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LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

ALPHA-PARTICLE OXIDATION AND REDUCTION IN AQUEOUS PLUTONIUM SOLUTIONS

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ALPHA-PARTICLE OXIDATION AND REDUCTION IN AQUEOUS PLUTONIUM SOLUTIONS

by

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ABSTRACT

Studies have been made of the rate of change of the mean oxidation number of plutonium solutions in perchloric, hydrochloric, and in mixed perchloric-hydrochloric acid solvents. Hydrogen peroxide concentrations have been determined in the plutonium solutions. The hydrogen peroxide concentrations in perchloric acid solutions of plutonium are markedly dependent upon the temperature. The higher hydrogen peroxide concentrations are found at the lower temperatures. The rate of alpha particle reduction of plutonium solutions in molar perchloric acid has been found to be only slightly influenced by temperature changes. From chemical analyses and gas analyses it has been concluded that the perchlorate ion is reduced to the chloride ion by the alpha particle radiation.

In hydrochloric acid solutions, the hydrogen peroxide concentrations and the rates of decrease of the mean oxidation number are much lower than in perchloric acid solutions of similar concentration. This inhibition of the reduction process presumably occurs through lowered yields of hydroxyl radicals and the interaction of chlorine and hypochlorous ion with hydrogen peroxide.

In perchloric acid solutions of plutonium containing bromide ion, an increase in the mean oxidation number, an alpha particle oxidation process, is found.

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1. Introduction

The chemical consequences of the interaction of the alpha particles from plutonium with the solvent must of necessity be considered in the study of the aqueous solution chemistry of this element. Plutonium-239,[1] the principal isotope used in this work, has a half-life of 24,360 years and an alpha particle energy of 5.15 Mev. This half-life and energy are of magnitudes which result in appreciable changes in the distribution of plutonium among the various oxidation states over a period of days.

Initially it was planned to make a complete, systematic study of the self-radiation effects of plutonium solutions. However, major kinetic problems appear to be involved, apart from the strictly radiation chemistry problems per se. Examples of these problems are the kinetics of the plutonium-hydrogen peroxide system and the interactions of chlorine and chloride ion with hydrogen peroxide.

The data which were obtained during the course of this study are summarized with comments and suggested mechanisms.

2. Reagents

α-plutonium from selected lots of high purity metal was used in this work. The oxide film was removed by mechanical means. The acidities of the solutions were known by using appropriate weights of standardized acid; allowances were made for the amount of acid consumed in dissolving the metal. Acids were standardized against c.p. mercuric oxide.

3. Apparatus

Gas samples from plutonium solutions were obtained by opening the glass containers in a vacuum system and were analyzed by mass spectrometric methods. End points of potentiometric titrations were obtained with the Beckman pH meter. The qualitative identification of hydrogen peroxide in plutonium solutions was confirmed by polarographic methods.

4. Experimental Procedure

It is convenient to use the average oxidation number of plutonium solutions as a means of expressing the relative proportions of this element in its four oxidation states. This quantity is defined by

$$\overline{ox} = \frac{\left(3\left[Pu^{+3}\right] + 4\left[Pu^{+4}\right] + 5\left[PuO_2^{+}\right] + 6\left[PuO_2^{+2}\right]\right)}{\Sigma[Pu]} \qquad (1)$$

In a solution in which the hydrogen peroxide is known to be small, a procedure has been developed[2] to determine $\overline{ox}$. It is found that the Pu(V) concentration is usually negligibly small in plutonium solutions in equilibrium at acidities between 0.1 and 1.0M or greater. The analytical method involves the oxidation of Pu(III) to the stable Pu(IV) sulfate complex with potassium permanganate; consequently, if $\overline{ox}$ is greater than four, it is necessary to add sufficient Pu^{+3} to reduce the $\overline{ox}$ below this value. Oxygen is swept from the vessel containing the plutonium solution, the sulfuric acid concentration is made 2 to 3M, three drops of 0.025M ferrous-phenanthroline indicator solution are added, and the solution is titrated with standardized 0.01N potassium permanganate from a microburet until the reddish-orange color of the indicator is discharged. The meq of oxidant equal the meq of reductant, i.e.,

$$\text{meq } KMnO_4 = \text{meq } Pu^{+3}_{\text{added}} - 2 \text{ meq } PuO_2^{+2} + \text{meq } Pu^{+3}_{\text{initial}} \qquad (2)$$

Combining equation 2 with equation 1, the value of $\overline{ox}$ is obtained

$$\overline{ox} = 4 - \frac{\left[\text{meq } KMnO_4 - \text{meq } Pu^{+3}_{\text{added}}\right]}{\Sigma Pu_{\text{meq}}} \qquad (3)$$

This procedure makes use of the reproportionation reaction

$$2Pu^{+3} + PuO_2^{+2} + 4H^{+} = 3Pu^{+4} + 2H_2O \qquad (4)$$

which is driven far to the right by the sulfate complexing of Pu^{+4} and by the relatively high acidity.

Another procedure[3] has been found useful in the event that the hydrogen peroxide concentration is to be determined. From two titrations on aliquots of the same sample of plutonium solution, the $\overline{ox}$ and the hydrogen peroxide concentrations can be determined. In this method, in titration I, an excess of $KMnO_4$ is added; then ferrous ion serves to react with the excess $KMnO_4$ and reduce the plutonium to the trivalent oxidation state. The titration is completed using standard potassium dichromate, and the end point is detected potentiometrically. In titration II, the same quantities of $KMnO_4$ and Fe^{+2} are added, but in reverse order. The titration is again completed with dichromate. In titration I, where x = meq H_2O_2, y = meq Pu^{+3}, a = meq $KMnO_4$, b = meq Fe^{+2}, and d = meq $K_2Cr_2O_7$

$$a + d = b + x + y \tag{5}$$

In titration II, all quantities are the same except e = meq $K_2Cr_2O_7$; then

$$a + x + e = b + y \tag{6}$$

Solving equations 5 and 6 simultaneously

$$2 \text{ meq } H_2O_2 = 2x = d - e \tag{7}$$

and

$$\text{meq } Pu^{+3} = y = a - b + \frac{(d + e)}{2} \tag{8}$$

With a knowledge of the total plutonium concentration and y, the fraction of Pu^{+3} can be computed. Since the remainder is Pu^{+4}, the value of $\overline{ox}$ can be computed. These titrations are also carried out in dilute sulfuric acid solution. As indicated in equations 5 and 6, in the first titration the MnO_4^- reacts with the Pu^{+3} and the hydrogen peroxide. In the second titration, the Fe^{+2} reacts with the hydrogen peroxide and the Pu^{+4}. The difference in the two titrations as indicated in equation 7 yields twice the meq of hydrogen peroxide.

