[Contribution from the University of California, Los Alamos Scientific Laboratory]

Chloride Complexing and Disproportionation of Pu(IV) in Hydrochloric Acid[1]

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Received May 18, 1955

From measurements of the formal potentials of the Pu^{+3}–Pu^{+4} couple in hydrochloric–perchloric acid solutions at constant total acidity and ionic strength it has been shown that the complex ion $PuCl^{+3}$ is formed. The dissociation quotient of this complex at 25° has been found to be 1.77 ± 0.10 at unit ionic strength and 1.70 ± 0.03 at an ionic strength of two. At 25° in molar hydrochloric acid the thermodynamic quantities for the reaction $PuCl^{+3} \rightleftarrows Pu^{+4} + Cl^-$ are $\Delta F = -0.34$ kcal./mole, $\Delta H = -1.9$ kcal./mole and $\Delta S = -5$ e.u. Equilibrium and rate measurements were made in hydrochloric acid solutions at 6, 25, 35 and 45° in a study of the disproportionation reaction $3Pu^{+4} + 2H_2O \rightleftarrows 2Pu^{+3} + PuO_2^{+2} + 4H^+$. In accord with this reaction, a fourth power hydrogen ion dependence of the equilibrium quotient was observed. The disproportionation reaction rate constant exhibited an inverse third power dependence upon the hydrogen ion concentration. Values of 39 kcal./mole and 53 e.u. were obtained for the heat of activation and for the entropy of activation, respectively, for the disproportionation reaction in molar hydrochloric acid. The change in the heat content at 25° for the reaction $Pu^{+3} + H^+ \rightleftarrows Pu^{+4} + {}^1/_2H_2$ was calculated to be 14.32 kcal./mole in molar hydrochloric acid and 13.63 kcal./mole in molar perchloric acid from measurements of the formal potential of the Pu^{+3}–Pu^{+4} couple as a function of temperature. The Pu^{+3}–PuO_2^{+2} potential in molar hydrochloric acid was calculated from the measured Pu^{+3}–Pu^{+4} formal potential and from the disproportionation equilibrium quotient at each temperature. For the reaction $Pu^{+3} + 2H_2O \rightleftarrows PuO_2^{+2} + H^+ + 3/2H_2$ in molar hydrochloric acid at 25°, $\Delta F = 70.8$ kcal./mole, $\Delta H = 78.4$ kcal./mole and $\Delta S = 25.4$ e.u. The ionic entropies of PuO_2^{+2} and Pu^{+4} have been calculated to be −28.9 and −87 e.u., respectively.

Introduction

From the previously reported[2] values of the Pu^{+3}–Pu^{+4} couple in molar perchloric and in molar hydrochloric acids it is possible to calculate the extent to which Pu^{+4} is complexed by chloride ion if the assumptions are made that Pu^{+3} is not complexed to any significant degree and that the formula of the Pu^{+4} complex is known. Measurements have been made in this work which show that the formula of the complex is $PuCl^{+3}$ up to an ionic strength of two.

Connick and McVey[3] calculated an apparent fifth power hydrogen ion dependence for the disproportionation equilibrium quotient and a −3.5 power hydrogen ion dependence for the disproportionation rate constant in hydrochloric acid solutions of varying ionic strength and chloride ion concentration. In the present study the expected fourth power hydrogen ion dependence of the equilibrium quotient was obtained from measurements at constant chloride ion concentration and at unit ionic strength. The disproportionation rate constant has been found to exhibit an inverse third power hydrogen dependence in hydrochloric acid solutions as has been previously shown to be the case in perchloric acid solutions.[3,4] The disproportionation of Pu(IV) has been studied as a function of temperature to obtain both rate and equilibrium data from which thermodynamic functions have been computed.

Experimental

Reagents.—The plutonium solutions were prepared by dissolving a known weight of oxide-free metal in the requisite weight of standardized Baker and Adamson reagent grade hydrochloric acid, followed by dilution to the desired acidity with water redistilled from alkaline permanganate. When necessary, the ionic strength was maintained at unity with the addition of purified sodium chloride. This salt was precipitated from a saturated solution with concentrated hydrochloric acid, washed with water, dried and ignited in an electric furnace at 600° overnight. The perchloric acid was Mallinckrodt 71% reagent grade. The potassium dichromate used in preparing a plutonium solution of known Pu(IV)/Pu(III) ratio was Mallinckrodt "primary standard" quality.

