THE ACCELERATION OF THE URANIUM (IV) - URANIUM (VI) ELECTRON EXCHANGE REACTION BY TARTARIC ACID

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ABSTRACT

THE ACCELERATION OF THE URANIUM(IV) – URANIUM(VI) ELECTRON EXCHANGE REACTION BY TARTARIC ACID

By E. Phillip Benson, Jr.

The effect of several organic acids on the exchange reaction between uranium(IV) and uranium(VI) in aqueous perchloric acid was studied. The catalytic effect of these acids was found to increase in the order malonic acid < maleic acid < malic acid << tartaric acid.

More detailed studies of the reaction in the presence of tartaric acid revealed that the order of the reaction is 1.3 with respect to uranium(IV) and 0.47 with respect to uranium(VI). The exchange is 0.90 order with respect to tartaric acid and hydrogen ion has an order of -2.9.

The predominant uranium species in solution are U^{+4} and UO_2^{++}. The following three paths for exchange

$$U^{+4} + H_2O \rightleftharpoons UOH^{+3} + H^+ \qquad \text{(fast)}$$

$$UOH^{+3} + UO_2^{+2} \rightleftharpoons Y^{+3} + 2H^+ \qquad \text{(fast)}$$

$$Y^{+3} + UOH^{+3} \rightleftharpoons Z^{+6} \qquad \text{(rate-determining)}$$

and

$$U^{+4} + H_2O \rightleftharpoons UOH^{+3} + H^+ \qquad \text{(fast)}$$

$$H_2Tar \rightleftharpoons HTar^- + H^+ \qquad \text{(fast)}$$

$$UOH^{+3} + HTar^- \longrightarrow (A.C.)^{+2} \qquad \text{(rate-determining)}$$

$$(A.C.)^{+2} + UO_2^{++} \longrightarrow \text{products} \qquad \text{(fast)}$$

and

$$U^{+4} + H_2O \rightleftharpoons UOH^{+3} + H^+ \qquad \text{(fast)}$$

$$H_2Tar \rightleftharpoons HTar^- + H^+ \qquad \text{(fast)}$$

$$UOH^{+3} + HTar^- \rightleftharpoons [(UOH)\cdot(HTar)]^{+2} \qquad \text{(fast)}$$

$$[(UOH)\cdot(HTar)]^{+2} + UO_2^{++} \longrightarrow (A.C.)^{+4} \qquad \text{(rate-determining)}$$

$$(A.C.)^{+4} \longrightarrow \text{products} \qquad \text{(fast)}$$

combine to give an expression for the overall rate

$$R = \frac{5.7 \times 10^{-4}[U^{+4}]^2[UO_2^{++}]}{[H^+]^4} + \frac{7.3 \times 10^{-5}[U^{+4}][H_2Tar]}{[H^+]^2}$$

$$+ \frac{1.2 \times 10^{-3}[U^{+4}][H_2Tar][UO_2^{++}]}{[H^+]^2}$$

Rates calculated using this expression agree well with rates obtained experimentally.

The rate of the reaction increased with increasing ionic strength and was markedly accelerated by temperature increases. Irradiation with an ultraviolet lamp caused a very large increase in the rate of the reaction.

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INTRODUCTION

In the last fifteen years, many papers have appeared which are concerned with the kinetics of inorganic oxidation-reduction reactions. The increase came partly as a result of the development of many new techniques of kinetic observation, and partly because of the increased availability of radioactive nuclides.

As a result of the increased activity in experimental work in this area, interest grew in the nature of the mechanisms by which such reactions occurred. Shaffer[1,2] and Michaelis[3] were the first to attempt to explain the observed rates of reactions as dependent on some factors other than thermodynamic considerations.

Michaelis' principle of "compulsory univalent oxidation steps" invokes the limitation that all oxidation-reduction reactions involving stable oxidation states that differ by two electrons (e.g. Tl^{+} - Tl^{+3}; Sn^{+2} - Sn^{+4}) occur by successive one electron steps. It evolved from consideration of a limited number of oxidation-reduction reactions and is now believed to be without universal validity.

