metal atom in the monomer and dimer, respectively. Although z will be positive, and may generally equal +2, the measured entropy changes for dimerization of both the $FeOH^{2+}$ and $CeOH^{3+}$ ions are negative. The loss in independent motion that the monomeric ions experience upon combination would contribute toward negative entropy changes. It is also likely that a dimeric ion of charge $+2n$ would exert a greater restrictive influence over surrounding water molecules than would two monomeric ions of charge $+n$. As yet no satisfactory approach has been made toward the quantitative estimation of entropies for these dimerization reactions. Before this problem can be attacked profitably, entropies for other dimerization reactions should be obtained.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

An Investigation of the Species Existing in Nitric Acid Solutions Containing Cerium(III) and Cerium(IV)[1]

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Extraction data and electromotive force measurements are interpreted as indicating the existence of cerium(IV)-cerium(IV) and cerium(IV)-cerium(III) polymers in 5.5 f nitric acid solutions. If the polymers are assumed to be dimers, the association constants for the reactions $2Ce^4 = (Ce^4)_2$, $Ce^4 + Ce^3 = Ce^4Ce^3$ in this medium are 17 ± 2 and 2.0 ± 0.7 at 30.0 ± 0.03° where total concentration of monomer and of dimer are used in the equilibrium expressions. Contradictory reports in the literature are reconciled by the existence of these dimeric species. The cerium(IV) species extracted by ether is shown to contain no ionizable hydrogen.

Introduction

The fact that ceric cerium forms complex ions with various anions has been known for some time.[2] The formal electrode potentials vary from −1.2 to −1.7 depending upon whether the solution contains hydrochloric, sulfuric, nitric or perchloric acids. Cerium(IV) migrates to the anode in 1 f[3a, 3b] sulfuric acid and in 6 f nitric acid; but it travels to the cathode in 1.8 f sulfuric acid and does not migrate in 2 f nitric acid. The formation constants for the various sulfate complexes of cerium(IV) have been measured.[4] More recently the ability of cerium(III) to form complex ions has been verified.[5] Several independent methods have been employed[6] to show the existence of cerium(IV) polymers in perchloric acid solutions even at high acidities. In spite of the existence of cerium(IV) complexes with nitrate, Noyes and Garner[7] present evidence that the cerium(IV)-cerium(III) electrode potential in nitric acid is essentially independent of nitric acid concentration. Yost, *et al.*,[2] postulate mixed hydroxide-nitrate complexes to account for these results. Cerium(IV) in nitric acid can be extracted by a number of solvents.[8] Wylie[8b] studied the nature of the compound extracted into diethyl ether and concluded that it has the formula $H_2Ce(NO_3)_6$.

The present investigation was initiated to study the nitrate complexes of cerium(IV) by an extraction procedure. In the course of the work, it was found that much of the cerium(IV) existed as polymers even in 5.5 f HNO_3 and the emphasis of the study was reoriented toward an investigation of these polymers.

Experimental

Materials.—Matheson, Coleman and Bell Practical Grade diisopropyl ether was purified by washing with alkaline permanganate, water, ceric nitrate in nitric acid and finally several more times with water. The ether, to which some hydroquinone had been added, was dried over $CaCl_2$ and $MgSO_4$, and then with some low-melting Na-amalgam (108 g. Hg/100 g. Na). The mixture was refluxed under nitrogen for two hours and then distilled in a nitrogen atmosphere at the rate of 400-500 ml./hr. The uncorrected boiling point of the material was 66° with a boiling range of 1°. The purified ether was made 2×10^{-5} f in hydroquinone to inhibit peroxide formation.[9] Ether purified in this fashion and stored for months in the dark before use contained no detectable amounts of peroxide, when tested either with a sulfuric acid solution of Ti(IV)[10] or with a 2% solution of KI and starch.

The stock solution of $LiNO_3$ (Mallinckrodt Analytical Reagent) was analyzed by converting an aliquot portion to Li_2SO_4 which was ignited and weighed as such.

The HNO_3 solutions were prepared by diluting either fresh, unopened Baker Analyzed Reagent concentrated nitric acid or a concentrated HNO_3 solution brought rapidly to a boil to expel nitrogen oxides and then cooled. The

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(1) This work was presented at the 130th meeting of the American Chemical Society at Atlantic City and is abstracted from a thesis submitted by B. D. Blaustein to the Faculty of Philosophy of The Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy.

(2) See, for example, D. M. Yost, H. Russell and C. S. Garner, "The Rare Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 61.

(3) (a) Concentration will be expressed in formality, f, formula weights per liter of solution. (b) V. J. Linnenbom and A. C. Wahl, THIS JOURNAL, **71**, 2589 (1949).

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(9) R. J. Myers, D. E. Metzler and E. H. Swift, THIS JOURNAL, **72**, 3767 (1950).

(10) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," 3rd ed., Vol. II, D. Van Nostrand and Co., Inc., New York, N. Y., 1949, p. 882.

acid was standardized against standard carbonate-free NaOH to the brom thymol blue–phenol red mixed indicator end-point.

The stock solutions of cerous nitrate (Amend Drug and Chemical Co., C.P.) in 6 *f* HNO_3 and of ceric nitrate were analyzed for total cerium by titration with standard ferrous sulfate, using *o*-phenanthroline-ferrous sulfate as indicator, after oxidation of the cerium by the method of Willard and Young.[11] The stock solution of ceric nitrate in 7 *f* HNO_3 was prepared by dissolving G. F. Smith Chemical Co., C.P. ceric hydroxide in 10 *f* HNO_3 and storing in the dark for seven weeks before filtering. The filtered solution was aged an additional four months before being used. The cerium(IV) concentration of this solution and of samples from the extractions were determined by titration with standard ferrous sulfate using *o*-phenanthroline ferrous sulfate as indicator. When titrating very dilute solutions of Ce^{IV}, the titration with 0.005 *f* ferrous sulfate was followed potentiometrically using platinum foil and glass electrodes with a Beckman, Model G, *p*H meter. Fifty milliliters of 1 *f* H_2SO_4 was added to the solution before titration. The ferrous sulfate solutions were restandardized frequently against a standard ceric sulfate solution, which in turn was standardized against Merck Primary Standard $Na_2C_2O_4$ using ICl as a catalyst.

