

## Electrolytic Reduction of Zinc Ions and of Zinc Cyanide Complex Ions from Aqueous Solutions of Zinc Perchlorate and Zinc Perchlorate with Potassium Cyanide

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Solutions of complex zinc cyanides have been investigated earlier in different ways. They have inter alia been the object of polarographic examination by Pines<sup>1</sup>. He was chiefly interested in finding an explanation of the fact that no zinc is electro-deposited from solutions of zinc salts if they contain a surplus of alkali cyanide, whereas cadmium is deposited under corresponding conditions. Pines concluded that slowness of dissociation of the potassium-zinc cyanide complexes hinders the deposition of zinc, whereas in cadmium-alkali-cyanide solutions the free ions are in reversible equilibrium with the complex ions<sup>2</sup>. Glasstone<sup>3</sup> on the other hand, in consequence of his researches on electrolytic polarization states that there is no reason to believe that any of the complex cyanides studied hitherto dissociate slowly. Glasstone studied the solutions by means of cathode-potential measurements and electrometric titrations. The shape of his titration curve suggests that  $\text{Zn}(\text{CN})_4^{--}$  is the chief complex ion present in solution. One of the earliest determinations of the instability constant for the  $\text{Zn}(\text{CN})_4^{--}$  ion and for the  $\text{Cd}(\text{CN})_4^{--}$  ion was made by v. Euler<sup>4</sup>. He found about the same values for both complexes. Britton and Dodd<sup>5</sup> also came to the conclusion that they are of the same order of magnitude. This seems strange in view of the fact that the zinc ion is a stronger acid than the cadmium ion. We must therefore, according to the Lewis conception of acids and bases expect the stability of the zinc cyanide complexes to be greater than that of the corresponding cadmium cyanide complexes. Pines (*l. c.*) concludes from his polarographic investigations that in solutions of cadmium chloride with potassium cyanide the greater part of the cadmium exists as  $\text{Cd}(\text{CN})_3^-$ , whereas the corresponding complex is excluded

from his reflections on zinc cyanide solutions. Kunschert<sup>6</sup> on the other hand maintains as a result of measurements with a silver electrode in potassium zinc cyanide solutions that the zinc in cyanide solutions is present partly in the form of  $\text{Zn}(\text{CN})_4^{--}$  ions and partly in the form of  $\text{Zn}(\text{CN})_3^-$  ions.

The aim of the present investigation is primarily to ascertain whether the "prewaves" which we formerly have recorded by the electro-reduction of divers metal ions as for instance the  $\text{Zn}^{++}$  ions and the  $\text{Cd}^{++}$  ions<sup>7</sup> can be reproduced also when complex forming anions, such as the  $\text{CN}^-$  ion are present. We chose first to examine the  $\text{Zn}^{++}$  ion, which ought to form the most stable cyanide complex ions of the two. An eventual impeding effect to the phenomenon might therefore be expected to be more pronounced in zinc salt solutions than in cadmium salt solutions.

#### EXPERIMENTAL PROCEDURE

For our experiments we employed a polarograph from Radiometer in Copenhagen with a photo-electric amplifier and automatic registrator. As by former investigations we made use of its counter current arrangement in order to vary the slopes of the curves.

We took extra precautions to secure against eventual oxygen waves. Not only were the solutions in the electrolytic vessels treated for a whole night before the readings were taken with hydrogen or nitrogen that had been purified over red hot copper; but the gas was also passed through solutions of chromous chloride. If the solutions were no longer sky-blue the copper as well as the solutions were renewed. As the slightest amount of oxygen changes the blue colour of chromous chloride to green, we can guarantee the purity of our gas. The solutions in the electrolytic vessel were kept under gas also during the readings.

The zinc perchlorate was prepared as usual by precipitation of zinc sulphate solutions with equivalent amounts of barium perchlorate solutions. The potassium cyanide solutions were freshly prepared for each series of measurements as it is well known that a solution of alkali cyanide decomposes on standing.

The molar concentration of the zinc ion varied between the order of magnitude of  $10^{-4}$  and  $10^{-3}$ . The molar concentration of the cyanide ion was increased from zero to six hundred times that of the zinc ion.