Shaffer's rule of "equivalence change" states that reactions between one-equivalent oxidizing agents and two-equivalent reducing agents (or vice-versa) are often slow, compared with those between one-equivalent reducing agents and one-equivalent oxidizing agents or between two-equivalent oxidizing and two-equivalent reducing agents. Examples are the slow reduction of Tl^{+3} by Fe^{++}, or of Ce^{+4} by Tl^{+} compared with the rapid reduction of Tl^{+3} by Sn^{+2} or of Ce^{+4} by Fe^{+2}. The slowness of the former types of reactions is explained by mechanisms which involve either a termolecular step or the formation of unstable intermediate oxidation states.

Although there is still no complete compilation of data for extensive comparison, Halpern[4] has compared three systems involving combinations of one and two electron equivalent oxidizing and reducing agents. While he concludes that one cannot draw any detailed results from the comparison, the rates for two of the systems studied (Fe^{+2} - Tl^{+3} and Tl^{+} - Co^{+3}) are not lower than those of the corresponding exchange reactions, as would be predicted, but are intermediate between them. This would indicate that the principle of equivalence change is not a uniquely applicable rule. Halpern considers the principle further in a recent review article.[5]

Accompanying the increase of experimental work on the kinetics of aqueous oxidation-reduction reactions has been an increase of interest in the theoretical aspect of electron transfer, since it is only recently that systems have been investigated in which clear-cut interpretation of results is possible. In an electron transfer reaction, it is not known if the electron lost by the reducing agent is the same one that is gained by the oxidizing agent and how this electron moves from the reducing agent to the oxidizing agent. Most of the systems studied have come to be explained by two important forms of the activated complex in electron transfer. These are usually denoted as the "outer sphere" activated complex and the "inner sphere" or "bridged" activated complex.[6] The distinction between the two is not always sharp and many reactions at this stage cannot be assigned with certainty to either class.[7]

In the "outer sphere" activated complex, the number and identity of the groups comprising the first coordination sphere remains unaltered by electron transfer. This means that substitution is a much less rapid process than transfer. In this case the readjustments which

accompany electron transfer take place largely in the solvent, and there is little change in the dimensions of the molecules on electron transfer.

Wahl[8] has summarized results for some reactions of this type.

The other general class of electron-transfer mechanisms involves the "bridged" activated complex. The first clear demonstration was by Taube[9] in the reaction of $[(NH_3)_5CoCl]^{+2}$ with Cr^{+2} to give NH_4^+, Co^{+2}, and $CrCl^{+2}$. Since both the Co^{+3} complex and the Cr^{+3} product are substitutionally inert, electron transfer must occur through a bridged intermediate of the type

$$[(H_3N)_5\ Co^{+3} - Cl - Cr^{+2}\ (OH_2)_5]^{+4}$$

in which Cl is simultaneously coordinated to both metal ions. It should be noted that although the bridging ligand is generally transferred from the oxidant to the reductant, this is not a necessary requirement for electron transfer. Also, catalysis by anions or incorporation of anions into the coordination sphere of the oxidized metal ion does not indicate the participation of the anion as a bridging ligand.[10] Fumarate and p-phthalate are of special interest as bridging ligands in the oxidation of Cr^{+2} by $[(H_3N)_5\ Co\,L]^{+2}$, since the rates are much higher than for other carboxylic acids.[11] This has been interpreted in terms of a bridged intermediate in which the two metal ions are coordinated through the "remote" carboxylate groups

$$[(H_3N)_5\ Co - O - C(=O) - CH = CH - C(OR) - O - Cr(OH_2)_5]^{+4}$$

where R = H, CH_3, or C_2H_5, with the electron being transferred between them by "conduction" through the conjugated π-electron system. This

attack is sterically favored over attack at the adjacent carboxyl group. The use of such conjugated bridging groups for distinguishing between the two types of mechanisms and for the systematic variation of structural parameters makes these systems extremely valuable.

