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CERIC-CEROUS SULFATES

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THE FORMAL OXIDATION POTENTIAL OF THE CERIC-CEROUS SULFATES

By

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A THESIS

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The Formal Oxidation Potential of the Ceric-Cerous Electrode
in the Presence of Ammonium Sulfate

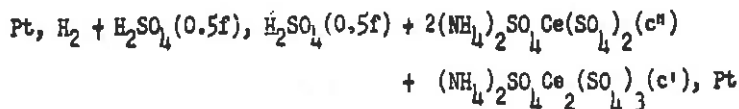
The oxidation-reduction potential of ceric and cerous salts has been studied by Baur and Glaessner (1), Kunz (2), Noyes and Garner (3), Smith and Getz (4), and Sherrill, King, and Spooner (5). Each of these authors has published one or more value, depending on the anion and the amount of acid present. Thus Baur and Glaessner obtained values of 1.84 and 1.70 volts in nitric and sulfuric acids respectively. Kunz obtained values of 1.444 and 1.460 in 1.0 and 0.5 molal sulfuric acid respectively. Noyes and Garner have published potential values of 1.6104, 1.6096, and 1.6085 volts for the cerous-ceric electrode in 2.0, 1.0, and 0.5 molal nitric acid respectively. Smith and Getz studied cerium chlorides, sulfates, nitrates, and perchlorates in the respective acids and obtained values in the order given ranging between 1.28 for chloride to 1.64 for perchlorate. Sherrill, King, and Spooner found the said standard potential, in perchlorate medium, to vary with the concentration of perchloric acid between 1.640 and 1.731 volts.

Ceric and cerous ammonium sulfates exhibit a greater solubility and greater stability in sulfuric acid solutions. Further, cerium solutions are often used volumetrically in the presence of ammonium salts. For these reasons, Ewing and Saltonstall (6) have measured the potential of the ceric-cerous electrode in sulfuric acid solution, utilizing double salts of cerium, ceric and

cerous ammonium sulfates, and with measurements at 15°, 25°, and 35°C have obtained a temperature coefficient for this cell. Recent completely independent measurements of the ceric-cerous electrode made in this laboratory with ceric and cerous ammonium sulfates, have corroborated results obtained by Ewing and Saltonstall.

The purposes of this investigation were, then, to measure the potential of the ceric-cerous electrode in sulfuric acid solution, utilizing double salts of cerium, ceric, and cerous ammonium sulfates; to determine the effect of the ammonium sulfate upon the potential of the electrode, and from these data to calculate the decrease in free energy and decrease in heat content for the reaction $\frac{1}{2}H_2 + Ce^{++++} - e \rightarrow Ce^{+++} + H^+$

The cell measured was:



Apparatus and Materials

Preparation and Analysis of Solutions.-Ceric and cerous ammonium sulfates corresponding to the formulas $2(\text{NH}_4)_2\text{SO}_4\text{Ce}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4\text{Ce}(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ were prepared especially for this work (7). A saturated solution of each of these salts was made in 0.5M sulfuric acid. The ceric salt was reduced with 30% hydrogen peroxide and an absorption spectrum was taken on each of these solutions using a 5cm. cell in a Cenco-Shearn Spectrophotometer. Since no absorption bands could be found, other rare-earth salts were presumed to be absent.

Lanthanum ammonium sulfate was added by increments to one of the cells until its concentration represented 10% of the salts present. The effect of this added impurity could not be detected.

A stock solution of 0.5000 ± 0.0005 molal sulfuric acid was made by diluting the acid with conductance water. The pre-calculated amounts of cerium salts needed were added to a portion of this acid. This solution was then analyzed according to the methods of Willard and Young (8), using o-phenathroline ferrous complex as indicator. A correction was made for the ferrous iron present in the indicator. The ferrous sulfate solution was standardized immediately before use with a ceric sulfate solution which had been standardized against a Bureau of Standards sodium oxalate. The method of Walden, Hammett, and Chapman (9) was

followed. Analyses for ceric and cerous cerium were made before and after a potential measurement and the latter analyses were used in calculations. Weight burettes were used throughout. All cerium concentrations are expressed in millimoles of cerium per thousand grams of solution.

The Electrolytic Cell.-The assembled cell consisted of four electrodes. Each half-cell, constructed from pyrex tubing, was closed by a ground glass joint bearing platinum electrodes. Each cerium electrode is connected to each hydrogen electrode through a flowing junction (10). This design permits the potential to be measured four ways and all values given are the average of four such measurements.

