

## **Ion Exchangers**



# Ion Exchangers

Editor Konrad Dorfner



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## Preface

This treatise on ion exchangers is, in a sense, a new edition of the book K. Dorfner, *Ion Exchangers — Properties and Applications*, which was the English translation of the third edition of K. Dorfner, *Ionenaustauscher*, Walter de Gruyter, Berlin, 1970. This fourth edition is being issued directly in English as there is no doubt that the international scientific and technological community can nowadays best communicate in this language. There will hardly be a country in which ion exchangers are not used and needed, depending on the extent of industrialization and scientific development, as a technical means or a scientific tool.

In order to achieve the utmost in expertise for every chapter and every detailed problem, the editor has chosen to form a team of authors. Thanks must be expressed that well-known and even great names in the field of ion exchangers and ion exchange have accepted the invitation to contribute. It was further the intention of the editor to maintain the character of a monograph to the greatest extent possible. We believe this has been achieved. The authors had full freedom in the arrangement of their chapters, with only some limitations on length. This freedom may, on the other hand, have resulted in differing opinions here and there, as well as in overlapping and repetition. The latter are considered to be of minor importance and are unavoidable in the preparation of such a volume within an acceptable time. Differing opinions, on the other hand, is more a positive aspect, making for fruitful discussion of the questions under consideration. Any pure mathematical approach to ion exchangers and ion exchange may be regarded by some as too extensive and too rigorous because the materials — whether they are natural, chemically modified, or even pure chemical products — can only be described by results from experimental work.

The relative independence of the various chapters should enable the reader to select the one or the other chapter of interest to him. The chapters on the applications of ion exchange resins, in particular, may be used in this way. It will be appreciated that for these chapters, experts were obtained who have summarized their experience of decades. Further, the necessity of an introduction into the field of ion exchangers and ion exchange has again in this expanded treatment been duly satisfied, in order to enable beginners to learn all that is necessary about this subject in a relatively short time. Further, the attempt was made to comprehensively place ion exchange as a phenomenon into the foreground, so that the results gained in one standardized product line might become more easily transferable to others where explanations and models are still needed to understand behavior and function. Synthetic ion exchange resins are defined and discussed for probably the first time with such consistency as reactive polymers, having the two main properties of storage capacity and selectivity. The result of all these endeavors is not only the

revision and enlargement of the volume but a considerable improvement in its contents.

It is a long way from the first idea of revising a monograph to the point when the whole manuscript can be handed over to the publishers. It is also a matter of the resources available to enable one to finish such a work at all. If the resources are rather poor, only enthusiasm and tenacity can help. Invaluable and kind help as rendered in the beginning by Robert Auer von Brunkau of The Dow Chemical Company must therefore be gratefully acknowledged. Thanks are also due to Dr. George P. Herz, who lent much support during the preparation of the volume, especially when it was most needed. On the other hand the conviction that research begins at the desk provided continual motivation for the editing of such a treatise, despite unfortunate setbacks which were overcome by the belief that the value of ion exchangers and ion exchange goes far beyond water purification. The work in this field of basic and applied science must go on.

Mannheim, 1990

K. Dorfner

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# 1 Ion Exchangers

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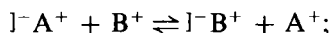
The term ion exchangers is not very old. The first inorganic synthetic products suitable for the uptake of free alkalinity from solutions were called permutites, a term which was used for a fairly long time and may even now still be found employed synonymously with ion exchangers. It was the application of permutites to remove undesired bases from solutions that led to the designation base exchange, as the whole phenomenon was named when it was discovered. The first synthetic organic ion exchangers had already been developed; they were called base exchange resins, with the important difference that a distinction was made between anion and cation exchangers. With these products the term ionic exchange came into use, which was employed together with the much more common base exchange. The introduction of the term ion exchangers can most probably not be exactly dated beyond to say that, for the underlying process, the expression ionic or ion exchange had been used from early on.

Base exchange and together with it, base exchangers are expressions that continued in use for decades, regardless of the fact that the chemical products had changed dramatically. Base exchange was understood as the property of the trading of base-producing entities or cations by certain insoluble materials, either natural or synthetic, inorganic or organic. It was as well the early name for water softening, which was the first industrial ion exchange process. The term base exchange has, in the meantime, come to be more and more replaced by the chemically correct name water softening by sodium exchange and the base exchangers are called cation exchangers in the sodium form. It can only be hoped that the terms base exchange and base exchangers will disappear completely from the literature, since it is sometimes difficult enough to make clear that with respect to ion exchangers one always has to distinguish clearly between cation exchangers and anion exchangers.

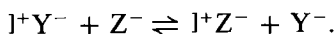
Ion exchangers is the name given to insoluble electrolytes containing labile ions that easily exchange with other ions in the surrounding medium without any major physical change occurring in the electrolytes' own structure. The process taking place is usually called the ion exchange reaction and the labile ions in the ion exchangers exchange reversibly. The ion exchanging electrolyte is in general of a complex nature and is macromolecular. Since after dissociation, all electrolytes exist only as either cations or anions, the ionic sites present in a macromolecular matrix in the case of ion exchangers can also only be either cationic or anionic. As a result, the different matrices consisting of repeating units in the macromolecules and which include inorganic materials, highly complex organic materials of natural origin, and the comparatively simply-structured synthetic resins, carry an electrostatic

charge in the form of a surplus charge or a fixed ion that is neutralized by the charge of the labile ion. These counterions are cations in a cation exchanger and anions in an anion exchanger. In other words — in the strictest sense with regard to the whole field — ion exchangers as such do not exist, but must first always be understood as either cation exchangers or anion exchangers. It is clear, therefore, that a cation exchanger consists of a macromolecular or polymeric anion with negative charges and labile cations and an anion exchanger of a macromolecular or polymeric cation with positive charges and labile anions. Collectively both may then be called ion exchangers.

Ion exchangers are thus insoluble polyelectrolytes having free ions that can reversibly interchange with ions in surrounding solutions. Generalized, a cation exchanger (for which the symbol  $I$  may be used) has negative anionic sites with cations  $A^+$  electrostatically bound but free to undergo exchange with cations  $B^+$ , according to the following equation



correspondingly, an anion exchanger (for which the same general symbol may be used) has positive cationic sites with anions  $Y^-$  again electrostatically bound, but free to undergo exchange with anions  $Z^-$ , according to the following equation



The double arrows indicate that an ion exchange process, if left to itself, reaches a state of equilibrium.

Ion exchangers are the tools for the established procedures and technologies of ion exchange. There are quite a number of different types of ion exchangers, but those based on solid organic polymers have become the most important. A binding nomenclature has, therefore, been found necessary, at least for the many analytical chemistry applications, and was issued by the International Union of Pure and Applied Chemistry (IUPAC), as Recommendations on Ion Exchange Nomenclature in 1971 [1]. Over 40 terms pertinent to ion exchangers and ion exchange were defined.

The solid organic polymeric ion exchangers usually called ion exchange resins predominate by far in technical applications. Their development and wide use in modern technology have made it necessary to elaborate at least a standardization of the test methods in order to have analytical methods to guarantee a qualitatively uniform functioning. Such test methods for ion exchangers are indispensable in research work, for the development of new or improved products, as well as in production to obtain reproducible product properties. The planning engineer cannot dimension an ion exchange unit without knowing the data of performance, and quality data are indispensable for operating the unit both in respect to examining the resins supplied and in following up on any drop in their efficiency, when they have been put into operation. Among others, the American Society for Testing and

Materials [2] and the West German Technical Standards Committee on Materials Testing (FNM) in DIN [3] have both elaborated standardized test methods as a quality control for ion exchange resins. It may be that this standardization of ion exchange testing methods may one day be extended to the production of standardized products which will be used by researchers everywhere instead of, as today, everyone's employing the resins from the next convenient source of supply.

The term ion exchange has often been closely related to or even used synonymously with adsorption and absorption. Exchange-adsorption was used instead of ion exchange during the transition in understanding from base exchange to modern cation exchange or anion exchange [4]. It is important first to distinguish between absorption and adsorption before one can identify ion exchange (Kunin).

Absorption refers to a uniform penetration of the component of a system into the, e. g., solid absorbing material following the old chemical rule of *similia similibus solvuntur* (like likes like), and with no change in concentration. Absorption is thus a process in which the solid engulfs another substance by distributing it very evenly throughout its own entire structure. The term adsorption on the other hand refers, e. g., to the interaction of a solute with a solid adsorbent through physical forces associated with the solid, resulting in a change in concentration of, e. g., a particular dissolved component of a system; it occurs mainly at the surface of the solid. Adsorption is thus characterized by an increase in concentration, which takes place at the interface of the liquid carrying the solute and the solid adsorbent.

It could be claimed, and it would make sense to do so, that ion exchange occurring at the surface only of a non-porous ion exchanger can safely be classified as adsorption. On the other hand, the exchange of a cation after it has wandered into the network of a porous cation exchange resin, could be regarded as absorption even though the mechanisms and energy factors for both cases are the same. But this would only be a phenomenological treatment: it disregards the fact that absorption, adsorption and ion exchange differ substantially, at least as far as synthetic polymers are concerned, in the mechanisms by which they retain solutes (Figure 1.1). All three are sorption processes. In absorption polar substances wander more easily into polar, e. g., plastic materials, just as non-polar substances wander more easily into non-polar plastics. In adsorption a solute is usually retained by the solid through physical (van der Waals) forces associated with the internal surface of the solid. In ion exchange a solute is retained by association or chemical reaction with ionic groups in the solid.

Still, so-called adsorbent resins have been described — and can be manufactured usually by condensation polymerisation — which are able to exchange ions only to a very slight extent, but can bind by adsorption organic coloring substances from solutions on their large surfaces. Most of these are amphoteric in character, which means that they contain both phenol and amine groups. Their main application has been similar to that of active carbon. Here, although the term adsorption for an ion exchange process may appear strange, phenomena associated with ion exchange have involved mechanisms other than the ionic exchange of ions. In the

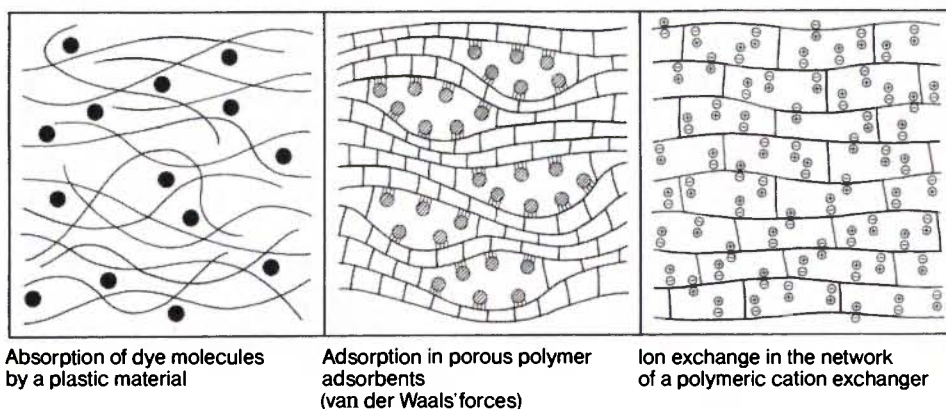


Figure 1.1 Sorption processes: examples of absorption, adsorption and ion exchange and their common way of schematic representation.

course of the increasing importance of addition polymerization materials, as opposed to condensation polymerisation products, a new class of porous polymeric sorbents has been developed, which are manufactured by suspension polymerization leading to polymer beads and which can be effectively used because of their porous structure as adsorbing media. These materials are truly non-ionic and are adsorbents because of their surface characteristics and van der Waals attractive forces. But over the years this group of polymeric adsorbents has been further developed, with polar groups – for instance hydroxyl, amine or halogens – being incorporated in a second reaction step into them. As a result, based on addition polymerization, products with a true porous structure are available.

The term ion exchangers denotes today insoluble polymeric or macromolecular substances with fixed ions. The reactive groups are dissociable and either present by nature in a naturally occurring exchange material or have later been incorporated during the manufacture of a synthetic ion exchanger. Ion exchangers are therefore reactive polymers or reactive macromolecules, but this term does not include macro-ions. In the case of ion exchangers as reactive polymers, the reactive groups are not functional, neither in the sense of the definition of functional groups in organic chemistry nor as defined in polymer chemistry. It is by reactions of polymers that ion exchangers can usually easily be obtained, and these are then called reactive polymers [5]. The fixed ions or reactive ionic groups of ion exchangers have the ability of undergoing ionic exchange reactions, but they are also able to store ionic species as counterions. As with all reactive polymers, the reactive ionic groups of ion exchangers are significant both because they are used to fulfil some sort of goal and are part of very important phenomena in nature.



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# 1.1 Introduction to Ion Exchange and Ion Exchangers

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## Introduction

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## Introduction

Ion exchange is a phenomenon or process involving the reversible exchange of ions in solution with ions held by a solid ion-exchanging material, in which there is no directly perceptible permanent change in the structure of the solid. Best known are the ion exchange phenomena in soils and the ion exchange processes used for the treatment of water. Ion exchange is also used in many other chemical processes, including simple or chromatographic separations and catalysis, and is well-established in analytical chemistry. Ion exchange processes are employed as well in hydrometallurgy and metal recoveries, in the manufacture of sugar, in pharmacy and medicine as well as in biochemistry and biotechnology, and in agriculture and food processing. The ion exchange process usually involves either inorganic or organic ions in predominantly aqueous solutions and proceeds, as it can be assumed, in two steps, i. e., an in-change of the solute ions into the ion exchanger and then the ex-change of the previously present ions out of the ion exchanger. The dynamic state of equilibrium resulting from these two steps is an interchange of ions [1].

Due to the development of special synthetic ion exchange polymers, processes have been developed which, even if somewhat reluctantly, are also called ion exchange processes, by which separations primarily can be achieved. Among these are to be found the ion exclusion method, the ion retardation method, the exchange of non-electrolytes via a process known as ligand exchange, specific and chelate exchangers for chromatographic purposes, as well as for water and waste water treatment, as well as processes based on crown ether polymers. With regard to the so-called redox exchangers the position has been taken in this monograph that their analogy with ion exchangers is only formal, since ion exchange is, in principle, not a redox reaction. We shall, therefore, dispense with a description of it [2].

What can be achieved by an ion exchange process depends largely on the ion exchanger used. Not all ion exchanging materials, with respect to, e. g., temperature and stability, can answer the requirements of a given ion exchange process.

An ion exchanger can be any material that has the ability to uptake ionic species from a solution with the simultaneous release of a chemically equivalent number of ions into this solution. These materials include cellulose, dextran and agarose derivatives, clays and clay minerals, zeolites and other non-siliceous inorganic ion exchangers, materials based on coal and other organic natural products, synthetic liquid ion exchangers and, last but not least, ion exchange membranes. While all the types just mentioned are of greater or lesser utility, in special applications, in this text by "ion exchanger" is meant synthetic ion exchange resins such as are in daily use in the laboratory and in chemical technology, if not otherwise stated. These ion exchangers can be made by oneself, but they are also available as commercial ion exchangers in a wide range of products. Because of their importance, they will almost exclusively be discussed in this introduction. They provide the highest exchange capacity and are of greatest interest in the laboratory as well as in industrial applications.

### 1.1.1 History

The history of ion exchange and ion exchangers can be interpreted from different angles. One can, if one wants, trace the history of ion exchange in nature back to approximately 3 000 years B. C.; or one can begin with the curiosity-driven search for the explanation of phenomena observed in experimenting with soils; or one can begin with the preparation of ion exchangers by man and their use for advantageous and necessary ion exchange processes.

Ion exchange is widespread in nature and might even be seen as the basic process in nature. This is due to the fact that ionic compounds are by far more frequent in nature than neutral molecules. It could be said that for countless millions of years ion exchangers have been active in the solid lithosphere, in soils and in organisms. But the first historical evidence for the use of ion exchange is given in the interpretation of the miracle performed by Moses: "And he cried upon the

Lord; and the Lord shewed him a tree, which when he had cast into the waters, the waters were made sweet: there he made for them a statute and an ordinance, and there he proved them" (Moses, Exodus 15: 22–25). The bitter water at Marah was thus made potable, and it is now known that rotten cellulose is a good exchanger for magnesium ions. It was also already known to Aristotle, 384–322 B. C., that sea and impure drinking water can be purified by percolating them through layers of sand or rocks because the water loses part of its original salt content during this filtration. Later Sir Francis Bacon, in *Sylva Sylvarum*, described experiments in passing salt water through earth, saying that "it hath become fresh when drayened through twenty vessels". In the early nineteenth century Sir Humphry Davy, Lambuschini, and Huxtable studied extensively the ability of clays and soils to absorb components of manure liquor, as was similarly done by Gazzari in 1819, and Liebig found that clays had the ability to adsorb ammonia. Fuchs in 1833 reported that certain clays released potassium and sodium when treated with lime.

But credit for the true observation of the phenomenon of ion exchange is generally ascribed to Thompson and Way. In 1850, Thompson [3] and Way [4] reported on the observation that cultivated soil can exchange various bases, such as ammonium, calcium or magnesium. In 1845, Spence, a pharmacist from York working under contract to Thompson, had prepared a bed of sandy clay treated with ammonium sulfate in a glass column and allowed water to flow through it. Instead of ammonium sulfate, he obtained gypsum in the eluate. Thompson commented on this: "This was a complete surprise". But although Thompson published these results earlier than Way, he has been characterized as follows: "He made a dive into the ocean of science, and brought up one scientific pearl of great price, ... but he was never a man of science". From the description of the personality of, as well as the work done by, Spence it follows that he must be considered as the discoverer of ion exchange. Way, on the other hand, was a professor of chemistry and after the results of Thompson and Spence became known to him in 1848 he studied the base exchange properties of soils very intensively. He writes: "... the acid comes away in the liquid not in the free state, but combined with lime, which it has taken in exchange for its previous saturating base". The term base exchange was born, and the process was so thoroughly investigated by Way in the years 1850 to 1854 that for decades thereafter it was not followed by any other comparable work.

Around 1950 the discovery of ion exchange was celebrated in the chemical literature as being 100 years old. But these 100 years must be subdivided into important periods, in which not only the phenomenon as such was elucidated and appropriately designated as ionic or ion exchange but also ion exchange materials were synthesized for employment in specific applications.

Curiosity as to the nature of the reaction of manure with soils led to the discovery of base exchange in 1850, but application of the process could not be properly utilized until the concepts of reversibility and stoichiometry and of the role played by ions were clearly formulated or applied in the following decades.

The phenomenon of base exchange was interpreted as a chemical process by Henneberg and Stohmann [5], and by Eichhorn [6] in 1858, when they succeeded in confirming the reversibility of such exchange processes. Several other names could also be cited, but it was only in 1870 that Lemberg [7], in his classical work, widened the knowledge of the chemical character of base exchange by furnishing proof of the stoichiometry of base exchange processes. Based on experiments, he demonstrated that a number of natural minerals, particularly the zeolites, are capable of exchanging bases in equivalent quantities. In his most striking experiments he succeeded in converting leucite,  $K[AlSi_2O_6]$ , into analcime,  $Na[AlSi_2O_6]$  using an NaCl-solution, and then analcime, using a KCl-solution, back into leucite. These experiments were the more striking because leucite contains little water while analcime contains approximately nine percent, and the experiments with these minerals showed, at all temperatures, an increase in water content when potassium was replaced by sodium. It should be noted that it was the opinion of the time that a reaction is chemical when its equivalency has been demonstrated. Why relatively little progress was made during the later second half of the 19th century is due to the fact that an authority like Liebig questioned Way's experimental results and considered base exchange a physical, not a chemical, process. The early physical school opposed the chemical interpretation of base exchange, did not agree with the stoichiometric views of the time, and even two conclusions arrived at by Way were found to be erroneous. In 1877 van Bemmelen published the first of a series of papers on absorption of salts by soils, further developing the point of view of Way and Lemberg [8]. The outstanding facts of van Bemmelen's are that in no case is there absorption of a neutral salt as a whole, but always an interchange of bases with the bases already present, and that the location of the exchange is in the silicates. It seems that mineralogists or, in modern terms, inorganic chemists were much earlier closer to an explanation of base exchange than were the agricultural chemists, but at the time the latter dominated the field.

After the work of Eichhorn and Lemberg base exchange had to be considered as reversible and stoichiometric, but the quantitative approach to relationships of the distribution of bases between the base-exchanging material and concentration in the solution went historically through an extensive evolutionary process during which already known or newly discovered physical-chemical phenomena or laws were applied. It is to be noted that in the book by Mulder [9] Berthelot's theorem of the state of equilibrium was applied for the first time to this field of investigation with a clarity which could not be much improved upon in modern times. This discovery was a guideline for several contemporary researchers for the understanding of the processes occurring in soils. But as the law of mass action was only discovered by Guldberg and Waage in 1867, the first attempts to solve mathematically the problem of the dependence of the quantity of the bases taken up in relation to the concentration were based on the assumption of a simple adsorption process. In both cases — the assumption of a simple adsorption process and the application of the law of mass action — contributions were made by various

scientists over the following decades. Around 1859 both Boedeker and Wolff suggested empirical equations, with the difference being that in the former case the initial concentration and in the latter the equilibrium concentration was included as being proportional to the exchange. Kroecker suggested another empirical equation in 1892 [10]. Interest focussed more and more on the question of the effect of concentration on the final equilibrium. Influenced by investigations of Ostwald on the solubility of alkaline earth sulphates in mineral acids showing it to be an exponential function of the concentration of the acid, investigators expected the silicate reactions to be similar, but the concentration curves both with the pure silicates and with soils were not as a rule strictly exponential. To explain this, Hall and Gunningham [11] in 1907 then put forward a formula for ammonium salts, but this also held only for a comparatively restricted range of concentration. As the Freundlich adsorption isotherm was developed in 1905 and the Langmuir isotherm in 1916, it is understandable that Wiegner in 1912 [12] set up an equation closely related to the Freundlich type, and Vageler and Woltersdorf in 1930 [13] set up one closer to the Langmuir isotherm. A formal analogue with an adsorption mechanism based on the Langmuir equation was more or less finally set up by Boyd, Schubert and Adamson in 1947 [14].

It would seem to be worthwhile to try to find out how and when base exchange became ionic and then ion exchange. The very general comment that this was not the case until the theory of electrolytic dissociation was developed by Arrhenius in 1884 is certainly true. Up to this time and even thereafter the scientific disputes on base exchange were mainly concerned with the phenomenon as it occurred in soils and the various early attempts using synthetic materials to describe it chemically or physically and quantitatively. Very slowly a change from base exchange to cation exchange took place, first being clearly denoted so by Wiegner in 1912 [12]. But in these studies of base exchange it was noticed and emphasized that the so-called acid radicals were not adsorbed in contrast to what had been reported in particular for phosphoric acid by Rostworoski and Wiegner [15]. The retention of, for instance, phosphate in soils was explained quite speculatively and, together with investigations on the absorption of citrate, oxalate, carbonates, borates and nitrate, it was concluded that the absorption of acid radicals somehow falls into line with the absorption of bases. Being thoroughly convinced that a rational method for the analysis of soils could only be expected when the principles of the reactions in soils were clarified, further investigations on base exchange were taken up and it was proved by Ramann and Spengel that base exchange is an ionic reaction [16]. Base exchange had thus, through cation exchange, arrived at ionic or ion exchange [17] but the term ion exchange was identical with the current cation exchange. True inorganic anion exchangers in the early days of ion exchange were never made, but it took the ingenious spirit of Jenny to show, over investigations of permutites, that a corresponding anion exchange must as well be taken into consideration [18].

The law of mass action was somewhat reluctantly applied during the first 100 years of base exchange. It was Gans who first employed it, in 1908, but with little

success, because of unsatisfactory conformity between experimental results and theory. Very detailed investigations on the base exchange equilibria by Rothmund and Kornfeld followed in 1918 [19] and Kerr was more successful in 1928 [20] with a true analysis of the applicability of the law of mass action. According to him the ionic exchange equilibrium could not be considered to be analogous to the simple equation of a double reaction with an insoluble precipitate, but he assumed that in base exchange the solid phases behaved as if they were dissolved in the solution, assuming further similar activity coefficients for the soluble species and insoluble species. Møller in 1937 still used the same approach, but in 1932 Vanselow had already presented a method based on the assumption that the two solids formed a series of continuous solid solutions and that the activity of each component was not unity, as Kerr had assumed, but is equal to its mole fraction in the solid [20]. Then Gapon in 1933 assumed for his formula that both the di- and monovalent ions behaved similarly on an equivalent basis on the absorbing surface and Kjelland in 1935 calculated from the equilibrium constants the free energies. Following investigations showed that the law of mass action is sometimes approximately obeyed within small concentration ranges. Thus Samuelson [21], Boyd, Schubert and Adamson [14], Marinsky [22], Kressman and Kitchener [23], and Duncan and Lister [24] finally succeeded, using a more rigorous application of the law of mass action to the phenomenon of ion exchange with more accurate data on “organic zeolites” and other newly available ion exchange resins.

All the initial fundamental studies of the mechanism, equilibria and rates of exchange reactions were difficult because of the chemical heterogeneity of the naturally occurring or poorly synthesized exchange materials available at the time; it was not known that for such physical-chemical investigations well-defined, uniform materials should be used. This is the reason why, on one hand, of the numerous experiments dealing with ion distribution between exchanger and solution only a small number is still of interest and, on the other, why Jenny for instance, at the beginning of the twentieth century emphatically welcomed such better defined synthetic products as the permutites.

It was Gans in 1905 who first synthesized suitable inorganic ion exchangers and called them permutites [25]. The fused sodium aluminosilicates,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$ , were granular cation exchangers stable in neutral media. Because of their solid glassy nature they had poor kinetics and were, after about ten years, discarded for modified natural mineral products, such as stabilized glauconites, bentonites and the synthetic amorphous sodium aluminosilicates [26]. The modified natural products had low operating capacities but the rate of regeneration was faster. On the other hand, the precipitated gels had a higher capacity to uptake ions but were very sensitive to low and high pH. The inorganic ion-exchanging materials were used for about forty years, then seemed to be completely abandoned because of limitations in their application; however, since 1950, many new developments have taken place in the field of inorganic ion exchangers.



An intermediate stage in the development of ion exchangers is represented by the period when ion exchange properties were recognized in various organic materials — for example, the sulfonated coals as cation exchangers stable in the hydrogen form were introduced in 1934 by Liebknecht [27]. In all cases these products contained  $-\text{SO}_3^-$  groups but had carboxylic acid groups as well, resulting from oxidation of the coal structure, in the case when coal was sulfonated with sulfur trioxide instead of with concentrated fuming sulfuric acid. In the hydrogen form these exchangers were insoluble polymeric acids. They could be used both in the sodium and in the hydrogen cycle. The first anion exchanger developed and used at that time was a precipitated black oxidation product of aniline called emeraldine. But this product was not used for very long because it hydrolyzed to produce chlorine leakage.

The next milestone in ion exchange, after its discovery by Spence, Thompson and Way, was the discovery of Adams and Holmes [28] in 1935 that it is possible to make truly synthetic organic ion exchange resins. Their original materials were the formaldehyde condensation products of polyhydric phenols or aromatic diamines, which yielded the required insoluble cation or anion exchange resins. In combination these resins were, in principle, able to exchange hydrogen for other cations and hydroxyl for other anions in aqueous solutions, leaving only water. It was not long before Holmes produced a more strongly acidic cation exchanger, analogous to the sulfonated coals, from phenolsulfonic acid. Somewhat later, the anion exchangers were also improved, by using the more strongly basic guanidine. Recognizing the importance of the discoveries of Adams and Holmes, IG-Farben-industrie in Germany purchased the patents on the subject and, since 1936, has continued developmental work in this field with the aim of systematic production of ion exchange resins to serve special purposes [29]. At the beginning of World War II the patents of Adams and Holmes were also given to the United States of America. Most of the cation exchangers developed there were based on phenol and formaldehyde as the resin matrix and  $-\text{SO}_3\text{H}$  as the exchanging group. The weak base amines varied in composition and were made from aromatic amines and formaldehyde, phenol, formaldehyde and polyamines or acetone, formaldehyde and polyamines. The first resin to contain highly basic groups which removed silicic acid was a condensation product of epichlorohydrin and amines, developed in 1947. These resins were referred to as epoxy or medium basic resins.

The ion exchangers first obtained by polycondensation came increasingly to be replaced by polymerization products after 1945, when D'Alelio succeeded in incorporating sulfonic acid groups into a crosslinked polystyrene resin [30]. The use of these copolymers of styrene and divinylbenzene as matrices for attaching the exchanging groups brought a tremendous expansion of ion exchange processes worldwide, as a result of intense research on the part of the manufacturers of ion exchangers. In 1947 the invention of McBurney [31], based again on styrene divinylbenzene co-polymerization, led to the modern range of anion exchange resins. These unifunctional synthetic polymeric ion exchangers rapidly became the standard

cation and anion exchangers. They were made in spherical bead form by the process of suspension polymerization, and were essentially monofunctional, in contrast to the granular polyfunctional resins of the Bakelite era. The new resins were also very stable over the total pH range and at higher temperatures.

Further developments led to improvements of ion exchange resins and the manufacture of resins with specific ion exchange properties. In 1948 Skogseid [32] developed by nitration, reduction and diazotization the first potassium specific exchanger; further, as new anion exchangers, pyridinium resins to be used in uranium recovery were synthesized. At this time investigators also began to attach a variety of exchanging groups to the resin matrix. The ease with which this could be done led researchers to investigate all conceivable types of properties, which they achieved simply by varying the reactive group on the matrix.

There is also the history of the applications of ion exchange and ion exchangers. The first suggestion to use ion exchange with a clay mineral was made by Harms in 1896; the aim was to exchange the calcium in the clay for the sodium and potassium in sugar solutions to reduce melassigenic formation, thus increasing the sugar yield. Gans then, in 1906, applied the ion exchange process successfully for water softening and described as further applications, in 1909, gold recovery from seawater, salt conversion, water purification, i. e. removal of manganese and iron, and manufacture of sugar [33]. Metzger in 1912 and Duggan in 1913 also attempted the recovery of gold and in 1915 a patent was taken out for the recovery of silver. In 1917 Folin and Bell employed for the first time ion exchange in analytical chemistry for the separation of ammonia from urine [34]. After the amorphous sodium aluminosilicates and greensands had become available — between 1914 and 1920 — water softening by ion exchange entered a new period of application lasting 30 years. Whitehorn showed first in 1923 that not only ammonia, but also other amines, including the amino acids histidine and lysine, were readily adsorbed by a synthetic aluminosilicate, either from aqueous solution or from solution in organic solvents [35]. In 1934 Austerweil and Jeanpost adsorbed copper from a solution with a greensand exchanger and then recovered the copper by elution with a salt, and Syrkin and Krynkin were issued a patent for the recovery of copper from a cuprammonium based liquor in 1937. The world's first commercial demineralising plant was set up in England in 1937 after — based on the work of Adams and Holmes — polycondensation cation as well as anion exchangers had become available. The recovery of vitamin B<sub>1</sub> from urine in an analytical procedure was first reported by Hennessy and Cerecedo in 1939, using a sodium aluminosilicate. The first pilot plant for the recovery of copper from cuprammonium waste liquors was built in Germany in 1939; the full-scale plant was built in 1941. By the use of improved synthetic resins both copper and water were recovered for reuse — the copper recovery was over 90% — and ammonia was also recovered for recycling. Griessbach and co-workers introduced in 1942 organic synthetic ion exchange resins in the hydrogen form into catalysis. The application of ion exchangers in chromatography was also suggested by Griessbach in 1939. Samuelson's

systematic investigations from 1939 on showed the importance of ion exchangers in general analytical chemistry and in ion exchange chromatography. Condensation products were still used in 1943 to 1945 for the desalination of water for trucks in desert areas, desalting kits for fliers, and, as described by Applezweig, for the recovery of quinine from cinchona barks. Anion exchangers for concentrating metal ions were used in Germany prior to 1945, e. g. for the recovery of silver from photographic film rinses. When, in 1947, the work done at the Manhattan Project was published by the US Atomic Energy Commission it showed tremendous achievements using ion exchangers for the separation of the rare earths, the discovery and identification of element 61 and many radionuclide separations. The biochemical separation of nucleic acids in 1950 and of carbohydrates in 1952 further showed the great potential of ion exchangers. At the same time ion exchangers with styrene-divinylbenzene matrices in bead form with excellent physical and chemical properties were commercially developed, and innumerable applications became feasible. The main application of ion exchangers, water purification, became easier and widespread. D'Ans, Klement and Hein used ion exchange resins very successfully in the early fifties in preparative chemistry.

The conversion of calcium nitrate to sodium nitrate was carried out on an industrial scale in Norway in 1955. The first 100 years of ion exchange had opened the door wide to the countless applications now known and practised.

In historical reviews of ion exchange usually little attention is paid to technical developments beyond the first industrial applications of ion exchangers. Further, unfortunately, one can find in these reviews nothing about suggestions prior to that made by Adams and Holmes that with the new products deionized water could be obtained by passing even seawater through a combination of phenolic with basic condensation products, thus rendering it potable. Only some time later, when the anion exchangers had also been improved, did it become possible for the first time in practice to remove essentially all the ionic impurities from water, to obtain the equivalent of distilled water by simple percolation techniques. By this time, E. Leighton Holmes had become chief chemist of The Permutit Co. Ltd., and the world's first commercial demineralizing plant was set up by Friary, Holroyd and Healy Ltd., at Guilford in England. The fixed-bed ion exchange equipment consisted of two columnar tanks, its design and operation obviously having evolved from experience with sand filtration columns. "Ten years and one World War later, unifunctional addition polymer resins based on polystyrene had become the standard cation and anion exchangers" (manufactured under licence granted by General Electric to Dow Chemical Company, under the name Dowex 50, and to Rohm and Haas Company, under the name Amberlite IR-120; then the first commercial strongly basic anion exchange resin containing quaternary ammonium groups, capable of removing weakly ionized anions such as carbonic acid, silicic acid and organic acids, was manufactured by Rohm and Haas Company) [36]. Thus, for the first time, the removal from water of all inorganic constituents together with trace amounts of natural organic acids had been achieved. But very little was disclosed

of the technically necessary modification of the equipment. For fixed-bed columns a basic design had evolved which has been in use since then. In 1949 the Rohm and Haas Company developed mixed bed deionizers, which they called Monobed, in which cation exchange resins and anion exchange resins were mixed in the same column permitting the production of high purity deionized water. This technology ushered in new age for the use of ultrapure water in various industries. Replacing the evaporator, the first large two-bed deionizer with a capacity of 190 000 m<sup>3</sup> per year seems to have been installed at a power plant in the USA in 1950; in 1951 in Japan the world's largest mixed bed deionizer was built, with a capacity of 600 m<sup>3</sup> per day. After that, many similar deionizers were installed throughout the world. The year 1957 may be considered as the beginning of ion exchange technology in nuclear technology. After several types of nuclear grade ion exchange resins had been made available by the Rohm and Haas Company, the world's first commercial nuclear power plant at Shipping Port Nuclear Power Station went into full operation, using mixed bed deionizers using Amberlite resins. From 1958 to 1961 the availability of macroporous cation and anion exchangers opened new areas in deionization systems, such as high flow rate deionization, external regeneration of condensate polishers, moving bed deionization and ultrapure water production. As early as 1962, in the Powdex Process, fine particle-size strongly acidic and strongly basic ion exchange resins were used as a new deionization system with, increasing the reaction velocity by a hundred-fold, much higher utilization than in ordinary processes, as well as removing suspended and colloidal matter. The following year, 1963, the Japan Organo Company and the Asahi Chemical Industry Company developed a new moving bed continuous ion exchange deionizer of, at first, a two-bed type, installing a commercial plant of 2 200 m<sup>3</sup> per day capacity, reducing the amount of ion exchange resins used, the regenerants consumed, and the land space required to half. After many improvements had been made, including a change from two-bed to a mixed bed, the technology was finally established in 1966 with the Continuous Mixed Bed Deionizer, which had a capacity of 2 400 m<sup>3</sup> per day. Another new technology for condensate water treatment – the mixed bed Ammonex Process, of the Cochrane Division of the Crane Company, USA – was developed in 1967, using the ammonium form of the cation exchange resin and the hydroxide form of the anion exchange resin. This process was first used at a power station; as a result, the removal of ammonium in the condensate was avoided, resulting in deionized water with less than 1 ppb of sodium, less than 5 ppb of silica, and with 90% of the iron sulfate removed. The operating time until sodium breakthrough was prolonged by a factor of about 10, and the operation cost was reduced by two-thirds. This resulted in a series of quick replacements of hydrogen/hydroxide form resins by ammonium/hydroxide resins in the mixed bed deionizers of existing plants. Reverting to developments in fixed bed technologies two techniques from 1968 should be mentioned: the stratified anion exchange system and the countercurrent regeneration (CCR) method. Kunin had pointed out that one of the main advantages of continuous ion exchange (CI) is the fact that it generally

employs countercurrent regeneration, and to make a proper comparison of fixed bed and moving bed (CI) processes one has to take fixed bed systems using countercurrent regeneration. It was primarily this comparison which has resulted, in Europe, in the increased use of countercurrent fixed bed systems and a slight decline in the use of continuous ion exchange. In 1969 the first systematic investigation in successful practice of pyrogen removal from water by the combined use of reverse osmosis, ultrafiltration and ion exchange resins was made by Shimizu, Okkido et al. in Japan, opening a new way for the production of pyrogen-free water. Since then work on ion exchange technology had been mainly concerned with the development and improvement of existing processes and techniques rather than with the development of radical new ones. Much attention has been paid to one of the most interesting new processes — the Sirotherm Process — in which specially developed resins are regenerated thermally. This has proven particularly suitable for the partial desalination of brackish waters.

The theory and application of ion exchange is over 100 years old. There have been times of basic research and milestone inventions alternating with periods of quiet development. Table 1.1 gives a chronological survey of developments, including some but by no means all the names of those who have contributed to them.

