TECHNIQUES OF CHEMISTRY

VOLUME VII

MEMBRANES IN SEPARATIONS

SUN-TAK HWANG

KARL KAMMERMEYER

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ARNOLD WEISSBERGER

Research Laboratories
Eastman Kodak Company
Rochester, New York

PROLOGUE, IN THE FORM OF A PERSONAL LETTER

TO KARL KAMMERMEYER*

Dear Karl,

When you asked me to write a largely historical "Prologue" to your book, you referred to my intimate association with the developments in the physical chemistry of membranes and stated that "what we would like to see is the personal touch," and further added: "It would be fascinating, especially to the younger people in the field, to get some historical perspective. For instance, how did you ever get interested in membranes and then what were some of the exciting events in your early work?" I gladly agreed to write such a prologue for which I can claim indeed some unusual qualifications: personal acquaintanceship with many of the old classical masters of "membranology" and active work on the physical chemistry, particularly the electrochemistry, of membranes which has occupied more than 80% of the last 45 years of my life. Also, writing this Prologue gave me a most welcome incentive to look systematically into the historical development of the physical chemistry of membranes, a topic about which I hope now to publish at length in the near future.

I use here the form of a personal letter, which frees me of many restrictions customary in scientific writing.

When I studied chemistry in my home town at the University of Vienna, Austria, in the first half of the 1920s one did not hear much about membranes. You got just a few bits of casual information. "Membranes" were not an organized field, a far cry from today's situation. In physical chemistry you learned that M. Traube developed in the 1860s "semipermeable" copperferrocyanide precipitation membranes which were used

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* The author of this letter is Dr. Karl Sollner, recently retired Chief of the Section on Electrochemistry and Colloid Physics, National Institute of Arthritis, Metabolism and Digestive Diseases, National Institutes of Health, Bethesda, Maryland 20014.

in 1877 by the "botanist" Pfeffer to measure the osmotic pressure of sucrose solutions, and that these measurements were in turn utilized by the great van't Hoff (1887) and Raoult (1884) as the basis for the classical theory of solutions. It also was impressed on you that the measurement of osmotic pressures by means of semipermeable membranes for the determination of molecular weights is a most difficult procedure, for practical purposes essentially useless.

In analytical chemistry word spread that one can prepare some very dense filters called "membrane filters" and "ultrafilters," which are useful with very fine precipitates. Although I was a teaching assistant in analytical chemistry from 1922 to 1926, I never saw this type of filter. In chemical technology you learned that parchment paper is used in the sugar and the dyestuff industries to remove by "dialysis" impurities, mainly salts. Only by chance did I hear that biologists were deeply interested in the "permeability" of living membranes. Thus, when I received a Ph.D. in 1926 the idea had never occurred to me that membranes and membrane effects per se could be worthwhile research topics.

After receiving my degree, I looked long and frantically for a position. For young scientists in Central Europe the job situation in those days was infinitely worse, and chronically so, than that which has confronted young American Ph.D.'s in the last few years. Soon I realized that in order to find a position as a chemist I must obtain postdoctoral training and that specializing in colloid chemistry might be a good bet. After considerable difficulties (postdoctorate fellowships at that time were virtually nonexistent) early in 1927 I arranged that I would join in the fall (at my family's expense) the laboratory of Professor Herbert Freundlich at the Kaiser Wilhelm-Institut (now Max Plank-Institut) for Physical Chemistry in Berlin, who was then the best authority on colloid chemistry in Germany. The interim period I used by working out a laboratory course in colloid chemistry for the Institute of Physical Chemistry of the Technical University of Vienna. In doing this I became somewhat acquainted with the use of membranes in dialysis, electrodialysis, and ultrafiltration. More importantly, I also familiarized myself thoroughly with the literature on colloids, paying particular attention to the 1922 and 1923 editions of Freundlich's "Kapillarchemie" and the 1920 and 1925/1927 editions of Zsigmondy's "Kolloidchemie."

