Polarization During the Electrolytic Reduction of Titanium Ions

By *O. Essin* [1]

I. Introduction

In a number of cases the process of the electrolytic reduction or oxidation of ions seems to involve the direct transfer of an electron from the electrode to the adsorbed ion, or the reverse. Therefore, an experimental study of the relation between the polarization η and the current density i in these processes may furnish data for checking the characteristic peculiarities of the electronic version of the slow discharge theory.

In a previous paper [2] it was shown that the relation between η and i during the electrolytic reduction or oxidation of tin ions is described by the following equation:

$$\pm i = k_1 [\mathrm{Sn}^{\cdots\cdot}] \left(1 \pm \frac{i}{i_\pi}\right) \exp. \left\{\frac{-\eta 2F}{\gamma_h RT}\right\} - k_2 [\mathrm{Sn}^{\cdot\cdot}] \exp. \left\{\frac{\eta 2F}{\gamma_n RT}\right\}. \quad (1)$$

On the basis of the considerations from which this equation may be derived, as well as from analysis of other possible explanations, it was concluded that the polarization which is here observed is the result of slow discharge complicated by the inadequate rate of dissociation of complex quadrivalent tin ions and retarded diffusion of its "simple" cations.

[1] Most of the experimental work described in this paper was carried out in collaboration with laboratory assistant K. N. Rusanova, and the preliminary experiments, with the students L. P. Khodak and E. A. Solovjev.

[2] O. Essin and M. Loschkarew, J. Phys. Chem. (Russ.), **13**, 794 (1939); Acta Physicochimica URSS, **10**, 513 (1939).

Although these measurements confirmed the fact that in the particular case of tin the slow discharge actually does take place in the processes of the electrolytic reduction of ions nevertheless, owing to the complications pointed out above (the extremely small value of the saturation current density, i_π, for retarded dissociation and diffusion), they did not allow verification of one of the most interesting conclusions[3] which follows from the electron transfer theory — namely, the existence of i_π for slow discharge at any value of the coefficient γ. It is possible that this was brought about by too great a difference in the values of the charges of the Sn^{++++}- and Sn^{++}-ions, which led to a considerable difference between the ground vacant and ground occupied electronic energy levels in the adsorbed ions.

Proceeding from such a hypothesis we thought it expedient to study the relation between η and i for pairs of ions that do not differ so sharply in the values of their charges. Under certain conditions (when the minima of the potential energy curves of the adsorbed ions correspond to points approximately equidistant from the metallic surface), it may be expected here that, even for comparatively small values of η, the slow discharge equation will assume a form similar to that of the expression for concentration polarization[3].

As Diethelm and Foerster[4] have shown, the cathodic reduction of solutions of sulphate salts of quadrivalent titanium is accompanied by polarization which depends very strongly upon the material of the electrode (a small value of η for platinized Pt and a considerable value for Pb and Cu), and, in certain cases, upon its history and the time (for example, for Pt, formation of a cathode film).

Inasmuch as the relative change in the value of the charge on transition of Ti^{++++} to Ti^{+++} is less than in the case of the electrolytic reduction of tin ions, and since Diethelm and Foerster's data permit us to assume that here there takes place chemical polarization, we thought it would be of interest to clear up the character of the relation between η and i in this case, adopting measures to eliminate the difficulties arising from the formation of a film on the electrode.

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[3] O. Essin, J. Phys. Chem. (Russ.), **14**, 717 (1940); Acta Physicochimica URSS, **13**, 123 (1940).

[4] B. Diethelm u. F. Foerster, Z. physik. Chem., **62**, 129 (1908).

II. Experimental procedure

To obviate these difficulties, a mercury jet was employed as electrode. The fact that the value of the equilibrium potential of the electrolytic reduction of titanium ions is close to that of the normal hydrogen electrode prevented the interaction of the metallic mercury with the electrolyte. The apparatus and procedure employed were essentially the same as those described in the preceding papers[5]. A correction for the ohmic voltage drop between the end of the siphon-tube and the mercury jet was introduced on the basis of special measurements (in the given electrolyser) of the relation between η and i for the discharge of $Na^{\cdot}$ from 1 N NaOH, and a comparison of the specific electrical conductivities of the latter and a corresponding solution of titanium ions. The working volume of the electrolyser amounted to about 100 cm.^{3}. The measurements were carried out at 25° C in electrolytes which contained different amounts of $Ti^{\cdot\cdot\cdot\cdot}$- and $Ti^{\cdot\cdot\cdot}$- ions. The desired ratio of concentrations of the two ions was attained by preliminary cathodic reduction of the initial solution of quadrivalent titanium. To avoid interaction between oxygen of the air and the electrolyte the latter was covered in all experiments with a layer of toluene. As control experiments showed, the presence of this layer does not strongly affect the magnitude of η, but makes the course of the curves smoother, especially at large values of i.