5. Experimental Results

A. Perchloric Acid Solutions

(1) The effect of oxygen on the alpha reduction rate. Two plutonium solutions $8.68 \times 10^{-3}\underline{M}$ were prepared in molar perchloric acid. The initial mean oxidation numbers were made nearly 4.0 by adding potassium dichromate to the plutonium solutions. One of the stock solutions was flushed with argon; the other was saturated with oxygen. Weighed quantities of these stock solutions were placed in glass ampoules, sealed, and placed in a water thermostat

maintained at 25.00 ± 0.05°. At intervals, the ampoules were opened and the mean oxidation numbers were determined. In Fig. 1 are given the results. A second, more concentrated plutonium stock solution from which the oxygen was removed with argon is also shown. It appears evident that the presence of oxygen in the perchloric acid solutions of plutonium does not significantly alter the alpha reduction rate. In each case a mean value of 0.014 was obtained for the decrease in the mean oxidation number per day.

(2) The influence of Cr(III) upon the alpha reduction rate. In the above reported experiments, the Pu^{+4} was prepared by the addition of potassium dichromate to Pu^{+3}. Plutonium(IV) can also be prepared by making use of the reproportionation reaction.[4] The PuO_2^{+2} is conveniently prepared by the prolonged ozonization of Pu^{+3}. With an initial mean oxidation number of 4.01, an alpha reduction rate of 0.014 per day was observed in this solution which did not contain Cr(III). Thus it can be concluded that the presence of Cr(III) does not alter the rate of alpha reduction.

(3) The dependence of alpha reduction rate upon the initial value of $\overline{ox}$. In this series of experiments, the initial mean oxidation number was equal to six. The PuO_2^{+2} solution was prepared by the ozonization of Pu^{+3} in molar $HClO_4$. Over a period of 46 days, the $\overline{ox}$ values decreased linearly at the rate of 0.014 per day. The initial value of the mean oxidation number (if it is significantly above the steady state value, see below) has little effect upon the rate of alpha reduction.

(4) The effect of temperature upon the alpha reduction rate. The rate of alpha reduction of molar perchloric acid solutions of plutonium has been measured between 5 and 45°. The results are given in Table I. No pronounced difference is noted between 5 and 45° in the rate of alpha reduction

TABLE I

TEMPERATURE DEPENDENCE OF ALPHA REDUCTION RATE IN 1$\underline{M}$ $HClO_4$

Temperature, °C	Time Interval, days	Initial $\overline{ox}$	$-d(\overline{ox})/dt$
5	40	3.95	0.0116 to 0.0138*
25	34	3.95	0.0140
45	36	3.95	0.0133

*The lower value represents the initial (0-20 days) period and curvature in the $\overline{ox}$ vs time plot gradually approached the higher rate of reduction.

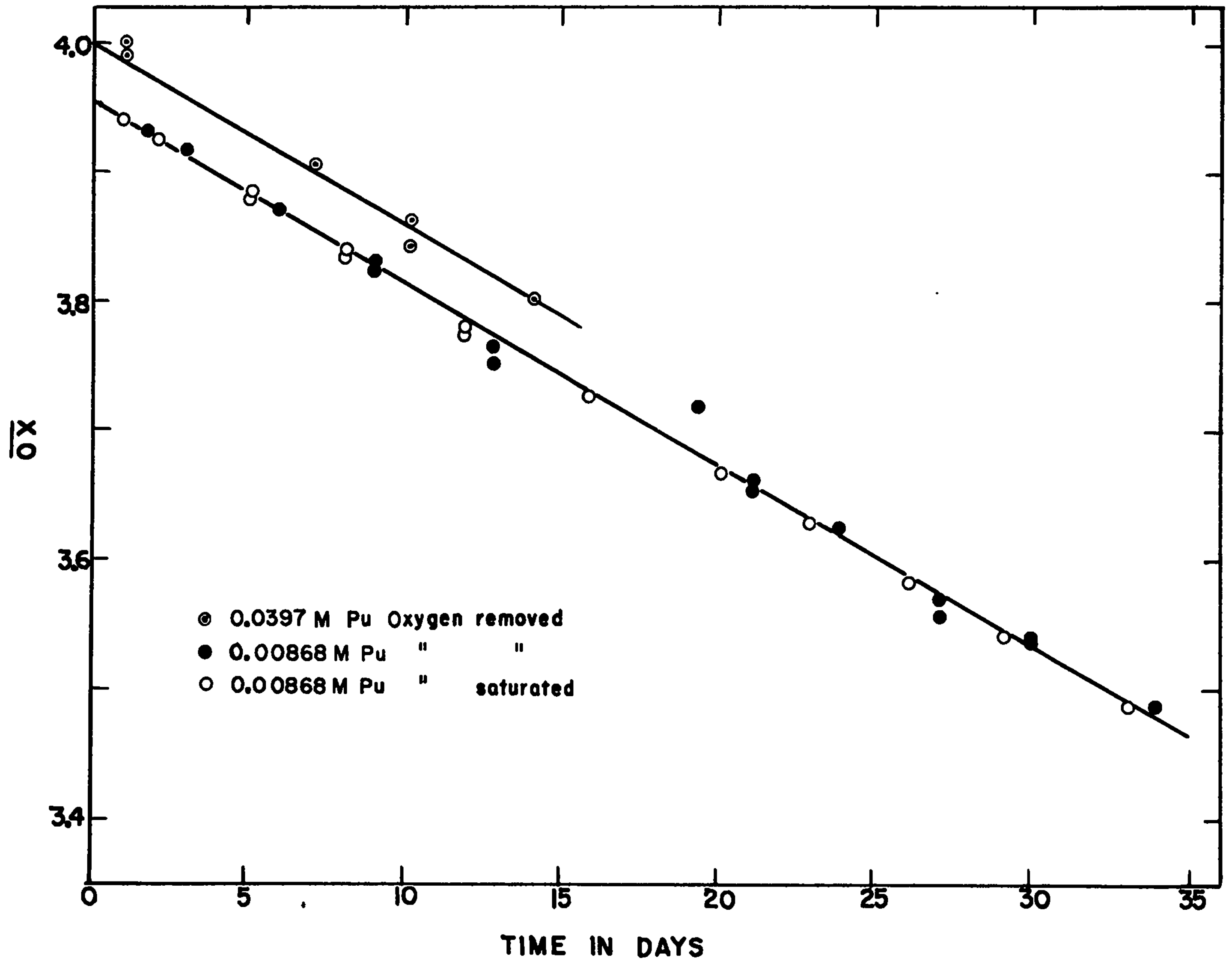

Fig. 1 The effect of oxygen and plutonium concentration on observed rate of alpha reduction.

in molar perchloric acid solutions after the low temperature run reaches its higher value.

(5) The growth of hydrogen peroxide in molar perchloric acid solutions as a function of temperature; alpha oxidation studies. As shown in Fig. 2, the steady state concentration of hydrogen peroxide is markedly temperature dependent. At 45° the hydrogen peroxide concentration was not detectable. At 25° the steady state concentration is sufficiently low so that this condition is essentially achieved within one day. The buildup of the hydrogen peroxide concentration in plutonium solutions at 5° required approximately 25 days to reach the steady state. From polarographic reduction waves, the presence of hydrogen peroxide in these plutonium solutions has been qualitatively established as well as quantitatively determined by the procedure described in the experimental procedure section of this report. The steady state concentration of hydrogen peroxide in the 25° experiment is calculated from the data of Fig. 2 to be 4×10^{-5} $\underline{N}$. The initial mean oxidation numbers of each of these solutions was about 3.9.