Some solutions of pure zinc cyanide were prepared by shaking a small amount with conductivity water under hydrogen in an electric shaker. The solubility of zinc cyanide has been determined by Masaki<sup>8</sup> by means of electrometric measurements. He found the molar solubility of  $\text{Zn}(\text{CN})_2$  to be  $4.49 \cdot 10^{-5}$ . Pines (*l. c.*) states that it is of the order of magnitude of  $10^{-4}$ .

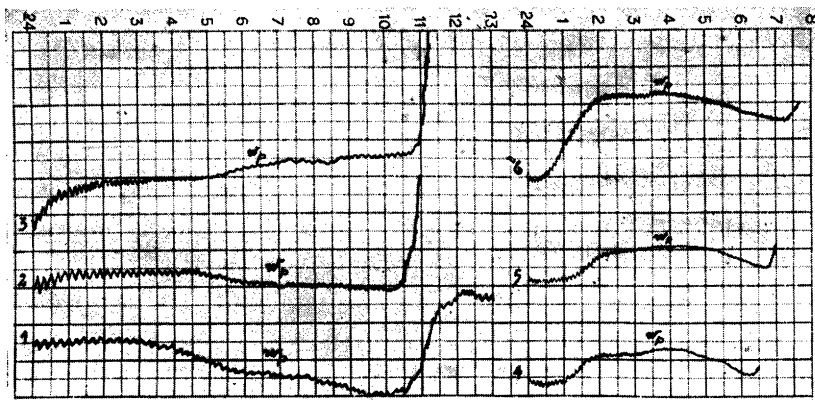


Fig. 1. Electro-reduction of zinc perchlorate in aqueous solutions.

No.	E. M. F. in volts	Counter current	1/sens	Mol. conc.	
				NaClO <sub>4</sub>	Zn(ClO <sub>4</sub> ) <sub>2</sub>
1	2	2	1 × 1	0	0.0001
2	2	2	1 × 1	0	0.001
3	2	2	1 × 1	0	0.005
4	3	3	1 × 1	0.1	0.0006
5	3	3	1 × 1	0.1	0.0012
6	3	3	1 × 1	0.1	0.004

### EXPERIMENTAL RESULTS

In the first instance we devoted ourselves to the checking of earlier results as regards stepwise reduction of zinc ions in pure zinc perchlorate solutions and in solutions of zinc perchlorate with 0.1 *M* sodium perchlorate as supporting electrolyte. Our experimental material is for these as for the following types of solutions too great to publish as a whole; but we have given several curves for each type. As will be seen from Fig. 1 the curves for pure zinc perchlorate solutions fully confirm earlier results, the "prewaves" being distinctly registered.

Next we tested some solutions of pure zinc cyanide. As will be seen from the height of the zinc wave the concentration of Zn<sup>++</sup> ions is not very great considering that we have used maximum of sensitivity, *viz.* 1 × 1 as in Fig. 1. The half wave potential for the zinc ion lies, as might be expected, at less negative values than when perchlorate ions are present, and the position of the pre-wave is correspondingly found between - 0.5 and - 0.6 volts.

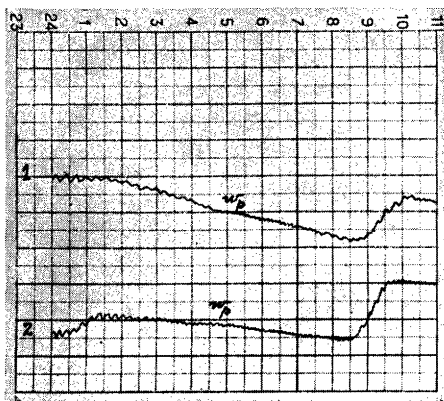


Fig. 2. Electro-reduction of saturated aqueous solutions of zinc cyanide.