III. Discussion of results

1. Branches of the cathodic curve. The graph in Fig. 1, in which lg i is plotted against η, represents the variation in the cathodic k and anodic a polarization with the current density (experiment 1). On comparing these curves, whose course is also characteristic for the other experiments with comparatively small concentrations of $Ti^{\cdot\cdot\cdot\cdot}$, one is struck by the following peculiarity. Whereas with an increase in anodic polarization lg i increases steadily, beginning from small currents and slowing down only as the current approaches

[5] See, for example, O. Essin, M. Loschkarew and K. Sofiysky, J. Phys. Chem. (Russ.), **10**, 132 (1937); Acta Physicochimica URSS, **7**, 433 (1937).

its saturation value $i_{\pi a}$, with an increase in cathodic polarization lg i changes at first extremely slowly, and only starting from values of η close to 0.3—0.4 V. does the curve begin to resemble the anodic one. A similar picture was observed by Diethelm and Foerster

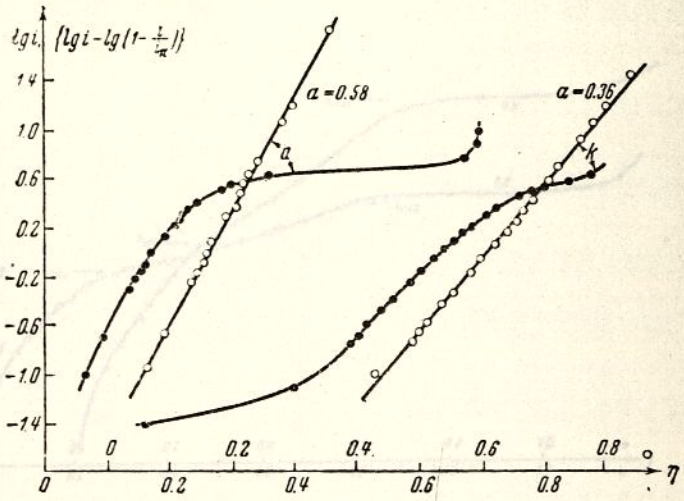

Fig. 1. Cathodic and anodic polarization for a solution with a comparatively small concentration of quadrivalent titanium.

(Fig. 7 in their paper) for copper and lead cathodes. Here a sharp increase in i also begins at a potential approximately 0.3—0.4 V. more negative than the equilibrium value. This led us to the conclusion th the cathodic curve has still another branch in the region of sm currents. And indeed this branch can be clearly seen in Fig. 2, whe the results of measurements with electrolytes containing large concen trations of $Ti^{\cdots\cdot}$ (experiments 2 and 4) are plotted.

Since the normal potential for $Ti^{\cdots\cdot} \rightleftarrows Ti^{\cdots}$ is equal to —0.04 V., while for $Ti^{\cdots} \rightleftarrows Ti^{\cdot\cdot}$ it amounts[6] to — 0.37 V., it is quite natural to assume that the first branch of the curve represents the reduction of quadrivalent titanium to the tervalent form, while the second branch,

[6] G. Forbers and T. Hall, J. Am. Chem. Soc., **46**, 385 (1924).

the reduction of the latter to the bivalent form. The following confirms the correctness of such an assumption:

With an increase in the concentration of Ti^{++++}, the saturation current density of the first branch $i_{\pi kI}$ also increases. Moreover, start-

