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The nature of cerium (IV) in aqueous nitric acid solution

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THE NATURE OF CERIUM(IV) IN AQUEOUS
NITRIC ACID SOLUTION

by

Lourdes Ocampo Tuazon

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Head of Major Department

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Dean of Graduate College

Iowa State College

Ames, Iowa

1959

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INTRODUCTION

Until a decade ago, only three metal ion nitrate complexes were known, those of cerium(IV), thorium(IV), and silver(II), whose formulas were not definitely established. Since then some seventeen mono-nitrate complexes (3) have been reported. Their association constants, though still unreliable, range from 0.2 to 18, as obtained from conductivity, solubility, potentiometric titration, ion exchange, spectrophotometric, kinetic, potentiometric, polarographic, and distribution measurements. One can see from the order of magnitude of the association constants that nitrate forms weak complexes with metal ions in aqueous solution.

Hydroxyl and sulfate ions, besides nitrate ion, have also been known for some time to complex cerium(IV). The nature of cerium(IV) in perchlorate and in sulfate media have been studied extensively; association constants for the various species have been evaluated. Nitric acid solutions containing higher concentration of cerium(IV) have also been investigated quantitatively and a dimerization constant has been reported. In this work an attempt was made to determine the predominating monomeric species in nitrate solutions.

REVIEW OF PREVIOUS WORK

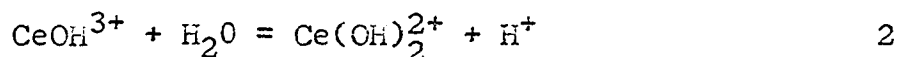
Cerium(IV) in perchlorate solution

The early reports on this system were contradicting. Smith and Goetz (26) found the formal oxidation potential of the cerium(III)-cerium(IV) couple to increase from 1.70 volts to 1.87 volts with increase in perchloric acid concentration. They therefore formulated the cerium(III)-cerium(IV) electrode potential relationship as

$$\frac{[\text{Ce}(\text{ClO}_4)_6^{2-}]}{(\text{Ce}^{3+})(\text{ClO}_4^-)^6} \quad 1$$

They considered the hydrogen ion to play a negligible part.

The hydrogen ion effect was studied by Sherrill, King and Spooner (24). The formal potential was shown to increase from 1.6400 volts to 1.7310 volts at 25° C with increase in hydrogen ion concentration from 0.2 M to 2.4 M, and yet was found to be independent of the perchlorate ion concentration. Cerium(IV) was varied from 0.001 M to 0.06 M and cerium(III) from 0.001 M to 0.02 M. They concluded that neither cerium(IV) nor cerium(III) reacts with perchlorate, that cerium(III) is not hydrolyzed in perchloric acid, that cerium(IV) is hydrolyzed in stages, forming CeOH^{3+} and $\text{Ce}(\text{OH})_2^{2+}$ even in 2.4 M perchloric acid, and that K for the reaction

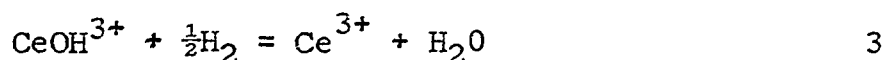


is 0.6. King and Pandow (13) observed that the spectra of their solutions containing 3.00 M perchlorate, 4×10^{-6} M and 6×10^{-4} M cerium(IV), and 0.33 M to 3.00 M hydrogen ion, from 470 m μ to 390 m μ are consistent with this value of k only if the extinction coefficients of $CeOH^{3+}$ and $Ce(OH)_2^{2+}$ are similar.

The qualitative results of Kraus, Holmberg, and Nelson (15) confirm essentially the conclusions of Sherrill et al. (24). pH measurements gave an average hydroxyl number "n" of somewhat less than 1.5 for 0.01 M ammonium hexanitratocerate(IV) (HNC) in 0.1 M perchloric acid, greater than zero for 10 M perchloric acid, and 2.35 for solutions of low HNC concentration and low acidity over a considerable acidity range. The extinction coefficients of 0.01 M HNC solutions were found to be acid independent from 0.1 M to 1.0 M hydrogen ion and rose rapidly with increasing acidity thereafter. However, from 210 m μ to 350 m μ the extinction coefficients of 3×10^{-4} M HNC solutions increased with increasing acidity from 0.10 M to 1.00 M perchloric acid, all of ionic strength 1.0. These spectral data were not thoroughly analyzed.

The photo-oxidation of water by ceric perchlorate was also used to elucidate further the species in perchlorate solution. This was observed qualitatively by Baur (1), first investigated by Weiss and Porret (30) who proposed a mechanism

involving Ce^{4+} , and was later studied quantitatively by Heidt and Smith (11). The latter measured in 254 m μ light the photolysis at 23^o C of 1.03 M perchloric acid solutions containing 0 to 0.08 M cerium(III) and 0 to 0.016 M cerium(IV). The net quantum yield led to an assumed mechanism of cerium(IV) dimers being deactivated by cerium(III) ions. With this finding, Heidt and Smith (11) went on to eliminate the anomaly in some of the data of Sherrill et al. (24), namely, the increase in the formal potential for



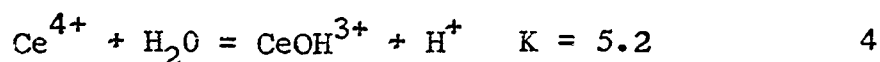
with decrease in cerium(IV) concentration in 0.8 M perchloric acid, by postulating the dimers, $(\text{HOce-O-CeOH})^{4+}$ and $(\text{CeO-CeOH})^{5+}$. The constancy of the corrected formal potential between 0.5 and 2.4 ionic strength (contribution mainly from perchloric acid) was attributed to the opposing effects of a decrease in ionic strength: it favors both the hydrolysis of CeOH^{3+} and the decrease in dimerization of cerium(IV) ions. Dimerization was not observed, however, by Heidt and Smith (11) from measurements of the extinction coefficients at 254 m μ of 1.03 M perchloric acid solutions containing 0 to 0.0094 M cerium(IV) and 7×10^{-5} M to 0.03 M cerium(III).

Working on the kinetics of the cerium(III)-cerium(IV) exchange in 4 M to 6.0 M perchloric acid, Duke and Parchen(5) found evidence for $\text{Ce}(\text{OH})_2^{2+}$, $\text{Ce}(\text{OH})_3^+$, and $(\text{CeOceOH})^{5+}$.

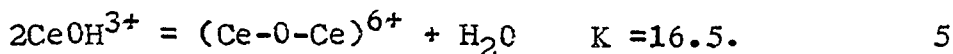
Consistent with the mechanism proposed by Heidt and Smith (11) are the rate data on the thermal reaction in perchloric acid between cerium(IV) and water obtained by Kolp and Thomas (14). A more recent mechanistic study by Fronaeus and Ostman (7) on the cerium(III)-cerium(IV) exchange at platinum surfaces in 3 M perchloric acid also indicated dimers. Their data are consistent with the formation constants calculated by Hardwick and Robertson (9). On the other hand, Evans and Uri (6) qualitatively and quantitatively reinterpreted the kinetic results of Heidt and Smith (11) in terms of a reaction scheme involving CeOH^{3+} ions and no dimers. They claimed that their spectrophotometric measurements showed conclusively the absence of dimers and that in molar perchloric acid, 92 per cent of the cerium(IV) is present as CeOH^{3+} . Likewise, Moore and Anderson (22) concluded that ceric perchlorate solutions obey Beer's law up to 0.01 M.

King and Pandow (13), however, found deviation from Beer's law from 440 m μ to 530 m μ for solutions 0.85 M and 2.57 M in hydrogen ion over a cerium(IV) concentration range of 4×10^{-4} M to 0.1 M. So did Hardwick and Robertson (9). Perchloric acid-sodium perchlorate solutions of the following compositions: 0.20 M to 2.00 M hydrogen ion, 7×10^{-4} M to 0.013 M cerium(IV) and of ionic strength 2.00, were examined from 395 m μ to 430 m μ and were shown to contain Ce^{4+} , CeOH^{3+} , and probably $(\text{Ce}-\text{O}-\text{Ce})^{6+}$, with the following forma-

tion constants, evaluated finally, at 25° C:



and



Their migration experiment confirmed the charges on the species, as did the observations of Linnenbom and Wahl (17).

Hardwick and Robertson (9) investigated also the effect of ionic strength on the preceding equilibria and found constant apparent molar extinction coefficients from ionic strengths of 1.10 to 4.00, suggesting no perchlorate complex. Duke and Bremer (4) pointed out that the observations of Smith and Goetz (26) cannot be due to perchlorate complexes but due to the fact that cerium(IV) effectively complexes more water than cerium(III) does and therefore in moderate concentrations of perchloric acid, cerium(IV) is apparently the tetrapositive hydrated cation. In relatively concentrated perchlorate solutions (>6M), whether perchloric acid or perchloric acid-sodium perchlorate solutions, the extinction coefficients were observed by King and Pandow (13) to be greater than in dilute solutions. They admitted their interpretation - that the increasing activity of perchlorate and decreasing activity of water may favor some sort of ceric - perchlorate ion pair in this sort of medium - to be rather uncertain.

