ture reaction takes several days to reach completion. Above 750–800°, however, the reaction goes to completion in a matter of minutes with the formation of V. Interplanar spacings for all anhydrous compounds are presented elsewhere.[10]

Comparison of Figs. 1 and 2 indicates a number of basic differences. In addition to the presence of two more compounds in Fig. 2, and the existence of an α,β-modification of $2K_2O \cdot V_2O_5$, large discrepancies exist in m.p. data. In the region 0–50 mole % K_2O Canneri observes that there are always three thermal arrests present. The first represents the liquidus, the second oxygen liberation referred to as "spitting," and finally a eutectic arrest. Our data in this same region never shows more than two arrests. Furthermore, careful weight loss experiments in this entire region are always in excellent agreement with theoretical weight loss corresponding to CO_2 evolution from the carbonate in the reaction mixture. It was observed that if oxygen stirring was dispensed with, then the phenomenon of "spitting" did indeed occur. Canneri attributes this O_2 evolution to the partial reduction of the V_2O_5. As the molten charges he examined were not maintained in an oxygen rich atmosphere it is undoubtedly the case that all of the charges employed for thermal analysis were strongly reduced. Thus his thermal analysis charges were not binary in character having relatively large quantities of reduced vanadic oxides which would most probably lower liquidus and eutectic data.

NEW YORK, N. Y.

[10] These data have been deposited as Document number 4760 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

[CONTRIBUTION NO. 431 FROM THE INSTITUTE FOR ATOMIC RESEARCH, DEPARTMENT OF CHEMISTRY AND VETERINARY RESEARCH INSTITUTE, IOWA STATE COLLEGE]

The Kinetics of the Ce(IV)–Ce(III) Exchange Reaction in Perchloric Acid[1]

BY FREDERICK R. DUKE AND FRANK R. PARCHEN

RECEIVED SEPTEMBER 1, 1955

The rate of the Ce(IV)–Ce(III) exchange reaction is found to be first order in Ce(III), first and second order in Ce(IV) and complex order in $[H^+]$. At high acidities, the Ce(IV) and $[H^+]$ dependencies are best explained by the reaction of Ce(III) with the species $Ce(OH)_2^{+2}$, $Ce(OH)_3^+$ and $[CeOCeOH]^{+5}$. At low $[H^+]$ more highly hydrolyzed and polymerized species appear to be involved.

Gryder and Dodson[2] demonstrated that the cerium(III)–cerium(IV) exchange rate could be determined when an ether extraction procedure was employed to effect separation of the reactants. This opened the way for further investigations on the exchange reaction.[3,4] They[3a] found that, in perchloric acid solution, the exchange rate was first order in cerium(III), but a fractional order between zero and one in cerium(IV). They also observed that the rate decreased as the acid concentration was increased.

Hornig and Libby[3b] found that both fluoride and chloride catalyzed the exchange reaction in nitric acid. The chloride catalytic effect was observed to be of lesser magnitude.

Experimental

Cerium Tracer.—Radioactive Ce^{144}, 275 day half-life, was obtained from the Oak Ridge National Laboratory on allocation from the U. S. Atomic Energy Commission. It was purified according to the method of Boldridge and Hume.[5] The final cerium oxalate precipitate was fumed with perchloric acid to destroy the oxalate ion. The cerium(III) perchlorate solution in concentrated perchloric acid was then diluted to give a cerium(III) perchlorate in *ca.* 6 *f* perchloric acid.

Measurement of Radioactivity.—All radioactive measurements were made using a dipping Geiger–Müller tube. Presumably the principal radiation being measured was the 3 mev. β-radiation of the 17.5 minute half-life Pr^{144} daughter. All solutions were allowed to stand at least three hours before counting to permit the daughter product to grow into equilibrium concentration. All samples were counted long enough to reduce the statistical counting error to 1.0% standard deviation or less.