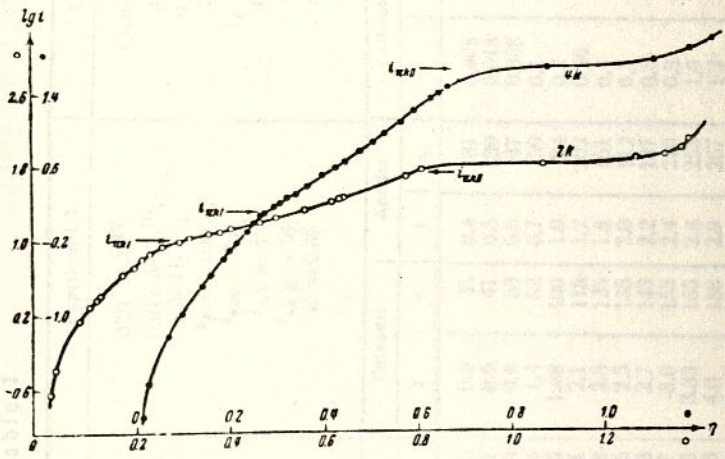

Fig. 2. The branches of the cathodic curve (experiments 2 and 4).

ing from a certain concentration of Ti^{++++}, the saturation current density becomes so large that the transition from one branch to the other loses its distinctness (see Fig. 2 and Table 1). Further, the saturation current density of the second branch $i_{\pi kII}$ after which noticeable evolution of hydrogen sets in, agrees in magnitude with $i_{\pi a}$ in all cases when the first branch lies in the region of small i, as, for example, in experiment 1, $i_{\pi kII} = 4.3$ mA, $i_{\pi a} = 4.6$ mA. In other words both of them are determined by the concentration of Ti^{+++}-ions. The Ti^{++}-ions, the formation of which is indicated by the second branch, interact in the electrolyte with Ti^{++++} giving Ti^{+++} again. The fact that at large concentrations of Ti^{++++} (and, consequently, at large values of $i_{\pi kI}$ also) $i_{\pi kII} > i_{\pi a}$, is explained by the appreciable amount of Ti^{+++}-ions which are continuously formed in this case in the region described by the first branch of the curve and markedly increase the content of Ti^{+++} in the

Table 1

Experiment 1	Experiment 2	Experiment 3	Experiment 4
0.08 M Ti^{IV}; 0.019 M Ti^{III}; 2 N H_2SO_4; $\varepsilon_p = 0.01$ V; $i_{\pi k\,II} = 4.3$; $i_{\pi A} = 4.6$; $i_{\pi kI} = 0.05$; $R = 0.36$	0.27 M Ti^{IV}; 0.015 M Ti^{III} 2 N H_2SO_4; $\varepsilon_p = 0.09$ V; $i_{\pi kI} = 10$; $i_{\pi A} = 2.8$; $i_{\pi kII} = 63$; $R = 3.6$	0.21 M Ti^{IV}; 0.017 M Ti^{III}; 2 N H_2SO_4; $\varepsilon_p = 0.095$ V; $i_{\pi kI} = 7.5$; $i_{\pi A} = 3.4$; $i_{\pi k\,II} = 56$; $R = 0.36$	Changed apparatus 0.17 M Ti^{IV}; 0.03 M Ti^{III}; 2 N H_2SO_4; $\varepsilon_p = -0.003$ V; $i_{\pi kI} = 1.4$; $i_{\pi A} = 6.5$; $i_{\pi kII} = 50$; $R = 0.38$

Cathodic		Anodic		Cathodic		Anodic		Cathodic		Anodic		Cathodic		Anodic	
i mA	η mV	i	η	i	η	i	η	i	η	i	η	i	η	i	η
0.04	162	0.1	63	0.22	16	0.2	15	0.5	35	0.4	31	0.008	10	0.1	146
0.08	402	0.2	95	0.4	29	0.4	31	0.6	41	0.5	39	0.018	25	0.2	192
0.1	431	0.5	138	1.4	79	0.7	55	0.8	53	0.6	47	0.058	70	0.4	231
0.18	494	0.6	146	1.9	102	0.8	64	1.4	83	0.7	59	0.1	96	0.6	260
0.22	504	0.7	155	2.3	115	0.9	75	1.68	100	1.0	84	0.2	141	1.1	298
0.26	516	0.8	158	2.6	126	1.1	91	2.1	118	1.2	102	0.26	157	1.2	312
0.34	540	1.0	169	4.29	173	1.3	108	2.3	125	1.8	151	0.4	186	1.4	319
0.42	561	1.4	195	4.96	188	1.6	135	2.5	135	2.0	172	0.5	198	2.0	338
0.60	589	1.7	207	6.29	214	1.7	143	2.7	143	2.2	187	0.6	212	2.6	375
0.74	606	1.9	216	7.33	230	2.0	177	3.0	153	2.4	210	0.8	239	3.0	390
0.94	629	2.1	222	8.66	256	2.1	186	3.33	163	2.8	253	1.0	251	4.33	441
1.1	644	2.3	227	10.0	293	2.2	196	4.0	188	2.9	267	1.2	264	6.0	519
1.3	661	2.6	245	11.0	313	2.8	269	5.33	221	3.0	285	1.3	273	6.6	546
1.5	672	3.33	285	12.0	353	2.9	287	7.33	278	4.33	559	1.5	292	7.3	577
1.7	690	3.62	302	13.0	376	3.0	299	8.0	307	4.66	576	1.7	306	8.0	701