A possible mechanism of electron transfer between metal aquo-ions, first suggested by Dodson and Davidson[12], is through transfer of a hydrogen atom between hydration shells. There is some evidence in support of such a mechanism. For example, the rates of the Fe^{+2} - Fe^{+3} and the Fe^{+2} - $FeOH^{+2}$ reactions are lowered by a factor of two in passing from H_2O to D_2O as the solvent.[13] In addition, the activation energies of a large number of diverse redox reactions involving metal aquo-ions are close to 10 kcal/mole, and their activation entropies close to -25 eu, suggesting that they proceed by a common mechanism involving water.

A modified view[14] of the role of water in these reactions is that the coupling of the hydration shells of the two ions by hydrogen bonding lowers the energy of the activated complex and, by increasing the overlap between the exchanging orbitals, provides a more effective conducting path for electron transfer. In this context transfer of hydrogen is incidental to its bridging role, and whether or not it occurs depends on the relative proton affinities of the two hydration shells after electron transfer.

In some cases redox processes proceed through mechanisms which do not involve direct reaction between the oxidizing and reducing agents. Such indirect mechanisms are frequently responsible for catalytic effects in redox systems.

One possible alternative is the release of an electron by the reducing agent to the solvent and its subsequent capture by the oxidizing agent. Also oxidizable or reducible ligands can act as electron carriers between metal ions. Intermediate oxidation of the bridging ligand without release from the bridged complex is another mechanism of electron transfer. In addition, ions which can exhibit two or more stable oxidation states may also serve to transport electrons in redox reactions through a chain mechanism.

Various theoretical aspects of electron transfer processes in solution have been considered by W. F. Libby,[15,16] R. A. Marcus,[17,18] N. S. Hush,[19] R. J. Marcus, B. Zwolinski, and H. Eyring,[20] and K. J. Laidler?[21,22] Nearly all these treatments have emphasized the dependence of the rate on the following factors: electrostatic interactions between the overall charges of the reactants, the reorganization energy of the ligands and of the surrounding medium prior to andduring electron transfer, associated with the Franck-Condon restriction, and the rate of the electron-transfer process itself in the activated complex.

Libby[15] discussed the formation of the activated complex and emphasized the restrictions of the Franck-Condon principle in its application to electron transfer in aqueous solution. The Franck-Condon principle states that transfer should be inhibited by the relatively long times required for movement of the heavy water molecules constituting the hydration spheres compared to the transit time for the electron. The differences in rates of movement of the electron and the extra energy of hydration due to the electron exchange process mean that the electron must make the transition against a barrier comparable in magnitude to the amount of energy involved in the subsequent slow orientation of the

water molecules to the new charge situation. This gives rise to the principle that electron exchange can be catalyzed by complexing the exchanging ions in such a way that the complexes are symmetrical. In a later article, Libby[16] applied the principle to oxidation-reduction reactions of the transition elements in which a bridged activated complex is operative.

R. A. Marcus[17] has attempted a quantitative treatment, incorporating the restriction of the Franck-Condon principle, to describe a mechanism for electron transfer. In the reaction between two reactants, A and B, the following steps may take place

$$(1) \qquad A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^*$$

$$(2) \qquad X^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X$$

$$(3) \qquad X \xrightarrow{k_3} \text{products}$$

where X^* is the activated complex. The overall rate is given by

$$(4) \qquad v = kc_a c_b$$

where c's denote concentration and k is the observed rate constant. If the forward step is at least as probable as the reverse step in reaction (1), then

$$(5) \qquad k \approxeq k_1$$

Using the restriction that only slight overlap of the electronic orbitals of the two reacting species in the activated complex is necessary, he obtains a value for the overall rate constant that is given by

$$(6) \qquad k \approx k_1 = Z \exp\left(-\Delta F^*/\underline{k}T\right)$$

where

Z = collision number in solution
ΔF^* = free energy of formation of X^* in excess of that for two neutral, nonreactive particles in solution
$\underline{k}$ = Boltzmann constant
T = absolute temperature

ΔF^* is obtained in terms of known quantities, such as ionic radii, charges, and the standard free energy of reaction. In a second article[18] he applied the model to some previously reported homogeneous isotopic exchange reactions and obtained impressive agreement with the experimental data.

