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[8] 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).

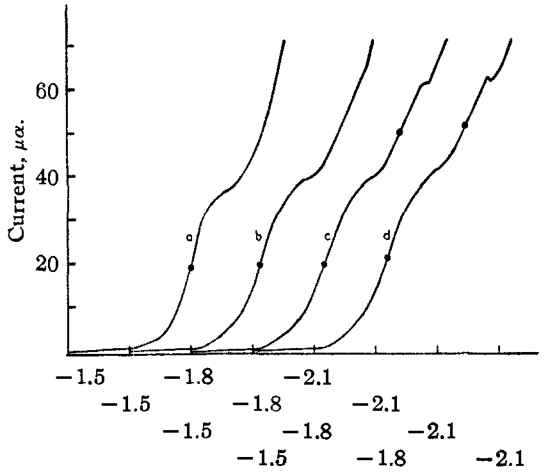

Fig. 1.—Samarium chloride, 5 millimolar, in various media: curves a-d, 1.0 *M* KCl, 0.1 *M* KCl, 0.1 *M* $(CH_3)_4NI$, 0.1 *M* LiCl, respectively.

samaric ion gave rise to well defined first steps as shown by Fig. 1, curves a–d respectively. In the 0.1 molar lithium chloride and 0.1 molar tetramethylammonium medium a second step seems to begin but is apparently terminated by the discharge of the supporting electrolyte. Figure 2 is a representative example of the variation of the ratio i_d/C observed in the polarograms recorded with the samarium chloride solutions shown in Fig. 1. It is evident that the expected proportionality of step height between the first and second step is not attained. Curves a and b are reproductions of the midpoint tracing of polarograms recorded with 0.1 molar tetramethylammonium iodide solutions containing 5 and 2.5 millimoles of samarium chloride, respectively. The residual current is shown by curve c.

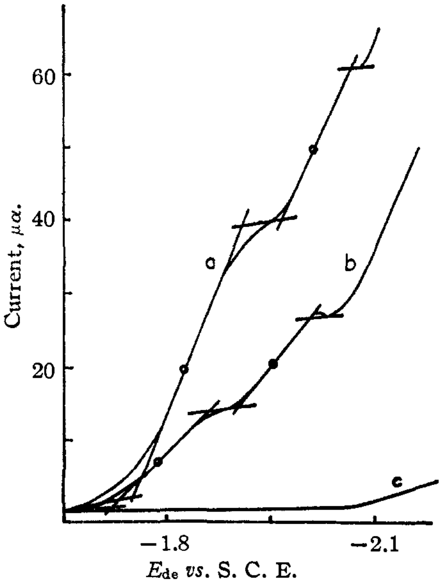

Fig. 2.—Relationship between concentration of samarium chloride and step height in 0.1 *M* tetramethylammonium iodide medium. Curves a and b are recorded with 5 and 2.5 millimolar solutions, respectively; c is the residual current.

Because of this variation in the current–concentration ratio, sulfate solutions of samarium were investigated.

Samarium Sulfate

No Supporting Electrolyte.—Several attempts to reproduce results reported[1] were made employing a mercury pool anode. Stock solutions of samarium sulfate which had stood a month or two yielded no waves, but a three step wave was recorded with a one day old 20 millimolar solution containing no gelatin. Discharge of hydrogen, observed from a wave with a half-wave potential at −1.64 volts against the mercury pool anode, occurred.

Supporting Electrolyte, 0.01% Gelatin.—Polarograms were recorded with various concentrations of samarium in 0.1 molar lithium chloride medium. With concentrations from 5 to 20 millimolar the polarograms consisted of two steps. At lower concentrations the second step terminated in a maximum. The results listed in Table I are corrected for *iR* drop.

Since the reduction of samarium ion proceeds at a potential more negative than the reduction of hydrogen ion, small amounts of dilute sulfuric acid were added to samarium solutions and polarograms recorded.[10] Two waves, one due to hydrogen and the other due to samarium discharge, were observed. In 0.1 molar lithium chloride solution (0.001 normal in sulfuric acid) containing varying concentrations of samarium, the half-wave potential of the hydrogen wave was −1.5 volts against the saturated calomel electrode. As shown in Table II the addition of acid reduced the

TABLE I

SAMARIUM SULFATE, 0.1 *M* LiCl, 0.01% GELATIN, $E_{1/2}$ *vs.* S. C. E.

Concn. Sm^{+++}	*p*H	i_d First step	i_d Second step	$E_{1/2}$ First step	$E_{1/2}$ Second step
20	. . .	113.1	17.7	−1.85	−2.07
10	4.0	55.9	15.2	−1.80	−1.97
5	4.4	28.4	15.4	−1.77	−1.92
2	4.8	10.7	Max.	−1.73	Max.