The mean oxidation numbers and the hydrogen peroxide concentrations were determined in another series of experiments in which the initial mean oxidation number of one series was 3.9 and the other 3.00. The results are given in Table II and are illustrated in Fig. 3. The value of $-d(\overline{ox})/dt$ in the solutions consisting initially chiefly of Pu^{+4} was 0.015 per day. The linearity of the rate of decrease of $\overline{ox}$ was maintained, even near the plutonium steady state $\overline{ox}$ value. The hydrogen peroxide concentrations appeared to be dependent upon the total plutonium ion concentrations at 4°. With the Pu^{+3} solutions, the steady state condition with respect to $\overline{ox}$ was attained within approximately 10 days. As shown in Table II the $\overline{ox}$ values at the steady state condition varied between 3.02 and 3.05 depending upon the plutonium ion concentration. The hydrogen peroxide concentrations at the steady state in the Pu^{+3} solutions were very similar to those obtained in the Pu^{+4} solutions of similar plutonium ion concentration.

(6) Effect of Acidity upon the Alpha Reduction Rate. To determine the acidity dependence of the alpha reduction rate, 0.3282 gram of plutonium metal was dissolved in sufficient perchloric acid to yield 100 ml of 3$\underline{M}$ acid. The initial mean oxidation number was made equal to 3.950 by the addition of potassium dichromate. Over a period of 19 days at 25° the value of $\overline{ox}$ decreased linearly, giving an average value of −0.0147 per day. This is essentially the value obtained in the molar perchloric acid solutions.[2,5] A difference was noted in the hydrogen peroxide concentrations in the two acids. Whereas in molar perchloric acid at 25° the hydrogen peroxide concentrations were small, in 3$\underline{M}$ acid the hydrogen peroxide level was essentially zero.

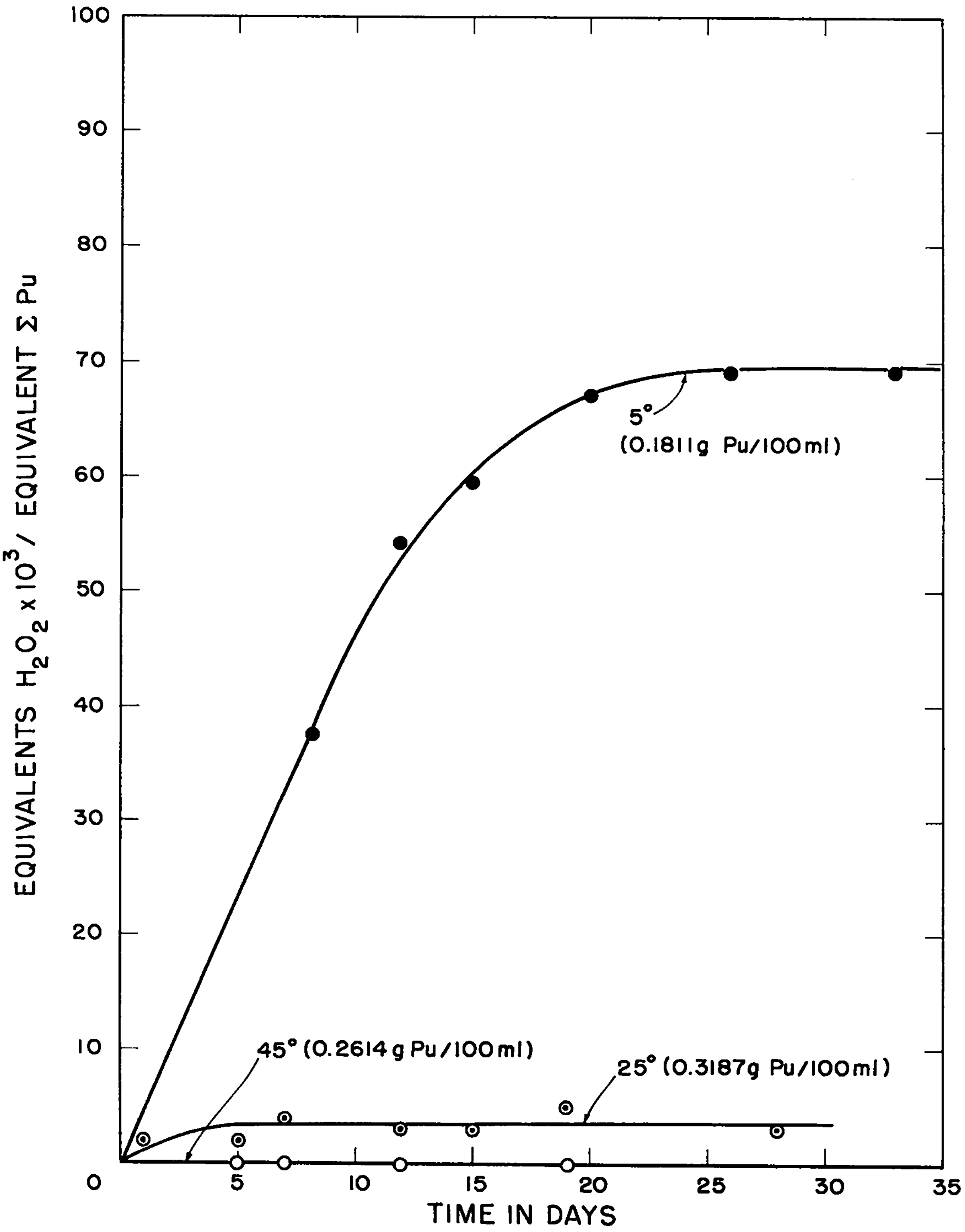

Fig. 2 Rate of formation of H_2O_2 as a function of temperature in molar perchloric acid.

