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CORRECTION TO THE REMARKS OF PROF. FRUMKIN IN "THE FIRST JAPAN-USSR SEMINAR ON ELECTROCHEMISTRY —GENERAL DISCUSSION—"[*] BY A. MATSUDA[1]

By

A. MATSUDA[**]

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Prof. A. FRUMKIN : ——

"I should say something about the establishment of the electrode potential. I should remember there have been two approaches in the history of electrochemistry and until now perhaps the question is not finally settled. The first approach goes back to NERNST. NERNST considered the establishment of the electrode potential as a result of one process, the ionization of the electrode metal or the backward process of the discharge of the ions in the solution.

RIDEAL and BOWDEN in the early thirties considered the establishment of the potential at the platinum hydrogen electrode under potentials between the reversible hydrogen and the reversible oxygen potentials as a result of accumulation on the platinum surface of dipoles formed by Pt–H or Pt–O bonds. Of course, as the potential changes the number of such bonds changes and so the potential is realized. This was the problem which occupied me since the early beginning of my studies in this field and which occupied me during the last years still.

In our first paper we showed that both approaches, if they are used without consideration of the existence of two simultaneous possibilities, cannot give correct results. First of course it is easy to show that the establishment of the potential is caused also by the specific adsorption or by the orientation of solvent molecules, this was the start of the work I have done. It was shown later the

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[1] A. MATSUDA This Journal **22**, 129 (1974).

[*] In this review article many errors due to mishearing of the tape record were pointed out by Prof. FRUMKIN. So the remarks of Prof. FRUMKIN in the General Discussion are reprinted in the present issue with special regard to his corrections. The author wishes to express many thanks to Prof. FRUMKIN for his kind cooperation.

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existence of a difference in point of zero charge between different metals, which is partly related to the potential difference arising at the metal-metal interface. This was the thing which NERNST completely neglected and which plays a definite role in the interpretation of electrochemical phenomena, but I must say until now very much practical use of this potential difference has not been done. We have tried to show in some cases that it is necessary to take it into account, for instance, in our study of thallium amalgams, but there was not much done in this direction.

What about the orientation of solvent dipoles? Especially during the last perhaps ten years much work has been done in our country and in Italy by TRASATTI. This line of research of TRASATTI and ours are in many respects similar however there are some differences in the interpretation of what is observed. The difference refers to the case of d-metals. In the case of sp-metals the interpretation of TRASATTI and ours practically coincide. Well, prehaps sometimes different words are used but the mathematical relations and the physical meaning are very similar.

As to the case of the orientation of water and other molecules on the surface of d-metals there is difference in approach, which is connected with the different evaluation of the experimental material. I make a more severe choice, I would say, then TRASATTI in the case of what we call d-metals. The available experimental material is not yet sufficient to draw the conclusions which TRASATTI draws. There is now some polemic which is not yet readily published, but the exchange of letters between TRASATTI and myself on this question will be published later. On my opinion TRASATTI uses experimental material for d-metals which is not perhaps so good as it should be for the building up of a theory.

Now in connection with what I am speaking a word about the paper of Prof. KITA which was given yesterday. I should draw your attention to one point. When we make classification of the reactions on metals we must be very careful. For instance, according to Prof. KITA gold is one which belongs to the category of d-metals. Now, Prof. TRASATTI quite from the beginning pretended that gold behaves specifically as sp-metals and at the beginning I was against it. But in this case I had to state that TRASATTI was right, because metallic gold is really not a d-metal, although in gold compounds gold becomes a d-metal. When we have metallic gold it does not behave as d-metal as far as the double layer structure is considered, for instance, the orientation of water melecules with the oxygen towards the metal is typical or qualitatively typical for d-metals and it is not observed at the gold electrode interface and in that respect gold behaves like mercury or even perhaps the orientation is still less pronounced than in the case of mercury. I showed a drawing in my paper that gold was quite at the beginning of the series of metals in which come mercury, cadmium, gallium and sp-metals, which by their behavior little by little approach the beahavior of d-metals. So one must be very careful when we classify the difference in groups because using different choice of the experimental material we can obtain quite different classification which depend very much on the author.