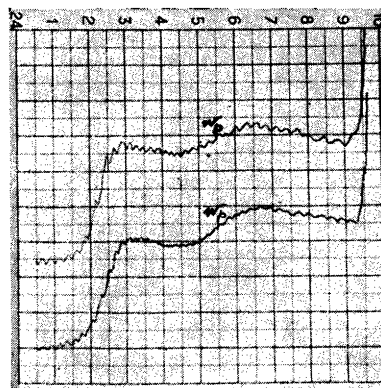


Fig. 3. Electro-reduction of solutions of zinc perchlorate with equivalent amounts of potassium cyanide.

No.	E. M. F. in volts	Counter current	l/sens	Gas stream in hours
1	2	2	1 × 1	1
2	2	2	1 × 1	20

No.	E. M. F. in volts	Counter current	l/sens	Mol. conc.		
				Zn(ClO <sub>4</sub> ) <sub>2</sub>	KCN	NaClO <sub>4</sub>
1	2	2	1 × 1	0.001	0.002	0.1
2	2	2	1 × 1	0.001	0.002	0.1

The principal part of our investigation was taken up with measurements of solutions of zinc perchlorate with gradually increasing amounts of potassium cyanide. We first examined solutions with equivalent amounts of Zn(ClO<sub>4</sub>)<sub>2</sub> and KCN. One might expect to get curves of the same shape as those for solutions of Zn(CN)<sub>2</sub>. The curves in Fig. 3, however, show more analogy to curves 4, 5 and 6 of Fig. 1 than to the curves in Fig. 2. It seems as if the Zn<sup>++</sup> ions and the CN<sup>-</sup> ions have not as yet had time to combine to Zn(CN)<sub>2</sub> in these dilute solutions, the zinc wave being much higher than those observed in a solution prepared from solid Zn(CN)<sub>2</sub>. The influence of the CN<sup>-</sup> ions is only seen in a lowering of the value for the half wave potential of Zn<sup>++</sup>. These effects will have to be the object of a separate investigation as regards the influence of ageing on solutions of Zn<sup>++</sup> ions with equivalent amounts of CN<sup>-</sup> ions.

When we have added as much as two equivalents of CN<sup>-</sup> per equivalent of Zn<sup>++</sup> conditions for formation of Zn(CN)<sub>4</sub><sup>2-</sup> ions ought to be present. We get, as will be seen from Fig. 4,1 a small wave at greater negative potential than the Zn wave. This wave is still more pronounced at curve 4,2. Its half-wave potential lies about - 1.3 volts.

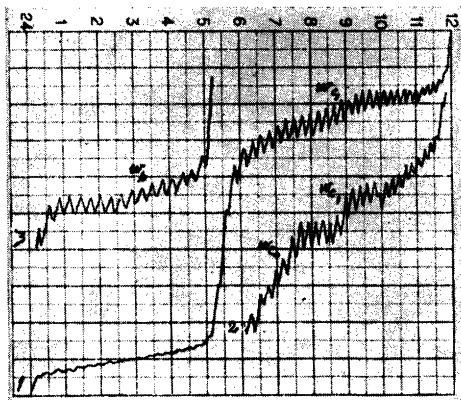


Fig. 4. Electro-reduction of solutions of zinc perchlorate with two equivalents of potassium cyanide per equivalent of zinc.

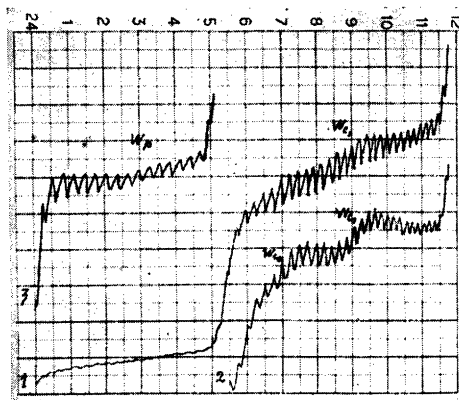


Fig. 5. Electro-reduction of solutions of zinc perchlorate with three equivalents of potassium cyanide per equivalent of zinc.