Cathodic		Anodic		Cathodic		Anodic		Cathodic		Anodic		Cathodic		Anodic	
i mA	η_i mV	i	η_i	i	η_i	i	η_i	i	η_i	i	η_i	i	η_i	i	η_i
2.1	713	4.33	363	14.0	401	3.3	366	9.33	352	5.33	588	1.9	322	9.3	715
2.4	728	4.62	413	16.0	465	3.63	480	11.0	415	6.0	595	2.1	339	10	722
3.0	764	6.0	677	18.0	497	3.96	526	13.0	455			2.6	364		
3.33	785	8.0	692	22.0	561	5.28	563	16.0	505			3.33	395		
3.66	804	10.0	701	27.0	616			20	545			4.0	423		
4.0	845			29	632			26	608			4.66	445		
4.62	882			30	642			30	641			6.0	478		
				50	778			50	763			7.7	503		
				60	808			60	846			9.7	529		
				70	1068			80	1178			13.0	563		
				80	1265							17.0	592		
				90	1329							23	627		
				100	1366							26	644		
				110	1380							30	666		
												50	875		
												60	1106		
												80	1179		
												100	1230		

electrolyte. Finally, if it is assumed that the normal potential for $Ti^{\cdots} \rightleftarrows Ti$ is approximately equal to —0.2 V., as follows from Botts and Krauskopf's data[7], recalculation according to Luther's rule gives a value of the normal potential for $Ti^{\cdots\cdot} \rightleftarrows Ti^{\cdot\cdot}$ equal to —0.2 V., and a value for $Ti^{\cdots\cdot} \rightleftarrows Ti$ equal to — 0.16 V. Comparison of these values of the potential shows that, of all the possible cathode processes (including even $Ti^{\cdot\cdot} \rightleftarrows Ti$, for which calculation gives $\varepsilon_0 = -0.12$ V.), the reduction of quadrivalent titanium to the tervalent form should take place first. Beginning, however, from a value of η equal, approximately, to — 0.2 V., the processes of the deposition of titanium from $Ti^{\cdots}$ and $Ti^{\cdots\cdot}$ and the formation of $Ti^{\cdot\cdot}$ from the latter also set in.

In our experiments, however, most of the experimental points on the first branch of the curve lay below $\eta = -0.2$ V., while a further increase in i rapidly led to the saturation current density and to $\eta = -0.4$ V. Furthermore, inasmuch as we did not succeed in detecting noticeable amounts of Ti in the washed cathodic mercury, and the formation of $Ti^{\cdot\cdot}$ from $Ti^{\cdots\cdot}$ changes the concentration of $Ti^{\cdots\cdot}$ just as the process $Ti^{\cdots\cdot} + \ominus \rightarrow Ti^{\cdots}$ does (as a result of the reaction between $Ti^{\cdots\cdot}$ and $Ti^{\cdot\cdot}$ in the electrolyte), it may be assumed, with a certain degree of approximation, that the remaining points of the first branch, or, in any case, the values of $i_{\pi k}$, are also sufficiently close to the values corresponding to the process of the transition of $Ti^{\cdots\cdot}$ to $Ti^{\cdots}$.