The dipole approach which goes back to RIDEAL and the time of early thirties was used recently again by BOCKRIS, who tried to show that the behavior of the platinum electrode in the oxygen region can be interpreted simply as the accumulation of the oxygen dipoles, and I already said in connection with the discussion which followed the paper of Prof. TAKAMURA that this approach leads to contradiction with thermodynamics. You cannot refer the building up of an electrode potential only to the accumulation of oriented dipoles. You have no enough variables such as to find equilibrium conditions in that case. So you must always consider both possible mechanisms, surface dipoles and surface adsorption phenomena and also ionization processes. In some cases one particular phenomenon is the most important and in other cases another one, but always you must consider that both exist.

Now the problem which interested us, not only personally myself, in Moscow last years was the theory of the surface layer of the platinum group metals. We have very strongly pronounced phenomena of adsorption of hydrogen or of oxygen or of both perhaps together. We tried first of all to develop a thermodynamical treatment which would be equivalent to the theory of the ideal polarized mercury electrode, which was developed well at the beginning by the work of KOENIG, directed by LANGE, and finally by GRAHAME and which for a certain time dominated completely modern electrochemistry. Of course the theory of the ideal polarized electrode is a very elegant theory, but it is, I think, rather a strange feature of this period of the development of electrochemistry, that the whole treatment of the double layer problem was based on the electrode which is in the usual sense of the word not an electrode at all, because it was the fundamental assumption that no possible electrochemical reaction occurs at this interface. Then this is not an electrode. This is some foreign body in the electrolyte solution and of course we should consider how to change the theory, so that you could adapt it to a real electrode, I mean an electrode at which electrode reactions can occur. If you look at the incorrect treatment given by MOHILNER quite recently to the physical meaning of the GIBBS adsorption Γ in the series edited by BARD, you see that on the basis of simple small corrections of the theory given by GRAHAME the problem cannot be solved and I think we gave a much better solution. Of course the question is still discussed in the literature. We had quite an argument recently with SCHULTZE and VETTER, but finally they had to state that at least in one respect they had been wrong. At any rate this is a question which is still debated and which PARSONS described as controversial. I hope this will be finally settled and I think the theory which have been worked out by myself, PETRY and DAMASKIN in Moscow will be accepted by everybody.

Now, I think it is practically all what I can say, but we see all effects must be considered, ionization, adsorption of ions, adsorption of neutral molecules, orientation of surface surfactants adsorbed from the solution, orientation of solvent dipoles, GALVANI potential difference at the interface between two metals, dipole effects caused by adsorption of atoms of hydrogen or oxygen, perhaps other atoms too and the different state of charge transfer between adsorbed particles and the electrode. This is a very interesting problem.

LORENZ in East Germany was the first one to draw attention to the last problem and I think this is a great merit of LORENZ, although the first treatment which has been given by LORENZ was not in all respects correct. It was criticized by DAMASKIN, but I think we have now especially thanks to the work done in Moscow by GRAFOV and PEKAR, come to some agreement with LORENZ. But we have to distinguish between two approaches to the treatment of charge transfer, one which is based on the molecular picture and must assume a definite model of the electrode, which is always something hypothetical but very interesting and very important, and the other is some definition of the charge transfer, which can be given on the basis of thermodynamic relations using either GIBBS thermodynamics or thermodynamics of irreversible processes which is given by ONSAGER relations. This was done recently by GRAFOV and leads to the same result. Well, in the paper which will be published soon this question is treated again and I will try to induce PETRY and DAMASKIN to give a final comparison between different approaches to the theory of charge transfer which is also an important factor in the establishment of the electrode potential.

How and to what degree an adsorbed ion begins to behave like an atom? How this problem can be treated? As I already stated there are two possible approaches which lead to different mathematical expressions, which have also a different physical meaning. This is, I think, an important electrochemical problem, but I shall not dwell further on it because it was not considered in this seminar, we might come back to it after two years in Moscow until when our last paper on this subject will be published. A very long paper of PETRY and myself is also in course of publication in Electrochimica Acta, which gives the review of all the work we have done on the platinum hydrogen system. There are also some considerations concerning the charge transfer but not in detail.

This is what I could say to this part of the discussion. I should like to say a few words later about instrumentation."

Prof. TAMAMUSHI : ——

"I would like to ask Prof. FRUMKIN one question on the role of point of zero charge in the kinetic theory of the charge transfer processes. In many cases when we analyze the irreversible process, the hydrogen scale is used as the reference potential. If you use the zero charge potential instead of the hydrogen scale, is there any merit or advantage of this scale?"

