Electrode Processes of Nickel(II) Ions at the Mercury Electrode in Concentrated Calcium Chloride Solutions

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The electrode reaction of nickel(II) ions at the mercury electrode seems to proceed with various mechanisms, depending on the kind of supporting electrolyte present in the solution. It has been known that the reduction of nickel(II) ions at the dropping mercury electrode (DME) in the concentrated solution of chloride occurs with a higher degree of reversibility at the potentials much more positive than those at which the reduction of hydrated nickel(II) ions takes place[1]. Reynolds and his coworkers[2,3] pointed out, from the results of the microcoulometry, that the reduction process of nickel(II) ions at the DME in 5 M calcium chloride solution is represented by

$$Ni^{2+} + 2e \rightarrow Ni$$

Recently, Vlček[4] reported that one continuous redox wave is obtained by the Kalousek's method[5,6] with nickel(II) ions in 6 M calcium chloride solution. From this result, he suggested that nickel(II) ions in 6 M calcium chloride solution is reduced at the mercury electrode to a zero-valent nickel complex, $NiCl_4^{4-}$, the life of which is estimated to be longer than 0.01 sec.

In this paper, an extensive and systematic study on the reduction of nickel(II) ions in concentrated calcium chloride solution at the mercury electrode is presented. The number of electrons which participate in the overall electrode reaction has been accurately determined by the coulometry at constant potential. The reduction product has been investigated by means of the controlled potential electrolysis at the mercury electrode. The reversibility of the electrode reaction is discussed from the analysis of the direct current (d. c.), the alternating current (a. c.) and the Kalousek's polarograms, and a possible mechanism for the reaction is proposed.

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[1] I. M. Kolthoff and J. J. Lingane, "Polarography", Vol. II, Interscience Publishers, Inc., New York (1952), p. 486.

[2] G. F. Reynolds, H. I. Shalgosky and T. J. Weber, *Anal. Chim. Acta*, **8**, 567 (1953).

[3] G. F. Reynolds and H. I. Shalgosky, ibid., **10**, 398 (1954).

[4] A. A. Vlček, *Z. Elektrochem.*, **61**, 1014 (1957).

[5] M. Kalousek, *Collection Czechoslov. Chem. Communs.*, **13**, 105 (1948).

[6] R. Tamamushi and N. Tanaka, *Repts. Inst. Sci. Technol. Univ. Tokyo*, **5**, 33 (1951).

Experimental

Apparatus.—Current-voltage curves were measured by a manual polarograph similar to that of Kolthoff and Lingane⁷⁾ or recorded automatically by a Yanagimoto Galvarecorder Y-GR 2. The Galvarecorder was also used for recording the a. c. and the Kalousek's polarograms and the current-time curves in coulometry.

The Kalousek's circuit used in this study is schematically shown in Fig. 1. The potential of the working electrode, e_1, is periodically changed from E_1 to E_2 and vice versa by the exchange switch b_2. When the reduction wave is concerned, E_2 is usually kept constant at a certain definite value in the potential region of the limiting current plateau. The value of E_1 is varied in the same way as in the ordinary polarograph, and only the current which flows when the electrode potential is E_1 is recorded. If the reduced substance produced at the electrode is oxidized at the potential of E_1, the anodic current is observed.

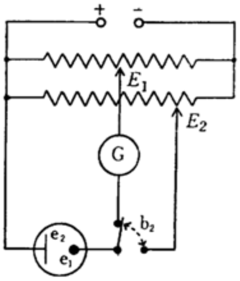

Fig. 1. Circuit of the Kalousek's method: G, Galvarecorder; e_1, working electrode (DME); e_2, unpolarizable electrode (S. C. E.); b_2, exchange switch (contact of relay B in Fig. 2).

A simple relay circuit as shown in Fig. 2 was used to exchange the electrode potential instead of a conventional mechanical commutator which consists of a synchronous motor and a rotary switch. Relay B in Fig. 2 has two pairs of contacts, b_1 and b_2, the latter of which is used for the exchange switch in Fig. 1. The exchange frequency can be easily changed from apporoximately 2 c/s to 30 c/s by adjusting the capacitors C_1 and C_2. The on-and-off intervals of the switch were made equal by adjusting R_1 and R_2. This switch proved to be preferable to the conventional mechanical commutator because of the constancy and reliability in its switching action as well as because of its wide range of exchange frequencies. In this study, the exchange frequency of approximately 5.6 c/s was employed unless otherwise stated.

