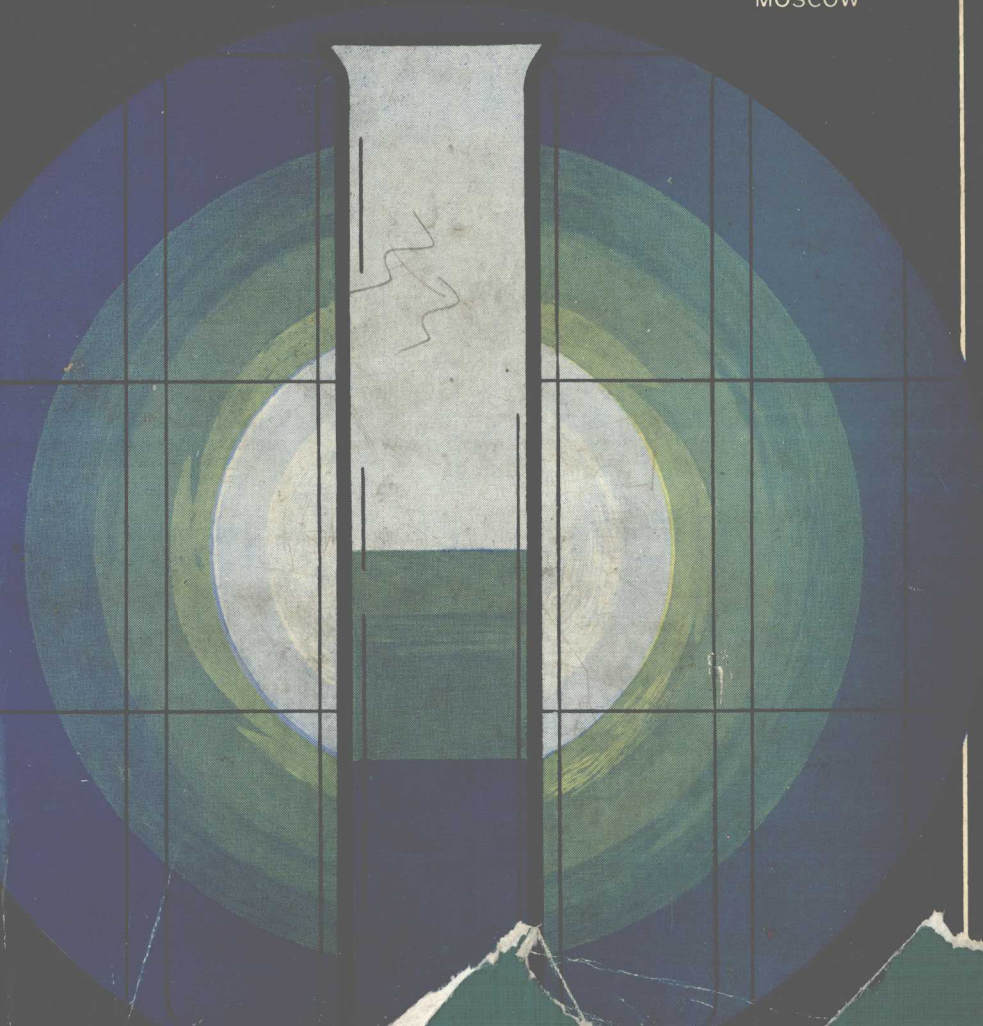


COLLOID CHEMISTRY

by S. Voyutsky

MIR PUBLISHERS
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С. С. ВОЮЦКИЙ
КУРС
КОЛЛОИДНОЙ ХИМИИ

ИЗДАТЕЛЬСТВО «ХИМИЯ»
МОСКВА

COLLOID CHEMISTRY

by S. Voyutsky

Translated from the Russian by
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PREFACE

S. S. Voyutsky's *Colloid Chemistry* has been for many years the main textbook for students of chemical engineering institutes and chemistry faculties of universities in the USSR.

Colloid chemistry has undergone considerable changes since the publication of the first edition. New problems have arisen and new approaches to colloidal phenomena have been found. This includes the concept of disjoining pressure, the formation of colloidal systems as a result of autodispersion, and the presence of periodic structures in colloidal systems. The science of physico-chemical mechanics has greatly developed. All this has made it necessary to considerably work over the textbook by introducing new concepts and, at the same time, deleting outdated material.

I hope S. S. Voyutsky's textbook, written simply and clearly on a high scientific level, will be useful to chemical engineering students and to all those wishing to become acquainted with the problems of modern colloid chemistry.

B. V. Derjaguin

AUTHOR'S PREFACE

More than ten years have passed since the publication of the first Russian edition of this textbook. During this time, colloid chemistry has undergone considerable changes as a result of the work of Soviet and other scientists. Several theoretically interesting and practically important sections are either new or have been greatly expanded, including the concept of stability and coagulation, physico-chemical mechanics, autodispersion, and physical chemistry of aqueous dispersions of rubber (latices).

All this has necessitated a revised edition of the textbook.

