A detailed microscopic image of a membrane surface, showing a dense layer of small, irregular, light green pores or cells against a dark green background.

Membrane Technology and Applications

Third Edition

Richard W. Baker

 **WILEY**



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Third Edition

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*Membrane Technology and Research, Inc.
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Membrane Technology and Applications

Preface

My introduction to membranes was as a graduate student in 1963. At that time membrane permeation was a sub-study of materials science. What is now called membrane technology did not exist, nor did any large industrial applications of membranes. Since then, sales of membranes and membrane equipment have increased more than 100-fold and several tens of millions of square meters of membrane are produced each year – a membrane industry has been created.

This membrane industry is very fragmented. Industrial applications are divided into six main sub-groups: reverse osmosis, ultrafiltration, microfiltration, gas separation, pervaporation, and electrodialysis. Medical applications are divided into three more: artificial kidneys, blood oxygenators, and controlled release pharmaceuticals. Few companies are involved in more than one sub-group of the industry. Because of these divisions it is difficult to obtain an overview of membrane science and technology; this book is an attempt to give such an overview.

The book starts with a series of general chapters on membrane preparation, transport theory, and concentration polarization. Thereafter, each major membrane application is treated in a single 20- to 50-page chapter. In a book of this size it is impossible to describe every membrane process in detail, but the major processes are covered. However, medical applications were short-changed somewhat and some applications – battery separators and membrane sensors, for example – are not covered at all.

Each application chapter starts with a short historical background to acknowledge the developers of the technology. I am conscious that my views of what was important in the past differ from those of many of my academic colleagues. In this book I have given more credit than is usual to the engineers who actually made the processes work.

Membrane technology continues to expand and change. For this reason, some change has been made to every chapter in this edition of the book to reflect these new developments. The use of bioreactors fitted with submerged-air scrubbed membranes – barely touched on in the second edition – is now a significant industry and so the ultrafiltration chapter has been completely rewritten. I also took this opportunity to rework the chapter on pervaporation and the section on membrane contactors, and included new sections on the use of membranes in fuel cells and the chlor-alkali industry. These updates and additions have added new figures and references, so the page count has increased more than 10% over the second edition.

Readers of the Theory section (Chapter 2) and elsewhere in the book will see that membrane permeation is described using simple phenomenological equations, most commonly, Fick's law. There is no mention of irreversible thermodynamics. The irreversible thermodynamic approach to permeation was very fashionable when I began to work

with membranes in the 1960s. This approach has the appearance of rigor but hides the physical reality of even simple processes behind a fog of tough equations. As a student and young researcher, I struggled with irreversible thermodynamics for more than 15 years before finally giving up in the 1970s. I have lived happily ever after.

Finally, a few words on units. Because a great deal of modern membrane technology originated in the United States, the US engineering units – gallons, cubic feet, and pounds per square inch – are widely used in the membrane industry. Unlike the creators of the Pascal, I am not a worshipper of mindless uniformity. Nonetheless, in this edition, I have used metric units to describe most of the processes covered in this book. British/US units are now only used when they are the industry standard and metric units would lead to confusion.

Acknowledgments

Acknowledgments for the First Edition

As a school boy I once received a mark of $\frac{1}{2}$ out of a possible 20 in an end-of-term spelling test. My spelling is still weak, and the only punctuation I ever really mastered was the period. This made the preparation of a polished final book draft from my yellow notepads a major undertaking. This effort was headed by Tessa Ennals and Cindi Wieselmann. Cindi typed and retyped the manuscript with amazing speed, through its numerous revisions, without complaint. Tessa corrected my English, clarified my language, unsplit my infinitives, and added every semicolon found in this book. She also chased down a source for all of the illustrations used and worked with David Lehmann, our graphics artist, to prepare the figures. It is a pleasure to acknowledge my debt to these people. This book would have been far weaker without the many hours they spent working on it. I also received help from other friends and colleagues at MTR. Hans Wijmans read, corrected, and made numerous suggestions on the theoretical section of the book (Chapter 2). Ingo Pinnau also provided data, references, and many valuable suggestions in the area of membrane preparation and membrane material sciences. I am also grateful to Kenji Matsumoto, who read the section on Reverse Osmosis and made corrections, and to Heiner Strathmann, who did the same for Electrodialysis. The assistance of Marcia Patten, who proofed the manuscript, and Vivian Tran, who checked many of the references, is also appreciated.