Apparatus.—The cell assembly, the potentiometric equipment, the folding-scale recording potentiometer and the thermostat have been described previously.[2,4] The temperature of the plutonium solution in the cell was obtained to ±0.001° from measurements of the resistance of a type 20D Western Electric thermistor. Over a period of several hours the temperature variation was ±0.01°. The thermistor was calibrated against a Beckmann thermometer which had been calibrated against a platinum resistance thermometer certified by the National Bureau of Standards. The hydrogen used for the hydrogen electrode was electrolytic grade purified by passing it through a uranium furnace heated to 600°. An atmosphere of helium was maintained over the plutonium solutions throughout the experiments. Both the hydrogen and the helium were saturated with water vapor at the cell temperature to minimize concentration changes because of evaporation.

Analyses.—The concentrations of Pu^{+3}, Pu^{+4} and PuO_2^{+2} were obtained as a function of time in the disproportionation studies from measurements of the potential of a cell of the type: Pt; Pu^{+3}, Pu^{+4}, $HCl(c_1)$, $NaCl(c_2)$; $HCl(c_1)$, $NaCl(c_2)$; H_2, Pt, where $c_1 + c_2 = 1$. As has been described previously,[4] from measurements of the cell potential, the mean oxidation number and the total plutonium concentration it is possible to calculate the concentrations of Pu^{+3}, Pu^{+4} and PuO_2^{+2}. In general, the experiments were devised such that the PuO_2^+ concentration was negligibly small. This was brought about by keeping the Pu^{+4} concentration relatively large in comparison with Pu^{+3} and PuO_2^{+2}.

Results

Chloride Complexing of Pu(IV).—If a plutonium(IV) chloride complex of the formula $PuCl^{+3}$ is formed, the dissociation of the complex may be represented by the reaction

$$PuCl^{+3} \rightleftarrows Pu^{+4} + Cl^-$$

and the equilibrium quotient is given by the expression $K = [Pu^{+4}][Cl^-]/[PuCl^{+3}]$. The uncomplexed species, Pu^{+4}, is related to the total Pu(IV) concentration, $\Sigma Pu(IV)$, by the equation

$$Pu^{+4} = k\Sigma Pu(IV)/(K + [Cl^-])$$

It is necessary to make an assumption concerning the chloride complexing of Pu^{+3}, and for this work it is assumed that Pu^{+3} is uncomplexed by chloride ion. (As has been discussed previously,[3] this assumption may not be strictly valid. Further studies of the chloride complexing of Pu^{+3} and PuO_2^{+2} are in progress.) Also, both Pu^{+3} and Pu^{+4} are con-

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[1] This work was done under the auspices of the A.E.C.

[2] S. W. Rabideau and J. F. Lemons, This Journal, **73**, 2895 (1951).

[3] R. E. Connick and W. H. McVey, *ibid.*, **75**, 474 (1953).

[4] S. W. Rabideau, *ibid.*, **75**, 798 (1953).

sidered to be uncomplexed in molar perchloric acid. The difference in the formal potentials of the Pu^{+3}–Pu^{+4} couple in molar perchloric acid and in the perchloric–hydrochloric acid solutions ($[H^+] = 1$) at 25° is related to the dissociation quotient of the complex by the equation

$$\Delta E^{0\prime} = 0.0591 \log K/(K + [Cl^-])$$

The formal potential of the Pu^{+3}–Pu^{+4} couple was determined over a tenfold change in the $\Sigma Pu(IV)/Pu^{+3}$ ratio for each of the perchloric–hydrochloric acid solutions. The results are given in Table I.

TABLE I

THE DETERMINATION OF THE DISSOCIATION QUOTIENT FOR $PuCl^{+3}$ AT 25°

$[Cl^-]$, moles/l.[a]	$E^{0\prime}$, v.	$\Delta E^{0\prime}$, v. × 10^3	K
0.0000	−0.9819	0.0	..
.1990	.9796	2.3	1.90
.2988	.9784	3.5	2.04
.3987	.9767	5.2	1.78
.4988	.9750	6.9	1.62
.5990	.9739	8.0	1.64
.6994	.9730	8.9	1.69
.7999	.9725	9.4	1.81
.9006	.9712	10.7	1.74
1.002	.9701	11.8	1.72
		Mean	1.77 ± 0.10

[a] $[H^+] = 1.000$ in each case.

