An Introduction to Integrated Chemical Systems

The chemist interested in catalysis, stereochemical specificity, polymer structure, metallo-organic reactions, surface effects and a hundred other facets of chemistry will be challenged and instructed by the myriad forms in biology.

—Arthur Kornberg
1988 Aharon Katzir Memorial Lecture
Weizmann Institute
Rehovot, Israel

1.1. Introduction

Large complex systems (macrosystems) generally have hierarchical structures; that is, they are assembled from smaller units that are, in turn, built from smaller and simpler ones, finally down to units with atomic and molecular dimensions. This general structure is illustrated in Figure 1.1.1, along with the approximate sizes of the different units. Consider, for example, a biological system (Fig. 1.1.2). At the molecular level are the simple chemical species (e.g., Cl\(^-\), water, phosphates) and molecular building blocks, the amino acids, sugars, nucleotides, and so on. These are components of the macromolecules at the next level, for example, polypeptides, proteins, polysaccharides, and nucleic acids. The structures that actually carry out the reactions are more complex, however, and involve the next level (the integrated chemical system level), where the different macromolecules and other components are assembled in a unique way to form a particular structure or carry out a certain process. For example, it might consist of several different
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**GENERAL SYSTEM**

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<th>SIZE</th>
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<td>nm</td>
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<td>MOLECULES</td>
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**FIGURE 1.1.1.** Schematic representation of the buildup of a general macrosystem from smaller and simpler components.

Enzymes contained in a membrane in contact with a liquid phase with dissolved reactants. These subsystems form the cells that are the building blocks of the tissues and finally the organism.

A complicated electronic system, such as a digital computer, is built up in an analogous manner (Fig. 1.1.3). At the molecular level are the atoms and molecules, including those that form the semiconductors Si and GaAs. The next level involves larger aggregates, up to bulk semiconductor crystals. However, the actual device depends on the construction of complex integrated chemical systems, such as transistors and integrated circuits, that require dopants, junctions, metal leads, contacts, and encapsulants. These are assembled into still larger units of different types, such as circuit boards, that contain the power supply, microprocessor, memory, and interconnections that make up the macrosystem—

**FIGURE 1.1.2.** Buildup of a general biological system following the scheme in Figure 1.1.1.
BIOLOGICAL SYSTEM

ORGANISM

TISSUES

CELLS

ORGANELLES

MEMBRANE-ENZYME SYSTEMS

PROTEINS

POLYPEPTIDES

AMINO ACIDS

H₂O, CO₂
ELECTRONIC SYSTEM

SIZE

m

COMPUTER

cm

SUB-ASSEMBLIES
CIRCUIT BOARD

mm

INTEGRATED CIRCUIT
TRANSISTOR

μm

Si CRYSTAL

nm

GaAs

o A

Si, Ga, As, Al

FIGURE 1.1.3. Buildup of an electronic system (computer) following the scheme in Figure 1.1.1.
the computer. In all cases, the system structures and interactions become more complex as one proceeds from the lowest boxes, containing simple atoms and molecules (the molecular level), to more complex molecules, to macromolecules, and so on up to the integrated chemical systems and larger entities. A feeling of the relative size of the various features of interest in these systems can be obtained from Figure 1.1.4.

The same concept of a hierarchical organization also holds for large structures and machines, such as buildings and automobiles. While this book does not deal with structural materials, the same concepts apply. Indeed, many advanced materials, such as composites and alloys, can be considered integrated chemical systems, whose behavior (strength, flexibility, stability) depends on the microstructure and the interactions between the components.