2. The relation between the overvoltage and the current density. Recalculations of the experimental data showed that the ralation between η and i is satisfactorily described by the following equations:

$$\eta_k = a - b \lg i + b \lg \left[\left(1 - \frac{i}{i_{\pi k}}\right) - \left(1 + \frac{i}{i_{\pi a}}\right) \times 10^{\eta_k / 0.06} \right], \qquad (2)$$

for cathodic polarization, and

$$\eta_a = a + b \lg i - b \lg \left[\left(1 - \frac{i}{i_{\pi a}}\right) - \left(1 + \frac{i}{i_{\pi k}}\right) \times 10^{-\eta_a / 0.06} \right] \qquad (3)$$

for anodic polarization. The results of a graphical analysis of these relations for the first branches of the cathodic and anodic curves of experiments 2, 3 and 4 are given in Fig. 3. As can be seen, when

[7] E. Botts and Krauskopf, J. Phys. Chem., **31**, 1404 (1927).

the experimental points are plotted using the co-ordinates η and φ, where

$$\varphi_{k,a} = \pm \lg i \pm \lg \left[\left(1 - \frac{i}{i_{\pi k,a}}\right) - \left(1 + \frac{i}{i_{\pi a,k}}\right) \times 10^{\pm \eta_{k,a}/0.06}\right],$$

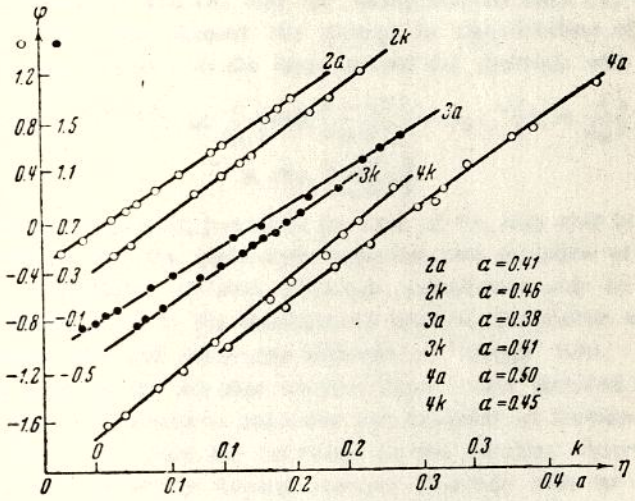

Fig. 3. Illustrating the applicability of equation (4).

straight lines are obtained in accordance with the form of equations (2) and (3). Putting

$$b = \frac{\gamma RT}{0.4343F}$$

we find from the slopes of the straight lines that the values for $\frac{1}{\gamma_{kI}}$ and $\frac{1}{\gamma_a}$ fluctuate within the interval 0.4—0.5. The second branch of the cathodic curve is also described by equation (2), as can be seen from the straight line k in Fig. 1. This was also confirmed by a number of other experiments with electrolytes containing small but different concentrations of $Ti^{\cdot\cdot\cdot\cdot}$ and $Ti^{\cdot\cdot\cdot}$. Since in our experiments the value of $i_{\pi a}$ for the process $Ti^{\cdot\cdot} - \ominus \rightarrow Ti^{\cdot\cdot\cdot}$ was not determined, a graphical check of equation (2) for this branch (the second cathodic branch) was made using the co-ordinates:

$$\gamma_k \Big/ \left[\lg (i - i_{\pi kI}) - \lg \left(1 - \frac{i - i_{\pi kI}}{i_{\pi kII} - i_{\pi kI}}\right)\right].$$

This is quite permissible since, starting with sufficiently negative values of η_{kII}, the term containing $i_{\pi a}$ may be neglected. In all the cases which we investigated the slopes of these straight lines gave values for $\frac{1}{\gamma_{kII}}$ close to 0.4.

Equations (2) and (3) may be easily derived from (1) if in the latter we take into account the change in concentration of the ion with a lower valency in the layer around the electrode with *i*, *i. e.*,

$$\pm i = k_1 c_h^0 \left(1 \mp \frac{i}{i_{\pi k}}\right) \exp. \left\{\frac{-\eta F}{\gamma_h RT}\right\} - k_2 c_n^0 \left(1 \pm \frac{i}{i_{\pi a}}\right) \times \times \exp. \left\{\frac{\eta F}{\gamma_n RT}\right\}. \quad (4)$$

The latter equation, just as in the case of tin, may also be derived if we assume that the electrolytic reduction and oxidation of titanium ions is accompanied by slow discharge, complicated only by a small rate of diffusion, or by the simultaneous retarded dissociation of complex titanium ions and inadequate diffusion of "simple" ions.