Prof. FRUMKIN : ——

"Well, I understand the question in the following way : whether we should abandon the usual way of presenting the electrochemical data referred to the standard hydrogen potential or express everything in the rational scale as it was called by GRAHAME, or reduced scale as it was called by ANTROPOV. For some period this was proposed also by BOCKRIS.

I think we should keep the use of the method which is used, because if we use the rational scale we must introduce a correction for the work function of the electrode. Otherwise we neglect that the extraction of the electron from the electrode to the solution at the point of zero charge requires different work for different metals.

There was a period when BOCKRIS advocated that we could use the *p.z.c.* scale or the rational scale, because at the point of zero charge every metal is in the same condition. This is not correct. It is the same condition so far as adsorption from the solution is considered, but it is not the same condition with respect to the extraction of the electron from the metal.

The most important agent in any electrochemical process is the electron. This should not be forgotten. The work necessary to extract an electron from metal into the solution is equal for all metals not at the potential of zero charge, but at any equal potential measured against any standard electrode. I should say this is a fundamental law. This can be directly shown without introduction of any clever concept like the electrochemical potential simply by considering the equilibrium of two electrodes in a solution. If you keep in mind that equilibrium must not suffer from any possible process and that we can assume always an electronic conduction of the solution, when you see at once that the work of extracting an electron from the metal into solution at equal potential must be independent of the metal nature. Well, I have said it already in 1935, although nobody payed any attention to it, this was not a paper, this was a footnote of the famous HORIUTI and POLANYI paper. This shows you clearly that you must use the standard scale and not the rational or the ANTROPOV's.

If the drop of potential in the diffuse double layer cannot be neglected, of course, you must apply the double layer correction, because what I have said concerning the electronic work function refers only to a point in the solution which is outside the limit of the diffuse double layer, and if you enter the limit of the diffuse double layer everything changes. This was shown clearly in the excellent paper of PLESKOV. I very greatly admire his work.

So I can quite clearly state my opinion that is the internationally accepted now. You should use the standard hydrogen electrode scale and apply the double layer correction when necessary and when possible.

You should not forget that the point of zero charge exists, but should not shift from this way of treating the experimental data to the idea of referring all processes to the point of zero charge, as it was proposed especially by ANTROPOV. ANTROPOV wrote a book which was published in New Delhi when he was in India for three years "Null point and Electrochemical Kinetics", which I think contains something like that, but this idea is not correct. I mean you should always remember the point of zero charge concept, but you must not forget that not everything can be in similar terms treated on the basis of this concept.

If you do so as BOCKRIS has done in some period of his work, that is if you try to introduce a correction for the work function, I mean the work function of the extraction of the electron into the solution at *p.z.c.*, you come back to the standard hydrogen scale, so this compensates. This was published in 64 or 65, I think. I published a paper in the Journal of Electroanalytical Chemistry on this subject and nearly at the same time Parsons published one or somewhat earlier. There was a paper in Russian published earlier by TEMKIN and myself on the same point in the Russian Journal of Physical Chemistry and this was already expressed in the foot note of HORIUTI and POLANYI paper. So I mentioned it in Hokkaido just to quote once more Prof. HORIUTI."

Prof. N. TANAKA: ——

"I would like to ask Prof. FRUMKIN two general questions. In most cases I have used a slowly dropping mercury electrode in the kinetic studies of the electrode processes, because it is very difficult to have a constant surface condition in the case of solid electrodes. A dropping mercury electrode is superior to a hanging mercury electrode which is easily deteriorated with surface active substances in solution, and I prefer a slowly dropping mercury electrode to a usual one because the usual dropping mercury electrode has not enough drop time to obtain constant surface area.

Now, my first question is how to standardize the surface condition when we use solid electrodes to obtain kinetic parameters, I mean, the rate constant and the transfer coefficient. The second question is on the dependence of the transfer coefficient on the electrode potential. Both are the complicated problems for the determination of the kinetic parameters. I would like to hear the opinion of the Russian delegates on these problems."

Prof. A. FRUMKIN : ——

"Well, first of all I think we should start a more wide use of solid electrodes because there are problems in electrochemical kinetics concerning the mechanism of the electrode process which cannot be solved so long as you use the electrodes from one metal. I'll give you one example which we met practically.

