) matrix elements between the absorbed species molecular orbitals and the surface d-band are inspected (symmetry), and (3) the adatom density of states is analysed (surface interactions).

4. Applications

The course ends with the application of these fundamental concepts to topics in adsorption and catalysis. This can be done through formal lectures or student special projects and reports. The latter procedure was followed at the University of Wisconsin, and below is a list of special projects recently chosen by students.

- Application of Woodward-Hoffmann rules to catalysis
- Alloy catalysis
- Electronic properties of metal clusters
- Electronic and structural factors for adsorption on semiconductors
- Surface diffusion in catalysis
- Absorbed atomic species (oxygen on metal oxides)
- Statistical mechanics of adsorption
- Hydrogen adsorption on metals.

CONCLUDING REMARK

The primary objective of the course is to provide the physical and chemical breadth that is necessary for a fundamental understanding of adsorption and catalytic phenomena. As a result, a significant fraction (ca. 30%) of the course enrollment at the University of Wisconsin has come from students in physics, chemistry and material science.

In the course, basic concepts pertinent to surface interactions are introduced and synthesized in various simple applications. The necessary proficiency in the use of the concepts for the interpretation of reaction kinetics and adsorption phenomena comes with further practice and study. This can be accomplished by subsequently following an interdisciplinary program of course study, and/or reading the literature. □

REFERENCES

The following is a list of texts that have been useful in various parts of the course.

I. Symmetry

1. Cotton, F. A., *The Chemical Applications of Group Theory*. (Second Edition), John Wiley and Sons, New York, 1971.
2. Pearson, R. G., *Symmetry Rules for Chemical Reactions, Orbital Topology and Elementary Proc-*

esses, John Wiley and Sons, New York, 1976.

3. *International Tables for X-ray Crystallography*, Vol. I, Kynoch Press, 1969.

II. Solid State

1. Kittel, C., *Introduction to Solid State Physics (Fourth Edition)*, John Wiley and Sons, New York, 1971.
2. Harrison, W. A., *Solid State Theory*, McGraw-Hill, New York, 1970.
3. Kröger, F. A., *The Chemistry of Imperfect Crystals (Second Edition)*, Vol. 2, North-Holland/American Elsevier, New York, 1974.

III. Surface Interactions

1. *NATO Advanced Study Institutes Series B: Physics*, Vol. 16, *Electronic Structure and Reactivity of Metal Surfaces* (E. G. Derouane and A. A. Lucas, editors), Plenum Press, New York, 1976.
2. *The Physical Basis for Heterogeneous Catalysis* (E. Drauglis and R. I. Jaffee, editors), Plenum Press, New York, 1975.
3. Clark, A., *The Chemisorptive Bond, Basic Concepts*, Academic Press, New York, 1974.

ACADEMIC POSITIONS

For advertising rates contact Ms. B. J. Neelands, CEE c/o Chemical Engineering Dept., University of Florida, Gainesville, FL 32611

RUTGERS

THE STATE UNIVERSITY OF NEW JERSEY

Department of Chemical and Biochemical Engineering

FACULTY POSITIONS IN CHEMICAL AND BIO-CHEMICAL ENGINEERING: Rutgers University, The State University of New Jersey, invites applications for several full-time faculty positions for undergraduate and graduate teaching and research in the fields of chemical and/or biochemical engineering. One tenure track assistant Professorship is open now to be filled in early 1978. It is expected that one or more similar positions can start later in the year. Applicants must have a doctoral degree in chemical and/or biochemical engineering at the time of the appointment and possess the dual abilities to develop sponsored research programs and teach in several areas of their field. Submit resumé, including at least three professional references, a list of journal publications, and a brief summary statement about your plans for research and teaching. Send your application to the Chairperson, Search Committee, Department of Chemical and Biochemical Engineering, Rutgers-The State University, New Brunswick, New Jersey 08903. Rutgers is an Affirmative Action/Equal Opportunity employer.