Hydrogen for the reference electrode was generated by electrolysis of a 15% solution of sodium hydroxide between nickel gauze electrodes. The gas was passed over a heated platinum spiral and through a saturating vessel containing sulfuric acid of the same concentration as that used in the half-cell. Nitrogen was passed through the cerium solution to exclude air and to gently agitate the solutions. Tank nitrogen was used after purification by bubbling through alkaline pyrogallol solution, washing with water, and passing over a heated copper gauze in a combustion furnace. The gas was passed through a saturator prior to entry into the cerium half-cells. Vapor traps assured a hydrogen, or a nitrogen, atmosphere and the entire apparatus was immersed in a bath maintained at 15.00, 25.00 or 35.00 \pm 0.01° C.

Platinum electrodes in the cerium half-cells were bright while those in the hydrogen half-cells were prepared according to the directions of Popoff, Kunz, and Snow (11) with the exception that they were not gold-plated.

Method of Potential Measurements.-Early measurements were carried out with a Queen Standard potentiometer, Model E-3040, in conjunction with a Leeds and Northrup Type R galvanometer. Recent duplicate values were obtained with a Wolff potentiometer, No. 7012, and a similar galvanometer. The system was shielded in the manner recommended by White (12). An Eppley standard cell, measured and certified by the U. S. Bureau of Standards, was the standard of e.m.f.

The cerium half-cells were flushed out with purified nitrogen for a time and hydrogen half-cells were flushed with purified hydrogen. The half-cells, the inlet tubes and traps, and the corresponding half of the flowing junction were rinsed several times with the solutions to be studied before filling. The complete cell unit was inserted in the constant temperature bath with very slow flow of hydrogen and nitrogen. The flowing junction was operated only a few minutes before taking a measurement.

Readings were taken every one or two hours until equilibrium values reoccurred. Only those values which checked four ways, i.e., against both hydrogen electrodes, were accepted as equilibrium values.

The partial pressure of the hydrogen gas was calculated as outlined by Ellis (13) except that no allowance was made for the variation of gravity at this latitude.

The Observed and Computed Electromotive Forces

In Table I are recorded the electromotive forces at various concentrations and at three temperatures. The formal oxidation potential E_f^0 has been derived with the electrode potential equation and the following considerations.

The change of state in the cells considered and for the passage of one faraday may be represented by $\frac{1}{2}H_2 + Ce^{++++} \rightarrow Ce^{+++} + H^+$ and the electromotive force is given by

$$E = E^0 - \frac{2.303RT}{F} \log \frac{a_{Ce^{+++}} \times a_{H^+}}{a_{Ce^{++++}} \times P_{H_2}^{1/2}}$$

where a denotes activity. Nothing is known of the activities of the ceric and cerous ions so that, in conformity with current methods for estimating oxidation-reduction potentials, concentrations are used in place of activities; that is, the ratio of the activity coefficients of the cerous and ceric ions is assumed to be unity.

The activity coefficient of the hydrogen ion is constant in all cells since the sulfuric acid concentration is constant. This quantity is difficult to estimate since it arises from an unsymmetrical electrolyte and non-thermo-dynamic assumptions become necessary. For these reasons, the correction is not made.

Thus all values are referred to the hydrogen electrode in 0.5 molal sulfuric acid. This method of calculation allows direct comparison of our data with values published by Kunz (2), who performed similar experiments with the ordinary ceric and cerous sulfates. At the same time sufficient data is included to allow future correction for reference to the standard hydrogen electrode. Mean activity coefficients of sulfuric acid are now available but their use in cases such as this is questionable. This point is under consideration.

The last column of Table I is thus calculated with the Equation:

$$E_{\text{(observed)}} = E_f^0 - \frac{2.303RT}{F} \log \frac{C_{\text{Ce}^{+++}}}{C_{\text{Ce}^{++++}} \times P_{\text{H}_2}^{1/2}}$$

Those cells marked "S" are measurements of Saltonstall (6); those marked "L" are measurements of McCallum (1947).

TABLE I

Observed and Corrected Electromotive Forces at 15, 25, and 35°C.

