as that observed with lithium chloride. The results of the polarographic reduction of gadolinium sulfate in potassium chloride are given in Table III.

TABLE III

GADOLINIUM SULFATE IN 0.1 *N* POTASSIUM CHLORIDE PLUS 0.01% GELATIN

Millimoles Gd^{+3} per liter	$E_{1/2}$ S. C. E. volts	$m^{2/3}t^{1/6}$	i microamp.	i_d/c	I_d
0.80	−1.75	1.780	5.2	6.5	3.9
1.60	−1.75	1.788	10.3	6.4	3.6
4.00	−1.77	1.728	26.9	6.7	3.7

Discussion

The values of the quantity $m^{2/3}t^{1/6}$ were determined at the potential at which the diffusion current was measured. The average value of the diffusion current constant, I_d, for Gd^{+3} was found to be 3.7. Using equivalent conductance data given by Pascal,[6] and extrapolating to infinite dilution, a value of 125 ohm^{-1} cm.^{2} was obtained for gadolinium sulfate. If the value 80 is used for the sulfate ion, the equivalent ionic conductance of gadolinium is then 45 ohm^{-1} sq. cm. By substituting the value of the ionic conductance of gadolinium into the Nernst relation

$$D_i^0 = 2.67 \times 10^{-7} (\lambda^0/Z)$$

the diffusion coefficient is found to be 4.0×10^{-6} sq. cm. sec^{-1}. With the above quantities substituted into the Ilkovic equation, the number of electrons involved in the electrode reaction is found to be three. Thus the results indicate that the reduction of gadolinium at the dropping electrode takes place according to the reaction

$$Gd^{+3} + 3e \longrightarrow Gd^0$$

An analysis of the polarographic waves was made by noting the slope of the line produced in plotting values of log $i/i_d - i$ *vs.* $E_{d.e.}$. The irreversibility of the electrode reaction is indicated by the fact that the slope is not as steep as would be expected on the basis of a three electron reduction.

Summary

1. The results of Noddack and Brukl were not confirmed with regard to the polarographic reduction of gadolinium sulfate.
2. An increasing acid concentration shifts the half-wave potential of gadolinium to more negative potentials.
3. A value of 4.0×10^{-6} sq. cm. sec.$^{-1}$ was calculated for the diffusion coefficient of Gd^{+3} at 25°.
4. The results indicate that the reduction of gadolinium at the dropping mercury electrode involves three electrons.
5. The average value of the diffusion current constant for Gd^{+3} was found to be 3.7 at 25° in a supporting electrolyte of 0.1 *N* lithium chloride or 0.1 *N* potassium chloride.
6. The half-wave potential for 4.0 millimolar Gd^{+3} was found to be −1.77 volts *vs.* the S.C.E. with 0.1 *N* lithium chloride, and with 0.1 *N* potassium chloride as the supporting electrolytes.

IOWA CITY, IOWA

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[6] Pascal, "Traité de Chimie Minérale," Masson et Cie., Éditeurs, Paris, 1933.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA]

Reduction of Neodymium at the Dropping Mercury Electrode

BY C. R. ESTEE AND GEORGE GLOCKLER

The polarographic behavior of neodymium in the presence of supporting electrolyte has not previously been described. The present study was undertaken to allow the application of the Ilkovic equation[1] to obtain the *n*-value for the reduction of the trivalent neodymium ion, and to establish under proper polarographic conditions the half-wave potential for the reduction. No evidence of the previously reported[2] two-step reduction from water solutions was obtained.

Experimental

The polarograms were recorded with a Sargent Model XX Visible Recording Polarograph of the Heyrovsky type, the design and operating characteristics of which have recently been discussed by Lingane.[3] A conventional dropping mercury cathode assembly was used, the stand tube being provided with an adjustable mercury reservoir. The usual H-type electrolysis vessel[4] with a sintered glass plug and agar bridge was employed. Measurements were made with respect to a mercury anode. Solution temperatures were maintained at 25.0 ± 0.1° by means of a thermostat. The drop time was varied between two and five seconds. Hydrogen or nitrogen was bubbled through the solution to remove dissolved oxygen.

