On the Irreversible Reduction Wave of Titanic Ion at the Dropping Mercury Electrode(1)

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It has been shown by Strubl's work(2) that the titanic-titanous system gives a well-defined polarographic oxidation-reduction wave of the irreversible type in the medium of hydrochloric acid. In the previous paper(3) the equation for the polarographic oxidation-reduction wave of the irreversible type was derived from the view-point of chemical kinetics. Now, in order to obtain the experimental supports on the results obtained by the theoretical consideration, the polarographic behavior of titanic ion in the sulfuric acid solution was investigated. In this paper, the results on the cathodic wave due to the electroreduction of titanic ion will be discussed.

Experiments

Apparatus. — Both the "manually operating polarograph" and the "photo-recording polarograph with the Kalousek's circuits"(4) were used. Most of the accurate measurements, *e. g.*, the determination of the half-wave potential, were carried out with the former. The Kalousek's method was used to test the reversibility of the polarographic electrode reaction. A normal calomel electrode (N. C. E.), which is connected with the solution of the polarographic cell by 1 *N* KCl solution and 1 *N* KNO_3-agar-bridge, was used as a reference electrode. The atmospheric oxygen was removed from the solution with a stream of pure hydrogen gas obtained by the electrolysis of NaOH solution. The temperature of the polarographic cell was maintained at 25.0 ± 0.1° in a thermostat.

The capillary constant, $m^{2/3}t^{1/6}$, of the dropping mercury electrode in 0.065 *N*-H_2SO_4 free from the oxygen was 1.14 mg.$^{2/3}$ sec.$^{-1/2}$ without applied potential and 1.13 mg.$^{2/3}$ sec.$^{-1/2}$ at −1.0 volt *vs.* N. C. E.

The Preparation of Ti^{4+}-H_2SO_4 Solution. — A small quantity of purified TiO_2 was dissolved in conc. H_2SO_4 with strong heating, and then this solution was diluted with distilled water. The concentration of the titanic ion was determined gravimetrically.

Experimental Results

Table 1

Ti^{4+}-Concn., mol/l.	I_d, amp.	$V_{1/2}$, volt *vs.* N.C.E.	K_o, amp./mol/l.	α
1.0 $\times 10^{-3}$	2.04×10^{-6}	−0.828	2.1×10^{-6}	0.58～0.56
〃 〃	2.02× 〃	−0.827	〃 〃	0.57～0.56
0.5 × 〃	9.95×10^{-7}	−0.826	2.06× 〃	0.62
0.25 × 〃	5.07× 〃	−0.829	2.11× 〃	0.61
0.125× 〃	2.44× 〃	−0.820	2.03× 〃	0.67

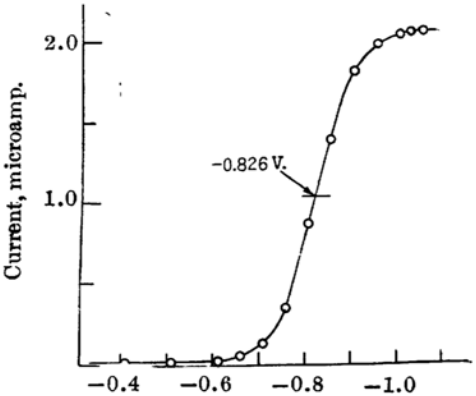

Fig. 1.—Reduction wave of Ti^{4+}-ion in 0.065 *N* H_2SO_4.

The Relation of Ti^{4+}-Concentration and Limiting-Current and that of Ti^{4+}-Concentration and Half-wave Potential. — The measurements were carried out with the solutions containing titanic ion from 0.05 × 10^{-3} to 1.0 × 10^{-3} *M* in concentration. Some of the results are shown in Table 1 and one of the polarographic waves obtained is shown in Fig. 1. The supporting electrolyte contained sulfuric acid of the same concentration as contained in the standard solution of titanic ion, so that the concentration of sulfuric acid in the measured solution was the same with changing the concentration of titanic ion. The experimental results indicated that the limiting

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(1) Presented at the 3rd annual meeting of the Chemical Society of Japan in April, 1950.

(2) R. Strubl, *Collection Czechoslovak Chemical Communications*, **10**, 475 (1938).

(3) R. Tamamushi and N. Tanaka, This Bulletin, **22**, 227 (1949).

(4) M. Kalousek, *Collection Czechoslovak Chemical Communications*, **13**. 105 (1948).

current (I_d) is proportional to the concentration of titanic ion, which is in agreement with the results obtained by Strubl.(2)

As for the half-wave potential of the Ti-wave, Strubl stated that the oxidation wave has the definite half-wave potential of − 0.18 volt *vs.* N. C. E. while the half-wave potential of the reduction wave appeared at the potential of about − 0.98 volt is not definite.(2) However, the present experiment showed that the polarograms obtained in 0.065 *N* sulfuric acid give the definite half-wave potential of −0.825 ±0.005 volt *vs.* N. C. E. (at 25.0°), which is independent of the concentration of titanic ion as shown in Table 1.

