THE PHOTOCHEMICAL ACCELERATION OF THE URANIUM (IV) - URANIUM (VI) ELECTRON EXCHANGE REACTION

> Thesis for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY JAMES DAVID HOESCHELE 1969



This is to certify that the

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presented by

James David Hoeschele

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Carl H. Brubal Major professor

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#### ABSTRACT

### THE PHOTOCHEMICAL ACCELERATION OF THE URANIUM(IV) - URANIUM(VI) ELECTRON EXCHANGE REACTION

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James David Hoeschele

The kinetics of the uranium(IV)-uranium(VI) electron exchange reaction were investigated in aqueous perchloric acid solutions under conditions of constant incident light intensity. A low-pressure mercuryvapor lamp, Model LO 735A-7 (Hanovia), was used as the light source which emitted principally 2537 Å radiation. The exchange was inhibited by uranium(VI) and hydrogen ion, but accelerated by uranium(IV) and by increasing the temperature. Non-linear order graphs were obtained for uranium(IV), uranium(VI), and hydrogen ion, having the approximate orders of 0.41, -1.3, and -0.65, respectively. Overall quantum yields for exchange ranged from 0.01 to 0.1, based on the absorption of light by uranium(VI), and were determined by means of potassium ferrioxalate actinometry.

Plausible exchange mechanisms are discussed in terms of a uranium(V) intermediate as produced by one or more of the following steps:

- (1)  $U(IV) + O_2 \longrightarrow U(V) + HO_2$
- (2)  $U(IV) + U(VI) \xrightarrow{} 2U(V)$
- (3)  $UO_2^{2+} \cdot H_2 O \xrightarrow{hv} UO_2^+ + OH + H^+$

A mechanism based on step (3) as the principal exchange path is in reasonable qualitative agreement with the experimental results. THE PHOTOCHEMICAL ACCELERATION

OF THE URANIUM(IV) - URANIUM(VI)

ELECTRON EXCHANGE REACTION

By

James David Hoeschele

A THESIS

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DEDICATION

To Todd, Lisa, David, Mark, and Heidi . . .

may they profit from my mistakes

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# TABLE OF CONTENTS

PAGE

I.	INTROI	DUCTION	
II.	HISTOR	RICAL	
	Α.	Aqueous Chemistry of Uranium	
		Hydrolysis	
		Spectra	
		Photochemistry of U(VI)	
		Electron Transfer Reactions	
	в.	Uranium(IV)-Uranium(VI) Exchange Studies	
		Thermal Exchange Studies	
		Photochemical Exchange Studies	
III.	THEORI	ETICAL	
IV.	EXPERI	IMENTAL	
	А.	Preparation and Standardization of Reagents	
		Sodium Hydroxide	
		Perchloric Acid	
		Sodium Perchlorate	
		Cerium(IV) in Sulfuric Acid	
		Nitrogen Purification	
		238 Uranium(VI) Perchlorate	
		233 U-enriched <sup>238</sup> Uranium(VI) Perchlorate	
		Uranium(IV) Perchlorate	
		Analysis of Uranium Stock Solutions.	

# PAGE

B. Exchange Experiments
Preparation of Exchange Solutions
Photolysis of Exchange Solutions 51
Processing of the Exchange Solutions
Separation
Preparation of Counting Samples 62
Counting Techniques
C. Chemical Actinometry
Preparation of Calibration Graph 65
Photolysis of Actinometer Solutions 67
Quantum Yield Determinations
V. RESULTS
A. Light Intensities and Overall Quantum Yields 76
B. Calculation of Exchange Results
Uranium(VI) Concentration Dependence 81
Uranium(IV) Concentration Dependence 83
Hydrogen Ion Concentration Dependence
Radiolysis and Temperature Dependences 96
Tartaric Acid Concentration Dependence (Thermal) 98
VI. DISCUSSION
A., Discussion of Errors and Reproducibility of Results 101
Photochemical Rate Data
Thermal Exchange Results
<b>B.</b> Interpretation of Photochemical Data
VII. SUMMARY
LIST OF REFERENCES
·

.

APPE	NDICES .
Α.	Relative Calibration of a Low-Pressure Mercury-Vapor Lamp (Model LO 735A-7, Hanovia)
В.	Light Absorption Data for Uranium(IV)-Uranium(VI) Solutions 130
с.	Computer Program and Sample of Input-Output Data 133
D.	Original Kinetic Data

:

.

# LIST OF TABLES

TABL	E	PAGE
1.	Selected decay properties for $233^{U}$ and $238^{U}$	42
2.	Emission intensities of a mercury-vapor lamp, Model LO 735A-7 (Hanovia)	54
3.	Total incident intensities for lamps I, II, and III	77
4.	Dependence of exchange rate and overall quantum yields on uranium(VI) concentration	84
5.	Dependence of exchange rate and overall quantum yields on uranium(IV) concentration	87
6.	Dependence of exchange rate and overall quantum yield on hydrogen ion concentration	93
7.	Dependence of exchange rate on the $233$ U concentration	96
8.	Dependence of exchange rate on temperature	98
9.	Dependence of exchange rate on tartaric acid concentration	100
10.	Exchange rates for comparable experiments	101
A1.	The spectral radiance and Cary response for the standard tungsten lamp (U-202) and the spectral response factors for a Cary 14 spectrophotometer	125
A2.	Cary Model 14 resolution parameters and relative intensity data for a mercury-vapor lamp, Model LO 735A-7 (Hanovia)	129
B1.	Molar absorptivities of uranium(IV) and uranium(VI) for the wavelengths of the mercury-vapor emission spectrum	130
B2.	Fractions of light absorbed by exchange solutions and uranium ions	131
вз.	Summary of data used in correlating exchange rates with calculated absorbed intensities	132
D1.	Dependence of exchange rate on concentration of uranium(IV) .	137
D2.	Dependence of exchange rate on uranium(VI) concentration	139

D3.	Dependence	of	exchange	rate	on	hydrogen ion concentration 142
D4.	Dependence	of	exchange	rate	on	temperature 145
D <b>5.</b>	Dependence	of	exchange	rate	on	the $233$ U concentration 146
D <b>6.</b>	Dependence	of	exchange	rate	on	tartaric acid concentration 148

# LIST OF FIGURES

FIGU	RE	P	AGE
1.	Formal reduction potentials of uranium in 1 $\underline{M}$ HClO <sub>4</sub> at 25°	•	11
2.	Absorption spectra of uranium(IV) and uranium(VI) and fluorescence (emission) spectrum of the uranyl ion in perchlorate media	•	16
3.	Nitrogen purification train	•	39
4.	Preparation and storage of uranium(IV) perchlorate	•	44
5.	Apparatus for the de-aeration and maintenance of a nitrogen atmosphere over exchange solutions	•	49
6.	Photolysis apparatus	•	52
7.	Lamp and associated circuitry	•	53
8.	Photolysis apparatus and associated equipment	•	57
9.	Flow diagram of exchange solution processing	•	59
10.	Absorbance <u>vs</u> length of photolysis	•	69
11.	Absorbance <u>vs</u> uranium(IV) concentration for uranium(IV) variation	•	71
12.	Absorbance <u>vs</u> uranium(VI) concentration for uranium(VI) variation	•	72
13.	Absorbance vs potassium ferrioxalate (K <sub>3</sub> [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ]) concentration	•	73
14.	Quanta absorbed (2537 Å radiation)/ml-sec vs absorbance of potassium ferrioxalate solutions at 2537 Å	•	75
15.	Typical graphs of ln(1 - F) vs time for the hydrogen ion dependence	•	82
16.	Logarithm of exchange rate <u>vs</u> logarithm of uranium(IV) and uranium(VI) concentrations	•	85
17.	Logarithm of overall quantum yield vs logarithm of uranium(VI) dependence.		86

18. Logarithm of overall quantum yield vs logarithm of uranium(IV) 89 19. 90 20. Logarithm of exchange rate vs logarithm of hydrogen ion 91 21. Logarithm of overall quantum yield vs logarithm of hydrogen ion concentration  $\ldots$   $\ldots$   $\ldots$   $\ldots$   $\ldots$ 94 22. Absorbance vs hydrogen ion concentration for exchange 95 Logarithm of exchange rate vs logarithm of <sup>233</sup>U tracer 23. 97 24. Logarithm of exchange rate vs logarithm of tartaric acid concentration  $\ldots$   $\ldots$   $\ldots$   $\ldots$   $\ldots$   $\ldots$   $\ldots$   $\ldots$  .99Arrangement of lamps, spherical mirror, and spectrophotometer A1. A2. 

### I. INTRODUCTION

During the past two decades, considerable progress has been made in understanding the kinetics and mechanisms of electron-transfer reactions. This progress has been attributed to the availability of specific tracers, advances in instrumentation (for direct rate measurements in any time range) and experimental techniques, as well as to the development of satisfactory quantitative theory. In this connection, the elegant theoretical treatment(s) of electron-transfer reactions by R.A. Marcus<sup>1</sup> is especially noteworthy. Marcus,<sup>1</sup> Sutin,<sup>2</sup> and Reynolds and Lumry<sup>3</sup> have critically reviewed the existing theories, while Taube,<sup>4</sup> Halpern,<sup>5</sup> and Sutin<sup>6</sup> have reviewed electron-transfer reactions in general.

Electron-transfer reactions generally include (1) isotopic or electron exchange processes, in which no net chemical change occurs, as in

$${}^{204}\text{T1}^{3+} + \text{T1}^{+} \xrightarrow{2}{}^{204}\text{T1}^{+} + \text{T1}^{3+} \tag{1}$$

and

$${}^{55-59}_{Fe(CN)}{}^{3-}_{6} + Fe(CN){}^{4-}_{6} \xrightarrow{55-59}_{Fe(CN)}{}^{4-}_{6} + Fe(CN){}^{3-}_{6}$$
(2)

and (2) the more familiar oxidation-reduction reactions, in which chemical change is involved, as in

$$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$$
 (3)

and

$$U^{4+} + T1^{3+} + 2H_2 0 \longrightarrow UO_2^{2+} + T1^+ + 4H^+$$
 (4)

Exchange reactions constitute a relatively "simple" class of reactions, since the reactants and products are identical, and therefore, the equilibrium constant K and standard free energy  $\Delta F^{\circ}$  may be assumed to be unity and zero, respectively. Their study has been of particular interest since they provide simpler models on which to base theoretical calculations.

There are two well-established general mechanisms for electrontransfer processes: the so-called <u>outer-sphere</u> and <u>inner-sphere</u> mechanisms. In the first of these, electron transfer occurs through an "extended" activated complex in which the primary coordination spheres of the reactant ions remain intact and unaltered with respect to the number and kind of ligands present; in the second, through a bridged activated complex in which the primary coordination spheres of the reactants are mutually linked by one or more bridging ligands. A distinction between the two mechanisms is usually possible experimentally when (1) electron transfer between substitution-inert reactants is rapid (outer-sphere) or (2) the reactant complex of one metal ion and the product complex of the other are substitution-inert, and the bridging ligand is incorporated into the substitution-inert product (innersphere). In other cases, it may be very difficult to distinguish between the two.

Outer-sphere electron transfer occurs principally by a <u>tunnel</u>-<u>ling process</u>. According to (R.J.) Marcus, Zwolinski, and Eyring,<sup>7,8</sup> tunnelling is a quantum-mechanical process in which the electron "passes through" a potential-energy barrier rather than over it (in the classical sense). Conceptually, this barrier is the region of space occupied by water molecules of hydration separating the metal ions. A <u>direct transfer</u> through delocalized overlapping metal ion orbitals is also possible when a very close approach can be achieved in the activated complex (somewhat analogous to gas-phase exchange reactions, e.g., Ne-Ne<sup>2+</sup>).

The rate constants of outer-sphere reactions, many of which are exchange reactions, cover a range of sixteen orders of magnitude, with  $k < 10^{-8} M^{-1} sec^{-1}$  for  $Co(NH_3)_6^{2+}-Co(NH_3)_6^{3+}$  and  $k > 10^8$  for  $Fe(CN)_6^{4-}$ -Fe (o-phenanthroline)<sup>3+</sup>. In general, complex ions containing unsaturated or large polarizable ligands (such as o-phenanthroline, bipyridyl,  $CN^$ or  $C1^-$ ) exchange rapidly and usually much faster than the corresponding aquo or ammine complexes. The pronounced rate dependence of certain outer-sphere reactions (Fe(CN)\_6^{3-}-Fe(CN)\_6^{4-} and MnO\_4^{--MnO}\_4^{2-}) on specific cations (Cs<sup>+</sup> > K<sup>+</sup> > Na<sup>+</sup>) indicates that in some instances electron transfer can occur through a bridged outer-sphere activated complex, e.g.,

$$[Fe(CN)_6...Cs...Fe(CN)_6^{6-}]^+$$

wherein the Cs<sup>+</sup> ion is perhaps acting as a bridge to conduct the electron, in addition to reducing the electrostatic repulsion between the anions.

In inner-sphere reactions, electron transfer is preceded by the formation of a singly- or doubly-bridged intermediate. The function of the bridging ligand(s) may simply be (1) to reduce the electrostatic repulsion between the reactant ions and bring them close enough together to permit a direct exchange and/or, (2) to provide a continuous pathway for electron "conduction" through  $\sigma$  or  $\pi$  metal-ligand bonds. The second alternative is an example of <u>double-exchange</u> in which the reductant loses an electron to the bridge as the bridge loses one to the oxidant (a concerted process). The use of vacant (but usually higher energy) orbitals of the bridging ligand for electron delocalization and migration has been called "<u>superexchange</u>." Temporary reduction or oxidation of the bridge may result in chemical change in the bridge (e.g., cis-trans isomerization) when the removal or addition of one or more electrons produces a relatively long-lived metastable intermediate. The name <u>chemical mechanism</u> has been suggested for such reactions. The names of the preceding three processes have been suggested by Halpern and Orgel.<sup>9</sup> Electron transfer can occur with or without the transfer of bridging ligand(s). However, the transfer of a bridge is incidental to the process and is strictly determined by the relative substitution labilities of the complex ions involved.

The recognition of the inner- and outer-sphere processes has been made possible largely through the pioneer work of Taube and co-workers on the general system

$$Co(NH_3)_5 x^{2+} + Cr^{2+} + 5H^+ \longrightarrow Cr(H_2^0)_5 x^{2+} + Co^{2+} + 5NH_4^+$$
(5)

where X = any of a large number (>100) of molecules or anions, e.g., halides,  $N_3^-$ , NCS<sup>-</sup>, OH<sup>-</sup>, H<sub>2</sub>O, (mono- and polyfunctional) organic acids, etc. Since Co(III) and Cr(III) complexes are substitution-inert, the original finding that Cl<sup>-</sup> was contained in the product, <sup>10</sup> Cr(H<sub>2</sub>O)<sub>5</sub>Cl<sup>2+</sup>, clearly demonstrated that electron transfer occurred through a bridged activated complex of the form

$$[(H_3N)_5Co--C1--Cr(OH_2)_5^{4+}]^+$$

Extensive studies involving the systematic variation of the X group in reaction (5) has led to the discovery that (i) lone-pair electrons (as in  $N_3^-$ ) can participate in the bridging and transfer process, (ii) the series  $N_3^- >> I^- > Br^- > CI^- > F^-$  (in the order of effectiveness as a bridging group) may be considered diagnostic of an inner-sphere mechanism, (iii) that rapid electron transfer can occur through a conjugated  $\pi$ -bonding system (conduction) in which the site attacked by  $Cr^{2+}$  may be "<u>adjacent</u>" to or "<u>remote</u>" from the point of attachment of Co(III), (iv) an unstable intermediate may be formed as a result of unorthodox coordination (S-bonded NCS<sup>-</sup>), plus others.

There is at least one system<sup>11</sup> studied thus far that proceeds by both general mechanisms; namely,  $Co(NH_3)_5 X^{2+}--Co(CN)_5^{3-}$ . The rate of the bridging mechanism path depends markedly on the identity of X, as is typical for inner-sphere mechanisms, whereas the outer-sphere path has a rate practically independent of X.

Many of the special properties of electron-transfer reactions are a result of Franck-Condon restrictions. Applied originally to electronic absorption and emission processes, the Franck-Condon principle states, that electronic movement is so fast compared to nuclear movement ( $\sim$ 100x) that the nuclear coordinates remain essentially unchanged during an electronic transition. This means that any rearrangement of the coordination and/or solvent shells (expansion, compression, asymmetric changes) which is necessary to establish the proper energy balance in the activated complex must occur <u>prior</u> to the actual electron-transfer act itself (for which  $\Delta F = 0^{1}$ ). Libby has recently considered transition metal exchange<sup>12</sup> and oxidation-reduction<sup>13</sup> reactions in light of this principle, and concludes that electron transfer occurs most readily when the activated complex assumes the most highly symmetrical configuration possible. Reactants which are normally symmetrical, therefore, would require relatively little energy for rearrangement (primarily of the solvent shells) whereas considerable energy and rearrangement (of both ligand and solvent shells) might be required for asymmetrical reactants. In this context, it is thought that the formation of a bridge(s) in a "symmetrical" activated complex can lower an otherwise appreciably higher activation energy. Sutin<sup>6</sup> has pointed out that inner-sphere mechanisms appear to be preferred when rearrangement energies are large.

Simultaneous two-electron transfers have been proposed for several transition elements, e.g., Tl, Sn, Sb, As, since their stable oxidation states differ by two electrons. Thus, a direct one-stage process, e.g., as in reaction (1), could occur in which two electrons are transferred from a single orbital on one of the reactants to a single orbital on the other. However, a direct two-electron transfer is difficult to distinguish kinetically from consecutive one-electron transfers. Reaction (4) is less likely to occur by a simultaneous twoelectron transfer since the two electrons transferred from U(IV) come from different orbitals and pairing must occur at some stage.<sup>14</sup>

Various atom-transfer processes (H, O, Cl) have been proposed and/or verified as alternative modes of "electron transfer." Dodson and Davidson<sup>15</sup> first proposed that electron transfer between aquo metal ions or related hydrolytic species (e.g.,  $Fe^{2+}-Fe^{3+}$  and  $Fe^{2+}-FeOH^{2+}$ ) may occur through transfer of a hydrogen atom between their hydration

spheres. With special reference to the Fe(II)-Fe(III) system, the evidence in support of such a mechanism is that the rates are much slower (1) in non-aqueous media (anhydrous alcohols and nitromethane) where H-atom transfer is less probable, and (2) in  $D_00$  by a factor of two which is consistent with, but not conclusive, that O-H bond formation and rupture occurs in the rate-determining step. Also, electron transfer has been demonstrated in ice<sup>16</sup> and the activation energies of a number of other aquo metal ion systems are comparable (~10 kcal/mole), suggesting that a common mechanism involving water may be operative. Alternatively, Stranks<sup>17</sup> has suggested that electron transfer in these systems occurs via a direct electron transfer or tunnelling process involving a hydrogen-bonded (outer-sphere) activated complex. Oxygenatom transfer has been demonstrated, by means of <sup>18</sup>0-labelling, in several systems, e.g.,  $Cr^{2+} + UO_2^{2+}$ , and U(IV) with a number of oxygen-containing oxidizing agents.<sup>19</sup> In this connection the kinetics of a number of actinide ion reactions have been interpreted in terms of (inner-sphere) oxygen-atom transfer, in addition to H-atom transfer and electron tunnelling as alternatives, (e.g., the Np(IV)-Np(VI) system). Newton and Rabideau<sup>20</sup> have reviewed the kinetics and mechanisms of actinide electron-transfer reactions.

Photoactivation and subsequent reaction of excited state species can lead to additional mechanistic possibilities. Photoexcitation may lead to (1) the catalysis of an existing thermal path or (2) a distinctively different reaction scheme(s) involving the (a) direct participation of an excited state species and/or (b) free-radicals, produced, for example, as a result of photodecomposition of the solvent (or ligands). Uri<sup>21</sup> has reviewed the photodecomposition of water by various ions from

which it appears that the following primary photooxidative process may have general validity for certain metal ions (given sufficiently energetic radiation),

$$M^{n+} \cdot H_{2}O \xrightarrow{h \cup} M^{(n-1)+} \cdot OH + H^{+}$$
(6)

where M = Fe(III), Ce(IV), T1(III), <sup>22</sup> and Np(VI). <sup>23</sup> A similar process involving H-atom photoproduction may be written for the photoreduction of H<sub>2</sub>O by various cations ( $Cr^{2+}$ ) and anions (halides).

The recent photochemical studies of Co(III) and Cr(III) complexes by Adamson and co-workers<sup>24</sup> have revealed that various types of excited states may have a <u>distinctive chemistry</u> which does not necessarily involve the traditional octahedral, square-planar, etc., geometries of complex ions and which is more understandable in terms of electronic structure and bonding than in terms of thermal reaction mechanisms. Adamson states that the excited state reaction is not necessarily a rapid one, but it may be activated and it may be stereospecific.

Only one photo-induced inorganic electron exchange system appears to have been studied, i.e., the Tl(I)-Tl(III) system. Exchange is thought to proceed through a chain-type mechanism (see p. 32 of the THEORETICAL section) involving Tl(II) and OH as transient intermediates as produced in a primary process corresponding to (6).

Several quantitative theoretical treatments of electron-transfer reactions have appeared in the literature. While none of these are "complete" in themselves, the treatments of Hush<sup>25</sup> and (R.A.) Marcus<sup>1</sup> have been applied most extensively. In general, they are equally applicable to electron-transfer reactions between (1) organic species, (2) metal complexes and organic molecules, and (3) non-metallic inorganic molecules as well as to reactions between complex ions. Thus far, the calculation of rate constants and free energies of activation has been limited to the simpler outer-sphere processes, the agreement between calculated and experimentally observed rate constants being within a factor of 10 (for the very fast reactions), which corresponds to a  $\Delta F^{\dagger}$  within  $\sim$ 1.3 kcal/mole.

The major factors considered in the calculation of these quantities are: (1) rearrangement free energies (ligand and solvation shells), (2) coulombic free energy, (3) the change-of-multiplicity contribution, and (4) the corrections for changes in ligand field effects. Reynolds and Lumry<sup>3</sup> have critically reviewed all present (quantitative) theories and cite the further refinements needed.

The purpose of the preceding section was to present a brief survey of the various types of processes that are thought to be involved in electron transfer reactions. The study of the catalytic effects of various anions on several electron transfer systems has been a major interest in this laboratory. In particular, kinetic studies of the U(IV)-T1(III),  $^{26,27}$  U(IV)-U(VI),  $^{28,29}$  and  $Fe(II)-Fe(III)^{30}$  systems have been carried out in  $HClo_4$  in the presence of one or more of the following dicarboxylic acids: oxalic, malic, malonic, succinic, maleic, fumaric, and (for all three systems) tartaric acid. Some of these acids caused inhibition of the rates, some were without effect, but for all the systems studied tartaric acid caused the greatest acceleration of the rates. Consequently, the studies involving tartaric acid are the most detailed. The results of these studies indicate that the reactions are complex and involve several competitive paths. In the U(IV)-U(VI) exchange study, a marked photoacceleration of the rate was

observed in the presence of tartaric acid. Photoinduced exchange had been reported previously for this system in other acid media, but not in the presence of organic acids. A kinetic study of this photocatalysis seemed particularly interesting and desirable since a direct comparison of the photochemical and thermal reaction kinetics could then be made. Furthermore, some interesting mechanistic alternatives are possible (see p. 7). Therefore, this system was selected as my major research problem. However, the preliminary photolysis experiments revealed that tartaric acid (as are most carboxylic acids) is photooxidized by the uranyl ion,  $UO_2^{2+}$ , itself being reduced to U(IV). Consequently, this "exchange" system was abandoned in favor of the "pure" U(IV)-U(VI) system in HClO<sub>4</sub> only. A knowledge of the kinetics and mechanism(s) of this parent system is prerequisite to the understanding of any future and perhaps more complicated studies involving organic compounds.

#### II. HISTORICAL

This section is a review (1) of selected aspects of the chemistry of uranium ions in acidic solutions and (2) of the previous work on the uranium(IV)-uranium(VI) exchange system. The first part is intended as background material and will cover, briefly, the hydrolysis, spectra, photolysis, and electron transfer reactions of U(IV), U(V), and U(VI), principally in perchloric acid. Thermal and photo-induced exchange studies are discussed in the second part. An excellent review of the aqueous chemistry of uranium is contained in the text by Katz and Seaborg.<sup>31</sup> Also, comprehensive reviews on the inorganic, <sup>31,32</sup> analytical,<sup>33</sup> and radiochemistry<sup>34</sup> of uranium have been published recently.

### A. Aqueous Chemistry of Uranium

Uranium can exist in four well-defined oxidation states in aqueous solution, i.e., III, IV, V, and VI. In acid solution, the III and IV oxidation states exist as the hydrated cations,  $U^{3+}$  and  $U^{4+}$ , whereas the higher oxidation states exist as the "-y1" ions,  $U0^+_2$  and  $U0^{2+}_2$ .

