CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE JOHNS HOPKINS UNIVERSITY, BALTIMORE 18, MARYLAND

The Kinetics of the Thallium(I)–Cerium(IV) Reaction in Nitric Acid[1]

BY MARY K. DORFMAN AND J. W. GRYDER

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Rate data for the oxidation of thallium(I) by cerium(IV) in 6.18 *f* nitric acid at 53.9 ± 0.1° are interpreted as indicating the following mechanism for the reaction

$$\begin{array}{lcl}
2\mathrm{Ce(IV)} & \overset{K}{=} & \mathrm{(CeIV)_2} \\
\mathrm{Ce(III)} + \mathrm{Ce(IV)} & \overset{K'}{=} & \mathrm{(CeIII\ CeIV)} \\
\mathrm{Ce(IV)} + \mathrm{OH^-} & \underset{2}{\overset{1}{\rightleftarrows}} & \mathrm{Ce(III)} + \mathrm{OH} \\
\mathrm{Tl(I)} + \mathrm{OH} & \underset{4}{\overset{3}{\rightleftarrows}} & \mathrm{Tl(II)} + \mathrm{OH^-} \\
\mathrm{Tl(I)} + \mathrm{Ce(IV)} & \underset{6}{\overset{5}{\rightleftarrows}} & \mathrm{Tl(II)} + \mathrm{Ce(III)} \\
\mathrm{Tl(II)} + \mathrm{Ce(IV)} & \xrightarrow{7} & \mathrm{Tl(III)} + \mathrm{Ce(III)}
\end{array}$$

where Ce(IV) is monomeric cerium(IV), $\mathrm{(CeIV)_2}$ is dimeric cerium(IV), and (CeIII CeIV) is a dimer of one cerium(III) and one cerium(IV). Employing a steady state approximation, microscopic reversibility, and an iterative least squares procedure, one obtains the following values for the equilibrium constants and groups of specific rate constants when the rate is expressed in terms of the disappearance of Ce(IV): $K = 18$, $K' = 2$, $k_1 = 1.33 \times 10^{-5}$, $k_5 = 2.81 \times 10^{-4}$, $k_2/k_3 = 0.021$, $k_2k_4/k_3k_7 = 5.4 \times 10^{-6}$, $k_4/k_7 = 2.6 \times 10^{-3}$, $k_6/k_7 = 1.52 \times 10^{-3}$. Concentrations are measured in moles/liter and time in seconds.

Introduction

The reaction between cerium(IV) and thallium(I) is of interest because it involves an oxidizing agent which can accept only one electron and a reducing agent which does not have a stable oxidation state corresponding to the loss of one electron. Indeed, Shaffer's postulate[2] of equivalent oxidation change in oxidation–reduction reactions was partially based upon the slow rate of this reaction. In recent years a number of authors[3] have discussed reactions involving non-equi-valent oxidation changes. This work was initiated with the goal in mind of using a comparison of the rate of the thallium(I)–cerium(IV) reaction with that of other oxidations of thallium(I) to establish whether or not a one-step oxidation of thallium(I) to thallium(III) occurs. A preliminary report indicating that such one step oxidations do occur has been published.[4]

Materials and Methods

Preparation and Analysis of Stock Solutions.—Cerium(IV) stock solutions were prepared by dissolving freshly precipitated cerium(IV) hydroxide in nitric acid. The cerium(IV) hydroxide was prepared in either of two ways: (a) ammonium hexanitrato cerium(IV) (G.F. Smith, Reagent Grade) was recrystallized three to five times, dissolved, and precipitated with ammonium hydroxide; (b) cerium(IV) hydroxide (Amend Drug and Chemical Co., C.P.) was dissolved in nitric acid and precipitated with ammonium hydroxide. In either case, the hydroxide was washed with water until it was free of ammonia.

Cerium(III) stock solutions were prepared by reduction of a cerium(IV) stock solution with hydrogen peroxide or by dissolving thrice recrystallized cerium(III) nitrate

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[2] P. A. Shaffer, *J. Am. Chem. Soc.*, **55**, 2169 (1933); *J. Phys. Chem.*, **40**, 1021 (1936).

[3] L. Michaelis, *Trans. Electrochem. Soc.*, **71**, 107 (1937); A. E. Remick, *J. Am. Chem. Soc.*, **69**, 94 (1947); W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discussions Faraday Soc.*, **29**, 49 (1960); A. M. Armstrong and J. Halpern, *Can. J. Chem.*, **35**, 1020 (1957); M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959); K. G. Ashurst, *J. Chem. Soc.*, 343 (1956); D. H. Irvine, *ibid.*, 1841 (1956); J. Halpern, *Can. J. Chem.*, **37**, 148 (1959).