Freundlich's book, for several decades a kind of "Bible" in colloid chemistry, impressed me by its emphatically physicochemical, not merely descriptive, approach. I was fascinated by his then unsurpassed presentation of the electrical aspect of colloids, colloid stability, electrokinetics and electrocapillarity, but found myself confused by a section on "Anomalous Osmosis, Electrostenolysis and the Becquerel Phenomenon." Freundlich's reviews of the mechanisms of these effects which had been suggested in the literature amazed me by their haziness and by their lack of a rigorous physicochemical reasoning.

In the fall of 1927 I started work in Professor Freundlich's laboratory and finished during the next ten months three experimental studies of a diversified nature. The nearly daily contact with Professor Freundlich was most stimulating and rewarding. The general atmosphere at the institute under the directorship of the Nobel laureate Fritz Haber of ammonia synthesis fame was one of intellectual fermentation with the emphasis on originality, and a great deal of independence for the younger scientists. By good luck I had fallen into a hothouse for the development of budding scientists about which I was to read thirty years later in the Encyclopedia Britannica: "This research institute, which he [Haber] headed until 1933, became the finest of its kind in the world and many mature chemists from all nations came there to work."

Thus I was highly pleased when toward the end of my first year at this institute I was awarded one of the few then available and therefore highly coveted "Haber fellowships," established by Professor Haber from his income as a director of the I. G. Farben Industries.

Now a few words about how I got into work on membranes: It occurred in a somewhat roundabout way, which I think now was significantly influenced by a strong boyhood interest in electricity. In the fall of 1928, when I looked for a sharply defined problem, I recalled the several aforementioned poorly understood electrical membrane effects, and decided to attempt to clarify the mechanism of the so-called electrocapillary Becquerel phenomenon, first described 60 years earlier by A. C. Becquerel (1867) as follows: when a cracked test tube or porous clay diaphragm filled with a Na_2S solution is placed into a solution of a copper or silver salt, CuS and Ag_2S precipitates are formed where the two solutions meet, and after some time beautiful copper or silver crystals appear at the crack or diaphragm on the side of the heavy-metal solution. The same effect is observed if solutions of Na_2Se or Na_2Te instead of Na_2S are used. The cracked test tubes and diaphragms, as was shown later, act only as convenient mechanical supports for the heavy-metal sulfide and other precipitation membranes.

The first modern attempt to explain this effect from the point of view of the newly established ion theory of electrolyte solutions was made in 1890 by Wilhelm Ostwald (1890), one of the founding fathers of physical chemistry. Ostwald's ideas, reported approvingly in Freundlich's book, did not make sense to me. Another explanation suggested by F. Braun (1891), however, seemed to be on the right track, but his view needed further clarification and reformulation in terms of modern electrochemistry.

The sulfides, selenides, and some other precipitates at which the Becquerel effect occurs are all metallic conductors, which when precipitated from aqueous solutions are highly porous. Accordingly short-circuited electrochemical cells of the type:

Soln. 1	Membrane	Soln. 2
	CuS (solid)	
Na_2S		$CuSO_4$
	Na_2SO_4 soln. in pore	

can form readily in which the heavy-metal sulfides act as electronically conducting electrodes. Cations and anions may be discharged continuously if the emf which arises in a particular cell surpasses the decomposition potential. Thus, the Bequerel effect turned out to be a rather trivial phenomenon and without wider significance. Nevertheless, I was elated by having solved this long open problem and greatly savored Haber's complimentary remarks when I presented my result in a seminar which I recall as a highlight of my budding career.

With great difficulty I persuaded Professor Freundlich to join me as coauthor on the Becquerel-effect paper (1928). I would have felt embarrassed to criticize my much beloved and admired master, and furthermore I felt that he had made a substantial contribution not only by leading me through his book to this problem but also by his interest in and encouragement of my effort. At that time I did not dream that this paper, which in my eyes was of a strictly electrochemical nature, would turn out to be the first step toward a lifetime's work on membranes. Similarly, I did not realize that Ostwald's aforementioned paper, aside from his obviously nonacceptable explanation of the electrocapillary Becquerel phenomenon, contains some most ingenious speculations concerning the electromotive properties of "semipermeable" membranes, which at that time already had been used by several, to me then still unknown, investigators as the seminal ideas of the rational electrochemistry of membranes.