Chemicals.—Stock reagent solutions were prepared from G. F. Smith Chemical Company hydrated cerium(IV) perchlorate (approximately 0.5 *f* cerium(IV) in 6 *f* perchloric acid) and 70% perchloric acid. The cerium(III) and cerium (IV) concentrations were determined by titration with standard iron(II), after oxidation of cerium(III) with persulfate in sulfuric acid. The acid solutions were analyzed by titration with standard alkali.

The *n*-butyl phosphate used was obtained from Commercial Solvents Corporation.

Separation of Reactants.—The separation of reactants was accomplished by extraction with *n*-butyl phosphate.[6] An aliquot of the exchange mixture was added to a solution 1 *f* each in nitric acid and ammonium nitrate. The cerium(IV) was then extracted with *n*-butyl phosphate. After separation the cerium(IV) was re-extracted with water from the solvent, first reducing cerium(IV) with hydrogen peroxide. Preliminary work on the extraction procedure indicated that the solvent caused very little reduction of cerium(IV). It was also determined that the cerium(IV) was quantitatively recovered from the solvent and that cerium(III) was not extracted.

Procedure.—Cerium(IV) perchlorate, perchloric acid and appropriate reagents were added to the exchange vessel. All solutions used in the exchange run were placed in a large refrigerated constant temperature bath at 0.1 ± 0.05°.

The exchange was started by the rapid addition of tagged cerium(III) perchlorate to the exchange vessel. The exchange solution was further agitated by the removal and re-injection of an aliquot plus gentle swirling of the exchange

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[1] Work was supported in part by the Ames Laboratory of the Atomic Energy Commission.

[2] J. W. Gryder and R. W. Dodson, THIS JOURNAL, **71**, 1894 (1949).

[3] (a) J. W. Gryder and R. W. Dodson, *ibid.*, **73**, 2890 (1951); (b) H. C. Hornig and W. F. Libby, *J. Phys. Chem.*, **56**, 869 (1952).

[4] G. E. Challenger and B. J. Masters, THIS JOURNAL, **77**, 1063 (1955).

[5] W. F. Boldridge and D. N. Hume, National Nuclear Energy Ser., Division IV, 9, "Radiochem. Studies: The Fission Products," Book **3**, 1693 (1951).

[6] J. C. Warf, THIS JOURNAL, **71**, 3257 (1949).

vessel. Approximately 20-ml. aliquots of the exchange solutions were removed from the reaction vessel at timed intervals and delivered into 250-ml. separatory funnels containing 50 ml. of solution 1 f each in nitric acid and ammonium nitrate. Seventy milliliters of *n*-butyl phosphate was then added immediately. The separatory funnel was shaken for approximately 30 seconds and separation completed by removing the aqueous phase. The solvent phase was then scrubbed using 50-ml. portions of the nitric acid-ammonium nitrate solution. One milliliter of 30% hydrogen peroxide was then added to the solvent phase to reduce the cerium(IV) and the cerium(III) was extracted with water. The sample was then collected and diluted to 100-ml. Six samples were taken in each experiment spread evenly over two half-times.

Two "infinite-time" samples (specific activity corresponding to complete exchange) were taken in each run. The "infinite-time" samples were taken after approximately ten half-times and the samples were treated exactly like the time samples.

In each experimental run aliquots of the exchange mixture were taken and analyses performed to determine the total cerium concentration and the cerium(IV) concentration. Duplicate analyses were run and the results averaged.

Errors.—Concentrations were known to only ±1% because corrections were not made for any volume change that occurred on cooling and because it was assumed that solution volumes were additive.

Although the exchange reactions were relatively rapid (half-times 5 to 60 min.), errors in the rate constants due to inaccuracies in timing the reaction are believed to be no more than a few per cent. This is because aliquots of the exchange mixture were separated in a very reproducible way so that although the exact time of separation might be uncertain by several seconds, the time interval between the separation of any two aliquots was known much more accurately. The time intervals between samples affects the slope of the exchange curves and therefore the measured rates and rate constants. Errors in the absolute times of separation, or the zero time, merely shift the exchange curve, affecting the apparent zero-time exchange but not the slope.

Duplicate runs performed months apart and with different sets of reagents generally agreed to within a few per cent.