[4] J. W. Gryder and M. K. Dorfman, *J. Am. Chem. Soc.*, **83**, 1254 (1961).

(Lindsay Chemical Company, C.P.) in water. When H_2O_2 was employed, the solution was boiled until the titanium(IV) test for peroxide was negative.

The cerium(IV) concentrations were determined by titration with standard ferrous sulfate to an orthophenanthroline ferrous sulfate end point. The cerium(III) concentrations and the total cerium concentrations in the cerium(IV) stock solutions were determined by the same procedure after oxidation of cerium(III) to cerium(IV) according to the method of Willard and Young.[5] The acid concentration in the cerium(IV) solutions was determined by titration with standard sodium hydroxide to the phenolphthalein end point after the cerium(IV) was reduced with H_2O_2 and precipitated with oxalate. A correction was made for the hydrogen ion produced in the reaction with H_2O_2.

Thallium(I) stock solutions were prepared by dissolving thallium metal (Amend Drug and Chemical Co., C.P, or Fairmount Chemical Co., assay 99.95% Tl) in concentrated nitric acid, recrystallizing thallium(I) nitrate several times, and finally dissolving the $TlNO_3$ in water. The concentration of thallium(I) was determined either gravimetrically[6a] as Tl_2CrO_4 or volumetrically[6b] with standard potassium bromate.

Thallium(III) stock solutions were prepared by dissolving thallium metal (from the sources mentioned above) in nitric acid, oxidizing the thallium(I) to thallium(III) with potassium ferricyanide, and precipitating thallium(III) hydroxide with ammonium hydroxide. The precipitate was washed by decantation until free of ammonia and ferricyanide and then dissolved in nitric acid. The concentration of thallium(III) was determined gravimetrically[7] as Tl_2O_3. Acid was determined by titration with sodium hydroxide after reduction of the thallium(III) with H_2O_2. A correction was made for the acid formed in the reduction of thallium(III).

Nitric acid stock solutions were prepared by diluting freshly opened concentrated nitric acid (Baker Analyzed Reagent, Fisher Reagent, or Mallinckrodt Analytical Reagent Grade) or concentrated nitric acid boiled to expel oxides of nitrogen. In a few runs, old nitric acid, red with nitrogen oxides, was employed. The source of HNO_3 had no effect on the rate of the reaction.

The water used in making up the stock solutions and reaction mixtures was treated to remove impurities. For some experiments distilled water from the laboratory tap was twice distilled from quartz. For other experiments water was distilled from a cerium(IV) solution in nitric acid, then from a sodium hydroxide solution, and finally twice distilled in a quartz still. Commercial distilled water (Cutter Laboratories, pyrogen free) also was used. The rates were insensitive to the source of water.

Tri-*n*-butyl phosphate (Matheson Coleman and Bell) was used without further purification after it was ascertained that duplicate results were obtained with different lots and with a redistilled sample.

Preparation and Analysis of Reaction Mixtures.—Reaction mixtures were prepared in volumetric flasks from stock solutions which had been immersed in a constant temperature bath at 53.9 ± 0.1° for 1 hr. before mixing. Light was excluded from the reaction vessels. Samples were withdrawn at measured times and either analyzed immediately or frozen in a Dry Ice–acetone slurry.

Reactions at very low concentrations of thallium(I) were followed radiochemically after extraction with tri-*n*-butyl phosphate. Thallium^{204} was added to the stock solutions of thallium(I) and thallium(III) to give the same specific activity in the two oxidation states. A sample to be analyzed was withdrawn from the reaction mixture and rapidly chilled, but not frozen, in a Dry Ice–acetone mixture. Five ml. of the chilled sample was immediately pipetted into a separatory funnel containing 10 ml. of tributyl phosphate and 5 ml. of 6.05 *f* $LiNO_3$. After phase equilibrium was obtained the aqueous phase was withdrawn and counted using a Radiation Counter Laboratories Model 10305 dipping counter. The extent of the reaction then was calculated from the observed counting rate and the apparent distribution constants for thallium(I) and thallium(III) determined under similar conditions.