No.	E. M. F. in volts	Counter current	I/sens	Mol. conc.		
				Zn(ClO <sub>4</sub> ) <sub>2</sub>	KCN	NaClO <sub>4</sub>
1	3	0	10 × 1	0.001	0.004	0.1
2	3	0	3 × 1	0.001	0.004	0.1
3	3	2	1 × 1	0.001	0.004	0.1

No.	E. M. F. in volts	Counter current	I/sens	Mol. conc.		
				Zn(ClO <sub>4</sub> ) <sub>2</sub>	KCN	NaClO <sub>4</sub>
1	3	0	10 × 1	0.001	0.006	0.1
2	3	1	3 × 1	0.001	0.006	0.1
3	3	2	1 × 1	0.001	0.006	0.1

The Zn<sup>++</sup> wave has shifted even more towards less negative values, but is still quite high, the pre-wave being less pronounced.

With three equivalents of CN<sup>-</sup> per equivalent of Zn<sup>++</sup> we should expect the Zn<sup>++</sup> wave to be less pronounced and the complex ion waves to be correspondingly more conspicuous. As will be seen from Fig. 5, 1 and 2 this is also the case. At this concentration, however, a complex ion wave unmistakably begins to appear at lower negative potential than the one marked  $w_{c1}$ . One might accordingly assume the formation of the complex ion Zn(CN)<sub>3</sub><sup>-</sup>, although Britton and Dodd (*l. c.*) in their investigation of the progressive formation in dilute solutions of the complex cyanides of zinc (and other metals) find no evidence for the existence of a Zn(CN)<sub>3</sub><sup>-</sup> ion. Kunschert<sup>9</sup>, however, found it necessary to postulate the existence of the zinc complex cyanide ion, Zn(CN)<sub>3</sub><sup>-</sup> in order to account for the potentials of silver electrodes in solutions containing both silver and zinc complex cyanides. This disputed ion is evidently not so easily formed as the well known Zn(CN)<sub>4</sub><sup>-</sup> ion. The prewave is still observable.

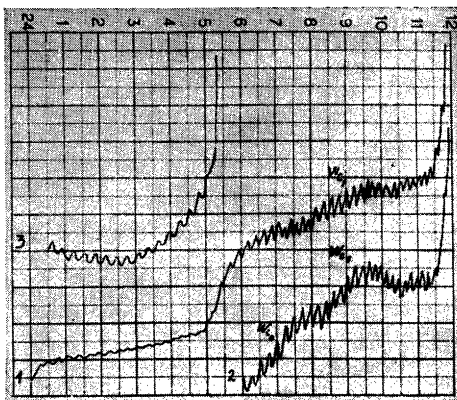


Fig. 6. Electro-reduction of solutions of zinc perchlorate with four equivalents of potassium cyanide per equivalent of zinc.

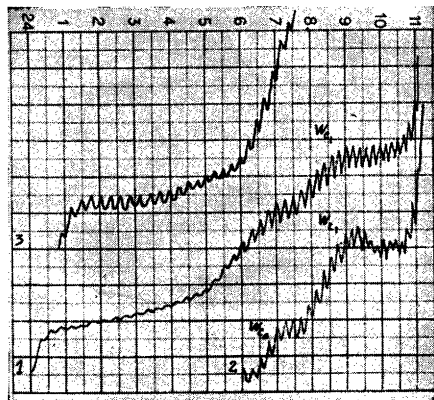


Fig. 7. Electro-reduction of solutions of zinc perchlorate with six equivalents of potassium cyanide per equivalent of zinc.

No.	E. M. F. in volts	Counter current	l/sens	Mol. conc.		
				Zn(ClO <sub>4</sub> ) <sub>2</sub>	KCN	NaClO <sub>4</sub>
1	3	0	10 × 1	0.001	0.008	0.1
2	3	2	3 × 1	0.001	0.008	0.1
3	3	3	1 × 1	0.001	0.008	0.1

No.	E. M. F. in volts	Counter current	l/sens	Mol. conc.		
				Zn(ClO <sub>4</sub> ) <sub>2</sub>	KCN	NaClO <sub>4</sub>
1	3	0	10 × 1	0.001	0.012	0.1
2	3	3	3 × 1	0.001	0.012	0.1
3	3	2	1 × 1	0.001	0.012	0.1

With the molar ratio 1 : 8 a complex ion wave also begins to appear at higher negative values than the one marked  $w_{c_1}$ . It has a half wave potential of about  $-1.5$  volts as against the mercury anode. This wave may be attributed to the complex ion  $Zn(CN)_5^{--}$ . Pines (*l. c.*) calculates with this ion on the assumption that the  $Zn(CN)_6^{--}$  ion is not polarographically reduced at lower negative values than  $-2$  volts.