The Effect of the Concentration of the Foreign Electrolyte on the Half-wave Potential. — The half-wave potential was measured with the solutions containing sulfuric acid in concentration from 0.026 to 0.452 *M* for the purpose of finding out the relation between the half-wave potential and the concentration of the electrolyte (Fig. 2). In this measurement, titanic ion was kept at the same concentration. The results showed that the half-wave potential shifts to more negative value with the increase in concentration of sulfuric acid. The same results were obtained by changing the concentration either of hydrochloric acid, ammonium sulfate, potassium nitrate, magnesium nitrate or aluminum nitrate (Fig. 3). Furthermore, it is to be mentioned here that Ti^{4+}-H_2SO_4 solution gave the quite different polarographic wave when the concentration of sulfuric acid became to be more than about 1 *N*.

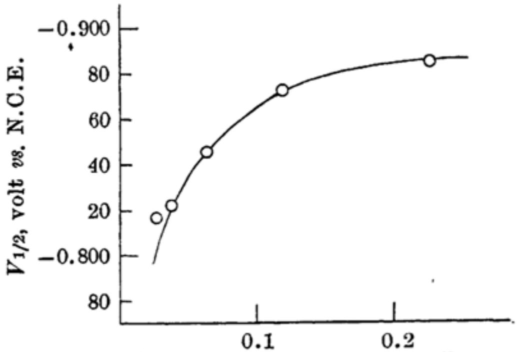

Fig. 2.—The effect of the concentration of sulfuric acid on the half-wave potential of Ti^{4+}-reduction wave.

Relation of log $I/(I_d - I)$ and V. — A plot of the potential V against log $I/(I_d - I)$ gave a straight line as shown in Fig. 4, which means that the reduction wave of titanic ion in 0.065 *N* sulfuric acid has a center of symmetry at the half-wave potential.

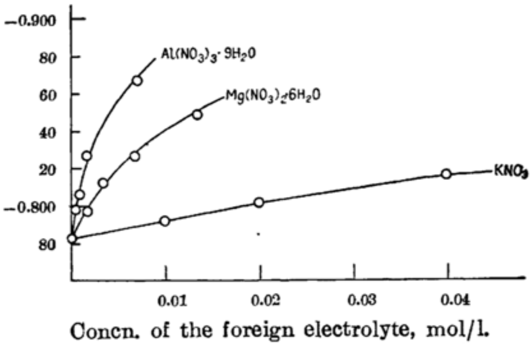

Fig. 3.—The effect of the concentration of the foreign electrolytes on the half-wave potential of Ti^{4+}-reduction wave. The salts mentioned in this figure was added to the Ti^{4+}-solution which contains 0.019 *M* H_2SO_4.

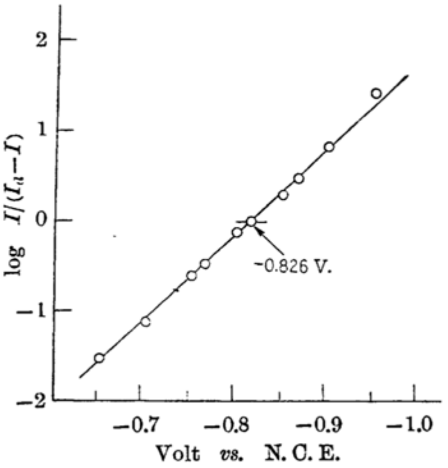

Fig. 4.—Relation between log $I/(I_d-I)$ and V.

The Test of Reversibility of the Electrode Process with the Kalousek's Method. — The results obtained with the Kalousek's method are shown in Figs. 5 and 6. The experimental results on the wave of Pb^{2+} ion in KOH solution are also shown in these figures as a typical example of the application of this method to a reversible wave. It can be seen from Fig. 5b that no oxidation current flows when the Kalousek's method I-a is applied to the reduction wave of titanic ion. Moreover, it was found by the Kalousek's method II that the anodic wave of the reduction product of titanic ion is obtained at the more positive potential than that of the cathodic wave of titanic ion. This means that, when the sufficient positive potential is given to the electrode, the reduction product of titanic ion

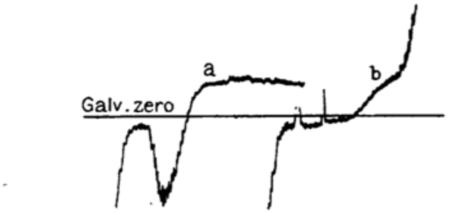

Fig. 5.—Polarograms obtained by Kalousek's method I-a: a, curve due to Pb^{2+} in KOH solution, difference 300 millivolts; b, curve due to Ti^{4+} in *ca.* 0.07 N H_2SO_4, difference 100 millivolts.