TABLE II

SAMARIUM SULFATE, $E_{1/2}$ *vs.* S. C. E.
0.1 *M* LiCl, 0.01% gel., 0.001 *N* H_2SO_4
$t = 3.074$, $m^{2/3}t^{1/6} = 1.760$

Concn.	*p*H	i_d	$E_{1/2}$
8	3.1	50.1	−1.82
4	3.1	25.3	−1.81
2	3.1	12.6	−1.79
1	3.0	6.5	−1.80
0.5	3.2	3.0	−1.80

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(10) R. H. Leach and H. Terrey, *Trans. Faraday Soc.*, **33**, 480 (1937).

half-wave potential shift by 0.03 volt in the samarium ion concentration range of 2 to 8 millimoles as compared to a 0.07 volt shift observed in an approximately similar concentration range without acid addition. The diffusion current varied directly with concentration in the acid series. Stabilization of *p*H could possibly explain the improved regularity.

From equivalent conductivity data[11] and application of Kohlrausch's law and the Nernst[12] equation, D was calculated to be 6.07 × 10^{-6} sq. cm. sec.^{-1}. Calculated I_d values for samarium ion would be 1.49 when n is 1 or 4.47 when n is 3. Experimentally the average I_d for the first step of the lithium chloride, sulfuric acid medium series of runs was found to be 3.57 which lies between the two theoretical values cited above. As shown by Fig. 3, a polarogram of the 4 millimolar solution of this series, the second step is terminated before its complete development and therefore no selection of the proper n value can be made. The two polarograms were recorded with the same solution but with different galvanometer sensitivities. The residual current is shown by curve a′.

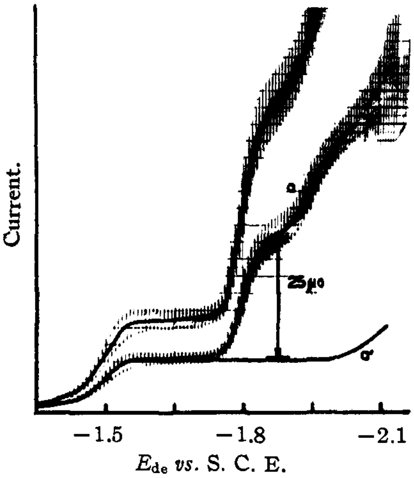

Fig. 3.—Sm^{+++} ion, 4 millimolar, in 0.001 N H_2SO_4, 0.1 M LiCl, 0.01% gelatin medium. Curve a′ is the residual current.

Figure 4 is a polarogram recorded with 4 millimolar samarium ion concentration in a 0.1 molar tetramethylammonium iodide and 0.001 N sulfuric acid medium. A well defined two step wave was obtained with an I_d of 3.56 for the first step and 6.49 for the second. As can be seen the two steps are approximately of equal height. This is not the case for a 1 millimolar solution in a similar medium as shown by Fig. 5. I_d for the first step was 3.85 and for the second 12.1 which would indicate a one electron reduction for the first step and a two electron reduction for the second. The multiple polarogram was recorded with various galvanometer sensitivities. The residual current is shown by curve a′ in Fig. 5.

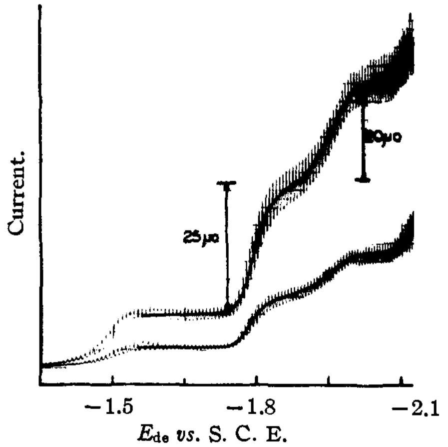

Fig. 4.—Sm^{+++} ion, 4 millimolar, in 0.001 N H_2SO_4, 0.1 M $(CH_3)_4NI$, 0.01% gelatin medium.

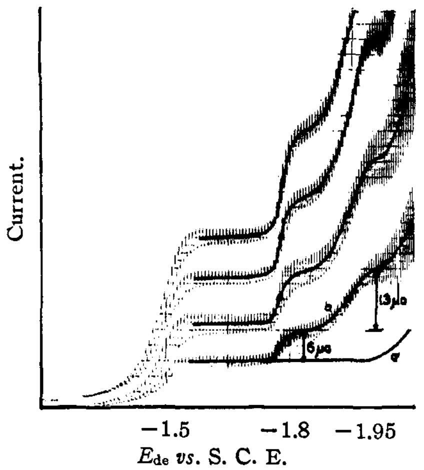

Fig. 5.—Sm^{+++}, 1 millimolar, in 0.001 N H_2SO_4, 0.1 M $(CH_3)_4NI$, 0.01% gelatin medium.

From the preceding observations it is obvious that the discharge of samarium ions at the dropping mercury electrode in aqueous solutions is a complex process. There is evidence of a two-step reduction but in most cases the second step is terminated by discharge of the supporting electrolyte.

It has been noted[6,7] that samarous ion is not very stable in aqueous solutions. It reverts to the samaric state with the evolution of hydrogen. This fact could possibly explain the anomalous results observed, in a manner similar to the case of ytterbium, mentioned by Laitinen and Taebel.[13]

Samarous ion is more unstable[14] than ytterbous ion and therefore hydrogen should be evolved more easily than in the ytterbous case, with greater discrepancy between the expected and ex-

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(11) "International Critical Tables," Vol. VI, p. 233.

