Kinetics of the Reaction of Americium(III) with Peroxydisulfate[1]

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Kinetic studies of the americium(III) oxidation have been made in aqueous solutions. The reaction rates are dependent on the concentrations of hydrogen, peroxydisulfate and the silver ion as catalyzers, and on the reaction temperature. The period of induction observed in the initial stage of reaction varies with the concentration of the reactant and with the reaction temperature. The data follow this rate expression:

$$-\frac{d[\mathrm{Am(III)}]}{dt} = K_h(k_1+k_2[\mathrm{Ag}^+])[\mathrm{S_2O_8}^{2-}][\mathrm{Am(III)}]\cdot 1/[\mathrm{H}^+]$$

where K_h is the dissociation constant of hydrogen peroxydisulfate, and where k_1 and k_2 refer to the silver-ion uncatalyzed and catalyzed paths respectively. The energies of activation were determined to be 28.6 kcal/mol for k_1 and 17.4 kcal/mol for k_2.

The oxidation of americium(III) with the peroxydisulfate ion in the presence of the silver ion is well known.[2,3] This reaction is used to prepare americium isotopes from the spent reactor fuels. Although many papers on the oxidation of Am(III) have been published,[4–7] our knowledge concerning the reaction kinetics of oxidation is rather limited, especially when a tracer concentration is involved. In previous papers[1,8] it was found that the rate data obtained by the tracer technique using the coprecipitation method were in good agreement with those measured specctrophotometrically and that the rate of oxidation appeared to be influenced by the concentrations of the reactants and the acidity of the reaction media. Kinetic studies of this reaction were carried out in order to obtain further information and in order to determine the reaction-rate law.

Experimental

Reagent. Americium-241 oxide which had been obtained from the Radiochemical Centre, Amersham, was dissolved in nitric acid. The solution was then evaporated to dryness, and the residue was dissolved in 0.1 M of a desirable acid. This solution served as the stock solution of americium. Before use, an aliquot of the stock solution was diluted to a suitable concentration with respect to americium and definite acids. The absorption spectrum indicated the tripositive state.[9] The radiochemical purity of ^{241}Am was confirmed by gamma-ray spectrometry.

Ammonium peroxydisulfate, silver nitrate and, all the other chemicals used were of an analytical reagent grade. The solution of ammonium peroxydisulfate was prepared freshly before use.

Apparatus. In order to check the radiochemical purity of ^{241}Am, the gamma-ray spectra were measured with a 2″×2″ NaI(Tl) detector connected with a TMC 400-channel pulseheight analyzer. For the determination of the distribution ratio of ^{241}Am by the coprecipitation method, the gamma-activity of ^{241}Am was counted with a 2″×2″ well-type NaI(Tl) detector connected with an Aloka scaler, Model TDC-5. A Hitachi Model EPS-2U and 124 spectrophotometer were used to determine the absorption spectra of americium. The samples were contained in silica cell which had a 1-cm path length and which contained about 0.8 m*l* of the solution. The silica cell was set in a cell holder thermostated with circulating water of a constant temperature. A Hitachi-Horiba pH meter, Model M-5, was used for the pH measurements.

Procedures. The solutions studied were made up from weighed amounts of ammonium peroxydisulfate, standardized nitric or perchloric acid, and an analyzed stock solution of americium salt. Solutions of ammonium peroxydisulfate containing silver nitrate and Am(III), which upon mixing would give the desired initial composition, were prepared separately and brought to the reaction vessel in a thermostat maintained to within ±0.2°C of the desired temperature. The reactions were followed by radiometry by means of the lanthanum trifluoride coprecipitation method.[8] In a typical experiment, the reaction mixture was pipetted out into a 10-m*l* centrifuge tube containing a cold solution of the lanthanum carrier and nitric acid. The unoxidized Am(III) was coprecipitated with the lanthanum trifluoride by the addition of an ammonium fluoride solution. The lanthanum trifluoride was centrifuged, and the americium content of the supernatant was determined by the measurement of the gamma-activity of ^{241}Am. The fraction of Am(III) may be described as:

$$1-\frac{\text{Am-remaining}}{\text{Am-taken}}$$

This determination was made for three samples at the same time. The mean value of the three measurements was employed for the kinetic data.