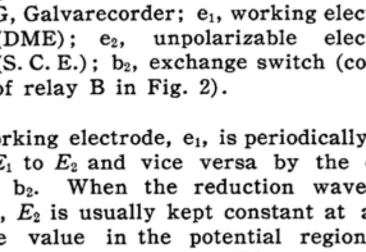

Fig. 2. Circuit of exchange switch: A, B, relay; a, contact of relay A; b_1, contact of relay B; R_1, R_2, 5 kΩ; C_1, C_2, 5∼50 μF.

The controlled potential electrolysis was carried out by using a Yanagimoto automatic potentiostat. In the coulometric study the current through the electrolysis cell during the constant potential electrolysis was automatically recorded with a Yanagimoto Galvarecorder⁸⁾. The quantity of electricity was determined by the graphical integration of the current-time curve thus obtained.

A simple beaker type cell was used for all polarographic measurements. A dropping mercury electrode, which had an m value of 1.94_8 mg./sec. and a drop time τ of 4.88 sec./drop in an air free 0.1 M potassium chloride solution at -0.60 V. vs. S. C. E., was used for the measurement of current-voltage curves. A saturated calomel electrode of a large surface area was used for the reference electrode, which was connected with the electrolytic solution by a Hume and Harris' type salt bridge⁹⁾. When a. c. polarograms were measured, a platinum plate electrode of a large surface area was inserted in the electrolytic solution as the third electrode, which was terminated at the saturated calomel electrode through a 100 μF capacitor in order to minimize the impedance of the cell¹⁰⁾. In the controlled potential electrolysis, the cathode was a mercury pool electrode whose surface area was approximately 20 cm², while the anode was a platinum spiral electrode which was connected with the electrolytic solution through a salt bridge. A saturated calomel electrode was used as a reference electrode, against which the electrode potential of the cathode was controlled.

All measurements were carried out in a thermostat of 25.00±0.01°C, and the dissolved oxygen in the electrolytic solution was removed by bubbling pure nitrogen gas through the solution. The d. c. and the Kalousek's polarograms given in this paper were corrected for the residual current and the ohmic potential drop of the cell circuit.

Reagents. — A standard solution of nickel chloride was prepared by the following procedure. An appropriate amount of pure nickel metal (Yokozawa Chemicals Co.: cobalt content, 0.004%) was dissolved in nitric acid, and the excess of nitric acid was removed by evaporation. By dilution with distilled water a nickel nitrate

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7) I. M. Kolthoff and J. J. Lingane, "Polarography", Vol. I, Interscience Publishers, Inc., New York (1952), p. 297.

8) N. Tanaka, T. Nozoe, T. Takamura and S. Kitahara, This Bulletin, **31**, 827 (1958).

9) D. N. Hume and W. E. Harris, *Ind. Eng. Chem. Analyt. Ed.*, **15**, 465 (1943).

10) B. Breyer, F. Gutmann and S. Hacobian, *Australian J. Sci. Research, Ser. A*, **4**, 595 (1951).

solution was obtained, to which a suitable amount of sodium carbonate was added to precipitate nickel(II) as carbonate. The precipitate was filtered off and washed thoroughly with distilled water. The resulting nickel carbonate was dissolved in dilute redistilled hydrochloric acid to prepare the standard solution of an appropriate concentration. The concentration of nickel was accurately determined by the conventional gravimetric method with dimethylglyoxime[11].

Calcium chloride which was free from organic surface-active substances was prepared. Reagent grade calcium chloride dihydrate was heated for 3 hr. at 470°C in an electric oven, and dissolved in redistilled water. After a small amount of insoluble substance was removed by decantation, the pH of the solution was adjusted to about 4.0 by adding hydrochloric acid. The chloride concentration of the solution was determined by the Volhard method[12].

All other chemicals used were of analytical reagent grade. Redistilled water was used to dilute the stock solutions and to prepare the electrolytic solutions.

Results

In a preliminary investigation, it was found that in 6 M unpurified calcium chloride solution nickel(II) ions are not reduced at the mercury pool electrode at the potentials where they are reduced at the DME. Their reduction at the mercury pool electrode occurred only at much more negative potentials. This phenomenon was not observed when the supporting electrolyte solution was prepared with purified calcium chloride, and therefore it was explained as due to the poisoning effect of surface-active substances which might have been present in the solution prepared with the unpurified reagent. The reduction potential of nickel(II) at the mercury pool electrode was found to shift to negative potentials upon the addition of polyoxyethylene lauryl ether to the electrolytic solution prepared with the purified calcium chloride. This clearly supports the above explanation. In this paper, only the experimental results which were obtained with purified calcium chloride are presented.