Chemists most frequently study reactions or synthesize species at the molecular level. Synthetic methods at this level have attained a highly developed state, and very complicated molecules, such as chlorophyll and large metal clusters, can be constructed. Such synthetic reactions are usually carried out by a series of reactions in homogeneous media, specifically, in the liquid or gas phase. The modes of reaction and bonding and the nature of intermolecular interactions at this level are well understood. The synthetic methods for larger molecules (polymers and macromolecules) are similarly highly developed, and a large number of polymers and copolymers with different chemical properties and structural characteristics can be produced at will. Again, these usually arise from reactions of one or more types of monomers (e.g., reactants A and B) that polymerize in a homogeneous medium to produce polymers of the form . . . AAAA . . . , . . . BEEE . . . , . . . AABBAA . . . , . . . ABABAB . . . , and so on. However, when one wants to synthesize a polymer chain made of a number of different monomeric units (W, X, Y, Z) in a specific sequence, for example, . . . WXWYXZ . . . , one must turn to synthesis at an interface. Thus polypeptides (1) and oligonucleotides (2) of known sequence are synthesized by a solid-phase method that involves attachment of the first monomer to a resin bead, followed by repeated treatments with different linking agents, monomers, and protective agents to grow the desired polymer structure. Polymers are of immense technological importance and macromolecules are involved in many biological processes, the details of reaction mechanisms and the nature of molecular interactions at this level are not as developed as those at the molecular level.

When we proceed to the next level, that of the "integrated chemical system" (3) (also sometimes called the nanostructure, microsystem, or
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FIGURE 1.1.4. Approximate size ranges of different small structures. Integrated-circuit features are those for smallest fabricated structures as of 1991. The top lines show the microscopic techniques that can be used for imaging at the size range: STM, scanning tunneling; AFM, atomic force; SEM, scanning electron; TEM, transmission electron. [Taken, in part, from G. W. Kreichbaum and P. Kleinschmit, Angew. Chem. Intl. Ed. Engl., 28, 1416 (1989).]

mesomeric level), we are concerned with structures that contain a number of different components and several phases. The operation at this level frequently requires consideration of interfacial processes and mechanisms of mass and charge transport. Although such systems can be building blocks to even larger, more complex ones that involve a number of different integrated chemical systems, they are also of interest in their own right in connection with the construction of smaller devices, such as ones that can carry out complicated, multistep reactions or processes or that can act as analytical sensors. For example, as discussed in more detail below, many biological systems involve a number of different
enzymes held in a membrane matrix. Systems for the utilization of solar energy to drive useful chemical reactions require several components that provide different functions: light absorption, charge separation, catalysis, and redox chemistry. The different components in this system are assembled on a suitable support in a structure that will produce the desired reactions when irradiated.

This monograph is concerned primarily with such systems. We define these integrated chemical systems (ICSs) as heterogeneous, multiphase systems involving several different components (e.g., semiconductors, polymers, catalysts, membranes) designed and arranged for specific functions or to carry out specific reactions or processes. Often the different components will be organized structurally and will show synergistic effects. Usually it is the interaction of the components of the ICS that determines its properties. Rather arbitrarily we limit the sizes of the structural elements of an ICS to the scale of molecular dimensions to a few micrometers. Thus the integrated circuits that are used in electronic devices are ICSs. Note that integrated circuits are constructed mainly by chemical fabrication techniques. Chemical reactions are not intentionally carried out with integrated circuits, but undesired reactions, such as electrochemically induced corrosion and current flow-induced metal migration, can occur in these systems. These processes become of greater importance as the size scale of the circuit is decreased. Integrated circuits are also of interest in connection with ICSs, because closely related devices have been used as analytical sensors and because some of the techniques used in the fabrication of integrated circuits are appropriate for the construction of ICSs as well, as discussed in Chapter 2.

1.2. EXAMPLES OF INTEGRATED CHEMICAL SYSTEMS

The character and applications of ICSs can be understood better by considering several examples of different types in more detail. Thus we discuss here, rather briefly, two biological organelles that are truly sophisticated ICSs, the chloroplast and the mitochondrion. We also describe several man-made ICSs, with examples of heterogeneous catalysts, photoelectrochemical systems, chemical microsensors, and a system employed in instant color photography.

1.2.1. Biological Integrated Chemical Systems

Living organisms depend on ICSs to carry out many functions, such as photosynthesis and oxidative phosphorylation. Consider a typical cell of