Next, I tried my hand on another of the poorly understood electrical effects described in Freundlich's book, namely "Electrostenolysis" and analogous "electrostenolytic effects," the formation of metallic precipitates at membranes and diaphragms on the passage of current, an effect which has been used as the basis of several farfetched and hazy speculations. I demonstrated that this phenomenon can be due to two entirely different mechanisms according to the experimental conditions (1929).

Electrostenolysis, like the electrocapillary Becquerel effect, also turned out to be readily explainable within the framework of conventional electrochemistry, in other words, trivial. Nevertheless, I felt rather pleased when more than 40 years later I read with reference to my electrostenolysis paper of 1929:

> "The subject of the electrolytic processes at membranes has been capably reviewed and discussed by Sollner and thus, there is no need for further treatment here."*

While trying to solve the riddle of electrostenolysis I immersed myself totally for many months in the rather widely scattered and never *in toto* systematically reviewed literature on the physical chemistry, particularly the electrochemistry of membranes. Fortunately, the literature on membranes, though already rather voluminous, was forty-five years ago still rather small compared with today's literature on this subject. It was then not too difficult even for a newcomer to identify the papers of the rather limited number of investigators who had made the major contributions. One can only marvel at the intuitive insight and experimental skill of the great masters and admire their ability to draw essentially correct, general, and far-reaching conclusions from limited experimental data, and it seems appropriate to review here briefly some of the most outstanding pre-1930 papers on the physical chemistry of membranes.

Thomas Graham, the father of systematic physicochemical membrane studies, described in 1829 the inflation (to the point of bursting) of water-wet (pig?) bladders containing some air, which were inserted into a jar filled with CO_2. He correctly explained this effect as the consequence of the solubility of the CO_2 in the water in the "capillary canals" of these membranes, and its diffusion through it followed by the release of the CO_2 into the air inside the bladder. In 1854 Graham also observed and clearly explained the process, which is referred to today as "pervaporation" and in 1866 reported extensively "On the absorption and dialytic separation of bases by colloidal septa" (1866). Exner (1874 and Stefan (1878) demonstrated that the rates of the movements of different gases across liquid (soap) lamellae are strictly proportional to the solubility of the various gases in water times their diffusion velocities. These and numerous similar papers were carefully reviewed by Waitz (1908) in an article that is an excellent guide to certain phases of the older literature. Lhermit in 1855 and Nernst in 1890 considered membrane systems consisting of three liquid phases and

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* A. Brenner and J. L. Sligh, Jr., *J. Electrochem. Soc.: Electrochemical Science*, **117**, 602 (1970).

proved that only those substances that are soluble in the middle phase, the membrane, can pass across it. For solid membranes, such as sheets of rubber, which act as solvents, the same was demonstrated by Flusin (1908).

The basic ideas concerning the *electrochemistry of liquid membranes*, particularly their electromotive behavior in concentration cells, were presented in a rather casual manner, as by-products of certain investigations directed toward other ends, which were carried out by the later Nobel laureates Walter Nernst and Fritz Haber and their collaborators.

In papers that deal mainly with the polarization of liquid–liquid phase boundaries under the influence of a direct current, Nernst and Riesenfeld came in 1902 to the following conclusion: the phase-boundary potential arising at the interface between two mutually sparingly soluble liquid phases, which are in a state of distribution equilibrium with respect to an electrolytic solute, is independent of the absolute concentrations of the latter. Accordingly, in a concentration cell $A^+L^-c_1$ |liquid membrane| $A^+L^-c_2$ in which the electrolyte A^+L^- is present in the membrane near the phase boundaries at the concentrations kc_1 and kc_2 (k being the distribution coefficient) the two phase-boundary potentials are equal and opposite. The measurable EMF of such cells is the liquid junction potential arising within the membrane due to the difference in the concentrations of A^+L^- within the membrane.

