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STUDIES ON THE DISPROPORTIONATION OF PLUTONIUM(V) IN OXALATE MEDIUM

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Abstract— Plutonium(V) in oxalate solutions in the pH region 2 to 5·5 has been found to be unstable to disproportionation giving rise to plutonium(VI) and plutonium(IV). The rate of disproportionation is proportional to the second power of the plutonium(V) concentration and decreases with decreasing hydrogen ion concentration. The dependence of the rate and extent of disproportionation on pH, oxalate concentration and plutonium concentration has been studied. An activation energy of 10·0 kcal/mole has been computed from the temperature dependence of the second order rate constant for the disproportionation of plutonium(V) in 0·03 M oxalate solution at pH 2.

INTRODUCTION

PLUTONIUM(V) is kinetically resistant to disproportionation in the pH range 1·5 to 6·0 in the absence of complexing agents[1, 2]. Cook, Foreman and Kemp[3] have shown that oxalate ions induce the disproportionation of plutonium(V) in the pH range 3·5–4·2. During the course of our preliminary work on the photochemistry of plutonium(VI), it was observed that plutonium(V) was highly unstable in oxalate medium at pH 3·5. The results of a detailed study of the disproportionation of plutonium(V) in oxalate medium in the pH range 2·0–5·5 are presented in this paper. The effects of temperature, oxalate concentration and plutonium concentration on the reaction have been studied.

EXPERIMENTAL

All the reagents used were of analytical grade. All solutions were prepared in double distilled water.

Preparation of solutions

Plutonium was purified using the standard anion exchange method[4] followed by one peroxide and two hydroxide precipitations. The purified hydroxide was dissolved in hot perchloric acid. Plutonium(VI) solution was prepared by oxidising the plutonium solution by passing ozonised oxygen through it for about 4 hr[5]. Plutonium(V) was prepared by the quantitative reduction of plutonium(VI) with iodide ion[6]. The end point was determined potentiometrically and the iodine liberated was removed by carbon tetrachloride extraction. Plutonium(IV) solution in perchloric acid was prepared by controlled electrolytic oxidation of plutonium(III), which was prepared by reducing the solution containing a mixture of valence states of plutonium by the addition of hydrogen peroxide. Dilute solutions of sodium hydroxide or perchloric acid were used for adjustment of pH.

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1. L. H. Gevantman and K. A. Kraus, *The Transuranium Elements*, Vol. 14B, p. 500, National Nuclear Energy Ser., Div. IV. McGraw-Hill. New York (1949).
2. K. A. Kraus, *The Transuranium Elements*, Vol. 14B, p. 241, National Nuclear Energy Ser., Div. IV. McGraw-Hill, New York (1949).
3. G. P. Cook, J. K. Foreman and E. F. Kemp, *Analitica chim. Acta* **19**, 174 (1958).
4. J. L. Ryan and E. J. Wheelwright, *USAEC Rep.* No. HW-55893 (1959).
5. C. K. Sivaramakrishnan, M.Sc. thesis, University of Bombay 1964.
6. S. W. Rabideau, *J. Am. chem. Soc.* **78**, 2705 (1956).

Estimation of plutonium(VI), (V) and (IV) in oxalate medium

Estimation of the different valence states of plutonium was carried out spectrophotometrically using a Beckman DU Spectrophotometer. Plutonium(VI) was estimated by measuring the optical density at 851–52 mμ. Calibration curves were prepared for the different pH's and oxalate concentrations used. The analytical method developed during the course of this work for the estimation of plutonium(V) in the presence of plutonium(VI) and (IV) in oxalate medium is as follows: Plutonium(V) was quantitatively oxidised to plutonium(VI) by excess cerium(IV) in 2·5M sulphuric acid and the concentration of plutonium(VI) in sulphuric acid was determined by measuring the optical density at 841–42 mμ after standing for half an hour to complete the oxidation of oxalate by cerium(IV). It was observed that the concentration of perchlorate had to be kept below 0·15 M during the oxidation process in order to avoid the precipitation of cerium. It was also verified by the following experiment that plutonium(IV) was not oxidised by cerium(IV) under the conditions used. A solution containing $1{\cdot}78 \times 10^{-3}$ M plutonium(IV), $3{\cdot}77 \times 10^{-2}$ M cerium(IV) and $1{\cdot}4 \times 10^{-2}$ M oxalate in 2·5 M sulphuric acid was allowed to stand for half an hour and the increase in optical density at 841–42 mμ peak was found to be less than 0·01 indicating that no measurable amount of plutonium(VI) was formed.