N. S. Hush[19] has also proposed a theory of electron transfer for processes in which the coordination shells about the ions are not disrupted on electron transfer. The central concept is that the probability density for electron transfer in each step can readily be found and the equations for the calculation of the free energy, enthalpy, and entropy of activation are then easily derived. Reasonably good agreement with experiment is found for isotopic exchange reactions. This method of approach is similar to that of R. A. Marcus and the general conclusions obtained by either method are similar.

R. J. Marcus, B. Zwolinski, and H. Eyring[20] have classified available data pertaining to electron-exchange reactions on the basis of the entropy of reaction: one group with negative entropies of activation and another with positive entropies of activation. In the oxidation-reduction reactions considered, the ions modify their structures in such a way that transfer of the electron leaves the total energy unchanged. During the approach of the reactive ionic species leading to the transition, ionic repulsion forces are overcome and the coordination and

hydration shells of both ions are rearranged until their electronic states are symmetrical, thus permitting a rapid transition to take place. Those configurations which give the fastest reaction will be the ones measured. Since these will not have too high a free energy of activation, any measurable rate for an oxidation-reduction reaction involves a transmission coefficient (probability of transition) less than unity. Its magnitude will be determined by the height and thickness of the electronic barrier for this transition. For convenience the electronic transmission coefficient (κ_e) can be represented in the following form:

$$(7) \qquad \kappa_e = \exp\left[\frac{-8}{3h}\, r_{ab}(2m\,(V - W))^{1/2}\right]$$

where

V = height of the electron barrier
W = kinetic energy of tunnelling electron
r_{ab} = tunnelling distance
m = electron mass
h = Planck's constant.

The class of reactions with positive entropies of activation have an electronic barrier that is quite thin at the transition point with the transmission coefficient near unity. The reactions characterized by apparent negative entropies of activation are those with appreciable electron barrier widths at the activated state, consistent with smaller energies of activation at larger critical distances of ion approach.

Laidler[21,22] has also given a theoretical treatment of electron-transfer reactions involving quantum-mechanical tunnelling. His more complete calculation also includes terms which account for repulsive

free energy and the energy of solvent reorganization. His calculation for the reaction

$$(8) \qquad Fe^{+2} + Fe^{*+3} \rightleftharpoons Fe^{+3} + Fe^{*+2}$$

predicts a minimum weighted value of 15.9 kcal/mole for free energy of activation at an interionic separation of 4.2 Å. This compares well with the experimental value of 16.8 kcal/mole.

Newton and Rabideau[23] have reviewed many of the aqueous oxidation-reduction reactions of uranium, neptunium, and plutonium. They summarized all of the kinetic information in terms of the equations for the net activation processes and the associated thermodynamic quantities of activation. Using the assumption that all of the reactions were one-electron oxidation-reduction reactions, the equations for the net activation processes were obtained from the rate laws. The equations were formulated in terms of any rapid equilibrium reactions which may have occurred prior to the rate-determining step. The result described the formation of the activated complex without regard to the detailed mechanism.

The thermodynamic quantities of activation, ΔF^{*}, ΔH^{*}, ΔS^{*}, were calculated from the equations of the absolute reaction rate theory.[24] The quantity called $\bar{S}^{*}_{complex}$ is the formal ionic entropy of the activated complex calculated from ΔS^{*} using the standard entropies of the ordinary species present or:

$$(9) \qquad \bar{S}^{*}_{complex} = \Delta S^{*} + \sum \bar{S}^{0}_{reactants}$$

The values for these standard entropies are calculated on the convention that $\bar{S}^{0}_{H^{+}} = 0$.

It was observed that the data reviewed did not fall into distinct classes as suggested by R. J. Marcus, B. Zwolinski, and H. Eying[20] but

instead exhibited a range of values. This wide range is reduced when allowance is made for the hydrolysis equilibria involved.

A relation between ΔH^* and the heat of reaction, ΔH^0, was found to hold for a large number of oxidation-reduction reactions of the actinide elements. Within this correlation, ΔH^* for purely "electron-transfer" reactions such as

$$(10) \qquad Pu^{+3} + PuO_2^{+2} \rightleftharpoons Pu^{+4} + PuO_2^{+}$$

appeared to be somewhat lower than for reactions involving hydrolytic or structural changes such as

$$(11) \qquad Np^{+4} + NpO_2^{+2} + 2H_2O \rightleftharpoons 2NpO_2^{+} + 4H^{+}$$

which presumably reflects an additional contribution to ΔH^* from bond rearrangement in the latter cases.