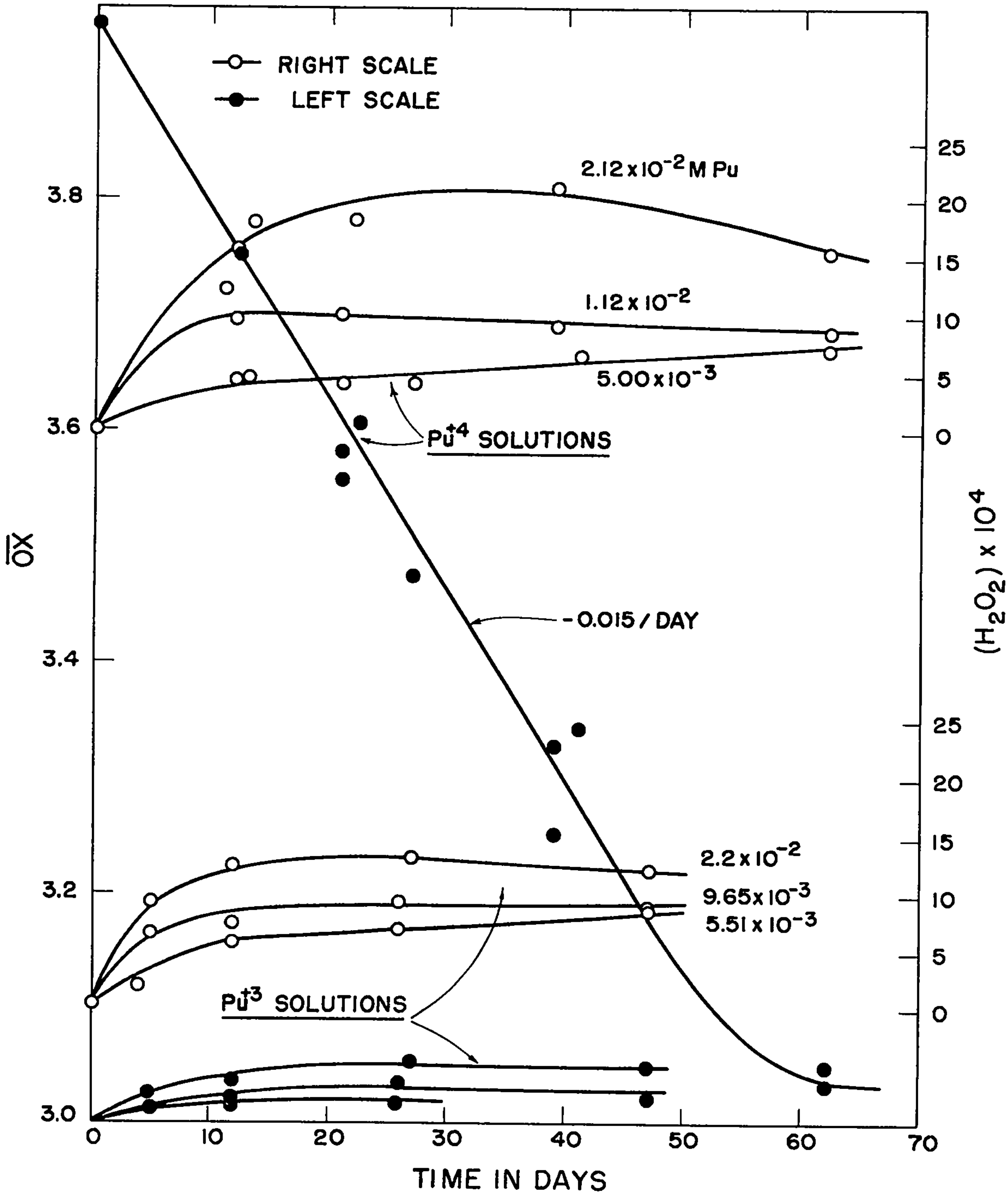

Fig. 3 Yield of H_2O_2 in plutonium solutions at 4°C

TABLE II

YIELD OF HYDROGEN PEROXIDE IN PLUTONIUM SOLUTIONS AT 4°

Σ Pu, moles/liter	Time, days	$\overline{\text{ox}}$	$[H_2O_2]$, eq/liter
I. Pu (IV) Solutions			
2.119×10^{-2}	11	3.811	12.07×10^{-4}
	13	3.775	18.12
	22	3.608	18.25
	39	3.328	20.86
	63	3.050	15.57
1.119×10^{-2}	12	3.752	9.68
	21	3.583	10.14
	39	3.251	8.97
	63	3.034	8.54
4.996×10^{-3}	12	3.756	4.42
	21	3.558	3.91
	27	3.474	4.00
	42	3.213	5.47
	63	3.033	7.02
II. Pu(III) Solutions			
2.211×10^{-2}	5	3.026	9.25
	17	3.041	12.4
	32	3.047	12.1
	52	3.049	12.1
9.654×10^{-3}	5	3.012	6.41
	12	3.018	6.89
	26	3.035	9.28
	48	3.019	9.16
5.506×10^{-3}	4	3.050	1.83
	11	3.016	5.75
	25	3.016	6.75
	48	-	9.35

(7) Evolution of Gases from Plutonium Solutions. A sample of Pu^{+3} (0.1960 g) was prepared in 100 ml of molar perchloric acid and the volume of gas produced was monitored over a period of 60 hours with the aid of a Töepler pump and a vacuum system equipped with calibrated volumes for quantitative measurements. (See Fig. 4.) Following this initial period of gas accumulation, the solution was kept at room temperature for 54 days. At the end of this period 1.81×10^{-4} moles of gas were collected. By mass spectrometric methods it was found that the gas contained 38.58% hydrogen and 61.42% oxygen. This experiment was repeated by continuing to collect the gas for an additional 21.2 days. At the end of this period 9.57×10^{-5} moles of gas were collected. Again the mass spectrometric results confirmed the unexpectedly large oxygen-hydrogen ratio. In the second sample the gas consisted of 62.33% oxygen and 37.67% hydrogen. Since the hydrogen peroxide reaches its steady state concentration quickly at room temperature, some other source of oxygen must be sought other than the water which would give rise to this predominance of oxygen in the evolved gases. The plutonium solution was examined for the presence of chloride ion by testing with silver nitrate solution. Significant amounts of chloride ion were observed, indicating that the reaction

$$ClO_4^- \xrightarrow{\alpha} Cl^- + 2O_2 \qquad (9)$$

occurs; this appears to be the explanation for the high oxygen content of the gas evolved from the plutonium solutions. Samples of molar perchloric acid were placed near a Co^{60} source so as to receive 0.18×10^{18} ev/sec, 0.092×10^{18} ev/sec, and 0.051×10^{18} ev/sec. The samples were exposed at these levels of activity for 16 hours. The amount of chloride in the latter two samples corresponded to 2 and 1 ml of 0.002M NaCl, respectively. Thus, it was demonstrated that the gamma radiation from Co^{60} also is effective in reducing perchlorate ion.

B. Hydrochloric Acid Solutions

(1) Alpha Reduction in Molar Hydrochloric Acid.[6, 7] The rate of change of $\overline{ox}$ of an $8.44 \times 10^{-3}M$ solution of plutonium in molar hydrochloric acid was measured. Air was removed from the solution by flushing with argon. The initial average oxidation number was 3.950. Over a period of 25 days the mean oxidation number remained at the initial value of 3.950. In a second experiment of a similar nature, the initial mean oxidation number was unchanged over a period of 75 days.