To clear up the question whether there occurs retarded dissociation during the electrolytic reduction and oxidation of titanium ions, it is expedient to compare the saturation current densities observed here with those found with a flowing mercury electrode, both for the processes accompanied only by concentration polarization (discharge of $Sn^{\cdot\cdot}$ to Sn in sulphate solutions), and for those involving sharply expressed retarded dissociation (the cathodic process of the reduction of tin ions). During the discharge of $Sn^{\cdot\cdot}$ to Sn the saturation current density for a 0.25 molal $SnSO_4$, 0.7 *N* H_2SO_4 solution is equal to 400—500 mA[8]; on addition of glue, it is equal to 80—100 mA. For the cathodic process of the reduction of tin ions from a saturated solution of $SnCl_4$ (about 1.5 molal), on the other hand, the saturation current density amounts to 1.1 mA[2]. Comparing these values with the values of $i_{\pi k\,I}$ and $i_{\pi a}$ (see Table 2), and assuming that the working surface of the mercury jet was approximately the same in all the experiments, we see that the value of the saturation current density for the reduction and oxidation of titanium ions lies somewhere between the values for these two extreme cases. Besides, the values of $i_{\pi a}$ are closer to those obtained

[8] According to the experimental data obtained by V. Sotnikova in our laboratory while working on her thesis. See also M. Loschkarew, O. Essin and V. Sotnikova, J. Gen. Chem. (Russ.), **9**, 1412 (1939).

Table 2

	Composition of electrolyte	i_π (in mA)			
		Experimental data		Recalculated for 0.25 molal solution	
		Cathodic	Anodic	Cathodic	Anodic
1.	0.25 molal $SnSO_4$, 0.7 N H_2SO_4 (a) without glue	400—500	—	400—500	—
	(b) with glue	80—100	—	80—100	—
2.	0.27 molal $Ti^{\cdots\cdot}$ 0.015 molal $Ti^{\cdots}$ 2 N H_2SO_4	10	2.8	9.3	48
3.	0.21 molal $Ti^{\cdots\cdot}$ 0.017 molal $Ti^{\cdots}$ 2 N H_2SO_4	7.5	3.4	9.0	50
4.	0.17 molal $Ti^{\cdots\cdot}$ 0.03 molal $Ti^{\cdots}$ 2 N H_2SO_4	1.4	6.5	2.1	52
5.	0.08 molal $Ti^{\cdots\cdot}$ 0.019 molal $Ti^{\cdots}$ 2 N H_2SO_4	0.05	4.6	0.15	59
6.	1.5 molal $SnCl_4$ 0.1 N $SnCl_2$ acidified	1.1	—	0.2	—

in the case of pure concentration polarization than the values of $i_{\pi k l}$; the latter, however, are still remote from the value of i_π for clearly pronounced retarded dissociation.

From the above considerations it may be assumed that a sufficiently stable complex ion of quadrivalent titanium is formed in a sulphuric acid solution; it is less stable, however, than the anion of quadrivalent tin. The fact that $i_{\pi k l}$ falls sharply with a decrease in the $Ti^{\cdots\cdot}$-ion content in solutions containing the same amount of hydrogen ions (see Table 2) as well as (as special experiments showed) with an increase (up to 4 N) in the H_2SO_4 concentration in solutions containing the same amount of $Ti^{\cdots\cdot}$-ions, is a further confirmation of the presence of such a complex ion in the solution [9]. As regards the complex ion of

tervalent titanium, the data given above are insufficient to allow us to speak of its existence with certainty. At any rate it must be less stable [9].

Thus, in summing up, we may state that the electrolytic reduction and oxidation of titanium ions in sulphuric acid solutions is accompanied by slow discharge, complicated, apparently, by an inadequate rate of dissociation of the complex ion and by a low rate of diffusion of the "simple" ions. In this case, however, the rôle played by retarded dissociation is smaller than in the case of the reduction of charge of tin ions in chloride solutions. Here the cathodic saturation current density is larger and, consequently, there are some chances for determining the value of i_{π} for slow discharge.