Besides cerium(IV) dimers, cerium(IV)-cerium(III) dimers

have recently been suggested in perchloric acid by Blaustein and Gryder (2). Some of the data of Sherrill et al. (24) were treated on this basis and the assumption was shown to be qualitatively true.

Cerium(IV) in nitrate solution

As with the perchlorate solution, the early interpretations of the data available in nitrate solution could not agree. First indication of a cerium(IV)-nitrate anion complex was obtained by Meyer and Jacoby (18) in their transference experiment in 6 M nitric acid. Smith, Sullivan and Frank (27) presented a number of chemical evidence which show that ammonium hexanitratocerate is a complex salt and not a double salt.

On the other hand, Noyes and Garner (23) observed that the formal potential of 1.61 volts at $.25^{\circ}$ of the cerium(III)-cerium(IV) couple in nitric acid is practically invariant with the following changes in concentration: 0.04 M to 0.09 M ceric nitrate, 0.03 M to 0.02 M cerous nitrate, and 0.5 M to 2.0 M nitric acid. They concluded that nitrate complexes are formed slightly if at all and that equation 4 is not appreciable at these concentrations. Similarly, Smith and Goetz (26) obtained a constant formal potential of 1.61 volts from 1 M to 4 M nitric acid solutions containing equimolar (0.025 M) ceric nitrate and cerous nitrate. This observation

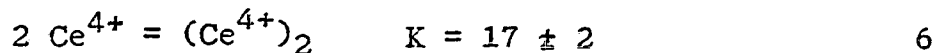
was interpreted on the other extreme - that in 2 M nitric acid, all or most of the cerium(IV) is $\text{Ce}(\text{NO}_3)_6^{2-}$. The substitution of sodium nitrate for nitric acid was claimed to have the same effect. Refuting this interpretation of Smith and Goetz (26) were the unpublished preliminary transference experiments of Garner as cited in Yost et al. (33), which gave no evidence of cerium(IV) migration towards the anode in 2 M nitric acid.

Like Noyes and Garner (23), Vetter (28) doubted the formation of complex nitrate ions. Once more he made a series of potential measurements. He explained the constancy of the formal potential up to 1 M nitric acid in solutions equimolar (0.001M) in cerium(IV) and cerium(III) as being due to hydrolysis and the opposing effect of the electrolytic development of oxygen. Hydrolyzed species were also suggested by Gryder and Dodson (8) to participate in the cerium(III)-cerium(IV) (0.002 M) exchange in 1.00 M to 6.18 M nitric acid solutions of ionic strength 6.18 as adjusted with sodium nitrate.

Yost, Russell and Garner (33) gave another explanation for the independence of the formal potential from nitric acid concentration between 0.5 M and 2.0 M. They postulated mixed hydroxide-nitrate complexes. Wylie (32) suggested that $[\text{Ce}(\text{OH})_n(\text{NO}_3)_m]^{(4-n-m)+}$ or $[\text{Ce}(\text{NO}_3)_m]^{(4-m)+}$ are first formed at low or intermediate acidities in nitrate solutions and

that conversion of these ions into anionic complexes takes place at higher acidities, corresponding to an increase in $n+m$. From 5 M to 6M nitric acid, Wylie (32) reported to have extracted into ethyl ether $H_2 [Ce(NO_3)_6]$, possibly mixed with $H [Ce(NO_3)_5(H_2O)]$.

The latest reinterpretation of the constant formal potential obtained by Noyes and Garner (23) is the one given by Blaustein and Gryder (2), namely, the presence of cerium-(IV)-cerium(III) dimers, besides cerium(IV) dimers, which have oxide or hydroxide bridges. Increasing the nitric acid concentration will have two opposing effects which are apparently comparable - an increase in nitrate complex formation and a decrease in dimerization. The extraction data of Blaustein and Gryder (2) were obtained using 5.5 M nitric acid solutions containing 0.33 M to 0.009 M ceric nitrate and about 0.2 M cerous nitrate. The species extracted into diisopropyl ether was found to contain no ionizable hydrogen, contrary to the report of Wylie (32). From their potential measurements on 5.5 M nitric acid solutions containing 0.11 M to 0.002 M ceric nitrate and 0.022 M to 0.029 M cerous nitrate, they estimated the following dimerization constants at 30° C:



and



They further supposed that cerium(IV) dimers may also be complexed with nitrate and that the monomers exist as various nitrate species.

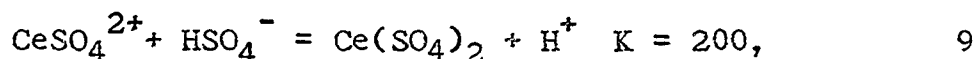
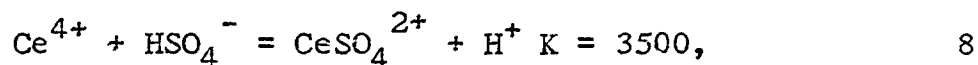
Cerium(IV) in sulfate solution

A number of workers obtained evidences for the formation of cerium(IV)-sulfate complexes. Jones and Soper (12) postulated $\text{H}_3\text{Ce}(\text{OH})(\text{SO}_4)_3$ in molar sulfuric acid and $\text{H}_4\text{Ce}(\text{SO}_4)_4$ in concentrated sulfuric acid from transport experiments. Smith and Goetz (26) obtained 1.44 volts as the formal potential of the cerium(III)-cerium(IV) couple from 1 M to 2 M sulfuric acid and interpreted this constant value to mean $\text{Ce}(\text{SO}_4)_3^{2-}$. An earlier potential measurement (16) gave a similar value. The potential drop in 1 M sulfuric acid solution which is 0.001 M in cerium(IV) and in cerium(III), was pointed out by Vetter (28) to be caused by complex formation. The constant formal potential from 0.1 M to 1.0 M sulfuric acid, he assumed to be due to the opposing effects of partial hydrolysis and complex formation.

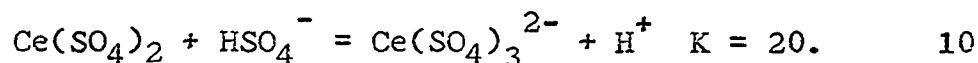
More evidence for sulfate complexes came from other sources. Weiss and Porret (30) did not observe reduction of cerium(IV) on irradiating ceric sulfate solution with ultra violet light, showing that free ceric ions must be nil. Moore and Anderson (21) found that the rate of reaction between cerium(IV) and arsenic(III) ions was decreased greatly

in sulfuric acid. Moore and Anderson (22) also made a spectrophotometric study of ceric perchlorate in perchloric acid-sodium perchlorate-sodium sulfate solution. Up to 0.01 M sulfate, $\text{Ce}(\text{SO}_4)^{2+}$ was reported to predominate and evidence for higher complexes was obtained.

Another spectral study, from 395 m μ to 430 m μ , was undertaken by Hardwick and Robertson (10) on solutions, 1.6×10^{-4} M to .0052 M in cerium(IV), 1.00 M in hydrogen ion, 0.001 M to 0.7 M in total sulfate, and all of ionic strength 2.00. Equilibrium constants were estimated at 25 $^{\circ}$ C for the following equilibria:



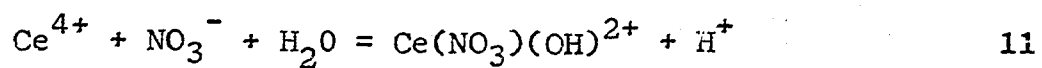
and



Migration experiments bore out the spectral results. Linnemann and Wahl (17), likewise, noted migration of cerium(IV) toward the anode and cerium(III) toward the cathode in their investigation of the cerium(III)-cerium(IV) exchange in sulfuric acid.

Wadsworth, Duke and Goetz (29) reviewed the variation of the formal potential of the cerium(III)-cerium(IV) couple with the type of anion present. The spectral data on sulfate complex formation and on hydrolysis were shown to correlate nicely with the potential data, yielding 1.74 volts for the

standard potential at an ionic strength of 2. To reconcile the acid independence of the formal potential from 0.5 M to 2 M nitric acid (23) with the evaluated standard potential, the following equilibrium was suggested:



whose K must have a value of 10^2 .

MATERIALS

Ceric perchlorate

The method of Sherrill, King and Spooner (24) was used to prepare ceric perchlorate. Ceric ammonium sulfate (obtained from the G. F. Smith Chemical Company) was dissolved in dilute nitric acid and reduced by 30 per cent hydrogen peroxide. A saturated solution of sodium oxalate was added to precipitate cerous oxalate, which was washed free from sulfate and was dissolved in concentrated nitric acid. The solution was treated with successive portions of concentrated hydrochloric acid, with each portion evaporated to fuming over a burner until all red fumes of nitrogen tetroxide were gone. Portions of 70 per cent perchloric acid were added next, with each portion evaporated to fuming. The solution was diluted and tested for chloride, nitrate, and ammonium ions. Electrolytic oxidation of this solution without use of a diaphragm as described by Smith, Frank, and Kott (25) gave the stock solution from which all subsequent dilutions were made.