The d. c. polarograms of nickel(II) ions which were obtained in the solutions containing various concentrations of calcium chloride are given in Fig. 3. In the presence of 6 M calcium chloride, nickel(II) ions gave a polarogram with a half-wave potential of −0.462 V. vs. S. C. E. A log-plot, i. e. a plot of $\log i/(i_l-i)$ against E, of the polarogram gave a straight line with a slope of 38 mV. (Fig. 4). The limiting current was found to be proportional to the bulk concentration of nickel(II) and also to the square-root of the effective pressure on the DME, as shown in Tables I and II.

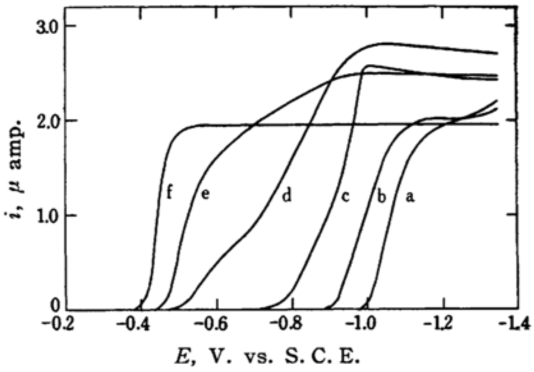

Fig. 3. D. C. polarograms of 0.844 mM Ni(II) ions in the solutions of various concentrations of calcium chloride: a, 1.0 M; b, 2.0 M; c, 3.0 M; d, 4.0 M; e, 5.0 M; f, 6.0 M $CaCl_2$.

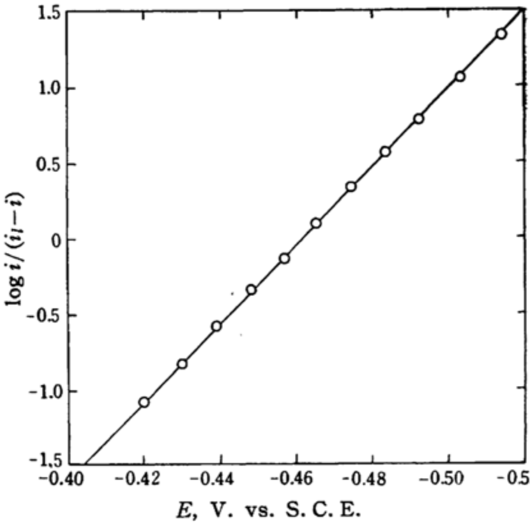

Fig. 4. Log-plot of the d. c. reduction wave of Ni(II) ions in 6 M $CaCl_2$ solution.

TABLE I. RELATION BETWEEN THE LIMITING CURRENT i_l AND THE BULK CONCENTRATION C OF NICKEL(II) IONS IN 6 M $CaCl_2$ SOLUTION

C, mM	i_l, μ amp.	i_l/C, μ amp./mM
0.844	1.95	2.31
1.68_7	3.89	2.31
2.53_1	5.85	2.31
3.37_5	7.79	2.31
6.75_0	15.58	2.31

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[11] F. P. Treadwell and W. T. Hall, "Analytical Chemistry", Vol. 2, John Wiley & Sons, Inc., New York (1951), p. 193.

[12] F. P. Treadwell and W. T. Hall, ibid., p. 650.

TABLE II. RELATION BETWEEN THE LIMITING CURRENT i_l OF 3.37_5 mM $NiCl_2$ IN 6 M $CaCl_2$ SOLUTION AND THE EFFECTIVE PRESSURE h ON THE DME

h, cmHg	i_l, μamp.	$i_l/\sqrt{h}$, μamp. cm$^{-1/2}$
40	6.55	1.04
55	7.79	1.05
85	9.78	1.06