An entirely different electromotive behavior of certain liquid–liquid phase boundaries, namely, an electromotive response to changes in the hydrogen-ion concentration in reasonably good conformity with the Nernst equation for concentration cells, was observed by Haber and Klemensiewicz (1909) in the course of an investigation that dealt mainly with the phase-boundary potentials at the interfaces between electrolytically conducting solid electrolytes and aqueous solutions having a common ion. The same paper also describes the glass-membrane electrode and presents its theory. The work on liquid membranes was later continued by Beutner (1912), a former student of Haber.

The papers of Nernst and Haber were difficult reading, at least for me, and things became much clearer when I found Michaelis' systematic, clear presentation of these matters in his book *Hydrogen Ion Concentration* (1926), which is a classic and still worthwhile reading.

Donnan's famous theoretical paper on the membrane equilibrium and membrane potential (1911), because of its generality (it applies equally to liquid and to porous membranes) and its rigorous mode of presentation, was somewhat awe-inspiring; it and subsequent experimental work created the feeling that everything that could be said about these problems had been expounded by Donnan. Professor Donnan was, indeed, a man of superior intellectual capacity as I could observe firsthand after joining his laboratory at University College, London, several years later.

The papers dealing with porous membranes were much more numerous than those on liquid membranes. Many of them were not membrane studies per se but described the use of such membranes for specific purposes, and thus contributed but little to the understanding of the basic physical chemistry of membranes, which was my primary interest. The outstanding examples of the use of porous membranes for the measurement of osmotic pressures were the careful experimental investigations by Morse and his school (1914) and by Berkeley and Hartley (1906–1916). There was also a considerable body of literature dealing with the use of membranes in dialysis, beginning with a paper by Graham (1861), and in ultrafiltration. Early papers by Bigelow and Gamberling and by Brown (1915) gave much useful information on the preparation of collodion membranes. The outstanding systematic investigation on various types of ultrafilters, however, originated in the laboratory of the Nobel laureate R. Zsigmondy (1918–1929). The technological literature on ultrafiltration and dialysis, as exemplified, for example, by a review of Hebler (1927), did not provide much of basic interest.

As to the nonelectrolyte permeability of membranes, considerably denser than those used ordinarily in dialysis and ultrafiltration, it was known that, aside from the porosity of the membrane, the deciding factor is the molecular weight (or size) of the permeants. With electrolytes, the situation was rather confused. The literature on these questions was reviewed briefly by Collander in three papers (1924–1926), on the permeability of copper ferrocyanide and of collodion membranes of graded porosities. In these systematic masterly studies, carried out with minimal facilities, Collander established definitely that the permeability of any given porous membrane for nonelectrolytic solutes depends on the molecular size of the latter, dropping off steeply above a certain molecular size characteristic for the membranes of a given porosity. Collander's results, taken today for granted, were 50 years ago a most important basic contribution. His findings on the electrolyte permeability of porous membranes were more complex, too complex to be reviewed here, but in the course of his work he corrected some long-standing erroneous ideas which had retarded progress for several decades.

As far as membranes in electrolytic systems were concerned, my first interest was to gain insight into the molecular mechanism of the electrochemical effects observed with porous membranes, particularly of their electromotive action. This blended later into a steadily growing desire to acquire all information that conceivably might be helpful in elucidating the mechanism of anomalous osmosis, a topic which tempted me as my next research project.

Anomalous osmosis, first described by Graham (1854), and assumed by him to be an electro-osmotic phenomenon, was one of the few electrical membrane effects that had attracted the interest of Bartell and his group (1914–1923). The explanations of this phenomenon suggested by them seemed unsatisfactory to me. Anomalous osmosis also was the topic of a long series of experimental studies by the biologist Jacques Loeb (1918–1920), famous for his work on parthenogenesis.