To determine the perchloric acid concentration in the ceric perchlorate stock solution, the method of Noyes and Garner (23) was followed. An aliquot was taken, was reduced by a few drops of 3 per cent hydrogen peroxide, and was precipitated with saturated sodium oxalate. The cerous oxalate

precipitate was washed several times and the filtrate was titrated with standard 0.1 M carbonate-free sodium hydroxide solution. The acid concentration thus obtained was corrected for the acid produced by the reduction of cerium(IV).

Cerium(IV) analysis was carried out by titrating an aliquot to the nitro-ferroin end point with weighed primary standard sodium oxalate dissolved in 2 M perchloric acid.

Ceric perchlorate-cerous perchlorate

A portion of the ceric perchlorate stock solution was treated with enough 30 per cent hydrogen peroxide to reduce about half of the cerium(IV) to cerium(III). The remaining cerium(IV) was determined by the same method as used in the preceding paragraph.

The cerium(III) concentration was taken as the difference between the total cerium and the remaining cerium(IV). The method of Willard and Young (31) was followed to determine the total cerium. An aliquot of the ceric perchlorate stock solution was taken, its perchloric acid was removed by evaporation with sulfuric acid to fumes of sulfur trioxide, and was oxidized with solid ammonium persulfate using silver nitrate as catalyst. The solution was titrated potentiometrically with standard 0.05 M ferrous ethylenediamine sulfate.

Nitric acid and perchloric acid

70 per cent freshly opened acid was diluted to approximately 5 M and standardized against standard sodium hydroxide solution.

Sodium nitrate and sodium perchlorate

Sodium nitrate (obtained from Baker and Adamson) and sodium perchlorate (obtained from the G. F. Smith Chemical Company) were used without further purification to prepare approximately 5 M solutions. The solutions were standardized by pouring an aliquot through a column of cation exchange resin (Amberlite IR-112(H)) and titrating the resulting acid solution with standard sodium hydroxide solution.

APPARATUS

A Model DU Beckman Quartz Spectrophotometer was used. Water at $24.5 \pm 0.05^{\circ}$ C was circulated through the walls of the cell compartment.

The absorption spectra of the solutions containing very dilute nitric acid were investigated using a Model 12 Cary Recording Spectrophotometer.

A Leeds and Northrup Students' Potentiometer was used for the approximate potential measurements. A saturated calomel electrode was used as the reference and for the indicator electrode, a 1 cm^2 bright platinum foil welded to a platinum wire was used.

PROCEDURE

Procedure for optical density measurements

Appropriate volumes of the stock ceric perchlorate solution, the acids, and the sodium salts were pipeted out and diluted to give solutions of the required cerium(IV) concentration, acidity, and ionic strength. The volume of solution made up was 100 ml, using 100 ml red volumetric flasks to minimize photolysis. The solutions were immersed in a bath at $24.5 \pm 0.05^\circ \text{C}$ for at least one hour before use. A 1.0 cm silica cell contained the test solution and the optical density was referred to another 1.0 cm silica cell containing a blank of the acids and sodium salts appropriate to the test solution. The optical density was measured from 400 m μ to 430 m μ in steps of 10 m μ , using the Beckman spectrophotometer.

At the time of each run, the stock ceric perchlorate solution was analyzed for cerium(IV).

The absorption spectra measurement using the Cary recording spectrophotometer was carried out as follows: A solution containing the required nitrate ion concentration, 3.01 M hydrogen ion, and of ionic strength 3.02 was prepared. Another solution of the same acidity and ionic strength and containing approximately 0.001 M ceric was prepared. Equal volumes of these solutions were mixed and the mixture introduced into a 2.00 cm Cary silica cell. This was the blank.

The sample holder had two 1.00 cm Cary silica cells lined up, one containing the nitric acid solution and the other, the cerium(IV) solution. The base line was set with all the cells, filled with 3.02 M perchloric acid, in their respective places.

Procedure for the approximate potential measurements

The calomel half-cell was placed directly in the cerium solution and the potential read with a reproducibility of about 0.01 volt or better.

RESULTS AND DISCUSSION

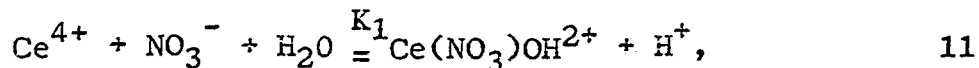
First complex

By apparent molar extinction coefficient is meant

$$\bar{\epsilon} = \frac{D}{C_T} \quad , \quad 12$$

where D is the optical density of the solution referred to the blank and C_T is the total ceric perchlorate concentration.

The two lower curves in Figure 1 show that an increase in acidity of solutions containing about 0.001 M nitrate, decreases the value of $\bar{\epsilon}$. Apparently, an equilibrium involving hydroxyl ions is present. Wadsworth, Duke and Goetz (29) suggested the equilibrium,



where

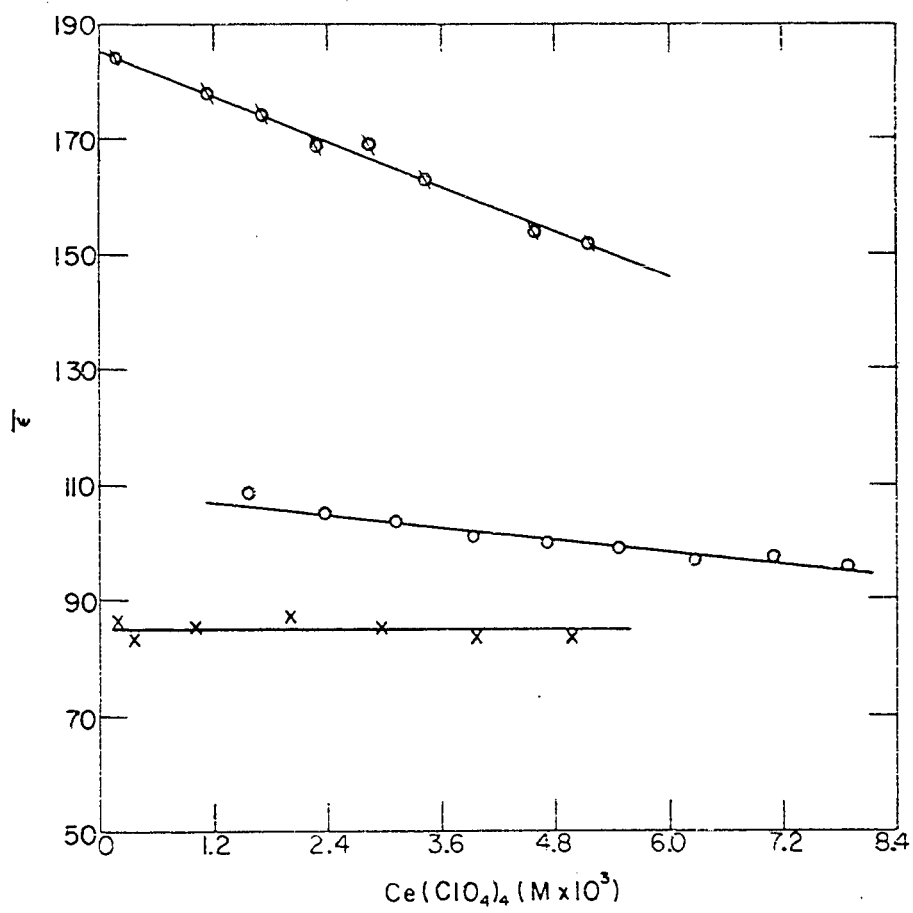
$$K_1 = \frac{[\text{Ce}(\text{NO}_3)\text{OH}^{2+}](\text{H}^+)}{(\text{Ce}^{4+})(\text{NO}_3^-)} \quad . \quad 11a$$

The lowest curve shows further that there is practically no polymerization of cerium(IV) up to a concentration of 0.005 M in solutions containing 5.02 M hydrogen ion and about 0.001 M nitrate.

K_1 was estimated as follows: The absorption spectra of solutions containing about 0.001 M and 0.004 M nitrate, 0.001 M cerium(IV), and 3.01 M hydrogen ion were measured in the ultra violet range, 240 m μ to 380 m μ , in such a manner

Figure 1. Apparent molar extinction coefficients as a function of ceric perchlorate concentration.