Table 1.1 Chronological order of developments of ion exchange and ion exchangers

Year	Development	Names
1845–52	Discovery and description of base exchange in soils	Spence, Thompson; Way
1858	Base exchange explained as a reversible chemical process	Eichhorn
1876	Zeolites recognized as carriers of base exchange in soils; equivalence of exchange of bases proved	Lemberg
1901	Artificial zeolites used for removal of potassium from sugar juices	Harms, Rümpler
1901–02	Manufacture of sulphonated coals and suggestion for removal of potassium from sugar juices	Majert, Halse
1906–10	Industrial manufacture of sodium Permutite	Gans
1912–16	Siliceous gel permutites	de Brüm, Rüdorff, Engel
1914–1920	Greensands of New Jersey stabilized to Neo Permutite	Borrowman
1912–18	Base exchange explained as cation and then ionic exchange	Wiegner; Ramann, Spengel
1925	Colloidal systems as ion exchangers; ion swarm theory	Wiegner, Jenny
1934–39	Industrial manufacture of sulphonated coals for water softening filters	Liebknecht; Smit
1935	Invention of sulphonated and aminated condensation polymers	Adams, Holmes

Year	Development	Names
1936–45	Development and introduction of commercial condensation ion exchangers	Holmes; Griessbach
1942	Invention of sulphonated polystyrene polymerization cation exchangers	D'Alelio
1947	Invention of aminated polystyrene polymerization anion exchangers	McBurney
1948	Preparation of a sodium specific polystyrene cation exchanger chelating resin	Skogseid
1949–56	Development of carboxylic addition polymers as weak acid cation exchangers	Hale, Reichenberg; Topp, Thomas
1946–65	Development and investigations of ion exchange polymers	Bonhoeffer, Schloegl
1951–56	New zeolites as molecular sieves with ion exchange properties	Barrer; Breck et al.
1952–71	Invention and development of chelating polymers	Gregor; Pepper; Morris
1956	Development of cellulose ion exchangers	Peterson, Sober
1956–58	Preparation and studies of non-siliceous inorganic ion exchangers: insoluble salts, heteropolyacids	Buchwald, Thistlewhaite
1957–59	Development of dextran ion exchangers	Porath, Flodin
1957	Invention of macroporous ion exchange resins	Corte, Meyer; Kunin, Metzner, Bostnick
1957	Snake cage resins and ion retardation process	Hatch, Dillon, Smith
1958	Development of liquid ion exchangers for analytical and technical applications	Schindewolf; Brown et al.; Coleman; Moore; Allen
1959	Foundations laid for the new theoretical treatment of ion exchange	Helfferich
1960	Invention and development of isoporous ion exchange resins	Kressman, Millar
1961	Development of continuous ion exchange processes	Higgins; Asahi Chem. Ind.
1964	Thermally regenerable ion exchange resins and water desalination based on them	Weiss et al.
1967–70	Pellicular ion exchangers for chromatographic use	Horvath et al.; Kirkland
1975	Development of exchangers with crown ethers as reactive groups	Blasius et al.
1984	Industrial chromatographic resin systems Dowex <sup>R</sup> Monosphere	Dow Chemical Company

This table is to be considered more as guideline than a complete representation of the history of ion exchange and ion exchangers. The complete history has been presented in a volume of its own [37]. The stormy development of ion exchange research after 1945 is evident from the graph of Figure 1.2, in which the number of scientific papers is plotted as a function of time (in years) (Kunin). The method

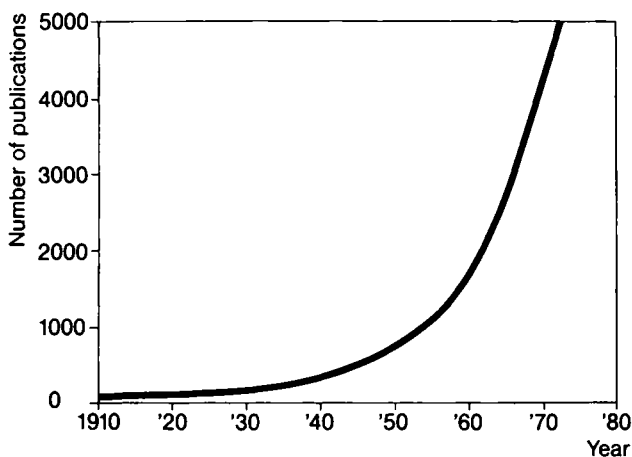


Figure 1.2 Number of publications on ion exchange as a function of time (Kunin).

of ion exchange has become an important modern tool widely accepted in the laboratory and in industry.

### 1.1.2 Types of ion exchangers

Ion exchange has become a general operating technique today. As indicated by the brief historical review at the beginning of this chapter, ion exchange was investigated first with inorganic materials; these found some industrial use, but were almost completely displaced by synthetic ion exchange resins. The demand for ion exchange materials that would satisfy the most diverse requirements led to the development of new products, which must be considered as separate ion exchanger types according to their special properties.

Among the available types, synthetic ion exchange resins have the greatest importance. But inorganic ion exchangers should not be neglected, since these have once again aroused interest because of their mechanical, thermal and chemical properties and because, in light of their mineralogical parallels, they offer information about numerous processes in soil science. The cellulose ion exchangers represent a separate type with their own characteristics related most closely to another group, i. e., the dextran ion exchangers. Both types have been rapidly accepted in ion exchange chromatography where they have become indispensable for analytical as well as preparative work. In addition, ion exchangers based on carbon have been produced and, together with a number of other materials with ion exchanging properties, have been investigated for their applicability. Liquid ion exchangers, as another type, probably are important primarily because of the technological possibilities they offer.

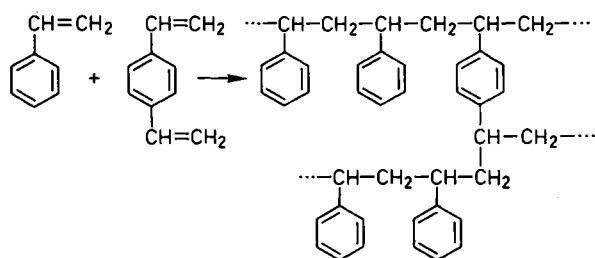
In the case of ion exchange membranes, interest was initially aroused not so much by questions of their structure as by their physicochemical mechanism of action and its possible utilization. This has continued until sufficiently sophisticated materials for general industrial applications have become available. Since then new membranes have been found that are being used in quite a number of industrial applications, although their full potential is yet to be realized.

### 1.1.2.1 Materials

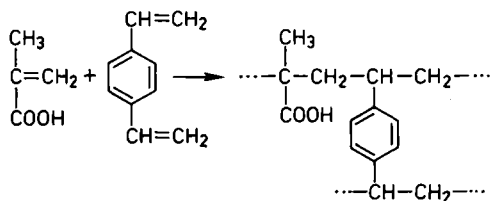
**Synthetic resin ion exchangers.** For the description as well as for an understanding of synthetic ion exchange resins and their properties, three factors are decisive: The raw material which is used for the construction of the skeleton or the matrix, bridging agents for crosslinking and insolubilization, and the type and number of the ionogenic groups. Synthetic ion exchange resins chemically are insoluble polyelectrolytes with a high but not unlimited moisture regain capacity. With regard to their function one speaks of cation exchangers, anion exchangers, and amphoteric ion exchanger types.

Polymerization and polycondensation can in principle be used as the synthesis routes to form the matrix. At the present time, polymerization resins have become more important than polycondensation resins, as they have a higher chemical and thermal stability.

The most important starting material, which is used nearly exclusively in exchangers of the strongly acidic and strongly basic types produced on a large scale, is styrene. The styrene is polymerized with itself and with divinylbenzene into a polymeric molecule:

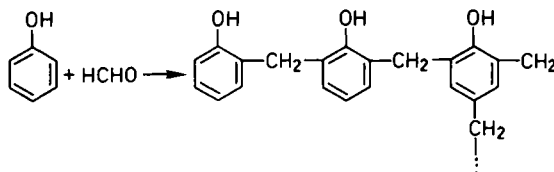


On the other hand, matrices for primarily weakly acidic cation exchangers are formed, also with divinylbenzene, from acrylic acid or methacrylic acid:





In polycondensation resins, the matrix is usually constructed of phenol and formaldehyde:



where the properties of the exchanger depend on the nature of the phenols, the quantity of starting materials used, and their side groups [38].

As far as the network of styrene-divinylbenzene copolymers is concerned, the reaction leading to their formation produces matrices which are not uniform in degree of crosslinking. Such ion exchange particles must accordingly be considered inhomogeneous substances in which relatively densely crosslinked regions, which are formed at the beginning of the polymerization process, are found connected with longer, more sparsely, crosslinked domains [39, 40]. From the standpoint of high polymer synthesis, it is probably impossible practically to obtain a uniform bridge distribution throughout the structure of a crosslinked copolymer. Naturally, the determination of significant thermodynamic values becomes difficult as a result and this must not be forgotten in all theoretical considerations. The degree of homogeneity of ion exchange structures depends on the purity, nature and properties of the starting materials used for their production, as well as on optimum conditions of polymer synthesis. In spite of the irregular structure of the matrix, however, it is possible to produce ion exchangers with a uniform distribution of the ionic groups [41]. Investigations of the ionogenic group distribution in common ion exchange resins established the heterogeneity of the gel type ion exchange resins contradicting the frequent assumption of a homogeneous gel that had been made in the study of the physicochemical properties of synthetic ion exchange resins. The ever-increasing experimental data of recent years suggests, however, that the heterogeneity of ion exchangers is of still a different nature, and at the molecular level of polymer chemistry it is basically associated with the structure of the initial copolymer [42].

Crosslinking naturally depends first of all on the quantity of divinylbenzene used as the crosslinking agent in production. Commercial ion exchangers of the gel type contain nominally between 2 and 12% divinylbenzene. The nature and degree of crosslinking have a decisive influence on the properties of ion exchange particles; additional details on this subject are described in the section on the properties of ion exchange resins.

With respect to the structure of the network of synthetic resin ion exchangers different types are now available with designations such as gel type, macroporous or macroreticular, and isoporous ion exchange resins. These terms refer to the

polymeric organic part of the exchanger resin and will first be considered with regard to their basic properties as well as in comparison with each other.

**Gel type ion exchange resins.** During polymerization of styrene and divinylbenzene (or similar reactants), which yields products to be used as the skeleton of an ion exchanger, the network formed is obtained as a gel. The term gel here refers to the fact that, macroscopically, a homogeneous network has been synthesized that is elastic in nature and contains solvent from the manufacturing process. The properties of such copolymers or matrices can be varied by changing the ratios of the amounts of the individual monomers used during the synthesis. It is already obvious from this brief description that the term “gel type resins” refers to polymer matrices that do not contain pores. As a result it is important to pay close attention to the influence of the amount of crosslinking agent used during polymerization, since this factor influences markedly the very important property of swelling. A gel ion exchanger whose matrix contains a low proportion of divinylbenzene swells strongly in aqueous solution; this opens its structure widely, permitting large ions to diffuse easily into the exchanger, and at a rapid rate. Ion exchangers with matrices containing a higher proportion of crosslinking agent ( $>10\%$  DVB) swell to a substantially lower degree in aqueous solutions. Porosity, which, strictly speaking, does not exist, may nonetheless be understood with respect to gel type resins as referring to the channels resulting from swelling that determine the size of the species, ion or molecule that may enter the structure, and the rate of diffusion and exchange. It is to be emphasized because of its importance, that gel type polymer structures have no appreciable porosity until they are swollen in a suitable medium; but such crosslinked polymers, as well as the ion exchangers derived from them, swell to a well-defined and reproducible degree in an appropriate solvent system, such as toluene for the basic copolymer, or water for the ion exchanger. This latent porosity may well be measured then in terms of the volume increase on exposure to the solvent. Other basic properties of gel type ion exchangers also depend on the amount of crosslinking. For example, the mechanical strength decreases with decreasing proportion of divinylbenzene, which means that the greater the crosslinking is the greater the mechanical strength is.

**Macroporous (macroreticular) ion exchange resins.** Macroporous ion exchangers are types in which a solvent is used during production from the monomers, so that a porous matrix structure is formed in the course of polymerization [43]. These macroporous structures, which have large internal surfaces, can be sulfonated very easily and completely and are much more resistant than gel type resins to osmotic shock. Furthermore, they are extremely uniform in external shape and, in contrast to the gel types, opaque. Pore sizes of several hundred nanometers in diameter and surface areas of up to  $100 \text{ m}^2/\text{g}$  and more can be obtained [44]. To prevent collapse of the structure, a larger portion of crosslinking agent needs to be used. However, in connection with the large internal porosity, this leads to a number of advantages such as a smaller swelling difference in polar and nonpolar solvents, a smaller loss

of volume during drying, and a higher oxidation resistance. Because of their higher porosity, larger molecules can also penetrate the interior. The economy of macroporous ion exchangers is somewhat limited by their lower capacities and higher regeneration costs, but, their suitability for catalytic purposes is unique. Macroporous ion exchangers are fully developed products, which are in frequent use because of their advantages [45].

In Figure 1.3 the clear gel type standard ion exchange resin is shown for comparisons together with the opaque macroporous ion exchange resin. Figure 1.4 then shows electron micrographs of fragments of typical gel and macroporous resin beads and in Figure 1.5 a two-dimensional diagram is given showing the mesh size

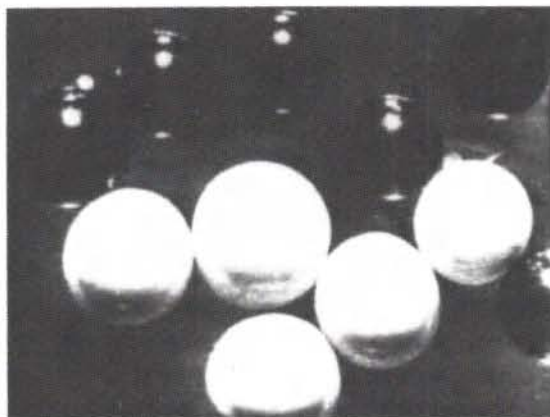


Figure 1.3 Types of ion exchangers. Gel type (above) and macroporous (below) ion exchange resin beads based on polystyrene-divinylbenzene.

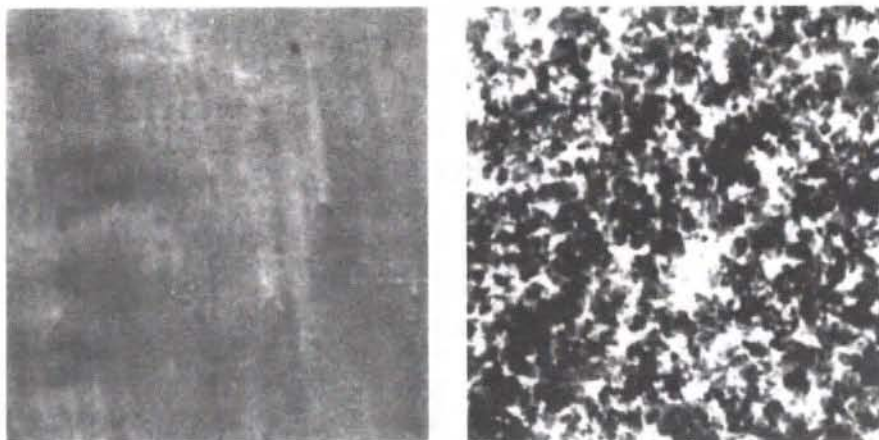


Figure 1.4 Electron micrographs of fragments of gel type (left) and macroreticular (right) ion exchange resins.

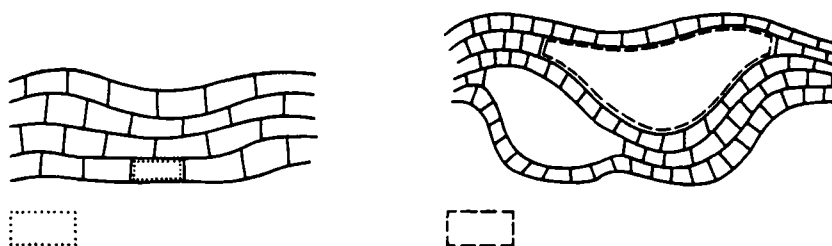




Figure 1.5 Two-dimensional diagram of ion exchange matrices.  mesh size of gel type,  pore size of macroporous exchange resins.

of a gel type matrix as compared with the pores of a macroporous resin. The latter should not lead to misconceptions about the three-dimensional structure of ion exchange matrices in general.

**Isoporous ion exchange resins.** The isoporous ion exchangers are a group in which crosslinking and pore structure are modified in a way to obtain polymers with a substantially uniform pore size. This is achieved by taking advantage of the possibility of forming methylene bridges during the standard process of chloromethylation of the preformed hydrocarbon beads [46]. The beads are manufactured using styrene, together with a temporary crosslinking agent which is unstable during chloromethylation, and is destroyed. Simultaneously, new crosslinks are formed, by a process which proceeds at a slow uniform velocity, and can be influenced to give an extremely even spacing of crosslinks. In practical application, the isoporous anion exchange resins show little sensitivity to organic fouling, have a higher capacity and regeneration efficiency, and a lower cost and price performance than the macroporous ion exchange resins. In some cases, they are particularly suited as anion exchangers for the removal of silicate. Probably the maximum structural homogeneity attainable up until now has been achieved in isoporous ion exchangers, since highly crosslinked regions are relatively rare and the crosslinking is more or less homogeneous [47].

The three structural models of ion exchange resins just described can be graphically depicted as shown in Figure 1.6, after Kressman. Following this representation a gel type ion exchange resin can be characterized by an alternation of expanded and contracted regions in the polymer network, in case the resin contains a solvent. In this swollen state ion exchangers of this type are characterized by a considerable specific permeability. Almost all their ionogenic groups are accessible to inorganic ions. If, however, the degree of crosslinking of such resins increases, the ionogenic groups may become screened off and inaccessible. The macroporous ion exchange resins are distinguished by a considerable heterogeneity, characterized by the presence of regions with higher and lower matrix densities. The resulting channels, which have a large internal area, exist also in the unswollen state, with the result

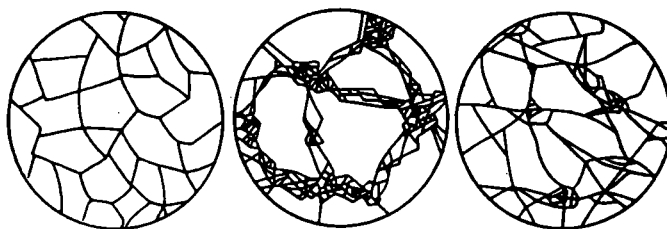


Figure 1.6 Structural models of gel type, macroporous, and isoporous (left to right) ion exchange resins, graphically depicted.

that when macroporous resins are hydrated, their degree of swelling does not change significantly. The regions with high matrix density are the reason for the considerable mechanical strength, and the porosity of macroporous ion exchange resins may be defined as an intrinsic porosity. In essence the structures of macroporous resins consist of agglomerates of quasi-spherical portions with interconnecting cavities between them. Kunin verified this by showing that the absorption of a solvent by macroporous resins takes place in two steps [48]. The isoporous ion exchange resins, then, are characterized by an enhanced permeability due to the consistent network they possess. This is certainly the case if, beyond methylene bridges, crosslinks with larger dimensions are used for their synthesis [49]. For all isoporous ion exchange resins the high permeability for organic ions is reflected in their capacity to sorb rapidly ions of higher molecular weight. But especially with respect to commercial isoporous ion exchange resins there are objections to a very strict classification of ion exchange matrices into gel type, macroreticular and isoporous, whereby a distinction of ion exchange materials into either gel type or macroporous is made [50].

For a complete understanding of practical classifications with respect to porosity it may be best to mention here that among anion exchangers a characterization is made depending upon the monomers used in building the polymer, with the porosity being expressed as the simple water retention capacity of the chloride form, and the ionogenic groups. Gel type quaternary ammonium resins are further divided into two broad classes, standard and porous. Standard types have less than fifty percent water retention in the chloride form, porous more than fifty percent. It is important to realize that here the term porous implies nothing about the nature of the polymer crosslinking mechanism (Fisher).

It must be added that there is still another way of classifying ion exchange resins, which is based upon the shape of the resin particles and their size. Polymerization ion exchangers are made by suspension polymerization in water and the resulting resins are beads. The modern range of ion exchangers consists nearly exclusively — at least in the basic products — of spherical types. The previous condensation resins were usually made in a bulk polymerization process and subsequently crushed to irregular particles of the desired size range. It is also possible to make polycon-

densation ion exchangers from water-soluble monomers in a polymerization process in a nonaqueous solvent, and then they are also obtained as beads. Ion exchange resins in bead form are by far predominant but the granular resins have certain inherent advantages, such as greater surface area and higher void space in columns. One can perhaps say that the more diversified the applications of synthetic resin ion exchangers will become the more classes of resins will be demanded. Ion exchange resins in powder form for precoat filters may be cited as one example here [51], and ultrafine ion exchange resins with a particle size of 0.5–1.5  $\mu\text{m}$  are also available in the form of microspheres or agglomerates of microspheres. Because of their large surface, the exchange rate here is higher, due to the greater accessibility of ionic sites, although their application in columns is limited. Particles of this size, however, have their own field of application in the production of ion exchange papers and for incorporation into plastics, films, coatings, and fibers [52].

**Pellicular ion exchangers.** Synthetic ion exchange resins can in principle also be manufactured in other shapes than in beads or granules. The different shapes that can be chosen in forming the ion-exchanging materials are films, fibres, fabrics, tubes, foams or plates, etc. But in all these cases the whole material consists of the same polymer or copolymer, which has been converted into an ion exchanger. In addition to these, pellicular ion exchangers have been developed for special chromatographic purposes, with much higher chromatographic efficiency than conventional resins. Pellicular ion exchangers are composed of thin layers of polymeric exchange material bonded to glass beads. The latter enables the material to withstand the high pressure required and the thin layer of ion exchanging material yields fast kinetics and sharp separations at high speeds. The preparation of both anion and cation pellicular exchangers is quite easy. Glass beads of approximately 50  $\mu\text{m}$  diameter are coated with a solution of styrene, divinylbenzene, and benzoylperoxide in ether and the solvent is evaporated. Polymerization and crosslinking is carried out at 90 °C in an aqueous suspension of the coated beads. The product is washed with water, acetone, benzene, and methanol, and then converted into the ion exchangers. The anion exchanger is prepared by chloromethylating the copolymer layer and reacting the product with dimethylbenzylamine. The pellicular ion exchanger is then sieved and washed with 2 mol/l NaOH and HCl solutions and dried. A pellicular cation exchanger is similarly prepared by sulfonating the coating of the glass beads with 98% sulfuric acid at 90 °C for 30 minutes. For making crosslinked poly(ethylene imine) pellicular exchangers, the water from commercial poly(ethylene imine) (Dow Chemical Co.) is removed by distillation with benzene. Glass beads are then coated with a solution of the dry poly(ethylene imine) in methylene chloride and the solvent is evaporated. The coated beads are exposed to methylene bromide vapor at 130 °C for 10 minutes in order to crosslink the polymer. The product is washed with acetone, water, diluted hydrochloric acid, then with water and dried (Horvath et al., [53]). With emphasis on controlled surface porosity in commercial pellicular ion exchangers (Zipax®; Trademark of DuPont de Nemours

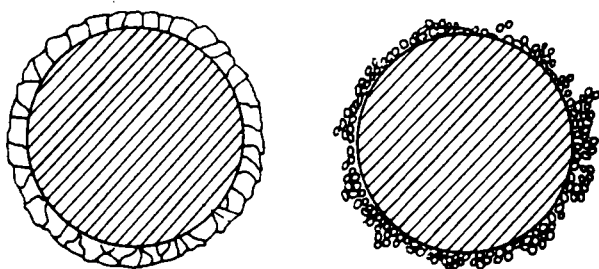


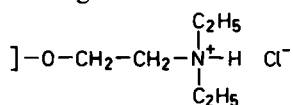
Figure 1.7 Pellicular ion exchangers with film-like (left) and porous (right) surface on solid inert core.

& Co., Wilmington, Del., USA) it was first shown that rapid separations of nucleotides and nucleic acid bases can be carried out due to the greatly improved mass transport effects [54]. The strong anion exchanger and the strong cation exchanger are still available for high pressure liquid chromatography since the hard, spherical nature of these exchangers permit their operation at high column input pressures. Figure 1.7 shows by way of comparison the structure of an ordinary pellicular ion exchanger and a superficially porous ion exchanger both built on a solid inert core. Further applications may be limited due to exchange capacities of only 0.162 mequ/ml as reported for similar ion exchangers [55].

**Partial ionogenic ion exchange resins.** It was as early as in 1952 that D. K. Hale stated during a Manchester ion exchange symposium that, when encountering difficulties in performing chromatographic separations with resins of low crosslinking, surface sulfonated polystyrene resins might be of help in making difficult separations [56]. A few researchers then investigated partially sulfonated ion exchange resin beads, but the results indicated that unless the beads had very low crosslinking and much care was taken, sulfonation occurred to a different extent within single beads in the same reaction mixture. No further attention was paid to this knowledge during the development of ion exchange chromatography until 1969, when Skafi and Lieser prepared superficially sulfonated exchange resins that were highly crosslinked styrene-divinylbenzene copolymers. Because particle diffusion was thus cut down the exchange equilibrium was attained rapidly with these resins and aside from the fact that the capacity was several orders of magnitude smaller than that of common exchange resins some excellent practical separations were obtained [57]. Further investigation then described the preparation of low capacity, partially sulfonated macroporous cation exchange resins and the measurement of distribution data and selectivity coefficients of multivalent metal ions on these resins. Macroporous resins are chemically and mechanically stable: they swell and shrink very little, and the liquid content is essentially the same no matter what the liquid is. These properties made such resins ideal for modern forced-flow chromatography [58]. With the introduction of the so-called ion chromatography Small et al. described the preparation of a resin of very low cation exchange

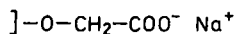
capacity by surface sulfonation of a styrene-divinylbenzene copolymer with 2% crosslinking. The manufacturing process involved heating at approx. 100 °C the copolymer for several minutes with an excess of concentrated sulfuric acid, which led to the formation of a thin surface shell of sulfonic acid groups. The capacity of a typical resin of this type is around 0.02 mequ/g of starting copolymer. Apart from being a resin of low capacity, the pellicular nature of the sulfonated material was expected to have favorable mass transfer characteristics due to the availability of all of the active sites [59]. The ion chromatography system of the same group of researchers uses a separation column containing a patented and commercially utilized anion exchange resin. For a simpler method called anion chromatography, which separates mixtures of anions without a suppressor column, an anion exchange resin with very low capacity was prepared by chloromethylation and amination with trimethylamine, starting from macroreticular highly crosslinked polystyrene beads XAD-1; this yielded a capacity of 0.007 mequ/g [60]. Systematic investigation of the preparation and ion chromatographic application of surface-sulfonated cation exchangers revealed, on the other hand, the effect of sulfonation temperature and time on the capacity of the materials from unswollen polystyrene-divinylbenzene copolymers, and it was found that ion-chromatographic separations can be advantageously influenced by optimization of the capacity and divinylbenzene content of the resins [61]. Finally it can be said that the efficiency of ion exchange chromatography is improved by decreasing the path length for the diffusion of ions to the place of sorption. This can be achieved by 1. granule size decrease, 2. using surface layer ion exchangers, and 3. using porous exchangers in which the diffusion is fast owing to the small dimensions of sorbent microgranules (which are immobilized by inert binder), and the presence of large transport pores [62].

New ion exchange chromatography gels based on vinyl polymers can fill the gap between the materials developed for use in HPLC and ion exchange chromatography with conventional ion exchangers. The matrix of these gels consists of hydrophilic vinyl polymers and, in contrast to other gels based on dextran, agarose or poly(acryl amide), contains pores between the intertwined polymer chains. This structure results in a mechanical stability hitherto unattainable with large-pore gels. Because of ether linkages and hydroxyl groups both the surface of the gel particles as the walls of the pores show strong hydrophilic properties. The basic gel is commercially available in five different pore sizes, covering in gel permeation chromatography separations in a molecular weight range from 100 to far beyond  $10^7$ . By modification ion exchangers are obtained. The semirigid crosslinked gel has excellent permeability as a result of the highly stable gel matrix. The ion exchangers DEAE-650 and CM-650 are stable at pressures up to 7 bar. In DEAE-650 the diethylaminoethyl groups are bound to the hydroxyl groups of the matrix via ether linkages





resulting in a weakly basic anion exchanger, and in CM-650 the carboxymethyl groups are also bound via ether linkages to the hydroxyl groups of the matrix



resulting in a weakly acidic cation exchanger. Both ion exchangers are available in two particle size ranges, i. e. Type S: particle size, moistened with water, 25–50  $\mu\text{m}$ , and Type M: particle size, moistened with water, 45–90  $\mu\text{m}$ .

The individual ionic groups of these ion exchangers have steep titration curves, as shown in Figure 1.8, and, as a result, do not have any buffer activity. The titration curves also show the ion exchange capacity and its dependence on pH.

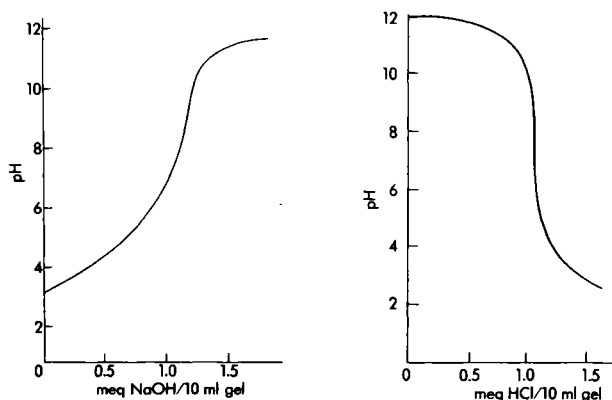
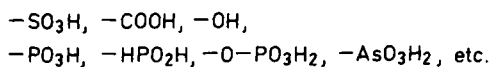


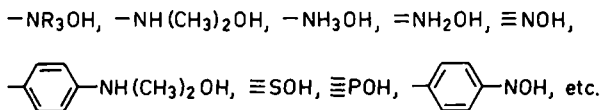
Figure 1.8 New ion exchanger gels. Titration curve of CM-650 (left) and DEAE-650 (right).

Further remarkable properties of these ion exchangers are: high pressure durability, negligible volume change with varying pH and ionic strength, high resolution at high flow rates, and the fact that the column can be packed to give uniform packing densities. The negligible change in the gel-bed volume means that the eluant can be changed or a gradient of pH or ionic strength can simply and rapidly be applied. Certain organic solvents can also be applied in the same manner. Packed in columns these ion exchangers can be regenerated in the presence of buffer solutions due to their high mechanical strength and chemical stability. Their exceptional mechanical strength permits these ion exchangers to be packed into stainless steel columns at packing pressures of 3–5  $\text{kg/cm}^2$ , which permits the connection of an HPLC system [63].

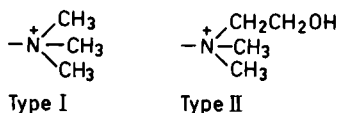
Regardless of the role played by the matrix in determining the properties of an ion exchanger, the decisive factor is the ionogenic group. Up to now, the following groups have been incorporated into cation exchangers:



and into anion exchangers:



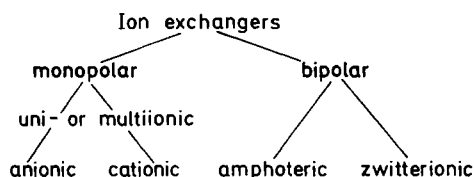
It is the ionogenic groups that confer the property of ion exchanger to the matrix. Depending on the acidity or basicity of the ionogenic group, one distinguishes between strong and weak acid and between strong and weak base ion exchangers. It has become accepted practice to distinguish between two types of strong base ion exchangers: Type I contains a trimethylamine group and Type II a dimethyl- $\beta$ -hydroxyethylamine group:



Type I is more strongly basic than Type II, but more difficult to regenerate. Type II has a higher thermal stability, but is more sensitive to oxidants.

An ion exchanger containing only one type of ionogenic group is called a monofunctional ion exchanger, an ion exchanger containing two types of ionogenic groups is called a bifunctional ion exchanger, and in general an ion exchanger containing more than one type of ionogenic group is called a polyfunctional ion exchanger (IUPAC). Cation exchangers containing two different ionogenic groups with the same charge, such as sulfonic acid and carboxylic acid groups, are in practice known as polyfunctional. For example, copolymers of acrylic acid or methacrylic acid with divinylbenzene have been sulfonated, and mixed sulfonic acid and phosphonic acid resins have also been produced. These would be called polyfunctional materials. In addition to cation and anion exchangers, amphoteric exchangers exist containing both acid and base groups. These would be called bifunctional materials. For example, condensation products of amines and phenols contain both very weakly acidic phenolic groups and basic amino groups. Bipolar exchange resins have also been prepared by the introduction of acidic and basic groups into the same matrix of a styrene-divinylbenzene copolymer.

A classification scheme based upon the type and number of ionic groups can therefore be propounded that includes — in a slight modification of an original proposal [64] — the important point that both anionic as well as cationic groups can be present as one (uni-) or as more than one (multi-) ionic site, this covering the fact that uniionic and multiionic materials of the same polarity must be distinguished:



According to this classification the bipolar ion exchanging materials are easier to subdivide further into amphoteric and zwitterionic, without yet specifying whether in this group there is still more to be elucidated.

The conditions required for a matrix, especially insolubility, are satisfied by a number of polymers. Many of these polymers, however, do not contain chemical groups with an ion exchange capacity. Although such groups can be introduced into most polymers, the end products still cannot be used in ion exchange, since their water solubility increases together with the ionic and thus with the hydrophilic groups. Consequently, only the cited polymers and copolymers are suitable for the synthesis of ion exchangers. Exceptions from this general practice are to be found in work done on the synthesis of certain phosphorylated ion exchange resins based on low molecular weight polyethylene (PE-515, Dow Chemical Company), used for the adsorption of uranium. The commercial polyethylene is phosphorylated with  $\text{PCl}_3$  and oxygen and then crosslinked with diamines and diols, yielding a product which is regular in size and insoluble in water. This resin shows a higher capacity than a commercial ion exchange resin of the styrene-divinylbenzene series [65].

**Strong acid cation exchangers of the sulfonic acid type.** The strong acid cation exchangers with ionogenic groups consisting of sulfonic acid have attained the greatest importance among ion exchangers produced from a matrix of styrene with divinylbenzene as the crosslinking agent, since they can be used industrially for water softening. They are produced by the sulfonation of suspension copolymer beads with sulfuric acid, sulfur trioxide, fuming sulfuric acid or chlorosulfonic acid. The  $\text{SO}_3$ -groups, which are the ionic groups yielding the cation exchange function, are probably primarily in para position and, for steric reasons, a double sulfonation is probably impossible. The ion exchange capacity of 5 mequ/g which is usually obtained confirms that only one aromatic ring on the average has been sulfonated, but experience has shown that at least one reactive site can be introduced for each aromatic ring in the copolymer, giving rise to the high exchange capacities.

The production of a strong acid cation exchanger of the sulfonic acid type involved a number of problems of detail which have only been solved with time. It is important to obtain undamaged crack-free beads. From the chemical standpoint, the sulfonation reaction leads to exchangers which contain hydrogen ions as the counter ions. By treatment with sodium hydroxide solution, the exchangers are then converted into the  $\text{Na}^+$ -form, in which form they are then used. Complete conversion into the Na-form is important because the hydrogen ions remaining in

an exchanger may lead to equipment corrosion when it is used, for example, in water softening.

**Weak acid cation exchangers of the carboxylic acid type.** In the most frequently used forms, the ionogenic group represented by carboxyl in weak acid cation exchangers is provided by one of the copolymer components, i. e. primarily acrylic or methacrylic acid that has been crosslinked with divinylbenzene, so that another production step becomes unnecessary. With dissociation constants of between  $10^{-5}$  and  $10^{-7}$ , they are weak acids which can be very effectively converted from the salt into the acid form by means of strong acids. Because of their high selectivity for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, a regeneration with sodium chloride is not very effective and practically not feasible. The carboxyl cation exchangers are primarily suited for the removal of cations from basic solutions and for the splitting of weakly alkaline salts of polyvalent cations. However, structural modifications can also increase the acidity of carboxyl cation exchangers to such a degree that a splitting of sodium and potassium salts is possible [66]. In general, the acrylic acid resin is a slightly stronger acid than the methacrylic acid product and is therefore more useful in water treatment, especially for alkalinity reduction [67].

**Phosphorus and arsenic-containing cation exchangers.** Although these types of cation exchangers are not of great significance for large industrial applications, they are of interest as medium-strong acid exchangers because of their selectivity and high capacities. Once a phosphonic acid resin called Duolite ES-63 was available in limited quantities commercially. A number of routes can be used for making resins containing phosphonic, phosphonous, phosphinic, or phosphoric acid groups [68]. When phosphorous trichloride is reacted with styrene-divinylbenzene beads, the dichlorophosphine derivative is formed. This can then be converted to the mono-basic phosphonous acid derivative by hydrolysis and then to the dibasic phosphonic acid derivative by oxidation. Alternatively, the dichlorophosphine can be oxidized and then hydrolyzed to give the dibasic acid [69]. The phosphonic acid resins are intermediate in acidity between the sulfonic and the carboxylic acid resins. The demand for this type of ion exchanger has been small, probably also because of its high price. Applications have been limited to special uses, for instance rare earth separations [70].

Arsenic-containing cation exchanger types have greater significance because of their selectivity, particularly with regard to their high affinity for uranium cations. On Soviet-made arsenic-containing ion exchangers the sorption of tantalum and niobium has been studied. A partition coefficient for tantalum more than 2–3 times that of the other exchangers compared [71] was obtained.

**Polyfunctional cation exchangers.** As mentioned before, polyfunctional or, preferably, multi-ionic cation exchangers are understood as containing two or more different ionic groups of the same charge, for instance sulfonic and carboxylic groups. The easiest approach to producing this type of bi-ionic exchanger is the

sulfonation of copolymers of acrylic acid or methacrylic acid with divinylbenzene. Other multi-ionic resins contain the sulfonic and phenolic or the sulfonic and phosphonic groups. The polyfunctional cation exchangers have been evaluated in a broader sense by scientists in both academic and industrial institutions, while ion exchange materials for water treatment containing either the sulfonic and carboxylic groups for cation exchangers or various amino groups for anion exchangers dominated the interest of the manufacturers of ion exchange resins. Commercial bifunctional acid resins (and it should be noted that this term is also in use) are found among the ion exchangers produced in Russia under the names Kationit KBU-1 — a styrene-methacrylic polymerization resin with sulfonic and carboxylic ionic groups — and KU-1 — a polycondensation resin made from phenolsulfonic acid and formaldehyde.