The potentials of the various oxidation states are shown in Figure 1.



Figure 1. Formal reduction potentials of uranium in 1  $\underline{M}$  HClO<sub>4</sub> at 25°.

In the presence of other anions the values differ as a result of complex ion formation. The  $U^{4+}/U^{3+}$  and  $UO_2^{2+}/UO_2^+$  potentials are reversible and attain equilibrium rapidly. The  $UO_2^+/U^{4+}$  and  $UO_2^{2+}/U^{4+}$  potentials, however, involve oxygen transfer and are therefore irreversible. Nevertheless, these potentials are very reproducible and are hydrogen ion dependent.

Solutions of uranium in the individual oxidation states (III-V) can be prepared by controlled-potential or chemical reduction (e.g., Zn amalgam) of  $UO_2^{2+}$  solutions, or by dissolving a suitable salt (anhydrous binary chloride) in solution.

Uranium(III) solutions are unstable and are oxidized by water (slowly) and oxygen (rapidly). It has also been reported<sup>35</sup> that the U(III) ion slowly reduces  $Clo_4^-$  to  $Cl^-$ . (The chemistry of U(III) is relatively unimportant to this study and, therefore, will not be considered further.)

Uranium(IV) solutions remain essentially unchanged at 25° in the absence of oxygen. Even in the presence of oxygen and at moderate acidities, U(IV) is oxidized only slowly (mechanism discussed below).

Uranium(V) is the least stable and most difficult oxidation state to observe in aqueous solution. Herasymenko<sup>36</sup> was the first to observe U(V) in solution by the polarographic reduction of  $UO_2^{2+}$  to  $UO_2^{+}$ . For a long time his conclusions were considered doubtful until the polarographic studies of Heal<sup>37</sup> and Harris and Kolthoff<sup>38</sup> confirmed the existence of  $UO_2^{+}$ . Uranium(V) exhibits the following characteristic disproportionation reaction:

$$2UO_{2}^{+} + 4H^{+} \rightleftharpoons UO_{2}^{2+} + U^{4+} + 2H_{2}O$$
 (7)

An equilibrium constant of  $1.05 \times 10^9$  was obtained by Nelson and Kraus<sup>39</sup> in polarographic studies at 25° at an ionic strength of 2.0. Kraus and co-workers also found that  $UO_2^+$  is relatively stable in the pH range 2-4, where (1) approximately millimolar solutions can be prepared and (2) the disproportionation rate is negligibly slow,<sup>40</sup>(In 24% HF solution U(V) exists as the UF<sub>6</sub><sup>-</sup> ion and is very stable.<sup>41</sup>)

The kinetics and mechanism(s) of the U(V) disproportionation reaction will be discussed under "Electron Transfer Reactions."

Uranium(VI) is the most stable oxidation state in solution, despite its positive reduction potential (see Figure 1). The high positive charge is stabilized by the formation of the  $UO_2^{2+}$  ion, which behaves more like a 3+ ion in solution, as indicated by hydrolytic studies and the fact that the uranyl ion entropy is unusually low for a divalent ion: -17 e.u. <u>vs</u> 2 to 4 e.u. for many 2+ ions. It is now generally accepted that the uranyl ion has a symmetrical, linear structure, O-U-O, which can be disturbed by strong local fields.

<u>Hydrolysis</u>: The hydrolytic behavior of uranium ions has been studied very thoroughly, particularly in the case of U(VI). The degree of hydrolysis increases in the order  $U^{3+} < U0_2^{2+} < U^{4+}$  as determined by the acid reaction of the respective salts in solution. The instabilities of the  $U^{3+}$  and  $U0_2^+$  ions, as noted previously, makes hydrolytic investigations of these ions very difficult. Numerous investigations, based principally on pH measurements, indicate that the hydrolysis of  $U^{3+}$  is similar to that of the lanthanide(III) ions. The acid constant for  $U0_2^+$  is estimated to be significantly less than  $10^{-3}$ .

The existence of  $U^{4+}$  as the unhydrolyzed species of U(IV) has been established unambiguously.<sup>42</sup> Kraus and Nelson<sup>43</sup> have shown that above a [H<sup>+</sup>]  $\sim 0.01$ ,  $U^{4+}$  is hydrolyzed according to the simple monomeric reaction

$$U^{4+} + H_2 O \xrightarrow{\rightarrow} UOH^{3+} + H^+$$
 (8)

with an acid constant K, at 25°, of 0.21 at zero ionic strength and 0.024 at an ionic strength of 2.00 (NaClO<sub>4</sub>). At lower acidities, further hydrolysis leads to polynuclear species of the general formula<sup>44</sup>  $U(UOOH)_{n}^{n+4}$ .

Uranium(VI) hydrolysis studies have shown that  $UO_2^{2+}$  is the only species present in solution below a pH of  $\sim 2.^{45}$  Recent equilibrium ultracentrifugation<sup>46</sup> and spectrophotometric work<sup>47</sup> indicate that the principal hydrolyzed species of  $UO_2^{2+}$  in HClO<sub>4</sub> at 25° are  $(UO_2)_2(OH)_2^{2+}$ and  $(UO_2)_3(OH)_5^+$ ; however, an equally satisfactory fit of the data is obtained if the species  $UO_2OH^+$  is included. Also, Hearne and White<sup>48</sup> proposed the species  $UO_2OH^+$  with a formation constant of  $4 \times 10^{-6}$  at an ionic strength of 0.35. Recent kinetic studies of  $UO_2^{2+}$  hydrolysis by relaxation methods<sup>49,50,51</sup> have provided additional evidence in support of  $UO_2OH^+$  as a major hydrolytic species. Sutton<sup>52</sup> and MacInnes and Longsworth<sup>53</sup> had previously proposed  $U_2O_5^{2+}$  and  $U_3O_8^{2+}$  as the major cationic species.

<u>Spectra</u>: The absorption spectra of the U(IV) and U(VI) ions consist of relatively narrow bands in the ultraviolet, visible and nearinfrared regions, as is characteristic of all actinide ion spectra. These bands arise from electronic transitions within the 5f<sup>n</sup> levels and are only moderately influenced by ligand field effects (as compared to the greater perturbation of the spectral bands of the d transition metal ions).

The ultraviolet and visible absorption spectra of U(IV) and U(VI) in 1 <u>M</u> HClO<sub>4</sub> are illustrated in Figure 2. This figure is a reproduction of the spectra which were experimentally observed in this study and which are discussed in the EXPERIMENTAL section on page 47. As regards U(IV) spectra in HClO<sub>4</sub>, two significant investigations have been reported. Cohen and Carnall<sup>54</sup> have measured the visible spectrum of U(IV) and U(III) both in HClO<sub>4</sub> and DClO<sub>4</sub> and have observed no discernible changes either in intensity or peak positions. The ultraviolet absorption spectra of U(IV) and U(III) in DClO<sub>4</sub> are also reported. Kraus and Nelson<sup>55</sup> investigated the U(IV) absorption spectrum over the wavelength range 4000-11000 Å. From a combination of hydrolytic and spectrophotometric data, they were able to deduce the absorption spectrum of UOH<sup>3+</sup>, which exhibits a maximum at ~6250 Å ( $\varepsilon \leq 20$ ). McKay and Woodhead,<sup>56</sup> and Stewart<sup>57</sup> report U(IV) spectra for HNO<sub>3</sub> and HCl media, respectively.

The uranyl ion spectrum is one of the most extensively investigated of all molecular spectra. A recent monograph<sup>58</sup> devoted to the spectroscopy and photochemistry of uranyl compounds reviews most of the early work up to about 1962. Very recent papers by McGlynn and Smith<sup>59</sup> and Bell and Biggers<sup>60</sup> have been concerned with the theoretical interpretation of the spectra. By using sophisticated computer-assisted resolution techniques, Bell and Biggers were able to resolve the complex overlapping uv and visible spectra (1795-5000 Å) into 24 discrete bands, comprising 7 major absorption bands (or band groups). Two major bands, located in the visible region, are in accord with the two (vibrationally



Absorption spectra:  $[H^{+}] = 1.00$ , I = 1.0  $\underline{M}$ , T = 25°; fluorescence spectrum:  $[U0_{2}^{2+}] = 0.218$ ,  $[H^{+}] = 2.35$ ; I = 3.00; T = 28°.

perturbed) triplet excited states as previously proposed by McGlynn. The remaining five broad bands, which show no vibrational structure, were ascribed to ground state-singlet excited state transitions  $({}^{*}S \leftarrow S_{n})$ . (Henceforth, \* represents an excited state species only.)

The fluorescence emission spectrum of the uranyl ion in aqueous solution consists of six bands arising from transitions from the first two excited levels to the five vibrational levels of the ground state. The lifetime of the emission process  $(T \rightarrow S)$  is of the order of  $10^{-4}$ to  $10^{-5}$  seconds. The line spectrum illustrated in Figure 2 was prepared from the peak height intensity data of the authors.

Uranyl ion fluorescence lifetimes and yields are affected by the viscosity of the medium (low viscosity -- strong quenching), temperature (primarily as it affects the viscosity), concentration of  $UO_2^{2+}$  (self-quenching), and a variety of inorganic (particularly halides), and organic quenching agents. (The perchlorate ion is "inactive" with respect to fluorescence quenching.) Practically all quenching ions are, in fact, reductants and are involved in reversible oxidation-reduction reactions, e.g.,

$$UO_2^{2+*} + I^- \to UO_2^+ + I$$
 (9)

$$I + UO_2^+ \rightarrow I^- + UO_2^{2+}$$
 (10)

$$\mathrm{UO}_2^{2+*} \to \mathrm{UO}_2^{2+} \tag{11}$$

Quenching (or self-quenching) may be "chemical" or "physical" in nature, depending on how the energy lost for fluorescence is used. "... A distinction can be made between three mechanisms of quenching: quenching caused by <u>association</u> of the light-excited molecules with the quenching

molecule preceding the excitation (quenching by <u>complexing</u>), quenching by <u>proximity</u> of the excited and the quenching molecule (quenching by <u>resonance transfer</u>), and quenching by kinetic <u>encounter</u> of the quencher with the excited molecule. (In all three cases quenching can be either chemical or physical.)"<sup>61</sup>

A quantum yield for fluorescence of uranyl sulfate (10 g/ $\ell$  at 10°; complete absorption) was estimated by Vavilov and Levshin<sup>62</sup> to be 0.28. No other fluorescence quantum yield data for  $U0_2^{2+}$  appear to be available.

<u>Photochemistry of U(VI)</u>: The photoactivity of uranyl compounds has been known for a long time. The recent monograph by Belford and Rabinowitch, mentioned previously, reviews chronologically the work up to about 1961. The majority of the systems studied pertain to uranylorganic compound photoreactions (principally carboxylic acids), among which the uranyl-oxalic acid system (chemical actinometer) is perhaps the best-known example. Relatively few reactions of  $UO_2^{2+}$  with inorganic compounds have been reported and, apparently, the  $UO_2^{2+}-I^-$  system is the only one which has been studied quantitatively.<sup>63</sup>

Photolyses induced by visible light are inherently slow (especially non-chain reactions) since the molar absorptivities of free  $UO_2^{2+}$ average  $\sim 5 \ M^{-1} cm^{-1}$  above 3500 Å. Consequently, secondary thermal reactions may develop and play an important part in the overall processes. Many uranyl reactions (especially with organic acids) proceed, however, by light absorption by complex ions which may have considerably higher molar absorptivities. The situation is more favorable for ultraviolet-induced reactions since the molar absorptivities of  $UO_2^{2+}$  increase

sharply with decreasing wavelength below  $\sim3500$  Å (see Figure 2).

Photoactivated  $UO_2^{2+}$  can function as a true oxidant, resulting in reduction to U(IV), and/or as a sensitizer (or catalyst) for oxidation by other oxidants, particularly molecular oxygen, in which case  $UO_2^{2+}$  undergoes no net change. Failure to rigorously exclude oxygen from uranyl photochemical systems can result in the superposition of both modes of reaction. This is true of organic  $acid-UO_2^{2+}$  photoreactions which characteristically involve a combination of sensitized decomposition (usually decarboxylation), direct photochemical oxidation, and, if oxygen is present, "auto-oxidation."

Uranium(V) is thought to occur quite generally as an intermediate in uranyl photochemistry. Heidt and  $Moon^{64}$  have shown indirectly that U(V) occurs transiently in the photo-oxidation of various carbohydrates and aqueous methanol by  $UO_2^{2+}$ . The kinetics of U(IV) produced after the photolysis (2537 Å light) was stopped indicated a second-order dependence on the intermediate, in accordance with the U(V) disproportionation step

$$-d[UO_{2}^{+}]/dt = k_{D}[UO_{2}^{+}]^{2}[H^{+}] .$$
 (12)

Values of  $k_D$  obtained for different substrates were the same and agree reasonably well with more recent data.<sup>66</sup> The results of the  $UO_2^{2+}$ -methanol study provided a confirmation of the steady-state (photostationarystate) hypothesis for a U(V) intermediate. Quantum yields for U(IV) production were ~0.14, and were not too strongly dependent upon  $UO_2^{2+}$ concentrations.<sup>65</sup>

Strong illumination of solutions  $(H_2SO_4 \text{ and } HClO_4, \text{ but } \underline{\text{not}} HCl)$  of  $UO_2^{2+}$  and  $U^{4+}$  causes a shift in the U(IV)-U(VI) reduction potential.

This photoelectrochemical effect, known originally as the Becquerel effect, was interpreted by Heal and Thomas<sup>37</sup> in terms of the displacement of the equilibrium

$$U(IV) + U(VI) \xrightarrow{\rightarrow} 2U(V)$$
(13)

to produce a higher ( $\sim$ 10 times) steady-state concentration of U(V). This interpretation is corroborated by the results of Sobkowski<sup>67</sup> who, in addition, revealed that the magnitude of the potential developed and rate at which the equilibrium potential is established is markedly dependent upon the nature of the electrode surface (smooth <u>vs</u> platinized), which varies itself with the nature of the medium used.

<u>Electron Transfer Reactions</u>: The oxidation of U(IV) by molecular oxygen in perchloric acid was investigated by Halpern and Smith.<sup>68</sup> The kinetics of the suggested overall reaction

$$2U^{4+} + O_2 + 2H_2O \xrightarrow{2} 2UO_2^{2+} + 4H^+$$
(14)

conform to the rate law

$$-d[U(IV)]/dt = k[U(IV)][0_2][H^+]^{-1}$$
(15)

where  $k = 5.6 \times 10^{-3} \text{ sec}^{-1}$  for  $0.5 \text{ M} \text{ Clo}_4$  at 30°. The inverse hydrogenion dependence suggests that UOH<sup>3+</sup>, rather than U<sup>4+</sup>, is involved. The reaction is catalyzed by Cu<sup>2+</sup> and inhibited by Fe<sup>2+</sup>, Ag<sup>+</sup>, and Cl<sup>-</sup>. All evidence indicates that H<sub>2</sub>O<sub>2</sub> is not an intermediate in the reaction. The results are interpreted in terms of the following chain mechanism involving UO<sub>2</sub><sup>+</sup> and HO<sub>2</sub> as chain carriers. Rapid pre-equilibrium:

$$U^{4+} + H_2^0 \stackrel{K}{\leftarrow} UOH^{3+} + H^+ . \tag{8}$$

Initiation step:

$$UOH^{3+} + O_2 + H_2O \xrightarrow{\kappa_1} UO_2^+ + HO_2 + 2H^+$$
 (16)

Chain propagation steps:

$$UO_2^+ + O_2^- + H_2^- O \xrightarrow{k_2}^- UO_2^{2+} + HO_2^- + OH^-$$
 (17)

$$HO_2 + UOH^{3+} + H_2O \xrightarrow{\kappa_3} UO_2^+ + H_2O_2^- + 2H^+$$
 (18)

Termination step:

$$uo_2^+ + Ho_2^- + H_2^- o \xrightarrow{k_4}^+ uo_2^{2+} + H_2^- o_2^- + OH^-$$
. (19)

Fast reaction:

$$U^{4+} + H_2O_2 \longrightarrow UO_2^{2+} + 2H^+ .$$
 (20)

Quantitative studies  $^{69-71}$  of the U(V) disproportionation reaction have established the form of the rate law

$$-d[UO_{2}^{+}]/dt = k[UO_{2}^{+}]^{2}[H^{+}]$$
(12)

where  $k^{72}$  is 436  $\underline{M}^{-2}$  sec<sup>-1</sup> for solutions of ionic strength 2 and at 25°. (All actinide(V) disproportionation reactions appear to be bimolecular with respect to the metal ion.) The mechanism<sup>73</sup> is considered to involve the reactions

$$UO_2^+ + H^+ \rightleftharpoons UO_2 H^{2+}$$
(21)

$$\mathrm{UO}_{2}^{+} + \mathrm{UO}_{2}\mathrm{H}^{2+} \longrightarrow \mathrm{UO}_{2}^{2+} + \mathrm{UO}_{2}\mathrm{H}^{+}$$
(22)

$$UO_2H^+ \longrightarrow stable U(IV) species .$$
 (23)

An isotope effect observed in  $D_2 0^{73}$  ( $k_D/k_H = 1.7$ ) is consistent with a pre-equilibrium step as in (21). Polarographic kinetic studies<sup>72</sup> indicate that Cl<sup>-</sup> and Br<sup>-</sup> ions accelerate the rate, whereas an emf investigation<sup>74</sup> indicates that Cl<sup>-</sup> retards the rate (citric acid is also present).

A recent spectrophotometric and kinetic study by Newton and Baker<sup>75</sup> has provided new insight into the mechanism of the U(V) disproportionation reaction. Evidence is presented for the formation of a moderately stable U(V)-U(VI) complex,  $U_2O_4^{3+}$ , as given by

$$uo_2^+ + uo_2^{2+} \stackrel{\rightarrow}{\leftarrow} u_2 o_4^{3+} . \tag{23A}$$

Appreciable complexation was first indicated by the observation that the U(V) disproportionation reaction is <u>greatly</u> inhibited by U(VI). The complex exhibits a characteristic absorption band at 7370 Å ( $\varepsilon = 27$  M<sup>-1</sup>cm<sup>-1</sup>.

A detailed analysis of the data indicated that the U(V) disproportionation most likely involves a binuclear intermediate, but that other possibilities cannot be considered disproved. An example of such a mechanism is:

$$200_{2}^{+} = 0_{2}0_{4}^{2+}$$
(24)

$$d[U_2O_4^{2+}]/dt = k_f[UO_2^+]^2 - k_r[U_2O_4^{2+}]$$
(25)

 $U_2 O_4^{2+} + H^+ = \text{products}$  (26)

$$-d[U_2O_4^{2+}]/dt = k_c[U_2O_4^{2+}][H^+] .$$
 (27)

Binuclear intermediates have been shown to be important in other systems (e.g.,  $NpO_2^+ - UO_2^{2+}$ ). The thermodynamic quantities of activation,  $\Delta H^+$  and  $\Delta S^+$ , are 11.0 kcal mole<sup>-1</sup> and -11.0 cal mole<sup>-1</sup> deg<sup>-1</sup>, respectively, and are not in agreement with previously reported values (10 and -17 respectively).

In the presence of U(VI), a minor path for disproportionation involving  $UO_2^+$  and  $U_2O_4^{3+}$  is thought to exist.

Gordon and Taube have studied the exchange reaction between  $UO_2^{2+}$ ion and  $H_2^{-18}O$  in perchloric acid solution. Two exchange paths were found: (1) a U(V) catalyzed path,<sup>77</sup> having the suggested mechanism

$$UO_2^+ + H_2^{18}O \rightleftharpoons U^{18}O_2^+ + H_2^{0}$$
 (28)

$$v^{18}o_2^+ + vo_2^{2+} \rightleftharpoons v^{18}o_2^{2+} + vo_2^+$$
 (29)

and (2) the intrinsic exchange path, presumably taking place through the ion  $UO_2OH^+$  (as indicated by a linear dependence of the rate on  $H^+$ ).<sup>78</sup> The specific rate for this intrinsic exchange in 1.00 <u>M</u> HClO<sub>4</sub> is < 4.8 × 10<sup>-8</sup>.

A minimum value of 52.0  $\underline{M}^{-1} \sec^{-1}$  was estimated for the rate of exchange of U(V) and U(VI). Masters and Perkins estimated this rate to be between the limits of 100 - 1000.<sup>79</sup>

### B. Uranium(IV)-Uranium(VI) Exchange Studies

The uranium(IV)-uranium(VI) exchange system has been studied very extensively. Betts,<sup>80</sup> and Bächmann and Lieser<sup>81</sup> have studied the system in sulfuric acid, Rona<sup>82</sup> and Kakihana <u>et al</u>.<sup>83,84</sup> in hydrochloric acid, Shimokawa and Nishio<sup>85</sup> in a mixed system of acidic solution and
cation exchange resin, Grinberg and Bykhovskii<sup>86</sup> in aqueous oxalate, Amis and co-workers<sup>87-89</sup> in a variety of aqueous-organic mixed solvent systems, Masters and Schwartz<sup>66</sup> and King<sup>90</sup> in perchloric acid, and Benson and Brubaker<sup>28,29</sup> in perchloric acid containing tartaric acid.

<u>Thermal Exchange Studies</u>: Studies on the uncatalyzed thermal system indicate that at least two parallel exchange paths exist. A path exhibiting second-order dependence on U(IV) concentration was observed by Rona<sup>82</sup> for dilute hydrochloric acid solutions. The exchange rate was not affected by light or added inert salts (NaClO<sub>4</sub> and NaCl). The rate equation presented by Rona is

$$R = k[U(IV)]^{2}[U(VI)][H^{+}]^{-3}$$
(30)

for which the suggested mechanism is

$$U^{4+} + H_2 0 \xrightarrow{\sim} UOH^{3+} + H^+$$
 (8)

$$UOH^{3+} + UO_2^{2+} + 2H_2O \xrightarrow{} [X_1]^{3+} + 2H^+$$
 (31)

$$[x_1]^{3+} + \text{UOH}^{3+} \xrightarrow{} [x_2]^{6+}$$
 (rate-determining) (32)

$$[x_2]^{6+} \longrightarrow \text{products}$$
 (33)

Thus far, this proposed mechanism is unique for a reaction of this kind involving one of the actinide elements.

The second path, found by Masters and Schwartz in perchloric acid solutions, exhibits a first-order dependence on U(IV) and predominates at or above 25° and at a [U(IV)] below 0.01. The rate equation obtained is of the form

$$R = k[U(IV)][U(VI)][H^{+}]^{-3}$$
(34)

where  $k = 2.13 \times 10^{-7} M^2 \text{ sec}^{-1}$  for I = 2.00 at T = 25.0°. This path was shown to proceed through a U(V) intermediate, in accordance with the equilibrium

$$U(IV) + U(VI) \xrightarrow{\rightarrow} 2U(V) . \tag{13}$$

A quantitative correlation of the exchange and disproportionation rates established that the activated complex formed in the exchange reaction was <u>identical</u> with that formed in the disproportionation reaction. The mechanism may be described schematically as

$$u^{4+} + uo_2^{2+} + 2H_2 O \xrightarrow{-3H^+}_{+3H^+} (HO \cdot U \cdot O \cdot UO_2)^{3+}$$
 (35)

and

$$(HO \cdot U \cdot O \cdot UO_2)^{3+} \xrightarrow{-H^+}_{+H^+} 2UO_2^+$$
(36)

This identical reaction sequence has been noted for other members of the actinide series.<sup>91</sup>

Exchange studies in media in which U(IV) and U(VI) are extensively complexed indicate that the U(IV)-U(V)-U(VI) equilibrium(a) is involved in the exchange process. Hence, in  $2 \leq H_2SO_4$  the exchange rate is described by the same rate expression given in equation (34), except k is  $10^3$  higher than in the uncomplexed system, and the disproportionation of U(V) is rate-determining.<sup>81</sup> The sulfate ion concentration was held constant throughout the study and no detailed mechanism was presented.

The U(IV)-U(VI) exchange in a solution containing ammonium oxalate,<sup>86</sup> of unspecified pH (but presumably >7), was found to be accelerated by oxalate ion and conformed to the following rate law at constant oxalate ion concentration:

$$R = k[U(IV)]^{1.7}[U(VI)]^{0.5}.$$
(37)

A three-step mechanism was proposed in which a U(IV)-U(V) exchange step is rate-determining.

$$U(IV) + {}^{233}U(V) \xrightarrow{233}U(IV) + U(V)$$
(38)

Uranium(IV) and -(VI) were present as the ions  $[U(C_2O_4)_4]^{4-}$  and  $[UO_2(C_2O_4)_2]^{2-}$ , respectively. An analogous exchange step has not been reported for any other actinide system.