Total plutonium concentration was determined by alpha counting.

Spectrophotometric measurements did not reveal any evidence for the presence of plutonium(III). Hence, the difference between the total plutonium and the sum of plutonium(VI) and plutonium (V) was taken to represent the concentration of plutonium(IV). In order to check this assumption, measurement of the concentration of plutonium(IV) formed was made in the case of pH 3·5 solution by following the 494 mμ peak. The extinction coefficient of plutonium(IV) at this wave length was found to be 81. Plutonium(VI) was also found to absorb significantly at this wave length with an extinction coefficient of 30. Plutonium (V) was found to have negligible absorption. The value of the plutonium(IV) concentration after making a correction for the absorption of plutonium(VI) was found to be practically equal to the difference between the total plutonium and the sum of plutonium(VI) and plutonium(V).

Kinetic runs

Rate of formation of plutonium(VI). Plutonium(V) solution in perchlorate medium at the desired pH and sodium oxalate solution at the same pH were kept separately in a compartment, the temperature of which was maintained constant by circulating water from a thermostat. The cell compartment in the spectrophotometer was also maintained at the same temperature by circulating the water through the spacers provided. A calculated volume of the plutonium(V) solution was pipetted into a spectrophotometer cell. The required volume of oxalate solution was then added to the plutonium(V) solution. The cell was stoppered immediately, shaken well and transferred back to the cell compartment. The optical density at 851–52 mμ was measured after about 3 min from the start of the reaction. The time of addition of half the amount of oxalate solution was taken as the starting time. Optical density measurements were taken at appropriate intervals for about 60 min.

Rate of disappearance of plutonium(V). Immediately after mixing the plutonium(V) and oxalate solutions, an aliquot of the solution was added to an excess of cerium(IV) sulphate in sulphuric acid. Aliquots were pipetted into different samples of ceric sulphate solutions periodically for about 60 min. The total plutonium(VI) in each sample was then measured by observing the optical density at 841–42 mμ.

For determining the activation energy, experiments were carried out at 15°C, 20°C, 28°C and 36°C. All other experiments were carried out at 28°C ± 0·2°C.

Potential measurements

The potentials of the plutonium solutions in oxalate medium were measured against a saturated calomel electrode using a NH_4NO_3 salt bridge and a Leeds and Northrup potentiometer. The European convention has been followed for expressing the values of the potentials.

RESULTS

The increase in the concentrations of plutonium(VI) and plutonium(IV) and the decrease in plutonium(V) concentration have been measured as a function of time at pH 3·5 and at an oxalate concentration of 0·03 M (Fig. 1). It may be noted