Results and Discussion

Changes in Absorption Spectra during the Reaction. The changes in the absorption spectra of americium during the course of oxidation were measured under

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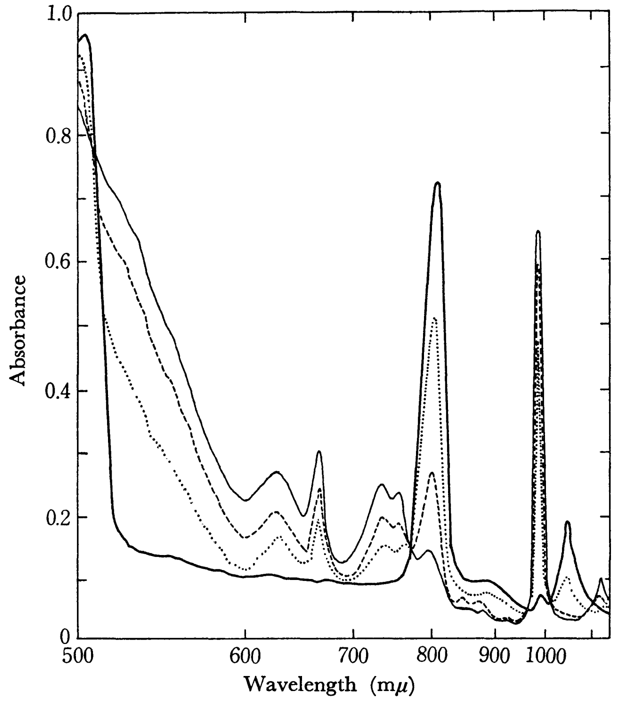

Fig. 1. Change of absorption spectrum of oxidizing americium solution with reaction time.
$[\text{Am(III)}]_0=6.4\times10^{-3}\text{M}$, $[(\text{NH}_4)_2\text{S}_2\text{O}_8]_0=5.0\times10^{-2}\text{M}$, $[\text{AgNO}_3]_0=5.0\times10^{-3}\text{M}$, $[\text{HNO}_3]_0=2.0\times10^{-2}\text{M}$, at 60°C.
Reaction time: —— 4 min, ······ 25 min, ---- 55 min, —— 125 min.

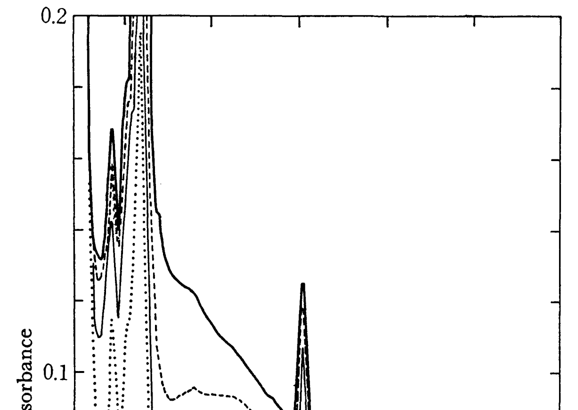

Fig. 2. Change of absorption spectrum of oxidizing americium solution at high acid concentration—I.
$[\text{Am(III)}]_0=3.2\times10^{-4}\text{M}$, $[(\text{NH}_4)_2\text{S}_2\text{O}_8]_0=5.0\times10^{-2}\text{M}$, $[\text{AgNO}_3]_0=1.0\times10^{-4}\text{M}$, $[\text{HNO}_3]_0=0.10\text{M}$ Temp.=60°C.
Reaction time: —— 1 min, ---- 6 min, —— 11 min, ······ 18 min.

