Studies on the Polarographic Analysis. XII. New Differential Polarography with One Dropping Electrode (2)

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Introduction

In the previous paper,(1) the authors reported on the construction of the new differential polarograph and its application was discussed from the standpoint of qualitative analysis. Here, they discuss the differential technique from the standpoint of quantitative analysis and of electrode reactions there-of.

Results and Discussion

On the Relation between the Peak Current (i_h) of the Differential Method and the Diffusion Current (i_d) of the Ordinary Method.—As easily concluded from Eq. (4) shown in the previous paper,(1) the peak current should be proportional to the diffusion current, taking $\varDelta E$ small enough to get the ideal differential curve. And also it would be less than one half of the diffusion current even though $\varDelta E$ is taken as large enough to cover the whole increasing part of the ordinary wave.

However, in many cases it is observed that the peak current is several times the height of the ordinary diffusion current, proving the increase of the sensitivity. But in some cases, contrary to this, the diminishing of the sensitivity is observed. So the differential curve obtained by the authors' method is not always the resultant one of $E\sim i$ curve and $E-\varDelta E\sim -i'$ curve.

The authors studied to clear these phenomena from the standpoint of electrode reaction, using the analysing circuit shown in Fig. 1. In the circuit of 1-a, when the switch is rotated, the electrolytic current i corresponding to the

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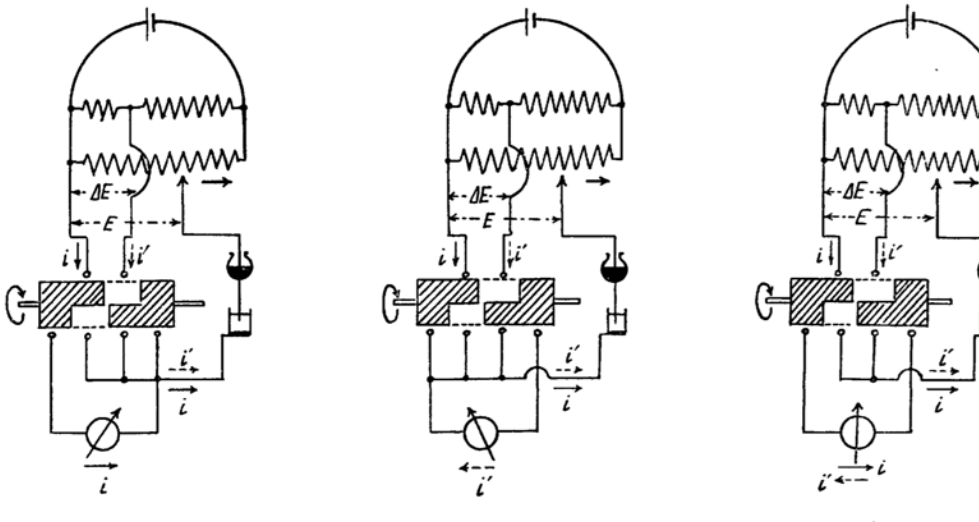
(1) M. Ishibashi and T. Fujinaga, This Bulletin, 25, 68 (1952).



Ia Ib I diff.

Fig. 1.—Scheme of the differential polarograph (1-diff.) and its analysing circuits (1-a and 1-b).

potential E flows through the galvanometer in the normal direction, while the current i' corresponding to the potential $E-\Delta E$ does not flow through it, but is short-circuited to the cell. We call the polarogram thus obtained by the rotation of the alternator in the circuit 1-a as $E\sim i$ rot. curve and to the contrary, in the circuit 1-b, the current i corresponding to E is short-circuited and i' corresponding to $E-\Delta E$ flows in the reverse direction through the galvanometer and we call this as $E-\Delta E\sim -i'$ rot. curve.

It is readily admitted that the differential polarogram obtained by the authors' method is the resultant curve of the $E\sim i$ rot. curve and $E-\Delta E\sim -i'$ rot. curve and that the experimental findings explain this point fairly well and are in good agreement with the considerations (see Fig. 2 and others). In addition, the scheme 1-a corresponds to the scheme 1-b in the experiment of Kalousek[(2)] and the scheme 1-b is a reversed circuit of the scheme 1-a in his experiment. Therefore, the authors' differential polarogram is explained to be the deduced curve of the two curves obtained by Kalousek's experiment.

