[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, COLUMBIA UNIVERSITY AND BROOKHAVEN NATIONAL LABORATORY]

The Kinetics of the Exchange Reaction between the Two Oxidation States of Cerium in Acid Solution[1a]

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The rate of the electron transfer exchange reaction between cerous and ceric cerium in nitrate and perchlorate solutions has been found to be measurable at 0° and to be complete within a few minutes at room temperature. The reaction is first order in cerous cerium, but has an order between zero and one in ceric cerium, depending on the cerium(IV) concentration and on the nature of the medium. The latter result is tentatively interpreted in terms of an excited electronic state of cerous cerium. The effect of acidity on the rate has been determined and suggests that hydrolyzed species participate more effectively in the reaction than unhydrolyzed species.

Introduction

Although the possibility of studying the rates of exchange reactions between various oxidation states of the same element was recognized soon after the discovery of radioactivity,[2] systematic experiments have only recently been carried out to measure the rates and determine the kinetics of such reactions. Several workers have studied the thallous–thallic exchange[3] and also the exchange between various cobaltous and cobaltic compounds.[4] In these cases it was found that the exchange reactions are relatively slow and are first order in the reacting species. The rates were also found to depend upon the acidity and the concentration of the anion present.

The present research was undertaken to study further the phenomenon of electron transfer with the hope that the results might give additional insight into oxidation–reduction reactions in general.[5] The cerium system was chosen because it is known that ceric cerium oxidizes thallous thallium extremely slowly at room temperature in spite of the fact that both form reversible electrodes. A comparison of the rate of this reaction with the two exchange reactions might elucidate the nature of ionic species existing in solution as well as the factors determining the rates of reaction. One of us (J.W.G.) is now studying the kinetics of the thallous–ceric reaction.

Procedure

Materials.—Radioactive cerous chloride (Ce^{144} 275 day) in hydrochloric acid solution was obtained from the U.S. Atomic Energy Commission, Oak Ridge, Tennessee. The active cerium was purified[6] by a precipitation of the fluorides of cerium and lanthanum in the presence of zirconium holdback carrier. The fluorides were dissolved in a solution of boric and nitric acids, oxidized with sodium bromate, and ceric iodate precipitated. The precipitate was dissolved with nitric acid and hydrogen peroxide, and ceric iodate was reprecipitated after oxidation with sodium bromate; this was repeated twice. Zirconium iodate was then precipitated in the presence of cerous ion. Finally cerous oxalate was prepared, dissolved in nitric acid and reprecipitated. The cerous oxalate was dissolved with nitric or perchloric acid, and the solution was fumed to destroy the oxalate. In this process some of the cerium was oxidized and therefore a drop of hydrogen peroxide was added and decomposed by heating the solution. The resulting solutions were used as stock reagents for introducing activity into the reaction materials.

Cerous perchlorate was obtained from G. Frederick Smith Chemical Company in reagent grade and used without further purification. Cerous nitrate and sodium perchlorate were obtained from Eimer and Amend. In a few cases the cerous salts were made by reduction of the ceric compound with hydrogen peroxide. No difference was noted in the rate of the reaction when different sources of material were used. Ammonium hexanitratocerate, ceric nitrate in 2 *f* nitric acid and ceric perchlorate in 6 *f* perchloric acid were obtained from G. Frederick Smith and used without further purification. Baker analyzed vacuum distilled 70% perchloric acid was employed. Mallinckrodt Analytical Reagent ethyl ether was used with or without previous treatment with ceric nitrate. All other chemicals were standard chemically pure reagents.

Stock solutions of cerous and ceric nitrate and perchlorate were prepared in 6 *f* acid. The ceric cerium concentration was determined by titration with standard ferrous solution. Cerous nitrate and total cerium in ceric nitrate were determined by this titration after first oxidizing with peroxysulfate with silver ion catalyst. The cerous perchlorate and total cerium in ceric perchlorate were determined by precipitating cerous 8-hydroxyquinolate, in the presence of hydroxylamine, and weighing as such.[7] Stock solutions of standard acid, sodium perchlorate and sodium nitrate were also prepared. The concentrations of the latter two solutions were obtained from their densities. Reaction mixtures were prepared from these solutions and the stock activity solutions.

Experimental.—Various workers have reported that the formation of a precipitate may induce the exchange of electrons between ionic species in solution,[3b,8] and consequently precipitation separations were avoided. The preliminary work with a diffusion separation has been reported previously.[9] Since this method proved to be unsatisfactory, an extraction procedure employing ethyl ether was developed.[10] The separation technique consisted of an extraction of ceric cerium into analytical reagent ether from a solution of the reacting ions in nitric acid. In the case of runs with perchloric acid, 20 ml. of the reaction mixture was diluted with 50 ml. of 4 *f* nitric acid before extraction. In spite of the fact that ceric cerium is slowly reduced by ether, consistent data were obtained because the fraction of cerium reduced in each separation was the same when a given lot of ether was employed. In some cases the ether was first treated with ceric nitrate to oxidize reducing impurities. The results with this ether were identical with those obtained with the unpurified reagent.