A series of formally identical reactions exhibited varying values of ΔS^* but had approximate agreement among the $\bar{S}^*_{complex}$ values. This indicates that an important source of the difference in the ΔS^* values lies in the differences in the entropies of the reactant ions.

The most important single factor which determines the entropy of the activated complex appears to be its charge. It was found that all reactions with an activated complex having a given charge type exhibited the same values of $\bar{S}^*_{complex}$. It was noted that the activated complexes of simple electron exchange reactions exhibited values of $\bar{S}^*_{complex}$ similar to those of other reactions.

Electron exchange reactions between uranium(IV) and uranium(VI) have been studied in sulfate solutions by Betts,[25] in chloride solutions by Rona,[26] and in perchlorate solutions by King,[27] and by Masters and Schwartz.[28]

King reported only that the exchange reaction was slow and suggested that this was due to the formation and breaking of metal-oxygen bonds. Betts reported the exchange in sulfate medium in the presence of constant external illumination. Although he presented no detailed mechanism for the exchange, it has been suggested that the active intermediate in the exchange is uranium (V). It has been shown by Heal[29] that illumination causes a considerable increase in the concentration of uranium (V).

Rona has studied the exchange reaction in chloride solutions and found that it is second order in uranium (IV), first order in uranium (VI), and negative third order in hydrogen ion concentration. She also noted no effect due to added ions or due to illumination of the solutions. The reaction was found to have an apparent activation energy, (E_a), of 33.4 kcal per mole.

She explained her results by means of the following mechanism. While uranium (VI) is present as UO_2^{++} in these solutions, uranium (IV) is present according to the following rapid equilibrium

$$(12) \qquad U^{+4} + H_2O \rightleftharpoons UOH^{+3} + H^+$$

The value of the equilibrium constant, K_h, had previously been evaluated by Kraus and Nelson.[30]

Rona suggests that UOH^{+3} will react more readily with UO_2^{++} to form an intermediate ion, Y^{+3}, containing an oxygen bridge according to the following equation:

$$(13) \qquad UOH^{+3} + UO_2^{++} + 2H_2O \rightleftharpoons Y^{+3} + 2H^+$$

The equilibrium constant for this reaction is K_1. This intermediate ion now reacts further with uranium (IV) in the rate determining step to form the activated complex, Z^{+6}

(14) $Y^{+3} + UOH^{+3} \longrightarrow Z^{+6}$

which breaks down into the final products

(15) $Z^{+6} \longrightarrow$ products.

This mechanism gives a calculated reaction rate, v, that agrees well with the experimental results.

(16) $v = k[Y^{+3}]\,[UOH^{+3}]$

and substituting

(17) $$v = kK_1 \frac{[U(IV)]^2\,[UO_2^{++}]}{\left[\frac{[H^+]}{K_h} + 1\right]^2 [H^+]^2}$$

More recently Masters and Schwartz have investigated the uranium (IV)-uranium (VI) system in perchlorate solutions. They confirmed Rona's work in perchlorate solutions and identified another path which predominates at conditions of low uranium (IV) ion concentrations and at temperatures above 25°C. This path was found to be first order in uranium (IV), first order in uranium (VI) and negative third order in hydrogen ion. The energy of activation, (E_a), was found to be 38.1 kcal per mole.

The strong effect due to ultraviolet irradiation suggested that the reaction path involved uranium (V) as an intermediate. The formation of U(V) can be given by the expression

(18) $$\frac{d}{dt}[UO_2^+] = 2k\,[U^{+4}]\,[UO_2^{++}]\,[H^+]^{-3}$$

which is twice the experimentally measured rate. The disproportionation of U(V) is given by

(19) $$-\frac{d}{dt}[UO_2^+] = k_D[UO_2^+]^2[H^+]$$

By equating the above equations, the equilibrium constant, K_E, may be determined

$$(20) \qquad K_E = k_D/2k$$

Masters and Schwartz obtained a value of 1.02×10^9 for K_E which agrees well with the value of 1.05×10^9 observed by Kraus and Nelson[31] in polarographic studies of the U(IV)-U(V)-U(VI) equilibrium.

