The Kinetics of the Oxidation-Reduction Reactions of Uranium, Neptunium, Plutonium, and Americium in Aqueous Solutions

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FOREWORD

From the inception of the Manhattan Project, one of the prerequisites for progress in the development and application of all forms of nuclear energy has been an understanding of the chemistry of the actinide elements. Questions of actinide chemistry enter into every aspect of nuclear energy activities, from prospecting for uranium ores to ultimate disposal of reactor waste products. The expansion of the nuclear energy industry to help meet critical power requirements has reinforced the basic need for detailed knowledge of the properties of the heavy elements. Much of the chemical behavior of uranium, neptunium, plutonium, and americium is governed by the kinetics of their oxidation–reduction reactions.

The Division of Military Application is pleased to have this review published in the Energy Research and Development Administration Critical Review Series.

Ernest Graves
Major General, U. S. Army
Director, Division of Military Application

PREFACE

Since in the near future there will quite probably be an increase in the number of nuclear reactors—particularly breeder reactors, which produce large quantities of plutonium—many more chemists must become concerned with uranium, plutonium, and the other actinide elements. The chemistry of these elements is complicated but is very important in the areas of fuel reprocessing, waste recovery or disposal, and chemical analysis. Since an important part of this chemistry involves ions of the elements in aqueous solution, this review is concerned with the many oxidation states that occur and with the rates of the reactions in which the oxidation states change.

Early work in this field, done during the second World War, helped solve some of the problems of the Manhattan Project. Much of this early work was, of necessity, rather fragmentary, but, since then, an ever increasing amount of careful research has been done on the oxidation–reduction reactions of the actinide elements. Now, after approximately 30 years, it is worthwhile to assemble and discuss the quantitative data available.

This review is addressed not only to the specialist but also to any chemist who would like to know more about the rates of the aqueous oxidation–reduction reactions of the lighter actinide ions. Some typical reactions are discussed in detail to show how we can arrive at, and then interpret, the rate laws and to show glimpses into the underlying mechanisms provided by the rate laws. Although the reader is assumed to have some knowledge of chemical kinetics, a brief discussion of the topics that are particularly important for oxidation–reduction kinetics is included.

In addition to these discussions, all the data available to me in the fall of 1973 are summarized in tables for convenient reference. This summary should be useful to

those who need to know what has been done on a particular reaction. The omissions indicate some of the areas in which future research is needed.

Since data are now available for many reactions of many types, we might expect to be able to find reactivity patterns that would help in predicting the rates of reactions not yet measured. Some of the generalizations that can be made are discussed, but the reader will note that the patterns are not clear and that detailed predictions must be made with caution. It is tempting to blame this difficulty, at least in part, on the fact that, because water is not a structureless solvent, individual water molecules influence the details of the transition state, or activated complex. Much clearer insight will be required, however, before this idea can be put on a quantitative basis for testing.

Over the past several years I have had helpful discussions with many colleagues. I particularly acknowledge those with Henry Taube and James C. Sullivan. Any errors in reporting, of omission, or in interpretation are my own responsibility, however; and I welcome correspondence on these points. Also, I gratefully acknowledge the careful editorial work done by Dee Jared, U. S. Energy Research and Development Administration, Office of Public Affairs, Technical Information Center, in preparing the original manuscript for publication.

This book is dedicated to William C. Bray, whose teaching and research did so much to lay the foundations for the study of oxidation-reduction kinetics.

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ABSTRACT

This is a review with about 250 references. Data for 240 reactions are cataloged and quantitative activation parameters are tabulated for 79 of these. Some empirical correlations are given. Twelve typical reactions are discussed in detail, along with the effects of self-irradiation and ionic strength.

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1 INTRODUCTION

In the next few years the use of nuclear reactors will increase, and many more chemists will be concerned with problems of analysis, fuel reprocessing, waste disposal, etc. It is the purpose of this review to provide these chemists with a complete survey of one of the important areas in this work. The aqueous ions of the actinide elements uranium, neptunium, plutonium, and americium show as many as five oxidation states with widely varying oxidation potentials; thus oxidation–reduction reactions form a very important part of the chemistry of these elements. A knowledge of the rates of these reactions is required for designing many chemical separation processes and for developing analytical procedures.

Understanding the kinetics of these reactions is aided by the fact that the ions of the elements in the same oxidation states differ only in the numbers of relatively well shielded *f* electrons. The ionic radii show the small actinide contraction, which for the +3 and +4 ions decreases by about 3% from uranium to plutonium. Thus the corresponding ions of the four elements are similar enough to make their reactions of particular interest to chemical kineticists who are trying to understand the various factors that influence the rates of oxidation–reduction reactions.

The history of the discovery and separation of neptunium, plutonium, and americium is discussed, for example, in the book by Katz and Seaborg.¹ The earlier work on oxidation–reduction reactions is also summarized there. At present a much larger body of kinetics data, almost all of which is summarized in the tables in Chap. 10, is available. Some of these data are only qualitative or semiquantitative, but fairly complete studies, including temperature coefficients, have been made on at least

79 reactions. These results are summarized in Table 8.1 in terms of ΔG^* , ΔH^* , and ΔS^* for the net activation processes involved.

No attempt will be made to consider all these reactions in detail; instead some typical examples, arranged roughly in order of increasing complexity, are discussed. Some interesting empirical correlations among the data have been found; these are discussed in Chap. 9.

Before discussing the kinetics of the reactions, we should consider the properties of the aqueous ions and review some of the general aspects of kinetics and mechanisms which are applicable to aqueous oxidation–reduction reactions; this is done in Chap. 2.

The new International System of Units, which is coming into general use in the scientific literature, has been adopted for this review. Thus energy values are given either in joules (J) or kilojoules (kJ), whichever is appropriate. Since the original literature cited used calories or kilocalories, however, values in these units are given in parentheses. Concentrations are given in kilomoles per cubic meter, defined at room temperature, and the usual symbol, M , is used. Temperatures are given in degrees Celsius. Seconds are the preferred unit of time, but for some of the less precise work the original units are retained.

2 PRELIMINARY CONSIDERATIONS

2-1

PROPERTIES OF THE AQUEOUS IONS

It is generally agreed (see Ref. 1) that the corresponding oxidation states of the four elements under consideration differ only in the numbers of f electrons and that the formulas are An^{3+} , An^{4+} , AnO_2^+ , and AnO_2^{2+} for the +3, +4, +5, and +6 oxidation states. The formulas for the recently discovered +7 oxidation states, particularly in acid solutions, are not known. For the first four oxidation states, the oxidation potentials and their temperature coefficients have been determined or have been estimated. The resulting values of E^0 , ΔG , ΔH , and ΔS for 1 *M* $HClO_4$ are summarized in Table 2.1. The oxidation of the An^{3+} hydrated cation to the An^{4+} hydrated cation is seen to involve widely differing values for the thermodynamic quantities, except those for ΔS , which are quite similar. This similarity is evidence that the structural changes are very similar for the reactions.

The oxidation of the +5 to the +6 state shows similarly varying potentials, but again the ΔS values are nearly the same. The oxidation of the +4 to the +5 state is more complicated since oxycations are formed from more simply hydrated cations. The ΔS values for uranium and plutonium are quite similar, but the value for neptunium is about 42 J/mol $\cdot$ K more positive. This might imply structural differences. We should note, however, that, because of the slowness of the reactions

Table 2.1
THERMODYNAMIC QUANTITIES FOR THE OXIDATION REACTIONS^a

Element	E ^o , V	ΔG, kJ/mol (kcal/mol)	ΔH, kJ/mol (kcal/mol)	ΔS, J/mol · K (cal/mol · deg)
$An^{3+} + H^+ = An^{4+} + \frac{1}{2}H_2$				
U	0.631 ^b	-60.9 (-14.55)	-99.2 (-23.7 ^c)	-128 (-30.5 ^d)
Np	-0.155 ^e	15.0 (3.58 ^e)	-23.8 (-5.7 ± 0.2 ^e)	-131 (-31.2 ± 0.8 ^e)
Pu	-0.9819 ^f	94.7 (22.64)	57.0 (13.63 ^g)	-126 (-30.2 ^g)
Am	-2.34 ± 0.1 ^{h,i}	-226 (54 ± 2.3 ^j)	187 (44.8 ± 2.3 ^j)	-128 (-30.7 ± 0.5 ^k)
$An^{4+} + 2H_2O = AnO_2^+ + 3H^+ + \frac{1}{2}H_2$				
U	-0.605 ^l	58.4 (13.95 ^m)	125.5 (30.0 ^m)	226 (54 ± 1 ^m)
Np	-0.739	71.3 (17.04 ^e)	149 (35.6 ± 0.3 ^e)	261 (62.3 ± 0.1 ^e)
Pu	-1.1702 ^f	112.9 (26.98)	178 (42.5 ± 0.6 ⁿ)	218 (52 ± 2 ⁿ)
Am	-1.31 ± 0.2 ^j	130 (31 ± 4 ^j)	198 (47.3 ± 2.5 ^o)	230 (55 ± 3 ^k)
$AnO_2^+ + H^+ = AnO_2^{2+} + \frac{1}{2}H_2$				
U	-0.063 ^b	6.1 (1.45)	12.1 (2.9)	20 (4.8 ± 1 ^p)
Np	-1.1373 ^e	109.7 (26.23 ^e)	118 (28.1 ± 0.2 ^e)	27 (6.4 ± 0.6 ^e)
Pu	-0.9164 ^f	88.4 (21.13 ^f)	92 (22.09 ^q)	13 (3.2 ± 2 ^q)
Am	-1.53 ± 0.05 ^{j,o,r}	148 (35.4 ± 1.2 ^j)	154 (36.9 ± 1 ^s)	21 (5 ± 1 ^k)

^aValues are for 25°C and 1M HClO₄.

^bRef. 2.

^cB. J. Fontana, quoted in Ref. 3.

^dRef. 3.

^eRef. 4.

^fRef. 5.

^gRef. 6.

^hRef. 7, based on measurements in 10 M H₃PO₄ extrapolated to 1 M HClO₄.

ⁱA previous estimate, -2.44 ± 0.2 V (Ref. 8), was based on the assumption that Am³⁺ quantitatively oxidizes water (see Ref. 9).

^jCalculated from the other quantities for the reaction using $\Delta G = \Delta H - T\Delta S = -nFE^o$.

^kBased on the corresponding reactions for uranium, neptunium, and plutonium.

^lThis would be -0.573 V if based on the U(V) disproportionation data (see Ref. 10).

^mValues for U⁴⁺ + 2H₂O = UO₂²⁺ + 2H⁺ + H₂ (Ref. 3) combined with those for UO₂⁺ + H⁺ = UO₂²⁺ + $\frac{1}{2}$ H₂.

ⁿFrom ΔS for Pu³⁺ + 2H₂O = PuO₂²⁺ + H⁺ + $\frac{3}{2}$ H₂ (Ref. 6) with the values for Pu³⁺ + H⁺ = Pu⁴⁺ + $\frac{1}{2}$ H₂ and PuO₂⁺ + H⁺ = PuO₂²⁺ + $\frac{1}{2}$ H₂.

^oFrom 92.1 ± 1.0 kcal/mol for Am³⁺ + 2H₂O = AmO₂²⁺ + 2H⁺ + H₂ (Ref. 11) and the value above for Am³⁺ + H⁺ = Am⁴⁺ + $\frac{1}{2}$ H₂.

^pFrom ΔS for Np³⁺ + UO₂²⁺ = Np⁴⁺ + UO₂⁺ (Ref. 12) combined with that for Np³⁺ + H⁺ = Np⁴⁺ + $\frac{1}{2}$ H₂.

^qRecomputed from the temperature dependence given in Ref. 5.

^rIn good agreement with -1.60 V, given in Ref. 13.

^sFrom the 92.1 in note o and 129.0 ± 0.3 kcal/mol for Am³⁺ + 2H₂O = AmO₂²⁺ + H⁺ + $\frac{3}{2}$ H₂ (Ref. 11).

involved, ΔS is difficult to determine, and most of the difference may be due to experimental error.

Np(VII) and Pu(VII) are very powerful oxidizing agents. No quantitative thermodynamic data are available on the ions in this oxidation state in acid solutions. Contrary to an early report, there is as yet no evidence for Am(VII) in aqueous solutions.¹⁴

The standard entropies of individual aqueous ions are determined from the heats of solution, entropies, and solubilities of appropriate crystalline solids and from the activities of the salts in the resulting solutions. Such measurements have been made for only three of the actinide ions. The results, in calories per mole per degree, are $S_{\text{UO}_2^{2+}}^0 = -17 \pm 5$ (Ref. 15), $S_{\text{NpO}_2^{2+}}^0 = -20 \pm 2$ (Ref. 16) and $S_{\text{Pu}^{3+}}^0 = -44.6(\pm 2)$ (Ref. 17). From these values, the entropies of the other actinide ions were estimated by using the heat and free-energy values for the $\text{NpO}_2^+ - \text{NpO}_2^{2+}$ couple and making corrections for the effects of mass and magnetic degeneracy.^{16,17} These estimates are listed in Table 2.2.

Table 2.2
STANDARD ENTROPIES OF THE ACTINIDE IONS^a

Element	An^{3+}	An^{4+}	AnO_2^+	AnO_2^{2+}
U	-176 (-42.1 ^b)	-392 (-93.7 ^c)	-29 (-7 ^d)	-94 (-22.5 ^d $\pm$ 1.1 ^e)
Np	-181 (-43.3 ^b)	-400 (-95.6 ^c)	-26 (-6.2 ^d)	-84 (-20 $\pm$ 2 ^{d,f})
Pu	-187 (-44.6 ^{b,f})	-401 (-95.9 ^c)	-24 (-5.8 ^d)	-80 (-19.2 ^d)
Am	-204 (-48.7 ^b)		-24 (-5.7 ^d)	-79 (-18.8 ^d)

^aValues are for 25°C and are given in J/mol · deg and cal/mol · deg (values in parentheses), based on $S_{\text{H}^+}^0 = 0.0$.

^bFrom Ref. 17.

^cValues are estimated from those in Table 2.1 and are corrected for effect of ionic strength.

^dFrom Ref. 16.

^eBased on the uncertainty in the method of estimating the magnetic contribution.

^fExperimental values.

The standard entropies apply to solutions of zero ionic strength; but it is valuable to convert them to unit ionic strength for use with other data, such as those in Table 2.1. The change in ionic entropy on going from zero to unit ionic strength depends on the ionic charge, and we estimate[†] that the entropies will be more positive at $\mu = 1M$ by about 0, 8, 23, and 46 J/mol · K for AnO_2^+ , AnO_2^{2+} , An^{3+} , and An^{4+} , respectively, based on $S_{\text{H}^+}^0 = 0.0$ for $\mu = 1.0M$.

[†]These estimates are based on the derivative with respect to temperature of an extended form of the Debye-Hückel equation: $\log K = \log K^0 + \{ (A \Delta z^2 \mu^{1/2}) / (1 + B \bar{a} \mu^{1/2}) \} + C\mu$. The results depend somewhat on the values chosen for $\bar{a}$ and C , but essentially the same values were obtained using $\bar{a} = 0.75$ nm and $C = 0$ as with $\bar{a} = 0.9$ nm and $C = 0.1$.

These corrections and the ΔS values in Table 2.1 were used to give the estimated values for the An^{4+} ions in Table 2.2. Values for the AnO_2^{2+} ions, found the same way, are $S_{\text{UO}_2^{2+}}^0 = -99 \text{ J/mol} \cdot \text{K}$, $S_{\text{NpO}_2^{2+}}^0 = -66 \text{ J/mol} \cdot \text{K}$, and $S_{\text{PuO}_2^{2+}}^0 = -123 \text{ J/mol} \cdot \text{K}$. Except for UO_2^{2+} , these values are not in good agreement with those in Table 2.2 and show that further work needs to be done on the thermodynamics of these actinide ions.

The actinide ions have characteristic, relatively sharp absorption bands that are often used to follow their reactions. The approximate locations and absorptivities of some of these bands are listed in Table 2.3. Detailed spectra may be found in the original references.

Table 2.3
ABSORPTIVITIES (ϵ) AND WAVELENGTHS (λ) OF IMPORTANT ABSORPTION BANDS
OF SOME ACTINIDE IONS IN AQUEOUS ACID SOLUTIONS

An(III)		An(IV)		An(V)		An(VI)		An(VII)	
ϵ , m ² /mol ^a	λ , nm	ϵ , m ² /mol ^a	λ , nm	ϵ , m ² /mol ^a	λ , nm	ϵ , m ² /mol ^a	λ , nm	ϵ , m ² /mol ^a	λ , nm
Uranium									
158.0	350 ^b	5.9	648 ^c	d		0.76	414 ^e		
17.1	526 ^f								
22.2	890 ^f								
22.6	910 ^f								
Neptunium									
229.5	233 ^e	12.7	723 ^g	2.3	617 ^g	4.5	1223 ^g	46.7	360 ^h
159.3	267 ^e	16.2	960 ^g	39.5	980 ^g			43.1	420 ^h
4.0	580 ^g								
4.4	786 ^g								
Plutonium									
150.0	244 ⁱ	5.65	470 ⁱ	41.0	274 ⁱ	1.35	504 ⁱ		
3.8	562 ⁱ			1.9	570 ⁱ	55.0	830 ⁱ		
3.7	600 ⁱ			2.2	1131 ⁱ				
Americium									
30.0	228 ^j			4.4	514 ^j	3.0	663 ^j		
40.0	503 ^j			5.9	718 ^j	8.3	996 ^j		
6.5	812 ^j								

^aThis unit (m^2/mol) is the same as $M^{-1} \text{ mm}^{-1}$.

^bRef. 18.

^cRef. 19.

^dIn the presence of U(VI) a band forms at 737 nm (Ref. 20).

^eRef. 21.

^fRef. 22.

^gRef. 23.

^hRef. 24.

ⁱRef. 25.

^jRef. 26.

The complexing of the actinide ions by other substances, usually anions, is important for our purposes because the reaction rates of the resulting complexes are usually different from those of the original ions. This also applies to the various hydrolyzed species that form as the pH of the solutions is increased. Discussions of complex formation and hydrolytic equilibria are beyond the scope of this review; the reader is referred to other sources, e.g., books by Katz and Seaborg,¹ Cleveland,^{2,7} and Keller.^{2,8}

In general, however, the tendency to hydrolyze or to form complexes with anions follows the charge density and has the order

In addition, the AnO_2^+ ions have a charge distribution such that they can form moderately stable complexes with cations such as Fe^{3+} (Ref. 29), Cr^{3+} (Refs. 30–32), Rh^{3+} (Ref. 33), and UO_2^{2+} (Refs. 20 and 34).

2-2

MECHANISM OF AQUEOUS OXIDATION-REDUCTION REACTIONS

The most important aspects of any reaction are its stoichiometry and equilibrium, followed by its rate and mechanism. Ideally, stoichiometry and equilibrium, as well as the complex ion and hydrolysis equilibria, are known from thermodynamic data before the reaction rates are measured. But even after the rates are known, the details of the mechanism may still be uncertain. By "mechanism" we mean the sequence of individual steps or elementary reactions occurring as the system goes from reactants to products. For aqueous oxidation-reduction reactions, the various steps may include:

1. Formation of reactive species, such as complex ions, hydrolyzed ions, or radicals.
2. Encounter of two (usually) reactive species; this can also be described as the formation of an outer-sphere complex.
3. Removal of a ligand from one of the reactant species to form an inner-sphere complex in which the reactants share a common ligand.
4. Distortion of the complex so that the electron(s) can transfer under Franck-Condon restrictions. These restrictions will not be required if the oxidation-reduction is accomplished by the transfer of a neutral atom or group.
5. Dissociation of the product complex.
6. Separation of the immediate products of reaction.
7. Further reaction of the individual immediate products to give the final products.

We should recognize that not all of these steps are required in every reaction. In fact, determination of the mechanism involves identifying the reactive species and

determining which steps are involved, whether some steps occur in parallel with others, and which steps are slowest. The mechanism will be called outer sphere if it can be shown or inferred that steps 3 and 5 are not involved. Some of the consequences of this mechanism are discussed in Sec. 2-5. If step 2 is the slowest step, the reaction will be diffusion controlled. Limiting rates for these reactions are given in Sec. 2-6.

2-3

RATE LAWS

We can learn much about the mechanism of a reaction by detecting reaction intermediates, by carefully comparing the data from similar reactions, and by studying the rate law. Although the rate law provides essentially no information about the rapid steps, it is important because it helps to specify the composition of the system at the highest barriers, which are associated with the slowest steps. The rate law is the quantitative function that gives the dependence of the reaction rate on concentrations of the various species in solution. In its most useful form the rate law is made up of individual terms each having the form $k[A]^n[B]^m[C]^p \dots$, where k is a rate constant and $[A]$, $[B]$, etc., are the concentrations of the indicated species.

The various steps or elementary reactions in a mechanism involve the crossing of energy barriers. The configuration of the reactants at the top of one of these barriers is called the activated complex or transition state. According to Eyring's absolute reaction-rate theory,³⁵ the activated complex can be treated as a special sort of molecule in quasi equilibrium with the reactants for that step. Formation of the activated complex from the reactants is called an activation process. The change in free energy for the process, ΔG^* , is called the free energy of activation. The rate of reaction is assumed to be proportional to the concentration of the activated complex, and the rate constant is given by

$$k_i = \kappa \frac{k_B T}{h} e^{-\Delta G_i^*/RT} = \kappa \frac{k_B T}{h} e^{\Delta S_i^*/R} e^{-\Delta H_i^*/RT} \quad (2.1)$$

where κ = transmission coefficient

k_B = Boltzmann constant

h = Planck's constant

T = absolute temperature

R = gas constant

ΔH^* = heat of activation

ΔS^* = entropy of activation

Thus the rate constant is defined in terms of ΔG^* for a particular activation process, and the rate law associated with it involves the concentrations and standard states implied by the activation process. Conversely, the numerical values of ΔG^* , ΔH^* , and

ΔS^* may depend on the concentration units employed, the composition of the solution, etc.

For many reactions the barrier for one of the steps is much higher than that for the others; the highest step will be rate determining and the others will be essentially at equilibrium. The rapid equilibria that precede the actual rate-determining step can be added to the activation process for the slow step to give a net activation process, written in terms of the principal species in solution,

The rate will be proportional to

$$\frac{[A]^m [B]^n [C]^p \dots}{[L]^q [M]^r \dots} \quad (2.3)$$

where A, B, C, ... are initial reactants and L, M, ... are products of the rapid pre-equilibria. Since the net activation process must formally balance, the composition of the activated complex can be determined from the form of the rate law even though the actual reactant species are unknown. Conversely, the form of the rate law does not identify the actual reactant species.

If two or more barriers are of nearly equal heights, the rate law will be more complicated in that it will have terms similar to those in Eq. 2.3 for each of the barriers. If the barriers are crossed in parallel, the rate law will consist of a sum of terms like those in Eq. 2.3. If the highest barriers are crossed sequentially, the rate law will involve the concentrations of the intermediates involved. If the concentrations of the intermediate(s) are small enough so that the net rates at which their concentrations change are small compared with the overall rate (the steady-state approximation), the rate law can be expressed in terms of the concentrations of the initial reactants.

Although the rate law for a reaction does not give the detailed mechanism, it does give the composition of the activated complexes at the highest barriers, as shown, and the pattern of paths for the reaction. By "pattern of paths," as contrasted with mechanism, we mean the various ways in which reactants can get to products without considering intermediates that are in rapid equilibrium with the initial reactants or final products. If only a single activated complex is kinetically important, only one pattern is possible: Reactants $\rightarrow$ products. If more than one activated complex is involved, the possible patterns of paths are analogous to the possible ways in which electrical resistors can be connected. In this analog the resistors correspond to kinetic barriers (activated complexes), the junctions correspond to intermediates, and the terminals correspond to reactants or products.

For two activated complexes there are two distinguishable patterns; for three activated complexes four patterns are generally distinguishable; for four activated complexes ten patterns are distinguishable; and so on. Figure 2.1 shows the first three of these sets of patterns, classified according to the number of activated complexes

Pattern	Number of kinetically distinguishable activated complexes	Number of intermediates	Electrical analog	Rate law
1-0	1	0		R_1
2-0	2	0		$R_1 + R_2$
2-1	2	1		$\frac{1}{\frac{1}{R_1} + \frac{1}{R_2}}$
3-0	3	0		$R_1 + R_2 + R_3$
3-1-a	3	1		$\frac{1}{\frac{1}{R_1} + \frac{1}{R_2 + R_3}}$
3-1-b	3	1		$R_1 + \frac{1}{\frac{1}{R_2} + \frac{1}{R_3}}$
3-2	3	2		$\frac{1}{\frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}}$

Fig. 2.1 Various patterns of paths. All the R_i are of the form $k_i[A]^{m_i}[B]^{n_i}[C]^{p_i} \dots$, where A, B, C, etc., are the initial reactants. (From *Lanthanide/Actinide Chemistry*, *Advances in Chemistry Series*, Vol. 71, p. 280, The American Chemical Society, 1967.)

and the number of intermediates involved. Note that none of the patterns are kinetically distinguishable from their mirror images.^{3,6}

We can see from the figure that, in general, the various R terms must be different functions of $[A]$, $[B]$, $[C]$, etc. For patterns 3-1-a and 3-1-b, R_1 may have the same form as either R_2 or R_3 ; if this occurs, however, the two patterns cannot be distinguished. An example of this is the Fe(II)–Pu(VI) reaction, which is discussed in Sec. 3-9.

An important feature of these electrical analogs is that, when the steady-state approximation is valid, the reciprocals of the indicated resistances are the analogs of $k[A]^m[B]^n[C]^p \dots$, where A, B, C, ... are the initial reactants and k is the effective rate constant for the formation of the activated complex directly from the initial reactants, even if intermediates are involved. This means that the overall rate law can be found by combining individual rate terms according to the rules for combining the analogous reciprocal resistances.

2-4

MEDIUM EFFECTS

To determine the rate law for a reaction, we must vary the concentrations of the species in solution over as wide a range as possible. Even though the ionic strength is held constant, it is important to consider the possibility that an observed effect on the rate is caused by changes in the activity coefficients of the reactants or activated complex rather than by a distinct step in the mechanism. Usually the species being oxidized and reduced are dilute enough so that changes in their concentrations will not influence the medium significantly. When the effect of a hydrogen ion or a complexing anion, such as chloride or sulfate, is studied, however, large changes in concentration are used. Typically the principal cation will be changed from H^+ to Li^+ or Na^+ , or the principal anion will be changed from ClO_4^- to Cl^- . Effects on the medium due to changes of this sort are often assumed to be negligible, but it is more reasonable to assume that the pertinent activity coefficient ratios are given by an equation like Harned's Rule.³⁷ Taking the hydrogen ion as an example, we would get

$$k = k_0 e^{\beta[H^+]} \quad (2.4)$$

If the coefficient β is small, the exponential can be expanded, and the expression can be rewritten as

$$k = k_0(1 + \beta[H^+] + \dots) \approx k_0 + k_0\beta[H^+] \quad (2.5)$$

If β is positive, this expression is indistinguishable from the two-term rate law for parallel paths. If β is negative, let $\beta' = -\beta$ and

$$k \approx \frac{k_0}{1 + \beta'[H^+]} = \left\{ \frac{1}{k_0} + \frac{1}{(k_0/\beta')[H^+]} \right\}^{-1} \quad (2.6)$$

which is indistinguishable from the rate law for consecutive reactions, pattern 2-1 in Fig. 2.1.

Thus the distinction between an actual step in a mechanism and a medium effect must be based on an estimate of the magnitude of the parameter β . If the reactant ions are of the same sign as the ion whose concentration is being changed, β is expected to be small.³⁸ This is supported by the data available. Values of β for equilibria among cations are known from measurements of the effect of substituting Li^+ or Na^+ for H^+ on the formal potentials of some oxidation-reduction couples. Results for Na^+ are 0, -0.012, and $0.096 M^{-1}$ for the $Fe(II)-Fe(III)$, $Hg(0)-Hg(I)$, and $Hg(I)-Hg(II)$ couples, respectively. For the $Np(V)-Np(VI)$ couple, β is $-0.059 M^{-1}$ for Li^+ and $-0.186 M^{-1}$ for Na^+ (Ref. 39). Similarly, β is less than $0.136 M^{-1}$ for the $Pu(III)-Pu(IV)$ couple in $HClO_4-NaClO_4$ mixtures.⁴⁰

Direct determinations of β for kinetic processes are not possible, but we should note that many reactions among cations have one-term rate laws with integral hydrogen-ion dependences. This implies that β is small or that there are fortuitous cancellations of medium effects by effects of actual paths.

The results discussed here indicate that β for $\text{Li}^+ - \text{H}^+$ substitutions is probably smaller than 0.1 or $0.15 M^{-1}$ but may be larger for $\text{Na}^+ - \text{H}^+$ substitutions.

2-5

OUTER-SPHERE REACTIONS

If steps 3 and 5 in the general mechanism given in Sec. 2-2 are not involved, the coordination shells of the two reactants may be distorted, but they will remain intact throughout the course of the reaction. A theory of such outer-sphere oxidation-reduction reactions has been developed by Marcus.^{4,1} The most readily applicable result of this theory is the expression

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \quad (2.7)$$

where $\log f = (\log K_{12})^2 / [4 \log (k_{11}k_{22}/Z^2)]$

k_{12} = rate constant for the net reaction

K_{12} = equilibrium constant

k_{11} and k_{22} = rate constants for the component self-exchange reactions

Z = collision frequency for the hypothetically uncharged reactant ions

In terms of free energies this equation becomes

$$\Delta G_{12}^* = 0.5(\Delta G_{11}^* + \Delta G_{22}^* + \Delta G_{12} + \Delta G^f) \quad (2.8)$$

where $\Delta G^f = (\Delta G_{12})^2 / [4(\Delta G_{11}^* + \Delta G_{22}^* - w_{11} - w_{22} - 20)]$ kJ/mol and w_{11} and w_{22} are the electrostatic work terms as usually defined^{4,1} and where we assume that $w_{11} + w_{22} = 2w_{12} = 2w_{21}$. The form of these expressions depends primarily on the assumptions that approximately harmonic distortions of coordination and solvent spheres about the ions occur before electron transfer under Franck-Condon restrictions, that the force constants for the distortions are essentially independent of reaction partner, and that the electrostatic work terms are small or cancel.

2-6

DIFFUSION-CONTROLLED REACTIONS

Diffusion in solutions is quite rapid, and most reactions are not limited by the rates at which the reactant species can diffuse together. However, collision frequencies

are greatly reduced for ions of like charge, and it is important to consider the possibility that some of the faster reactions between actinide ions and other highly charged cations might be diffusion controlled.

Debye⁴² used a plausible model to derive a relatively simple expression for collision frequencies of ions in solution. For dilute aqueous solutions at 25°C and zero ionic strength, the second-order rate constant is given (in units of $M^{-1} \text{ sec}^{-1}$) by $k = 7.4 \times 10^9 [x/(e^x - 1)]$, where $x = 0.7(z_1 z_2)/r$ (z_1 and z_2 are the charges on the ions[†] and r is the average radius in nanometers).

To illustrate the magnitude of the charge effect on diffusion-controlled reactions, we assumed that r is 0.4 nm and calculated k for a range of ($z_1 z_2$) values. The results are summarized in Table 2.4

Table 2.4
EFFECTS OF IONIC CHARGE ON DIFFUSION-
CONTROLLED RATES^{a,b}

$z_1 z_2$	$k, M^{-1} \text{ sec}^{-1}$	$z_1 z_2$	$k, M^{-1} \text{ sec}^{-1}$
0	7.4×10^9	6	2.1×10^6
1	2.7×10^9	9	1.7×10^4
2	8.1×10^8	12	1.2×10^2
4	4.8×10^7		

^aValues are for 25°C and $\mu = 0$.

^bA hydrodynamic effect has been shown^{4,3} to reduce these values by about 15%; this has been neglected, however, because of the other approximations involved.

These results are only approximate, but they do indicate that diffusion-controlled reactions between a +3 and a +4 ion, or even between a pair of +3 ions, are slow enough to be measured by rapid-mixing techniques. One of the fastest actinide oxidation–reduction reactions that had been measured by 1971 is the reduction of $\text{Co}(\text{NH}_3)_5 \text{N}_3^{2+}$ by U^{3+} (Ref. 18). A second-order rate constant of about $10^6 M^{-1} \text{ sec}^{-1}$ was reported for 25°C and $\mu = 0.2 M$. A reasonable extrapolation to $\mu = 0$ reduces the rate constant to about $7 \times 10^4 M^{-1} \text{ sec}^{-1}$, only about $1/30$ the diffusion-controlled limit.

[†] These charges are in multiples of the charge on the electron.

3 KINETICS OF SOME TYPICAL REACTIONS

In this chapter the kinetics of 12 typical oxidation–reduction reactions of uranium, neptunium, and plutonium ions are discussed. Since their reactions are complicated by radiolytic effects, americium ions are discussed separately in Chap. 6. The reactions discussed here were chosen to illustrate the various ways rates can be determined, the different rate laws observed, and the possible ways these rate laws are interpreted.

3-1

THE Pu(IV)–V(III) REACTION⁴⁴

The kinetics of the Pu(IV)–V(III) reaction are discussed in detail because it is typical of oxidation–reduction reactions between highly charged cations. The reactants undergo hydrolysis, and two activated complexes are involved in parallel paths.

The overall reaction in terms of the principal species in acid solution is

The potentials in Table 2.1 and those given by Latimer⁴⁵ lead to $\Delta G = -59.8$ kJ/mol and to an equilibrium quotient of about $3 \times 10^{10} M^2$. Thus the reaction will go essentially to completion in 1M acid at 25°C. Since the reaction in which V(IV) is

further oxidized to V(V) by Pu(IV) has an equilibrium quotient of only about 0.5, it is unimportant. The stoichiometry indicated by Eq. 3.1 was confirmed by direct experiment. Reaction rates were followed spectrophotometrically at 469.6 nm where Pu(IV) is the principal absorbing species. The reactant concentrations were varied between $1.24 \times 10^{-3}M$ and $2.52 \times 10^{-3}M$ for Pu(IV) and between $1.17 \times 10^{-3}M$ and $3.29 \times 10^{-3}M$ for V(III). In all cases the absorbance-vs.-time data agree with the integrated form of a second-order rate law, i.e., first-order in each reactant, and the individual experimental second-order rate constants are independent of initial reactant concentrations. The reaction rate decreases with increasing hydrogen-ion concentration between 0.25M and 2.0M at a constant ionic strength of 2.0M made up with NaClO₄. A graph of the logarithm of the apparent second-order rate constant vs. log [H⁺] is approximately linear, with a slope of about –1.5. Thus the experimental results can be described in terms of the rate law:

$$-\frac{d[\text{Pu(IV)}]}{dt} = k[\text{Pu(IV)}][\text{V(III)}][\text{H}^+]^{-1.5} \quad (3.2)$$

This is called an empirical rate law because it is not written in terms of actual species present in the solution and because not all the exponents are integers. It is useful as a step in determining the composition of the activated complexes and the pattern of paths because it indicates that an average of 1.5 hydrogen ions are released when the activated complex is formed from one Pu(IV) and one V(III). This is not surprising since a total of two hydrogen ions is released in the overall reaction. The rate law in terms of species actually present in the solution can be written as

$$-\frac{d[\text{Pu(IV)}]}{dt} = (k_1 [\text{H}^+]^{-1} + k_2 [\text{H}^+]^{-2})[\text{Pu}^{4+}][\text{V}^{3+}] \quad (3.3)$$

Both reactants are known to hydrolyze, and their stoichiometric concentrations are given by $[\text{Pu(IV)}] = [\text{Pu}^{4+}] + [\text{PuOH}^{3+}] + \dots$ and $[\text{V(III)}] = [\text{V}^{3+}] + [\text{VOH}^{2+}] + \dots$ or by $[\text{Pu}^{4+}] = [\text{H}^+][\text{Pu(IV)}]/([\text{H}^+] + K_{\text{Pu}})$ and $[\text{V}^{3+}] = [\text{H}^+][\text{V(III)}]/([\text{H}^+] + K_{\text{V}})$, where hydrolysis beyond the first stage has been ignored. When these expressions are substituted into Eq. 3.3, the rate law becomes

$$-\frac{d[\text{Pu(IV)}]}{dt} = [\text{Pu(IV)}][\text{V(III)}] \frac{k_1 [\text{H}^+] + k_2}{([\text{H}^+] + K_{\text{Pu}})([\text{H}^+] + K_{\text{V}})} \quad (3.4)$$

At 25°C, $K_{\text{Pu}} = 5.4 \times 10^{-2}M$ for $\mu = 2M$, but K_{V} is negligible with respect to [H⁺]; the value is only about $2 \times 10^{-3}M$. Thus Eq. 3.4 can be simplified by omitting K_{V} . The simplified expression was confirmed by the linearity of graphs of $k''([\text{H}^+] + K_{\text{Pu}})$ vs. $[\text{H}^+]^{-1}$, where k'' is the second-order rate constant observed at a particular [H⁺] and temperature. At 20°C, k_1 was found to be 11.9 sec^{–1} and k_2 to be 20.1M sec^{–1}. Values for the rate constants were also determined at four other temperatures down to 2.4°C.