(a) **A case when the electrode reaction is reversible and the dissociation rate of the reducible substances is fast.**—Cadmium and its ion can be oxidized or reduced reversibly at the dropping mercury electrode. The behavior of electrolytic dissolution and deposition of cadmium in potassium chloride solution is shown in Fig. 2. The curve 1 shows the ordinary polarogram i. e. the $E\sim i$ curve (taken with the switch stopped in 1-a or 1-

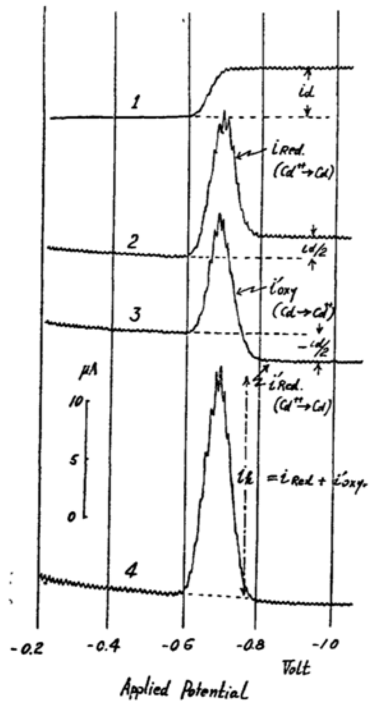


Fig. 2.—Polarograms of cadmium ion in potassium chloride: ΔE=50 millivolts, sensit.=1:200.

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(2) M. Kalousek, *Collection Czech. Chem. Communs.*, **13**, 105 (1948).

diff.), the curve 2 the $E\sim i$ rot. curve (the switch rotated in 1-a), the curve 3 the $E-\Delta E \sim -i'$ rot. curve (the switch rotated in 1-b) and the curve 4 the resultant differential curve *i.e.* $E\sim \Delta i/\Delta E$ curve (the switch rotated in 1-diff.). In these polarogram ΔE is 50 millivolts. Comparing the curve 1 with the curve 4, the diffusion current i_d is 4.1 microamperes in the ordinary polarogram while the peak current i_h is 18.3 microamperes in the differential one; in short, the sensitivity is increased by *ca.* 4.5 times. In the curve 2, the maximum is seen at the half-wave potential of the ordinary curve and the magnitude is about $2.7 \times i_d$ and in the part of the diffusion current, the current falls down to about $i_d/2$. And in the curve 3 analogous maximum is seen and the current falls down to *ca.* $-i_d/2$ in the same part. Considering the isochronism of the rotating switch, it is well recognized that the current of *ca.* $i_d/2$ flows in normal and reverse directions in the part of diffusion current. As for the maximum at the halfwave potential, it could be explained, as Kalousek did, to depend on the reversibility of the electrode reactions. However, as for the curve 3, the current flows in the reverse direction contrary to Kalousek's scheme 1-a by the change of the switch connection. More precisely, the current caused by the reduction of cadmium ions flows in normal direction at the potential E, but in the next instant when E-ΔE is applied the reduction of them takes place no longer, but the dissolution of cadmium begins from the cadmium amalgam yielded by the reduction at the potential E thus effecting the oxidation current, which flows through the galvanometer still in normal direction. At the next instant when the potential E is again applied, the cadmium ions dissolved out of the electrode are again reduced at the same time together with other diffused ions. As a result of these, the concentration of cadmium ion at the electrode surface becomes much larger than it is in the ordinary polarography and the concentration instead of the diffusion layer is brought at the mercury-solution interface. Therefore the concentration of cadmium amalgam at the electrode surface also becomes larger in the same manner. Thus in the circuit 1-a the large reduction current and in the circuit 1-b the large oxidation current are yielded respectively, but by the action of the switch both these currents flow always in normal direction through the galvanometer in spite of the opposite electrode reaction. As the result, as shown in curve 4 of Fig. 2, the prominent maximum is seen in the differential method. Now, when the applied potential is so increased as both the potential E and $E-\Delta E$ come into the part of diffusion current, the above mentioned reverse reaction no longer takes place and consequently the currents have each definite value, $i_d/2$ or $-i_d/2$. The differential curve 4 which is a resultant curve of these curves 2 and 3, therefore, indicates zero current in the stationary parts before and after the wave. Thus the peak current (i_h) is larger by several times than the diffusion current (i_d) of the ordinary polarogram.