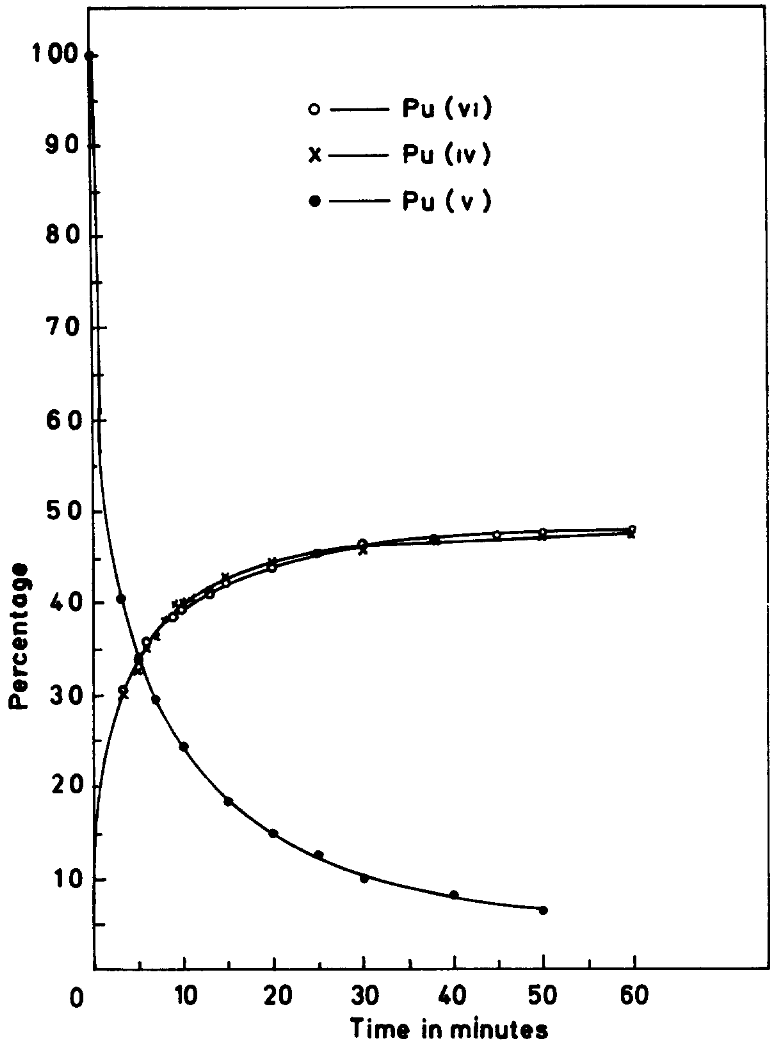

Fig. 1. Growth of Pu(VI) and Pu(IV) and decay of Pu(V) in oxalate-perchlorate medium.
Initial Pu(V) concentration = 0·0065 M
Oxalate concentration = 0·03 M
Perchlorate concentration = 0·15 M
pH = 3·5.

that more than 90 per cent of plutonium(V) has disappeared in about 50 min giving rise to nearly equal amounts of plutonium(IV) and plutonium(VI) showing that the reaction occurring was the disproportionation of plutonium(V) as follows:

$$2Pu(V) \longrightarrow Pu(IV) + Pu(VI). \qquad (1)$$

Plutonium(III) was absent throughout the course of the reaction. The rate and extent of formation of plutonium(VI) were found to be practically the same when the reaction was carried out in argon atmosphere. It indicates that air oxidation of plutonium(V) is not taking place and that disproportionation is the cause for the instability of plutonium(V). The pH of the solution was observed to increase from 3·5 to 3·9 during the reaction. Hence, the results given in Fig. 1 could not be utilized for determining the order of the reaction. The experiment was repeated with a solution having an initial pH of 2 and it was observed that the final pH was also nearly 2. The results obtained in this experiment have been used to plot 1/[Pu(V)] against time (Fig. 2) and the values of the second order rate constant was found to be 107 $M^{-1}min^{-1}$ at 28°C.

