PHYSICOCHEMICAL MECHANICS

Physicochemical mechanics is a self-contained theoretical framework that can be used to study and model physicochemical processes, based on well-known concepts taken from classical mechanics. This intuitive approach exploits the principles of Newtonian mechanics alongside Einstein's theory of Brownian motion in order to accurately describe complex biochemical systems, and can be used to model a broad range of phenomena including thermodiffusion, transmembrane transport and protein folding. The book begins by presenting the basic principles of classical mechanics and thermodynamics, before introducing the two new postulates of physicochemical mechanics. It is shown that these foundational concepts can be applied to systematically describe all major mass transport and equilibrium equations, and many practical applications of the theory are discussed. This text will be of interest to advanced undergraduate and graduate students in biological physics, biochemistry and chemical engineering, and a useful resource for researchers seeking an introduction to this modern theoretical approach.

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PHYSICOCHEMICAL MECHANICS

With Applications in Physics, Chemistry, Membranology and Biology

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To the memory of my parents, Lidiya and Meir Kocherginsky, PhDs.

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Preface

Physicochemical Mechanics and Its Place in Physics, Chemistry, Biology and Engineering

When you read a physical chemistry textbook, one of the natural questions is: Why does it have so many laws? The situation is very different in classical mechanics, based on the three laws formulated by Newton in 1687. One of the major areas of physical chemistry describes the relations between the initial and final states of a chemical system. It is called equilibrium chemical thermodynamics, and it is also based on three major laws. Gibbs formulated them between 1875 and 1878. But then you have to study the rates of transitions from one state to another, which is done in courses dealing with mass transport and chemical kinetics. In these courses, you are introduced to many different laws and equations, and the relationship between them is not always clear. A lot of physical chemistry laws are empirical and seemingly unrelated. Many of them carry the names of great scientists. For example, mass transport from high to low concentration is described by Fick's first and second laws. Driven by an electric field, transport of charged species is described by Faraday's laws, and it is related to Ohm's law. When you study chemical kinetics, you are certain to be introduced to the law of mass action (Guldberg and Waage), the Arrhenius equation and so forth. To describe an equilibrium of chemical reactions, you need van't Hoff's law, and for electrochemical equilibrium, you should remember the Nernst equation. Many other examples are well known, but they are not derived systematically, based on two or three fundamental equations, like Newton did in mechanics or even Gibbs in thermodynamics.

Mechanics says that a body moves toward decreasing its potential energy, but thermodynamics tells us that an isolated system evolves toward increasing entropy. The major instrument of nonequilibrium thermodynamics is the rate of entropy production. According to Newton's mechanics, a force leads to acceleration, but in chemical transport a thermodynamic "force" leads to a constant transport rate. Moreover, rates of chemical reactions are exponential functions of energy. Do mechanical and thermodynamic principles contradict each other? We will show how to describe all these laws from one point of view.

This book uses essentially just two additional postulates, but we develop a simple unifying description of the rates of all major physicochemical processes, including transport and chemical reactions. This approach is based on energy and forces acting on a substance, so we call it physicochemical mechanics (PCM). The primary purpose is to show how PCM may connect physics, chemistry, biology and chemical engineering. Thus, it will be possible to answer three crucial questions for scientists and engineers: How much? How fast? And, finally, why?

Introductory courses in mechanics consider so-called ideal systems without friction. Traditional textbooks on thermodynamics mainly deal with so-called simple systems, that is, the macroscopically homogeneous systems that are isotropic, uncharged and sufficiently large, so that the surface effects may be neglected. In addition, simple systems are not affected by external electric, magnetic and gravitational fields. They are isolated. This book will pay attention to all these missing factors, especially friction, external fields and surface effects.

In 1905, Albert Einstein published his papers describing Brownian motion of small particles. Surprisingly, the particles do not stop their movement even though the average acting force is zero. Now it is common knowledge that heat and freedom of motion are the reasons for the molecular movement in space at any temperature unless it is near absolute zero. We suggest a unified way to derive relations of different transport processes and easily derive Onsager's relations for transport coefficients in simple cases. In more complicated cases, we explain, for example, why transport coefficients for magnetic and other velocity-dependent phenomena change their sign, and why Onsager's reciprocal relations are not valid for multicomponent diffusion of noncharged species. Not only do we describe multicomponent diffusion but we also explain why the same substance may be transported to either a hot or cold area in thermodiffusion and so forth.