This result meant that the activated complex formed in the exchange reaction was identical with that formed in the disproportionation reaction. The mechanism may be described schematically as

$$(21) \qquad U^{+4} + UO_2^{++} + 2H_2O \underset{+3H^+}{\overset{-3H^+}{\rightleftharpoons}} (HO\text{-}U\text{-}O\text{-}UO_2)^{+3}$$

and

$$(22) \qquad (HO\text{-}U\text{-}O\text{-}UO_2)^{+3} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} 2UO_2^{+}$$

This reaction sequence is formally identical with that encountered in reactions of other members of the actinide series.[23]

THEORETICAL

In an exchange reaction

(23) $AX + BX^{*} = AX^{*} + BX$

where X^{*} designates the isotopically labeled compound, let R be the rate of exchange.[32] If the concentrations are designated as follows,

(24) $[AX] + [AX^{*}] = a$

(25) $[BX] + [BX^{*}] = b$

(26) $[AX^{*}] = x, [AX] = a - x$

(27) $[BX^{*}] = y, [BX] = b - y$

then the net rate is given by

(28) $$\frac{dx}{dt} = -\frac{dy}{dt} = R\,\frac{y}{b}\,\frac{(a - x)}{a} - R\,\frac{x}{a}\,\frac{(b - y)}{b} = \frac{R}{ab}\,(ay - bx)$$

But since

(29) $y - y_{\infty} = x - x_{\infty}$

and

(30) $x_{\infty}/y_{\infty} = a/b$

therefore

(31) $$\frac{dx}{dt} = \frac{R}{ab}\,[(a + b)\,(x_{\infty} - x)\,]$$

On integration one obtains

(32) $$\ln [x_{\infty}/(x_{\infty} - x)] = \frac{R}{ab}\,(a + b)t$$

The more familiar form of the equation is

$$(33) \quad \ln [1 - x/x_\infty] = - \frac{a + b}{ab} Rt$$

The quantity x/x_∞ is the fraction of exchange and is often merely designated as F. An exchange system conforms to this rate expression if a graph of ln (1-F) vs t is rectilinear. If a straight line is obtained, then R may be determined directly from the slope of the line.

The fraction of exchange can be conveniently determined in a variety of ways. If the separation is not quantitative or reproducible, it is often convenient to use the specific activity (counts per unit time per unit weight) of one of the exchanging species. Prestwood and Wahl[33] have shown that

$$(34) \quad F = \frac{S - S_0}{S_\infty - S_0}$$

where S is the specific activity of AX at time t, S_0 the specific activity at zero time, and S_∞ the specific activity when complete exchange has occurred.

The rate of the exchange reaction, R, is equal to some function of the various concentrations involved and one or more rate and equilibrium constants. For example, for a simple bimolecular reaction

$$(35) \quad R = k[a][b]$$

where k is the specific reaction rate constant. The order with respect to each species in solution may be determined by systematically varying its concentration while all others are kept constant.

This dependence of reaction rate on temperature[34] has been quantitatively formulated by Arrhenius as

$$(36) \quad \ln k = \ln A - E_a/RT \quad \text{or} \quad k = A \exp(-E_a/RT)$$

E_a is the activation energy for the reaction and A is known as the pre-exponential (or Arrhenius) factor. Experimentally a graph of ln k *vs* the reciprocal of the absolute temperature gives E_a from the slope and ln A as the intercept.

It should be pointed out that the above discussion applies only to individual specific reaction rate constants. A complex reaction may appear to follow a simple kinetic order over a limited range of experimental conditions. The apparent rate constant for such a reaction is not a rate constant for a single process but may be a complicated function of many rate constants. If this rate constant is plotted against temperature it may be expected that the Arrhenius equation will not be obeyed. This lack of agreement is often useful in indicating the complexity of the reacting system.