The nitric acid in the stock solutions of cerous and ceric nitrate and in the samples from the extractions was determined by first reducing Ce^{IV} by titrating to a slight excess with 0.5 *f* H_2O_2, adding a twofold excess of $K_2C_2O_4$ solution, and titrating the mixture slowly with standard NaOH to a brom thymol blue–phenol red end-point. A correction was made for the extra acid produced in the reduction of the Ce^{IV}. The cerous oxalate precipitate remains white in color at the end-point, indicating no oxidation to Ce^{IV}. However, the end-point is not as sharp as in the absence of the precipitate. Potentiometric titrations using a *p*H meter indicate that when HNO_3 is titrated with NaOH in the presence of cerous oxalate, excess oxalate, and the mixed indicator, the equivalence point is near *p*H 7.5 and the indicator is pale violet in color.

Methods.—The solutions for extraction were prepared from the stock solutions and equilibrated in a water-bath at 30.0 ± 0.03°. Fifty milliliters of the aqueous solution and 50 ml. of diisopropyl ether (previously cooled to 0°) were transferred to a 100-ml. ground glass stoppered graduate cylinder and placed in the bath for 12 min. The two phases were mixed at frequent intervals during the equilibration. The volumes of each phase were noted, and samples were taken for analysis without removing the cylinder from the bath.

The samples for acid analysis were immediately reduced with H_2O_2, diluted, excess oxalate added, and titrated as before. Each Ce^{IV} sample was diluted immediately with 1 *f* H_2SO_4 and titrated. The titrations of the ethereal phase were performed in the same fashion in the presence of the ether. The final concentration of lithium was determined from the initial concentration and the final volume of the aqueous phase. The final concentration of Ce^{III} was determined from its initial concentration, the final Ce^{IV} concentration, the loss in total Ce^{IV} during extraction, and the final volume of the aqueous phase.

Some reduction of Ce^{IV} occurred in the extraction, varying from 3 to 50%, depending upon the conditions. Since the loss of Ce^{IV} was independent of the method of analysis and increased with time of standing in the bath, we conclude that cerium(IV) reacts with some residual impurity in the ether or with the ether itself. The material balance for hydrogen ion was within 0.5% of the theoretical value. The results of duplicate experiments agreed to within 2%.

A modified H-cell, described elsewhere,[12] was employed for the e.m.f. measurements. A Leeds and Northrup type K2 potentiometer and a No. 2500 galvanometer were used for the measurements. Platinum spiral electrodes were employed and the cell and its contents were placed in a water-bath maintained at 30.0 ± 0.03°. Readings were taken for 40 minutes with the values usually becoming constant after ten minutes and with duplicate runs agreeing within 0.1 mv.

Results and Discussion

Extraction Studies.—Table I gives the results of extraction experiments at varying concentrations of Ce^{IV} with relatively constant concentrations of Ce^{III}, H^+, NO_3^- and Li^+ for a series of different total H^+ concentrations. In all cases it is seen that the fraction of Ce^{IV} extracted decreases markedly with increasing final concentrations of aqueous ceric ion. This observation is consistent with the assumption that the Ce^{IV} is polymerized in aqueous solution to a greater extent than in ether. In view of the results in the literature on the polymerization of cerium(IV) in perchloric acid,[6] the simplest assumption is that the cerium(IV) exists principally as monomer and dimer in the aqueous phase and as a monomer in ether. Under these assumptions it is possible to calculate both an overall association constant and an extraction coefficient. The cerium(IV) monomer will undoubtedly exist as various nitrate species and presumably the dimer will also be complexed with nitrate to some extent.

Total cerium(IV) monomer, $C^4{}_m$, is given by the following expression

$$C^4{}_m = \sum_{i=0}^{6} (C^4)\beta i(NO_3^-)^i = (C_4)f(NO_3^-)$$

where (C^4) is the concentration of uncomplexed monomer, β_i is the association constant of the ith complex and $f(NO_3^-)$ is a function of nitrate ion concentration. Similarly it can be shown that the total monomer concentration is equal to the product of the concentration of any particular monomeric species and some function of the nitrate concentration. If hydroxide complexes are present the unspecified function will also depend upon the hydrogen ion concentration. Likewise, the total concentration of dimer, $C^4{}_2$, is equal to the concentration of any particular dimeric species times a function of nitrate and hydrogen ion. For any particular series in Table I the concentrations of nitrate ion and of hydrogen ion remain essentially constant. Therefore, the undetermined functions are constant and can be included in the association constant for the dimer and in the extraction coefficient. Thus, we can write

$$K = C^4{}_2/(C^4{}_m)^2 \qquad (1)$$

and

$$D = C^4{}_m/C^4{}_e$$

where $C^4{}_e$ is the total concentration of cerium(IV) in the ether phase. The total cerium(IV) in the aqueous phase, $C^4{}_T$, is given by

$$C^4{}_T = C^4{}_m + 2C^4{}_2 = C^4{}_m + 2K(C^4{}_m)^2 \qquad (2)$$

Combining eqs. 1 and 2 and rearranging, we have

$$C^4{}_T/C^4{}_e = D + 2KD^2C^4{}_e$$

Thus a plot of $C^4{}_T/C^4{}_e$ *vs.* $C^4{}_e$ should give a straight line with intercept equal to the apparent extraction coefficient for monomer and with the slope equal to the product of twice the apparent dimer association constant and the extraction coefficient squared. Graphs are shown in Fig. 1 for the three series. It is evident that the experiments are in reasonable accord with this interpretation although the graphs deviate from linearity at high cerium(IV) concentrations. It is also to be noted that the dimerization constant varies with acidity although the ex-

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[11] H. H. Willard and P. Young, THIS JOURNAL, **50**, 1379 (1928).