- φ (NO₃⁻) = 2.00 M; (H⁺) = 2.00 M; μ = 4.00;
430 mμ; 25.4 ± 0.1° C.
- (NO₃⁻) = 0.95 × 10⁻³ M; (H⁺) = 1.02 M; μ = 3.03;
410 mμ; 24.5 ± 0.05° C.
- x (NO₃⁻) = 1.15 × 10⁻³ M; (H⁺) = 5.01 M; μ = 5.02;
410 mμ; 24.5 ± 0.05° C.



that

$$D_{\text{obs'd}} = \epsilon_0 C_T + \epsilon_n N_T - \epsilon_0 C - \epsilon_1 C_1 - \epsilon_n N, \quad 13$$

where C , C_1 and N are the equilibrium concentrations of Ce^{4+} , $\text{Ce}(\text{NO}_3)\text{OH}^{2+}$, and NO_3^- respectively and ϵ_0 , ϵ_1 and ϵ_n are the corresponding molar extinction coefficients,

$$C_T = C + C_1, \quad 14$$

and

$$N_T = N + C_1. \quad 15$$

Combination of equations 11a, 13, 14 and 15 leads to

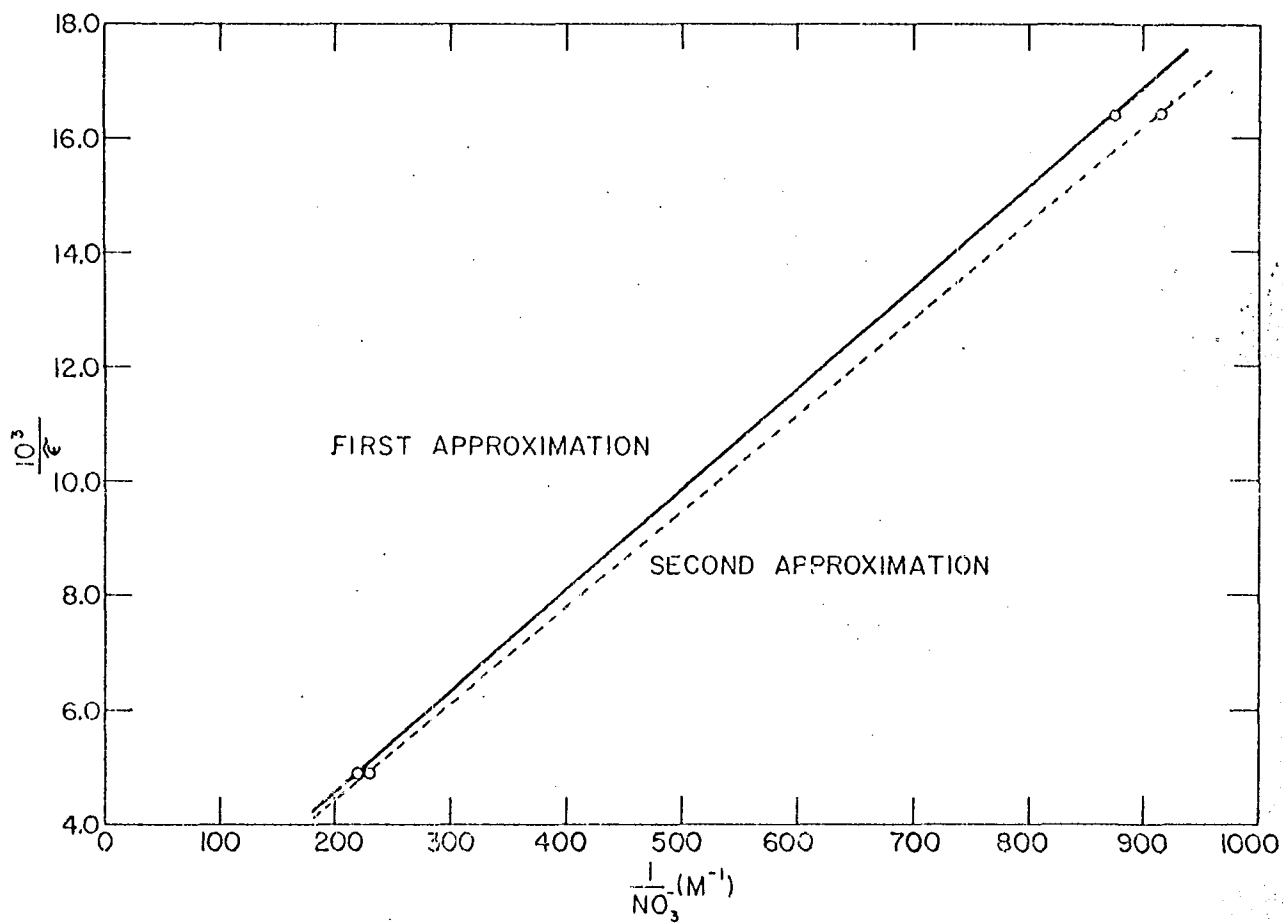
$$\frac{D_{\text{obs'd}}}{C_T} = \frac{(\epsilon_0 + \epsilon_n - \epsilon_1) \frac{K_1}{(\text{H}^+)} N}{1 + \frac{K_1}{(\text{H}^+)} N}. \quad 16$$

A plot of $C_T/D_{\text{obs'd}}$ (designated as $\tilde{\epsilon}$ in Figure 2) against $1/N$ is a straight line with an x-intercept equal to $+K_1/(\text{H}^+)$. The hydrogen ion concentration was not corrected since the acidity of the medium used was rather high. As a first approximation, the total nitrate was used in the solid curve in Figure 2. Convergence was achieved after the second approximation. K_1 was evaluated to be about 171.

The solutions were also investigated in the visible range, 400 m μ to 800 m μ . $D_{\text{obs'd}}$ was found to be zero. Apparently, Ce^{4+} and $\text{Ce}(\text{NO}_3)\text{OH}^{2+}$ have comparable molar extinction coefficients in this range.

Figure 2. Reciprocals of "apparent molar extinction coefficients" as a function of the reciprocal of nitrate concentration.

$[\text{Ce}(\text{ClO}_4)_4] = 0.98 \times 10^{-3} \text{ M}$; $(\text{H}^+) = 3.01 \text{ M}$; $\mu = 3.02$; 290 m μ .



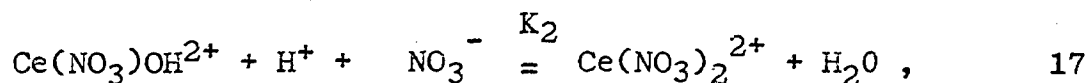
Second complex

The optical densities at $24.5 \pm 0.05^\circ$ C of ceric perchlorate solutions whose compositions are shown in Table 1 were measured at 400 m μ , 410 m μ , 420 m μ and 430 m μ .

Table 1. Compositions of solutions investigated to estimate K_2 and K_3

Series	NO_3^- (M)	$\text{Ce}(\text{ClO}_4)_4$ (M)(10^3)	H^+ (M)	μ
A	0-1.85	0.80-0.99	5.01	5.02
B	0-4.99	0.80-0.99	3.01	5.02
C	0-2.95	0.79-0.99	3.01	3.02
D	0-2.98	0.79-0.99	2.01	3.02
E	0-2.88	0.79-0.99	1.02	3.02

Figure 3 shows that increasing the acidity produces a corresponding increase in the value of $\bar{\epsilon}$. The equilibrium



where

$$K_2 = \frac{[\text{Ce}(\text{NO}_3)_2^{2+}]}{[\text{Ce}(\text{NO}_3)\text{OH}^{2+}](\text{H}^+)(\text{NO}_3^-)} \quad 17a$$

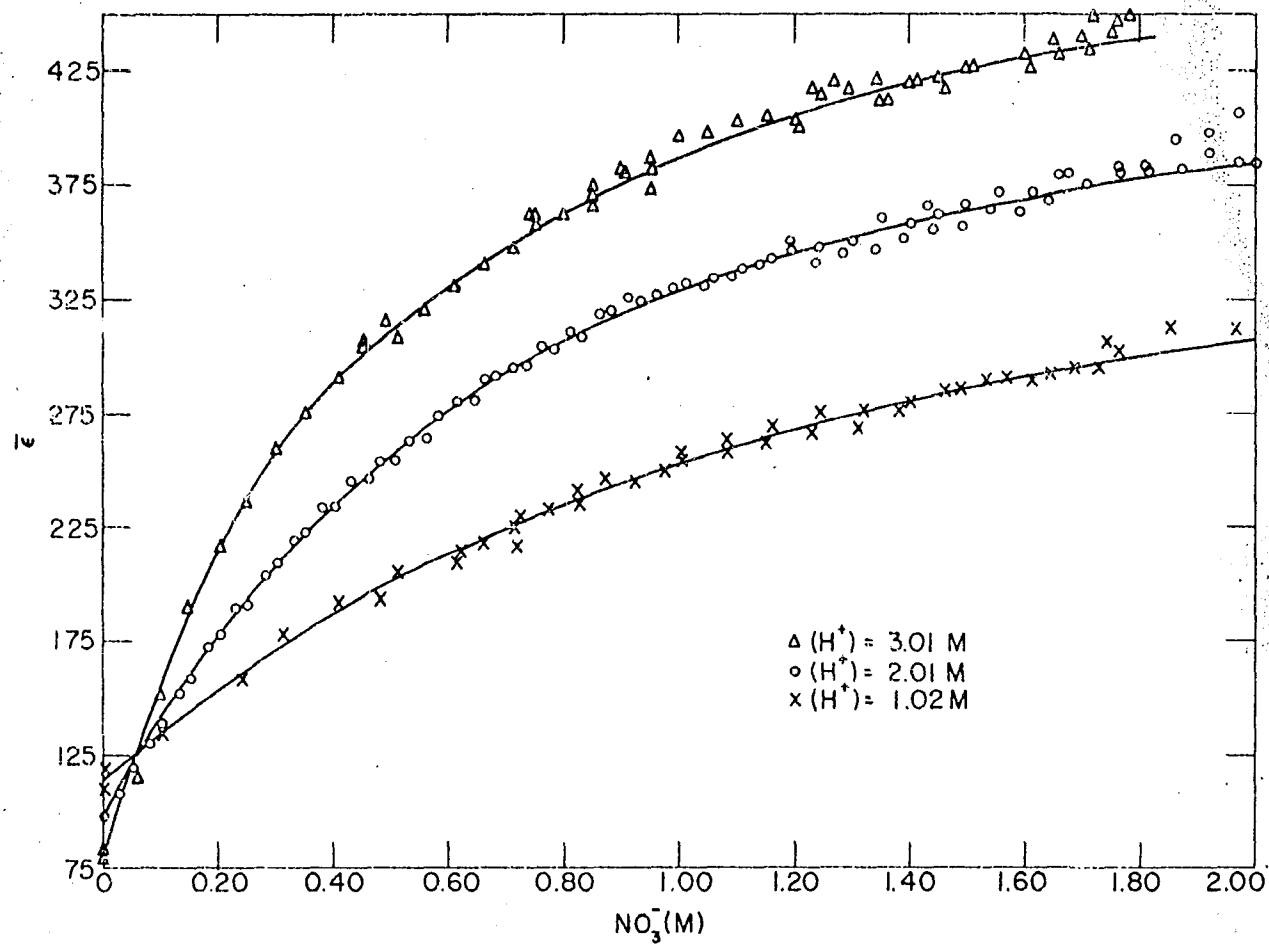
may then be written.