Temp.	Cell #	Ce ⁺⁺⁺⁺ + Ce ⁺⁺⁺	Ce ⁺⁺⁺ /Ce ⁺⁺⁺⁺	E (observed)	E _F ^o (volts)	
15°C.	1M	20.28	1.014	1.4603	1.4610	
	2S	19.84	1.013	1.4604	1.4612	
	4S	15.86	1.013	1.4608	1.4617	
	11S	12.00	1.025	1.4618	1.4624	
	1M	11.94	1.012	1.4623	1.4631	
	15S	8.059	1.034	1.4618	1.4631	
	22S	5.296	1.699	1.4502	1.4639	
	25S	4.042	1.051	1.4623	1.4641	
	28S	2.025	1.055	1.4630	1.4649	
	25°C.	5M	20.28	1.014	1.4570	1.4577
3S		19.85	1.013	1.4569	1.4582	
5S		16.05	1.016	1.4578	1.4589	
13S		11.94	1.012	1.4583	1.4595	
2M		11.94	1.012	1.4592	1.4595	
19S		7.954	1.021	1.4591	1.4604	
24S		5.323	1.692	1.4468	1.4610	
27S		2.007	1.057	1.4597	1.4619	
35°C.		6M	20.28	1.014	1.4541	1.4547
		1S	19.86	1.020	1.4532	1.4558
	7S	16.00	1.007	1.4551	1.4565	
	9S	12.08	1.027	1.4555	1.4572	
	3M	11.94	1.012	1.4562	1.4576	
	20S	7.962	1.026	1.4563	1.4582	
	23S	5.299	1.701	1.4436	1.4586	
	26S	2.012	1.058	1.4570	1.4596	

Summary and Discussion

It may be seen from Table I that the formal oxidation potential, E_f^0 , is decreased by an increase in the concentration of the cerium salts. This effect is opposite to that observed by Kunz. At 25°C. an extrapolation to zero concentration of cerium leads to a value of 1.4626 volts. This is the value which should include no liquid-junction potential and may be compared with Kunz's formal oxidation potential of 1.4602 volts.

The effect of ammonium sulfate upon the formal oxidation potential of the ceric-cerous electrode in sulfate medium is small (at most 4.0mv in the range studied.) Its presence, however, tends to decrease the observed electro-motive forces. Kunz has demonstrated that a decrease is also produced by additional sulfuric acid.

Table II has been obtained by a graphical extrapolation to zero cerium concentration. The formal oxidation potentials thus obtained were used in the calculation of the temperature coefficient of the cell, the decrease in free energy ($-AF$), and the decrease in heat content ($-\Delta H$) for the reaction $\frac{1}{2}H_2(1 \text{ atm.}) + Ce^{++++} \longrightarrow Ce^{+++} + H^+$ in 0.5 molal sulfuric acid. The Gibbs-Helmholtz equation was used for the calculation of $-\Delta H$.

TABLE II

Temp. (°C)	Temperature Coefficient (Volts/degree)	- ΔF (calories)	- ΔH (calories)	E _f ^o (volts)
15	-0.00033	36,033	33,795	1.4656
25	-0.00027	35,547	33,726	1.4626
35	-0.00020	35,050	33,673	1.4603

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The Formal Oxidation Potential of the Ceric-Cerous Sulfates

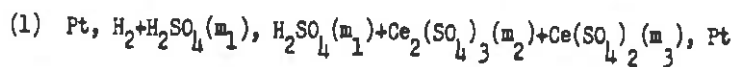
Oxidation-reduction potentials of ceric-cerous salts have been reviewed in our previous paper (1). All these previous determinations have been carried out in solutions with relatively high acid concentrations. Kunz (2) measured the potentials in 0.5 and 1.0 molal sulfuric acid. Noyes and Garner (3) made measurements in 0.5, 1.0, and 2.0 molal nitric acid. Smith and Getz (4) extended the measurements to acid concentrations as high as 8 normal. Sherrill, King, and Spooner (5) have measurements in perchloric acid from 0.2 to 2.4 molal. In all these studies, the concentration of the cerium salts was of the order of 0.001 to 0.1 molal.

Kunz, and Noyes and Garner, found little change in potentials for different acid concentrations in sulfate or nitrate solutions, but Smith and Getz and Sherrill, King and Spooner found the potential to increase over 100 millivolts as the concentration of perchloric acid increased. This effect is opposite to that observed in sulfate medium where Kunz has shown an increase in concentration of sulfuric acid produces a decrease in the computed e.m.f.