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[1] (a) This work was carried out at Brookhaven National Laboratory under the auspices of the United States Atomic Energy Commission. (b) Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland.

[2] G. Hevesy and L. Zechmeister, *Ber.*, **53**, 410 (1920); G. T. Seaborg, *Chem. Revs.*, **27**, 199 (1940).

[3] (a) G. Harbottle and R. W. Dodson, Columbia University Thesis; Brookhaven National Laboratory Report No. BNL-C-8; unpublished data. (b) R. J. Prestwood and A. C. Wahl, THIS JOURNAL, **71**, 3137 (1949).

[4] (a) K. J. McCallum and S. A. Hoshowsky, *J. Chem. Phys.*, **16**, 254 (1948); K. J. McCallum, Brookhaven National Laboratory Report BNL-C-8. (b) W. B. Lewis and C. D. Coryell, *ibid.*; W. B. Lewis, Massachusetts Institute of Technology Technical Report No. 19

[5] (a) J. W. Gryder, *Trans. N. Y. Acad. Sci.*, **12**, 18 (1949) Series II. (b) also see A. E. Remick, *Record Chem. Progress*, **9**, 95 (1948).

[6] N. E. Ballou, Plutonium Project Report Volume 9B, 8. 243

[7] R. Berg and E. Becker, *Z. anal. Chem.*, **119**, 1 (1940).

[8] (a) C. L. Van Alten and C. N. Rice, THIS JOURNAL, **70**, 883 (1948); (b) see also M. H. Gorin, *ibid.*, **58**, 1787 (1936).

[9] (a) J. W. Gryder and R. W. Dodson, *ibid.*, **71**, 1894 (1949); (b) see also V. J. Linnenbom and A. C. Wahl, *ibid.*, **71**, 2589 (1949).

[10] We have since found that various solvents have been used for the extraction of tetravalent cerium: L. Imre, *Z. anorg. allgem. Chem.*, **164**, 214 (1927); J. C. Warf, Atomic Energy Commission Report AECD 2524, and THIS JOURNAL, **71**, 3257 (1949).

After extraction, the ethereal phase was washed with 8*f* nitric acid and the ceric cerium re-extracted with water. This second aqueous phase was diluted to constant volume and counted with a dipping thin wall Geiger–Müller tube with reproducible geometry. The counting rates were below 1000 c./min. thus obviating need for coincidence corrections. The solutions counted were always of the same composition so that corrections for the effect of density on counting rate were unnecessary. In all cases the samples were allowed to stand at least three hours before counting to permit the 17-minute praseodymium daughter to grow into equilibrium concentration. A Tracerlab Autoscaler was employed, and three separate counts of 4096 were always made to check the reproducibility of geometry.

The fraction exchanged was obtained by comparing the observed count with the experimentally determined counting rate at infinite time. This was done to eliminate the necessity of determining the fraction of cerium extracted in each run. The method was validated by the observed exponential time dependence of the fraction of exchange[11] and by confirmatory experiments in which it was found that the specific activity of experimental infinite time runs agreed with the calculated values. All exchange runs were carried out at constant volume formal ionic strength in a constant temperature bath with temperature regulation of about 0.1°. The individual determinations of reaction rate constants are believed to be accurate within a relative standard deviation of about 10%.

Results

Nitrate System.—A series of runs was performed to determine the dependence of the rate of reaction on the concentrations of cerous and ceric cerium. For the case in which there are no slow consecutive reactions and in which the concentrations of the reactants do not vary with time, the time dependence of the fraction of activity exchanged is given by[11]

$$\ln (1 - x/x_\infty) = -Rt(a + b)/ab \qquad (1)$$

in which x is the activity of the originally inactive material at time t and x_∞ is this quantity when equilibrium with respect to isotopic mixing has been achieved. R is the rate of the reaction being studied, and a and b are the over-all concentrations of the reactants. Representative experimental curves are given in Fig. 1. If the rate of the reaction is assumed to have a simple power dependence upon the concentrations of the reacting materials one can write

$$R = ka^\alpha b^\beta \qquad (2)$$

Employing this in equation (1), substituting $T^{1/2}$ for the time for half reaction, and taking logarithms we obtain

$$\ln T^{1/2}(a + b) + (\alpha - 1) \ln a + (\beta - 1) \ln b + \ln k/0.693 = 0 \qquad (3)$$

