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THE KINETICS OF THE $\text{Ce(IV)} - \text{Ce(III)}$ EXCHANGE REACTION
IN PERCHLORIC ACID.

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The Kinetics of the Ce(IV)-Ce(III) Exchange Reaction in Perchloric
Acid

by

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The Kinetics of the Ce(IV)-Ce(III) Exchange Reaction in Perchloric Acid

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Abstract

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 $[CeO_2CeOH]^{+5}$. At low $[H^+]$ more highly hydrolized and polymerized species appear to be involved.

¹
Gryder and Dodson demonstrated that the cerium(III)-cerium(IV)

(1) J. W. Gryder and R. W. Dodson, J. Am. Chem. Soc. 71, 1894 (1949).

exchange rate could be determined when an ether extraction procedure was employed to affect separation of the reactants. This opened the way for further investigations on the exchange reaction.^{2,3,4}

(2) J. W. Gryder and R. W. Dodson, J. Am. Chem. Soc. 73, 2890 (1951).

(3) H. C. Hornig and W. F. Libby, J. Phys. Chem. 56, 869 (1952).

(4) G. E. Challenger and B. J. Masters, J. Am. Chem. Soc. 77, 1063 (1955).

They² 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 Libby³ found that both fluoride and chloride catalyzed the exchange reaction in nitric acid. The chloride catalytic effect was observed to be of smaller 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

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

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 γ -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

(6) J. C. Warf, J. Am. Chem. Soc. 71, 3257 (1949).

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 $0.1^{\circ} \pm 0.05^{\circ}\text{C}$

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 reinjection of an aliquot plus gentle swirling of the exchange 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 timed 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 $\pm 1\%$ 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 law⁷ as applied to the cerium(III)-

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

cerium(IV) exchange is

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

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 apparent zero-time exchange may be corrected by using the following relationship,⁸

(8) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry", John Wiley and Sons, Inc., New York, N. Y., 1951, p. 17.

$$F = \frac{F' - F'_0}{1 - F'_0} \quad (2)$$

where F' and F'_0 are the fraction exchange observed for the exchange reactants separated at time t and time zero.

Heterogeneous Catalysis

The data in Table I show that within experimental error the exchange rate is not affected by a change in surface material of the reaction vessel, by the presence of potentially catalytic materials, 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

Figure 1 shows 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

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

The value of m is obtained from the slope of the plot of $\log R$ against $\log [\text{Ce(III)}]$, at constant total cerium(IV) $T_{\text{Ce(IV)}}$, concentration. The slope of the line in Fig. 1 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

Heterogeneous Catalysis

Experimental Conditions	Ce(IV) mf.	Ce(III) mf.	t _{1/2} min.
Control	3.83	2.23	26.2
Glass beads (775-6 mm)	3.83	2.23	26.7
Pt. wire (24 in. of 24 gauge)	3.83	2.23	26.7
Pt. foil (5 in. diameter)	3.83	2.23	30.5
Polyethylene exchange vessel	3.83	2.23	26.5
Control	1.79	2.05	18.9
Pt. block (1 in. x 0.5 in.)	1.79	2.05	17.7
Control	1.83	1.72	7.5, 8.1
Clear Glass exchange vessel	1.83	1.72	9.3, 8.2
Control	1.74	1.19	49.5
Nitrogen atmosphere	1.74	1.19	44.0, 46.8

6.0 f HClO₄, 0.0°C, 500 ml. low actinic erlenmeyer reaction vessel
except where noted.

FIG. 1. DEPENDENCE OF THE Ce(IV) Ce(III) EXCHANGE RATE ON Ce (III)

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

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

where $f[\text{Ce(IV)}]$ represents some function of the cerium(IV) concentration.

The data are shown on Fig. 2, in which the rate divided by cerium(III) concentration is plotted against total cerium(IV) concentration. The curve on Fig. 2 shows a straight line portion at low total cerium(IV) concentration suggesting first order dependency at these concentrations. At higher total cerium(IV) concentrations the dependency appears to be more complicated.

Including a second order dependency term for cerium(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. 3. The straight line obtained in Fig. 3 indicates that a second order dependency in total cerium(IV) is also involved.

Perchloric Acid Dependence

One experimental technique employed in studying the acid dependence was to determine experimental plots like those in Fig. 3 at different hydrogen ion concentrations, using sodium perchlorate to maintain a constant ionic strength. The experimental points are shown on Fig. 4.

Table II presents the experimental data obtained from a series of experiments in which the hydrogen ion concentration was varied

FIG. 2 DEPENDENCE OF THE $Ce(IV)$ - $Ce(III)$ EXCHANGE RATE ON $Ce(IV)$

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FIG. 3 PLOT SHOWING VALIDITY OF EQUATION 5

FIG. 4. EFFECT OF VARIATION IN H^+ ON FIRST AND SECOND ORDER IN Ce(IV) RATE AT HIGH ACIDITIES

with the cerium(III), cerium(IV) concentrations, and the ionic strength essentially maintained constant.