**Strong base quaternary ammonium anion exchangers.** These anion exchangers are obtained by a relatively simple method from the chloromethylation products of styrene-divinylbenzene copolymers by their conversion with tertiary amines. The exchangers obtained are extremely stable and have a high exchange capacity. As strongly basic products they are also capable of exchanging silicate and carbonate. They are easily converted from the chloride form into the OH-form by treatment with NaOH. This regeneration is difficult, however, with  $\text{Na}_2\text{CO}_3$ , and almost impossible with  $\text{NH}_4\text{OH}$ . By conversion with trimethylamine one obtains the strongly basic anion exchanger known as Type I, which, in general, is the most common one. For reasons of regeneration feasibility, a Type II was finally developed with dimethylethanolamine which proved to be less stable, and did not become as important as expected, since the Type I resin is favored for the high temperature applications where chemical stability differences are most apparent [72]. Recently a new type of strongly basic anion exchanger based on an acrylamide matrix has been introduced, with test results showing an increase in the operating capacity of nearly a hundred percent as compared with conventional Type I resins [73].

**Weak base anion exchangers of the amine type.** This group of synthetic ion exchange resins comprises a rather complex range of products — there are more variations in composition and properties among weak base resins than in any other class of ion exchange material. The group includes materials with ionogenic groups of primary ( $-\text{NH}_2$ ), secondary ( $=\text{NH}$ ) and tertiary amine ( $\equiv\text{N}$ ) functionality, individually or in mixtures. The latter would be themselves have to be classified as polyfunctional or multi-ionic weak base amine anion exchangers [74]. In building the matrix polycondensates and addition polymers serve for their production. Besides the previous aminated condensation products of phenol and formaldehyde, three principal types of weak base resins have been developed: Condensation products of epichlorohydrin with amines or ammonia, acrylic polymers, and amine derivatives of chloromethylated styrene-divinylbenzene copolymers. The ion exchangers thus obtained are suitable for sorbing strong acids with good capacity,

but they are limited kinetically. The kinetics can be improved by the incorporation of about 10% of quaternary ammonium groups, thus creating another mixed-ionogenic or polyfunctional anion exchanger; it is then more a medium base resin with the good capacities of the weak base resin together with the superior kinetics required for acceptable rinse, especially in the practical application of water demineralization following the regeneration with caustic soda.

The classic weak base anion exchangers, because of their low basicity, sufficiently exchange only anions of strong acids, such as HCl or H<sub>2</sub>SO<sub>4</sub>; the anions of weaker acids, such as SiO<sub>3</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup>, are not extensively exchanged. For the same reason, however, these anion exchangers can also be converted into hydroxyl form by weak bases, such as sodium carbonate or ammonia. Their customary commercial chloride form is easily hydrolyzed. The weakly basic ionogenic groups cannot exchange neutral salt anions.

To improve the kinetic properties of weak base anion exchange resins the development has gone towards macroporous matrices with true porosity and high surface area. This structure has in commercial ranges almost displaced the gel structure used in the original styrene-divinylbenzene-based weak base resins.

**Anion exchangers of the pyridine type.** Gel type polymers with pyridine as the group with exchange activity are weakly basic anion exchangers. Little was published in the early years about their production and application. Materials of this type have always been expected to have good chemical, thermal, and radiation resistance as well as good kinetic characteristics [75]. It was then found that macroporous poly(vinylpyridine) anion exchangers possess a number of advantages, e. g., higher mechanical and osmotic stability, improved kinetic properties, over the above-mentioned gel type analogues [76]. Novel polyfunctional or multiionic anion exchangers on the basis of amino-substituted vinylpyridines have been described as being of interest as extractive sorbents for metals such as molybdenum, tungsten, gold, etc., with high capacity and chemical resistance, and as catalysts for certain chemical reactions [77]. Most of the research and development on anion exchangers of the pyridine type was as a result of the search for resins with specific exchange properties. This started with investigations into poly(1-hydroxy-4-vinylpyridine) ion exchangers [78] and led then mainly to the synthesis of amphoteric exchangers based on 4-vinylpyridine.

Depending on the counterion attached to the fixed group to maintain electroneutrality, the individual types can be classed under different forms. In the case of cation exchangers one speaks of an H-form or a Na-form and in anion exchangers of an OH-form or a Cl-form, etc. The exchangers can either be used in their delivered ionic form or they must be converted first into another form. The composition of the solution to be treated and the selectivity of an exchanger for certain ions generally determine the choice of an exchanger and its particular form. The choice of appropriate ion exchangers to solve a concrete chemical or other scientific problem is dictated by the application. The choice of a suitable resin for

Table 1.2 Conversion of ion exchange resins

Type of resin	Conversion	Reagent	Volume reagent per volume resin	Flow rate (cm/min)	Volume rinse water per volume resin	Method to test completeness
Strong acid Sulfonic acid cation exchanger	$\text{Na}^+ \rightarrow \text{H}^+$	2 N HCl	5	2	6	pH > 5 neutral
	$\text{H}^+ \rightarrow \text{Na}^+$	1 N NaCl,	5	2	6	$\text{Cl}^-$ negative
	$\text{Ca}^{2+} \rightarrow \text{Na}^+$	1 N NaOH	5	2	6	$\text{Cl}^-$ negative
		2 N NaCl				
Weak acid Carboxylic cation exchanger	$\text{H}^+ \rightarrow \text{Na}^+$	2 N NaOH	8	1	15	pH < 8
	$\text{Ca}^{2+} \rightarrow \text{Na}^+$	1 N NaCl	10	1	15	$\text{Cl}^-$ negative
	$\text{Ca}^{2+} \rightarrow \text{H}^+$	0.5 N HCl	4	1	15	pH > 5
Strong base anion exchanger Type I	$\text{Cl}^- \rightarrow \text{OH}^-$	2 N NaOH	8	2	8	pH < 9
	$\text{HCO}_3^- \rightarrow \text{OH}^-$	2 N NaOH	4	2	8	pH < 9
	$\text{OH}^- \rightarrow \text{formate}^-$	2 N formic acid	5	2	8	pH > 5
	$\text{Cl}^- \rightarrow \text{formate}^-$	use $\text{Cl}^- \rightarrow \text{OH}^-$ , then $\text{OH}^- \rightarrow \text{formate}^-$				
	$\text{Cl}^- \rightarrow \text{acetate}^-$	same as formate with HAc				
	$\text{Cl}^- \rightarrow \text{OH}^-$	2 N NaOH	5	2	10	pH < 9
	$\text{Cl}^- \rightarrow \text{NO}_3^-$	1 N $\text{NaNO}_3$	4	2	6	Na flame test negative
Type II	$\text{OH}^- \rightarrow \text{Cl}^-$	1 N HCl	3	1	4	pH > 6
	$\text{Cl}^- \rightarrow \text{OH}^-$	1 N $\text{NH}_4\text{OH}$	8	1	10	pH < 8

a given purpose may give rise to difficulties. It is to be hoped that the chapters of this volume dealing with the use of ion exchangers in industry and the various other fields will prove to be guidelines for the selection of an appropriate ion exchanger.

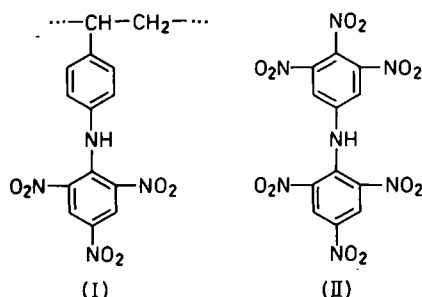
The conversion of an ion exchange resin from one ionic form to another is known as resin conversion and/or regeneration. The slight difference in meaning between these two terms lies in whether this process is carried out under economical aspects or not. In the laboratory the costs of the chemicals for converting a resin are usually negligible and it is more important to convert the resin sample quantitatively to a desired form using a considerable excess of the corresponding conversion reagent. Table 1.2 shows a survey of the common types of ion exchange resins and the conditions under which on a laboratory scale ion exchange resins are converted from one ionic form to another. Such conversions are normally performed in columns; it is then to be remembered that the resin may shrink, or it may swell by as much as hundred percent, depending on the conversion. Usually a test is carried out to determine the completeness of the conversion. As a rule, conversion is then complete when the first ion is no longer detected in the effluent. In addition, the easiest test method for completeness of conversion depends on the particular conversion: in many cases it can be evaluated by pH measurements or by simple qualitative tests. Rinsing the column using deionised water after completeness of conversion is the most common technique. In general, for any conversion for which the converting conditions are unknown, information can be gathered from the relative selectivities of the various counterions for the resin in use. If the conversion of a resin is to be achieved to an ionic form with a higher selectivity, the column is to be treated with two or three bed volumes of a 1M solution of the desired counterion. To convert to an ionic form with a lower relative selectivity for the resin in use, the volume of counterion solution needed will depend on the difference in selectivity, generally being one bed volume of 1M counterion solution for each unit difference in relative selectivity.

Certain special synthetic ion exchange resins require separate consideration, since they differ from customary resin types either because they have a special matrix or because of their particular reactive groups.

**Specific and chelate ion exchangers.** Specific ion exchangers are those types in which active groups have been introduced having the properties of a specific reagent. The specificity is based on the chemical structure of the ion exchanger itself and must not be confused with the phenomenon of selectivity. Because of its specificity, such an ion exchanger can sorb one ionic species to the exclusion of others under a broad range of conditions. Their mechanism of action will first be explained by a historical example.

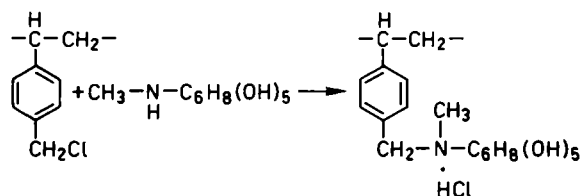
Skogseid [79] subjected polystyrene to nitrogenation, reduction, conversion of the formed polyaminostyrene with picrylic chloride, and renewed nitrogenation, obtaining an exchanger containing the following building blocks (I):





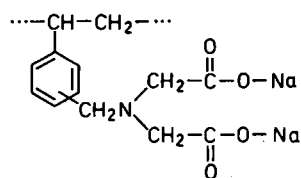
Dipicrylamine (II) is a specific precipitating agent of potassium, and the above ion exchanger shows, as a result, an excellent specific uptake of potassium ions.

A next step in the development of specific ion exchangers was the report on a boron specific resin by Kunin and Preuss [80]. To introduce a respective group the principle was employed that boric acid reacts readily with polyhydric alcohols to form an acid considerably stronger than the original boric acid. The boron specific ion exchange resin was, therefore, synthesized by aminating a chloromethylated styrene-divinylbenzene copolymer with *N*-methylglucamine according to the following diagrammatic equation

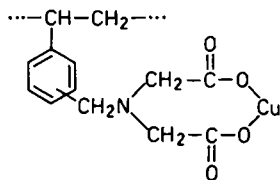


This resin shows a unique specificity on the grounds of the incorporated *N*-methylglucamine, which is known to form salts with acids and complexes with metals. Column tests indicated the utility of this ion exchange resin for removing boron from irrigation water and solutions containing unacceptable quantities of this trace element. The most important point is that the resin is readily regenerated with sulfuric acid.

Specific ion exchangers would, if seen in contrast to selective ion exchangers, include the entire group of chelate resins, whose specificity is based on the chelate or complex-forming reactive group. The best known commercial type is the iminodiacetate ion exchanger, Dowex A-1, in which the iminodiacetate groups are directly attached to the styrene matrix:



and which can fix polyvalent ions with a high affinity by the formation of heterocyclic metal chelate complexes:



A series of specific and chelating ion exchangers has been produced, but their main application was in the field of analysis [81]. The above chelate-forming polymers have ion exchange properties by virtue of their carboxylic acid groups. It is therefore recommended to equilibrate them with the same buffer solution from which the cations are to be removed in order to avoid ion shifts during their application. This dependence on the pH is shown for Dowex A-1 in the fact that the uptake of ions is very low below pH 2, increases sharply from pH 2 to pH 4, and reaches a maximum above pH 4. Since a true ion exchange takes place, any metal removed from solution is replaced by an equivalent amount of the ions originally on the resin. For regeneration, e. g. in a column, the chelate ion exchanger is washed with two bed volumes 1 N HCl, 5 bed volumes water, two bed volumes 1 N NaOH and then five bed volumes water.

Interest in the synthesis and investigation of chelating resins has again increased, as limitations in the use of the standard ion exchangers with well-known polar groups, such as sulfonic, carboxylic, or amine groups have become obvious. These resins are characterized by their selectivities, but if the relative selectivities of ions in a mixture are close to each other, these exchangers will take up all ions, regardless of whether this is desired or not. As a result an increased amount of regenerant is needed than would be required if certain ions were removed specifically. Further, a regenerant effluent having a mixture of ions makes reuse of the specific ions more difficult. It may then be especially difficult to remove toxic from non-toxic metals in standard operations. The relative selectivity coefficients of the standard sulfonic cation exchangers are close to each other in magnitude and are often overestimated in practical application. With the requirements for emissions of many metal ions into the environment being in parts per billion, new types of exchangers are essential that are either highly selective or specific for a particular ion to the exclusion of other ions.

Several types of specific ion exchangers are already on the commercial market. The first one, based on dipicrylamine, and synthesized by Skogseid has not proven practical commercially. In principle, given organic reagents that act as specific precipitants of specific ions, there is no reason for these molecules not to be attached to a polymeric matrix. An example of a specific resin for mercury ions, containing thiol as an active group, with a high operating capacity of more than 1 000 mequ/l, and a leakage of about 2 µg/l, has become known under the name Imac TMR

[82]. In operation, when a solution containing 10 mg/l each of cadmium, lead, copper and mercury ions is percolated through a thiol exchanger bed, the mercury ions even replace the cadmium, lead and copper ions (in this order), and still continue to be removed from the solution until breakthrough occurs.

In contrast to the use of the term “chelate ion exchangers” for the resins mentioned above, the term should be reserved for resins carrying reactive groups that are able to form inner complexes, i. e. real chelates, with selected ions. These resins combine the processes of ion exchange and complex formation. Reactive groups resulting in chelate formation are usually introduced into a premanufactured macromolecular matrix of either gel or macroporous type. During this process the matrix structure must remain unchanged. Reactions involving the ring formation of chelates with metal ions are characteristic for chemical groups of only a few elements that can act as electron donors in exchanging groups, namely oxygen, nitrogen, sulfur, phosphorus or arsenic. Such chelate ion exchangers are then distinguished from ordinary type ion exchangers in that the affinity of a particular metal ion depends mainly on the nature of the chelating groups, with the size of the ion, its charge and other physical properties being of secondary importance. The strength of the binding forces in an ordinary exchanger is of the order of 8 to 12 kJ/mol; it is appreciably higher in a chelating ion exchanger being of the order of 60 to 100 kJ/mol. The exchange process in chelate ion exchangers is slower than that in ordinary type ion exchangers and seems to be controlled either by particle diffusion or by a second order chemical reaction. Chelate ion exchangers with macroporous matrix structure have faster exchange rates.

Among the synthetic ion exchange resins described above, those of the gel type still have the greatest importance, and continue to be used most frequently in industry. The production of an ion exchanger requires specialized knowledge, so that it would hardly be worthwhile to attempt homemade preparation. Ion exchangers also assume a sort of intermediate position between a chemical product, which is manufactured and further processed, and equipment serving for the manufacture of a particular product. They are highly sophisticated chemical materials, but they are used only as processing aids; they are therefore only the transfer agents of a chemical process without being completely changed or turned to another purposes. Because of the possibility of reversible conversion into different forms, they have diverse applications and it would seem that they should have an unlimited life. Naturally, like any material, they are subject to chemical and mechanical wear and have only a limited life.

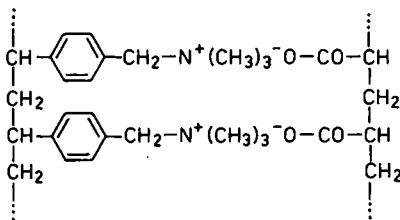
The synthetic resin ion exchangers available today are commercial products with registered tradenames, made by various manufacturers. In the Russian literature, on the other hand, ion exchangers are usually referred to as cationites or anionites, etc. Since in this case it has become customary to designate individual types only by letters or numbers, such as SBS, EDE- 10 P, etc., this somewhat confusing dual nomenclature must be retained. Appendix 1 of this volume lists a selection of

important commercial ion exchangers frequently cited in the literature. The number of available types is so large that it has become almost confusing. Data on their characteristics have been obtained from the technical literature of the manufacturers — the best source of information concerning the applicability of an available synthetic ion exchange resin.

The tables in the Appendix give the specification of an ion exchanger by covering the necessary data resulting from its properties. The acidity and basicity follow from the ionogenic group with its exchange activity and thus are immediately understandable. The production process determines the external form of an ion exchanger. While polymerization resins are generally delivered in the form of beads, polycondensation resins are available as milled granulates. The color of individual types ranges from white through yellow, brown, and dark brown to black. Important additional characteristics are their total exchange capacity, moisture content, particle size distribution, physical structure and stability, as well as data on elutable components. In practice, a knowledge of the intended application is necessary, which frequently needs to be determined specifically for special uses.

In conclusion, it may be said that the present significance of synthetic ion exchange resins results from their great mechanical strength and chemical resistance, high exchange rates, high capacity and the possibilities of varying their properties as a consequence of their synthetic nature. Their only disadvantage is a limited range of operating temperatures, although this range is sufficient for most purposes.

**Snake-cage ion exchangers.** The so-called snake-cage ion exchangers were developed as a separate group of ion exchange materials to permit the removal of salts from a single polyelectrolyte and regenerate the exhausted resin with water. In these snake-cage resins, a polymeric linear “snake” is formed by the polymerization of suitable monomers with a given charge in such a way that it is located in a polymeric crosslinked “cage” of opposite charge. Since the distance between charged groups determines their effect, considerable effort was needed to obtain a controlled structure of the effective interstices between negative and positive ionogenic groups. This was achieved by the polymerization of acrylic or methacrylic acid into different quaternary ammonium anion exchange resins [83]:



Such a snake-cage ion exchanger can exchange salts from aqueous solutions of organic compounds, such as glycerol, by simple sorption and can be regenerated subsequently by washing with water [84]. Since the snake-cage ion exchangers can

also have a selective action, they permit the separation of electrolytes, such as NaCl and NaOH. The ion retardation process is carried out with snake-cage ion exchangers. With respect to classification of synthetic ion exchangers snake-cage resins belong to the amphoteric ion exchangers.

**Inorganic ion exchangers.** Historically, it was inorganic ion exchangers that were first studied for the practical applicability of ion exchange [85]. Synthetic inorganic ion exchangers were prepared by Gans on the basis of findings obtained on mineral exchangers. They consisted of fused sodium aluminosilicates and had, because of their glassy nature, very poor kinetics. As permutites or hydrothermal synthetic zeolites they were used for water softening, but to regenerate these exchangers took longer than the softening cycle. They were of great interest for scientific investigation of ion exchange but they lasted only about ten years on the industrial market. The inorganic ion exchangers that followed were then modified natural products such as greensands (glauconites), bentonites and clay type minerals, with low operating capacities but faster regeneration rates. The synthetic sodium aluminosilicates had a longer lifetime under practical application aspects. They were precipitated out of solutions consisting of alum, sodium aluminate and sodium silicate. These precipitated gels had higher capacities but were very sensitive to low and high pH and readily fouled by iron present in water.

The principle of ion exchange is the same for the synthetic ion exchangers [86] as for the modified mineral exchangers [87]. The skeleton carries an excess charge which is compensated for by mobile counterions, as they are called in ion exchange nomenclature. In the case of the zeolites, this was found to be a consequence of the fact that a part of the  $\text{Si}^{4+}$  building blocks is replaced by  $\text{Al}^{3+}$  in the silicate lattice. The lacking positive charge is replaced by alkali or alkaline earth ions, which are as counterions freely mobile in the inorganic skeleton. The natural and the older synthetic inorganic ion exchangers are no longer of industrial significance. Nevertheless, driven by the wish to obtain ion exchange materials that are stable at higher temperatures and radiation-resistant, intensive research and development work has resumed in this field in recent years. Based on the data available, this involves the production or modification, as well as the characterization and application, of clays and clay minerals, new zeolites and the combined group of non-siliceous inorganic ion exchangers. These groups of inorganic ion exchangers are, because of their increasing importance, treated in detail in separate chapters of this volume. For commercial inorganic ion exchangers see Appendix 1.

**Cellulose, Dextran and Agarose ion exchangers.** As a result of a small number of carboxyl groups in its structure natural cellulose has ion exchange properties. Numerous reaction products can be obtained by the oxidation of cellulose. These products include hydroxycellulose with 15% COOH-groups, and which, in powdered form, must theoretically be considered ion exchangers, although they find little practical use because of their solubility in water. Powdered cellulose ion exchangers, which are now used in columnar processes, have become very important

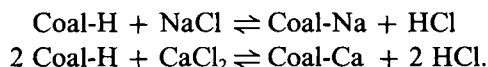
as a result of the studies of Peterson and Sober on protein separation — as was already mentioned in the section on the history of ion exchange and ion exchangers. Cellulose ion exchangers have ion-exchanging properties just as do the synthetic ion exchange resins, but they differ from the latter in a few important points. They are treated therefore in detail in a separate chapter of this volume. For commercial cellulose ion exchangers see Appendix 1.

The polysaccharide dextran (poly- $\alpha$ -1,6-glucan), which is produced from sucrose by microbiological methods, consists of fibrous molecules that can be converted with epichlorohydrin and, as a result of this crosslinking, be transformed into polymers with a three-dimensional structure. According to the studies of Porath and Flodin, these can be used for the fractionation of water-soluble substances. These dextrans, which are obtained as beads from the suspension polymerization process, have proven to be useful as molecular sieves in gel filtration and in molecular sieve chromatography for chromatographic separations based on molecular weight. They can be obtained in standardized form under the tradename Sephadex. Since the number of hydroxyl groups is only insignificantly modified by crosslinking, it is possible to prepare esters and ethers by further reactions with suitable reactants and to introduce ionic groups into the dextran molecule, thus arriving at ion exchange materials with polysaccharide as the matrix. In an early study Porath and Lindner demonstrated that oxytocin and vasopressin can be separated on dextran diethylaminoethylether by the ion exclusion process. Dextran ion exchangers are treated in detail in a separate chapter of this volume.

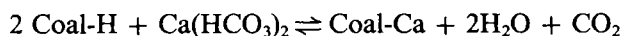
Agar and agarose derivatives were first prepared for chromatography, electrophoresis and gel-bound enzymes by Porath and coworkers whose aim was to produce alkalistable and thermostable, insoluble spherical agar particles with a very low adsorption capacity. For this purpose the sulfate ester groups present in the original agar are removed by alkaline hydrolysis of crosslinked agar, in bead form, at an elevated temperature. The reaction is performed in the presence of sodium borohydride to prevent simultaneous oxidation. Further reduction of the adsorption capacity may be accomplished by treatment of the gel with lithium aluminum hydride in dioxane. It was found that desulfated and reduced agar and agarose gels can be packed in beds with excellent flow and molecular sieve properties [88].

**Coal based ion exchangers and other materials with ion-exchanging properties.** If wood, peat, firewood, soft coal, or anthracite is treated with oxidizing reagents or concentrated sulfuric acid, it is possible to introduce additional groups with an exchange capacity, beyond the existing OH- and COOH-groups with their exchange capacities. Also heating with caustic soda under anhydrous conditions permits the production of coals with ion exchange properties. Another group, the ammoniated coals, are also anion exchangers based on coal. The most important coal ion exchangers, which are also commercially available, are the sulfonated coals. These products contain a mixture of sulfonic, carboxylic and phenol groups of very different acid strengths. Depending on these different acid strengths, only phenol

and carboxylic groups or, with a sufficient excess, also the sulfonic acid groups are transformed into the  $H^+$ -form during regeneration. If sulfonic acid groups are also present in the H-form, sulfonated coals are capable of neutral salt splitting according to the following equations:



If about 100% of theory is used for regeneration, only a conversion with the alkaline salts takes place according to:



a reaction which is very economically used in the "starvation process" for partial deionization.

Among previously available commercial coal ion exchangers, the products Dusarit S and Imac C 19 of the former Imacti Industriële Maatschappij Activit N. V., Amsterdam, should be mentioned. Dusarit S was a multiionic cation exchanger of high physical stability, in the form of granulate (0.3–1.2 mm) based on sulfonated coal and with the properties of activated carbon. It was delivered in the Na-form and served for the treatment of water and purification of glucose juices in the Na- and H-cycle. Imac C 19 was a multiionic strong and weak granular cation exchanger (0.3–1.2 mm) delivered in the H-form. It was used for the decarbonation of carbonate-rich water with a high regenerant effect. Table 1.3 lists the other properties of these coal ion exchangers, together with other commercial products. Occasionally, coal ion exchangers produced commercially or in the laboratory are also used for ion exchange chromatography.

Table 1.3 Coal ion exchangers (cation exchangers)

Designation	Capacity	Heat stability (°C)	Permissible range (pH)
Dusarit S	20 or 10 g CaO/l	80	0–14
Imac C 19	28 g CaO/l	80	4–14
Permutit S 53	10–15 g CaO/l	40	0–11
Permutit HI 53	1–28 g CaO/l	40	0–10
Zerolit Na	1.8 mequ/g		
Zeo-Carb HI		30	0–8

A number of other natural and industrial materials can also be converted into ion exchangers by chemical treatment. Tar, paper, cotton, pectin, tannin, and lignin are well-known examples. Under the influence of sulfuric acid, lignin is converted into lignic acid, with ion exchange properties which were recognized by Freudenberg at the time when the first synthetic ion exchange resins were produced. By treating lignin-containing substances, particularly sawdust, with sodium sulfite solutions,

very inexpensive ion exchangers which can be used for the adsorption of radionuclides are obtained. Alginic acid has always been of some interest as a cation exchanger. Occasionally, it was also used for separations by ion exchange chromatography. The possible therapeutic applications of alginates are of particular interest because of their Sr-Ca-ion exchange reactions. Further details on carbonaceous as well as other ion exchange materials can be found in a separate chapter of this volume. Liquid ion exchangers and ion exchange membranes are also described in detail in separate chapters.

### 1.1.2.2 Structures

Structural chemistry is, in general, a part of physical chemistry that aims at the elucidation of the structures of molecules, in particular the arrangement and bonding of atoms. The term structure is used in many kinds of connexions in chemistry – in particular in the everyday language of organic chemistry by the structure of an organic compound the structural formula is actually meant. Structural formula are the words in the language of organic chemistry and they are basic to understanding and communicating everything else in the subject. Geometric structures are also important in inorganic chemistry, where crystalline structures especially are investigated in order to get an idea of the total molecular structure and the reactions that can be expected from the crystals.

The structure of organic polymers, in particular, is necessarily complicated because the possibilities of synthesizing such polymeric substances are numerous. In the simplest case one has what could be called a repetition of structural units along a chain. The next step in building polymeric structures is to form copolymers. Here a very wide variety of combinations is feasible, not only by the formation of branched macromolecules, but especially because, besides random copolymers, graft and block copolymers can be made up; further, there are many copolymers that do not fall under any distinct classification. It is also well known that polymer molecules can be linked together by including in the polymerization formulation a monomer having two or more functional groups. When polymer molecules are connected to one another by a sufficient number of interchain bonds, the network formed is, in effect, one giant molecule. The character of a network polymer depends primarily on the concentration of the crosslinking agent and the type and concentration of diluent present when the network is formed. The general principles of structural chemistry can hardly be applied to such network polymers.

It may sometimes be quite difficult to understand the title of a publication on ion exchangers that contains the word “structure”, i. e. precisely what meaning this word has in the context of the paper. The synthetic organic ion exchangers are, in the majority, based on random polymeric networks consisting of styrene or an acrylic component crosslinked with divinylbenzene into which ionogenic groups have been incorporated. When the structures of such products are being discussed,



and this also includes matrices that have been formed by the simpler but less practiced polycondensation reaction, it is important to note that in the literature several types of investigation of the structure of ion exchangers can be found. These comprise the following categories:

The structure of the complete ion exchanger, including an investigation into the distribution of the fixed ions.

The structure of the matrix copolymer or polycondensate network as it was formed during polymerization.

The structure relative to the fixation of the counterions.

The structure or structural changes due to interaction with solvents.

In an early attempt Grubhofer [89] suggested a model for the molecular structure of polystyrene ion exchangers crosslinked with divinylbenzene, which served to calculate the distances within the structure limiting ion diffusion through the ion exchanger. If  $x$  is the molar percentage of the crosslinking agent divinylbenzene, then the number of ethylene groups per crosslink between the points of attachment of the latter is  $N_{\text{Eth}} = 50/x + 0.5$ . The distance between two branching points in the network, when taking into account the thickness of the benzene ring at  $4.5 \text{ \AA}$ , the length of two carbon-carbon bonds in the phenyl group at  $2 \cdot 1.5 \text{ \AA}$ , and the size of a single monomer unit at  $2.2 \text{ \AA}$  is  $a = 2.2N_{\text{Eth}} + 7.5 \text{ \AA}$ . The angle between the main chain and the crosslink is assumed to be  $90^\circ$ . To obtain the dimensions of the cell accessible to the diffusion of ions, it is necessary to subtract from the resulting cell diameter the thickness of the polystyrene chain, i. e.  $15 \text{ \AA}$ . The results obtained for a high content of crosslinking agent in the resin agree well with independent estimates of the cell dimensions and with what is known from diffusion studies. For low content of the crosslinking agent they agree with data obtained by electron microscope studies of the same specimens in the dry state. This shows that the model describes correctly the fundamental structural characteristics of resins based on styrene and divinylbenzene. From the polymer chemistry point of view such a model is undoubtedly still a quite rough approximation, disregarding as it does a whole series of phenomena belonging to the formation of copolymer structures and especially to sulfonated ion exchange resin structures, e. g., the presence of amorphous regions, the entanglement of chains, non-uniform sulfonation or new reactions during sulfonation, etc.

Marcus and Kertes in their reflections on the structure of polystyrene-divinylbenzene-type ion exchangers based on the models shown in Figure 1.9 assume that the skeleton of such an exchanger, which consists of aliphatic  $-\text{CH}_2\text{CH}-$  chains with attached benzene rings and the divinylbenzene bridges, is fairly elastic, and considerable changes of volume are, therefore, possible. Considering a fully swollen cation or anion exchange resin 10% crosslinked, the aromatic rings are connected to the skeleton in repeating units, about  $8 \text{ \AA}$  apart, with the rings striving to be parallel to each other in order to minimize mutual interaction. The fixed groups

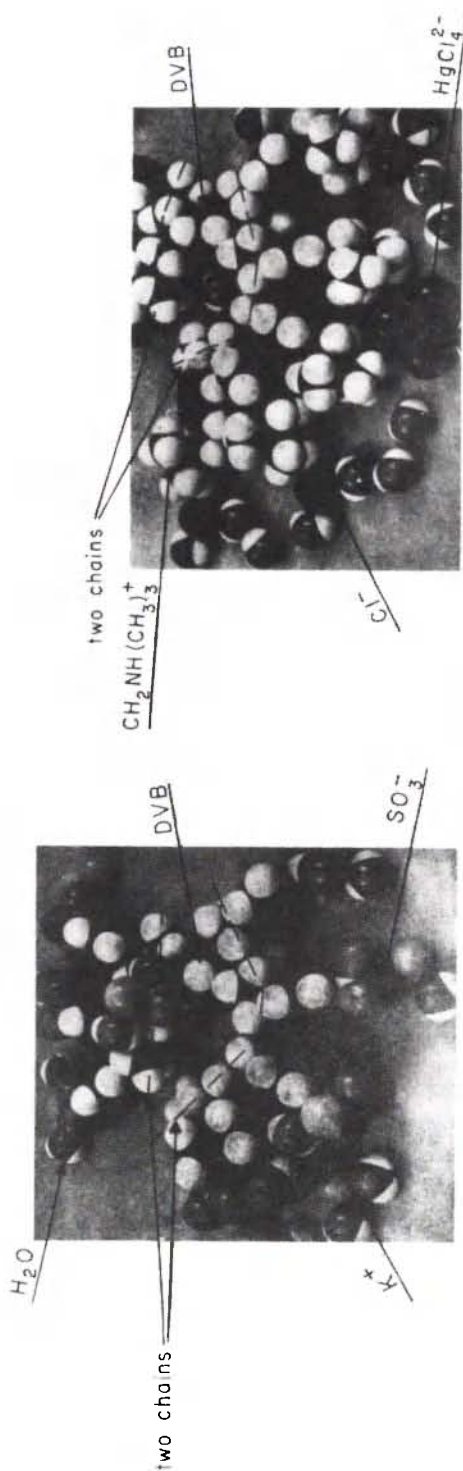


Figure 1.9 Three-dimensional models of polystyrene-divinylbenzene ion exchange resins with nominal 12% crosslinking showing the relative size of ionogenic groups, counterions, hydrocarbon skeleton and free space. Left: strong acid cation exchanger K-form; right: strong base quaternary ammonium anion exchanger Cl-form. (From Ion Exchange and Solvent Extraction of Metals: Conplexes, Y. Marcus and A. S. Kettle, Wiley, London, 1969).

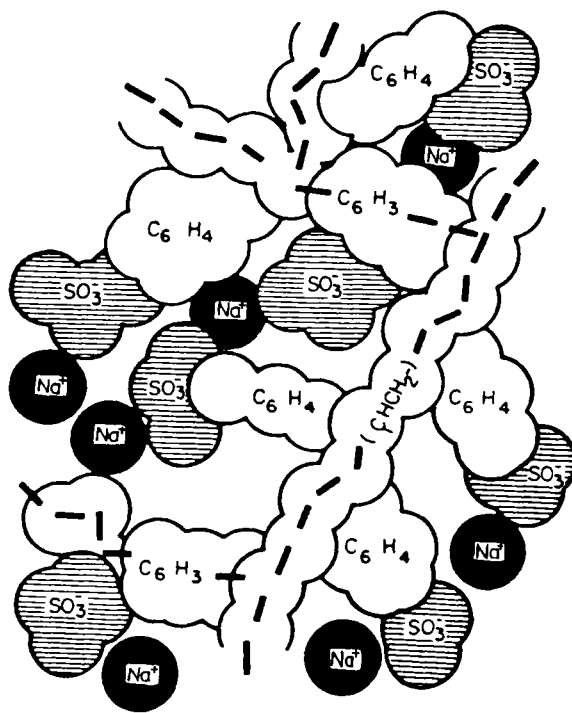


Figure 1.10 Two-dimensional projection of a strong acid sulfonic polystyrene-divinylbenzene cation exchanger with nominal 16% crosslinking. (From *Molecular Science and Engineering*, ed. A. R. von Hippel. M.I.T. Press, Cambridge, 1959).

are located at the ends of the benzene rings. Crosslinking has the effect of producing cavities  $50 \text{ \AA}$  in average diameter which are lined by the exchange sites. These cavities are filled by water. With reference to the schematic representation of a fragment of a cation exchanger as shown in Figure 1.10 it should be pointed out that this two-dimensional projection of the model appears somewhat more crowded than the model actually is. But it must also be pointed out that an important feature of such ion exchange resins is the randomness of the crosslinks, resulting in a completely disordered structure of the exchanger. It is further assumed that there is a wide range of distances between sites, and that the environment of a site may vary from preponderately of organic material to freely available space occupied by mobile solvent. The flexibility of the chains, it is said, causes, of course, changes in the environment with time (and pressure?) [90].

But it would seem to be more appropriate to approach the structural questions of ion exchangers from a synthetic point of view in order to elucidate what the structure might be. In this light Arden has presented in a series of lectures in 1974 a philosophy of ion exchange resin structures [91]. Arden argues that it is probably

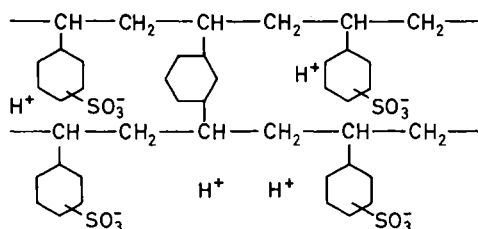


Figure 1.11 Standard method of presenting the structure of a strong acid sulfonic polystyrene-divinylbenzene cation exchanger leading to the basic misconception that the structure is an open network, with parallel chains, uniform crosslinks, and a virtually flat structure.

true to say that the whole of early thinking on ion exchange resins was incorrect, as a result of the standard method of writing out the structure of the polystyrene resin as shown in Figure 1.11; he emphasizes that this first basic misconception led investigators to conceive of the resins as an open network, with parallel chains, uniform crosslinks, and a virtually flat structure. But in reality this is very far from the truth. When the original styrene-divinylbenzene mixture starts to polymerize under the influence of the catalyst, a very large number of different crosslinked chains start to form simultaneously. As they grow, they intermingle with each other and grow through each other, as depicted in Figure 1.12. The diagrammatic molecule A on the left is 8% crosslinked, as is the one B in the middle. If these two molecules are separate from each other then they give a certain pore size which determines the measured characteristics of the resin. If the same two prototype molecules are formed so that they are entangled as shown in diagram C, then because the crosslinks are closed they cannot be separated from each other. They are still exactly 8% crosslinked, but the effective pore size is now only half of what it was before, and the apparent measured crosslinking is consequently considerably higher than 8%. In reality, while the original polymer is being manufactured the chains entangle and there are no resins which are not entangled, although the degree of entanglement may be modified by special procedures. The measured crosslinking of every resin in existence is in fact not the true crosslinking, but the

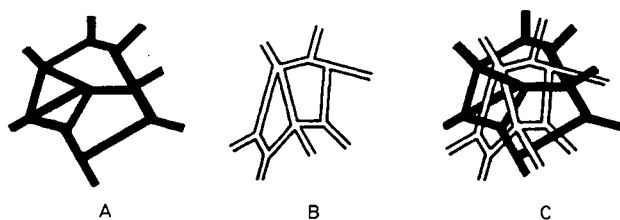


Figure 1.12 Chain entanglement of different crosslinked chains.