Results

The exponential exchange law[7] as applied to the cerium(III)–cerium(IV) exchange is

$$Rt = -\frac{[\mathrm{Ce(III)}][\mathrm{Ce(IV)}]}{[\mathrm{Ce(III)}] + [\mathrm{Ce(IV)}]} \ln(1 - F) \qquad (1)$$

where R is the constant rate at which cerium(III) becomes cerium(IV) and cerium(IV) becomes cerium(III), and F is the fraction exchange attained at time t, determined in our experiments by comparing the observed counting rate with the experimentally determined counting rate at infinite time.

Apparent Zero-time Exchange.—The straight line plots of log $(1 - F)$ against time do not pass through one at time zero (apparent zero-time exchange); this is due mainly to exchange induced during the separation procedure, but may in part be due to some uncertainty in the time a reaction was started relative to the times of separation. In any case the apparent zero-time exchange was reproducible for a given run and therefore did not affect the slope of the exchange curve. The zero time exchange in these experiments varied from 12 to 19%.

Heterogeneous Catalysis.—Experiments were run which show that the exchange rate is not affected by a change in surface material of the reaction vessel, by the presence of bright platinum and platinized platinum, by an atmosphere of nitrogen, or by ordinary diffuse light. The lack of catalysis by Pt is surprising and indicates that Pt may not act as a reversible electrode in the Ce(IV)–Ce(III) perchlorate system.

Cerium(III) Dependence.—Data in Table I where [Ce(III)] varies at approximately constant [Ce(IV)] show the dependence of the exchange half-time on the cerium(III) concentration. The general rate expression, for this particular case, may be described by the following

$$R = k[\mathrm{Ce(III)}]^m[\mathrm{Ce(IV)}]^n \qquad (3)$$

If m or n are not integral constants, a more complex function is indicated. The value of m is obtained from the slope of the plot of log R against log [Ce(III)], at constant Ce(IV) concentration. The slope of the line indicates that the order, m, with respect to cerium(III) is 0.90.

Cerium(IV) Dependence.—In the experiments to determine the dependence of the reaction rate on cerium(IV) concentration, the cerium(III) concentration was never held strictly constant. This is due to the fact that some cerium(III) is always present in cerium(IV) perchlorate solutions. Consequently, it is not possible to determine the dependence of the rate on cerium(IV) in the same manner as employed for cerium(III) dependence.

TABLE I

DEPENDENCE OF THE RATE OF EXCHANGE ON CERIUM(IV)
[$HClO_4$] = 6.0 f; 0.1°

[Ce(IV)], $f \times 10^3$	[Ce(III)], $f \times 10^3$	$t_{1/2}$, min.	R/[Ce(III)], min.$^{-1}$ × 10^2	R/[Ce(III)] [Ce(IV)], f^{-1} min.$^{-1}$
0.870	5.03	34.1	0.300	3.45
1.17	5.25	29.9	.421	3.61
1.43	5.15	26.2	.523	3.68
1.62	4.33	28.2	.670	4.12
1.63	3.11	36.1	.659	4.05
1.63	5.17	26.2	0.623	3.89
2.01	5.01	21.2	0.930	4.65
3.22	3.08	23.9	1.48	4.60
3.48	1.77	30.4	1.51	4.33
3.60	0.810	35.0	1.61	4.49
3.92	1.18	29.2	1.91	4.62
3.82	4.47	18.7	1.71	4.52
3.88	5.52	16.9	1.70	4.42
3.86	6.26	16.7	1.60	4.13
3.82	6.74	15.2	1.64	4.37
3.79	7.75	15.1	1.50	4.04
3.76	0.865	28.1	2.00	5.34
3.80	3.05	19.8	1.96	5.04
3.91	2.09	23.0	1.83	4.66
4.45	3.48	15.1	2.57	5.80
5.46	1.05	17.4	3.49	6.22
6.01	1.09	14.7	4.00	6.65
6.96	1.33	10.5	5.55	7.96
8.06	1.46	10.0	5.86	7.28
8.17	2.68	8.70	5.99	7.35
9.14	1.56	8.60	6.88	7.53
9.86	1.75	6.65	8.85	8.97
10.2	2.37	6.50	8.65	8.48

Since the cerium(III) dependence is unity the general rate expression becomes

$$R = k[\mathrm{Ce(III)}]f[\mathrm{Ce(IV)}] \qquad (4)$$

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(7) H. A. C. McKay, *Nature*, **142**, 997 (1938).

where f[Ce(IV)] represents some function of the cerium(IV) concentration.