Investigations at high HCl concentrations  $^{83,84}$  have shown that the exchange rate is markedly accelerated in 6-10 <u>M</u> HCl. Deuterium enrichment caused a slight acceleration of the rate. A mechanism was proposed involving an activated complex composed of U(IV), U(VI), Cl<sup>-</sup>, and undissociated HCl (bridged).

Benson and Brubaker<sup>29</sup> examined the effects of several organic dicarboxylic acids on the exchange reaction in perchloric acid. The catalytic effect of these acids increased in the order: malonic < maleic < malic << tartaric acid. The following three-term rate law was deduced for the exchange system in the presence of tartaric acid (HaTar).

$$R = \frac{5.7 \times 10^{-4} [U^{4+}]^{2} [U0^{2+}]}{[H^{+}]^{4}} + \frac{7.3 \times 10^{-5} [U^{4+}] [H_{2} Tar]}{[H^{+}]^{2}} + \frac{1.2 \times 10^{-3} [U^{4+}] [H_{2} Tar] [U0^{2+}_{2}]}{[H^{+}]^{2}}$$
(39)

Rates calculated by means of this expression agree well with those obtained experimentally. The light-catalyzed exchange reported for this system was, apparently, partly the result of net photochemical reduction of U(VI) by tartaric acid.

Exchange studies in the ethylene glycol-water, ethanol-water, and acetone-water solvent systems  $^{87-89}$  indicate a marked dependence on the composition of the solvent. Wear  $^{92}$  has reviewed these systems and has attempted to write reasonable rate laws that will reproduce the observed rates of reaction.

Photochemical Exchange Studies: No definite study of the photoinduced U(IV)-U(VI) exchange system has been carried out in any medium heretofore. In several of the above-mentioned studies, <sup>28,66,80,81,86</sup> the exchange rate was observed to be markedly accelerated by light (primarily from tungsten lamps) and U(V) was presumed to be the active intermediate. However, the experiments were, for the most part, isolated ones and the light intensities involved were unknown.

Betts' study in sulfuric acid<sup>80</sup> provided the following rate law for the conditions of constant illumination and sulfate concentration (1.9 M):

$$R = k' [U(IV)]^{0.5} [U(VI)^{0.5} [H^+]^{-0.30}$$
(40)

Photo-induced rates were  $\sim 20$  times faster than the corresponding thermal rates. Poor agreement between an observed and calculated rate (assuming a U(V) disproportionation mechanism) lead Betts to conclude that U(V) disproportionation was insufficient, in itself, to account for the observed rate of exchange. No detailed mechanism was presented. The results of irradiations using low intensity monochromatic light (as supplied by a conventional spectrophotometer during normal operation) pointed to U(VI) as the light sensitive ion. Exchange was catalyzed by 340 mµ light (absorbed by U(VI) only) but not by 650 mµ light (absorption by U(IV) only). [No definite conclusions can be made concerning the U(IV) photoactivity since the intensity of light absorbed by each ion was not determined.]

Masters and Schwartz<sup>66</sup> obtained the first quantitative photochemical data for the U(IV)-U(VI) exchange system. Irradiation of a solution, containing  $0.00132 \ M$  U(IV),  $0.00484 \ M$  U(VI) and  $0.24 \ M$  hydrogen ion at ionic strength 2.0 with ultraviolet light (principally 2537 Å light) caused the rate to be increased a 1000-fold over the expected thermal rate. No change in reactant concentrations was detected and, an overall quantum yield of about 0.01 was estimated for the induced exchange. In order to explain the accelerative effect, it was assumed that photolysis brought about an increase in the steady-state concentration of U(V) without causing a net reduction of the solute.

Zielen, Sullivan and Cohen<sup>23</sup> studied the photochemical reduction and autoreduction of Np(VI) in HClO<sub>4</sub> at 25°. An "apparent" quantum yield for Np(V) formation of 0.032 ± 0.011 was obtained for photolyses with 2537 Å light. The first order rate constant for the autoreduction of Np(VI) to Np(V) was measured as  $k = 3.1 \pm 0.2 \times 10^{-9} \text{ sec}^{-1}$ .

## III. THEORETICAL

The rate of isotopic exchange is mathematically described in terms of the first-order exchange law, the McKay equation<sup>93</sup>

$$\ln(1 - F) = -R(\frac{a + b}{ab})t$$
, (41)

The derivation of this equation and its modified forms, which take into account radiation-<sup>94</sup> and separation-induced<sup>95</sup> exchange and appreciable isotope effects,<sup>96</sup> can be found elsewhere in the literature and will not be repeated here.

As applied to the general isotopic exchange reaction

$$AX + BX \xrightarrow{\star} AX + BX$$
(42)

R is the rate at which X is being exchanged between the two species AX and BX, whose total concentrations are given by a and b. F is the fraction of exchange occurring in time, t. ( $\stackrel{\star}{X}$  is an isotopic tracer introduced into the system in AX (or BX) in order to follow the rate of exchange). Exchange rates are evaluated from the slope of a plot of ln(1 - F) <u>vs</u> t.

Equation (41) is equally applicable to photochemical as well as thermal exchange systems, since it does not depend on the form of R, assuming that isotopic effects are negligible, and that there is no net change in the reactant concentrations. By varying the reaction conditions systematically, the dependence of R upon concentration, (the empirical rate law), temperature, and other experimental variables may be determined. The rate law for a simple bimolecular reaction is of the form:

$$R = k[AX][BX]$$
(43)

where k is the specific rate constant in  $\underline{M}^{-1} \sec^{-1}$ . Plausible thermal mechanisms are then based on and directly correlated with the empirical rate law so obtained.

The interpretation of a photochemical exchange reaction mechanism, however, is based on the variation of the overall quantum yield for exchange,  $\phi_{ex}$ , with reactant concentrations and absorbed light intensities. For exchange resulting from absorption of light by AX (see equation (42)),  $\phi_{ex}$  is defined as

$$\phi_{ex} = \frac{R'}{I_{abs}} = \frac{No. \text{ of ions (or molecules) of } BX \text{ exchanged/ml-sec}}{No. \text{ of quanta absorbed by } AX/ml-sec} (44)$$

where the numerator is the exchange rate, R' (now in terms of ions exchanged/ml-sec) and is obtained as mentioned above. The denominator is the intensity of light of wavelength  $\lambda$  absorbed by AX (I<sub>abs</sub>).

Primary quantum yields are of great theoretical importance but are difficult to estimate. True primary quantum yields are independent of reactant concentrations and absorbed intensities. It follows from the second law of photochemistry that the sum of all  $\underline{n}$  of the primary quantum yields of the n different primary processes is equal to unity

$$\sum_{i=1}^{n} \phi_{i} = 1.00.$$
 (45)

This includes the primary photophysical processes of collisional deactivation, fluorescence, radiationless transitions, and other similar processes. Primary quantum yields of photoinitiated exchange reactions may be determined in the following simple manner.<sup>97</sup> For the exchange reaction in equation (42), in which exchange is initiated by light absorption by AX, the rate will be given by

$$R = \phi_1 I_{abs} = \phi_1 I_0 (1 - 10^{-\varepsilon ad})$$
(46)

(at low [AX]) where  $\epsilon$  is the molar absorptivity of AX, d the path length of light, a the [AX], and I<sub>0</sub> the incident light intensity of wavelength  $\lambda$ .

Expressing R in terms of the exchange half-life,  $t_{1/2}$ ,

$$R = \frac{0.693}{t_{1/2}} \frac{ab}{a+b}$$
(47)

and combining it with equation (46), the exchange law may be rewritten

$$\frac{0.693}{t_{1/2}} \cdot \begin{pmatrix} ab \\ a+b \end{pmatrix} = \phi_1 I_0 (1 - 10^{-\varepsilon ad})$$
(48)

Hence, at known reactant concentrations, the primary quantum yield may be evaluated by determining the half-time as a function of the incident light intensity. However, overall quantum yields are generally more useful and often provide crucial information about the reaction system. A small  $\phi_{ex}$  (<<1) indicates the importance of deactivation, fluorescence, or other processes that lead to no net chemical change whereas a  $\phi_{ex}$  >1 indicates that a chain mechanism is operative.

A generalized kinetic treatment of photoinitiated exchange involving a chain-type reaction has been presented by Stranks and Yandell. For the general exchange process

$$\overset{*}{A} + B \underset{\longleftarrow}{\longrightarrow} A + \overset{*}{B}$$
(42)

(X's have been omitted for the sake of simplicity; labelling is still represented by \*) occurring in liquid or gaseous phase, the following general mechanism is proposed

(i) 
$$A + hv \rightarrow C + X$$
 (initiation)  $\phi_1$  (49)

(ii) 
$$C + \hat{A} \xrightarrow{\sim} \hat{C} + A$$
 (propagation)  $k_1$  (50)

(111) 
$$\hat{C} + B \xrightarrow{B} \hat{B} + C$$
 (propagation)  $k_2$  (51)

followed by either

(iv) 
$$C + X \rightarrow A$$
 (termination) (52)

or

$$(v) C(+S) \longrightarrow A(+S') \quad (termination) \quad k_{+} \qquad (53)$$

Absorption of light or radiation  $(x, \gamma, \alpha, \beta)$  by species A generates the species C and X which can be either radicals or ions. For a two-electron exchange system in solution [e.g., the T1(I) -T1(III) system], charge-transfer absorption can generate C in an oxidation state intermediate between the oxidation states of A and B.

The rate of process (i) is equal to  $I_{abs}\phi_1$  where  $I_{abs}$  is the absorbed intensity in quanta liter<sup>-1</sup>sec<sup>-1</sup> and  $\phi_1$  (<1) is the primary quantum yield for the photolysis step itself. For liquid systems, where diffusion of geminate radicals is important,  $\phi_1$  is a measure of the efficiency with which a single absorbed quantum of light can produce the two species C and X which have escaped primary and secondary recombination. The essential requirement of this mechanism, which leads to  $\phi_{ex} > 1$ , is that C, as a chain carrier, must be capable of exchanging with <u>both</u> A and B at a rate much faster than its own rate of destruction, as in the sequence (ii) to (iv) or (v).

The two alternative termination reactions (iv) and (v) are examples of quadratic and linear termination reactions, both of which lead to very complex expressions for the rate and overall quantum yield,  $\phi_{ex}$ , for each of the two cases. For example, the rate expression for the quadratic case is of the form

$$R = \frac{k_{1}a \cdot k_{2}b}{k_{1}a + k_{2}b + (k_{t}I_{abs}\phi_{1})^{1/2}} \left(\frac{\phi_{1}I_{abs}}{k_{t}}\right)^{1/2} + \frac{k_{2}b \cdot \phi_{1}I_{abs}}{k_{1}a + k_{2}b + (k_{t}I_{abs}\phi_{1})^{1/2}}$$
(54)

where a and b represent the total concentrations of the species A and B. The expression for  $\phi_{ex}$  is obtained directly from (54) by the relationship

$$\phi_{ex} = \frac{R}{I_{abs}}$$
(55)

and is of the form

$$\phi_{ex} = \frac{k_{1}a \cdot k_{2}b}{k_{1}a + k_{2}b + (k_{t}I_{abs}\phi_{1})^{1/2}} \left(\frac{\phi_{1}}{k_{t}I_{abs}}\right)^{1/2} + \frac{k_{2}b \cdot \phi_{1}}{k_{1}a + k_{2}b + (k_{t}I_{abs}\phi_{1})^{1/2}}$$
(56)

The second term in (56) cannot exceed unity and arises from the non-chain

path, <u>via</u> reactions (i), (iii), and (iv). Quantum yields greater than unity arise from the first term in (56) and the contribution from this term depends on a balance between propagation and termination rates and the absorbed light intensity.

The general conclusion is made that for a linear chain termination exchange reaction,  $\phi_{ex}$  is independent of  $I_{abs}$ , whereas for a quadratic chain termination, equation (52),  $\phi_{ex}$  is proportional to  $I_{abs}^{-1/2}$  under appropriate conditions.

## **IV.** EXPERIMENTAL

## A. Preparation and Standardization of Reagents

Starting materials were reagent grade chemicals and were used without further purification, except for tartaric acid, sodium perchlorate monohydrate, and uranyl nitrate hexahydrate.

Demineralized water was used in the preparation of all stock solutions. Such purified water, denoted hereafter simply as water, was obtained by passing distilled water through a mixed bed resin, Crystalab DEEMINIZER, Model CL-5. This water contained less than 0.5 parts per million ionic impurities (measured as NaCl).

All glassware was scrupulously cleaned prior to use, especially the numerous items used in the preparation of exchange solutions. Ordinary cleaning with a detergent was followed by an overnight treatment with aqua regia, and subsequently, by successive rinsings with hot, distilled, and demineralized water.

Class A volumetric ware (pipets, burets, and flasks) was employed in all (1) standardization procedures and (2) the preparations of solutions for actinometric and exchange experiments. When Class A volumetric apparatus was unavailable, but required, volumetric apparatus was calibrated in accordance with the procedures outlined by the National Bureau of Standards.<sup>99</sup>

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<u>Sodium Hydroxide</u>: Carbonate-free sodium hydroxide  $(0.3\underline{N})$  was prepared and standardized according to the procedure of Kolthoff and Sandell. <sup>100</sup> The sodium hydroxide solution was prepared in a polystyrene vessel by diluting a saturated solution with de-aerated water. The

vessel was fitted with a delivery assembly which enabled the solution to be dispensed without introducing atmospheric carbon dioxide into the vessel. Under these conditions, the titer of the standard solution changed only 0.1% during a two-year period.

Sodium hydroxide solutions were standardized against primary standard potassium acid phthalate, which had been dried for two hours at 100° and using phenophthalein as the indicator.

<u>Perchloric Acid</u>: Perchloric acid stock solutions were prepared by diluting Baker Analyzed (70-72%) perchloric acid to the required volume. Numerous perchloric acid stock solutions were prepared during the course of this investigation, but one particular stock solution (3.944 M) was used in preparing the majority of the exchange solutions.

Perchloric acid stock solutions were standardized with sodium hydroxide and phenolphthalein was used as the indicator.

<u>Sodium Perchlorate</u>: Sodium perchlorate was used to adjust the ionic strength to 2.00 <u>M</u> in all exchange experiments. One major stock solution was prepared from triply-recrystallized sodium perchlorate, and used specifically for this purpose. The recrystallization procedure employed was developed, principally, by Love.<sup>101</sup> First, the starting material, reagent sodium perchlorate monohydrate from G. Frederick Smith Chemical Co., was dissolved in hot water to prepare a saturated solution. This solution was filtered through a fine fritted disc to remove dirt particles, placed on a hot plate and boiled until surface crystallization was observed (at  $\sim$ 142°). The crystals were dissolved in a minimum amount of water and then the solution was placed in an oven, thermostatted at 60°, where cooling and crystallization were allowed to take place

undisturbed during one day. (Crystallization from aqueous solutions of temperatures above 50° yields non-deliquescent prismatic crystals of anhydrous sodium perchlorate, whereas below 50° a deliquescent monohydrate is formed.<sup>102</sup>) The resulting crystals of anhydrous sodium perchlorate were collected in a coarse-fritted funnel, with care taken to keep out airborne dust, but were not washed because of their high solubility in water even at 0°. Three additional crops of crystals were collected by treating the resulting filtrate in the same way as the starting solution and repeating the steps just described. The once-recrystallized sodium perchlorate was recycled twice through the entire recrystallization procedure, and a total of four crops per cycle was collected in obtaining the final product. Sufficient purified product was obtained to prepare two liters of a 7.508 M sodium perchlorate solution.

To standardize the sodium perchlorate stock solution, one milliliter aliquots were delivered into weighed porcelain crucibles and then evaporated to dryness in a 160° oven. The crucibles containing the anhydrous sodium perchlorate were reweighed and the stock concentration was computed.

<u>Cerium(IV) in Sulfuric Acid</u>: Standard solutions of cerium(IV) in sulfuric acid were prepared from the salt,  $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ , according to the procedure of Wilson and Wilson.<sup>103</sup> This salt was obtained from the G. Frederick Smith Chemical Company.

Cerium(IV) solutions were standardized against (1) primary standard arsenic(III) oxide, with osmium(VIII) oxide as a catalyst and ferroin as the indicator,  $^{104}$  or (2) sodium oxalate (NBS certified) at 70° by a potentiometric procedure by use of a saturated calomel and

platinum electrode set.

Cerium(IV) solutions were used primarily for the determination of uranium in the respective stock solutions; the potentiometrically standardized cerium(IV) was used in the actinometric studies which will be discussed later.

<u>Nitrogen Purification</u>: Oxygen-free nitrogen was used as an inert cover gas in (1) all kinetic experiments and (2) during the preparation, transfer, and storage of all uranium(IV) stock solutions in order to prevent air oxidation of uranium(IV).<sup>106</sup>

The inert cover gas was prepared from Matheson pre-purified nitrogen (oxygen assay, 8 ppm) by passing it through a purification train, which consisted of the following components, in series, and which is schematically illustrated in Figure 3:

- (A) a tube furnace containing fine copper turnings at  $450^{\circ}$ ,
- (B) a heated glass column packed with activated copper adsorbed on Fuller's earth<sup>107</sup> (center at 175°).
- (C) duplicate gas scrubbing towers containing chromium(II)
   sulfate solution<sup>108</sup> over Zn amalgam,
- (D) a gas scrubbing tower of demineralized water and, finally,

(E) a gas scrubbing tower of 2  $\underline{M}$  sodium perchlorate (I = 2.00). Component (A) is the "rough," high-capacity oxygen getter, whereas components (B) and (C) are very efficient and high-capacity oxygenremoval units.

Connections between components were made with thick-walled polyvinyl chloride tubing, which is nearly impervious to oxygen.<sup>109</sup>

Detailed information on the purification scheme, including the



Figure 3. Nitrogen purification train.

procedures for column construction and operation, preparation and <u>in situ</u> regeneration of getter materials, can be found elsewhere.<sup>27</sup>

Henceforth, any reference to nitrogen means oxygen-free nitrogen. Occasionally, "tank nitrogen" will be used to refer to pre-purified nitrogen.

 $\frac{238}{\text{Uranium(VI) Perchlorate}}: \text{ Three types of uranium stock solutions}$ were prepared and used during the course of the work: (1) 238 uranium(VI) perchlorate, (2) 233 U-enriched 238 uranium(VI) perchlorate, and (3) 238 uranium(IV) perchlorate stock solutions. Except where noted, any reference to exchange and uranium(VI) stock solutions automatically implies enrichment with 233 U. 238 Uranium(VI) perchlorate will be specified as such. No uranium(IV) stock solutions were enriched, therefore, no isotopic designation is applicable.

Specially purified <sup>238</sup>uranium(VI) perchlorate was the starting solution used in preparing stock solutions of categories (2) and (3) above. <sup>238</sup>Uranium(VI) perchlorate stock solutions were prepared by a following procedure similar to that used by Love,<sup>111</sup>Benson,<sup>112</sup> and Quinn.<sup>26</sup>

A hot solution (85-95°) of recrystallized uranyl nitrate hexahydrate (99.9% assay, J.T. Baker Chemical Co.) was treated with a two-fold excess of 6% (w/w) hydrogen peroxide, to precipitate the gelatihous lemon-yellow uranium(VI) peroxide,  $UO_4 \cdot 2H_2O$ . ( $UO_4 \cdot 2H_2O$  is precipitated above 70°,  $UO_4 \cdot 4H_2O$  below 50°. A mixture of the two results between 50 and 70°.)<sup>113,114</sup> This precipitate was digested overnight at 80°, filtered, washed with water, and then dissolved in a minimum of hot 1 <u>M</u> perchloric acid. Dissolution was appreciably slow and usually a full day was required to complete it. The resulting solution was cooled, and then treated with dilute ammonium hydroxide to adjust the pH to  $\sim 2$ . The UO<sub>4</sub>·2H<sub>2</sub>O was then reprecipitated by adding more H<sub>2</sub>O<sub>2</sub>, and subsequently recycled through the dissolution-precipitation procedure. A total of four complete cycles was carried out in order to obtain a high-purity product. The final UO<sub>4</sub>·2H<sub>2</sub>O precipitate (of considerably improved crystallinity) was filtered, washed thoroughly, and was initially dried for a week in an oven at 105-110°. During the oven drying, part of the UO<sub>4</sub>·2H<sub>2</sub>O had decomposed to give the orange peroxide, U<sub>2</sub>O<sub>7</sub>.<sup>115</sup> Consequently, the entire batch of UO<sub>4</sub>·2H<sub>2</sub>O was converted to U<sub>2</sub>O<sub>7</sub> by heating it in an oven at 165° for a week. Although U<sub>2</sub>O<sub>7</sub> is slightly hygroscopic, no significant uptake of water was observed during the analytical weighings that followed.

Uranium(VI) perchlorate stock solutions of the desired composition were prepared by dissolving weighed quantities of  $U_2O_7$  in the stoichiometric amount of perchloric acid in accordance with the following equation:

$$U_2O_7 + 4H^+ \rightarrow 2UO_2^{2+} + 1/2 O_2 + 2H_2O$$
. (57)

Before making the final dilutions, the solutions were boiled vigorously for 2-3 hours to insure the complete destruction of any trace amounts of hydrogen peroxide. No detectable amounts of  $H_2O_2$  were found when solutions were titrated with 0.1 <u>N</u> cerium(IV) sulfate.

Three liters of 0.2  $\underline{M}$  uranium(VI) perchlorate was prepared in all. Two liters were used specifically for uranium(IV) preparations and had a slightly higher perchloric acid concentration.

 $\frac{233}{\text{U-enriched}} \frac{238}{\text{Uranium(VI) Perchlorate:}} 233 \text{U-enriched uranium(VI)}$ perchloric acid stock solutions were prepared by adding 10 or 25 ml of the tracer stock solution to the desired volume of the <sup>238</sup>uranium(VI) stock solution described above. The tracer stock solution, which had been prepared by Benson,<sup>116</sup> contained 0.51 g of <sup>233</sup>UO<sub>3</sub> (97.3% isotopic purity) dissolved in 100 ml of solution 3.00 <u>M</u> in HClO<sub>4</sub> [1.74 × 10<sup>-3</sup> <u>M</u> <sup>233</sup>UO<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]. The <sup>233</sup>U had been separated from its daughter products, primarily <sup>229</sup>Th, by anion-exchange chromatography in an 11 <u>M</u> HCl medium. Table 1 presents a comparison of the mode of decay, half-life, and specific activity for <sup>233</sup>U and <sup>238</sup>U.

Table 1.	Selected	decay	117 properties	for	<sup>233</sup> U	and	<sup>238</sup> u.
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Nuclide	Decay mode	<sup>T</sup> 1/2, y	Specific activity (d/m/µg)	Daughter, T <sub>1/2</sub>
233 <sub>U</sub>	α	$1.62 \times 10^5$	$2.103 \times 10^4$	$^{229}$ Th, 7.34 × 10 <sup>3</sup> y
238 <sub>U</sub>	α	$4.51 \times 10^9$	0.739	<sup>234</sup> Th, 24.1 d

Two principal stock solutions were prepared and used in making up exchange solutions. For preliminary and uranium(IV) variation experiments, a uranium(VI) stock was used having  $0.01\%^{233}$ U enrichment. This enrichment level was found to be unsatisfactory and therefore, a second stock, used for the H<sup>+</sup>, U(VI), and temperature variation experiments, was prepared with a  $0.025\%^{233}$ U enrichment. (Masters and Schwartz,<sup>66</sup> and Benson<sup>28</sup> used an isotopic enrichment of  $2\%^{233}$ U).

<u>Uranium(IV) Perchlorate</u>: Uranium(IV) perchlorate stock solutions were prepared by the electrolytic reduction of uranium(VI) perchlorate in perchloric acid solution. The procedure used was similar to that described by several previous workers.<sup>26,27,28,77,78</sup> The account given by Love<sup>27</sup> is particularly comprehensive; hence, only a brief description of the procedure used will be presented here.

Electrolyses were conducted in the dual-compartmented cell, illustrated in Figure 4, part I, and a four-inch diameter mercury-pool cathode and a 1 cm<sup>2</sup> platinum foil anode were used. The pool was reagent grade mercury and had been cleaned just prior to use.<sup>119</sup> The anode, fabricated from 22 gauge platinum wire and 4 mil foil, was placed in the anode compartment which contained perchloric acid of the same concentration as that in the final uranium(IV) solution.

Typically, 800 ml of 0.1 <u>M</u> uranium(VI) perchlorate, prepared from the <sup>238</sup>uranium(VI) stock solution mentioned above, was electrolyzed at 0° for ~21 hrs at 0.25-0.3 A and 5-7 V. An Electro, Model D-612T, was used as the (filtered) dc power supply. Higher currents were avoided since (1) the perchlorate ion is reduced to chloride ion at or above 0.7 A,<sup>118</sup> and (2) there is a greater tendency to produce the brownishblack hydrous oxide,  $UO_2 \cdot xH_2O$ , frequently observed <sup>27,28</sup>during the electrolysis (presumably resulting from localized depletion of acid). Solutions being electrolyzed were agitated by N<sub>2</sub> sparging but were not stirred mechanically. The electrolysis cell was maintained at 0° in an ice-salt bath to insure quantitative reduction of U(VI) to U(IV).<sup>77, 78</sup>

Before beginning an electrolysis, the uranium(VI) solution was purged rapidly with N<sub>2</sub> overnight in order to provide an oxygen-free atmosphere for the electrolysis. (The <u>entire</u> apparatus, including tubing and transfer routes, had been thoroughly flushed out prior to the addition of the uranium(VI) solution).