two different sets of experimental conditions. The spectral changes in the visible region of a weak acidic solution are given in Fig. 1. It may be seen that Am(III) exhibits λ_{max} at 814 and 1050 mμ, and that the absorbances at 995 and 666 mμ due to Am(VI) increase with the decrease in those of Am(III) during the reaction time elapsed. In a highly acidic solution, the absorption peak of 503 mμ due to Am(III) does not change immediately after the reactants are mixed, but the broad absorptions in the UV and visible regions obviously change, as is shown in Fig. 2. These absorption band decreased for about 30 min; then, the absorption at 503 mμ began to decrease and a new broad absorption began to appear over the range from 600 to 800 mμ. After this absorption band reached a maximum, it then decreased with the longer reaction time, as is shown in Fig. 3. These changes can be attributed to both the disintegration of Am(III) and the formation of some intermediate compounds. This absorption band shifted towards the lower wavelength region with its increase. After about one hour, this broad band began to decrease, and the absorption peak at 660 mμ due to Am(VI) appeared, though it was not visible because of the low extinction coefficient. The plot of log D_{814} (absorbance at 814 mμ) against the reaction time shows a linear relationship. The same relation was found in the results obtained from the radiochemical measurements.[8] The plots on the

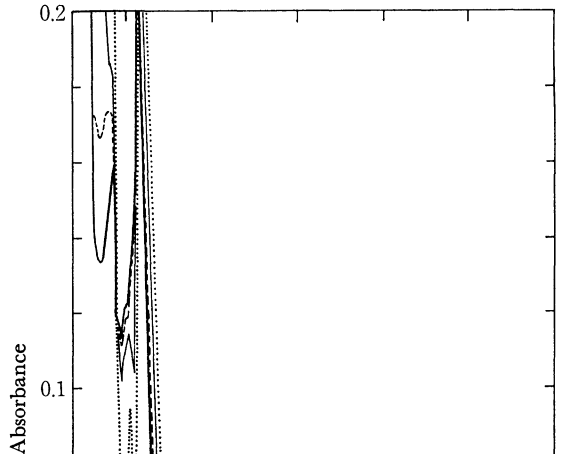

Fig. 3. Change of absorption spectrum of oxidizing americium solution at high acid concentration—II.
$[\text{Am(III)}]_0=3.2\times10^{-4}\text{M}$, $[(\text{NH}_4)_2\text{S}_2\text{O}_8]_0=5.0\times10^{-2}\text{M}$, $[\text{AgNO}_3]_0=1.0\times10^{-4}\text{M}$, $[\text{HNO}_3]_0=0.10\text{M}$, Temp.=60°C.
Reaction time: —— 39 min, ---- 50 min, —— 60 min, ······ 70 min.

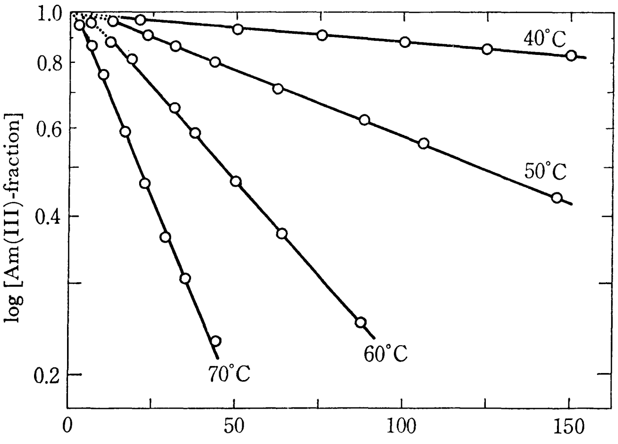

Fig. 4. Plots of the logarithm of Am(III) fraction *vs.* reaction time at various temperatures.
$[\mathrm{Am(III)}]_0 = 4.0 \times 10^{-6}\mathrm{M}$, $[(\mathrm{NH_4})_2\mathrm{S_2O_8}]_0 = 2.0 \times 10^{-2}\mathrm{M}$, $[\mathrm{AgNO_3}]_0 = 1.0 \times 10^{-3}\mathrm{M}$, $[\mathrm{HNO_3}]_0 = 6.0 \times 10^{-2}\mathrm{M}$, $\mu = 0.50$.