Nevertheless, in the presence of a nonpermeable wall, which separates two volumes and is one of the most straightforward engineering constructions, a transition from a phase with high concentration to another with low concentration will never happen. Membranes are constructions, separating space into two parts, but they are different. They have selective permeability for some and not for other substances. As a result, the simple separation of three-dimensional space into two parts leads to directed transport. Thus, instead of being scalar, as they are in chemical reactions, physicochemical processes become vectorial. This is a significant and fundamental difference.

Based on the ideas from physicochemical mechanics, we describe fundamental aspects of transmembrane transport and illustrate these ideas using very simple artificial constructions, called biomimetic membranes. These membranes imitate many quantitative parameters of biological membranes, including selective barrier properties, active transport, redox reactions coupled with ion transport and even spontaneous electrical oscillations, usually considered an experimental proof of protein channels, which may be open or closed in biomembranes. In addition to the barrier properties, chemical and biological membranes may serve as sensors, send electric signals and catalyze different reactions. Biomimetic membranes can find new applications, including small chemical sensors, medium-sized drug-delivery systems, prebiological drug screening and bioengineering and large-scale separation and purification in chemical and environmental engineering.

Biological membranes are functionally active. They not only protect cellular content but are also involved in chemical transport, energy metabolism, work production, recognition, regulation and so forth. Many diseases are related to membrane abnormalities. Without biological membranes, there would be no compartmentalization, and all cellular components would be mixed. To separate and then use these components would require too much energy and, because of that, the cells would die. In biological membranes, we can find the molecular-size motors and pumps, leading to an active transport. Based on the PCM ideas and knowledge of biomimetic membranes, we suggest a simple mechanism of active transport, a description of an action potential on a nerve membrane and a possible principle of oxidative phosphorylation.

Many phenomena can be explained based on very fundamental ideas similar to classical and physicochemical mechanics. It is even possible to extend these ideas to evolution, human society and financial markets. Constraints and limitations imposed by laws and governments serve not only as restrictions of our freedom but they also serve or at least should serve as a construction helping new social processes and human development. At the end of the book, we suggest that it should be possible to use an analog of the equation for the rate of chemical transport to describe the pace of social progress.

A fundamental and unified description of the expanded body of scientific knowledge, including mechanics, equilibrium and nonequilibrium thermodynamics, chemical and heat transport, kinetics of chemical reactions and so forth, is vital for education and a broader vision of surrounding processes. In any course, the students should be able to absorb knowledge early enough and learn what must be retained during the course so that later it will be possible to use this knowledge in many different applications. Physicochemical mechanics is an example of this approach. We try to mention the names of scientists who developed one or another key idea, and many of them were awarded a Nobel Prize. It could be helpful for a reader to know who those bright and outstanding individuals were who brought our science to the modern state. As Isaac Newton wrote in 1675 (English translation): “If I have seen further, it is by standing on the shoulders of Giants.” The reader will find references to major names and major journal publications, including recent papers and reviews, so that it will be possible to delve further into one or another topic after reading this book.

Though we review the basics from related courses in several chapters (Chapters 2 through 5), it would help if the reader were familiar with introductory undergraduate textbooks in mechanics, physical chemistry and biophysics. We tried to connect many aspects from different areas but kept the chapters more or less independent (which should help). As a result, a careful reader will find slight overlapping of described subjects with previous chapters. Another problem we had was with notation. We tried to avoid situations when the same notation is used in different chapters for different variables, but we preferred to use notation accepted in textbooks. To prevent confusion, if necessary, we introduce notation again and again in related chapters.

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This text is the result of many years of work and teaching at several universities, but it could not have been accomplished without collaboration with Professor Martin Gruebele. His interest, understanding and many years of support are highly appreciated. Without many discussions with him, this book would be very different. He is also the first to have used the major ideas from this book when teaching physical chemistry class at the University of Illinois at Urbana-Champaign. I am also much obliged to my wife, Svetlana, for her patience and understanding. English is not my native language, but I hope with her help the book became a readable and self-contained account accessible to a reader with basic knowledge of natural sciences.

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