Ceric salts hydrolyze easily but extended measurements to the more dilute acid concentrations should provide additional insight to the discrepancies that exist in ceric-cerous systems. To this end two series of measurements have been carried out in

the more dilute solutions; one in which the concentration of cerium sulfates was kept constant and the sulfuric acid content was lowered and a second in which the concentration of all constituents was decreased by the simple addition of water.

Measurements were made on cells of the type,



The measurements on Series II have been carried out at three temperatures.

Apparatus and Materials

Preparation and Analysis of Solutions.--Cerium salts purchased from the G. F. Smith Chemical Co. were used. Ceric hydrogen sulfate, calculated as $\text{Ce}(\text{HSO}_4)_4$, was analyzed to be 91% pure. This salt was used without further purification. The cerous sulfate was heated at 400-450° C according to directions by Mellor (6). This dried salt, calculated as $\text{Ce}_2(\text{SO}_4)_3$, was analyzed to be 90% pure and was used in this form.

A saturated solution of each of the salts was made in 0.5m sulfuric acid. The ceric salt was reduced with C. P. 30% hydrogen peroxide and an absorption spectrum was taken on each of these solutions using a 5cm. cell in a Genco-Shear Spectrophotometer. Since no absorption bands could be found, the remaining percentage impurities of the above cerium salts was assumed to be water.

The cell solutions for the first series of measurements were made up as follows. A stock solution of 0.5000 ± 0.0005 molar sulfuric acid was made by diluting the acid with a good grade of conductance water. For the first cell, the pre-calculated amount of cerium salts needed to make the solution 0.005m with respect to $\text{Ce}(\text{SO}_4)_2$ and 0.0025m with respect to $\text{Ce}_2(\text{SO}_4)_3$ were added to a portion of this acid. This solution was then analyzed according to the methods of Willard and Young (7) using o-phenanthroline ferrous complex as indicator. In this and

subsequent cells, a correction was made for the ferrous iron present in the indicator. The ferrous sulfate solution was standardized immediately before use with a ceric sulfate solution which had been standardized against a Bureau of Standards sodium oxalate. The method of Walden, Hammett, and Chapman (8) was followed. Analyses for ceric and cerous cerium were made before and after a potential measurement and the latter analyses were used in calculations. For the remaining cells of this first series, a portion of the stock acid was diluted with conductance water and standardized. The resulting acid solution was then divided, cerium salts being added to half, as above, while the other half was used for the hydrogen electrode.

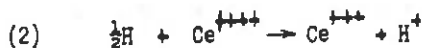
The cell solutions for the second series of measurements were obtained from two stock solutions. These solutions were prepared by making a large quantity of approximately 0.5M sulfuric acid. This was standardized and divided. To half was added cerium salts as for cell #1 in the first series. A portion of each stock solution was then diluted with water in exactly the same manner so that the sulfuric acid content in each solution would be the same. Standardization of each was carried out before and after a measurement at each temperature and the average of all analyses were used in the calculations.

The Electrolytic Cell and Method of Potential Measurements are exactly the same as described in our previous paper (1) to which the reader is referred for details. For observed potentials

beyond the range of the potentiometer, a secondary standard cell was placed in series.

The Observed and Computed Electromotive Forces

The change of state for the passage of one Faraday through cell (1) may be represented by



and the electromotive force is evaluated by the thermodynamic equation

$$(3) \quad E = E^{\circ} - \frac{RT}{F} \ln \frac{a_{Ce^{+++}} a_{H^+}}{a_{Ce^{++++}} a_{H_2}} + E_L$$

where E_L arises from the small amount of cerium present in one half-cell, and a denotes activity.

As nothing is known of the activity of the cerous and ceric ions and since the activity of the hydrogen ion in sulfuric acid is unknown, current methods for estimating oxidation-reduction potentials employ a quantity known as the "formal" oxidation-potential, $E^{\circ}(\text{formal})$. This is taken to mean the potential exhibited when all constituents are present in the amount of one formula weight per thousand grams of solvent without regard to ionization. Further, Kunz, Noyes and Garner, and our previous paper have shown that E_L of equation (3) is practically negligible so that under these conditions

$$(4) \quad E^{\circ}(\text{formal}) = E + \frac{RT}{F} \ln \frac{m_{Ce^{+++}} m_{H^+}}{m_{Ce^{++++}} m_{H_2}}$$

The electromotive forces at various concentrations of total cerium and sulfuric acid are recorded in Table I. The last column, E° (formal) was calculated by means of equation (4). The molality of the hydrogen ion is taken to be twice that of the sulfuric acid.