$$\text{Let } D = \epsilon_0 C + \epsilon_1 C_1 + \epsilon_2 C_2 \quad 18$$

and

$$C_T = C + C_1 + C_2, \quad 19$$

Figure 3. Apparent molar extinction coefficients as a function of total nitrate concentration. $[\text{Ce}(\text{ClO}_4)_4] = 0.79 \times 10^{-3} \text{ M}$; $\mu = 3.02$; $410 \text{ m}\mu$; $24.5 \pm 0.050 \text{ C}$.



where C_2 is the equilibrium concentration of $Ce(NO_3)_2^{2+}$ and

ϵ_2 is its molar extinction coefficient. Equations 11a, 17a, 18 and 19 can be combined to the form

$$\bar{\epsilon} - \epsilon_0 = \frac{(\epsilon_1 - \epsilon_0) \frac{K_1}{(H^+)} + (\epsilon_2 - \epsilon_0) K_1 K_2 N}{\frac{1}{N} + \frac{K_1}{(H^+)} + K_1 K_2 N} \quad 20$$

If $1/N$ is neglected in the denominator (for $N_T = 0.16$ M, $(H^+) = 1.02$, this amounts to neglecting 3 per cent of the denominator) and if ϵ_0 and ϵ_1 are assumed to be comparable as previous evidence showed, equation 20 may be reduced to the form

$$\frac{1}{\bar{\epsilon} - \epsilon_0} = \frac{1}{(\epsilon_2 - \epsilon_0)(H^+)K_2} \left(\frac{1}{N} + \frac{1}{(\epsilon_2 - \epsilon_0)} \right) \quad 20a$$

Plots of equation 20a are shown in Figures 4, 5, 6, 7 and 8. The total nitrate concentration was plotted and the total hydrogen ion concentration was used since the corrections were not appreciable under the conditions used. The x-intercepts gave the values of $K_2(H^+)$ which are shown in Table 2. The mean values of K_2 thus obtained are 0.6 and 1.0 at ionic strengths of 3.02 and 5.02 respectively.

Third complex

It may be noted in Figures 4 and 5, both at an ionic strength of 5.02, that the slope increases at higher nitrate concentration. The change in slope starts at about 1.58 M

Figure 4. Reciprocals of apparent molar extinction coefficients as a function of the reciprocal of total nitrate concentration.
[Ce(ClO₄)₄] = 0.80 x 10⁻³ M; (H⁺) = 5.01; μ = 5.02; 410 mμ;
24.5 ± 0.05° C.

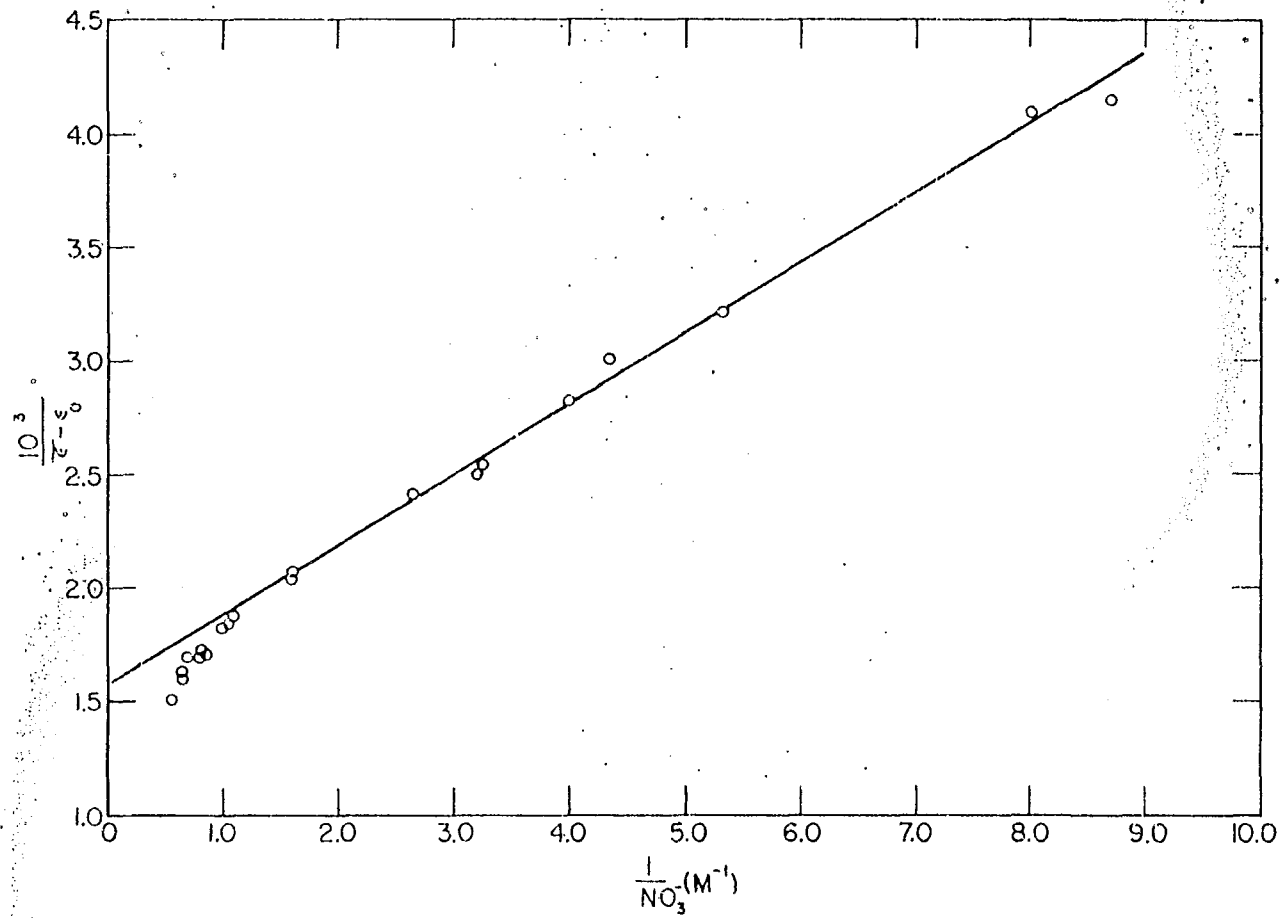
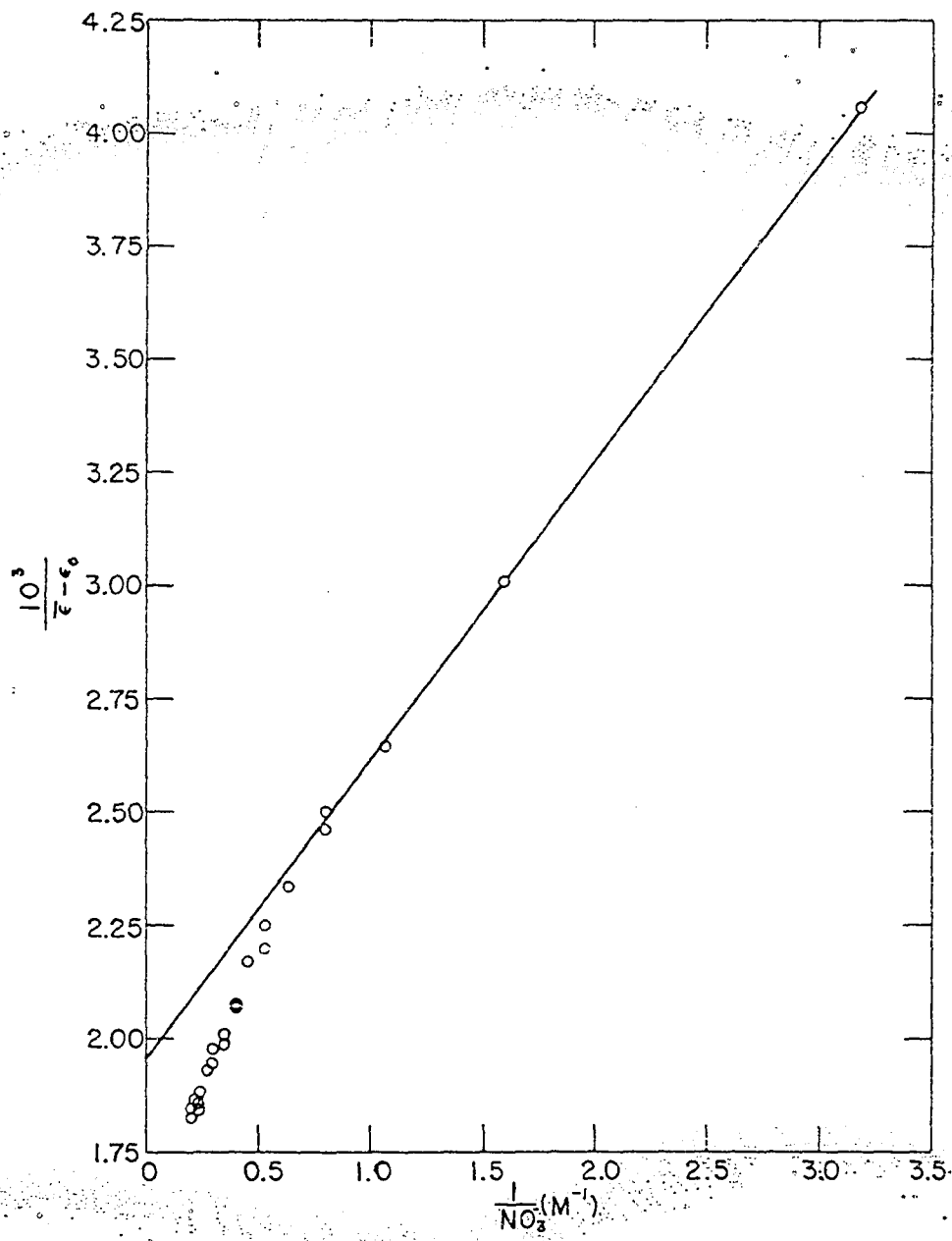


