

Principles of Colloid and Surface Chemistry

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MARCEL DEKKER, INC. New York and Basel

Library of Congress Cataloging in Publication Data

Hiemenz, Paul C 1936-

Principles of colloid and surface chemistry

(Undergraduate chemistry; v. 4)

Includes bibliographical references and index:

1. Colloids. 2. Surface chemistry. I. Title.

QD549.H53

541'.345

76-55600

ISBN 0-8247-6573-7

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MARCEL DEKKER, INC.

270 Madison Avenue, New York, New York 10016

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

Principles of Colloid and Surface Chemistry

UNDERGRADUATE CHEMISTRY

A Series of Textbooks

edited by

J. J. Lagowski

Department of Chemistry

The University of Texas at Austin

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Preface

Colloid and surface chemistry occupy a paradoxical position among the topics of physical chemistry. These are areas which have traditionally been considered part of physical chemistry and are currently enjoying more widespread application than ever due to their relevance to environmental and biological problems. At the same time, however, colloid and surface chemistry have virtually disappeared from physical chemistry courses. These topics are largely absent from the contemporary general chemistry course as well. It is possible, therefore, that a student could complete a degree in chemistry without even being able to identify what colloid and surface chemistry are about.

The primary objective of this book is to bridge the gap between today's typical physical chemistry course and the literature of colloid and surface chemistry. The reader is assumed to have completed a course in physical chemistry, but no prior knowledge of the topics under consideration is assumed. The book is, therefore, introductory as far as the topic subjects are concerned, although familiarity with numerous other aspects of physical chemistry is required background.

Since physical chemistry is the point of departure for this presentation, the undergraduate chemistry major is the model reader toward whom the book is addressed. This in no way implies that these are the only students who will study the material contained herein. Students majoring in engineering, biology, physics, materials science, and so on, at both the undergraduate and graduate levels will find aspects of this subject highly useful. The interdisciplinary nature of colloid and surface chemistry is another aspect of these subjects that contributes to their relevance in today's curricula.

This is primarily a textbook, written with student backgrounds, needs, and objectives in mind. There are several ways in which this fact manifests itself in the organization of this book. First, no attempt has been made to review the literature or to describe research frontiers in colloid and surface chemistry. A large literature exists which does these things admirably. Our purpose is to provide the beginner with enough background to make intelligible the journals and monographs which present these topics. References have been limited to monographs, textbooks, and reviews which are especially comprehensive and/or accessible. Second, where derivations are presented, this is done in sufficient detail so that the reader should find them self-explanatory. In areas in which undergraduate chemistry majors have minimal backgrounds or have chronic difficulties—for example, fluid mechanics, classical electromagnetic theory, and electrostatics—the presentations begin at the level of general physics, which may be the student's only prior contact with these topics.

Third, an effort has been made to facilitate calculations by paying special attention to dimensional considerations. The cgs-esu system of units has been used throughout, even though this is gradually being phased out of most books. The reason for keeping these units is the stated objective of relating the student's experiences to the existing literature of colloid and surface chemistry. At present, the cgs-esu system is still the common denominator between the two. A fairly detailed list of conversions between cgs and SI units is included in Appendix C. Finally, a few problems are included in each chapter. These provide an opportunity to apply the concepts of the chapter and indicate the kinds of applications these ideas find.

Not all who use the book will have the time or interest to cover it entirely. In the author's course, about two-thirds of the material is discussed in a one-quarter course. With the same level of coverage, the entire book could be completed in a semester. To cover the amount of material involved, very little time is devoted to derivations except to answer questions. Lecture time is devoted instead to outlining highlights of the material and presenting supplementary examples.

The underlying unity which connects the various topics discussed here is seen most clearly when the book is studied in its entirety and in the order presented. Time limitations and special interests often interfere with this ideal. Those who choose to rearrange the sequence of topics should note the subthemes that unify certain blocks of chapters. Chapters 1 through 5 are primarily concerned with particle characterization, especially with respect to molecular weight; Chapters 6 through 8, with surface tension/free energy and adsorption; and Chapters 9 through 11, with flocculation and the electrical double layer. Subjects of special interest to students of the biological sciences are given in Chapters 2 to 5, 7, and 11.

