



# HOKKAIDO UNIVERSITY

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(Review)

## EARLY DAYS IN ELECTROCHEMISTRY<sup>\*)</sup>

By

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I have entitled my talk "Early Days in Electrochemistry" but not so early as impressed by these words ; to be precise I should better say early days in the application of hydrogen isotope to the electrochemistry of hydrogen electrode reaction.

The stage of play was a rather spacious room in a basement of the Owens College of the Manchester University named after the contributor. Characters were Prof. A. FRUMKIN, Prof. M. POLANYI and myself. What was going on there was the experiment on the catalyzed exchange of hydrogen between 10 cc liquid water and hydrogen gas of *ca.* 100 mm.Hg pressure in 100 cc space in the presence of platinum as catalyst ; hydrogen gas was enriched with deuterium by a few percent<sup>\*\*\*)</sup> and the exchange reaction was to be followed by the decrease of deuterium content in the hydrogen gas.

Prof. FRUMKIN was concerned about the disturbing effect of oxide film on the surface of platinum and advised us to reduce the film beforehand. We have effected his advice by heating the platinum plate to be used as the catalyst beforehand from outside a reactor *in situ* in dry hydrogen gas. And for this purpose a quartz glass vessel was used as the reactor which will be called FRUMKIN reactor. The partner of exchange, *i. e.* 10 cc liquid water was distilled into the FRUMKIN reactor after evacuation of the hydrogen gas.

The FRUMKIN reactor F was fitted to another work G of ordinary glass by a ground joint ; G was provided with two taps as shown in the Figure 1, which, if closed, excluded F from outside. The two taps were

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<sup>\*)</sup> Talk to the Japan-Soviet Colloquium on Electrochemistry, October 4, 1974.

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<sup>\*\*\*)</sup> One gm nearly 100% deuterium oxide was provided us by Late Sir Hugh, *i. e.* Prof. H. S. TAYLOR in Princeton at that time in so early days, to whom our best thanks are due.

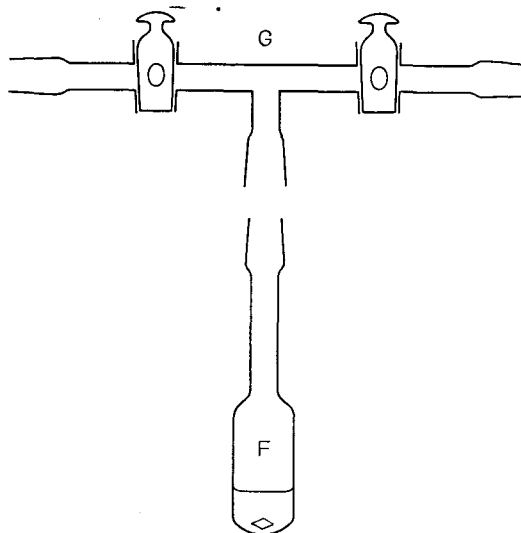
*Early Days in Electrochemistry*

Fig. 1.

connected each with one of the two ground joints directed outwards in line with each other. G enabled us to charge F with water and deuterium-shifted hydrogen gas by vacuum processes, to extract hydrogen gas thus treated and to charge F with a fresh portion of deuterium-shifted hydrogen gas. The hydrogen thus treated was now led to a furnace packed with pieces of copper oxide kept at *ca.* 200°C in order to burn it to form *ca.* 10 mg water; its specific gravity was measured by means of a micro-pyknometer of GILFILLAN and POLANYI<sup>\*)</sup> and the deuterium content was determined from the known relation between the density and the deuterium content.

The experiment in view was now started one day in Autumn 1933 in the spacious basement. I myself was manipulating taps and POLANYI was, sitting on a low wooden box, shaking the FRUMKIN reactor in order to mix up the content around the axis through these ground joints fitted respectively to adapting ones. The platinum plate was jumping crazily about in the shaken water in the FRUMKIN reactor. And Prof. FRUMKIN was walking around the room muttering about the effect of the oxide film.

After about one hour we finished with the experiment and the hydrogen gas thus treated was extracted and analysed for deuterium content. It took a few hours and the result was negative. In other words the deuterium percentage was found unchanged by the treatment within the experimental

<sup>\*)</sup> E. S. GILFILLAN and M. POLANYI: *Z. physik. Chem.* A 166 (1933), 254.

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error of the analysis.

Afterwards we could observe a good decrease of deuterium content in hydrogen gas quite exceeding the experimental error; the effect of acid, alkali or of change of hydrogen pressure on the exchange rate could be quantitatively confirmed. Why failed at first?

I must confess this was due to my ridiculous mistake. We have arrived at Manchester from Germany in August, but we found there no available apparatus nor deuterium. Professor POLANYI advised me to investigate the reaction we were going to deal with theoretically until the apparatus was ready and deuterium was supplied. I was reading papers of VOLMER, FRUMKIN and GURNEY and drawing every day on my note book one cm square platinum surface and estimating according to the elaborated theory of VOLMER and FRUMKIN the rate of conversion of hydrogen atoms formed from hydrogen molecule into hydrogen ion and metal electron. The FRUMKIN's elaboration was published just in 1933. He visited the Manchester Laboratory we were working several times and I had a good fortune to be post-doctorally trained in electrochemistry. On the other hand I had a hard luck to be totally possessed by the occult of one cm square Pt surface, cut out from plenty of this platinum plate a piece of one cm square plate quite seriously fitting a measure to the plate and stored the plenty of the rest in a closet.

The secret of later successes was quite simple; I just packed the FRUMKIN reactor with platinum plate as much as practicable.