TABLE I

Observed and Computed Electromotive Forces

Series #	Temperature	Cell #	m_{Ce_3} x10	m_{Ce_2} x10	m_{H}	P_{H_2}	E (observed)	E° (formal) (volts)
I	25°C.	6	5.474	5.346	1.0000	0.9500	1.4609	1.4617
		7	5.220	5.035	0.6142	.9549	1.4714	1.4605
		8	8.144	5.285	.3928	.9550	1.4690	1.4567
		9	4.972	5.224	.2934	.9500	1.4841	1.4521
		10	4.996	5.081	.2026	.9480	1.4836	1.4428
II	25°C.	13	5.738	5.735	1.0032	0.9522	1.4619	1.4625
		16	2.896	2.808	0.4970	.9505	1.4767	1.4615
		17	1.974	1.886	.3300	.9562	1.4867	1.4599
		21	1.182	1.079	.1967	.9482	1.4990	1.4602
		24	0.7336	0.6735	.1222	.9526	1.5101	1.4589
		27	0.3718	0.3058	.06134	.9425	1.5185	1.4526
II	15°C.	11	5.738	5.735	1.0032	0.9537	1.4647	1.4652
		14	2.896	2.808	0.4970	.9696	1.4809	1.4658
		18	1.974	1.886	.3300	.9778	1.4900	1.4639
		22	1.182	1.079	.1967	.9711	1.5020	1.4643
		23	0.7336	0.6735	.1222	.9621	1.5134	1.4639
		26	0.3718	0.3058	.06134	.9634	1.5255	1.4616
II	35°C.	12	5.738	5.735	1.0032	0.9363	1.4596	1.4604
		15	2.896	2.808	0.4970	.9355	1.4734	1.4577
		19	1.974	1.886	.3300	.9363	1.4835	1.4562
		20	1.182	1.078	.1967	.9237	1.4956	1.4559
		25	0.7336	0.6735	.1222	.9176	1.5061	1.4538
		28	0.3718	0.3058	.06134	.9328	1.5089	1.4409

Discussion and Summary

Two cells shown in Table I showed visible evidence of hydrolysis. These are Cells #10 and #28. Excluding these values, we see that the formal oxidation potential is practically constant over a 15 fold change of concentration of any or all constituents. There is a tendency for $E^{\circ}(\text{formal})$ to decrease as the amount of acid decreases. However, neglecting this trend for the time being, we obtain the following averages:

$$15^{\circ} \quad E^{\circ}(\text{formal}) = 1.4634 \pm 0.003 \text{ volts}$$

$$25^{\circ} \quad E^{\circ}(\text{formal}) = 1.4587 \pm 0.006$$

$$35^{\circ} \quad E^{\circ}(\text{formal}) = 1.4568 \pm 0.004$$

These values may be compared with values obtained by Kunz and in our previous paper when calculated with equation (4):

$$\text{Kunz} \quad \left\{ \begin{array}{lll} 25^{\circ} & 0.5\text{m H}_2\text{SO}_4 & E^{\circ}(\text{formal}) = 1.4603 \\ 25^{\circ} & 1.0\text{m H}_2\text{SO}_4 & E^{\circ}(\text{formal}) = 1.4611 \end{array} \right.$$

$$\begin{array}{l} \text{Ewing,} \\ \text{Saltonstall,} \\ \text{and} \\ \text{McCallum} \end{array} \quad \left\{ \begin{array}{lll} 15^{\circ} & 0.5\text{m H}_2\text{SO}_4 & E^{\circ}(\text{formal}) = 1.4656 \\ 25^{\circ} & " & E^{\circ}(\text{formal}) = 1.4626 \\ 35^{\circ} & " & E^{\circ}(\text{formal}) = 1.4603 \end{array} \right.$$

The above values are seen to be well within the limits indicated and thus extend the range of applicability of equation (4) over a concentration range greater than thirty fold. The greatest discrepancy, however, is the constancy with which the formal potentials increase with increasing acid concentration. This effect corroborates that observed by Sherrill, King, and Spooner in

perchlorate medium and is opposite to the lowering of potential which is often inferred from Kunz's data.

Equation (4) and "formal" oxidation potentials in general are non-thermodynamic in that no allowance is made for incomplete chemical dissociation, activities, or the liquid junctions which are usually present. Such potentials are, however, of great practical use and the above data does show that equation (4) gives practically constant values over a wide range of concentrations.