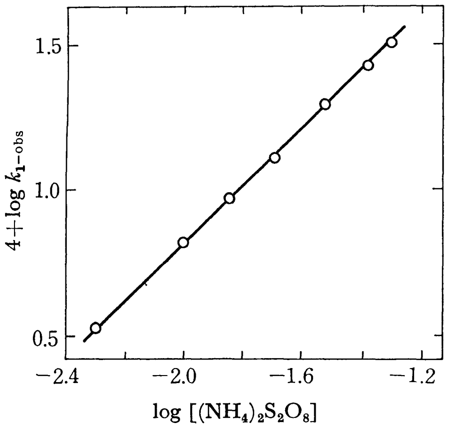

Fig. 5. The plot of log $k_{1\text{-obs}}$ *vs.* log$[(\mathrm{NH_4})_2\mathrm{S_2O_8}]$
$[\mathrm{Am(III)}]_0 = 3.3 \times 10^{-7}\mathrm{M}$, $[\mathrm{AgNO_3}]_0 = 5.0 \times 10^{-4}\mathrm{M}$, $[\mathrm{HNO_3}]_0 = 8.0 \times 10^{-2}\mathrm{M}$, $\mu = 0.50$, Temp. = 50°C.

straight lines indicate that the oxidation of Am(III) is first-order with respect to Am(III) over the temperature range of 40—70°C, as is shown in Fig. 4. Thus, the rate of oxidation may be expressed as follows:

$$\mathrm{Rate} = k_{1\text{-obs}}[\mathrm{Am(III)}] \qquad (1)$$

Effects of Other Reactant Concentrations. The variation in the rates as a function of the concentration of the peroxydisulfate ion was studied at 50°C. Assuming the observed rate constants, $k_{1\text{-obs}}$, to be $k_{2\text{-obs}}\ [\mathrm{S_2O_8}^{2-}]^n$, the slope of the straight line (Fig. 5) obtained by plotting log $k_{1\text{-obs}}$ against log$[\mathrm{S_2O_8}^{2-}]$ indicated that n was equal to unity; thus, the rate of oxidation may be expressed by the following equation:

$$\mathrm{Rate} = k_{2\text{-obs}}[\mathrm{Am(III)}][\mathrm{S_2O_8}^{2-}] \qquad (2)$$

In order to ascertain the role of the silver-ion catalyst in the kinetics of the oxidation, the study was carried out using $\mathrm{AgNO_3}$ of different concentrations. The plots of $[k_{2\text{-obs}} - k_1]$ *vs.* $[\mathrm{AgNO_3}]$ give curves, as is illustrated in Fig. 6, where the k_1 value is the rate constant obtained in the case of $[\mathrm{AgNO_3}] = 0$. It appears that the effect of the silver nitrate concentration makes the reaction rate increase and approach a limiting value. Therefore, the $k_{2\text{-obs}}$ is given by the following equation under the limiting conditions.

$$k_{2\text{-obs}} = k_1 + k_2[\mathrm{Ag^+}] \qquad (3)$$

where the k_1 is the rate constant of the uncatalyzed reaction and where the k_2 obtained from the initial slope of the linear part of the curve in Fig. 6 corresponds to the rate constant of the catalyzed path of the oxidation. These values are exhibited in Table 1.