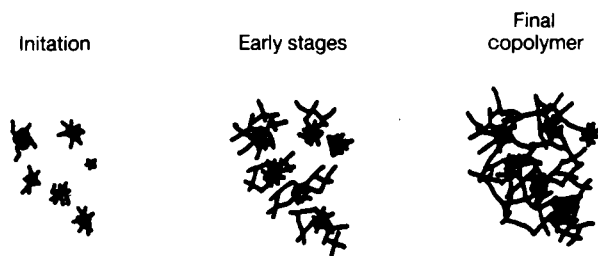


Figure 1.13 Progress of copolymerization from initiation to the final copolymer matrix.

sum of the two effects of divinylbenzene crosslinks together with the entanglement factor. It is in fact possible to deliberately introduce entanglement, and it has also been possible to synthesize so-called re-entangled structures. What is noticeable, however, is that as the degree of deliberate entanglement is increased, the resin becomes more brittle, and mechanically fragile. It follows that chain entanglement is a negative feature, which should be avoided as much as possible. The second basic misconception in at least the simplified picture of ion exchange macromolecules is that the crosslinking is uniform. This is not the case, since in the polymerization of styrene and divinylbenzene, there are three separate processes, not counting the ones due to the presence of ethylstyrene in the divinylbenzene: a) DVB-DVB polymerization, which is rapid, b) DVB-styrene polymerization, which is intermediate and c) styrene-styrene polymerization, which is slow. From this it results that, as polymerization starts at the catalyst centres, the first polymer to form has an excessively high DVB content, and is thus highly crosslinked. As the reaction proceeds, over a period of several hours, however, the later polymer is less and less crosslinked, until the final chains are completely linear. These process steps are shown in Figure 1.13. The final copolymer, and the exchangers made from it, are extremely heterogeneous, with highly crosslinked regions, surrounded by more loosely crosslinked areas. The disadvantages resulting from this heterogeneity will be discussed elsewhere. In fact, the development of newer resins was brought about by the problem of organic poisoning and the need to overcome this problem. Thus new types of resin structures were developed which had either been “disentangled” or which had “sintered”, “spongelike” or “macroporous” structures. It is in fact possible, by the use of deliberate re-entanglement or disentanglement, to produce ranges of different resins, containing from 0% to over 30% DVB, that are very similar in their normal characteristics (Arden, Kressman and Millar). Figure 1.14 gives an overview of possible structures. If a resin material has a lower entanglement than a normal DVB polymer, it possesses a much larger pore size for the same DVB content. As a result, the water content of the drained resin — the factor used to measure apparent crosslinking — is very much higher for the same DVB content, and the volumetric capacity of the resin is correspondingly reduced. To compensate

















% DVB	Multiple re-entangled	Re-entangled	Normal	Disentangled
2				
4				
8				
16				

Figure 1.14 Possible structures obtained by the use or deliberate re-entanglement or disentanglement.

for this factor, the DVB content can be increased, and it is thus possible, by using increasing proportions of DVB under the special conditions of the polymerization, to produce very different resins, all having the same apparent crosslinking, but with increasing real crosslinking and decreasing entanglement. As the disentanglement increases, with increasing real crosslinking to compensate, the resultant resins become harder and tougher.

Whatever the method of polymerization used, it is possible to separate the polymer chains to a greater extent than the normal limits of intermolecular distance, so that the polymer beads contain holes (termed macropores) from the first stage of synthesis. The ion exchange resins made from these beads were already called “macroporous”. In all these synthetic processes the polymers obtained have a structure that has also been called “sintered” or “sponge-like”, as depicted in Figure 1.15. Decisive is — and this applies to several other methods of more recent years as well — that from the method of synthesis it follows that in the latter cases the structures must contain large pores.

A progressive summary similar to the one above was given by Millar of the discrepancies between the more or less ideal assumptions of a molecular model and a practical synthetic approach to the structure of ion exchange resins [92]. The complex of questions related to crosslinking and entanglement, as well as to pores



Figure 1.15 Sintered or sponge-like structure obtained by a polymerization technique separating the polymer chains.

and heterogeneity, are analyzed with an eye towards the validity of a number of assumptions made in simplifying kinetic expressions dependent on structure, with Millar emphasizing the non-ideality of real materials. With respect to crosslinking and entanglement from a synthetic point of view as a factor decisive for the structure of the resulting ion exchangers and their properties, the quality of the commercial DVB must be taken into consideration, when comparing, for instance, the early theoretical work of Pepper and his colleagues, or that of Gregor and others, with later results. Modifications in the structure of ion exchange polymers can be achieved by using solvents during their manufacture. In the production of commercial DVB, the divinylbenzene isomers are obtained mixed with their precursors in the original raw material, and are separated by distillation. Current commercial DVB contains about 60% DVB isomers, with the rest consisting almost entirely of ethylstyrene, and concentrates with up to 88% DVB isomers are available. In the late forties, however, the content of crosslinking component was only 25–35%, with the ethylstyrene content being about the same. The rest in those days was mainly the original diethylbenzene starting material. Thus — and this is the important point — the higher DVB content materials of those days were in fact solvent modified, with the resultant physicochemical differences described in Millar's paper, cited above [92]. Further reflection on pores and heterogeneity and basic considerations regarding the synthesis and formation mechanisms of cross-linked polymers have led to the conclusion that in synthetic organic polymers the occurrence of structural homogeneous networks seems to be the exception rather than the normal case [93].

A third approach to the elucidation of the structure of ion exchange resins is to run investigations based on chemical, physicochemical or physical methods. Chemical investigation of the network structure of crosslinked polymers would require the splitting of the polymer chains by unambiguous reactions. But up to now very little has been developed regarding chemical methods suitable for investigation of the structure of ion exchange resins [94]. It is obvious that results showing an almost linear correlation between the quantity of DVB in the polymerization starting material and in the pyrolysate of copolymers made from styrene and DVB to be converted to cation exchangers, can only be used as an indication for a characterization of the crosslinking conditions and do not allow any assertions as to the

density of the network, etc.; they may, after a corresponding calibration, indicate the quantity of divinylbenzene incorporated into such a resin [95].

Physicochemical methods on the other hand, can be used, such as:

- Measurement of the swelling in equilibrium
- Application of the theory of capillary condensation
- Measurement of the steric accessibility of ionic sites to organic ions with increase in their dimensions
- Depression of the freezing point of the solvent in resins
- Determination of the specific absorbing surface by the BET method, the porosity and the average pore diameter
- Measurement of gas permeabilities
- Microradiographic study of resin sections
- Nuclear spin echo studies
- Measurement of the hydrolysis kinetics of the ionogenic group

as well as physical methods, such as:

- Determination of microhardness
- Electron microscope methods
- X-ray diffraction
- Optical properties in transmitted and reflected polarised light beams
- Absorption spectra in the visible region
- Reflection spectra in the visible region
- UV spectroscopy
- IR spectroscopy
- Nuclear magnetic resonance spectroscopy (NMR)
- Electron spin resonance spectroscopy (ESR)
- Mößbauer spectroscopy
- Measurement of magnetic susceptibility
- Temperature dependence of the dynamic mechanical moduli.

The results obtained are then used to propose more or less generalized structure models; but up to now it seems that none can be better used for the elucidation of the network structure of ion exchange resins than the investigation of the formation of the network polymer during its synthesis by measuring the consumption of the reactant and by investigating the changes in physicochemical or physical parameters during or after the incorporation of the ionogenic groups. Experience has shown that the structure of ion exchange resins depends as much on the method of preparation as on the chemical composition. As a result labelling of the exchangers with, e. g., radioactive uranium, and radiography were proven particularly effective



in such studies, as they permit the elucidation of the heterogeneity of the internal structure of resin ion exchangers.

Contrary to resin ion exchangers the open-structured ion exchange materials, as for instance cellulose ion exchangers, consist of a loose network that permits the penetration of large molecules to the reactive sites from which the molecules are then readily eluted. Structural aspects can be derived from the native cellulose, either from wood or cotton fibers. In the native state, adjacent polysaccharide chains are extensively hydrogen-bonded, forming microcrystalline regions. These higher-oriented fibrillar chains are interspersed with amorphous regions of longer axial fibers with less hydrogen bonding. Hydrogen bonding between the neighboring cellulose chains, and especially in the fibril centers, provides dimensional stability for the cellulose matrix, and it is these forces that restrict the matrix to only moderate swelling, making cellulose insoluble in water. Limited acid hydrolysis results in preferential loss of the amorphous regions, yielding so-called microcrystalline cellulose. Within and in-between the cellulose chains are located "openings" or pores with a wide size range. When ionizable groups are introduced into such a matrix, the natural polymer cellulose becomes an ion exchange material with the open structure shown diagrammatically in Figure 1.16a. By modification by mild acid hydrolysis the characteristic structure of cotton cellulose undergoes chain splitting and recrystallization within the interfibrillar regions, so that the crystallite fibrils are enhanced, causing much of the amorphous portion of the cellulose microstructure to be removed. During this regeneration microgranular cellulose is obtained, which is strengthened by crosslinking with epichlorohydrin, although the main structure-forming bonds are still hydrogen bonds. The impact of such modifications on the native structure of cellulose are shown in Figure 11.6b. The ionogenic groups are attached by ether linkages directly to the glucose units of the

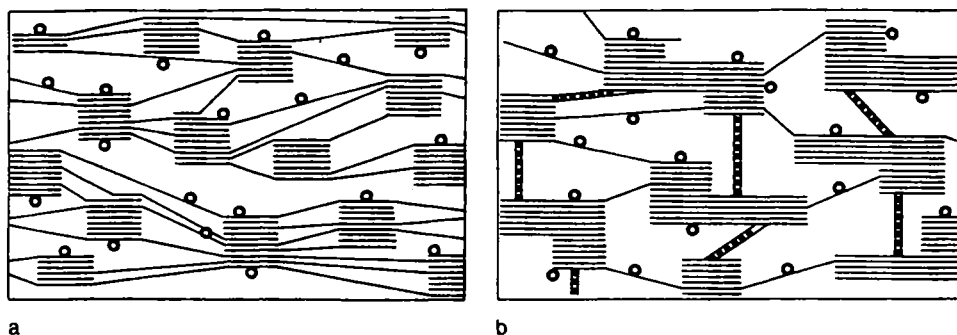


Figure 1.16 Microstructures of ion exchange cellulose. Left: diagrammatic microstructure of a fibrous material, the solid lines representing the aggregates of carbohydrate chains and the dotted circles being the ion exchange sites; right: the same of a microgranular material with highly oriented regions, the wider dotted lines showing the crosslinks introduced and the dotted circles again being the ion exchange sites.

polysaccharide chains. The modification also results macrostructurally in the production of shorter particles that are dense and almost bead-shaped [96].

The best known exchanger structures are found among inorganic ion exchangers. It must even be emphasized that before the cation exchange behavior of inorganic ion exchangers can be fully understood a general appreciation of their structure is essential. However, since quite a number of inorganic ion exchangers are now available, structure must also be considered individually [97]. The principle of ion exchange is the same for the mineral exchangers as for the synthetic ion exchange resins [98]. The skeleton or crystal structure carries an excess charge which is compensated for by mobile counterions. In the case of the zeolites, this is known to be a consequence of the fact that a part of the  $\text{Si}^{4+}$  building blocks is replaced by  $\text{Al}^{3+}$  in the silicate lattice. The lacking positive charge is replaced by alkali or alkaline earth ions, which are present with free mobility in the mineral skeleton as counterions. As an illustration of these facts, the structure of chabazite is shown

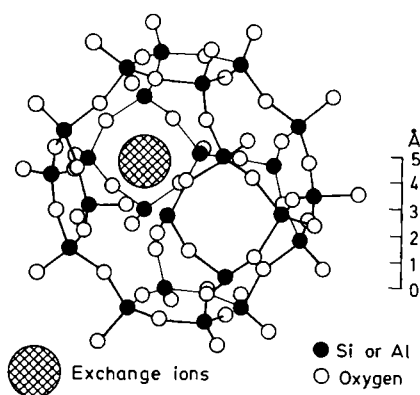


Figure 1.17 Stereostructure of chabazite.

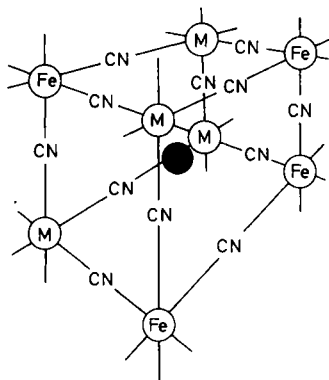


Figure 1.18 Cubic arrangement of the metal cyanide octaeders in the structure of ferrocyanide and the mobile exchangeable cation.

in Figure 11.7. As a further example, the complex salts based on ferrocyanide may be mentioned, which were developed in the search for new inorganic exchange materials. In relation to the general formula  $M_2^I M^{II}Fe^{II}(CN)_6 \cdot n H_2O$  their structure is usually represented as shown in Figure 1.18. This figure shows the cubic arrangement of the metal cyanide octaeters with the mobile, exchangeable cation in the resulting cavity.

### 1.1.3 Fundamentals and definitions

Ion exchangers are solid or suitably insolubilized high molecular weight polyelectrolytes which can exchange their mobile ions for ions of the same charge from the surrounding medium. The resulting ion exchange is reversible and stoichiometric, with the displacement of one ionic species by another on the exchanger. Viewed in a different light, ion exchangers can be considered to be acids with a high molecular weight anion or bases with a high molecular weight cation, which can exchange their hydrogen or hydroxyl ions for equally charged ions, thus being converted into high molecular weight salts. If such a solid acid is neutralized by a base into a salt, however, the cations bound to the polyelectrolytes can again be displaced by other cations. The resulting process is known as cation exchange and the polyelectrolyte as the cation exchanger. In the second case, a solid base is obtained which is capable of hydroxyl exchange and which can be neutralized with an acid, and the anion from this acid which was bound first can again be displaced by another anion, a process then known as anion exchange. The polyelectrolyte on which this process takes place is called the anion exchanger.

The most widely used modern ion exchangers are organic materials based on synthetic polymers. The fundamental process can be described most easily for these and, on the other hand, all — even the general — phenomena of ion exchange can be more easily understood on the basis of these descriptions. Figure 1.19 shows some types of ion exchange resins.

The polymeric molecule of an ion exchanger is in the most general case — because of crosslinkages — a three-dimensional network with a large number of attached ionogenic groups. Polymer molecules can be linked together by including a monomer with two or more functional groups in the polymerization. When polymer molecules are connected to one another by a sufficient number of interchain bonds, the network formed, is, in effect, one giant molecule. Crosslinks confer unique properties to such polymers. Networks that form in solution and remain intimately associated with the solvent are gels. Polymers whose crosslinks are permanent chemical bonds are insoluble in all nondegrading liquids, but can often swell enormously in liquids that would be solvents if the crosslinks were absent. The crosslinks in ion exchange resins occur randomly and the network structures can vary over very wide ranges. It is therefore quite difficult to depict ion exchangers in constitutional formula [99].

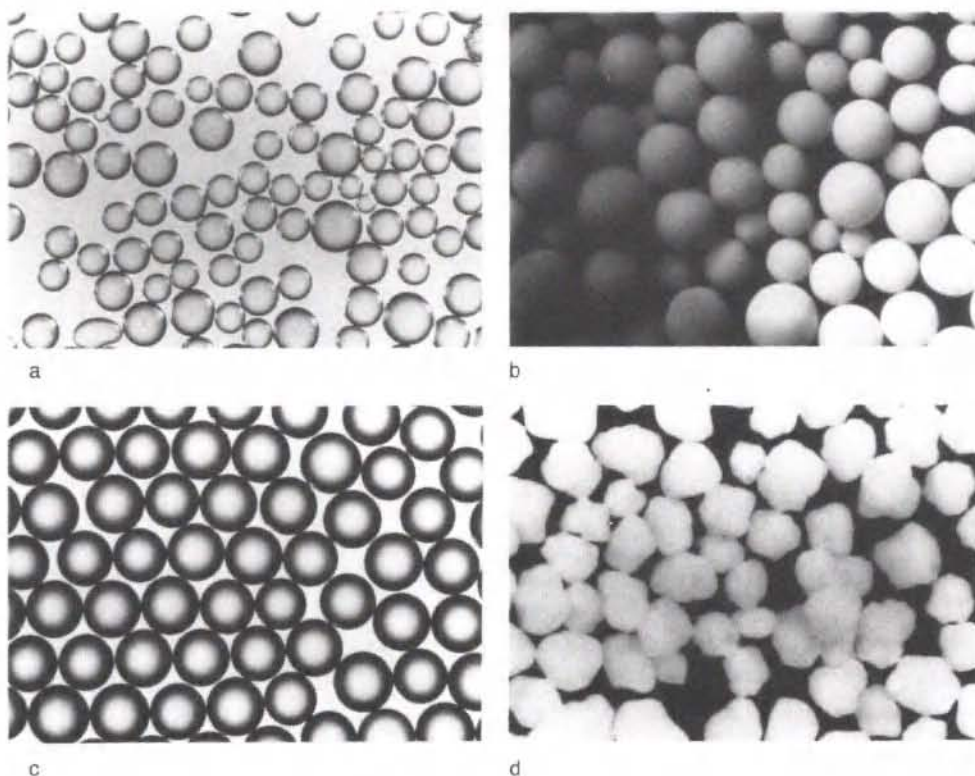
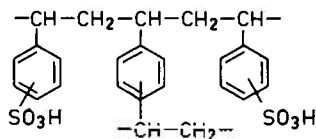
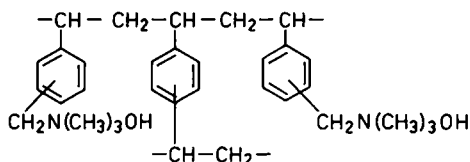


Figure 1.19 Some common types of ion exchangers: a) gel type strong acid cation exchanger; b) macroporous type strong base anion exchanger; c) Monosphere® cation exchanger with exceptional uniform bead size; d) granular form of a weak base anion exchanger. (®Trademark of the Dow Chemical Company).

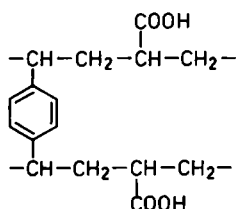
The most important starting material used in synthetic resin ion exchangers is styrene. First, styrene is crosslinked with divinylbenzene into a polymeric network and then the reactive groups are introduced. One may therefore depict a cation exchanger containing sulfonic acid groups or an anion exchanger containing quaternary ammonium groups best by a quasi-constitutional formula that contains, irrespective of the structure, the three principal building entities, i. e. the basic polymer-forming constituent or chain, the crosslinking agent and the ionizable site. For instance, for a copolymeric styrene-divinylbenzene sulfonic acid cation exchanger the quasi-constitutional formula would be:



and for a styrene-divinylbenzene quaternary ammonium anion exchanger the quasi-constitutional formula would be:



Matrices for synthetic resin ion exchangers are also formed from acrylic acid with divinylbenzene, and can be represented by the quasi-constitutional formula



Such quasi-constitutional formula can be used advantageously for the representation of synthetic polymeric ion exchangers in order to depict their basic structural elements, and, above all, for writing down further reactions, as well as for more special ion exchange polymers.

A common depiction of the basic structure of synthetic ion exchange resins based on styrene and divinylbenzene with their anionic fixed groups in the case of cation exchangers or cationic fixed groups in the case of anion exchangers, is by figures showing schematically the charged matrix including the exchangeable ions in a circular outline to suggest the bead form of such ion exchangers, as in Figure 1.20. Such schematic drawings do not represent the true polymeric structure

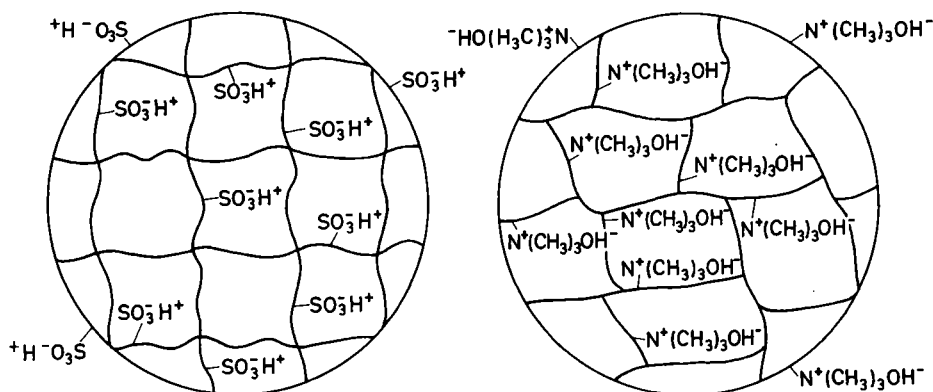


Figure 1.20 Schematic drawings of a strong acid cation exchanger (left) and a strong base anion exchanger (right) showing the charged matrix and the exchangeable ions.

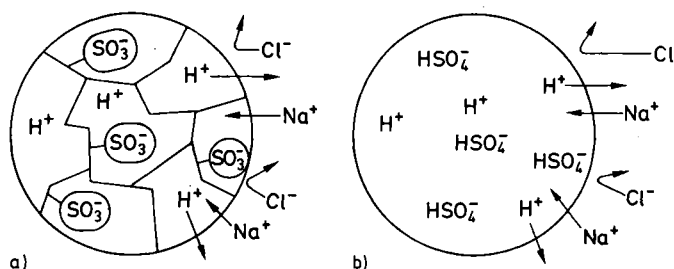
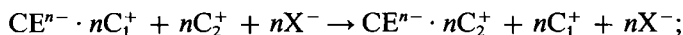


Figure 1.21 Comparison of cation exchange resin bead with sulfuric acid droplet. Left: schematic section through cation exchange resin bead; right: imaginary droplet of sulfuric acid surrounded by cation permeable membrane (Arden).

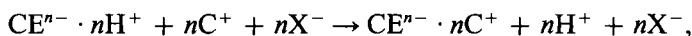
but are intended to give a visual impression of the basic structure. If the cation exchange resin is shown diagrammatically as in Figure 1.21, it can easily be understood that the sulfonic groups are immoveably attached to the resin skeleton, while the corresponding hydrogen ions are free to move throughout the structure. As a result, a sodium ion can enter freely, causing the ejection of a hydrogen ion, whereas a chloride ion approaching the surface of the bead is repelled by the fixed negative charges, and cannot enter. The effect is thus exactly as if the bead were a droplet of sulfuric acid solution, surrounded by a membrane through which cations, but not anions can pass (Arden).

Ion exchange processes require a mediating agent, generally water, in which the ions to be exchanged are dissolved. The ion exchanger in water contains water in its structure, so that when the exchange process is initiated, the solute ions penetrate the structure and immediately begin to exchange places, so to speak, with the original ions and, since electroneutrality must be maintained, join the co-existent ions which have penetrated previously. From the physicochemical standpoint, therefore, diffusion appears to be an important process during ion exchange.

It is therefore feasible to write ion exchange processes like chemical equations. If one uses the symbol  $CE^{n-}$  for a cation exchanger consisting of any matrix carrying ionogenic groups with a number  $n$  of negative charges, and the symbol  $C_1^+$  for a monovalent cation, cation exchange can generally be described as follows:



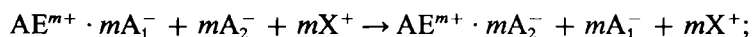
for hydrogen ion exchange, which already represents a special case, this simplifies to:



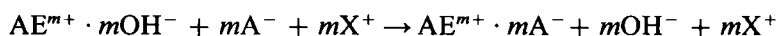
becoming a process analogous to neutralization when the cation intended for the exchange is used in the hydroxide form, i. e., as a base:



Using the symbol  $AE^{m+}$  for an anion exchanger in the same manner, one obtains the general formula for anion exchange:



for hydroxyl exchange, which also represents a special case:



and again, for the process analogous to neutralization:



As it will be seen, these fundamental formulas can be applied to all ion exchange processes and can be useful as a generalizing scheme when certain processes are to be interpreted as ion exchange events.

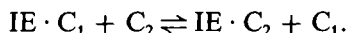
**Nomenclature.** The nomenclature on ion exchange and ion exchangers contains certain fundamental terms [100]. Those related to fundamentals are given below with their definitions, whereas other terms will be explained as the need arises. The following definitions are recommended (IUPAC):

Resin matrix:	The molecular network of an ion-exchange resin that carries the ionogenic groups.
Fixed ions:	In an ion exchanger, the non-exchangeable ions that have a charge opposite to that of the counter-ions.
Counter-ions:	In an ion exchanger, the mobile exchangeable ions.
Ionogenic groups:	In an ion exchanger, the fixed groupings that are either ionized or capable of dissociation into fixed ions and mobile counter-ions.
Co-ions:	In an ion exchanger, mobile ionic species with a charge of the same sign as the fixed ions.
Cation exchanger:	An ion exchanger with cations as counter-ions. The term cation-exchange resin may be used in the case of solid organic polymers.
Anion exchanger:	An ion exchanger with anions as counter-ions. The term anion-exchange resin may be used in the case of solid organic polymers.
Cation exchange:	Process of exchanging cations between a solution and a cation exchanger.
Anion exchange:	Process of exchanging anions between a solution and an anion exchanger.
Acid form of cation exchanger:	The ionic form of a cation exchanger in which the counter-ions are hydrogen ions (H-form) or the ionogenic groups have added a proton, forming an undissociated acid.
Base form of anion exchanger:	The ionic form of an anion exchanger in which the counter-ions are hydroxide ions (OH-form) or the ionogenic groups form an uncharged base, e. g. $-NH_2$ .

Salt form of ion exchanger:	The ionic form of an ion exchanger in which the counter-ions are neither hydrogen nor hydroxide ions. When only one valence is possible for the counter-ion, or its exact form or charge is not known, the symbol or the name of the counter-ion without charge is used, e. g. sodium form (Na-form) tetramethylammonium form, orthophosphate form. When one of two or more possible forms is exclusively present, the oxidation state may be indicated by Roman numerals, e. g. Fe(II)-form, Fe(III)-form.
Monofunctional ion exchanger:	An ion exchanger containing only one type of ionogenic group.
Bifunctional ion exchanger:	An ion exchanger containing two types of ionogenic group.
Polyfunctional ion exchanger:	An ion exchanger containing more than one type of ionogenic group.

In selecting terms used in the experimental and discussion sections of publications it is requested that one pays attention to these IUPAC recommendations on nomenclature (Inczedy).

**Equilibria.** If a system set up in the manner described above is left to itself an equilibrium forms, as in all chemical reactions; for the general case of an ion exchanger IE with the counterion  $C_1$  and a solute ion  $C_2$  for a binary exchange system, an equation can be written in the usual way for the reaction between the ion exchanger and the ionic solute:



For the further treatment of this equation a full generalization for all types of ion exchangers is unfortunately not possible, since the gel type ion exchange resins swell whereas the so-called macroreticular resins swell only little and zeolites practically not at all; clays and clay minerals swell only in one dimension and inorganic ion exchanger gels behave, depending on their structure, similarly to macroreticular or to common ion exchange polymers. All further statements are therefore related to the common gel type ion exchange resins and their equilibria with respect to swelling, ion exchange and sorption. In other words, when an ion exchange resin is immersed in a solution containing an electrolyte some or all of several processes may occur. Firstly, the resin swells by imbibing solvent from the external phase. Secondly, especially when an exchanger phase with one type of counterion and an external solution with a second but different counterion exist, an ion exchange process usually takes place. Thirdly, some electrolyte penetrates the ion exchanger gel to an extent which can no longer be explained by the underlying stoichiometry of ion exchange processes. All three processes can occur at the same time and obviously influence the total distribution of freely diffusible species in the system.



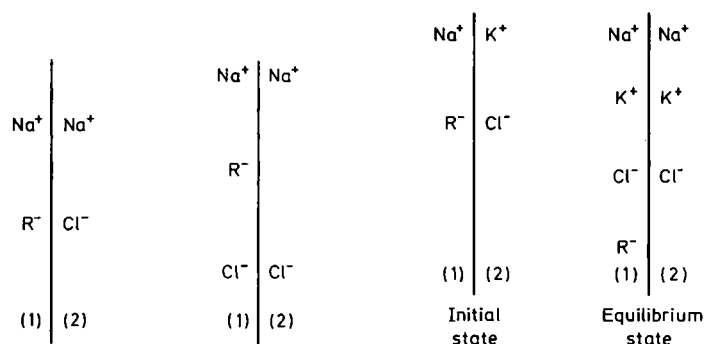


Figure 1.22 Donnan membrane equilibria.

Because the Donnan membrane equilibrium has often been applied to both molecular as well as theoretical models of ion exchange, this will be briefly described [101]. Donnan made use of the simple model shown in Figure 1.22, left, in which the vertical line indicates that the salt  $\text{NaR}$  is located on one side of the membrane which is impermeable to the anion  $\text{R}^-$ , while  $\text{NaCl}$  is on the other side.  $\text{NaCl}$  will then diffuse from (2) to (1), so that an equilibrium state is finally reached as shown in Figure 1.22, second left. This picture can also be extended to the case of an electrolyte with no common ion, in which only  $\text{NaR}$  is present on one side of the membrane and only  $\text{KCl}$  on the other (Figure 1.22, second right and right).  $\text{KCl}$  will then diffuse through the membrane in one direction, but  $\text{NaCl}$  will also permeate the membrane in the opposite direction. An equilibrium state results, which can be evaluated qualitatively as follows: the anion  $\text{R}^-$ , which cannot diffuse through the membrane, apparently attracts the cation of a second, quite different, electrolyte whose anion, however, apparently diffuses through the membrane to the same degree as  $\text{R}^-$  remains behind. This model can also be applied to ion exchange, if the interface between the exchange resin and the aqueous phase is seen as a membrane and the resin or the ion fixed on it is taken as the indiffusible component on one side. The counterion of the resin matrix is freely mobile. Therefore, if the exchanger is surrounded by an electrolyte solution containing a common or also not a common ion, an equilibrium will form according to the Donnan concept, which can therefore be treated according to the principles of membrane theory. For the case in which the membrane is permeable only to the solvent, the well-known theory of osmotic equilibrium, as well as the derivation of the osmotic pressure, result from the membrane theory. In ion exchange the capillary or swelling pressure plays the role of osmotic pressure, bringing about an equilibrium between the two phases with respect to the entire system.

The development of a Donnan potential at the interface of an exchanger resin and a solution can diagrammatically be illustrated as shown in Figure 1.23. Regarding a hypothetical pore of a cation exchanger before immersion on the left and after immersion in water on the right, the latter demonstrates that as the exchanger

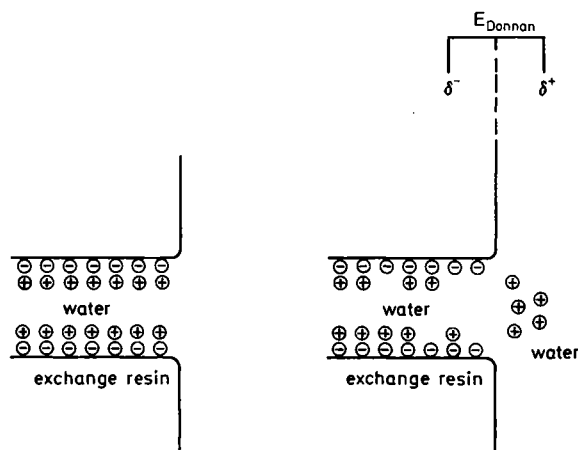


Figure 1.23 Development of a Donnan potential at an ion exchange resin and solution interface. Left: schematic pore of a cation exchanger in the dry state; right: the system after immersion in water.

comes to an equilibrium with a solution some diffusion of ions from the exchanger into the solution occurs, but only to a very small degree since only counterions are available for diffusion. Each counterion which does leave the exchanger phase leaves behind an uncompensated charge on the matrix of the exchanger. The ions which do diffuse out into the solvent remain near the surface of the resin in a diffuse double layer. A separation of charges takes place in this process and sets up an electrical potential across the exchanger and solution interface. This is the Donnan membrane potential. This situation makes it more difficult for the counterions to move because they would now have to do an increased amount of electrical work in wandering. But, in fact, very few ions are sufficient to set up quite substantial voltages. Moreover, the developed potential tends to return the counterions of the diffuse double layer to the fixed sites bound to the matrix. With respect to the capacity of the ion exchange resin the ions of this double layer never form a significant proportion so that it can still be considered that electroneutrality is maintained within the exchanger. But these few ions and the Donnan potential developed in their moving away are of the utmost importance for an understanding of all ion exchange processes. This is because what is called the ion exchange process has already begun when the counterions of the double layer are in dynamic equilibrium with those of the exchanger phase. Then foreign counterions introduced into the external solvent mix with and displace the original counterions of the diffuse layer and thus occupy sites within the exchanger. The presence of the Donnan potential at the resin and solution interface also explains naturally the fact that ion exchangers are permselective to their counterions, meaning that they virtually exclude all co-ions. This will be referred to in several contexts as the Donnan exclusion effect.

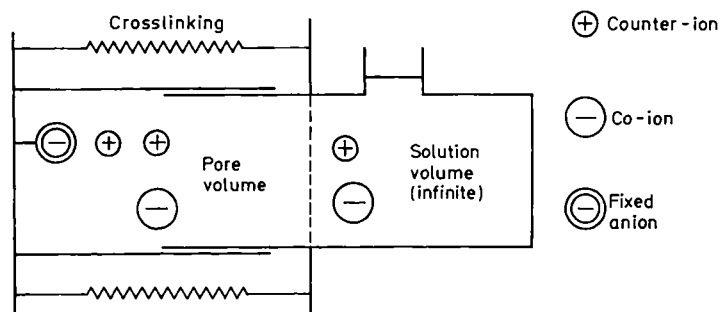


Figure 1.24 Gregor model for an ion exchange resin.

Further, for the phenomenological understanding of ion exchange, and because this approach has had a pronounced influence upon subsequent studies, the Gregor model of ion exchangers will be described [102]. As shown in Figure 1.24, in the matrix of the ion exchanger the crosslinking can be represented by elastic springs. The chemical components of this system are the matrix with the solvated fixed anion for the case of a cation exchanger, the solvated permeant ions, and the free solvent. The exchange resin is supposed to behave like a salt which becomes hydrated as the resin imbibes water and swells. During swelling the crosslinked network of the matrix exerts a pressure on the liquid inside the polymer structure, which is interpreted as an internal swelling pressure acting on the liquid within the resin. The counterions, on the other hand, dissociate, forming a concentrated electrolyte solution within the resin, thus causing by osmotic activity further amounts of water to enter the resin phase, which therefore continues to swell. The swelling of the resin is accompanied by a stretching of the crosslinked matrix or, following Gregor's model, an extension of the elastic springs. In Figure 1.24 it is further shown that co-ions can also penetrate the ion exchanger resins together with corresponding surplus counterions. On the basis of this model, whereby newly developed theoretical aspects have been disregarded, several phenomena of ion exchange and its equilibria can still be profitably discussed.

**Swelling equilibria.** The swelling of an ion exchanger gel after immersion into a solvent — in most cases water — is phenomenologically postulated as being, in principle, an osmotic process. In the literature this is referred to as the osmotic theory of the concept of osmotic pressure in the swelling of ion exchange resins. This theory postulates that the solvent retention is a reproducible, equilibrium quantity, which can be explained as the effort towards dilution made by the many existing fixed ions and counterions in the network or the tendency of these ionic groups to become hydrated. Water swelling must therefore increase with an increase in the number of ionogenic groups, up to the limits imposed by the crosslinking. The swelling equilibrium is reached when the tension of the network equals the osmotic pressure difference between the interior of the ion exchanger gel and the surrounding solution.

Investigations of the swelling of ion exchangers are important both for the study of their physicochemical properties and for the elucidation of ion exchange mechanisms. For the experimental determination of the degree of swelling, e. g. for the dependence of swelling on the degree of crosslinking and the valence of the counterion [103], and the dependence of swelling on the concentration of the solution [104], several methods have been found convenient and useful, among which the pycnometric determination of the external volume [105, 106], the gravimetric measurements of the weight of a gel in a given salt form [105], and the calibrated tube or the sealed column method for determinations of the influence of the surrounding liquid on the bed volume of the gel [107] should be mentioned. But the most useful and quantitative characteristic of the interaction of an ion exchange resin with a solvent is given by the isopiestic determination of vapor sorption isotherms [108]. These so-called isopiestic lines are measured in the vapor pressure range from negligibly low values up to the vapor pressure of the pure solvent. In Figure 1.25 isotherms for different degrees of crosslinking are given for the H-form of sulfonated polystyrene resins, showing that the influence of crosslinkings is greater for  $X > 0.6$ . Isopiestic lines are in general of great importance for the evaluation of thermodynamic parameters that are usually based on the equilibrium pressure [109]. It can be said that swelling pressure and resin hydration studies have been a significant milestone in the theoretical treatment of ion exchange resins, for instance for the determination of the enthalpy of swelling [106, 110, 111]. It should also be mentioned that the application of the thermodynamic method to resins has been developed, at least to some extent, in analogy with the thermodynamics of the hydration of natural macromolecular substances [112, 113].

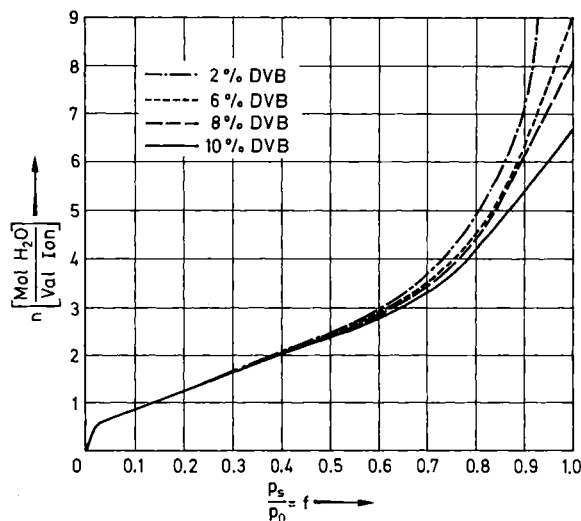


Figure 1.25 Water vapor sorption isotherms of ion exchange resins in the H-form (Dickel et al., 1959).

Mainly from the results of the studies of Gregor and Pepper and their coworkers, the influence of various factors on the swelling properties and equilibria have led to certain general conclusions. For polar solvents it can be concluded:

1. Swelling equilibria of gel type ion exchangers depend on the nature of the ionogenic site. Highly dissociated strong acid cation exchangers with the  $-\text{SO}_3\text{H}$  group — as compared with the weak acid  $-\text{COOH}$  group with the same degree of crosslinkage — swell more because of a higher number of osmotic active ions.
2. Swelling is greatly influenced by the nature of the counterions. Resin volumes change when the resins are converted to different ionic forms, with a sequence for monovalent counterions for the sulfonic acid type cation exchanger generally being  $\text{H}^+ > \text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+ > \text{Ag}^+$ ; for polycarboxylic gels, one has,  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{H}^+$  (with the possibility of inversions).
3. The effect of counterions of higher valency on the swelling can even be negative, i. e. some ion exchangers can shrink when they are loaded with divalent ions. In general the swelling is lower with counterions of higher valence because of a lower number of osmotic active ions being present inside the exchanger. With polyvalent ions swelling is reduced usually according to the sequence  $\text{Na}^+ > \text{Ca}^{2+} > \text{Al}^{3+}$ .
4. Swelling equilibria of gel type resins depend largely on the degree of crosslinking, because higher crosslinking means a more rigid structure. Reasons for the decrease in swelling at higher degrees of crosslinking are: increase in the swelling pressure, changes in the number of bound water molecules, the difficulty of interpreting external volume and thermodynamic functions with the swelling pressure as variable.
5. Swelling is favored by an increase in the number of ionogenic groups (capacity) because of a higher ion concentration in the exchanger.
6. The external solution can determine the swelling with varying concentrations. Swelling is decreased by an increase in concentration of the external solution since this decreases the difference in the osmotic activity between the two phases.
7. Swelling of resins that are not immersed in water is dependent on the relative humidity, especially as 100% relative humidity is reached. Water sorption from solutions is always higher than swelling in water vapor.
8. The increase in resin swelling with increase in temperature is not great, even in the range of several tens of degrees, but is significant in certain operations, this being one of the reasons why thermodynamic treatments of swelling equilibria are difficult to make.