The major electrochemical half-reactions occurring during electrolysis are the following:

(1) 
$$H_2^0 \rightarrow 2H^+ + 1/2 0_2 + 2e^-$$
 (anode) (58)

(2) 
$$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2^0$$
 (cathode) (59)

$$(3) \quad U^{4+} + e^- \rightarrow U^{3+} \qquad (cathode) \qquad (60)$$

Half-reaction (3) occurs only when the U(VI) has been reduced quantitatively and is indicated by the appearance of the characteristic red color of the  $U^{3+}$  ion which is readily observed by viewing the transmitted light from a tungsten lamp placed directly behind the electrolysis cell. Electrolyses were terminated at the first appearance of the red color, since the  $U^{3+}$  ion is known to reduce slowly the perchlorate ion.<sup>35,54</sup>

After electrolysis, oxygen (scrubbed and filtered) is bubbled through the solution briefly to re-oxidize U(III) to U(IV). The uranium(IV) solution is then transferred and filtered <u>en route</u> to the storage vessel (Figure 4, part II) where it was purged again and then stored under a positive-pressure inert atmosphere. When special precautions are taken to eliminate the re-entry of air, uranium(IV) solutions can be stored for several months without detectable change. An average change of 5%/year was observed for the solutions considered herein (with most of the change occurring during the last six months).

A precision 10 ml buret, part III of Figure 4, was installed as an integral part of the storage unit. Thus, solutions for exchange experiments and analysis could be prepared by dispensing a known volume of the stock solution directly into the make-up vessel without the need for an additional volume measurement. In this way, oxygen contamination of the prepared solution was greatly minimized and virtually eliminated in the case of the storage vessel. <u>Analysis of Uranium Stock Solutions</u>: Uranium(IV), uranium(VI), and free perchloric acid concentrations in the various stock solutions were determined by titrimetric methods of analysis using 5-10 milliequivalents of uranium and acid (free) in each triplicate analysis.

Uranium(IV) solutions, made 2 M in  $\text{H}_2\text{SO}_4$ , were titrated with 0.1 <u>N</u> cerium(IV) sulfate at room temperature by using Fe(III) as a catalyst and ferroin as the indicator.<sup>120</sup> Reagent blanks were always less than 0.010 ml.

Uranium(VI) solutions, also made 2 M in  $\text{H}_2\text{SO}_4$ , were first passed through a Jones reductor in which the uranium(VI) was reduced to a mixture of U(III) and U(IV).<sup>106</sup> The reductor column effluent was sparged briefly with air to reoxidize the U(III) to U(IV), which was then titrated with cerium(IV) as above.

Free acid concentrations,  $[H_0^+]$ , in the uranium stock solutions ranged from 0.1-1 <u>M</u> as  $HClO_4$  and were determined by the method of Ahrland.<sup>118</sup> Appropriate volumes of a stock solution, U(IV) or U(VI), were passed through a cation-exchange column containing Dowex-50 X8 resin (strong cation exchanger) in the hydrogen ion form to liberate hydrogen ions in an amount equivalent to the  $UO_2^{2+}$  and  $U^{4+}$ . After rinsing the column with water, the effluent was titrated with 0.1 <u>N</u> sodium hydroxide and the number of free acid equivalents,  $nH_0^+$ , determined from the following relationship:

$$nH_0^+ = nH_{total}^+ - 4[U(IV)] - 2[U(VI)] .$$
 (61)

On the basis of the hydrogen ion and uranium(IV) analyses, the loss of U(IV) in the stock solutions with time was accounted for quantitatively in terms of the following reaction:

$$U^{4+} + 1/2 O_2 + H_2 O \rightarrow UO_2^{2+} + 2H^+ .$$
 (62)

This oxidative loss route was suspected, of course, but had not been confirmed previously.

Results of cerium(IV) titrations of freshly prepared  $^{238}$ uranium(VI) stock solutions indicated that no significant oxidizable substances (H<sub>2</sub>O<sub>2</sub>) were present in the solutions to within the sensitivity of the method (0.2 microequivalents).

Visible and ultraviolet absorption spectra (see Figure 2) of freshly prepared stock solutions were recorded over the wavelength range 2200-7200 Å by means of a Cary Model 14 spectrophotometer. Except as noted below, agreement with published spectra<sup>54,60</sup> was excellent. Molar absorptivities computed for each of the major peaks (7) of the U(IV) spectrum were the same (within 1%) as those reported for  $DC10_4^{54}$  with the exception of the 2454 Å peak. This discrepancy indicates that either (1) U(VI) was present in low concentration (undetected by titration) and/or (2) U(IV) spectra in  $DC10_4$  vs  $HC10_4$  differ slightly in this region. (Molar absorptivities for the wavelengths of the mercury-vapor emission spectrum are listed in Table B1.)

## B. Exchange Experiments

This section describes the procedures used in (1) preparing exchange solutions, (2) conducting exchange experiments and (3) processing the resultant solutions.

Two types of exchange experiments were performed. Thermal experiments were performed in order to (1) duplicate and extend a portion of the work of Benson,<sup>28</sup> (2) determine any radiolytic dependence of the rate

(variation of  $^{233}$ U tracer level), and (3) determine the exchange rate for the condition of lowest acidity employed in the photochemical experiments. Photochemical experiments constituted the majority of the experiments performed and were concerned with the dependence of the exchange rate upon reactant concentrations [H<sup>+</sup>, U(IV), and U(VI)] and temperature.

All exchange experiments were conducted at an ionic strength of 2.00  $\underline{M}$  (NaClO<sub>4</sub>), a temperature of 25.0° (except for the temperature variation) and under a protective atmosphere of nitrogen.

Uranium(IV) is oxidized slowly by oxygen under thermal conditions; <sup>68</sup> however, the rate of oxidation is greatly accelerated under ultraviolet excitation, and, particularly, in the presence of high uranium(VI) concentrations. Consequently, special procedures were employed to exclude air completely from the exchange solutions and vessels.

<u>Preparation of Exchange Solutions</u>: Exchange solutions for all thermal and most photochemical experiments were prepared as follows. The required volumes of labeled U(VI), NaClO<sub>4</sub>, (and tartaric acid, where appropriate) and HClO<sub>4</sub> stock solutions were dispensed into 50 or 100 ml volumetric flasks from burets or pipets. A flush adaptor connected to a detachable extension by tubing, as shown in Figure 5, was inserted into each flask which was then mounted either singly or in series in a thermostated bath. Nitrogen was bubbled through the solutions vigorously for approximately twelve hours to completely displace the oxygen present. After de-aeration, a given flask was removed from the bath momentarily, the flush insert was removed, and the required amount of U(IV) stock solution was added from the in-line inert atmosphere buret.



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De-aerated water, prepared by a boiling-cooling-nitrogen purge sequence, was added to dilute to the volumetric mark. The void space was flushed out with nitrogen and the flask stoppered before the contents were thoroughly mixed. After mixing, the sighting area was covered with black tape, the flush adaptor head was substituted for the stopper, and the flask was returned to the bath for equilibration and sampling a short time later.

The addition of the U(IV) stock solution effectively initiated thermal exchange. The progress of a thermal exchange was followed by periodically withdrawing aliquots of exchange solution, quenching them (if necessary), and then processing them exactly as described below for the photolyzed solutions. The uranium(IV) concentration was monitored periodically at 6500 Å by use of a Beckman DU spectrophotometer. No change in uranium(IV) concentration was detected during the course of any thermal exchange experiment.

A slightly modified procedure was used to prepare solutions for photochemical experiments at the highest uranium(VI) and lowest hydrogen ion concentrations, and at a temperature above 25°. Fifty or 100 ml of a solution was prepared to contain, in 5 ml of solution, the required amounts of uranium(VI), perchloric acid, and sodium perchlorate for a given exchange experiment. Five-milliliter aliquots were pipetted into individual 10 ml volumetric flasks, which were subsequently fitted with miniaturized flush-adaptor assemblies, and then placed in a thermostated bath. The remainder of the procedure was the same as described previously. The modified procedure was necessary in order to prevent significant oxidative losses of uranium(IV) during photolysis. It meant, however, that solutions had to be prepared just before each photolysis (the

so-called single-point kinetic technique), whereas in thermal exchanges samples were drawn from a 100 ml reserve of previously prepared solution.

Photolysis of Exchange Solutions: Photolyses were carried out by using the apparatus illustrated in Figure 6. The entire assembly consisted of three major parts: (1) lamp, (2) lamp housing, and (3) photolysis vessel. No filters or optics were interposed in the light path. The basic arrangement of the components was originally recommended by Adamson.<sup>121</sup>

Two low-pressure, quartz, mercury-vapor lamps (Hanovia, Model LO 735A-7) were used individually as the light sources and were operated in accordance with data file specifications, i.e., at a lamp current of 1.0 A at approximately 40 Vdc. A schematic diagram of the lamp and associated circuitry is given in Figure 7.

According to the lamp data file<sup>122</sup> the principal band emitted is the highly concentrated 2537 Å band, having a direct current intensity value of 15.75  $\mu$ W/cm<sup>2</sup> at a distance of 20 in from the quartz end of the lamp bulb. Other prominent bands include the blue band at 4358 Å and the ultraviolet band at 3130 Å, but no dc intensity data are given for these wavelengths. (For ac operation, the ratio of energy at 2537 Å was measured by Hanovia to be 34:5.) No measurable 1849 Å radiation is transmitted by the regular quartz envelope.<sup>123</sup>

A reliable spectral intensity distribution for a typical lamp was needed in order to correlate the exchange data with the wavelength and intensity of the absorbed radiations. Therefore, a lamp (lamp III) was calibrated by comparison with an NBS-calibrated tungsten ribbon-strip lamp (No. U-202) in conjunction with a Cary Model 14 spectrophotometer.



Figure 6. Photolysis apparatus.



Figure 7. Lamp and associated circuitry.

This calibration was checked independently by means of a procedure employing the 0.15 <u>M</u> potassium ferrioxalate actinometer (see section entitled "Chemical Actinometry") in combination with two filters (Pyrex #7740 and Corning #3391) which allowed intensity data to be obtained for the following three spectral regions:  $\lambda < 2730$  Å, 2730 Å  $<\lambda < 4085$  Å, and  $\lambda > 4085$  Å. The results of the calibration and actinometric check are listed in Table 2. More details are presented in Appendix A.

Table 2. Emission intensities of a mercury-vapor lamp, Model LO 735A-7 (Hanovia).

	<u>NBS-la</u>	mp Compari	Chemical Actinometry <sup>b</sup>		
Wavelength <sup>a</sup>	<u>Relative</u> Int	ensity Dis	Absorbed Intensities		
Å	Energy	Quanta	(%)	(quanta/sec)	
2537	100.0	100.0	(88.1)	$4.10 \times 10^{15}$ (86%)	
3126-32	1.69	2.09	(1.84)		
3650	1.71	2.11	(1.86)	$\longrightarrow 4.51 \times 10^{14} (14\%)$	
4047-78	1.06	1.69	(1.49)		
4358	1.68	2.89	(2.54)	$2.2 \times 10^{14}$ (5%)	
5461	2.23	4.79	(4.22)		

<sup>a</sup>The 5770-90 Å region is omitted since neither the exchange nor actinometer solutions absorb appreciably in this region.

<sup>b</sup>The 0.15 <u>M</u> actinometer (15 mm depth of solution) is  $\sim$ 110 times more sensitive for 4358 Å radiation than for 5461 Å radiation which is  $\sim$ 6 times more sensitive than for 5770-90 Å radiation; hence, the last value given (2.2 × 10<sup>14</sup>) is essentially for 4358 Å light.

The calibrated lamp was not used for any of the photolyses. Details of the calibration can be found in Appendix A.

Constant light output was achieved by (1) regulating the power input to 1.00 A and (2) controlling the temperature of the lamp envelope. Under these conditions, the voltage (and consequently wattage), and  $N_2$  airflow could be varied appreciably without changing the spectral distribution or output. These observations are consistent with those of Heidt and Boyles<sup>124</sup> who studied the effect of several experimental parameters on the output of the 2537 Å radiation. Constant power input was facilitated by regulating ( $\pm 0.2\%$ ) the 115 Vac line supply by means of a Sorenson (Model 1000 S) ac voltage regulator. Temperature control was accomplished primarily by mounting the lamp in a water-jacketed housing maintained at 25.0°.

In the housing, which was fabricated to close tolerances from an inner 34/45 § joint, the lamp was supported by a circular "shoulder" on which the edge of the lamp base rested. There was virtually no "play" in the lamp once it was seated.

Six interchangeable photolysis vessels were fabricated from inner 34/45 § joints. When fitted onto the housing, the distance, L, between the outer tip of the lamp envelope and the bottom, inside surface of the photolysis vessel was reproducibly  $6.10 \pm 0.05$  in. The lamp-to-solution distance is estimated at about 5.4 in when there is 5 ml of solution in the vessel. Both housing and vessels were made of Pyrex glass and were painted black on the outside; the housing also had an undercoat of silver paint.

Solutions undergoing photolysis were stirred continuously by a stirring bar ("peanut") which was magnetically activated by an underwater stirring unit. The underwater unit, as shown in Figure 6, was powered externally by a flexible cable attached to a standard stirring motor (also see Figure 8).

A nitrogen atmosphere was maintained over the solutions at all times during photolysis. After passing through a scrubbing tower of

 $2 \underline{M}$  sodium perchlorate (same ionic strength as the exchange solutions) at the temperature of the bath, the nitrogen was metered in through a flowmeter at a fixed, reproducible rate. It exited through the extremely narrow, annular clearances at the top of the housing and served to further cool the lamp envelope. A schematic drawing of the complete photolysis apparatus as arranged in the bath is shown in Figure 8.

The temperature of the photolyte remained constant during photolysis. This point was checked out specifically during an extended (60 minutes) photolysis of an exchange solution [#P(7)]. The post-photolysis temperature measured was identical to the bath temperature to within 0.05°, the limit of sensitivity of the thermometer used.

The following operational procedure was used in conducting the exchange solution photolyses;

- (1) A photolysis vessel, containing only a stirring bar, was sinserted in place. The whole assembly was lowered to a preset position (by a mechanical stop) at which the water level of the bath was just below the side-arm **s** joint.
- (2) The lamp was turned on and allowed to warm up for at least a half-hour before a series of photolyses were begun. The stirring unit and circulating pump were turned on immediately after the lamp.
- (3) The entire apparatus was flushed for 5-10 minutes with a rapid flow of tank nitrogen <u>via</u> a by-pass. Nitrogen was then re-routed into the flush route for the photolysis.

 $\xi_{ij}$ 

(4) After stable operating conditions were attained (primarily the lamp current), 5 ml of the photolyte was pipetted (jetted) into the vessel through the side-arm. A timer was



Figure 8. Photolysis apparatus and associated equipment.

tripped and the time recorded when half the sample had been delivered. The lamp current was checked frequently, but adjustments were seldom necessary. The remainder of the unphotolyzed exchange sample (10 ml initially) was used to measure the solution absorbance at 6500 Å by using a Beckman DU spectrophotometer.

(5) Upon completion of the photolysis, which usually lasted from one to twelve hours, the sample was removed from the light path (quenching the exchange) and the lamp remained on for the next photolysis. The solution absorbance was remeasured at 6500 Å and compared with the initial measurement. In general, only slight losses (<3%) of uranium(IV) were experienced. Photolyses were repeated (or the respective samples discarded) in which the change in uranium(IV) concentration exceeded 5%.

The photolyzed solution was then processed as described below. Essentially the same procedure was followed in photolyzing actinometer solutions. These along with other pertinent items will be discussed in the section entitled "Chemical Actinometry."

<u>Processing of the Exchange Solutions</u>: The progress of an exchange was followed by (1) separating uranium(IV) from uranium(VI), (2) preparing counting samples, and, subsequently, (3) determining, by  $\alpha$ -counting, the rate of grow-in of <sup>233</sup>U in the originally unlabeled U(IV) species. Several procedures discussed in the following three subsections (Separation, Preparation of Counting Samples, and Counting Techniques) were adapted from the work of Benson.<sup>28</sup> A flow diagram of the overall processing procedure is given in Figure 9.



Figure 9. Flow diagram of exchange solution processing.
Separation: The separation procedure used was essentially the same as that of Masters and Schwartz.<sup>66</sup> The exchange solution (5 ml) was delivered into a 30 ml separatory funnel containing an equal volume of 0.1 <u>M</u> 2-thenoyltrifluoroacetone (TTA) solution in benzene. The separatory funnel was shaken vigorously for two minutes and the lower, aqueous phase drained off and discarded. The uranium(IV) was extracted into the benzene phase as a 1:4 neutral molecule,  $U(TTA)_{L}^{125}$ 

$$U^{4+}_{(aq)} + 4 \text{ TTA } -H_{(org)} \stackrel{\rightarrow}{\leftarrow} U(\text{TTA})_{4(org)} + 4H^{+}_{(aq)}$$
(63)

Five milliliters of a 0.5  $\underline{M}$  perchloric acid wash solution was added and the funnel shaken vigorously for one-half minute. The aqueous layer was drained off and discarded. Normally, two such washes were adequate; however, for solutions at high uranium(VI) concentration, a third wash was found necessary, since traces of uranium(VI) in the wash could be detected by spectrophotometry. Finally, uranium(IV) was re-extracted into the aqueous phase, as a chlorocomplex, by vigorously contacting the benzene layer with 5 ml of 3.0  $\underline{M}$  hydrochloric acid for two minutes. This final aqueous extract normally contained 65-75% of the uranium(IV) and virtually none of the uranium(VI) originally present in the aliquot. [U(VI) is not extracted at a pH <3.<sup>126</sup>] Three 0.5 ml aliquots were taken and used to prepare triplicate counting samples (see below) and the remainder of the solution was used for the spectrophotometric determination of the uranium(IV) concentration.

Exchange solutions at acidities <1  $\underline{M}$  were quenched immediately before separation by adding acid to adjust the perchloric acid concentration to 1  $\underline{M}$ . In order to minimize the differences in the total amount of uranium extracted, less volume of exchange solution was used in the separations for certain solutions of the uranium(IV) variation. The actual volume of solution used was determined usually from the results of a preliminary extraction. Alternatively, estimation could have been made from available solvent extraction data.<sup>125,127</sup> No exchange was induced by the separation procedure(s) used.

For thermal experiments, the first sample withdrawn was designated as the "zero time" sample. The separation time was taken as the time the sample was delivered into the separatory funnel. For photochemical experiments, the unphotolyzed solution was used as the "zero time" sample and was processed coincident with the first photolysis of the "run" sequence. Occasionally, a second "zero time" sample was processed toward the end of the experiment. For photochemical experiments, separation times corresponded to the time a photolysis was terminated.

"Infinite" or "complete exchange" rates could not be calculated accurately, since the separation was not quantitative or precisely reproducible. Therefore, special samples were prepared for each exchange experiment, taking advantage of the fact that the specific activity of uranium is the same in both oxidation states when the exchange is complete. "Complete exchange" samples were obtained by electrolyzing an aliquot of an exchange solution to convert all the uranium present to the U(IV) oxidation state. Electrolyses were carried out in a 150 ml beaker by means of a mercury-pool cathode and platinum anode and at a potential of 6 Vdc and a current of 0.2-0.3 A. The operating conditions were very similar to those described for the preparation of uranium(IV) stock solutions, except no inert atmosphere was provided. The "synthesized" solutions were processed as described above.

The uranium(IV) in 3 <u>M</u> hydrochloric acid solution from above was placed in a one centimeter quartz cell and the absorbance,  $A_s$ , measured at a wavelength of 6500 Å, by means of a Beckman DU spectrophotometer. Solutions of uranium(IV) in 3 <u>M</u> hydrochloric acid obey Beer's law<sup>128</sup> and exhibit a molar absorptivity,  $\varepsilon$ , of 58 <u>M</u><sup>-1</sup> cm<sup>-1</sup>. (Using a solution of 0.1231 <u>M</u> U(IV) in 3.0 <u>M</u> HCl, the molar absorptivity was found to be 58.0.) The uranium(IV) concentration, C, in moles/liter can be determined from the following relationship:

$$C = A_{cl}$$
(64)

where l is the cell path length in centimeters, and  $A_s$ ,  $\varepsilon$ , and C are as indicated above. The uranium(IV) concentrations, or at least absorbances, were needed for the determination of specific activities.

<u>Preparation of Counting Samples</u>: The triplicate 0.5 ml aliquots taken for counting sample preparation were delivered onto 30 mm watchglasses, in earlier experiments, and then onto quartz discs one inch in diameter in later experiments. The edges of the sample mounts were ringed with a ceramic wax pencil to prevent sample losses through creepage during drying. The samples were evaporated to dryness rapidly under a heat lamp and then transferred to a muffle furnace. When the temperature reached 500°, the furnace was turned off; the samples were allowed to cool and then removed from the oven. When possible, all samples for a given experiment were heated at the same time. For the most part, adherent, uniform coatings (thickness and distribution) of  $UO_3$  were obtained by using this procedure. Considerably better coatings were obtained by incorporating into the procedure, a technique in use at

Argonne National Laboratory.<sup>129</sup> As before, samples were evaporated to dryness under a heat lamp. After a short cooling period, ~0.5 ml of water was added to redissolve the residue and then the sample was reevaporated under a heat lamp, but under an atmosphere of ammonia. These samples were heated in the furnace as above.

Approximately 0.4 mg of uranium was deposited on each sample mounting (density thickness of  $\sim.08 \text{ mg/cm}^2$ ). At this level, selfabsorption of  $\alpha$ -particles is significant. However, differences in selfabsorption from sample to sample were virtually negligible, since the amount of uranium(IV) extracted in each separation of a given experiment was relatively constant.

<u>Counting Techniques</u>: Samples were counted for  $\alpha$ -particles by use of the proportional region in one of two different windowless, flow, counting systems. A manual system incorporating a detector (Radiation Instrument Development Laboratory, Model 2-7) with an external preamplifier, and a glow-tube scaler (Baird Atomics, Inc., Model 309) was used initially. Samples from five experiments, P(24)-P(29), were counted by use of a Nuclear Chicago automatic counting system, complete with its associated detector, pre-amplifier (input sensitivity at 10), scaler (Model 8160), and sample changer (Model 1042). The input line voltage was regulated ( $\pm 0.2\%$ ) using an ac voltage regulator (same one mentioned previously). A 90% argon-10% methane gas mixture (The Matheson Co.) was used for the counting.

Samples were counted from 2 to 60 minutes in order to obtain at least a total of 10,000 counts. ("Infinite time" samples were counted up to 30,000 total counts.) This was sufficient to reduce the

statistical variation to well within 1%, as is shown below. For the longlived isotopes considered herein (e.g.,  $^{238}$ U and  $^{233}$ U), the standard deviation for a single observed value (total number of counts), S<sub>i</sub>, in a set (triplicate) is given by the relation:  $^{130}$ 

$$\sigma_{S_{i}} = (\bar{S}_{i})^{1/2} .$$
 (65)

Similarly, the standard deviation in a measured rate, R<sub>1</sub>, is given by the following:

$$\sigma_{\mathbf{R}_{i}} = \sigma_{\mathbf{S}_{i}/t} = (\overline{\mathbf{R}}_{i}/t)^{1/2} .$$
 (66)

Corrections for instrument variation and background were made by counting a single "standard" and blank sample before, during, and after a given counting session. The "standard" sample was identical in composition to the normal counting samples, having been prepared from leftover exchange solution by the same processing procedure. Counting rates were normalized relative to the initial counting rate of the "standard" by applying a correction factor for any non-statistical variation noted.

## C. Chemical Actinometry

Potassium ferrioxalate [potassium tris(oxalato)ferrate(III)] actinometry was used to determine incident and absorbed light intensities. Overall quantum yields for exchange,  $\phi_{ex}$ , were calculated from the intensity (and exchange rate) data.

Rated as the best solution-phase actinometer available today for photochemical research,  $^{131}$ the ferrioxalate actinometer is simple to use and is sensitive over the wavelength range, 2500-4800 Å. A detailed

description of the actinometer, including its nature, preparation and purification, and use, has been published by Hatchard and Parker.<sup>132</sup>

When sulfuric acid solutions of  $K_3[Fe(C_2O_4)_3]$  are photolyzed with light in the range 2500-5700 Å, simultaneous oxidation of the oxalate and reduction of from to Fe(II) occur. The quantity of Fe(II) produced can be determined by first complexing the Fe(II) with 1,10-phenanthroline (in an acetic acid-sodium acetate buffer of pH 3.5) and then measuring the absorbance,  $A_s$ , of the complex at 5100 Å by using a spectrophotometer. The high molar absorptivity of the Fe(II) complex,  $\varepsilon = 1.11 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , makes possible convenient exposures about one hundred times shorter than those required for the classical uranyl oxalate actinometer.