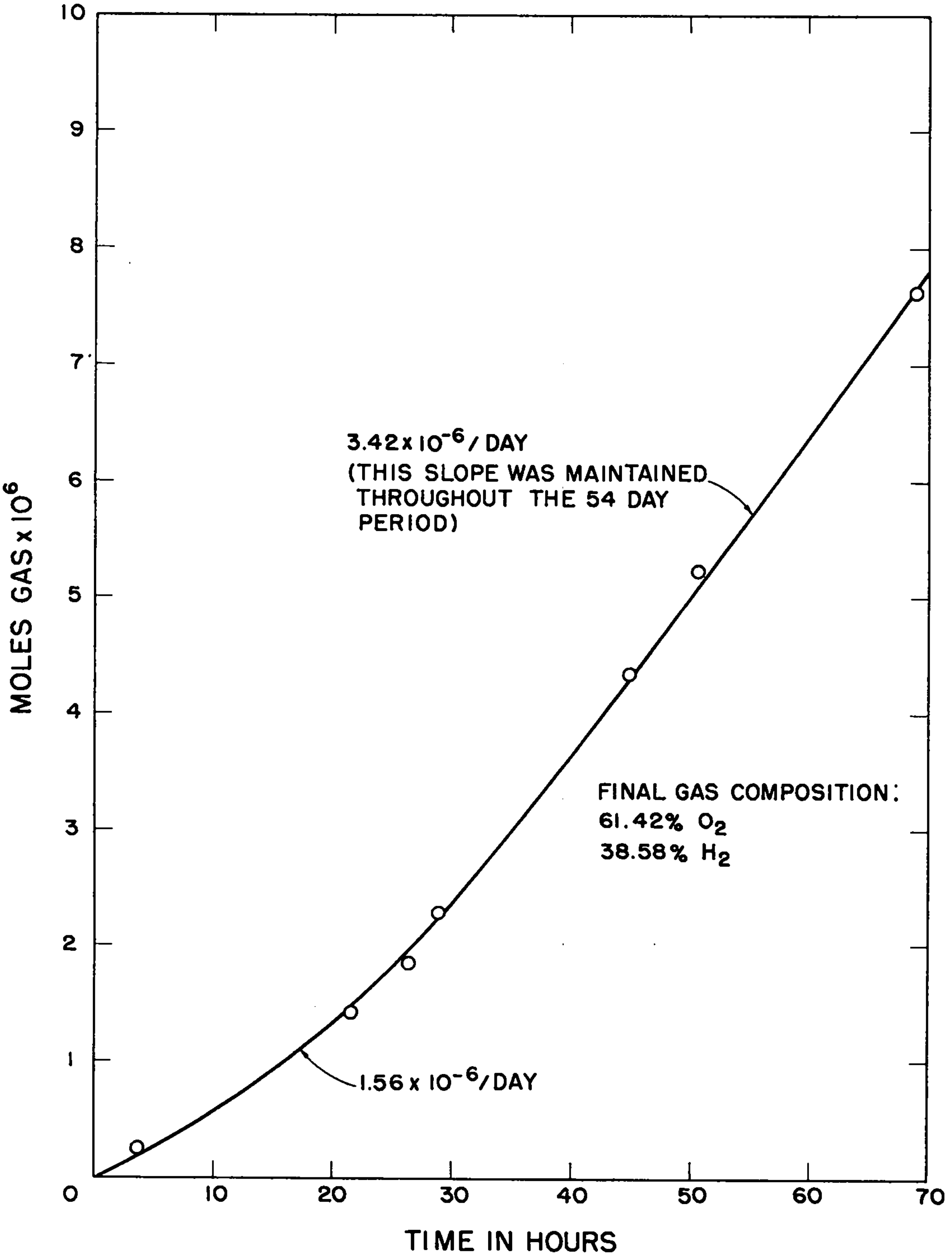

Fig. 4 Evolution of gas from plutonium(III) perchlorate solution in molar perchloric acid at 23°.

(2) Alpha Reduction in Hydrochloric-Perchloric Acid Solutions. In Table III are given the results of a series of alpha reduction experiments made at constant total plutonium ion concentration but with various amounts of chloride ion. The total acidity was maintained at 1.00M.

TABLE III

ALPHA REDUCTION RATES IN MIXED $HClO_4$-HCl SOLUTIONS AT 25°

$[HClO_4]$, M	[HCl], M	$-d(\overline{ox})/dt$
1.00	0.00	0.0140
0.90	0.10	0.0084
0.80	0.20	0.0070
0.60	0.40	0.0040
0.20	0.80	0.0015
0.00	1.00	0.000

Σ Pu = 1.5×10^{-2} M

$\overline{ox}_i = 3.95$

The data for Table III are illustrated in Fig. 5. As shown, the linearity of the alpha reduction rates in the perchloric-hydrochloric acid mixtures is well maintained over the period of 20 days. The plutonium solutions were kept in 100 ml volumetric flasks at room temperature with the ground glass stoppers in place. After 17 days the 0.20M perchloric-0.80M hydrochloric acid solution of plutonium was flushed with helium. As shown in Fig. 5 the removal of chlorine (later identified as such) by the helium markedly increased the rate of alpha reduction from −0.0015 to −0.005 per day.

Chlorine was detected in the mixed perchloric-hydrochloric acid solutions after a period of several days. The gas turned moist starch iodide paper blue. The gas was absorbed in water, reduced with sodium sulfite, and precipitated as the silver halide. Rather large amounts of iodine were released as helium was bubbled through the plutonium solution and into a solution of potassium iodide. [See section B(7)].

(3) Acidity Dependence of Rate of Alpha Reduction in $HClO_4$-HCl Solutions. In Table IV the results of experiments to determine the influence of acidity upon the rates of alpha reduction are given.