The mechanism of the uptake of water by ion exchangers of the gel type can be elucidated on the basis of swelling equilibria changes with regard to the exchange of different counterions. Interrelations between the degree of crosslinking and the hydration water of the mobile ions can be deduced from the Gregor model, leading to the conclusion that the higher the degree of crosslinking of the resin and, hence,

the less the swollen volume, the closer will the mobile cations be forced towards the anionic groups fixed to the resin inducing a stronger interaction between them. By this interaction water molecules are displaced from the hydration shell of the counter-cation and its degree of hydration is reduced. The hydration number is not constant, but upper and lower limits do result [114]. For the salt forms of sulfonated resins the hydration of ion exchange resins is, on the other hand, regarded as a stepwise adsorption process. This is deduced from thermodynamic functions with the conclusion that the first water molecule is exclusively sorbed by an  $\text{SO}_3^-$ -group fixed on the matrix, while the second and subsequent hydration shells are formed as a result of the hydration of the cation [115]. Analysis of the temperature variation of the water vapor adsorption isotherms has led also to the conclusion that, if there is one molecule per fixed group, then its interaction with the counterion and also the interaction of the counterion with the water molecule, is not a linear function of the ionic radius alone, i. e. is not purely coulombic, but factors such as polarisation may play an important role. The discussions along these lines have not been terminated yet [106, 111]. The mechanism of hydration has also been studied by physical methods. From the infrared spectra of thin films of sulfonated polystyrene it was earlier concluded that the hydration of the salt forms of sulfonated resins begins with the interaction of water with the counterion [116]. There are results of later years which would seem to contradict these findings but they are based on different substrates: they show that ion pairs and not individual ions are hydrated in sulfonated polymer films. If different explanations of the mechanism of primary hydration have to be applied it may well be that different mechanisms do exist for different ion exchanging polymers. NMR studies for the characterization of moisture absorption by hydrogen forms of Dowex 50 resins with different crosslinking show that water molecules in the resin phase are in a state of rapid if restricted motion. Water molecules in several different states in the resin would then have to be expected at low moisture content, with an exchange between the protons of the water within the resin and outside it. But the NMR method enables the heterogeneity of resins to be quantitatively determined.

From experimental results elucidating various relationships and from mechanisms obtained either from analysing differential thermodynamic functions or from interpreting the more rigorous investigations by a wide variety of physical methods, diagrammatic representations can be figured out, but this can easily lead to misconceptions due to oversimplification. It seems better therefore to refer only to the theoretical models which have been proposed and on which quantitative treatments of the swelling equilibria and other interrelated properties of ion exchangers have been based. The model proposed by Gregor was described above. This so-called osmotic theory was also applied by others [115], and was in part the subject of intense discussion over the following years [109, 117]. These may all be considered as mechanical models in contrast with molecular models as treated by Rice and Harris [118] and Katchalsky and coworkers [119]. The latter can be considered as extensions of the early polyelectrolyte theories where the resin gel is described as a

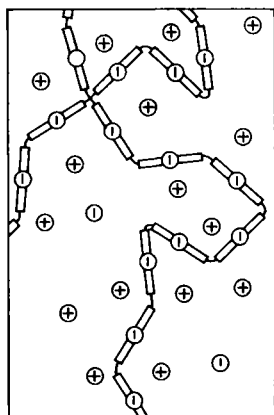


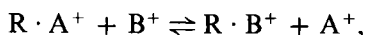
Figure 1.26 The Katchalsky molecular model.

network of rigid segments, each of them carrying only one ionic site, as shown in Figure 1.26. From thermodynamic considerations the necessary elasticity of the resin matrix for swelling is reflected by entropy changes, and the conformational entropy contribution is calculated in detail from the statistical theory of nonpolar gels (Flory). Due to their molecular nature electrostatic interactions are introduced in both models, in the Rice and Harris model for moderately and highly crosslinked resins as interactions between sites over the whole gel volume if no ion pairs have been formed, and in the Katchalsky model for slightly crosslinked polyelectrolyte gels as interactions between neighboring sites of the same chain. Both models require the introduction of empirical parameters, making it difficult to predict correctly and quantitatively theoretical values, which must be evaluated by experimental results (Rinaudo).

**Ion exchange equilibria.** Since ion exchange processes are stoichiometric and reversible, whenever an ion exchanger is brought into contact with an aqueous solution containing a counterion different from that initially bound to the resin, an exchange of ions occurs until equilibrium is reached, as shown in the previously given general equations. To describe this exchange process quantitatively well-known physical-chemical formulations can be applied, which fall essentially into two categories. One considers the exchange process as an adsorption phenomenon, the other classifies it as the interaction of coulombic forces in electrolytes, such as described either by the Donnan equilibrium theory or the law of mass action. Although it may be justifiable to treat an ion exchange process under operational aspects as an adsorption process using the Freundlich or Langmuir isotherms, this seems strange for ionic interactions concerning ion exchangers, and may be left to discussions in the literature (Cassidy [120] and Morris and Morris [121]). The Donnan membrane theory, with the Donnan exclusion effect, explains how co-ions are prevented from penetrating the interior of a high capacity ion exchanger and

simultaneously force an equivalent quantity of counterions into the exchanger whenever the first counterions wander out of the resin. However, with the exceptions of ion exchange reactions of low capacity resins in dilute solution, the discrepancies between experimental results and calculations made according to a simplified Donnan membrane theory [122] are too great.

However, because in ion exchange reactions equivalent amounts of ions participate, the law of mass action describes ion exchange equilibria quite adequately. Given the ion exchange resin R with fixed ions and counterions  $A^+$  — for instance in the case of a strong sulfonic acid cation exchanger — which undergo exchange with the counterions  $B^+$ , according to the equation



then, by application of the law of mass action, and taking into consideration the fact that the activities of ions in the resin phase cannot be evaluated accurately, an apparent exchange constant  $K_c$  is obtained

$$K_c = \frac{[R \cdot B^+][A^+]}{[R \cdot A^+][B^+]}$$

As this is not a true thermodynamic equilibrium constant it is called the equilibrium quotient. For practical purposes, and in order to measure the values analytically, the activity coefficients of the ions in both the resin and aqueous phase are usually ignored and the concentrations determined are used uncorrected. In the equation the brackets represent the concentrations of the reactants as expressed in some convenient units. Normality is often the unit chosen for the aqueous phase, while the concentration in the resin phase is usually expressed as equivalents of counterion per unit weight of exchanger

This empirical equilibrium quotient depends, however, on the properties of the ion exchanger and the nature and concentration of the electrolytes; as a result different empirical equilibrium quotients are obtained for different ions and this has led to the introduction of the concept of selectivity.

One quite often presented derivation of a thermodynamic ion exchange equilibrium constant and a selectivity relation is made in the following way. Based on the above equilibrium equation and considering that co-ions have no effect on this equilibrium — unless specifically complexing or, indirectly, on the activity coefficient in the solution — and therefore may be ignored, a thermodynamic equilibrium constant,  $K_{th}$ , may be written for the ion exchange

$$K_{th} = \frac{a_{RB} \cdot a_A}{a_{RA} \cdot a_B} = \frac{[RB] \cdot [A]}{[RA] \cdot [B]} \cdot \frac{\gamma_{RB} \cdot \gamma_A}{\gamma_{RA} \cdot \gamma_B},$$

this is generalized for the case where the exchanging ions have valencies  $z_A$  and  $z_B$ , to the thermodynamic equilibrium constant

$$K_{th} = \frac{(a_{RB})^{z_A} \cdot (a_A)^{z_B}}{(a_{RA})^{z_B} (a_B)^{z_A}},$$



where  $a$  represents the activity of the species involved and is, in turn, equal to the concentration of that species multiplied by an activity coefficient such that for a species  $i$

$$a = [i] \cdot \gamma_i.$$

This extension gives the thermodynamic equilibrium constant as the usual product of two terms, the first being a concentration and the second an activity coefficient quotient. But in experimental practice use is mainly made of the concentration term only, as already mentioned above, which is then termed the selectivity coefficient because of the reasons outlined above as well. The selectivity coefficient is often given the symbol  $K_A^B$ , since it measures the tendency of the exchanger to prefer B over A. This means that

$$K_A^B = \frac{[RB] \cdot [A]}{[RA] \cdot [B]},$$

if  $K_A^B$  is greater than unity, the exchanger selects ion B, if it is less than unity, it selects ion A, and if it is equal to unity then the exchanger shows no preference for either ion.

Since the first investigations of ion exchange phenomena it has been shown that, in general, and in dilute solutions of electrolytes ( $< 0.1$  N mol/l), an ion exchanger or an ion exchange resin will show a preference for one ion over another, that is, that the affinities of ions towards an ion exchanger are not equal. This phenomenon of preference is called selectivity of the ion exchanger for the counter-ion and is characterized by the selectivity coefficient,  $k_{A/B}$ . The IUPAC Recommendations on Ion Exchange Nomenclature define:

Selectivity coefficient,  $k_{A/B}$ : Equilibrium coefficient obtained by formal application of mass action law to ion exchange, characterizing quantitatively the relative ability of an ion exchanger to select one of two ions present in the same solution.

Exchange  $[Mg^{2+} - Ca^{2+}]$ :

$$k_{Mg/Ca} = \frac{[\overline{Mg}] [Ca]}{[Mg] [\overline{Ca}]}$$

Exchange  $[SO_4^{2-} - Cl^-]$ :

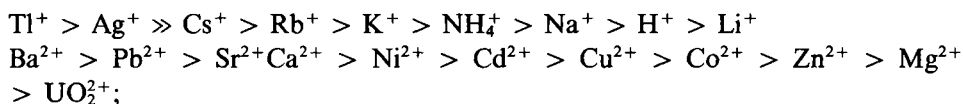
$$k_{SO_4/Cl} = \frac{[SO_4]_r [Cl]^2}{[SO_4] [Cl]_r}$$

Over-bars or subscript letters, "r", are used to designate concentrations in the ion exchanger. For exchanges involving counter-ions differing in their charges, the numerical value of

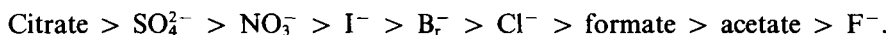
$k_{A/B}$  depends on the choice of the concentration scales in the ion exchanger and the solution (molal scale, molar scale, mole fraction scale, etc). Concentration units must be clearly stated in exchange of ions of differing charges.

Corrected selectivity Concentrations of external solution in  $k_{A/B}$  are replaced by coefficient,  $k_{A/B}$ : activities.

For any given series of ions the selectivities can be arranged in a relative order and selectivity sequences can be established. For counterions of the same valence that do not form complexes, the affinities are ruled by electrostatic reciprocal effects with the fixed ion, by disturbance of the solvent structure in the exchanger and by changes in the swelling. For a general purpose cation exchanger and aqueous solutions usually the following selectivity sequences are valid for the most common cations:



likewise for anions with respect to a general purpose anion exchanger:



If measurements are to be made to investigate the ion exchange behavior of cations or anions it is common practice to determine the concentration distribution ratio  $D_c$ , the distribution coefficient  $D_g$  or the volume distribution coefficient  $D_v$  for which in the IUPAC Recommendations on Ion Exchange Nomenclature the following definitions are given:

Concentration distribution ratio $D_c$ :	The ratio of the total (analytical) concentration of a solute in the ion exchanger to its analytical concentration in the external solution. The concentrations are calculated per $\text{cm}^3$ of the swollen ion exchanger and $\text{cm}^3$ of the external solution.
Distribution coefficient $D_g$ :	The ratio of the total (analytical) amount of solute per gramme of dry ion exchanger to its concentration (total amount per $\text{cm}^3$ ) in the external solution.
Volume distribution coefficient $D_v$ :	The ratio of the total (analytical) amount of a solute in the ion exchanger calculated per $\text{cm}^3$ of column or bed volume to its concentration (total amount per $\text{cm}^3$ ) in the external solution. ( $D_v = D_g \rho$ , where $\rho$ is the bed density, g of dry resin per $\text{cm}^3$ bed.) This quantity is most conveniently determined from column experiments and it is recommended to use the $D_v$ values in describing the results from chromatographic separations.

The employment, especially of  $D_g$ ,

$$D_g = \frac{\text{concentration of solute in resin}}{\text{concentration of solute in liquid}}$$

is, in practice, much easier than for instance trying to obtain the separability from selectivity sequences; from  $D_g$  it is, e. g., much more convenient to predict the column behavior of an ion, for any given set of conditions. The distribution coefficients of a large number of inorganic and organic ions have been measured over wide ranges of conditions and are available from the literature [123].

The ratio of the distribution coefficients for two different ions is then the separation factor, which is defined as

Separation factor      Ratio between the distribution coefficients of solutes A and B  
 $\alpha_{A/B}: \alpha_{A/B} = D_A/D_B$       in a specified medium at a specified temperature. In exchange of counter-ions of equal charge the separation factor is equal to the selectivity coefficient provided that only one type of ion represents the analytical concentration (e. g., in exchanges of  $K^+$  and  $Na^+$ , but not in systems where several individual species are included in the analytical concentrations);

this can also be written as

$$\alpha_{A/B} = \frac{\bar{C}_A \cdot C_B}{\bar{C}_B \cdot C_A}.$$

The separation factor, as the quotient of the distribution coefficients, is for practical purposes the most useful value. In general, if  $\alpha_{A/B} > 1$  the ions A are more selectively taken up than the ions B by the ion exchanger, and the easier it will be to separate them on a column of ion exchange resin. In addition — and under the important restriction that the selectivity coefficient is different from the separation factor only in the case of the uptake of ions of different valence — from analogous considerations the various methods for the regeneration of ion exchangers can be dealt with [124]. In Table 1.4 average separation factors are given for a commercial polystyrene sulfonic acid ion exchange resin of various crosslinking in equilibrium with diluted chloride solutions.

Further fundamental facts are of interest with respect to ion exchange equilibria. In conclusion, it should be remarked that, as a rule, some properties of a counterion favor a particular uptake over others. These are, higher valence (especially in dilute solutions), smaller solvated volume, greater polarizability, stronger complex formation with the fixed ion and weaker complex formation with co-ions. If a counterion has the tendency of being more easily associated with the fixed ion, then the exchange equilibrium is altered in its favor. Based on this principle (Le Chetelier) weak acid exchangers prefer, in contrast to strong acid exchangers, hydrogen ions as against almost all monovalent metal cations. This applies also to

Table 1.4 Mean separation factors of customary styrene sulfonic acid resins of different crosslinkages in equilibrium with dilute chloride solutions

Counterions	Crosslinking (% DVB)		
	4	8	16
Li <sup>+</sup> /H <sup>+</sup>	0.75	0.78	0.70
Na <sup>+</sup> /H <sup>+</sup>	1.2	1.5	1.6
NH <sub>4</sub> <sup>+</sup> /H <sup>+</sup>	1.4	2.0	2.3
K <sup>+</sup> /H <sup>+</sup>	1.7	2.3	3.0
Cs <sup>+</sup> /H <sup>+</sup>	2.0	2.6	3.2
Ag <sup>+</sup> /H <sup>+</sup>	3.6	6.7	15.5
Zn <sup>2+</sup> /Mg <sup>2+</sup>	1.1	1.1	1.1
Co <sup>2+</sup> /Mg <sup>2+</sup>	1.1	1.1	1.1
Cu <sup>2+</sup> /Mg <sup>2+</sup>	1.1	1.2	1.3
Ni <sup>2+</sup> /Mg <sup>2+</sup>	1.2	1.3	1.3
Ca <sup>2+</sup> /Mg <sup>2+</sup>	1.4	1.6	2.1
Ba <sup>2+</sup> /Mg <sup>2+</sup>	2.5	3.5	5.9

chelating resins, as long as the reactive groups are weak acids; the metal ion can easily be exchanged against hydrogen ions, with the complex formation being very selective and very strong in neutral or alkaline solutions. On the other hand, the exchange equilibrium is altered unfavorably for the uptake of a counterion if it is removed either by association, complex formation or precipitation. Thus it is possible, due to the binding of  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ , to convert a weak acid exchanger with NaOH from the  $\text{H}^+$ -form into the  $\text{Na}^+$ -form, which is only partially feasible with NaCl. The addition of complex-forming agents to a solution with metal ions leads to complex-ion formation with selectivities not achieved otherwise; the most remarkable example for this is the separation of the rare earth and other fission products in spectroscopic purities, for which complex-ion formation and control of pH was the key to sharp differentiation among the rare earths by ion exchange processes [125]. The technique of changing the charge of a cation by complex-ion formation, thus modifying its attraction as an anion complex to an anion exchanger, e. g.  $\text{AuCl}_4^-$ , is of use in that this may happen to a varying degree for each species competing for the complexing reagent. Changes in the dielectric constant, the solvation and the structure of the solvent can deeply influence the selectivity on going over to nonaqueous or mixed-aqueous systems, which are used especially for analytical purposes; this is unpractical in technical applications because exchange velocities are too low. It must finally be mentioned that the thermodynamic equilibrium constant including both the activity coefficients and the correction factors is difficult to evaluate and is therefore treated in the chapter on the theory of ion exchange.

Apart from the application of mathematical relations for the quantitative description of ion exchange, a commonly used method of investigation of an estab-

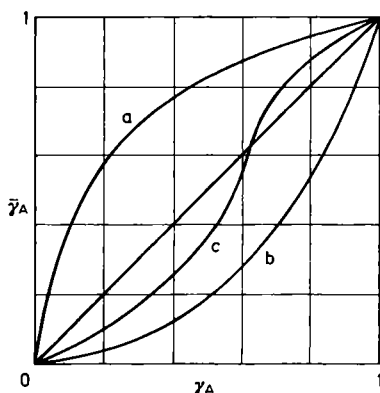


Figure 1.27 Ion exchange isotherms.  $\bar{\gamma}_A$  and  $\gamma$  are the relative exchange concentrations in resin phase and solution, respectively; c shows a sigmoidal characteristic of the ion exchanger.

lished ion exchange equilibrium is to determine the concentrations of a solute in the solution and in the resin and to construct what is called an ion exchange isotherm. An ion exchange isotherm is defined as the concentration of a counterion in the ion exchanger expressed as a function of its concentration in the external solution under specified conditions and at constant temperature (IUPAC). For plotting it, the equivalent in part  $\bar{\gamma}_A$  of the ion A in the exchanger is plotted as a function of the equivalent  $\gamma_A$  of the ion A in the solution, as shown in Figure 1.27. The numerical value of the equivalent is independent of whether the concentration is given molaly, molarly or in mole fractions. Figure 1.27 shows the three curves possible depending on various selectivities, i. e. a straight diagonal line in this so-called quadratic equilibrium representation if the state of equilibrium was reached without any selectivity, and non-linear curves for the possibilities of selectivity of one counterion over another. With respect to eventual connections between ion exchange and sorption, a sorption isotherm has been defined: it is the concentration of a sorbed species in the ion exchanger expressed as a function of its concentration in the external solution under specified conditions and at constant temperature (IUPAC). In accordance with the different forces that may become effective in relation to sorption processes, and which frequently appear side by side, the exchange plus superimposed sorption isotherms are (except for simple ions) often quite complicated, resembling complex equilibria. In practical studies much can be read from sorption isotherms, and sometimes even more from the subsequent desorption curves. Isotherms are also called either favorable, unfavorable or linear. Favorable isotherms, a in Figure 1.27, favor the uptake of the ionic species; unfavorable isotherms, b in Figure 1.27, do not favor uptake over the full range of concentration. The linear isotherm is obtained for  $\bar{\gamma}_A = \gamma_A$ . In addition there are also so-called sigmoidal isotherms, representing a selectivity reversal. Viewed practically, the sigmoidal isotherm is in general very undesirable. For an understanding

Figure 1.27 it must be mentioned that per definition the respective concentrations  $\bar{\gamma}_A$  and  $\gamma_B$  are relative concentrations of the component that is being taken up by the exchanger, which therefore range from zero to one.

According to Lieser selectivity may be defined by the following equation

$$S = \log K_d(1) - \log K_d(\text{others}),$$

in which  $K_d(1)$  is the distribution coefficient of the element, ion or compound under consideration and  $K_d(\text{others})$  the highest value of the distribution coefficients of all other species that may be present. The highest possible selectivity results when a substance reacts with only one element, ion or compound. It is the aim of many scientists working in the field of analytical chemistry to find such substances. But substances of high selectivity are also very important in radiochemistry and nuclear or environmental technology where special radionuclides, long-lived fission products or trace amounts of elements or compounds are to be separated from other elements or compounds. High selectivity is not restricted to certain classes of compounds. Inorganic compounds, organic compounds or resins, and special groups show high selectivity for certain elements, ions or compounds. Lieser and coworkers have applied this equation to many separation problems.

**Sorption equilibria.** Sorption is defined with respect to ion exchangers as the uptake of electrolytes or non-electrolytes by ion exchangers through mechanisms other than pure ion exchange. In order to make the terminology clearer one has, in other words, to distinguish between non-exchange electrolyte adsorption and the adsorption of non-electrolytes. It is further important to realize that the terms electrolyte and co-ion uptake by an ion exchange resin are synonymous.

Discussing first the equilibrium between a resin containing the fixed ion with counterion A and an aqueous solution of an electrolyte containing the same ion A and co-ion X, the usual depiction shows that in both the above cases, either by diffusion or as a result of other special conditions, with the least quantity of counterions A migrating out of the resin or the uptake of co-ions X, the latter must, because of electroneutrality, be accompanied by an equivalent number of counterions A. Consequently, and because the fixed ion of the resin cannot migrate from the resin phase to the aqueous, the particular type of equilibrium called a Donnan equilibrium arises. The Donnan equilibrium that can be reached is governed by the Donnan potential established during the above-described migration processes, which tends to pull in ions A and to repel co-ions X. Qualitatively seen, the Donnan potential at the interface is negative for cation exchangers and positive for anion exchangers. Important is that the Donnan potential is greatest, and therefore co-ions almost entirely excluded, when the concentration difference between the resin phase and the external solution is large. A high exchange capacity, high crosslinking, and increasing dilution of the external solution are, therefore, factors favoring the exclusion of electrolyte from the exchanger. The potential required to counteract the initial migration of the counterion is least for those of

higher valence and the effect of electrolyte (or Donnan) exclusion is consequently lower. Further, a given Donnan potential excludes multivalent co-ions to a greater extent than monovalent ions. An increase in the external electrolyte concentration is favorable for the penetration of electrolyte into the exchanger, but this is also accompanied by a shrinking of the resin due to a lowering of the water activity in the external solution relative to the exchanger phase. An equilibrium is reached, i. e. the Donnan equilibrium, at which the electrochemical potential of each ionic species is the same in both phases, with electroneutrality prevailing everywhere. A number of models have been proposed to describe the Donnan non-exchange electrolyte sorption equilibrium quantitatively. Ignoring the activity coefficients and the swelling pressure, it is generally accepted that from equating the electrochemical potentials of the co-ion in both phases and using the thermodynamic relationships concerned, the following equation is obtained as a general statement for the existing Donnan equilibrium for an electrolyte AX dissociating into  $\nu$  ions

$$\frac{\bar{C}_A^{\nu_A}}{C_A^{\nu_A}} = \frac{\bar{C}_X^{\nu_X}}{C_X^{\nu_X}},$$

This equation can be discussed for various conditions. At high concentrations of counterions in the resin and low concentrations of the same species in solution ( $C_A, C_X \ll \bar{C}_A$ ) the uptake of co-ions ( $C_X$ ), and implicitly of electrolyte, into the exchanger is small. This phenomenon is known as Donnan exclusion. It is larger for higher valence of the co-ion ( $\nu_X$ ) and lower valence of the counterion ( $\nu_A$ ). As the concentration of the solution is increased the Donnan exclusion becomes less effective and conditions for the situation known as electrolyte invasion are reached. In other words, the distribution coefficient

$$K_d = \frac{\bar{C}_X}{C_X}$$

of the co-ion or of the electrolyte increases with increasing concentration of the solution [126]. Some other consequences of the Donnan exclusion are also of interest to ion exchange fundamentals. Since it is caused by electrostatic effects and disappears at lower dissociation of the electrolyte or the exchangeable groups, cation exchangers, e. g., adsorb weak acids well but their dissociated salts only a little. In a similar way, weak acid exchangers adsorb strong acids well but their salts hardly at all. In all these cases the sorption depends greatly on the pH of the solution. As the internal structure of the ion exchange resins is highly decisive for all ion exchange phenomena, it must be concluded that the Donnan theory is valid only for homogeneous exchangers and constant electrical potentials within the resin, whereas under certain practical conditions it is not strictly applicable. Thus counterion association in the resin, specific interactions between the co-ions and the fixed ionic groups, and complex-ion formation in the external solution can greatly influence the degree of non-exchange electrolyte sorption.

The sorption of non-electrolytes is best brought into the picture by drawing attention to the fact that ion exchangers in the dry state can already sorb a great variety of substances besides water. Gas sorption by zeolites for drying and to remove polar impurities from non-polar gases is one example. For all sorptions of non-electrolytes either from the gas phase or from a liquid phase or solution it is a prerequisite for a large amount of sorption that there be a strong interaction with the constituents of the resin, the hydrocarbon network, the fixed and counterions, and any solvent already present. The interaction with the matrix occurs through van der Waals forces. Interaction with the fixed ions may occur through solvation, although this is not the only mechanism feasible, since solutes may be sorbed from aqueous solutions, where hydration is preferred over solvation by the solute. Hydrogen bonds formed between certain kinds of solutes, like alcohols, with the water of hydration, may then be the major factor. Because of the fixed ions the ion exchanger represents a strong polar medium which means that polar molecules are generally taken up and non-polar ones largely rejected. The properties of the ion exchange resin, i. e. degree of crosslinking, swelling and concentration of water-preferring ions, the kind of counterions, the solvent and additives in a solvent system all influence the sorption and allow room to vary the sorption conditions. For weak acid and weak base exchangers the same pH-dependent effects can be encountered as discussed for the sorption of electrolytes.

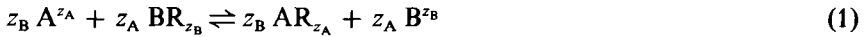
Besides investigations of the mechanisms of sorption of non-electrolytes by ion exchangers quite a number of investigations have been made in order to elucidate the sorbing behavior of individual chemical substances, as well as of homologous series. As typical for the sorption of non-electrolytes it must be mentioned that Langmuir adsorption isotherms are usually determined at 20 °C and in dependence on the pH. The Langmuir adsorption isotherms are, in most cases, convex and permit the calculation of the maximum sorption capacity. Included in the investigations of the sorption properties were many studies of the distribution of organic solvents between ion exchange resins and aqueous solutions. Among the individual substances studied phenol is an outstanding example, with a distribution coefficient higher than unity in strongly basic anion exchangers. For several aliphatic acids and alcohols in strong acid cation exchangers a general trend of a decreasing distribution coefficient with increasing external organic concentration and increasing crosslinking has been demonstrated. Because of the lack of a general quantitative theory for the sorption of non-electrolytes by ion exchange resins phenomenological solutions are presented [127]. Otherwise strong adsorption effects are to be expected for solutes that can form complexes with the counterions. For instance, anion exchangers in the  $\text{Br}^-$  or  $\text{I}^-$ -form strongly absorb bromine and iodine, probably forming  $\text{Br}_7^-$  and  $\text{I}_7^-$  adducts in a stoichiometric process, reaching saturation of the resin beyond a certain concentration of solute, which is shown by a flattening out of the sorption isotherm.



**Ligand exchange.** This standard method developed by Helfferich is a special sorption procedure based on cation exchangers with transition metals as counterions. In this process the complex water molecules of the metallic ion bound to a cation exchanger of the carboxylic acid type are exchanged for ammonia. The method can be extended, with the ammonia being then exchanged for diamine. In contrast to ion exchange in general, this method — which is in accordance with complex chemistry — leads to an exchange of ligands on the counterion while the latter is retained in the resin phase. Carboxylic resins are used for this purpose, because of their higher selectivity compared with sulfonic acid exchangers. Ligand exchange is for the preparation of salts, and is suitable as well for the separation of amines, amino acids, etc. [128].

A very valuable approach to the fundamental question of ion exchange and the law of mass action was presented by Bobleter, yielding an equilibrium determination of cation exchangers through distribution and activity coefficients. It has often been denied that equilibrium constants and distribution coefficients are related to the law of mass action. It can, however, be shown that these coefficients and constants can be deduced directly from the law of mass action, provided ion activities and true molar concentration values are considered for the liquid part of the ion exchange phase [129]. The following is a gratefully included direct contribution from O. Bobleter, and the reader should note that slightly deviating notations have been used.

The exchange of the ion A for B on the monovalent exchange site R can be written



whereby  $z_A$  and  $z_B$  represent the valency state of the ions A and B. The activities of the ions A and B must be equal in the solution and the ion exchanger phase. Therefore

$$a_{AR_{z_A}} = a_A z_A \quad \text{and} \quad a_{BR_{z_B}} = a_B z_B.$$

This leads directly to the thermodynamic equilibrium coefficient,  ${}^0K_B^A$ , which by definition is equal to (1):

$${}^0K_B^A \equiv \frac{a_{AR_{z_A}}^{z_B} \cdot a_{B^{z_B}}^{z_A}}{a_A^{z_B} \cdot a_{BR_{z_B}}^{z_A}} \equiv \frac{C_{AR_{z_A}}^{z_B} \cdot C_{B^{z_B}}^{z_A}}{C_A^{z_B} \cdot C_{BR_{z_B}}^{z_A}} \cdot \frac{\gamma_{AR_{z_A}}^{z_B} \cdot \gamma_{B^{z_B}}^{z_A}}{\gamma_A^{z_B} \cdot \gamma_{BR_{z_B}}^{z_A}} \equiv 1 \quad (2)$$

(For reasons of simplicity the lower indices  $z_A$  and  $z_B$  have been omitted). In the second part of equation (2), the activities are replaced by the product of the corresponding concentrations  $C$  and the activity coefficients ( $\gamma$ ). The molar equilibrium coefficient  $K_B^A$  is therefore

$$K_B^A = \frac{C_{AR}^{z_B} \cdot C_B^{z_A}}{C_A^{z_B} \cdot C_{BR}^{z_A}} = \frac{\gamma_A^{z_B} \cdot \gamma_{BR}^{z_A}}{\gamma_B^{z_A} \cdot \gamma_{AR}^{z_B}} \quad (3)$$

A further simplification has been introduced: the ion A is present in traces only and B is the macroelectrolyte.

Activity coefficients in the outer solution. The activity coefficient of the macroelectrolyte ion is equal to that of the compound (BX)

$$\gamma_{BZ_B} = \gamma_{BX} \quad (4)$$

Only  $\gamma_{BX}$  can be determined experimentally. The activity coefficients of many electrolytes in dependence on their concentration are listed in the literature.

The evaluation of the trace ion activity coefficient is more complicated, owing to the fact that its activity is influenced by the activity of the macroelectrolyte ion. By the use of the Harned rule this influence can be determined:

$$\log \gamma_{AX(0)} = \log \gamma_{AX(1)} + \alpha_{AX} \cdot C_{BX} \quad (5)$$

In this equation,  $\gamma_{AX(0)}$  indicates the activity coefficients of the neutral compound AX at the trace concentration, and  $\gamma_{AX(1)}$  that of AX at the concentration at which the macroelectrolyte BX occurs in the solution. The  $\alpha$  coefficients of several electrolytes at different macroelectrolyte concentrations are also given in the literature.

Activity coefficients in the ion exchanger phase. The exchanger loaded with the ion B has an activity coefficient of  $\gamma_{BR}$ . The determination of these values is relatively difficult, but at least for certain liquid exchanger systems the coefficients have been measured. In [129 a], for example, the activity coefficients for the Li-, Na- and K-salts of toluene sulfonic acid (Tsa) are given. It can be assumed that no essential differences exist between these liquid exchangers and an equivalent polystyrene DVB-crosslinked resin. The activity coefficients of the solid exchangers are therefore taken as equal to those of the liquid ones:

$$\gamma_{BR} = \gamma_{BTsa} \quad (6)$$

Evaluation of the Kraus and Moore experiments (Chapter 5.1) has shown, however, that only the water-containing part of the exchanger phase is involved in exchange processes. This is comprehensible because both the polystyrene matrix and the toluene fraction of liquid exchangers can be classified as inert materials, which means that they don't contribute to the electrolyte activities.

In Figure 1.28 the activity coefficients for Li and Na toluene sulfonic acids are plotted. The original molal concentrations have been transformed into molar values after determination of the density of the solutions. The inert part of the exchangers is deducted by subtracting the volume of the toluene molecule for every fixed site exchanger group.

The water content in the exchanger phase can be calculated for strongly acidic polystyrene exchangers [129 b] by the equation

$$\frac{W^0}{\rho_0} = \bar{V}^0 - 0.63 \quad (7)$$

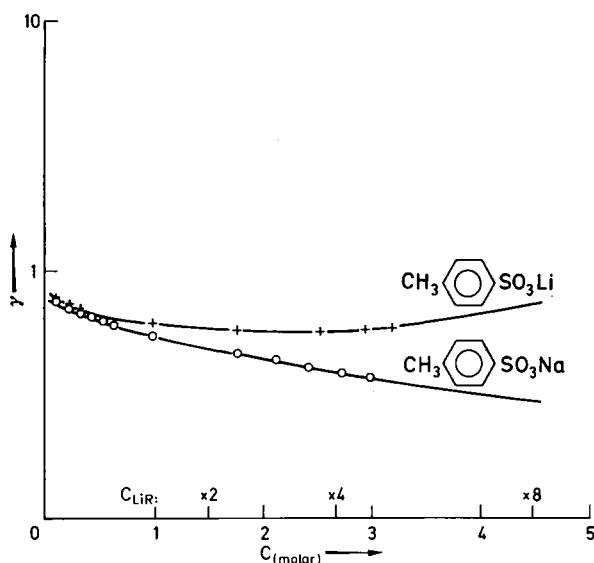


Figure 1.28 Activity coefficients of Na and Li toluene sulfonic acids in dependence on their concentration. The molal values were transformed into molar values and then the concentration was calculated for the inert free solution by deducting the volume of the toluene (conversion factor 1.12 per exchanger equivalent). For low outer electrolyte concentration the  $C_{LiR}$  values for three exchangers with different degrees of crosslinking (X2, X4, and X8) are indicated (Bobleter).

$W^0$  is the amount of water in grams of the specific exchanger volume  $V^0$  (of 1 gram dry exchanger in the  $H^+$  or  $Cl^-$ -form) and  $\rho_0$  the density of the water at the relevant temperature.

The concentration  $C_{BR}$  of the B-loaded exchanger is given by the relation of the capacity  $K_{sp}$  of the specific ion exchange volume to the water volume of the same amount of exchanger:

$$C_{BR} = \frac{K_{sp}}{W^0 \rho_0} = \frac{K_{sp}}{\bar{V}^0 - 0,63} \quad (8)$$

By this means the concentration is related to the amount of water in the exchanger phase.

A contraction (shrinking) of the exchanger phase usually occurs when the outer concentration of the electrolyte BX is increased. The specific volume of the exchanger must therefore be determined for every electrolyte concentration of interest. At low electrolyte concentrations Donnan exclusion is prevalent, but at higher concentrations Donnan invasion becomes increasingly important.

According to equation 3 in Chapter 5.1

$$\bar{C}_{BR} = \frac{C_{BR} \pm \sqrt{C_{BR}^2 + 4\left(\frac{\gamma_{BX}}{\bar{\gamma}_{BX}}\right)^2 C_{BX}^2}}{2} \quad (9)$$

– the invasion is negligible at low BX concentrations ( $\bar{C}_{BR} \approx C_{BR}$ ) but it can constitute a relatively large contribution at higher concentrations.

In a first step the activity coefficient of the macroelectrolyte ion in the exchanger phase can be equated with that of the liquid exchanger:  $\gamma_{BR} = \gamma_{BTsa}$ . In addition, the invasion of the electrolyte BX has to be considered. This again is done by introducing an equation equivalent to the Harned rule.

$$\log \bar{\gamma}_{BR(1)} = \log \gamma_{BTsa(1)} + \alpha_1 \bar{C}_{BR} \quad (10)$$

In the case of the trace ion the Harned rule must be extended because, in addition to the BX invasion, the coefficients are further influenced by the macroelectrolyte concentration

$$\log \bar{\gamma}_{AR(0)} = \log \gamma_{ATsa(1)} + \alpha_1 \bar{C}_{BR} + \alpha_2 C_{BR} \quad (11)$$

The relation  $\gamma_{BR(1)}/\gamma_{AR(0)}$  is of a special interest. From equation 10 and 11 it can be concluded that

$$\frac{\bar{\gamma}_{BR(1)}}{\bar{\gamma}_{AR(0)}} = \frac{\gamma_{BTsa(1)}}{\gamma_{ATsa(1)} \cdot 10^{\alpha_2 C_{BR}}} \quad (12)$$

Example of a  $\text{Na}^+/\text{Li}^+$  exchange. According to equation 3, the equilibrium constant for the exchange of  $\text{Na}^+$  trace ions for  $\text{Li}^+$  is given by

$$K_{Li}^{\text{Na}} = \frac{C_{\text{NaR}} C_{\text{Li}^+}}{C_{\text{Na}^+} C_{\text{LiR}}} = k_d \frac{C_{\text{Li}^+}}{C_{\text{LiR}}} = \frac{\gamma_{\text{NaCl}(0)} \bar{\gamma}_{\text{LiR}(1)}}{\gamma_{\text{LiCl}(1)} \bar{\gamma}_{\text{NaR}(0)}} \quad (13)$$

The constant  $k_d$  represents the molar distribution coefficient. With increasing outer LiCl concentrations, the concentration  $C_{\text{LiR}}$  of the  $\text{Li}^+$  ions adsorbed at the fixed exchanger sites increases, according to equation 8, due to the exchanger shrinking. As can be seen from Table 1.5 a the total Li concentration  $C_{\text{LiR}}$  is even higher owing to the LiCl invasion (shrinking and invasion according to equation 9).