If one determines $T^{1/2}$ as a function of a with b constant and plots $\ln T^{1/2}(a + b)$ against $\ln a$, the slope will be equal to $1 - \alpha$. This plot has an advantage over the usual graph of $\ln R$ against $\ln a$ at constant b in that the divergence from first order is magnified. The results of experiments carried out to determine the dependence upon cerous and ceric cerium in the nitrate system at 0° are given in Table I, and the data are plotted according to equation 3 in Figs. 2 and 3. The slopes of the lines in Figs. 2 and 3 indicate that the order with respect to cerium(III) is 1.06 ± 0.10 and with respect to cerium(IV) is 0.89 ± 0.05. Although the order is amost unity, it is believed that the trend in the ceric cerium dependence is real. This will be discussed subsequently.

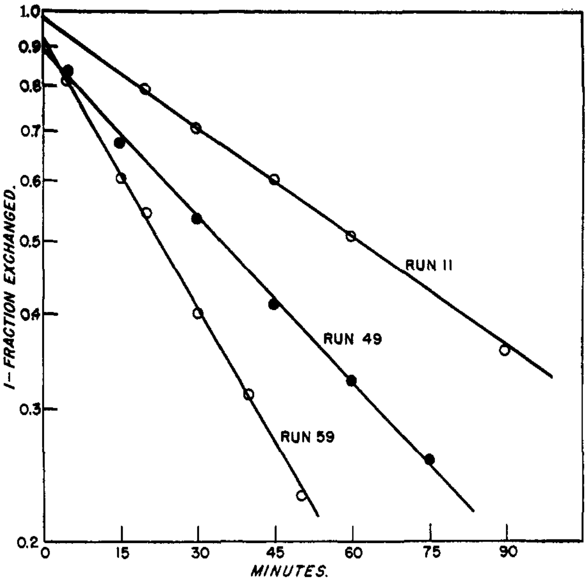

Fig. 1.—Representative curves of original data.

TABLE I

CERIUM(III) AND CERIUM(IV) DEPENDENCE IN NITRATE SYSTEM

6.18 *f* HNO₃ at 0.0 ± 0.1°

Ce(III), *f*	Ce(IV) *f*,	$T^{1/2}$, min.
0.00181	0.00171	88
.00453	.00171	45
.00905	.00171	25.1
.0181	.00171	16.7[a]
.0181	.00171	13.3
.00176	.00167	94
.00176	.00416	61
.00176	.00831	35
.00176	.0171	20.5
.00176	.0167	23

[a] Probably in error due to temperature fluctuation.

Another series of experiments was performed to determine the dependence upon acidity and temperature. The results of these runs are given in Table II. In all cases the volume formal ionic

TABLE II

ACID AND TEMPERATURE DEPENDENCE IN THE NITRATE SYSTEM

Ionic strength adjusted to 6.18 *f* with NaNO₃

Temp., °C.	HNO₃, *f*	Ce(III), *f*	Ce(IV), *f*	$T^{1/2}$, min.	*k*, formal⁻¹ min.⁻¹
25.0	6.18	0.00181	0.00171	11.2	17.6
0.0	6.18	.00181	.00171	88	2.24
0.0	3.68	.00181	.00171	81	2.43
0.0	3.68	.00181	.00171	75	2.62
0.0	2.42	.00194	.00148	45	4.50
0.0	2.01	.00194	.00148	34.5	5.86
−1.1	2.01	.00194	.00148	42	4.82
−9.7	2.01	.00194	.00148	112	1.81
0.0	1.00	.00194	.00148	10.6	19.1
−5.7	1.00	.00194	.00148	29	6.97
−9.8	1.00	.00194	.00148	49	4.13

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[11] H. A. C. McKay, *Nature*, **142**, 997 (1938); R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

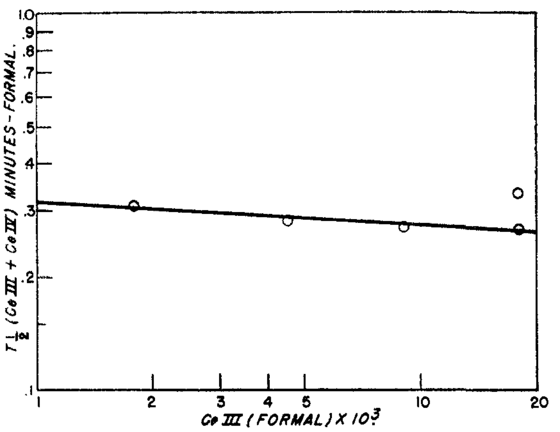

Fig. 2.—Cerium(III) dependence in the nitrate system (0.0°, 6.18 *f* HNO_3, 0.00171 *f* Ce(IV)).