Acknowledgments for the Second Edition

Eighteen months after the first edition of this book appeared, it was out of print. Fortunately, John Wiley and Sons agreed to publish a second edition, and I have taken the opportunity to update and revise a number of sections. Tessa Ennals, long-time editor at Membrane Technology and Research, postponed her retirement to help me finish the new edition. Tessa has the standards of an earlier time, and here, as in the past, she gave the task nothing but her best effort. I am indebted to her, and wish her a long and happy retirement. Marcia Patten, Eric Peterson, David Lehmann, Cindy Dunnegan, and Janet Farrant assisted Tessa by typing new sections, revising and adding figures, and checking references, as well as helping with proofing the manuscript. I am grateful to all of these colleagues for their help.

Acknowledgements for the Third Edition

As with the earlier editions of this book, I would not have been able to produce this manuscript without the support of my co-workers at Membrane Technology and Research, Inc. I work with a group of scientist-engineers interested in many aspects of membrane technology. This has kept me informed on new developments affecting our own company's interests and on developments across the membrane field. I also had the assistance of Sara Soder, our company's technical editor, who by mastering my spelling and handwriting was able to provide me with a polished manuscript draft, and who then had the patience to allow me to change and re-change the draft as I clarified my thoughts. Crystal Min and David Lehmann added to and revised the nearly 400 figures, and Beth Godfrey, Jenny Valcov, and Linda Szkoropad pitched in to assist with the figure permissions and final manuscript preparation. I am grateful to all of these colleagues for their help.

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1

Overview of Membrane Science and Technology

1.1 Introduction

Membranes have gained an important place in chemical technology and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. In controlled drug delivery, the goal is to moderate the permeation rate of a drug from a reservoir to the body. In separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other components.

This book provides a general introduction to membrane science and technology. Chapters 2–4 cover membrane science, that is, topics that are basic to all membrane processes, such as transport mechanisms, membrane preparation, and boundary layer effects. The next six chapters cover the industrial membrane separation processes that represent the heart of current membrane technology. Carrier facilitated transport is covered next, followed by a chapter reviewing the medical applications of membranes. The book closes with a chapter that describes various minor or yet-to-be-developed membrane processes, including membrane reactors, membrane contactors, and piezodialysis.

1.2 Historical Development of Membranes

Systematic studies of membrane phenomena can be traced to the eighteenth century philosopher scientists. For example, Abbé Nolet coined the word “osmosis” to describe permeation of water through a diaphragm in 1748. Through the nineteenth and early twentieth centuries, membranes had no industrial or commercial uses, but were used as laboratory tools to develop physical/chemical theories. For example, the measurements of solution osmotic pressure made with membranes by Traube and Pfeffer were used by van’t Hoff in 1887 to develop his limit law, which explains the behavior of ideal dilute

solutions; this work led directly to the van't Hoff equation. At about the same time, the concept of a perfectly selective semipermeable membrane was used by Maxwell and others in developing the kinetic theory of gases.

Early membrane investigators experimented with every type of diaphragm available to them, such as bladders of pigs, cattle or fish, and sausage casings made of animal gut. Later, collodion (nitrocellulose) membranes were preferred, because they could be made reproducibly. In 1907, Bechhold devised a technique to prepare nitrocellulose membranes of graded pore size, which he determined by a bubble test [1]. Other early workers, particularly Elford [2], Zsigmondy and Bachmann [3], and Ferry [4] improved on Bechhold's technique, and by the early 1930s microporous collodion membranes were commercially available. During the next 20 years, this early microfiltration membrane technology was expanded to other polymers, notably cellulose acetate.

Membranes found their first significant application in the testing of drinking water at the end of World War II. Drinking water supplies serving large communities in Germany and elsewhere in Europe had broken down, and filters to test for water safety were needed urgently. The research effort to develop these filters, sponsored by the US Army, was later exploited by the Millipore Corporation, the first and still the largest US microfiltration membrane producer.

By 1960, the elements of modern membrane science had been developed, but membranes were used in only a few laboratory and small, specialized industrial applications. No significant membrane industry existed, and total annual sales of membranes for all industrial applications probably did not exceed US\$20 million in 2012 dollars. Membranes suffered from four problems that prohibited their widespread use as a separation process: they were too unreliable, too slow, too unselective, and too expensive. Solutions to each of these problems have been developed during the last 40 years, and membrane-based separation processes are now commonplace.