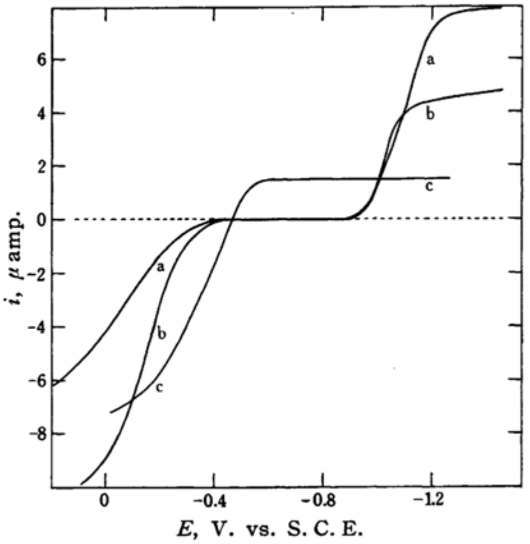

Fig. 5. Kalousek's polarograms of Ni(II) ions obtained at exchange frequency of 5.6 c/s. a; 2.0 mM $Ni(NO_3)_2$ in 0.2 M KNO_3, $E_2 = -1.45$ V. vs. S. C. E.: b; 1.7 mM $NiCl_2$ in 0.2 M KCl, $E_2 = -1.40$ V. vs. S. C. E.: c; 1.7 mM $NiCl_2$ in 6 M $CaCl_2$, $E_2 = -0.75$ V. vs. S. C. E.

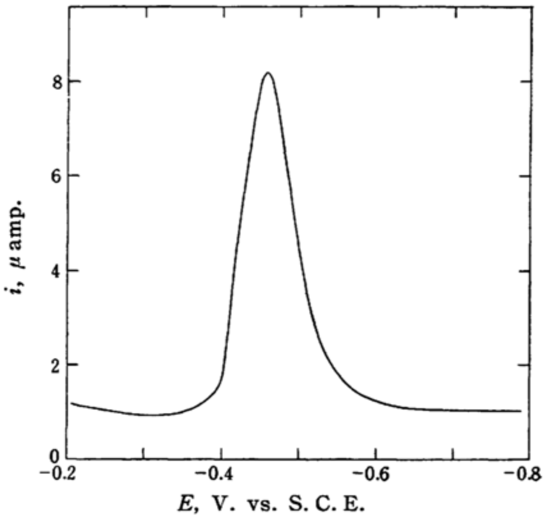

Fig. 6. A. C. polarogram of 3.37_5 mM Ni(II) ions in 6 M $CaCl_2$ solution.

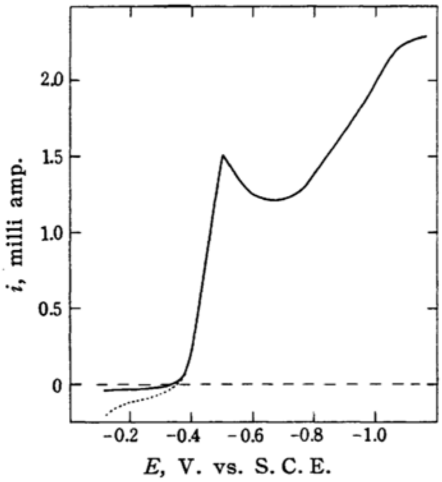

Fig. 7. Current—potential curve of Ni(II) ions in 6 M $CaCl_2$ solution at the mercury pool electrode.

The Kalousek's polarograms in Fig. 5 were recorded in 6 M calcium chloride, 0.2 M potassium chloride and 0.2 M potassium nitrate solutions. In the 6 M calcium chloride solution one continuous redox wave (Fig. 5, c) was observed as has been reported by Vlček[4)], while in the 0.2 M potassium chloride and the 0.2 M potassium nitrate solution no continuous redox wave was obtained, the anodic waves being far separated from the cathodic ones. It may be interesting to note that the potentials at which the anodic waves appear are almost identical in the three different solutions investigated.

In the 6 M calcium chloride solution a typical a. c. polarogram of nickel(II) as shown in Fig. 6 was obtained, the summit potential of which was nearly equal to the half-wave potential of the d. c. polarogram.

An example of the d. c. polarograms of nickel(II) ions obtained at the mercury pool electrode in the 6 M calcium chloride solution is given in Fig. 7. An apparent anodic current was observed when the working electrode was polarized at −0.1∼−0.3 V. vs. S. C. E. immediately after it had been polarized for 20 to 30 min. at the potential where the reduction of nickel(II) takes place (dotted line in Fig. 7). This anodic current remained nearly constant for several minutes if the solution was stirred by nitrogen gas bubbled through it. On the other hand, no anodic current was observed at the dropping mercury electrode with the same solution with which the anodic current was observed at the mercury pool electrode.