The neodymium salt was obtained as the nitrate and an examination of the absorption curve found with a Bell and Coleman spectrophotometer showed no detectable impurities. Neodymium oxide was prepared by ignition of the oxalate precipitated from a warm acid solution of the nitrate. The oxide was treated with an excess of sulfuric acid and heated for eight hours at 440° to give the octahydrate of neodymium sulfate. Solutions of supporting electrolytes prepared from analytical grade reagents showed no detectable impurities.

Diffusion coefficients of 6.03×10^{-6} sq. cm./sec. for the neodymium ion and 8.15×10^{-6} sq. cm./sec. for

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[1] Ilkovic, *J. chim. phys.*, **35**, 129 (1938).

[2] Noddack and Brukl, *Angew. Chem.*, **50**, 362 (1937).

[3] Lingane, *Ind. Eng. Chem., Anal. Ed.*, **18**, 734 (1946).

[4] Lingane and Laitinen, *ibid.*, **11**, 504 (1930).

neodymium sulfate were calculated by means of conductance data[5] and the Nernst equation.[6]

Half-wave potentials were measured in the usual manner, with all values being calculated with respect to the saturated calomel anode and corrected for the iR drop in the cell to an accuracy of ±0.01 volt.

Data and Discussion

No Supporting Electrolyte.—No indication of the double waves (Inset, Fig. 1) reported by Noddack and Brukl[2] was found; a single wave (Fig. 1) resulted when water solutions of neodymium sulfate were reduced at the dropping mercury electrode. The suggestion[7] has been made that the first wave reported by Noddack and Brukl[2] might be due to the discharge of hydrogen ion from the hydrolyzed solutions. However, although fresh solutions of both neodymium and praseodymium sulfate were slightly acidic, no indication of such a wave could be found. Recent work by Thomas and Kurbatov[8] with yttrium likewise makes doubtful the existence of the two-step waves reported by Noddack and Brukl.[2]

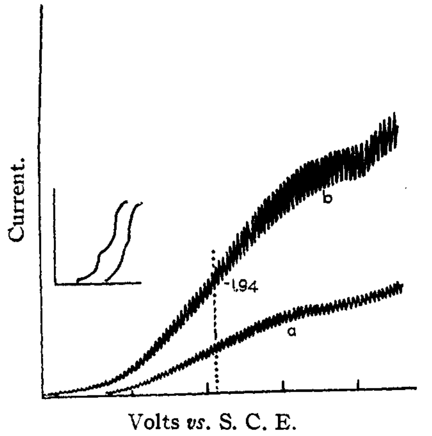

Fig. 1.—Neodymium sulfate, 4.0 molar, no supporting electrolyte. Inset shows curves of Noddack and Brukl.[2]

Lithium Chloride as Supporting Electrolyte.—The half-wave potential was found to vary with the concentration when lithium chloride (0.01% gel added) was used as the supporting electrolyte; no consistent linear relationship between step height and concentration was observed (Table I). The variation in the step heights is probably caused by the simultaneous deposition of hydrogen and neodymium. To separate the two waves sulfuric acid was added to the solutions; as the concentration of acid increased, the hydrogen preceded and was well separated from the neodymium wave (Fig. 2). With the use of 2.0 millimolar sulfuric acid solutions fairly well defined waves were obtained (Fig. 3); the half-wave potential was constant, and a linear relationship between concentration and step height was found.

TABLE I

EFFECT OF CONCENTRATION ON THE HALF-WAVE POTENTIAL OF NEODYMIUM WITH 0.1 MOLAR LiCl AS ELECTROLYTE

Concentration millimoles/l.	$E_{1/2}$	i_d microamp.	i_d/c
1.6	−1.77	17.9	11.2
1.6	−1.78	18.0	11.2
4.0	−1.81	31.1	7.8
4.0	−1.81	28.6	7.2
8.0	−1.83	49.2	6.2
8.0	−1.83	49.6	6.2

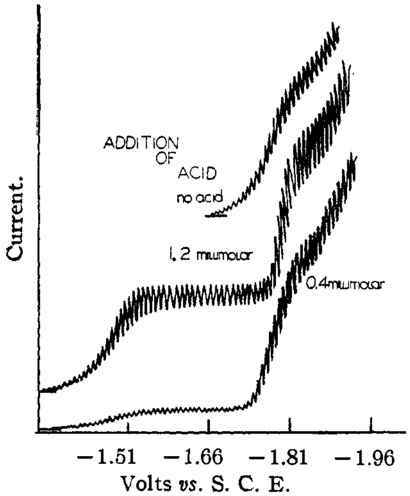

Fig. 2.—Addition of acid with lithium chloride as a supporting electrolyte.