The only difference which the curves of Fig. 6 show from those of Fig. 5 is that the height of the  $Zn^{++}$  wave has decreased perceptibly while that of the complex waves has increased.

An increase of  $CN^-$  to six equivalents of  $CN^-$  ion per equivalent of  $Zn^{++}$  ions only augments the effects just mentioned, as will be seen from Fig. 7.

An increase of  $CN^-$  ions to twelve equivalents of  $CN^-$  ions per equivalent of  $Zn^{++}$  ions brings  $w_{c_2}$  into prominence as seen from Fig. 8.

Increasing the amount of  $CN^-$  ions to sixty equivalents of  $CN^-$  ions per equivalent of  $Zn^{++}$  ions, we obtain a new polarographic wave at about  $-1.65$  volts as against

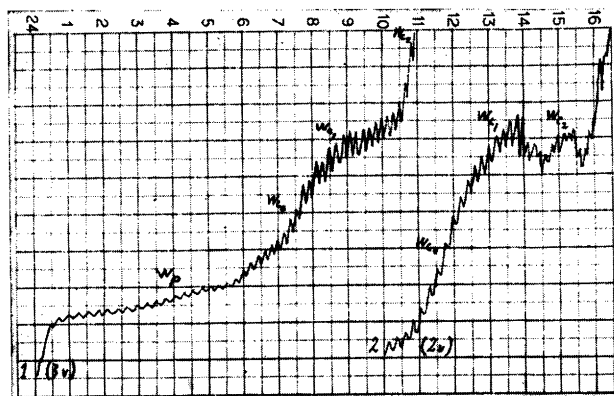


Fig. 8. Electro-reduction of solutions of zinc perchlorate with twelve equivalents of potassium cyanide per equivalent of zinc.

No.	E. M. F. in volts	Counter current	l/sens	Mol. conc.		
				Zn(ClO <sub>4</sub> ) <sub>2</sub>	KCN	NaClO <sub>4</sub>
1	3	0	10 × 1	0.001	0.024	0.1
2	2	4	3 × 1	0.001	0.024	0.1

the mercury anode. We have called it  $w_{c_3}$  and we may assume that wave to be due to the presence of  $Zn(CN)_6^{--}$  ions. The assumption that this ion has a more negative reduction potential than the potassium ion, (Pines, *l. c.*) does evidently not tally with our experimental results as given in Fig. 9.

The last and greatest concentration of  $CN^-$  ions that we used was three hundred equivalents to one equivalent of zinc. With the usual concentration of  $Zn^{++}$ , *viz.* 0.001, we did not get any distinct complex waves, though the pre-wave appeared, as shown in Fig. 10 a.

To test the effect of an increased dissociation of the complexes we next repeated the polarographic treatment of solutions in the same equivalent proportions but a hundred times more diluted. The most conspicuous result was a very great rise of the  $Z^{++}$  wave as will be seen from Fig. 10b;  $w_{c_0}$  and  $w_{c_1}$  are also observable.

Lastly we wanted to try out the effect of lesser ionic strength, that is, to dispense with the supporting electrolyte. We have earlier found that many effects that otherwise hardly may be traceable seem to appear in such solutions. As will be seen from Fig. 11 both the prewave, the  $Zn^{++}$  wave, and the complex ion waves are unmistakable. We even seem to get a  $w_{c_4}$  that lies at about, — 1.8 volts, just before the potassium wave.