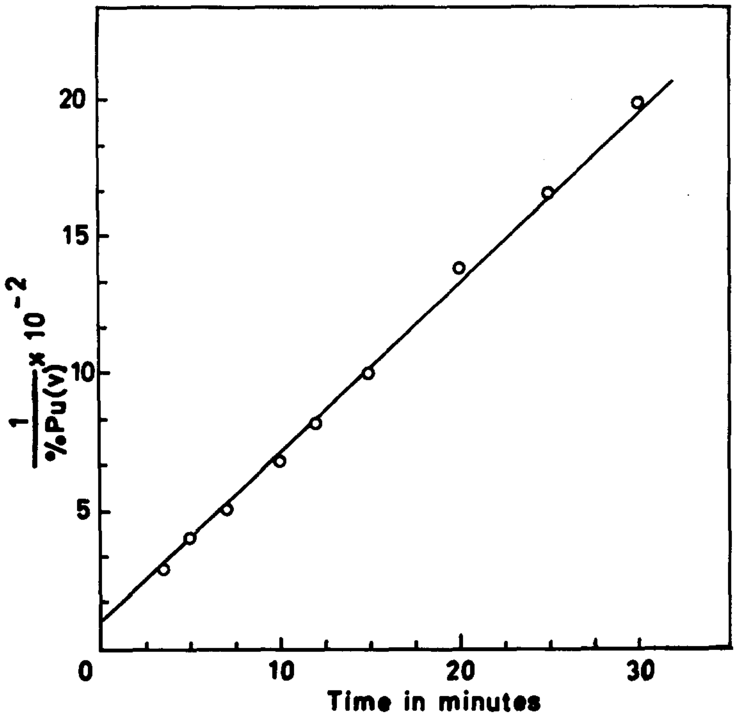

Fig. 2. Second order plot of the disproportionation of Pu(V).
Initial Pu(V) concentration = 0·0065 M
pH = 2 Temperature = 28°C.

Effect of temperature

The rates of disproportionation of plutonium(V) in oxalate medium at pH 2 were measured at 15°C, 20°C, 28°C and 36°C. The plot of 1/T against log (rate constant) is a straight line (Fig. 3). A value of 10·0 Kcal/mole was calculated for the activation energy of the rate determining step in the disproportionation of plutonium(V). The heat, free energy and entropy of activation for the disproportionation reaction were calculated from the rate expression from the transition state theory[7]. The calculated values of ΔH^*, ΔF^* and ΔS^* are 9·4 Kcal/mole, 17·1 Kcal/mole and −25·8 cal/deg mole respectively.

Effect of pH

The rates of formation of plutonium(VI) from plutonium(V) solutions of initial pH 2·0, 3·5, 3·8, 4·0, 4·5, 5·0, and 5·5 have been measured (Fig. 4). It may be

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7. S. Glasstone, K. Laidler and H. Eyring, *The Theory of Rate Processes*. McGraw-Hill, New York (1941).

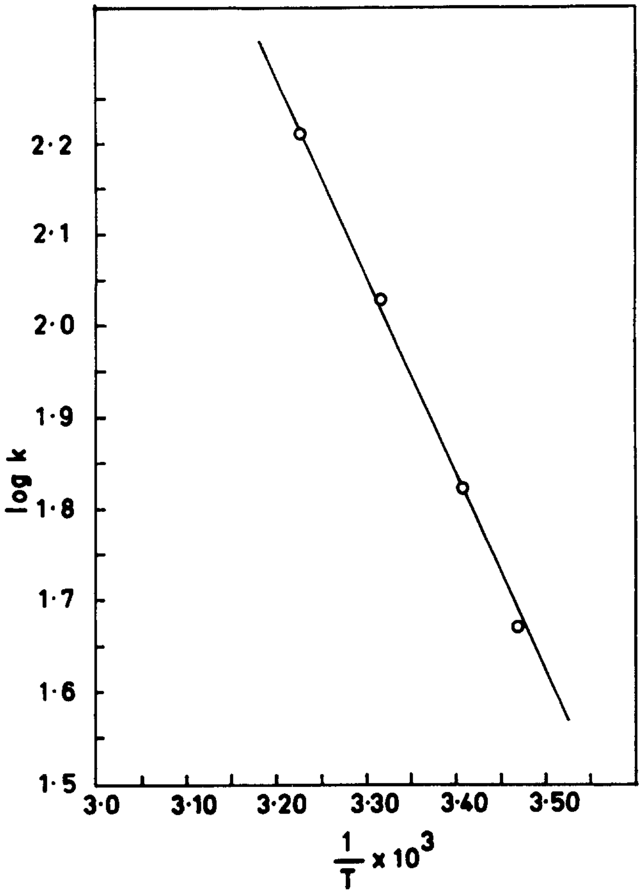

Fig. 3. A plot between 1/T and log k at pH = 2.

seen that the rate and extent of formation of plutonium(VI) decrease with increase in pH. The pH of the solution increases appreciably during disproportionation in all cases except that with an initial pH 2 (see Table 1).

In solutions where the final pH values are 2 and 3·9 plutonium(V) has disproportionated almost completely. In the case of other solutions where the final pH values vary from 6·3 to 7·2, the ratio [Pu(VI)]/[Pu(V)] at equilibrium decreases with increase in pH (Table 1).