A thorough study of the papers of these and various other investigators convinced me that a satisfactory explanation of the mechanism of anomalous osmosis could result only from a deeper understanding of the electrochemistry of porous membranes. This topic had never been reviewed in a comprehensive, truly constructive manner. Even Freundlich in 1916 discussed at length only one investigation on porous membranes, a study of Bethe and Toropoff (1915) "On electrolytic processes at membranes" in which the polarization effects arising at porous membranes are treated in detail. The presentation of this subject was so overwhelmingly impressive that a brief introductory section was generally overlooked, which from the systematic point of view is really of much greater basic importance than the polarization studies. It was only much later that I began to realize, at least in part, the vast amount of insight present in it.

Bethe and Toropoff outlined clearly the most basic concept of the electrochemistry of membranes, namely, the correlation of the electrokinetic charge of the membranes and their electromotive properties, their electrolyte permeability, and their polarization behavior. Those charges (ions) which are fixed to the pore wall, and form the immovable part of electrical double layer at the membrane-matrix-solution interface, cannot participate in the movement of ions across the membrane either by thermal motion (diffusion) or under the influence of an electric current. Their counterions, however, which are dissociated off into the pore water, are freely movable and can move under the influence of a concentration or potential gradient. This concept is the ultimate basis of today's highly developed electrochemistry of porous membranes. The prolonged neglect of these and related insights of Bethe and Toropoff has undoubtedly retarded the development of the electrochemistry of porous membranes.

Relatively well known in the late 1920s was the then still current systematic work on the basic electrochemistry, particularly the electromotive behavior, of dense, "molecular sieve," collodion membranes of extreme ionic selectivity by Michaelis and collaborators (1925–1927). Michaelis expounded in a quantitative manner the relationship of the ratio of the "mean mobilities" (in reality the ratio of the transference numbers) of the anions and cations in a membrane to the electromotive action of the latter. His papers are still a delight to read; his review of his then still progressing work is a classic, showing a great mind at work. By his rigorous systematic work Michaelis laid the firm basis for all later work in this field in spite of the fact that it left many basic questions still open. It was my good fortune to have in later years many discussions with Professor Michaelis on membranes and other electrochemical topics. He was an exceedingly modest man of great scientific sagacity, originality, and amazing intuitive understanding.

For me, familiarity with Michaelis' work paid off soon. It furnished an essential part of the information which I utilized in 1929 to develop a theory of the mechanism of anomalous osmosis, which later was verified experimentally (1932). This work, to my great delight, found the approval not only of Professor Freundlich but also of such experts in electrochemistry as Nernst and Haber, and later also of Planck. This theory is based on the concept that porous membranes have pores of different diameter which, according to Michaelis, yield different pore potentials in concentration cells. Consequently, they must interact electrically with each other; local electric currents are set up and cause electro-osmosis, that is, anomalous osmosis. Expanding the view of membranes as micromosaic structures, I developed the quantitative theory of mosaic membranes composed of ideally anion and ideally cation selective parts (1932). It correlates in a rigorous manner the electrolyte permeability of such membranes under defined conditions to the electrical characteristics of their component parts. This is the first instance in which an exhaustive quantitative treatment of a complex electrochemical membrane system was shown to be feasible. Much later, after suitable "permselective" membranes had been developed in my laboratory, this theory was verified quantitatively; such membranes have recently attracted considerable interest.

After 1932, my feeling, and that of several older and much more experienced investigators I consulted, was that physicochemical-membrane research as carried out in the past had seemingly run its course. Some new theoretical idea and experimental approach seemed necessary to revitalize this field. The first step in this direction occurred when Theorell in 1935, and soon afterwards Meyer and Sievers (1936–1937) at greater length, proposed what is today known as the "fixed-charge theory of ionic membranes," which is the basis of today's electrochemical-membrane research. From then on, first slowly and later with increasing speed and breadth, research on electrolytic-membrane systems has been carried out both in academic and industrial laboratories; and soon nonelectrolyte-membrane systems also became a favored research topic. Today the literature on membranes and membrane effects is overwhelming. Therefore it is good to see that you have entered the ranks of those who try to organize and present in a book some large and important part of the current knowledge in this field.

Kind regards!