Reactions at moderate concentrations of the reactants were analyzed by titration of the cerium(IV) with standard ferrous sulfate to an orthophenanthroline ferrous sulfate end point. Samples were pipetted from the reaction mixture, transferred into 50 ml. of ice-cold 1 *f* H_2SO_4, and titrated immediately. Any reduction of thallium(III) is negligible, as shown by thirteen experiments in which the cerium(IV) determined by titration agreed with that added (0.0382 to 0.4120 *f*) to within 0.8% except for two experiments for which the added Ce(IV) was 0.0404 *f* and the added Tl(III) was 0.0484 *f* and for which titration gave 0.411 *f* Ce(IV). The variation in Tl(III) for all these experiments was from 0.0086 to 0.0550 *f*.

Reaction mixtures in which the initial concentration of cerium(IV) was low were analyzed spectrophotometrically.[8] Two-ml. samples were withdrawn, frozen rapidly in a Dry Ice–acetone slurry, and refrigerated in the dark. For analysis, 1 ml. of a sample was pipetted into 25 ml. of 6 *f* H_2SO_4, and its absorption at 330 mμ was measured with a Beckman Model DK recording spectrophotometer. The concentration of cerium(IV) was determined by interpolation on a calibration curve. Reduction of cerium(IV) occurred at a rate of about 0.1% per second under exposure to the hydrogen discharge lamp. Readings were taken sufficiently rapidly so that the error due to reduction was never greater than 1%.

Stoichiometry.—The stoichiometry of the reaction was checked two ways. For some experiments, duplicate samples were taken, of which one was analyzed for Ce(IV) by titration with ferrous sulfate and the other for Tl(I) by gravimetric determination as Tl_2CrO_4. The duplicates agreed with the required stoichiometry to within experimental error. In other experiments, the final concentration of Ce(IV) was determined by titration and compared with the difference between the initial Ce(IV) concentration and two times the initial Tl(I) concentration. The results are presented in Table I.

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[5] H. Willard and P. Young, *J. Am. Chem. Soc.*, **50**, 1379 (1928).

[6] (a) O. Forscheimer and R. Epple, *ibid.*, **74**, 5772 (1952); (b) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Volume III, Interscience Publishers, Inc., New York, N. Y., 1957, p. 519.

[7] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 377.

[8] A. I. Medalia and B. J. Byrne, *Anal. Chem.*, **23**, 453 (1951).

TABLE I

TEST OF STOICHIOMETRY

(CeIV) initial, *f*	(TlI) initial, *f*	(CeIV) final (calcd.), *f*	(CeIV) final (obsd.), *f*
0.2260	0.0218	0.1824	0.1824
.1373	.0484	.0404	.0411
.0549	.0121	.0307	.0324
.1098	.0121	.0856	.0865
.0986	.0107	.0772	.0775
.0986	.0107	.0772	.0776
.0554	.00859	.0382	.0384
.0554	.00859	.0382	.0385

TABLE II

RATES IN PRESENCE AND ABSENCE OF Tl(III)

(CeIV), *f*	(TlIII)I, *f*	(CeIII), *f*	(Tl), *f*	R × 10^3
0.1810	0.0247	0.117	0.114	4.00
.1810	.0247	.117	.000	4.00
.1845	.0262	.000	.000	4.80
.0095	.0430	.0156	.0184	0.60
.0095	.0430	.0156	.000	.58

TABLE III

RESULTS IN ABSENCE OF Ce(III)[a]

(CeIV), *f*	(TlI), *f*	$R \times 10^3$ (obsd.)	$R \times 10^3$ (calcd.)	$100R(_{\text{obs}} - R_{\text{cal}})/R_{\text{obs}}$
0.2274	0.0218	5.77	5.23	9
.0549	.0242	2.45	2.25	8
.0549	.0364	2.73	2.71	1
.0549	.0531	3.09	3.34	8
.2080	.0247	4.76	5.21	9
.1645	.0242	4.62	4.50	2
.1816	.0247	4.36	4.81	10
.1845	.0262	4.80	4.98	4
.0986	.0107	2.81	2.55	9
.0197	.0430	1.39	1.43	3
.0554	.0644	3.84	3.78	2
.0554	.0644	3.84	3.78	2
.0554	.0859	4.52	4.60	2
.0554	.0859	4.52	4.60	2
.0554	.1074	5.33	5.42	2
.0019	.0430	0.190	0.192	1
.0038	.0430	0.388	0.363	6
.0554	.00859	2.04	1.67	18
.0554	.00859	2.04	1.67	18
.0270	.00032	0.830	0.834	0
.0549	.000725	1.67	1.36	18
.0095	.0430	0.775	0.803	4
.0554	.0644	3.61	3.78	5
.00887	.0773	1.08	1.09	1
.00887	.0859	1.19	1.17	2
.00887	.0601	0.962	0.924	4
.2260	.0218	6.00	5.21	13
.2274	.0218	6.45	5.23	19

[a] Rates for disappearance of Ce(IV), concentrations in formula weights/l., time in hr., 53.9 ± 0.1°, 6.18 *f* HNO_3.