From the mean value of the dissociation quotient of the complex ion, $PuCl^{+3}$, it can be calculated that in molar hydrochloric acid approximately 36% of the total Pu(IV) is in the form of the complex ion. The measurements of Ahrland and Larsson[5] indicate that U^{+4} is complexed to about the same degree (*ca.* 33% at $\mu = 1$) by chloride ion, whereas Waggener and Stoughton[6] found that the first chloride complex of thorium is of somewhat greater stability, about 60% existing in the complexed form at unit ionic strength. From the difference in the heat of reaction for the Pu^{+3}–Pu^{+4} couple in molar perchloric and in molar hydrochloric acids, −0.70 kcal./mole (*vide infra*), together with the dissociation quotient of $PuCl^{+3}$, it can be calculated that for the reaction $PuCl^{+3} \rightleftarrows Pu^{+4} + Cl^-$ in molar hydrochloric acid at 25°, $\Delta F = -0.34$ kcal./mole, $\Delta H = -1.9$ kcal./mole and $\Delta S = -5$ e.u. The Pu^{+3}–Pu^{+4} formal potential measurements were also made in perchloric–hydrochloric acid mixtures at a constant acidity of 2 *M* and at an ionic strength of two. The value of the dissociation quotient under these conditions was 1.70 ± 0.03 at 25°. Thus it appears that the single complex, $PuCl^{+3}$, is sufficient to explain the data even in 2 *M* hydrochloric acid.

Disproportionation of Pu(IV) in Hydrochloric Acid Solutions.—Connick[7] has shown that the over-all disproportionation reaction can be considered to consist of a rate-determining step

$$Pu(IV) + Pu(IV) \underset{k_2}{\overset{k_1}{\rightleftarrows}} Pu(III) + Pu(V)$$

and the fast reaction

$$Pu(V) + Pu(IV) \underset{k_4}{\overset{k_3}{\rightleftarrows}} Pu(III) + Pu(VI)$$

In perchloric acid solutions it was necessary to consider in addition to these two steps the diminution of the mean oxidation number as a result of the α-particle reduction. The rate law for the disproportionation reaction both in perchloric and in hydrochloric acid solutions as derived[3] from the above reactions is

$$-\,d(Pu(IV))/dt + d(Pu(V))/dt = 3k_1Pu(IV)^2 - 3k_1[Pu(III)^2Pu(VI)/Pu(IV)K'] + \alpha$$

where K' is the equilibrium quotient, $Pu(III)^2Pu(VI)/Pu(IV)^3$, without acidity or hydrolysis corrections and α is the rate of α-reduction in the solution. Kasha and Sheline[8] reported a decrease in the mean oxidation number of 0.0038 day^{-1} in 0.95 *M* hydrochloric acid at 25°. This rate is approximately 40% of the α-reduction rate observed in perchloric acid. However, in the present work it has been found that in hydrochloric acid solutions of plutonium at 25°, with the ionic strength held at unity with added sodium chloride, the α-reduction rate is essentially *zero*. Additional details on α-reduction studies in perchloric and in hydrochloric acids as well as in solutions of these two acids will be given in a later publication. Thus the "α" term in the rate law may be omitted in the disproportionation experiments in hydrochloric acid solutions. In general, the Pu(V) concentration was less than 1% of the total plutonium concentration, and thus the term $d(Pu(V))/dt$ may also be omitted from the rate law. Values of the specific rate constant for the forward reaction, k_1, can be obtained from the expression

$$k_1 = -d(Pu(IV))/dt/(1 - K^*/K')3Pu(IV)^2$$

where K^* is the apparent equilibrium quotient, $Pu(III)^2Pu(VI)/Pu(IV)^3$, at a given time. In Table II are listed the disproportionation equilibrium quotients together with the fourth power hydrogen ion dependence of this quotient. In the fourth column of Table II the results have been corrected for the effect of the hydrolysis of Pu^{+4}.[2]

TABLE II

DISPROPORTIONATION EQUILIBRIUM QUOTIENTS IN HYDROCHLORIC ACID AT 25°

$[H^+]$, moles/l.	[NaCl], moles/l.	$Pu(III)^2Pu(VI)/Pu(IV)^3$	$Pu(III)^2Pu(VI)K'(H^+)^4/Pu(IV)^3$
1.000	0.000	$1.75 \pm 0.2 \times 10^{-3}$	1.92×10^{-3}
0.500	.500	$2.40 \pm 0.04 \times 10^{-2}$	1.80×10^{-3}
.200	.800	$7.7 \pm 0.1 \times 10^{-1}$	1.90×10^{-3}

The results given in Table II for the quantity $Pu(III)^2Pu(VI)/Pu(IV)^3$ represent the mean values of about five separate equilibrium experiments at each acidity. Equilibrium was approached from both disproportionation and reproportionation directions with good concordance in the equilibrium quotient values. The reproportionation experiments were carried out by heating the plutonium solution at disproportionation equilibrium to 70°

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[5] S. Ahrland and R. Larsson, *Acta Chim. Scand.*, **8**, 137 (1954).

