

## The Potentiometric Titration of Phenolic Hydroxyl Groups. I. Description of a "Calomel Electrode"

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In the last decades, water-free solvents have been widely used in the titrations of weak acids and bases. One of the main difficulties encountered in such determinations has been to find electrodes with sufficiently high stability. Moss, Elliot, and Hall<sup>1</sup> have used antimony electrodes, and have stated that platinum electrodes do not give good results. In connection with investigations on the possibility of determining phenolic hydroxyl groups by titration in water-free solvents, the present authors were not able to obtain satisfactory results with either platinum or antimony electrodes arranged according to Moss, Elliott, and Hall<sup>1</sup>. Later, however a "calomel electrode" was developed, which has given very good results<sup>2</sup>. Investiga-

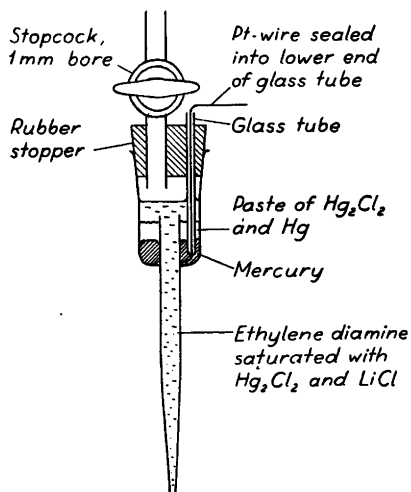


Fig. 1. Schematic drawing of the "calomel electrode".

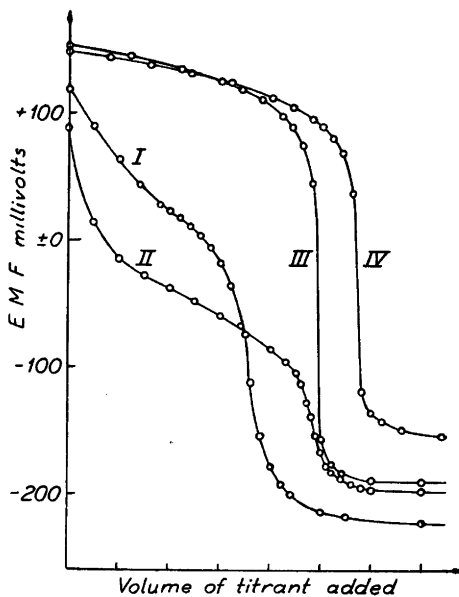


Fig. 2. Titration curves obtained from titrations of various acidic substances using the electrode described.

- I Lignin derivative
- II Phenol
- III Benzoic acid
- IV Methyl *p*-hydroxybenzoate

tions on the solvent effect have shown ethylene diamine to be the most satisfactory solvent for use with the above-mentioned "calomel electrode".

**Description of the "calomel electrode".** The electrode is shown in Fig. 1. It is made of Pyrex glass and consists of a wide, upper tube with a capillary tube (2.0 to 2.5 mm bore) sealed through the bottom. The lower part of the capillary is drawn out to a smaller diameter. The upper tube has a ring-formed bottom, where mercury is placed. On the mercury is placed a paste consisting of mercurous chloride and mercury. The upper tube is closed by a rubber stopper with two holes, through which lead a glass stopcock (1 mm bore) and a glass tube with a sealed in platinum wire, which gives contact with the mercury. The electrode vessel is filled with a saturated solution of mercur-

## 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.

1. Moss, M. L., Elliott, J. H., and Hall. R.T. *Anal. Chem.* **20** (1948) 784–788.
2. Gran, G. *Acta Chem. Scand.* **4** (1950) 559–577.

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