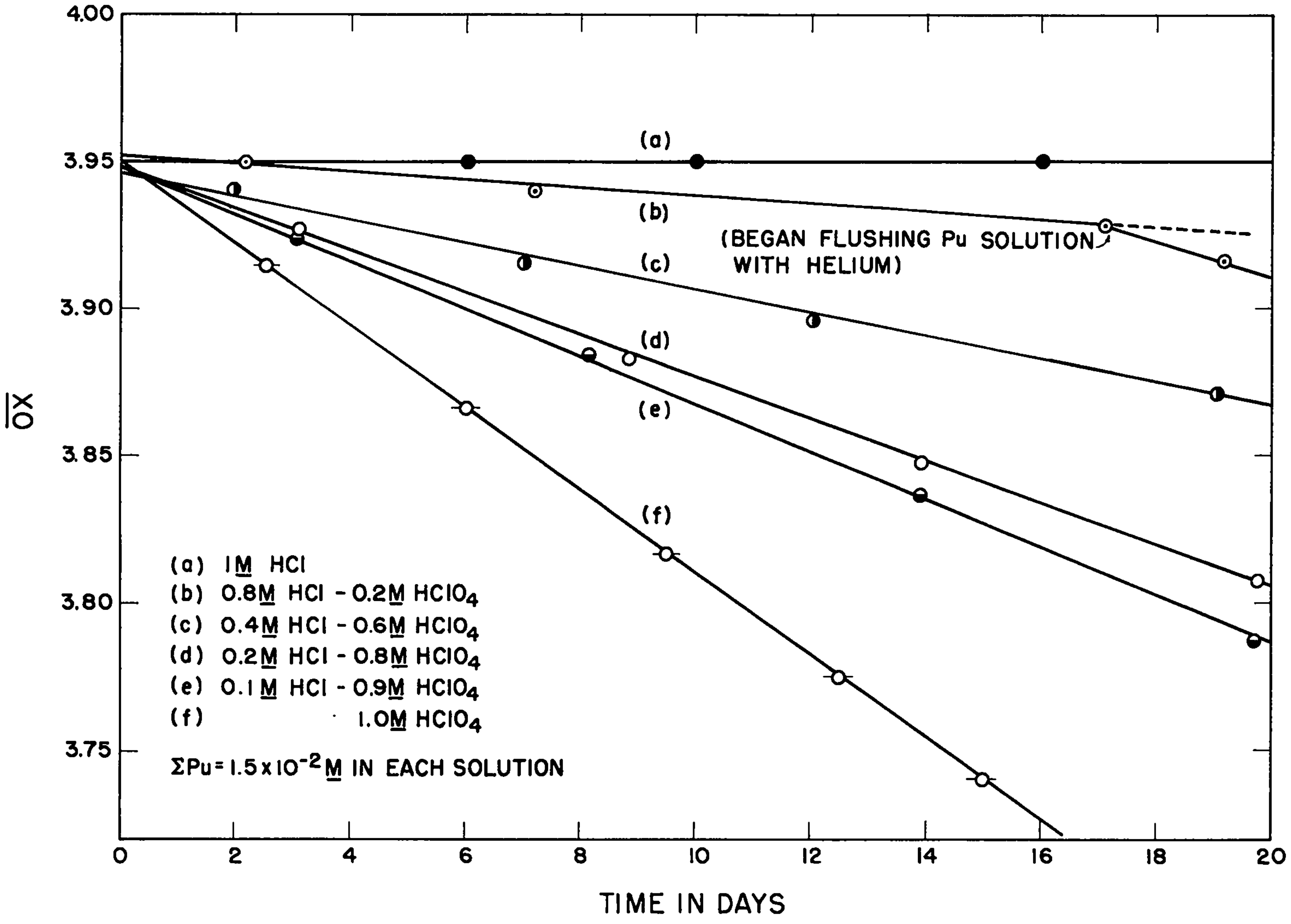

Fig. 5 Inhibition of alpha reduction by chloride ion in plutonium solutions.

TABLE IV

ACIDITY DEPENDENCE OF ALPHA REDUCTION RATE IN HCl-HClO$_4$ SOLUTIONS AT CONSTANT CHLORIDE ION CONCENTRATION

[HClO$_4$], M	[HCl], M	g Pu/100	Alpha Reduction Rate/Day
0.400	0.100	0.302	−0.0081
0.900	0.100	0.369	−0.0084
1.900	0.100	0.326	−0.0081
2.900	0.100	0.165	−0.0056

Up to a total acidity of two molar, little change is noted in the alpha reduction rate in the mixed perchloric-hydrochloric acid solutions of constant chloride concentration. However, a 32% reduction in the alpha reduction rate is noted as the total acidity reached three molar. It is believed that the effect of acidity on the alpha reduction rate arises through its effect upon the equilibrium

$$H^+ + Cl^- + HClO = H_2O + Cl_2 \qquad (10)$$

with the higher acidities favoring increased amounts of chlorine.

(4) Alpha Reduction Rate as a Function of Chloride Ion Concentration at Total Acidity of Three Molar. In this series of experiments, the total plutonium ion concentration was held constant, the acidity maintained at 3M, but the chloride ion concentration was varied between 0.1 and 0.8M. The data obtained over a 15 day period are shown in Fig. 6. As the chloride ion concentration was increased to 0.2M, and above, the alpha reduction was supplanted by an alpha oxidation. The larger chloride ion concentrations gave rise to the greater rates of oxidation. The data of Fig. 6 together with the results given in Table IV support the explanation that the lower alpha reduction rates, or the incidence of alpha oxidation, is related to the equilibrium of reaction 10. Both increased chloride at constant acidity and increased acidity at constant chloride ion resulted in reduced alpha reduction rates. Makower and Bray[8] have studied the kinetics of the reaction between hydrogen peroxide and chlorine in the presence of hydrochloric acid. The over-all reaction appears to be

