[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Cerium Amalgam Electrode and the Thermodynamics of Aqueous Cerium(III) Sulfate Solutions[1]

BY GEORGE C. WALTERS[2] AND THOMAS DE VRIES

The only use which has been made of electrodes prepared from cerium amalgam and whose reactions involve Ce^{+++} ions has been by Müller and Schmidt,[3] who measured the e. m. f. of the cell Ce(Hg, two phase) | $CeBr_3$ (in pyridine) | $AgNO_3$ (in pyridine) | Ag. They also measured the potential of the metal against the two phase amalgam.

In this investigation a study was made of the reproducibility of the cerium amalgam electrode in aqueous solutions, using the cell Ce(Hg, two phase) | $Ce_2(SO_4)_3$ (m) | Hg_2SO_4, Hg. The free energy, heat content and entropy changes of the cell reaction and the activity coefficients of the cerous sulfate were calculated from the e. m. f. measurements at 15, 25 and 35°, using 0.0071 to 0.0937 molal solutions. A saturated solution of cerous sulfate is approximately 0.1 molal at 25°.

Experimental

Purification of the Cerium Material.—The starting material used for obtaining the final purified cerium compound was 500 g. of basic ceric nitrate. This material in itself was of fairly high purity, having been hydrolyzed several times from a neutral solution as a means of purification. The cerium material was treated with concentrated nitric acid and heated to a temperature just below the decomposition of the nitric acid. At this point hydrogen peroxide was added in small amounts with vigorous stirring. Complete dissolution of the starting material was obtained. The solution was diluted to a volume of 20 to 25 liters in a large evaporating dish, then boiled free from hydrogen peroxide and marble added. With marble present it was boiled down to a volume of about 10 liters. This procedure resulted in obtaining a practically neutral solution of the cerium ion. Next about 100 g. of potassium bromate was added to the solution and heated. After oxidation to Ce^{++++} was thought to be complete, 5 liters of water was added and the diluted solution was again heated. Within a short time after the application of heat, a precipitate of white basic ceric nitrate was obtained. Only a portion of the total cerium content was removed by such hydrolysis and the last portion to precipitate was set aside. The foregoing procedure was repeated twice on the freshly precipitated material. A spectrographic analysis of the final purified product showed the presence of traces only of lanthanum, praseodymium and thorium as impurities.

Cerium(III) Chloride.—Pure basic cerium(IV) nitrate was transposed to the hydroxide by heating with 6 N sodium hydroxide for five hours. The cerium(IV) hydroxide was washed with water until the washings were neutral, dissolved in concentrated hydrochloric acid and the resulting solution was evaporated down to a viscous liquid over a Meker burner. Upon cooling, crystals of $CeCl_3 \cdot 7H_2O$ were obtained which had a pale yellow color. The hydrated salt was heated in an electric oven at 45–50° for three hours, this treatment resulting in the transformation of almost all of the hepta-hydrate to the monohydrate.

Cerium(III) Sulfate.—Cerium(III) hydroxide, which was prepared by transposing cerous chloride with 6 N sodium hydroxide, was dissolved in dilute sulfuric acid. During the dissolution of the hydroxide the mixture was kept in a container cooled with ice. Fine crystals of hydrated cerous sulfate crystallized from the solution upon heating since the solubility decreases rapidly with increase of temperature. Three recrystallizations from conductivity water were used to prepare the final product. Stock solutions were made by dissolving the hydrated salt in conductivity water. Solutions of lower concentration were prepared by successive weight dilutions. The solutions were analyzed by oxidizing the cerium with an excess of ammonium persulfate in the presence of a few drops of silver nitrate solution as catalyst. After boiling for five minutes to decompose excess persulfate the cerium content was determined by adding a measured excess of ferrous ammonium sulfate and back-titrating with potassium permanganate solution.