Colloid chemistry and surface chemistry each span virtually the entire field of chemistry. The former may be visualized as a chemistry whose "atoms" are considerably larger than actual atoms; the latter, as a two-dimensional chemistry. The point is that each encompasses all the usual subdivisions of chemistry: reaction chemistry, analytical chemistry, physical chemistry, and so on. The various subdivisions of physical chemistry are also represented: thermodynamics, structure elucidation, rate processes, and so on. As a consequence, these traditional categories could be used as the basis for organization in a book of this sort. For example, "The Thermodynamics of Surfaces" would be a logical chapter heading according to such a plan of organization. In this book, however, no such chapter exists (although not only chapters but entire volumes on this topic exist elsewhere). The reason goes back to the premise stated earlier: These days most undergraduates know more about thermodynamics than about surfaces, and this is probably true regardless of their thermodynamic literacy/illiteracy! Accordingly, this book discusses surfaces: flat and curved, rigid and mobile, pure substances and solutions, condensed phases and gases. Thermodynamic arguments are presented—along with arguments derived from other sources—in developing an overview of surface chemistry (with the emphasis on "surface"). A more systematic, formal presentation of surface thermodynamics (with the emphasis on "thermodynamics") would be a likely sequel to the study of this book for those who desire still more insight into that aspect of two-dimensional chemistry. Similarly, other topics could be organized differently as well. Only time will tell whether the plan followed in this book succeeds in convincing

students that chemistry they have learned in other courses is also applicable to the "in between" dimensions of colloids and the two dimensions of surface chemistry.

The notion that molecules at a surface are in a two-dimensional state of matter is reminiscent of E. A. Abbott's science fiction classic, *Flatland*.^{*} Perusal of this little book for quotations suitable for Chapters 6, 7, and 8 revealed other parallels also: the color revolt and light scattering, "Attend to your Configuration" and the shape of polymer molecules, and so on. Eventually, the objective of beginning each chapter with a quote from *Flatland* replaced the requirement that the passage cited have some actual connection with the contents of the chapter. As it ends up, the quotes are merely for fun: Perhaps those who are not captivated by colloids and surfaces will at least enjoy this glimpse of *Flatland*.

Finally, it is a pleasure to acknowledge those whose contributions helped bring this book into existence. I am grateful to Maurits and Marcel Dekker for the confidence they showed and the encouragement they gave throughout the entire project. I wish to thank Phyllis Bartosh, Felecia Granderson, Jennifer Woodruff, and, especially, Mickie McConnell and Lynda Parzick for making my sloppy manuscript presentable. My appreciation also goes to Bob Marvos, George Phillips, and, especially, Dottie Holmquist for their work on the figures, which are such an important part of any textbook. I also wish to thank Michael Goett for helping with proofreading and indexing. Finally, due to the diligence of the class on whom this material was tested in manuscript form, the book has 395 fewer errors than when it started. For the errors that remain, and I hope they are few in number and minor in magnitude, I am responsible. Reports from readers of errors and/or obscurities will be very much appreciated.

Paul C. Hiemenz

^{*} E. A. Abbott, *Flatland* (6th ed.), Dover, New York, 1952. Used with permission.

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Colloid and Surface Chemistry: Their Scope and Variables

1

Next . . . come the Nobility, of whom there are several degrees, beginning at Six-Sided Figures, . . . and from thence rising in the number of their sides till they receive the honorable title of Polygonal . . . Finally when the number of sides becomes so numerous, and the sides themselves so small, that the figure cannot be distinguished from a circle, he is included in . . . the highest class of all. [From Abbott's Flatland]

1.1 INTRODUCTION

"Yesterday, I couldn't define colloid chemistry; today, I'm doing it." This variation of an old quip could apply to many a recent chemistry graduate upon entering employment in the "real world." Two facts underlie this situation. First, colloid and surface chemistry, although traditional parts of physical chemistry, have largely disappeared from introductory physical chemistry courses. Second, in research, technology, and manufacture, countless problems are encountered which fall squarely within the purview of colloid and surface chemistry. Later in this section, we shall enumerate some examples which illustrate this statement.

The paradoxical situation just described means that it is entirely possible for a chemistry student to have completed a course in physical chemistry and still not have any clear idea of what colloid and surface chemistry are about. A book like this one is therefore in the curious position of being simultaneously "advanced" and "introductory." Our discussions are often advanced in the sense of building on topics from physical chemistry. At the same time, we shall have to describe the phenomena under consideration pretty much from scratch, since they are largely unfamiliar. In keeping with this, this chapter is concerned primarily with a broad description of the scope of colloid and surface chemistry and the kinds of variables with which they deal. In subsequent chapters, different specific phenomena are developed in detail.

Our first tasks are to define what we mean by colloid chemistry and how this is related to surface chemistry. For our purposes, any particle which has some linear dimension between 10^{-7} cm (10 \AA) and 10^{-4} cm ($1 \mu\text{m}$ or 1μ)* is considered a

* Appendix C contains a fairly detailed list of conversion factors between cgs and SI units.

colloid. For us, linear dimensions rather than particle weights or the number of atoms in a particle will define the colloidal size range. However, other definitions may be encountered elsewhere. It should be emphasized that these limits are rather arbitrary. Smaller particles are considered within other branches of chemistry and larger ones are considered within sciences other than chemistry. The preceding statement may be expanded still further. Colloid chemistry is interdisciplinary in many respects; its field of interest overlaps physics, biology, materials science, and several other disciplines. It is the particle dimension—not the chemical composition (organic or inorganic), source of the sample (biological or mineralogical), or physical state (one phase or two)—that consigns it to our attention. With this in mind, it is evident that colloid chemistry is the science of both large molecules and finely subdivided multiphase systems.