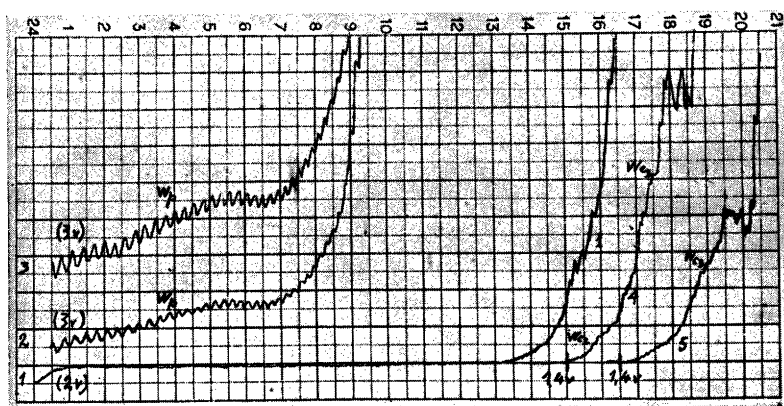


Fig. 9. Electro-reduction of solutions of zinc perchlorate with sixty equivalents of potassium cyanide per equivalent of zinc.

No.	E. M. F. in volts	Counter current	1/sens	Mol. conc.		
				Zn(ClO <sub>4</sub> ) <sub>2</sub>	KCN	NaClO <sub>4</sub>
1	3	0	100 × 1	0.001	0.120	0.1
2	3	0	3 × 1	0.001	0.120	0.1
3	3	0	2 × 1	0.001	0.120	0.1
4	2	0	100 × 3	0.001	0.120	0.1
5	2	0	100 × 5	0.001	0.120	0.1

#### DISCUSSION

The chief experimental data as regards the polarographic behaviour of zinc in cyanide medium have been summarized in Table 1.

As one might expect, the prewave for Zn<sup>++</sup> comes out most strongly in those solutions where the complex ions have not as yet been formed and the zinc wave is still the dominant one. With increasing concentration of CN<sup>-</sup> ions, complex formation takes place and the Zn<sup>++</sup> wave gets correspondingly smaller.

A complex wave,  $w_{c1}$ , with a half wave potential of about — 1.3 volts as against the mercury anode gets very distinct at the molar ratio Zn<sup>++</sup>:CN<sup>-</sup> = 1 : 4, and does not disappear till the ratio has reached 1 : 120. It is natural to



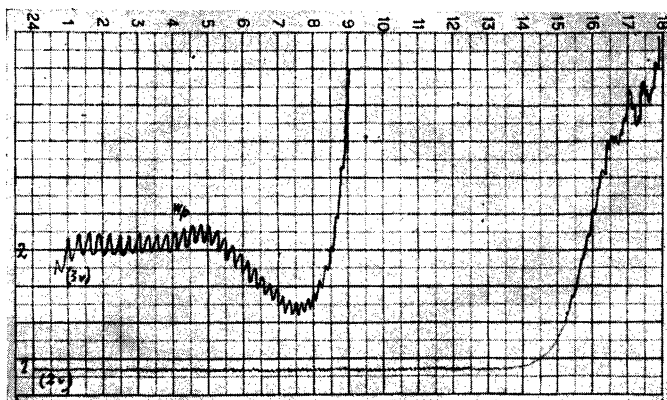


Fig. 10 a. Electro-reduction of solutions of zinc perchlorate with three hundred equivalents of potassium cyanide per equivalent of zinc.

No.	E. M. F. in volts	Counter current	l/sens	Mol. conc.		
				Zn(ClO <sub>4</sub> ) <sub>2</sub>	KCN	NaClO <sub>4</sub>
1	2	0	100 × 5	0.001	0.600	0.1
2	3	1	1 × 1	0.001	0.600	0.1

attribute this to the complex ion  $\text{Zn}(\text{CN})_4^{--}$  inasmuch as it is usually considered the dominant complex ion, the zinc ion readily forming tetracoordinated complexes. At the same ratio however a small wave,  $w_{c_0}$ , with a somewhat lower half wave potential just begins to appear. At the ratio 1 : 8 it is fairly distinct and does not disappear as long as the  $w_{c_1}$  is present. Not until the molar ratio has become 1 : 8 does the third complex wave,  $w_{c_2}$ , make its appearance. Its half wave potential lies about 1.5 volts. It gets distinct at the ratio 1 : 24, and is still apparent at the ratio 1 : 120, when both  $w_{c_0}$  and  $w_{c_1}$  have disappeared. At that ratio however a fourth half wave,  $w_{c_3}$ , appears with a half wave potential of about — 1.65 volts. as against the mercury anode. It may be natural to attribute those last two waves to the complex ions  $\text{Zn}(\text{CN})_5^{---}$  and  $\text{Zn}(\text{CN})_6^{----}$  although Pines (*l. c.*) with the concentrations and the sensitivity he disposed of, did not observe any wave corresponding to the last ion.