As pointed out in Sec. 2-3, the rate law alone does not identify the actual reactant species. In the present case, reactions either between VOH^{2+} and Pu^{4+} or between V^{3+} and PuOH^{3+} are consistent with the k_1 term in Eq. 3.3. The k_2 term can be explained in terms of reactions between VOH^{2+} and PuOH^{3+} , between V^{3+} and $\text{Pu}(\text{OH})_2^{2+}$, or between $\text{V}(\text{OH})_2^+$ and Pu^{4+} . For the last possibility, k_2 would be given by $K_V K'_V k'$, where K_V and K'_V are the first and second hydrolysis constants for V^{3+} and k' is the second-order rate constant defined in terms of the species $\text{V}(\text{OH})_2^+$ and Pu^{4+} . Values for K_V and K'_V are about $2 \times 10^{-3}M$ and $2.5 \times 10^{-4}M$, respectively; thus k' would be about $4 \times 10^7 M^{-1} \text{sec}^{-1}$. Table 2.4 shows that this value is near the diffusion-controlled limit for reactions between +1 and +4 ions. We should note, however, that the diffusion limits apply to infinitely dilute solutions and k' applies to $\mu = 2M$. Reactions between ions of like charge become slower as the ionic strength is decreased, and using reasonable values for the parameters in the extended Debye-Hückel expression (see Chap. 7) gives a factor of about 30 between $\mu = 2M$ and $\mu = 0M$ for reactions between +1 and +4 ions. This calculation shows that, although $\text{V}(\text{OH})_2^+$ is a very minor constituent of the solution, its concentration is large enough to be kinetically important. Similar conclusions can be reached about $\text{Pu}(\text{OH})_2^{2+}$.

Despite the uncertainty about the actual rate-determining steps, the formal processes for formation of the two activated complexes from the principal reactants are unambiguous. The two net activation processes, together with their thermodynamic quantities of activation, are listed in Table 3.1.

Table 3.1
NET ACTIVATION PROCESSES AND THERMODYNAMIC QUANTITIES OF ACTIVATION
FOR THE $\text{Pu}(\text{IV})-\text{V}(\text{III})$ REACTION[†]

Net activation process	ΔG^* , kJ/mol (kcal/mol)	ΔH^* , kJ/mol (kcal/mol)	ΔS^* , J/mol · K (cal/mol · deg)
$\text{Pu}^{4+} + \text{V}^{3+} + \text{H}_2\text{O} = [*]^{6+} + \text{H}^+$	65.6 ± 0.04 (15.68 ± 0.01)	71.5 ± 2 (17.1 ± 0.5)	20 ± 7 (4.8 ± 1.7)
$\text{Pu}^{4+} + \text{V}^{3+} + \text{H}_2\text{O} = [*]^{5+} + 2\text{H}^+$	64.0 ± 0.04 (15.30 ± 0.01)	90 ± 1.7 (21.5 ± 0.04)	87 ± 6 (20.8 ± 1.4)

[†] Values are for 25°C and $\mu = 2.0M$.

3-2

THE $\text{U}(\text{IV})-\text{Fe}(\text{III})$ REACTION⁴⁶

The $\text{U}(\text{IV})-\text{Fe}(\text{III})$ reaction is another example of a reaction between highly charged cations both of which undergo appreciable hydrolysis. The pertinent oxidation potentials indicate that the reaction should be

The stoichiometry indicated by this equation was confirmed by experiments showing that 1.98 moles of Fe(II) formed for each mole of U(IV) consumed. Rates were determined by removing samples of the reacting mixture periodically and quenching them in solutions of *o*-phenanthroline containing an equimolar mixture of NH_4F and $\text{NH}_4(\text{CH}_3\text{COO})$ at a pH of 4. This solution effectively stopped the reaction and provided a convenient colorimetric determination of the product, Fe(II). The data are in accord with the integrated form of the second-order rate law:

$$-\frac{d[\text{U(IV)}]}{dt} = k'' [\text{U(IV)}] [\text{Fe(III)}] \quad (3.6)$$

This rate law was further tested by varying the initial concentrations of Fe(III) in the range 1.2 to $52 \times 10^{-5}M$ and U(IV) in the range 1.7 to $3.6 \times 10^{-5}M$. Over this very wide range in concentrations, the experimental values of k' agreed with the average with a mean deviation of only 5%.

The rate law, Eq. 3.6, shows that the rate-determining step (or steps) involves a reaction between one U(IV) and one Fe(III) to give the intermediate U(V) or possibly a binuclear complex such as $\text{Fe} \cdot \text{UO}_2^{3+}$. The details of the reactions that follow the rate-determining step are difficult to determine, but the intermediate probably reacts rapidly with more Fe(III) to give the final products.

The reaction rate increases markedly between $1.0M$ and $0.1M$ HClO_4 at constant ionic strength. Graphs of $\log k''$ vs. $\log [\text{H}^+]$ give an empirical hydrogen-ion dependence of -1.8 . This suggests the following rate law in terms of the principal species present in the solutions:

$$\frac{d[\text{U(IV)}]}{dt} = [\text{U}^{4+}] [\text{Fe}^{3+}] (k_1 [\text{H}^+]^{-1} + k_2 [\text{H}^+]^{-2}) \quad (3.7)$$

If we allow for hydrolysis, $[\text{Fe}^{3+}]$ is equal to $[\text{Fe(III)}] [\text{H}^+] / ([\text{H}^+] + K_{\text{Fe}})$ and $[\text{U}^{4+}]$ is equal to $[\text{U(IV)}] [\text{H}^+] / ([\text{H}^+] + K_{\text{U}})$. These expressions are valid when the hydrogen-ion concentrations are greater than about $0.1M$, where the concentrations of hydrolyzed species other than FeOH^{2+} and UOH^{3+} are negligibly small. When we substitute these expressions into Eq. 3.7, we get

$$k'' = \frac{k_1 [\text{H}^+] + k_2}{([\text{H}^+] + K_{\text{Fe}})([\text{H}^+] + K_{\text{U}})} \quad (3.8)$$

Since the hydrolysis constants, K_{Fe} and K_{U} , are known, the applicability of Eq. 3.8 could be confirmed by the linearity of graphs of $k''([\text{H}^+] + K_{\text{Fe}})([\text{H}^+] + K_{\text{U}})$ vs. $[\text{H}^+]$ for the data at the various temperatures. Values for k_1 and k_2 were determined from the slopes and intercepts of the graphs.

The rate law, Eq. 3.7, shows that there are two parallel rate-determining steps, but the actual reacting species are unknown. The rate law does specify the net activation processes, which are given in Table 3.2.

Measurements were made between 3.1 and 24.8°C, and values for k_1 and k_2 were determined as described. Graphs of $\log k_1$ and $\log k_2$ vs. $1/T$ were good straight lines, indicating activation energies of 22.5 and 24.4 kcal/mol. Similarly, graphs of $\log (k_1/T)$ and $\log (k_2/T)$ vs. $1/T$ are straight lines, in accordance with Eq. 2.1, giving ΔH^* values of 21.5 ± 0.2 and 23.6 ± 0.3 kcal/mol.

Table 3.2
NET ACTIVATION PROCESSES AND THERMODYNAMIC QUANTITIES OF ACTIVATION
FOR THE U(IV)–Fe(III) REACTION†

Net activation process	$\Delta G^*, \ddagger$ kJ/mol (kcal/mol)	$\Delta H^*,$ kJ/mol (kcal/mol)	$\Delta S^*, \ddagger$ J/mol · K (cal/mol · deg)
$U^{4+} + Fe^{3+} + H_2O = [*]^{6+} + H^+$	71.2 (17.01)	75 ± 11 (17.9 ± 2.6)	13 ± 39 (3 ± 9)
$U^{4+} + Fe^{3+} + H_2O = [*]^{5+} + 2H^+$	66.9 (16.00)	101 ± 2 (24.1 ± 0.5)	113 ± 7 (27.1 ± 1.7)

† Values are for 25°C and $\mu = 1.02M$.

‡ Values are calculated under the assumption that the overall rate is twice that of the rate-determining step.

Treating the two sets of k values separately has the drawback that the best fit of one set will generally be inconsistent with the best fit of the other. Also, since the two sets are not independent of each other, reliable estimates of the precision of the activation parameters cannot be determined from the fit of the individual sets to the individual lines. It is better to use a least-squares procedure to find values of the activation parameters (ΔH_1^* , ΔS_1^* , ΔH_2^* , and ΔS_2^*) which best reproduce all the hydrogen-ion- and temperature-dependence data simultaneously. Values determined this way are listed in Table 3.2, which shows that the ΔH^* values are distinctly different from those obtained from the individual k values.

Three different rate-determining steps are all consistent with the second net activation process in Table 3.2. They are the reactions between UOH^{3+} and $FeOH^{2+}$ (with a second-order rate constant k_{11}), between $U(OH)_2^{2+}$ and Fe^{3+} (k_{20}), and between U^{4+} and $Fe(OH)_2^+$ (k_{02}). It is of interest to see if any of these possibilities can be ruled out because of inconsistencies with other requirements. If the k_{11} path is important, the observed rate constant k_2 will be related to k_{11} by the equation $k_{11} = k_2/(K_{Fe}K_U)$. At 25°C and $\mu = 1M$, k_{11} is $2.34 \times 10^5 M^{-1} sec^{-1}$, a value well within the diffusion-controlled limit (see Table 2.4). Also, for the heat of activation, $\Delta H_1^* - \Delta H_2^* - \Delta H_{Fe} - \Delta H_U$, where the two last terms are for the hydrolysis of Fe^{3+} and U^{4+} ,

respectively. Using the known values for the heats of hydrolysis, we find that $\Delta H^\ddagger_1$ is $101 - 52 - 44 = 5$ kJ/mol. Although this is quite small, it is not an impossible value in view of other low values that have been observed; e.g., for the U^{3+} – NpO_2^{2+} reaction, $\Delta H^\ddagger = 4.2$ kJ/mol, and for the U^{3+} – UO_2^+ reaction, $\Delta H^\ddagger = 7.5$ kJ/mol.

Not enough is known about the formation of $U(OH)_2^+$ and $Fe(OH)_2^+$ to enable us to apply similar quantitative arguments to the k_{20} and k_{02} paths. However, reasonable values for the hydrolysis constants and heats of hydrolysis lead to plausible values for the rate constants. Thus the Fe(III)–U(IV) reaction illustrates a typical situation in which the formulas of the activated complexes can readily be determined but the detailed mechanism of their formation can be determined only with great difficulty, if at all.

3-3

THE Np(V)–Co(III) REACTION

The Np(V)–Co(III) reaction⁴⁷ illustrates the various ways of interpreting a small observed hydrogen-ion dependence.

The reaction was studied spectrophotometrically at 980.5 nm, where NpO_2^+ is the principal absorbing species. The stoichiometry is given by

in acid solutions. The rate of the reaction was studied at six hydrogen-ion concentrations from 0.26*M* to 2.1*M* and at four temperatures between 5 and 25°C. The rate is strictly first order in each of the metal ions, but the apparent second-order rate constants decrease about 25% when concentrations of $HClO_4$ increase from 0.26*M* to 2.1*M* at constant ionic strength ($LiClO_4$). A satisfactory empirical rate law is

$$-\frac{d[NpO_2^+]}{dt} = k'' [NpO_2^+] [Co^{3+}] [H^+]^n \quad (3.10)$$

where *n* ranges from –0.06 at 5°C to –0.112 at 25°C. The discussion in Sec. 2-4 shows that small hydrogen-ion dependences such as this can be explained in several ways. For this reason the apparent second-order rate constants were treated by least squares, as described in Sec. 3-2, with three different functional forms for k'' : (1) $k'' = k_0 + k_1 [H^+]^{-1}$, (2) $k'' = \{k_0^{-1} + (k_1 [H^+]^{-1})^{-1}\}^{-1}$, and (3) $k'' = k_0 \exp \{ \beta(1 + \alpha t)[H^+] \}$. The temperature dependence of β was assumed to be linear, as indicated; the temperature dependences of the rate constants were assumed to be given by the Eyring equation; and best values for the parameters were determined by least squares. The calculations showed that the temperature dependence of β is not statistically significant; repeating the calculations without it gave essentially the same results.

Table 3.3
INTERPRETATIONS OF THE HYDROGEN-ION DEPENDENCE OF THE Np(V)–Co(III) REACTION†‡

Apparent second-order rate constant	ΔH_0^* , kJ/mol (kcal/mol)	ΔS_0^* , J/mol · K (cal/mol · deg)	ΔH_1^* , kJ/mol (kcal/mol)	ΔS_1^* , J/mol · K (cal/mol · deg)	β , M^{-1}	α , deg ⁻¹	Deviation §
$k'' = k_0 + k_1 [H^+]^{-1}$	50.2 ± 0.9 (12.0 ± 0.2)	-29.5 ± 3.2 (-7.0 ± 0.8)	82 ± 10 (19.7 ± 2.4)	61 ± 34 (14.5 ± 8)			6.3
$k'' = \{k_0^{-1} + (k_1 [H^+]^{-1})^{-1}\}^{-1}$	57.0 ± 4.6 (13.6 ± 1.1)	-4.1 ± 15 (-1.0 ± 3.7)	26 ± 31 (6.3 ± 7.4)	-93 ± 104 (-22 ± 25)			14.2
$k'' = k_0 \exp \{ \beta (1 + \alpha) [H^+] \}$	56.1 ± 4.6 (13.4 ± 1.1)	-7.1 ± 15.5 (-1.7 ± 3.7)			-0.45 ± 0.1	0.086 ± 0.3	14.6
	52.3 ± 1.5 (12.5 ± 0.4)	-20.5 ± 5 (-4.9 ± 1.2)			-0.11 ± 0.02	0 (fixed)	13.5

†The rate law is $-d[Np(V)]/dt = k''[Np(V)][Co(III)]$.

‡The uncertainties listed for the parameters are the standard deviations.

§Root-mean-square deviation between observed and calculated k'' values. The data were weighted according to their individual standard deviations. The root-mean-square average of these individual standard deviations was $3.7 M^{-1} \text{ sec}^{-1}$.

The results of these calculations, summarized in Table 3.3, show that the activation parameters for the major, hydrogen-ion-independent, path do not depend strongly on the form assumed for the minor term in the rate law. We recommend the interpretation based on parallel paths since it fits the data much better than the others. Other interpretations cannot be excluded with certainty, however, because they may also fit the data within the experimental error. For example, the root-mean-square deviation of $14.2 \text{ M}^{-1} \text{ sec}^{-1}$, found in the second calculation, corresponds to a mean deviation of only 5.3%.

The oxidation of Np(V) complexed with Cr(III) was also studied. When a mixture of hexaquo Cr^{3+} is allowed to stand in solution with NpO_2^+ , a definite complex, $\text{Cr} \cdot \text{NpO}_2^{4+}$, is formed. This can be separated from the mixture by ion-exchange techniques.^{29,33} Similar complexes containing uranium³⁰ or plutonium³² can also be made.

The stoichiometry of the reaction between the complex and Co(III) is given by

This reaction, too, was studied spectrophotometrically over a range of temperatures and hydrogen-ion concentrations. The empirical rate law has the form

$$\frac{d[\text{NpO}_2^{2+}]}{dt} = k'' [\text{Cr} \cdot \text{NpO}_2^{4+}] [\text{Co}^{3+}] [\text{H}^+]^{-1.1} \quad (3.12)$$

Thus the reaction is predominantly inverse first power in $[\text{H}^+]$. Again, the small deviation from this dependence can be explained by parallel reactions, by consecutive reactions, or by a medium effect. Our calculations show that the three different assumptions are about equally satisfactory with respect to fitting the observed hydrogen-ion- and temperature-dependence data. We got the best fit by assuming consecutive reactions and the poorest by assuming parallel reactions. The differences among the possibilities are not significant, however, since the weighted average deviation for the best fit is only 4% less than that for the poorest. Thus there is no evidence that the minor term in the rate law results from a distinct activation process occurring either in parallel with or consecutive to the principal one. The activation parameters for the principal path, inverse in $[\text{H}^+]$, calculated under the three assumptions agree within their standard deviations. The average values are given in Table 3.4, along with those for the reaction of uncomplexed Np(V).

When we compare the second and third processes, we see that, although the presence of Cr(III) decreases ΔH^* , the decrease is more than compensated for by the effect of the higher charge in decreasing ΔS^* . Thus the net effect is a reduction in the rate.

Table 3.4
NET ACTIVATION PROCESSES AND THERMODYNAMIC QUANTITIES OF ACTIVATION
FOR Np(V)–Co(III) REACTIONS[†]

Net activation process	ΔG^* , kJ/mol (kcal/mol)	ΔH^* , kJ/mol (kcal/mol)	ΔS^* , J/mol · K (cal/mol · deg)
$\text{Co}^{3+} + \text{NpO}_2^+ = [*]^{4+}$	59.0 (14.1)	50.2 ± 0.8 (12.0 $\pm$ 0.2)	-29 ± 3 (-7 $\pm$ 1)
$\text{Co}^{3+} + \text{NpO}_2^+ + \text{H}_2\text{O} = [*]^{3+} + \text{H}^+$	64.4 (15.4)	82.4 ± 10 (19.7 $\pm$ 2.4)	62 ± 34 (14.8 $\pm$ 8)
$\text{Co}^{3+} + \text{Cr} \cdot \text{NpO}_2^{4+} + \text{H}_2\text{O} = [*]^{6+} + \text{H}^+$	70.3 (16.8)	77.0 ± 3.3 (18.4 $\pm$ 0.8)	23 ± 11 (5.4 $\pm$ 2.7)

[†] Values are for 25°C and $\mu = 2.1M$ (LiClO_4).

3.4

THE Np(V)–V(III) REACTION⁴⁸

The Np(V)–V(III) reaction is interesting because the rate law shows the operation of parallel paths that do not differ merely by one or two hydrogen ions as in the reactions discussed previously (e.g., the Fe(III)–U(IV) reaction).

The course of the reaction was followed spectrophotometrically by use of either the Np(V) band at 980 nm or the Np(VI) band at 960 nm. At hydrogen-ion concentrations greater than 0.5M, the stoichiometry of the reaction is given by

At lower acidities, however, appreciable concentrations of Np^{3+} were formed by the rapid equilibrium:

for which the equilibrium quotient, Q_{14} , was found to be about $6 \times 10^{-4}M^2$ at 25°C in 3M (H,Li)ClO₄.

The rate was found to be first order in each of the reactants V(III) and Np(V) but to be catalyzed by Np(IV) and inhibited by V(IV). At constant hydrogen-ion concentration, the rate is given by

$$-\frac{d[\text{Np(V)}]}{dt} = k_a'' [\text{V(III)}] [\text{Np(V)}] + \frac{k_b'' [\text{V(III)}] [\text{Np(IV)}] [\text{Np(V)}]}{[\text{V(IV)}]} \quad (3.15)$$

The k_a'' and k_b'' terms show that there are two parallel rate-determining steps. The first term corresponds to the direct reaction (Eq. 3.13) and the form of the second term shows that its activated complex is formed from V(III), Np(IV), and Np(V) with the prior loss of V(IV). This means that the activated complex contains no vanadium and has an average oxidation number of +4. This suggests a mechanism consisting of reactions 3.13 and 3.14, followed by the rate-determining oxidation of Np(III) by Np(V):

If we assume that Np(III) is formed at essentially the same rate as that at which it reacts (so that its net rate of change is small compared with the rate of the overall reaction), the steady-state approximation can be applied:

$$[\text{Np(III)}] = \frac{k_{14} [\text{V(III)}] [\text{Np(IV)}]}{k_{-14} [\text{V(IV)}] + k_{16} [\text{Np(V)}]} \quad (3.17)$$

where k_{14} refers to Eq. 3.14, k_{-14} to the reverse of Eq. 3.14, and k_{16} to Eq. 3.16. The rate of the overall reaction is then given by

$$\frac{d[\text{Np(V)}]}{dt} = k_{13} [\text{Np(V)}] [\text{V(III)}] + \frac{k_{14} k_{16} [\text{V(III)}] [\text{Np(IV)}] [\text{Np(V)}]}{k_{-14} [\text{V(IV)}] + k_{16} [\text{Np(V)}]} \quad (3.18)$$

Since $k_{-14} [\text{V(IV)}]$ is known to be much larger than $k_{16} [\text{Np(V)}]$, Eq. 3.18 reduces to Eq. 3.15, where the experimental rate constant k_b'' is given by $k_{14} k_{16} / k_{-14}$ or $k_{16} Q_{14}$. Both k_{16} and the equilibrium quotient, Q_{14} , were measured separately, and their product was found to be significantly less than k_b'' . This discrepancy is attributed to unknown catalytic impurities.

The experimental rate constant k_a'' is independent of $[\text{H}^+]$, and k_b'' shows an inverse 1.6 power dependence, consistent with the $[\text{H}^+]$ dependences of equilibrium 3.14 and reaction 3.16 and the proposed mechanism. The heat of activation for reaction 3.13 was determined from the temperature dependence of k_a'' between 15 and 35°C; the value is $\Delta H^* = 61 \pm 3 \text{ kJ/mol}$.

3-5

THE V(II)—U(VI) REACTION

The reaction between V(II) and U(VI)⁴⁹ shows one way that U(VI) can act as a catalyst for oxidation–reduction reactions and how this action can be used to determine the rate of reduction of U(VI).

The reaction between V(II) and V(IV) to give V(III) is relatively slow in acid solution; e.g., the second-order rate constant at 25°C is $1.6 \text{ M}^{-1} \text{ sec}^{-1}$ in 1M

HClO_4 — $1M$ LiClO_4 (Ref. 50). When as little as $10^{-4}M$ U(VI) is present, however, the initial value of the apparent second-order rate constant is increased by a factor of 2.75 if the V(IV) concentration is $2.5 \times 10^{-3}M$. This catalytic effect is in accord with the following reaction scheme:

Additional reactions that might be considered are the disproportionation of U(V) or its reduction by either V(II) or V(III) . No U(IV) is detected during the catalytic reaction, however; thus these reactions can be ignored. Making the usual steady-state approximation for the concentration of U(V) , we find that the rate law for reactions 3.19, 3.20, and 3.21 is

$$-\frac{d[\text{V(IV)}]}{dt} = k_{21} [\text{V(II)}] [\text{V(IV)}] + \frac{k_{19} [\text{V(II)}] [\text{U(VI)}]_T}{1 + k_{19} [\text{V(II)}] / (k_{20} [\text{V(IV)}])} \quad (3.22)$$

where $[\text{U(VI)}]_T$ is the total concentration of U(VI) added.

If the initial concentration of V(II) is approximately equal to that of V(IV) , or if $k_{19} [\text{V(II)}]$ is much smaller than $k_{20} [\text{V(IV)}]$, the denominator term in Eq. 3.22 will be essentially constant, and an apparent rate constant, $k' = k_{19} \{1 + k_{19} [\text{V(II)}] / (k_{20} [\text{V(IV)}])\}^{-1}$, can be defined.

The reaction was followed spectrophotometrically at 760 nm where V(IV) is the predominant absorbing species and the data were in good agreement with the rate law, Eq. 3.22, written in terms of k' . Values for k_{21} were taken from work on the uncatalyzed reaction, and consistent values for k' were found over a 20-fold change in $[\text{U(VI)}]$, from $5 \times 10^{-5}M$ to $10^{-3}M$, and V(III) concentrations up to $10^{-2}M$. However, varying the initial $[\text{V(IV)}] / [\text{V(II)}]$ ratio from 1.1 to 5.5 caused a 4% increase in the apparent value for k' . This is outside the experimental error and suggests that $k_{20} [\text{V(IV)}]$ is not much greater than $k_{19} [\text{V(II)}]$. The observed effect is consistent with $k_{20} / k_{19} \approx 20$.

Rate constants were determined at hydrogen-ion concentrations from $0.05M$ to $2.0M$ and at temperatures from 0.6 to 36.8°C . That the rate constant, k_{19} , is essentially independent of the hydrogen-ion concentration shows that the principal net activation process is

The temperature dependence of k_{19} leads to $\Delta H^* = 30 \pm 0.4 \text{ kJ/mol}$ and $\Delta S^* = -110 \pm 2 \text{ J/mol} \cdot \text{K}$.

The uranyl ion has also been shown to catalyze the Fe(III)–V(III) (Ref. 51), the Fe(III)–Np(III) (Ref. 12), and the oxygen–ascorbic acid^{5,2} reactions. The last reaction is of a different type, however, since U(V) is apparently not involved.

3-6

THE Np(VII)–Hg(I)₂ REACTION

Neptunium in the +7 state is a very powerful oxidizing agent in acid solutions but reacts slowly with water under these conditions.^{2,4,5,3} Reducing agents that react more slowly than water are difficult to study, but a variety of faster ones has been examined. The reactions between Np(VII) and the one-electron reducing agents Ag⁺, Ce³⁺, Co²⁺, and NpO₂⁺ are all too rapid for convenient measurement. The oxidation of Tl⁺ (Ref. 54) or Hg₂²⁺ is readily measurable, however. Because of its many interesting features, the Hg₂²⁺ reaction^{5,5} is discussed in detail.

Solutions of Np(VII) in 1M NaOH were prepared electrolytically by use of a platinum gauze anode with a current density of about 12 A/m² (Ref. 56). Solutions of Hg(I)₂, defined as Hg₂²⁺ plus any hydrolyzed species, were prepared by reducing recrystallized Hg(ClO₄)₂ with metallic mercury and then adding a small excess of Hg(II), presumably to remove suspended or colloidal Hg⁰. The rate experiments were started by injecting samples of the alkaline Np(VII) solution into acidic solutions of the other reactants. The heat of neutralization was compensated by precooling the Np(VII) solution. The stoichiometry is given by

In six separate measurements the consumption ratio, $\Delta[\text{Np(VII)}]/\Delta[\text{Hg(I)}_2]$, was found to be 2.001 ± 0.038 .

Rates were followed spectrophotometrically at 440 nm, where Np(VII) absorbs strongly. First-power dependences were found for both Hg(I)₂ and Np(VII) in experiments in which the initial concentration ranges were 5.9 to $23.7 \times 10^{-4}M$ and 0.63 to $13.3 \times 10^{-4}M$, respectively. The concentration of Hg(II) was without effect from $1.2 \times 10^{-3}M$ to $3.9 \times 10^{-2}M$. Thus Np(VII) is like the other strong oxidizing agents Ag(II) and Co(III) in that inhibition by Hg(II) is not observed. By contrast, inhibition is observed when Mn(III) and Tl(III) are used.^{5,7}

The hydrogen-ion dependence of the apparent second-order rate constant is linear in the range $0.08M$ to $0.94M$ at constant ionic strength, made up with LiClO₄. Thus the rate law can be written

$$-\frac{d[\text{Np(VII)}]}{dt} = 2(k_0 + k_1 [\text{H}^+]) [\text{Np(VII)}] [\text{Hg(I)}_2] \quad (3.25)$$

This result indicates parallel rate-determining steps with the two net activation processes given in Table 3.5.

The rates of the reaction were studied as a function of the hydrogen-ion concentration over a 33° temperature interval (between 2 and 35°C). We have used the combined hydrogen-ion- and temperature-dependence data to determine the best values for the thermodynamic quantities of activation for the two net activation processes. The results, which are in good agreement with the published activation energies, are given in Table 3.5.

Table 3.5
NET ACTIVATION PROCESSES AND THERMODYNAMIC QUANTITIES OF ACTIVATION
FOR THE Np(VII)–Hg(I)₂ REACTION†

Net activation process	ΔG^* , ‡ kJ/mol (kcal/mol)	ΔH^* , kJ/mol (kcal/mol)	ΔS^* , ‡ J/mol · K (cal/mol · deg)
Np(VII) + Hg ₂ ²⁺ = [*] ⁿ⁺² §	66.51 (15.90)	49.4 ± 1.2 (11.8 ± 0.3)	–58 ± 4 (–14 ± 1)
Np(VII) + Hg ₂ ²⁺ + H ⁺ = [*] ⁿ⁺³	68.10 (16.28)	31.0 ± 4.2 (7.4 ± 1.0)	–125 ± 15 (–30 ± 3.5)

†Values are for 25°C and $\mu = 1.0M$ (LiClO₄).

‡Values were calculated under the assumption that the overall rate is twice that of the rate-determining step.

§n is the unknown charge on the Np(VII) species in acid solution.

Since the stoichiometry of the rate-determining steps is not the same as for the overall reaction (Eq. 3.24), a reactive intermediate must be involved. Plausible mechanisms, without regard to hydrogen ions, are

or

For either of these mechanisms, the rate of disappearance of Np(VII) is twice that of the rate-determining step. It is possible, however, that the monomeric Hg(I) produced in reaction 3.26 will dimerize, in which case the overall rate will equal that of the

rate-determining step. This ambiguity introduces an uncertainty of a factor of 2 into the values for the rate constants for the rate-determining steps and a corresponding uncertainty into the values for ΔG^* and ΔS^* . The values in Table 3.5 are based on the assumption that Np(VII) is consumed in a rapid reaction after the rate-determining step. If Np(VII) is not consumed in this way, the ΔG^* values in the table should be decreased by 1.72 kJ/mol and the ΔS^* values increased by 5.77 J/mol · K.

For the analogous oxidation of Tl(I) by Np(VII), the predominant term in the rate law is first power in $[H^+]$ (Ref. 55). The corresponding net activation process is $Np(VII) + Tl^+ + H^+ = [^*]^{n+2}$, for which $\Delta H^* = 29.0 \pm 0.8$ kJ/mol and $\Delta S^* = -142 \pm 3$ J/mol · K. These are quite close to the corresponding values for the Hg(I)₂ reaction. This agreement may imply that the energetics for the hydrogen-ion-dependent path are relatively insensitive to the nature of the reductant.

Although the charge, n , on Np(VII) in acid solution has not been determined, the effect of ionic strength on the Np(VII)–Hg₂²⁺ reaction indicates that its sign is positive. The rate increases with increasing ionic strength, and, in 0.09M HClO₄ solutions up to $\mu = 3.7M$ with LiClO₄, the data are consistent with an extended Debye–Hückel equation (Eq. 7.1) for any value of n from +1 to +3.

3-7

THE Np(VI)–H₂O₂ REACTION

The rate law for the Np(VI)–H₂O₂ reaction⁵⁸ is more complicated than the rate laws discussed previously and gives evidence for a reactive intermediate and an inhibiting back reaction.

The net reaction was found to be

As long as the initial $[Np(VI)]/[H_2O_2]$ ratio was greater than 2, no decomposition of H₂O₂ was detected. Because concentration-vs.-time data were not in accord with the integrated form of the second-order rate law, the kinetics were studied by use of initial rates. Adding NpO₂⁺ was found to decrease the initial rates markedly. Graphs of $[NpO_2^{2+}][H_2O_2][H^+]^{-1}(d[NpO_2^+]/dt)^{-1}$ vs. $[NpO_2^+][NpO_2^{2+}]^{-1}$ were found to be linear with positive intercepts. This shows the rate law to be

$$\left(\frac{d[NpO_2^+]}{dt}\right)_0 = \frac{k' [NpO_2^{2+}]_0 [H_2O_2]_0 [H^+]_0^{-1}}{1 + b [NpO_2^+]_0 [NpO_2^{2+}]_0^{-1}} \quad (3.31)$$

Values for k' and b were found to be 8.9 sec⁻¹ and 1.9, respectively, at 25°C in 3M (H,Na)ClO₄. The temperature dependences of the rate constants between 5 and 25°C give activation energies of 51.9 ± 4.6 and -6.3 ± 5.9 kJ/mol for k' and b , respectively.

The form of this rate law indicates consecutive reactions (Fig. 2.1, pattern 2-1), and rearranging Eq. 3.31 shows the compositions of the two activated complexes involved:

$$\left(\frac{d[\text{NpO}_2^+]}{dt}\right)_0^{-1} = (k' [\text{NpO}_2^{2+}]_0 [\text{H}_2\text{O}_2]_0 [\text{H}^+]_0^{-1})^{-1} + \left(\frac{k'}{b} [\text{NpO}_2^{2+}]_0^2 [\text{H}_2\text{O}_2]_0 [\text{H}^+]_0^{-1} [\text{NpO}_2^+]_0^{-1}\right)^{-1} \quad (3.32)$$

Here the reciprocal of the rate is equal to the sum of the reciprocals of two terms, each of which corresponds to one of the activation processes. These are shown in Table 3.6 along with their activation parameters.

Table 3.6
NET ACTIVATION PROCESSES AND THERMODYNAMIC QUANTITIES OF ACTIVATION
FOR THE $\text{Np(VI)}-\text{H}_2\text{O}_2$ REACTION†

Net activation process	ΔG^* , kJ/mol (kcal/mol)	ΔH^* , kJ/mol (kcal/mol)	ΔS^* , J/mol · K (cal/mol · deg)
$\text{NpO}_2^{2+} + \text{H}_2\text{O}_2 = [*]^{1+} + \text{H}^+$	69.5 ± 0.4 (16.6 ± 0.1)	49.4 ± 4.6 (11.8 ± 1.1)	-67 ± 15 (-16.1 ± 3.7)
$2\text{NpO}_2^{2+} + \text{H}_2\text{O}_2 = [*]^{2+} + \text{NpO}_2^+ + \text{H}^+$	71.1 ± 0.2 (17.0 ± 0.5)	55.6 ± 7.5 (13.3 ± 1.8)	-52 ± 25 (-12.4 ± 6)

† Values are for 25° and $\mu = 3.0M$.

A plausible mechanism that involves the indicated activated complexes is

If the usual steady-state approximation is made for the radical intermediate, HO_2 , this scheme leads to the rate law, Eq. 3.31, where $k' = 2k_{3.4}K_{3.3}$ and $b = k_{-3.4}/k_{3.5}$. Since $K_{3.3}$ is about $10^{-5}M$ to $10^{-6}M$, $k_{3.4}$ is about $10^6 M^{-1} \text{sec}^{-1}$.

The kinetically equivalent mechanism in which reactions 3.33 and 3.34 are replaced by

and

can be rejected because the equilibrium concentration HO_2^- is too low. The acid dissociation constant for H_2O_2 , K_{33a} , is about $10^{-11} M$ at 25°C and $\mu = 3M$ (Ref. 59); thus $k_{34a} = 8.9/(2 \times 10^{-11}) = 4.4 \times 10^{11} M^{-1} \text{sec}^{-1}$ and is probably about 3×10^{12} at $\mu = 0$. Since this value is about 100 times larger than the diffusion-controlled limit, we can conclude that this alternate mechanism is unsatisfactory.

The analogous reduction of Pu(VI) has been investigated.⁶⁰ Inhibition by Pu(V) was considered but was not explicitly studied. Some of the concentration-vs.-time curves show decreases in the apparent second-order rate constants as the reaction proceeds, however. The reported rate law for initial rates is

$$-\frac{d[\text{PuO}_2^{2+}]}{dt} = 6.3 \times 10^{-3} [\text{PuO}_2^{2+}] [\text{H}_2\text{O}_2] [\text{H}^+]^{-1} M \text{sec}^{-1} \quad (3.36)$$

with an activation energy of 50 ± 4 kJ/mol. Thus, for the net activation process studied, $\text{PuO}_2^{2+} + \text{H}_2\text{O}_2 = [\text{*}]^+ + \text{H}^+$, $\Delta G^* = 86$ kJ/mol, $\Delta H^* = 48.4$ kJ/mol, and $\Delta S^* = -125$ J/mol $\cdot$ K. These results show that the plutonium reaction is much slower, primarily because of the more negative entropy of activation. No explanation is readily apparent for the surprising difference between the ΔS^* values reported for the reactions of NpO_2^{2+} and of PuO_2^{2+} .

3-8

THE U(IV)–Pu(VI) REACTION

The rate law of the U(IV)–Pu(VI) reaction⁶¹ provides evidence for consecutive rate-determining steps and a binuclear intermediate, the 2-1 pattern discussed in Sec. 2-3.

In acid solutions U(IV) is a strong enough reducing agent to reduce Pu(VI) all the way to Pu(III) (Table 2.1). In dilute solutions, however $[1.8 \times 10^{-4} M \text{ Pu(VI)}]$ and $0.62 \times 10^{-4} M \text{ U(VI)}$ in $1M \text{ HClO}_4$, about 96% of the U(IV) reacts according to

The rest reacts according to

The reaction rates, studied by use of the Pu(VI) absorption peak at 830.2 nm, were all in good agreement with the rate law:

$$-\frac{d[\text{Pu(VI)}]}{dt} = 2k'' [\text{Pu(VI)}] [\text{U(IV)}] \quad (3.39)$$

at constant ionic strength, $[\text{H}^+]$, and temperature. This rate law requires that the activated complexes be formed from one Pu(VI) and one U(IV). The mechanism, without regard to hydrogen ions, is probably

followed by the rapid reaction

The disproportionation of U(V)

is too slow to account for the disappearance of U(V). This can be shown by calculating the steady-state concentration of U(V) required to make the rate of reaction 3.42 equal to the observed rate. If the mechanism were reaction 3.40, followed by reaction 3.42, the relative concentration of U(V) under steady-state conditions would be given by

$$\frac{[\text{U(V)}]}{\{[\text{Pu(VI)}] [\text{U(IV)}]\}^{1/2}} = \left(\frac{k_{40}}{2k_{42}} \right)^{1/2} \quad (3.43)$$

In $0.1M \text{ H}^+$ at 25°C and $\mu = 2M$, k_{40} is approximately equal to $70 M^{-1} \text{ sec}^{-1}$ and $2k_{42}$ is approximately equal to $50 M^{-1} \text{ sec}^{-1}$ (Ref. 20); thus the relative concentration of U(V) would be about 1.2. Such a large steady-state concentration could not be reached quickly enough for second-order kinetics to be observed. Thus the disproportionation of U(V) will be unimportant with respect to its reaction with Pu(VI). The factor of 2 in Eq. 3.39 reflects the supposition that two Pu(VI) ions are consumed each time reaction 3.40 occurs.