Table II
($\mu = 5.89, 0.1^\circ$)

$[\text{HClO}_4]$ f	$^T\text{Ce(IV)}$ mf.	$[\text{Ce(III)}]$ mf.	$t_{1/2}$ min.	R mole $\cdot$ liter $^{-1}$ min $^{-1} \times 10^{-5}$
2.04	1.35	0.429	5.79	39.1
3.00	1.38	0.376	9.30	22.0
3.97	1.39	0.333	13.8	13.4
4.98	1.39	0.345	21.5	8.86
5.89	1.40	0.336	33.3	5.65

Dependence of the rate of exchange on $[\text{H}^+]$

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.

Homogeneous Exchange

The nature of cerium(IV) perchlorate solutions is undoubtedly complex. Recent evidence suggests that in perchloric acid cerium(IV) undergoes considerable hydrolysis and may exist to some extent as a polymer of the form $\text{CeO}^+\text{Ce}^{+6}$ or a similar type

structure.^{9,10} Cerium(III) complexes in perchloric acid are not

(9) L. J. Heidt and M. E. Smith, J. Am. Chem. Soc. 70, 2476 (1948).

(10) T. J. Hardwick and E. Robertson, Can. J. Chem. 29, 818 (1951).

well-known and in general are assumed not to exist.

The above considerations lead to the general rate expression.

$$R = k \frac{[\text{Ce(III)}]}{[\text{Ce(IV)}]} + k_2 \frac{[\text{Ce(III)}]}{[\text{CeOH}^{+3}]} + k_3 \frac{[\text{Ce(III)}]}{[\text{Ce(OH)}_2^{+2}]} + k_4 \frac{[\text{Ce(III)}]}{[\text{Ce(OH)}_3^{+}]} + k_5 \frac{[\text{Ce(III)}]}{[\text{CeO}^{+6}]} + k_6 \frac{[\text{Ce(III)}]}{[\text{HO}^{+5}\text{CeO}]} + k_7 \frac{[\text{Ce(III)}]}{[\text{HO}^{+4}\text{CeO}]} + \text{etc.} \quad (6)$$

This leads to

$$R = \frac{\frac{[\text{Ce(III)}]}{[\text{H}^{+}]} T_{\text{Ce(IV)}}}{[\text{H}^{+}] + K} \left[\frac{k}{[\text{H}^{+}]} + k_2 K_1 + \frac{k_3 K_1 K_2}{[\text{H}^{+}]} + \frac{k_4 K_1 K_2 K_3}{[\text{H}^{+}]^2} + \right. \\ \left. + \frac{k_4 K_1^2 K_4 T_{\text{Ce(IV)}}}{[\text{H}^{+}] + K_1} + \frac{k_6 K_1^2 K_5 T_{\text{Ce(IV)}}}{[\text{H}^{+}] [\text{H}^{+} + K_1]} + \frac{k_7 K_1^2 K_6 T_{\text{Ce(IV)}}}{[\text{H}^{+}]^2 [\text{H}^{+} + K_1]} \right] \quad (7)$$

in which $\frac{[\text{Ce(III)}]}{[\text{H}^{+}]}$ and $T_{\text{Ce(IV)}}$ 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 the equation.

Equation 7 was analyzed termwise in order to determine which, if any, of the included unhydrolyzed or hydrolyzed forms of cerium(IV) were involved as the rate determining exchange reactions. The specific rate constant or pseudo-rate constant for first order

cerium(IV) dependence as the case may be, was individually evaluated from the intercept of curve A, Figure 4, 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 Robertson¹⁰ 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 5.04f, 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. 4. The ordinate value of 8.88 corresponds to the hydrolyzed form $\text{Ce}(\text{OH})_3^+$ and can be concluded to best agree with experimental data which are plotted as solid dots on Fig. 4. The calculated slopes yield curves B, C and D of Fig. 4 which correspond to the dimers, CeO^{+6} , $\text{HO}^{+5}\text{CeO}^{+5}$, and $\text{HO}^{+4}\text{CeO}^{+4}\text{CeOH}^{+4}$, 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 $\text{HO}^{+5}\text{CeO}^{+5}$, equation 7 may be simplified to give the rate expression.

$$R = \frac{[\text{Ce(III)}] T_{\text{Ce(IV)}}}{[\text{H}^+][\text{H}^+ + K_1]} \frac{k_4 K_1 K_2 K_3}{[\text{H}^+]} + \frac{k_6 K_1^2 K_5 T_{\text{Ce(IV)}}}{[\text{H}^+ + K_1]} \quad (8)$$

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 2 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 form 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 H of hydrolysis would have to be 15 kcal, a reasonable value, in order to get the ca 25 kcal observed by Gryder and Dodson.