The seminal discovery that transformed membrane separation from a laboratory to an industrial process was the development, in the early 1960s, of the Loeb–Sourirajan process for making defect-free, high-flux, anisotropic reverse osmosis membranes [5]. These membranes consist of an ultrathin, selective surface film on a much thicker but much more permeable microporous support, which provides the mechanical strength. The flux of the first Loeb–Sourirajan reverse osmosis membrane was 10 times higher than that of any membrane then available and made reverse osmosis a potentially practical method of desalting water. The work of Loeb and Sourirajan, and the timely infusion of large sums of research and development dollars from the US Department of Interior, Office of Saline Water (OSW), resulted in the commercialization of reverse osmosis and was a major factor in the development of ultrafiltration and microfiltration. The development of electrodialysis was also aided by OSW funding.

Concurrent with the development of these industrial applications of membranes was the independent development of membranes for medical separation processes, in particular, the artificial kidney. Kolf and Berk [6] had demonstrated the first successful artificial kidney in The Netherlands in 1945. It took almost 20 years to refine the technology for use on a large scale, but these developments were complete by the early 1960s. Since then, the use of membranes in artificial organs has become a major life-saving procedure. More than 800 000 people are now sustained by artificial kidneys and a further million people undergo open-heart surgery each year, a procedure made possible by development

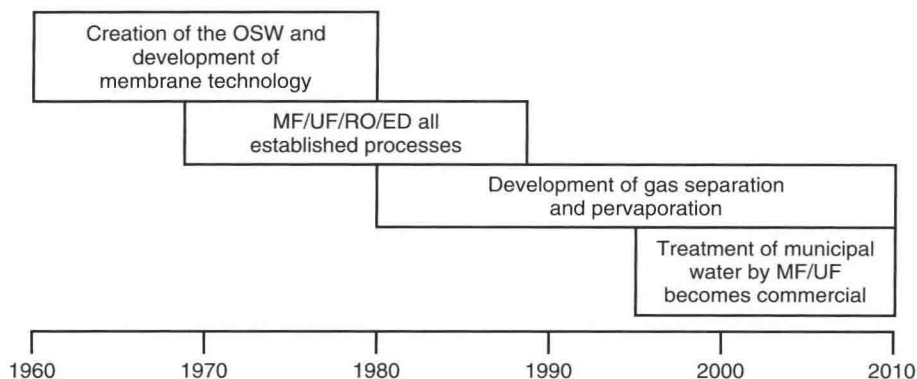


Figure 1.1 The development of the membrane separation industry, 1960–2010

of the membrane blood oxygenator. The sales of these devices comfortably exceed the total industrial membrane separation market. Another important medical application of membranes is for controlled drug delivery systems. A key figure in this area was Alex Zaffaroni, who founded Alza, a company dedicated to developing these products, in 1966. The membrane techniques developed by Alza and its competitors are widely used in the pharmaceutical industry to improve the efficiency and safety of drug delivery.

The modern membrane separation industry began in the 1960s. The creation of this industry can be divided into the four phases shown in Figure 1.1. In the first phase, building on the original Loeb–Sourirajan technique, other membrane formation processes, including interfacial polymerization and multilayer composite casting and coating, were developed for making high-performance membranes. Using these processes, membranes with selective layers as thin as $0.1\mu\text{m}$ or less are now being produced by a number of companies. Methods of packaging membranes into large-membrane-area spiral-wound, hollow-fine-fiber, capillary, and plate-and-frame modules were also developed, and advances were made in improving membrane stability. The support of the OSW was key to these developments.

In the second phase, beginning in the early 1970s, the developments that came out of the OSW program began to appear in commercial membrane units; by the 1980s, microfiltration, ultrafiltration, reverse osmosis, and electrodialysis were all established processes. The third phase, which began in the 1980s, was the emergence of industrial membrane gas separation processes. The first major product was the Monsanto Prism® membrane for hydrogen separation, introduced in 1980 [7]. Within a few years, Dow was producing systems to separate nitrogen from air, and Cynara and Separex were producing systems to separate carbon dioxide from natural gas. Gas separation technology is continuing to evolve and expand; further growth will be seen in the coming years. Another development of the 1980s was the introduction by GFT, a small German engineering company, of the first commercial pervaporation systems for dehydration of alcohol and other solvents. Pervaporation has been slow to take off and 2010 sales were still not more than \$20 million. However, the development of bioethanol from biomass has produced a new, very large potential market for the technology, which may lead to future growth.