[6] W. C. Waggener and R. W. Stoughton, *J. Phys. Chem.*, **56**, 1 (1952).

[7] R. E. Connick, THIS JOURNAL, **71**, 1528 (1949).

[8] M. Kasha and G. E. Sheline, "The Transuranium Elements," National Nuclear Energy Series, Div. IV, 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 180.

for about ten minutes, then cooling the solutions to 25°. This short heating period shifted the equilibrium to produce concentrations of Pu^{+3} and PuO_2^{+2} which were greater than the equilibrium values at 25°.

Inasmuch as a fourth power hydrogen ion concentration dependence of the disproportionation equilibrium quotient in hydrochloric acid solutions is found, it appears that the stoichiometry of the disproportionation reaction in hydrochloric acid is the same as has been found to be the case in perchloric acid solutions.[3,4]

Temperature Dependence of the Pu^{+3}–Pu^{+4} Couple.—Because the ratio $[Pu^{+4}]/[Pu^{+3}]$ constitutes an essential part of the analytical method used in the disproportionation studies, the formal potential of the Pu^{+3}–Pu^{+4} couple in molar hydrochloric acid was measured as a function of temperature. These results permit the calculations of the thermodynamic functions to be made for the reaction

$$Pu^{+3} + H^+ \rightleftharpoons Pu^{+4} + {}^1/_2H_2$$

In Table III are given the formal potentials *vs.* temperature for one atmosphere of hydrogen, and for equal and small concentrations of Pu^{+3} and Pu^{+4}.

TABLE III

THE TEMPERATURE DEPENDENCE OF THE Pu^{+3}–Pu^{+4} FORMAL POTENTIAL IN 1 *M* HCl

T, °K.	$E^{0\prime}$, volts	$1/T \times 10^3$	$E^{0\prime}/T \times 10^3$
279.47	−0.94815	3.5782	3.3927
298.16	.97019	3.3539	3.2539
308.40	.98208	3.2425	3.1844
318.26	.99356	3.1421	3.1218

From the slope of the plot of $E^{0\prime}/T$ *vs.* $1/T$, a value of ΔH = 14.32 kcal./mole was calculated and at 25° the values of ΔF = 22.37 kcal./mole and ΔS = −27.0 e.u. for the reaction $Pu^{+3} + H^+ \rightleftharpoons Pu^{+4} + {}^1/_2 H_2$ (see Fig. 1). The temperature dependence of the Pu^{+3}–Pu^{+4} couple in 1 *M* perchloric acid has been measured previously,[9] and the results which have been obtained in the present work are in good agreement with the earlier findings. The values found in this work are ΔH = 13.63 kcal./mole, ΔF = 22.6 kcal./mole, and ΔS = −30.2 e.u.

Temperature Dependence of Pu(IV) Disproportionation.—The disproportionation equilibrium quotient was measured in molar hydrochloric acid as a function of temperature from 6 to 45°. From the disproportionation equilibrium quotient and the Pu^{+3}–Pu^{+4} formal potential at a given temperature, the formal potential of the Pu^{+3}–PuO_2^{+2} couple can be calculated (see Table IV).

TABLE IV

VARIATION OF DISPROPORTIONATION EQUILIBRIUM QUOTIENT WITH TEMPERATURE IN MOLAR HYDROCHLORIC ACID

T, °K.	$(Pu^{+3})^2(PuO_2^{+2})[H^+]/(Pu^{+4})^3$	$E^{0\prime}{}_{Pu^{+3}-PuO_2^{+2}}$	$E^{0\prime}/T \times 10^3$	$1/T \times 10^3$
279.59	3.76×10^{-5}	−1.0301	3.6843	3.5767
298.16	1.42×10^{-3}	1.0238	3.4337	3.3539
308.40	1.35×10^{-2}	1.0202	3.3080	3.2425
318.32	9.67×10^{-2}	1.0150	3.1886	3.1415