Cerium Amalgam.—Cerium amalgam was prepared by electrolyzing a saturated solution of $CeCl_3 \cdot H_2O$ (25 g.) in ethanol (75 ml.), using purified mercury as the cathode (area about 20 cm.^{2}). The anode was a graphite disk, 2 cm. in diameter, fitted to the end of a graphite rod and placed parallel to and about 2 cm. from the cathode surface. The electrolysis cell consisted of a 250-ml. wide-mouthed Florence flask with a platinum wire sealed into the bottom for an electrical connection. Through a stopper, which fitted the mouth of the flask, were introduced the anode rod, an outlet vent and a stirrer which was so adjusted that it agitated slightly the surface of the mercury cathode. A current of 2.0 amperes was passed through the cell for fifteen to forty hours. Under these conditions a liquid to semi-solid amalgam was formed containing up to 2.7% cerium by weight. The amalgam was washed with water, then with acetone and stored in a glass container in a hydrogen atmosphere.

The cerium amalgam was analyzed by allowing a weighed sample to stand exposed to air for seven to ten days. The resulting cerium(IV) oxide was dissolved in sulfuric acid, diluted and precipitated with oxalic acid. The cerium oxalate was washed with hot water, dried, ignited and weighed as CeO_2.

Mercury(I) Sulfate.—The method of Smith[4] was used to prepare mercury(I) sulfate. One hundred grams of

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[1] Abstracted from the Ph.D. thesis of G. C. Walters.

[2] Present address: Pittsburgh Plate Glass Co., Barberton, Ohio.

[3] R. Müller and H. J. Schmidt, *Monatsh.*, **53**, 224 (1929).

[4] F. E. Smith, *Trans. Roy. Soc.* (London), **A207**, 395 (1908).

pure mercury was treated with 15 ml. of concentrated nitric acid. When all action had ceased the crystals of mercury(I) nitrate that had formed were removed and dissolved in 200 ml. of dilute nitric acid. The solution was allowed to run from a fine-pointed pipet into 1000 ml. of cold dilute sulfuric acid. The mercury(I) sulfate thus formed was washed several times, first with alcohol, then with ether. It was stored in a desiccator.

Apparatus and Procedure.—The apparatus was designed by Ivett and De Vries[5] and their experimental technique was employed in this investigation. Hydrogen was used to displace air from the apparatus and the solutions. It was bubbled through chromium(II) sulfate and copper sulfate successively to remove traces of oxygen[6] and hydrogen sulfide.[7]

Measurements of the potentials of the cells were made at 15, 25 and 35° with cerous sulfate concentrations ranging between 0.0071 and 0.0937 molal. A water thermostat with a maximum deviation of not more than ±0.02° was used. The potentials of one-phase and two-phase cerium amalgams with different cerium content were also measured. These measurements were made at only 25° and the concentration of the cerous sulfate solution was kept constant at 0.0937 molal. The e. m. f. measurements were made with a Rubicon Type B potentiometer. Since the voltages to be measured exceeded the range of the potentiometer, a Weston standard cell was connected in opposition to the cell to reduce the voltage to a measurable value. The voltage of the standard cell was checked before each potential determination. A cell recently checked by the Bureau of Standards was used as the ultimate standard.

Each cell was allowed to stand for at least six hours at constant temperature in order to attain equilibrium. During the potential measurements the amalgam was allowed to flow from the capillary electrode at the rate of one drop every two to three seconds and the cerous sulfate solution was allowed to flow through the cell at about three times that rate While the amalgam was flowing potential measurements were made every fifteen seconds and were practically constant at the end of two minutes. Repeat determinations at several hour intervals gave practically the same value. The results of a typical potential measurement are given in Table I. Due to the high reproducibility of the cell only one cell was prepared in later work for each different electrolyte concentration. The potentials have a probable precision of ±0.1 mv.

TABLE I

VARIATION OF POTENTIAL WITH TIME

Ce(Hg, two phase) $Ce_2(SO_4)_3$ (0.0281 *m*) Hg_2SO_4, Hg

Time, min.	E. m. f., v.
0	2.16058
0.25	55
0.50	53
60.50	60
60.75	58
61.00	51
121.00	51
121.25	53
121.50	55