3. The electrolytic saturation current. The experimental data obtained may also be interpreted in a different way. From the electron transition theory it follows [3] that, starting from a certain value of the overvoltage, the usual equation for slow discharge reduces to an expression which is identical in form with the formula for concentration polarization. The term representing the limiting current density which enters into this expression may be called, just as the similar term in thermoionic emission, the electrolytic saturation current i_{π}. The fact that the experimental results are satisfactorily described by equation (4) may be explained from this point of view as follows. At values of the current density remote from i_{π}, the overvoltage obeys the usual form of the equation for slow discharge:

$$\eta = a - b \lg i.$$

The fact that the quantity $\lg\left(1 - \frac{i}{i_{\pi}}\right)$ is absent in the equation does not contradict the experimental data, since at such values of i it plays no essential rôle. And conversely, for values of i close to i_{π}, the equation changes into another, *viz.*:

$$\eta = b \lg\left(1 - \frac{i}{i_{\pi}}\right),$$

which must also fit the experimental data, since here $\lg i$ becomes secondary to $\lg\left(1 - \frac{i}{i_{\pi}}\right)$. In other words the experimental results may be described by the equation for slow discharge, which changes

[9] See for example, R. Abegg, Handb. anorg. Chem., **3**, 2 (1909) Leipzig, pp. 417, 426, 444.

in form at a certain value of η; the limiting current density observed is the electrolytic saturation current.

The value of the coefficient b, which remains approximately equal to 0.12 even in the region where the influence of $\lg\left(1-\frac{i}{i_\pi}\right)$ is sufficiently great, whereas in accordance with the electron transition theory this coefficient should approach [3] 0.06 $\left(i.\ e.,\ \frac{RT}{0.4343F}\right)$, contradicts this conclusion. If, further, it is assumed that along with slow discharge, there also occurs retarded dissociation and diffusion (which, evidently, is not far from the actual state of things, at least in the case of ions of quadrivalent titanium), then the quantity i_π which enters into the equation $\eta_i(i)=0$ should be connected (for large values of η_i) with the saturation current densities at individual stages by the following expression [2, 3]:

$$\frac{1}{i_\pi'}=\frac{1}{i_s}+\frac{1}{i_{\pi k}+i_{\pi g}}.$$

In other words, for comparable values of i_s and $(i_{\pi k}+i_{\pi g})$, the quantity i_π' will be less than either of them and, consequently, less than the value of the saturation current density obtained experimentally (*i. e.*, any one of them). This leads to a decrease in the value of the coefficient b $\left(\text{or an increase in } \frac{1}{\gamma}\right)$. However, even in the best case, when

$$i_s=(i_{\pi k}+i_{\pi g}),$$

i. e., when i_π' is one half of the experimental value of i_π, the value of b remains almost constant, barring the points lying very close to the actual saturation current density, which are hardly worth calculating, since the accuracy in measuring η_i in these regions of i decreases considerably. Thus the experimental value of i_π is probably less than that of i_s and is determined by the rate of diffusion and dissociation of the ions, just as in the process of the reduction of tin ions.

It is necessary to mention, however, that in the experiments in which the saturation current density for the first branch of the cathodic curve is sharply expressed, the sum of the coefficients $\frac{1}{\gamma_{kI}}$ and $\frac{1}{\gamma_a}$ differs noticeably from unity (see, for example, Fig. 2). It only becomes equal to unity if the value of $i_{\pi kI}$ substituted in equation (4) is reduced to about $^2/_3$ of the experimental value. It is possible that this

is explained [10] by the fact that in the case of the reduction of titanium ions ($Ti^{++++} + \ominus \rightarrow Ti^{+++}$), the value of i_s is not very large as compared with the value of $(i_{\pi k} + i_{\pi g})$.

Summary

1. Measurements were made of the cathodic and anodic polarizations taking place on a flowing mercury electrode in the process of the electrolytic reduction and oxidation of titanium ions in sulphuric acid solutions.

2. It was established that under certain conditions the cathodic curve has two distinct branches, one of which refers, in the main, to the process of the transition of quadrivalent titanium to the tervalent form, and the other, to the transition of the latter to the bivalent form.

3. Analysis of the data obtained showed that both these processes, just as in the case of tin ions, are accompanied by slow discharge complicated by an inadequate rate of diffusion of ions and retarded dissociation, at least of the complex ions of quadrivalent titanium. The latter, however, plays a lesser rôle than in the case of tin.

4. A hypothesis is advanced that the existence of an electrolytic saturation current influences the form of the relation between η and i for the reduction of titanium ions, although its magnitude, in this case also, remains greater than the saturation current density observed experimentally.

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[10] It is hardly possible that such a large increase in the experimental value of the saturation current density could be due to other possible electrode processes (such, for example, as $Ti^{++++} \rightarrow Ti$) (see the section dealing with the cathodic branches).