Potential measurements

The potential measurements on solutions containing plutonium(IV), (V) and (VI) in equilibrium are given in Table 1. Since only the plutonium(VI)/(V) potential is reversible, it can be assumed that the measured potentials refer to the plutonium(VI)/(V) couple. Moreover, the observed potentials when plotted against log [Pu(VI)]/[Pu(V)] gave a straight line of slope −0·06. The formal half-cell-potential for unit ratio of plutonium(VI) to plutonium(V) evaluated by assuming zero liquid-junction potential and +0·244 V for the standard potential of the calomel electrode, is found to be +0·69 ± 0·01 V.

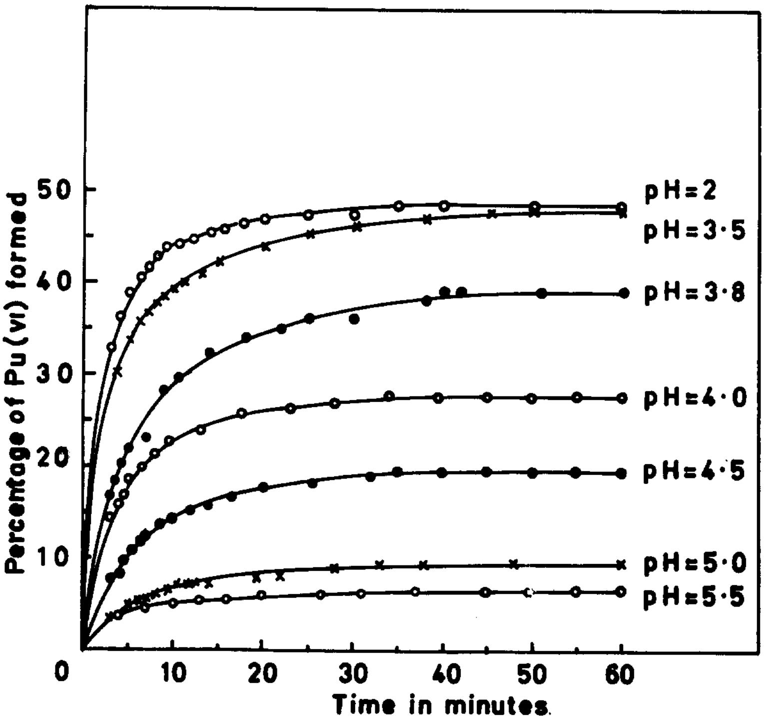

Fig. 4. Effect of pH on the disproportionation of Pu(V).
Initial Pu(V) concentration = 0·0065 M
Oxalate concentration = 0·03 M
Perchlorate concentration = 0·15 M.

Table 1. Equilibrium measurements of pH, e.m.f. and [Pu(VI)]/[Pu(V)] ratio
Initial plutonium(V) concentration = $6 \cdot 5 \times 10^{-3}$ M
Oxalate concentration = 0·03 M
Perchlorate concentration = 0·15 M.

Initial pH	Final pH	$\frac{[Pu(VI)]}{[Pu(V)]}$ at equilibrium	$K = \frac{[Pu(VI)]^2}{[Pu(V)]^2[H^+]^4}$ $\times 10^{-26}$	Potential of Pu(VI)/(V) couple measured w.r.t. SCE in volts
2	2	Almost completely disproportionated	—	—
3·5	3·9		—	—
3·8	6·3	1·77	0·50	+0·464
4·0	6·8	0·61	5·89	+0·437
4·5	7·0	0·321	10·30	+0·413
5·0	7·1	0·117	3·44	+0·390
5·5	7·2	0·0747	3·52	+0·379

Effect of oxalate concentration

The disproportionation studies reported above were carried out with solutions of 3×10^{-2} M oxalate. The effect of variation of oxalate concentration by a factor of ten on the reaction has been studied with solutions of initial pH 3·5 and 5·5 and the results are given in Fig. 5. With the pH 3·5 solutions plutonium(V) undergoes practically complete disproportionation when the oxalate concentration is 0·03 M and 0·1 M.When the oxalate concentration is brought down to 0·01 M, about 50 per cent of plutonium(V) undergoes disproportionation. The rate of disproportionation also falls down considerably. At 0·001 M oxalate concentration there was practically no disproportionation even in 2 hr. With the pH 5·5 solutions also a similar trend of a decrease in the rate and extent of disproportionation with decrease in oxalate concentration was observed.