The number of electrons n which participate in the overall electrode reaction of nickel(II) was determined coulometrically by the controlled potential electrolysis. It can be calculated from the relation

$$n=\frac{Q}{FM}\times\frac{(i_d)_1}{(i_d)_1-(i_d)_2}$$

where Q is the quantity of electricity required for the electrolysis expressed in coulomb, M the initial amount of nickel(II) ions present in the solution expressed in mole, and $(i_d)_1$ and $(i_d)_2$ are the diffusion currents of nickel(II) before and after the electrolysis, respectively. The value of Q was corrected for the quantity of electricity that was measured with the supporting electrolyte solution under the same conditions of actual electrolysis. The results are presented in Table III.

TABLE III. THE NUMBER OF ELECTRONS n CONCERNING THE OVERALL ELECTRODE REDUCTION OF Ni(II) IN 6 M $CaCl_2$ SOLUTION*

Expt.	$(i_d)_1$, μ amp.	$(i_d)_2$, μ amp.	Q, coulombs	n
1	7.79	6.02	2.95_9	2.00
2	7.71	5.62	3.53_2	2.00

* The initial amount of Ni(II) was 0.0675 millimol.

In order to know whether the reduced substance of nickel(II) in 6 M calcium chloride solution is contained in the solution or in the mercury of the electrode, the nickel content of the mercury was determined after the electrolysis. Twenty milliliters of 3.37_5 mM of nickel(II) solution containing 6 M calcium chloride was subjected to the controlled potential electrolysis at −0.80 V. vs. S. C. E. with a mercury pool electrode. After 30 to 40% of the total amount of nickel(II) was reduced, the mercury electrode was separated from the solution, washed carefully with distilled water, and then treated for about 30 hr. with 30 ml. of 3 M hydrochloric acid to extract nickel in the mercury. The precipitate of mercurous chloride produced was filtered off. The volume and pH of the filtrate were adjusted to be about 130 ml. and 6.0∼6.5, respectively, by adding distilled water and ammonium hydroxide solution. Then, 15 ml. of 2 M potassium iodide solution was added to the solution, and the solution was kept standing for 30 min. The nickel content of the solution was determined by titration with a 0.01 M ethylenediaminetetraacetate solution using murexide as an indicator[13]. Preliminary experiments indicated that the nickel content can be determined with this procedure in the presence of an excess of mercuric ions. The amounts of nickel(II) ions reduced by the controlled potential electrolysis and those of nickel found in the mercury electrode are given in Table IV.

TABLE IV. DETERMINATION OF THE AMOUNT OF NICKEL IN THE MERCURY POOL ELECTRODE

Amount of Ni(II) ion reduced, millimol.	Amount of Ni(II) ion found in the mercury pool electrode, millimol.	Recovery of nickel, %
0.0287	0.0276	96
0.0216	0.0203	94

Discussion

The color of the solution containing nickel(II) ions and 6 M calcium chloride is yellowish green. This suggests the formation of chloronickel(II) complexes. According to Kiss and his coworkers[14] and Kiseleva and Khodeeva[15], the predominant species of these complexes is considered to be $NiCl_4^{2-}$.

The results given in Table II shows that the limiting current of nickel(II) ions in 6 M calcium chloride solution is diffusion-controlled. The relatively low value of the diffusion current for the unit concentration (Table I) is supposed to be due to the high viscosity of the solution. It is known that the diffusion coefficient of ions in the electrolyte solution is inversely proportional to the viscosity of the solution[16]. If the relation

$$D=D^\circ/\eta$$

where D° is the diffusion coefficient of Ni^{2+} ions at infinite dilution and η the viscosity of the 6 M calcium chloride solution referred to that of water as unity, is applied to the present case, the diffusion coefficient D of nickel(II) ions in 6 M calcium chloride solution is calculated to be 8.1×10^{-7} cm²/sec., when 6.9×10^{-6} cm²/sec. is used for D°[17] and 8.5 for η[18]. With the value of D thus obtained, the number of

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[14] Á. v. Kiss and P. Csokán, *Z. anorg. u. allgem. Chem.*, **245**, 355 (1941).

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[17] I. M. Kolthoff and J. J. Lingane, ibid., p. 52.