From the view-point of quantitative analysis this magnification ratio i_h/i_d would be constant, since then, the peak current is proportional to the concentration. In practice, however, taking ΔE small enough the magnification ratio is particularly large in dilute solution and it diminishes as the concentration increases. Nevertheless, when ΔE is taken as large enough to cover the potential width of the ordinary wave, the ratio becomes constant independently of the concentration and so the peak current is directly proportional to the concentration (see Fig.3). This increase in sensitivity based upon the reversibility is observed as well with the following ions and substances; free ions of copper, zinc, lead etc. and alkali-metal ions and ammonium ion also and oxygen.

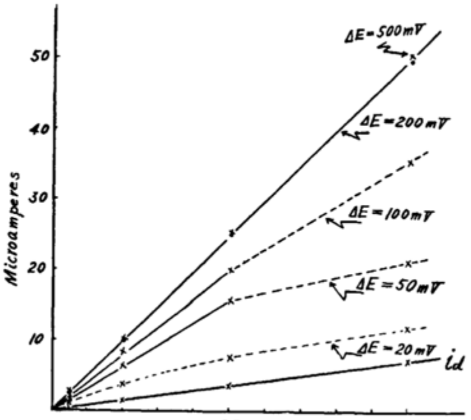

Fig. 3.—Relation between the peak current (i_h) and the diffusion current (i_d) of the cadmium ion in potassium chloride.

(b) **A case when the electrode reaction is irreversible and the dissociation rate of the reducible substance is fast.**—Zinc ion indicates an irreversible electrode reaction in ammoniacal solution. Fig. 4 as well as Fig. 2 shows the normal order, curve 1; $E\sim i$ curve, curve 2; $E\sim i$ rot. curve, curve 3; $E-\Delta E\sim -i'$

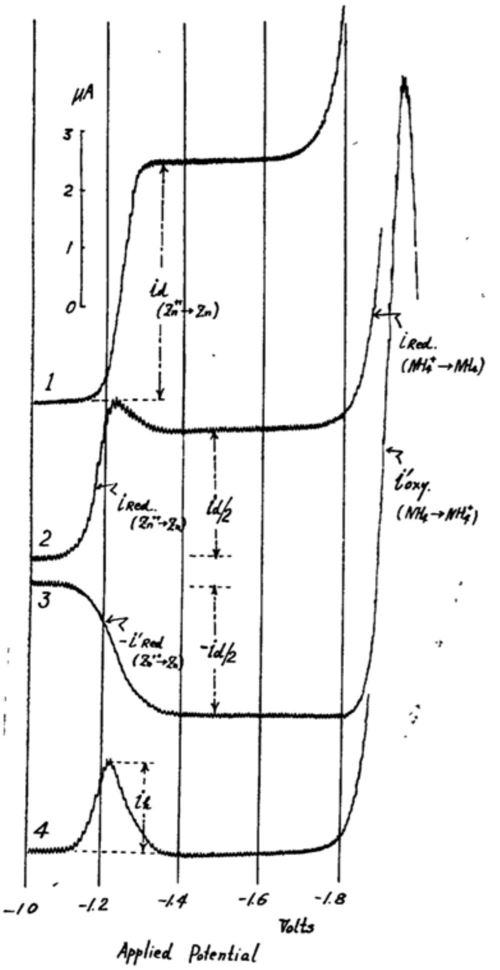

Fig. 4.—Polarograms of zinc ion in ammoniacal solution: ΔE=40 millivolts, sensit.=1:50.

rot. curve and curve 4; $E\sim\Delta i/\Delta E$ curve, which are all in regard to the same zinc ammine solution. The explanation about the case of such irreversible reaction is very easy and the differential curve in this case is in almost a perfect agreement with that in an ideal state. The electrode reaction is scarcely different from cases of ordinary polarography. It would be needless to discuss the curves 1 and 3. Though the curve 2 has likewise its maximum, this maximum is never beyond the height of diffusion current so long as ΔE is less than 300 millivolts. This maximum is explained as follows; the reduction takes place when the potential E is applied and the vacuum layer is formed on the electrode surface. In the next instant when the potential falls to $E-\Delta E$ its reduction still does not take place and also the oxidation does not happen due to the irreversible process. Therefore the vacuum layer is soon almost filled with zinc ions by the diffusion from the bulk of the solution at the potential $E-\Delta E$. In the next instant, when E is again applied, those zinc ions are together reduced at this time. Therefore the height of the peak in curve 2 is greater than