As in the first edition, I have sought to bring the material as close as possible to practical problems without making the book a prescription of recipes and a description of the processes of various technological fields. I have tried to present my material clearly, drawing attention mainly to the physical meaning of phenomena.

This textbook of colloid chemistry fits the curriculum of chemical engineering specialties of higher educational institutions, approved by the Educational and Methodological Board of the Ministry of Higher and Secondary Specialized Education of the USSR in 1974. Moreover, it gives information, which will be useful to students and post-graduate students of chemistry faculties of universities. I believe that in this form the book will also be useful to various researchers and engineers working in the field of applied colloid chemistry.

I take this opportunity to express my thanks to the professors and research assistants of colloid chemistry departments of the Moscow State University, the Leningrad State University, the Leningrad Technological Institute, the Moscow Chemical Engineering Institute

Author's Preface

and the Moscow Technological Institute of Light Industry, and also to professors G. A. Martynov, A. A. Trapeznikov, G. I. Fuchs and several other persons for their valuable advice on this book. I am especially grateful to the Corresponding-Member of the USSR Academy of Sciences, Prof. B. V. Deryagin (Derjaguin), for his valuable instructions and assistance in writing the textbook.

S. S. Voyutsky

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INTRODUCTION. COLLOIDAL SYSTEMS AND THE SUBJECT MATTER OF COLLOID CHEMISTRY

1. CONCEPT OF COLLOIDAL SYSTEMS AND THE DEFINITION OF COLLOID CHEMISTRY AS A SCIENCE

Colloid chemistry was at first only a chapter of physical chemistry, but in the course of time it has grown enormously and become an independent science with its own concepts underlying the interpretation of experimental facts. In addition, special and quite specific colloid-chemistry methods of investigation have been worked out, such as ultramicroscopy, electron microscopy, ultracentrifugation, and electrophoresis. Practice has shown that colloid chemistry is extremely important to modern technology. At present, there is no branch of the economy where colloidal systems and colloidal processes are not used and their methods of investigation are not applied. All this has made colloid chemistry an independent science.

To have a good idea of this science, it is first necessary to know what are colloids and colloidal systems. Man has been acquainted with natural colloidal systems from time immemorial, but it was only comparatively recently that they began to be studied.

In the 1840's the Italian scientist Francesco Selmi drew attention to the anomalous properties of some solutions which, according to modern concepts, are typical colloidal systems. These solutions strongly scatter light; substances dissolved in them precipitate when even very small quantities of salts which do not react with the solute are added to them; dissolution of a substance and its precipitation are not accompanied with a change in temperature and volume of a system, as is the case when crystalline substances are being dissolved. Selmi called such solutions *pseudo-solutions* in order to distinguish them from the ordinary ones. Later, they became known as *sols*.

In the 1860's the English chemist Thomas Graham thoroughly studied the properties of those solutions which interested Selmi. Graham termed these solutions, and the substances which form them, *colloids*, because he believed that glue, or *kolla* in Greek, is their typical representative.

Let us consider the specific features of colloidal solutions that were known as early as the 1860's.

1. All colloidal solutions are capable of scattering light or, in other words, *opalescing*. Opalescence becomes especially noticeable if a beam of converging rays is passed through a colloidal solution, by putting a lens between the light source and the cuvette containing the solution, as Tyndall had done. Under these conditions, a bright glowing cone (the *Tyndall cone*) is seen in the colloidal solution when looking at it sideways. Intensive opalescence is not conclusive proof of the presence of interfaces in a system, but it undoubtedly indicates heterogeneity of colloidal solutions.

2. Diffusion of particles in colloidal solutions is very slow.

3. Colloidal solutions have very low osmotic pressure, which is often even difficult to detect.

The last two properties, i.e., slow diffusion and low osmotic pressure, indicate that colloidal solutions contain relatively large particles of the solute. Indeed, diffusion is affected by the size of particles because, as they grow in size, greater friction makes it more and more difficult for them to move in the solution. Osmotic pressure is a colligative property, i.e., at constant temperature it depends only on the number of particles in the volume, its small value indicates the large size of particles because, at the same gravimetric concentration and the same density of the solute, the larger the particles, the smaller is their amount in the solution.

4. Colloidal solutions are capable of undergoing *dialysis*, i.e., they can be separated, by means of a semipermeable partition (membrane), from the impurities of low molecular weight substances dissolved in them. During dialysis, the molecules of a low molecular weight solute pass through the semipermeable membrane while the colloidal particles which are incapable of passing through the membrane (dialyzing, to use Graham's term) remain behind it as a purified colloidal solution. The ability for dialysis also indicates that the size of particles in colloidal solutions is considerably larger than the size of molecules in true solutions.

The impurities in colloidal solutions can play a very substantial role. In his day, D. Mendeleev noted that not even a single colloidal solution can be obtained without an admixture of foreign substances, and that all attempts to obtain perfectly pure colloidal solutions had failed. Later, he indicated that some substances, formerly regarded as admixtures, were in the complex composition of colloids. The importance of such impurities, which serve as stabilizers, i.e., substances without which colloidal solutions cannot be obtained, was later revealed by N. Peskov.