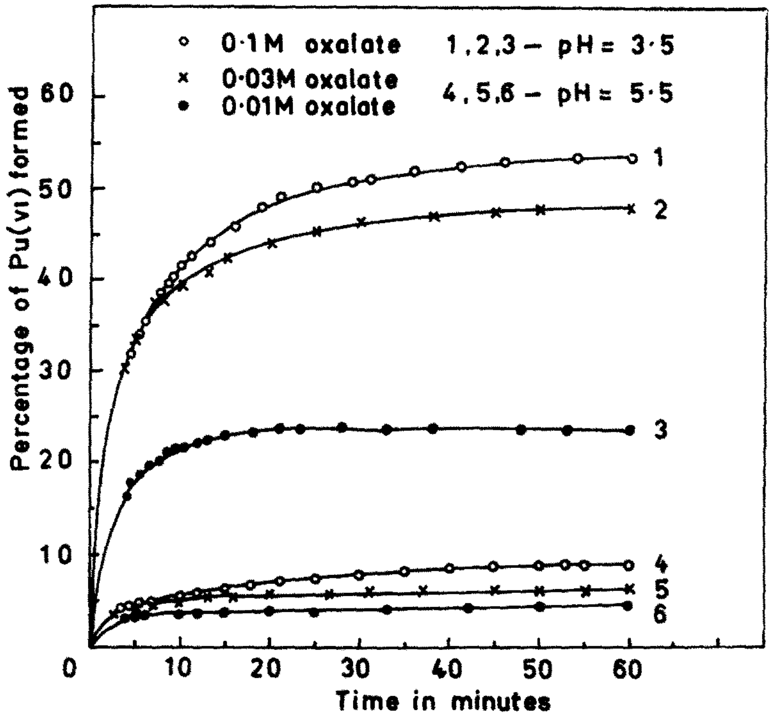

Fig. 5. Effect of oxalate concentration on the disproportionation of Pu(V). Initial Pu(V) concentration = 0·0065 M.

Effect of plutonium concentration

The studies reported above were limited to solutions of $6{\cdot}5\times10^{-3}$ M plutonium. A higher plutonium(V) concentration was not tried since the concentration of plutonium(IV) formed would be exceeding the solubility of plutonium(IV) oxalate, which was determined during the present work to be about $3{\cdot}1\times10^{-3}$ M. The effect of changing the plutonium(V) concentration on the disproportionation reaction was, therefore, studied with lower plutonium(V) concentrations only at pH 3·5. With the pH 5·5 solutions, however, a higher plutonium(V) concentration could be tried, since only about 10 per cent of plutonium(V) undergoes disproportionation at that pH. The curves I and II shown in Fig. 6 indicate that the initial concentration of plutonium(V) has no effect on the extent of disproportionation. The curve III does not show complete dispro-