$$H_2O_2 + Cl_2 = O_2 + 2H^+ + 2Cl^- \qquad (11)$$

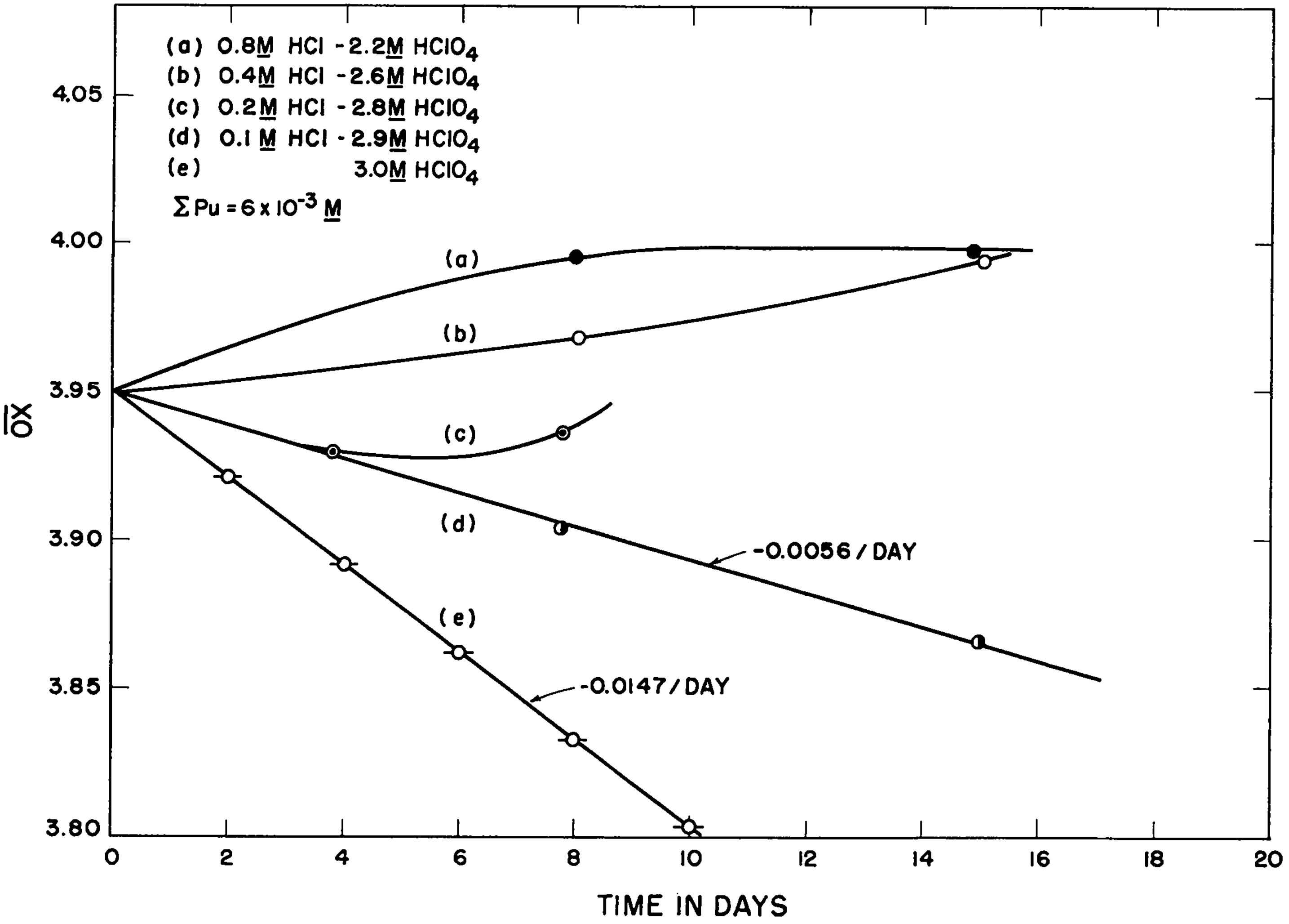

Fig. 6 Effect of chloride ion concentration upon alpha reduction rate at constant total acidity of three molar.

with the rate-determining step involving the bimolecular step

$$H_2O_2 + HOCl \rightarrow O_2 + H_2O + H^+ + Cl^- \qquad (12)$$

Connick[9] has re-examined the reaction between hydrogen peroxide and hypochlorous acid in acid solution containing chloride ion and has reached the conclusion that the rate of the reaction could best be explained by the mechanism

$$H_2O_2 + Cl_2 \underset{k_b}{\overset{k_a}{\rightleftharpoons}} H^+ + Cl^- + HOOCl \text{ (peroxy compound)} \qquad (13)$$

$$HOOCl \xrightarrow{k_c} Cl^- + H^+ + O_2 \qquad (14)$$

The rate law obtained was

$$\frac{-d\left(H_2O_2\right)}{dt} = \frac{k_c k_a\left(H_2O_2\right)\left(Cl_2\right)}{k_b(H^+)(Cl^-) + k_c} \qquad (15)$$

(5) Hydrogen Peroxide Concentrations in Perchloric-Hydrochloric Acid Solutions at 5°. Since as shown in Fig. 5 the alpha reduction rate in solutions of constant total acidity is markedly dependent upon the chloride ion concentration, it would be predicted that because of the equilibrium of equation 10 and because of reaction 11 together with the reaction

$$OH + Cl^- = OH^- + Cl \qquad (16)$$

the hydrogen peroxide concentration would also be a function of the chloride ion concentration. This result is observed as shown in Fig. 7; the presence of even 0.1$\underline{M}$ hydrochloric acid markedly lowers the maximum hydrogen peroxide concentration attained.[10] It is not clear why the hydrogen peroxide concentration should fall off so markedly in both the 0.1 and the 0.2$\underline{M}$ hydrochloric acid solutions after 25 days.

(6) Dependence of Alpha Reduction Rate on Initial $\overline{ox}$ in Molar Hydrochloric Acid. The alpha reduction rate in molar hydrochloric acid solutions in which the initial mean oxidation number was 3.950 has been shown to be

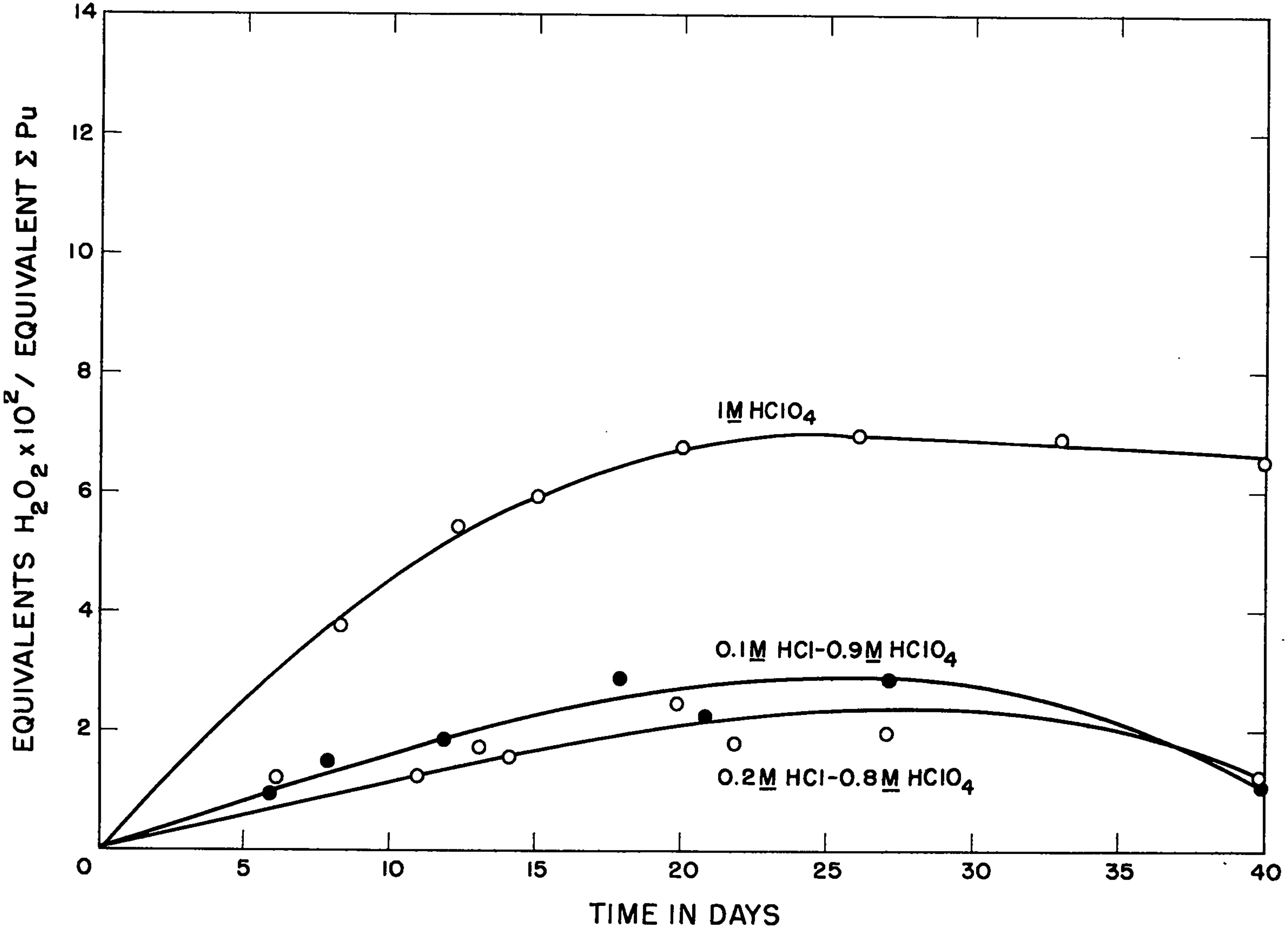

Fig. 7 Growth of hydrogen peroxide in perchloric and in perchloric-hydrochloric acid solutions at 5°.

zero in section B(2) of this report. Plutonium solutions in molar hydrochloric acid were prepared in which the initial mean oxidation numbers were 3.59 and 5.54. In both these solutions over a period of 75 and 68 days, respectively, the alpha reduction rate was found to be zero.