The data (Table I) are shown in Fig. 1, in which the rate divided by cerium(III) concentration is plotted against total cerium(IV) concentration.

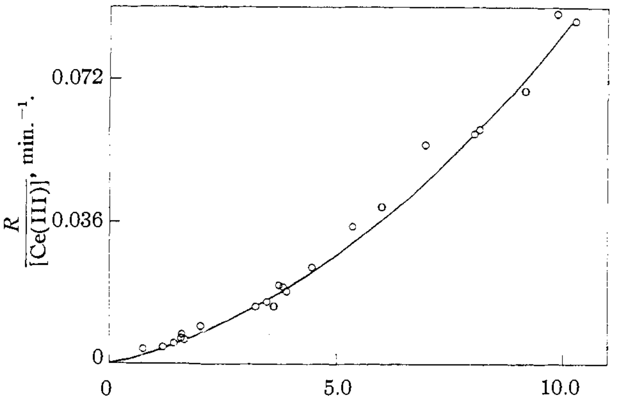

Fig. 1.—Dependence of the Ce(IV)–Ce(III) exchange rate on Ce(IV).

Including a second order dependency term for Ce(IV) in the general rate expression, gives

$$R = k[\text{Ce(III)}][\text{Ce(IV)}] + k'[\text{Ce(III)}][\text{Ce(IV)}]^2 \quad (5)$$

A plot of $R/[\text{Ce(III)}][(\text{Ce(IV)}]$ *vs.* Ce(IV) is shown in Fig. 2. The straight line obtained in Fig. 2 indicates that a second-order dependency in total cerium(IV) is also involved.

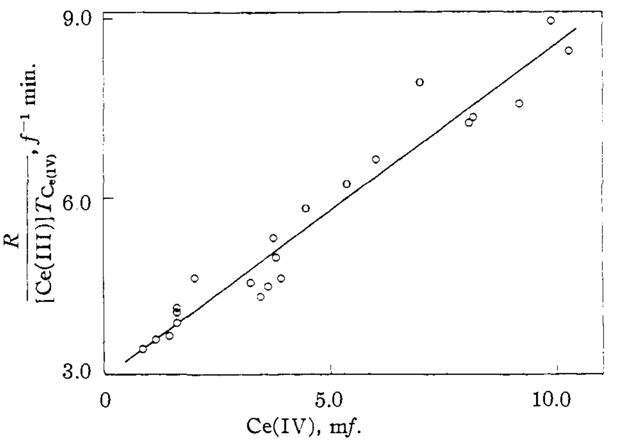

Fig. 2.—Plot showing validity of equation 5.

Perchloric Acid Dependence.—One experimental technique employed in studying the acid dependence was to determine experimental plots like those in Fig. 2 at different hydrogen ion concentrations, using sodium perchlorate to maintain a constant ionic strength. The experimental points are shown on Fig. 3 from the data in Table II.

Table II also presents the experimental data obtained from a series of experiments in which the hydrogen ion concentration was varied with the cerium(III) and cerium(IV) concentrations and the ionic strength essentially maintained constant.

Discussion

Heterogeneous Catalysis.—Within experimental error it appears that the exchange rate is not affected by the various potential catalysts, the surface material, ordinary diffuse light, or the presence of molecular oxygen.