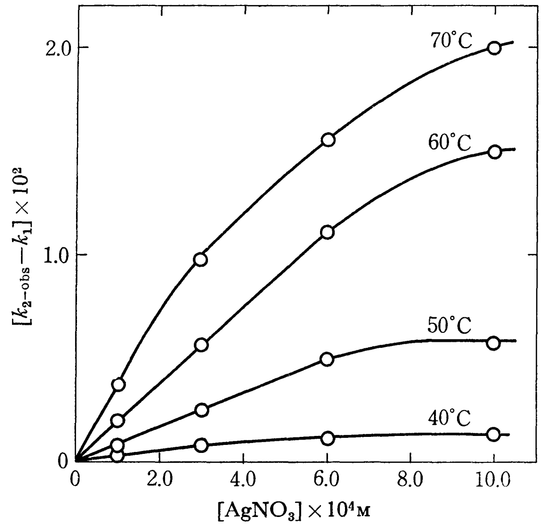

Fig. 6. Difference of total and uncatalyzed reaction rate constants for Am(III) oxidation as a function of the silver nitrate concentration at various temperatures.
$[\mathrm{Am(III)}]_0 = 4.0 \times 10^{-6}\mathrm{M}$, $[(\mathrm{NH_4})_2\mathrm{S_2O_8}]_0 = 2.0 \times 10^{-2}\mathrm{M}$, $[\mathrm{HNO_3}]_0 = 6.0 \times 10^{-2}\mathrm{M}$, $\mu = 0.50$.

TABLE 1. THE VALUES OF RATE CONSTANTS FOR SILVER CATALYZED (k_2) AND UNCATALYZED PATH (k_1).
$[\mathrm{Am(III)}]_0 = 4.0 \times 10^{-6}\mathrm{M}$, $[(\mathrm{NH_4})_2\mathrm{S_2O_8}]_0 = 2.0 \times 10^{-2}\mathrm{M}$, $[\mathrm{HNO_3}]_0 = 6.0 \times 10^{-2}\mathrm{M}$, $\mu = 0.50$.

Temp., °C	k_2 $\mathrm{M^{-2}min^{-1}}$	k_1 $\mathrm{M^{-1}min^{-1}}$
40	162	0.013
50	420	0.093
60	915	0.36
70	1820	1.45

Effect of the Hydrogen-ion Concentration on the Rate. The experiment were performed at a constant ionic strength and temperature. The hydrogen-ion concentration was varied by the addition of nitric acid. The ionic strength was maintained constant with sodium nitrate. At concentrations of the hydrogen ion higher than 0.4M, no oxidation of Am(III) was observed. The rate increases with the decrease in the hydrogen ion concentration and reaches a constant value at $[\mathrm{H^+}] = 0.06\mathrm{M}$.

A kinetic study of the decomposition of peroxydisulfates has been made by Kolthoff and Miller.10) It decomposes according to the reaction(4) in a dilute acid solution:

$$\mathrm{S_2O_8}^{2-} + \mathrm{H_2O} = 2\mathrm{HSO_4}^- + 1/2\mathrm{O_2} \qquad (4)$$

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10) K. I. M. Kolthoff and I. K. Miller, *J. Amer. Chem. Soc.*, **73**, 3055 (1951).

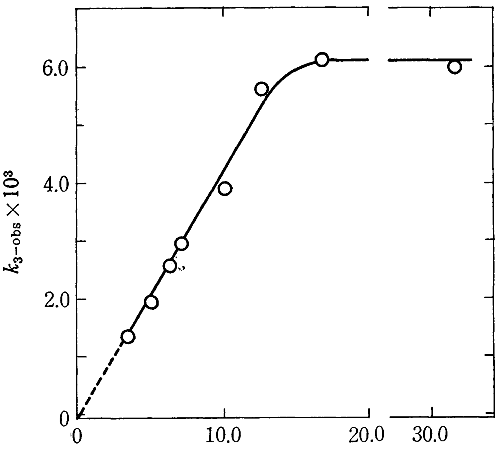

Fig. 7. A plot of the observed rate constants *vs.* reciprocal of the initial hydrogen ion concentration.
$[Am(III)]_0=4.0\times10^{-6}$M, $[(NH_4)_2S_2O_8]_0=2.0\times10^{-2}$M, $[AgNO_3]_0=1.0\times10^{-3}$M, $\mu=0.50$, Temp.=60°C.