[18] "International Critical Tables", Vol. V, McGraw-Hill Book Co., Inc., New York (1929), p. 14.

electrons which participate in the overall electrode reaction is calculated to be 2.0 with the modified Ilkovič equation[19)]

$$i_d=607\,nD^{1/2}m^{2/3}\tau^{1/6}C\left(1+\frac{34\tau^{1/6}D^{1/2}}{m^{1/3}}\right)$$

This value of n is in agreement with that obtained by coulometry at constant potential (Table III), and leads to a conclusion that the nickel(II) ions in 6 M calcium chloride solution are reduced at the mercury electrode to either nickel metal or some chloro complexes of zero-valent nickel.

It has been reported by Vlček[4)] that the anodic wave of the Kalousek's polarogram obtained with nickel(II) ions in 6 M calcium chloride solution is due to the oxidation of zero-valent nickel complex, $NiCl_4^{4-}$, formed on the surface of the electrode. On the other hand, it has been known that nickel amalgam is easily obtained by the reduction of aqueous solutions of nickel chloride or sulfate at the mercury electrode[20),21)]. Breckpot[22)] reported that the oxidation of nickel amalgam occurred at +0.10 V. vs. N. H. E. at 75°C under the current density of 15 amp./m^2. This value of oxidation potential agrees approximately with those which were determined from the Kalousek's polarograms given in Fig. 5. The anodic wave is clearly observed on the Kalousek's polarogram which was obtained at the exchange frequency of about 2 c/s. This seems to be an indication that the life of the substance which is actually oxidized by the Kalousek's method must be longer than 0.5 sec. These facts strongly suggest that the anodic current observed with the Kalousek's method is due to the oxidation of nickel amalgam. It should be noted that the oxidation of nickel amalgam proceeds at almost the same potential in all of the solutions (the 6 M calcium chloride, the 0.2 M potassium chloride and the 0.2 M potassium nitrate solution), while the reduction takes place at entirely different potentials in these three solutions depending on the species and the concentration of supporting electrolyte.

Table IV shows that the amount of nickel reduced at the mercury electrode in 6 M calcium chloride solution is almost completely recovered from the mercury electrode. This excludes any possible contribution of the monovalent nickel compounds to the overall electrode reaction, but supports the conclusion that the reduced substance is nickel metal which is dissolved in mercury as nickel amalgam. However, any possibility that the zero- or monovalent nickel complexes exist as the reaction intermediate of very short lives is not excluded.

The experimental results of the a. c. and the Kalousek's polarograms and the log-plot analysis of the d. c. current-voltage curves indicate that the electrode reaction of nickel(II) ions in 6 M calcium chloride solution proceeds with a relatively high degree of reversibility in comparison with that of hydrated nickel(II) ions. It has been pointed out by Senda[23)] et al. that the value of $i_p/(n\sqrt{\tau}\,i_d)$, where i_p is the peak current of the a. c. polarogram, represents the degree of reversibility of the electrode reaction. The value for nickel(II) ions in 6 M calcium chloride solution was calculated to be 0.20, which is smaller than the values for the well-known reversible systems such as cadmium(II) or lead(II) ions in potassium nitrate solutions, but nearly equal to those of quasi-reversible systems such as zinc(II) ions in potassium nitrate solutions.

From the foregoing discussion, it can be concluded that the electrode reaction of nickel(II) ions in 6 M calcium chloride proceeds quasi-reversibly at the mercury electrode according to the reaction

$$NiCl_4^{2-}+2e+Hg \rightleftarrows Ni(Hg)+4Cl^-$$

Summary

A typical reduction wave with a half-wave potential of −0.462 V. vs. S. C. E. was obtained with nickel(II) ions in 6 M calcium chloride solution. The a. c. and the Kalousek's polarograms revealed that the electrode reaction is a quasi-reversible one. From the coulometric measurement carried out at the constant potential, the overall electrode reaction proved to be a two-electron reduction. Nearly the total amount of nickel reduced by the controlled potential electrolysis with the mercury electrode was recovered from the mercury, indicating that the nickel(II) ions are reduced to nickel metal to form probably

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[23)] M. Senda, M. Senda and I. Tachi, *J. Electrochem. Soc. Japan* (*Denki Kagaku*), **27**, 83 (1959).

nickel amalgam. From these experimental results the electrode reaction of nickel(II) ions in 6 M calcium chloride at the mercury electrode was concluded to proceed quasi-reversibly according to the equation

$$NiCl_4^{2-} + 2e + Hg \rightleftarrows Ni(Hg) + 4Cl^-$$

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