

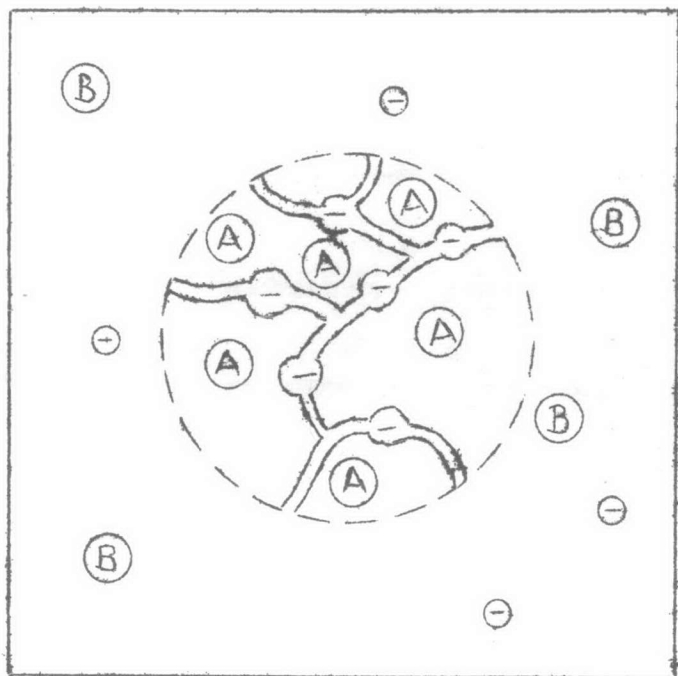
CHAPTER I

INTRODUCTION

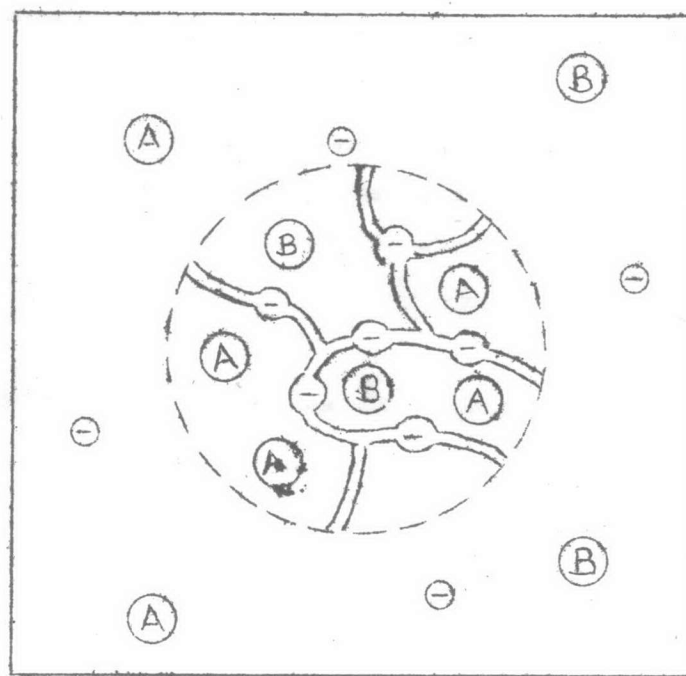
Ion exchangers are insoluble solid materials, acid or base. They consist of a framework which is held together by chemical bonds or lattice energy, so that they are fixed. This framework carries a positive or negative electric charge which is compensated by ions of opposite sign called counter ions. The counters are free to move within the framework and can be exchanged under suitable conditions, for a stoichiometrically equivalent amount of other ions of the same sign when the ion exchange is in contact with an electrolyte solution. The material is called a cation (electropositive) or an anion (electro-negative) exchanger, according to the sign of the mobile ion. Carriers of exchangeable cations are called cation exchangers. Certain materials are capable of both cation and anion exchange. These are called amphoteric ion exchangers. The framework of a cation exchanger may be regarded as a macromolecular or crystalline polyanion, that of an anion exchanger as a polycation.

When an ion exchanger in A form (where A is an arbitrary counter ion) is placed in a solution of an electrolyte BY, counter ions A will migrate from the exchanger into the solution and counter ions B from the solution into the ion exchanger, i.e., an exchange of counter ions takes place. After a certain time, ion-exchange equilibrium is attained. Now, both the ion exchanger and the solution contain both counter-ion

Initial State



Equilibrium



Matrix with fixed charges



Counter ions

Co-ions

Fig. 1-1 Ion exchange with a solution (schematic). A cation exchanger containing counter ions A is placed in a solution containing counter ions B (left). The counter ions are redistributed by diffusion until equilibrium is attained (right).

species A and B. The concentration ratio of the two counter ions, is not necessarily the same in both phases. According to this definition all ionic species with charge sign opposite to that of the exchanger framework will be called counter ions, and all ionic species with the same charge sign as the exchanger framework will be called (1) co-ions.

As a rule, the pores, the interstices in the framework, are occupied not only by counter ions but also by solvent and solutes which can enter the pores when the ion exchanger is in contact with a solution. Uptake of solvent may result in swelling of the ion exchanger. Uptake of solutes is usually called sorption, though it is essentially a distribution of the solute between two liquid phases, namely the pore liquid and the solution outside.

Ion exchange is, with very few exceptions, a reversible process. In ion exchange equilibrium, the concentration ratios of the competing counter-ion species in the ion exchanger and in the solution are not the same. The ion exchanger prefers one species to the other. The preference for one species may have several causes. The most important of these are:

(1) The electrostatic interactions between the charged framework and the counter ions depend on the size and the valence of the counter ion.

(2) Other electrostatic forces, interactions between the ions and their environment.

(3) Large counter ions may be sterically excluded from the

narrow pores of the ion exchanger.

All these effects depend on the nature of the counter ion and thus may lead to preferential uptake of a species by the ion exchanger.

Ion-exchangers are generally classified into two types:⁽²⁾

(1) Organic ion-exchange resins, the diffusion medium is generally the imbibed water or electrolyte.

(2) Inorganic ion-exchange materials, the diffusion medium may be the solution surrounding the solid particles or crystallines.

The early ion exchangers were largely inorganic in origin, but subsequently, the ion exchange scene was dominated by the synthetic organic resins because of the ease with which reproducible preparations could be made, and their excellent mechanical and chemical stability. In addition, the organic resins possessed physical characteristics and exhibited ion exchange behaviour which could be reproduced from sample to sample. In recent years interest in the inorganic exchangers has been revived with the need for the high temperature separation of ionic components in radioactive wastes. In order to make such separations, highly selective exchangers are required which are not only stable at high temperatures but which also have exchange properties unaffected by acidity and high levels of radiation. Organic ion exchange resins are unsuitable for such applications, as changes in selectivity and capacity occur on exposure to radiation, and degradation takes place at the high temperatures of interest. As a result of this renewed interest in the inorganic materials, two types of ion exchangers were developed:⁽³⁾

(1) The insoluble salts of polybasic acids with polyvalent metals, such as ammonium molybdophosphate.

(2) The hydrous oxides of polyvalent metals, such as oxides of tin and zirconium, iron, aluminium, chromium, bismuth.

The inorganic ion exchangers though numerous in number but very few have been subject to thorough kinetic studies.⁽⁴⁾ It has been accepted that equilibrium is established between two phases, liquid and solid. It should be of interest to know the type of equilibria, the rate at which equilibrium is approached in order to set an optimum working condition.