The activity coefficients for the outer solution  $\gamma_{\text{NaCl}(0)}/\gamma_{\text{LiCl}(1)}$  are calculated by equation 4 and 5. At low electrolyte concentrations they are close to 1, but they decrease considerably at higher concentrations of the solution (Table 1.5 b). The coefficient of equation 5 is between 0.034 and 0.037.

Equation 12 can be written

$$\frac{\bar{\gamma}_{\text{LiR}(1)}}{\bar{\gamma}_{\text{NaR}(0)}} = \frac{\gamma_{\text{LiTsa}(1)}}{\gamma_{\text{NaTsa}(1)} \cdot 10^{\alpha_2 C_{BR}}} \quad (14)$$

Table 1.5 a Concentrations of a Li<sup>+</sup> loaded cation exchanger (Dowex 50WX4) at different outer LiCl concentrations

Outer solution $C_{\text{LiCl}}$ (mol/l)	Concentration in the exchanger phase (according to equations 8 and 9)	
	$C_{\text{LiR}}$ (mol/l)	$\bar{C}_{\text{LiR}}$ (mol/l)
0.1	2.66	2.67
0.25	2.78	2.83
0.5	2.91	3.08
1.0	3.13	3.67
2.0	3.50	5.05
3.92	4.19	7.96

Table 1.5 b Activity coefficients and equilibrium constants of a Na<sup>+</sup>/Li<sup>+</sup> exchange on Dowex 50WX4 (according to equation 14)

a	b	c	d
Outer solution $C_{\text{LiCl}}$ (mol/l)	Activity coeff. in outer solution $\frac{\gamma_{\text{NaCl}}(0)}{\gamma_{\text{LiCl}}(1)}$	Activity coeff. in resin phase $\frac{\bar{\gamma}_{\text{LiR}}(1)}{\bar{\gamma}_{\text{NaR}}(0)}$	$K_{\text{Li}}^{\text{Na}}$ (column b $\times$ c)
0.1	0.995	1.356	1.35
0.25	0.984	1.382	1.36
0.5	0.962	1.415	1.36
1.0	0.921	1.520	1.40
2.0	0.839	1.680	1.41
3.92	0.670	1.963	1.32
average			1.37

The  $\gamma$  values of Na and Li toluene sulfonic acid can be taken from Figure 1.28. The  $\alpha_2$  coefficient was estimated to be 0.01.

The relation  $\bar{\gamma}_{\text{LiR}}(1)/\bar{\gamma}_{\text{NaR}}(0)$  thus obtained is also given in Table 1.5 b. The value of the equilibrium constant  $K_{\text{Li}}^{\text{Na}}$  resulting from these experiments was found to be 1.37 and lies very well within experimental errors.

According to equation 13, the molar distribution coefficient  $k_d$  is

$$k_d = K_{\text{Li}}^{\text{Na}} \frac{C_{\text{LiR}}}{C_{\text{Li}^+}} \quad (15)$$

In Figure 1.29 a the corresponding values are given for an increasing LiCl concentration in the solution. The logarithmic plot represents a straight line, which can be obtained only when correct thermodynamic parameters are used.

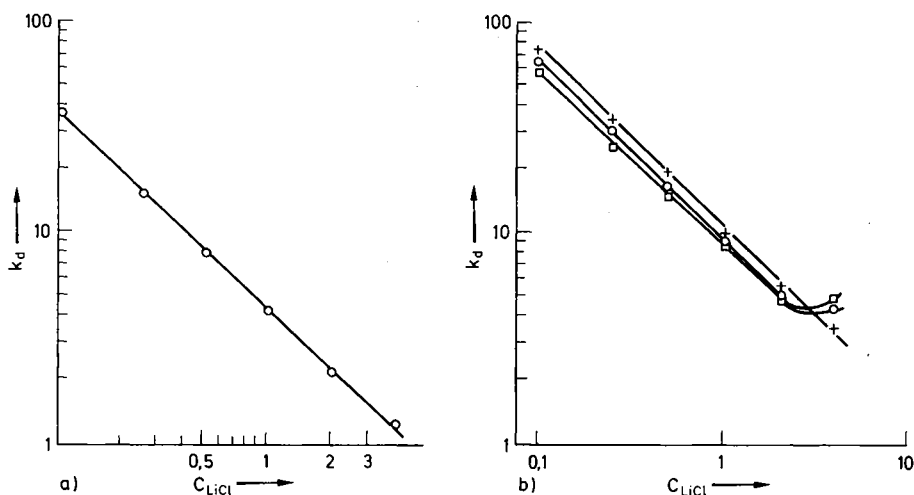


Figure 1.29 Distribution coefficients for the Na<sup>+</sup>/Li<sup>+</sup> exchange. + Dowex 50WX8, O Dowex 50WX4 and □ Dowex 50WX2.

a) The molar distribution coefficient,  $k_d$ , is given in dependence on the LiCl concentration in the solution.

b) The weight distribution coefficient,  $k_D$ , is given in dependence on the LiCl concentration in the solution (Bobleter).

In Figure 1.29 b the weight distribution coefficients for the same experiments are given

$$k_D = {}^{wt}K_{Li}^{Na} \frac{M_{LiR}}{C_{Li^+}} \quad (16)$$

$M_{LiR}$  is the specific capacity of the exchanger. Several characteristic features can be observed in this figure. The stronger crosslinked exchangers (Dowex 50W X 4 and 8) deviate greatly from linearity at higher LiCl concentrations. The parameter  ${}^{wt}K_{Li}^{Na}$  is no longer a constant but changes for every measured point between 1.13 and 2.45.

To summarize, it can be said that the law of mass action is a good basis for the evaluation of thermodynamic ion-exchange parameters. The necessary condition, however, is that true molar concentration values are applied, which means that the shrinking or swelling, as well as Donnan invasion, are also taken into account. Under these premises equilibrium constants and distribution coefficients can be deduced in astonishingly good agreement with the experiments [129].

The fundamentals of ion exchange and ion exchangers require some further definitions related to or derived from the chemical or physical properties of ion exchangers. Given the general validity of the principles of electrical neutrality and stoichiometry, there must at first be a constant counterion content that is directly

proportional to the fixed electrical charges of the matrix. In other words an ion exchanger has, depending on the number of fixed ions, a certain capacity for the uptake of counterions.

The capacity of an ion exchanger can, in general, be quantitatively expressed by the number of counterions relative to the number of exchange sites per unit weight of material. The capacity is usually expressed on a dry-weight or wet-volume basis and capacity ratings are assumed, unless otherwise stated, to relate to the hydrogen form of cation exchangers and the chloride form of anion exchangers. Depending on whether the capacity of an ion exchanger is regarded independent of or dependent on experimental conditions the following definitions are valid (IUPAC), with the term bed volume being used synonymously with column volume for the application of an ion exchanger in a packed column.

Theoretical specific capacity, $Q_0$ :	Milliequivalents of ionogenic group per gramme of dry ion exchanger. If not otherwise stated the capacity should be reported per gramme of the H-form of a cation exchanger and Cl-form of an anion exchanger.
Volume capacity, $Q_v$ :	Milliequivalents of ionogenic group per $\text{cm}^3$ (true volume) of swollen ion exchanger. (The ionic form of the ion exchanger and the medium should be stated.)
Bed volume capacity:	Milliequivalents of ionogenic group per $\text{cm}^3$ of bed volume determined under specified conditions (should always be given together with specification of conditions).
Practical specific capacity, $Q_A$ :	Total amount of ions expressed in milliequivalents or millimoles taken up per gramme of dry ion exchanger under specified conditions (should always be given together with specification of conditions).
Break-through capacity of ion exchanger bed, $Q_B$ :	The practical capacity of an ion exchanger bed obtained experimentally by passing a solution containing a particular ionic or molecular species through a column containing the ion exchanger, under specified conditions, and measuring the amount of species which has been taken up when the species is first detected in the effluent or when the concentration in the effluent reaches some arbitrarily defined value. The breakthrough capacity may be expressed in milliequivalents, millimoles or milligrammes taken up per gramme of dry ion exchanger or per $\text{cm}^3$ of bed volume.

The volume capacity  $Q_v$  and the bed volume capacity are related to the true volume and bulk volume respectively and depend on the type of counterions, the solvent and other conditions. The practical specific capacity,  $Q_A$ , covers, in contrast to the theoretical specific capacity, only the quantity of active fixed ions under specific conditions. The break-through capacity,  $Q_B$ , gives the uptake that can be achieved

under practical conditions, whereby the requirements on the purity of the effluent have to be taken into consideration.

Porosity is, besides being an important fundamental property, one of the most difficult subjects to describe and explain in general terms for all ion exchanger types. No general definition is included in the IUPAC Recommendations on Ion Exchange Nomenclature except the term macroporous ion exchanger for which the definition is given as ion exchangers with pores which are large compared to atomic dimensions. The channels which enclose the ion exchanger skeleton are usually called pores, and represent the porosity. The term gel type resin refers to ion exchangers prepared with polymers that do not contain pores. The pore structure of these gels is quite difficult to describe since the distances between crosslinks and chains vary considerably. These resins are elastic three-dimensional polymers which cannot have a definite pore size. A steadily increasing resistance of the polymer network limits the uptake of ions and molecules of increasing size. The resins have no appreciable porosity until swollen in some suitable solvent such as water. Among the synthetic ion exchange materials due to a new polymerization technique, ion exchange resins with a crosslinked structure have been developed, which are entirely different from the conventional so-called homogeneous gels in that they have a rigid macroporous structure superimposed on the gel structure similar to those of conventional adsorbents. In reality, however, these synthetic ion exchangers are also gels. Ion exchange materials referred to as macroporous are very tightly crosslinked gels in which larger holes have been formed artificially. The term isoporous, which had been introduced, can obviously not be accepted without criticism, since all gel ion exchange resins are more or less isoporous. That ion exchange resins have a microporous structure is quite often claimed in the literature but this property has not yet been clearly defined. For application in high pressure liquid chromatography so-called porous types of ion exchangers have been developed — they are in fact superficially porous materials of a special kind, which are treated in detail elsewhere in this volume.

Much has been described already in the foregoing sections of the swelling of ion exchangers. Confining the following comments to the swelling behavior of synthetic gel type resins, the main fact with regard to their swelling is that it is in principle an osmotic process, whereby the osmotic activity of the internal ionogenic groups being present in high concentration causes (because of the inclination to become diluted) water to enter the resin structure, which therefore swells. This swelling of the resin is accompanied by a stretching of the crosslinked hydrocarbon matrix. The crosslinking of the exchanger network then limits the swelling, and the net restoring force of the crosslinks is interpreted as an internal swelling pressure acting on the pore liquid within the resin. Equilibrium is reached when the swelling pressure of the matrix counterbalances the osmotic pressure difference between the interior of the resin and the surrounding solution. This approach roughly explains the most important factors the swelling depends on. To express it quantitatively a weight swelling and a volume swelling have been defined (IUPAC):



Weight swelling in solvent, $w_s$ : (e. g., $w_{H_2O}$ )	Gramme of solvent taken up by one gramme of dry exchanger.
Volume swelling ratio:	Ratio of the dry swollen volume to the true dry volume.

Swelling is necessary for the diffusion; if diffusion is hindered by too little swelling the exchange process becomes too slow.

Diffusion processes are essential for the whole field of ion exchange. In accordance with the above general equation for the ion exchange equilibrium the counter-ion  $A^+$  moves during the exchange process from the ion exchanger into the solution and the ionic species  $B^+$  moves from the solution into the exchanger. It was first recognized at the beginning of this century that basic ion exchange is essentially a redistribution of the exchanging counterions  $A^+$  and  $B^+$  by diffusion, a process therefore, that does not include an actual chemical reaction. In other words, basic ion exchange is in essence an equilibrium process that comes about by diffusion (Helfferich). In the following more or less only basic ion exchange and the role played in it by diffusion with respect to gel type ion exchange polymers can be regarded, neglecting for instance the diffusional sorption processes. In searching for mechanisms and models two have proven to be of basic importance, and have been used to develop the theory of the kinetics of ion exchange.

Based on extensive research into the rate factor in ion exchange Boyd and coworkers concluded that the ordinary exchange of ions is indeed not a chemical reaction of a kinetic order corresponding to its stoichiometric coefficients but a diffusion mechanism, in particular either diffusion in the adherent stagnant liquid layer to and from the exchanger particle or diffusion within the ion exchanger particle [130]. The discussions concerned were restricted to the exchange of counterions between ion exchanger particles and well-stirred electrolyte solutions, and did not include the much more complex behavior of columns. At that time it seemed evident that cases where a chemical exchange reaction is rate-controlling are extremely rare, if occurring at all. This basic diffusion concept is depicted in Figure 1.30. One comes to this figurative representation following Boyd's work by

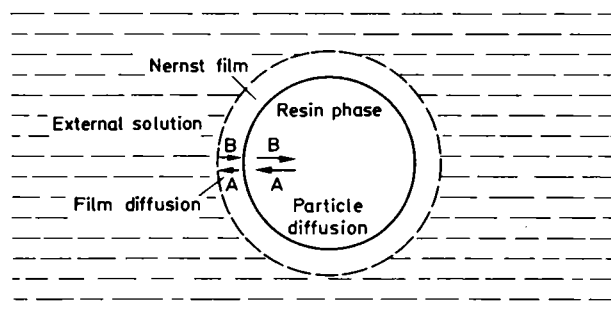


Figure 1.30 Film diffusion and particle diffusion in ion exchange kinetics.

assuming that at first, two different diffusion mechanisms exist during ion exchange. In the region of low external concentration (about 0.001 N), the rate is determined by the diffusion of ions through the liquid film enveloping the exchanger particle, while at high external concentrations (about 0.3 N), diffusion of ions through the exchanger particle itself represents the rate-controlling step. On the basis of this division, a distinction is made between film diffusion and particle or, better, gel diffusion. The outer boundary of the spherical exchanger particle represents the interface between the adhering Nernst film (the thickness of which was determined to be  $3 \cdot 10^{-4}$  cm [130, Dickel]) which has film diffusion, and the exchanger particle, which has gel diffusion [131]. In an intermediate range of conditions both mechanisms may affect the rate factor of the exchange of ions. But if only film or gel diffusion are considered, especially under practical considerations, and it is to be determined which of them is rate-controlling, a quantitative criterion derived by Helfferich can be applied. These relations for the theoretical prediction of the rate controlling step are based on the effect of ion exchange capacity  $\bar{C}$ , solution concentration  $C$ , particle size  $r_0$  (particle radius in cm), film thickness  $\delta$ , diffusion coefficients  $D$ , and the separation factor  $\alpha$ :

$$\text{Particle diffusion control } \frac{\bar{C} \bar{D} \delta}{C D r_0} (5 + 2\alpha_{A/B}) \ll 1 \equiv N$$

$$\text{Film diffusion control } \frac{\bar{C} \bar{D} \delta}{C D r_0} (5 + 2\alpha_{A/B}) \gg 1 \equiv N.$$

Using the dimensionless number,  $N$ , which is to be called the Helfferich number, the following criteria are obtained:

if  $N \ll 1$  particle diffusion control

if  $N \gg 1$  film diffusion control.

The thickness of the fictitious Nernst film is related to the engineer's Sherwood number by  $\delta = 2r_0/Sh$ . It is true that a low solution concentration favors film diffusion control, but a first difficulty arises from the selectivities of the exchanging ions. If the selectivity is sufficiently high, it is possible that exchange of A for B is film diffusion controlled, while the reverse exchange of B for A under identical conditions is particle diffusion controlled. An early method for distinguishing experimentally between film and particle diffusion control was developed by Kressman and Kitchener [132] with the so-called interruption test, in which the ion exchange process is stopped by removing the particles from the solution for a short period of time; only with particle diffusion control is the exchange rate higher upon reimmersion than at the moment of interruption, because internal concentration gradients have had time to level out. The difference in exchange rate that may be observed is schematically shown in Figure 1.31.

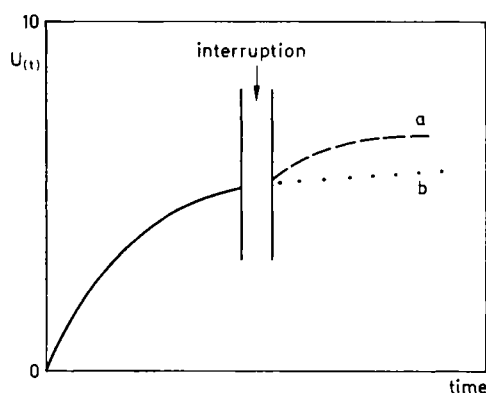


Figure 1.31 Diagrammatic representation of the interruption test and its effect on the observed exchange rate. After interruption the dashed line in continuation of the exchange indicates that the rate is controlled by concentration gradients in the particle or by mixed particle and film diffusion, and the dotted line that the unaffected film diffusion is rate determining.

Already with regard to this first model, and in particular with gel (particle) diffusion as the rate-controlling step in ion exchange materials, the problem of predicting diffusion coefficients in ion exchangers immediately arises. Diffusion in ion exchanger gels is slower than in solutions for several reasons. Part of the ion exchanger structure is not available for diffusion. The diffusion paths in the ion exchanger are more twisted and therefore longer. The size of ions influences their mobility in and through highly crosslinked and therefore denser portions of the gel, retarding larger ions more with increasing size of the diffusing species, preventing with very large species, the exchange equilibrium from being reached. These and several other conditions lead to a retardation in the diffusion in ion exchange resins and are also related to the question of whether a quasi-homogeneous model can be used for discussions of diffusion processes. The above model has been employed in various ways to relate the self-diffusion coefficients in ion exchanger gels to those in solution.

However, the diffusion of the counterions is — as was discovered some ten years later by Helfferich et al. — not as simple as it looks, and is moreover subject to the restriction of electroneutrality. This means that as ions of species  $A^+$  initially present as counterions move into the solution, a stoichiometric amount of species  $B^+$  must move into the exchanger to balance the electric charges of the fixed sites. The ions are carriers of electric charges and, therefore, their diffusion generates an electric potential — the diffusion potential — which influences the motion of the ions and which has to be taken into account in describing ion exchanging diffusion processes. Fluxes of counterions thus become coupled with one another, which is achieved by the corrective action of an automatically arising electric field, i. e. the diffusion potential. In ion exchange, diffusion processes are therefore the diffusion

of ions with an electric field as the mechanism because of electroneutrality conservation [133]. Resorting to Nernst, Planck, Teorell, K. H. Meyer and even Warburg [134] it was shown that in ion exchange diffusion there is a net flux

	Counterion 1	Counterion 2
Diffusion	→	←
Transference	←	←
Net flux (equal in magnitude)	→	←

which results from an initial disparity of diffusion fluxes caused by a minute deviation from electroneutrality. The electric potential gradient produces electric transference of both ions, in the direction of the diffusion flux of the slower ion, which in effect retards the faster ion and accelerates the slower one. As the mechanisms of ion diffusion in the resin are a fundamental question for theoretical kinetic investigations, it cannot be ignored that, besides other refinements necessary, there are situations where ion exchange processes are accompanied by a chemical reaction – for instance the neutralization of a weak acid cation exchanger in free acid form by a strong base,  $\text{RCOOH} + \text{Na}^+ + \text{OH}^- \rightarrow \text{RCOONa} + \text{H}_2\text{O}$ . Taking this, although reportedly remote possibility into account – which will be treated below as ion exchange accompanied by reactions – and trying to sum up what the mechanism of ion diffusion in an ion exchange resin is it can for now be assumed that the ion diffusion inside the resin can be approached hypothetically by at least three major different mechanisms [135]. As shown in Figure 1.32 besides the gradient or Fickian diffusion mechanism based on Fick's theory, there are two other feasible mechanisms that may be expected to occur, namely the homogeneous or progressive conversion mechanism as discussed for noncatalytic heterogeneous solid fluid re-

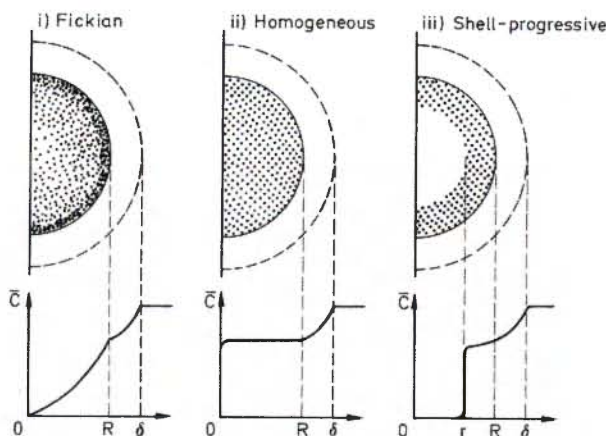


Figure 1.32 The fundamental diffusion mechanisms in question which may be basic as the rate determining step.

action models by Wen [136] and by Kunii and Levenspiel [137], or the shell progressive or unreacted core mechanism first developed by Yagi and Kunii [138]. From each of these hypothetical mechanisms theories of ion exchange kinetics can be derived, depending on whether they are based on Fick's laws [139], the Nernst-Planck equation, which contains in addition to the Fickian component a term for the electric field [133], or, in more recent times, the Stefan-Maxwell equation [140]. As far as values of diffusion coefficients are concerned, it has been shown that there is a relation between the effective diffusion coefficient  $\bar{D}$  inside the resin and the diffusion coefficient  $D$  in aqueous solution, which as a quotient yield a retardation factor according to the following formula

$$\frac{\bar{D}}{D} = \frac{(2 - \varepsilon)^2}{\varepsilon^2},$$

with  $\varepsilon$  the fractional pore volume [141]. For this and similar relations a quasi-homogeneous model for the exchange polymer was employed in most cases. It has always been a question whether such a model can be used for the treatment of diffusion processes in resins and theories of kinetics based upon them. The various retarding effects have been taken into account in the quasi-homogeneous model by the use of the effective diffusion coefficients. For customary ion exchange resins this model is considered as entirely adequate, as has been shown by experimental results — very accurate tracer-diffusion measurements agree closely with theoretical rate equations. Nevertheless, for other non-uniform exchange materials it is necessary to determine the effective diffusion coefficients for a particular combination of ion and ion exchanger. The above equation is reasonably successful for univalent counterions, co-ions and small molecules in moderately crosslinked polymers, but predicts too little retardation in other cases in which other effects, as e. g. partial localization of the counterions by association, contribute significantly. In customary gel type ion exchange resins the diffusion coefficients increase with increasing particle size and decreasing crosslinking. If the degree of crosslinking decreases, swelling increases, and with an increasing water content of the exchanger phase the diffusion coefficients become increasingly similar to the values of ordinary dilute solutions. In most commercial ion exchange resins, the values of particle diffusion of univalent ions are approximately 1/3 to 1/10, those of bivalent ions 1/5 to 1/100 and those of trivalent ions 1/10 to 1/1000 of the diffusion values in aqueous solutions. Table 1.6 shows measured values of diffusion coefficients in various commercial ion exchangers. It can be seen that the values depend on the valence of the ion and the degree of crosslinking.

When it comes to the employment of diffusion coefficients in theoretical kinetic models, however, the very important question arises of whether they are constant or variable. This question must certainly be gone into in those discussions where diffusion is considered as the only rate control factor. The earlier models of ion exchange kinetics of particle diffusion controlled binary exchange employed con-

Table 1.6 Tracer particle diffusion coefficients (at different temperatures)

Ion exchanger	Counterion	Diffusion coefficient ( $\text{cm}^2 \cdot \text{s}^{-1}$ )	Acti- vation energy (kcal/mol)	Source
Dowex 50 X 4	Na	$1.4 \cdot 10^{-6}$	4.93	G. E. Boyd et al., 1953
	Sr	$2.3 \cdot 10^{-7}$	5.64	
	Y	$7.5 \cdot 10^{-8}$	6.77	
	La	$6.9 \cdot 10^{-8}$	5.52	
Dowex 50W X 8	Na	$1.6 \cdot 10^{-6}$		J. C. W. Kuo et al., 1963
Dowex 50 X 8	Zn	$6.3 \cdot 10^{-8}$	7.34	G. E. Boyd et al., 1953
	La	$9.2 \cdot 10^{-9}$		
Dowex 50 X 8.6	Na	$9.4 \cdot 10^{-7}$	6.50	
	K	$1.3 \cdot 10^{-6}$	5.22	
	Ag	$6.4 \cdot 10^{-7}$	5.90	
	Sr	$3.4 \cdot 10^{-8}$	8.28	
	Y	$3.2 \cdot 10^{-9}$	7.53	
Dowex 50 X 12	K	$4.3 \cdot 10^{-6}$		M. Tetenbaum et al., 1954
Dowex 50 X 16	Na	$2.4 \cdot 10^{-7}$	8.40	G. E. Boyd et al., 1953
	Ag	$1.1 \cdot 10^{-7}$	7.20	
	Sr	$3.0 \cdot 10^{-9}$	10.98	
	Zn	$1.2 \cdot 10^{-8}$	8.52	
KU-2 X 2	methylene blue	$2.78 \cdot 10^{-10}$	15.0	G. S. Libinson et al., 1963
KU-2	NH <sub>4</sub>	$2.6 \cdot 10^{-6}$		L. N. Peletaev et al. 1986
PS-DVB X 10	Na	$2.1 \cdot 10^{-6}$		G. Dickel et al., 1968
	H	$0.98 \cdot 10^{-6}$		
	K	$3.2 \cdot 10^{-6}$		
	H	$0.98 \cdot 10^{-6}$		
Dowex 50W X 8	Na	$20.5 \cdot 10^{-7}$		M. G. Rao, 1974
	Mn	$2.22 \cdot 10^{-7}$		
	Sr	$1.95 \cdot 10^{-7}$		
PS-DVB X 8	Na	$7.1 \cdot 10^{-7}$		P. Frölich, 1976
		$1.9 \cdot 10^{-7}$		
Dowex 1 X 8	Cl	$3.3 \cdot 10^{-6}$		J. Eliasek, 1968
	OH	$0.5 \cdot 10^{-6}$		
Kastel A 500	SO <sub>4</sub>	$2.0 \cdot 10^{-6}$		L. Liberti et al., 1978
SBW	Cl	$2.0 \cdot 10^{-6}$		B. Mehlich et al., 1986
	OH	$0.3 \cdot 10^{-6}$		
Dowex 2 X 2	Br	$6.4 \cdot 10^{-7}$	5.0	B. A. Soldano et al., 1953
Dowex 2 X 6	Cl	$3.5 \cdot 10^{-7}$	6.8	
	Br	$3.9 \cdot 10^{-7}$	6.0	
	I	$1.3 \cdot 10^{-7}$	8.8	
	BrO <sub>3</sub>	$4.6 \cdot 10^{-7}$	6.2	
	WO <sub>4</sub>	$1.8 \cdot 10^{-7}$	7.2	
	PO <sub>4</sub>	$5.7 \cdot 10^{-8}$	8.7	
Dowex 2 X 16	Br	$2.6 \cdot 10^{-7}$	9.3	
Dowex A-1	Na	$1.2 \cdot 10^{-7}$		A. Schwarz et al., 1964
	Zn	$6 \cdot 10^{-9}$		
	Co	$7 \cdot 10^{-9}$		

stant interdiffusion coefficients, for instance when Fick's first law was used as the flux equation with  $\bar{D} = \text{const}$ . This approach is considered as correct for counterions with equal mobility  $\bar{D}_A = \bar{D}_B = \bar{D}$ . But on the basis of the Nernst-Planck model its validity for counterions with different mobilities, has been challenged, because here, as mentioned above, the effect of electrical-potential gradients is taken into account. In deriving the flux equations according to the Nernst-Planck model it has been found that the interdiffusion coefficient  $\bar{D}$  is not constant, but depends, according to the relation

$$\bar{D} = \bar{D}_A \bar{D}_B \frac{(z_A^2 \bar{C}_A + z_B^2 \bar{C}_B)}{(z_A^2 \bar{C}_A \bar{D}_A + z_B^2 \bar{C}_B \bar{D}_B)},$$

on the relative concentrations of A and B (Helfferich). With vanishing concentration of either ion, the interdiffusion coefficient then approaches the diffusion of that ion. In other words, the interdiffusion rate is predominantly controlled by the ion which is in the minority. The corrective action of the electric field is mainly directed against the high-concentration species, so that the interdiffusion rate is predominantly controlled by Fickian diffusion of the low concentration species, as is shown on the left of Figure 1.32. Two limiting cases are still to be mentioned, namely, either where ions of equal mobility are involved or where the concentration of one counterion is always much smaller than that of the other, as in exchange of trace components, where the interdiffusion coefficient equals the diffusion coefficient of the trace ion: e. g.,  $\bar{C}_B \ll \bar{C}_A$ ,  $\bar{D} = \bar{D}_0$ . In film diffusion-controlled binary ion exchange the earlier models all used the Nernst film concept on the premise that film diffusion is a quasi-stationary process in a planar layer. In Boyd's theory, developed for isotopic exchange for the use of Fick's first law, constant diffusion coefficients were applied:  $D_A = D_B = D = \text{const}$ . Adamson, as well as Dickel and Meyer and subsequent workers, later tried to include systems with counterions of different mobilities, with ion exchangers exhibiting selectivity. It was postulated that the fluxes of the ions in the film could obey Fick's law, but each with its own constant diffusion coefficient:  $D_A, D_B = \text{const}$ . The weaknesses of these approaches were discussed by Schlögl and Helfferich [142], who pointed out that a self-consistent treatment is achieved if one uses the three Nernst-Planck equations for A, B and the co-ion. Then again, for  $D_A \neq D_B$  a concentration gradient of the co-ion appears, but now Fickian diffusion of the co-ion in one direction is compensated for by electric transference in the opposite direction. Schlögl's Nernst-Planck film model also clarifies the accumulation or depletion of electrolyte at the particle surface. The driving force here is the electrical-potential difference between bulk solution and particle surface, resulting from counterion interdiffusion. This force pushes co-ions into the film if the faster counterion is initially in the solution, and pulls co-ions out of the film in the opposite case (Helfferich). In a detailed study of the theory of film diffusion Bunzl and Dickel made measurements in small concentration intervals in which the equilibrium constant  $K$  can actually be considered

constant [143]. The diffusion coefficients observed by Dunlop [144] in the ternary electrolyte for the system  $\text{Li}^+/\text{K}^+$  were used as a basis for calculations and led to a quantitative agreement between calculated and measured values.

Transport phenomena in ion exchangers can most rigorously be treated by the thermodynamics of irreversible processes [145]. Diffusion processes in ion exchange are here considered as transport phenomena in a concentrated electrolyte, with the use of the chemical potential as the driving force for dealing with the simultaneous diffusion of several species. But since neither the transport coefficients nor the chemical potential gradients needed in the corresponding equations are generally known, these quantities are replaced by the diffusion coefficients, which are first determined empirically. It must again be emphasized that every diffusion coefficient refers to a given reference system [146]. Using the Nernst-Planck equation in thermodynamic transport theories obviously yields a differential equation in which, in addition to Helfferich's diffusion coefficient, there is a coefficient involving the heat of reaction [147].

Attempts to include selectivity into diffusion processes in ion exchange resins seem to show that the Nernst-Planck equations are only limiting laws valid for ideal systems. Helfferich corrected his relation for the diffusion coefficient with an additional term, which leads then to

$$\bar{D} = D_A D_B \frac{z_A^2 \bar{C}_A + z_B^2 \bar{C}_B + z_A \bar{C}_A z_B \bar{C}_B \left[ \frac{d \ln K_a}{d(z_A \bar{C}_A)} \right]}{z_A^2 \bar{C}_A \bar{D}_A + z_B^2 \bar{C}_B \bar{D}_B},$$

where the actual existing gradients of activity coefficients have been expressed in terms of the molar selectivity coefficient  $K_a = \frac{\bar{y}_B^{z_A}}{\bar{y}_A^{z_B}}$ . But also according to Helfferich,

the role of selectivity in particle-controlled diffusion processes is such that it does not affect the flux equation, since only the derivative  $d \ln K_a / d(z_A \bar{C}_A)$  appears in the above equation and the absolute value of  $K_a$  is of no consequence. This relates to a constant boundary condition, so that the rate is independent of selectivity. But if the solution volume is not large compared with the amount of ion exchanger, so that  $C_A$  increases with conversion, the selectivity affects the boundary condition. Then, for any given solution concentration  $C_A$ , the boundary concentration  $\bar{C}_A(r_0, t)$  is lower if the ion exchanger prefers B more strongly. In such systems selectivity for the ion B does indeed increase the rate and the conversion eventually attained. In film diffusion the influence of selectivity is rather different, as it has no effect on the flux equations, only on the boundary condition at the film/particle interface. In film diffusion the concentrations of both ions A and B at the interface are finite over the course of exchange, even if the concentration of A in the bulk solution remains negligible, and the boundary concentration  $C_A(r_0, t)$  is thus affected by the selectivity even in this case. As a consequence, the rate of film-diffusion-controlled exchange increases with increasing selectivity for the ion B, even in cases in which



particle-diffusion-controlled exchange is independent of such preference. This difference between the two mechanisms with respect to selectivity accounts for the appearance of the separation factor  $\alpha_{A/B}$  in the Helfferich number  $N$ . It is important to note that the selectivity effect, which may be drastic, is taken into account differently in the different theories of ion exchange kinetics.

Very practically conceived investigations of the selective exchange of  $\text{SO}_4^{2-}$  against  $\text{Cl}^-$  on anion exchangers of different basicity by Liberti and coworkers under particle-diffusion-controlled conditions showed that, in general, because of the diffusive nature of the ion exchange mechanism, it must be concluded that selectivity may adversely influence the over-all kinetics of ion exchange processes. This must obviously be taken into account each time one is dealing with selective applications of ion exchange [148]. Two cases have been studied extensively: the chloride/sulfate exchange when particle diffusion is rate-determining because of the concentration conditions; and very dilute systems where resin selectivities for the divalent sulfate ion are drastically raised due to the electroselectivity effect. For the first case it was found that for this actual system also an apparently variable interdiffusion coefficient can be determined experimentally, thus avoiding the problem of the knowledge of the individual ion diffusion coefficients for each exchange (which is the explanation for the lack of experimental evaluation of the Nernst-Planck model and the use, whenever possible, of Fick's simpler model); further, that from  $\bar{D}$  vs.  $U$  plots the single ion diffusion coefficients can be extrapolated as limiting  $\bar{D}$  values, and that the more rigorous rate laws for ion exchange can be applied to the investigated process. For the second case it was discovered that rate mechanisms do not seem to obey the well-known models based on diffusion only, but convincing evidence was obtained to show that the chemical reaction rate on fixed charges controls the overall process kinetics. In particular the activation energies — up to 16.83 kcal/equ, — are definitely beyond the range of usual diffusion controlled kinetics. Therefore, a spherically-symmetrical diffusion model with a billiard-ball-like mechanism of site-to-site jumping of ions inside the resin was suggested.

The determination of diffusion coefficients of ion exchangers is usually made by independent radioactive tracer or conductivity measurements. For the first case only measurements performed on spherical granules will be considered here. For such ion exchange materials the shallow bed technique is the most frequently used method. Initially introduced as the thin bed method for general kinetic investigations on cation exchange water softening it was adopted under the current term by Boyd and coworkers to study the self-diffusion of cations and anions, etc., in and through exchange polymers. This method makes possible the determination of rates of exchange down to very short times. Further, it makes it possible to obtain rate data under conditions of constant solution concentration of the exchanging ions. The first such experimental arrangement is shown in Figure 1.33. Later researchers have used the shallow bed method with more or less significant modifications, and with not only a small volume of exchanger but with as few as five resin beads.

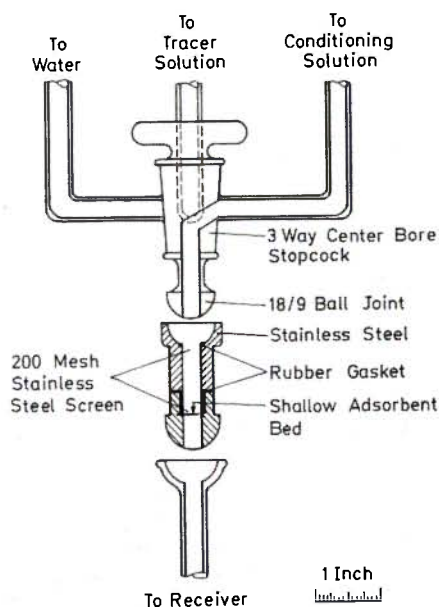


Figure 1.33 Equipment for the determination of exchange rates according to the shallow bed method.

Other experimental procedures can only be mentioned, for instance the disc method of Helfferich (for polycondensation ion exchange resins) or the shallow fluidized bed method of Streat. The diffusion coefficient is obtained from rate relations containing it, depending on the theoretical model used. Solving the many still unsolved problems and existing anomalies in describing diffusion in ion exchange and related ion exchange systems is a task remaining for ion exchange kinetics. Conductivity measurements for the determination of the mobilities in ion exchange materials were first carried out for investigations on membranes [149] but can as well be used for the determination of diffusion coefficients in ion exchanger beads [150]. In all these cases, evidently, quite special experimental equipment has to be designed, which may be the reason why for the determination of diffusion coefficients in ion exchangers the radioactive tracer method is much more frequently applied.

Among the ion exchange materials the diffusion processes occurring in macroporous ion exchange polymers deserve to be considered separately, because such resins are now widely used industrially. Macroporous (or porous) ion exchangers are heterogeneous and can be modelled as an agglomeration of microspheres within the bead macrosphere. In other words, a bead of a macroporous ion exchanger is formed of clusters of microspheres, which arrange in groups to give an open, porous structure containing comparatively large voids, called macropores. The microspheres also contain water, and it is essential to realize that ion exchange by diffusion

proceeds within the macropores and the microspheres. In the macropores the self-diffusion coefficients of exchanging ions have values lower than, but comparable to, their values in the free aqueous solution. But in the microspheres, the diffusion coefficients are orders of magnitude lower than measured for even quite highly crosslinked gel type materials. It has been shown that diffusion coefficients in both phases are in agreement with the Nernst-Planck theory with regard to their dependence on composition. For a complete understanding, the fluxes in the macropores and the diffusion in the microspheres have to be brought together, resulting in parameters that affect the shape of the conversion vs. time curve, but which have a very simple physical explanation. If the parameter,  $\beta$ , is large, it means that macropore diffusion is rate limiting, while very small values indicate that diffusion into microspheres controls the overall exchange rate.  $\alpha/\beta$  is the ratio of the relative uptake in the microspheres and macropores at equilibrium. When  $\beta$  is small, the uptake is a two-stage process. Diffusion in the macrostructure is very much faster than in the microstructure. The macropores are in equilibrium before any measurable uptake by the micropores occurs. If  $\beta$  is large, the composition of each small sphere is practically uniform, though changing over time in equilibrium with the composition of the macropore at that location. The other special case exists for  $\alpha = 0$ . In this situation there is no uptake by the microspheres and the model reduces to the simple homogeneous diffusion case (Patell and Turner, [150]). Thus it can be understood why the open, porous structure of the macroporous ion exchange resins does not lead to markedly improved exchange kinetics. The increased rate of diffusion into the centre of a bead through the macropores is counteracted by the much slower diffusion within the microspheres.