Sincerely yours,

Karl* [Sollner]

* *Comment.* The early experiences of Karl Sollner, the dean of American membranologists and equally esteemed on a global basis, should be an inspiration to all scientists. The sequel to Sollner's writings is regrettably too long to present here. It constitutes a masterful history and review of membrane science and is expected to be published as a separate work. (Karl Kammermeyer)

PREFACE

The purpose of this volume is to provide a unified treatise of all membrane separation processes. Much of the development of membrane technology is fairly recent, even though the history of membranes itself dates far back. Membranology is a multidisciplinary field. Various membrane processes have been developed so rapidly in several different disciplines of science and technology that the highly compartmentalized state of the art hardly allows full communication among the investigators. The literature covering membrane phenomena is also diversified and numerous. As a result, the terminologies are confusing and the theories need to be generalized in many cases. Thus, this book is written not only for those who are actively involved in membrane research but also for people who would like to know about membrane separations.

Biological membranes are important and hold a key in many questions of basic biology and medicine. However, since they exhibit distinct characteristics from artificial membranes, they should be treated separately. Indeed, there are many excellent books on this subject and we feel that it would be redundant to include it in this volume.

The first three chapters deal with basic definitions of membrane processes and present brief descriptions of various transport mechanisms. A generalized view is emphasized. In Chapters IV and XIII, we attempt to unify the existing theories in formulating engineering analysis. Chapters V through X discuss individual processes in detail. These are followed by two chapters covering what quantities are used and how they are measured in membrane processes. Chapter XIV explains how the membranes are prepared, and the last three chapters are devoted to specific applications.

Finally, we would like to express our appreciation to Miss Edna Wilson for typing the manuscript and to Dr. H. Rhim for his extensive assistance in preparing the manifold aspects of liquid-phase operations.

SUN-TAK HWANG
KARL KAMMERMEYER

Iowa City, Iowa
July 1974

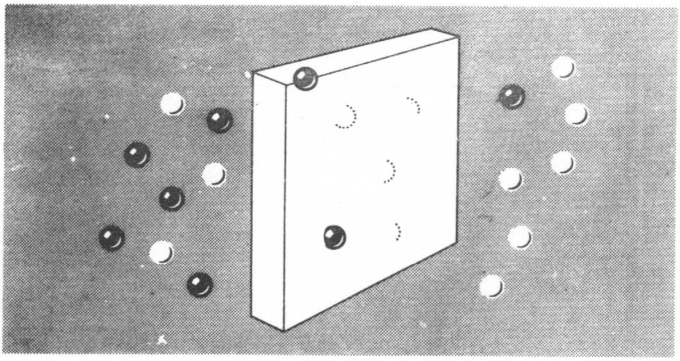
HISTORY

In 1954 I had my first opportunity to present the results of many years of study in the gaseous diffusion field to a distinguished group at a Gordon Research Conference. I am greatly indebted to Letcher Jones for the opportunity to address the Conference on Separation and Purification. This event was a momentous occasion as it led to many friendships that have lasted through the years.

It also taught me a lesson. In my eagerness to put on a good show I attempted to cover too much in too short a time. Fortunately, I received good advice. One of the elder statesmen took me aside after the session and in a most friendly way said "Karl, I know you wanted to tell us all you did, but it would have helped a great deal if at the very beginning you would have told us what you were going to talk about."

So, here is the very basic explanation of what is involved in discussing membranes in separation. A membrane, usually a solid film, is placed in a vessel so that two compartments are established (see figure).

A feed stream of a mixture, gaseous or liquid, is introduced on the upstream side of the membrane. As it flows along the membrane some constituents permeate selectively, and an enriched permeate and a depleted reject stream are generated. It is now already evident that the process is



almost always one resulting in partial enrichment. Consequently, the usual installation will contain multiple stages.

With this admittedly very elementary introduction I have now followed my friend's advice, and it remains only to express Sun-Tak Hwang's and my appreciation to Karl Sollner for writing the Prologue. We find Dr. Sollner's philosophical approach fascinating and hope that the readers will enjoy his unique manner of presentation as much as we do.

KARL KAMMERMEYER

July 1974