Results

Preliminary results established that the mechanism of the reaction is not simple. In the presence of low initial concentrations of cerium(IV) and high thallium(I), the reaction is first order in cerium(IV). With a large excess of cerium(IV) over thallium(I) and cerium(III), the reaction appears to be much less than first order with respect to thallium(I), but with increasing initial concentrations of cerium(III) the reaction velocity is decreased markedly and the order in thallium(I) approaches unity. The data in Table II show that the reaction is independent of Tl(III).

Because of this behavior, the reaction was first studied in the absence of added cerium(III). The reaction rates were determined as the initial slopes of graphs of either the concentration or the logarithm of the concentration of one of the reactants or products *vs.* time, depending upon the initial conditions and which curve was most nearly linear. The results are given in Table III.

The Empirical Rate Law in the Absence of Cerium(III).—For a constant initial concentration of cerium(IV), a graph of rate of disappearance of Ce(IV), *R*, *vs.* (TlI) is a straight line with finite intercept and positive slope, indicating the presence of two concurrent pathways, one zero order with respect to thallium(I) and one first order in thallium(I).

However, at constant thallium(I), *R*/(CeIV) decreases as (CeIV) is increased. No simple dependence upon the total cerium(IV) concentration could be found. It is known that cerium(IV) is partially dimerized in nitric acid solutions.[9] The decrease in *R*/(CeIV) as (CeIV) increases is consistent with the postulate that the reactive species is monomeric cerium(IV). In order to test this hypothesis, vaues of $R/(C_{4\text{m}})$ were calculated for various assumed values of the dimerization constant, *K*, and were plotted against (TlI). For $K = 20$, this graph is a straight line, as shown in the figure in reference 4. Thus, the empirical rate law in the absence of cerium(III) is

$$R_0 = k_1C_{4\text{m}} + k_5C_{4\text{m}}(\text{TlI}) \qquad (1)$$

where R_0 denotes the rate of disappearance of Ce(IV) in the absence of cerium(III), $C_{4\text{m}}$ is the concentration of cerium(IV) monomer, and k_1 and k_5 are constants. The best value for the dimerization constant of cerium(IV) under the conditions employed was first determined by minimizing the function

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(9) B. D. Blaustein and J. W. Gryder, *J. Am. Chem. Soc.*, **79**, 540 (1957).

$$F = [1 - k_1C_{4m}/R_0 - k_5C_{4m}(\text{TlI})/R_0]^2$$

with respect to k_1 and k_5, for various assumed values of the dimerization constant. This form of the function was chosen because the percentage error in R is estimated to be approximately independent of the concentrations involved. Each pair of values for k_1 and k_5 then was used in eq. 1 to calculate rates, and the quantity $\delta = (R_{\text{obs}} - R_{\text{calc}})/R_{\text{calc}}$ was determined for each of the assumed dimerization constants. A graph of δ *vs.* K gave a minimum for $K = 18$ which is therefore the best value for K. The best values for k_1 and k_5 are 0.055 hr.$^{-1}$ and 1.22 l. mole^{-1} hr.$^{-1}$, respectively.

The Rate Law in the Presence of Cerium(III).—Three mechanisms are consistent with the empirical rate law and the observations that the rate is markedly reduced by cerium(III) and independent of Tl(III). These are

Mechanism I

$$\text{Ce(IV)} + \text{NO}_3^- \underset{2}{\overset{1}{\rightleftarrows}} \text{Ce(III)} + \text{NO}_3$$

$$\text{Tl(I)} + \text{NO}_3 \underset{4}{\overset{3}{\rightleftarrows}} \text{TlO}^+ + \text{NO}_2$$

$$\text{Ce(IV)(NO}_3^-) + \text{Tl(I)} \underset{6}{\overset{5}{\rightleftarrows}} \text{TlO}^+ + \text{NO}_2 + \text{Ce(III)}$$

$$\text{Ce(IV)(OH}^-)_2 + \text{NO}_2 \xrightarrow{k_7} \text{Ce(III)} + \text{NO}_3^- + \text{H}_2\text{O}$$