The hydrogen-ion dependence was determined at four temperatures in $2M (\text{H,Li})\text{ClO}_4$ solutions from $0.1M$ to $1.5M \text{ H}^+$. In this range U(IV) hydrolyzes, but Pu(VI) does not. Thus $[\text{U(IV)}]$ is equal to $[\text{U}^{4+}] \{1 + (K/[\text{H}^+])\}$ and $[\text{Pu(VI)}]$ is equal to $[\text{PuO}_2^{2+}]$, where K is the first hydrolysis constant for U(IV). Thus, in terms of species actually present in the solution, the rate law in Eq. 3.39 becomes

$$-\frac{d[\text{Pu(VI)}]}{dt} = 2k'' \left(1 + \frac{K}{[\text{H}^+]} \right) [\text{PuO}_2^{2+}] [\text{U}^{4+}] \quad (3.44)$$

Graphs of $\log \{k''(1 + K/[H^+])\}$ vs. $\log [H^+]$ show small amounts of curvature. For the 25°C data the slopes are -1.03 and -1.27 at $0.1M$ and $1.5M$ H^+ , respectively. This hydrogen-ion dependence suggests that the most important activated complex is formed with the prior loss of one H^+ and that a second activated complex, formed with the loss of two hydrogen ions may be involved also. The decrease in the apparent H^+ dependence with decreasing $[H^+]$ is not consistent with parallel rate-determining steps but suggests consecutive reactions instead. Thus the rate law to be tested is that for a 2-1 pattern:

$$-\frac{d[Pu(VI)]}{dt} = \frac{2[Pu(VI)][U(IV)]}{1 + K/[H^+]} \left(\frac{1}{k_1 [H^+]^{-1}} + \frac{1}{k_2 [H^+]^{-2}} \right)^{-1} \quad (3.45)$$

The correctness of this rate law is confirmed by the linearity of graphs of $\{k''([H^+] + K)\}^{-1}$ vs. $[H^+]$ for the data at each temperature. The rate constants k_1 and k_2 are given by the reciprocals of the intercepts and slopes of the graphs. The possibility that the k_2 term in the rate law is due to medium effects must be considered. In Sec. 2-4 it was shown that medium effects can give rate laws of the same form as Eq. 3.45 and that the Harned parameter, $-\beta$, would be given by k_1/k_2 . At 25°C the values of k_1 and k_2 are 4.4 sec^{-1} and $11 M \text{ sec}^{-1}$; thus β would be -0.4 . This would require a 50% change in the pertinent activity-coefficient ratio on going from $1M$ $HClO_4$ to $1M$ $LiClO_4$ and is unreasonably large. On this basis it is concluded that most, if not all, of the k_2 term is due to an actual path and not merely to a medium effect.

Many detailed mechanisms are consistent with the rate law, Eq. 3.45. All require a binuclear intermediate that can react to give products or dissociate to give reactants at relative rates depending on the hydrogen-ion concentration. Perhaps the simplest such mechanism is

The binuclear intermediate, formed in the second step of this mechanism, must be an inner-sphere complex because its rate of formation is relatively low.

The two net activation processes required by the rate law, Eq. 3.45, do not depend on the details of the mechanism. The activation parameters, $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$, for these processes were determined from a simultaneous treatment of the hydrogen-ion and temperature data. The results are listed in Table 3.7.

Table 3.7

NET ACTIVATION PROCESSES AND THERMODYNAMIC QUANTITIES OF ACTIVATION
FOR THE U(IV)–Pu(VI) REACTION†

Net activation process	ΔG^* , kJ/mol (kcal/mol)	ΔH^* , kJ/mol (kcal/mol)	ΔS^* , J/mol · K (cal/mol · deg)
$U^{4+} + PuO_2^{2+} + H_2O = [*]^{5+} + H^+$	69.33 (16.57)	73.8 ± 0.5 (17.6 $\pm$ 0.1)	15 ± 2 (3.6 $\pm$ 0.4)
$U^{4+} + PuO_2^{2+} + H_2O = [*]^{4+} + 2H^+$	67.07 (16.03)	89.2 ± 1.3 (21.3 $\pm$ 0.3)	74 ± 5 (17.8 $\pm$ 1.3)

† Values are for 25°C and $\mu = 2.0M$.

3-9

THE Pu(VI)–Fe(II) REACTION⁶²

The Pu(VI)–Fe(II) reaction illustrates that even a very simple reaction can have a very complicated rate law and mechanism. The data are consistent with either of the 3-1 patterns of paths (Fig. 2.1).

When Fe(II) is added to an excess of Pu(VI), the predominant reaction is

Using a 60% excess of Pu(VI), we found that the number of moles of Pu(VI) reduced per mole of Fe(II) oxidized ranged from 0.92 to 1.01 as the acid concentration was varied from 2.0M to 0.05M at constant ionic strength. However, Fe(II) is capable of reducing plutonium all the way to Pu(III), and, with excess Fe(II), we observe appreciable amounts of Pu(IV). The additional reactions that are important are

The rate of reaction 3.46 was determined in stirred, thermostated absorption cells. The Pu(VI) band at 830.3 nm was used to determine the extent of reaction vs. time. The rate law with excess Pu(VI) and at constant hydrogen-ion concentration was found to be

$$-\frac{d[PuO_2^{2+}]}{dt} = k'[PuO_2^{2+}][Fe^{2+}] \quad (3.49)$$

The metal-ion dependences shown in Eq. 3.49 were confirmed in experiments in which the plutonium and iron concentrations were varied by factors of 2 and 4, respectively, without significantly affecting the experimental value of k' .

The hydrogen-ion dependence, studied between 0.05*M* and 2.0*M* at constant ionic strength, was found to be quite complicated. The simplest function capable of reproducing the data satisfactorily is

$$-\frac{d[\text{PuO}_2^{2+}]}{dt} = \{ A + (B + C[\text{H}^+])^{-1} \} [\text{PuO}_2^{2+}] [\text{Fe}^{2+}] \quad (3.50)$$

The fact that three parameters are required shows that there are three rate-determining steps and three important activated complexes. Referring to Fig. 2.1, we see that there are three possible patterns of paths to be considered. Since Eq. 3.50 does not reduce to the forms for either the 3-0 or the 3-2 patterns, these can be rejected. The equation can be reduced to forms corresponding to either of the 3-1 patterns, however.

Equation 3.50 is readily rearranged to give

$$\frac{d[\text{PuO}_2^{2+}]}{dt} = A[\text{PuO}_2^{2+}] [\text{Fe}^{2+}] + \left(\frac{1}{B^{-1}[\text{PuO}_2^{2+}] [\text{Fe}^{2+}]} + \frac{1}{C^{-1}[\text{PuO}_2^{2+}] [\text{Fe}^{2+}] / [\text{H}^+]} \right)^{-1} \quad (3.51)$$

which has the 3-1-b form. For this pattern parameter A is associated with the path that leads directly to products, and the B and C terms involve the consecutive reactions. One of several possible mechanisms consistent with this pattern is

It is obvious that the equilibrium hydrolysis of PuO_2^{2+} instead of Fe^{2+} would be equally acceptable. Note also that the intermediate could just as well be formed without the loss of H^+ but that it hydrolyzes before reaction to products. This alternative corresponds to the mirror image of the pattern given by Eqs. 3.52 to 3.55.

Equation 3.50 can also be rearranged to give

$$\frac{d[\text{PuO}_2^{2+}]}{dt} = \left\{ \frac{1}{A(1 + AB)[\text{PuO}_2^{2+}][\text{Fe}^{2+}] + (1 + AB)^2 C^{-1} [\text{PuO}_2^{2+}][\text{Fe}^{2+}]/[\text{H}^+]} + \frac{1}{(1 + AB)B^{-1} [\text{PuO}_2^{2+}][\text{Fe}^{2+}]} \right\}^{-1} \quad (3.56)$$

In this form the rate law corresponds to pattern 3-1-a. The activated complexes involved in this pattern have the same compositions as before, but the effective rate constants for the formation of these complexes are not the same. This shows that although the activation parameters, k , ΔG^* , ΔH^* , and ΔS^* , do not depend on the detailed mechanism for a given pattern of paths, they can depend on the pattern. The activation parameters for the Pu(VI)–Fe(II) reaction calculated for the two patterns are compared in Table 3.8.

The nature of the activated complexes indicated in Table 3.8 is unclear, but some limited conclusions can be reached. For either pattern the activated complexes in processes (2) and (3) in the table are formed sequentially and involve the formation or disappearance of a metastable intermediate. The transfer of the electron may occur either during the formation of the intermediate or during its reaction to give products. Thus it is unknown which of the two activated complexes is for the substitution reaction and which is for the redox reaction. The redox process is almost certainly inner sphere, however, because the binuclear intermediate is the immediate product (or reactant). By the same reasoning, the activated complex in process (1) is for an outer-sphere redox reaction if the pattern is 3-1-b but is for either a substitution reaction or an inner-sphere reaction if the pattern is 3-1-a.

3-10

THE Cr(II)–Np(V) REACTION⁶³

The Cr(II)–Np(V) reaction illustrates the complexities that may arise when competitive–consecutive reactions have rate constants such that the steady-state approximation cannot be applied. It also illustrates the use of ^{18}O to prove that the mechanism is predominantly inner sphere.

The reaction was carried out in 0.2M (H,Li)ClO₄ solutions with an excess of Np(V). The rate of appearance of Np(IV), which was followed spectrophotometrically at 732 nm, did not adhere to second-order kinetics. In addition, examination at 276 nm showed the formation of appreciable concentrations of Np(III). For example, in 0.1M HClO₄ with an initial reactant ratio of $[\text{Np(V)}]/[\text{Cr(II)}] = 4$, the product ratio $[\text{Np(III)}]/[\text{Np(IV)}]$ was 0.12 after 75% of the Cr(II) had been consumed. A similar experiment in 0.05M HClO₄ gave a product ratio of 0.48.

Table 3.8
NET ACTIVATION PROCESSES AND THERMODYNAMIC QUANTITIES OF ACTIVATION
FOR THE Pu(VI)–Fe(II) REACTION†

Net activation process	Pattern 3-1-a			Pattern 3-1-b		
	ΔG^* , kJ/mol (kcal/mol)	ΔH^* , kJ/mol (kcal/mol)	ΔS^* , J/mol · K (cal/mol · deg)	ΔG^* , kJ/mol (kcal/mol)	ΔH^* , kJ/mol (kcal/mol)	ΔS^* , J/mol · K (cal/mol · deg)
1. $\text{PuO}_2^{2+} + \text{Fe}^{2+} = [*]^{4+}$	55.4 (13.25)	16.0 ± 0.8 (3.83 ± 0.2)	-132 ± 3 (-31.6 ± 0.7)	55.9 (13.36)	20.5 ± 0.8 (4.91 ± 0.18)	-118 ± 3 (-28.3 ± 0.6)
2. $\text{PuO}_2^{2+} + \text{Fe}^{2+} = [*]^{4+}$	51.6 (12.34)	33.3 ± 1.3 (7.95 ± 0.31)	-62 ± 5 (-14.7 ± 1.1)	52.0 (12.44)	39.0 ± 1.9 (9.31 ± 0.46)	-44 ± 7 (-10.5 ± 1.6)
3. $\text{PuO}_2^{2+} + \text{Fe}^{2+} + \text{H}_2\text{O} = [*]^{3+} + \text{H}^+$	55.6 (13.28)	36.2 ± 2.2 (8.66 ± 0.52)	-65 ± 8 (-15.5 ± 1.8)	56.6 (13.54)	42.6 ± 2.0 (10.17 ± 0.48)	-47 ± 7 (11.3 ± 1.7)

† Values are for 25°C and $\mu = 2M(\text{LiClO}_4)$.

A plausible reaction sequence to explain the observations is

This scheme is similar to that proposed for the reduction of Np(V) by V(III), discussed in Sec. 3-4, but differs in that reaction 3.59 and the reverse of reaction 3.58 are relatively slow and appreciable concentrations of Np(III) build up. Since the usual steady-state approximation is not applicable, it is necessary to use two differential equations to describe the concentration changes that occur. These are

$$\begin{aligned} \frac{dx}{dt} = & k_{57}(A - x - y)(B - x - 2y) - k_{58}(x)(B - x - 2y) \\ & + 2k_{59}(A - x - y)(y) \end{aligned} \quad (3.60)$$

and

$$\frac{dy}{dt} = k_{58}(x)(B - x - 2y) - k_{59}(A - x - y)(y) \quad (3.61)$$

where A and B are the initial concentrations of Np(V) and Cr(II), respectively, and x and y are the instantaneous concentrations of Np(IV) and Np(III), respectively. These differential equations cannot be solved in closed form but are readily solved by numerical methods.

In principle the concentration-vs.-time data could be used to determine all three rate constants, but more-accurate values for k_{57} were obtained by using values for k_{58} and k_{59} which were determined in separate experiments. Values for k_{57} which best reproduce the observed data were found by use of a computer program that couples a Runge-Kutta method for solving Eqs. 3.60 and 3.61 to a nonlinear least-squares program.⁵¹

In this way values for k_{57} were determined for temperatures ranging from 5 to 25°C and for hydrogen-ion concentrations from 0.026M to 0.21M, all at a constant ionic strength of 0.21M made up with LiClO₄. In addition, k_{57} increases by a factor of 4.1 between ionic strengths of 0.11M and 1.01M. The reaction is markedly catalyzed by sulfate; as little as 10⁻³M in 0.11M HClO₄ at 17°C increases the rate by a factor of 4.7.

Like the rates of most other reactions in which an actinide AnO₂⁺ ion is reduced, the rate increases with increasing hydrogen-ion concentration. Graphs of log k_{57} vs. log [H⁺] give the empirical expression $k_{57} = k'[\text{H}^+]^n$, where the exponent varies from 0.76 to 0.86 depending on the temperature. This suggests that the major term in the rate law is first order in [H⁺] but that another term, due to an additional path or to a medium effect, is present also. Thus two rate laws were tested for consistency with the data:

$$\frac{d[\text{Np(IV)}]}{dt} = (k_a + k_b [\text{H}^+]) [\text{NpO}_2^+] [\text{Cr}^{2+}] \quad (3.62)$$

$$\frac{d[\text{Np(IV)}]}{dt} = (k_c [\text{H}^+] e^{\beta [\text{H}^+]}) [\text{NpO}_2^+] [\text{Cr}^{2+}] \quad (3.63)$$

All the hydrogen-ion- and temperature-dependence data were treated simultaneously to find the values of the heats and entropies of activation and the value of β and its temperature coefficient which best reproduce the observed values of k_5 . The results of these calculations are summarized in Table 3.9.

Table 3.9

ALTERNATE INTERPRETATIONS OF THE HYDROGEN-ION- AND TEMPERATURE-DEPENDENCE DATA FOR THE Cr(II)–Np(V) REACTION†

Parameter	Rate law 3.62	Rate law 3.63
$\Delta H_{b/c}^*$, kJ/mol (kcal/mol)	8 ± 3 (2.0 ± 0.7)	11 ± 2 (2.6 ± 0.4)
$\Delta S_{b/c}^*$, J/mol · K (cal/mol · deg)	-162 ± 10 (-39 ± 2.5)	-149 ± 6 (-35.7 ± 1.4)
ΔH_a^* , kJ/mol (kcal/mol)	32 ± 16 (8 ± 4)	
ΔS_a^* , J/mol · K (cal/mol · deg)	-116 ± 54 (-28 ± 13)	
β , M^{-1}		$-1.45 \pm 0.32_{\ddagger}$
Root-mean-square deviation, %	8.1	9.1

†The original authors used six adjustable parameters: ΔH_c^* , ΔS_c^* , and a different value for β for each of the four temperatures. This gives activation parameters very similar to those listed for rate law 3.63 and a root-mean-square deviation of about 9.5%.

‡Temperature dependence of β is taken as zero because the least-squares best value is $0.0053 \pm 0.0345 \text{ deg}^{-1}$, which is not statistically significant.

It is seen that the activation parameters for the predominant term, first power in $[\text{H}^+]$, do not depend significantly on which rate law is assumed. The rate law, Eq. 3.62, is preferred, however, because the value required for β in the rate law, Eq. 3.63, is about 10 times the reasonable upper limit discussed in Sec. 2-4.

The exchange of oxygen between NpO_2^+ and H_2O is fairly slow³³ and between $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and solvent water is very slow.⁶⁴ This means that it is possible to use ^{18}O tracer experiments to determine the fate of the coordinated oxygens when NpO_2^+ is reduced by Cr^{2+} , as in Eq. 3.57, which can be rewritten in terms of the species present as

Dry NpO_2ClO_4 in which the $^{18}\text{O}/^{16}\text{O}$ ratio was about 0.01 was prepared, dissolved in a small amount of ordinary water, and injected into less than the stoichiometric

amount of Cr^{2+} in dilute HClO_4 . The product $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ was separated as $\text{Cr}(\text{H}_2\text{O})_6\text{F}_3$. The water was removed from this salt and equilibrated with CO_2 for analysis using an isotope-ratio mass spectrometer. If the activated complex for reaction 3.64 is inner sphere, so that one of the neptunyl oxygens is coordinated to chromium, and if all the Cr^{3+} is produced by this reaction, then one-sixth of the water coordinated to the $\text{Cr}(\text{III})$ products will come from the NpO_2^+ . Two experiments in $1M$ HClO_4 gave values for the isotope ratio which were 0.90 ± 0.08 of that expected on this basis. A single experiment in $0.17M$ HClO_4 gave a value only 0.68 of that expected. This low value is undoubtedly caused by the fact that, although reaction 3.58 is relatively unimportant in $1M$ HClO_4 , the hydrogen-ion dependences are such that the ratio k_{57}/k_{58} is about 6.4 in $0.17M$ HClO_4 . Under these conditions an appreciable fraction of the $\text{Cr}(\text{III})$ is produced by reaction 3.58.

3-11

THE U(IV)–Cl(III) REACTION⁶⁵

The stoichiometry of the U(IV)–Cl(III) reaction is quite complicated. When U^{4+} and HClO_2 are mixed, the ratio $[\text{Cl(III)}]_{\text{consumed}}/[\text{U(IV)}]_{\text{consumed}}$ varies between 1.5 and 2.5 depending on the initial concentrations.⁶⁶ With an appropriate scavenger, such as phenol, the ratio becomes 1.0, however. These results are accounted for by the following reactions:

and

Separate experiments showed that reactions 3.66 and 3.67 are fast compared with 3.65; thus the net reaction is

Second-order rate constants, determined spectrophotometrically at the U(IV) peak at 648 nm, were found to be independent of initial phenol concentrations if these were greater than the initial U(IV) concentrations. Over wide ranges of reactant and hydrogen-ion concentrations the rate law was found to be

$$-\frac{d[\text{U(IV)}]}{dt} = \frac{k[\text{U(IV)}][\text{HClO}_2][\text{H}^+]^{-1}}{1 + K[\text{HClO}_2]} \quad (3.69)$$

Note that the total Cl(III) concentration is given by $[Cl(III)] = [HClO_2](1 + K_a [H^+]^{-1})$, where $K_a \approx 0.03M$ at $25^\circ C$ and $\mu = 2M$. Thus, in acid solutions greater than about $0.1M$, Cl(III) is predominantly $HClO_2$.

The denominator term in Eq. 3.69 suggests the possibility of consecutive reactions (pattern 2-1). Rearranging the equation gives

$$\left(-\frac{d[U(IV)]}{dt}\right)^{-1} = \frac{1}{k[U(IV)][HClO_2][H^+]^{-1}} + \frac{1}{kK^{-1}[U(IV)][H^+]^{-1}} \quad (3.70)$$

This equation implies that one activated complex is made from U(IV) and $HClO_2$ with the prior loss of one H^+ and that a second activated complex is made from only U(IV) with the loss of H^+ . Consistent with this, we would write

where $(UOH^{3+})^*$ is a reactive form of UOH^{3+} . Making the usual steady-state approximation with respect to its concentration, we readily derive the following rate law:

$$-\frac{d[U(IV)]}{dt} = \frac{(k_{72}k_{73}K/k_{-72})[U(IV)][HClO_2][H^+]^{-1}}{1 + (k_{73}/k_{-72})[HClO_2]} \quad (3.74)$$

which has the same form as Eq. 3.69, the observed rate law.

Before accepting this mechanism, which requires a "reactive form" of UOH^{3+} , we should note that the two-term denominator in Eq. 3.69 can arise also from the formation of significant concentrations of a U(IV)–Cl(III) complex. Consider the following mechanism:

$[U^{4+}]$ will equal $[U(IV)](1 + K_{76}[HClO_2])^{-1}$, and the rate law will be

$$-\frac{d[U(IV)]}{dt} = k_{77}K_{75}[U(IV)][HClO_2][H^+]^{-1}(1 + K_{76}[HClO_2])^{-1} \quad (3.78)$$

again in agreement with the observed rate law. The fact that two radically different mechanisms lead to the same rate law illustrates the necessity of knowing the

equilibria in a system before attempting a mechanistic interpretation. In this case a rapid increase in absorbance was observed at 360 nm when the reactants were mixed. This was probably a result of reaction 3.76 because, although Cl(III) is known to react with U(VI) to give a colored complex, only about 1% of the uranium used was in the form of the +6 oxidation state.

For either mechanism the principal net activation process is

The more plausible second mechanism was assumed, and the temperature-dependence data were used to evaluate the activation parameters: $\Delta H^* = 86.1 \pm 1.7$ kJ/mol and $\Delta S^* = 66.5 \pm 6.3$ J/mol · K.

Further information about the mechanism was gained by the use of ^{18}O -labeled HClO_2 . Efficient oxygen transfer to the product UO_2^{2+} was observed; an average of 0.76 ± 0.04 of an oxygen is transferred from the HClO_2 reactant to the UO_2^{2+} product. This implies an inner-sphere activated complex and a two-electron oxidation of U^{4+} to UO_2^{2+} since the one-electron intermediate, UO_2^+ , exchanges oxygen rapidly with the solvent.

3-12

THE U(IV)–Cr(VI) REACTION^{6,7}

The U(IV)–Cr(VI) reaction is particularly interesting because it shows how in certain circumstances we can learn more about a mechanism than is given by the rate law. If a reaction produces intermediates capable of reacting with substances other than the usual reactants or products, these reactions may provide important additional information. In the U(IV)–Cr(VI) reaction, although I^- reacts very slowly with HCrO_4^- and I_2 reacts very slowly with U(IV), significant amounts of I_2 are formed if I^- is present during the reaction between U(IV) and Cr(VI). This is an example of an induced reaction; other such reactions involving Cr(VI) and I^- are discussed in a review by Westheimer.^{6,8}

In the absence of I^- or other reducing agents, the stoichiometry of the U(IV)–Cr(VI) reaction is just what would be expected on the basis of the potentials:

In fact, standard volumetric methods of analysis are based on this reaction.

Important equilibria influencing the interpretation of the kinetics are the hydrolysis of U(IV),

and the acid dissociation of H_2CrO_4 ,

Other equilibria, such as $2\text{HCrO}_4^- = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ and $\text{HCrO}_4^- = \text{H}^+ + \text{CrO}_4^{2-}$, with equilibrium quotients of $98M^{-1}$ and $3 \times 10^{-7}M$, respectively, are not important in the solutions studied.

The reaction is quite rapid, and the rates were studied spectrophotometrically with a commercial stopped-flow apparatus.[†]

At a constant hydrogen-ion concentration, the rate law is

$$\frac{d[\text{U(IV)}]}{dt} = k'' [\text{U(IV)}] [\text{Cr(VI)}] \quad (3.83)$$

The second-order rate constant defined by this equation was determined over a wide range of $[\text{H}^+]$ (from $0.15M$ to $2.99M$) and was found to be given by

$$k'' = (0.86 + 8.83[\text{H}^+]^{-1}) \times 10^4 \left(1 + \frac{K_{81}}{[\text{H}^+]}\right)^{-1} \left(1 + \frac{[\text{H}^+]}{K_{82}}\right)^{-1} \quad (3.84)$$

The second and third terms are due to equilibria 3.81 and 3.82 and are relatively small because $K_{82} > [\text{H}^+] > K_{81}$. This rate law shows that the principal net activation process is

The fact that the stoichiometry for the formation of the activated complex does not correspond to that for the overall reaction shows that one or more intermediates are involved in the reaction. After the rate-determining step, these intermediates must react rapidly with the original reactants or with themselves to complete the overall reaction. Since iodide reacts rapidly with Cr(V), one of the possible intermediates, a study of the formation of I_2 gives additional information about the mechanism.

When the induction factor, the ratio (equivalents of I^- oxidized)/(equivalents of U(IV) oxidized), was measured, it was found to depend on the $[\text{U(IV)}]/[\text{I}^-]$ ratio. The induction factor approaches a limiting value of 2.0 as the stoichiometric ratio approaches zero.

[†]This apparatus uses a flow system consisting of syringes for the two reactants, an efficient mixing chamber, a flow-through absorption cell, and a receiving syringe for the mixed solution. In operation, solutions are rapidly ejected from the reactant syringes through the mixer and absorption cell and into the receiving syringe until it is filled. Flow is then stopped abruptly. At this moment an oscilloscope (or other rapid recorder) connected to the output of a phototube is triggered to display light absorption vs. time in the now stationary sample in the absorption cell.

A plausible scheme for the reactions that occur during the overall reaction might be.⁶⁸

Scheme 1

When Np(IV) or Pu(IV) is oxidized with Cr(VI), significant amounts of Cr(III) · Np(V) or Cr(III) · Pu(V) complexes are known to form.³² Therefore it is reasonable to expect the analogous U(V) complex to form in the second step and to react in the third. The fourth and fifth reactions in Scheme 1 show a competition for Cr(V). When $[\text{I}^-] \gg [\text{U(IV)}]$, the overall reaction would be

which gives a limiting induction factor of 0.5. Since the observed limiting factor is 2.0, the mechanism must be rejected.

Another possibility⁶⁷ might be

Scheme 2

For this scheme, when $[\text{I}^-] \gg [\text{U(IV)}]$, the stoichiometry is given by

which is in agreement with the observed induction factor. This mechanism requires that Cr(IV) react much faster with Cr(VI) than with U(IV). This is puzzling since Cr(IV) appears to react rapidly with either Np(IV) or Pu(IV), both of which are poorer reducing agents than U(IV). Also, there is some doubt⁶⁹ that the reaction between Cr(IV) and Cr(VI) occurs rapidly at all.

Another possibility, which avoids the objections mentioned, is

Scheme 3

This scheme has the same limiting stoichiometry as Scheme 2 and is in agreement with the observations. The intermediate Cr(IV) does not appear in Scheme 3, because the Cr(V) is postulated to be reduced directly to Cr(III) by U(IV) (or I⁻). The potentials suggest that this is much less likely for Np(IV) or Pu(IV); this is consistent with the apparent formation of Cr(IV) and the observation of significant concentrations of the Cr(III) · An(V) complexes when either Np(IV) or Pu(IV) is oxidized with Cr(VI).

Oxygen-18 transfer studies⁷⁰ have shown that under some circumstances up to 1.2 of the two oxygen atoms on the UO₂²⁺ product come from the HCrO₄⁻. One explanation for this involves a doubly oxygen-bridged activated complex for one of the steps in the mechanism. This efficiency of oxygen transfer also requires that, if U(V) is formed in a series of reactions such as those in Scheme 3, it must be consumed fairly rapidly. This follows from the fact that U(VI) exchanges its oxygens rapidly with the solvent water in the presence of U(V) (Ref. 71).

4 REACTIONS AMONG THE IONS OF URANIUM, NEPTUNIUM, AND PLUTONIUM

Reactions among the ions of uranium, neptunium, and plutonium are particularly interesting because they provide sets of formally similar reactions that differ only in the driving force, ΔG . Also, the reactions among the various oxidation states of the same element are important because they determine the stability of partially oxidized or reduced solutions of the element and often influence the course of reactions with other oxidizing or reducing agents.

The +7 states of neptunium and plutonium can be made in alkaline solution, either electrolytically or by the use of strong oxidizing agents such as ozone.⁷¹ They are extremely powerful oxidizing agents, especially in acid solutions, and are capable of rapid reaction with actinide ions in their lower oxidation states. The reaction between Pu(VII) and Np(VI) has been observed in 1 *M* NaOH (Ref. 72), but no quantitative information is available in acid solutions. Qualitative experiments in acid solutions have shown that Np(VII) reacts very rapidly with Pu(III) but at measurable rates with Pu(IV) (Ref. 73).

Excluding the +7 state, a variety of different reaction types are possible among actinide ions in the other four oxidation states. The simplest reactions involve the transfer of an electron without the making or breaking of metal–oxygen bonds. General equations for these reactions are

where An and An' represent uranium, neptunium, or plutonium. The directions in which these reactions proceed and the positions of the equilibria depend on the oxidation potentials of the individual ions involved (see Table 2.1). The only examples of reaction type 1 or 2 which have been studied thoroughly are the Pu^{3+} – Pu^{4+} (Ref. 74) and the NpO_2^+ – NpO_2^{2+} (Ref. 75) exchange reactions. A preliminary experiment has indicated that the PuO_2^+ – NpO_2^{2+} reaction is quite rapid.³²

In addition to these three reaction types, there are three others in which metal–oxygen bonds are formed or broken. These are

We will discuss the known examples of reaction types 3 to 6 after we consider the reactions for which both An and An' are plutonium.

The reactions among the plutonium ions are particularly noteworthy because the rates and equilibria are such that under many circumstances reactions of three different types are important simultaneously. To illustrate this, we will consider first the reaction between Pu^{3+} and PuO_2^+ in $1M\text{HClO}_4$. The individual reactions that must be considered are of types 3, 5, and 6. Written in terms of the oxidation states and without regard to hydrogen ions, they are

Reaction 4.2 is the most rapid of the three, and under most circumstances the system will be near equilibrium with respect to it at all times. Reaction 4.1 is significantly slower and is effectively rate determining. Reaction 4.3 is enough slower than 4.1 so that it is relatively unimportant. The system is governed by two simultaneous differential equations. To simplify the notation, we will use a Roman numeral for plutonium in the indicated oxidation state. A convenient pair of differential equations is

$$-\frac{d(\text{III})}{dt} = k_1(\text{III})(\text{V}) - k_{-1}(\text{IV})^2 + k_2(\text{III})(\text{VI}) - k_{-2}(\text{IV})(\text{V}) \quad (4.4)$$

$$-\frac{d(V)}{dt} = k_1(III)(V) - k_{-1}(IV)^2 - k_2(III)(VI) + k_{-2}(IV)(V) + 2k_3(V)^2 - 2k_{-3}(IV)(VI) \quad (4.5)$$

Rate constants applicable to 1M HClO₄ and 25°C were taken from Tables 4.1, 4.2, and 4.3, and the equations were solved numerically to give the concentrations of all the plutonium species as a function of time. Since the actual rates depend on the plutonium concentration, to make the results more general, we show in Fig. 4.1 a graph of relative concentration vs. τ , which is the time in seconds multiplied by the total plutonium concentration.

Although reaction 4.1 is essentially rate determining, the overall stoichiometry changes during the course of the reaction, depending on the extent and direction of reaction 4.2 as it rapidly approaches equilibrium. At the start there is a net production of Pu(III), and the stoichiometry is given by

As Pu(III) builds up, this stoichiometry changes, and, when its concentration reaches a maximum, the stoichiometry is given by Eq. 4.3. Soon after this the concentration of Pu(VI) reaches its maximum, and the stoichiometry is that of Eq. 4.1. Finally, near the end of the reaction when the Pu(V) is essentially gone, the stoichiometry is approximated by

An even more complicated example is illustrated in Fig. 4.2, which shows the behavior of a solution that is initially pure Pu(V). Again the calculation applies to 1M HClO₄ at 25°C. Initially, when [Pu(III)] = 0, reaction 4.3 is the only rate-determining step. It is followed by the rapid reverse of reaction 4.2 so that Pu(III) is formed by the overall net reaction Eq. 4.6. As Pu(III) builds up, reaction 4.1 rapidly becomes important, and, when τ is about 18.8 *M* sec, reactions 4.1 and 4.3 have equal rates. At this point the system is far from equilibrium, even with respect to reaction 4.2; its forward rate is only about 87% of the reverse rate. By 50 *M* sec, however, the forward and reverse rates agree within 1.7%, and from there on reaction 4.2 is essentially at equilibrium. As in the previous example, the stoichiometry changes during the course of the reaction and has integral values only when $d(III)/dt$ or $d(VI)/dt$ equals zero.

Only one example of a type 4 reaction has been reported. The oxidation of U⁴⁺ by NpO₂⁺ was found⁸⁸ to have the rate law $-d[U(IV)]/dt = k_8[U(IV)][Np(V)] + k_9[U(IV)][Np(IV)]$. This is consistent with a type 4 reaction,

and a type 5 reaction,

followed by the rapid oxidation of both Np(III) and U(V) by Np(V). Reaction 4.8 is quite slow, with an activation energy of 134 ± 8 kJ/mol and an apparent second-order rate constant of $8.3 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ in 0.1 M HClO_4 at 25°C . The Np(IV)–Np(V) exchange reaction might be expected to be type 4, but the observed rate law^{8,9} shows that this is not the case.

Data for the five reactions of type 3 which have been studied are listed in Table 4.1. The most important term in the individual rate laws is $k'[\text{An}^{3+}][\text{An}'\text{O}_2^{2+}][\text{H}^+]^0$. A lack of hydrogen-ion dependence is not surprising since the overall reactions do not involve hydrogen ions. However, the Pu(III)–Np(VI) and the Np(III)–U(VI) reactions show additional small terms inverse in $[\text{H}^+]$. This suggests the participation of hydrolyzed species, but why it is observed for these two reactions alone is not clear.

The free energies for the reactions range widely from -95 to $+9$ kJ/mol, and, in general, the rates decrease as the driving force for reaction decreases. This is shown in Fig. 4.3, where ΔG^* is plotted vs. ΔG . The rates for the two reactions involving UO_2^{2+} are unexpectedly large in that the points for these reactions fall below the line through the points for the other reactions.

The heats of activation for the five reactions are all quite low, ranging from 4.2 to 20 kJ/mol. The entropies of activation are negative as would be expected for reactions between ions of like sign. Except for the U(III)–U(VI) reaction, ΔS^* trends toward more positive values as ΔG increases.

Six of the nine possible reactions of type 5 have been studied, and the results are summarized in Table 4.2. The oxidation potentials are such that two of the plutonium reactions proceed in the direction opposite to the others. The rate constants and other activation parameters for these reactions have been recalculated for the reverse direction for comparison. On this basis all the reactions show a common term in their rate laws: $k[\text{An}^{3+}][\text{An}'\text{O}_2^+][\text{H}^+]^n$, where $n = 1$ —except for the Pu^{3+} – UO_2^+ reaction, where $n = 2$. The observed $[\text{H}^+]$ dependence suggests that the species $\text{HOAn}'\text{O}^{2+}$ is a reactive intermediate. It must be a strong acid, however, because no other evidence for its existence has been found.

The overall reduction of AnO_2^+ to An^{4+} requires four hydrogen ions to convert the two oxide ligands to water. Since the activated complex has a configuration that lies along the reaction path, it is reasonable that one or more of these hydrogen ions is required for the formation of the activated complex, as is observed. Interestingly, the reaction with the smallest driving force is the one for which $n = 2$. Also, the U^{3+} – UO_2^+ reaction, which has the largest driving force of the series, has a small term in the rate law for which $n = 0$. These results are consistent with the idea that, in a series of similar reactions, the activated complexes will more nearly resemble the reactants if the driving force is large but will tend to resemble the products if the driving force is small.

Table 4.1
TYPE 3 REACTIONS AMONG THE IONS OF URANIUM, NEPTUNIUM, AND PLUTONIUM†

Reaction	ΔG , kJ/mol (kcal/mol)	ΔH , kJ/mol (kcal/mol)	ΔS , J/mol·K (cal/mol·deg)	k'' , $M^{-1} \text{ sec}^{-1}$	ΔG^* , kJ/mol (kcal/mol)	ΔH^* , kJ/mol (kcal/mol)	ΔS^* , J/mol·K (cal/mol·deg)	Ref.
$\text{Np}^{3+} + \text{NpO}_2^{2+} =$	-94.8	-141.0	-157	1.05×10^5	44.4	4.2	-134	
$\text{Np}^{4+} + \text{NpO}_2^+ =$	(22.65)	(33.8)	(-37.6)		(10.6)	(1.0)	(-32)	76
$\text{U}^{3+} + \text{UO}_2^{2+} =$	-66.9	-112.5	-148	5.5×10^4	46.0	18.1	-93	
$\text{U}^{4+} + \text{UO}_2^+ =$	(-16.0)	(-26.9)	(-35.5)		(11.0)	(4.3 ± 0.2)	(-22.3 ± 0.6)	76
$\text{Pu}^{3+} + \text{NpO}_2^{2+} =$	-15.1	-60.7	-153	$35.5 +$	64.2	14.6	-166	
$\text{Pu}^{4+} + \text{NpO}_2^+ =$	(-3.6)	(-14.5)	(-36.6)	$3.1 [\text{H}^+]^{-1}$	(15.34)	(3.49)	(-39.7 ± 0.2)	77
$\text{Pu}^{3+} + \text{PuO}_2^{2+} =$	6.3	-35.6	-140	2.7	70.5	20.2	-169	
$\text{Pu}^{4+} + \text{PuO}_2^+ =$	(1.51)	(-8.5)	(-33.4)		(16.86)	(4.83 ± 0.1)	(-40.4 ± 0.3)	78
$\text{Np}^{3+} + \text{UO}_2^{2+} =$	8.9	-35.9	-151	$38.8 +$	64.0	10.9	-178	
$\text{Np}^{4+} + \text{UO}_2^+ =$	(2.13)	(-8.6)	(-36)	$1.4 [\text{H}^+]^{-1}$	(15.29)	(2.6 ± 0.16)	(-42.6 ± 0.6)	12

† Values are for 25°C and $\mu = 1 M$.