Calculations

The potential of the cell Ce(Hg, two phase) | $Ce_2(SO_4)_3$ (*m*) | Hg_2SO_4, Hg, may be expressed by the Nernst equation with certain terms transposed as

$$E_{\text{obs.}} + \frac{5RT}{6F} \ln 108^{1/5}m = E^0 - \frac{5RT}{6F} \ln \gamma$$

where the left side of the equation shall be denoted by E'. When the concentration of the electrolyte is low, the mean activity coefficient, γ, is given by an equation based on the Debye–Hückel theory, namely, $\log \gamma = -6A\sqrt{15m}/(1 + B\sqrt{15m})$, in which A and B are constants at a given temperature (*e. g.*, 0.5047 was used for A at 25°). Substituting this value of $\log \gamma$ in the above equation and rearranging terms, the following equation is obtained.

$$E_{\text{obs.}} + \frac{5RT}{6F} \ln 108^{1/5}m - \frac{5ART}{F}\sqrt{15m} = E^0 - (E' - E^0)B\sqrt{15m}$$

If the values on the left side of the equation, sometimes represented by E'', are plotted against $(E' - E^0)\sqrt{15m}$, a straight line should be obtained in the lower range of concentrations and extrapolation to $m = 0$ will give the standard molal potential, E^0, of the cell.[8] Electromotive force measurements were made of approximately 30 cells and the average values are listed in Table II. By a series of approximations the E^0 for the cell was found to be 2.0506, 2.0525 and 2.0543 volts at 15, 25 and 35°, respectively. The results of the last approximation are graphed in Fig. 1.

TABLE II

ELECTROMOTIVE FORCE OF CELLS

m	15°	25°	35°
0.0071	2.1653	2.1715	2.1777
.0170	2.1585	2.1648	2.1709
.0281	2.1543	2.1605	2.1668
.0382	2.1518	2.1579	2.1642
.0529	2.1501	2.1562	2.1625
.0818	2.1451	2.1513	2.1575
.0937	2.1445	2.1507	2.1569

Using the standard molal potential of the mercury–mercurous sulfate electrode at 15, 25 and 35° according to Harned,[9] the E^0 of the Ce(Hg, two phase) Ce^{+++} electrode was calculated to be 1.4275, 1.4373 and 1.4473 volts for 15, 25 and 35°, respectively.

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[5] R. W. Ivett and T. De Vries, THIS JOURNAL, **63**, 2821 (1941).

[6] H. W. Stone, *ibid.*, **58**, 2591 (1936).

[7] Traces of hydrogen sulfide are formed in the chromous sulfate solution, J. R. Branham, *U. S. Bureau Stds. Bull.*, **21**, 45 (1938).

[8] A. S. Brown and D. A. MacInnes, THIS JOURNAL, **57**, 1356 (1935).

[9] H. S. Harned and W. J. Hamer, *ibid.*, **57**, 31 (1935).

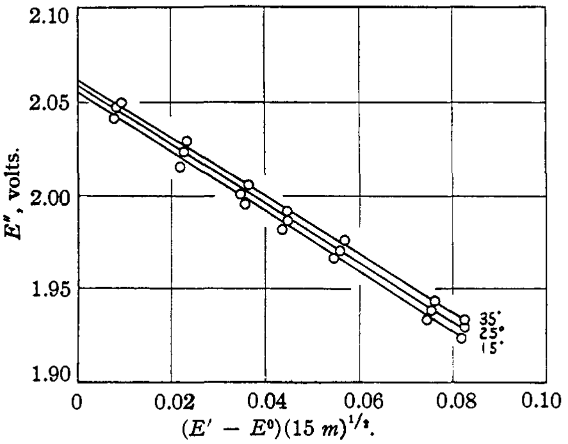

Fig. 1.—Extrapolation to obtain E^0.

According to Müller and Schmidt[3] the difference in potential between pure metallic cerium and the two-phase amalgam is 0.2451 volt at 25°. Using this value, the E^0 of the Ce, Ce^{+++} electrode is calculated to be 1.6824 volt at 25°.

Potentials of Cerium Amalgams of Varying Cerium Content.—The potentials of cells with different cerium amalgam concentrations were determined at 25° with a constant cerium(III) sulfate concentration of 0.0937 molal. The data for all the measurements are given in Table III and the plot of potential against the logarithm of the cerium concentration is shown in Fig. 2. By the method of least squares the intersection was calculated to be at 0.312% cerium, by weight, above which concentration a two-phase amalgam exists.