Figure 5. Reciprocals of apparent molar extinction coefficients as a function of the reciprocal of total nitrate concentration.

$[\text{Ce}(\text{ClO}_4)_4] = 0.80 \times 10^{-3}\text{M}$; $(\text{H}^+) = 3.01 \text{ M}$;
 $\mu = 5.02$; $410 \text{ m}\mu$; $24.5 \pm 0.05^\circ \text{ C}$.



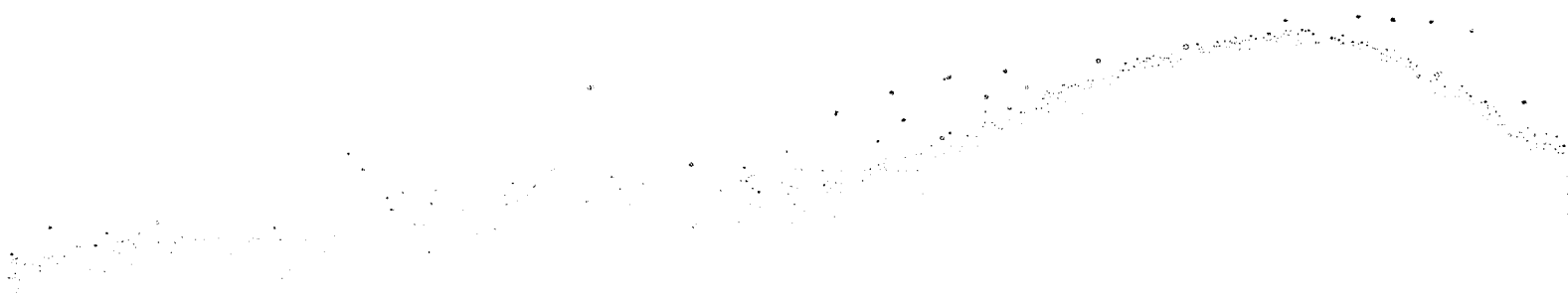


Figure 6. Reciprocals of apparent molar extinction coefficients as a function of the reciprocal of total nitrate concentration.

$[\text{Ce}(\text{ClO}_4)_4] = 0.89 \times 10^{-3}$ and 0.99×10^{-3} M;
 $\mu = 5.02$; $24.5 \pm 0.05^\circ \text{C}$.

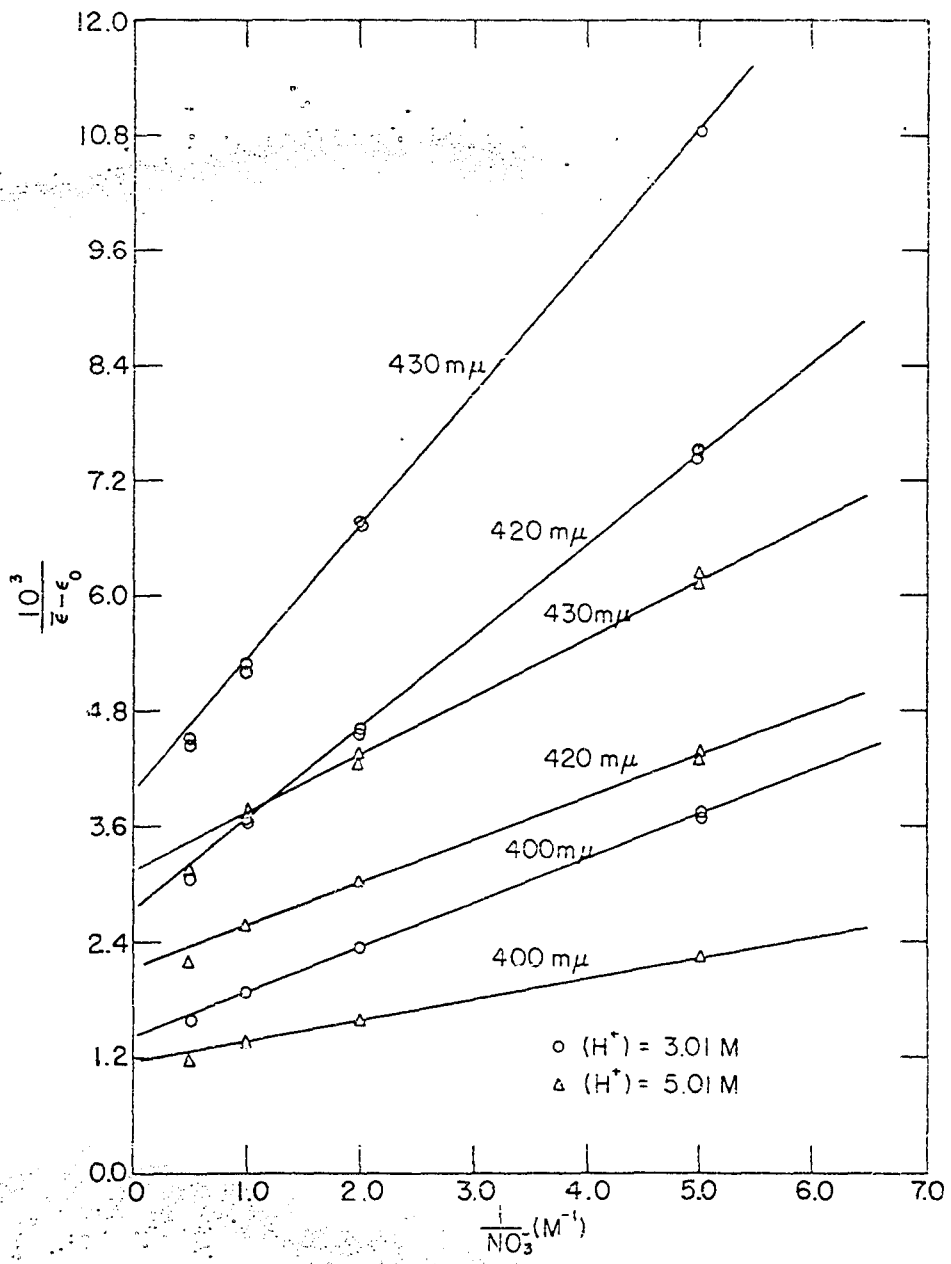


Figure 7. Reciprocals of apparent molar extinction coefficients as a function of the reciprocal of total nitrate concentration.

$[\text{Ce}(\text{ClO}_4)_4] = 0.89 \times 10^{-3}$ and 0.99×10^{-3} M;

$\mu = 3.02$; $24.5 \pm 0.05^\circ$ C.