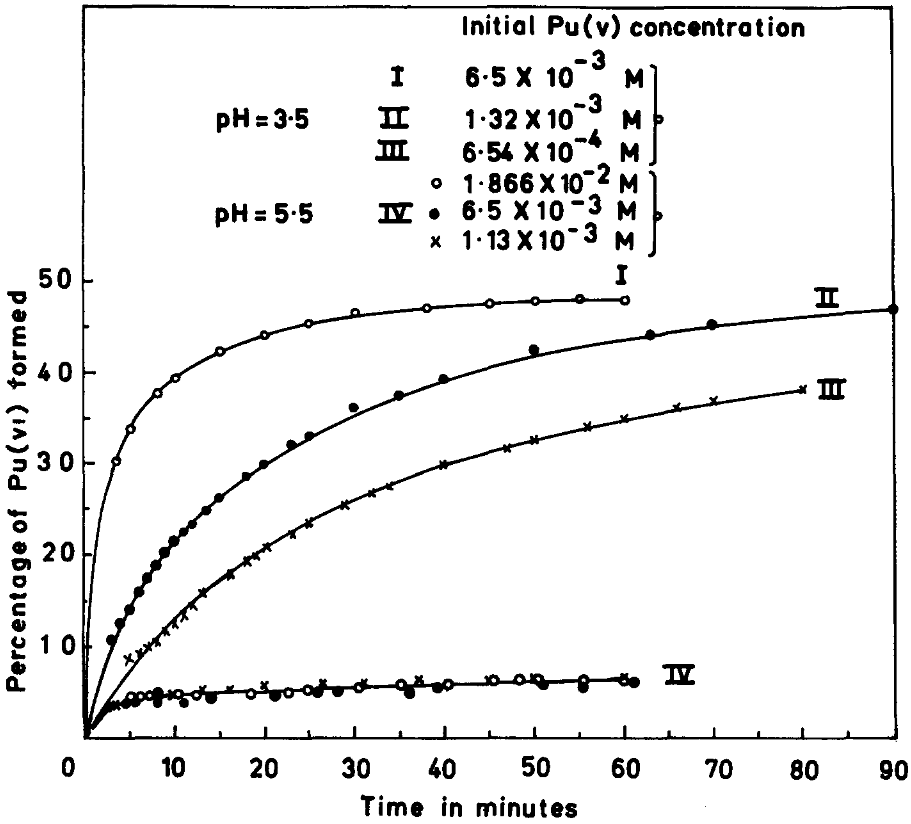

Fig. 6. Effect of initial Pu(V) concentration on the disproportionation of Pu(V).
Oxalate concentration = 0·03 M.
Perchlorate concentration = 0·15 M.

portionation during the time for which observations have been made. Since it is going upwards, disproportionation is likely to be complete after a considerable time. The rate of disproportionation, however, markedly decreases with a decrease in plutonium(V) concentration in the case of pH 3·5 solutions. A similar effect is expected in the case of pH 5·5 solutions also, where the results show that the rate is practically unaltered by the initial concentration of plutonium(V). It is possible that the effect was not noticed, since the rate of disproportionation is very small at this pH.

IV. DISCUSSION

Plutonium(V) is known to disproportionate in highly acidic solutions into plutonium(III) and plutonium(VI) [8–11]. Since the plutonium(IV)/(III) potential (+0·96 V) is more positive than the plutonium(VI)/(V) potential (+0·93 V) in

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[8] R. E. Connick, *The Transuranium Elements*, Vol. 14B, p. 268, National Nuclear Energy Ser., Div. IV. McGraw-Hill, New York (1949).

[9] R. E. Connick, *J. Am. chem. Soc.* 71, 1528 (1949).

[10] S. W. Rabideau, *J. Am. chem. Soc.* 79, 6350 (1957).

[11] P. I. Artyukhim, U. I. Medredouskii and A. D. Gel'man, *Zh. neorg. Khim.* 4, 1324 (1959).

1 M perchloric acid the plutonium(IV) formed initially is reduced to plutonium(III) by plutonium(V). While the plutonium(VI)/(V) potential does not change with pH, the plutonium(IV)/(III) potential decreases rapidly with the increasing pH owing to the formation of plutonium(IV) polymer above pH 1·5[2]. Hence, beyond pH 1·5 disproportionation of plutonium(V) involves only plutonium(IV) and plutonium(VI)[1]. In the present work also plutonium(III) was found to be absent throughout the course of the reaction, showing that the plutonium(IV)/(III) potential must be lower than +0·69 V, the value obtained for the plutonium(VI)/(V) potential in 0·03 M oxalate medium. In this connection it may be noted that a value of +0·205 V relative to saturated calomel electrode has been reported for the plutonium(IV)/(III) couple in 1 M oxalate[12].