TABLE III

VARIATION OF POTENTIAL WITH CERIUM CONCENTRATION

Cerium, %	E. m. f., v.	Cerium, %	E. m. f., v.
1.522	2.15073	0.256	2.14841
1.160	2.15072	.223	2.14526
0.746	2.15071	.182	2.14580
.540	2.15073	.163	2.14460
.404	2.15070	.141	2.14385
.382	2.15069	.066	2.13683
.315	2.15074		

Mean Activity Coefficients of Cerous Sulfate.—Values of the mean activity coefficients of cerous sulfate were calculated at concentrations at which measurements had been made by using the equation $5RT/6F \ln \gamma = E^0 - E'$. At other concentrations the values were obtained by substituting the values of B, the slopes of the lines in Fig. 1, in the Debye–Hückel equation. The values of B were 1.3433, 1.3679 and 1.3653 at 15, 25 and 35°, respectively. The values of γ are tabulated in Table IV, together with the γ of indium sulfate[10] at 25° for comparison purposes.

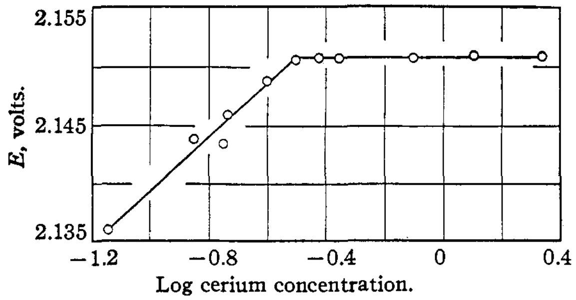

Fig. 2.—Potential of cell with varying cerium concentration at 25° with 0.0937 m $Ce_2(SO_4)_3$.

TABLE IV

ACTIVITY COEFFICIENTS OF CEROUS SULFATE

m	15°	25°	35°	$In_2(SO_4)_3$, 25°
0.0071	0.210	0.207	0.202	
.0100	.174	.171	.167	0.142
.0170	.123	.121	.116	
.0200	.115	.112	.109	.095
.0281	.092	.090	.087	
.0300	.089	.087	.085	.071
.0382	.077	.074	.072	
.0400	.074	.072	.070	
.0500	.065	.063	.061	.054
.0529	.060	.055	.056	
.0600	.055	.053	.051	
.0700	.051	.050	.049	
.0800	.049	.048	.047	
.0818	.049	.047	.045	
.0900	.045	.044	.043	
.0937	.043	.042	.041	
.1000	.042	.041	.040	.035

Free Energy, Heat and Entropy Changes of the Cell Reaction.—In Table V are given the free energy and heat changes for the cell reaction $2Ce + 3Hg_2SO_4 = Ce_2(SO_4)_3(aq.) + 6Hg$. The heats of the reaction were calculated from the change of e. m. f. with temperature, using the Gibbs–Helmholtz equation. A constant value of 85.8 was obtained for ΔS, equal to $-d(\Delta F)/dT$. The probable error of the e. m. f. measurements was about 0.1 mv., therefore the values of

TABLE V

ΔF AND ΔH OF THE REACTION $2Ce + 3Hg_2SO_4 = Ce_2(SO_4)_3(aq.) + 6Hg$

m	$E_{25°}$	ΔF	ΔH
0.0071	2.4166	−334,360	−308,790
.0170	2.4099	−333,430	−307,860
.0281	2.4056	−332,840	−307,270
.0382	2.4030	−332,480	−306,910
.0529	2.4013	−332,240	−306,670
.0818	2.3964	−331,570	−306,000
.0937	2.3958	−331,480	−305,910

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(10) E. M. Hattox and T. De Vries, THIS JOURNAL, **58**, 2126 (1936).

ΔF are accurate to about 25 cal., those of ΔH to about 100 cal. and the value of ΔS to about 0.5 cal. per degree.

We thank D. W. Pearce of this Laboratory for his helpful suggestions concerning the purification and preparation of the cerium compounds.