[12] R. J. Gross and J. W. Gryder, *ibid.*, **77**, 3695 (1955).

TABLE I

EXTRACTION DATA

Initial (Ce^{IV}), $f \times 10^2$	Final vol., ml.[a]	Aqueous phase Final (H^+), f	Final (Li^+), f	Final (Ce^{III}), $f \times 10^2$	Final (Ce^{IV}), $f \times 10^2$	Ether phase Final vol., ml.	Final (H^+), f	Final (Ce^{IV}), $f \times 10^2$	$\frac{(Ce^{IV})_{water}}{(Ce^{IV})_{ether}}$
Series I, Initial $(H^+) = 7.661 f$, $(Li^+) = 0$									
33.42	38.4	5.480[b]		18.33	9.923	60.3	2.78	18.69	0.531
22.28	39.7	5.437		22.09	4.956	59.3	2.770	13.25	.374
22.72	40.0	5.497		23.29	4.529	58.3	2.792	12.81	.354
17.82	40.2	5.494[c]		22.94	3.599	58.9	2.775	10.88	.331
11.36	41.0	5.427		24.62	1.767	58.0	2.747	6.883	.257
6.816	41.9	5.421		25.11	0.922	56.9	2.745	4.184	.220
2.272	42.1	5.302		26.13	.216	57.4	2.712	1.201	.180
0.909	42.3	5.346		26.19	.0605	57.0	2.719	0.376	.161
Series II, Initial $(H^+) = 5.822 f$, $(Li^+) = 1.827 f$									
22.72	40.3	3.435	2.267	21.13	5.614	58.8	2.556	13.29	0.422
18.18	41.0	3.47	2.228	21.97	3.950	58.0	2.542	10.91	.362
11.36	41.7	3.445	2.191	23.73	2.016	57.1	2.535	7.136	.283
6.816	42.0	3.463	2.175	24.73	0.972	57.2	2.516	4.358	.223
2.272	43.0	3.443	2.124	25.44	.223	56.9	2.490	1.298	.172
0.909	43.0	3.457	2.124	25.77	.0648	56.7	2.4	0.374	.173
0.909	43.0	3.45	2.124	25.77	.0671	56.7	2.4	0.379	.177
Series III, initial $(H^+) = 5.094 f$, $(Li^+) = 2.558 f$									
22.72	40.9	2.729	3.127	20.77	6.020	58.1	2.430	13.15	0.458
18.18	41.5	2.755	3.082	21.68	4.323	57.4	2.424	10.95	.395
11.36	42.0	2.772	3.045	23.44	2.108	57.5	2.39	7.090	.297
6.816	42.8	2.794	2.988	24.36	1.017	55.9	2.401	4.339	.234
2.272	43.0	2.801	2.974	25.46	0.2366	55.8	2.381	1.298	.182
0.909	43.5	2.787	2.940	25.47	0.0694	55.7	2.346	0.3764	.184

[a] Initially 50 ml. of aqueous phase and 50 ml. of ether. Initial $(H^+) = 7.601 f$. [c] Initial $(H^+) = 7.692 f$.

traction coefficient, D, remains relatively constant.

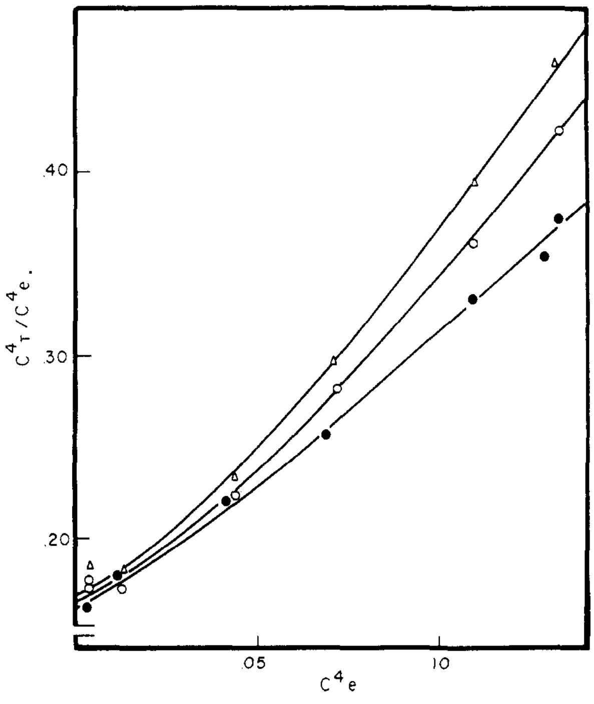

Fig. 1.—Distribution ratio as function of (Ce^4) in ether: Δ, 2.8 f HNO_3; ○, 3.5 f HNO_3; ●, 5.5 f HNO_3; $\mu = 5.5 f$.

The relative constancy of D with respect to acidity makes Wylie's conclusion that the extracted species is $H_2Ce(NO_3)_6$ questionable and therefore we reinvestigated this problem. Table II gives the results of nitric acid extraction in the presence and absence of cerium(IV) under conditions similar to those employed for the data in Table I. The ratio of acid in ether to acid in water is almost constant for comparable acidities regardless of the presence of cerium(IV) in the system. In addition, the increase in concentration of acid in the ether phase is much less than the concentration of cerium(IV) in the ether. The slight increase in ethereal acid is accounted for by the increase in aqueous acid. If the species extracted contained ionizable hydrogen, the acidity in the ether should be greater in the presence of cerium than in its absence by an amount equal to N times the ethereal cerium(IV), where N is the number of hydrogen ions per cerium extracted. Thus we conclude that there is no ionizable hydrogen extracted with the cerium(IV). Wylie's data[8b] are in agreement with this conclusion. Table III presents Wylie's results on the excess nitric acid extracted per formula weight of cerium(IV) extracted, at varying total concentrations of nitric acid. We