Table 4.2
TYPE 5 REACTIONS AMONG THE IONS OF URANIUM, NEPTUNIUM, AND PLUTONIUM†

Reaction	ΔG , kJ/mol (kcal/mol)	ΔH , kJ/mol (kcal/mol)	ΔS , J/mol·K (cal/mol·deg)	k'' , $M^{-1} \text{ sec}^{-1}$	μ , M	ΔG^* , kJ/mol (kcal/mol)	ΔH^* , kJ/mol (kcal/mol)	ΔS^* , J/mol·K (cal/mol·deg)	Ref.
$U^{3+} + UO_2^+ + 4H^+ =$ $2U^{4+} + 2H_2O$	-119.2 (-28.5)	-225 (-53.7)	-354 (-84.5)	$(0.9 + 4.7[H^+])10^5$ $(0.55 \pm 1.3[H^+])10^5$	1.0 0.2	40.6 (9.7) 43.9 (10.5)	8.4 ± 1.7 (2 ± 0.4) 7.5 ± 1.7 (1.8 ± 0.4)	-109 ± 5 (-26 ± 1.3) -121 ± 5 (-29 ± 1.3)	76 76
$Np^{3+} + NpO_2^+ + 4H^+ =$ $2Np^{4+} + 2H_2O$	-56.3 (-13.46)	-173 (-41.3)	-391 (-93.5)	$43[H^+]$ $15[H^+]$	2.0 1.0	63.7 (15.22) 66.1 (15.8)	24.7 ± 2 (5.9 ± 0.5) 24.7 ± 2 (5.9 ± 0.5)	-128 ± 8 (-31 ± 2) -138 ± 10 (-33 ± 2)	79 Estimate
$Np^{3+} + UO_2^+ + 4H^+ =$ $Np^{4+} + U^{4+} + 2H_2O$	-43.4 (-10.37)	-149 (-35.7)	-356 (-85.2)	$38[H^+]$	1.0	64.0 (15.29)	21.3 ± 1.7 (5.1 ± 0.4)	-143 ± 5 (-34.1 ± 1.2)	12
$Pu^{3+} + PuO_2^+ + 4H^+ =$ $2Pu^{4+} + 2H_2O$	-18.2 (-4.34)	-121 (-28.9)	-344 (-82.2)	$4.4 \times 10^{-2}[H^+]$	1.0	80.8 (19.3)	33.5 ± 0.5 (8.0 ± 0.1)	-158 ± 2 (-37.8 ± 0.4)	80
$Np^{4+} + Pu^{4+} + 2H_2O =$ $NpO_2^+ + Pu^{3+} + 4H^+$	-23.4 (-5.60)	92 (22.0)	387 (92.5)	$0.253[H^+]^{-3}$ $2.2 \times 10^{-5}[H^+]$	2.0 1.0	76.6 (18.3) 99.6 (23.8)	142 ± 6 (33.9 ± 1.5) 50 (11.9)	218 ± 21 (52 ± 5) -167 ± 21 (-40 ± 5)	81 ‡
$U^{4+} + Pu^{4+} + 2H_2O =$ $UO_2^+ + Pu^{3+} + 4H^+$	-36.4 (-8.69)	68.5 (16.4)	352 (84.2)	$34.4[H^+]^{-2}$ $1.9 \times 10^{-5}[H^+]^2$	2.0 1.0	64.3 (15.36) 100 (23.9)	102 ± 2.5 (24.3 ± 0.6) 33.1 (7.9)	126 ± 8 (30 ± 2) -216 ± 8 (52 ± 2)	82 ‡

† Values are for 25°C.

‡ An estimate for the reverse action.

Table 4.3
TYPE 6 REACTIONS AMONG THE IONS OF URANIUM, NEPTUNIUM, AND PLUTONIUM^a

Reaction	ΔG , kJ/mol (kcal/mol)	ΔH , kJ/mol (kcal/mol)	ΔS , J/mol·K (cal/mol·deg)	k'' , $M^{-1} \text{ sec}^{-1}$	μ , M	ΔG^* , kJ/mol (kcal/mol)	ΔH^* , kJ/mol (kcal/mol)	ΔS^* , J/mol·K (cal/mol·deg)	Ref.
1. $U^{4+} + NpO_2^{2+} + 2H_2O =$ $UO_2^{2+} + NpO_2^{2+} + 4H^+$	-51.4 (-12.3)	7.9 (1.9)	199 (48)	$21.3[H^+]^{-1}$	2	67.2 (16.05)	76 ± 1 (18.2 $\pm$ 0.2)	31 ± 3 (7.4 $\pm$ 0.8)	83
2. $Np^{4+} + NpO_2^{2+} + 2H_2O =$ $2NpO_2^{2+} + 4H^+$	-38.5 (-9.2)	31.4 (7.5)	234 (56)	$0.043[H^+]^{-2} +$ $1.2 \times 10^{-3}[H^+]^{-3}$	2	80.8 (19.3)	105 ± 2.5 (25 $\pm$ 0.6)	82 ± 8 (19.5 $\pm$ 2)	84 ^b
3. $U^{4+} + PuO_2^{2+} + 2H_2O =$ $UO_2^{2+} + PuO_2^{2+} + 4H^+$	-30.0 (-7.18)	33 (7.9)	213 (51)	$\{(4.35[H^+]^{-1})^{-1} +$ $(11.25[H^+]^{-2})^{-1}\}^{-1}$	2	69.5 (16.6)	73.6 ± 0.4 (17.6 $\pm$ 0.1)	15 ± 2 (3.6 $\pm$ 0.4)	85 61
4. $Np^{4+} + PuO_2^{2+} + 2H_2O =$ $NpO_2^{2+} + PuO_2^{2+} + 4H^+$	-17.1 (-4.09)	56.5 (13.5)	247 (59)	$5 \times 10^{-3}[H^+]^{-2}$	2	85.3 (20.4)	133 ± 18 (32 $\pm$ 4.4)	162 ± 62 (39 $\pm$ 15)	87 ^b
5. $Pu^{4+} + PuO_2^{2+} + 2H_2O =$ $2PuO_2^{2+} + 4H^+$	24.5 (5.85)	85.3 (20.4)	204 (49)	$1.2 \times 10^{-7}[H^+]^{-3}$ $3.6 \times 10^{-3}[H^+]^e$	2	112.5 (26.9)	164 (39.2) ^a	172 (41) ^b	d
6. $U^{4+} + UO_2^{2+} + 2H_2O =$ $2UO_2^{2+} + 4H^+$	52.3 (12.5)	112 (26.8)	205 (49)	$6.6 \times 10^{-8}[H^+]^{-3}$ $240[H^+]^e$	2	87.0 (20.8)	79 ± 11 (19 $\pm$ 2.6)	25 ± 38 (-6 $\pm$ 9)	86
					2	114.1 (27.0)	158 (37.8)	151 (36)	d
					2	59.8 (14.3)	46 ± 2 (11 $\pm$ 0.4)	-46 ± 6 (-11 $\pm$ 1.5)	20

^aValues are for 25°C.

^bRecalculated from the original data.

^cFor the second term in the rate law.

^dCalculated from the reverse action.

^eThe reaction was measured in the opposite direction, with this result.

Fig. 4.1 The course of the Pu(III)–Pu(V) reaction in 1 M HClO₄ at 25°C.

This same argument can be used to rationalize the observation that the ΔS^* values become more positive as the ΔG^* values decrease. The overall reactions show large decreases in entropy as highly charged +4 ions are formed from ions of lesser charges. Lower values of ΔG^* (and ΔG) imply smaller reorganization of the reactant ions toward the product ions and hence less negative ΔS^* values than for the reactions with larger ΔG^* values.

The reaction rates vary widely, by a factor of about 10^{10} , but depend primarily on the driving force. This is shown in Fig. 4.4, where ΔG^* is plotted vs. ΔG . The value for the Pu^{3+} – UO_2^+ reaction, shown as a Δ in the figure, lies below the function through the other points. This is as expected because the hydrogen-ion dependence is different. For this reaction ΔG^* for the undetected term in the rate law which is first power in $[\text{H}^+]$ should be at least 8 kJ/mol greater than the value for the observed term.

Although it is not known whether the mechanism of these reactions should be classed as inner sphere or outer sphere, it is interesting to apply Marcus's cross relation (Eq. 2.8) to the data since most of the assumptions on which it is based might be expected to apply to either case. The work required to bring the ions to reaction distance, the work terms in Eq. 2.8, are usually quite small, but for these reactions they must include the work of forming the presumed intermediates, HOAnO^{2+} and HOAnO^+ . A reasonable estimate for the total of these terms lies between 20 and 40 kJ/mol. If Eq. 2.8 is used as a semi-empirical function to describe the data, the best values for the parameters are $\Delta G_1^* + \Delta G_2^* = 176 \pm 4$ kJ/mol and

Fig. 4.2 The course of the disproportionation of Pu(V) in 1 M HClO₄ at 25°C.

$w_{11} + w_{22} = 12 \pm 40$ kJ/mol. The line in Fig. 4.4 was drawn using these parameters. Since the large uncertainty in the work-term parameter includes all reasonable estimates for its value, the Marcus expression is physically reasonable. It should be emphasized, however, that this agreement is not proof that these type 5 reactions proceed by an outer-sphere mechanism.

The results for type 6 reactions are summarized in Table 4.3. The last two reactions, with positive ΔG values, were measured in the opposite direction but have been recalculated for comparison with the others. The rate laws for all the reactions were found to be first power in each actinide ion, but different hydrogen-ion dependences were observed. Since terms in the rate laws showed hydrogen-ion dependences ranging from -1 to -3 , the net activation processes can be written

with $n = 1, 2$, and 3 . In addition, the $\text{U}^{4+} - \text{PuO}_2^{2+}$ reaction occurs by consecutive rate-determining steps (the 2-1 pattern described in Fig. 2.1 and Sec. 2-3). The observed hydrogen-ion dependences, or the number of hydrogen ions released when

Fig. 4.3 ΔG^* vs. ΔG for type 3 reactions: $An^{3+} + AnO_2^{2+} = An^{4+} + AnO_2^+$.

Fig. 4.4 ΔG^* vs. ΔG for type 5 reactions: $An^{3+} + AnO_2^+ + 4H^+ = An^{4+} + An^{4+} + 2H_2O$.

the activated complex is formed, shows a rough dependence on ΔG . The reaction with the largest driving force shows an inverse first-power dependence, but the two reactions with the smallest driving forces are inverse third power in $[H^+]$.

Figure 4.5 shows a graph of ΔG^* vs. ΔG for six type 6 reactions that have been studied carefully. In addition, a preliminary value⁷⁷ for the $Pu^{4+}-NpO_2^{2+}$ is shown.

Fig. 4.5 ΔG^* vs. ΔG for type 6 reactions: $An^{4+} + AnO_2^{2+} + 2H_2O = AnO_2^+ + AnO_2^+ + 4H^+$, where n on the figure is the number of H^+ released in the net activation process.

Three separate lines were drawn to distinguish among the reactions with different hydrogen-ion dependences. Because they are based on rate constants with different dimensions, the ΔG^* values for the different dependences are not comparable. For $n = 1, 2$, and 3 , the dimensions are sec^{-1} , $M \text{ sec}^{-1}$, and $M^2 \text{ sec}^{-1}$, respectively. Thus, except for $n = 1$, the numerical values of ΔG^* depend on the concentration units employed, and meaningful intercomparisons are difficult.

Within groups with the same values for n , the effect of ΔG on ΔG^* is smaller than that shown by the type 3 and type 5 reactions. A possible explanation is that the rate-determining step in the type 6 reactions is the formation of an inner-sphere complex (step 3 in the general mechanism given in Sec. 2-2) rather than the electron transfer itself. The conclusion that the $U(IV)-Pu(VI)$ reaction involves two consecutive rate-determining steps is consistent with this idea if the first step involves substitution and electron transfer occurs in the second step. This would also explain the fact that the point for $n = 2$ for this reaction is not in agreement with the other points with $n = 2$. In this connection we should note that consecutive rate-determining steps were shown to be consistent with the hydrogen-ion dependence observed for the disproportionation of UO_2^+ , the reverse of the $U^{4+}-UO_2^{2+}$ reaction.

5 EFFECTS OF SELF-IRRADIATION IN PLUTONIUM SOLUTIONS

The most common isotope of plutonium, ^{239}Pu , emits alpha particles with an average energy of about 5.15 MeV and a half-life of 24,360 years. For plutonium in solution this amounts to the deposition of energy at a rate of 0.401 eV per day per atom of plutonium. Alpha radiation ionizes water in dense tracks, probably producing H_2O^+ and e^- initially; in acid solutions these are equivalent to the radicals H and OH . In the tracks these radicals can recombine, react to give the molecules H_2 and H_2O_2 , or diffuse out into the bulk of the solution. Interaction between the radiation and various solutes will be relatively unimportant because their concentrations will usually be much less than the concentration of water. The reaction between H_2O_2 and OH in the alpha-particle tracks probably produces an additional species, the radical HO_2 . In addition, various solutes can probably react with radicals in the tracks.

The yields of the various species that diffuse out of the radiation tracks are expressed by the symbol G in units of molecules (or radicals) per 100 eV absorbed. For alpha radiation of about 5 MeV, the yields of the most important species are: $G_{\text{H}_2} \approx 1.6$, $G_{\text{H}_2\text{O}_2} \approx 1.35$, $G_{\text{H}} \approx 0.6$, $G_{\text{OH}} \approx 0.4$, and $G_{\text{HO}_2} \approx 0.22$ (Ref. 90).

The observed radiolytic effects depend on the reactions of the plutonium ions and other solutes with the radicals H , OH , and HO_2 , as well as with H_2O_2 . Since all these radiolytic species are capable of reacting as either oxidizing or reducing agents depending on conditions, it is not surprising that the resulting chemistry is quite complicated.

In HClO_4 solutions both Pu(VI) and Pu(IV) are reduced at rates such that the mean oxidation number, $\overline{\text{ox}}$,† decreases by 0.013 (Refs. 91, 92) to 0.015 (Ref. 93) per day. These values correspond to radiolytic yields from $G = 3.2$ to $G = 3.7$ atom equivalents (at. eq.) per 100 eV. The lower of these values is in good agreement with the value for the reduction of Ce(IV) in $0.8N \text{ H}_2\text{SO}_4$, where $G = 3.2$ for irradiation by alpha particles from polonium. This result is consistent with the reasonable assumption that H_2O_2 , HO_2 , and H are acting as reducing agents while OH acts as an oxidizing agent.⁹⁰

The alpha-particle reduction rates for ^{239}Pu are essentially independent of temperature between 5 and 45°C and independent of HClO_4 concentration between $0.1M$ and $3.0M$ (Refs. 91, 93). The rates are also independent of plutonium concentration and initial oxidation number as long as $\overline{\text{ox}}$ is greater than about 3.1. Apparently Pu(V) is not reduced significantly by radiolytic species but disappears by disproportionation reactions.⁸⁶ Essentially the same G values for reduction were observed with much higher dose rates obtained by dissolving small amounts of ^{210}Po in the solutions.⁹² Thus the radiolytic yields are apparently independent of alpha dose rates and can be applied to other isotopes of plutonium with different half-lives. It should be noted, however, that for the analogous autoreduction of Np(VI) a G value of 6.4 atoms reduced per 100 eV was observed.⁹⁴ This large value was attributed to the fact that relatively high concentrations of neptunium were used ($0.044M$ to $0.304M$) so that reduction was occurring in the tracks, presumably reducing the hydrogen yield. This cannot be the complete explanation, because the reduction rate in a $0.04M \text{ Pu(IV)}$ solution corresponded to $G = 3.5$ atoms reduced per 100 eV.

On long standing, plutonium solutions in HClO_4 reach a steady state in which the rate of reduction of Pu(IV) equals the rate of oxidation of Pu(III) . At 4°C the mean oxidation number was found to depend slightly on the total plutonium concentration, being 3.05 in $0.022M$ solutions and 3.016 in $0.0055M$ solutions. The steady-state H_2O_2 concentrations under these conditions were found to be $1.2 \times 10^{-3}N$ and $0.93 \times 10^{-3}N$, respectively. Under these steady-state conditions, there is a net decomposition of water and some decomposition of ClO_4^- . Radiolytic yields in $1M \text{ HClO}_4$ at 23°C were $G_{\text{H}_2} = 0.4$ molecules of H_2 per 100 eV and $G_{\text{ClO}_4^-} = 0.44$ molecules of O_2 from ClO_4^- per 100 eV. Chloride ion was detected in the solutions,⁹³ and ClO_3^- might possibly be produced also.⁹⁵

The reduction of Pu(VI) in H_2SO_4 solutions is similar to that in HClO_4 in that the G values are essentially the same (3.2). Important differences are that Pu(V) is not observed and the reduction stops at Pu(IV) (Ref. 92). This is consistent with the fact that H_2O_2 oxidizes Pu(III) rapidly to Pu(IV) in H_2SO_4 . Apparently no experiments have demonstrated the alpha oxidation of Pu(III) in H_2SO_4 although this has been observed under gamma irradiation.⁹² Other effects of gamma and X irradiation have been summarized in a recent book by Cleveland.²⁷

†The mean oxidation number is defined by the equation $\overline{\text{ox}} = \{3[\text{Pu(III)}] + 4[\text{Pu(IV)}] + 5[\text{Pu(V)}] + 6[\text{Pu(VI)}]\} / [\Sigma \text{Pu}]$.

Early work in HCl solutions indicated that alpha-reduction rates were 0.2 to 0.7 as great as in HClO₄ solutions.⁹¹ More-recent work⁹³ has indicated essentially zero reduction rates for Pu(VI) and Pu(IV) in 1M HCl. Mixed solutions of HCl and HClO₄ at constant acidity show that even low concentrations of chloride reduce the rates significantly. This is illustrated in Table 5.1.

Table 5.1
ALPHA REDUCTION RATES IN 1M HCl-HClO₄
MIXTURES AT 25° C (Ref. 93)

[Cl ⁻], M	0.00	0.10	0.20	0.40	0.80	1.00
-d(δx)/dt, day ⁻¹	0.014	0.0084	0.007	0.004	0.0015	0.00
G, at. eq./100 eV	3.5	2.1	1.7	1.0	0.37	0.0

At a constant chloride concentration of 0.1M, the reduction rate was found to be essentially independent of total acidity between 0.5M and 2M, but at higher acidities the rate dropped slightly. In 0.8M HCl-2.2M HClO₄, an initial oxidation due to the alpha irradiation was observed. In 3M HCl solutions significant amounts of chlorine were produced, and the G value was found to be 0.96 molecule of Cl₂ per 100 eV. Bromide ion, 0.1M in 1M HClO₄, was also observed to lead to an increase in ox with time in Pu(III)-Pu(IV) mixtures.⁹³

The radiation chemistry of plutonium in nitrate solutions has been discussed extensively in a review by Miner and Seed,⁹⁶ so only a brief summary will be given here.

In solutions containing HNO₃ or the nitrate ion, the effect of alpha irradiation is more complicated than in H₂SO₄ or HClO₄ solutions because of the formation of HNO₂ and oxides of nitrogen. This probably accounts for the fact that different observers have reported different results and that inhibition periods are often observed.⁹⁶ Russian chemists⁹⁷ have observed initial rates of disappearance of Pu(VI) equal to about 0.016 per day in 0.05M NaNO₃ solution with pH values of either 2 or 4.7. In 0.4M HNO₃, however, the rate of reduction of Pu(VI) was essentially zero at the start and increased slowly for about 20 days; finally -d(δx)/dt became constant at about 0.017 per day. This final rate agrees with that observed at higher pH values and is only slightly higher than the rates observed in HClO₄ and H₂SO₄ solutions. It should be noted that other workers have observed longer inhibition periods.^{92,98}

Increasing the nitrate concentration at a constant pH of 3 increases the rates significantly; a rate of 0.016 per day was found in 0.05M NaNO₃ and 0.033 per day in 5M NaNO₃. These rates correspond to G values of 4 and 8 at. eq./100 eV, respectively. The higher value is consistent with the idea that decomposition products from NO₃⁻ play an important role.

6 REACTIONS OF AMERICIUM IONS

The kinetics of aqueous americium reactions are difficult to study because the experimental observations tend to be dominated by radiation effects. Since even the two most stable isotopes of americium, ^{241}Am and ^{243}Am , have relatively short half-lives (433 and 7370 years, respectively), intense alpha-particle self-irradiation occurs in solution.

The formulas and potentials of the americium ions are given in Table 2.1. As shown in the table, the hydrated Am^{4+} ion is very unstable in the absence of strong complexing agents and is relatively stable only in concentrated fluoride solutions,⁹⁹ concentrated phosphoric acid, or pyrophosphate solutions.¹⁰⁰

The few oxidation–reduction reactions of americium which have been studied quantitatively are discussed here, but, since the effects of radiation are so important, they are discussed first.

6-1

RADIOLYTIC EFFECTS

Radiolytic effects for americium are similar to those discussed previously for plutonium but are more pronounced. Solutions of Am(III) , unlike those of Pu(III) , are stable with respect to oxidation induced by alpha radiation. This is almost certainly due to the fact that the higher oxidation states of americium are much better oxidizing

agents than are those of plutonium. The net reactions in Am(III) solutions are the decomposition of water and the production of hydrogen peroxide. Production of H_2O_2 depends on the acidity and, in 0.1M and 1.0M H_2SO_4 solutions, corresponds to 1.2 and 0.7 molecules per 100 eV absorbed in the solution.¹⁰¹ For ^{241}Am these two values mean that the increase in H_2O_2 concentration per hour will be about 1.2 and 0.7% of the total concentration of the americium in solution.

The reduction of solutions of $^{241}\text{Am(VI)}$ occurs in two distinct stages. First Am(VI) reduces to Am(V), and, when the Am(VI) is essentially gone, Am(V) reduces to Am(III). Since Am(VI) does not react with Am(III) and reacts relatively slowly with Am(IV), the presence of distinct stages means that Am(VI) reacts with the radiolytically produced reducing agents about 100 times faster than Am(V) does. This conclusion is consistent with the fact that H_2O_2 reacts very rapidly with Am(VI) (Ref. 102) but quite slowly with Am(V) (Ref. 106).

The net reduction rate, or the change in the average oxidation number, $(\overline{\text{ox}})$, with time, depends primarily on the total concentration of ^{241}Am in solution, to a lesser extent on the concentrations and nature of the acid present, and practically not at all on the relative amounts of americium in the various oxidation states. Several sets of data indicate that the net reduction rate is a few percent lower in the second stage than in the first, however.^{101,103,104} Typical results from three investigations, in terms of $d(\overline{\text{ox}})/dt$, are summarized in Table 6.1. The significantly larger values for the reduction-rate constant in HNO_3 solutions suggest that the alpha particles react directly with HNO_3 and/or the radicals react with HNO_3 to produce species that change the mechanism.

Table 6.1
REDUCTION OF ^{241}Am SOLUTIONS (k VALUES)^a

Reaction	Acid	Acid concentration, M					
		0.1	0.2	1.0	2.0	4.0	6.0
Am(VI) → Am(V)	HClO ₄		0.0404 ^b 0.031 ^d 0.044 ^{d,e}	0.058 ^c	0.032 ^b	0.032 ^b	0.034 ^b
	H ₂ SO ₄	0.0404 ^b		0.0285 ^b	0.025 ^b	0.0202 ^b	0.0180 ^b
	HNO ₃			0.075 ^{b,f}		0.086 ^b	0.087 ^b
Am(V) → Am(III)	HClO ₄		0.024 ^d	0.046 ^c	0.028 ^{b,e}		
	H ₂ SO ₄	0.032 ^c		0.026 ^{b,e}			

^aReduction rate constant is defined by $k = (-d(\overline{\text{ox}})/dt)/[\text{Am}]_{\text{total}} \text{ hr}^{-1}$.

^bRef. 101.

^cRef. 103.

^dRef. 104.

^eFrom graph in Ref. 101.

^fBy interpolation.

The alpha reduction rates given in the table are reasonable in magnitude. For example, Ce(IV) in 0.4M H₂SO₄ irradiated with alpha particles from polonium undergoes reduction at the rate of 3.2 atoms per 100 eV absorbed.⁹⁰ The analogous reduction of Am(VI) gives a value (by interpolation) of about 3.5 atoms per 100 eV. Since the agreement is satisfactory, we conclude that Am(VI) and Ce(IV) react in much the same way upon radiolysis of their solutions.

6-2

REACTION RATES

Most of the common reducing agents have been observed to react rapidly with either Am(V) or Am(VI), but very few quantitative data are available. Similarly, qualitative observations show that a variety of strong oxidizing agents react rapidly with Am(III) or Am(V). The various qualitative observations have been summarized by Gourisse.¹⁰⁵ Quantitative kinetic data are available for only five oxidation-reduction reactions of americium; these are discussed in the following sections.

6-3

THE Am(V)-H₂O₂ REACTION¹⁰⁶

Since H₂O₂ is one of the observed products of the radiolysis of water, we need to know its rate of reaction with Am(V) and Am(VI). Reaction with Am(VI) is very fast, but reaction with Am(V) is quite slow (experiments were done in 0.1M HClO₄ with ²⁴¹Am). The rate law is

$$-\frac{d[\text{Am(V)}]}{dt} = k[\text{AmO}_2^+][\text{H}_2\text{O}_2] \quad (6.1)$$

Unfortunately the hydrogen-ion dependence was not determined. The observed rate constants were 14.8 ± 1.5 , 21.6 ± 2.2 , and $30.3 \pm 3.0 \text{ M}^{-1} \text{ hr}^{-1}$ at 25, 30, and 35°C, respectively. These values lead to an activation energy of $55 \pm 9 \text{ kJ/mol}$. The H₂O₂ concentrations chosen were large enough (0.0137M to 0.040M) so that the alpha reduction of the Am(V) amounted to less than 10% of the observed reduction. However, the apparent second-order rate constants were observed to increase as the reaction proceeded in accordance with the known rate of alpha reduction. Correction for this effect will reduce the reported rate constants by about 10%.

Thus the direct reaction between Am(V) and H₂O₂ is too slow to be important in the alpha-radiation-induced reduction of Am(V) (Ref. 101) even though about 75% of the radiolytically produced reducing equivalents are H₂O₂ (Ref. 90). The H₂O₂ is

probably consumed by reaction with Am(IV) or with Am(VI), which is produced by the rapid reaction between Am(IV) and Am(V).

6-4

THE Am(VI)—H₂O₂ REACTION

The reaction between Am(VI) and H₂O₂ (Ref. 102a) was studied with ²⁴³Am and stopped-flow techniques. At 25°C in 1M (H,Li)ClO₄, the rate is first power in both Am(VI) and H₂O₂ but shows a small inverse hydrogen-ion dependence:

$$-\frac{d[\text{Am(VI)}]}{dt} = k[\text{AmO}_2^{2+}][\text{H}_2\text{O}_2][\text{H}^+]^{-0.12} \quad (6.2)$$

The rate constant, *k*, is $(3.91 \pm 0.06) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$. The hydrogen-ion dependence may indicate either a medium effect or a small contribution from a parallel path. The analogous reactions between H₂O₂ and either Np(VI) (Ref. 58) or Pu(VI) (Ref. 60) are predominantly inverse first power in [H⁺]. This difference in the hydrogen-ion dependences is consistent with the fact that Am(VI) is a much better oxidizing agent than either Np(VI) or Pu(VI). (See Chap. 4, p. 47.)

The rate constant given here can be used to estimate an upper limit for the steady-state concentration of H₂O₂ present during the alpha reduction of solutions of ²⁴¹Am(VI). Using the data from Table 6.1 for 1M HClO₄ and the limiting assumption that all the Am(V) is formed by reaction with H₂O₂, we can write: $(0.058 \text{ hr}^{-1}) [\text{Am(VI)}] = (3.9 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}) (3600 \text{ sec hr}^{-1}) [\text{Am(VI)}] [\text{H}_2\text{O}_2]$ and $[\text{H}_2\text{O}_2] \leq 4 \times 10^{-10} \text{ M}$.

6-5

OXIDATION OF Am(III) AND Am(V) BY PEROXYDISULFATE

Since peroxydisulfate is a useful reagent for preparing Am(V) or Am(VI) from Am(III), it is important to understand the kinetics of the reactions involved. The reactions apparently involve radicals such as SO₄^{•−}, SO₄[•], and HO[•] and are quite complicated. Two separate studies have given varying results in different Am(III) concentration ranges.

Russian investigators¹⁰⁷ studied the reactions in HNO₃ solutions using millimolar concentrations of the long-lived ²⁴³Am so that radiolytic effects were negligible. The stoichiometries of the reactions are presumably

and

Simultaneous decomposition of $\text{S}_2\text{O}_8^{2-}$ is also possible, but apparently this was not investigated. The oxidations of both Am(III) and Am(V) show three stages: (1) a short induction period, (2) a region of constant rate, if $\text{S}_2\text{O}_8^{2-}$ is in excess, and (3) a region of decreasing rate. The effects of initial concentrations of americium, $\text{S}_2\text{O}_8^{2-}$, and HNO_3 were determined for the predominantly linear parts of the reactions. Even though the ionic strength of the solutions was not held constant, the results can be summarized by the following fairly simple rate equations:

$$-\frac{d[\text{Am(III)}]}{dt} = (a - b[\text{H}^+])[\text{S}_2\text{O}_8^{2-}] [\text{Am(III)}]^0 \quad (6.5)$$

and

$$-\frac{d[\text{Am(V)}]}{dt} = (a' - b'[\text{H}^+])[\text{S}_2\text{O}_8^{2-}] [\text{Am(V)}]^0 \quad (6.6)$$

The rate parameters for 50.6°C are $a = 4.9 \times 10^{-5} \text{ min}^{-1}$, $b = 0.9 \times 10^{-4} M^{-1} \text{ min}^{-1}$, $a' = 15 \times 10^{-5} \text{ min}^{-1}$, and $b' = 2.7 \times 10^{-4} M^{-1} \text{ min}^{-1}$. Note that the americium dependences are zero and that the corresponding parameters for the two reactions differ by factors of almost exactly three. These observations indicate that Am(III) and Am(V) do not react directly with $\text{S}_2\text{O}_8^{2-}$ but do react rapidly with a constant fraction of the intermediates in the thermal decomposition of $\text{S}_2\text{O}_8^{2-}$. The unusual H^+ dependence, valid only when a is greater than $b[\text{H}^+]$, is consistent with a plausible mechanism based on that proposed for the thermal decomposition of $\text{S}_2\text{O}_8^{2-}$ (Ref. 108). The rate law for this decomposition is

$$-\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = (k_1 + k_2[\text{H}^+])[\text{S}_2\text{O}_8^{2-}] \quad (6.7)$$

The acid-independent term is thought to involve the radicals SO_4^- and HO , which are oxidizing agents. The acid-dependent term involves SO_4^+ , which can form the reducing agent H_2O_2 by the reaction $\text{SO}_4^+ + \text{H}_2\text{O} = \text{SO}_3 + \text{H}_2\text{O}_2$ (Ref. 108). Thus, at an acid concentration at which the production of oxidizing agents equals the production of reducing agents, the net rate of oxidation of americium will be zero, as indicated by Eqs. 6.5 and 6.6. At 50.6°C , k_1 is about $6.6 \times 10^{-5} \text{ min}^{-1}$ (Ref. 108), and, if the intermediates for this path react quantitatively with Am(III) , the stoichiometry will be given by Eq. 6.3 and the parameter a will be $\frac{2}{3} k_1$, or 4.4×10^{-5} , in satisfactory agreement with the observed value of $4.9 \times 10^{-5} \text{ min}^{-1}$. The rate parameter b should

be less than $\frac{2}{3}$ of k_2 because not all the $\text{SO}_4^\cdot$ formed produces H_2O_2 . The data indicate that only relatively small amounts of H_2O_2 are produced since k_2 is about $2.5 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}$ at 50°C in a solution with an ionic strength of $0.7M$ (Ref. 108) and b is only $9 \times 10^{-5} \text{ M}^{-1} \text{ min}^{-1}$ under similar conditions.

In carbonate solutions it was found¹⁰⁹ that the oxidation of Am(III) to Am(V) depends on the decomposition of $\text{S}_2\text{O}_8^{2-}$ and is independent of the concentration of americium or CO_3^{2-} . The oxidation of Am(V) to Am(VI), however, was shown to be directly proportional to the concentrations of americium and $\text{S}_2\text{O}_8^{2-}$ but inversely proportional to the K_2CO_3 concentration.

The Japanese investigators¹¹⁰ studied the oxidation of $^{241}\text{Am(III)}$ using micromolar concentrations. Unreacted Am(III) was determined radiometrically with a lanthanum fluoride precipitation technique. A typical $[\text{S}_2\text{O}_8^{2-}]$ -to- $[\text{Am(III)}]$ ratio was about 5000, and the rate of oxidation of Am(III) was less than 1% of the rate of decomposition of the $\text{S}_2\text{O}_8^{2-}$. Under these conditions the concentration of Am(III) is too low for efficient scavenging of the radicals and the rate is first power in $[\text{Am(III)}]$ as well as in $[\text{S}_2\text{O}_8^{2-}]$. Silver ion catalyzes the decomposition of $\text{S}_2\text{O}_8^{2-}$ and also the rate of the oxidation of Am(III). At low concentrations of Ag^+ (less than about 3×10^{-4}) and at constant $[\text{H}^+]$ and ionic strength, the rate law is

$$-\frac{d[\text{Am(III)}]}{dt} = (k_1 + k_2 [\text{Ag}^+])[\text{S}_2\text{O}_8^{2-}] [\text{Am(III)}] \quad (6.8)$$

At 50°C in $0.06M$ HNO_3 solutions with an ionic strength of $0.5M$ (NaNO_3), $k_1 = 0.093 \text{ M}^{-1} \text{ min}^{-1}$ and $k_2 = 420 \text{ M}^{-2} \text{ min}^{-1}$. The activation energies associated with the two rate constants are 139 ± 6 and $72 \pm 2.5 \text{ kJ/mol}$, respectively.[†] The activation energy for the uncatalyzed decomposition of $\text{S}_2\text{O}_8^{2-}$ is 142 kJ/mol . The close agreement means that the fraction of the radical intermediates that react with Am(III) is essentially independent of temperature.

The effect of hydrogen-ion concentration is similar to that observed with higher americium concentrations. The rate decreases as $[\text{H}^+]$ increases (becoming zero at $0.4M$), increases with decreasing $[\text{H}^+]$, and becomes constant at about $0.06M$.

6-6

DISPROPORTIONATION OF Am(V)

The oxidation potentials in Table 2.1 indicate that Am(V) is unstable with respect to disproportionation into Am(III) and Am(VI) according to

[†]These values have been recalculated from k vs. T data in the original article.¹¹⁰ The value reported there for the k_1 path (120 kJ/mol) is clearly in error.

In addition, if ^{241}Am is used, alpha reduction will also occur. Early experiments with this isotope in HCl (Ref. 111), HNO_3 (Ref. 106), HClO_4 (Refs. 11, 104, 106, and 112), and H_2SO_4 (Ref. 106) showed that reaction 6.9 occurs at measurable rates in acid solutions greater than about $2M$. In addition, some of the data indicate that less Am(VI) is formed than is required by the equation. The rate of disappearance of Am(V) was found to be proportional to the square of its concentration and to approximately the fourth power of the acid concentration. An exact interpretation of these experiments is difficult because in most cases the alpha-reduction rate was approximately equal to the rate of disproportionation.

The most recent work¹¹³ on reaction 6.9 employed the long-lived isotope ^{243}Am , so that radiolytic effects were small enough to be ignored. Changes in the concentrations of Am(III) , Am(V) , and Am(VI) were followed spectrophotometrically, and the stoichiometry was given accurately by Eq. 6.9. As expected from the much lower alpha-radiation level, the mean oxidation number decreased by only about 0.0035 hr^{-1} . As in the earlier work, the rate of disproportionation was proportional to the square of the Am(V) concentration. Thus the most probable rate-determining step is

The Am(IV) formed in this way is very unstable and probably disappears by either

or

but not by both reactions.[†] It is thermodynamically possible for Am(IV) to oxidize water, but, if this were to occur to an appreciable extent, contrary to observations, the mean oxidation number would decrease. Even though the potential for reaction 6.11 is about 0.2 V greater than that for reaction 6.12, it is very likely that the latter is much faster, particularly at the low Am(IV) concentrations and relatively high acid concentrations involved. (See Chap. 4). If we make this plausible assumption,

$$-\frac{d[\text{Am(V)}]}{dt} = 3k[\text{Am(V)}]^2 \quad (6.13)$$

where k is the rate constant for reaction 6.10.

[†]If both reactions occur significantly, the overall reaction will not be second order in Am(V) (see Ref. 61).