Summary

A two phase cerium amalgam has been used as an electrode with cerium(III) sulfate solutions. The standard molal potential has been calculated for 15, 25 and 35° from the data. From the measurement of the cell potentials it was determined that a two phase cerium amalgam is obtained at concentrations greater than 0.312% cerium by weight. The mean activity coefficients of cerous sulfate from 0.007 *m* to saturation and the free energy, heat and entropy changes for the cell reaction have been calculated.

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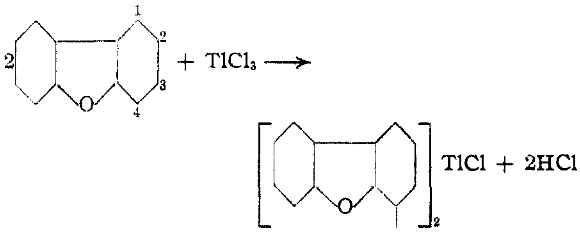
NOTES

The Direct Thallation of Dibenzofuran[1]

BY HENRY GILMAN AND R. K. ABBOTT, JR.

In view of the known direct replacement of nuclear hydrogen by gold (auration) and by mercury (mercuration), it appeared that a similar substitution should take place with thallium (thallation). We have observed that a reaction of this kind does take place with dibenzofuran and thallium trichloride. The position of thallation was established by treating the R_2TlCl compound with iodine to give the known 4-iododibenzofuran. It is interesting to note that all metalations of dibenzofuran (by metals, inorganic salts or RM compounds) involve the 4-position, which is not the case with some related heterocycles like dibenzothiophene.[2] The metalation reaction which has been shown to take place with gold, mercury and thallium does not appear to take place to any significant extent with related lead compounds.



Although trivalent thallium forms complexes[3] with many compounds, these have not been converted to carbon–thallium types. We had no success in attempts to rearrange the thallium trichloride–pyridine complex[4] to a dipyridylthallium chloride. Goddard,[5] some years ago, tried a related reaction with the thallium trichloride complex of *p*-aminophenylmercury chloride. Numerous complexes have been prepared of thallium trichloride with diazonium salts,[6] but there is no record of their having been converted to organothallium compounds. Various phenols have been treated with thallium trichloride and thallium tribromide.[7] In some of these reactions a complex is formed; in others, the thallium trichloride acts as a chlorinating and oxidizing agent, being reduced to thallous chloride. This latter mode of reaction is common with many amines. For example, Renz[8] showed that α-naphthylamine hydrochloride is oxidized to a deep violet dye, in striking contrast to β-naphthylamine hydrochloride which gives a crystalline complex.

There is no significant tendency for a thallous salt to undergo oxidation–reduction to a trivalent thallic salt and metallic thallium. Exploratory experiments in which thallous acetate was heated with furan, thiophene, dibenzofuran and N-phenylcarbazole gave in every case complete recovery of the thallous acetate.

Experimental

In a three-necked flask equipped with nitrogen inlet, stirrer and short delivery tube were placed 31 g. (0.1 mole) of thallium trichloride, as a saturated aqueous solution,

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[1] Paper XLVIII in the series "Relative Reactivities of Organometallic Compounds."

[2] Gilman, Meals, O'Donnell and Woods, THIS JOURNAL, **65**, in press (1943).

[3] Meyer, *Z. anorg. Chem.*, **24**, 321 (1900); Rabe and Steinmetz, *Ber.*, **35**, 4447 (1902).

[4] Meyer, *Ber.*, **35**, 1319 (1902).

[5] Goddard, *J. Chem. Soc.*, **123**, 1161 (1923).

[6] Nesmeyanov, Kocheshkov and Klimova, *Ber.*, **68**, 1877 (1935); Nametkin and Mel'nikov, *J. Gen. Chem.* (U. S. S. R.), **5**, 373 (1935); Kocheshkov and Nesmeyanov, *ibid.*, **6**, 144 (1936).

[7] Mel'nikov and Gracheva, *ibid.*, **7**, 467 (1937); see also Marino, *Gazz. chim., ital.*, **371**, 55 (1907).

[8] Renz, *Ber.*, **35**, 1110, 2768 (1902).