Mechanism II

$$\text{Ce(IV)} + \text{NO}_3^- \underset{2}{\overset{1}{\rightleftarrows}} \text{Ce(III)} + \text{NO}_3$$

$$\text{Tl(I)} + \text{NO}_3 \underset{4}{\overset{3}{\rightleftarrows}} \text{Tl(II)} + \text{NO}_3^-$$

$$\text{Ce(IV)} + \text{Tl(I)} \underset{6}{\overset{5}{\rightleftarrows}} \text{Ce(III)} + \text{Tl(II)}$$

$$\text{Ce(IV)} + \text{Tl(II)} \xrightarrow{7} \text{Ce(III)} + \text{Tl(III)}$$

Mechanism III

$$\text{Ce(IV)} + \text{OH}^- \underset{2}{\overset{1}{\rightleftarrows}} \text{Ce(III)} + \text{OH}$$

$$\text{OH} + \text{Tl(I)} \underset{4}{\overset{3}{\rightleftarrows}} \text{OH}^- + \text{Tl(II)}$$

$$\text{Ce(IV)} + \text{Tl(I)} \underset{6}{\overset{5}{\rightleftarrows}} \text{Ce(III)} + \text{Tl(II)}$$

$$\text{Ce(IV)} + \text{Tl(II)} \xrightarrow{7} \text{Ce(III)} + \text{Tl(III)}$$

As is implied by the notation used in describing the above mechanisms, the exact nature of the various species is not known. For example, in mechanism III, step 1 could be a cerium(IV) hydroxide complex reacting to give cerium(III) and hydroxyl radical, or a mixed complex of cerium(IV) with hydroxide and nitrate as ligands reacting to give a cerium(III) nitrate complex and hydroxyl radical, or some species of cerium(IV) reacting with water to give hydrogen ion, hydroxyl radical, and cerium(III). Furthermore a number of analogous mechanisms could be proposed as is discussed in reference 4. The essential aspect of mechanism I is that cerium participates in reactions involving an oxidation number change of 1 while thallium reacts with an oxidation number change of 2. The essential aspect of mechanisms II and III is that both cerium and thallium react with an oxidation number change of one.

Using the steady state approximation for the concentrations of NO_3 and NO_2, the fact that only cerium(IV) monomer is kinetically active, the assumption that only cerium(III) monomer is kinetically active, and the observation that the rate is independent of thallium(III), one can derive from mechanism I

$$R = \frac{k_1k_3(\text{TlI})C_{4m}}{k_3(\text{TlI}) + k_2C_3} + k_5C_{4m}(\text{TlI}) \qquad (2)$$

Where C_{4m} as before is the concentration of monomeric cerium IV and C_3 is that of monomeric cerium(III). The rate in the absence of Ce(III) is again given by eq. 1. Equations 1 and 2 can be combined to give

$$\frac{C_{4m}}{R_0 - R} = \frac{k_3(\text{TlI})}{k_1k_2C_3} + \frac{1}{k_1}$$

Hence a graph of $C_{4m}/(R_0 - R)$ *vs.* $(\text{TlI})/C_3$ should be a straight line if this mechanism is correct. Such a graph is not even a smooth curve and therefore mechanism I is eliminated.

Mechanisms II and III are indistinguishable by means of the experimental data because the concentrations of NO_3^- and H^+ were not varied. Furthermore, kinetic data for such a variation would suffer from the fact that activity coefficients also would vary. For convenience, therefore, the remaining treatment will be given in terms of mechanism III with the understanding that mechanism II will fit equally well.

Using the steady state approximation for the concentrations of OH and Tl(II), and the fact that the reaction is irreversible, one can derive from mechanism III

$$R = \frac{k_1(\mathrm{TlI})(C_{4\mathrm{m}})^2 + \frac{k_5k_2}{k_3}(\mathrm{TlI})(C_{4\mathrm{m}})^2C_3 + k_5(\mathrm{TlI})^2(C_{4\mathrm{m}})^2}{\frac{k_2k_4}{k_3k_7}C_3 + \frac{k_2}{k_3}C_3C_{4\mathrm{m}} + (\mathrm{TlI})C_{4\mathrm{m}} + \frac{k_6}{k_7}\left[\frac{k_2}{k_3}(C_3)^2 + (\mathrm{TlI})C_3\right]} \qquad (3)$$

where the acid dependence is included in the constants.