The dependence of the rate constant on the HClO_4 concentration, from $3M$ to $8M$ at 25°C , is given by the empirical equation

$$3k = (2.25 \times 10^6)[\text{HClO}_4]^5 + (3.3 \times 10^{13})[\text{HClO}_4]^{13} \text{ M}^{-1} \text{ sec}^{-1} \quad (6.14)$$

This equation indicates an acid dependence slightly greater than fifth power. This fails to confirm the earlier,¹⁰⁶ less precise results obtained with ^{241}Am . A mechanistic interpretation of the acid dependence in these concentrated solutions is not possible, because of unknown changes in the activity coefficients of the reactants and of the water. The hydrogen-ion dependence was further examined at 75.7°C in LiClO_4 – HClO_4 solutions at a constant ionic strength of $2M$ to avoid these difficulties. Under these conditions and in $0.97M$ to $1.9M$ acid, the second-order rate constant depends on $[\text{H}^+]^{2.5}$. This dependence suggests that two activated complexes are involved, one formed from two AmO_2^+ and two hydrogen ions and the other from two AmO_2^+ and three hydrogen ions. If these activated complexes are involved in parallel rate-determining steps, the rate law will be

$$-\frac{d[\text{Am(V)}]}{dt} = [\text{AmO}_2^+]^2 (k_2 [\text{H}^+]^2 + k_3 [\text{H}^+]^3) \quad (6.15)$$

The values for k_2 and k_3 are $(6.94 \pm 1.01) \times 10^{-4} \text{ M}^{-3} \text{ sec}^{-1}$ and $(4.63 \pm 0.71) \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$, respectively. These parameters reproduce the six experimental values with a root-mean-square deviation of 3.3% and a maximum deviation of 6.5%.

Despite the fact that the rate law, Eq. 6.15, is very satisfactory, an ambiguity in interpretation remains. If the same two activated complexes are formed consecutively rather than in parallel steps, the rate law is

$$-\frac{d[\text{Am(V)}]}{dt} = [\text{AmO}_2^+]^2 \left(\frac{1}{k'_2 [\text{H}^+]^2} + \frac{1}{k'_3 [\text{H}^+]^3} \right)^{-1} \quad (6.16)$$

This equation fits the experimental results just as well as Eq. 6.15. Values for k'_2 and k'_3 are $(2.57 \pm 0.36) \times 10^{-3} \text{ M}^{-3} \text{ sec}^{-1}$ and $(2.06 \pm 0.33) \times 10^{-3} \text{ M}^{-4} \text{ sec}^{-1}$, respectively. These values reproduce the data with a root-mean-square deviation of 3.2% and a maximum deviation of 6.6%. A distinction between the two rate laws would require measurements at least down to $0.7M$ HClO_4 , where the two calculated values for the apparent second-order rate constants would differ by 10%.

The temperature dependence of the disproportionation was determined for $1.92M$ HClO_4 solutions from 59.6 to 85.4°C . Since only one acid concentration was used, the data give only a single value for ΔH^* , $54 \pm 17 \text{ kJ/mol}$ for k_1 , and $54 \mp 17 \text{ kJ/mol}$ for k_2 . These estimates can probably be improved on the basis of the reasonable assumption that the difference between the two associated ΔS^* values is the same as for other actinide reactions. Fourteen such oxidation–reduction reactions are known for which the two activated complexes differ by one hydrogen ion. These are discussed in Chap. 9, Sec. 9-1, where it is shown that the weighted average difference is 79 ± 9

Table 6.2

NET ACTIVATION PROCESSES AND THERMODYNAMIC QUANTITIES OF
ACTIVATION FOR THE DISPROPORTIONATION OF Am(V)[†]

Net activation process	ΔG^* , kJ/mol (kcal/mol)	ΔH^* , kJ/mol (kcal/mol)	ΔS^* , J/mol·K (cal/mol·deg)
$2\text{AmO}_2^+ + 2\text{H}^+ = [\text{*}]^{4+}$	109.5(26.17)	$64 \pm 1.2(15.4 \pm 0.3)$	$-130 \pm 4(-31 \pm 1)$
$2\text{AmO}_2^+ + 3\text{H}^+ = [\text{*}]^{5+}$	112.2(26.81)	$39 \mp 2(9.4 \mp 0.5)$	$-209 \mp 5(-50 \mp 1.2)$

[†]Values are for 75°C and $\mu = 2M$.

J/mol·K. This average value was applied to the calculation of ΔH^* and ΔS^* for the two net activation processes. The results are essentially the same for the parallel reaction mechanism and the consecutive reaction mechanism discussed previously and are summarized in Table 6.2.

It is of interest to compare the H^+ dependences for disproportionation reactions of U(V), Np(V), Pu(V), and Am(V). For this set of similar reactions, the metal-ion dependence is the same but the hydrogen-ion dependences are not. For the uranium and plutonium reactions, the free energies are negative, and rates are proportional to the first power of the hydrogen-ion concentration. On the other hand, the free energies are positive for the neptunium and americium reactions, and the hydrogen-ion dependences are significantly larger, $[\text{H}^+]^{1.86}$ and $[\text{H}^+]^{2.5}$, respectively. Since a total of four hydrogen ions are required for the overall reaction, these results illustrate the general idea that, the smaller the driving force for a reaction, the more the activated complex will resemble the products.

6-7

REACTION^{102b} BETWEEN Am(VI) AND Np(V)

The reaction between AmO_2^{2+} and NpO_2^+ was studied in $1M$ $(\text{H,Li})\text{ClO}_4$ with a commercial stopped-flow apparatus. The rate is proportional to the concentrations of Am(VI) and Np(V) but is independent of $[\text{H}^+]$ between $0.1M$ and $1.0M$. Thus the rate law is

$$-\frac{d[\text{Am(VI)}]}{dt} = k[\text{Am(VI)}][\text{Np(V)}] \quad (6.17)$$

At 25°C k is $(2.45 \pm 0.4) \times 10^4 M^{-1} \text{sec}^{-1}$. Measurements at three other temperatures, which range from 2.3 to 36.2°C, give $\Delta H^* = 27.9 \pm 0.3 \text{ kJ/mol}$ ($6.66 \pm 0.08 \text{ kcal/mol}$) and $\Delta S^* = -67.9 \pm 1.1 \text{ J/mol·K}$ ($-16.2 \pm 0.3 \text{ cal/mol·deg}$).

7 EFFECT OF IONIC STRENGTH

Oxidation—reduction reactions of actinide ions often show rather large ionic-strength dependences. An understanding of these effects is important because we must frequently estimate the value of a rate constant at an ionic strength at which it has not been measured. It has been found that the available data are in accord with an extended form of the Debye—Hückel equation despite the high charges on the ions involved and the high ionic strengths usually used. The equation is

$$\log k = \log k_0 + \frac{A \Delta z^2 \mu^{1/2}}{1 + B a_i^0 \mu^{1/2}} + C \mu \quad (7.1)$$

where μ is the ionic strength; Δz^2 is the change in the sum of the squares of the charges in the net activation process associated with the measured rate constant, k ; k_0 , a_i^0 , and C are adjustable parameters; and A and B depend on the temperature, solvent, and fundamental constants. The equation is based on the assumptions that the activity coefficients of the reactants, as well as the activated complex, are given by $\log \gamma_i = z_i^2 A \mu^{1/2} / (1 + B a_i^0 \mu^{1/2}) + C_i \mu$ and that the individual a_i^0 's are similar enough so that some sort of average can be used for all the species involved.

As an example, the rate law for the oxidation of Np(III) by Fe(III) was found to be

$$-\frac{d[\text{Np(III)}]}{dt} = k[\text{Np}^{3+}][\text{Fe}^{3+}][\text{H}^+]^{-1} \quad (7.2)$$

Hence the principal net activation process is

for which $\Delta z^2 = 5^2 + 1^2 - 3^2 - 3^2 = 8$. The ionic strength was varied between 0.2M and 2.0M; both LiClO_4 and NaClO_4 were used. The adjustable parameters in Eq. 7.1 were determined by a least-squares procedure. For LiClO_4 solutions at 0.8°C, the results were $k_0 = 1.59 \pm 0.012 \text{ sec}^{-1}$, $\overset{\circ}{a} = 0.89 \pm 0.025 \text{ nm}$, and $C = 0.059 \pm 0.008 \text{ M}^{-1}$. These parameters reproduce the eight observed values with a mean deviation of 0.8%. The corresponding values for NaClO_4 solutions are $1.61 \pm 0.026 \text{ sec}^{-1}$, $0.96 \pm 0.06 \text{ nm}$, and $0.051 \pm 0.016 \text{ M}^{-1}$; these give a mean deviation of 2%. The uncertainties here are the standard deviations. It should be noted that, although $\overset{\circ}{a}$ and C are somewhat different for the two salts, k_0 is essentially the same. The data from seven other actinide reactions were treated in the same way, and in all cases Eq. 7.1 describes the ionic-strength dependences with good precision. The average values found for $\overset{\circ}{a}$ and C are summarized in Table 7.1, and the values for the individual reactions are given in Table 7.2. For a particular salt, values for both $\overset{\circ}{a}$ and C fall within fairly narrow limits, essentially independent of Δz^2 . Thus it appears that Eq. 7.1, together with appropriate values from Table 7.1, might be used for approximate estimates for the ionic-strength dependences for reactions similar to those listed in Table 7.2.

To get an idea of how reliable such estimates might be, using the average values for $\overset{\circ}{a}$ and C , we calculated the ratio of the value of the rate constant at $\mu = 0.2\text{M}$ to the value at $\mu = 1.0\text{M}$ for both LiClO_4 and NaClO_4 at 25°C and at 0°C for the various Δz^2 values. These ratios were then compared with the observed ratios. The average deviation was 8.2%, with a range from 0.6 to 28%. A similar calculation using $\mu = 2\text{M}$ and $\mu = 1\text{M}$ gave an average deviation of 8.2% and a range of 0.3 to 25%.

Table 7.1 AVERAGE DEBYE-HÜCKEL PARAMETERS FOR ACTINIDE REACTIONS

$$\log k = \log k_0 + \frac{A \Delta z^2 \mu^{1/2}}{1 + B a_\mu^{1/2}} + C \mu$$

Temp., °C	A, $M^{-0.5}$	B, $\text{nm}^{-1} M^{-0.5}$	$\overset{\circ}{a}$, nm		C, M^{-1}		Deviation, ‡ %	
			Range	Average†	Range	Average†	Range	Average†
LiClO ₄								
25	0.5115	3.291	0.83–0.99	0.896	0.021–0.173	0.1275	1.3–7.0	3.6
0.5	0.4921	3.249	0.80–0.89	0.824	0.059–0.148	0.1009	0.2–2.5	1.3
NaClO ₄								
25	0.5115	3.291	0.83–1.07	0.936	0–0.116	0.0977	1.7–3.6	2.8
0.5	0.4921	3.249	0.86–0.97	0.838	0.052–0.129	0.0972	0.7–2.4	1.7

† Weighted according to the individual standard deviations.

‡ Mean percent deviation between observed and calculated values.

Table 7.2 DEBYE-HÜCKEL PARAMETERS FOR EIGHT REACTIONS

Net activation process	Δz^2	Range of μ, M	Salt	Temp., °C	$\bar{a}, \text{nm}$	C, M^{-1}	Mean deviation, %
$\text{Fe}^{2+} + \text{PuO}_2^{2+} = [*]^{4+}$	8	0.05–2.0	LiClO_4	0.1	0.821 ± 0.016	0.1367 ± 0.007	1.5
			NaClO_4	0.1	0.856 ± 0.033	0.1079 ± 0.013	2.4
$\text{V}^{2+} + \text{UO}_2^{2+} = [*]^{4+}$	8	0.08–2.0	LiClO_4	0.1	0.804 ± 0.004	0.0988 ± 0.0018	0.2
			NaClO_4	0.1	0.858 ± 0.017	0.0776 ± 0.0061	0.7
			LiClO_4	25.1	0.833 ± 0.016	0.1094 ± 0.006	1.3
			NaClO_4	25.1	0.909 ± 0.023	0.0952 ± 0.008	1.7
			$\text{La}(\text{ClO}_4)_3$	25.1	1.159 ± 0.037	0.1437 ± 0.007	1.6
$\text{Np}^{3+} + \text{Fe}^{3+} + \text{H}_2\text{O} = [*]^{5+} + \text{H}^+$	8	0.2–2.0	LiClO_4	0.8	0.887 ± 0.025	0.0591 ± 0.008	0.8
			NaClO_4	0.8	0.957 ± 0.058	0.0515 ± 0.0157	1.7
			LiClO_4	25.1	0.842 ± 0.212	0.0214 ± 0.062	7.0
			NaClO_4	25.1	0.829 ± 0.10	-0.005 ± 0.030	2.8
$\text{Np}^{3+} + \text{UO}_2^{2+} = [*]^{5+}$	12	0.12–2.57	LiClO_4	0.6	0.894 ± 0.039	0.148 ± 0.015	1.2
$\text{Pu}^{3+} + \text{NpO}_2^{2+} = [*]^{5+}$	12	0.24–3.2	LiClO_4	0.6	0.836 ± 0.020	0.140 ± 0.006	1.1
			NaClO_4	0.6	0.969 ± 0.031	0.129 ± 0.007	1.5
			$\text{La}(\text{ClO}_4)_3$	0.6	1.269 ± 0.048	0.151 ± 0.005	1.3
$\text{U}^{3+} + \text{UO}_2^{2+} = [*]^{5+}$	12	0.053–1.0	LiClO_4	0.8	0.884 ± 0.019	0.139 ± 0.02	2.5
			LiClO_4	25.1	0.941 ± 0.055	0.173 ± 0.048	4.3
$\text{Np}^{4+} + \text{V}^{2+} = [*]^{6+}$	16	0.275–3.73	LiClO_4	25.2	0.988 ± 0.037	0.1532 ± 0.010	4.0
		0.275–4.00	NaClO_4	25.2	1.068 ± 0.046	0.1156 ± 0.011	3.6
		0.275–3.90	$\text{La}(\text{ClO}_4)_3$	25.2	1.141 ± 0.061	0.1302 ± 0.012	4.3
$\text{U}^{3+} + \text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+} = [*]^{6+}$	18	0.12–3.2	LiClO_4	0.8	0.935 ± 0.011	0.080 ± 0.005	1.7
			LiClO_4	25.1	0.924 ± 0.013	0.087 ± 0.05	1.4

The reaction between Pu^{3+} and the complex CrOPuO^{4+} differs from the reactions listed in Table 7.2 in that one of the reactants is considerably larger and that Δz^2 is 24. For this reaction in LiClO_4 at 25°C , the data are satisfactorily reproduced by Eq. 7.1, with $\overset{\circ}{a} = 0.11 \pm 0.013 \text{ nm}$ and $C = 0.233 \pm 0.006 M^{-1}$ (Ref. 80). These values are considerably higher than the corresponding values given in Table 7.2 and illustrate the need for caution in estimating the parameters for Eq. 7.1.

8 THERMODYNAMIC QUANTITIES FOR THE OVERALL PROCESSES AND ACTIVATION PROCESSES

The quantitative data available are summarized in Table 8.1 in terms of the overall processes, the net activation processes, and the thermodynamic quantities (ΔG , ΔH , and ΔS) associated with these processes. Where possible, the overall processes were chosen to be the simplest net reactions that include the actual rate-determining steps. For example, the overall reaction

is thought to involve two net steps:

and

Only the first of these is rate determining, and only its properties may be kinetically important. The thermodynamic quantities for the net reactions were taken from standard sources.

The Eyring equation (Eq. 2.1) has been applied to the temperature dependence of the reaction rates to get ΔG^* , ΔH^* , and ΔS^* . The experimental uncertainty is indicated for ΔS^* only. Note, however, that a corresponding uncertainty also applies to ΔH^* since these two quantities are highly correlated. Some of the original data were recalculated for the table; references from which these data came are indicated. The data are arranged so that similar reactions appear in sets.

Table 8.1
ACTINIDE OXIDATION-REDUCTION REACTIONS, OVERALL PROCESSES AND ACTIVATION PROCESSES

No.	Process	Pattern (Fig. 2.1)	μ , M	ΔG , kJ/mol (kcal/mol)	ΔH , kJ/mol (kcal/mol)	ΔS , J/mol · K (cal/mol · deg)	S_{complex}^* , J/mol · K (cal/mol · deg)	Ref.
Oxidation of An^{3+}								
1	$Np^{3+} + Fe^{3+} = Np^{4+} + Fe^{2+}$ $Np^{3+} + Fe^{3+} + H_2O = [*]^{5+} + H^+$	Net 1-0	2	-59.4 (-14.2) 57.3 (13.7)	-69.0 (-16.5) 61.1 (14.6)	-33.5 (-8.0) 12.6 ± 1.3 (3.0)	-368 (-88)	114
2	$Pu^{3+} + *Pu^{4+} = Pu^{4+} + *Pu^{3+}$ $Pu^{3+} + Pu^{4+} + H_2O = [*]^{6+} + H^+$	1-0	2	0.0 (0.0) 56.1 (13.4)	0.0 (0.0) 31.0 (7.4)	0.0 (0.0) -85.4 ± 16.7 (-20.4)	-536 (-128)	74 ^b
3	$U^{3+} + UO_2^{2+} = U^{4+} + UO_2^+$ $U^{3+} + UO_2^{2+} = [*]^{5+}$	Net 1-0	1	-66.9 (-16.0) 46.0 (11.0)	-112.5 (-26.9) 18.1 (4.3)	-148.5 (-35.5) -93.3 ± 2.5 (-22.3)	-331 (-79)	76
4	$Np^{3+} + UO_2^{2+} = Np^{4+} + UO_2^+$ $Np^{3+} + UO_2^{2+} = [*]^{5+}$ $Np^{3+} + UO_2^{2+} + H_2O = [*]^{4+} + H^+$	Net 2-0	1	8.9 (2.1) 64.0 (15.3) 72.4 (17.3)	-37.2 (-8.6) 10.9 (2.6) 47.3 (11.3)	-151 (-36) -178.2 ± 2.5 (-42.6) -83.7 ± 27.2 (-20.0)	-423 (-101) -259 (-62)	12
5	$Np^{3+} + NpO_2^{2+} = Np^{4+} + NpO_2^+$ $Np^{3+} + NpO_2^{2+} = [*]^{5+}$	Net 1-0	1	-94.8 (-22.6) 44.4 (10.6)	-141.4 (-33.8) 4.2 (1.0)	-157.3 (-37.6) -133.9 ± 4.2 (-32.0)	-368 (-88)	76
6	$Pu^{3+} + NpO_2^{2+} = Pu^{4+} + NpO_2^+$ $Pu^{3+} + NpO_2^{2+} = [*]^{5+}$ $Pu^{3+} + NpO_2^{2+} + H_2O = [*]^{4+} + H^+$	Net 2-0	1	-15.1 (-3.6) 64.0 (15.3) 70.3 (16.8)	-60.7 (-14.5) 14.6 (3.5) 53.6 (12.8)	-153.1 (-36.6) -166.1 ± 0.8 (-39.7) -55.6 ± 1.7 (-13.3)	-406 (-97) -226 (-54)	77
7	$Pu^{3+} + PuO_2^{2+} = Pu^{4+} + PuO_2^+$ $Pu^{3+} + PuO_2^{2+} = [*]^{5+}$	Net 1-0	1	6.3 (1.5) 70.7 (16.9)	-35.6 (-8.5) 20.2 (4.8)	-139.7 (-33.4) -169.0 ± 1.3 (-40.4)	-406 (-97)	78
8	$U^{3+} + UO_2^+ + 4H^+ = 2U^{4+} + 2H_2O$ $U^{3+} + UO_2^+ + H^+ = [*]^{5+}$	Net 2-0	1	-119.2 (-28.5) 40.6 (9.7)	-224.7 (-53.7) 8.4 (2.0)	-353.5 (-84.5) -108.8 ± 5.4 (-26.0)	-293 (-70)	76
9	$Np^{3+} + UO_2^+ + 4H^+ = Np^{4+} + U^{4+} + 2H_2O$ $Np^{3+} + UO_2^+ + H^+ = [*]^{5+}$	Net 1-0	1	-43.5 (-10.4) 64.0 (15.3)	-149.4 (-35.7) 21.3 (5.1)	-356 (-85.2) -142.7 ± 5.0 (-34.1)	-326 (-78)	12
10	$Np^{3+} + NpO_2^+ + 4H^+ = 2Np^{4+} + 2H_2O$ $Np^{3+} + NpO_2^+ + H^+ = [*]^{5+}$	Net 1-0	2	-56.5 (-13.5) 63.6 (15.2)	-172.8 (-41.3) 24.7 (5.9)	-391 (-93.5) -129.7 ± 8.4 (-31.0)	-314 (-75)	79

11	$\text{Pu}^{3+} + \text{NpO}_2^+ + 4\text{H}^+ = \text{Pu}^{4+} + \text{Np}^{4+} + 2\text{H}_2\text{O}$ $\text{Pu}^{3+} + \text{NpO}_2^+ + \text{H}^+ = [\ast]^{5+}$	Net 1-0	1	23.4 (5.6) 99.6 (23.8)	-92.0 (-22.0) 49.8 (11.9)	-387.0 (-92.5) $-167.4 \pm 20.9 (-40.0)$	-356 (-85)	81 ^c
12	$\text{Pu}^{3+} + \text{PuO}_2^+ + 4\text{H}^+ = 2\text{Pu}^{4+} + 2\text{H}_2\text{O}$ $\text{Pu}^{3+} + \text{PuO}_2^+ + \text{H}^+ = [\ast]^{5+}$	Net 1-0	1	-18.2 (-4.3) 80.8 (19.3)	-120.9 (-28.9) 33.5 (8.0)	-343.9 (-82.2) $-158.2 \pm 1.7 (-37.8)$	-347 (-83)	80
13	$\text{U}^{3+} + \text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+} = \text{U}(\text{IV}) + \text{Co}(\text{II})$ $\text{U}^{3+} + \text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+} = [\ast]^{6+}$	Net ^d 1-0	2	54.8 (13.1)	15.5 (3.7)	$-131.8 \pm 1.3 (-31.5)$		115
14	$\text{U}^{3+} + \text{Co}(\text{NH}_3)_5\text{Cl}^{2+} = \text{U}(\text{IV}) + \text{Co}(\text{II})$ $\text{U}^{3+} + \text{Co}(\text{NH}_3)_5\text{Cl}^{2+} = [\ast]^{5+}$	Net ^d 1-0	0.2	47.3 (11.3)	11.3 (2.7)	$-121.3 \pm 4.2 (-29.0)$		18
15	$\text{U}^{3+} + \text{Co}(\text{NH}_3)_5\text{Br}^{2+} = \text{U}(\text{IV}) + \text{Co}(\text{II})$ $\text{U}^{3+} + \text{Co}(\text{NH}_3)_5\text{Br}^{2+} = [\ast]^{5+}$	Net ^d 1-0	0.1	49.4 (11.8)	8.4 (2.0)	$-138.1 \pm 4.2 (-33.0)$		18
16	$\text{Np}^{3+} + \text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+} = \text{Np}^{4+} + \text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$ $\text{Np}^{3+} + \text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+} = [\ast]^{6+}$	Net 1-0	1	6.9 (1.6) 76.1 (18.2)	-36.4 (-8.7) 17.7 (4.2)	-145.6 (-34.8) $-196.2 \pm 3.8 (-46.9)$		116 116
17	$\text{Np}^{3+} + \text{Ru}(\text{NH}_3)_6^{3+} = \text{Np}^{4+} + \text{Ru}(\text{NH}_3)_6^{2+}$ $\text{Np}^{3+} + \text{Ru}(\text{NH}_3)_6^{3+} = [\ast]^{6+}$	Net 1-0	0.5	8.6 (2.1) 76.1 (18.2)	-51.9 (-12.4) 16.3 (3.9)	-202.5 (-48.4) $-201.3 \pm 14.6 (-48.1)$		116 116
Reduction of An^{4+}								
18	$\text{Np}^{4+} + \text{V}^{2+} = \text{Np}^{3+} + \text{V}^{3+}$ $\text{Np}^{4+} + \text{V}^{2+} = [\ast]^{6+}$	Net 1-0	2	-38.9 (-9.3) 70.7 (16.9)	-26.8 (-6.4) 40.6 (9.7)	41.8 (10.0) $-100.4 \pm 0.8 (-24.0)$	-561 ¹ (-134)	117
19	$\text{Np}^{4+} + \text{Cr}^{2+} = \text{Np}^{3+} + \text{Cr}^{3+}$ $\text{Np}^{4+} + \text{Cr}^{2+} + \text{H}_2\text{O} = [\ast]^{5+} + \text{H}^+$ $\text{Np}^{4+} + \text{Cr}^{2+} + \text{H}_2\text{O} = [\ast]^{4+} + 2\text{H}^+$	Net 2-0	1	-54.4 (-13.0) 69.9 (16.7) 74.1 (17.7)	-44.8 (-10.7) 67.8 (16.2) 86.2 (20.6)	33.5 (8.0) $-6.7 \pm 5.9 (-1.6)$ $41.0 \pm 13.8 (9.8)$	-402 (-96) -356 (-85)	118 ^b
20	$\text{Pu}^{4+} + \text{Fe}^{2+} = \text{Pu}^{3+} + \text{Fe}^{3+}$ $\text{Pu}^{4+} + \text{Fe}^{2+} + \text{H}_2\text{O} = [\ast]^{5+} + \text{H}^+$	Net 2-0		-20.5 (-4.9) 63.2 (15.1)	-12.6 (-3.0) 79.9 (19.1)	29.3 (7.0) $54.4 \pm 4.2 (13.0)$	-360 ¹ (-86)	119
21	$\text{Pu}^{4+} + \text{V}^{3+} + \text{H}_2\text{O} = \text{Pu}^{3+} + \text{VO}^{2+} + 2\text{H}^+$ $\text{Pu}^{4+} + \text{V}^{3+} + \text{H}_2\text{O} = [\ast]^{6+} + \text{H}^+$ $\text{Pu}^{4+} + \text{V}^{3+} + \text{H}_2\text{O} = [\ast]^{5+} + 2\text{H}^+$	Net 2-0	2	-59.8 (-14.3) 65.7 (15.7) 64.0 (15.3)	12.6 (3.0) 72.0 (17.2) 90.4 (21.6)	246.9 (59.0) $20.9 \pm 12.6 (5.0)$ $87.9 \pm 8.4 (21.0)$	-523 (-125) -456 (-109)	44
22	$\text{Pu}^{4+} + \text{Ti}^{3+} + \text{H}_2\text{O} = \text{Pu}^{3+} + \text{TiO}^{2+} + 2\text{H}^+$ $\text{Pu}^{4+} + \text{Ti}^{3+} + \text{H}_2\text{O} = [\ast]^{6+} + \text{H}^+$	Net 1-0	1	-84.9 (-20.3) 62.8 (15.0)	-1.3 (-0.3) 69.9 (16.7)	280.3 (67.0) $25.1 \pm 8.4 (6.0)$	-515 (-123)	120

Note: Footnotes begin on p. 79.

(Table continues on following page.)

Table 8.1 (Continued)

No.	Process	Pattern (Fig. 2.1)	μ , M	ΔG , kJ/mol (kcal/mol)	ΔH , kJ/mol (kcal/mol)	ΔS , J/mol · K (cal/mol · deg)	$S^*_{\text{complex}, a}$ J/mol · K (cal/mol · deg)	Ref.
Oxidation of An^{4+}								
23	$U^{4+} + Fe^{3+} + 2H_2O = UO_2^+ + Fe^{2+} + 4H^+$	Net		-15.9 (-3.8)	85.4 (20.4)	338.9 (81.0)		
	$U^{4+} + Fe^{3+} + H_2O = [*]^{6+} + H^+$			71.1 (17.0)	75.3 (18.0)	12.6 ± 37.7 (3.0)	-556 (-133)	
	$U^{4+} + Fe^{3+} + H_2O = [*]^{5+} + 2H^+$	2-0	1	66.9 (16.0)	100.8 (24.1)	113.0 ± 8.4 (27.0)	-456 (-109)	46 ^b
24	$Np^{4+} + Fe^{3+} + 2H_2O = NpO_2^+ + Fe^{2+} + 4H^+$			-2.9 (-0.7)	100.4 (24.0)	351.5 (84.0)		
	$Np^{4+} + Fe^{3+} + 2H_2O = [*]^{4+} + 3H^+$	1-0	1	79.9 (19.1)	144.8 (34.6)	217.6 ± 8.4 (52.0)	-289 (-69)	121
25	$U^{4+} + Ti^{3+} + H_2O = UO_2^+ + Ti^+ + 4H^+$	Net ^d		-175.7 (-42.0)	-46.0 (-11.0)	418.4 (100.0)		
	$U^{4+} + Ti^{3+} + H_2O = [*]^{6+} + H^+$			82.4 (19.7)	103.3 (24.7)	71.1 ± 16.7 (17.0)	-393 (-94)	
	$U^{4+} + Ti^{3+} + H_2O = [*]^{5+} + 2H^+$	2-0	2.9	82.4 (19.7)	85.8 (20.5)	12.6 ± 16.7 (3.0)	-452 (-108)	122 ^b
26	$U^{4+} + CeOH^{3+} + H_2O = UO_2^+ + Ce^{3+} + 3H^+$	Net		-100.4 (-24.0)	-25.1 (-6.0)	259.4 (62.0)		
	$U^{4+} + CeOH^{3+} = [*]^{6+} + H^+$	1-0	2	50.6 (12.1)	58.6 (14.0)	27.2 ± 8.4 (6.5)	-494 (-118)	123
27	$Pu^{4+} + CeOH^{3+} + H_2O = PuO^+ + Ce^{3+} + 3H^+$	Net		-41.8 (-10.0)	25.1 (6.0)	230.1 (55.0)		
	$Pu^{4+} + CeOH^{3+} + H_2O = [*]^{5+} + 2H^+$	1-0	2.5	65.7 (15.7)	58.6 (14.0)	-24.3 ± 12.6 (-5.8)	-485 (-116)	124
28	$U^{4+} + Pu^{4+} + 2H_2O = Pu^{3+} + UO_2^+ + 4H^+$			-36.4 (-8.7)	68.6 (16.4)	352.3 (84.2)		
	$U^{4+} + Pu^{4+} + H_2O = [*]^{6+} + 2H^+$	1-0	2	64.4 (15.4)	101.7 (24.3)	125.5 ± 8.4 (30.0)	-506 (-121)	82
29	$U^{4+} + NpO_2^{2+} + 2H_2O = UO_2^+ + NpO_2^+ + 4H^+$	Net		-51.5 (-12.3)	7.9 (1.9)	199.2 (47.6)		
	$U^{4+} + NpO_2^{2+} + H_2O = [*]^{5+} + H^+$	1-0	2	67.4 (16.1)	76.1 (18.2)	31.0 ± 3.3 (7.4)	-322 (-77)	83
30	$U^{4+} + PuO_2^{2+} + 2H_2O = UO_2^+ + PuO_2^+ + 4H^+$	Net		-30.0 (-7.2)	33.1 (7.9)	212.5 (50.8)		
	$U^{4+} + PuO_2^{2+} + H_2O = [*]^{5+} + H^+$			69.5 (16.6)	73.6 (17.6)	15.1 ± 1.7 (3.6)	-335 (-80)	
	$U^{4+} + PuO_2^{2+} + H_2O = [*]^{4+} + 2H^+$	2-1	2	66.9 (16.0)	89.1 (21.3)	74.5 ± 5.4 (17.8)	-272 (-65)	61
31	$Np^{4+} + NpO_2^{2+} + 2H_2O = 2NpO_2^+ + 4H^+$	Net		-38.5 (-9.2)	31.4 (7.5)	233.9 (55.9)		
	$Np^{4+} + NpO_2^{2+} + H_2O = [*]^{4+} + 2H^+$	2-0	2	80.8 (19.3)	105.0 (25.1)	81.6 ± 7.9 (19.5)	-276 (-66)	84 ^b
	$Np^{4+} + NpO_2^{2+} + H_2O = [*]^{4+} + 2H^+$			79.9 (19.1)	92.5 (22.1)	41.8 ± 20.9 (10.0)	-318 (-76)	
	$Np^{4+} + NpO_2^{2+} + 2H_2O = [*]^{3+} + 3H^+$	2-0	2	82.8 (19.8)	146.4 (35.0)	213.4 ± 54.4 (51.0)	-75 (-18)	125 ^b

32	$\text{Np}^{4+} + \text{PuO}_2^{2+} + 2\text{H}_2\text{O} = \text{NpO}_2^+ + \text{PuO}_2^+ + 4\text{H}^+$ $\text{Np}^{4+} + \text{PuO}_2^{2+} + \text{H}_2\text{O} = [\ast]^{4+} + 2\text{H}^+$	Net 1-0	2	-17.2 (-4.1) 85.4 (20.4)	56.5 (13.5) 133.5 (31.9)	247.3 (59.1) 163.2 ± 62.8 (39.0)	-192 (-46)	87
33	$\text{U}^{4+} + \ast\text{UO}_2^{2+} = \text{UO}_2^{2+} + \ast\text{U}^{4+}$ $2\text{U}^{4+} + \text{UO}_2^{2+} + 2\text{H}_2\text{O} = [\ast]^{6+} + 4\text{H}^+$	Net 1-0	0.14	0.0 (0.0) 105.0 (25.1)	0.0 (0.0) 137.2 (32.8)	0.0 (0.0) 108.8 ± 8.4 (26.0)	-527 (-126)	126
34	$\text{Np}^{4+} + \ast\text{NpO}_2^+ = \text{NpO}_2^+ + \ast\text{Np}^{4+}$ $\text{Np}^{4+} + \text{NpO}_2^{2+} + \text{H}_2\text{O} = [\ast]^{4+} + 2\text{H}^+$ $2\text{NpO}_2^+ + \text{H}^+ = [\ast]^{3+}$	Net e	1.2	0.0 (0.0) 66.9 (16.0) 101.3 (24.2)	0.0 (0.0) 83.3 (19.9) 73.6 (17.6)	0.0 (0.0) 130.1 ± 7.1 (31.1) -92.9 ± 2.9 (-22.2)	-0 (-0) -230 (-55) -146 (-35)	89
35	$5\text{Pu}^{4+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} = 5\text{PuO}_2^{2+} + 2\text{Mn}^{2+} + 4\text{H}^+$ $\text{Pu}^{4+} + \text{Mn}^{2+} + \text{H}_2\text{O} = [\ast]^{4+} + 2\text{H}^+$	d		62.8 (15.0)	90.8 (21.7)	94.1 ± 4.2 (22.5)	-310 (-74)	127
Reduction of AnO_2^+								
36	$2\text{UO}_2^+ + 4\text{H}^+ = \text{U}^{4+} + \text{UO}_2^{2+} + 2\text{H}_2\text{O}$ $2\text{UO}_2^+ + \text{H}^+ = [\ast]^{3+}$	Net 2-1	2	-52.3 (-12.5) 59.8 (14.3)	-112.1 (-26.8) 46.0 (11.0)	-205.0 (-49.0) -46.0 ± 6.3 (-11.0)	-105 (-25)	20
37	$2\text{PuO}_2^+ + 4\text{H}^+ = \text{Pu}^{4+} + \text{PuO}_2^{2+} + 2\text{H}_2\text{O}$ $2\text{PuO}_2^+ + \text{H}^+ = [\ast]^{3+}$	Net 1-0	2	-24.5 (-5.8) 87.0 (20.8)	-85.4 (-20.4) 78.7 (18.8)	-204.2 (-48.8) -25.1 ± 37.7 (-6.0)	-75 (-18)	86
38	$2\text{AmO}_2^+ + 4\text{H}^+ = \text{Am}^{4+} + \text{AmO}_2^{2+} + 2\text{H}_2\text{O}$ $2\text{AmO}_2^+ + 2\text{H}^+ = [\ast]^{4+}$ $2\text{AmO}_2^+ + 3\text{H}^+ = [\ast]^{5+}$	Net 2-0	2	18.4 (4.4) 102.1 (24.4) 102.9 (24.6)	-41.8 (-10.0) 53.6 (12.8) 53.3 (12.7)	-209.2 (-50.0) -161.1 ± 54.4 (-38.5) -168.6 ± 54.4 (-40.3)	-138 (-33) -146 (-35)	113
39	$\text{NpO}_2^+ + \text{Cr}^{2+} + 4\text{H}^+ = \text{Np}^{4+} + \text{Cr}^{3+} + 2\text{H}_2\text{O}$ $\text{NpO}_2^+ + \text{Cr}^{2+} = [\ast]^{3+}$ $\text{NpO}_2^+ + \text{Cr}^{2+} + \text{H}^+ = [\ast]^{4+}$	Net 2-0	0.2	-110.5 (-26.4) 66.5 (15.9) 56.5 (13.5)	-213.4 (-51.0) 31.8 (7.6) 7.9 (1.9)	-351.5 (-84.0) -117.2 ± 54.4 (-28.0) -163.2 ± 10.5 (-39.0)	-255 (-61) -301 (-72)	63 ^b
40	$\text{NpO}_2^+ + \text{V}^{3+} + 2\text{H}^+ = \text{Np}^{4+} + \text{VO}^{2+} + \text{H}_2\text{O}$ $\text{NpO}_2^+ + \text{V}^{3+} = [\ast]^{4+}$	Net 1-0 ^e	3	-36.8 (-8.8) 76.1 (18.2)	-75.3 (-18.0) 61.1 (14.6)	-125.5 (-30.0) -51.5 ± 10.9 (-12.3)	-335 (-80)	48
41	$\text{NpO}_2^+ + \text{U}^{4+} = \text{Np}^{4+} + \text{UO}_2^+$ $\text{NpO}_2^+ + \text{U}^{4+} + \text{H}_2\text{O} = [\ast]^{3+} + 2\text{H}^+$	Net e	1	-15.9 (-3.8) 102.1 (24.4)	-25.1 (-6.0) 132.2 (31.6)	-33.5 (-8.0) 104.6 ± 29.3 (25.0)	-197 (-47)	88
42	$\text{CrUO}_2^{3+} + \text{Cr}^{2+} + 4\text{H}^+ = \text{U}^{4+} + 2\text{Cr}^{3+} + 2\text{H}_2\text{O}$ $\text{CrUO}_2^{3+} + \text{Cr}^{2+} = [\ast]^{6+}$	Net 1-0	2	-104.6 (-25.0) 57.1 (13.6)	-188.3 (-45.0) 13.2 (3.2)	-284.5 (-68.0) -147.3 ± 4.2 (-35.2)	-623 (-149)	128
43	$\text{CrPuO}_2^{4+} + \text{Pu}^{3+} + 4\text{H}^+ = 2\text{Pu}^{4+} + \text{Cr}^{3+} + 2\text{H}_2\text{O}$ $\text{CrPuO}_2^{4+} + \text{Pu}^{3+} = [\ast]^{7+}$	Net 1-0	1	-23.4 (-5.6) 63.6 (15.2)	-108.8 (26.0) 18.2 (4.3)	-284.5 (-68.0) -152.3 ± 0.8 (-36.4)	-674 (-161)	80

(Table continues on following page.)