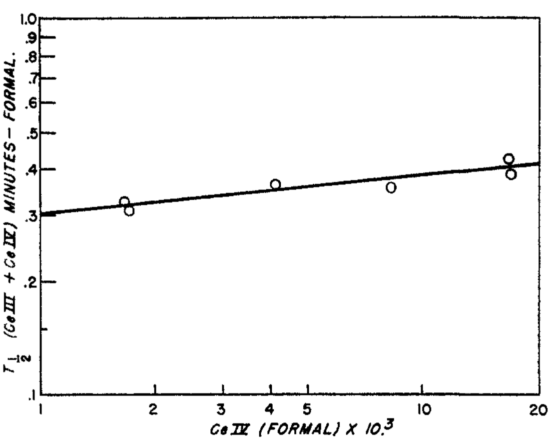

Fig. 3.—Cerium(IV) dependence in the nitrate system (0.0°, 6.18 *f* HNO_3, 0.00171 *f* Ce(III)).

strength was maintained at 6.18 *f* by the addition of suitable amounts of sodium nitrate solution. The rate constant *k* given in Table II is calculated on the assumption that the reaction is first order with respect to both cerous and ceric cerium.

The data in Table II show that the rate of the reaction increases as the acid concentration is decreased. This trend is exhibited clearly in Fig. 4, which shows plots of over-all rate constant against $1/(H^+)^2$ at 0° and −10°. This was the only simple plot which could be found to give a straight line. The values for −10° were obtained by extrapolation of the data in Table II. All of the data thus far presented can be expressed in the empirical equation

$$\text{rate}\,(f\,\text{min.}^{-1}) = (\text{Ce(III)})(\text{Ce(IV)})\left\{2.09 \times 10^6\, e^{\frac{-7700}{RT}} + \frac{2.61 \times 10^{20}}{(H^+)^2}\, e^{\frac{-24,000}{RT}}\right\} \quad (4)$$

where *RT* is expressed in calories.

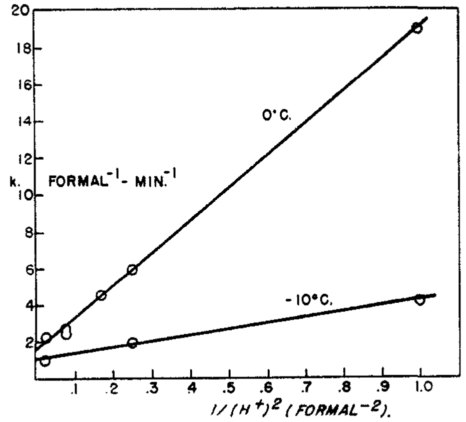

Fig 4.—Acid dependence in nitrate system (μ = 6.18 *f*).

Perchlorate System.—A series of experiments was performed to determine the order of the reaction with respect to cerous and ceric cerium. The results are given in Table III. A plot according to equation (3) is given in Fig. 5 for the determination of the dependence upon cerous

Table III

Cerium(III), Cerium(IV), and Temperature Dependence in the Perchlorate System

Temp., °C.	Ce(III), *f*	Ce(IV), *f*	$T^{1/2}$, min.	R/Ce(III) × 10^3, min.$^{-1}$
0.0	0.00215	0.00425	62	
.0	.00215	.00425	68	
.0	.00507	.00425	48	
.0	.00985	.00425	25	
.0	.00985	.00425	26	
.0	.00985	.00425	27	
.0	.0195	.00425	19	
.0	.0195	.00425	17	
.0	.0195	.00425	18	
.0	.0195	.00425	16.5	
15.0	.00985	.00425	4.8	
15.0	.00507	.00425	6.7	
15.0	.00215	.00425	10.5	
0.0	.00490	.00170	24	7.43
.0	.00236	.00850	62	8.75
.0	.00278	.0170	58	10.3
.0	.00567	.0170	52	10.0
.0	.00609	.0254	40	13.9
.0	.00695	.0425	24	24.8
10.0	.00490	.00170	9.3	19.2
10.0	.00507	.00425	14.0	22.6
10.0	.00525	.00850	15.2	28.1
10.0	.00567	.0170	15	34.5
10.0	.00609	.0254	12.8	43.6
10.0	.00695	.0425	8.2	72.5