TABLE II

EXTRACTIONS IN THE PRESENCE AND ABSENCE OF Ce^{IV}

Water phase (H^+), f	(Ce^{III}), $f \times 10^2$	Ether phase (H^+), f	(Ce^{IV}), $f \times 10^2$	$\frac{(H^+)_{ether}}{(H^+)_{water}}$
5.370	21.85	2.716	0.00	0.506
5.497	23.29	2.792	12.81	.508
5.437	22.09	2.770	13.25	.509
5.494	22.94	2.775	10.88	.505
5.319	24.50	2.718	0.00	.511
5.427	24.62	2.747	6.88	.506

TABLE III

EXCESS FORMULA WEIGHTS OF H^+ EXTRACTED PER FORMULA WEIGHT Ce^{IV}—DATA OF A. W. WYLIE[8b]

Initial conditions: 40 ml. HNO_3 solution (+5 g. $(NH_4)_2Ce(NO_3)_6$) + 40 ml. diethyl ether. Method of recalculation: the initial conditions and the % extraction data were used to calculate the f.wts. of HNO_3 extracted in the presence (A) and in the absence (B) of Ce^{IV}, and the f.wts. of Ce^{IV} extracted (C). The values in the last column are (A − B)/C.

Initial (HNO_3), *f*	% HNO_3 extracted With Ce^{IV}	No Ce^{IV}	% Ce^{IV} extracted	Excess f.wts. of H^+ extracted per f.wt. Ce^{IV} Wylie's value	Recalcd. value
1.0	15	7	1.1	27	32
2.0	23	13	4.5	16	19.5
3.0	31	21.5[a]	39	2.7	3.2
4.0	36	28.5[a]	69	2.2	1.91
5.0	40	35	88	1.6	1.25
6.0	44	41	93	1.6	+0.85
7.0	45	46	93	1.4	−0.33
8.0	49	48	94	1.4	+0.37
9.0	53	52	94	1.0	0.42

[a] Interpolated from Wylie's data.

were unable to obtain the values reported by Wylie from the data given in the paper and both Wylie's values and our recalculated values are presented. Either set of numbers, however, can be explained on the basis of the fact that the concentration of nitrate ion was greater in the presence of the ceric ammonium nitrate than in its absence. This is particularly true at low acid concentrations in which the cerium(IV) is less complexed with nitrate ion and where the fraction of nitrate coming from the added ceric ammonium nitrate is greatest. The amount of nitric acid extracted would certainly increase with increasing NO_3^- concentration in the water as a result of the common ion effect and therefore additional acid would be extracted regardless of any acid going with the cerium(IV). Since Wylie's solutions were approximately 0.23 formal in ceric ammonium nitrate before extraction, it is evident that the concentration of nitrate is indeed considerably greater in his runs in the presence of cerium than in those runs containing nitric acid alone. The values in Table III for excess nitric acid per mole of cerium(IV) extracted are therefore too high, and since they are below two and approaching zero for all acidities above 4 *f* on either basis of calculation we conclude that the data are compatible with the assumption that no ionizable hydrogen ion is associated with the extracted cerium.

Potentiometric Studies.—Although the extraction results appear to be conclusive in showing the existence of cerium(IV) dimers, the aqueous phase after extraction contains a large amount of ether and the decrease in $C^4{}_e/C^4{}_T$ with increasing cerium(IV) could be an artifact caused by abnormal activity relationships in the medium. This appears unlikely because the media in both the ether and aqueous phases remain almost constant as the cerium(IV) concentrations are changed within each series. In order to eliminate the possibility of an artifact and to obtain values for the dimerization constant in the absence of ether, an independent approach was employed. The method adopted was to measure the potential of a concentration cell of such a nature that the e.m.f. measured was a direct indication of any dimerization. The two half-cells employed contained large amounts of nitric acid and much smaller amounts of cerium(IV) and cerium(III). The ratio of cerium(III) to cerium(IV) was equal in the two half-cells but the total amount of cerium differed. If dimers are not formed and if junction potentials and activity effects are neglected, the cell should show zero e.m.f. The junction potential should, indeed, be very small because the bulk of the current will be carried by the hydrogen ion, which is constant throughout the cell and most of the remaining current will be carried by nitrate which is approximately constant in all parts of the cell. In addition, the activity coefficients of the various species in solution should be almost equal in the two half-cells because of the nearly constant nature of the medium. A quantitative check of these assumptions will be presented in a later section of this paper.

Table IV shows the concentrations in the half-cells employed and Table V shows the results obtained from a number of cells. It is evident that the potentials are not close to zero as would be expected in the absence of dimerization. Furthermore in all cases the solution with the higher concentration of cerium(IV) is less oxidizing than the solution containing the smaller concentration of cerium(IV). Table V also gives values for the e.m.f. obtained in intercomparisons between the various series. In these cases, of course, we would not expect zero potential in the absence of dimerization because the ratio of total cerium(IV) to cerium(III) is different in the two half-cells.

If dimerization of cerium(IV) is the only phenomenon responsible for the e.m.f., we can determine the association constant for the dimer. Solving for $C^4{}_m$, the monomer concentration, from eq. 1 and 2 we obtain

$$C^4{}_m = [-1 + (1 + 8KC^4{}_T)^{1/2}]/4K$$

and for the concentration cell of the type discussed, the Nernst equation at 30° becomes

$$\Delta E/60.15 = \log \{-1 + [1 + 8K(C^4{}_T)_1]^{1/2}\}(C^3)_2/ \{-1 + [1 + 8K(C^4{}_T)_2]^{1/2}\}(C^3)_1$$

where C^3 is the cerium(III) concentration, the subscripts refer to the two solutions making up the half-cell, and ΔE is the potential difference in millivolts. If the substitutions $R = (C^3)_2/(C^3)_1$ and $A = \{[1 + 8K(C^4{}_T)_1]^{1/2} - 1\}$ are made, we have after algebraic manipulation

$$[(C^4{}_T)_2/R]10 \exp (\Delta E/60.15) = [(A^2R/8K) 10 \exp (-\Delta E/60.15)] + A/4K \quad (3)$$