The best values for the various specific rate constants and equilibrium constants explicitly and implicitly contained in eq. 3 were determined by a rather tedious least squares procedure. If, for the present, we assume that $(k_6/k_7)[(k_2/k_3)(C_3)^2 + (\mathrm{TlI})C_3]$ is negligible, eq. 3 can be rewritten as

$$R = \frac{ax + bk_5y + cz}{du + bv + w} \qquad (4)$$

where $a = k_1$, $b = k_2/k_3$, $c = k_5$, $d = (k_2k_4)/(k_3k_7)$, and x, y, z, u, v, w have obvious relationships to the variables of eq. 3. From eq. 4 we obtain

$$R = ax/w + bk_5y/w + cz/w - Rdu/w - Rbv/w$$

Since the percentage error in R is approximately constant, the first approximation to the best values for the constants was obtained by minimizing the function

$$G \equiv \left[1 - \frac{ax}{Rw} + b\left(\frac{v}{w} - \frac{k_5y}{Rw}\right) - \frac{cz}{Rw} + \frac{du}{w}\right]^2 \qquad (5)$$

with respect to a, b, c, and d. In order to mitigate algebraic complexities involving cross terms arising from k_5 in the coefficient of b in eq. 5, the value of k_5 determined in the absence of Ce(III) was used to calculate the coefficient of b. Now for each chosen value of K and K', values for $C_{4\mathrm{m}}$ and C_3 were calculated by the procedure given in reference 9 and G was minimized. The new value of k_5 was used to calculate a new value of the coefficient for b in eq. 5 and the procedure repeated until convergence in k_5 was obtained.

Applying the principle of microscopic reversibility to the first three steps of the mechanism one obtains $k_4/k_6 = (k_1k_3)/(k_5k_2) = a/(bc)$. Furthermore, from the definition of b and d it is evident that $k_4/k_7 = b/d$. Hence $k_6/k_7 = cd/a$.

Using the values of the constants obtained in this fashion and the experimental concentrations, one finds that the terms involving k_6/k_7 in the denominator of eq. 3 are not negligible for all experimental conditions. Hence the constants were refined by an iterative least squares procedure. If the complete denominator of eq. 3 is retained, u becomes $C_3 + (k_6/k_4)(C_3)^2 + (k_3k_6/k_2k_4)(\mathrm{TlI})C_3$. New values of u were calculated from the values of the constants previously determined and G again was minimized with respect to a, b, c, and d. Iteration was continued until convergence in k_6/k_7 was obtained. In principle one could repeat the above procedures for different values of K and K' and finally determine the best values for all the constants in a fashion analogous to that employed in reference 9. The improvement in constants which might be expected did not seem to warrant the required effort. Therefore only values of $K = 18$ and 22 and of $K' = 0$, 2, and 6 were employed. The value of $K' = 6$ is clearly unreasonable because it leads to a negative value for k_2k_4/k_3k_7. A value of $K' = 2$ gave a better fit than did a value of 0. The best values of the various constants are given in Table IV. It is seen that k_1 and k_5 are insensitive to the value of K' and that k_2/k_3 is not markedly sensitive to the value of K'. However k_2k_4/k_3k_7 is very sensitive to the value chosen for K'. Tables III and V give the experimental and calculated rates as well as the per cent deviations for all the data obtained using the following values for the various constants: $K = 18$, $K' = 2$, $k_1 = 0.048$, $k_2 = 1.37$, $k_2/k_3 = 0.021$, $k_2k_4/k_3k_7 = 5.4 \times 10^{-5}$, and $k_6/k_7 = 1.5 \times 10^{-3}$. Time is in hours, concentrations in moles/liter, and the rate for the disappearance of Ce(IV). The agreement between experimental and calculated values is within experimental error. If time is expressed in seconds, k_1 and k_2 become 1.33×10^{-5} and 3.81×10^{-4}, respectively.

TABLE IV

SPECIFIC RATE CONSTANTS[a]

K	K'	k_1	k_5	k_2/k_3	$(k_2k_4/k_3k_7) \times 10^5$
18[b]	..	0.055	1.22	...	...
18	0	.044	1.45	0.011	23.6
18	2	.048	1.37	.021	5.4
18	6	.049	1.38	.024	−1.9
22[b]	..	.060	1.28	...	...
22	0	.050	1.47	.011	25.8
22	2	.052	1.45	.021	6.3
22	6	.053	1.45	.024	−1.4

[a] For disappearance of Ce(IV), time in hr., concentrations in moles/l., 53.9 ± 0.1°, 6.18 *f* $\mathrm{HNO_3}$. [b] From data in absence of Ce(III).