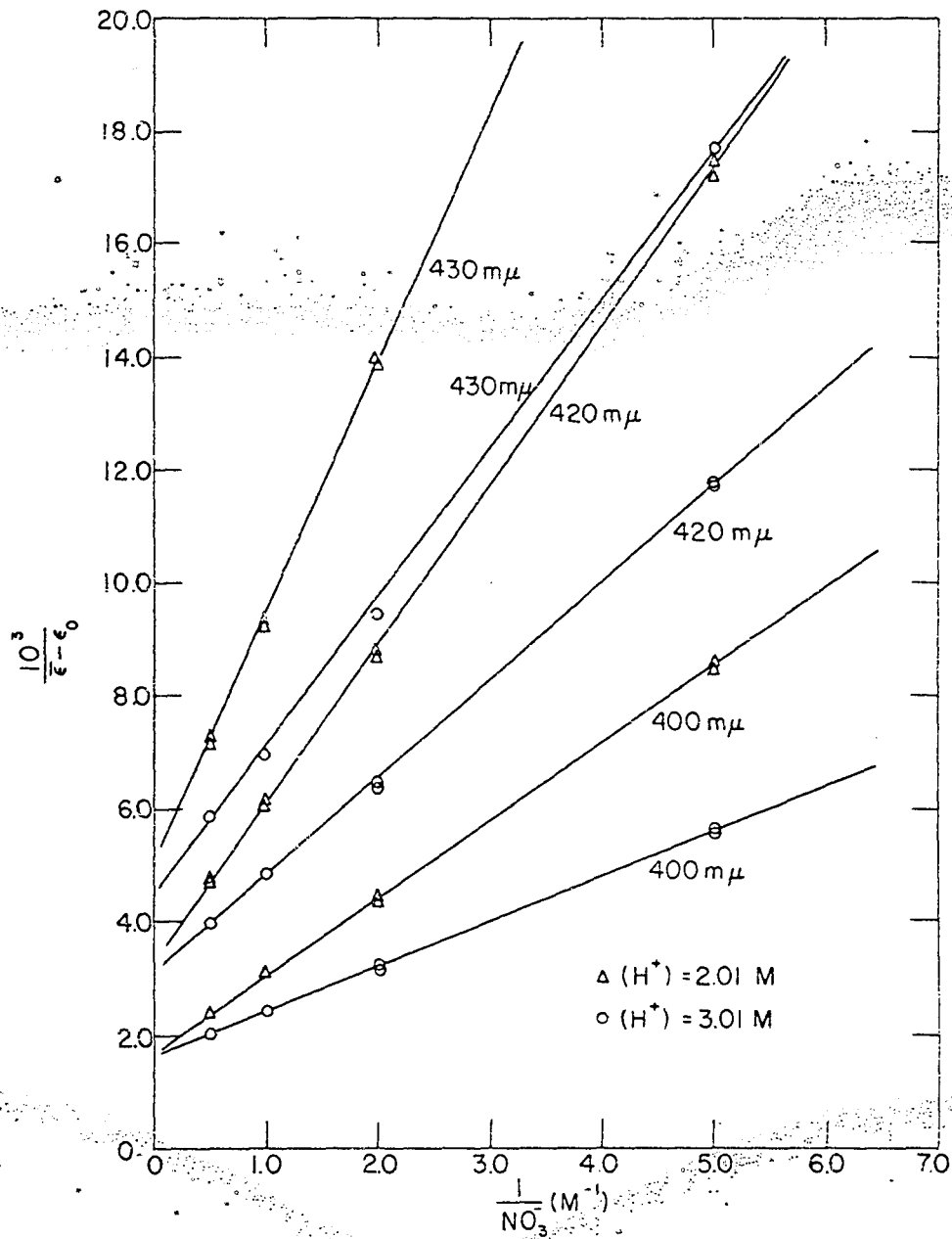


Figure 8. Reciprocals of apparent molar extinction coefficients as a function of the reciprocal of total nitrate concentration.

$[\text{Ce}(\text{ClO}_4)_4] = 0.89 \text{ and } 0.99 \times 10^{-3}\text{M}; (\text{H}^+) = 1.02\text{M}; \mu = 3.02; 24.5 \pm 0.05^\circ \text{C}.$

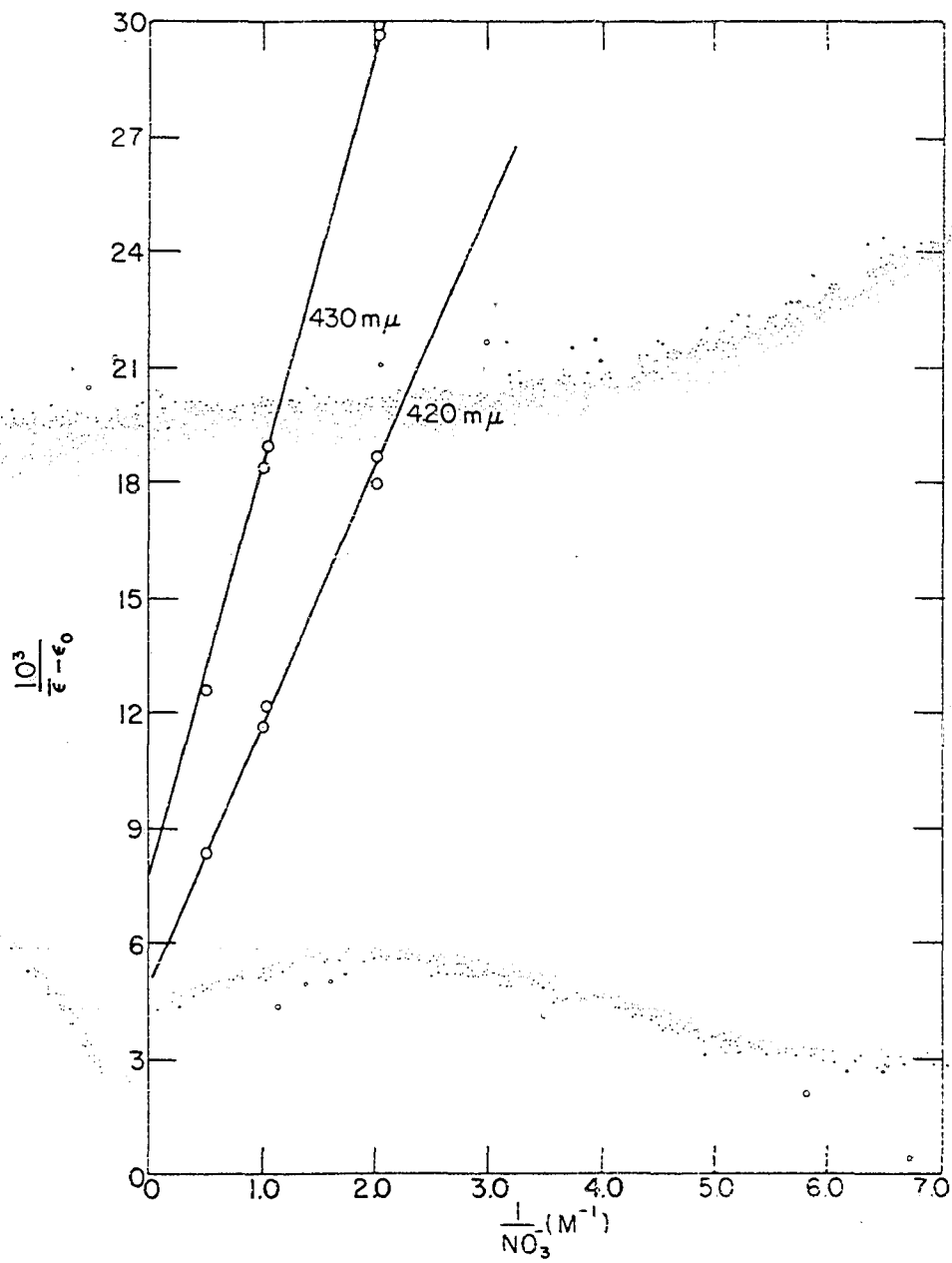
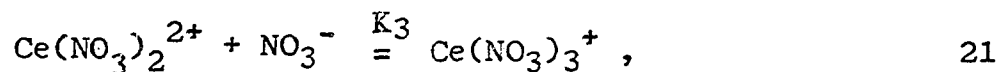


Table 2. Graphically estimated K_2 in the different series

Series	$K_2(H^+)$				K_2
	400 μ	410 μ	420 μ	430 μ	
A	5.3	5.1	4.9	4.9	1.0
B	3.0	3.0	2.9	2.8	1.0
C	2.0	1.9	1.8	1.7	0.6
D	1.3	1.2	1.2	1.2	0.6
E		0.6	0.7	0.7	0.65

and 0.93 M nitrate in solutions containing 3.01 M and 5.01 M hydrogen ion respectively. This seemingly is evidence for a higher complex, probably $Ce(NO_3)_3^+$. If it is assumed that this complex and the second complex predominate at these higher nitrate concentrations, then one can write



where

$$K_3 = \frac{[Ce(NO_3)_3^+]}{[Ce(NO_3)_2^{2+}] (NO_3^-)}, \quad 21a$$

$$D = \epsilon_2 C_2 + \epsilon_3 C_3, \quad 22$$

and

$$C_T = C_2 + C_3, \quad 23$$

where C_3 is the equilibrium concentration of $Ce(NO_3)_3^+$ and ϵ_3 is its molar extinction coefficient. Summing up equation 21a, 22, and 23 leads to

$$\frac{1}{\bar{\epsilon}} = \frac{1 + K_3N}{\epsilon_2 + \epsilon_3 K_3 N} \quad 24$$

A plot of $1/\bar{\epsilon}$ against $1/N_T$ gave a straight line with an x-intercept of 1.7 ± 0.3 . The nitrate concentration was not corrected. If the approximation, that ϵ_2 is small compared to the product $\epsilon_3 K_3 N$, is made, this value may be interpreted as K_3 .