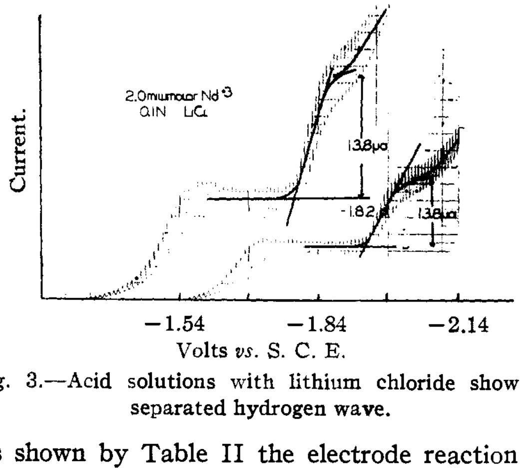

Fig. 3.—Acid solutions with lithium chloride showing separated hydrogen wave.

As shown by Table II the electrode reaction is $Nd^{+3} \rightarrow Nd^0$. The calculated diffusion current was obtained by the use of the Ilkovic equation, assuming that $n = 3$.

Tetramethylammonium Iodide as Supporting Electrolyte.—A single wave (Fig. 4) is obtained from sulfuric acid solutions of this supporting

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(5) "International Critical Tables, Vol. VI," 233 (1933).

(6) W. Nernst, *Z. physik Chem.*, **2**, 613 (1888).

(7) Lingane and Kolthoff, "Polarography," New York Interscience Publishers, Inc., New York, N. Y., Revised Reprint, 1936, p. 305.

(8) Thomas and Kurbatov, Paper No. 16, Division of Physical and Inorganic Chemistry, Atlantic City Meeting, American Chemical Society, April, 1947.

TABLE II

EXPERIMENTAL VALUES OF n WITH 0.1 M LiCl AS SUPPORTING ELECTROLYTE (0.01% GEL + 2.0 MILLIMOLAR H_2SO_4 ADDED)

Concentration millimoles/l.	$E_{1/2}$	i_d exp.	i_d calcd.	n exp.
0.4	−1.82	2.8	2.9	2.9
0.8	−1.82	5.6	5.8	2.9
1.2	−1.82	8.7	8.9	2.9
2.0	−1.82	13.8	14.4	2.9
4.0	−1.82	28.2	29.4	2.9

electrolyte; the apparent second wave in the range −1.94 to −2.04 being characteristic of the supporting electrolyte used. In the absence of acid, variations in half-wave potentials and diffusion currents occur (Table III) which are not evident when a 2.0 millimolar acid solution is used (Table IV). These data serve to indicate that in neutral media the measured diffusion currents are the result of the simultaneous deposition of neodymium and hydrogen since the measured currents are larger than those expected by the application of the Ilkovic equation. When acid is added to cause a definite prewave due to hydrogen the measured diffusion currents are less than those predicted on the basis of the Ilkovic equation; this is to be expected. The diffusion current constant (I_d) obtained in 2.0 millimolar sulfuric acid solution agrees closely with the theoretical value of 4.46 obtained if the reaction at the electrode is assumed to be $Nd^{+3} \rightarrow Nd^0$.

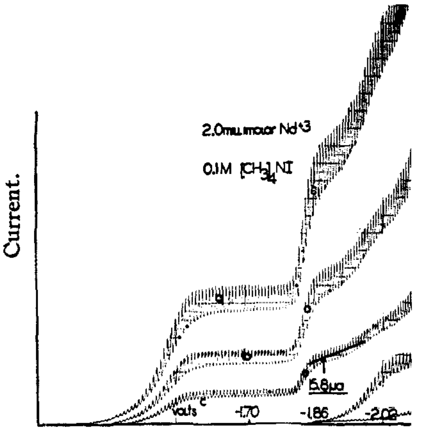

Fig. 4.—Acid solution with tetramethylammonium iodide: recorder sensitivity, (a) 3–75; (b) 3–50; (c) 3–25.