Discussion

Since the above results show that the cerium(IV)–thallium(I) reaction proceeds *via* unit oxidation changes for thallium, we conclude from the

TABLE V

RESULTS IN PRESENCE OF Ce(III)[a]

(CeIV), f	(CeIII), f	(TlI), f	$R \times 10^3$ (obsd.)	$R \times 10^3$ (calcd.)	$100(R_{obs} - R_{cal})/R_{obs}$
0.0540	0.0795	0.0016	0.674	0.650	4
.0540	.0795	.000532	.334	.380	8
.0254	.0288	.00149	.544	.549	1
.0254	.0288	.000596	.301	.364	21
.0338	.0544	.000596	.306	.308	1
.0422	.0686	.000596	.312	.321	3
.0422	.0801	.000596	.262	.276	5
.00887	.1874	.00344	.118	.119	1
.00887	.2499	.00344	.100	.092	8
.00887	.3124	.00344	.0775	.074	5
.00887	.1250	.00344	.1628	.161	1
.00887	.3436	.00344	.0623	.066	6
.0549	.0786	.0242	2.12	2.04	4
.0549	.0786	.0121	1.53	1.53	0
.1098	.0791	.0121	2.33	2.45	5
.1098	.0791	.0242	3.36	3.25	3
.1373	.1184	.0484	5.09	5.27	4
.0986	.0390	.0107	2.63	2.35	11
.0986	.0781	.0107	2.28	2.19	4
.0540	.00142	.0016	1.47	1.36	8
.0540	.00142	.000532	1.67	1.27	24
.1373	.0012	.0484	5.33	5.66	6
.1373	.0012	.0484	5.42	5.66	4
.0095	.00624	.0430	0.747	0.793	6
.0095	.0156	.0430	.730	.741	[b]
.0095	.0156	.0430	.600 → 0.810	.741	[b]
.0095	.0156	.0089	.626 → .566	.426	[b]
.0095	.0625	.0089	.394 → .322	.355	[b]
.0095	.0625	.0043	.233 → .313	.271	[b]
.0095	.0156	.0089	.44	.426	[b]
.0038	.0625	.0043	.097 → .138	.129	[b]
.0095	.1560	.0430	.47	.604	[b]

[a] Rates for disappearance of Ce(IV), concentrations in formula weights/l., time in hr., 53.9 ± 0.1°, 6.18 f HNO_3. [b] The experimental data for these runs were unreliable because of scatter or because of insufficient data. Range of possible rates is given for some runs and a best guess for others. These runs were not used in the least squares treatment.

argument given in a previous publication[4] that the Tl(I)–Tl(III) exchange reaction occurs *via* a single step involving an oxidation number change of 2. The single step can of course be a Tl(I) and Tl(III) trapped in a liquid cage with two one-electron transfers occurring before separation of the two thallium ions. It is evident, however, that no free Tl(II) can be formed.

A number of investigations are in agreement with our results. The values of K and K' for the two dimerization constants for Ce(IV)–Ce(IV) and Ce(IV)–Ce(III) are in excellent agreement with the values of 17 ± 2 and 2.0 ± 0.7, respectively, obtained from potentiometric data[9] gathered for systems containing 5.5 f HNO_3 at 30°. Attempts were made to study the system potentiometrically at 53.9° with $(HNO_3) = 6.18\ f$, but the problems of solvent evaporation and increased diffusion rate resulted in large experimental errors. The crude data did, however, indicate that the constants were of the same order of magnitude under these conditions as under the experimentally more tractable conditions.

The quantitative agreement between the kinetically and potentiometrically determined dimerization constants coupled with qualitative indications of cerium(IV) polymers from extraction[9] and spectrophotometric[10] data would seem to prove that polymerization of Ce(IV) occurs in high concentrations of HNO_3.

The mechanism proposed also is consistent with preliminary data for the reaction in $HClO_4$ obtained by Halpern[11] and is not inconsistent with the data for the catalyzed reaction in H_2SO_4 reported by Krishna and Sinha.[12] The mechanism,

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(10) L. O. Tuazon, Dissertation, Iowa State College, 1959.