The possibilities of ion exchange accompanied by reactions mentioned only briefly above have been presented in a comprehensive analysis by Helfferich [151]. It has to be realized that the ion exchange processes described above as a redistribution of counterions is based, for theoretical treatments, on the assumption that the exchanging ions retain their identity. This is reasonable and justifiable for the simple and most extensively studied systems, such as the exchange of uni- or divalent cations with strongly acidic cation exchangers, a case that is very important in practice. This assumption is, however, questionable with counterions which are hydrolyzed, and is wrong when the ion exchange process is accompanied by chemical reactions such as, for instance, neutralization or complex formation. Helfferich has grouped the ion exchange processes accompanied by reactions into four general classes covering eleven typical cases. As presented in Table 1.7 processes like association, dissociation, precipitation and complex formation can accompany ion exchange, exercising — either by the binding or releasing of counterions — substantial influence. In class I the counterion released from the exchanger is consumed by a reaction. This is the case when  $H^+$  or  $OH^-$  released by strong acid or strong base ion exchangers is removed by neutralization with solution of base or acid (reaction I a and I b), or when released  $H^+$  or metal counterions form undissociated acid (reaction I c) or complexes (reaction I d) or are precipitated (reaction I e).

Table 1.7 Ion exchange with reaction. Classification and examples as grouped by Helfferich

Class Reaction		Examples			
	Initial state	Final state	Initial state	Final state	
I	$-\text{R} + \text{A} \rightarrow \text{B} + \text{Y} \rightarrow -\text{R} + \text{B}$	a) $-\text{SO}_3^- + \text{H}^+$ b) $-\text{N}^+ \text{R}_3 + \text{OH}^-$ c) $-\text{SO}_3^- + \text{H}^+$ d) $2 -\text{SO}_3^- + \text{Ni}^{2+}$ e) $-\text{N}^+ \text{R}_3 + \text{Cl}^-$	+ AY	$-\text{SO}_3^- + \text{Na}^+ \rightarrow$ $-\text{N}_3^+ \text{R} + \text{Cl}^- \rightarrow$ $-\text{SO}_3^- + \text{Na}^+ \rightarrow$ $2 -\text{SO}_3^- + 2 \text{Na}^+ \rightarrow$ $-\text{N}^+ \text{R}_3 + \text{NO}_3^- \rightarrow$	+ H <sub>2</sub> O + H <sub>2</sub> O + AcOH + 2Na <sup>+</sup> + Ni(EDTA) <sup>2-</sup> + AgCl
II	$-\text{R} + \text{A} \rightarrow \text{B} + \text{Y} \rightarrow -\text{RB}$	a) $-\text{COO}^- + \text{Na}^+$ b) $-\text{NH}_3^+ + \text{Cl}^-$ c) $-\text{N}(\text{CH}_2\text{COO}^-)_2 + 2 \text{Ba}^+$	+ A + Y	$-\text{COOH} \rightarrow$ $-\text{NH}_2 \rightarrow$ $-\text{N}(\text{CH}_2\text{COO}^-)_2 \text{Ni} \rightarrow$	+ Na <sup>+</sup> + Cl <sup>-</sup> + Na <sup>+</sup> + Cl <sup>-</sup> + H <sub>2</sub> O + 2 Na <sup>+</sup> + 2 Cl <sup>-</sup>
III	$-\text{RA} \rightarrow \text{B} + \text{Y} \rightarrow -\text{R} + \text{B}$	a) $-\text{COOH}$ b) $-\text{NH}_2$ c) $-\text{N}(\text{CH}_2\text{COO})_2 \text{Ni}$	+ AY	$-\text{COO}^- + \text{Na}^+ \rightarrow$ $-\text{NH}_3^+ + \text{Cl}^- \rightarrow$	+ H <sub>2</sub> O
IV	$-\text{RA} \rightarrow \text{B} + \text{Y} \rightarrow -\text{RB}$	$-\text{N}(\text{CH}_2\text{COO})_2 \text{Ni}$	+ A + Y	$-\text{N}(\text{CH}_2\text{COO}^-)_2 + 2 \text{Na}^+ \rightarrow$ $\text{N}(\text{CH}_2\text{COOH})_2 \rightarrow$	+ 2 Na <sup>+</sup> + Ni(EDTA) <sup>2-</sup> + Ni <sup>2+</sup> + 2 Cl <sup>-</sup>

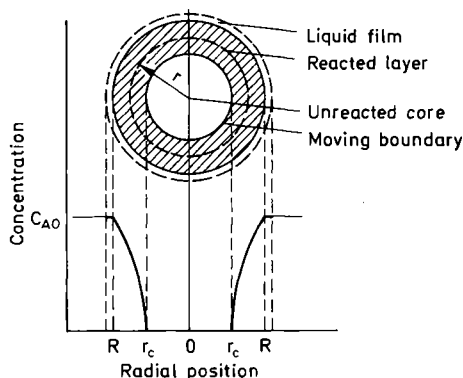


Figure 1.34 Schematic representation of the shell progressive mechanism in an ion exchanger bead according to Schmuckler and coworkers.

Helfferich predicted that the rate laws which could be derived for such ion exchange processes would appreciably differ from those for ordinary ion exchange in the absence of ionic reactions. This was later confirmed by the results of kinetic studies on the neutralization of strong acid and weak base ion exchange resins [152]. In class II and class IV the counterion to be taken up by the exchanger from the solution is characteristically consumed by a fast chemical reaction, and the interacting ions progress in shells into the resin matrix. Under the microscope a sharp moving boundary can be observed during the exchange process, when a completely reacted shell envelops an unreacted core. From a diffusion perspective, this is the so-called shell progressive mechanism (also known as shell-core, shrinking core or moving boundary mechanism) which is illustrated in Figure 1.34 [153], where the development of the concentration gradient from  $C_{Bo}$  to zero is traced. This model shows that the rate of these processes is controlled by the diffusion of the reactant through the reacted layer. The likelihood of a moving boundary in a spherical ion exchanger bead was first suggested by Helfferich for the elution of the sodium form of a weak acid carboxylic exchanger with hydrochloric acid (reaction II a). In this case a change of the resin from a dissociated to a non-dissociated species accompanies the exchange, but it was also realized that this was the exchange mechanism for, among others, the chloro-palladate-chloride interaction on a strong base anion exchanger and the chelation of copper on Dowex A-1. The description of the rate of ion interdiffusion in complex-forming ion exchangers (reaction II c) by using the isotherm yield dependences of the mass transfer rate on the exchange selectivity as the ratio between the dissociation constants for the complexes of the desorbed ion and the sorbed ion, was used as the parameter characterizing the exchange isotherm [154]. An optical verification of the sharp loading profiles inside the resin phase of weak electrolyte resins in their salt forms was presented by Hoell for weak acid cation exchangers or weak base anion exchangers (reaction II b), together with an isotherm close to rectangular in form. The corresponding fronts can be made visible

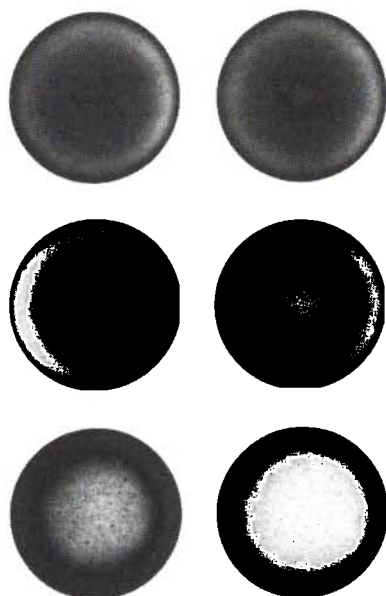


Figure 1.35 Succession of pictures of the exchange  $\text{Ca}^{2+} \rightarrow \text{H}^{+}$  of a weak acid cation exchanger bead after 2, 4, 8, 11, 13, and 15 min with 1 N HCl (Höll).

in transparent resins, and observation is possible due to gradients of the refractive indices or to transitions in color [155]. Evaluation of photographs, as e. g. shown in Figure 1.35, provides exact evidence for the exchange processes in the resin types concerned. For reactions of class III two mechanisms are possible. One is dependent on electrolyte invasion caused by the counterion B and the co-ion Y — as a typical case (reaction IIIa) the  $\text{OH}^{-}$  ion as a co-ion is the minority ion in the shell, which means that ion exchange is controlled by diffusion of a co-ion. For more general considerations it is of interest to discuss what the rate control is for the ion exchange in systems with reaction (Helfferich). A chemical reaction may affect the rate of ion exchange in two ways. In the first case, the reaction rate is slow compared with diffusion. In the limiting condition, diffusion is fast enough to compensate for any concentration gradients within the ion exchanger bead. The reaction at the fixed site is then the rate-controlling factor and the rate of the ion exchange is entirely independent of particle size. In the second, the reaction may be faster than diffusion, and is binding ions on the diffusion of which the ion exchange depends. The binding of the ions then inhibits their diffusion and slows the exchange down. The rate of exchange is controlled by slow diffusion which, in turn, is affected by the equilibrium of the reaction. The rate, then, is diffusion-controlled and depends on particle size. This is also a situation which often, although not always, leads to a progressive shell mechanism. It is still possible, for all the above-described ion exchange and reaction processes to calculate fairly accurately all the necessary kinetic parameters,

as well as to determine its extent of deviation from ordinary ion exchange, when one knows the nature of variation of the ion concentration through the diffusion zone [156].

**Acidity and basicity.** Ion exchangers have also been defined as high molecular weight solid acids or high molecular weight solid bases whereby these terms are equivalent to the more common expressions cation exchangers or anion exchangers. It is, therefore, of interest and considerable importance to examine in any exchange material the chemical properties from the point of view of acidity and basicity as well, and to determine the chemical nature of the ionogenic group. In principle, chemically, there are two fundamental types of ion exchanger, those in which under all normal conditions the ionogenic group is essentially completely dissociated and those where the extent of dissociation is markedly pH-dependent, corresponding to whether the ionogenic groups represent strong or weak acids, and strong or weak bases. Briefly summarizing, phenolic OH-groups or carboxylic acid groups remain partially or completely undissociated at low pH values, so that, for instance, the exchange capacity of exchangers with such ionogenic groups with respect to metal cations from acidic and neutral solutions is lower than from alkaline solutions. Anion exchangers with primary, secondary and tertiary amino groups exchange acid anions from alkaline and neutral solutions to a lesser degree than from acidic solutions. However, ion exchangers with strongly acidic or strongly basic groups — in the latter case quaternary ammonium groups — are capacity-independent over a broad pH range. Accordingly, they are also active over a wide pH range and can be used under acidic, neutral and alkaline conditions. Table 1.8 shows a summary of the effective pH ranges of customary types of ion exchangers. In other words, ion exchangers show a certain acidity or basicity as an important chemical property. To evaluate the acidity or basicity of any exchange material, inorganic or organic, so-called pH titration curves are determined, which involves the titration of the exchanger with either base or acid at various ionic strengths of the solution.

Table 1.8 Effective pH range of different customary types of ion exchangers

Type of ion exchanger	Approximate pH range
Strong acid cation exchanger	0–14
Weak acid cation exchanger	5–14
Weak base anion exchanger	0–9
Strong base anion exchanger	0–14

These titration curves are an aid, moreover, in the determination of the total number of ionogenic groups and the number of types of ionogenic groups present. It may be added that optimum operating pH ranges have been obtained based on theoretical considerations from titration curves of cation (sulfonic and carboxylic) and

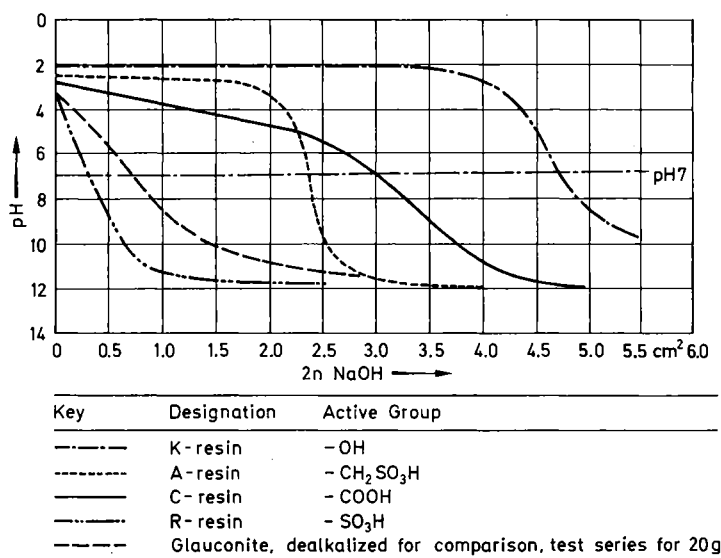


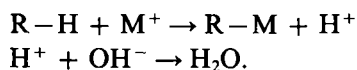
Figure 1.36 pH-titration curves of some cation exchangers according to Griebbach.

anion (strong and medium base) ion exchange resins, and are recommended as follows: sulfonic pH = 4.7–9.3, carboxylic 7.3–9.3, medium base 4.7–8.0 and strong base 4.7–10.1 [157]. In the case of cation exchangers Griessbach has introduced the method of pH titration, again based on the fact that cation exchangers in the H-form can be titrated with alkalis like ordinary acids, with the advancing neutralization process being evaluated by measurement of the pH. To perform this direct titration, 5 g of the cation exchanger were first transformed into the H-form with hydrochloric acid, then washed with distilled water, and finally treated with 0.1 N NaCl solution as a neutral salt in a beaker. Small amounts of 2 N sodium hydroxide were added with vigorous stirring, and the pH adjustment was observed on the glass electrode. For an evaluation of the test results, the measured pH values were plotted as a function of the consumed quantity of alkali. Figure 1.36 shows the titration curves of some cation exchangers according to Griessbach [158]. The capacity of the exchanger can be read from these curves at the intersection of the curve with the line for pH 7. Moreover, these curves can be used to evaluate the exchangers for their acid strength, operating interval, and buffering power. Further, from pH titration curves information on the nature and concentration of the acidic or basic groups in both types of ion exchangers, cation as well as anion, can be obtained. A very important fact in this connexion is that, if the direct titration of a cation exchange resin in the H-form is attempted, there will be no pH change in the external solution until the endpoint of the titration is reached. The reaction for, e.g., a strong acid cation exchanger can be written  $R-SO_3H + NaOH = R-SO_3Na + H_2O$ , whereby the actual titration takes place



inside the resin, and the pH changes cannot be measured directly. Griessbach has given an exact empirical expression describing the exchange reaction with  $(\text{Na}^+)_{\text{R}}/(\text{H}^+)_{\text{R}} \cdot [(\text{H}^+)_{\text{S}}/(\text{Na}^+)_{\text{S}}]^n = K$ , where the subscripts refer to the resin and external solution phases. Concentrations are used in place of activities, since the ratio of the activity coefficients of the univalent cations used is nearly equal to unity. But if a large excess of a neutral salt of sodium is added, the ratio  $(\text{Na}^+)_{\text{R}}/(\text{Na}^+)_{\text{S}}$  becomes small, since  $n$  is 0.8–1.0 and  $K$  is 0.5–2.0 for most resins. The ratio  $(\text{H}^+)_{\text{S}}/(\text{H}^+)_{\text{R}}$  must become very large which means that virtually all of the hydrogen ions are in the solution phase. Thus the addition of a neutral salt displaces an ion into solution upon dissociation, and yields results comparable to those which would be obtained if the resin were soluble. This is also the case for weak acid resins. For anion exchangers the same principle is valid. Therefore the direct pH titration of strong base anion exchangers is also carried out in the presence of a large excess of neutral salt. An experimental alternative but one definitely necessary, however, for the determination of pH titration curves of weak acid and weak base ion exchangers was adopted by Topp and Pepper in the method of weighed samples. Briefly, with cation exchangers, different amounts of base were added to weighed samples, 0.5 g, of the hydrogen form of the resin in separate flasks. After 48 hours of shaking, the pH of the solution was determined and aliquot samples were withdrawn for analysis. A parallel series of experiments was made in the presence of neutral electrolyte. The results obtained provide a basis for the interpretation of the titration curves of multiionic exchangers. Thus, resins containing both hydroxyl and sulfonic or carboxylic groups give titration curves which consist of segments characteristic for each ionisable group present. Anion exchangers available at that time were also studied with the conclusion, for instance, that a *m*-phenylenediamine-formaldehyde resin was ill-defined since the corresponding titration curve showed that it contained a variety of weakly basic groups, including primary aromatic amino and mixed aliphatic-aromatic secondary and tertiary amino groups [159].

Kunin and coworkers then studied in depth the acidity and basicity behavior of ion exchangers. For cation exchangers in the H-form titration curves for various ionogenic groups such as the methylene sulfonic  $-\text{CH}_2\text{SO}_3\text{H}$ , nuclear sulfonic  $-\text{SO}_3\text{H}$ , carboxylic  $-\text{COOH}$ , phosphonic  $-\text{PO}_3\text{H}_2$ , phosphonous  $-\text{PO}_2\text{H}_2$ , and phenolic  $-\text{OH}$  groups were plotted, as shown in Figure 1.37 [160]. It can be seen that the titration curves, which were determined for different ionic strengths of the solution, are quite similar to the corresponding curves of the analogous soluble acids. The apparent ionization constants ( $\text{p}K_1$ ) can be calculated from these curves from the relationship  $\text{pH} = \text{p}K_1 + \log \text{salt/acid}$ . It is important, however, to realize that upon changing the ionic strength or upon changing the base the titration curve of a cation exchange resin is a result not simply of the basic neutralization reaction  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ , but must be interpreted as a combination of two reactions, i. e.,



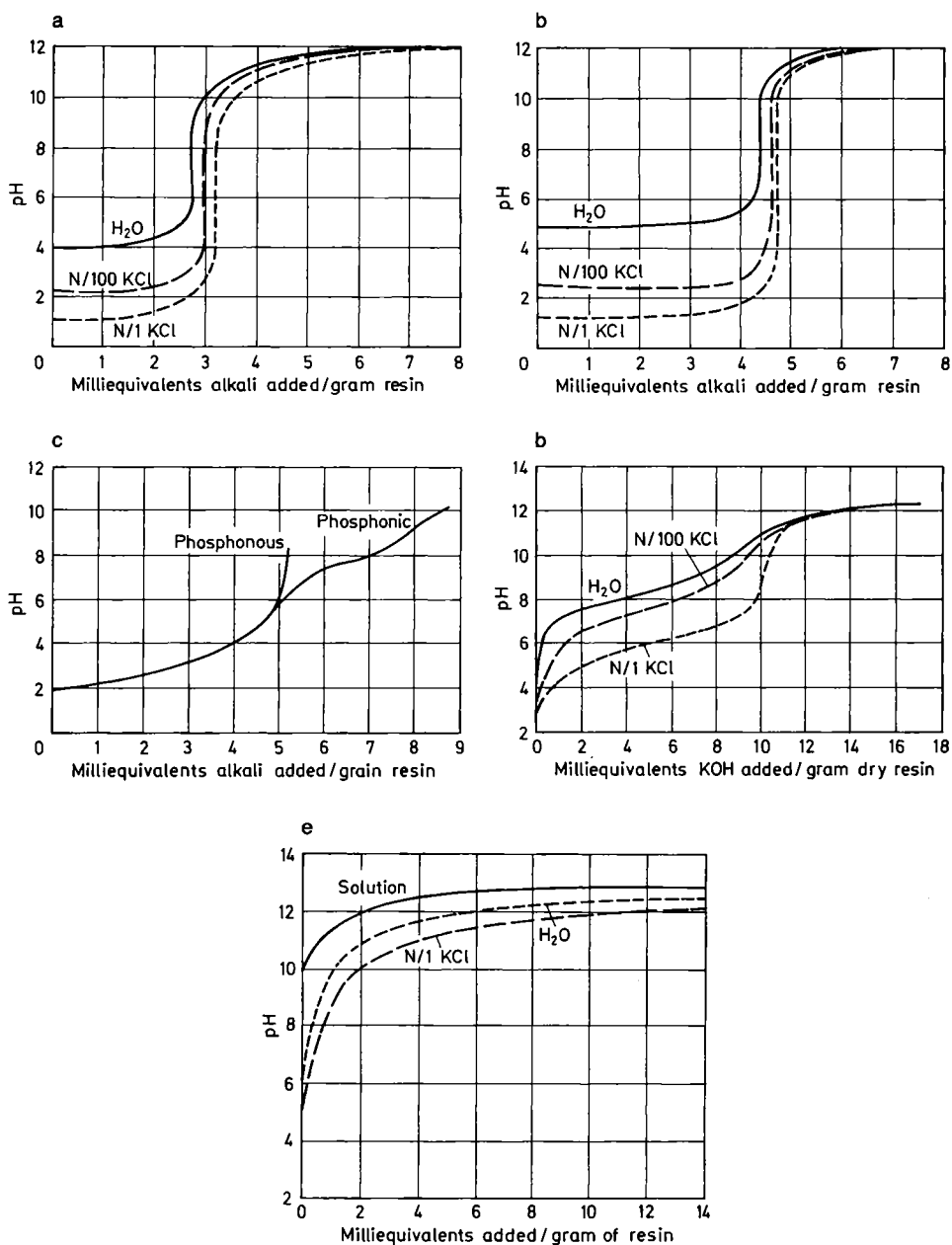


Figure 1.37 pH-titration curves of cation exchangers with various ionogenic groups:  $-CH_2SO_3H$ ;  $-SO_3H$ ,  $pK_1 = 2$ ;  $-PO_3H_2$ ,  $pK_1 = 3$ ;  $-PO_2H_2$ ,  $pK_1 = 3$ ;  $-COOH$ ,  $pK_1 = 5-6$ ; and  $OH$ ,  $pK_1 = 10$  (Kunin).

It thus becomes dependent on the equilibrium, including the selectivity of the fixed site for the exchanging ion. However, since the equilibrium of the exchange is also dependent on the acid strength ( $pK$  value) of the acid group, the equilibrium constant becomes, at first sight, essentially a measure of the acid strength of the fixed group. From the curves in Figure 1.37 it can also be seen, as already mentioned, that different ionic strengths or, in other words, the presence of salt, have distinct effects upon the shape and position of the titration curve. The magnitudes of these effects are dependent on the acid strength of the ionogenic group. Gregor and Bregman [161] first determined the order of increasing acid strength for the three major resinous cation exchangers



But at very high ionic strengths the titration curves of the various cation exchangers become quite independent of the ionic species.

Practically, the titration curves reveal that with cation resins of the sulfonic acid type the hydrogen ion behaves much like an alkali metal ion. However, the carboxylic group titrates with KOH between pH 7 and 11 in the absence of a salt, and is half-neutralized at about pH 9. In the presence of 0.1 N KCl, the titration curve extends from pH 4 to 10, half-neutralization being at about pH 7. The values are lowered by about 1 pH unit if  $\text{Ba}(\text{OH})_2$  is used in place of KOH [162]. The phenolic group in the phenol-formaldehyde resins is weaker and takes up base from about pH 10 upwards or pH 8 in 0.1 N KCl.

As described above Griessbach has already set up an empirical equation for the effect of the various cationic species upon the position and shape of the titration curve, based on the equilibrium constant; a somewhat similar one can be easily derived that qualitatively describes quite well the effect of concentration on the position of the titration curve. But such an approach does not take into consideration the physical chemistry of the polymer structures. Helpful for the field of ion exchangers in gaining knowledge of the whole electrochemical situation of the system, i. e. polymeric matrix versus ionized ionogenic groups, are similar endeavours in the field of polyelectrolytes, the latter being the soluble, polymeric (because they are not crosslinked) analogues of monomeric acids. The electrochemistry of these important reactive polymers has been studied intensively by Kern, Fuoss, Katchalsky, Mandel, Oosawa and several others.

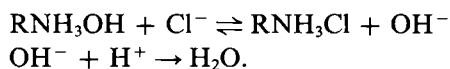
It is state of the art for polyelectrolytes to use as a basis for potentiometric investigations the Henderson-Hasselbach equation derived from the dissociation equilibrium of monovalent electrolytes: the equation is  $\text{pH} = \text{p}K_a + \log \alpha/(1 - \alpha)$ , with  $K_a$  the dissociation equilibrium constant according to the law of mass action and  $\alpha$  the degree of neutralization calculated from the amount of base added. On investigating the specific effects of solutions of polyelectrolytes it was found necessary to modify this equation (Overbeck, Katchalsky and Spitnik, Mandel [163]); the form then used, in most cases, is the empirical Katchalsky and Spitnik version of the Henderson-Hasselbach equation:  $\text{pH} = \text{p}K_a + n \log \alpha/(1 - \alpha)$ , with  $\text{p}K_a$  the

apparent  $pK_a$  value of the polyacid and  $n$  another constant. Fisher and Kunin have attempted to bridge the gap between the polyelectrolytes and the polymeric ion exchangers by using this equation [164], and Kuhn et al. [165] as well as Helfferich, have, for the description of the neutralization curve of a carboxylic cation exchanger in the presence of a monovalent counterion, proposed the following equation

$$pH = pK_a + \log \frac{\alpha^2}{1 - \alpha} + \log [\bar{X}] - \log [M^+],$$

with pH the pH measured in the equilibrium solution,  $K_a$  the apparent acidity constant,  $\alpha$  the degree of dissociation,  $[\bar{X}]$  the total concentration of ionogenic groups in the exchanger, and  $[M^+]$  the concentration of counterions in the equilibrium solution. But in order to determine the nature of the binding between a carboxylic ion exchanger and a monovalent counterion including very weak dissociations, Auclair et al. used a system of equations for three different assumptions [166], relative to the different ways of binding.

For anion exchangers also titration curves show one of the important characteristic properties. The anion exchange resins that were originally and for quite some time available were of the weak base type, functioning only in acid media; it has become possible with the availability of strong base anion exchangers to extend the scope of anion exchange operations to neutral and alkaline media as well. Kunin and coworkers studied intensively the behavior of all types of anion exchange resins, and it became apparent that the range of basicities covers a range corresponding to strong, weak and very weak bases. Since it was realized that the ionic strength of the solution showed a marked effect on the titration curves, especially for the weakly basic exchangers, this was seen as an indication that the acid neutralization of these basic resinous exchangers might well proceed as a combination of two reactions, i. e.



For anion exchangers in the OH-form the titration curves for various anionic groups are shown in Figure 1.38 [167]. The hydroxyl ion with the strongly basic resins behaves much like chloride. However, with weak base resins pH plays a special role, as a weak base resin passes into the undissociated base form at high pH values. Strong base anion exchangers as quaternary ammonium resins are ionized at all pH values and are fully neutralized with chloride from pH 8 downwards. The weakly basic groups  $-\text{NH}_2$ ,  $-\text{NHR}$  and  $-\text{NR}'\text{R}''$  take up HCl between pH 7 and pH 1. With respect to the ionic strength or the presence of salts, the magnitude of the ionic strength effect increases as the basicity of the resin decreases. For example, the half-neutralization point of a resin can be at pH 4 with HCl, and at pH 5.5 with HCl plus 0.1 N KCl. However, acid strength and the anion valence also have pronounced effects on the nature of the titration curves. Increases in acid strength and the valence of the ion favor the replacement of the hydroxyl ion.

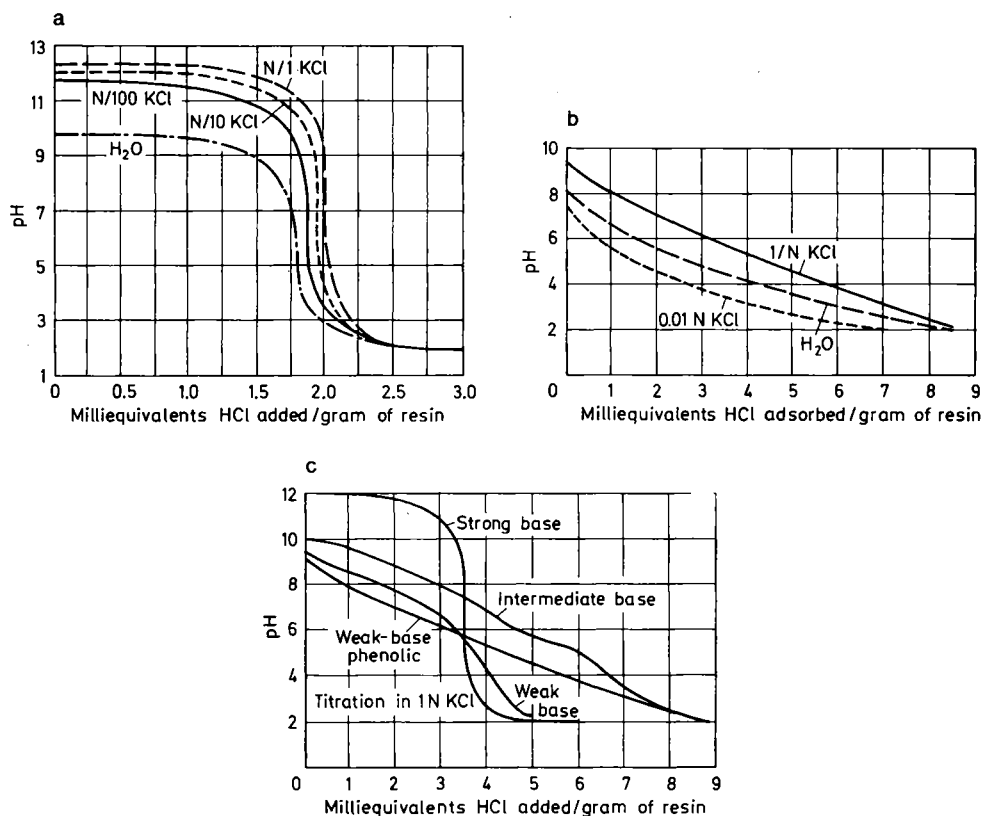


Figure 1.38 pH-titration curves of anion exchange resins: strong base, weak base and some resins of different basicity (Kunin).

Because, in spite of the increasing technological importance of weak base ion exchange resins, so little information concerning their basicities had been obtained, Kunin and coworkers examined the basicities of a series of weak base ion exchange resins [168]. In this work the precautions necessary and the techniques to be applied are critically reviewed. For the given calculations it would seem best to follow the descriptions exactly. The dissociation of the protonated form of a weakly basic resin may be described by the equilibrium



$$K_a = \frac{(\text{RN})(\text{H}^+)}{(\text{RNH}^+)},$$

where the parentheses indicate activities. This expression may be written as

$$K_a = \frac{\alpha[\text{H}^+]}{1 - \alpha},$$

where  $\alpha$  is the fraction of the resin in the dissociated form, if activity coefficients are neglected. The hydrogen ion concentration term refers to the resin phase which is, of course, inaccessible to measurement. It may be determined indirectly from the measurement of the pH of the aqueous phase by the use of the Donnan relationship,

$$[H^+]_r[Cl^-]_r = [H^+]_s[Cl^-]_s,$$

in which activity coefficients and the pressure-volume term have been neglected. Subscripts r and s refer to the resin and solution phases, respectively. Substitution of the last equation into the previous one gives

$$K_a = \frac{\alpha [H^+]_s [Cl^-]_s}{1 - \alpha [Cl^-]_r}$$

or

$$pH = pK_a + \log \frac{\alpha}{1 - \alpha} + \log \frac{[Cl^-]_s}{[Cl^-]_r}$$

where  $[Cl^-]_s$  and  $[Cl^-]_r$  represent the molality of the Cl ion in the outer solution phase and in the resin phase, respectively. Using this equation, Dragan and co-workers have reported sequences for the order of increasing base strength for tertiary alkyl-, hydroxyl alkyl- and aryl amine groups for fourteen anion exchange resins with differing ionogenic groups on a copolymer gel in bead form with 92% styrene and 8% divinylbenzene [169]. The variation of the derived basicity data was correlated with the measurements on retained water in the standard state and volume changes during transformation from Cl- to OH-form of the anion exchange resins. The results derived by the potentiometric titration curves in 1 M NaCl solutions, by the pH values of the water in equilibrium with the anion exchange resins in OH-form, by the studies of the ion exchange  $OH \leftrightarrow Cl$  at equivalent concentrations, as well as by measurements of the volume changes from one ionic form to another, all lead to the same sequence of basicity for the fourteen anion exchange resins. In the series of strongly basic anion exchange resins synthesized with tertiary alkyl amines, the basicity decreased with the increase of the chain length of the alkyl substituent, inversely to the basicity of the free amine. The strongly basic anion exchange resins synthesized with hydroxy alkyl amines had a weaker basicity than those obtained with alkyl amines, and the replacement of an alkyl substituent at the quaternary nitrogen by a hydroxy alkyl substituent of a similar volume, decreased the basicity. The anion exchange resins synthesized with primary and secondary aromatic amines could not be titrated in a satisfactory way in an aqueous medium.

There have been repeated recent investigations based on titration curves. The two methods now established for titration curves are the method of direct titration or the method of individually weighed samples. The method of direct titration can be used for exchangers with easily dissociated ionogenic groups and with fast

exchange kinetics. Exchangers containing weakly dissociated ionogenic groups and with slow exchange equilibration are treated by the method of individually weighed samples. The latter, however, can be used for any type of exchanger. Babkin and Kiseleva reviewed the testing of ion exchangers by stepwise potentiometric titration and Michaeli and Kinrot discussed the salt effects on pH titration curves of weak acid or weak base ion exchangers [170]. Of interest seems to be that the determination of ionization constants and exchange capacities of ion exchangers by potentiometric titration at 80 °C decreases the duration of the determination ten to twenty-fold, as compared with titrations performed at room temperature; the  $pK$  values of the cation exchangers examined were linearly dependent on the ionic strength of the solutions, and were virtually independent of temperature at 20 °C to 80 °C [171]. For the analysis of copolymers based on 2-methyl-5-vinylpyridine as well as of polyamine ion exchange resins from polyepichlorohydrin titration curves were used [172].

**Ion exchange resin buffers.** It has been mentioned that in the titration curves of weakly acidic ion exchangers the range of buffering activity can be clearly seen. This means that, in analogy to buffers in solution consisting of a weak acid and its salt, mixtures of an ion exchange resin in the H-form and a neutralized exchanger are also very good buffer systems. The same applies to a weak base anion exchanger mixed with a resin, e. g., in the  $SO_4$ -form. Comparing the buffering effects of ion exchange resins with those of weak acids and bases the advantages for the ion exchange technique are a wider buffering range, fewer ion effects on physiological experiments, low osmotic pressure effects and the ability to change the pH during

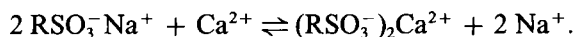
Table 1.9 The pH of Murashige and Skoog's culture medium containing various proportions of Amberlite IRC-50 charged with either hydrogen or calcium ions. The pH values for + cells are for five-day-old carrot cultures, the pH values are mean and standard error of three replicates. (From 174)

Grams Resin		Medium pH	
H <sup>+</sup>	Ca <sup>2+</sup>	– Cells	+ Cells
0.0	5.0	8.6 ± 0.08	8.0 ± 0.05
0.5	4.5	7.1 ± 0.08	6.6 ± 0.1
1.0	4.0	6.6 ± 0.02	6.2 ± 0.02
1.5	3.5	6.3 ± 0.02	5.9 ± 0.01
2.0	3.0	5.9 ± 0.01	5.7 ± 0.01
2.5	2.5	5.7 ± 0.03	5.4 ± 0.0
3.0	2.0	5.4 ± 0.04	5.2 ± 0.0
3.5	1.5	5.2 ± 0.03	4.9 ± 0.0
4.0	1.0	4.9 ± 0.03	4.7 ± 0.01
4.5	0.5	4.5 ± 0.06	4.4 ± 0.04
5.0	0.0	2.9 ± 0.03	2.9 ± 0.01
0.0	0.0	5.0 ± 0.12	4.6 ± 0.07

an experiment without changing the rest of the composition of the suspending media. The buffer capacity of ion exchangers has been determined by automated direct recording of potentiometric titration curves in a broad range of pH under conditions for maximum measurement reproducibility [173]. The practical applicability of ion exchange resin buffers was demonstrated in connexion with liquid plant cell cultures as a simple and effective method for reducing pH fluctuations in liquid cultures of carrot cells — it involves adding to the culture medium before autoclaving a cation exchanger system consisting of a mixture of the H- and Ca-forms of the carboxylic acid resin. The pH conditions achieved are shown in Table 1.9. The resin is nontoxic and nonabrasive to the carrot cells and can be stored in its treated form for an extended period of time [174].

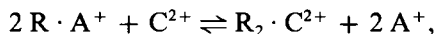
**Suspension effect.** A phenomenon quite closely related to acidity and basicity of ion exchangers is the so-called suspension effect. Discovered by Jenny and interpreted first by Pallmann mainly on clay, the suspension effect was ascribed to a more or less strong adsorption of hydrogen ions, with its intensity decreasing with decreasing density of the adsorbed layer. Experimentally it can be shown that cation exchangers in the H-form give rise to a low pH when stirred in water around a glass electrode, while anion exchangers increase the pH because the latter supposedly contain adsorbed hydroxyl ions. When stirring is interrupted the resin particles sediment quickly and the supernatant liquid is neutral [175]. Chernoberezhskii and coworkers have intensively investigated the suspension effect of ion exchange resins in suspension and defined  $\Delta\text{pH} = (\text{pH of suspension} - \text{pH of equilibrium solution})$ . Its magnitude of 2–3 pH units generally depends, among other things, on the concentrations and sizes of the solid phase particles, on the density of the electric charge, and on the concentration of electrolyte [176]. The two hypotheses persisting regarding the cause of the suspension effect have been critically re-examined, based on the data obtained by three independent methods [177]. The conclusion drawn is, that not the traditional hypothesis, which attributes the effect to a different activity of ions in the suspension than in the dialyzate, but the hypothesis that attributes the effect largely to a junction potential at the calomel-suspension boundary, is correct. The suspension effect for compacted ion exchanger resin beads was analyzed with very positive results in terms of an ionic, space charge generated phase boundary potential difference between the supernatant and slurry phases [177].