TABLE II

DEPENDENCE OF THE RATE OF EXCHANGE ON ACID CONCENTRATION[a]

μ = 5.85–5.9; 0.1°

[HClO$_4$], f	[Ce(IV)], $f \times 10^3$	[Ce(III)], $f \times 10^3$	$t_{1/2}$, min.	$R/[\text{Ce(III)}][\text{Ce(IV)}]$, f^{-1} min.$^{-1}$
5.85	1.97	0.380	41.3	7.15
	2.95	0.550	27.6	7.20
	3.96	0.705	18.8	7.90
	3.98	0.740	18.8	7.80
	5.95	1.07	10.8	9.15
	6.96	1.23	8.75	9.69
5.04	1.94	0.396	27.0	10.9
	1.98	0.394	28.8	10.1
	2.99	0.608	16.3	11.8
	3.92	0.770	12.1	12.2
	5.00	0.875	8.85	13.3
	5.90	1.06	6.60	13.1
	5.91	1.09	7.44	13.3
2.04	1.35	0.429	5.79	67.5
3.00	1.38	0.376	9.30	42.3
3.97	1.39	0.333	13.8	28.9

[a] Dependence of the rate of exchange on [H$^+$].

Homogeneous Exchange.—The nature of cerium(IV) perchlorate solutions undoubtedly is complex. Recent evidence suggests that in perchloric acid cerium(IV) undergoes considerable hydrolysis and may exist to some extent as a

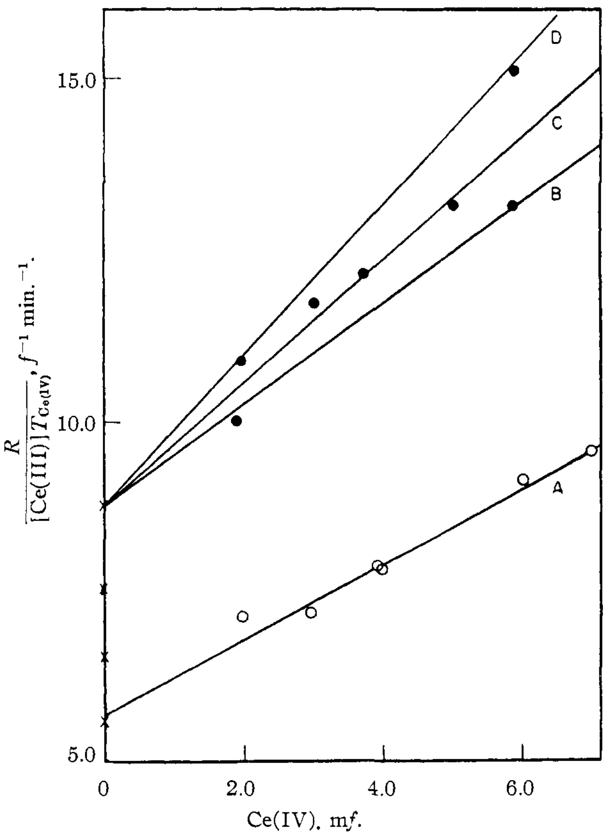

Fig. 3.—Effect of variation in [H] on first and second order in Ce(IV) rate at high acidities.

polymer of the form $CeOCe^{+6}$ or a similar type structure.[8,9] Cerium(III) complexes in perchloric acid are not well-known and in general are assumed not to exist.

The above considerations lead to the general rate expression

$$R = k_4[\mathrm{Ce(III)}][\mathrm{Ce(OH)_3}^+] + k_6[\mathrm{Ce(III)}][\mathrm{HOCeOCe}^{+5}] \qquad (6)$$

including only those pairs of reactants which, according to the data, are pertinent to the data. Inclusion of other terms does not improve the fit of the data. This leads to

$$R = \frac{k_4K_1K_2K_3[\mathrm{Ce(IV)}]}{[\mathrm{H}^+]^2[(\mathrm{H}^+) + K_1]} + \frac{k_6K_1{}^2K_5[\mathrm{Ce(IV)}]^2}{(\mathrm{H}^+)[(\mathrm{H}^+) + K_1]^2} \qquad (7)$$

in which [Ce(III)] and Ce(IV) are the over-all concentrations of cerium(III) and cerium(IV), small *k*'s are specific rate constants, large *K*'s are the equilibrium constants for the reactions involving the various hydrolyzed species listed in equation 6.