(11) J. Halpern, *Can. J. Chem.*, **35**, 1020 (1957).

with the exception of dimerization, is identical to that proposed by Sworski[13] for the catalysis by Tl(I) of the photoreduction of Ce(IV). If one considers the difference in medium and experimental procedures, the value of k_2/k_3 of 0.021 obtained in this work is in amazingly good agreement with the values of 0.023, 0.024, and 0.026 determined by Sworski. One is tempted to conclude that this agreement argues that OH rather than NO_3 is the kinetic intermediate.

[12] B. Krishna and B. P. Sinha, *Z. physik. Chem.*, **212**, 149, 177 (1959).

[13] T. J. Sworski, *J. Am. Chem. Soc.*, **79**, 3655 (1957); *Radiation Res.*, **4**, 483 (1956).

CONTRIBUTION FROM THE METALLURGICAL ENGINEERING DEPARTMENT, RESEARCH LABORATORIES, GENERAL MOTORS CORPORATION, WARREN, MICHIGAN

The Effect of Ultrahigh Pressure on the Melting Point of Bismuth Telluride

BY DONALD L. BALL

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The effect of pressure up to 50 kb. on the melting point of Bi_2Te_3 has been determined. A maximum in melting point is indicated at approximately 610° and 15 kb. The Clapeyron–Clausius equation predicts that at one atmosphere the rate of increase of the melting point (585°) with increasing pressure is 3.3°/kb. However, above about 15 kb. the melting point was observed to decrease with pressure, reaching a value of about 535° at 50 kb. An effort is made to interpret this unusual dependence of melting point on pressure in terms of the structural changes in Bi_2Te_3 on fusion.

Introduction

In recent years the physical properties of bismuth telluride (Bi_2Te_3) have been investigated rather extensively. The particular interest in this substance has resulted from its relatively efficient performance capabilities in certain thermoelectric devices.

Conventional thermal analyses of the bismuth–tellurium system generally reveal only one intermediate phase,[1] the compound Bi_2Te_3, which displays only the rhombohedral, "Strukturbericht" type C33 structure.[2] However, the existence of three other intermediate phases, which form by peritectic reactions, has been reported.[3] One of these, containing approximately 50 atom % Bi and Te, forms at 540° by the reaction of solid Bi_2Te_3 with a bismuth-rich melt. The preparation of a compound BiTe by an evaporated film technique has been reported also[4]; its structure was investigated by electron diffraction and found to be of the B1 (rock salt) type with a lattice parameter of 6.47 Å. at room temperature.

Because of the wide interest in Bi_2Te_3 it was decided to investigate the effect of pressure and temperature on the condensed phase equilibria of the compound. The purpose was to demonstrate whether or not any new phase structures of Bi_2Te_3 are stable at elevated pressure and to determine the effect of pressure on the melting point. A more limited study was made of specimens containing 50 atom % Bi and Te.

Experimental

Sample Preparation.—Bi_2Te_3 was prepared by the reaction of the elements (99.999% purity) within evacuated Vycor capsules. Four separate preparations were employed in the high pressure experiments; each was made using stoichiometric amounts of the elements. Two additional preparations were used in the comparison experiments at one atmosphere. These preparations (designated as specimens I and II) originally were made as part of a program for the evaluation of thermoelectric materials. Specimen I contained Bi_2Te_3 + $^1/_8$ atom % Te; specimen II contained Bi_2Te_3 saturated with NaI (an amount less than $^1/_8$ atom %).

High Pressure Experiments.—These experiments were performed with a 600-ton tetrahedral anvil apparatus constructed at this Laboratory with the consultation of the inventor, H. Tracy Hall, Brigham Young University, Provo, Utah. The principal design and operation characteristics of the device are described elsewhere.[5] In

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[1] M. Hansen and K. Anderko, "Constitution of Binary Alloys," McGraw-Hill Book Co., Inc., New York, N. Y., 2nd Ed., 1958, p. 340.

[2] M. H. Francombe, *Brit. J. Appl. Phys.*, **9**, 415 (1958).

[3] M. Kh. Abrikosov and V. F. Bankina, *Zh. Neorgan. Khim.*, **3**, 659 (1958); *Chem. Abstr.*, **52**, 19377d.

[4] S. A. Semiletov, *Tr. Inst. Krist., Akad. Nauk SSSR*, **10**, 76 (1954).

[5] H. T. Hall, *Rev. Sci. Instr.*, **29** 267 (1958).