When you try to solve the question what is the charge of the reactant particle in the case of the electroreduction of anions, which was very much discussed in the literature by Gierst, by us and others, in the recent analysis which is not yet published, but soon will appear in Jour. of Electroanalytical Chemistry, we could show this question cannot be solved so long as you work only with mercury. You can attempt to solve this question only if you compare the behaviors of different electrodes.

Now, if you start to use different electrodes, the choice of liquid metals is rather limited because there are only mercury and gallium as well as gallium alloys and amalgams. Gallium is in many respects interesting, but not a very convenient electrode because it is very easily oxidized. So we are interested in the use of solid electrodes.

How can you control the state of the solid electrode to be sure at least you have reproducible results, and how can you obtain the electrode in a good state? These are two different questions.

I think the most unambiguous method of control is to take a set of differential capacity *vs.* potential curves at different concentrations of the supporting electrolyte. There is a normal set of curves, which was shown primarily in our work in Moscow and later in the work of GRAHAME, and if you get a similar set of curves, there is a definite relation between the capacity at a higher electrolyte concentration and at a lower electrolyte concentration, which was established by the work done in Moscow and by GRAHAME. Then you can be sure that the electrode really has a clean surface which can be used for any measurements. Of course, in many cases it becomes spoiled during the reaction. You cannot help it. You must simply renew it.

There are different methods. You can scrape the electrode as proposed by EYRING. This is a practically easily realized method. Some similar work was done by TOMASHOV in Moscow, but you must not forget that the scraped electrode in its behavior is markedly different from a smooth electrode. So you cannot identify the results obtained with the scraped electrode with the results obtained with a smooth electrode.

The best method, but which cannot be used in all cases, is to get a monocrystalline face just by splitting the monocrystal, but this method is limited to a number of metals. In the case of zinc, of course, you have a wonderful (0001) face which is a perfect face. It works absolutely well. It has a coefficient of flexuosity very close to unity, not perhaps 1 but 1.05 or something like that. The method is very good and very easily applied but only to a limited number of metals. You can split also the bismuth crystal. We have done some work on such faces. Probably they are quite good but this has not yet been investigated.

If you cannot obtain such a face by splitting, you can in many cases obtain it by chemical or electropolishing the surface and by reducing the oxide layer, but very carefully. There has been tendency in the electrochemical work to strongly polarize in the cathodic region assuming that a strong cathodic polarization is something very good to obtain a clean surface. This is wrong, because when you go over a certain limit you introduce foreign metal cations into the electrode, as it is shown by many data obtained by KABANOV in Moscow, and instead of oxide layer you get contamination by sodium atoms or something like that. To what extent? That depends on the material, we have no general rules presently.

But in many cases how can you control? You can control it just by taking again good differential capacity *vs.* potential curves at low supporting electrolyte concentration. Very extensive work in this direction has been done by the group of Dr. LEIKIS at the Institute of Electrochemistry. We have quite a program on the point of zero charge in our country. When she started studying silver, new or old data obtained in USA, in our country and elsewhere were all related to oxidized surfaces. So she started to polarize cathodically, but she soon saw that she got electrodes which were absolutely useless. Then she started to work out conditions at which you should remove the oxide layer. This must be done rather in acid solution even if you have to work afterwards in alkaline solutions. You should better remove the oxide layer in an acid solution, then substitute the acid one to an alkaline one under control of the cathodic potential and if you take differential capacity *vs.* potential curves, then you see that you have a good surface.

Of course, there are some definite cases where splendid surface have been obtained by Bulgarian electrochemists. They worked out a method of growing in a capillary a dislocation free metallic surface with a definite crystallographic index. At first it was a quartz capillary and now it is a teflon capillary. We had from them a cubic face and a octahedral face.

Somewhat later French people in the Laboratoire d'Electrolyse du C.N.R.S.

which is directed by Prof. BONNEMAY, miss Antoinette HAMELIN started also work on silver and now I am very glad I can tell you that they obtained also good results; not first results obtained with a monocrystalline face, first was the work which has been done by Bulgarian electrochemists with us. But they obtained for the first time data for the (110) face of a dodecahedron. Presently we have data for three different faces of silver monocrystals and for polycrystalline silver which are absolutely reproducible.