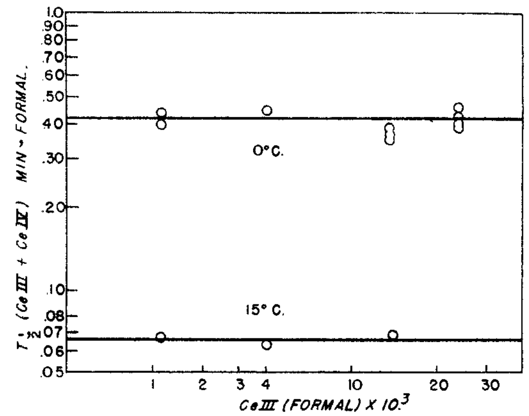

Fig. 5.—Cerium(III) dependence in perchlorate system (6.18 *f* $HClO_4$, 0.00425 *f* Ce(IV)).

cerium. It is seen that the cerous dependence is unity. In the experiments on ceric dependence, the cerous concentration was never held strictly constant because cerous cerium was present in the ceric perchlorate sample; and consequently one is unable to determine the dependence upon ceric cerium in the manner employed for the cerium(III) dependence. However from Fig. 5 it is evident that the dependence upon cerous cerium is unity and hence one may write

$$R = (\mathrm{Ce(III)})f[(\mathrm{Ce(IV)})] \qquad (5)$$

R can be obtained from the half time and concentration of reactants by the use of equation (1), and hence $f[(\mathrm{Ce(IV)})]$ can be determined by plotting $R/(\mathrm{Ce(III)})$ against $(\mathrm{Ce(IV)})$. Such plots are given in Fig. 6 for two temperatures. Since the curves in Fig. 6 do not go to zero when the concentration of ceric cerium vanishes, one must conclude that the reaction becomes first order at low ceric cerium concentrations and that

$$f[(\mathrm{Ce(IV)})] = k + k'(\mathrm{Ce(IV)}) \qquad (6)$$

Solving for the constants as exponential functions of temperature, one finally obtains the empirical equation

$$\text{rate } (f \text{ min.}^{-1}) = (\mathrm{Ce(III)}) \left\{ 1.60 \times 10^{13}\, e \frac{-19{,}400}{RT} + (\mathrm{Ce(IV)})\, 1.11 \times 10^{13}\, e \frac{-16{,}800}{RT} \right\} \qquad (7)$$

where RT is in calories. This expression applies to solutions $6.18 f$ in $HClO_4$.

In order to check the effect of the change in ionic strength as the cerium concentration was increased to $0.05 f$, one run (cerium(III) $0.00525 f$, cerium(IV) $0.00850 f$, $HClO_4$ $6.18 f$) was performed at 10° in which $0.05 f$ lanthanum perchlorate was added. The half time in the absence of lanthanum was 15.2 min. and in its presence 14.5 min. Thus no appreciable effect was observed. A few runs were made to check the acid dependence. The results are given in Table IV.

TABLE IV

ACID DEPENDENCE IN THE PERCHLORATE SYSTEM

$(\mathrm{Ce(III)}) = 0.00507 f$, $(\mathrm{Ce(IV)}) = 0.00425 f$, Ionic strength adjusted to $6.18 f$ with $NaClO_4$, 0.0°

$(H^+), f$	$T_{1/2}$, min.	$R \times 10^5, f$ min.$^{-1}$
6.18	48	3.34
4.00	25	6.40
2.00	10.8	15.0
1.00	5.1	31.4

Discussion

Cerium Dependence.—The first order dependence upon cerium(III) and (IV) found in the nitrate system is to be compared with similar results for other exchange reactions which have been reported.[3,4,12] The obvious interpretation of such results is that the reaction is indeed bimolecular and that specific ionic species are responsible for the exchange. A study of the kinetics as a function of the concentration of various added salts then gives an indication of the complexes formed and the reactivity of various ions from the standpoint of ability to give up or receive electrons. Such an approach was planned in order to gain a better knowledge of the nature of solutions of cerium(III) and cerium(IV).

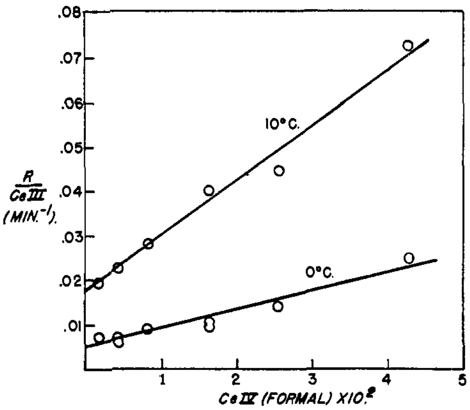

Fig. 6.—Ceric dependence in perchlorate system (6.18 $HClO_4$).