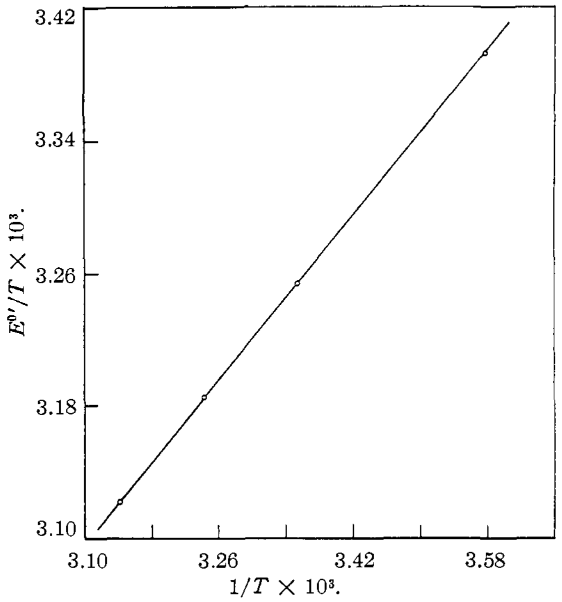

Fig. 1.—Evaluation of heat content change in 1 *M* hydrochloric acid for the reaction: $Pu^{+3} + H^+ \rightleftharpoons Pu^{+4} + {}^1/_2H_2$. ΔH_{298} = 14.32 kcal./mole.

The value of ΔH = 78.4 kcal./mole was obtained from the slope of the line in Fig. 2. This change in heat content is for the reaction

$$Pu^{+3} + 2H_2O \rightleftharpoons PuO_2^{+2} + \overset{+}{H} + {}^3/_2H_2$$

in molar hydrochloric acid at 25°. The other thermodynamic functions at this temperature are ΔF = 70.8 kcal./mole and ΔS = 25.4 e.u.

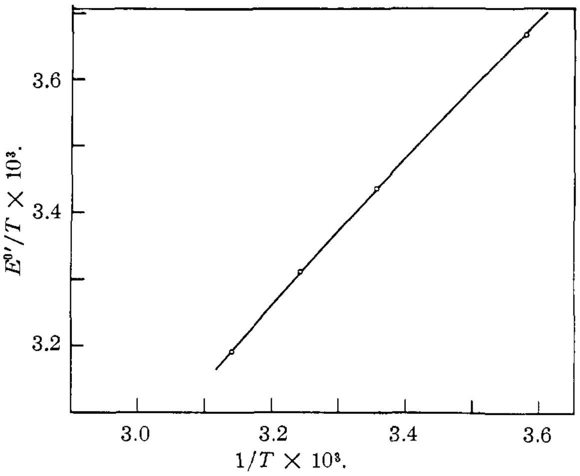

Fig. 2.—Temperature dependence of the formal potential for the reaction $Pu^{+3} + 2H_2O \rightleftharpoons PuO_2^{+2} + H^+ + {}^3/_2H_2$ in 1 *M* hydrochloric acid, ΔH_{298} = 78.4 kcal./mole, data derived from variation of disproportionation equilibrium quotient and Pu^{+3}–Pu^{+4} couple with temperature.

With Latimer's[10] values of the entropies of H^+, H_2 and H_2O it can be calculated from the entropy change for the Pu^{+3}–PuO_2^{+2} couple that the entropy difference, $S_{PuO_2^{+2}} - S_{Pu^{+3}}$ = 12.1 e.u. Also, from measurements of the Pu^{+3}–Pu^{+4} couple in

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[9] R. E. Connick and W. H. McVey, THIS JOURNAL, **73**, 1798 (1951).

[10] W. M. Latimer, "Oxidation Potentials," Second Edition, Prentice-Hall, Inc., New York, N. Y., 1952.

molar perchloric acid as a function of temperature it is found that $S_{Pu^{+4}} - S_{Pu^{+3}} = -45.8$ e.u. (The entropy difference between Pu^{+4} and Pu^{+3} obtained in perchloric acid was used to eliminate from this calculation the effect of the chloro complex of Pu^{+4}. However, any entropy contribution as a result of the chloride complexing of PuO_2^{+2} has been neglected.) A value of −41 e.u. has been estimated[3] for $S_{Pu^{+3}}$ in molar perchloric acid at 25°, and it is assumed that this estimate is valid in molar hydrochloric acid as well. Thus, the entropies of Pu^{+4} and PuO_2^{+2} are calculated to be −87 and −28.9 e.u., respectively. This result for the entropy of the plutonyl ion is considerably more negative than the entropy of the uranyl ion (−17 e.u.) which is somewhat surprising since from charge and size considerations alone, these oxy-cations would be expected to have comparable ionic entropies.