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

(13) H. A. Laitinen and W. A. Taebel, *Ind. Eng. Chem., Anal. Ed.*, **13**, 825 (1941).

(14) W. Klemm and W. Schuth, *Z. anorg. Chem.*, **184**, 352 (1929).

perimentally obtained diffusion currents and thus offer an explanation for the anomalous diffusion current constant in the case of samarium.

Acknowledgment.—This work was undertaken while one of us (A. T.) held a graduate college research assistantship at the State University of Iowa.

Summary

Solutions of samarium chloride and sulfate were studied polarographically without supporting electrolyte and in the presence of lithium chloride, potassium chloride and tetramethylammonium iodide. Addition of sulfuric acid to the sulfate solutions stabilized the half-wave potential. With one millimolar samarium ion, in 0.001 normal sulfuric acid, 0.1 molar tetramethylammonium iodide and 0.01% gelatin medium a two step polarogram was obtained. The half-wave potentials were -1.80 and -1.96 volts against the saturated calomel electrode. The diffusion currents were, respectively, 6.0 and 13.0 microamp., corresponding to $Sm^{+++} \rightarrow Sm^{++}$, and $Sm^{++} \rightarrow Sm^0$. However, in 4 millimolar solution the behavior is anomalous.

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[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Capacities at Low Temperatures and Entropies of $3CaO\cdot B_2O_3$, $2CaO\cdot B_2O_3$, $CaO\cdot B_2O_3$, and $CaO\cdot 2B_2O_3$[1]

BY K. K. KELLEY,[2] S. S. TODD[3] AND C. H. SHOMATE[4]

In a recent paper, Torgeson and Shomate[5] presented data for the heats of formation of the crystalline calcium borates, $3CaO\cdot B_2O_3$, $2CaO\cdot B_2O_3$, $CaO\cdot B_2O_3$, and $CaO\cdot 2B_2O_3$. These are all the compounds in the CaO–B_2O_3 system, according to the work of Carlson.[6] The present paper reports low temperature heat capacity and entropy determinations of these same substances, thus enabling the calculation of their free energies of formation. There are no previous similar data for any of these compounds.

Materials.—The samples of calcium borates used in the present measurements were virtually the same as those employed in the heat of formation studies of Torgeson and Shomate.[5] Their paper included the method of preparation of the samples, their densities, and X-ray diffractions, and repetition here appears unnecessary. About one mole of each compound was used in the present measurements and all weighings were corrected to vacuum. The chemical purity of the samples is indicated by the following analyses:

Substance	Actual analysis		Theoretical analyses	
	CaO, %	B_2O_3, %	CaO, %	B_2O_3, %
$3CaO\cdot B_2O_3$	70.75	29.31	70.72	29.28
$2CaO\cdot B_2O_3$	61.71	38.41	61.69	38.31
$CaO\cdot B_2O_3$	44.59	55.26	44.61	55.39
$CaO\cdot 2B_2O_3$	28.57	71.02	28.71	71.29

Only the calcium diborate contained any appreciable impurity. As mentioned by Torgeson and Shomate,[5] this material contained 0.42% of insoluble impurity from superficial reaction with the nickel crucible in which it was prepared. No correction for this impurity was made in the present results.

Heat Capacities.—The heat capacities were measured by means of previously described[7] apparatus and methods. The results, expressed in defined calories,[8] are listed in Table I and shown graphically in Fig. 1. The molecular mass figures in the headings of Table I accord with the 1947 International Atomic Weights.[9] The precision error in the results is under 0.1% and it is believed they are accurate on the average to within ±0.3% in the absolute sense.

The heat capacities of all four calcium borates are higher at the lower temperatures, and lower at the higher temperatures, than the sum of the heat capacities of the component oxides. The greatest average deviation from additivity is shown by $CaO\cdot 2B_2O_3$, the heat capacity of which averages over 2 cal. per deg. per mole lower than the sum of the heat capacities of the component oxides in the temperature range 100 to 298.16°K. In this connection it is of interest to note that this substance also has the highest atomic density (lowest mean atomic volume). Other things being equal, high atomic density generally parallels low heat capacity at low temperatures.

Entropies at 298.16°K.—In each instance, the entropy increment between 52.00 and 298.16°K. (measured portion, Table II) was obtained, as usual, by numerical integration of a large-scale plot of C_p against log T. To obtain the entropy

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[4] Formerly chemist, Pacific Experiment Station, Bureau of Mines.

(5) Torgeson and Shomate, THIS JOURNAL, **69**, 2103 (1947).

(6) Carlson, *Bur. Standards J. Research*, **9**, 825 (1932).

(7) Kelley, Naylor and Shomate, *Bur. Mines Tech. Paper* 686 (1946).

(8) Mueller and Rossini, *Am. J. Phys.*, **12**, 1 (1944).

(9) Baxter, Guichard and Whytlaw-Gray, THIS JOURNAL, **69**, 731 (1947).