The fact that ceric cerium forms complexes with various anions has been known for some time.[13] The formal electrode potentials vary from −1.2 to −1.7 depending upon whether the solution contains hydrochloric, sulfuric, nitric, or perchloric acid. Cerium(IV) migrates to the anode in $1 f$ sulfuric acid[9b] and in $6 f$ nitric acid; but it travels to the cathode in $1.8 f$ perchloric acid and in $2 f$ nitric acid. A marked color change occurs when nitric or sulfuric acid is added to a perchloric acid solution of cerium(IV). No ceric nitrate is precipitated when nitric acid is added to a concentrated solution of ceric nitrate, but ceric ammonium hexanitrate is precipitated when ammonium nitrate is added. These observations indicate that chloride and sulfate form rather strong complexes with ceric cerium while nitrate forms a weaker complex and perchlorate probably does not enter into a complex formation.[14] The nature of ceric cerium solutions is undoubtedly complex, and it appears likely that no single species predominates. Recent evidence suggests that in perchloric acid cerium(IV) undergoes considerable hydrolysis and probably exists to some extent as a polymer of the form $CeOCe^{+6}$ or a similar structure.[15] Such ions have been postulated for plutonium, uranium and neptunium in the plus four oxidation state.[15c] Complexes of cerium(III) are not well known and in most instances have been assumed not to exist. However, the cerous–ceric electrode potential in nitric acid is essentially independent of the nitric acid concentrations; and, since cerium(IV) complexes with nitrate exist, one must either assume cerous complexes or, as suggested by Yost, *et al.*,[13] suppose that hydroxide takes part in the complexing of cerium(IV). Freed

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[12] A recent paper on the exchange of Sb(III), Sb(V) reports a 0.6 order dependence with respect to Sb(III); N. A. Bonner, THIS JOURNAL, **71**, 3909 (1949).

[13] For a general survey see 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.

[14] The statements made by G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938), in support of $Ce(ClO_4)_6^{=}$ are based on insufficient evidence and in view of the above are probably in error.

[15] (a) L. J. Heidt and M. E. Smith, THIS JOURNAL, **70**, 2476 (1948); (b) K. A. Kraus, Atomic Energy Commission Report Number AECD 2070; (c) K. A. Kraus and F. Nelson, *ibid.*, AECD 1888.

and co-workers[16] have found evidence for order of arrangement of nitrate around europium(III) by a study of the absorption spectrum of solutions. The exact nature of these complexes is not well understood, but they probably exist in the case of cerium(III) also.

A study of the complex formation by determining the rate of the exchange reaction in various media proved unsatisfactory since the rate did not change markedly when the medium was changed from 6 *f* nitric to 6 *f* perchloric acid. Moreover, the striking result that the ceric dependence departs widely from first order required separate consideration. As indicated in the preceding section, the dependence upon ceric cerium in the perchlorate system is not first order but is a combination of a first order and zero order reaction with respect to this variable. A mechanism suggested to account for these data is

$$\mathrm{Ce(IV)} + \mathrm{Ce(III)} \underset{k_1}{\overset{k_1}{\rightleftarrows}} \text{exchange} \tag{8}$$

in parallel with the reactions

$$\mathrm{Ce(III)} + \mathrm{S} \underset{k_3}{\overset{k_2}{\rightleftarrows}} \mathrm{Ce(III)}^* + \mathrm{S} \tag{9}$$

where Ce(III)* is an excited state of cerium(III) and S is any substance in the solution which is capable of exciting the cerous cerium upon collision.

$$\mathrm{Ce(III)}^* + \mathrm{Ce(IV)} \underset{k_4}{\overset{k_4}{\rightleftarrows}} \text{exchange} \tag{10}$$

If $k_4(\mathrm{Ce(IV)}) > > k_3\mathrm{S}$ the rate equation

$$R = k(\mathrm{Ce(III)}) + k'(\mathrm{Ce(III)})\,(\mathrm{Ce(IV)}) \tag{11}$$

is obtained which is in agreement with equation (7).

The hypothesis of an excited state of cerium(III) is in agreement with spectral and theoretical considerations. The lowest electronic configuration of cerous cerium is a $^2F_{5/2,7/2}$, and due to spin–spin and spin–orbit coupling this will give rise to energy levels[17] with separation of the order of magnitude of 1000 cm.$^{-1}$. Kröger and Bakker and Lang[18] observed experimental splittings of 1620–2250 cm.$^{-1}$ for the lowest level depending upon the chemical state of the cerium. A simple Boltzman calculation indicates that $10^{-3}\%$ of the cerous cerium exists in the excited state at room temperature. This is certainly enough to make the above mechanism possible. The fact that the excitation is slow is also expected since the transition is a forbidden one and must take place by collision with solvent molecules.[19]