Since the actinometer is highly sensitive to the normal level of room illumination, all solution preparation, handling, and storage were carried out in total darkness or, at most, in the presence of a Kodak OB safelight (weak red illumination). Stock solutions were prepared, as recommended, <sup>132</sup> from solid  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$  which had been recrystallized three times from demineralized water and, subsequently, dried at 45°. Weighed amounts of the solid were first dissolved in  $0.1 \ N \ H_2SO_4$  and the resulting solutions transferred quantitatively into blackened and/or actinic volumetric flasks (painted by dipping). After final dilutions were made with  $0.1 \ N \ H_2SO_4$ , the flasks were stored in a darkened cabinet until use.

<u>Preparation of Calibration Graph</u>: As recommended,<sup>132</sup> a standard calibration graph was prepared for the analysis of the tris (1,10-phenanthroline) iron(II) complex for the particular spectrophotometer (Beckman

DU spectrophotometer) used in recording the absorbance data. The procedure followed in preparing the calibration graph was developed by Hatchard and Parker and is briefly presented here because of its relevance to the analysis of the photolyzed actinometer solutions. A standard solution (a),  $5.026 \times 10^{-4}$  <u>M</u> in Fe(II) and 0.1 <u>N</u> in H<sub>2</sub>SO<sub>4</sub>, was freshly prepared by diluting a 0.1 <u>N</u> FeSO<sub>4</sub> solution (also 0.1 <u>N</u> in H<sub>2</sub>SO<sub>4</sub>) with 0.1 <u>N</u> H<sub>2</sub>SO<sub>4</sub>. Both Fe(II) solutions were prepared with de-aerated water and were standardized potentiometrically with the 0.1 <u>N</u> Ce(IV) sulfate described previously. Also necessary for the calibration and for subsequent use in the actinometry were: a solution (b), containing 0.125% (by weight) 1,10-phenanthroline in water, and a buffer solution (c) prepared from 600 ml of 1.25 <u>N</u> NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and 360 ml of 1.25 <u>M</u> H<sub>2</sub>SO<sub>4</sub> diluted to one liter.

The following volumes of solution (a) were added to eleven calibrated 25 ml volumetric flasks: 0 (blank), 0.5, 1.0, ..., 5.0 ml. Sufficient 0.1  $\underline{N}$  H<sub>2</sub>SO<sub>4</sub> was added to make the total number of milliequivalents of acid present equal to 1.25. After 2 ml of (b) and 5 ml of (c) were added, the solution was diluted to volume, mixed, and allowed to stand for at least one-half hour. The absorbance of each solution was measured with the Beckman DU spectrophotometer at 5100 Å in a 1-cm cell, with the blank in the reference beam. A graph of A<sub>s</sub> vs [Fe(II)] was found to be linear and conforms to the following least-squares equation:

$$A_{g} = (1.108 \times 10^{4})[Fe(II)] + 0.003$$
 (67)

where the slope,  $\epsilon d$ , is numerically equal to  $\epsilon$ ,  $\underline{M}^{-1}cm^{-1}$ , since the path length, d, was constant at 1.00 cm. The value of  $\epsilon$  obtained is identical with that reported previously.<sup>131,132</sup>

<u>Photolysis of Actinometer Solutions</u>: Actinometer solutions were photolyzed under essentially the same conditions as the exchange solutions (see pp. 51-58). The only minor changes were (1) the termination of the photolysis by turning off the lamp instead of just physically removing the photolyte from the light path, and (2) the substitution of a  $0.1 \ \underline{N} \ H_2SO_4$  scrubber solution for the 2.0  $\underline{M} \ NaClO_4$  scrubber.

Two different actinometer solutions were used in the experiments. A  $6.00 \times 10^{-3} \text{ M K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$  solution was (1) used in all "standard" photolyses and (2) diluted to prepare the solutions required for the quantum yield determinations discussed below. The second actinometer solution, 0.15 M, was photolyzed twice, in order to verify that the incident light was completely absorbed by the more dilute solution. A "standard" photolysis consisted of photolyzing 5.00 ml of the  $6.00 \times 10^{-3} \text{ M}$  actinometer solution for five minutes. Four milliliters of this solution was used for analysis of the [Fe(II)] photo-produced, which, for a five-minute irradiation, corresponded to a solution absorbance of about 0.7. [The analytical procedure used was identical to that used in preparing the calibration graph, except the 4 ml of photolyte replaces solution (a)]. The number of quanta absorbed per second can be calculated by the following equation:

$$Quanta/sec = \frac{A_{s}V_{1}V_{3}(6.023 \times 10^{20})}{\varepsilon l V_{2}^{t\phi}}$$
(68)

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 $V_1$  = the volume of actinometer solution photolyzed (5 ml)  $V_2$  = the volume of aliquot taken for analysis (4 ml)  $V_3$  = the final volume to which  $V_2$  is diluted (25 ml)  $A_s$  = the measured (and corrected) absorbance of the solution at 5100 Å

- $\ell$  = the path length of the cell used (1 cm)
- $\epsilon$  = the molar absorptivity of the Fe(II) complex (1.11 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>)
- the quantum yield for Fe(II) formation for light of 2537 Å wavelength (1.25)
- t = the length of the photolysis in seconds

Such "standard" photolyses were carried out periodically in order to detect and correct for any appreciable change in the lamp output caused by aging or deviations from the normal operating conditions.

As mentioned above, two low-pressure Hg-vapor lamps were used as the source of the ultraviolet radiation. Lamp I was used for all the exchange solutions comprising the uranium(IV),  $H^+$ , and part of the uranium(VI) concentration variations. Lamp II was used in the temperature variation experiments and in three experiments, P(26)-(28), of the uranium(VI) variation. Actinometry experiments involved the use of the second lamp only. However, the lamps were compared by means of the "standard" irradiation procedure.

In a series of preliminary experiments the length of photolysis was varied systematically from one to ten minutes using the  $6.00 \times 10^{-3}$ <u>M</u> actinometer solution. As shown in Figure 10, the relationship of  $A_g$ (5100 Å) <u>vs</u> photolysis time, t, in minutes is linear over the time interval studied and extrapolates through zero.

Quantum Yield Determinations: Overall quantum yields for exchange were determined by using the approach of Claesson, <sup>133,134</sup> which entailed equating the fractions of the 2537 Å light absorbed (and therefore the number of quanta) by the exchange and actinometer solutions. The concentrations of the actinometer and exchange solutions which absorb the



Photolyte: 5.00 ml of 6.00 ×  $10^{-3} \text{ M} \text{ K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$  in 0.1 N H<sub>2</sub>SO<sub>4</sub>;  $\lambda = 5100 \text{ Å}$ .

same fraction of light were determined by measuring solution absorbances at 2537 Å for (1) each exchange condition studied at 25° and (2) a series of actinometer solutions for which the absorbance values overlapped the range observed in (1). The calculated absorbances of the exchange solutions ranged from 12 to 50 absorbance units for a onecentimeter path length. Because of these very high values, mock exchange solutions were prepared with uranium(IV) and uranium(VI) concentrations 10-100 fold less than in the actual photolyzed solutions. The acidity and ionic strength were maintained at the normal levels; namely, 1.00 and 2.00 <u>M</u>, respectively. Measured absorbances were then multiplied by the respective dilution factors in order to obtain the full-scale values.

The actinometer solutions used for the measurements varied from (0.06-5) ×  $10^{-3}$  <u>M</u> in K<sub>3</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] and were prepared by diluting the 6.00 ×  $10^{-3}$  <u>M</u> actinometer solution with 0.1 <u>N</u> H<sub>2</sub>SO<sub>4</sub>. The measured absorbances for the series ranged from 0.2 to 26.

Graphs of the absorbance data used to verify Beer's law are shown in Figures 11, 12, and 13, corresponding to the U(IV), U(VI), and  $K_3[Fe(C_2O_4)_3]$  variations, respectively. As indicated in Figure 13, a slight deviation from Beer's law occurs at concentrations <6 × 10<sup>-4</sup> <u>M</u>. Molar absorptivities and concentrations of the invariant components were calculated from the slopes and intercepts, respectively, obtained from the least-squares treatment of the data.

All solution cells used for the absorbance measurements were quartz, and were calibrated for use at the 2537 Å wavelength. The majority of the measurements were made by using a matched set of stoppered cells having exceptional ultraviolet transparency. The high absorbances of the actinometer solutions were measured directly with the





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Figure 13. Absorbance vs potassium ferrioxalate  $(K_3[Fe(C_2O_4)_3])$  concentration.

$$[H_2SO_4] = 0.1 \text{ M}; T = 25.0^\circ; \lambda = 2537 \text{ Å}.$$

aid of precision 9 mm solution cell spacers.

Each actinometer solution used in the absorbance measurements was subsequently photolyzed for 5 minutes and the absorbed quanta/ml-sec computed. A graph of the quanta absorbed (of 2537 Å radiation)/ml-sec  $\underline{vs}$  the  $A_g$  for the actinometer solutions, shown in Figure 14, was constructed from which quanta/ml-sec for the corresponding exchange solution absorbances could be obtained graphically. These intensity data were used in computing the apparent quantum yields for exchange.

50  $U(IV), U(VI), H^+$ : Range of measured absorbances (at  $\lambda$  =2537Å ) for the U(IV), U(VI), and H<sup>+</sup> variations. 40 Absorbance of K<sub>3</sub> [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] Solutions ğ 0 - U(VI) 20 (VI)U Ŧ ę 0 15.0 **1**0.0 5.00 Quanta absorbed/ml-sec(x10<sup>-14</sup>)

Quanta absorbed (2537 Å radiation)/ml-sec <u>vs</u> absorbance of potassium ferrioxalate solutions at 2537 Å. Figure 14.

$$K_3[Fe(C_2O_4)_3] = 6.00 \times 10^{-4}$$
 to  $6.00 \times 10^{-3}$  M.

## V. RESULTS

## A. Light Intensities and Overall Quantum Yields

Incident light intensities for each of the lamps used were computed from the actinometric and lamp calibration data in accordance with the following relationship:

$$I_{o} = \frac{\eta F e^{2+}/sec}{\sum \phi_{i} D_{i} f_{i}}, \qquad (69)$$

where  $I_{o}$  is the total incident light intensity in quanta/sec (for  $\lambda \leq 5461$  Å, nFe<sup>2+</sup>/sec is the number of Fe<sup>2+</sup> ions produced/sec during a five-minute photolysis and is computed from a measured absorbance,  $A_{s}$ , using equation (68),  $\phi_{i}$  and  $f_{i}$  are the quantum yield for Fe<sup>2+</sup> production by light of  $\lambda_{i}$  and the fraction of that light absorbed by a 1 - cm path length of the 6.0 × 10<sup>-3</sup> M actinometer solution, <sup>135</sup> and  $D_{i}$  is the fraction of the lamp output as  $\lambda_{i}$  (NBS lamp calibration data, Table 2).

The denominator in equation (69) is equal to 1.18 and is essentially an average quantum yield, weighted in accordance with the lamp spectral distribution and modified to correct for any incomplete absorption of  $\lambda_i$ . The results for three lamps are listed in Table 3. A value of 1.23 was used in computing the incident intensity for lamp III. This value is based on the fractions of light absorbed and quantum yields for the 0.15 <u>M</u> ferrioxalate actinometer, but is higher principally because 5461 Å radiation was not considered in the computation.

Since lamp deterioration does not materially affect the spectrum of a properly cleaned quartz mercury arc, it was assumed that all lamps

Lamps	A <sub>s</sub> (daily av)	nFe <sup>2+</sup> /sec (× 10 <sup>-15</sup> )	Incident Intensities, I <sub>o</sub> (quanta/sec × 10 <sup>-15</sup> )
I or II (new)	0.870 ± 0.039	4.92 ± 0.22	4.17
I (aged)	$0.522 \pm 0.013$	2.95 ± 0.07	2.50
IIa	0.545 ± 0.050	$3.08 \pm 0.28$	2.61
<b>I</b> II	0.895	5.06	4.11

Table 3. Total incident intensities for lamps I, II, and III.

involved, new or aged, exhibited the same relative spectral distribution and, consequently, that the incident intensities were directly proportional to the gross actinometric yields ( $nFe^{2+}/sec$ ). Moreover, lamp I (new) was assumed to have the same output as lamps II or III, which were observed to be identical within experimental error. Lamp IIa is the same as lamp II, except that the output had been reduced temporarily by a mineral coating which had encrusted the lamp tip. It is believed that P(25) is the only experiment affected by the lower intensity.

Overall quantum yields for exchange,  $\phi_{ex}$ , were determined by two different procedures. The first procedure consisted of computing  $\phi_{ex}$ directly from the experimentally observed exchange rates, R, and corresponding absorbed intensity data in accordance with Claesson's principle<sup>133</sup> and the following general expression for quantum yields:<sup>137</sup>

$$\phi_{ex} = \frac{\text{No. of ions exchanged}}{\text{No. of quanta absorbed}} \text{ (per unit time and volume)}$$
(44)

More specifically,

$$\phi_{ex} = \frac{(R \times 10^{-8} \text{ M/sec})(0.005l)(6.023 \times 10^{23} \text{ ions/g-ion})}{(L)(\text{quanta absorbed/m1-sec} \times 10^{14})(5 \text{ ml})} . \quad (70)$$

Values of the quanta absorbed (of 2537 Å radiation)/ml-sec for the various exchange conditions were interpolated from the graph illustrated in Figure 14 (see also p. 74) and, depending upon the lamp used, were adjusted for differences in the lamp outputs by means of the correction factor, L. The computed  $\phi_{av}$  values are tabulated with the rate data of each concentration variation study. Although the quantum yields are based on the absorption of 2537 Å light, they do not apply exclusively to this wavelength, since the actinometer and exchange solutions absorb the longer wavelength light (>3130 Å) to slightly different extents. But since the 2537 Å radiation comprised 90-96% of the total light intensity absorbed by either the actinometer or exchange solutions, it may be assumed that the  $\phi_{\rm av}$  values apply equally well to either the total absorbed intensity (all wavelengths) or to the 2537 Å radiation. The least reliable quantum yields are those for the U(IV) variation, wherein the fraction of the 4358 and 5461  ${\rm \AA}$  radiation absorbed increases with progressively higher [U(IV)].

The second procedure for obtaining overall quantum yields involved the use of <u>calculated</u> (as opposed to experimentally observed) absorbed intensities. From a knowledge of the molar absorptivities,  $\varepsilon$ , for each uranium species at each wavelength of light involved (see Table Bl in Appendix B), the total incident light intensity,  $I_0$ , and the lamp spectral distribution ( $D_i$  values mentioned above), absorbed intensities (for each uranium species) were calculated by use of equations derived from the Beer-Lambert law.<sup>138</sup> The fraction F, of the incident light intensity, I of wavelength  $\lambda_i$ , absorbed by a solution of path length d, containing two absorbing species [U(IV) and U(VI)] is given by:

$$F = 1 - T = 1 - 10^{-d(\varepsilon_1 C_1 + \varepsilon_2 C_2)},$$
(71)

where T is the transmittance,  $\varepsilon_1$ ,  $\varepsilon_2$  and  $C_1$ ,  $C_2$  are the molar absorptivities and concentrations of the two absorbing species, respectively. The distribution of the absorbed light,  $I_a = FI_o$ , between the two absorbing species is given by

$$I_{a} \frac{(\varepsilon_{1}C_{1})}{(\varepsilon_{1}C_{1} + \varepsilon_{2}C_{2})} = f_{1}, \text{ etc. for } f_{2}, \qquad (72)$$

where  $f_1$  and  $f_2$  are the fractions of the light,  $I_a$ , that is absorbed by each species. A summary of the solution and ion absorption data is presented in Table B2 in Appendix B.

By using the above series of equations, the intensity of light of  $\lambda_1$  absorbed by each uranium ion was calculated for each exchange condition [of the U(IV) and U(VI) variations] and for each of the six major wavelengths absorbed, with d = 1.00. The  $\phi_{ex}$  values, designated as  $\phi_{ex}$  (calc), were then calculated as before, but by use of the total calculated light intensity absorbed by each exchange solution. These results are also listed in the appropriate concentration variation section. Correlations of the exchange rate with the light intensity absorbed by each uranium ion(s) will be mentioned later.

## B. Calculation of Exchange Results

The logarithmic form of the McKay equation, 93 as applied to the U(IV)-U(VI) exchange system, is as follows:

$$\ln(1 - F) = -R \frac{[U(IV)] + [U(VI)]}{[U(IV)][U(VI)]} t .$$
(73)

F represents the fraction of exchange in time t, and is equal to the following, expressed in terms of specific activities;<sup>139</sup>

$$F = (S - S_{0})/S_{m} - S_{0})$$
 (74)

S is the specific activity (counts per minute per absorbance unit) of the U(IV) fraction of the sample photolyzed for (or removed at) time t,  $S_0$  the U(IV) specific activity at "zero time," and  $S_{\infty}$  the specific activity at the "complete exchange."

Specific activities were calculated from the averaged sample activities (triplicate set) and their corresponding absorbances and were, in turn, used to calculate a series of fractions of exchange. Writing the McKay equation in the form of (73), the slope would be equal to  $-R\{[U(IV)] + [U(VI)]/[U(IV)][U(VI)]\}$  and the intercept would be zero in the absence of induced exchange. Exchange rates were computed from the most probable slope, as determined by a linear least-squares treatment of the data, and use of the formulas given by Youden.<sup>140</sup> The requirement that the error in x (time) be small as compared with the error in y, or ln (1 - F), was clearly met.

The standard deviations  $\sigma$  in the slope and intercept were computed

by using standard formulas.<sup>140</sup> The standard deviation in the slope was used to determine the standard deviation in the rate. A comparison of the least-squares intercept values and the associated standard deviations indicated that no exchange had been induced by the separation methods since all values were within  $\pm 3\%$  of the theoretical value. Benson<sup>141</sup> and Masters and Schwartz<sup>66</sup> also reported no induced exchange.

The data were tested for the rejection of deviant points according to a  $2\sigma$ -rejection criterion. If the absolute difference between the least-squares value of ln (1 - F) and the experimental value exceeded  $2\sigma$ , the point was rejected. A new slope and intercept were then recalculated, based on the remaining data, with only one revision permitted. The McKay equation for each experiment was hand plotted to certify visually that linear graphs were obtained and, therefore, that the system conformed to the exchange law. Some typical graphs for experiments at different hydrogen ion concentrations are presented in Figure 15. Occasionally, curvature (tailing) was detected at longer photolysis times, but this always coincided with change in the [U(IV)]. Consequently, a second restriction was imposed on the data. Data for any photolysis in which the change in [U(IV)] exceeded 5% were discarded.

Computations were carried out by means of a computer program, written in FORTRAN IV and executed on a Control Data Corporation 3600 Computer. The program and a sample of the input and output data are presented in Appendix C.

<u>Uranium(VI) Concentration Dependence</u>: The effect of uranium(VI) concentration on the exchange rate was evaluated over a 15-fold concentration range:  $7.40 \times 10^{-3}$  to 0.111 M. The data are summarized in



Typical graphs of ln(1 - F) vs time for the hydrogen ion dependence. Figure 15.

 $[U(IV)] = 1.20 \times 10^{-2}$ ;  $[U(VI)] = 2.76 \times 10^{-2}$ ; I = 2.00 M;  $T = 25.0^{\circ}$ ;  $[H^{+}]$ : shown on graph with experimental code.

Table 4. Figure 16 shows the graphs of reaction order, log R vs log [U(VI)], which were obtained. Data for experiments P(17)-P(21), employing lamp I, constitute the lower curve in set B, whereas those for experiments P(26)-P(28), employing lamp II, are for the upper plot, which has a least-squares slope of  $-1.37 \pm 0.21$ . It is apparent that the exchange rate exhibits a non-linear and inverse dependence on [U(VI)]. At low [U(VI)] an approximate zero-order dependence is indicated, while at higher concentrations a decreasing order is in effect. Experiments P(26)-P(28) were performed last and solely for the purpose of verifying the results of the first set. A log-log plot of  $\phi_{av}$  vs [U(VI)] is illustrated in Figure 17. It is observed that the rate data conform to a single curve (at high [U(VI)]), having a least-squares slope of -1.31 ± 0.17, when absorbed intensities are taken into account.  $\phi_{out}(calc)$ , based on calculated absorbed intensities, are plotted on the same curve showing the agreement between the two sets of data listed in Table 4. The appearance of this curve is similar to that in Figure 16 (set B, lower curve), since the intensity of the light absorbed (all  $\lambda$ ) was nearly constant.

<u>Uranium(IV) Concentration Dependence</u>: The effect of the uranium(IV) concentration on the exchange rate was evaluated over the range 0.00598 to 0.0837 <u>M</u>, at a constant  $[U(VI)] = 2.76 \times 10^{-2}$ . The data are summarized in Table 5 and graphed in Figure 16 (set A) along with the U(VI) data for comparative purposes. A positive non-linear order was obtained as indicated in the upper curve (solid circles). A leastsquares straight line through these same points would have a slope of 0.42 ± 0.04. If one included P(6), the order would be 0.33 ± 0.11.

Experiment	[U(VI)] ( <u>M</u> × 10 <sup>2</sup> )	$(\underline{M} \text{ sec}^{-1} \times 10^8)$	¢ <sub>ex</sub> (ove	rall) × 10 <sup>2</sup>
			Observed	Calculated
P(17)	0.740	1.95 ± 0.14	3.55	2.53
P(18)	1.47	$2.05 \pm 0.14$	3.18	2.61
P(19)	2.96	1.79 ± 0.03	2.40	2.26
P(20)	5.92	1.61 ± 0.37	2.02	2.01
P(21)	8.87	1.09 ± 0.10	1.37	1.36
P(26)	7.44	$1.94 \pm 0.18$	1.46	1.51
P(27)	9.66	$1.45 \pm 0.11$	1.09	1.12
P(28)	11,14	$1.10 \pm 0.12$	0.826	0.85

Table 4. Dependence of exchange rate and overall quantum yields on uranium(VI) concentration.  $[U(IV)] = 5.87 \times 10^{-3}$ ;  $[H^+] = 1.00$ ; I = 2.00 <u>M</u>; T = 25.0°; P(17-21), lamp I; P(26-28), lamp II.



Logarithm of exchange rate vs logarithm of uranium(IV) and uranium(VI) concentrations. Figure 16.

 $[H^{+}] = 1.00; I = 2.00 \text{ M}; T = 325.0^{\circ}; A: [U(IV)] varied, [U(VI)] = 2.76 \times 10^{-2}; B: [U(VI)] varied, [U(IV)] = 5.87 \times 10^{-3}.$ 



$$U(IV)$$
] = 1.20 × 10<sup>-4</sup>; [H<sup>T</sup>] = 1.00; I = 2.00 M; T = 25.0°



concentration. = 2537 Å, λ <sub>5</sub> = 4358 Å,
Dependence of exchange rate and overall quantum yields on uranium(IV $[U(VI)] = 2.76 \times 10^{-2}$ ; $[H^+] = 1.00$ ; $I = 2.00 \underline{M}$ ; $T = 25.0^\circ$ ; lamp I; $\lambda_6 = 5461 \underline{A}$ ; I = absorbed intensity.
Table 5.

0.613 0.911	5.80	6.20	7.80 ± 0.98 (4)		
0.417 0.619	3.94	4.21	$5.30 \pm 1.02$ (6)	8.37	P(9)
0.399 0.548	3.27	3.37	<b>4.37 ± 1.32</b>	5.98	P(6)
0.747 0.925	3.64	3.70	4.76 ± 0.46	2.39	P(5)
1.03 1.23	3.00	3.13	3.87 ± 0.20	1.20	P(4)
•	I	I	1.85 ± 0.57	0.598	P(8) <sup>a</sup>
1.20 1.42	1.93	2.00	2.46 ± 0.15	0.598	P(7)
(6) (7) (7) (7)	carcutated (5)	(4)		(2)	(1)
$\sum_{\{\lambda_1,\dots,\lambda_n\}} \text{for:} (\lambda_1,\dots,\lambda_n)$	r all λ) Calculated	(∑I <sub>a</sub> fo) Observed	R (M sec <sup>-1</sup> × 10 <sup>8</sup> )	$[U(IV)]$ $(M \times 10^{2})$	Experiment
$\phi_{ex}(overall),"$ (calculated)	all) × 10 <sup>2</sup> "	φ <sub>ex</sub> (over,			

<sup>a</sup>[H<sup>+</sup>] = 1.86

1.14

It should be pointed out that the condition of highest [U(IV)] = 0.0837, P(9), is based only on four experimental points. Originally there were six points; however, two values had been discarded because of known determinate errors. Had these points been retained, the R would be 5.30, instead of 7.80,  $\times 10^{-8}$  M sec<sup>-1</sup>, and the lower curve (dashed) would apply. Also, the standard deviation in the R would be 6% higher. The somewhat greater scatter in the data of this variation, especially at high [U(IV)], is related to the inherent error associated with a slow exchange rate and a low tracer level. The tracer level used in this series was 0.01% (of the [U(VI)]) vs 0.025% for most other experiments.