If the same solution is always used as a reference in one half-cell, we can drop the designation of subscript 2 in the other half-cell, and since A is a constant under these conditions a plot of

$$(C^4{}_T)/R \ 10(\Delta E \exp)/60.15) \ vs. \ R \ 10 \exp(-\Delta E/60.15)$$

should be a straight line with intercept of $A/4K$ and slope of $A^2/8K$. Figure 2 shows such a plot for the experimental data in Table V with intercomparisons being used to refer all of the values back to solution 21 as standard. Two observations are immediately evident. The curves are not

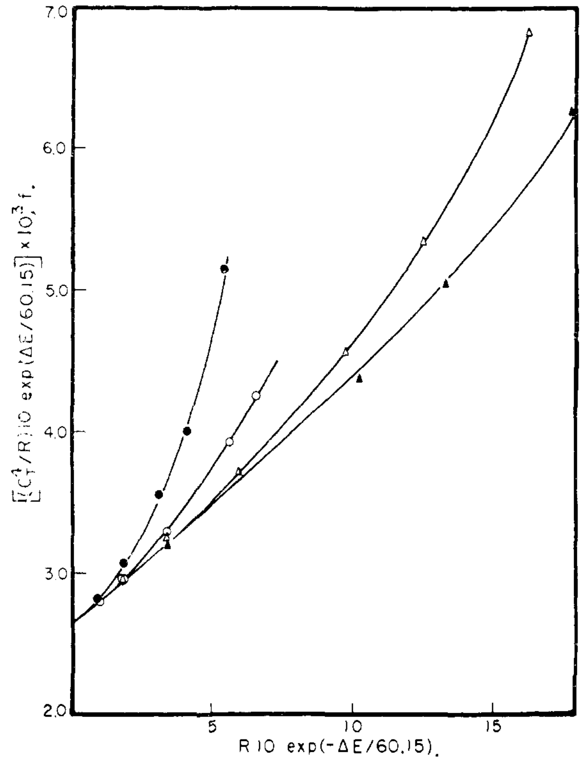

Fig. 2.—E.m.f. results: ▲, series I; △, series II; O, series III; ●, series IV.

TABLE IV

CONCENTRATION OF SOLUTIONS USED FOR E.M.F. MEASUREMENTS[a]

Soln.	(Ce^{IV}), $f \times 10^2$	(Ce^{III}), $f \times 10^2$	Soln.	(Ce^{IV}), $f \times 10^2$	(Ce^{III}), $f \times 10^2$
1	11.14	2.26	17	2.785	10.96
2	6.684	1.356	18	2.228	8.764
3	4.456	0.9040	19	1.114	4.382
4	2.228	0.4520	20	0.5570	2.191
5	1.114	0.226	21	0.2785	1.096
11	11.14	10.05	25	2.783	29.14
12	6.684	6.032	26	2.226	23.31
13	4.456	4.021	27	1.670	17.48
14	2.228	2.011	28	1.113	11.66
15	1.114	1.005	29	0.5565	5.828
16	0.5570	0.5027	30	0.2783	2.914

[a] $[HNO_3] = 5.5 f$ in all solutions.

TABLE V

OBSERVED AND CALCULATED E.M.F.'S FOR $K = 17$ AND $K' = 2.0$

E.m.f. of soln. pairs	ΔE(mv.) Obsd.	Calcd.	δE	$(\delta E)^2$
		Series I		
1–5	17.19	15.78	−1.41	1.99
2–5	11.50	11.51	+0.01	0.00
3–5	7.85	8.36	+ .51	.26
4–5	3.55	3.68	+ .13	.02
		Series II		
11–16	21.95	19.20	−2.75	7.56
11–15	19.75	16.53	−3.22	10.37
12–15	13.38	12.01	−1.37	1.88
13–15	9.32	8.71	−0.61	0.37
14–15	3.80	3.83	+0.03	.00
		Series III		
17–21	11.00	11.30	+0.30	.09
18–21	8.92	9.58	+ .66	.44
19–21	4.40	5.13	+ .73	.53
20–21	1.50	2.00	+ .50	.25
		Series IV		
25–30	15.62	14.50	−1.12	1.25
26–30	12.56	12.30	−0.26	0.07
27–30	9.20	9.70	+ .50	.25
28–30	6.02	6.63	+ .61	.37
29–30	2.18	2.60	+ .42	.18
		Intercomparisons		
21–5	73.00	73.65	+0.65	0.42
21–3	65.73	65.29	−0.44	.19
21–1	56.45	57.87	+1.42	2.02
21–15	34.77	34.41	−0.36	0.13
21–13	25.79	25.70	−0.09	.01
21–11	15.37	17.90	+2.53	6.40
15–3	30.65	30.86	+0.21	0.04
15–1	21.55	23.48	+1.93	3.72
30–21	25.90	26.35	0.45	0.20
		Σ|δE|	23.21	
		$\Sigma(\delta E)^2$		39.00
		Av.	0.86	1.44
	Excluding soln. 1 and 11	Σ|δE|	9.94	
		$\Sigma(\delta E)^2$		6.94
		Av.	0.47	0.33