5. Unlike true solutions, which are stable systems, colloidal solutions are aggregatively unstable (labile), i.e., a colloid is capable of being separated from a solution (to coagulate) rather readily under

the action of inconsiderable extraneous effects. As a result, a precipitate (*coagulate*) consisting of aggregates of agglomerated primary particles is formed in the colloidal solution. The aggregative instability of colloidal systems is usually the greater, the larger is their concentration. Therefore, typical colloidal systems of sufficient concentration often cannot be obtained.

Among the effects that cause coagulation are heating, freezing, intensive stirring and especially introduction of very small quantities of electrolytes into a solution. Coagulation under the action of electrolytes occurs even when they do not react with the colloid. Hence, coagulation is a physical, not chemical, process.

6. Colloidal solutions can be subjected (not always) to *electrophoresis*. Discovered by F. Reiss in Russia in 1808, this phenomenon consists in the transfer of colloidal particles to one of the electrodes in the electric field. Consequently, colloidal particles, like ions, can carry an electric charge. Contrary to electrolysis where its products are deposited on electrodes in equivalent quantities, in electrophoresis substances are transferred only in one direction. Since Faraday's laws, which quantitatively characterize electrolysis, do not hold in electrophoresis, it was long believed that the two phenomena were not directly connected with each other. In fact, as we will see later, such a conclusion was incorrect.

Colloidal systems may be gaseous, liquid, or solid. At the beginning of this textbook, we will consider mainly colloidal solutions because they have been best investigated and are of great practical importance. Only in the subsequent chapters will we become acquainted with emulsions and foams, and also with gaseous and solid colloidal systems.

Examples of colloidal systems are ordinary water mist, smokes, colloidal solutions of metals (e.g., solutions of platinum, gold, silver), colloidal solutions of silver iodide and arsenic sulphide, solutions of some organic dyes and soaps, milk, and also pumice, ruby glass, opal, cast iron, and some metal alloys.

Colloidal properties may be exhibited by systems consisting of not only inorganic, but also organic substances. Moreover, colloidal systems are widespread in nature and can be obtained in the laboratory. Consequently, the colloidal properties of a system do not depend on its state of aggregation, chemical nature, and origin. How does a colloidal system differ from a non-colloidal one?

Graham believed, at least at first, that colloids differ from ordinary substances (crystalloids) by their nature. Proceeding from this, he divided all substances into two realms: the crystalloid realm and the colloid realm with its special laws. However, he was wrong in his opinion.

A contemporary of Graham's, I. Borshchov, indicated that particles present in colloidal solutions may have a crystalline structure.

Later, at the beginning of this century, the Russian scientist P. Weimarn showed that a substance can possess crystalloid properties under some conditions and produce colloidal solutions under others. For example, colophony forms a true solution when it dissolves in alcohol and a colloidal solution in water. Sodium chloride produces a true solution in water and a colloidal one in benzene. Hence, we would be closer to the truth by saying "the colloidal state of a substance" instead of "the colloidal substance".

Decades of extensive research have shown that the colloidal state of a substance is a highly dispersed (greatly disintegrated) state in which separate particles are not molecules but aggregates consisting of numerous molecules. In accepting this definition of the colloidal state (colloidal system), we may formulate the basic features which distinguish colloidal systems from true solutions. Since colloidal particles consist of numerous molecules, apparently all the thermodynamic properties of a phase may be ascribed to them. Likewise, the molecules of a medium in which colloidal particles are dispersed form another phase. Consequently, unlike true solutions which are homogeneous systems, any colloidal solution is a heterogeneous, multiphase (in the simplest case, two-phase) system and a prerequisite of its formation is the insolubility (or very low solubility) of a substance of one phase in a substance of another one (physical interfaces can exist only between such substances).

Since the components of a system number two or more, colloidal systems are usually multicomponent systems. However, single-component colloidal systems may be formed under certain conditions. An example of these systems, termed *iso-colloidal systems* by Wolfgang Ostwald, are liquids in which molecules form sufficiently large aggregates as a result of the action of molecular forces. Such systems are found rather rarely, and therefore they will not be considered in this textbook.

The accepted definition of colloidal systems is confirmed by the aforementioned properties of colloidal solutions. It is precisely such heterogeneous systems that strongly scatter light, possess low diffusibility, are capable of dialysis, and can be aggregatively unstable.

Solid colloidal systems do not possess all the typical colloidal properties enumerated above. For example, all solid colloidal systems are aggregatively stable under ordinary conditions. This is due only to the enormous viscosity of these systems, which does not allow the particles of a solute to move and form larger aggregates as a result of agglomeration. The aggregative instability of these systems may manifest itself when they melt. Metallic alloys also do not possess opalescence properties. But this is due only to the non-transparency of a metal. Other solid colloidal systems having a clear dispersion medium (e.g., ruby glass, opal) opalesce noticeably. No wonder the term "opalescence" is derived from opal.