**Exchange of monovalent ions for ions of higher valence.** When an ion exchanger is described as a solid electrolyte having a “free” ion that can reversibly interchange with ions in solution, the example given is quite often that of a cation exchanger with fixed sulfonic acid groups on a polymeric matrix R in the sodium form, which is used for the important application of water softening, i. e. the exchange against calcium ions according to the equation





Attention is not drawn, however, to the fact that this process might not be as easily explainable as the exchange of monovalent ions. In an attempt to give a more adequate explanation one may revert to the above-introduced practice of application of the law of mass action to the exchange process, in which monovalent and bivalent ions are involved as represented by the general equation



and then by the apparent exchange constant relationship

$$K_c = \frac{[R \cdot A^+]^2 [C^{2+}]}{[R \cdot C^{2+}] [A^+]^2}$$

with  $[RA^+]$  and  $[RC^{2+}]$  the concentrations of the ions in the resin and  $[A^+]^2$  and  $[C^{2+}]$  their concentrations in solution. If the same units are used to express the concentration of the ions in the resin and in the solution, then  $K_c$  will be dimensionless, but its value will depend on the units employed. By introducing the equivalent fractions of the ion C this equation may also be written in the form

$$\frac{[\bar{X}_c]}{[1 - \bar{X}_c]} = K_c \frac{[\bar{C}^{2+}]}{[C^{2+}]} \frac{[X]}{[1 - X]^2}$$

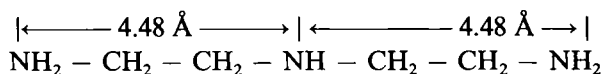
where  $[\bar{X}_c]$  and  $[X_c]$  are the equivalent fractions of the ion  $C^{2+}$  in the resin and in solution and  $[\bar{C}^{2+}]$  and  $[C^{2+}]$  are the total concentrations of the exchanging ions in the resin and in the solution. Unlike the corresponding equation which can be derived for monovalent ions, this equation involves the term  $[\bar{C}^{2+}]/[C^{2+}]$ , so that the effective selectivity of the resin is determined by the value of  $K_c([\bar{C}^{2+}]/[C^{2+}])$ . Since  $[\bar{C}^{2+}]$  is fixed by the exchange capacity it will be determined by the resin being used, and will not be affected by changes in the concentration of the external solution. The value of  $[C^{2+}]$ , however, will depend on the total concentration of the ions in the solution. It follows that the value of  $[\bar{C}^{2+}]$  will depend not only on  $K_c$  and  $[X]$  but also on  $[C^{2+}]$ , and the effective selectivity of the resin for the divalent ion will be inversely proportional to the concentration of the solution, which means that the relative uptake of the divalent ion will be much greater in dilute solution. The effect of solution concentration has been described in the literature either by non-linear curves, when the theoretical values of  $[\bar{X}_c]$  are plotted against  $[X_c]$  for different values of  $K_c([\bar{C}^{2+}]/[C^{2+}])$ , or as straight lines, if the appropriate mass action functions are plotted [178]. In exchange processes with strong acid cation exchangers involving monovalent and trivalent ions, the effect of the ionic strength of the solution is much greater. In this case the equivalent fraction of the trivalent ion in the resin will be inversely proportional to the square of the total solution concentration.

For weak acid carboxylic cation exchangers the exchange of monovalent for divalent counterions has also been intensively studied in order to determine the nature of the binding. For anionic polyelectrolytes and copper, as well as for

alkaline earth cations, it had been postulated in prior investigations by one group of researchers that the binding is a complex formation, and by an other group that it is of electrostatic nature. For carboxymethylcelluloses and the divalent ions  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  it was found that the degree of association depends little on the nature of these cations but is entirely determined by the charge density of the polyelectrolyte and should, therefore, be of purely electrostatic nature. In all the studies in question it was shown that the binding of a divalent cation and a weak acid polyelectrolyte takes place between two ionizable groups of the polyion, whereby these bound sites can be either on one polymer chain or on two different ones. Then with respect to weak and carboxylic cation exchangers and taking into consideration the different modes possible between compensating ions and dissociated ionogenic groups and the relative disposition of the carboxylic groups in the ion exchange resin, a series of equations was set up, representing the exchange reaction. From these it was concluded that carboxylic cation exchangers occur as diacids during the exchange of divalent ions, but that  $\text{Ba}^{2+}$  is only weakly bonded [179]. When one includes ions of higher valence than divalent in studies of metal ion adsorption on carboxylic cation exchangers (i. e. other than  $\text{Cu}^{2+}$ ,  $\text{Pr}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Ca}^{2+}$ ), it seems evident that there is an additional charge formed after the exchange of  $\text{H}^+$  for the metal ion. Further, it was found that the cations  $\text{UO}_2^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{ZrO}^{2+}$  and  $\text{Th}^{4+}$  have high distribution coefficients even at pH 2.0 from aqueous acidic solutions with a weak acid cation exchanger which contradicts the idea that carboxylic exchangers have a high affinity for the hydrogen ion. The affinity for  $\text{Cu}^{2+}$  and  $\text{Al}^{3+}$  above pH 4.0 was comparable to the affinity for  $\text{H}^+$  [180]. It might also be said that the more complicated nature of the binding of divalent cations on carboxylic ion exchangers is also shown by work done on the determination of the effective exchange constants of ions and the dissociation constants of complexes of these ions in the ion exchanger phase. The values of theoretical constants for the weakly acidic carboxylic exchanger KB-4P-3 for alkali metal ions were in good agreement with the experimental values whereas for alkaline earth ions the agreement was only satisfactory [181].

Anion exchange resins show basically similar effects towards divalent anions: in general polyvalent anions are preferentially taken up from a dilute solution. An investigation of the  $\text{Cl}^- - \text{X}^{n-}$  exchange, where  $\text{X}^{n-}$  were  $\text{NO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ , on a strong base anion exchanger, showed that the ion exchange selectivity of the multivalent anions is not controlled by electrostatic forces. It was concluded that the hydration effects are predominantly responsible for the selectivity, and a correlation was found between the ion hydration energy and selectivity constant values. These values decreased on this particular anion exchanger with increasing  $n$  value of  $\text{X}^{n-}$  [182]. In similar studies, Soldatov and coworkers have extended the investigation to the influence of crosslinking and the sorption of water with regard to the equilibrium of exchange of anions of different valences on a strong base anion exchanger. Using Dowex 1 X 1, 1 X 4 and 1 X 10 the ion exchange equilibria of the anions  $\text{SO}_4^{2-} - \text{Cl}^-$ ,  $\text{SO}_4^{2-} - \text{OH}^-$  and  $\text{PO}_4^{3-} - \text{OH}^-$  and sorption

of water of the  $\text{Cl}^-$ -,  $\text{OH}^-$ -,  $\text{SO}_4^{2-}$ - and  $\text{PO}_4^{3-}$ -forms were determined at  $25^\circ\text{C}$ . With increasing crosslinking of the exchanger, the ion exchange constant of the  $\text{SO}_4^{2-} - \text{Cl}^-$  system decreased and of the remaining systems changed in a complicated way [183]. The most conclusive investigation, however, of the exchange of monovalent for divalent anions as well as of the selectivity of anion exchangers is based on structural considerations of the resin phase, making use of the distance-of-charge-separation theory of Clifford and Weber. The results of this research demonstrate that it is the distance of fixed-charge separation in the resin which is the primary determinant of monovalent-divalent selectivity. The goal of the research was to determine the causes of sulfate and nitrate selectivity in anion resins and it was found that the resin matrix and the type of ionogenic group were the most important factors. Because the uptake of a divalent ion, e. g. sulfate, requires the distance of two closely-spaced positive charges, a resin is highly sulfate selective if the electrostatically-active nitrogen atoms (amine) are in the continuous polymer structure. It is hypothesized in this theory that this extreme divalent ion preference is due to the proximity ( $4.48 \text{ \AA}$  apart) of two active nitrogen atoms in the polymer backbone. This distance,  $4.48 \text{ \AA}$ , is the nitrogen separation distance due to the single ethylene group in the amine monomers diethylenetriamine and triethylenetetraamine, commonly used to provide reactive sites and crosslinking in anion exchange resins:



Fixed pairs of properly-spaced positively charged ionic sites will tend to prefer single divalent anions to pairs of monovalent ions for both electrostatic and entropic reasons. In order to bring positive charges into close proximity within a resin one can: 1. Incorporate the amine ionic groups into the polymer chains, as opposed to having them pendant on the chains. 2. Minimize the size and number of organic groups attached to the N atom, i. e. minimize the size of the amine. 3. Minimize the resin flexibility, i. e. its ability to reorient to satisfy divalent counterions, by minimizing the degree of crosslinking [184]. This theory would also seem to provide as stimulus to further investigate both structure of the copolymer and distribution of the ionic groups as the actual chemical basis of ion exchange and ion exchange selectivity, since the distance-of-charge-separation theory is not restricted to divalent anion exchanges but also applies to cation exchanges and to polyvalent ions in general.

**Ion exchange in multicomponent systems.** Ternary and higher multicomponent systems in the field of ion exchange are understood as systems in which the exchange of one bound counterion is performed in a solution offering more than one ion for exchange. If one also includes ions of higher valence for both cation and anion exchangers, it is obvious that this field becomes quite wide, since several other chemical interactions and mutual ion effects must be expected and it would,

therefore, be necessary to examine such systems with respect to equilibrium conditions, selectivity and diffusion conditions, etc. Although practically speaking, just such multicomponent systems are usually involved in ion exchange, they have unfortunately been described far less than binary systems, regardless of whether the approach has been theoretical, mechanistic or purely chemical.

One empirical effect found in ternary systems must be mentioned at the outset. This is that under certain conditions the concentration of a counterion in either phase can go beyond its eventual equilibrium value. This can occur if the respective counterion is more mobile than a competing one originating in the same phase. For the case that an ion exchanger in the A-form is in contact with a solution containing counterions B and C, of which B is the much more mobile one, one has that in the early stages of exchange, A and B exchange while C, because of its low mobility, barely begins to penetrate into the resin particle. C will subsequently exchange, although slowly, and will in part displace the B ions taken up earlier.

Several investigators have nonetheless attempted to describe and predict multicomponent ion exchange equilibria but because the number of experimental manipulations increases enormously with each additional ionic component, methods for the correlation of binary and ternary, as well as quaternary to multicomponent systems have been sought. Thus have J. Dranoff et al. (1957–8, 1961, 1963), V. S. Soldatov et al. (1968–9), S. E. Smith (1986), A. Jasz et al. (1961–3) and Gopala Rao et al. (1969, 1973–4) adopted a semi-empirical approach by ignoring the effect of the third component on the remaining pair of ions.

These and some other earlier investigators have claimed that the presence of a third ionic species does not interfere with the equilibrium relationship of the other two ions. This general assumption was disproved and some doubt arose about the validity of certain previous fundamental rules. V. S. Soldatov, V. A. Bichkova and coworkers (1970, 1973–5) and R. K. Bajpai et al. (1973) attempted a more rigorous method of prediction. In the former case, ternary data were predicted from binary results by taking into account the effect of the third component on the binary system. The method applied is similar to that used in the prediction of vapor-liquid equilibria and depends on the applicability of Harned's rule, which says that at constant ionic strength the ratio of the activity coefficients of electrolytes in a mixture is constant and equal to the ratio for the pure electrolyte solutions at the same ionic strength. The activity coefficients of the resin and salts in their ternary mixtures were calculated from the equilibrium of the three binary systems. In the latter case a method was proposed of predicting weighted activity coefficients in the resin phase in order to derive ternary data from binary equilibrium results. Furthermore, it was observed that ternary data could be predicted most successfully if the binary pairs containing the most favoured ion were used. Hence, it was found that for a selectivity sequence  $A > B > C$ , good correlation between ternary and derived binary data could be obtained for the ionic pairs A–B and A–C. In an investigation on ion exchange equilibrium in polyionic systems by Danes and Danes [185] starting from the thermodynamic dependences between the activity coefficients

in the ionic phase and the excess free mixing enthalpy of resins correlations were deducted for the apparent ion exchange equilibrium constants in systems of more than two counterions. As is common practice, Gibbs' triangle with arrows for the graphical representation of the equilibrium in systems with three competing ions was used. The basis of the arrows represents the composition of a solution, which is in equilibrium with an ion exchange resin of given composition (arrow-head). But such a diagram is only valid for one total concentration of the solution and is by no means a closed description. Streat and coworkers presented some experimental ternary equilibrium data and showed the application of simple empirical graphical extrapolations to predict ternary results from the corresponding binary data. Two alternative graphical methods of prediction of ternary ion exchange equilibrium data were presented. In this paper ternary equilibrium data were obtained directly from actual experimental binary measurements for the three respective components. It was shown that methods assuming constant selectivity coefficients are unreliable in most cases. The method of prediction recommended in this work uses a triangular representation of the data. The accuracy and reliability of the graphical method of prediction were shown to be as good as a more rigorous calculation using derived resin-phase activity coefficients and it was suggested that these techniques are suitable for the prediction of equilibrium data in process design calculations for chromatographic separation processes [186]. Kolnenkov and coworkers have dedicated most of their work to the calculation of quaternary ion exchange systems using data for binary systems as well as ion exchange isotherms of binary systems [187]. The anion exchange equilibria and kinetics in the ternary system chloride-sulphate-phosphate was studied by Gregory because of its significance for the removal of phosphate from waters and effluents. In this work equilibrium and kinetic data were obtained from shallow bed experiments, using radioactively-labelled sulphate and phosphate and three strong base anion exchangers. The equilibrium uptake of phosphate, in the presence of sulphate and chloride, was always low and became still lower with decreasing pH. From the kinetic data it was found that the exchange of phosphate from a ternary system shows the above-mentioned empirical effect and can overshoot the equilibrium value. This effect was most apparent for resins with a low affinity for phosphate and at low flow rates [188]. A very interesting approach for the description and calculation of isolated and simultaneous ion exchange equilibria seems to be the one presented by Froelich et al. Based on the empirical equation  $\bar{x}_B = [(1 + k)/(1 + kx_B)] x_B^n$  with  $k$  and  $n$  the respective characteristic constants under the restriction  $-1 < k < n/(1 - n)$ , this equation can also be applied to systems with three counterions, if for the dependences of  $k$  and  $n$  on the total concentration  $c$  the equations

$$K = k_{00} + k_{10} \lg c + k_{01} y_C + k_{11} y_C \lg c$$

and

$$n = n_{00} + n_{10} \lg c + n_{01} y_C + n_{11} y_C \lg c,$$

are used, whereby  $y_C$  corresponds to the amount of  $y_C = c_C/(x_A + x_C)$  of the counterion C in solution. Applied to the ternary system  $H^+/Zn^{2+}/Cd^{2+}$  on a strong acid styrene-divinylbenzene cation exchanger, it was shown that the equation of isotherms used is suitable for the description of real systems [189]. Diffusion phenomena in ternary systems were also studied with the goal of verifying the Nernst-Planck equation for the description of ion exchange under the conditions of the gel-kinetics in a ternary ion exchange system [190]. To predict the selectivity in multicomponent systems with monovalent ions, equations have been derived by Soldatov and Bichkova, which have been proven to be applicable to non-ideal exchange systems with two or three exchangeable ions; they also made the suggestion for a method for predicting the ion exchange equilibria in multicomponent systems. Further, for the ternary systems  $Zn^{2+}/Cd^{2+}/H^+$  and  $Cu^{2+}/Ag^+/H^+$  on a strong acid cation exchanger, the possibility of predicting ternary data by use of the pair of binary exchange results containing the most preferred ion was examined by Sengupta and Paul using the graphical procedure of Streat. They found that the correlation between the experimental and the theoretically predicted results was reasonably good for both the above ternary systems [191]. The possibility of predicting multicomponent ( $n$  ion) exchange from  $(n-1)$  isotherms for the constituent pairs of ions was examined. This new approach treats ion exchange as a phase equilibrium by using standard procedures developed for solution thermodynamics. Surface effects were taken into account [191].

**Ion exchange mechanisms.** In organic chemistry the goal of investigating the mechanisms of a reaction is to predict what products will be formed, to understand how the rate of reaction depends on the structure of the reactants and how the spatial arrangement of groups in reactants is affected by the reaction. There are some general characteristics of mechanisms and it is sometimes defined that a reaction mechanism is a concise history of the detailed way in which reactant molecules are transformed into product molecules. Disregarding the formation of the polymer matrices of ion exchangers and the mechanisms involved there, it is assumed that in the ion exchange process itself important mechanisms must be involved. Within polymer chemistry certain mechanisms can also be determined relative to the reactions of polymers, but related only to chains or networks without reactive groups. Taking ion exchangers as one kind of reactive polymer, the determination of mechanisms aims at a direct observation and elucidation of the concrete steps that make up the overall ion exchange process [192]. It should be noted that "ion exchange mechanisms" and not "the mechanism of ion exchange reactions" was used. Ion exchange is a phenomenon in and of itself and ion exchange reactions may occur as part of the process of ion exchange depending on the chemical nature of the ion-exchanging material or the nature of the surrounding solution. A survey of the results of the determination of the mechanisms of ion exchange up to the present follows, there is still a long way to go until standard mechanisms for ion exchange will be obtained. Kinetic measurements and the elucidation of diffusion phenomena are only one field of study with regard to ion exchange mechanisms.

The most important methods applied for the investigation of ion exchange mechanisms are visible and UV light, IR spectroscopy, Raman spectroscopy, nuclear magnetic resonance (NMR), electron spin resonance (ESR), and magnetic susceptibility measurements [193], Mößbauer spectroscopy [194], proton magnetic resonance measurements [195], electron probe microanalysis [196] and extended X-ray absorption fine structure spectroscopy [197]. With regard to results based on the latter method it has been claimed that each of the other techniques has its limitations, giving only a very partial picture of the site occupied by the metal, whereas exafs spectroscopy is capable of probing bond distances and coordination numbers directly, whatever the state of the sample or its degree of loading. This would help to place ion exchange phenomena — obviously first with respect to inorganic materials — on a firm structural foundation. But there are still many questions regarding ion exchange and only the future will show which method can bring the best results under particular circumstances.

To begin with, since most of the ion exchange processes occur in aqueous media the state of water in swollen ion exchange resins is of general interest. The discussion of whether and to what extent water exists in swollen ion exchange resins as “bound” or “free” water was initially based on the enthalpy and entropy of swelling. Bound water is usually considered as the water that hydrates counterions. However, the enthalpy and entropy of swelling are the mean values of simultaneously occurring processes, such as simple sorption, dissociation of the ionogenic groups or ion pairs, dissolution of the “internal” solution formed and conformational changes in the chains of the resin matrix. It is, therefore, of interest to use other means to obtain information on the interaction of water with ion exchangers. Thus, in order to observe the relations directly, spectral methods, especially IR and NMR, have been applied, to study either the ion–water interaction or the hydration number of various ions. For cation exchangers of the sulfonic acid type it was found that the hydration numbers of, e. g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  and  $\text{Mg}^{2+}$  in the resin phase are lower than those found by the same method for cations in electrolyte solution. The hydration numbers in strong base anion exchangers are approximately one and are consistent with the hydration numbers of  $\text{N}(\text{CH}_3)_4\text{Cl}$  and  $\text{N}(\text{CH}_3)_4\text{Br}$  in solution. The hydration numbers increase with a decrease in crosslinking, i. e. as the resin phase becomes more dilute. In another work, where the hydration numbers of strong ion exchange resins were studied by the NMR method, it was shown that the hydration number of monovalent counter-cations in the cation exchanger varies around 3, and that the hydration number of anions increases in the series  $\text{I}^-$  to  $\text{F}^-$  [198]. For multivalent counter-cations the hydration numbers obtained are usually around 6. Concerning the state of water in swollen carboxylic resins without hydration of counterions but containing undissociated or ion-paired groups, the data obtained elsewhere were examined by using the Bradley isotherm and proton magnetic relaxation data. The latter were obtained with a pulse NMR spectrometer operating at 19.2 MHz for the longitudinal,  $T_1$ , relaxation times by the Carr-Purcell method and the transverse relaxation times,  $T_2$ , by the Carr-Purcell method as

modified by Meiboom and Gill and by the Hahn method, indicating that water is bound to the matrix rather than to counterions. The data obtained seem to imply that water molecules in this resin (Zeo-Karb 226; 25% nominal DVB crosslinking) exist in a state of steeply decreasing restriction on rotational motion, perhaps multilayers, but this state can hardly be compared to that in liquid water; this seems at least to be true at that stage of swelling which corresponds to a water activity of 0.9 [199].

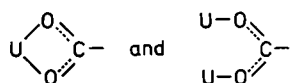
In describing the mechanism of the binding of counterions in ion exchangers the formation of ion-pairs has quite often been postulated. Originally it was claimed that a movable exchange ion forms an associated ion-pair with a fixed exchange group in an ion exchange resin, as represented by  $A^- + R^+ = RA$ , where  $A^-$  is a movable anion,  $R^+$  the fixed exchange group, and  $RA$  is the ion-pair. Since  $R^+$  and  $RA$  are both fixed to the resin matrix, and are at a finite distance of separation ( $7-10 \text{ \AA}$ ), they do not possess translational degrees of freedom and should be regarded as separate, solid phases. The exchanger system has, then, four phases: the external solution, the internal solution and the two solid phases  $R^+$  and  $RA$  [200]. The association of counterions into ion-pairs was also postulated at that time in order to explain the different electrochemical properties of two different ion exchange resins. However, besides providing one explanation for the selectivity of ion exchangers, the term ion-pair formation has remained quite vague.

There have been numerous studies of the mechanisms of the exchange of cations on strong acid cation exchangers. The aim of such investigations is to obtain additional insight into the ion exchange process from information concerning the structure of the sorbed ion. It might also be that such data could — by providing the correct formulation of chemical stages encountered in the exchange process — permit the quantitative mass-action expression of such equilibria. Furthermore, the Mößbauer spectroscopic study results confirm that the resin phase in strong acid cation exchangers with a degree of divinylbenzene crosslinking  $\geq 8\%$  must be regarded as a concentrated solution of a strong electrolyte. The counterions are hydrated in equilibrium with dilute aqueous solutions, and the solid electrolyte is completely dissociated. Spherical ion associations at higher crosslinkages occur also and are more pronounced for counterions with high charge densities. Depending on the moisture content, e. g. air-dried resin or dehydrated or hydrated, copper ions were found in different states in a KU 2X8 resin. Of interest is also the study of uranyl sulfate species or uranyl halide species sorbed on ion exchangers, as well as the cobalt coordination in cation exchange resins [201]. Metal coordination in general and the mechanisms of ion selectivity on ion exchangers would seem still be fruitful fields of research in ion exchange [202].

It is generally known that a characteristic feature of weak acid cation exchange resins is to show poor dissociation in the free acid form. Nevertheless, it is possible to exchange the proton of a weak acid carboxylic cation exchanger against metal cations. On the other hand, the exchange of protons and metal ions at macromolecular binding sites is a process of considerable importance in a variety of fields,



not least in biochemistry. For this reason and because ion exchange resins offer a simple system for studies of the mechanism, Schowen and coworkers used this system for the characterization of certain features of the transition state for proton release from the resin, which state appears to be that for migration of a preformed hydronium ion through the matrix. The migration generates a hole which is rapidly occupied by the metal ion [203]. With respect then to the mechanism of the uptake of metal ions the state of hydrogen as compared with sodium can be examined by the paramagnetic probe method. The state of copper ions depends on the degree of hydration, which can be determined by ESR spectra. From the first investigations on visible and near-infrared spectra of divalent nickel, cobalt and copper ions sorbed on a cation exchanger with carboxylic groups, where it was assumed that there is at least a partial coordination of ions by the carboxylic groups [204], the intensive work of Chuveleva and coworkers on the mechanism of the sorption of metal ions has shown, e. g., for  $\text{UO}_2^{2+}$  that their interaction with carboxylic resins is the formation of complexes of the type



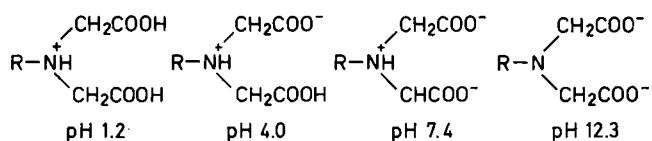
with more or less covalently bonded groups [205]. Numerous similar studies have followed, using the same methods [206] or one or the other of the above mentioned techniques [193, 202].

With regard to phosphoric acid type cation exchangers, study of the IR absorption of a resin in H- and Na-form saturated with U, Cu or Ni revealed that the sorption of U on the resin leads to the formation of a 4-membered coordination uranyl-phosphoryl ring compound, whereas the formation of similar 4-membered compounds in the resin containing Cu and Ni was not observed. The investigation of Cr(III) by EPR showed the formation of Cr(III) of distorted symmetry, revealing non-uniform distribution of sorbed Cr(III) ions in the exchanger matrix, and the study of iron(III) on phosphorus-containing ion exchangers by Mößbauer spectroscopy revealed that macromolecular complexes containing only O atoms in the 1st coordination sphere form on Fe(III) sorption on all types of these ion exchangers [207].

It could be expected that strong base anion exchangers would behave similarly to strong acid cation exchangers, since the states of sorbed species are simple, often being only the hydrated metal ion. Such conditions are not relevant for common anions, but one still has to distinguish between the uptake of customary anions and that of anionic metal complexes. For the first group NMR investigations of small molecules like  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , formate, acetate,  $\text{C}_2\text{O}_4^{2-}$  and benzoate showed that relaxation times are significantly lower than in bulk solution, suggesting that interaction with the resin limits molecular motion. An attempt was made to elucidate the equilibrium conditions of the system Zerolite FF- $\text{H}_3\text{PO}_4$  in water solutions by conductometric titration with a sodium base. It was found that the nature of

the process occurring depended on the concentration of the phosphoric acid solution used [208]. The results on complex species sorbed on anion exchangers are numerous [193]. The behavior of molybdenum was examined by IR spectroscopy; when sorbed from pH 7 or 9 solutions it polymerized in the exchanger on increasing concentration of the solutions; consequently the spectra reflect the presence of  $\text{MoO}_4^{2-}$  as well as of polymeric  $\text{H}_2\text{MoO}_4$  with H bridges; the sorbed Mo composition is more complexed when sorbed from pH 5 solutions, consisting of paramolybdates and  $\text{Mo}_8\text{O}_{26}^{4-}$  [209]. A new method of distribution analysis in anion exchange resin phases was developed — because of the peculiar nature of the internal solution in the resin — which involves equilibrium analyses on the simultaneous distribution among the three phases, i. e. the cation exchange resin phase, the anion exchange resin phase and the solution. It was applied to the visible absorption spectra and compositions of copper(II)-bromide and nickel(II)-thiocyanate sorbed in Dowex 1 X 4 [210]. The interpretation of mechanisms occurring in weak base anion exchangers seem to be much more difficult because these products are less well-defined reactive polymers. An infrared spectroscopic study of the sorption mechanism of vanadium(V) by porous vinylpyridine ion exchangers showed that the vanadium ions are sorbed as polyanions and a carboxylated polymer takes up vanadium as  $\text{VO}_2^+$ , forming an additional coordination bond between nitrogen and the sorbed cation.

In the following ion exchange mechanisms for chelating ion exchangers will be only briefly discussed for the two currently most important chelating polymers, iminodiacetic acid and amino phosphoric acid, with comments on some other resins that have been studied with interesting results. It has long been known that the kinetics of chelate resins are slower and that, since the selectivity for a given ion by a chelate is higher, the elution requires higher concentrations or higher dosages of the eluting agent. It is only now that spectral studies have been able to provide insight into the nature of the bonds formed and have been applied to examine the iminodiacetic and amino phosphoric resins. The iminodiacetic group dissociates differently depending on the pH



and accordingly acts differently. Visible light and ESR measurements have clearly shown that the complexes  $\text{CuCl}_4^{2-}$  and  $\text{CoCl}_4^{2-}$  are taken up from hydrochloric acid solutions, just as was found for the same species with Dowex 1. Heitner-Wirguin and coworkers have further found that the species formed from neutral solutions are chelated by the carboxylate groups, however no conclusive evidence was found for chelation through nitrogen as well. ESR measurements of copper ions on the chelating resin have shown that the bonding is partially ionic. For

uranyl species more details are available: in neutral solutions the Dowex A-1 resin sorbs uranyl ions strongly, added salt leads to coordination of the neutral salt anion, and from the corresponding spectral shift the anions may be classified according to their coordinating power:  $\text{NO}_3^- \approx \text{SO}_4^{2-} < \text{Br}^- < \text{Cl}^- < \text{SCN}^-$ . The amino phosphoric ion exchanger is primarily an amphoteric material. Copper sorption and structure of the H-, Na- and Cu-forms were studied by IR spectroscopy. An equilibrium of the dissociated H-form was established. Sorption of copper involves complex formation. It must be realized that very little work has been done on the mechanisms by which metal ions are sorbed by chelating ion exchange resins. On two polycondensation resins containing 8-hydroxyquinoline or salicylaldehyde/salicylaldoxime and a macroporous polyhydroxamic acid copolymer the role of the co-ion was studied showing that it accompanies the ion sorbed but remains labile, being easily eluted by buffer solutions. Vernon, therefore, comes to the conclusion that, initially, the co-ion is intimately connected with the sorption of the metal and does not remain within the polymer lattice simply to effect charge neutralization. 1 : 1 metal : co-ion complexes are fairly commonplace but, with the statistical spatial distribution of chelating groups attached to a random polymer backbone, some 1 : 2 metal : resin sorption is inevitable. With structures involving regularity of chelating group attachment to the polymer backbone, the probability of a divalent co-ion spanning two sites and thereby neutralizing the charge on two sorbed metal cations is greatly increased. Finally it should clearly be seen that in chelating ion exchange the total metal sorption involves all species  $\text{MR}_n$  to  $\text{RM-X}_{n-1}$ , where X represents a monovalent co-ion. Each species will have its own metal-resinate stability constant and overlap of the different species of two sorbed metals results in a decrease in selectivity [211].

**Effect of temperature on ion exchange.** Temperature has an influence on ion exchange, but under the practical aspects of operating ion exchanger units an increase in temperature does not improve ion exchange rates sufficiently to justify the extra expense of installing special heating equipment. Certain advantages can be gained by operating at elevated temperatures if the solution is at this temperature initially or if the solution is viscous at normal room temperature. In more specific applications, a warm regenerate solution is beneficial. But since all ion exchange resins are subject to chemical degradation and structural changes at rather high temperatures, temperature limits should be determined from the technical literature on each resin.

With respect to equilibria, in particular the swelling equilibrium, the change in the solvent content of an ion exchange resin with temperature changes in the range of several tens of degrees is small. This leads to a low accuracy in the determination of the enthalpy of swelling from the temperature variation. Together with the effect of temperature on ion exchange equilibria, selectivity should be considered since this factor is influenced by the temperature. Bonner and coworkers and Kraus and coworkers have studied temperature dependence and have found that the selectiv-

ities of monovalent cations as against hydrogen in a Dowex 50 resin decreased with increasing temperature. In the same system divalent cations showed a slight, and trivalent ions a strong increase in selectivity [212]. The influence of temperature on the kinetics of ion exchange is also important, since an increase in temperature produces a substantial increase in diffusion. It was reported that the self-diffusion coefficient of sodium in a strong acid cation exchanger and of chloride in a strong base anion exchanger increases almost three-fold on increasing the temperature from 3 to 25 °C. The diffusion rate of complexed metal ions in an anion exchanger was reported to have been increased by a factor of approx. forty during a temperature increase from 20 to 180 °C. On the other hand the desorption of different cations from a strong acid cation exchanger was studied and it was found that increasing the desorption temperature from 35–40 °C to 50–55 °C reduces the desorption time from 9 to 2 hours. Most important is the influence of temperature on the dissociation of weakly dissociating ion exchange resins. Furthermore, the capacity in both resin types increases with increasing temperature. More important is that the dependence of the dissociation of weak acid cation exchangers and weak base anion exchangers on temperature may be used for a thermal regeneration of such resins, thus eliminating for the environment the problems caused by using regeneration chemicals.

**Effect of pressure on ion exchange.** External pressure exerted on an ion exchange resin has a certain influence on the ion exchange system. The exchange equilibria, which were the first properties examined under this aspect, are not influenced, because (from a thermodynamic point of view) there is no volume change of the exchanger phase with its surrounding solution. The hydrostatic pressure of a total ion exchange system has also been investigated with more or less the same result, except that some increase in the electrolyte dissociation, and change in the structure and properties of the solvent or the degree of solvation of ions were found. As far as ion exchanger powders are concerned the effect of pressure can become an operative factor because of the particle size. But what was theoretically derived and then experimentally proven is that if external pressure is applied to a styrene-divinylbenzene cation exchanger resin it influences swelling and the selectivity in the same way as an increase in the degree of crosslinking by divinylbenzene does. This could be shown for the ion exchanges hydrogen against copper and hydrogen against iron(III). As an application, regeneration can be accomplished without pressure, which results in better exchange kinetics and lower ion selectivities for this step. An external mechanical pressure simulates a further crosslinking of the matrix, also in the case of anion exchange resins, influencing in this way the selectivity of anion exchangers. But the effect was found to be not uniform, in contrast with cation exchange resins. The pressure applied causes here both an increase and a decrease in selectivity. Especially in the case of chromate anions high ion selectivities were observed [213]. Effects of pressure on ion exchange and ion pairing chromatography were also studied.

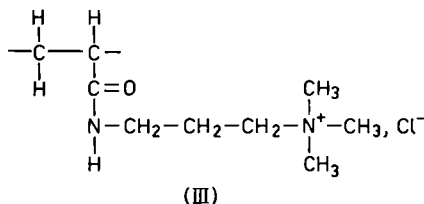
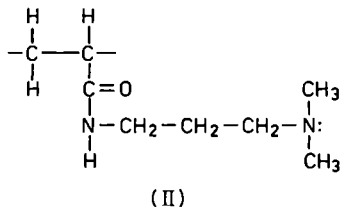
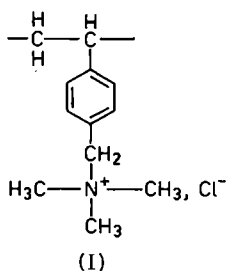
**Ion exchange of ampholytes.** In biochemistry, of all the applications of ion exchangers, ion exchange chromatography has been extensively used for the fractionation of complex mixtures of amphoteric molecules (also called ampholytes) such as amino acids, peptides, proteins, and nucleotides. In general, ampholytes can, with respect to their behaviour towards ion exchange materials, be treated either like organic bases or organic acids. For example, amino acids can be separated by displacement development on a strong acid ion exchange resin in the H-form with sodium hydroxide as displacing agent, or on a strong base resin with hydrochloric acid. With respect to ampholytes the early work with ion exchangers was pretty much empirical. Nevertheless attempts were made to find relations between ionization constants and sorption constants of amphoteric electrolytes, such as glycine,  $\alpha$ -alanine, phenylalanine, and lysine. Further, a general method was suggested for determining the sorption equilibrium constant of an aqueous solution of an ampholyte-cation exchanger system. With proteins adsorption is confined to the surface of the particles and van der Waals interactions appear to be of considerable importance. The equilibrium principles of the sorption of nucleotides on anion and cation exchange resins was intensively studied. It was found that the mechanism of nucleotide sorption is not significantly different from the sorption of inorganic ions. Since the analysis of the sorption of partially deaminated resins has shown that, for a resin with a small sorption capacity the nucleotide sorption capacity approaches the full exchange capacity of the ion exchangers, one can expect that there will be a demand for special exchangers for other special molecules.

The fundamentals and definitions of ion exchange and ion exchangers are in principle all related to ion exchange in an aqueous solution. Nevertheless ion exchange between solids has also been investigated. A direct ion exchange has, for instance, been observed between  $\alpha$ -Zr phosphate and several anhydrous metal halides. The exchange reaction occurs at 115 to 375 °C, and proceeds by continuous removal of the volatile acid. This type of exchange process between solids must be considered as a general property of ion exchangers in the H-form [225]. It might well be a matter of definition whether the exchange of ions between ion exchanger grains in fully deionized water can not also be considered an ion exchange between solids. Results of corresponding investigations are available showing mainly that exchange takes place on a limited surface area rather than over the whole surface of the grains [226].

**Ion exchange with organic ions.** That ion exchange is not confined to inorganic ions was first shown by Kressman and Kitschener in a study on the ion exchange equilibria of large organic cations on a phenolsulfonate resin. The affinity of some large organic cations, namely, tetramethylammonium, tetraethylammonium, trimethyl-n-amylammonium, phenyldimethylethylammonium, phenylbenzyl-dimethylammonium and the quininium ion increases with the size of the ion, which is in contrast to the simple inorganic cations. As an explanation of this it was suggested that van der Waals forces contribute largely to the affinity, with the electrostatic

forces being less important. The rate of exchange, on the other hand, decreases with increasing ionic size. As the saturation capacity was found the same for the largest of the quaternary ions studied, namely phenylbenzyltrimethylammonium, as for inorganic ions, this was taken as a clear indication that all the molecular pores within the resin are larger than the effective diameter of the ion. No physical adsorption was observed from solutions of the highly dissociated salts of large cations [214]. Although several studies of the binding of organic cations by cation exchange resins followed, virtually no investigations of the selectivities of anion exchangers for organic ions had been undertaken although it was becoming apparent that an understanding of the nature of such binding is of considerable importance: one of the chief problems associated with the use of anion exchange resins in water treatment is the virtually irreversible fouling of the resins by such naturally occurring materials as fulvic and humic acids. Further knowledge concerning the binding of organic ions by anion exchangers will aid in the proper development and selection of resins for use in situations in which organic fouling is a potential problem. In a pertinent study by Gustafson and Lirio, therefore, the influence of the chemical structure of the resin upon the equilibria and kinetics of binding of model organic species were evaluated.

The selectivities of poly (*N,N,N*-trimethylvinylbenzylammonium) chloride (I), the protonated form of poly (3-*N,N*-dimethylaminopropylacrylamide) (II) and poly-(3-*N,N,N*-trimethylammoniumpropylacrylamide) chloride (III) anion exchange



resins for ethanesulfonate (ES), benzenesulfonate (BS), 2-naphthalenesulfonate (NS), 2-anthraquinonesulfonate (AQS), tert-butylcatecholsulfonate (TBCS), dodecylbenzenesulfonate (ABS), and gallate (GAL), ions were measured at 25 °C and  $\mu = 0.10$ . The following values of molal selectivity coefficients,  $K_{\text{Cl}}^0$ , for the binding of organic ions by resin I were obtained: ES, 0.67; BS, 7.4, NS; 133, GAL; 150,