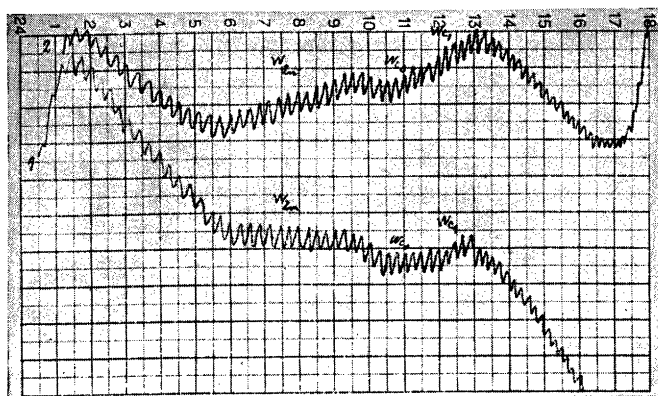


Fig. 10 b. Electro-reduction of highly dilute solutions of zinc perchlorate with three hundred equivalents of potassium cyanide per equivalent of zinc.

No.	E. M. F. in volts	Counter current	I/sens	Mol. conc.		
				Zn(ClO <sub>4</sub> ) <sub>2</sub>	KCN	NaClO <sub>4</sub>
1	2	6	1 × 1	0.00001	0.006	0.001
2	2	5	1 × 1	0.00001	0.006	0.001

When we used extremely dilute solutions, and when we lowered the ionic strength by dispensing with supporting electrolyte, the complex waves were still more plainly seen, and in the solutions that did not contain NaClO<sub>4</sub> we even obtained a complex wave with a half wave potential of about — 1.8 volts. One might perhaps attribute this wave to the forming of still higher complexes with this extremely high excess of CN<sup>-</sup> ions. The observation of Pines that the complex waves disappear when the CN<sup>-</sup> excess is very great seems only to hold good for relatively concentrated solutions, but dilution evidently brings about sufficient dissociation of the complexes for reaching equilibrium. From these observations we may conclude that the Zn(CN)<sub>4</sub><sup>-</sup> complex ion is predominant in dilute solutions of zinc salts on addition of CN<sup>-</sup> ions, and is perhaps even formed before the Zn(CN)<sub>3</sub><sup>-</sup> ion. With great excess of CN<sup>-</sup> ion the coordination number 4 is seemingly exceeded.

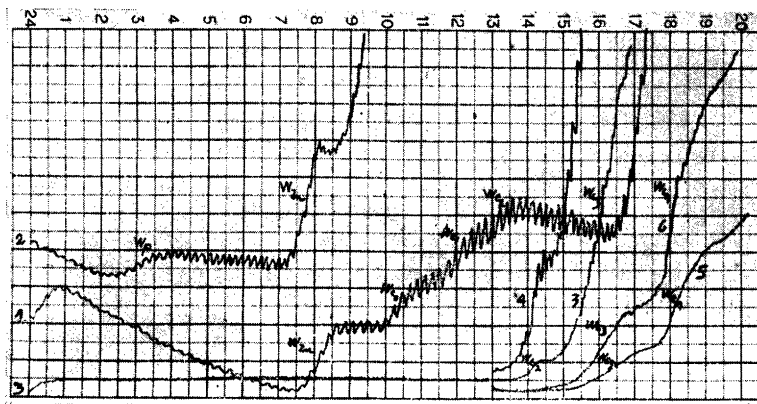


Fig. 11. Electro-reduction of zinc perchlorate with gradually increasing amounts of potassium cyanide, but without supporting electrolyte.