TABLE III

NEUTRAL SOLUTION OF 0.1 M TETRAMETHYLAMMONIUM IODIDE AS SUPPORTING ELECTROLYTE (0.1% GEL ADDED)

Concentration millimoles/l.	i_d exp.	i_d calcd.	I_d exp.	$E_{1/2}$
2.0	16.2	16.0	4.47	−1.80
2.0	15.8	15.9	4.42	−1.80
0.8	6.9	6.5	4.71	−1.73
.8	6.9	..	..	−1.73
.4	3.6	3.2	4.96	−1.75
.4	3.6	3.2	4.94	−1.75

TABLE IV

SULFURIC ACID (2.0 MILLIMOLAR) SOLUTION OF 0.1 M TETRAMETHYLAMMONIUM IODIDE AS SUPPORTING ELECTROLYTE (0.01% GEL)

Concentration millimoles/l.	i_d exp.	i_d calc.	I_d exp.	$E_{1/2}$
2.0	15.6	16.0	4.32	−1.83
2.0	15.9	16.0	4.41	−1.83
0.8	6.4	6.4	4.48	−1.83
.8	6.4	6.4	4.46	−1.83
.4	3.1	3.2	4.26	−1.83
.4	3.2	3.2	4.45	−1.83

Other Supporting Electrolytes.—A single step curve (Fig. 5) was obtained from potassium chloride solutions; half-wave potential was −1.83 from a 2.0 millimolar sulfuric acid solution of 0.1 M potassium chloride. Again the single step indicates the reduction $Nd^{+3} \rightarrow Nd^0$. Ammonium chloride was not satisfactory as a supporting electrolyte, the curves being poorly defined.

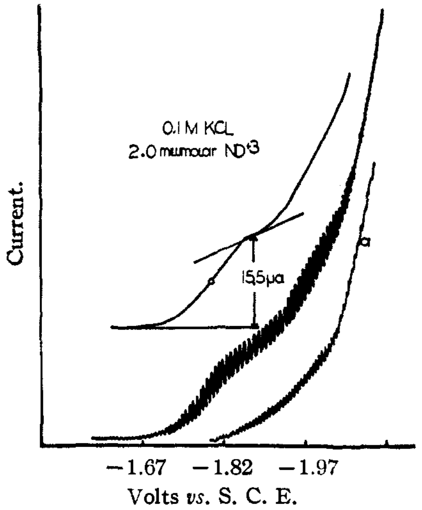

Fig. 5.—Neutral potassium chloride solution: (a) residual current.

Summary

A single wave is obtained from water solutions of neodymium sulfate; this is in contradiction to the results of earlier investigators. Similar single waves are obtained when lithium chloride, tetramethylammonium iodide or potassium chloride is used as supporting electrolyte.

By means of the Ilkovic equation it is shown that the reduction corresponds in all cases to $Nd^{+3} \rightarrow Nd^0$.

The half-wave potentials are found to be dependent upon the concentration and acidity of the solution. From solutions of the above-mentioned electrolytes containing 2 millimoles of sulfuric acid per liter (with 0.01% gel added) diffusion currents proportional to the concentration of neodymium ion were obtained. The half-wave potentials remained constant in the range studied (0.01 *M* and below) at −1.83 ± 0.01 volt *versus* the saturated calomel electrode in all cases.

IOWA CITY, IOWA RECEIVED JUNE 9, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA]

The Half-Wave Potential of Samarium

BY ANDREW TIMNICK AND GEORGE GLOCKLER

Noddack and Brukl[1] who studied the electrolytic decomposition of 0.01 molar rare earth sulfate solutions, containing no supporting electrolyte, report that samarium undergoes a two-step reduction at the dropping mercury electrode. In an earlier report[2] outlining the progress of the work, Brukl announced their intentions of publishing the inflection points, (Knickpunkte) of the *c–v* curves representing the stepwise reduction of the rare earth ions. In the discussion following the report, Hohn[2] suggested that if the half-wave potentials[3] of the steps were reported, the results would be expressed as a reproducible constant which is independent of concentration. It was also suggested that if an indifferent electrolyte were added to the solutions the diffusion current[4] or step height would be directly proportional to the concentration. The advice evidently was disregarded for only the inflection points were reported.[1]