It seems likely that the rate of activation by collision depends upon the medium. As mentioned above, the degree of splitting varies with the compound employed. Furthermore rates of electronic excitations should be sensitive to the change of electron density resulting from complex formation and to the electromagnetic fields set up in the neighborhood of the ion by the other constituents of the solution. Consequently a difference in the rate of the first order reaction should be observed in changing from perchloric to other acids. In actuality the data for the nitrate system do not show the first order part of the reaction, although the order with respect to cerium(IV) appears to be slightly less than unity. The assumption that the divergence from unity is real and that reactions similar to those in equations (9) and (10) may also be operative in this medium seems reasonable. Since, however, the second order part of the reaction in nitrate is faster than in perchlorate, no conclusion can be made concerning the relative rates of the first order reactions. Further experiments at lower ceric cerium concentration in the nitrate system would be desirable to check this hypothesis. However, a new separation technique would be necessary because of the reduction of the ceric–cerium.

Acid Dependence.—The dependence of the exchange rate upon acid in the nitrate system indicates the existence of an acid dependent and acid independent path for exchange. Furthermore it appears that the acid dependent path is between an unhydrolyzed species and a substance containing two hydroxyl groups or their equivalent or between two singly hydrolyzed species.[20] The former is in good agreement with the hypothesis concerning hydroxide complexing to explain the constancy of the cerium(III)–(IV) electrode potential as nitric acid concentration is changed. An alternative explanation is that a polymeric form of cerium(IV) involving an oxygen bridge becomes important as the acidity is decreased. This could be checked by determining the dependence upon ceric cerium at low acidity.

The acid dependence in the perchlorate system has not been studied in sufficient detail to permit an unequivocal interpretation. The data of Table IV show that the rate is a linear function of the reciprocal of the acid concentration. Since the ceric cerium concentration was 0.00425, we see from Fig. 6 that most of the exchange occurred by way of equations (9) and (10) and not by the direct path of equation (8). Hence one might suppose that hydroxyl ion is required in the activation of cerium(III). This is further substantiated by the fact that the rate approaches zero as the acid concentration becomes very large. The mechanism of exchange may alter, however, as the acidity is decreased; and experiments in which the cerium(III) and -(IV) dependence are measured at various acid concentrations are necessary to establish this point unambiguously.

The above discussion is subject to the assumption that the activity coefficients of the reactants do not vary widely as sodium ion is substituted for hydrogen ion at constant ionic strength.

Temperature Dependence.—The empirical equations (4) and (7) indicate apparent energies of activation ranging from 7700 to 24,000 calories

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(16) S. Freed, S. I. Weissman and F. E. Fortess, THIS JOURNAL, **63**, 1079 (1941); S. Freed, *Rev. Mod. Phys.*, **14**, 105 (1942).

(17) S. Freed, *Phys. Rev.*, **38**, 2122 (1931).

(18) (a) F. A. Kröger and J. Bakker, *Physica*, **8**, 628 (1941); (b) R. J. Lang, *Can. J. Research*, **14A**, 127 (1936).

(19) From an analogy with the mean life for fluorescence of the uranyl ion and the calculated population of the excited state of cerium, one can show that the observed value for the first order rate constant is reasonable.

(20) In order to get the simple inverse hydrogen ion squared dependence it is necessary that the amount of hydrolyzed material be very small, *i.e.* $K(\text{hydrolysis}) \ll (\mathrm{H}^+)^2$. For a more extensive treatment see reference in footnote 3a.

per mole. The values have uncertainties of about ±1000 calories per mole. Beyond the fact that they are of the same order of magnitude as those reported for other electron transfer exchange reactions, little can be said about the values because of the complex nature of the solutions. The actual reactants in some, and possibly all, of the reaction paths suggested by our data are hydrolyzed or complexed species present in unknown concentrations. Hence, the apparent activation energies include unknown contributions from the heats of the reactions in which they are formed. It is correspondingly impossible to estimate meaningful values of the entropies of activation. It is of some interest to note, however, that if nitrate complexes of both cerous and ceric species are assumed to be essentially saturated in 6 *f* nitric acid, the data would lead to an entropy of activation[21] of about −40 cal./deg.-mole. Such a large negative value is consistent with expectation[21] for a reaction between two ions of large, and like, charge.

The apparent activation energy of the first order term of the rate in the perchlorate system is much larger than the excitation of the state through which, it is suggested, the exchange may occur. This is not particularly surprising since the observed temperature coefficient may simply be a measure of the heat of formation of the species in which activation by collision occurs.