straight lines and different curves are obtained for each series. The results are therefore incompatible with the assumptions made thus far. The original data in Table V also indicate that an additional parameter is necessary. If the only reaction responsible for variation in the e.m.f.'s is the dimerization, the potential difference would be independent of the concentration of cerium(III) at constant cerium(IV) concentrations. However, comparison between series I and series II and especially between series III and series IV indicate that the observed e.m.f. increases with increasing cerium(III) concentration. The effect is not due to cerium(III)–cerium(III) polymerization since it is in the wrong direction. It could, however, be caused by dimer formation between cerium(IV) and cerium(III). If such dimers exist, an increase in cerium(III) would have a twofold effect. It would decrease the concentration of monomeric cerium(IV) and increase the concentration of monomeric cerium(III) with the greatest fractional change in concentration occurring in the most concentrated solutions. The change in e.m.f. with addition of cerium(III) could be either positive or negative depending upon the ratio of cerium(III) to cerium(IV), the total cerium concentration, and the values of the equilibrium constants. Although, as previously stated, we would expect the junction potentials and activity effects to be small, the possibility existed that the differences between series I and II and between series III and IV are caused by these effects. In order to check the results, sufficient solid $Sr(NO_3)_2$ was added to solutions 17 and 21 to make solution 17 two-tenths f in $Sr(NO_3)_2$ and solution 21 two-hundredths formal in $Sr(NO_3)_2$. The potential difference between the two solutions increased 0.6 mv. over its value in the absence of strontium. Since cerium(III) complexes with nitrate to such an extent that it would exist, under our conditions, principally as the mononitrate complex, the strontium nitrate should have approximately the same non-specific effect as added cerous nitrate. However, the e.m.f. for solutions 25–30 (which should correspond closely to solutions 17–21 with added strontium) is 4.62 mv. greater than for solutions 17–21 and we therefore conclude that the cerium(III) is indeed acting in a specific fashion. Since the greatest activity and junction effects should occur in solution pair 25–30, we conclude from the strontium nitrate results that the maximum non-specific effect is 0.6 mv. and in most cases is much smaller. Therefore the data will be interpreted on the basis of Ce^{IV}–Ce^{IV} and Ce^{IV}–Ce^{III} dimers.

In principle two potential measurements involving three solutions would give 14 equations and 14 unknowns and allow the direct calculation of values for the two equilibrium constants. However, the algebraic complexity of the situation prohibits a direct approach of this sort. Rather, a modified least squares procedure was developed to determine if two constants could be chosen which would predict potentials in satisfactory agreement with the experimental values. Although the procedure developed is tedious, reasonable results can be obtained in a finite time.

The conservation equations become

$$C^4{}_T = (1 + K'C^3)C^4{}_m + 2K(C^4{}_m)^2 \qquad (4)$$

$$C^3{}_T = C^3 + K'(C^3)(C^4{}_m) \qquad (5)$$

where $C^3{}_T$ is total cerium(III), C^3 is the concentration of cerium(III) monomer, K' is the association constant for the cerium(III)–cerium(IV) dimer, and the other symbols have their previous significance. From eq. 4 and 5 we obtain

$$C^3 = C^3{}_T/(1 + K'C^4{}_m) \qquad (6)$$

$$C^4{}_T = [1 + K'(C^3{}_T + C^4{}_m)]C^4{}_m/[1 + K'C^4{}_m] + 2K(C^4{}_m)^2 \qquad (7)$$

Since the effect of varying total cerium(III) concentration is small in comparison to variations in total cerium(IV), it is evident that K is considerably greater than K'. First approximations to K can therefore be obtained from the graphs in Fig. 2. This gives 10 as the order of magnitude for K. From the variation of the cell potential with cerium(III), it would appear that K' is about an order of magnitude less than K. Now particular values of K and K' are chosen and the concentration of $C^4{}_m$ in each solution determined by an iterative process which involves first neglecting $C^4{}_m$ in the square brackets in eq. 7, solving for $C^4{}_m$ from the resultant quadratic equation, substituting this value of $C^4{}_m$ in the square brackets, solving for a new $C^4{}_m$ and repeating the procedure until convergence is achieved. Under the conditions employed, convergence is very rapid. The cerium(III) monomer can then be obtained from eq. 6. Knowing C^3 and $C^4{}_m$ for each solution, ΔE can be calculated for each pair of solutions. Graphs of calculated ΔE *vs.* K for various values of K' were made for each pair of solutions employed. For each pair of solutions a number of values for the two constants would be consistent with the experimental values. However, fewer values for the constants would fit two of the cells simultaneously. By inspecting all 27 graphs, the possible variation in the constants was reduced significantly; and it was determined that a K in the vicinity of 18 and a K' of around 2 would be necessary to fit all the available data. A graphical least squares procedure was then employed to determine the best values for the constants. A plot of $\overline{(\delta E)^2} = \overline{(\Delta E_{\text{calcd}} - \Delta E_{\text{exp}})^2}$ *versus* K for a particular K' has a minimum value which corresponds to the best K for the particular K'. A plot of the minimum values of $\overline{(\delta E)^2}$ for the particular (K')'s *versus* the K' to which they correspond should give another minimum from which the best value of both K and K' can be determined. The results of these calculations are shown in Fig. 3. Uniqueness of the solution is not assured except in the immediate vicinity of the values for the constants which were used in drawing the graph. However, the graphs of calculated ΔE *versus* K for various values decrease the probability of the existence of a second solution with real, positive values for the constants. No values for the constants could be chosen which would fit e.m.f.'s for cells involving solutions 1 or 11 and the other cells simultaneously. These two solutions had relatively high concentrations of cerium(IV) and differed from the calculated values in the direction to indicate the formation of higher polymers. Since the possibility of higher cerium(IV) polymers is reasonable, these solutions were not used in calculating the square deviation, although their inclusion would not have affected the results markedly.

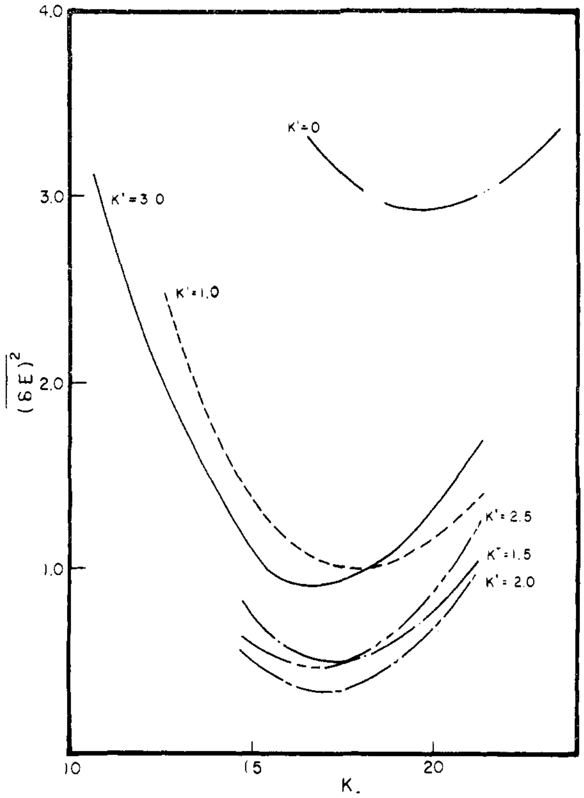

Fig. 3.—Calculated mean square deviation *versus* K.