Approximate potentials

The approximate formal cerium(III)-cerium(IV) oxidation potentials were measured in a few nitrate solutions of ionic strength 3.02. The potentials were also calculated using the equation

$$E = E^{\circ} - 0.059 \log \left(1 + \frac{K_1 N_T}{(H^+)} + K_1 K_2 N_T^2 \right) \quad 25$$

where

$$E^{\circ} = 1.77 \text{ volts for ionic strength of 3}$$

(interpolated from Wadsworth, Duke, and Goetz (29)), $K_1 = 171$, and $K_2 = 0.6$. The cerium(IV) species assumed here were Ce^{4+} , $Ce(NO_3)OH^{2+}$, and $Ce(NO_3)_2^{2+}$. Table 3 shows the comparison between the calculated and the observed formal oxidation potentials of the cerium(III)-cerium(IV) couple.

Wadsworth et al. (29) reported 1.61 volts and 1.62 volts

Table 3. Comparison between the calculated [$E^{\circ} = 1.77$ (29), $K_1 = 171$, $K_2 = 0.6$] and the observed Ce(III)-Ce(IV) formal oxidation potentials.
 $[\text{Ce}(\text{ClO}_4)_4] = 0.017 \text{ M}$; $[\text{Ce}(\text{ClO}_4)_3] = 0.018 \text{ M}$;
 $\mu = 3.02$

Total NO_3^- (M)	$(\text{H}^+) = 3.01 \text{ M}$		$(\text{H}^+) = 2.01 \text{ M}$		$(\text{H}^+) = 1.02 \text{ M}$	
	E obs'd volts	E calc'd volts	E obs'd volts	E calc'd volts	E obs'd volts	E calc'd volts
0.50	1.66	1.67	1.66	1.66	1.66	1.65
1.00	1.64	1.64	1.65	1.64	1.65	1.63
2.00	1.62	1.61	1.62	1.61	1.62	1.60

as the formal potentials in 1 M and 2 M nitric acid respectively. The corresponding calculated values are 1.61 and 1.60. E° was taken to be 1.75 volts and 1.76 volts (29) for ionic strengths of 1 and 2 respectively and the same values of K_1 and K_2 as previously used were assumed.

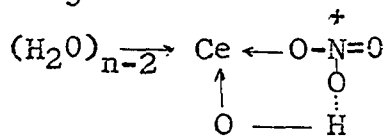
Discussion

The solutions invariably contained small amounts of cerium(III) ions from the incomplete oxidation of the stock cerium solution and from reduction of cerium(IV) by water. However, these ions were found to have negligible effect on the spectra under the conditions used. Perchlorate and nitrate solutions containing equimolar ceric perchlorate and cerous perchlorate had the same optical densities at 410 $\text{m}\mu$, as the corresponding solutions without added cerous perchlo-

rate. Seemingly, the mononitrate complex of cerium(III), whose association constant in 0.89 M nitric acid is reported to be 1.4 (3), is non-absorbing at 410 m μ .

There is some uncertainty in the value of K_1 obtained. This may be due to water reduction of ceric perchlorate in the blank in the absence of stabilizing nitrate ions upon the incidence of ultra-violet light in which range the spectrum was measured. The value estimated may therefore be slightly higher than the true value.

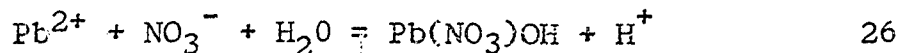
The order of magnitude of K_1 appears to be unusually high for a metal ion nitrate complex. This may be explained by the stabilizing effect of a hydrogen bond if the following structure of $\text{Ce}(\text{NO}_3)\text{OH}^{2+}$ is assumed:



The coordination of the OH^- to the cerium increases the positive charge on the oxygen atom which donates the proton in hydrogen bond formation, and thus increases the ionic character of the O-H bond and the positive charge of the hydrogen atom. The strength of the hydrogen bond is therefore increased.

K_1 may be compared with the only analogous one available so far. The formation constant of $\text{Pb}(\text{NO}_3)\text{OH}$ according to the

equilibrium



was obtained by Misra and Pani (19) from a study of the solubility of $\text{Pb}(\text{IO}_3)_2$ in nitric acid. They reported a fairly low constant, 0.712. The empirical ionic (crystal) radii for coordination number six of Pb^{2+} and Ce^{4+} are 1.32 Å and 1.02 Å respectively, and their corresponding outer electron configurations are $6s^2$ and $4f^05s^25p^6$ (20). These differences may partly explain the unusually high stability of $\text{Ce}(\text{NO}_3)\text{OH}^{2+}$ compared to that of $\text{Pb}(\text{NO}_3)\text{OH}$.

K_2 was seen to increase with increase in ionic strength. This means that changes in the activity coefficients of the ions in equation 17a do not cancel numerically.

No attempt was made to calculate the spectral curves by assigning definite molar extinction coefficients to the various species. There is a probable error in the calculated value of K_1 . Besides, the situation may possibly be more complex than the picture deduced with other species probably present which, although may not really be predominating, cannot entirely be ruled out. Some dimers with oxide or hydroxide bridges and complexed with nitrate may also be present especially in solutions high in nitrate and in ionic strength and low in acidity. Such dimers were suggested by Blaustein and Gryder (2). The highest curve in Figure 1

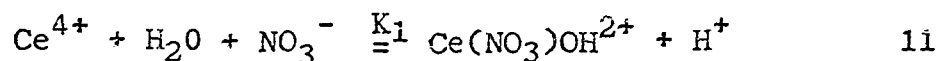
shows this tendency. Gryder and Dodson (8) admitted that the nature of cerium(IV) in nitrate solution is a complex one with no single species really predominating.

The charges on the species up to 2 M nitrate agree with the transference experiments of Garner as cited in Yost et al. (33), which gave no evidence of cerium(IV) migration towards the anode in 2 M nitric acid.

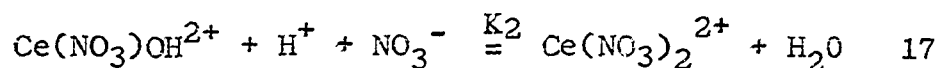
The observed formal oxidation potentials of the cerium-(III)-cerium(IV) couple are open to question. Vetter (28) pointed out that the high potential measured in 1 M nitric acid is actually a mixed potential with the oxygen electrode. The disagreement in Table 3 between the observed and the calculated potentials is higher at lower acidity. This may be due to the electrolytic evolution of oxygen. Furthermore, Duke and Parchen (5) observed that platinum does not catalyze the exchange between cerium(III) and cerium(IV) in perchloric acid and so platinum may not act as a reversible electrode in such system. This may well be extended to the nitrate system.

SUMMARY

The monomeric cerium(IV) species in nitrate solutions of ionic strengths 3 and 5 were studied spectrophotometrically at 24.5° C. Evidence was obtained for the presence of Ce^{4+} (aquated), $\text{Ce}(\text{NO}_3)\text{OH}^{2+}$, and $\text{Ce}(\text{NO}_3)_2^{2+}$ in solutions of the following composition: 0.001 M ceric perchlorate, from 1 M to 3 M hydrogen ion, ionic strength 3, and up to 2 M nitrate. To interpret the data obtained, the following equilibria were assumed:

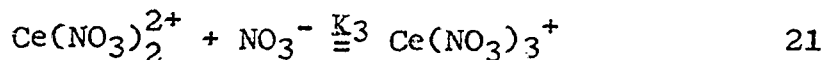


and



and values of 171 and 0.6 were estimated for K_1 and K_2 respectively.

In solutions containing 0.001 M ceric perchlorate, 3 M and 5 M hydrogen ion, and of ionic strength 5, the above equilibria were found to be valid up to about 1 M nitrate. K_2 was evaluated to be 1. K_1 at this higher ionic strength was not calculated; a lower value than 171 may be expected. At higher nitrate concentration, from 1 M to 4 M, $\text{Ce}(\text{NO}_3)_2^{2+}$ and $\text{Ce}(\text{NO}_3)_3^+$ seemed to predominate. K_3 for the equilibrium



was approximated as 1.7 ± 0.3 .

Evidence for the possibility of dimers with oxide or hydroxide bridges and complexed with nitrate in solutions high in nitrate and in ionic strength and low in acidity was also observed.

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