By this I mean you must find out a good method in each case. I must state that there are many cases of published modern work from people who have not realized this. I would give you now as an example a series of papers of HAMPSON and others published in England, I think in Middlesex. We had quite a polemic about cadmium. LEIKIS group published papers on the cadmium electrode, and HAMPSON's group wrote: We don't believe you can obtain such data with a cadmium electrode. Then I wrote a letter to Parsons and he apologized this was published in his absence. But when they published a paper, LEIKIS and others had to explain that you must work out your method, you cannot use the first method which you have read in the literature about electropolishing. Because if you electropolish using, for instance, cyanide solution, it is impossible to get rid of the cyanide groups from the metal surface. So there is an experimental work which must be done to find out a good method.

Now you see how to state which method is a good one. Well, we might say, the method is a good one which gives a point of zero charge which you like to obtain. No, that is not so, not the point of zero charge, but a series of differential capacity *vs.* potential curves which correspond to a reasonable structure of the electric double layer. The point of zero charge is afterwards some product of this work and it is not the criterion. The criterion is the dependence on the concentration which semi-quantitatively corresponds to the theory of the double layer. I said semi-quantitatively because in the theory enters a constant about which we are not sure. This is the dielectric constant of the liquid *e.g.* the water in the diffuse double layer. GRAHAME assumed that it has always the bulk value 81 at room temperature. Now we are not quite sure about it. It appears that it can deviate somewhat in this respect. But this is not very important, because at any rate the shape and relative position of these curves do not depend very much on the numerical value of this constant. So you can see always whether you got a good electrode. We can say HAMPSON didn't get a good electrode. Really if we would obtain such results elsewhere published for many metals, we would say we have not yet worked out the method to get a good electrode.

Well, let us quote another work, *e.g.* HACKERMAN's work on solid electrodes.

He was also one of the first to do the measurements on solid electrodes, however his results cannot be used. You see from the relative position of the curves those measurements were not correct. It is very easy to obtain with solid electrodes quite wrong data because of course a solid surface is very much easier to contaminate and it is difficult to get rid of contamination compared with a mercury drop. This is quite clear, but still it is possible to do this. But it requires some work.

Now, there is one case where it is very easy to obtain an absolutely reproducible solid electrode. That is when this electrode has a large surface. In that case it is quite easy to get it clean. So platinized platinum or other platinum group metals are quite easily obtained, at least in an absolutely reproducible form, if you use some standard method of depositing platinum black. This is important. The method must be a standard one. You can get an absolutely reproducible surface after you get forward and backward from anodic to cathodic potentials quite a plenty of times, and it changes only very slowly and you can check it from time to time. That is, I should say, as good as a mercury electrode, although it has quite different properties of course, but this is because it has a very large surface.

Now, what I think must be kept in mind in the work with solid electrodes is the purity of water. This is a difficult problem too. I think in most works the difficulty of removing organic impurities from water is very much underestimated. This is quite a problem because when you take up water and you add sodium-permanganate and distil it twice or three times, you don't get water free of organic contaminations. It can be shown that you must use more elaborate methods. Some have been proposed in Moscow and some by CONWAY. We have not yet compared both methods but I think they give identical results. I think CONWAY's method is a good one too, but we haven't used his method. At any rate you must control water and you must get rid of organic contaminations.

The simplest way to control is by measuring the polarographic maxima of the second kind. They are very sensitive to organic contaminations and the method is very easy to handle and doesn't require any special apparatus. This is described in the literature and for details you can look at the work of NIKOLAEVA-FEDOROVICH which was published in Soviet Electrochemistry.

So, of course, the requirement is becoming more and more strict. I mean it is becoming more difficult to work. Fourty years ago a very good electrochemical investigation was very easily done and now it requires much more work, but we can't help it."

Prof. A. FRUMKIN : ——

"I should like to draw your attention to one point. The validity of the slow discharge theory has been, well I should say at least in the case of mercury, finally demonstrated by photoelectroemission work. Because what remained not quite clear for the second step of the reaction when you have a slow discharge mechanism, was cleared by photoelectrical measurements.

So I think I would like to say, some Japanese electrochemists should not spend so much time in trying to show that the slow discharge theory cannot be applied to any electrode reaction. I think this is a hopeless attempt and we should better work together on the perfection of this theory."