Table V lists the experimental and calculated values of the e.m.f. and the deviation and square deviation for the values of 17 and 2 for K and K', respectively. The calculated and experimental values for the e.m.f. are seen to agree well with all of the experimental points, with the exception of those involving solutions 1 and 11. In view of the rather complex treatment and the possibility of small junction potentials and activity variations, we choose 17 ± 2 and 2.0 ± 0.7 as the best values for K and K', respectively. The results could be interpreted on the basis of other types of polymerization such as $\mathrm{Ce^{III}}$–$\mathrm{Ce^{IV}}$ dimers and $\mathrm{Ce^{IV}}$ trimers. However, the interpretation given is the simplest and most reasonable of the various possibilities.

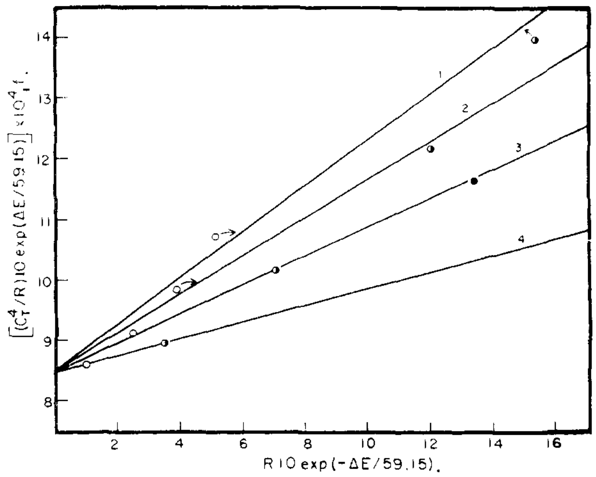

Fig. 4.—E.m.f. data for perchlorate system from Sherrill, King and Spooner, $\mathrm{Ce^{IV}/Ce^{III}}$: 1 = 1.2 to 1.6, 2 = 0.7, 3 = 0.3, 4 = 0.1; total cerium: ○, 0.009865 *f*; ◑, 0.03463 *f*; ●, 0.0732 *f*.

The extraction experiments intentionally had been conducted in the presence of a large amount of cerium(III) in order to minimize any effects caused by the formation of cerium(III) resulting from the reduction of cerium(IV) by the organic matter during extraction. Consequently the extraction data cannot be used to add further support for the existence of cerium(IV)–cerium(III) dimers. Likewise the extraction data cannot be used to obtain association constants for the two dimers, although they can be used to place a lower limit on the cerium(IV)–cerium(IV) association under the conditions of the extraction. In all of these experiments C^3_T is essentially constant and much greater than C^4_m. If we neglect C^4_m in comparison with C^3_T and assume that $K'C^4_m$ is sufficiently less than 1 to justify the approximation $(1 + K'C^4_m)^n = 1 + nK'C^4_m$, eq. 7 becomes

$$C^4_T \approx (1 + K'C^3_T)(1 - K'C^4_m)C^4_m + 2K(C^4_m)^2 \qquad (8)$$

Combining eq. 1 and 8 and rearranging we have

$$C^4_T/C^4_e \approx (1 + K'C^3_T)D + [2K - K'(1 + K'C^3_T)]D^2C^4_e \qquad (9)$$

and under the conditions that C^3_T is constant, a plot of C^4_T/C^4_e *versus* C^4_e is a straight line as was found to be approximately true in Fig. 1. If m is the slope of the line and b the intercept, we have from eq. 9

$$m/b^2 = 2K/(1 + K'C^3_T)^2 - K'/(1 + K'C^3_T)$$

or

$$K = \left(\frac{m}{b^2} + \frac{K'}{1 + K'C^3_T}\right)(1 + K'C^3_T)^2/2$$

Thus K is greater than $m/2b^2$ with its value depending upon the value of K'. The minimum value of K found in 5.5 *f* acid saturated with ether is about 35. Although this result is considerably higher than that determined by e.m.f. measurements, it is not surprising because ether is very soluble in these acid solutions and certainly exists as the oxonium ion, thus binding a large amount of acid and decreasing the effective hydrogen ion concentration. This conclusion is further substantiated by the fact that the acid concentration in the ether phase is almost the same when in equilibrium with 2.5 *f* acid in the aqueous phase as it is when the aqueous acid is 5.5 *f*, indicating that the activity of acid in the aqueous phase does not change markedly. This increase of cerium(IV)–cerium(IV) dimerization with decreasing activity of acid is in agreement with the results in perchloric acid medium and suggests hydroxide or oxide bridges in the dimer.

Studies by Previous Workers.—One would expect that cerium(III)–cerium(IV) dimers would also be possible in a perchloric acid medium. That this is probably true can be deduced from the data of Sherrill, King and Spooner.[13] In only one of the series reported by these workers is it possible to check the hypothesis, because in most cases sufficient variation in the cerium concentrations was not made. The data for series 2 reported by these authors was treated in the following fashion. The values for the e.m.f. of concentration cells of the type employed in our work were calculated relative to solution VIIId of series 2 in the paper of Sherrill, *et al.*, by first calculating E' from

$$E' = E^0{}_f + 0.05915 \log \frac{C^4_T}{C^3_T}$$

ΔE values were then obtained by subtracting from E' for solution VIIId the other (E')'s. These ΔE values were treated by eq. 3 above and plotted in Fig. 4. Because of the difference in temperature, the constant 59.15 is used instead of 60.15. Solutions VIa, b, and c were not included because the acidity was considerably different for these solutions. If the only effect were cerium(IV) dimerization a single straight line should be obtained in this graph. Actually, as was the case for the nitrate data, a different curve is obtained for each ratio of C^4_T/C^3_T again indicating the existence of cerium(IV)–cerium(III) dimers. Because of the difficulty in determining the constants and the insufficiency of suitable experimental values, this work was not subjected to further analysis. Heidt and Smith, in their reinterpretation of Sherrill, King and Spooner's data did not include the data from series 2, presumably because of the difference in acidity in this case. However, Fig. 4 indicates that their method would not have been successful for this series.