(7) Evolution of Chlorine from Plutonium Solutions. A sample of 0.2530 gram of Pu was dissolved in sufficient concentrated hydrochloric acid to prepare 100 ml of 3M acid. Helium gas was slowly bubbled through the plutonium solution and then into a neutral potassium iodide solution. Periodically the potassium iodide solution was acidified and the iodine was titrated with standard sodium thiosulfate solution. The sodium thiosulfate was added from a weight buret to the starch-iodide endpoint. The results are given in Table V.

TABLE V

DETERMINATION OF CHLORINE YIELD FROM PLUTONIUM SOLUTIONS IN 3M HCl

Elapsed time, hr	Ml 0.01N $Na_2S_2O_3$ Required	Meq Chlorine/day
71.0	2.380	8.05×10^{-3}
6.25	0.220	8.45
19.30	0.641	7.96
		Mean: 8.15×10^{-3}

Since the half-life of plutonium is 24,360 years, and the alpha particle has an energy of 5.15 Mev, the G_{Cl_2} value (molecules Cl_2/100 ev) equals 0.24 in this solution.

C. Perchloric Acid-Sodium Bromide Solutions[11]

The influence of bromide ion upon the rate of alpha reduction of plutonium solutions at 25° was studied. A solution containing 0.2276 gram of plutonium metal was made 0.1M in sodium bromide and 1.0M in perchloric acid. The initial mean oxidation number of the solution was made equal to about 3.90. Instead of observing an alpha reduction, an alpha oxidation process occurred. In Fig. 8 the experimentally observed values of the mean oxidation number as a function of time are plotted. It is very likely that disproportionation of Pu^{+4} has occurred in this molar perchloric acid solution

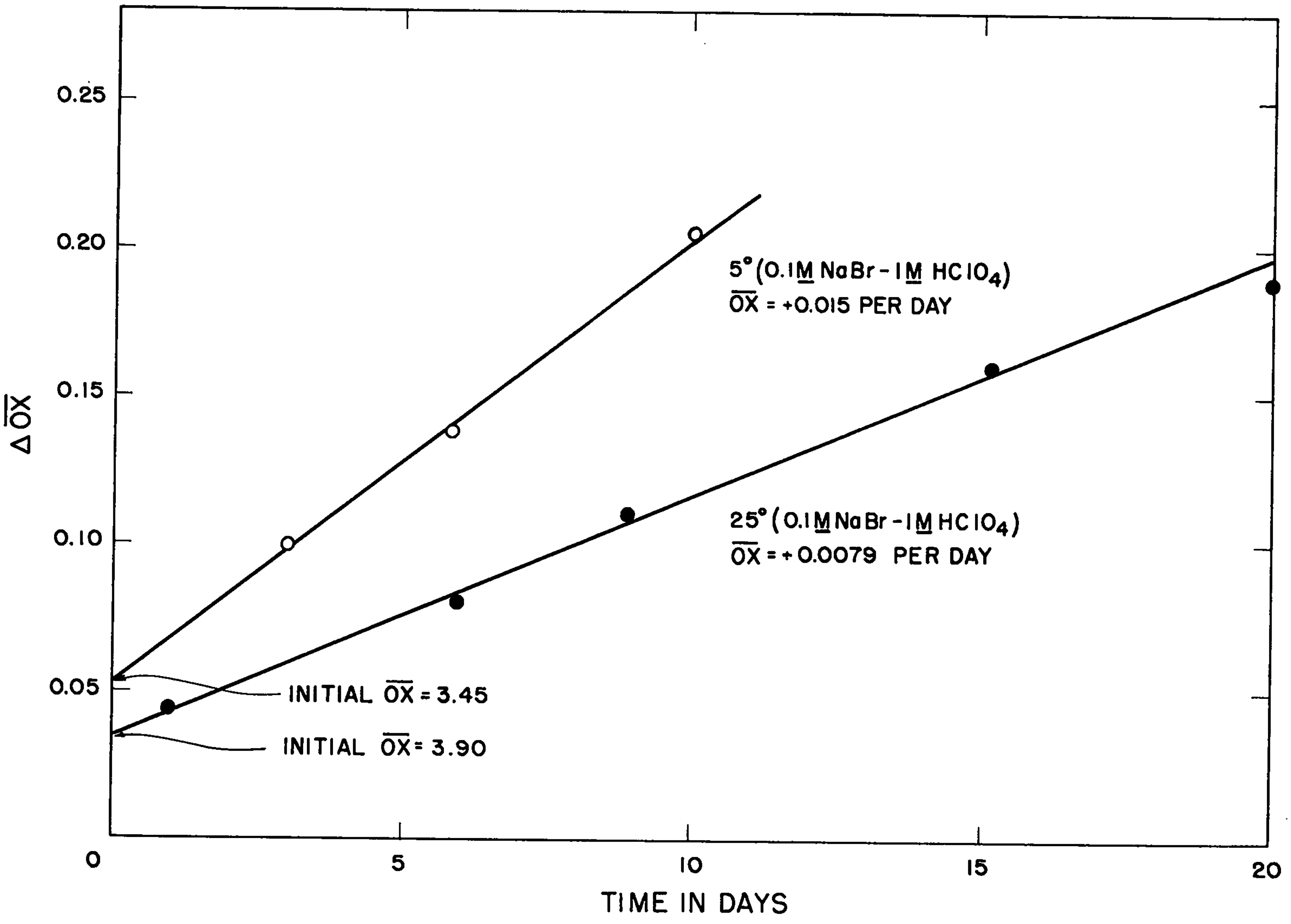

Fig. 8 Effect on alpha reduction rate of added bromide in perchloric acid solutions of plutonium.

to an extent that permits the mean oxidation number of the solution to rise above four. With higher acidity the mean oxidation number would probably have levelled off close to four as was observed in the three molar hydrochloric acid solutions.

In another experiment, the initial mean oxidation number of the solution was about 3.45. The solution was kept at a temperature of 5°. Again, the alpha oxidation process was observed. (See Fig. 8). At 5° the rate of increase of the value of $\overline{ox}$ was found to be 0.015 per day, while at 25° it was observed to be 0.0079 per day. The bromine color was evident in the solutions.

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