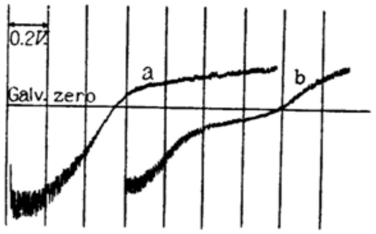

Fig. 6.—Polarograms obtained by Kalousek's method II: a, curve due to Pb^{2+} in KOH solution; b, curve due to Ti^{4+} in *ca.* 0.07 N H_2SO_4.

can be oxidized at the dropping mercury electrode. This is in agreement with the fact that titanous ion can be oxidized at the dropping mercury electrode, and it gives the separated anodic wave from the cathodic wave of titanic ion.⁽²⁾

Discussion

Since, according to R. Strubl, the number of electrons concerning the reduction of titanic ion is one,⁽²⁾ it will be assumed that the reduction of titanic ion proceeds as shown in the following;

$$Ti^{4+} + \varepsilon \rightleftharpoons Ti^{3+} \qquad (1)$$

From the results of the Kalousek's method, it can be said that the polarographic electrode process of titanic ion proceeds irreversibly and that at the potential region of the reduction wave the velocity of the oxidation process is vanishingly small. Then, it is quite certain that the reduction wave of titanic ion is one of the irreversible type, and it may be considered that the activation process involving the transfer of an electron at the electrode surface is the rate-determining step of the over-all process. According to the theoretical treatment described in the previous paper⁽³⁾ the formulae of the current-voltage curve of the reduction wave in the activation-controlled case can be represented as follows:

$$V = \text{const.} - \frac{RT}{n\alpha F}\ln\frac{I}{I_d - I} + \frac{RT}{n\alpha F}\ln f_o \quad (2)$$

$$I_d = nFK'_o[A_o]^\circ = nFK_o[C_o]^\circ \qquad (3)$$

where I_d represents the limiting current of the reduction wave, F, the Faraday constant, n, the number of electrons which participate in the reaction, f_o, the activity coefficient of the oxidized ion, and K_o and K'_o are the constants concerning to the diffusion process, and $[C_o]^\circ$ and $[A_o]^\circ$, the concentration and the activity of the oxidized ion in the body of the solution, respectively. The term α is the portion of the electrode potential which promotes the reduction process, and it takes the value between 0 and 1.

If Eqs. (2) and (3) can be applied to the reduction wave of titanic ion, the half-wave potential will be independent of the activity or concentration of titanic ion, so far as the activity coefficient of the titanic ion remains constant, and the linearity of the relation between log $I/(I_d - I)$ and V will be satisfied on the polarographic waves obtained experimentally. The experimental results indicated in Table 1 and Fig. 4 show clearly that they are in accord with the theoretical considerations. Consequently, it can be concluded that the reduction wave of titanic ion in the medium of sulfuric acid (less than about 1 N) is one of the activation-controlled type and the formulae of its polarographic wave are represented by Eqs. (2) and (3).

It must be mentioned here that the half-wave potential of the reduction wave of titanic ion varied with the change of the foreign electrolyte in the solution. It was experimentally found that the effect of the concentration of the electrolyte on the half-wave potential became larger when the valency of the cation of the foreign electrolyte increased. A similar result on the deposition potential of the hydrogen ion was reported by Herasymenko and Šlendyk,⁽⁵⁾ and it was explained by them by considering the adsorption of the ion. A. Frumkin⁽⁶⁾ developed his theory on the hydrogen overvoltage, and he interpreted reasonably the effect of the foreign electrolyte by introducing the conception of ζ-potential of Stern.⁽⁷⁾ In the present case, the shift of the half-wave potential of the reduction wave of titanic ion is expected to occur when either one or all of

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(5) P. Herasymenko and I. Šlendyk, *Z. physik. Chem.*, **A 149**, 123 (1930).

(6) A. Frumkin, *ibid.*, **A 164**, 121 (1933).

(7) O. Stern, *Z. Elektrochem.*, **30**, 510 (1924).

the following conditions is fulfilled, namely: (1) when the state of titanic ion in the solution changes with the change of electrolytes; (2) when the activity coefficient of the titanic ion changes with the change of the ionic strength of the solution; and (3) when ζ-potential of the surface of the dropping mercury electrode changes with the change of the electrolytes and the value of the half-wave potential is affected by ζ-potential. The experimental results are, though qualitatively, in accord with the change of half-wave potential which is calculated on the assumption that the activity coefficient of titanic ion changes with the change of ionic strength of the solution. It is highly probable that the property of the double layer at the dropping mercury electrode and the value of ζ-potential will play an important role on the value of the half-wave potential. However, from the present study no conclusion can be driven out on the reason of the shift of the half-wave potential due to the change of the concentration of the foreign electrolytes.

Summary

The reduction wave of titanic ion in sulfuric acid medium was investigated in order to give some experimental supports to the theoretical results on the irreversible wave which were derived from the standpoint of chemical kinetics. The Kalousek's method was used to test the reversibility of the reduction process of titanic ion at the dropping mercury electrode, and it was found that this process proceeds irreversibly. From the constancy of the half-wave potential, which is independent of the concentration of titanic ion, and from the linear relation between log $I/(I_d - I)$ and V, which were proved by the experiments, it can be said that the theoretical equation (2) explains the feature of the irreversible reduction wave such as that of titanic ion. Furthermore, the effect of the foreign electrolytes on the half-wave potential was measured, on which some discussions were carried out.

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