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# Intercalation Chemistry

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# Intercalation Chemistry

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# Preface

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The study of reactions between guest molecules or ions and solid host lattices, which retain the major features of their structures, has continued since 1841 when Schaufaustl first reported the intercalation of graphite by sulfate ions. However, it was not until the 1960s that interest in intercalation chemistry began to grow significantly and to extend into many scientific disciplines. Although the term intercalation has been used widely to describe reactions of guests with layered host lattices, many other reactions have characteristics in common. We decided to draw together in this volume a number of these related areas in which host lattices maintain some essential structural features during the reaction. The volume therefore aims to introduce the specialist reader to the breadth of intercalation chemistry and the newcomer to the diverse research opportunities and challenges available in synthetic and reaction chemistry and also in the controlled modification of physical properties.

After an introductory paper, the next chapter describes the intercalation chemistry of graphite. Graphite is perhaps the simplest host lattice structure but shows varied chemistry due to its ability to react with both oxidants and reductants and to incorporate neutral molecules. Its chemistry is further complicated by staging, which is more prevalent than in any other layered system. The second group of materials described are complex oxides with both two (clays and acid phosphates)- and three (zeolites)-dimensional structures. These systems are currently of considerable interest, because of technological applications in heterogeneous catalysis, as sorbents and inorganic ion exchangers. Their chemistry is dominated primarily by the intercalation of neutral molecules and by ion exchange rather than by the redox chemistry observed in both graphite and the layered chalcogenides. The  $\beta$ -aluminas (Chapter 6) have been mostly studied for applications as solid ion conductors in electrochemical cells, but much of their chemistry is analogous to that of the clays, though



limited to small molecules and ions by the fixed interlayer separation imposed by the bridging oxygen.

Four chapters describe the intercalation chemistry of layered chalcogenides and halides with simple and hydrated cations and organic and organometallic ions. The reactions are mainly characterized by reduction of the host lattice; unlike graphite, no host oxidations accompanied by anion insertions have been observed, though attempts have been made to intercalate electron-accepting molecules, such as TCNQ, into the filled d-band group-VI dichalcogenides, for example,  $\text{MoS}_2$ . Once formed, these intercalation compounds show ion-exchange behavior that is similar to clays. In the redox systems, however, the ion-exchange capacity is set by the degree of host reduction, whereas in clay and zeolite chemistry, it is determined by cation substitution, e.g., Si for Al, in zeolites.

The next two chapters discuss areas that are not normally considered by the inorganic chemist. The first of these is concerned with the chemistry, thermodynamics, and applications of intermetallic compounds that incorporate hydrogen. The reader will observe many similarities and differences in behavior when compared with lithium intercalation in the dichalcogenides and oxides. Chapter 14 discusses intercalation in the context of biological systems and shows how the intercalation model was developed for the interaction of molecules with DNA. Crystallographic shear structures (Chapter 15) are not usually considered as related to intercalation compounds. However, there are important similarities, particularly in the way in which the structure imposes constraints on reactions. Reduction reactions, for example, leave the main part of the crystal lattice unperturbed and are accommodated by rearrangements of small numbers of atoms on specific sites. In the following two chapters, intercalation reactions of oxides and chalcogenides of vanadium, molybdenum, and tungsten are described. The final chapter touches on the physical properties of some intercalation compounds of the dichalcogenides.

In collecting these contributions, we have not attempted to cover all the aspects of intercalation chemistry, nor to describe, in any detail, their technological applications. Rather, we have concentrated on the chemistry and structural principles of a wide range of systems. It is our hope thereby to stimulate wider interactions among researchers in the various materials science disciplines.

*M. Stanley Whittingham  
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