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(13) M. S. Sherrill, C. B. King and R. C. Spooner, THIS JOURNAL, **65**, 170 (1943).

The results of Noyes and Garner are also compatible with our interpretation. If the dimers involve oxide or hydroxide bridges, increasing the nitric acid concentration will tend to decrease the free cerium(IV) concentration by forming nitrate complexes but at the same time will tend to increase free cerium(IV) by decreasing the extent of dimerization and apparently the two effects are comparable. This of course is similar to the suggestion of Yost, Russell and Garner[2] involving hydroxide complexes. The very small change in the standard formal potential when the ratio of Ce^{IV} to Ce^{III} is varied keeping total cerium constant can be accounted for on the basis of the fact that as the ratio is changed, the expected change in free cerium(IV) which would result from a change in the per cent. of dimerization of cerium(IV) is approximately balanced by a change in the amount of cerium(IV)–cerium(III) dimerization. The small residual change is in the direction which would be expected if the cerium(IV)–cerium(IV) association constant were larger than the cerium(IV)–cerium(III) association constant.

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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Thermal Decomposition of Aqueous Chromic Acid and Some Properties of the Resulting Solid Phases[1]

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Aqueous chromic acid solutions in closed containers evolve oxygen at an appreciable rate at 300 to 325°. The equilibrium has been investigated at oxygen pressures between 50 and 200 atmospheres. The decomposition is first order at 300° but it is approximately of order **1$^1/_2$** at 325°. The solid decomposition products are chromium dioxide (cassiterite structure, $a_0 = 4.421 \pm 0.002$ Å., $c_0 = 2.916 \pm 0.001$ Å.) and $HCrO_2$ (diffraction symbol $\overline{3}mR$---, $a_0 = 4.787 \pm 0.005$ Å., $\alpha = 36.3 \pm 0.1°$, $Z = 1$).

Introduction

The kinetics of the decomposition of chromic acid in sulfuric acid solutions and the effect of the resulting chromic sulfate have been studied by Snethlage[2] and Aynsley[3] in the range 14 to 100% oleum. Birjukov[4] observed that boiling aqueous chromic acid evolved oxygen, but no measurements appear to have been made of the decomposition equilibrium or kinetics in this system, nor have the decomposition products been identified. Such data are reported herein as the result of experiments conducted on aqueous chromic acid solutions in a closed system at 300 and 325°. The solid decomposition products, chromium dioxide and $HCrO_2$, were studied by chemical, X-ray, optical and morphological methods.

Thermal Decomposition of Aqueous Chromic Acid

Experimental.—The solutions used in the experiments were prepared from Mallinckrodt Analytical Reagent CrO_3 and distilled water, and the chromate content of all solutions used in the experiments or obtained therefrom was determined volumetrically. The experiments were performed with the solutions contained in bombs made of Type 347 Stainless Steel. The inside of the bomb had a protective platinum cladding in only one experiment but in all experiments corrosive attack on the wall was slight. Temperatures were measured with a calibrated chromel–alumel thermocouple inserted in a well in the bomb wall and connected to a Brown recorder. The recorder controlled the voltage to the electric furnace containing the bomb, thus controlling the bomb temperature to within $^1/_2°$ of the desired temperature. The upper end of the bomb was connected to a water-filled Heise pressure gage by capillary tubing of negligible volume.

For each equilibration the bomb was filled exactly half full with the chromic acid solution to be equilibrated at the elevated temperature. On reaching the temperature at which equilibration was to be made the bomb was rocked continuously. It is estimated that in each equilibration less than 1% of the hexavalent chromium had decomposed by the time the equilibration temperature had been reached. No samples were taken during the equilibration period. Hence the reaction proceeded in a closed system. Pressure readings indicated the degree of completion of the reaction and provided information on reaction kinetics. After constant pressure readings over several days indicated that equilibrium had been attained, the bomb was allowed to cool to room temperature, the liquid phase was filtered and analyzed for its hexavalent chromium content, and the solid phases were identified.

Results and Conclusions.—Data pertinent to the equilibrium state are presented in Table I. In each equilibration all or part of the oxygen present at equilibrium had been produced by the decomposing chromic acid. Column E of Table I was

TABLE I

THERMAL DECOMPOSITION OF AQUEOUS CHROMIC ACID

	A	B	C	D	E	F
Run	CrO_3 molality[a] of the aqueous charge	Gaseous charge (room temp.)	Temp. (°C.) at equilibration	CrO_3 molality[a] as removed from bomb	Equil. CrO_3 molality[a], equilibration temp.	Equil. O_2 pressure (atm.), equilibration temp.
1	1.590	Helium, 1 atm.	300	0.116	0.120	50.5
2	3.348	Helium, 1 atm.	300	.473	.489	84.8
3	3.348	Oxygen, 68.4 atm.	300	.784	.810	209.2
4	3.348	Helium, 1 atm.	325	.384	.400	91.5

[a] The molality is the number of gram formula weights of CrO_3 per 1000 grams of water.

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[1] Work done under the auspices of the Atomic Energy Commission.

[2] H. C. S. Snethlage, *Rec. trav. chim.*, **57**, 1341 (1938); **57**, 459 (1938); **55**, 874 (1936).

[3] E. E. Aynsley, *J. Chem. Soc.*, 368 (1950).

[4] N. D. Birjukov, *J. Gen. Chem. U. S. S. R.*, **10**, 942 (1940).