Influence of Acidity and Temperature on Rate of Pu(IV) Disproportionation.—The rate of disproportionation of Pu(IV) has been measured as a function of both acidity and temperature. Within a fivefold change in the hydrogen ion concentration the specific rate constant, k_1, has been found to be inversely dependent upon the third power of the hydrogen ion concentration, as shown in Table V. This parallels the observations made in perchloric acid solutions.[3,4] However, it is of interest to observe that the rate of disproportionation of Pu(IV) is approximately five times greater in hydrochloric acid than in perchloric acid of the same acidity. Connick and McVey[3] noted rather marked discrepancies in the value of k_1 in molar hydrochloric acid depending upon the direction from which the equilibrium was approached. This anomaly was not observed in the present study. The reproportionation results were within the experimental error of the determination of the rate constants. It was not possible to obtain accurate values of k_1 from reproportionation studies in 0.5 and in 0.2 M hydrochloric acid because the PuO_2^+ concentration was not sufficiently small to be neglected during the early stages of the reproportionation reaction which were most suited to the determination of k_1. The method of analysis used in this work presumes that the PuO_2^+ concentration is negligibly small. Sufficiently accurate values of the PuO_2^+–PuO_2^{+2} couple in hydrochloric acid solutions are not available. These potentials together with the other available analytical data would permit the concentrations of all four ionic species to be computed.

TABLE V

DISPROPORTIONATION RATE CONSTANTS IN HYDROCHLORIC ACID SOLUTIONS AT 25°

$[H^+]$, moles/l.	[NaCl], moles/l.	ΣPu, moles/l.	k_1, moles^{-1} l. hr.$^{-1}$	$k_1[H^+]^3$
1.000	0.000	5.623 × 10^{-3}	0.47	0.47
		6.410	.53	.53
		7.385	.54	.54
		7.385	.50[a]	.50
		7.798	.48	.48
		9.201	.58[a]	.58
		10.04	.63	.63
			Mean	0.53
0.500	.500	7.138 × 10^{-3}	4.76	0.595
		7.757	4.88	.610
		8.063	4.72	.590
			Mean	0.60
0.200	.800	5.096 × 10^{-3}	73.1	0.585
		5.573	61.1	.489
		6.954	74.9	.607
		7.192	77.5	.620
			Mean	0.575

[a] Obtained from reproportionation studies.

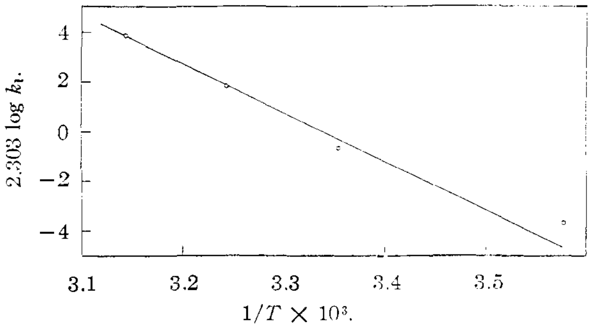

Fig. 3.—Determination of heat of activation for the disproportionation reaction $3Pu^{+4} + 2H_2O \rightleftarrows 2Pu^{+3} + PuO_2^{+2} + 4H^+$ in molar hydrochloric acid, $\Delta H_{298}^{\ddagger} = 39$ kcal./mole.

The rate constant, k_1, was obtained as a function of temperature over the interval 6 to 45°. From a plot of 2.303 log k_1 *vs.* $1/T$, the heat of activation for the disproportionation reaction was found to be 39 kcal./mole. The results are listed in Table VI and plotted in Fig. 3. An entropy of activation of 53 e.u. was calculated from this study of the effect of temperature upon the rate of disproportionation.

TABLE VI

TEMPERATURE VARIATION OF DISPROPORTIONATION RATE CONSTANT IN MOLAR HYDROCHLORIC ACID

T, °K.	k_1	2.303 log k_1	$1/T \times 10^3$
279.56	2.40 ± 0.15 × 10^{-2}	−3.730	3.577
279.57	2.79 ± 0.10 × 10^{-2}	−3.580	3.577
298.16	0.53 ± 0.04	−0.635	3.354
308.39	6.10 ± 0.10	1.809	3.243
308.44	6.19 ± 0.07	1.823	3.242
318.14	48.4 ± 3.3	3.880	3.143
318.32	45.8 ± 3.8	3.825	3.141

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