Log-log plots of overall quantum yields (calculated and observed) <u>vs</u> [U(IV)] are shown in Figure 18. These curves are based on the averages of the values in columns (4) and (5) in Table 5. Curve P(9)-1 is based on R =  $7.80 \times 10^{-8} \text{ M sec}^{-1}$  (excluding P(6) as before), and P(9)-2 on R =  $5.30 \times 10^{-8} \text{ M sec}^{-1}$ . A least-squares line through the points considered for P(9)-1 has a slope of 0.41 ± 0.04.

"Quantum yields" were also computed on the basis of the total light intensity absorbed by the U(IV) ion for the wavelengths 2537, 4358, and 5461 Å. One set is based on the sum of all three wavelengths; a second set is based on the sum of the latter two. These data are also listed in Table 5, columns (6) and (7), and graphed in B and A of Figure 19. At the very most, only qualitative significance may be attached to these "quantum yields."

<u>Hydrogen Ion Concentration Dependence</u>: The effect of the hydrogen ion concentration on the exchange rate is illustrated in Figure 20.







 $\sum I_{a4}$  = the sum of light intensities absorbed by U(IV). P(9)-1, -2: lines based on R = (7.80 and 5.30) × 10<sup>-8</sup>  $\underline{M}$  sec<sup>-1</sup>, respectively; d, cm.





The data are tabulated in Table 6. The  $[H^+]$  was systematically varied over a 10-fold concentration range, 1.80-0.179 <u>M</u>, in the experiments P(10)-P(16), while the [U(IV)] and [U(VI)] were maintained constant at  $1.20 \times 10^{-2}$  and  $2.76 \times 10^{-2}$  <u>M</u> respectively. The ionic strength and temperature were maintained at 2.00 <u>M</u> and 25.0° respectively. As indicated in Figure 20, the reaction order graph exhibits curvature in the high acid region ( $\geq 0.7$  <u>M</u> acid). A reaction order of -0.65 ± 0.05 would be obtained from a linear least-squares slope of a line including all solid-circled points. The result for the thermal experiment, T(16), has been plotted on the same graph since thermal exchange is competitive under the conditions of the lowest  $[H^+]$  employed, i.e., at  $[H^+] = 0.179$ .

The log of overall  $\phi_{ex}$  <u>vs</u> log of [H<sup>+</sup>] are plotted in Figure 21. The whole curve could be slightly low by a constant factor, since the measured solution absorbances were higher than the calculated values for the 1 <u>M</u> acid region. Calculations indicate that at a [H<sup>+</sup>] = 1.00 <u>M</u>, [experiment P(12)] the UO<sub>2</sub><sup>2+</sup> ion absorbs >99% of the incident 2537 Å radiation.

Calculation of  $\phi_{ex}(\text{calc})$  for the  $[\text{H}^+]$  variation was not possible, since molar absorptivity data for U(IV) is not available for the ultraviolet region as a function of acidity. However, the gross changes in absorbance for the low acidity region in Figure 22 may be attributed primarily to the absorption of 2537 Å light by the U(IV) species, presumably UOH<sup>3+</sup>, since the molar absorptivities for the UO<sub>2</sub><sup>2+</sup> ion (1) have been reported <sup>45</sup> to be constant (±2-3%) over the entire spectrum for the pH range 0.1 to 1.5 and (2) are known to be nearly invariant (<1% change) over the acidity range, 0.125 to 1.00 <u>M</u> above 3400 Å.<sup>142</sup> Presumably this holds true for the lower wavelength region also.

Experiment	[н <sup>+</sup> ] ( <u>м</u> )	$\frac{R}{(\underline{M} \text{ sec}^{-1} \times 10^8)}$	¢ <sub>ex</sub> (overall) (× 10 <sup>2</sup> )
P(10)	1.80	2.00 ± 0.24	1.63
P(11)	1.50	$2.17 \pm 0.12$	1.70
P(12)	1.00	$2.49 \pm 0.07$	2.03
P(13)	0.750	3.01 ± 0.07	2.43
P(14)	0.500	$4.40 \pm 0.12$	3.55
P(15)	0.250	6.85 ± 0.25	5.51
P(16)	0.179	11.4 ± 0.5	9.12
T(16) <sup>a</sup>	0.179	1.70 ± 0.18	

Table 6. Dependence of exchange rate and overall quantum yield on hydrogen ion concentration.  $[U(IV)] = 1.20 \times 10^{-2}; [U(VI)] = 2.76 \times 10^{-2}; I = 2.00 \text{ M}; T = 25.0^{\circ}; \text{lamp I.}$ 

<sup>a</sup> Thermal experiment


 $[U(IV)] = 1.20 \times 10^{-3}; [U(VI)] = 2.76 \times 10^{-3}; [H^{+}] = 1.00; I = 2.00 \underline{M}; T = 25.0^{\circ}; lamp I.$ Figure 21. Logarithm of overall quantum yield vs logarithm of hydrogen ion concentration.





<u>Radiolysis and Temperature Dependencies</u>: The possibility of a radiolytic effect on the exchange rate was evaluated by varying the  $[^{233}U]$  in four thermal experiments over the range, (2.16 to 13.2) ×  $10^{-6}$ . The other invariant experimental conditions were: [U(IV)] =0.0250, [U(VI)] = 0.0274,  $[H^+] = 1:00$ , [Tartaric acid] = 0.130, I = 2.00 <u>M</u>, and the temperature at 25.0°. The data are listed in Table 7. The log-log plot shown in Figure 23 indicates an order of 0.10 ± 0.17. Although a different <sup>233</sup>U-U(VI) stock solution was used in T-4, one is not justified in discarding this experiment. However, it is conceivable that this point is deviant and that the actual radiolytic dependence is somewhat more pronounced than indicated above. The level employed in T-1 was the same as that used in the solutions of the U(IV) variation.

Table 7. Dependence of exchange rate on the  $^{233}$ U concentration. [U(IV)] = 2.50 × 10<sup>-2</sup>; [U(VI)] = 2.74 × 10<sup>-2</sup>; [H<sup>+</sup>] = 1.00; [Tartaric acid] = 0.130; I = 2.00 <u>M</u>; T = 25.0°.

Experiment (thermal)	[ <sup>233</sup> U(VI)] ( <u>M</u> × 10 <sup>6</sup>	$(\underline{M} \text{ sec}^{-1} \times 10^9)$
T-1	4.52	4.08 ± 0.38
T-2	8.83	4.96 ± 0.31
T-3	13.2	$6.82 \pm 0.43$
т-4	2.16	5.60 ± 0.22

The effect of temperature on the exchange rate was evaluated at the temperatures 14.2°, 25.0°, and 32.0° for the following conditions:  $[U(IV)] = 5.87 \times 10^{-3}$ ,  $[U(VI)] = 7.60 \times 10^{-3}$ , I = 2.00 <u>M</u>, and  $[H^+] = 1.00$ . The data are listed in Table 8. A marked increase in the rate was observed when the temperature was increased from 14.2 to 25.0°. The rate for P(25) is lower presumably because of the lower incident



c ?

$$[U(IV)] = 2.50 \times 10^{-4}; [U(VI)] = 2.74 \times 10^{-4}; [tartaric acid] = 0.130;  $[H^{+}] = 1.00; I = 2.00 \underline{M}; T = 25.0^{\circ}; thermal experiments.$$$

	Temperature	R
Experiment	(°C)	$(\underline{M} \text{ sec}^{-1} \times 10^8)$
P(24)	14.2	1.41 ± 0.08
P(23)	25.0	$2.95 \pm 0.08$
P(25)	32.0	2.45 ± 0.20

Table 8. Dependence of exchange rate on temperature.  $[U(IV)] = 5.87 \times 10^{-3}; [U(VI)] = 7.60 \times 10^{-3}; [H^+] = 1.00;$ I = 2.00 M; P(23,24), lamp II; P(25), lamp IIa.

intensity involved (lamp IIa). In view of the apparent complexity of the exchange reaction, as indicated by the fractional order dependencies, the determination of an activation energy was not even attempted.

<u>Tartaric Acid Concentration Dependence (Thermal)</u>: The effect of the concentration of tartaric acid,  $[H_2Tar]$ , on the thermal exchange rate was evaluated over the 30-fold concentration range, 0.00910 to 0.260 <u>M</u>. Ten experiments (plus five duplicates) were performed under conditions identical with those of Benson<sup>29</sup> i.e.,

[U(IV)] = 0.0250	I = 2.00 <u>M</u>
[U(VI)] = 0.0274	$T = 25.0^{\circ}$
$[H^+] = 1.00 \text{ (and } 0.85)$	[H <sub>2</sub> Tar] = varied

in an effort to extend part of his work and therefore better define the limits of his tartaric acid dependence study.

The results are shown in Table 9 and graphed in Figure 24 from which an order of  $1.19 \pm 0.03$  was obtained (for all plotted data) from the slope of the log-log plot. Slight deviation from linearity is discernible for the low limit of the variation. A value of  $1.28 \pm 0.03$  is obtained for the slope based on the data points for the seven highest tartaric acid concentrations.



Figure 24. Logarithm of exchange rate vs logarithm of tartaric acid concentration.

 $[U(IV)] = 2.50 \times 10^{-2}; [U(VI)] = 2.74 \times 10^{-2}; [H^+] = 1.00;$ I = 2.00 <u>M</u>; T = 25.0°; thermal experiments.

	[Tartaric Acid]	R
Experiment	( <u>M</u> × 10)	$(\underline{M} \text{ sec}^{-1} \times 10^{10})$
2	0.0910	2.04
3	0.130	2.81
4	0.390	9.28
5	0.650	18.1
6	0.910	24.8
7 <sup>a</sup>	1.30	54.0
8	1.69	57.0
9	1.95	74.4
10	2.21	84.3
11	2,60	106.0

Table 9. Dependence of exchange rate on tartaric acid concentration.  $[U(IV)] = 0.0250; [U(VI)] = 0.0274; [H^+] = 1.00; I = 2.00 M;$ and T = 25.0°; thermal experiments.

 $a[H^+] = 0.850$ 

## VI. DISCUSSION

#### A. Discussion of Errors and Reproducibility of Results

Photochemical Rate Data: As indicated by the standard deviation in the exchange rates, the data for a given experiment are fairly consistent,  $\sigma(av) = 10\%$ . The uncertainties in the data arise from two main sources of error: (1) change in the [U(IV)] during photolysis, resulting from presumably, photocatalyzed oxidation of U(IV) by oxygen, and (2) gradual change in the output of lamp I (main one) through aging. In general, the net effect of a U(IV) loss would be slightly lower rates than would be found with no loss of U(IV). Slightly higher rates could be observed for the high [U(VI)] conditions, however. In any case, the uncertainty should not exceed  $\sim 5\%$ . Although no definite trends in the data are discernible to indicate a major effect by (oxidative) loss of U(IV), a mechanism involving oxygen-catalyzed exchange is still a possibility.

A second source of error becomes evident on examining the rates of comparable experiments as listed in Table 10.

Table 10. Exchange rates for comparable experiments.

Experiment	[U(IV)] ( <u>M</u> × 10 <sup>2</sup> )	[U(VI)] ( <u>M</u> × 10 <sup>2</sup> )	$\frac{\underline{R}}{(\underline{M} \text{ sec}^{-1} \times 10^8)}$	Order in which performed
P(4)	1.20	2.76	3.87	1
P(12)	1.20	2.76	2.49 64% of	P(4) 3
P(7)	0.598	2.76	2.46	2
P(19)	0.587	2.96	1.79 73% of	P(7) 4

$$[H^{T}] = 1.00; I = 2.00 \underline{M}; T = 25.0^{\circ}; lamp I.$$

The agreement is poor for both sets of experiments, but slightly better for the second set when the differences in U(IV) and U(VI) concentrations are taken into account. The decreasing trend of R with order of performance suggests that (1) the lamp output (I\_) had gradually diminished over this time period through aging and, consequently, that (2) the U(IV) and hydrogen ion dependences might be somewhat more pronounced than was observed since the experiments, P(4 to 21), were performed in consecutive numerical order. However, no gross effects were apparent from the McKay plots, all of which were linear except where noted previously (page 81). This uncertainty does not apply to the experiments of the U(VI) variation, however, since the lamp outputs were periodically monitored by means of chemical actinometry. Good reproducibility is apparent for these experiments for which a log-log graph of  $\phi_{av}$  vs [U(VI)] conforms to a single curve (see Figure 17). The two sets of experiments were performed at different times by using different lamps and, for P(26-28), in random order.

The incident light ( $\lambda$  <3650) was completely absorbed in all solutions and usually within a very thin layer of solution. The question of whether  $R_{local} = R_{overall}$  was considered and specifically with regard to the U(VI) variation. Since the solutions were stirred moderately rapidly and the exchange rates were very slow, any possible differences in the local <u>vs</u> overall rates were judged to be small.<sup>143</sup>

<u>Thermal Exchange Results</u>: The thermal exchange rate observed for T(16),  $[H^+] = 0.179$ , is  $1.70 \times 10^{-8} \text{ M sec}^{-1}$ . This rate agrees satisfactorily with 1.23 and  $1.6 \times 10^{-8} \text{ M sec}^{-1}$  as computed from the rate laws of Masters and Schwartz, equation (34), and Rona, equation (30),

respectively. A rate constant of  $2.5 \times 10^{-5}$  <u>M</u> sec<sup>-1</sup>, as reported by Stranks and Wilkins,<sup>144</sup> for Rona's work was used in computing the latter value.

The observed photochemical rate is approximately 7 times the corresponding thermal exchange rate. Calculations of thermal rates for higher acidities by using either of the thermal rate expressions which have been reported, indicated that the thermal contribution to the gross rate would be essentially small for the other conditions studied. For example, at a  $[H^+] = 1.00$ , the thermal rate would be slower by at least a factor of  $10^2$ . For the condition of highest [U(IV)], P(9), the thermal rate is calculated to be  $\sim 1/20$  that of T(16), assuming a second-order dependence on U(IV). T(16) is the only thermal experiment performed in which tartaric acid was not present.

The agreement between comparable thermal and photochemical (one) exchange rates obtained by Benson and those of the present study is very poor. In all cases, the rates obtained by Benson are higher by at least a factor of 2 and often by a full order of magnitude. (This holds true for the above-mentioned thermal condition). All attempts to duplicate the results of his tartaric study were unsuccessful; furthermore, a different reaction order with respect to tartaric acid was obtained; namely,  $1.19 \pm 0.03 \text{ vs} 0.89 \pm 0.11$  as obtained by Benson. It also should be pointed out that the rates obtained by Benson were consistently higher than those of Rona for comparable conditions. The exact reasons for the discrepancies are not known, but could include one or more of the following in the suspected order of importance: (1) uncertainties in the measurement of the acidities of exchange solutions, <sup>145</sup> (2) <sup>233</sup>U radiolytic effects, (3) contamination of stock solutions by trace catalytic impurities. With respect to a possible radiolytic explanation, Benson reported using a 2% enrichment of  $^{233}$ U. If this figure is correct, it would mean that the tracer level used in his experiments was  $\sim 10^2$  higher than in the comparable experiments reported herein. As noted previously, the exchange rate is accelerated slightly with increasing tracer concentration.

### B. Interpretation of Photochemical Data

The following empirical rate law is established from the experimental results for conditions of constant incident light intensity:

$$R = k' [U(IV)]^{0.41} [U(VI)]^{-1.4} [H^+]^{-0.65}$$
(74)

The fractional exchange orders shown are only approximate and apply to a limited portion of the region investigated, since all of the order graphs exhibited curvature. The presence of fractional orders in this expression indicates that the exchange system is not simple and that probably <u>several</u> exchange paths are operative. It is obvious from the form of the rate law that the exchange is not simply the result of photoacceleration of an existing thermal path.

The relative unimportance of radiolysis products in the exchange process(es) is illustrated as follows. From a knowledge of the tracer level normally employed, the specific activity of  $^{233}$ U (2.103 × 10<sup>4</sup> d/m/µg, Table 1), and the energy of its  $\alpha$ -particles (4.8 Mev), the concentrations of the radiolytically produced species, (OH + H)/ $\ell$  sec can be computed by using a value of G(OH + H) of  $\sim$ 4,  $^{146}$  where G is the conventional radiation yield or molecules produced per 100 eV of absorbed energy. For the U(IV) variation, the rate of production of OH and H

would be  $\sim 1 \times 10^{-12} \text{ M} \text{ sec}^{-1}$  as compared with (2.5 and 10)  $\times 10^{-12} \text{ M} \text{ sec}^{-1}$ for the H<sup>+</sup> and U(VI) variations (for the highest [U(VI)] employed). Implicit in the above calculation is the assumption that the  $\gamma$ -rays associated with the  $\alpha$ -decay of <sup>233</sup>U do not make a significant contribution to the radiolysis of the solution. The rate of photoactivation of uranyl ions (U0<sup>2+\*</sup>) would be  $\sim 8 \times 10^{17}$  ions/ $\ell$  sec and would correspond to  $\sim 1 \times 10^{-6}$  mole of excited state species/ $\ell$  sec , or a factor of  $10^5 - 10^6$ greater than the radiolytic production. On the basis of the above, it is doubtful that the steady-state concentrations of the radiolytic products are high enough to compete effectively with the concurrent photochemical process(es).

The following relationships could be important in the overall exchange process(es).

Excitation and de-excitation of  $UO_2^{2+}$  occur in solution according to the processes:

$$UO_2^{2+} + hv \stackrel{k_1}{\underset{k_2}{\leftarrow}} UO_2^{2+*}$$
 (excitation and fluorescence) (75)

and

$$UO_2^{2+*} + UO_2^{2+} \xrightarrow{k_3} 2UO_2^{2+} (self-quenching)$$
(76)

where  $UO_2^{2+*}$  and  $UO_2^{2+}$  represent the excited and ground states of the uranyl ion, respectively, and  $k_1$ ,  $k_2$ , and  $k_3$  are the appropriate specific rate constants. From Vavilov's self-quenching experiments on uranyl (sulfate) solutions it appears that  $k_3 \simeq 99 k_2$ .<sup>58</sup> Under conditions of constant absorbed intensity,  $I_a$ , (and for the moment assuming no subsequent reaction of  $UO_2^{2+*}$ ) the steady-state (photostationary-state) concentration of  $UO_2^{2+*}$  would be given by

$$[UO_{2}^{2+*}]_{ss} = \frac{I_{a}}{k_{2} + k_{3}[UO_{2}^{2+}]}, \qquad (77)$$

where  $I_a = I_o[1 - 10^{-(\varepsilon[U0_2^{2+}]d)}]$ , and as indicated, would be dependent upon the bulk  $[U0_2^{2+}]$ .  $(I_o, \varepsilon$ , and d have been described previously.) This self-quenching mechanism could qualitatively explain the inhibitory effect of  $U0_2^{2+}$  on the exchange rate, if  $U0_2^{2+*}$  initiates exchange.

Photodecomposition of  $UO_2^{2+*}$  could generate U(V) and an OH radical according to the process

$$UO_2^{2+*} \cdot H_2^{0} \longrightarrow UO_2^{+} + OH + H^{+}$$
(78)

which could involve coordinated or free  $H_2^{0}$ , although the former seems more reasonable. This process or a closely related one involving OH<sup>-</sup>, instead of  $H_2^{0}$ , has been proposed for the photooxidation of  $H_2^{0}$  by bromate (uranyl-sensitized)<sup>152</sup> or could be inferred from the work of Gordon and Taube on the U(V)-catalyzed oxygen exchange between  $U0_2^{2+}$  and  $H_2^{-18}O$ . Iron(III),<sup>147</sup> T1(III),<sup>22</sup> Ce(IV),<sup>148</sup> and Np(VI)<sup>23</sup> are involved in analogous process(es), as mentioned previously. Although reaction (78) is feasible on energetic grounds ( $\sim$ 117 kcal/Einstein for 2537 Å radiation), the back-reaction (reverse of (78), which corresponds to primary and secondary recombination, would have to be very efficient since no net change in  $U0_2^{2+}$  or formation of  $O_2$ , through OH recombination and subsequent decomposition, are observed in irradiations of  $U0_2^{2+}$  solutions alone. Competition for U(V) and/or OH would result, however, when suitable species are present. Neither  $H_2O^{-149}$  nor the  $C10_4^{-}$  ion<sup>150</sup> are photodecomposed by light of  $\lambda > 2000$  Å.

Uranium(V) could also be produced by a photoinitiated process as

$$U(IV) + U(VI)^* \longrightarrow 2U(V)$$
 (79)

where the U(IV) species is probably UOH<sup>3+</sup> rather than U<sup>4+</sup>, in view of the observed inverse dependence on H<sup>+</sup>. The U(VI)<sup>\*</sup> species might be  $UO_2^{2+*}$  (a triplet-excited state) or a species derived directly from it, e.g., as in photohydrolysis

$$UO_2^{2+*} \cdot H_2 O \longrightarrow UO_2 OH^+ + H^+$$
(80)

This hydrolytic species is thought to be involved in the intrinsic  $UO_2^{2+}$ - $H_2O$  exchange, and conceivably could result from the recombination reaction in (78).

In turn, the resultant U(V) would interact by one or more of the following steps which would lead to exchange:

(i) formation of a complex intermediate with  $UO_2^{2+}$ , 75

$$\mathrm{UO}_{2}^{+} + \overset{233}{\simeq} \mathrm{UO}_{2}^{2+} \xrightarrow{\simeq} [\mathrm{U}_{2}\mathrm{O}_{4}^{3+}] \xrightarrow{\simeq} \overset{233}{\simeq} \mathrm{UO}_{2}^{+} + \mathrm{UO}_{2}^{2+}$$
(81)

(ii) disproportionation  $^{39}$  (essentially the reverse of equation (14),

$$2UO_2^+ + 4H^+ \xrightarrow{} UO_2^{2+} + U^{4+} + H_2^0$$
(7)

(iii) exchange with U(IV), as postulated for the U(IV)-U(VI) system in oxalate media.<sup>86</sup>

$$^{233}\mathrm{U}(\mathrm{V}) + \mathrm{U}(\mathrm{IV}) \xleftarrow{} \mathrm{U}(\mathrm{V}) + ^{233}\mathrm{U}(\mathrm{IV}). \tag{38}$$

No evidence exists to support reaction (38) in any actinide system in acid perchlorate media; therefore, it is considered to be of little significance here.

The complex intermediate in equation (81) is formed to a significant extent even in  $1 \leq \text{HClO}_4$ . At progressively higher  $[\text{UO}_2^{2+}]$ , the increased formation of this complex would decrease any free [U(V)], thereby inhibiting the disproportionation reaction (7) and, hence, the observed exchange rate (assuming exchange proceeds through a U(V) intermediate).

An exchange path initiated by, or as a result of, photoactivated U(IV) could provide a partial explanation of the positive U(IV) dependence. Although U(IV) has not been well-established as a photoactive species.<sup>151</sup> the following evidence supports such a hypothesis. The exchange rate increases (but perhaps at a decreasing rate), (see Figures 18 and 19) as the fraction of light absorbed by U(IV) increases. Also, enhanced exchange rates were observed for preliminary experiments using filtered light<sup>153</sup> (>4910 Å, wherein the increase in the rate is clearly related to the absorption (most likely of 5461 Å radiation) by U(IV). since the  $UO_2^{2+}$  doesn't absorb above  $\sim 4800$  Å (see Figure 2). In this context, if  $UO_2^{2+}$  fluorescence yields were at all appreciable under the exchange conditions (an estimate of 28% has been made for uranyl sulfate solutions<sup>62</sup>), a significant fraction of the emitted light,  $\lambda > 4700$  Å, would be reabsorbed by U(IV). Exchange initiated by photoactivated U(IV) could occur, conceivably, as a result of one of the photohydrolysis steps represented in equations (82) and (83)

$$U^{4+} + H_2 O - \frac{hv}{m} UOH^{3+} + H^+$$
 (82)

$$UOH^{3+} + H_2O - \frac{hv}{2} U(OH)_2^{2+} + H^+$$
 (83)

followed by exchange with U(VI) or less likely U(V) as represented by equations (79) or (81), respectively. The increased absorption of 2537 Å light by U(IV) as a function of decreasing acidity, as noted previously for solutions of the H<sup>+</sup> variation is consistent with (83). A negative second or third order dependence on  $[H^+]$  would have to be obtained experimentally in order for exchange to proceed through and be consistent with the path represented by equation (79) and involving  $U(OH)_2^{2+}$  or  $UOH^{3+}$ , respectively and  $UO_2^{2+}$ . Since (1) an inverse first-order dependence approximately on hydrogen ion was observed, and (2) this mechanism does not account for the pronounced inverse dependence on U(VI), neither of the latter possibilities are likely to constitute a major step involving exchange photoinduced by U(IV). Also, if the observed exchange rate R were determined solely by the light absorbed by U(IV),  $I_{a4}$ , which it is not,  $\phi_{ex}$  values near or >1 would be observed (see Table 5, column 4).