In highly acidic solutions, though, reactions(5) and (6) occur:

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4 \tag{5}$$

$$H_2SO_5 + H_2O = H_2O_2 + H_2SO_4 \tag{6}$$

The oxidation of Am(III) with the peroxydisulfate ion may be disturbed by the H_2O_2 produced in Eq. (6) because the hydrogen peroxide is an efficient reductant of Am(VI). Figure 7 represents the plot of the observed rate constants against $1/[H^+]_0$. The rate increases with the decrease in the hydrogen-ion concentration but eventually reaches at a constant value, $k_{3\text{-obs}}=6.0\times10^{-3}\ \text{min}^{-1}$ at $[H^+]=0.06$M. The results shown in Fig. 7 clearly indicate an inverse first-order dependence of the oxidation rate on the hydrogen-ion concentration. The reaction can thus be expressed by a relation of the type:

$$k_{3\text{-obs}} = A\cdot K_h/[H^+] \tag{7}$$

where A is the constant defined by the experimental conditions. The K_h constant, which has the dimension of molarity, was determined from the slope of straight line in Fig. 7 as follows: $K_h=1.4\times10^{-2}$M. This value is close to the secondary dissociation constant of H_2SO_4 ($K_2=1.2\times10^{-2}$M). Thus, it is possible to consider that K_h is the dissociation constant of the hydrogen peroxydisulfate ion, $HS_2O_8^-$.

From the results obtained by the effects of the reaction variables, the over-all rate equation of the Am(III) oxidation reaction may be expressed as follows:

$$-\frac{d[Am(III)]}{dt} = K_h(k_1+k_2[Ag^+])[Am(III)][S_2O_8^{2-}]\cdot 1/[H^+] \tag{8}$$

where k_2 and k_1 refer to the reaction paths catalyzed and uncatalyzed by the silver ion respectively.

From the kinetic relationship, it may be concluded that Am(III) disappears upon reaction with the SO_4^- produced in the decomposition reaction. The kinetics are consistent with the following mechanism:

$$S_2O_8^{2-} \longrightarrow 2SO_4^- \tag{9}$$

$$SO_4^- + Am(III) \longrightarrow Am(VI) \tag{10}$$

If the radicals produced in the reaction(9) react rapidly with Am(III), then the rate is proportional to the concentration of the peroxydisulfate ion and it follows that the measured rate law refers to the unimolecular dissociation of the peroxydisulfate ion. Kolthoff and Miller[10] have shown that a second decomposition reaction occurs in acid media:

$$H^+ + S_2O_8^{2-} \rightleftarrows HS_2O_8^- \longrightarrow HSO_4^- + SO \tag{11}$$

The fact that the rate of the disappearance of Am(III) was dependent of the reversed hydrogen-ion concentration showed conclusively that Am(III) did not react with SO_4; furthermore, the oxidation of Am(III) might be hindered by the reaction (11). This is in agreement with the above-described mechanism that the two modes of dissociation occur at a comparable rate at these particular hydrogen-ion concentrations.

A mixture of the silver ion and the peroxydisulfate ion forms more powerful oxidizing system than $S_2O_8^{2-}$ alone. The existence of the divalent silver ion is well established,[11] and the influence of Ag^+ in the decomposition of the peroxydisulfate ion can be accounted for by the formation of Ag^{2+} according to the reaction:

$$Ag^+ + S_2O_8^{2-} \longrightarrow Ag^{2+} + SO_4^{-\cdot} + SO_4^{2-} \tag{12}$$

The Period of Induction. When the Am(III) solution was added to a solution containing the ammonium peroxydisulfate and silver nitrate, the oxidation reaction did not start immediately, but after a certain time interval following the mixing of the reactants. This time interval is termed the induction period and is listed in Table 2 for various experimental conditions.