Table 8.1 (Continued)

No.	Process	Pattern (Fig. 2.1)	μ , M	ΔG , kJ/mol (kcal/mol)	ΔH , kJ/mol (kcal/mol)	ΔS , J/mol · K (cal/mol · deg)	$S^*_{\text{complex}, a}$ J/mol · K (cal/mol · deg)	Ref.
Oxidation of AnO_2^+								
44	$\text{NpO}_2^+ + \text{CeOH}^{3+} + \text{H}^+ = \text{NpO}_2^{2+} + \text{Ce}^{3+} + \text{H}_2\text{O}$	Net		-55.6 (-13.3)	-46.0 (-11.0)	29.3 (7.0)		
	$\text{NpO}_2^+ + \text{CeOH}^{3+} + \text{H}^+ = [*]^{5+}$	1-0	2	44.8 (10.7)	0.0 (0.0)	-150.6 ± 20.9 (-36.0)	-351 (-84)	129
45	$\text{NpO}_2^+ + \text{Co}^{3+} = \text{NpO}_2^{2+} + \text{Co}^{2+}$	Net		-67.4 (-16.1)	-33.5 (-8.0)	117.2 (28.0)		
	$\text{NpO}_2^+ + \text{Co}^{3+} = [*]^{4+}$			59.0 (14.1)	50.2 (12.0)	-29.3 ± 3.3 (-7.0)	-351 (-84)	
	$\text{NpO}_2^+ + \text{Co}^{3+} + \text{H}_2\text{O} = [*]^{3+} + \text{H}^+$	2-0	2	64.4 (15.4)	82.4 (19.7)	60.7 ± 34.3 (14.5)	-192 (-46)	
	or $\text{NpO}_2^+ + \text{Co}^{3+} = [*]^{4+}$	1-0 ^f	2	58.3 (13.9)	56.1 (13.4)	-7.1 ± 15.5 (-1.7)	(-79)	47 ^b
46	$\text{CrNpO}_4^{4+} + \text{Co}^{3+} = \text{NpO}_2^{2+} + \text{Co}^{2+} + \text{Cr}^{3+}$	Net		-71.1 (-17.0)	-20.9 (-5.0)	175.7 (42.0)		
	$\text{CrNpO}_4^{4+} + \text{Co}^{3+} + \text{H}_2\text{O} = [*]^{6+} + \text{H}^+$	1-0 ^f	2.1	70.8 (16.9)	77.4 (18.5)	22.6 ± 15.9 (5.4)	-565 (-135)	47 ^b
47	$\text{NpO}_2^+ + \text{NpO}_2^{2+} = \text{NpO}_2^{2+} + * \text{NpO}_2^+$	Net		0.0 (0.0)	0.0 (0.0)	0.0 (0.0)		
	$\text{NpO}_2^+ + \text{NpO}_2^{2+} = [*]^{3+}$	2-0	3	58.6 (14.0)	44.4 (10.6)	-50.2 ± 12.6 (-12.0)	-151 (-36)	75
48	$\text{NpO}_2^+ + \text{AmO}_2^{2+} = \text{NpO}_2^{2+} + \text{AmO}_2^+$	Net		-38.4 (-9.2)	-37.0 (-9)	6 (1.4)		
	$\text{NpO}_2^+ + \text{AmO}_2^{2+} = [*]^{3+}$	1-0	1	48.1 (11.5)	27.9 (6.7)	-67.9 ± 1.1 (-16.2)	-172 (-41)	101b
Reduction of AnO_2^{2+}								
49	$\text{UO}_2^{2+} + \text{Cr}^{2+} = \text{CrUO}_4^{4+}$	Net		-4.2 (-1.0)	-100.4 (-24.0)	-192.5 (-46.0)		
	$\text{UO}_2^{2+} + \text{Cr}^{2+} = [*]^{4+}$	1-0		49.4 (11.8)	2.1 (0.5)	-159.0 ± 6.3 (-38.0)	-356 (-85)	130
50	$\text{UO}_2^{2+} + \text{Eu}^{2+} = \text{UO}_2^+ + \text{Eu}^{3+}$	Net		-39.7 (-9.5)	-87.9 (-21.0)	-159.0 (-38.0)		
	$\text{UO}_2^{2+} + \text{Eu}^{2+} = [*]^{4+}$	1-0	2	49.4 (11.8)	6.3 (1.5)	-143.9 ± 4.2 (-34.4)	-218 (-52)	131 ^c
51	$\text{UO}_2^{2+} + \text{V}^{2+} = \text{UO}_2^+ + \text{V}^{3+}$	Net		-30.5 (-7.3)	-62.8 (-15.0)	-108.8 (-26.0)		
	$\text{UO}_2^{2+} + \text{V}^{2+} = [*]^{4+}$	1-0	2	62.3 (14.9)	29.7 (7.1)	-109.2 ± 1.7 (-26.1)	-301 (-72)	49
52	$\text{PuO}_2^{2+} + \text{Fe}^{2+} = \text{PuO}_2^+ + \text{Fe}^{3+}$	Net		-13.8 (-3.3)	-48.1 (-11.5)	-117.2 (-28.0)		
	$\text{PuO}_2^{2+} + \text{Fe}^{2+} = [*]^{4+}$			55.6 (13.3)	18.4 (4.4)	-125.5 ± 6.7 (-30.0)	-335 (-80)	
	$\text{PuO}_2^{2+} + \text{Fe}^{2+} = [*]^{4+}$			51.9 (12.4)	36.0 (8.6)	-52.7 ± 8.4 (-12.6)	-264 (-63)	
	$\text{PuO}_2^{2+} + \text{Fe}^{2+} + \text{H}_2\text{O} = [*]^{3+} + \text{H}^+$	3-2	2	56.1 (13.4)	39.3 (9.4)	-56.1 ± 8.4 (-13.4)	-197 (-47)	62

53	$\text{UO}_2^{2+} + \text{V}^{3+} + \text{H}_2\text{O} = \text{UO}_2^+ + \text{VO}^{2+} + 2\text{H}^+$	Net			28.9	(6.9)	64.9	(15.5)	121.3	(29.0)			
	$\text{UO}_2^{2+} + \text{V}^{3+} + \text{H}_2\text{O} = [*]^{4+} + \text{H}^+$				69.5	(16.6)	74.1	(17.7)	15.9 ± 3.8	(3.8)	-259	(-62)	
	$\text{UO}_2^{2+} + \text{V}^{3+} + \text{H}_2\text{O} = [*]^{3+} + 2\text{H}^+$	2-1	2		76.6	(18.3)	92.5	(22.1)	54.0 ± 2.1	(12.9)	-222	(-53)	51
54	$\text{NpO}_2^{2+} + \text{V}^{3+} + \text{H}_2\text{O} = \text{NpO}_2^+ + \text{VO}^{2+} + 2\text{H}^+$	Net			-74.9	(-17.9)	-41.8	(-10.0)	113.0	(27.0)			
	$\text{NpO}_2^{2+} + \text{V}^{3+} + \text{H}_2\text{O} = [*]^{4+} + \text{H}^+$	1-0 ^f	2		64.9	(15.5)	66.9	(16.0)	4.2 ± 25.1	(1.0)	-259	(-62)	
	or												
	$\text{NpO}_2^{2+} + \text{V}^{3+} + \text{H}_2\text{O} = [*]^{5+}$				69.0	(16.5)	133.9	(32.0)	217.6 ± 67	(52.0)	-117	(-28)	
	$\text{NpO}_2^{2+} + \text{V}^{3+} + \text{H}_2\text{O} = [*]^{4+} + \text{H}^+$	2-0	2		65.7	(15.7)	54.4	(13.0)	-37.7 ± 25	(-9.0)	-301	(-72)	132 ^b
55	$\text{PuO}_2^{2+} + \text{Ti}^{3+} + \text{H}_2\text{O} = \text{PuO}_2^+ + \text{TiO}^{2+} + 2\text{H}^+$	Net			-78.2	(-18.7)	-39.3	(-9.4)	129.7	(31.0)			
	$\text{PuO}_2^{2+} + \text{Ti}^{3+} + \text{H}_2\text{O} = [*]^{4+} + \text{H}^+$	1-0	1		61.5	(14.7)	43.1	(10.3)	-61.5 ± 5.4	(-14.7)	-272	(-65)	133
56	$\text{PuO}_2^{2+} + \text{V}^{3+} + \text{H}_2\text{O} = \text{PuO}_2^+ + \text{VO}^{2+} + 2\text{H}^+$	Net			-53.1	(-12.7)	-19.2	(-4.6)	113.0	(27.0)			
	$\text{PuO}_2^{2+} + \text{V}^{3+} + \text{H}_2\text{O} = [*]^{4+} + \text{H}^+$				71.5	(17.1)	65.3	(15.6)	-20.9 ± 16.7	(-5.0)	-280	(-67)	
	$\text{PuO}_2^{2+} + \text{V}^{3+} + \text{H}_2\text{O} = [*]^{3+} + 2\text{H}^+$	2-0	2		76.6	(18.3)							134
57	$\text{NpO}_2^{2+} + \text{N}_2\text{H}_5^+$	Net ^d											
	$\text{NpO}_2^{2+} + \text{N}_2\text{H}_5^+ + \text{H}_2\text{O} = [*]^{2+} + \text{H}^+$				78.2	(18.7)	66.5	(15.9)	-39.7 ± 11.0	(-9.5)	97	(23)	
	$\text{NpO}_2^{2+} + \text{N}_2\text{H}_5^+ + \text{H}_2\text{O} = [*]^{+} + 2\text{H}^+$	2-0	2		80.3	(19.2)	58.0	(13.9)	-74.6 ± 31	(-18.0)	63	(15)	135 ^b
58	$\text{PuO}_2^{2+} + \text{N}_2\text{H}_5^+$	Net ^d											
	$\text{PuO}_2^{2+} + \text{N}_2\text{H}_5^+ + \text{H}_2\text{O} = [*]^{2+} + \text{H}^+$	1-0	2		90.4	(21.6)	64.9	(15.5)	-85.4 ± 2.5	(-20.4)	63	(15)	136

Reduction of Np(VII) (n Is the Charge on the Np(VII) Ion)

59	$\text{Np(VII)} + \text{HCOOH} =$	Net ^d											
	$\text{Np(VII)} + \text{HCOOH} = [*]^n$				77.0	(18.4)	24.5	(5.8)	-176.1 ± 4.2	(-42.1)			
	$\text{Np(VII)} + \text{HCOOH} = [*]^{n-1} + \text{H}^+$	2-0	1		82.0	(19.6)	41.4	(9.9)	-136.0 ± 2.9	(-32.5)			137
60	$\text{Np(VII)} + \text{Hg(I)}$	Net ^d											
	$\text{Np(VII)} + \text{Hg}_2^{2+} = [*]^{n+2}$				66.5	(15.9)	49.4	(11.8)	-57.7 ± 4.2	(-13.8)			
	$\text{Np(VII)} + \text{Hg}_2^{2+} + \text{H}^+ = [*]^{n+3}$	2-0	1		68.2	(16.3)	31.0	(7.4)	-124.7 ± 14.6	(-29.8)			55
61	$\text{Np(VII)} + \text{Ti}^+ =$	Net ^f											
	$\text{Np(VII)} + \text{Ti}^+ + \text{H}^+ = [*]^{n+2}$	1-0	1		71.1	(17.0)	28.9	(6.9)	-142.3 ± 3.3	(-34.0)			54
62	$\text{Np(VII)} + \text{V(IV)} = \text{Np(VI)} + \text{V(V)}$	Net											
	$\text{Np(VII)} + \text{VO}^{2+} = [*]^{n+2}$	1-0	1		55.0	(13.1)	28.0	(6.7)	-92.0 ± 12.6	(-22.0)			138

(Table continues on following page.)

Table 8.1 (Continued)

No.	Process	Pattern (Fig. 2.1)	μ , M	ΔG , kJ/mol (kcal/mol)	ΔH , kJ/mol (kcal/mol)	ΔS , J/mol · K (cal/mol · deg)	$S^*_{\text{complex}, a}$ J/mol · K (cal/mol · deg)	Ref.
Reactions Involving Chloride Ion								
63	Pu(IV) + Fe(II) $\text{Pu}^{4+} + \text{Fe}^{2+} + \text{Cl}^- = [*]^{5+}$	Net ^d	2	59.4 (14.2)	60.2 (14.4)	2.5 ± 20.9 (0.6)	-427 (-102)	119
64	Np(IV) + V(II) $\text{Np}^{4+} + \text{V}^{2+} + \text{Cl}^- = [*]^{5+}$	Net ^d	2	63.3 (15.1)	56.1 (13.4)	-23.4 ± 2.5 (-5.6)	-427 ₁ (-102)	117
65	U(VI) + V(II) $\text{UO}_2^{2+} + \text{V}^{2+} + \text{Cl}^- = [*]^{3+}$	Net ^d	2	59.8 (14.3)	44.4 (10.6)	-51.9 ± 8.4 (-12.4)	-184 (-44)	49
66	Np(V) + Np(VI) $\text{NpO}_2^+ + \text{NpO}_2^{2+} + \text{Cl}^- = [*]^{2+}$	Net ^d	3	56.9 (13.6)	37.7 (9.0)	-58.6 ± 41.8 (-14.0)	-105 (-25)	139
67	Pu(IV) + Sn(II) $\text{Pu}^{4+} + \text{SnCl}_2 + 3\text{Cl}^- = [*]^{1+}$	Net ^d		64.0 (15.3)	87.9 (21.0)	79.5 ± (19.0)	58 (14)	140 ^b
	$\text{Pu}^{4+} + \text{SnCl}_2 + 2\text{Cl}^- = [*]^{2+}$	2-0	2	66.9 (16.0)	96.2 (23.0)	108.8 ± (26.0)	33 (8)	
	or $\text{Pu}^{4+} + \text{Sn}^{2+} + 5\text{Cl}^- = [*]^{1+}$			54.8 (13.1)	100.8 (24.1)	154.8 ± (37.0)	58 (14)	
	$\text{Pu}^{4+} + \text{Sn}^{2+} + 4\text{Cl}^- = [*]^{2+}$	2-0	2	56.9 (13.6)	112.5 (26.9)	187.0 ± (44.7)	33 (8)	
68	Pu(VI) + Sn(II) = Pu(IV) + Sn(IV) $\text{PuO}_2^{2+} + \text{SnCl}_2 + \text{Cl}^- = [*]^{1+}$	Net ^g		62.8 (15.0)	45.1 (10.8)	-59.4 ± 27.2 (-14.2)	88 (21)	141 ^b
	$\text{PuO}_2^{2+} + \text{SnCl}_2 + 2\text{Cl}^- = [*]^0$	2-1	2	61.0 (14.6)	48.8 (11.7)	-40.7 ± 22.6 (-9.7)	163 (39)	
	or $\text{PuO}_2^{2+} + \text{Sn}^{2+} + 3\text{Cl}^- = [*]^{1+}$			53.1 (12.7)	58.1 (13.9)	18.4 ± 27 (4.1)	88 (21)	
	$\text{PuO}_2^{2+} + \text{Sn}^{2+} + 4\text{Cl}^- = [*]^0$	2-0	2	51.1 (12.2)	61.8 (14.3)	33.7 ± 23 (8.5)	163 (39)	
Reactions Involving Anionic or Nonmetallic Agents								
69	$\text{U}^{4+} + \text{BrO}_3^- + \text{H}_2\text{O} = \text{UO}_2^{2+} + \text{HBrO}_2 + \text{H}^+$			-175.7 (-42.0)	-117.2 (-28.0)	196.6 (47.0)		142 ^b
	$\text{U}^{4+} + \text{BrO}_3^- + [*]^{3+}$			75.3 (18.0)	117.2 (28.0)	140.6 ± 6.3 (33.6)	-42 (-10)	
	$\text{U}^{4+} + \text{BrO}_3^- + 2\text{H}^+ = [*]^{5+} + \text{H}_2\text{O}$	2-0	4	77.8 (18.6)	95.4 (22.8)	58.6 ± 4.2 (14.0)	-192 (-46)	

70	$3\text{U(IV)} + 2\text{Cr(VI)} = 3\text{U(VI)} + 2\text{Cr(III)}$ $\text{U}^{4+} + \text{HCrO}_4^- = [\ast]^{2+} + \text{H}^+$	Net			45.1	(10.8)	55.6	(13.3)	35.6 ± 20.9	(8.5)	-126	(-30)	67
71	$\text{NpO}_2^+ + \text{HCrO}_4^- = \text{NpO}_2^{2+} + \text{Cr(V)}$ $\text{NpO}_2^+ + \text{HCrO}_4^- + 2\text{H}^+ = [\ast]^{2+} + \text{H}_2\text{O}$ $2\text{NpO}_2^+ + \text{HCrO}_4^- + 4\text{H}^+ = [\ast]^{3+} + \text{NpO}_2^{3+} + 2\text{H}_2\text{O}$	Net			70.3	(16.8)	56.1	(13.4)	-49.0 ± 4.2	(-11.7)	38	(9)	
		2-1	2		71.1	(17.0)	47.7	(11.4)	-78.2 ± 12.6	(-18.7)	0	(0)	143
72	$\text{U}^{4+} + \text{HClO}_2 + \text{H}_2\text{O} = \text{UO}_2^{2+} + \text{HOCl} + 2\text{H}^+$ $\text{U}^{4+} + \text{HClO}_2 = [\ast]^{3+} + \text{H}^+$	Net			-252.3	(-60.3)	-205.9	(-49.2)	140.2	(33.5)			
		1-0	2		66.5	(15.9)	86.2	(20.6)	66.5 ± 6.3	(15.9)	-92	(-22)	65 ^b
73	$\text{U}^{4+} + \text{Fe(CN)}_6^{3-} + 2\text{H}_2\text{O} = \text{UO}_2^+ + \text{Fe(CN)}_6^{4-} + 4\text{H}^+$ $\text{U}^{4+} + \text{Fe(CN)}_6^{3-} + \text{H}_2\text{O} = [\ast]^0 + \text{H}^+$				12.1	(2.9)							
		1-0	2		70.3	(16.8)	70.7	(16.9)	1.7 ± 8.4	(0.4)	42	(10)	144 ^b
74	$\text{PuO}_2^{2+} + \text{H}_2\text{O}_2 = \text{PuO}_2^+ + \text{HO}_2 + \text{H}^+$ $\text{PuO}_2^{2+} + \text{H}_2\text{O}_2 = [\ast]^{1+} + \text{H}^+$	Net			-56.5	(-13.5)							
		1-0	1		85.8	(20.5)	47.7	(11.4)	$\pm 12.6 \pm 12.6$	(-30.0)	-54	(-13)	60
75	$\text{NpO}_2^{2+} + \text{H}_2\text{O}_2 = \text{NpO}_2^+ + \text{HO}_2 + \text{H}^+$ $\text{NpO}_2^{2+} + \text{H}_2\text{O}_2 = [\ast]^{1+} + \text{H}^+$ $2\text{NpO}_2^{2+} + \text{H}_2\text{O}_2 = [\ast]^{2+} + \text{NpO}_2^+ + \text{H}^+$	Net			35.1	(8.4)							
					69.5	(16.6)	49.4	(11.8)	$-67.4 \pm$	(-16.1)	0	(0)	
		2-1	3		71.1	(17.0)	55.6	(13.3)	$-51.0 \pm$	(-12.2)	-33	(-8)	58
76	$\text{NpO}_2^{2+} + \text{H}_2\text{Q} = \text{NpO}_2^+ + \text{H}^+ + \text{HQ}\cdot$ $\text{NpO}_2^{2+} + \text{H}_2\text{Q} = [\ast]^{2+}$	Net ^h			16.7	(4.0)							
		1-0	1		48.1	(11.5)	34.3	(8.2)	-46.9 ± 4.6	(-11.2)	75	(18)	145
77	$\text{Pu}^{4+} + \text{H}_2\text{Q} = \text{Pu}^{3+} + \text{H}^+ + \text{HQ}\cdot$ $\text{Pu}^{4+} + \text{H}_2\text{Q} = [\ast]^{4+}$	Net ^h			16.7	(4.0)							
		1-0 ^h	1		44.4	(10.6)	47.7	(11.4)	10.5 ± 12.6	(2.5)	-146	(-35)	146
78	$\text{PuO}_2^{2+} + \text{H}_2\text{Q} = \text{PuO}_2^+ + \text{H}^+ + \text{HQ}\cdot$ $\text{PuO}_2^{2+} + \text{H}_2\text{Q} = [\ast]^{1+} + \text{H}^+$	Net ^h			20.9	(5.0)							
		1-0 ⁱ			54.8	(13.1)	63.2	(15.1)	34.7 ± 1.3	(8.3)	159	(38)	146
79	$6\text{Pu}^{3+} + \text{XeO}_3 + 6\text{H}^+ = 6\text{Pu}^{4+} + \text{Xe} + 3\text{H}_2\text{O}$ $\text{Pu}^{3+} + \text{XeO}_3 = [\ast]^{3+}$	Net											
		1-0 ^j	2		84.1	(20.1)	64.0	(15.3)	-66.9 ± 29.3	(-16.0)			147

^aThe ionic entropies for the reactant ions, required for calculating S_{complex}^* , are not known with much certainty. For the actinide ions, we have corrected the values given in Table 2.2 to unit ionic strength. For the various other reactants, we have chosen the values: -31, -27, -25, -28, -31, and 3 cal/mol·deg for Fe^{2+} , Cr^{2+} , V^{2+} , Mn^{2+} , Co^{2+} , and Eu^{2+} , respectively; -70, -66, -62, -61, -71, and -40 cal/mol·deg for Fe^{3+} , Cr^{3+} , V^{3+} , Ti^{3+} , Co^{3+} , and Ti^{3+} , respectively; and 13.5, 39, 44, 34, 45, and 36 cal/mol·deg for Cl^- , BrO_3^- , HCrO_4^- , H_2O_2 , HClO_2 , and N_2H_7^+ , respectively. These estimates are

(Table continues on following page.)

Table 8.1 (Continued)

based on published values^{1,4,8} and the Powell–Latimer correlation^{4,5} and are corrected to unit ionic strength. The average uncertainty may be about 5 cal/mol·deg.

^bOriginal data were recalculated for the table.

^cValues are estimated from those for the reverse reaction.

^dThe simplest net reaction that includes the rate determining step is unknown.

^eComplicated; see original reference.

^fA small $[H^+]$ dependence has been assumed to be a medium effect given by Harned's Rule.

^gThere is good evidence that this is a two-electron reaction.

^h H_2Q stands for hydroquinone.

ⁱPattern is 2-1 for overall reaction.

^jThe values for ΔG^* and ΔS^* are based on the assumption that all the xenon intermediates disproportionate. If instead they oxidize Pu^{3+} , ΔS^* will be about 15 J/mol·K more negative and ΔG^* will be about 4.4 kJ/mol greater than the tabulated values.

9 EMPIRICAL CORRELATIONS

Many factors influence the rates of oxidation–reduction reactions; some are properties of the individual reactants (such as ionic charge, size, and the availability of bridging groups and appropriate orbitals), and some may be properties of the overall rate-determining reaction (such as ΔH and Δz^2). It is often difficult, however, to identify the appropriate overall reaction. Since the actual rate-determining step is usually *unknown*, the best we can do is take the simplest net reaction in terms of reasonably well-characterized reactants and products which includes the rate-determining step. The most elusive factors are those peculiar to particular reactant pairs.

Since rather large amounts of data on actinide oxidation–reduction reactions are now available, it is worthwhile to examine the data empirically to see if we can identify some general factors that influence the activation parameters and hence the reaction rates.

9-1

HYDROGEN-ION DEPENDENCES

For most of the reactions studied, the number of hydrogen ions gained or released in the net activation process lies between zero and the total number *gained or released* in the corresponding net process. This is consistent with the idea that the composition of the activated complex will be somewhere between the compositions of the reactants and of the products. Important exceptions to this generalization are the cases in which a hydrogen ion is lost in the net activation process but is not involved in the overall

process. This can be viewed as a tendency for an activated complex to hydrolyze and thus reduce an otherwise high charge.

We can examine the concept of hydrolysis of activated complexes further by considering reactions involving two different net activation processes that differ by one hydrogen ion. For example, the rate law for the reduction of Np(IV) by Cr(II) is

$$\frac{-d[\text{Np(IV)}]}{dt} = [\text{Np}^{4+}] [\text{Cr}^{2+}] (k_1 [\text{H}^+]^{-1} + k_2 [\text{H}^+]^{-2}) \quad (9.1)$$

and the two net activation processes are

and

If the first process is subtracted from the second, we have, in a purely formal way, the hydrolysis of the first activated complex. Fourteen pairs† of activation processes which can be treated this way are found in Table 8.1. The results are shown in Table 9.1. We see that, even though different charges and compositions are involved, the ΔH^* and ΔS^* values for all but one of these formal processes are quite similar. The weighted average values and standard deviations (excluding process 11) are 20.2 ± 0.09 kJ/mol and 79 ± 9 J/mol · K for ΔH^* and ΔS^* , respectively. These values are similar to those for highly charged actinide ions; for example, for $\text{Pu}^{4+} + \text{H}_2\text{O} = \text{PuOH}^{3+} + \text{H}^+$, ΔH is 30.5 ± 2 kJ/mol and ΔS is 79 ± 9 J/mol · K.¹⁴⁹ If the data are correct, the discordant value for the U(IV)–Ti(III) reaction (process 11) suggests that the two activated complexes have quite different structures.

It has recently been suggested¹⁵⁰ that reactions with nonintegral hydrogen-ion dependences, such as the Np(IV)–Cr(II) reaction and the others discussed in this section, actually have only one activated complex and one ΔH^* but that ΔS^* is a function of $[\text{H}^+]$. Since this suggestion is contrary to the conventional interpretation given here, the available data were examined to see whether they are consistent with a single ΔH^* value for each reaction independent of temperature. According to this hypothesis, the hydrogen-ion and temperature dependences should be given by the equation

$$k_{\text{obs}} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) [\text{H}^+]^{(n_H + a[\text{H}^+])} \quad (9.4)$$

† The data for the V(III)–Np(VI) reaction were not included, because they give the improbable value of -255 ± 84 J/mol · K for ΔS^* of hydrolysis. The original hydrogen-ion and temperature dependence have been recalculated under the assumption that activity effects are important (see Chap. 2, Sec. 2-4). Since this interpretation fits the data nearly as well as the assumption of parallel paths, it seems likely that only one activated complex is involved.

Table 9.1
HYDROLYSIS OF ACTIVATED COMPLEXES

	Process	ΔG^* , kJ/mol (kcal/mol)	ΔH^* , kJ/mol (kcal/mol)	ΔS^* , J/mol · K (cal/mol · deg)	RMS ratio†
1	$\{\text{Fe} \cdot \text{PuO}_2^*\}^{4+} + \text{H}_2\text{O} = [*]^{3+} + \text{H}^+$	0.4 (0.1)	21 (5.0)	71 (17 ± 2)	2.15
2	$\{\text{Co} \cdot \text{NpO}_2^*\}^{4+} + \text{H}_2\text{O} = [*]^{3+} + \text{H}^+$	5.4 (1.3)	32 (7.7)	90 (21.5 ± 9)	1.12
3	$\{\text{V} \cdot \text{OH} \cdot \text{UO}_2^*\}^{4+} (+\text{H}_2\text{O}) = [*]^{3+} + \text{H}^+$	7.1 (1.7)	18 (4.4)	38 (9 ± 2)	2.02
4	$\{\text{Np} \cdot (\text{OH})_2 \cdot \text{NpO}_2^*\}^{4+} (+\text{H}_2\text{O}) = [*]^{3+} + \text{H}^+$	2.7 (0.65)	29 (6.9)	171 (41 ± 17)	0.95
5	$\{\text{Cr} \cdot \text{NpO}_2 \cdot \text{H}^*\}^{4+} = [*]^{3+} + \text{H}^+$	10.0 (2.4)	24 (5.7)	46 (11 ± 13)	1.05
6	$\{\text{Cr} \cdot \text{OH} \cdot \text{Np}^*\}^{5+} (+\text{H}_2\text{O}) = [*]^{4+} + \text{H}^+$	4.2 (1.0)	18 (4.4)	46 (11 ± 4)	1.23
7	$\{\text{U} \cdot \text{OH} \cdot \text{PuO}_2^*\}^{5+} (+\text{H}_2\text{O}) = [*]^{4+} + \text{H}^+$	-2.5 (-0.6)	15 (3.7)	59 (14 ± 2)	2.41
8	$\{\text{Pu} \cdot \text{NpO}_2^*\}^{5+} + \text{H}_2\text{O} = [*]^{4+} + \text{H}^+$	5.9 (1.4)	22 (5.3)	109 (26 ± 1)	1.23
9	$\{\text{Np} \cdot \text{UO}_2^*\}^{5+} + \text{H}_2\text{O} = [*]^{4+} + \text{H}^+$	8.4 (2.0)	36 (8.7)	96 (23 ± 7)	0.95
10	$\{\text{V} \cdot \text{Pu} \cdot \text{OH}^*\}^{6+} (+\text{H}_2\text{O}) = [*]^{5+} + \text{H}^+$	-1.7 (-0.4)	18 (4.4)	67 (16 ± 4)	1.09
11	$\{\text{Tl} \cdot \text{U} \cdot \text{OH}^*\}^{6+} (+\text{H}_2\text{O}) = [*]^{5+} + \text{H}^+$	0(0)	-18 (-4.2)	-59 (-14 ± 8)	1.14
12	$\{\text{Fe} \cdot \text{U} \cdot \text{OH}^*\}^{6+} (+\text{H}_2\text{O}) = [*]^{5+} + \text{H}^+$	-4.0(-1)	26 (6.1)	100 (24 ± 10)	0.95
13‡	$[\text{Np(VII)} \cdot \text{Hg}_2 \cdot \text{H}^*]^{n+3} = [*]^{n+2} + \text{H}^+$	-1.7 (-0.4)	18 (4.4)	67 (16 ± 4)	1.18
14‡	$[\text{Np(VII)} \cdot \text{HCO}_2\text{H}^*]^n = [*]^{n-1} + \text{H}^+$	5.0 (1.2)	17 (4.1)	42 (10 ± 2)	1.56

†The root-mean-square deviation found by Eq. 9.4 over the same quantity based on two activated complexes.

‡n is the unknown charge on Np(VII) in acid solution.

where n_H is the empirical $[H^+]$ dependence and a is an allowance for small curvature in graphs of $\log k_{obs}$ vs. $\log [H^+]$. The data for the 14 reactions in Table 9.1 were fitted to this equation by a least-squares procedure, and the root-mean-square deviations were compared with those obtained by the conventional equations. The ratios of these deviations are given in the last column of the table. For three of the reactions, Eq. 9.4 fits the data better than the conventional one; for four of the reactions, the equation is only a little poorer; and, for the remaining seven reactions, the fit is significantly poorer. These calculations, together with the reasonably consistent values for ΔH^* and ΔS^* for hydrolysis shown in the table, support the usual concept of distinct activated complexes formed with definite numbers of hydrogen ions and indicate that Eq. 9.4 is not generally satisfactory.

9-2

ENTROPIES OF ACTIVATION

The entropy of activation depends on the structural changes that occur in the reactant ions and solvation shells when the activated complex is formed. Some of these changes depend on the particular reaction, but some more general effects can be expected also. For example, ΔS^* is expected to depend on Δn , the change in the number of nonsolvent molecules (or ions) in the activation process. This is related to the fact that Δn determines the purely mixing part of the entropy change.¹⁵¹ Changes in the symmetry numbers should also affect ΔS^* .¹⁵² We are forced to ignore this factor because the details of the structures of the activated complexes are unknown. The entropy of activation is also expected to have an electrostatic component that depends on Δz^2 , the change in the sum of the squares of the ionic charges in the activation process.¹⁵³ Since, in addition, rapid reactions involve the crossing of lower free-energy barriers and presumably involve less distortion during activation, ΔG^* might also show an influence. A correlation between ΔS^* and ΔH^* , described as a compensatory effect, has been noted previously.^{154,155} Such an effect would also imply a correlation between ΔS^* and ΔG^* since $\Delta H^* = \Delta G^* + T\Delta S^*$.

Table 8.1 lists 96 ΔS^* values that can be used; these range from -201 to $+218$ J/mol $\cdot$ K, with an average of -31.66 and a root-mean-square deviation of 97 J/mol $\cdot$ K. If the factors discussed have an influence on ΔS^* , the expression

$$\Delta S^* = a + b \Delta n + c \Delta z^2 + d \Delta G^* \quad (9.5)$$

can be fit to the data; the coefficients will have relatively small uncertainties; and the difference between the observed and calculated values will be smaller than the deviation from the average value. A standard least-squares procedure was used to find the best values for the four parameters and their standard deviations. These are listed in Table 9.2, along with the root-mean-square deviation between observed and

Table 9.2
CORRELATION OF ENTROPIES OF ACTIVATION[†]‡
($\Delta S^* = a + b \Delta n + c \Delta z^2 + d \Delta G^*$)

No. of data	a, J/mol · K	b, J/mol · K	c, J/mol · K	d, J/kJ · K	RMS dev.,§ J/mol · K
96	-26.6 ± 35.2	27.9 ± 5.4	-6.2 ± 0.9	0.62 ± 0.50	66
96	16.4 ± 8.4	28.2 ± 5.4	-6.3 ± 0.9	0 (fixed)	67
96	-31.7 ± 9.9	0 (fixed)	0 (fixed)	0 (fixed)	97
79¶	-23.6 ± 31.4	37.3 ± 4.9	-7.8 ± 0.8	0.92 ± 0.44	52
79	40.2 ± 8.3	37.8 ± 5.0	-8.0 ± 0.8	0 (fixed)	54
79	-33.9 ± 11.5	0 (fixed)	0 (fixed)	0 (fixed)	102

[†] All pertinent data from Table 8.1.

[‡] Uncertainties are standard deviations.

[§] Root-mean-square deviation between observed and calculated values.

[¶] Data for processes involving nonmetallic and anionic substances are omitted.

calculated values. We see that, since the coefficient for ΔG^* is less than twice its standard deviation, it is not statistically significant. Repeating the calculation with d fixed at zero gives essentially the same deviation.

Most of the data showing large deviations involve reactions of nonmetallic or anionic substances, such as BrO_3^- or H_2O_2 . The 17 processes in this class were excluded, and the calculations were repeated. These results, also given in Table 9.2, show that the values for the various parameters are not changed significantly but the root-mean-square deviations are greatly reduced.

These calculations show that both Δn and Δz^2 are important factors in determining ΔS^* but that ΔG^* probably is not. No correlation with ΔG^* alone was found. We should note, however, that the smallest root-mean-square deviation in the table (52 J/mol · K) is very much larger than the usual experimental uncertainty in ΔS^* ; this indicates that other very important factors remain to be identified.

The effect of Δn , as indicated by the size of parameter b , seems quite reasonable since the use of a simple lattice model gives 34 J/mol · K for the coefficient for Δn .¹⁵¹ On the other hand, the effect of Δz^2 , indicated by c , is smaller than might be expected but does have the expected sign. The electrostatic contribution to ΔS^* at infinite dilution in water at 25°C is given by $-42 z_a z_b$ for an approach of ions charged z_a and z_b to a distance of 0.2 nm.¹⁵³ This corresponds to $-4.2 \Delta z^2 / r^*$, where r^* is the effective distance of approach in nanometers in the formation of the activated complex. The effect becomes smaller at larger ionic strengths, and, using parameters from Chap. 7, we estimate $[(-4.2/r^*) + 2.5] \Delta z^2$ for unit ionic strength. Thus a coefficient for Δz^2 of -8 J/mol · K implies that r^* is 0.4 nm, which seems to be at least 50% too high.

9-3

ENTROPIES OF THE ACTIVATED COMPLEXES

A somewhat different approach to activation entropies involves the calculation of the formal ionic entropies of the activated complexes themselves. The entropies of ordinary aqueous ions have been shown to depend strongly on ionic charge and to a lesser extent on radius and mass.⁴⁵ A similar but much rougher correlation has been noted for activated complexes.¹⁵⁶

The formal ionic entropy of an activated complex, S_{complex}^* , is defined by the relation

$$S_{\text{complex}}^* = \Delta S^* + \sum S_{\text{reactants}}^0 - \sum S_{\text{other products}}^0 \quad (9.6)$$

This definition can be ambiguous because the number of moles of water involved in a net activation process is not known with certainty. For example, the net activation process for the second term in the rate law for the Pu(IV)–V(III) reaction (see Chap. 3, Sec. 3-1) can be written as either

or

In this example the value for S_{complex}^* defined in terms of the second process will be about 70 J/mol · K more positive than the value defined in terms of the first process. For consistency, we have defined all S_{complex}^* values in terms of minimum hydration.