As additional alternatives of exchange involving U(IV), exchange could be catalyzed conceivably by photochemical oxidation of U(IV) by oxygen or by trace concentrations of radiolytic products, since the thermal oxidation of U(IV) apparently proceeds by a chain mechanism involving U(V) and HO<sub>2</sub> as chain carriers.<sup>68</sup> The photoinduced exchange could involve reaction (78) or (79) as the initial step, followed by exchange through (81) and the propagation steps

$$UO_2^+ + O_2^- + H_2^0 \longrightarrow UO_2^{2+} + HO_2^- + OH^-$$
(17)

and

$$HO_2 + UOH^{3+} + H_2O \longrightarrow UO_2^+ + H_2O_2 + 2H^+$$
 (18)

etc. as in the thermal route (page 21). Since slight U(IV) loss occurred in many experiments, this or an equivalent oxygen-catalyzed path undoubtedly contributes to the overall observed exchange.

Exchange proceeding primarily through reaction (79), as a ratedetermining step, is a definite possibility since (1) U(IV) would be expected to exhibit a positive and perhaps non-linear exchange order, since at the higher [U(IV)], U(IV) could act as an inner-filter (for 4358 and 2537 Å light), and (2) the inverse dependence on U(VI) can be accounted for (under constant  $I_a$ ) in terms of the self-quenching and U(V)-U(VI) complexation effects as noted above. Evidence for a positive (and perhaps linear) dependence of R upon  $I_a$  is provided by the results of the two independent sets of experiments of the U(VI) variation (coincidence of the  $\phi_{ex}$  curves at the higher [U(VI)]). The major shortcoming of this mechanism is in accounting for the observed H<sup>+</sup> dependence. If reaction (79) is of the form

$$\operatorname{UOH}^{3+} + \operatorname{UO}_{2}\operatorname{OH}^{+} \xrightarrow{} 2\operatorname{UO}_{2}^{+} + 2\operatorname{H}^{+}$$
(84)

or

$$UOH^{3+} + UO_2^{2+*} + H_2O \longrightarrow 2UO_2^+ + 3H^+$$
 (85)

and is assumed to proceed through the same activated complex as the thermal exchange,<sup>66</sup> i.e.,  $(HO \cdot U \cdot O \cdot UO_2^{3+})^+$ , then the predicted dependences would be at least third and fourth-order, respectively. However, if the reaction proceeded through a different activated complex, involving a lower H<sup>+</sup> dependence, better qualitative agreement with the observed dependence would be realized.

An exchange mechanism based on the photoinitiation step (78) appears to offer the best general qualitative explanation of the experimental results. A summary of the processes that could be involved is as follows:

(1) 
$$UO_2^{2+} \cdot H_2^{0} \xrightarrow{hv} UO_2^{2+*} \cdot H_2^{0}$$
 (excitation-fluorescence) (75)

(11) 
$$UO_2^{2+*} + UO_2^{2+} \longrightarrow 2UO_2^{2+}$$
 (self-quenching) (76)

(iii) 
$$UO_2^{2+*} \cdot H_2^{0} \longrightarrow UO_2^{+} + 0H + H^{+}$$
 (photoinitiation,  $\phi_1$ ) (78)

(iv) 
$$UO_2^+ + {}^{233}UO_2^{2+} \xrightarrow{} [U_2O_4^{3+}] \xrightarrow{} {}^{233}UO_2^+ + UO_2^{2+}$$
 (81)

$$(v) \xrightarrow{233} UO_2^+ + U(IV) \xrightarrow{233} U(IV) + UO_2^+$$
(86)

(vi) 
$$UOH^{3+} + OH \longrightarrow UO_2^+ + 2H^+$$
 (87)

(vii) 
$$UO_2^+ + OH + H^+ \longrightarrow UO_2^{2+} + H_2^0$$
 (88)

(viii) 
$$2UO_2^+ + H^+ \longrightarrow \text{products}$$
 (rate-determining) (7)

Steps (i to iii) may occur as shown or absorption of 2537 Å radiation may cause (iii) to occur directly, thereby eliminating the necessity of the two preliminary steps (and therefore the self-quenching feature) as kinetic steps. The inhibition of the U(VI) variation would then depend only on step (iv), the formation of the U(V)-U(VI) complex. Step (v) occurs slowly, if at all; it is only included to point out that  $\phi_{ex} > 1$  would not be expected, even though a chain-mechanism is proposed (since  $UO_2^+$  would not exchange with  $UO_2^{2+}$  and U(IV) faster than its own rate of destruction, i.e., through the rate-determining step (viii)). The magnitude of the  $\phi_{ex}$  might then be an indication of the importance of this path. Steps (vi and vii) would be necessary so that no net change in U(IV) or U(VI) would be observed with time.

The mechanism accounts for a first or second-order  $H^+$  dependence, a positive U(IV) dependence (but perhaps not as pronounced as observed) since U(IV) would be expected to compete more effectively with the secondary recombination processes(es) (step vii) for the OH radical at higher [U(IV)]. The low quantum yields observed are (1) understandable in terms of the back-reaction (88), plus the competitive processes of fluorescence emission and self-quenching, and (2) in good agreement with the previously reported value of 0.01.<sup>66</sup> The fact that Np(VI) is photoreduced in an analogous photoinitiation step and that the observed overall  $\phi_{ex}$  is about the same order of magnitude (= 0.032) lends additional plausibility to the proposed mechanism.

## VII. SUMMARY

The kinetics of the uranium(IV)-uranium(VI) electron exchange reaction were investigated in aqueous perchoric acid solutions under conditions of constant incident light intensity. A low-pressure mercuryvapor lamp, Model LO 735A-7 (Hanovia), was used as the light source which emitted principally 2537 Å radiation. The exchange was inhibited by uranium(VI) and hydrogen ion, but accelerated by uranium(IV) and by increasing the temperature. Non-linear order graphs were obtained for uranium(IV), uranium(VI), and hydrogen ion, having the approximate orders of 0.41, -1.4, and -0.65, respectively. Overall quantum yields for exchange ranged from 0.01 to 0.1, based on the absorption of light by uranium(VI), and were determined by means of potassium ferrioxalate actinometry.

Plausible exchange mechanisms are discussed in terms of a uranium(V) intermediate as produced by one or more of the following steps:

(1)  $U(IV) + O_2 \longrightarrow U(V) + HO_2$ (2)  $U(IV) + U(VI) \xrightarrow{} 2U(V)$ (3)  $UO_2^{2+} \cdot H_2) \xrightarrow{hv} UO_2^+ + OH + H^+$ 

A mechanism based on step (3) as the principal exchange path is in reasonable qualitative agreement with the experimental results.

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APPENDICES

APPENDIX A

RELATIVE CALIBRATION OF A LOW-PRESSURE MERCURY-VAPOR LAMP (MODEL LO 735A-7, HANOVIA)

#### APPENDIX A

# RELATIVE CALIBRATION OF A LOW-PRESSURE MERCURY-VAPOR LAMP (MODEL LO 735A-7, HANOVIA)

A low-pressure mercury-vapor lamp, identical to the type used in the photolysis experiments, was calibrated by comparison with a tungsten ribbon-filament lamp having a quartz window. The tungsten lamp, a secondary standard of spectral radiance ( $\mu$ W/ster-nm-mm<sup>2</sup>), was supplied by the National Bureau of Standards as lamp No. U-202 and had been calibrated against a blackbody.

Figure Al shows the geometrical arrangement of the lamps, spherical mirror, and Cary Model 14 spectrophotometer used in the calibration. The spherical mirror was mounted on a pivot which allowed the lamps to be switched alternately into the optical path without changing the position of either lamp. The lamps were operated in strict accordance with their specifications which are as follows: the NBS lamp at 35A at 6Vac, and the mercury-vapor lamp at 1.0A at 36 Vdc. For the mercury-vapor lamp all other operating conditions were the same as described in the Experimental section of the thesis. The 115 Vac primary power supplies for the lamps were regulated by means of Sola transformers.

The emission spectrum of the tungsten lamp was recorded by means of the Cary 14 spectrophotometer. Figure A2 shows a composite graph of this spectrum, W, and the absolute output (spectral radiance), A, of the standard tungsten lamp. The scale of the ordinate is in terms of relative energy for curve W, but in spectral radiance for curve A. In recording this spectrum, the slit width was changed at 3100 Å from



Figure Al. Arrangement of lamps, spherical mirror, and spectrophotometer for lamp calibration.





For NBS tungsten lamp: A is the absolute output (spectral radiance), W the response on Cary spectrophotometer (relative energy).

0.030 to 0.300 mm in order to obtain the entire region shown. A factor of 100 was taken into account in computing the relative energies for the lower wavelength region since the energy passing through the slits is proportional to the square of the slit width. As for the plots of the two sets of data, some uncertainty (perhaps 5%) arises from the fact that the lower region was not a perfect continuation of the upper wavelength region. Presumably, this uncertainty is associated with the reproducibility and accuracy of the slit settings.

Spectral response correction factors, characteristic of the composite effect of the grating, prism, and phototube were obtained from the ratios,  $A_i/W_i$ , of the two curves at each wavelength  $\lambda$  of the mercury-vapor spectrum. The spectral data and calculated ratios are listed in Table Al. Curve R in Figure A2 is the spectral response correction curve for the entire region investigated (2500-6000 Å).

Table A1. The spectral radiance and Cary response for the standard tungsten lamp (U-202) and the spectral response factors for a Cary 14 spectrophotometer.

	Tungsten	Spectral response	
Wavelength	Spectral radiance	Cary response	Correction factors
λ, Å	$\mu W/ster-nm-mm^2$	(relative energy)	A <sub>i</sub> /W <sub>i</sub>
2537	$1.50 \times 10^{-2}$	$1.80 \times 10^{-2}$	0.833
3126-32	$3.75 \times 10^{-1}$	1.09	0.343
3650	2.15	8.90	0.242
4047	5.51	$2.50 \times 10^{1}$	0.221
4358	9.80	$4.54 \times 10^{1}$	0.216
5461	$4.12 \times 10^{1}$	$8.63 \times 10^{1}$	0.477
5770-90	5.21 × $10^{1}$	$7.53 \times 10^{1}$	0.692

With respect to the mercury-vapor lamp, the maximum signal response, T, of each of the emission lines was recorded essentially manually and the values, as relative energies, are listed in Table A2. A complete and undistorted spectrum could not be recorded even at the slowest instrument scanning speed (1/2 Å/sec) because of the inability of the pen to keep up with the signal for the most intense lines. Ideally, a mercury-vapor lamp should be calibrated against a standard lamp of the same type (i.e., low-pressure lamp with low-pressure lamp, etc.). In such cases, a relative calibration is obtained directly as the normalized ratios of the corresponding outputs, since the spectral band widths are essentially the same. In general, "in experiments where [similar] sources of radiation are being compared, no knowledge of the spectral reflectance of the auxiliary mirrors, the spectrometer transmission characteristics, or the spectral sensitivity of the detector is required. Furthermore, when the same auxiliary optics are employed no measure need be taken of the spectrometer slit widths, or slit areas, provided the slit is fully and uniformly filled in both cases." The foregoing is strictly valid only when the same type of spectra are being compared (continuum vs continuum, etc.), since the energy passed through the slits is proportional to the square of the slit width in the case of a continuum, but only proportional to the slit width for a line spectrum.

For the geometry employed, the entrance slit was fully and uniformly filled for both lamps.

The calibration of a mercury-vapor lamp (line spectrum) against a tungsten-lamp (continuum) is not as straightforward a procedure since the spectral interval being investigated differs significantly (1) from one band to another (for the mercury-vapor spectrum) and (2) for the two
types of spectra being considered. Hence, the resolution of the measuring instrument must be taken into account.

For a Cary Model 14 spectrophotometer the spectral band width (resolution) is given by:

Spectral band width (SBW),  $Å = D \cdot S + C + L$ where

> D is the reciprocal dispersion in Å/mm S is the slit width in mm C is the slit curvature mismatch in Å L is the Rayleigh diffraction limit in Å

Graphs of these quantities <u>vs</u> wavelength (all are a function of wavelength) may be found in two Applied Physics Corporation publications. In short, each of the three right-hand terms compensates for the reduction in intensity because the incident energy is distributed over a wider wavelength span. The observed response (T) for each band was corrected in accordance with the following relationship which takes into account the instrument resolution and spectral response factors:

$$T\left(\frac{A_{i}}{W_{i}}\right)SBW = \alpha I$$

where

- I is the integrated intensity (in arbitrary energy units) of a given band having the center wavelength  $\lambda$ .
- a proportionality constant for the Cary response and the
   absolute output graphs in Figure A2.

The quantities T, SBW, A, and H have been described previously. The

relative band intensities (energy) were converted into relative band intensities (quanta) by applying the factor,  $\lambda$ , Å/2537 Å; both sets of data were then normalized with respect to the 2537 Å line. The Cary resolution data and relative spectral intensity data for the mercuryvapor lamp are given in Table A2.

The reliability of the calculated spectral band width (SBW) data was checked for the 2537 Å band for three different slit widths (1.0, 2.0, and 3.0 mm). For each slit width used, the experimentally determined SBW was 5-6% higher than the calculated value (i.e., using the Applied Physics data). It was assumed that the deviation for the other slit settings would be in the same direction and about the same order of magnitude, since a plot of the square root of the instrument response at 5150 Å (plateau region) by using the tungsten lamp <u>vs</u> slit setting was linear over the region 0.030 to 0.005 mm.

	Reciprocal	Slit Curvature	Diffraction Limit	Spectral Band width	Mer	cury-va	por lamp	
Wavelength	Dispersion	Mismatch	(Rayleigh)	(Resolution)	Response	Relat	ive inte	nsities
λ, Å	D, Å/mm	s, Å	L, Å	SBW, Å	н	αΤ	Energy	Quanta
2537	19.4	0.478	0.061	0.636	156.3	82.8	100.0	100.0
3132	26.8	0.370	0.082	0.586	7.00	1.40	1.69	2.09
3650	30.8	0.215	0.100	0.469	12.5	1.42	1.71	2.11
4047	32.8	0.118	0.116	0.398	10.0	0.88	1.06	1.69
4358	33.8	0.033	0.124	0.326	19.8	1.39	1.68	2.89
5461	35.8	0.191	0.166	0.536	8.55	1.85	2.33	4.79

Cary Model 14 resolution parameters and relative intensity data for a mercury-vapor lamp, Model LO 735A-7 (Hanovia). Table A2.

APPENDIX B

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LIGHT ABSORPTION DATA FOR URANIUM(IV)-URANIUM(VI) SOLUTIONS

#### APPENDIX B

LIGHT ABSORPTION DATA FOR URANIUM(IV)-URANIUM(VI) SOLUTIONS

Table B1. Molar absorptivities of uranium(IV) and uranium(VI) for the wavelengths of the mercury-vapor emission spectrum. Sodium perchlorate-perchloric acid media,  $T \sim 25^{\circ}$ ,

Columns (1) and (2):	$[H^+] = 0.974, I = 1.00 M_{\odot}$
Column (3):	$[H^+] = 1.00, I = 3.00 M.$

	Molar a	bsorptivity, ε(M <sup>-1</sup> cm <sup>-1</sup>	1 <u>)</u>
Wavelength	Uranium(IV)	Uraniu	<u>n(VI)</u>
Å	(1) <sup>a</sup>	(2) <sup>a,f</sup>	(3) <sup>b,f</sup>
2537	7.2 (5.07) <sup>C</sup>	423 (435) <sup>d</sup>	
3130	<0.08 <sup>C</sup>	47.8	
3656 ·	<0.08	2.0	2.23
4047	0.7	6.67	6.80
4078	∿0.7	6.11	6.37
4358	11.6	2.89	3.17
5461	17.7		ration
5770-90	0.8 <sup>e</sup>	0 >~480	

<sup>a</sup>Interpolated from spectra, Figure 2.

<sup>b</sup>Unpublished data.

<sup>C</sup>From intercept of Beer's law plot for the conditions of the U(VI) concentration variation.

<sup>d</sup>From slope of Beer's law plot for the conditions of the U(VI) concentration variation.

<sup>e</sup>Doubtful if Beer's law is obeyed at these wavelengths.

<sup>f</sup>Averages of values in columns (2) and (3) were used in calculating the fractions of incident light absorbed by the exchange solutions.

Waveleng	ch. J. Å			2537			3130			3656			4047			4358			5461	
Incident	Intensity,	I <sub>o</sub> (X 10 <sup>-15</sup> )		3.67			0.077			0.078			0.062			0.106			0.176	
Ŷ	lar Absorpt	ivity, c	2	5.07)			(<0.08)			(\$0.08)			(1.0.)			(11.6)			(17.7)	
Variant	Exchange Solution	[Variant] $(\underline{M} \times 10^2)$	~	ZV	9 (4	* *	ZV	80 1-1	۳,	ZV	8 1	٩	2V	88  24	٩	72	L	~	۸z	
U(IV)	P(4)	1.196	0.061	0.50	1.00	0.001	0.075	0.952	0.001	1.67	0.129	0.0084	4.30	0.362	0.139	62.3	0.402	0.212	1002	0.386
	P(5)	2.392	0.121	1.00	1.00	0.002	0.15	0.952	0.002	3.28	0.129	0.017	8.33	0.376	0.277	76.8	0.564	0.423		0.622
	P(6)	5.980	0.303	2.45	1.00	0.005	0.38	0.952	0.005	7.81	0.137	0.042	18.3	0.411	0.694	89.2	0.833	1.06		0.913
	P(7)	0.598	0.0303	0.25	1.00	0.001	0.075	0.952	0.000	6	0.127	0.0042	1.83	0.357	0.069	45.1	0.297	.106		0.217
	P(9)	8.372	0.424	3.41	1.00	0.007	0.53	0.953	0.007	10.6	0.141	0.059	24.0	0.432	0.971	92.0	0.901	1.48		0.967
[(IA)]	- 2.764	× 10 <sup>-2</sup>	12.02			1.321			0.059			0.187			0.084			ş		
£	lar Absorpt	lvity, ε		(435)			(47.8)			(2.12)			(6.75)			(3.04)			9	
U(VI)	P(17)	0.7395	3.22	1.66	0.999	0.353	6.99	0.557	0.016	97.0	0.37	0.050	92.4	0.117	0.022	24.4	0.187	0	0	660.0
	P(18)	1.479	6.43	39.5	1.000	0.707		0.804	0.031	98.4	0.070	0.100	96.1	0.215	0.045	39.8	0.229			660.0
	P(19)	2.958	12.9	8.66	1.000	1.41		0.962	0.063	99.2	0.136	0.200	98.0	0.376	060.0	57.0	0.305			660.0
	P(20)	5.916	25.7	6.99	1.000	2.83		666.0	0.125		0.251	0.399	0.66	0.609	0.180	72.6	0.435			660°C
	P(21)	8.874	38.6	100.0	1.000	4.25		1.000	0.188		0.352	0.599	6.9	0.753	0.270	79.9	0.541			660.0
	P(26)	7.438	32.4	6.99	1.000	3.56		1.000	0.158		0.306	0.502	99.2	169.0	0.226	76.9	0.492			660.0
	P(27)	9.657	42.0	100.0	1.000	4.62		1.000	0.205		0.377	0.652	99.4	0.780	0.294	81.2	0.565			660.0
	P(28)	11.14	45.5	100.0	1.00	5.33 ]	0.00	1.00	0.236	99.8	0.420	0.752	5.99	0.825	0.334	83.3	0.608			660.0
[(AI)n+	<b>-</b> 5.87	× 10 <sup>-3</sup>	0.030			~0.0005		-	-0.0005			0.0041			0.068					

Table B2. Fractions of light absorbed by exchange solutions and uranium ions.

A<sub>5</sub> - Absorbance of variant ion
 F<sub>a</sub> = Fraction of light intensity, I<sub>o</sub> of A absorbed by solution
 X = X of absorbed light absorbed by variant ion

(Assumed depth of solution = 1.00 cm)

131

	Ξ	(2)	(3)	(7)	(2)	(9)	(2)	(8)	(6)	(10)
	a na ha n Na ha na ha	[Variant]	P	∑IalO // 200-1 / 10-15/	AD / A 7 T	[Iav // con-l / 10-15/	* E 1 (1)	χ, Σι <sub>av</sub>	∑Ia4 (~ 200-1 ~ 10-15)	[134] [134]
Variant	Solution	$(\underline{M} \times 10^2)$	هم ۲۰۱۳) ( <u>M</u> × ۱۰ <sup>8</sup> )	all à	an/421410	all à	*2,3,4	01 (4)	$\lambda_{1,5,6}$	(1 sec × 10 ) λ5,6
U(IV)	P(4)	1.196	3.87 ± 0.20	3.89	28.2	0.114	0.88	16.1	0.113	0.095
	P(5)	2.392	4.76 ± 0.46	3.94	23.0	0.194	1.10	18.9	0.192	0.155
	P(6)	5.980	4.37 ± 1.32	4.03	10.1	0.335	1.49	26.8	0.330	0.240
	P(7)	0.598	2.46 ± 0.15	3.84	reference	0.062	0.74	14.8	0.062	0.052
	P(9)	8.372	7.80 ± 0.98	4.05	25.4	0.390	1.78	32.1	0.383	0.258
			(5.30 ± 1.02)		(13.5)					
U(VI)	P(17)	0.7395	1.95 ± 0.14			2.32	1.39	1.96		
	P(18)	1.479	2.05 ± 0.14			2.36	2.10	98.3		
	P(19)	2.958	1.79 ± 0.03			2.38	2.82	97.5		
	P(20)	5.916	1.61 ± 0.37			2.41	3.48	96.3		
	P(21)	8.874	1.09 ± 0.10			2.42	3.92	95.3		
	P(26)	7.438	1.94 ± 0.18			3.85	3.74	94.8		
	P(27)	9.657	$1.45 \pm 0.11$			3.87	3.98	94.8		
	P(28)	11.14	1.10 ± 0.12			3.88	4.14	94.6		

Summary of data used in correlating exchange rates with calculated absorbed intensities. Table B3.

132

 $^{\lambda}_{1,2,3,4,5} = 2537, 3130, 3650, 4047-78, 4358, 2461A, respectively; deptn or solution; u = 1.00 cm, r = 40$  $Total light intensity absorbed by: U(IV), <math>\sum_{a_4}$ ; U(VI),  $\sum_{a_6}$ ; U(IV) + U(VI),  $\sum_{a_{10}}$ ; variant U ion,  $\sum_{a_{10}}$ .

