

## Exchange of Isotopic Ions in Cation Exchangers

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In theories published on the mechanism of cation exchange it has been postulated that there is a dynamic equilibrium between the cations sorbed and the cations of the same element in the surrounding solution. No direct experimental proof has been given, although it seems very probable in view of the many successful separations of different cation species<sup>1</sup> and especially Taylor and Urey's classical separations of isotopes<sup>2</sup>.

In 1947 one of the authors<sup>3</sup> observed that a cation exchanger (Wofatit KS) saturated with thorium ions did not seem to be in dynamic equilibrium with a solution containing the thorium isotope  $UX_1$ . The possibility that a dynamic equilibrium really exists even in this case, is not excluded because of the high affinity of the thorium ions caused by their high charge. Another conceivable explanation is that thorium forms radiocolloids which are physically adsorbed on the exchanger and removable only by complexing agents and not by ion exchange alone.

In order to get a better understanding

of this problem an investigation was started concerning the dynamic equilibrium in ion exchange systems. In this paper is reported a study of the exchange between silver ions using  $Ag^{111}$ , which is a pure beta-emitter with a maximum energy of 1.0 Mev. and a half-life of 7.5 days. A commercial quality of the synthetic cation exchange resin, Dowex 50, was used, the spherical particles of which had an average size of 10–30 mesh. Experiments were carried out both as single-stage operations and as column operations.

*Single-stage experiments.* A beaker containing "labelled" silver nitrate solution was supplied with a proper amount of Dowex 50 previously saturated with inactive silver ions. During the experiment the solution was stirred vigorously and samples of the solution were withdrawn at suitable time intervals for radioactivity measurements. Another single-stage experiment was made with the labelled silver saturated exchanger obtained in the experiment just mentioned. Its performance was the same except that in this case the outer solution was originally inactive. In both experiments the volume of the silver nitrate solution was 30 ml and its concentration 0.080 *N*. The amount of ion exchanger was chosen so as to have about as many exchanging groups as there were cations in the outer solution. If there is

ous chloride and lithium chloride in ethylene diamine by gentle suction through the stopcock tube. When the vessel is filled the stopcock is closed, and the electrode is left for at least one day to reach equilibrium. When in use, the platinum wire is connected to the potentiometer and the drawn out capillary tube is put in the reaction solution. An ignited, bright platinum electrode is used as indicator electrode.

In Fig. 2 are shown some titration curves obtained from titrations of various substances of different acidity. An ethylene

diamine solution of sodium aminoethoxide was used for the titrations of benzoic acid and methyl *p*-hydroxybenzoate, while sodium methoxide, in ethylene diamine, was used for the lignin derivative and phenol. A *Radiometer* potentiometer model PHM 3f was used for measuring the potential differences.

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any exchange between isotopic ions, this will result in the first experiment in a total decrease of about 50 % in the specific activity when equilibrium is reached; a magnitude of decrease which gives the best experimental accuracy.

Two different types of *column experiments* were carried out. In the first case the column was saturated with hydrogen ions and after washing with distilled water a labelled silver nitrate solution was percolated at a rate of 2.5 ml/cm<sup>2</sup>/min. The silver content of this solution corresponded only to a small fraction of the total exchanger capacity. After washing the activity of the column was measured by means of a "scanning" device (previously shortly described<sup>3</sup>) containing an end-window Geiger-Müller counting tube. Then a solution of inactive silver nitrate was allowed to flow through the exchanger. The silver content of this solution was chosen to displace the active silver ions previously sorbed for a distance of a few centimetres provided that there is an exchange. After washing the column activity was measured again. Another portion of inactive silver nitrate solution was percolated and so on. The other type of column experiment was similar to the one just described except that in this case the exchanger originally was completely loaded with inactive silver ions. All experiments were carried out at room temperature.

All experiments showed clearly that there is a rapid exchange between ions bound to the exchanger and their isotopic ions in the surrounding solution. Thus, in the single-stage experiments the specific activity of the outer solutions changed as expected from the exchanger capacity and the cation content of the outer solution. As would be anticipated this change was exponential with a half-time of the exchange of the order of 1–2 minutes under the conditions here employed. In the column experiments the maxima of the sorption bands of the active silver moved

a distance, the length of which was equivalent to the cation content of the displacing silver nitrate solution. As the displacement progressed, the band width increased with a corresponding decrease of the maximum.

In a paper, which appeared after this work was completed, Borland and Reitemeier<sup>4</sup> reported the exchange of calcium ions between a calcium solution labelled with Ca<sup>45</sup> and a number of clays, saturated with inactive calcium ions. They state that the equilibration is virtually complete after ½ to 1 hour, their techniques preventing the study of shorter periods. Apparently this calcium exchange is slower than the silver exchange studied by us. The chemical and structural differences, however, between clays and synthetic sulphonic acid cation exchange resins plays probably a much more important rôle in this rate difference, than the higher charge of the calcium ions.

The work will be continued with isotopic ions of higher charge and the single-stage techniques improved by using immersion Geiger-Müller counters to make possible the study of rather fast exchanges. Together with the column experiments this may be of fundamental interest for processes involving ion exchange. A more detailed report will be published later.

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1. *E. g.* a number of papers in *J. Am. Chem. Soc.* **69** (1947) 2 769–2 881.
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3. Westermarck, T. *Ing. Vetenskaps Akad. Medd.* FKO No. 7 (1948) 28.
4. Borland, J. W., and Reitemeier, R. F. *Soil Sci.* **69** (1950) 251.

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