No.	E. M. F. in volts	Counter current	l/sens	Mol. conc.		
				Zn(ClO <sub>4</sub> ) <sub>2</sub>	KCN	NaClO <sub>4</sub>
1	2	2	5 × 1	0.001	0.0147	0
2	2	1	10 × 1.5	0.001	0.048	0
3	2	0	10 × 10	0.001	0.240	0
4	2	0	10 × 2	0.001	0.240	0
5	2	0	100 × 10	0.001	0.240	0
6	2	0	100 × 5	0.001	0.240	0

#### SUMMARY

1. The polarographic behaviour of the system Zn(ClO<sub>4</sub>)<sub>2</sub>—KCN—H<sub>2</sub>O has been investigated.

2. As previously found, the Zn<sup>++</sup> ions in very dilute solutions show a step-wise polarographic reduction when a sufficiently sensitive apparatus is used. The double waves previously obtained were repeatedly reproduced.

3. As the CN<sup>-</sup> ion concentration is increased beyond the point Zn<sup>++</sup> : CN<sup>-</sup> = 1 : 4 complex waves appear. At first only a wave with  $w_{1/2}$  = ca. — 1.3 volts as against the mercury anode is manifest. This is attributed to the ion Zn(CN)<sub>4</sub><sup>---</sup>. With increasing concentration of CN<sup>-</sup>, however, a wave appears at lesser  $w_{1/2}$ .

Table 1. Main points in the polarographic behaviour of the system  
 $Zn(ClO_4)_2 - NaClO_4 - KCN - H_2O$ .

Fig. no.	Mol. ratio Zn <sup>++</sup> : CN <sup>-</sup>	Pre-wave	Zn <sup>++</sup> wave	$w_{c_0}$	$w_{c_1}$	$w_{c_2}$	$w_{c_3}$
1	1 : 0	Distinct	Dominant	Non existent	Non existent	Non existent	Non existent
2	1 : 2 Zn(CN) <sub>2</sub>	Observable	Low	Not considered	Not considered	Not considered	Not considered
3	1 : 2 Zn(ClO <sub>4</sub> ) <sub>2</sub> + KCN	Distinct	Dominant	Not considered	Not considered	Not considered	Not considered
4	1 : 4	Still observable	Still dominant	Just appeared	Distinct	Not appeared	Not appeared
5	1 : 6	Still observable	Still dominant	Unmistakeably appeared	Distinct	Not appeared	Not appeared
6	1 : 8	Disappeared	Distinct	Fairly distinct	Distinct	Just appeared	Not appeared
7	1 : 12	Just reappeared	Not distinguishable	Distinct	Distinct	Just appeared	Not appeared
8	1 : 24	Reappeared	Not distinguishable	Distinct	Distinct	Distinct	Not considered
9	1 : 120	Reappeared	Disappeared	Disappeared	Disappeared	Distinct	Distinct
10 a	1 : 600	Reappeared	Distinct	Disappeared	Disappeared	Disappeared	Indistinct
10 b	1 : 600	Not observable	Distinct	Observable	Observable	Not observable	Not observable

This may be owing to the formation of  $Zn(CN)_3^-$  ions, which are evidently not as dominant as the  $Zn(CN)_4^{--}$  ions. With gradually increasing amounts of  $CN^-$  a wave is obtained with  $w_{1/2} = -1.5$  volts, which may be due to  $Zn(CN)_5^{---}$  ions, and still another wave with  $w_{1/2} = -1.65$  volts. The last wave seems to indicate that the  $Zn(CN)_6^{----}$  ion is polarographically reduced before the  $K^+$  ion, and not as formerly supposed at negative potentials greater than 2 volts. In dilute solutions without any supporting electrolyte we even got a separate wave with  $w_{1/2} = -1.8$  volts.

4. The assumption made by earlier polarographic investigators, that no complex wave is to be observed when a large excess of potassium cyanide is added to a zinc solution, seems not to hold when the solutions are sufficiently dilute and the apparatus correspondingly sensitive.

The authors are indebted to Anne Lise Kallevig for her careful and reliable work as our assistant.

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