APPENDIX C

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COMPUTER PROGRAM AND SAMPLE OF INPUT-OUTPUT DATA

## APPENDIX C

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COMPUTER PROGRAM AND SAMPLE OF INPUT-OUTPUT DATA
 COOP, 11499, HOESCHELE, 'G
 FTN,L,E,G.
      PROGRAM RATES
      DIMENSION X(100), Y(100), D(100), CPM(100),
     1ABS(100), EN(100), COMP(200), Z2(100)
      READ 11, NRUN
С
      NRUN=NO. OF RUNS FOR WHICH DATA HAS BEEN SUBMITTED
   11 FORMAT (12)
    1 \text{ READ 5, (COMP(I), I=1,12)}
С
      COMP(I)=IDENTIFICATION OF THE DATA FOR A GIVEN EXCHANGE RUN
    5 FORMAT(18A4)
      READ 100, A4, A6, BKG
C
      A4 AND A6 ARE THE CONCENTRATIONS OF U(IV) AND U(VI), RESPECTIVELY
      BKG=BACKGROUND ACTIVITY IN COUNTS/MINUTE
С
  100 FORMAT(3F10.0)
      READ 100, CO, ABO, ENO
С
      CO, ABO, ENO=COUNTS/MINUTES, ABSORBANCE, AND NORMALIZATION
С
      FACTOR FOR THE ZERO-TIME SAMPLE, RESP.
      READ 100, CINF, ABINF, ENINF
С
      CINF, ABINF, ENINF=COUNTS/MINUTE, ABSORBANCE, AND NORMALIZATION
С
      FACTOR FOR THE INFINITE-TIME SAMPLE, RESP.
      READ 101, J, (CPM(I), ABS(I), EN(I), X(I), I=1, J)
С
      CPM(I), ABS(I), EN(I), X(I), = COUNTS/MINUTE, ABSORBANCE
С
      NORMALIZATION FACTOR, AND CORRESPONDING TIME (MINUTES) OF A
С
      GIVEN SAMPLE(I)
  101 FORMAT (13/(4F10.0))
      BKG=BKG/60.0
      PRINT 200
      PRINT 5, (COMP(I), I=1,12)
      PRINT 102, A4, A6, BKG
      PRINT 102, CO, ABO, ENO
      PRINT 102, CINF, ABINF, ENINF
  102 FORMAT (3F13.6)
      PRINT 103, J, (CPM(I), ABS(I), EN(I), X(I) = I = 1, J)
  103 FORMAT (13/(4F13,6))
С
      CALCULATION OF SPECIFIC ACTIVITIES, SO+HINF
      CO = CO / 60.0
      CINF=CINF/60.0
      SO=((CO-BKG)*ENO)/ABO
      HINF=((CINF-BKG)*ENINF)/ABINF
С
      CALCULATION OF LN(1-F) VALUES
      DO 78 I=1, J
С
      CONVERSION OF MINUTES TO SECONDS
      X(I) = X(I) * 60.0
      CPM(I) = CPM(I)/60.0
      Z=((CPM(I)-BKG)*EN(I))/ABS(I)
```

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133
```

1

```
Z=1.0-(Z-SO)/(HINF-SO)
      Z2X(I)=Z
С
      Z2X(I) = 1 - F FOR SAMPLE(I)
      Y(I) = LOGF(Z)
С
      LOGF(Z) CORRESPONDS TO THE LN(1-F) FOR SAMPLE(I) - --LN(1-F)
С
      VALUES ARE THE Y TERMS IN THE LEAST SQUARES ROUTINE
   78 CONTINUE
      K=J
С
      BEGIN LEAST SQUARES ROUTINE
    2 SUMXY=0.0
      SUMX=0.0
      SUMY=0.0
      SUMX2=0.0
      DO 70 I=1, J
      SUMXY=SUMXY+Y(I)*X(I)
      SUMX=SUMX+X(I)
      SUMY=SUMY+Y(I)
   70 SUMX2 = X(I) * 2 + SUMX2
      Z=K
      SLOPE=(Z*SUMXY-SUMX*SUMY)/(Z*SUMX2-SUMX**2)
      B=(SUMY*SUMX2-SUMXY*SUMX)/(Z*SUMX2-SUMX**2)
      DO 120 I=1, J
      CALCULATION OF STANDARD DEVIATIONS.
С
  120 D(I) = SLOPE * X(I) + B - Y(I)
      DO 123 I=1, J
      IF(X(I)) 122, 122, 123
  122 D(I)=0.0
  123 CONTINUE
      SUMD2=0.0
      DO 130 I=1, J
  130 SUMD2=SUMD2+D(I)**2
      STDEV=SQRTF(SUMD2/(Z-2.))
      CONST=2.0
      OPTDEV=CONST*STDEV
      IF(J-K) 23, 23, 400
   23 DO 140, I=1, J
      IF(ABSF(D(I))-OPTDEV) 140, 25, 25
   25 Y(I)=0.0
      X(I) = 0, 0
      K=K-1
  140 CONTINUE
      IF (J-K) 400, 400, 2
  400 SDEVS=STDEV/(SORTF(SUMX2-(SUMX**2)/Z))
      SDEVI=STDEV*SQRTF(SUMX2/(Z*SUMX2-SUMX**2))
С
      CALCULATION OFHALF-TIME, THALF
      THALF= -(LOGF(2,0))/SLOPE
      OMF = EXPF(B)
      PRINT 200
  200 FORMAT (1H1, ///)
      PRINT 205
  205 FORMAT(10X, 31HMCKAY DATA FOR J.D. HOESCHELE/)
      PRINT 210, (COMP(I), I=1, 12)
```

```
210 FORMAT(10X,12A4///)
С
      CALCULATION OF THE RATE OF EXCHANGE, RXG
      AX = (A4 * A6) / (A4 + A6)
      PRINT 220, SLOPE
  220 FORMAT(10X, 8HSLOPE = E12.4/)
      PRINT 230, B
  230 FORMAT(10X, 12HINTERCEPT = E12.4/)
      PRINT 231, OMF
  231 FORMAT(10X, 14HAT T=0, 1-F = E12.4/)
      RXG=-SLOPE*AX
      PRINT 240, RXG
  240 FORMAT(10X, 27HRATE OF EXCHANGE, M/SEC. = E12.4/)
      PRINT 250, THALF
  250 FORMAT(10X, 18HHALF TIME, SEC. = E12.4/)
      PRINT 260, STDEV
  260 FORMAT(10X, 24HSTD. DEV. FOR SINGLE Y = E12.4/)
      PRINT 270, SDEVS
      SDRXG=AX*ADEVS
      PRINT 271, SDRXG
  271 FORMAT(10X, 19HVARIATION IN RXG= E12.4/)
  270 FORMAT(10X, 21HVARIATION IN SLOPE= E12.4/)
      PRINT 280, SDEVI
  280 FORMAT(10X, 25HSTD. DEV. FOR INTERCEPT= E12.4///)
      PRINT 289
  289 FORMAT(10X, 47H
                        TIME, SECONDS
                                           LN(1-F) 1-F /)
      DO 300 I=1, J
      PRINT 290, X(I), Y(I), Z2X(I)
  290 FORMAT(10X, 3E16.4)
  300 CONTINUE
      NRUN=NRUN-1
      IF(NRUN) 500, 500, 1
  500 CONTINUE
     END
EXECUTE.
```

#### INPUT DATA

P(5)-U(IV)	VARIATION	(H+)=1.00,	I=2.00 M,	T=25.0
0.023920	0.02	27640	0.466667	
402.500000	0.47	2000	1.021000	
4205.600000	0.38	39000	1.000000	
7				
403,500000	0.42	28000	1.010400	46.00000
414.200000	0.44	8000	1.005100	80,00000
576.700000	0.45	0000	1.017300	180,000000
511.500000	0.46	64000	1.000600	250.000000
644.200000	0.46	8000	0.999500	285.000000
657.400000	0.42	28000	1.003500	325,000000
835.600000	0.50	0000	0.997800	400.300000

### OUTPUT DATA

P(5)-U(IV) VARIATION (H+)=1.00, I=2.00 M, T=25.0

SLOPE = -3.5954-006 INTERCEPT = 7.2309-003 AT T=0, 1-F = 1.0073+000 RATE OF EXCHANGE, M/SEC. = 4.6104-008 HALF TIME, SEC. = 1.9279+005 STD. DEV. FOR SINGLE Y= 1.2698-002 STD. DEV. FOR SLOPE= 6.6914-007 STD. DEV. FOR RXG= 8.5804-009 STD. DEV. FOR INTERCEPT= 1.0185-002

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TIME, SECONDS	LN(1-F)	1-F
2.7600+003	-7.7208-003	9.9231-001
4.8000+003	-5.6919-003	9.9432-001
1.0800+004	-4.4307-002	9.5666-001
1.5000+004	-2.3700-002	9.7658-001
1.7100+004	-5.2296-002	9.4905-001
1.9500+004	-6.9388-002	9.3296-001
2.4018+004	-8,4172-002	9.1927-001

APPENDIX D

ORIGINAL KINETIC DATA

# APPENDIX D

# ORIGINAL KINETIC DATA

Table D1. Dependence of exchange rate on concentration of uranium(IV).  $[U(VI)] = 2.76 \times 10^{-2}; [H^+] = 1.00; I = 2.00 \text{ M}; T = 25.0^\circ;$ lamp I.

	Experiment	1-F	t(min)
-2	P(4)		
$[U(IV)] = 1.20 \times 10^{-2}$	1	0.998	30.0
$R = 3.87 \pm 0.20 \times 10^{-8} M$ sec	-1	0.976	66.0
<b>Intercept = 0.998</b> ± 0.004		0.972	100.0
		0.945	180.0
		0.885	410.0
		0.858	565.0
2	P(5)		
$[U(IV)] = 2.39 \times 10^{-2}$	_	0.992	46.0
$R = 4.76 \pm 0.46 \times 10^{-8} M$ sec	-1	0.994	80.0
<b>Intercept = <math>1.005 \pm 0.005</math></b>		0.957	180.0
		0.949	285.0
		0.933	325.0
		0.919	400.3
	P(6)		
$[U(VI)] = 4.37 \pm 1.32$	_	0,998	60.0
$R = 4.37 \pm 1.32 \times 10^{-8} M$ sec	-1	0.961	130.0
Intercept = 0.992 ± 0.011		0.953	222.0
		0.957	300.0
		0.933	460.0

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	Experiment	1-F	t(min)
	P(7)		
$[U(IV)] = 5.98 \times 10^{-3}$	•	0.980	75.1
$R = 2.46 \pm 0.15 \times 10^{-8} M$ sec	-1	0.939	150.0
<b>Intercept = 0.997</b> ± 0.007		0.943	185.0
		0.935	250.0
		0.897	350.0
		0.858	525.0
		0.855	530.0
		0.812	650.0
	P(8)		
$[U(IV)] = 5.98 \times 10^{-3}$	1	1.031	90.0
$R = 1.85 \pm 0.57 \times 10^{-6} M$ sec	-1	1.035	180.0
Intercept = 1.083 ± 0.03		1.027	225.0
		1.068	375.0
		0.943	525.0
	_	0.891	794.0
	P(9)		
$[U(IV)] = 8.37 \times 10^{-2}$	1	0.998	125.0
$R = 7.80 \pm 0.98 \times 10^{-6} M$ sec	-1 (4 pts)	0.956	300.0
Intercept = 1.028 ± 0.016		0.951	400.0
		0.894	600.0
		(0.898)	(750.0)
		(0.908)	(800.0)

	Experiment	1-F	t(min)
-3	P(17)		
$[U(VI)] = 7.40 \times 10^{-5}$	_1	0.947	110.0
$R = 1.95 \pm 0.14 \times 10^{-6} M$ sec	-1	0.935	175.0
Intercept = 0.985 ± 0.010		0.892	272.0
		0.866	320.0
		0.869	350.3
		0.852	400.0
		0.816	585.1
		0.781	614.8
	P(18)		
$[U(VI)] = 1.47 \times 10^{-1}$	-1	0.988	50.3
$R = 2.05 \pm 0.14 \times 10^{\circ} M$ sec	-	0.961	115.3
Intercept = $0.999 \pm 0.008$		0.952	150.0
		0.940	200.2
		0.909	335.0
		0.889	475.0
		0.812	625.0
		0.799	780.0
	P(19)		
$[U(VI)] = 2.96 \times 10^{-8}$	-1	0.994	25.0
$R = 1.76 \pm 0.03 \times 10^{\circ} M$ sec	-	0.992	50.0
Intercept = $1.002 \pm 0.001$		0.986	75.2
		0.976	110.0
		0.968	160.0
		0.948	265.0
		0.901	495.1
		0.888	541.1
		0.886	550.3

Table D2. Dependence of exchange rate on uranium(VI) concentration.  $[U(IV)] = 5.87 \times 10^{-3}; [H^+] = 1.00; I = 2.00 M;$ T = 25.0°; P(17-21), lamp I; P(26-28), lamp II.

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	Experiment	1-F	t(min)
	P(20)		
$[U(VI)] = 5.92 \times 10^{-1}$	1	0.992	25.2
$R = 1.61 \pm 0.37 \times 10^{-6} M$ sec	-	0.984	60.2
<b>Intercept = <math>0.992 \pm 0.012</math></b>		0.975	100.1
		0.942	225.0
N Contraction of the second se		0.960	275.0
		0.932	359.2
		0.891	400.0
		0.927	500.0
	P(21)		
$[U(VI)] = 8.87 \times 10^{-1}$	.1	0.998	20.0
$R = 1.09 \pm 0.10 \times 10^{-6} M$ sec	-	0.994	50.1
<b>Intercept = 0.9962</b> ± 0.004		0.983	75.0
		0.978	151.3
		0.970	200.1
		0.969	300.0
		0.935	410.0
		0.932	510.0
		0.940	550.5
		0.921	701,2
<b></b> 2	P(26)		
$[U(VI)] = 7.44 \times 10^{-1}$	.1	0.998	20.2
$R = 1.94 \pm 0.18 \times 10^{-6} M$ sec	-	0,992	65.0
Intercept = $1.002 \pm 0.004$		0.982	100.0
		0.972	140.0
		0.957	181.2
		0.959	200.0
		0.946	250.0
		0.946	305.0

	Experiment	1-F	t(min)
	P(27)		
$[U(VI)] = 9.66 \times 10^{-2}$		0.993	36.3
$R = 1.45 \pm 0.11 \times 10^{-8} M$ sec	-1	0.987	60.0
Intercept = 0.996 ± 0.003		0.983	95.0
		0.966	155.0
		0.967	205.0
		0.956	250.1
		0.955	300.0
		0.940	360.0
- 1	P(28)		
$[U(VI)] = 1.11 \times 10^{-1}$	_	0.980	60.0
$R = 1.10 \pm 0.12 \times 10^{-8} M$ sec	-1	0.985	100.0
Intercept = 0.993 ± 0.004		0.984	130.0
		0.964	205.0
		0.964	250.0
		0.948	405.0
		0.939	460.0

	Experiment	1-F	t(min)
. +.	P(10)		
$[H^{-}] = 1.80$	-1	0.986	110.0
$R = 2.00 \pm 0.24 \times 10^{\circ} M$ sec	-	0.978	210.0
Intercept = $1.006 \pm 0.009$		0.979	275.0
		0.941	360.0
		0.948	450.0
		0.914	565.0
		0.931	678.0
		0.891	775.0
		0.894	836.0
·+.	P(11)	0.005	<i>(</i> <b>0 0</b>
[H] = 1.50	-1	0.985	60.0
$R = 2.17 \pm 0.12 \times 10^{\circ} M$ sec	-	0.979	130.0
$Intercept = 0.999 \pm 0.005$		0.973	226.0
		0.954	325.0
		0.917	480.0
		0.934	600.0
		0.891	715.0
		0.892	. 770.0
		0.876	835.0
	P(12)		
[H'] = 1.00	-1	0.990	58.0
$R = 2.49 \pm 0.07 \times 10^{\circ} M$ sec	-	0.987	100.0
Intercept = $1.003 \pm 0.002$		0.964	250.0
		0.950	275.2
		0.933	415.0
		0.914	501.5
		0.898	600.0
		0.864	840.0

Table D3. Dependence of exchange rate on hydrogen ion concentration.  $[U(IV)] = 1.20 \times 10^{-2}; [U(VI)] = 2.76 \times 10^{-2}; I = 2.00 \text{ M};$  $T = 25.0^{\circ}; \text{ lamp I}.$ 

	Experiment	1-F	t(min)
	P(13)		
[H <sup>T</sup> ] = 0.750	1	0.981	60.0
$R = 3.01 \pm 0.07 \times 10^{-6} M$ sec	T	0.970	100.1
Intercept = 0.988 ± 0.003		0.948	180.2
		0.927	280.1
		0.911	350.0
		0.889	485.3
		0.860	650.8
		0.858	740.1
		0.841	770.4
		0.812	900.0
	P(14)		
[H <sup>+</sup> ] = 0.500	1	0.979	50.3
$R = 4.40 \pm 0.12 \times 10^{-6} M$ sec	1	0.968	108.0
Intercept = 0.997 ± 0.005		0.875	400.0
		0.813	670.0
		0.793	700.9
		0.776	800.0
±	P(15)		
[H <sup>+</sup> ] = 0.250	1	0.986	25.0
$R = 6.85 \pm 0.25 \times 10^{-6} M$ sec	<b>L</b>	0.957	61.0
Intercept = 0.997 ± 0.006		0.937	156.0
		0.871	, 258.0
		0.836	350.7
		0.803	450.8
		0.730	625.5

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	Experiment	1-F	t(min)
	P(16)		
[H <sup>+</sup> ] = 0.179		0.932	54.0
$R = 11.4 \pm 0.5 \times 10^{-8} M$ sec	1	0.925	80.0
Intercept = 0.984 ± 0.010		0.929	100.0
		0.835	180.0
		0.803	257.0
		0.768	300.0
		0.699	400.0
		0.648	525.0
T(1	6) (thermal)		
[H <sup>+</sup> ] = 0.179		0.964	50.2
$R = 1.70 \pm 0.18 \times 10^{-8} M$ sec	-1	0.965	100.4
Intercept = 0.972 ± 0.008		0.952	239.9
		0.952	300.4
		0.917	360.0
		0.877	650.0
		0.815	1514.0

E	xperiment	1-F	t(min)
	P(23)		
$T = 25.0^{\circ}$		0.992	20.0
$R = 2.95 \pm 0.08 \times 10^{-6} M sec^{-1}$		0.978	52.8
Intercept = $1.005 \pm 0.005$		0.967	100.0
		0.911	175.2
		0.873	250.0
		0.824	356.0
		0.790	460.0
		0.726	615.0
	P(24)		
$T = 14.23^{\circ}$		0.996	30.3
$R = 1.41 \pm 0.08 \times 10^{-5} M$ sec		0.987	60.9
Intercept = $1.000 \pm 0.003$		0.972	100.0
		0.960	135.5
		0.951	190.2
		0.941	235.5
		0.932	300.0
		0.911	355.0
	P(25)		
$T = 32.0^{\circ}$		0.974	25.5
$R = 2.45 \pm 0.20 \times 10^{\circ} M$ sec		0.982	55.0
Intercept = $1.000 \pm 0.007$		0.975	80.0
		0.943	125.0
		0.915	185.0
		0.906	225.0
		0.907	250.5
		0.848	350.0

Table D4. Dependence of exchange rate on temperature.  $[U(IV)] = 5.87 \times 10^{-3}; [U(VI)] = 7.60 \times 10^{-3}; [H^+] = 1.00;$ I = 2.00 <u>M</u>; P(23,24), lamp II; P(25), lamp IIa.

Table D5. Dependence of exchange rate on the  ${}^{233}$ U concentration. [U(IV)] = 2.50 × 10-2; [U(VI)] = 2.74 × 10-2; [H<sup>+</sup>] = 1.00; [Tartaric acid] = 0.130; I = 2.00 <u>M</u>; T = 25.0°. Thermal experiments.

	Experiment	1-F	t(min)
	R(1)		
$[^{233}U(VI)] = 4.52 \times 10^{-6}$	_	0.969	931.0
$R = 4.00 \pm 0.38 \times 10^{-9} M$ sec	-1	0.940	1423.0
Intercept = 0.977 ± 0.010		0.957	2481.0
		0.907	3901.0
		0.910	4377.0
		0.845	5753.0
		0.833	7203.0
		0.837	9606.0
		0.817	10096.0
		0.802	11642.0
		0.758	12521.0
222 6	R(2)		
$[^{233}U(VI)] = 8.83 \times 10^{-0}$	1	0.950	934.0
$R = 4.96 \pm 0.31 \times 10^{-9} M$ sec	-T	0.930	1404.0
Intercept = 0.962 ± 0.010		0.870	3882.0
		0.871	4358.0
		0.837	5734.0
		0.818	7184.0
		0.797	9587.0
		0.753	10077.0
		0.754	11623.0
		0.706	12502.0

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	Experiment	1-F	t(min)
	R(3)		
$[^{2}J^{3}U(VI)] = 13.2 \times 10^{-6}$	1	0.983	463.0
$R = 6.82 \pm 0.43 \times 10^{-9} M$ sec	-1	0.976	1540.0
Intercept = 1.020 ± 0.010		0.964	2935.0
		0.904	3428.0
		0.879	4788.0
		0.833	6240.0
		0.800	8638.0
		0.758	9145.0
		0.702	11563.0
	R(4)		
$[^{233}U(VI)] = 2.16 \times 10^{-6}$	-	0.990	917.0
$R = 5.60 \pm 0.22 \times 10^{-9} M$ sec	-1	0.967	1380.0
Intercept = 1.007 ± 0.008		0.952	2457.0
		0.898	3852.0
		0.897	4345.0
		0.870	5705.0
		0.885	7157.0
		0.806	9555.0
		0.761	10062.0
		0.745	11592.0
		0.726	12480.0

Exp	eriment 1-F	t(min)
$[T_{\text{entends}}, \text{edd}] = 0, 10 \times 10^{-3}$	2	12080
$[1artaric acid] = 9.10 \times 10^{-1}$	0.944	13009
$R = 2.04 \pm 0.72 \times 10$ <u>M</u> sec	0.964	22275
$intercept = 0.972 \pm 0.014$	0.985	34826
	0.946	41896
	0.929	49274
	0.906	64904
	3	
$[Tartaric acid] = 1.30 \times 10^{-2}$	1.00	4941
$R = 2.81 \pm 0.49 \times 10^{-10} \text{ M sec}^{-1}$	0.997	8714
Intercept = $1.00 \pm 0.010$	0.987	13090
	0.986	22340
	0.954	33159
	0.937	40982
	0.935	49019
	0.926	53354
	0.946	64944
	4	
[Tartaric acid] = $3.90 \times 10^{-2}$	0.997	4985
$R = 9.28 \pm 0.65 \times 10^{-10} M sec^{-1}$	0.964	9465
Intercept = 1.00 ± 0.010	0.943	13842
	0.916	21783
	0.856	31708
	0.853	34951
	0.838	41009
	0.819	47780
	0.820	52661

Table D6. Dependence of exchange rate on tartaric acid concentration.  $[U(IV)] = 2.50 \times 10^{-2}; [U(VI)] = 2.74 \times 10^{-2}; [H^+] = 1.00;$  $I = 2.00 \text{ M}; T = 25.0^\circ; \text{ thermal experiments.}$ 

· · · · · · · · · · · · · · · · · · ·	Experiment 1-F	t(min)
	5	
[Tartaric acid] = $6.50 \times 10^{-2}$	0.925	9400
$R = 18.1 \pm 1.57 \times 10^{-10} M set$	c <sup>-1</sup> 0.936	10879
Intercept = 0.990 ± 0.022	0.894	12253
	0.862	15133
	0.862	20443
	0.795	23407
	0.727	29546
	0.693	40602
	0.664	4787 <b>6</b>
	0.668	52684
	6	
$[Tartaric acid] = 9.10 \times 10^{-2}$	0.922	5830
$R = 24.8 \pm 1.75 \times 10^{-10} M$ set	c <sup>-1</sup> 0.927	10103
Intercept = 1.00 ± 0.024	0.876	10998
	0.880	12950
	0.844	15896
	0.796	21200
	0.762	24155
	0.636	29684
	0.679	33948
	0.640	41327
	0.594	45564
	0.560	53152

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	Experiment	1-F	t(min)
•	7		
[Tartaric acid] = $1.30 \times 10^{-1}$		0.929	1629
[H <sup>+</sup> ] = 0.850		0.881	2687
$R = 54.0 \pm 3.69 \times 10^{-10} M$ sec	-1	0.884	4252
Intercept = 0.980 ± 0.024		0.826	5566
		0.812	10143
		0.733	11631
		0.732	12986
		0.714	15980
		0.584	19950
		0.554	21285
		0.506	25650
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$[Tartaric acid] = 1.69 \times 10^{-1}$		0.940	1243
$R = 57.0 \pm 5.98 \times 10^{-10} M$ sec	-1	0.892	2732
Intercept = 0.985 ± 0.036		0.950	4469
		0.856	5785
		0.833	7577
		0.742	10082
		0.689	11546
		0.738	12921
		0.617	14776
		0.624	16499
		0.539	20473
		0.624	22009

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	Experiment	1-F	t(min)
	9		
[Tartaric acid] = $1.95 \times 10^{-1}$		0.940	1273
$R = 74.4 \pm 4.59 \times 10^{-10} M$ sec	-1	0.867	2755
Intercept = $1.00 \pm 0.028$		0.871	4428
		0.820	5739
		0.800	7611
		0.687	10116
		0.707	11459
		0.662	12946
		0.614	14805
		0.623	16531
		0.491	20505
		0.431	22044
	10		
$[Tartaric acid] = 2.21 \times 10^{-1}$		0.918	1423
$R = 84.3 \pm 5.53 \times 10^{-10} M$ sec	-1	0.825	2722
Intercept = 0.962 ± 0.031		0.756	4483
		0.886	5793
		0.747	7669
		0.668	10168
		0.619	11514
		0.617	13003
		0.500	14851
		0.550	16576
		0.438	20559
		0.318	22099

Exp	periment 1-F	t(min)
	11	
[Tartaric acid] = $2.60 \times 10^{-1}$	0.983	1564
$R = 106.4 \pm 5.51 \times 10^{-10} M$ sec <sup>-1</sup>	0.926	2470
Intercept = 1.04 ± 0.018	0.897	2957
	0.832	3789
	0.828	4459
	0.772	5495
	0.748	6853
	0.737	7327
	0.709	8024
	0.698	8794
	0.606	9763
	0.635	10217
	0.608	11177

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