TABLE 2. VARIATIONS OF THE INDUCTION PERIOD

		Induction Period, min					
$[AgNO_3]\times10^3$M		0	0.1	0.3	0.5	0.6	1.0
Temp, °C	40	1800	100	35	—	10	0
	50	385	60	25	—	16	1
	60	41	28	8	—	7	6
	70	9	8	5	—	2	2
$[(NH_4)_2S_2O_8]\times10^2$M	0.5				11		
	1.4				7		
	2.0				5		
	3.0				5		
	4.2				10		
	5.0				6		
μ[a]	0.12	25	15	5	—	2	1
	0.25	47	18	8	—	3	2
	0.50	41	28	8	—	7	6
	0.75	120	35	15	—	13	7
	1.00	68	34	10	—	4	6

a) μ was adjusted by the addition of sodium nitrate.

No change in the absorption spectrum due to Am(III) was observed at 503 mμ; however, visible changes were observed in the wavelength region lower than 503 mμ during the induction period (Fig. 2). An increase in the concentration of any of the reactants or an increase in the temperature decreased the period of induction. Thus, it appears that the induction period is related to

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[11] C. E. H. Bawn and D. Margerison, *Trans. Faraday Soc.*, **51**, 925 (1955).

the mechanism of the oxidation of Am(III). In view of the mechanism, the induction period is the time required for the thermal activation of the peroxydisulfate ion to split into SO_4^- radicals, which then produce the Ag^{2+} responsible for the oxidation of Am(III). An increase in the temperature increases the rate of the chain-initiating process, resulting in a decrease in the induction period. Similarly, an increase in the concentration of either the silver ion or the peroxydisulfate ion increases the rate of SO_4^- radical production by means of reaction (12) or (13) respectively, thereby decreasing the period of induction.

$$S_2O_8^{2-} \rightleftarrows S_2O_8^{2-*} \longrightarrow 2SO_4^- \qquad (13)$$

where (*) denotes the activated state; therefore,

$$SO_4^- + \mathrm{Am(III)} \longrightarrow SO_4^{2-} + \mathrm{Am(VI)} \qquad (14)$$

Energies of Activation. The plots of log k_1 and k_2 against $1/T$ have been represented in Fig. 8. From the slopes of the straight lines, the activation energies of the silver-ion-catalyzed and uncatalyzed reactions were calculated to be 17.4±0.6 kcal/mol and 28.6±0.8 kcal/mol respectively.

These values are the same as the activation energies calculated in the decomposition of the peroxydisulfate ion[11] in the absence or presence of a silver-ion catalyzer. Such an agreement of values suggests that the same mechanism may be involved in the rate-determining steps of the reactions.

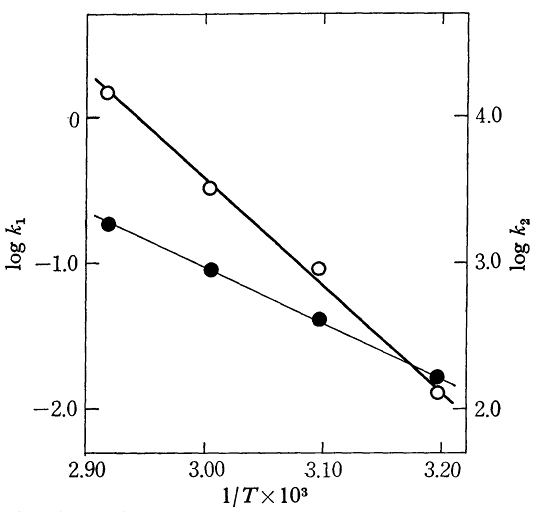

Fig. 8. Arrhenius plots for the silver ion uncatalyzed (k_1) and catalyzed (k_2) reactions.
○ ··· log k_1 ● ··· log k_2