Holleck[5] electrolyzed 0.02 molar samarium chloride solutions, without supporting electrolyte, at the dropping mercury electrode but his interest was the detection of the conversion of the samarium ion from one isoelectronic form to another. He obtained single and double waves, the form varying with methods of preparation of the salt, the temperature of the solution being electrolyzed and with the addition of zinc chloride. Neither half-wave potentials, nor diffusion currents were reported. Divalent samarium compounds have been prepared.[6,7] It is known that samarous ions are stable in aqueous solutions under limited conditions. A two-step reduction can logically be predicted.

The present study was undertaken to evaluate the diffusion current and half-wave potentials of samarium ion from its chloride and sulfate solutions. The influence of concentration, *p*H and supporting electrolyte was also observed.

Experimental Procedure

A 0.02 molar samarium chloride stock solution was prepared with C. P. $SmCl_3 \cdot 6H_2O$. Spectrographic examination indicated only traces of gadolinium and europium. Samarium sulfate was prepared by converting the chloride to the oxide followed by the conversion to the sulfate. This was done by adding excess sulfuric acid to the oxide, heating the resulting mixture to 450° on a hot-plate until the excess acid was decomposed, and followed by heating in a regulated furnace at 600° for two hours to ensure complete acid decomposition and dehydration. The product was recrystallized from water solutions with subsequent acid and heating treatments. Excellent yellow translucent crystals (octahydrate) were obtained, some 5 mm. long, after the third treatment. These were washed, broken up, mixed with sulfuric acid and heated to the anhydrous form. A 0.01 molar samarium sulfate stock solution was made with this material. The salts employed as supporting electrolyte were of C. P. grade. An H-cell with a saturated calomel anode[8] was used. The salt bridges consisted of saturated potassium chloride solution containing 4% agar. The resistance of the cell and calomel electrode was 230 ohms. This value was used to correct the half-wave potentials for *iR* drop when the magnitude of the diffusion current warranted this procedure.

All measurements were made at 25.0 ± 0.1°. Nitrogen was used to remove dissolved air from the solutions. The *m* and *t* values of the Ilkovic equation[4] were found for twenty-five drops of mercury at the applied potential at which the diffusion current was measured. Polarograms were recorded with a Sargent Model XX Polarograph. The operating characteristics of this instrument have been described by Lingane.[9] Accurate checks of applied potential were made with a K-type potentiometer. The polarographic waves for measurement purposes were obtained by connecting the midpoints of the galvanometer oscillations recorded by the instrument. The *p*H of solutions was measured with a glass electrode Type 200 Coleman *p*H Electrometer. This instrument was tested with buffer solutions and found to be accurate to 0.1 unit. The concentration *c* in all cases is expressed in millimoles of samarium ion per liter.

Results and Discussion

Samarium Chloride

No Supporting Electrolyte, No Gelatin.—The preliminary determinations were made with samarium chloride solutions ranging in concentration from 0.5 millimolar samarium ion to 20 millimolar. Some potassium chloride would be expected to diffuse from the agar plug into the solution being electrolyzed, but poorly defined waves were nevertheless obtained.

Supporting Electrolyte, No Gelatin.—Supporting electrolyte media of 1.0 molar potassium chloride, 0.1 molar potassium chloride, 0.1 molar tetramethylammonium iodide, or 0.1 molar lithium chloride, containing 5 millimolar

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[1] W. Noddack and A. Brukl, *Angew. Chem.*, **50**, 362 (1937).

[2] W. Noddack and A. Brukl, *ibid.*, **49**, 533 (1936).

[3] J. Heyrovsky and D. Ilkovic, *Coll. Czechoslov. Chem. Commun.*, **7**, 198 (1935).

[4] D. Ilkovic, *ibid.*, **6**, 498 (1934).

[5] L. Holleck, *Z. Elektrochem.*, **45**, 249 (1939).

[6] C. A. Matigon and E. Cazes, *Compt. rend.*, **142**, 83 (1906).

[7] G. Jantsch, H. Rupig and W. Kunze, *Z. anorg. Chem.*, **161**, 212 (1927).

[8] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 459.

[9] J. J. Lingane, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 734 (1946).