The extent of disproportionation of plutonium(V) into plutonium(IV) and plutonium(VI) is determined by the difference in the potentials of plutonium(V)/(IV) and plutonium(VI)/(V) couples. The former is considerably more positive than the latter in acid medium. As the pH increases, the difference in the values becomes less and results in the stability of plutonium(V) towards disproportionation in the pH range 1·5 to 6·0[1]. In presence of oxalate the plutonium (VI)/(V) couple has fallen to +0·69 V from the value of +0·93 V in perchlorate indicating the preferential complexing of plutonium(VI). In this connection it may be noted that Cook, Foreman and Kemp [3] have obtained a value of −0·21 V relative to the standard calomel electrode for the half-wave potential of the plutonium(VI) reduction in 0·5 M oxalate solution at pH 4·0, and have suggested that the large shift in half-wave potential from the formal potential of the plutonium (VI)/(V) couple in essentially non-complexing media implies that plutonium (VI) is much more strongly complexed by oxalate than is plutonium(V). The plutonium(V)/(IV) couple would have increased owing to the considerable complexing of plutonium(IV). The difference in potentials of plutonium(V)/(IV) and plutonium (VI)/(V) couples makes plutonium(V) thermodynamically unstable in an oxalate medium. This is borne out by the results obtained in the present work with different oxalate concentrations.

Cook, Foreman and Kemp[3] have reported that on the addition of sodium oxalate-oxalic acid solution to a solution of plutonium(V) at pH 3·5 plutonium(IV) is formed predominantly along with small amounts of plutonium(VI) and have suggested that the disproportionation of plutonium(V) is accompanied by direct reduction of it by oxalate ion. In the present work it has been shown that when plutonium(V) disappears nearly equal amounts of plutonium(IV) and plutonium(VI) are formed and that therefore reduction of plutonium(V) by oxalate ion is not taking place to any significant extent under the conditions used. Plutonium(VI) solutions in oxalate medium have also been found to be stable to reduction on standing overnight. It is, therefore, concluded that there is no oxidation of oxalate ion during the disproportionation process, though no measurements of oxalate concentration have been carried out during disproportionation.

At a constant oxalate concentration an increase in pH decreases the extent of disproportionation. This result coupled with the observation that the pH of the solution increases during the course of disproportionation shows that the

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12. V. V. Fomin, S. P. Vorobler and M. A. Andreeva, *Soviet J. atom. Energy* **4**, 57 (1958).

reaction involves hydrogen ions and can be represented by the equation

$$2\text{Pu(V)}^* + 4\text{H}^+ \longrightarrow \text{Pu(IV)}^* + \text{Pu(VI)}^* + 2\text{H}_2\text{O} \qquad (2)$$

where the symbols Pu(V)*, Pu(VI)* and Pu(IV)* refer to the oxalate complexes of the respective plutonium ions. Since a number of oxalate complexes are known to be formed by plutonium in different valence states, no attempt has been made to balance Equation (2). It may be assumed that hydrolysis of plutonium would be negligible in the presence of oxalate. The values of the equilibrium constant for reaction (2) at different pH have been given in Table 1. The mean value is of the order of 10^{26}. This value does not take into account the participation of oxalate ions in reaction (2).

The rate of disproportionation in an oxalate medium at pH2 is found to be second order with respect to plutonium(V) concentration as observed by other workers in acid media[10, 11]. The second order rate constant increases with temperature and a value of 10·0 kcal/mole is obtained for the activation energy of the rate determining step in the disproportionation reaction. The value may be compared with 19·6 kcal/mole reported for the activation energy in 1 M perchloric acid[10]. It is difficult to evaluate the order of the reaction with respect to H^+ concentration, since the pH of the solution increases appreciably during the reaction. The only conclusion that could be reached from the results obtained with solutions of different initial pH is that the rate determining step involves the participation of hydrogen ions.

Note added in proof. A paper by Eromolaev *et al.* [13] has come to our notice subsequent to communicating our present paper. Under the conditions employed by these authors disproportionation of plutonium(V) in oxalate solutions is reported to proceed irreversibly, whereas our results show that disproportionation is incomplete under certain conditions. Work on the reproportionation reaction is in progress and the results will be communicated later.

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13. N. P. Eromolaev, N. N. Krot and A. D. Gelman, *Radiokhimiya* **9**, 178 (1967).