The values for S_{complex}^* defined this way are plotted vs. the charge on the activated complex in Fig. 9.1. The data show considerable scatter, but a definite trend is quite obvious. If S_{complex}^* is assumed to be linear in the charge on the activated complex, the scatter (measured by the root-mean-square deviation) is about 15% greater than for the ΔS^* values according to Eq. 9.5.

9-4

HEATS OF ACTIVATION

A graph of the available values for ΔH^* vs. ΔH showed that most of the data fall in a band with a small positive slope. The ΔH^* values for the net activation processes that do not involve hydrogen ions tended to be lower than average, however, and those for processes in which two hydrogen ions are released tended to be above average. This leads us to postulate an empirical correlation of the form

Fig. 9.1 Formal entropy vs. charge for the activated complexes. Reaction numbers are from Table 8.1. Open circles (o) refer to reactions with nonmetallic or anionic reagents.

$$\Delta H^* = a + b \Delta H + c |h| \quad (9.9)$$

where $|h|$ is the absolute value of the number of hydrogen ions gained in the net activation process. The data for the 71 pertinent processes in Table 8.1 were used to find the best values for the parameters. These values are $a = 41.4 \pm 6.2$ kJ/mol, $b = 0.16 \pm 0.05$, and $c = 23.0 \pm 3.9$ kJ/mol. The data scatter considerably, giving a root-mean-square deviation of 25 kJ/mol, which is much less than the 37.6 kJ/mol for the ΔH^* values themselves. As was the case for the ΔS^* values, the processes involving nonmetallic and anionic substances show the most scatter. When these four processes

were omitted, the root-mean-square deviation was reduced to 19 kJ/mol,[†] but the values for a , b , and c were changed very little. Thus we conclude that ΔH^* correlates with both ΔH and $|h|$.

To illustrate this correlation and to show the range of values involved, we plotted the quantity $\Delta H^* - 23.9|h|$ vs. ΔH in Fig. 9.2.

The observed dependence on $|h|$ implies that, on the average, about 24 kJ/mol are contributed to ΔH^* for each hydrogen ion. This may be the average value required for the formation of a reactive intermediate by either loss or gain of a hydrogen ion. This is consistent with the results in Table 9.1, where it was shown that ΔH^* averages about 20 kJ/mol for the loss of a hydrogen ion from one activated complex to form another.

9.5

FREE ENERGIES OF ACTIVATION

Since ΔH^* correlates with ΔH and $|h|$ and ΔS^* correlates with Δn and Δz^2 , ΔG^* is expected to correlate with these quantities also. The function

Fig. 9.2 Heat of activation vs. heat of reaction. Reaction numbers are from Table 8.1. Open circles (○) refer to reactions with nonmetallic agents.

[†]This can be reduced to 17 kJ/mol if a term for Δz^2 is included.

$$\Delta G^* = a + b \Delta H + c |h| + d \Delta n + e \Delta z^2 \quad (9.10)$$

was tested as before by using the 71 net activation processes from Table 8.1 for which the necessary data are available. The results of the calculations are summarized in Table 9.3. The first calculation shows that ΔG^* apparently does not depend on Δz^2 even though ΔS^* does. The calculation was repeated with $e = 0$ with little effect on any of the remaining parameters or on the deviations between observed and calculated values. The observed values of ΔG^* corrected for the effects of $|h|$ and Δn are plotted vs. ΔH in Fig. 9.3. The scatter shows that one or more important terms have yet to be recognized. However, 82% of the points have deviations less than 11.4 kJ/mol, which corresponds to a factor of 100 in actual rate.

If ΔG is used instead of ΔH in Eq. 9.10, calculations show that ΔG^* correlates with $|h|$ and Δn but with neither ΔG nor Δz^2 . This is to be contrasted with the results for actinide-actinide reactions where good correlations were observed (Chap. 4).

The correlations discussed in this section are interesting in that they show the relative importance of the physical factors $|h|$, Δn , and Δz^2 . They are of very little predictive value, however, since they strongly support the old teaching that, in general, the rate of a reaction is not determined by its equilibrium.

Fig. 9.3 Free energy of activation, corrected for $|h|$ and Δn , vs. heat of reaction. Reaction numbers are from Table 8.1. Open circles (○) refer to reactions with nonmetallic reagents.

Table 9.3
 CORRELATION OF FREE ENERGIES OF ACTIVATION[†] _‡
 ($\Delta G^* = a + b \Delta H + c |h| + d \Delta n + e \Delta z^2$)

a, kJ/mol	b	c, kJ/mol	d, kJ/mol	e, kJ/mol	RMS dev., [§] kJ/mol
63 ± 4	0.065 ± 0.025	8.2 ± 1.8	6.8 ± 1.8	0.44 ± 0.27	10.6
60 ± 3	0.057 ± 0.024	9.3 ± 1.7	5.1 ± 1.5	0 (fixed)	10.9
69 ± 2	0 (fixed)	0 (fixed)	0 (fixed)	0 (fixed)	14.2

[†]Data from 71 activation processes.

_‡Uncertainties are standard deviations.

[§]Root-mean-square deviation between observed and calculated values.

10 CATALOG OF REACTION RATES

The data on the oxidation–reduction reactions of uranium, neptunium, plutonium, and americium which were available in the fall of 1973 are listed in Tables 10.1 to 10.24 in this chapter. Results of the older work were adapted from the compilations by Magnusson and coworkers¹⁵⁷ and by Connick.¹⁵⁸ Although some of these results are only qualitative, they are included because they provide good bases for further work.

Semiquantitative results are given in terms of half-lives under the specified conditions of concentration and temperature. Where possible, typical values for the rate constants are given; k is used for first-order rate constants, k' , for second-order rate constants written in terms of uncomplexed or unhydrolyzed species, and k'' , for second-order rate constants written in terms of the stoichiometric concentrations. The rate constants apply to the rate of change of concentration of the actinide ion or, if both reactants are actinides, to the actinide ion being oxidized; for example, in the reaction $2\text{Pu(IV)} + \text{U(IV)} = 2\text{Pu(III)} + \text{U(VI)}$,

$$-\frac{d[\text{U(IV)}]}{dt} = -\frac{1}{2} \frac{d[\text{Pu(IV)}]}{dt} = k'' [\text{Pu(IV)}] [\text{U(IV)}] = k' [\text{Pu}^{4+}] [\text{U}^{4+}]$$

The available temperature dependences are given either by E_a in terms of the Arrhenius equation or by ΔH^* in terms of the Eyring equation (Eq. 3.1). These quantities are related by $\Delta H^* = E_a - RT$. The values of these quantities are given both in kilojoules per mole and in kilocalories per mole, the latter in parentheses.

The significance of the uncertainties given by the various authors is not always clear. Usually they appear to be estimates of precision rather than of accuracy and can be taken to approximate one standard deviation.

Table 10.1
OXIDATION OF URANIUM(III) TO URANIUM(IV)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
ClO_4^-		0.5 <i>M</i> HClO_4	22	$k = 1.8 \times 10^{-5} \text{ sec}^{-1}$ $E_a = 92 \text{ (22)}$	159
		6.0 <i>M</i> HClO_4	22	$k = 8.7 \times 10^{-4} \text{ sec}^{-1}$	
$\text{Co}(\text{NH}_3)_5 \text{Cl}^{2+}$	3×10^{-4}	0.2 <i>M</i> (H,Li) ClO_4	25	$k'' = (3.24 \pm 0.05) \times 10^4 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	18
$\text{Co}(\text{NH}_3)_5 \text{Br}^{2+}$	10^{-3}	0.2 <i>M</i> (H,Li) ClO_4	25	$k'' = (1.42 \pm 0.01) \times 10^4 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	18
$\text{Co}(\text{NH}_3)_5 \text{N}_3^{2+}$	5×10^{-5}	0.2 <i>M</i> (H,Li) ClO_4	25	$k'' = (1.08 \pm 0.08) \times 10^6 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	18
$\text{Co}(\text{NH}_3)_5 \text{F}^{2+}$	1.2×10^{-4}	0.2 <i>M</i> (H,Li) ClO_4	25	$k'' = (5.4 \pm 0.13) \times 10^5 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	18
$\text{Co}(\text{NH}_3)_5 \text{OAc}^{2+}$	8×10^{-4}	0.2 <i>M</i> (H,Li) ClO_4	25	$k'' = (1.5 \pm 0.14) \times 10^4 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	18
$\text{Co}(\text{NH}_3)_5 \text{CN}^{2+}$	1.2×10^{-3}	0.2 <i>M</i> (H,Li) ClO_4	25	$k'' = (3.45 \pm 0.22) \times 10^3 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	18
$\text{Co}(\text{NH}_3)_5 \text{NCS}^{2+}$	8×10^{-4}	0.2 <i>M</i> (H,Li) ClO_4	25	$k'' = (18.2 \pm 0.6) [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	18
<i>cis</i> - $\text{Co}(\text{en})_2 \text{Cl}_2^{2+}$	4×10^{-4}	0.2 <i>M</i> (H,Li) ClO_4	25	$k'' = (2.15 \pm 0.05) \times 10^4 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	18
<i>trans</i> - $\text{Co}(\text{en})_2 \text{Cl}_2^{2+}$	1×10^{-4}	0.2 <i>M</i> (H,Li) ClO_4	25	$k'' = (2.15 \pm 0.08) \times 10^5 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	18
<i>cis</i> - $\text{Co}(\text{en})_2 (\text{H}_2\text{O}) \text{Cl}^{2+}$	4×10^{-4}	0.2 <i>M</i> (H,Li) ClO_4	25	$k'' = (1.94 \pm 0.06) \times 10^4 [\text{H}^+]^{-0.06} M^{-1} \text{ sec}^{-1}$	18
<i>trans</i> - $\text{Co}(\text{en})_2 (\text{H}_2\text{O}) \text{CN}^{2+}$	7×10^{-4}	0.2 <i>M</i> (H,Li) ClO_4	25	$k'' = (\sim 8) \times 10^4 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	18
$\text{Co}(\text{NH}_3)_6^{3+}$	10^{-3}	0.2 <i>M</i> (H,Li) ClO_4	25	$k'' = (1.32 \pm 0.04) [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	18
$\text{Co}(\text{en})_3^{3+}$	10^{-3}	0.2 <i>M</i> (H,Li) ClO_4	25	Catalyzed by halide ions $k'' = 0.133 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	18
$\text{Co}(\text{NH}_3)_5 (\text{H}_2\text{O})^{3+}$	1.3×10^{-3}	0.1 <i>M</i> HClO_4 – 0.1 <i>M</i> LiClO_4	25	Catalyzed by halide ions $k'' = 28.4 \pm 1.2 M^{-1} \text{ sec}^{-1}$ Complicated $[\text{H}^+]$ dependence	18

<i>trans</i> - Co(en) ₂ (NH ₃)(H ₂ O) ³⁺	9 × 10 ⁻⁴	0.1M LiClO ₄	25	k'' = 40.1 ± 0.1 M ⁻¹ sec ⁻¹ Complicated [H ⁺] dependence	18
<i>cis</i> -Co(NH ₃) ₄ (H ₂ O) ₂ ³⁺	3 × 10 ⁻⁴	0.2M (H,Li)ClO ₄	25	k'' = 210 ± 2 + (0.47 ± 0.03)[H ⁺] ⁻¹ M ⁻¹ sec ⁻¹ ΔH* = 15.4 ± 0.02(3.67 ± 0.04) at μ = 2M	115
Cr ³⁺ (aquo)	10 ⁻³	0.2M (H,Li)ClO ₄	25	k'' = (6.0[H ⁺] ⁻¹ + 0.19[H ⁺] ⁻²) × 10 ⁻³ M ⁻¹ sec ⁻¹	160
CrCl ₂ ²⁺	10 ⁻³	0.2M (H,Li)ClO ₄	25	k'' = 0.48[H ⁺] ⁻¹ M ⁻¹ sec ⁻¹	160
CrBr ₂ ²⁺	10 ⁻³	0.2M (H,Li)ClO ₄	25	k'' = 1.42[H ⁺] ⁻¹ M ⁻¹ sec ⁻¹	160
CrF ₂ ²⁺	10 ⁻³	0.2M (H,Li)ClO ₄	25	k'' = 17 + 0.31[H ⁺] ⁻¹ M ⁻¹ sec ⁻¹	160
CrN ₃ ³⁺	10 ⁻³	0.2M (H,Li)ClO ₄	25	k'' = 40 + 0.41[H ⁺] ⁻¹ M ⁻¹ sec ⁻¹	160
CrNCS ₂ ²⁺	10 ⁻³	0.2M (H,Li)ClO ₄	25	k'' = (14[H ⁺] ⁻¹ + 0.74[H ⁺] ⁻²) × 10 ⁻³ M ⁻¹ sec ⁻¹	160
CrSCN ₂ ²⁺	10 ⁻³	0.2M (H,Li)ClO ₄	25	k'' = 9 × 10 ³ M ⁻¹ sec ⁻¹	160
<i>cis</i> -CrCl ₂ ⁺	10 ⁻³	0.2M (H,Li)ClO ₄	25	k'' = 51 + 4.35[H ⁺] ⁻¹ M ⁻¹ sec ⁻¹	160
<i>trans</i> -CrCl ₂ ⁺	10 ⁻³	0.2M (H,Li)ClO ₄	25	k'' = 44 + 5.5[H ⁺] ⁻¹ M ⁻¹ sec ⁻¹	160
Cr(NH ₃) ₅ Cl ²⁺	10 ⁻³	0.2M (H,Li)ClO ₄	25	k'' = 8 × 10 ⁻³	161
H ₂ O (or H ⁺)	55.5	10 ⁻⁴ M HCl	22	k = 4.27 × 10 ⁻⁴ sec ⁻¹	161
	55.5	0.5M HCl	22	k = 1.84 × 10 ⁻⁷ sec ⁻¹ ; rate increased by LiCl	161
	55.5	8.3M HCl	22	k = 2.9 × 10 ⁻⁴ sec ⁻¹	161
	55.5	0.25M H ₂ SO ₄	22	E _a = 42 (10) in 6M HCl k = 8.52 × 10 ⁻⁷ sec ⁻¹	159
	55.5	4.0M H ₂ SO ₄	22	E _a = 54 (13) k = 4.66 × 10 ⁻⁵ sec ⁻¹	159
	55.5	0.05M H ₂ SO ₄	20	k = 1.7 × 10 ⁻⁶ sec ⁻¹	162
UO ₂ ⁺	10 ⁻⁵	0.1M HClO ₄	25	E _a = 30 (7.1) k'' = (5.0 ± 0.2) × 10 ⁴ [H ⁺] ⁰ M ⁻¹ sec ⁻¹ ΔH* = 8(2)	76
UO ₂ ²⁺	2.5 × 10 ⁻⁵	0.1M HClO ₄	25	k'' = (1.20 ± 0.04) × 10 ⁴ [H ⁺] ⁰ M ⁻¹ sec ⁻¹ ΔH* = 17.4 (4.15)	76

Table 10.2
OXIDATION OF URANIUM(IV)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Br ₂	0.07	2 <i>M</i> (H,Na)ClO ₄ 1 <i>M</i> Na(Br,ClO ₄)	25	$k'' = 5.3 \times 10^{-4} [\text{H}^+]^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ Catalyzed by Fe(III) and Mn(II)	163
BrO ₃ ⁻	4×10^{-3}	4 <i>M</i> (H,Na)ClO ₄	25	$k'' = 0.41 + 0.14 [\text{H}^+]^2 \text{ M}^{-1} \text{ sec}^{-1}$ $\Delta H^* = 115 \pm 0.4$ (27.6 $\pm$ 0.1) and 95 $\pm$ 0.4 (22.8 $\pm$ 0.1) for the respective rate constants	142
Ce(IV)	5×10^{-5}	2 <i>M</i> (H,Na)ClO ₄	25	$k'' = 8.7 \times 10^3 [\text{H}^+]^{-1.2} \text{ M}^{-1} \text{ sec}^{-1}$ $E_a = 64 \pm 3$ (15.4 $\pm$ 0.7) Rates are lower in solutions of tributyl phosphate Reaction also studied in acidic sulfate media $E_a = 71 \pm 2$ (17 $\pm$ 0.4)	123 164 165
ClO ₃ ⁻	0.075	0.5 <i>M</i> (H,Na)ClO ₄	Room	$k'' = 2.9 \times 10^{-3} [\text{H}^+] \text{ M}^{-1} \text{ sec}^{-1}$ Catalyzed by Fe(II) and V(V)	166 167
Fe ³⁺	2×10^{-4}	1 <i>M</i> (H,Na)ClO ₄	25	$k' = 2.98 [\text{H}^+]^{-1} + 10.6 [\text{H}^+]^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ $E_a = 77 \pm 11$ (18.5 $\pm$ 2.6) and 103 $\pm$ 2 (24.7 $\pm$ 0.5) for the respective rate constants† Rate is increased in aqueous solutions of CH ₃ OH, C ₂ H ₅ OH, or (CH ₃) ₂ CO Also studied in HNO ₃ by a catalytic method Effect of sulfate determined	46 168 169 190
Fe(CN) ₆ ³⁻	10 ⁻³	2 <i>M</i> (H,Na)ClO ₄	25	$k'' = 3.2 [\text{H}^+]^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ $\Delta H^* = 71 \pm 4$ (16.9 $\pm$ 0.9) Rate is inhibited by Cl ⁻ Rate decreased significantly in D ₂ O solutions	144 170
HClO ₂	0.1	2 <i>M</i> (H,Na)ClO ₄ 0.1 <i>M</i> C ₆ H ₅ OH	25	$k'' = (291 \pm 4)(1 + 4 [\text{HClO}_2])^{-1} (1 + 21 [\text{H}^+])^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ $\Delta H^* = 107 \pm 1$ (25.5 $\pm$ 0.3) for the second-order rate constant	65a

				Phenol scavenges the Cl(I) species and forms chlorophenols; the rate is independent of $[C_6H_5OH]$ Also studied in H_2SO_4	65b
$HCrO_4^-$	3×10^{-5} (U^{4+} in excess)	$3M (H,Li)ClO_4$	25	$k' = (0.85 + 8.76[H^+]^{-1}) \times 10^4 M^{-1} sec^{-1}$ The reaction induces the oxidation of I^-	67
HNO_2	0.03	$3M (H,Na)NO_3$	25	Reaction catalyzed by $(0.5 - 10) \times 10^{-3} M Fe(III)$ $-d[U(IV)]/dt = (1.01 \pm 0.02) \times 10^3 [U(IV)] [Fe(III)] [HNO_2]^0 [H^+]^{-1.15} M sec^{-1}$ $E_a = 74 (17.8)$ Uncatalyzed reaction is much slower	169
H_2O_2	2×10^{-3}	$2M (H,Li)ClO_4$	25	$k'' = 1 [H^+]^{-0.21} M^{-1} sec^{-1}$ $E_a = 67 - 79 (16 - 19)$ Reaction is inhibited by $Cu(II)$ and $Co(II)$ Higher rates have been reported	171
$Np(V)$	2×10^{-3}	$1M (H,Na)ClO_4$	25	$-d[U(IV)]/dt = k_1 [Np(V)] [U(IV)] + k_2 [Np(IV)] [U(IV)]$ For $[H^+] = 0.1M$ $k_1 = 8.3 \times 10^{-4} M^{-1} sec^{-1}$ $k_2 = 5.3 \times 10^{-3} M^{-1} sec^{-1}$ $E_a = 134 \pm 8 (32 \pm 2)$ and $63 \pm 13 (15 \pm 3)$ for the respective rate constants Reaction is catalyzed by Cl^-	88
$Np(VI)$	8×10^{-4}	$2M (H,Na)ClO_4$	25	$k' = 21.7 [H^+]^{-1} M^{-1} sec^{-1}$ $\Delta H^* = 76 \pm 1 (18.2 \pm 0.2)$ Deuterium isotope effect given by $k_H/k_D = 1.6$	83
O_2	10^{-3}	$1M (H,Na)ClO_4$	25	$k' = (1.49[H^+]^{-1} + 0.24[H^+]^{-2}) \times 10^{-2} M^{-1} sec^{-1}$ $E_a = 81 \pm 4 (19.3 \pm 1)$ in $0.95M HClO_4$ Reaction is inhibited by Cl^- , Ag^+ , and Fe^{2+} and catalyzed by Cu^{2+} and Hg^{2+}	173
Pu^{4+}	2×10^{-3}	$2M (H,Li)ClO_4$	25	$k' = 34 [H^+]^{-2} M^{-1} sec^{-1}$ $\Delta H^* = 102 \pm 2.5 (24.3 \pm 0.6)$ Reaction is catalyzed by $P_2O_7^{4-}$, PO_4^{3-} , SO_4^{2-} , and Cr^{3+}	174
					82
					175

(Table continues on following page.)

Table 10.2 (Continued)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Pu(VI)	2×10^{-4}	$2M$ (H,Li)ClO ₄	25	$k'' = \frac{k_1}{(1 + \{k_1 [H^+]\} / k_2)([H^+] + K)}$ $k_1 = 4.4 \text{ sec}^{-1}$; $k_2 = 11M \text{ sec}^{-1}$; $K = 0.024M$ $\Delta H^* = 74 \pm 2$ (17.6 ± 0.4) and 90 ± 1 (21.4 ± 0.3) for the respective rate constants Rate law shows evidence for consecutive reactions and a metastable intermediate	61
S ₂ O ₈ ²⁻	0.03	0.5 <i>M</i> H ₂ SO ₄	Room	$k'' = 7.2 \times 10^{-3} [H^+]^0 M^{-1} \text{ sec}^{-1}$	176
Tl ³⁺	0.01	2.9 <i>M</i> (H,Na)ClO ₄	25	$k' = (2.11 [H^+]^{-1} + 2.13 [H^+]^{-2}) \times 10^{-2} M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 103 \pm 8$ (24.6 ± 2) and 91 ± 8 (21.7 ± 2) for the respective rate constants Reaction is catalyzed by Fe(III); tartaric acid increases rate and causes departure from second-order kinetics CH ₃ OH causes departure from second-order kinetics Second-order rate law not followed over wide ranges in reactant concentrations	122 177 178 179
U(VI)	0.03	Cl ⁻ solutions	25	Exchange rate = $1.2 \times 10^{-5} [U(IV)]^2 [U(VI)] [H^+]^{-3} M \text{ sec}^{-1}$ $E_a = 140 \pm 3$ (33.4 ± 0.8) for pH = 0.85	126
	0.005	2 <i>M</i> (H,Na)ClO ₄	25	k' (for exchange) = $2.13 \times 10^{-7} [H^+]^{-3} M^{-1} \text{ sec}^{-1}$ Low concentration of U(IV) used to minimize the contribution of the $[U(IV)]^2$ term $E_a = 159 \pm 2$ (38.1 ± 0.5) Exchange is induced by UV light; quantum yield is about 0.01 Also studied in sulfate (181) and in aqueous HCl-ethanol solutions	180 182

†Original data recalculated.

Table 10.3
OXIDATION OF URANIUM(V)

Agent	Typical concentration, M	Solution	Temp., °C	Results	Ref.
Fe(III)	3×10^{-3}	$1M \text{ HClO}_4 - 1M \text{ LiClO}_4$	25	$k'' = 2.5 \times 10^5 M^{-1} \text{ sec}^{-1}$, estimated from the effect of Fe(III) and V(IV) on the V(III)–U(VI) reaction	51
U(V)	10^{-3}	$2M (\text{H,Li})\text{ClO}_4$	25	$k'' = 240[\text{H}^+]^{0.82} M^{-1} \text{ sec}^{-1}$ Effect of the U(V) • U(VI) complex allowed for by extrapolation to $[\text{U(VI)}] = 0$ $\Delta H^* = 46 \pm 2 (11.0 \pm 0.4)$ The reaction has also been studied by electro-chemical methods Also studied in sulfate solutions	20 183, 184 185

Table 10.4
REDUCTION OF URANIUM(V)

Agent	Typical concentration, M	Solution	Temp., °C	Results	Ref.
Cr(II)	0.06	$2M (\text{H,Na})\text{ClO}_4$	20	$k'' = (416 \pm 15) \exp(0.16[\text{H}^+]) M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 13 \pm 1.2 (3.2 \pm 0.3)$ The U(V) is in the form of the U(V) • Cr(III) complex	128

Table 10.5
REDUCTION OF URANIUM(VI)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Cr(II)	2.5×10^{-3}	2 <i>M</i> (H ₂ Na)ClO ₄	25	$k'' = 1.42 \times 10^4 [H^+]^0 M^{-1} \text{ sec}^{-1}$ $E_a = 5.8 \pm 1.7 (1.4 \pm 0.4)$ A Cr(III) · U(V) complex is formed	130 30
Eu(II)	4.7×10^{-4}	2 <i>M</i> (H ₂ Na)ClO ₄	20	$k'' = 1.43 \times 10^4 \exp (0.15 [H^+]) M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 6.3 \pm 1.3 (1.5 \pm 0.3)$ Reaction is catalyzed by added sulfate; rate is nearly tripled by 0.003 <i>M</i> SO ₄ ²⁻	131
Fe(II)		3.7 <i>M</i> H ₃ PO ₄	25	$t_{1/2} = 160 \text{ to } 170 \text{ min}$; [Fe(II)] not specified	186
Np(III)				(See Table 10.6)	
Sn(II)	1	1 <i>M</i> HCl	30	$k'' = 2.75 \times 10^{-3} M^{-1} \text{ hr}^{-1}$ $E_a = 76 (18)$ Rate increases with increasing HCl concentration Evidence for optical interaction absorption	187 188
Ti(III)	2×10^{-3}	0.5 <i>M</i> (H ₂ Li)ClO ₄	25	$k'' = 13.7([H^+] + 0.0136)^{-1} M^{-1} \text{ sec}^{-1}$ E_a unknown [Cl ⁻] has no effect up to 0.3 <i>M</i> Reaction is inhibited by V(IV), which is reduced to V(III)	189
V(II)	1.5×10^{-3}	2 <i>M</i> (H ₂ Li)ClO ₄	25	$k'' = 73 M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 29.7 \pm 0.4 (7.1 \pm 0.1)$	49
V(III)	3×10^{-3}	2 <i>M</i> (H ₂ Li)ClO ₄	25	$k'' = 0.28 [H^+]^{-1.8} M^{-1} \text{ sec}^{-1}$ [H ⁺] dependence suggests consecutive reactions and a binuclear intermediate $E_a = 92.5 \pm 0.4 (22.1 \pm 0.1)$ for 1 <i>M</i> H ⁺	51

Table 10.6
OXIDATION OF NEPTUNIUM(III)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Co(NH ₃) ₄ (H ₂ O) ₂ ³⁺	5 × 10 ⁻²	2 <i>M</i> (H,Li)ClO ₄	25	$k'' = 4.4 \times 10^{-3} + 9 \times 10^{-3} [\text{H}^+]^{-1} M^{-1} \text{ sec}^{-1}$	115
Fe(III)	10 ⁻³	2 <i>M</i> (H,Li)ClO ₄	25	$k'' = 676 [\text{H}^+]^{-0.94} M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 60.9 \pm 0.4 (14.6 \pm 0.1)$	114
FeCl ²⁺	4 × 10 ⁻⁵	1.96 <i>M</i> HClO ₄ – 0.04 <i>M</i> HCl	1	$k' = 3.4 \times 10^3 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$	191
H ₂ O ₂	3.5 × 10 ⁻⁴	1 <i>M</i> HClO ₄	25	$k'' = 35 \pm 3 M^{-1} \text{ sec}^{-1}$ Np(V) apparently forms in first step	192
NpO ₂ ⁺	6 × 10 ⁻⁴	0.25 <i>M</i> HClO ₄ – 1.75 <i>M</i> NaClO ₄	25	$k'' = 43 [\text{H}^+]^{1.05} M^{-1} \text{ sec}^{-1}$	79
		0.25 <i>M</i> (H,Li)ClO ₄	25	$k'' = 1.0 + 14.3 [\text{H}^+] M^{-1} \text{ sec}^{-1}$	63
NpO ₂ ²⁺	7 × 10 ⁻⁶	0.1 <i>M</i> HClO ₄	25	$k'' = 2.2 \times 10^4 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$ $\Delta H^* \approx 4 (1)$	76
O ₂	Saturated	1 <i>M</i> HClO ₄	25	Complete in 10 sec	192
Ru(NH ₃) ₅ OH ₂ ³⁺	1.2 × 10 ⁻²	1 <i>M</i> (H,Li)O ₃ SCF ₃	25	k'' (forward) = 0.27[H ⁺] ⁰ <i>M</i> ⁻¹ sec ⁻¹ $\Delta H^* = 17.7 \pm 1 (4.24 \pm 0.25)$ Reverse reaction important, <i>Q</i> = 0.062	116
Ru(NH ₃) ₆ ³⁺	1.9 × 10 ⁻²	0.5 <i>M</i> (H,Li)O ₃ SCF ₃	25	k'' (forward) = 0.305[H ⁺] ⁰ <i>M</i> ⁻¹ sec ⁻¹ $\Delta H^* = 16 \pm 4 (3.9 \pm 1)$ Reverse reaction important, <i>Q</i> = 0.031	116
UO ₂ ⁺	2 × 10 ⁻⁴	1 <i>M</i> HClO ₄	25	$k'' = 38 [\text{H}^+] M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 21 \pm 0.8 (5.1 \pm 0.2)$	12
UO ₂ ²⁺	1.5 × 10 ⁻³	1 <i>M</i> HClO ₄	25	$k'' = 39 [\text{H}^+]^{-0.13}$ $\Delta H^* = 11 \pm 0.7 (2.6 \pm 0.16)$	12

Table 10.7
OXIDATION OF NEPTUNIUM(IV)

Agent	Typical concentration, M	Solution	Temp., °C	Results	Ref.
Ag(II)			Room	Very rapid	157
BrO_3^-	0.09	$1M \text{ H}_2\text{SO}_4$	25	Initial $k'' \approx 6 \times 10^{-4} M^{-1} \text{ sec}^{-1}$ Catalyzed by Np(V) and Ce(III)	157
Cl_2		$1M \text{ HCl}$	25	Very slow (quite rapid at 75°C)	157
Fe(III)	2×10^{-3}	$1M (\text{H},\text{Na})\text{ClO}_4$	25	$k'' = 5.7 \times 10^{-2} [\text{H}^+]^{-3} M^{-1} \text{ sec}^{-1}$ $E_a = 146 (35)$ Recent work suggests three parallel paths	121 193
MnO_4^-		H_2SO_4 or HNO_3		Rates are greater in aqueous solutions of CH_3OH or $\text{C}_2\text{H}_5\text{OH}$	194
Np(VI)	5×10^{-3}	$2M (\text{H},\text{Na})\text{ClO}_4$	25	Very rapid	157
				$k'' = 4.5 \times 10^{-2} [\text{H}^+]^{-2} M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 105 \pm 2.5 (25.1 \pm 0.6)^\dagger$	84
		$2.2M (\text{H},\text{Na})\text{ClO}_4$	25	HSO_4^- causes a maximum in the rate at $5 \times 10^{-2} M$ $k'' = (4.27[\text{H}^+]^{-2} + 0.504[\text{H}^+]^{-3}) \times 10^{-2} M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 103 \pm 1.3 (24.6 \pm 0.3)$ in $0.27M \text{ H}^+\dagger$	85 195
		$2M (\text{H},\text{Na})\text{ClO}_4$	25	$k' = (5.69[\text{H}^+]^{-2} + 1.52[\text{H}^+]^{-3}) \times 10^{-2} M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 93 \pm 6 (22.3 \pm 1.4)$ and $145 \pm 21 (34.6 \pm 4.6)$ for the respective rate constants $\dagger$	125
				NO_3^- causes a maximum in the rate at $0.575M$	196
				Also studied in aqueous alcohol and acetone solutions	168
O_2	10^{-3} (saturated)	$0.01M \text{ HClO}_4$	25	$k'' = 9 \times 10^{-3} M^{-1} \text{ sec}^{-1}$	192
Pu(IV)	3×10^{-3}	$2M (\text{H},\text{Na})\text{ClO}_4$	25	$k' = 0.253[\text{H}^+]^{-3} M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 142 \pm 6 (33.9 \pm 1.5)$	81
Pu(VI)		$2M (\text{H},\text{Na})\text{ClO}_4$	25	$k'' = 5 \times 10^{-3} [\text{H}^+]^{-2.3} M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 134 \pm 17 (32 \pm 4)$	87

$\dagger$ Original data recalculated.

Table 10.8
OXIDATION OF NEPTUNIUM(V)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
BrO ₃ ⁻	10 ⁻³	3 <i>M</i> H ₂ SO ₄	25	-d[BrO ₃ ⁻]/dt = 6.1[BrO ₃ ⁻] ² [Np(V)] ⁰ <i>M</i> sec ⁻¹ Δ <i>H</i> * = 77.4 ± 0.8 (18.5 ± 0.2) Same rate parameters observed when Mn(II) or Ce(III) oxidized Similar results were obtained in perchlorate solutions; [H ⁺] ^{1.5}	197a
Ce(IV)	3 × 10 ⁻⁴	2 <i>M</i> (H,Na)ClO ₄	25	<i>k</i> ' = 9.2 × 10 ⁴ [H ⁺] <i>M</i> ⁻¹ sec ⁻¹ Δ <i>H</i> * ≈ 0	129
Co(III)	4 × 10 ⁻⁴	2.1 <i>M</i> (H,Li)ClO ₄	25	<i>k</i> ' = 311 [H ⁺] ^{-0.11} <i>M</i> ⁻¹ sec ⁻¹ <i>E</i> _a = 54 ± 2.5 (12.9 ± 0.6) Or <i>k</i> ' = 282 + 29[H ⁺] ⁻¹ <i>M</i> ⁻¹ sec ⁻¹ <i>E</i> _a = 52.7 ± 0.8 (12.6 ± 0.2) for first rate constant Oxidation of Np(V) in the Cr(III) · Np(V) complex also studied: <i>k</i> ' = 2.28[H ⁺] ^{-1.1} <i>M</i> ⁻¹ sec ⁻¹ <i>E</i> _a = 75 ± 4 (18 ± 1)	47
Cr(VI)	3 × 10 ⁻⁴	2 <i>M</i> (H,Li)ClO ₄	25	<i>k</i> ' = 4.3[H ⁺] ^{1.6} /[1 + 0.76[Np(VI)][H ⁺] ^{-1.8} /[Np(V)]] <i>M</i> ⁻¹ sec ⁻¹ <i>E</i> _a = 48.5 (11.6) for first rate constant	143
MnO ₄ ⁻		H ₂ SO ₄	Room	Very rapid	157
NO ₃ ⁻	2.9	2.9 <i>M</i> HNO ₃	20	<i>t</i> _{1/2} = 17 min; rate depends on [HNO ₃] ⁴ <i>E</i> _a = 50 (12) Rate increased by the products of the nitration of nitropropane	198 199
Np(VI)	9 × 10 ⁻⁵	1 <i>M</i> HClO ₄	0	<i>k</i> ' = 29 <i>M</i> ⁻¹ sec ⁻¹ <i>E</i> _a = 35 (8.3) Exchange rate unaffected by NO ₃ ⁻ but catalyzed by Cl ⁻ Unaffected by the dielectric constant in aqueous ethylene glycol or sucrose solutions Decreased 20 to 40% in D ₂ O	200 139 75 201

(Table continues on following page.)