It is in systems of more than one phase that colloid and surface chemistry meet. The word "surface" is thus used in the chemical sense of a phase boundary, rather than in a strictly geometrical sense. Geometrically, a surface has area, but not thickness. Chemically, however, it is a region in which the properties vary from those of one phase to those of the adjoining phase. This transition occurs over distances of molecular dimensions at least. For us, therefore, a surface has a thickness which we may imagine as shrinking to zero when we desire a purely geometric description.

It is self-evident that the more finely subdivided a given weight of material is the higher the surface area will be for that weight of sample. In the following section we discuss this in considerable detail since it is the basis for combining a discussion of surface and colloid chemistry in a single book.

In subsequent sections of this chapter, we shall discuss further the distinction between macromolecular colloids and multiphase dispersions (Sect. 1.3), the use of the term "stability" in colloid chemistry (Sect. 1.4), the size and shape of colloidal particles (Sect. 1.6), states of aggregation among particles (Sect. 1.7), and the distribution of particle sizes that is typical of virtually all colloidal preparations (Sect. 1.8). The fact that particles in the colloidal size range are not all identical in size also requires a preliminary discussion of statistics which is the subject matter of several sections at the end of this chapter.

One of the basic premises underlying the selection of topics included in this book is that areas of similarity between diverse fields should be stressed. This is not to say, of course, that differences are unimportant. Rather, it seems more valuable to point out to the beginner that useful methods and insights are frequently part of the well-established procedures of other disciplines which deal with related phenomena. Too provincial a viewpoint, especially at the beginning, is apt to isolate the worker from many potentially valuable sources of information. In the long run, this seems like a greater loss than the loss of time that occurs when a worker concludes too hastily that a technique which works well in one system should work equally well in another system where the particles are larger or smaller by several orders of magnitude. Errors of this last sort are generally discovered quickly enough!

Any attempt to enumerate the areas in which surface and colloid chemical concepts find applicability is bound to be incomplete and quite variable with time

because of changing technology. Nonetheless, we shall conclude this section with a partial listing of such applications. If there is any difficulty in doing this, it is because of the abundance rather than scarcity of such examples.

Some areas of science and technology in which particles in the colloidal size range are regularly encountered are the following:

1. In analytical chemistry: adsorption indicators, ion exchange, nephelometry, precipitate filterability, chromatography, and decolorization.
2. In physical chemistry: nucleation; superheating, supercooling, and supersaturation; and liquid crystals.
3. In biochemistry and molecular biology: electrophoresis; osmotic and Donnan equilibria and other membrane phenomena; viruses, nucleic acids, and proteins; and hematology.
4. In chemical manufacturing: catalysis, soaps and detergents, paints, adhesives, ink; paper and paper coating; pigments; thickening agents; and lubricants.
5. In environmental science: aerosols, fog and smog, foams, water purification and sewage treatment; cloud seeding; and clean rooms.
6. In materials science: powder metallurgy, alloys, ceramics, cement, fibers, and plastics of all sorts.
7. In petroleum science, geology, and soil science: oil retrieval, emulsification, soil porosity, flotation, and ore enrichment.
8. In household and consumer products: milk and dairy products, beer, water-proofing, cosmetics, and encapsulated products.

It is evident from this partial list how many materials or phenomena of current scientific or everyday interest touch on colloid and surface chemistry to some extent. Many of these areas, of course, have enormous technological and/or theoretical facets which are totally outside our perspective. Nevertheless, all share a common interest in small particles and/or large molecules.

1.2 THE IMPORTANCE OF THE SURFACE FOR SMALL PARTICLES

The contemporary science student is probably aware that the concept of the atom is traceable to early Greek philosophers, notably Democritus. More than likely, however, few have bothered to follow through the hypothetical subdivision process that led to the original concept of an atom. The time has come to remedy this situation since the colloidal size range lies between microscopic chunks of material and individual atoms.

Consider a spherical particle of some unspecified material in which the sphere has a radius of exactly 1.0 cm. What we propose to do is to "reapportion" this fixed quantity of material by subdividing it, first, into an array of spheres, each with a radius half that of the original sphere. In a second subdivision, the radius of each of these spheres will be cut in half again. In the third "cut" the radii will be halved again, and so on. The results of such an exercise are summarized in Table 1.1.

The first line in Table 1.1 shows the volume and area of the original sphere whose radius is 1.0 cm. The second line in the table defines the symbols we use to signify