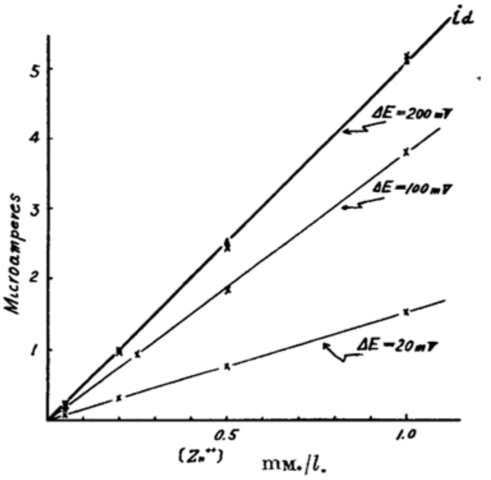

Fig. 5.—Relation between the peak current (i_h) and the diffusion current (i_d) of the zinc ion in ammoniacal solution.

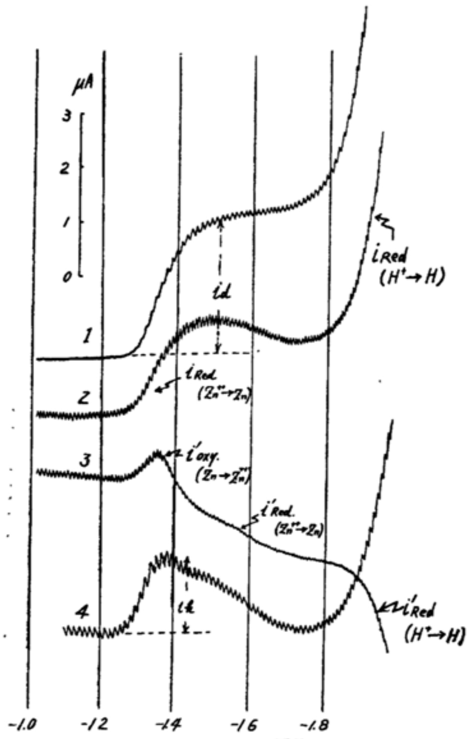

Fig. 6.—Polarograms of zinc ion in acidic tartrate solution: ΔE=100 millivolts, sensit.=1:50.

$i_d/2$ and less than i_d. Increasing the applied potential as high as the potential $E-\Delta E$ is sufficient to reduce zinc ion, the current drops to $i_d/2$ owing to the stop of supplying the ions at $E-\Delta E$. Thus the little peak appears in the curve 2 and also in the differential curve (curve 4), but differing from the case of reversible reaction, the peak current is always less than i_d. Viewed from the standpoint of quantitative analysis, such a case is the most ideal one in which the peak current is proportional to the concentration even though ΔE is small. The results obtained are shown in Fig. 5. Such irreversibility like that of zinc ammine should also be observed as to bismuth ion in tartrate solution, hydrion, many organic substances and hydrogen peroxide.(2)

(c) **A case when the dissociation rate is slow.**—In the ordinary polarogram, zinc in tartrate solution shows a wave of more gentle slope than the theoretically expected one. The differential polarogram shows only a little peak even when ΔE is taken so large. Judging from this fact, it is concluded that the rate of the dissociation of zinc ion from its tartrate complex is very slow compared with the electrodeposition of zinc from its simple ion. Fig. 6 shows from above to below, curve 1; $E\sim i$, curve 2; $E\sim i$ rot., curve 3; $E-\Delta E\sim -i'$ rot., and curve 4; $E\sim \Delta i/\Delta E$ curves. In the electrode reaction the over-voltage is required for the dissociation, and with the increase of the applied potential the dissociation is reasonably accelerated and the reduction current increases gradually to the extent of diffusion control. However, until the appearance of its influence, the potential interval is so wide that the peak becomes very low compared with the expected one. Concerning the little peak of the curve 3, it may be concluded that the electrode reaction has yet reversibility to some extent. The similar phenomena are expected in the following cases; the complex ions of nickel or cobalt and some organic substances which generate, for instance, the kinetic current. These cases are now under investigation.

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