Table 10.8 (Continued)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
V(V)	10 ⁻³	2 <i>M</i> HNO ₃	24	$k'' = 0.2[\text{H}^+]^{2.3} \text{ M}^{-1} \text{ sec}^{-1}$ $E_a = 49 \pm 1.7 (11.7 \pm 0.4)$	202
XeO ₃	4 × 10 ⁻³	2 <i>M</i> (H,Li)ClO ₄	60	$-\text{d}[\text{Np(V)}]/\text{dt} = k[\text{XeO}_3][\text{Np(V)}]^0[\text{H}^+]^0$ Photochemical reaction, $k = 6.3 \times 10^{-6} \text{ sec}^{-1}$ in strong light from a W source	203

Table 10.9

OXIDATION OF NEPTUNIUM(VI)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
BrO ⁻	0.1	6.5 <i>M</i> NaOH	70	$k = 5.7 \times 10^{-4} \text{ sec}^{-1}$; first order in Np(VI); other dependences: $[\text{BrO}^-]^{0.6}$, $[\text{NaOH}]^{1.6}$ $E_a = 88 \pm 4 (21 \pm 1)$ Catalyzed by Cu(II), Ni(II), Co(II)	204
Fe(CN) ₆ ³⁻	1.5 × 10 ⁻⁵	3.2 <i>M</i> KOH	23	Equilibrium established in 2 to 3 min $\{[\text{Np(VII)}][\text{Fe(II)}]\} / \{[\text{Np(VI)}][\text{Fe(III)}][\text{OH}^-]^3\} = 0.061 \text{ M}^{-3}$	205
Mn(VII)	2.5 × 10 ⁻⁴	1 <i>M</i> NaOH	Room	Rapid; reaction complete in several seconds with equimolar concentrations	72
Pu(VII)	2.4 × 10 ⁻⁴	1 <i>M</i> NaOH	Room	$k'' = 2 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$, if first order in each reactant	72
S ₂ O ₈ ²⁻	0.10	0.7 <i>M</i> NaOH	60	$-\text{d}[\text{Np(VI)}]/\text{dt} = 3.7 \times 10^{-6} [\text{S}_2\text{O}_8^{2-}][\text{Np(VI)}]^0 \text{ M sec}^{-1}$ $E_a = 140 \pm 4 (33.5 \pm 1)$	206
O ₃	0.1% (gas vol.)	1 <i>M</i> KOH	20	$t_{1/2} = 55 \pm 5 \text{ sec}$; first order in Np(VI); other dependences: $[\text{O}_3]^{0.5}$, $[\text{KOH}]^{0.5}$	207

Table 10.10
REDUCTION OF NEPTUNIUM(IV)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Cr ²⁺	2 × 10 ⁻³	1 <i>M</i> HClO ₄	25	$k'' = (4.3 \pm 0.2)[H^+]^{-1.27} M^{-1} \text{ sec}^{-1}$ $E_a = 75 \pm 4 (18 \pm 1)$	118
V ²⁺	1.3 × 10 ⁻³	2.0 <i>M</i> (H,Li)ClO ₄	25	$k' = 2.53 + 3.8 \times 10^{-2} [H^+]^{-1} + 6 \times 10^{-4} [H^+]^{-2} M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 40.6 \pm 0.2 (9.7 \pm 0.05)$	117

Table 10.11
REDUCTION OF NEPTUNIUM(V)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Cr(II)	5 × 10 ⁻⁴	0.21 <i>M</i> (H,Li)ClO ₄	25	$k'' = 1.15 \times 10^3 [H^+] \exp(-1.14 [H^+]) M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 7.7 \pm 1 (1.85 \pm 0.23)$ Or $k'' = (14.2 + 860 [H^+]) M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 32 \pm 16 (7.6 \pm 3.8)$ and 7.9 ± 2.9 (1.9 ± 0.7) for the respective rate constants†	63
Fe(II)	4 × 10 ⁻³	1 <i>M</i> (H,Na)ClO ₄	25	$k'' = 0.078 [H^+] M^{-1} \text{ sec}^{-1}$ Also studied in aqueous solutions of CH ₃ OH and C ₂ H ₅ OH	121 194
H ₂ C ₂ O ₄	0.17	2 <i>M</i> (H,Na)ClO ₄	68	$\{d[Np(IV)]/dt\}_0 = [NpO_2^+][C_2O_4^{2-}][H^+](k_1 + k_2[NpO_2^+][C_2O_4^{2-}][H^+] + k_3[NpO_2^+][C_2O_4^{2-}])$ $k_1 = 32 M^{-2} \text{ sec}^{-1}$, $k_2 = 5.3 \times 10^{10} M^{-5} \text{ sec}^{-1}$, $k_3 = 7 \times 10^{12} M^{-4} \text{ sec}^{-1}$ The association quotients for NpO ₂ C ₂ O ₄ ⁻ and NpO ₂ (C ₂ O ₄) ₂ ³⁻ were taken as 3 × 10 ⁻³ M ⁻¹ and 1 × 10 ⁻⁶ M ⁻² , respectively. The acid dissociation quotients for H ₂ C ₂ O ₄ were taken as 6.3 × 10 ⁻² <i>M</i> and 1.7 × 10 ⁻⁴ <i>M</i> , respectively Also studied in (NH ₄) ₂ C ₂ O ₄ solutions	208

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(Table continues on following page.)

Table 10.11 (Continued)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
H ₂ O ₂		0.5 <i>M</i> HNO ₃	Room	No reaction detectable in 24 hr	157
		7.5 <i>M</i> HNO ₃	20	$k'' = 9.3 M^{-1} \text{ min}^{-1}$ $E_a = 55 \pm 2 (13.2 \pm 0.5)$	210
I ⁻	10 ⁻²	3.3 <i>M</i> HCl	25	$k'' = 0.103 [\text{Np(V)}]^{-0.14} [\text{I}^-]^{0.55} [\text{H}^+]^{2.61} M^{-1} \text{ min}^{-1}$ $E_a = 118 (28.3)$ Or $k'' = (1.82 \times 10^{-2} [\text{H}^+]^2 + 0.54 [\text{I}^-] [\text{H}^+]^3) M^{-1} \text{ min}^{-1}$	211
NH ₃ OH ⁺		1 <i>M</i> acid	Room	Very slow	157
N ₂ H ₅ ⁺		1 <i>M</i> acid	Room	Very slow	157
		HNO ₃ (conc.)		Rapid	212
N ₂ H ₅ ⁺	0.5	5 <i>M</i> (H,Na)ClO ₄	92	$k'' = (9.7 \pm 0.6) \times 10^{-6} M^{-1} \text{ sec}^{-1}$ $E_a = 103 \pm 2 (24.5 \pm 0.5)$ A parallel path which involves the disproportionation of Np(V) is also important	215
Np(III)				(See Table 10.6)	
Sn(II)		HCl	Room	Very slow	157
SO ₂		H ₂ SO ₄	Room	Very slow, catalyzed by F ⁻	157
U(IV)				(See Table 10.2)	
V(III)	1.5 × 10 ⁻³	3 <i>M</i> (H,Li)ClO ₄	25	$k'' = (0.30 + 0.16 [\text{Np(IV)}]) [\text{V(IV)}]^{-1} [\text{H}^+]^{-1.5} M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 61 \pm 3 (14.6 \pm 0.8)$ for first rate constant	48

†Original data recalculated.

Table 10.12
REDUCTION OF NEPTUNIUM(VI)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Cl ⁻	1.0	1 <i>M</i> HCl	Room	Very slow, catalyzed by Pt or Au	157
EDTA	5 × 10 ⁻³	1 <i>M</i> (H,Na)ClO ₄	25	$k'' = 0.1 [H^+]^{-1.5} M^{-1} \text{ sec}^{-1}$ $E_a = 97.5 \pm 0.4 (23.3 \pm 0.1)$	213
Fe(II)	10 ⁻⁴	1 <i>M</i> HClO ₄	1	$k'' \approx 3 \times 10^3 M^{-1} \text{ sec}^{-1}$ (preliminary observation)	
H ₂ C ₂ O ₄	2 × 10 ⁻²	1 <i>M</i> (H,Na)ClO ₄	25	$k'' = 0.012 [H^+]^{-1} M^{-1} \text{ sec}^{-1}$ $E_a = 54 \pm 4 (13 \pm 1)^\dagger$ Net reaction is reported to be $4\text{NpO}_2^{2+} + \text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O} = 4\text{NpO}_2^+ + 2\text{CO}_2 + \frac{1}{2}\text{O}_2 + 4\text{H}^+$	214
HNO ₂		1 <i>M</i> HNO ₃	Room	Very rapid	157
H ₂ O ₂		3 <i>M</i> (H,Na)ClO ₄	25	$k'' = 8.9 [H^+]^{-1} / \{1 + 1.9 [\text{Np(V)}] / [\text{Np(IV)}]\} M^{-1} \text{ sec}^{-1}$ $E_a = 52 \pm 4.6 (12.4 \pm 1.1)$ for first rate constant	58
<i>p</i> -hydroquinone	10 ⁻³	1 <i>M</i> (H,Li)ClO ₄	25	$k'' = 4.5 \times 10^4 [H^+]^0 [\text{Np(V)}]^0 M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 34.2 \pm 1.4 (8.17 \pm 0.34)$ Reaction with <i>p</i> -toluhydroquinone is very similar; k'' is about 40% greater and $\Delta H^* = 38.4 \pm 1.2 (9.2 \pm 0.3)$	145
NH ₃ OH ⁺		1 <i>M</i> acid	Room	Very rapid	145
N ₂ H ₅ ⁺	0.03	2 <i>M</i> (H,Na)ClO ₄	25	$k'' = (11.8 [H^+]^{-1} + 5.3 [H^+]^{-2}) 10^{-2} M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 66 \pm 3 (15.9 \pm 0.8)$ and $58 \pm 9 (13.9 \pm 2.3)$ for the respective rate constants [†]	135
Np(III)				(See Table 10.6)	
Np(IV)				(See Table 10.7)	
Pu(III)				(See Table 10.14)	

(Table continues on following page.)

Table 10.12 (Continued)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Pu(V)	10 ⁻⁴	1 <i>M</i> HClO ₄	2	$k'' \approx 5 \times 10^3 M^{-1} \text{ sec}^{-1}$ (preliminary observation)	157
Sn(II)		HCl	Room	Very rapid	
U(IV)				(See Table 10.2)	
V(III)	10 ⁻³	2 <i>M</i> (H,Na)ClO ₄	25	$k'' = 5.7 + 22.6[H^+]^{-1} M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 134 \pm 21$ (32 ± 5) and 54 ± 8 (13 ± 2) for the respective rate constants†	132
V(IV)	10 ⁻³	2 <i>M</i> HClO ₄	25	$k'' = 13 M^{-1} \text{ sec}^{-1}$ (preliminary result)	132

†Original data recalculated.

Table 10.13

REDUCTION OF NEPTUNIUM(VII)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Ag(I)	0.02	1 <i>M</i> HClO ₄	25	$k'' = (3.54 \pm 0.05) \times 10^3 [H^+] M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 3.4 \pm 0.3$ (0.81 ± 0.08)	216
C ₂ O ₄ ²⁻	0.2	0.1 <i>M</i> NaOH	65	$t_{1/2} = 1900 \text{ sec}$ (>6000 sec at 25°C or in 2 <i>M</i> NaOH)	217
C ₂ H ₅ OH	1.5	0.1 <i>M</i> NaOH	65	$t_{1/2} = 300 \text{ sec}$ (1800 sec in 2 <i>M</i> NaOH)	217
Citrate	0.09	0.1 <i>M</i> NaOH	25	$t_{1/2} = 720 \text{ sec}$	217
Co(II)	1.5 × 10 ⁻³	1 <i>M</i> (H,Li)ClO ₄	25	$k'' = k_1 [H^+] (1 + k_1 [H^+] / k_2)^{-1}$ $k_1 = 9.51 \times 10^4 M^{-2} \text{ sec}^{-1}$ $k_2 = 5.85 \times 10^4 M^{-1} \text{ sec}^{-1}$	216

				$\Delta H_1^* = -15 \pm 2$ (-3.6 ± 0.5) $\Delta H_2^* = 40 \pm 2$ (9.65 ± 0.5)	
EDTA	0.01	0.1M NaOH	25	$t_{1/2} = 4500$ sec (66 sec at 65°C, 2700 sec in 2M NaOH)	217
HCHO	0.06	0.1M NaOH	25	$t_{1/2} = 90$ sec	217
HCO ₂ ⁻	0.09	0.1M NaOH	25	$t_{1/2} = 300$ sec	217
HCOOH	0.02	1M (H,Li)ClO ₄	25	$k'' = 0.402 + 0.0538[H^+]^{-1} M^{-1} \text{ sec}^{-1}$ $E_a = 27 \pm 1$ (6.4 ± 0.3) and 44 ± 1 (10.5 ± 0.2) for the respective rate constants Deuterium isotope effect determined	137
H ₂ O	55.5	3M (H,Li)ClO ₄	25	$k = 7.64 \times 10^{-4} [H^+]^{1.15} + 4.41 [\text{Np(VII)}] [H^+]^{0.15} \text{ sec}^{-1}$	24
H ₂ O	55.5	1M (H,Na)NO ₃	40	$k = 10^{-3} (0.5 + 1.7[H^+]) \text{ sec}^{-1}$ $E_a = 66 \pm 4$ (15.8 ± 1) in 1M HNO ₃	53
		1M (H,Na)ClO ₄	40	$k = 10^{-3} (0.87 + 2.38[H^+]) \text{ sec}^{-1}$	
Hg(I)	10 ⁻³	1M (H,Li)ClO ₄	25	$k'' = 28.1 + 13.4[H^+] M^{-1} \text{ sec}^{-1}$ $E_a = 51 \pm 13$ (12.3 ± 3) and 35 ± 3 (8.3 ± 0.8) for the respective rate constants	55
I ⁻	0.14	0.0155M NaOH 0.6M NaNO ₃	25	Reaction is autocatalytic and is half complete in 420 sec; I ₃ ⁻ is apparently the reactive species	217
NO ₂ ⁻	0.07	0.1M NaOH	65	$t_{1/2} \approx 6000$ sec (NH ₃ and CH ₃ O ₂ ⁻ are also reduced slowly)	217
SO ₃ ²⁻	0.07	0.7M Na(OH,NO ₃)	25	$k'' = 10^{-3} (1.5[OH^-] + 0.67[OH^-]^2) M^{-1} \text{ sec}^{-1}$ $E_a = 92 \pm 8$ (22 ± 2) for $[OH^-] = 0.5M$ Reaction is catalyzed by Cu(II), Co(II), Mn(VII), Fe(III), and Np(VI)	217
S ₂ O ₃ ²⁻	0.05	0.1M NaOH	25	$t_{1/2} = 3900$ sec	217
Tl(I)	5×10^{-3}	1M (H,Li)ClO ₄	25	$k'' = 4.46[H^+]^{0.9} M^{-1} \text{ sec}^{-1}$ $E_a = 32 \pm 2$ (7.7 ± 0.4)	54
V(IV)	0.023	1M (H,Li)ClO ₄	25	$k'' = 1.44 \times 10^3 [H^+]^{-0.1} M^{-1} \text{ sec}^{-1}$ $E_a = 31 \pm 4$ (7.3 ± 0.9)	138

Table 10.14
OXIDATION OF PLUTONIUM(III)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
BrO ₃ ⁻	0.016	0.84 <i>M</i> HClO ₄	25	Autocatalytic; reaction complete in 130 sec (preliminary result)	218
Ce(IV)	3 × 10 ⁻³	0.5 <i>M</i> HCl	Room	<i>t</i> _{1/2} ≤ 5 sec	158
Cl ₂	0.025	1.5 <i>M</i> HCl	Room	<i>k</i> = 7 × 10 ⁻⁶ sec ⁻¹ [Cl ₂] dependence not clear, rate increases with [HCl] Reaction is catalyzed by Cu(II) and Fe(III) Reaction also studied in sulfate solutions	219a 219b 219c
Cr(III) + Pu(V)	10 ⁻⁴	2 <i>M</i> (H,Li)ClO ₄	25	<i>k</i> '' = 122 [H ⁺] ⁰ <i>M</i> ⁻¹ sec ⁻¹ Δ <i>H</i> * = 19.2 ± 0.4 (4.6 ± 0.1)	80
Cr(VI)	1.5 × 10 ⁻⁵	2 <i>M</i> (H,Li)ClO ₄	25	<i>k</i> '' = 2.4 × 10 ⁴ [H ⁺] ² <i>M</i> ⁻¹ sec ⁻¹ Inhibited by Pu(IV)	218
H ₂ O ₂	0.3	1 <i>M</i> H ₂ SO ₄	Room	Essentially complete in 1 to 2 min; slower in HCl	158
IO ₃ ⁻	0.0156	1 <i>M</i> HClO ₄	25	<i>k</i> ≈ 10 ⁻⁶ sec ⁻¹ (preliminary result)	218
MnO ₄ ⁻		Dilute acid	Room	Extremely rapid	158
NpO ₂ ²⁺	3 × 10 ⁻³	1 <i>M</i> (H,Li)ClO ₄	25	<i>k</i> '' = 35.3 + 3.1 [H ⁺] ⁻¹ <i>M</i> ⁻¹ sec ⁻¹ Δ <i>H</i> * = 14.6 ± 0.2 (3.49 ± 0.05) for the larger term	77

NO_3^-	0.2 (NaNO ₃)	0.5M HCl	Room	$t_{1/2} \approx 600$ hr; autocatalytic; rapid in 16M HNO ₃	158
HNO_2	3×10^{-4}	1M to 2M HCl	25	$-\text{d}[\text{Pu(III)}]/\text{dt} = 0.3[\text{Pu(III)}][\text{HNO}_2]^{0.83}[\text{HCl}]^{1.28} \times (1 + 5[\text{NO}_3^-]) M \text{ sec}^{-1}$	220a
		2M (H,Na)NO ₃	25	$k = 1.55[\text{HNO}_2]^{0.5} \text{ min}^{-1}$	220b
O_2	Saturated at 0.74 atm	2M (H,Na)ClO ₄	25	$k'' = [\text{Pu(III)}](5.5[\text{SO}_4^{2-}]^2 + 179[\text{SO}_4^{2-}]^3)/(1 + 10[\text{SO}_4^{2-}] + 50[\text{SO}_4^{2-}]^2) \text{ atm}^{-1} \text{ sec}^{-1}$ $E_a \approx 79$ (19)	221
Pu^{4+}	3×10^{-6}	2M (H,Li)ClO ₄	25	$k'' = 6.4 \times 10^4 [\text{H}^+]^{-1} M^{-1} \text{ sec}^{-1}$ $E_a = 31 \pm 5$ (7.4 $\pm$ 1)	74
PuO_2^+	2×10^{-3}	0.5M HCl	25	$k'' = 0.058 [\text{H}^+] M^{-1} \text{ sec}^{-1}$	222
	1.5×10^{-3}	1M HClO ₄	25	$k'' = 4.44 \times 10^{-2} M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 33 \pm 1$ (8.0 $\pm$ 0.3)	80
PuO_2^{2+}	10^{-4}	1M HClO ₄	25	$k'' = 2.68 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$ $\Delta H^* = 20.2 \pm 0.4$ (4.8 $\pm$ 0.1) The reaction has also been studied in anhydrous acetic acid	78 223
Tl^{3+}		Dilute HClO ₄	Room	Very slow	158
XeO_3	10^{-3}	2M (H,Li)ClO ₄	30	$k'' = 1.8 \times 10^{-2} M^{-1} \text{ sec}^{-1}$	147

Table 10.15
OXIDATION OF PLUTONIUM(IV)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Ag(II)	0.1	1.1 <i>M</i> HNO ₃	Room	Complete in <60 sec	158
Ag ₂ O		45% K ₂ CO ₃	75	>90% complete in 45 min	158
Bi(V) (NaBiO ₃)	0.84 g/liter	5 <i>M</i> HNO ₃	Room	Complete in <5 min	158
BrO ₃ ⁻	0.2	0.2 <i>M</i> HNO ₃	95	<i>t</i> _{1/2} ≈ 13 min; slower at higher [HNO ₃] or in H ₂ SO ₄	158
Br ₂	Saturated	1.5 <i>M</i> HNO ₃	50	<i>t</i> _{1/2} ≈ 4 hr	158
Ce(IV)	5 × 10 ⁻⁴	2.5 <i>M</i> (H,Na)ClO ₄	28	<i>k</i> ' = 23 [H ⁺] ⁻² <i>M</i> ⁻¹ sec ⁻¹ <i>E</i> _a = 61 ± 4 (14.6 ± 1) In 0.04 <i>M</i> to 0.2 <i>M</i> sulfate solutions: <i>k</i> ' = 10 ⁻³ (165 + 0.3 [H ⁺] ⁻¹ [HSO ₄ ⁻] ⁻¹) [HSO ₄ ⁻] ⁻² <i>M</i> ⁻¹ sec ⁻¹	124
Cl ₂	0.025	0.1 <i>M</i> HClO ₄ 0.056 <i>M</i> Cl ⁻	22	<i>t</i> _{1/2} ≈ 2 hr; 85 times slower in 1 <i>M</i> HClO ₄ and extremely slow in 1 <i>M</i> H ₂ SO ₄	158
Cl(I) (HOCl-ClO ⁻)	0.1 to 0.2	4.5 to 8.2 pH 45% K ₂ CO ₃	80	Complete in 15 min	158
Co(III) acetate			Room	Complete in 5 to 10 min	158
			75	Complete in 10 min	158
HClO ₄	12	Concentrated	Fuming	Rapid	158
HCrO ₄ ⁻	0.04	0.1 <i>M</i> HClO ₄	25	<i>k</i> ' ≈ 0.29 <i>M</i> ⁻¹ sec ⁻¹ Slower in H ₂ SO ₄ ; catalyzed by Co(II) Complicated by the formation of Pu(IV) · Cr(VI) and Cr(III) · Pu(V) complexes	158 32
H ₅ IO ₆	0.02	0.22 <i>M</i> HNO ₃	Room	<i>t</i> _{1/2} ≈ 100 min; rate decreases with increasing acidity	158
MnO ₄ ⁻	2 × 10 ⁻⁴	3 <i>M</i> (H,Na)ClO ₄	25	-d[Pu(IV)]/dt = (4070 ± 210)[Pu(IV)][Mn(II)][Mn(VII)] ⁰ [H ⁺] ⁻² <i>M</i> min ⁻¹ Δ <i>H</i> [*] = 91 ± 1 (21.7 ± 0.2) Δ <i>S</i> [*] = 94 ± 4 (22.5 ± 1)	127

Mn(III)	3.8×10^{-3}	$3M$ (H,Na)ClO ₄	25	$k' = 11[H^+]^{-2} + 53.2[H^+]^{-3} M^{-1} \text{ sec}^{-1}$ Hydrolysis constants for Pu ⁴⁺ and Mn ³⁺ taken as 0.077 <i>M</i> and 0.88 <i>M</i> , respectively $E_a = 68 \pm 4$ (16.3 $\pm$ 1) for $[H^+] = 2.9M$	224
MnO ₂	2 g/ml	HNO ₃	Room	$t_{1/2} \approx 2.5$ hr, with shaking; column operation indicated	225
NO ₃ ⁻	0.52	0.52 <i>M</i> HNO ₃	95	$t_{1/2} = 45$ min; very slow in presence of HSO ₄ ⁻	158
O ₃		0.03 <i>M</i> H ₂ SO ₄	0	Catalyzed by Ce(III) or Ag(I); essentially complete in 30 min with $1.5 \times 10^{-3}M$ catalyst	158
		1 <i>M</i> (H,Na)NO ₃	20	$k = (1.32 \pm 0.13) \times 10^{-2} [O_3]^0 [H^+]^{-1} \text{ min}^{-1}$ $[Pu(IV)] = 10^{-6} M$ to $10^{-5} M$ $E_a = 19 \pm 5$ (4.6 $\pm$ 1.2)	226
Pb(CH ₃ COO) ₄		5 <i>M</i> HNO ₃	50	Complete in 1 hr	158
S ₂ O ₈ ²⁻	0.09	0.055 <i>M</i> to 1.05 <i>M</i> H ₂ SO ₄	0 to 72	Complete in 1 min in the presence of $9 \times 10^{-3}M$ Ag(I)	158
V(V)		HNO ₃	24	Slow	202

Table 10.16
OXIDATION OF PLUTONIUM(V)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Ce(IV)	6×10^{-5}	2 <i>M</i> HClO ₄	23	Very rapid; $k'' > 7 \times 10^5 M^{-1} \text{ sec}^{-1}$	32
Cr(VI)	1.3×10^{-3}	0.1 <i>M</i> HClO ₄	25	$k'' = 5.5 M^{-1} \text{ sec}^{-1}$ initially; decreases as reaction proceeds	32
Pu(V)				(See Table 10.18)	
Np(VI)				(See Table 10.12)	

Table 10.17
REDUCTION OF PLUTONIUM(IV)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Ag metal		2 <i>M</i> HClO ₄	25	Rate controlled by diffusion to surface; diffusion coefficient is $\sim 1.1 \times 10^{-5}$ cm ² sec ⁻¹ Similar results for Cu and Pb	227
Ascorbic acid		4.7 <i>M</i> HNO ₃	Room	Complete in a few minutes in presence of NH ₂ SO ₃ H to inhibit the ascorbic acid-HNO ₃ reaction Similar results for <i>iso</i> -ascorbic acid	228
Fe ²⁺	2×10^{-3}	2 <i>M</i> (H,Li)ClO ₄	20	$k'' = 27[\text{H}^+]^{-1} M^{-1} \text{ sec}^{-1}$ $E_a = 82 \pm 2.5$ (19.7 $\pm$ 0.6) Rate increased by Cl ⁻	119
H ₂ on platinized Pt		2.4 <i>M</i> HCl	Room	$t_{1/2} < 5$ min; >99% reduced in 45 min Rate very low without catalyst	229
		0.25 <i>M</i> H ₂ SO ₄	Room	96% complete in 45 min	230
		3.5 <i>M</i> H ₂ SO ₄	Room	85% complete in 45 min	
H ₂ O ₂	7.9×10^{-4}	0.5 <i>M</i> HCl	25	$t_{1/2} = 64$ min (excess H ₂ O ₂) Complicated by rapid formation of Pu(IV)-H ₂ O ₂ complexes	158 231
H ₂ O ₂ in the PuO ₂ PuOH ⁵⁺ complex	2.8×10^{-3}	2 <i>M</i> (H,Na)ClO ₄	25	Decomposition gives Pu(III); rate is first order in complex $k = 1.4 \times 10^{-4} \text{ sec}^{-1}$ $E_a = 92 \pm 13$ (22 $\pm$ 3)	232
H ₂ S		Acid	Room	Pu(IV) "readily reduced"	158
Hydroquinone	10^{-5}	1 <i>M</i> (H,Li)ClO ₄	25	$k'' = 1.9 \times 10^5 [\text{H}^+]^0 M^{-1} \text{ sec}^{-1}$ $E_a = 50 \pm 4$ (12 $\pm$ 1) Reaction is inhibited by Pu(III) but not by quinone	146
I ⁻	0.1	0.4 <i>M</i> HCl	Room	$t_{1/2} \approx 2$ min; the I ⁻ -O ₂ reaction is induced	158

NH ₃ OH ⁺	0.1	2.5M (H,Na)(NO ₃ ,ClO ₄)	25	Initial $k'' = (k_1 + k_2 [\text{NH}_3\text{OH}^+]) / \{[\text{H}^+]^2 (1 + 2[\text{NO}_3^-])\}$ $k_1 = 7 \pm 1.1 \text{ M sec}^{-1}$; $E_a = 88 \pm 5 (21 \pm 1.3)$ $k_2 = 48 \pm 9 \text{ sec}^{-1}$; $E_a = 107 \pm 11 (25.5 \pm 2.7)$ Rate is inhibited by Pu(III) Stoichiometry is complicated in that both N ₂ and N ₂ O are products. Catalyzed by Fe(III)	233
	0.1	0.5M HNO ₃	Room	$k'' > 0.2 \text{ M}^{-1} \text{ sec}^{-1}$	158
N ₂ H ₅ ⁺	0.02	1.0M HNO ₃ – 0.02M H ₂ SO ₄	Room	$t_{1/2} = 8.2 \text{ min}$ (tracer concentration of Pu)	234
	0.197	1M HClO ₄	Room	$t_{1/2} \approx 100 \text{ min}$ [$1.3 \times 10^{-3} \text{ M Pu(IV)}$]	218
Np ⁴⁺	3×10^{-3}	2M (H,Na)ClO ₄	25	$k'' = 0.253 [\text{H}^+]^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ $E_a = 144 \pm 6 (34.5 \pm 1.5)$	81
Pu ⁴⁺ (disproportionation)	1×10^{-2}	1.0M (H,Na)ClO ₄	25	$-d[\text{Pu(IV)}]/3dt = [\text{Pu}^{4+}]^2 (2.56 \times 10^{-5} [\text{H}^+]^{-3} + 3.9 \times 10^{-6} [\text{H}^+]^{-4}) \text{ M sec}^{-1}$ Also studied in HNO ₃ solutions	235 236
Sn ²⁺	2×10^{-3}	2.0M (H,Na)(ClO ₄)	25	$k'' = 17 [\text{Cl}^-]^{1.9} [\text{H}^+]^0 \text{ M}^{-1} \text{ sec}^{-1}$ Rate law corrected for Cl [–] complexing is $-d[\text{Sn(II)}]/dt = [\text{Pu}^{4+}] [\text{Sn}^{2+}] (332 [\text{Cl}^-]^4 + 850 [\text{Cl}^-]^5) \text{ M sec}^{-1}$ at 20°C	140
SO ₂ (H ₂ SO ₃)	2×10^{-2}	0.5M HCl	Room	$t_{1/2} > 0.1 \text{ min}$; rate is much lower in H ₂ SO ₄	158
Ti ³⁺	2×10^{-3}	1.0M HClO ₄	25	$k'' = 65.5 [\text{H}^+]^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ $E_a = 72 \pm 3 (17.3 \pm 0.7)$ (See Table 10.2)	120
U(IV)					
V ³⁺	1.5×10^{-3}	2.0M (H,Na)ClO ₄	20	$k' = 11.9 [\text{H}^+]^{-1} + 20.1 [\text{H}^+]^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ in terms of [Pu ⁴⁺] and [V ³⁺] $E_a = 74 \pm 2 (17.7 \pm 0.5)$ and $92 \pm 1.6 (22.1 \pm 0.4)$ for the respective rate constants	

Table 10.18
REDUCTION OF PLUTONIUM(V)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Fe(II)	1.6×10^{-3}	1 <i>M</i> (H,Na)ClO ₄	25	$k'' = 30[\text{H}^+] M^{-1} \text{sec}^{-1}$ (preliminary result)	32
HNO ₂	0.1	0.2 <i>M</i> (H,Na)NO ₃	Room	Slower than the disproportionation of Pu(V)	158
H ₂ O ₂	2×10^{-3}	0.5 <i>M</i> HCl	25	Slower than the disproportionation of Pu(V)	158
I ⁻	pH 2		Room	Very slow	158
NH ₂ NH ₃ ⁺	0.05	0.5 <i>M</i> HCl	Room	Slower than the disproportionation of Pu(V)	158
NH ₃ OH ⁺	0.015	0.5 <i>M</i> HCl	Room	Slower than the disproportionation of Pu(V)	158
Pu(III)				(See Table 10.14)	
Pu(V)	$\sim 10^{-3}$	1 <i>M</i> (H,Na)ClO ₄	25	$k'' = 3.6 \times 10^{-3} [\text{H}^+] M^{-1} \text{sec}^{-1}$ $\Delta H^* = 79 \pm 4 (19 \pm 1)$ Also studied in oxalate solutions	86 237,238
Sn(II)	2×10^{-3}	0.5 <i>M</i> HCl	2.4	$k'' < 0.15 M^{-1} \text{sec}^{-1}$	141
SO ₂	2×10^{-2}	0.5 <i>M</i> HCl	Room	Slower than the disproportionation of Pu(V)	158
Ti ³⁺	10^{-4}	2 <i>M</i> (H,Na)ClO ₄	25	Rapid; $k'' \geq 100 M^{-1} \text{sec}^{-2}$	133
V ³⁺	2×10^{-3}	1 <i>M</i> HClO ₄	2.4	Slow; $k'' \ll 0.24 M^{-1} \text{sec}^{-1}$	134

Table 10.19
REDUCTION OF PLUTONIUM(VI)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
Cr(II)	2.5×10^{-4}	1 <i>M</i> HClO ₄	14.5	$k'' > 10^5 M^{-1} \text{ sec}^{-1}$	130
EDTA	2×10^{-3}	1 <i>M</i> NaClO ₄ pH 3 to 5	Room	$k'' = 4.3 \pm 1.6 M^{-1} \text{ sec}^{-1}$	239
Fe(II)	4×10^{-5}	2 <i>M</i> (H,Li)ClO ₄	25	$k'' = 1000 + (2 \times 10^{-4} + 1.3 \times 10^{-3} [H^+])^{-1} M^{-1} \text{ sec}^{-1}$ Evidence for a binuclear intermediate $E_a = 22.6 \pm 0.8$ (5.4 ± 0.2) for first rate constant	62
H ₂ C ₂ O ₄	0.02	1 <i>M</i> HClO ₄	80	Conveniently measurable rate $E_a = 117$ (27.9)	240
HNO ₂	0.1	0.1 <i>M</i> HNO ₃ – 0.1 <i>M</i> NaNO ₃	Room	$t_{1/2} < 25 \text{ sec}$	158
	0.027	0.1 <i>M</i> HNO ₃ – 0.45 <i>M</i> NaNO ₃	20	Initial $t_{1/2} = 72 \text{ sec}$	241
H ₂ O ₂	10^{-3}	1 <i>M</i> (H,Na)ClO ₄	22	$k'' = 6.3 \times 10^{-3} [H^+]^{-1} M^{-1} \text{ sec}^{-1}$ $E_a = 50 \pm 4$ (12 ± 1) Rates also determined in NO ₃ [–] and SO ₄ ^{2–} solutions	60
Hydroquinone	10^{-4}	1 <i>M</i> (H,Li)ClO ₄	25	$k'' = 3.2 \times 10^3 [H^+]^{-1} M^{-1} \text{ sec}^{-1}$ $E_a = 65.7 \pm 0.4$ (15.7 ± 0.1) Reaction is inhibited by Pu(V) but not by quinone	146
NH ₃ OH ⁺	0.015	0.5 <i>M</i> HCl	Room	$t_{1/2} = 36 \text{ min}$; NH ₃ OH ⁺ in excess, its dependence not determined	158
N ₂ H ₅ ⁺	0.02	2 <i>M</i> (H,Na)(NO ₃ ,ClO ₄)	40	$k'' = (0.314 \pm 0.042)[H^+]^{-1} [NO_3^-]^0 M^{-1} \text{ min}^{-1}$ $E_a = 67.4 \pm 0.8$ (16.1 ± 0.2)	136
Np(IV)				(See Table 10.7)	
Pu(III)				(See Table 10.14)	

(Table continues on following page.)

CH ₃ OH	0.55	2.5 <i>M</i> KOH		$t_{1/2} = 69 \text{ sec (105 sec for C}_2\text{H}_5\text{OH under the same conditions)}$	242
C ₂ O ₄ ²⁻				Reacts slower than the reaction with H ₂ O	242
CH ₃ COO ⁻				Reacts slower than the reaction with H ₂ O	242
H ₂ CO	4×10^{-3}	2.5 <i>M</i> KOH		$t_{1/2} = 75 \text{ sec}$	242
H ₂ O	55.5	0.06 <i>M</i> NaOH – 0.94 <i>M</i> NaNO ₃	25	$\frac{-d[\text{Pu(VII)}]}{dt} = \frac{4.7 \times 10^{-4} [\text{Pu(VII)}]^2}{K_0 [\text{Pu(VII)}]_0 + (1 - K_0)[\text{Pu(VII)}]}$ <i>M</i> sec ⁻¹ (the value of the constant K_0 is not given) The rate is proportional to $[\text{OH}^-]^{-1}$ and is catalyzed by Fe(III), Cu(II), Ni(II), and Co(III)	243
I ⁻	6.2×10^{-4}	1 <i>M</i> KOH	25	$k'' = 110 \text{ } M^{-1} \text{ sec}^{-1}$, first power in each reactant Rate is proportional to $[\text{KOH}]^{-3.6}$, μ not constant Product is IO ⁻ if $[\text{OH}^-] < 2M$ $E_a = 25 \text{ (6)}$	242
IO ₃ ⁻		1 <i>M</i> KOH	25	$k'' = 18.3 \text{ } M^{-1} \text{ sec}^{-1}$, first power in each reactant $E_a = 25 \text{ (5.9)}$ Rate increases linearly with $[\text{KOH}]$	242
Np(VI)				(See Table 10.9)	
S ₂ O ₃ ²⁻		2.5 <i>M</i> KOH		$t_{1/2} = 120 \text{ sec}$	242

Table 10.21
OXIDATION OF AMERICIUM(III)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
$S_2O_8^{2-}$		HNO_3	50.6	$-d[Am(III)]/dt = (4.9 - 9[H^+]) \times 10^{-5} [S_2O_8^{2-}] [Am(III)]^0 M \text{ hr}^{-1}$ Millimolar concentrations of ^{243}Am used	107
	5×10^{-3}	$0.5M (H,Na)NO_3$	50	Reaction is catalyzed by Ag^+ $-d[Am(III)]/dt = (0.093 + 420[Ag^+])[S_2O_8^{2-}][Am(III)]^1 M \text{ min}^{-1}$ for $[H^+] = 0.06M$ $E_a = 139 \pm 6 (33.3 \pm 1.4)$ and $72 \pm 2.5 (17.2 \pm 0.6)$ for the respective rate constants† Micromolar concentrations of ^{241}Am used	110

†Original data recalculated.

Table 10.22
OXIDATION OF AMERICIUM(V)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
$Am(V)$	2.5×10^{-3}	$2M (H,Li)ClO_4$	75.7	$k'' = (6.9 \pm 1) \times 10^{-4} [H^+]^2 + (4.6 \pm 0.7) \times 10^{-4} [H^+]^3 M^{-1} \text{ sec}^{-1}$ $E_a = 57 \pm 2 (13.6 \pm 0.5)$ for $[H^+] = 1.92M$ (r)	113
$S_2O_8^{2-}$		HNO_3	50.6	$-d[Am(V)]/dt = (1.5 - 2.7[H^+]) \times 10^{-4} [S_2O_8^{2-}] [Am(V)]^0 M \text{ hr}^{-1}$ Millimolar concentrations of ^{243}Am used	107

Table 10.23
REDUCTION OF AMERICIUM(V)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
H ₂ O ₂	0.02	0.1 <i>M</i> HClO ₄	25	$k'' = 14.8 \pm 1.5 \text{ M}^{-1} \text{ hr}^{-1}$ $E_a = 55 \pm 9 \text{ (} 13.1 \pm 2.2 \text{)}$ ²⁴¹ Am was used	106

Table 10.24
REDUCTION OF AMERICIUM(VI)

Agent	Typical concentration, <i>M</i>	Solution	Temp., °C	Results	Ref.
H ₂ O ₂	6.9×10^{-4}	1 <i>M</i> HClO ₄	25	$k'' = 3.9 \times 10^4 [\text{H}^+]^{-0.12}$	101a
NpO ₂ ⁺	1.5×10^{-3}	1 <i>M</i> (H,Li)ClO ₄	25	$k'' = (2.45 \pm 0.04) \times 10^4 [\text{H}^+]^0 \text{ M}^{-1} \text{ sec}^{-1}$ $\Delta H^* = 27.9 \pm 0.3 \text{ (} 6.7 \pm 0.1 \text{)}$	101b

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