Equation 7 including more terms was analyzed termwise in order to determine which, if any, of the possible unhydrolyzed or hydrolyzed forms of cerium(IV) were involved as the rate-determining exchange reactions. The specific rate constant or pseduo-rate constant for first-order cerium(IV) dependence as the case may be, was individually evaluated from the intercept of curve A, Fig. 3, neglecting all other first-order cerium(IV) dependency terms. Similarly, the pseudo-rate constant for each term representing second-order cerium(IV) dependence was individually evaluated from slope of the same curve, neglecting all the other second-order dependency terms.

Extrapolating the data of Hardwick and Robertson[9] to 0.1°, the value of K_1 involving the species $CeOH^{+3}$, was found to be 0.52. Similar values for the slopes and intercepts were calculated for the case where the hydrogen ion concentration is 5.04 *f*, using the above values. The intercept values increase progressively as the degree of hydrolysis of the monomer increases. These values are plotted as X's on the ordinate of Fig. 3. The ordinate value of 8.88 corresponds to the hydrolyzed form $Ce(OH)_3^+$ and can be concluded to best agree with experimental data which are plotted as solid dots on Fig. 3. The calculated slopes yield curves B, C and D of Fig. 3 which correspond to the dimers, $CeOCe^{+6}$, $HOCeOCe^{+5}$ and $HOCeOCeOH^{+4}$, respectively. As can be seen, the experimental results might fit any of the calculated curves. Assuming that the best fit is to curve C, corresponding to dimer $HOCeOCe^{+5}$, equation 7 above is the fitted rate expression.

As the hydrogen ion concentration is decreased (Table II), the equilibria favor formation of hydrolyzed and polymerized forms of cerium(IV). Qualitatively the data in Table II indicate that at lower acidities the exchange rate is relatively fast due to the comparatively large total concentration of hydrolyzed species and the possible existence of different hydrolyzed or polymerized forms of cerium(IV).

At the higher hydrogen ion concentrations the total concentration of hydrolyzed species becomes relatively small and the curve indicates that the exchange rate approaches zero or a very low value at high acid concentration. On the basis of this the exchange rate between cerium(III) and the unhydrolyzed cerium(IV) species must be slow compared to the exchange rate involving hydrolyzed and polymerized forms of cerium(IV).

The participation of the hydrolyzed and polymerized species of cerium(IV) in the exchange mechanisms aids in explaining the comparatively high experimental activation energies obtained by Gryder and Dodson. That is, if one takes an activation energy of about 10 kcal. for the electron exchange reaction, the ΔH of hydrolysis would have to be 15 kcal., a reasonable value, in order to get the *ca.* 25 kcal. observed by Gryder and Dodson.

AMES, IOWA

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Isotopic Exchange Reactions of Neptunium Ions in Solution. IV. The Effect of Variation of Dielectric Constant on the Rate of the Np(V)–Np(VI) Exchange[1]

BY DONALD COHEN, J. C. SULLIVAN, E. S. AMIS[2] AND J. C. HINDMAN

RECEIVED OCTOBER 28, 1955

The isotopic exchange reaction between Np(V) and Np(VI) ions has been studied at zero degrees C, in a medium of aqueous perchloric acid containing varying weight percentages of ethylene glycol or sucrose. The data show that the reaction rate for the isotopic exchange is negligibly affected by the variation of the macroscopic dielectric constant in these solvents. This result is discussed in terms of the current theories of the mechanism of electron exchange reactions.

Although arguments have been presented in favor of the interpretation that the Np(V)–Np(VI) exchange proceeds *via* an atom transfer process in chloride media,[3] the mechanism of the exchange in a non-complexing system is subject to considerably more uncertainty. In an attempt to differentiate further between possible mechanisms, experiments have been carried out in media of varying dielectric constant.

From simple electrostatic considerations it is expected that the rate will decrease with a decrease in dielectric constant[4] if the actual reaction is between two ions of like charge. For more sophisti-

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Resident Research Associate from the University of Arkansas.

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