It has been variously suggested[22] that the rates of oxidation–reduction reactions are predominantly governed by electrostatic interactions between the reactants, the number of electrons donated or received, or by the free energy change of the reaction. The results reported here and those obtained by other workers on electron transfer exchange reactions show that no one of these hypotheses is an adequate guide in predicting the rate of an oxidation reduction reaction. Other factors include the nature of any complexes which may be formed, the number of degrees of freedom of the intermediate complex, and, possibly, the electronic state of the reactants. This subject has been discussed more fully elsewhere.[5]

[21] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.

[22] J. Weiss, *J. Chem. Soc.*, 309 (1944); B. Krishna, *J. Chem. Phys.*, **17**, 846 (1949); P. A. Shaffer, THIS JOURNAL, **55**, 2169 (1933); L. Michaelis, *Trans. Electrochem. Soc.*, **71**, 107 (1937); A. E. Remick, THIS JOURNAL, **69**, 94 (1947).

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

The Potential of the Pu(III)–Pu(IV) Couple and the Equilibrium Constants for Some Complex Ions of Pu(IV)[1]

BY SHERMAN W. RABIDEAU AND JOE F. LEMONS

The formal potentials of the Pu(III)–Pu(IV) couple *vs.* the H_2–H^+ couple in perchloric acid and in hydrochloric acid were measured at 25.2 ± 0.1° through potentiometric titrations of Pu(III) in cells with negligible liquid junction potentials. Values of −0.9821 ± 0.0005 volt and −0.9703 ± 0.0005 volt were obtained for this couple in molar perchloric and in molar hydrochloric acid, respectively. A value of 3.1×10^{-2} was obtained for the hydrolysis constant of Pu(IV) at 25.1 ± 0.03° from a study of the variation of the Pu(III)–Pu(IV) formal potential with acidity at unit ionic strength. The formulas and the dissociation constants of a Pu(IV) sulfate and a Pu(IV) nitrate complex have been obtained from the shift of the cell potential to more positive values with the addition of the complexing agent. A value of $2.17 \pm 0.05 \times 10^{-4}$ was found for the dissociation constant of $\mathrm{PuSO_4}^{++}$ and 0.287 ± 0.004 for the dissociation constant of $\mathrm{PuNO_3}^{+++}$ at 25.2 ± 0.1°.

Introduction

The formal potential of the Pu(III)–Pu(IV) couple has been reported by Howland, Hindman and Kraus[2] to be −0.953 ± 0.01 volt in 1 *M* perchloric acid and −0.966 ± 0.002 volt in 1 *M* hydrochloric acid. However, Connick and McVey[3] obtained a value of −0.982 ± 0.001 volt in molar perchloric acid for the formal potential of the reaction: $\mathrm{Pu}^{+++} + \mathrm{H}^+ \rightleftarrows \mathrm{Pu}^{++++} + {}^1/_2\ \mathrm{H}_2$. The more negative potential in 1 *M* perchloric acid as compared to that in 1 *M* hydrochloric acid is in agreement with the accepted relative complexing tendencies of the perchlorate and chloride ions; however, Connick and McVey[3] encountered unexplained difficulties in the analysis of the mixed Pu(III)–Pu(IV) solutions which limited somewhat the reliability of their determination.

Kraus and Nelson[4] by a spectrophotometric method obtained a value of 0.025 for the first hydrolysis constant of Pu(IV) in acidic perchlorate solutions at an ionic strength of 0.5. The association constant for the reaction $\mathrm{Pu}^{++++} + \mathrm{NO_3}^- \rightleftarrows \mathrm{PuNO_3}^{+++}$ was determined by Hindman.[5] He obtained a value of 2.9 ± 0.6 by spectrophotometric means. It is of interest to determine these constants by independent methods.

No precise value has been reported for the dissociation constant of a Pu(IV) sulfate complex.

In this investigation the formal potentials of the Pu(III)–Pu(IV) couple in 1 *M* perchloric acid and in 1 *M* hydrochloric acid have been determined by means of potentiometric titrations of Pu(III) solutions. The hydrolysis constant of Pu(IV) has been evaluated from a study of the formal potential of the Pu(III)–Pu(IV) couple as a function of acidity at unit ionic strength. The dissociation constants of a plutonium sulfate complex ion with the formula

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[2] J. J. Howland J. C. Hindman and K. A. Kraus, Natl. Nuclear Energy Ser., Div. IV, 14B, Transuranium Elements, Pt. I, 133 (1949).

[3] R. E. Connick and W. H. McVey, THIS JOURNAL, **73**, 1798 (1951).

[4] K. A. Kraus and F. Nelson, *ibid.*, **72**, 3901 (1950).

[5] J. C. Hindman, Natl. Nuclear Energy Ser., Div IV, 14B. Transuranium Elements, Pt. I, 388 (1949).