In the theory of absolute reaction rates,[24] the equilibrium between reactants and the activated complex can be represented as

$$(37) \quad aA + bB + \ldots\ldots \rightleftharpoons M^*$$

where M^* represents the activated complex and the equilibrium constant can be represented as

$$(38) \quad K = \frac{C^*}{C_A^a \; C_B^b \ldots\ldots}$$

where C^* is the concentration of the activated complex. The rate of reaction of the activated complex formed is given by

$$(39) \quad \text{rate} = k_r \, C_A^a \, C_B^b \ldots\ldots$$

where k_r is the rate constant. From the theory of reaction rates a pseudo equilibrium constant, K^*, can be defined that is related to the

rate constant for the reaction by

$$(40) \quad k_r = \left(\frac{kT}{h}\right) K^*$$

where k is the Boltzmann constant, T is the absolute temperature, and h is Planck's constant. Thus, the definition of quantities analogous to the thermodynamic functions associated with equilibrium constants is possible.

$$(41) \quad \Delta F^* = - RT \ln K^*$$

$$(42) \quad \Delta H^* = RT^2 \frac{d \ln K^*}{dT}$$

or

$$(43) \quad \Delta H^* = RT^2 \frac{d \ln k_r}{dT} - RT$$

and

$$(44) \quad \Delta S^* = \frac{\Delta H^* - \Delta F^*}{T}$$

It follows that

$$(45) \quad K^* = \exp(-\Delta F^*/RT) = \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$$

or in terms of the rate constant

$$(46) \quad k_r = (kT/h) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$$

The relations derived from the theory of absolute reaction rates can be compared with the Arrenhius equation to calculate thermodynamic quantities. The differential form of the Arrhenius equation is

$$(47) \quad \frac{d \ln k}{dT} = E_a/RT^2$$

If this equation is compared with equation (43) it can be seen that

$$(48) \quad \Delta H^* = E_a - RT$$

By substituting the above equation in (46), the entropy of activation,

ΔS^*, can be determined from the result

$$(49) \quad k_r = e\underline{k}T/h \exp(\Delta S^*/R) \exp(-E_a/RT)$$

if the rate constant at a given temperature and the experimental activation energy are known.

EXPERIMENTAL

Materials

All reagents used were reagent grade chemicals or were purified before use.

The perchloric acid used was Baker's Analyzed Reagent which was used without further purification.

Stock solutions of sodium perchlorate were made up from sodium perchlorate monohydrate obtained from the G. Frederick Smith Chemical Company. It was dissolved in demineralized water, filtered to remove the inevitable insoluble material, and placed on the hot plate to reduce the solution volume. This process was continued until a thin crust of salt appeared on the surface of the solution. The walls of the beaker were then washed down with a minimum of demineralized water to dissolve the crust. A narrow, more dilute, aqueous phase formed above the phase containing the concentrated sodium perchlorate solution. The beaker was then transferred to an oven held at 50-60°C. It was kept there until a large crop of needle-like crystals appeared. The needles were filtered off and the filtrate was returned to the hot plate and the process was repeated. The crystals were dissolved in demineralized water and recrystallized twice more before being used. After the sodium perchlorate had been recrystallized three times it was dissolved in the minimum amount of demineralized water, giving a solution which was about 8.4 M. This solution was then stored in a volumetric flask and used as the stock in making up solutions for kinetic runs.

Demineralized water was used in all experimental work. This was prepared by passing distilled water through a mixed bed of cation and anion exchange resins. The unit used was a Crystal Research Laboratories, Inc. Deeminizer, Model CL-5. Love[35] observed no difference in the results of kinetic experiments carried out in distilled water and those in conductivity water which had been prepared by repeated distillation from an alkaline permanganate solution.

The uranium isotope used as the tracer in the kinetic studies was $^{233}_{92}U$ having a half-life of 1.62×10^5 years. The $^{233}_{92}U$ isotope was obtained from the Nuclear Materials and Equipment Corporation, Apollo, Pennsylvania, in the form of the oxide powder. The analysis of this material is given in Table I.

Table I. The composition of uranium tracer

Uranium Isotope	Per cent of Total
^{233}U	97.3 ± 0.1
^{234}U	1.6 ± 0.1
^{235}U	< 0.1
^{238}U	1.1 ± 0.1

The ^{233}U tracer was purified by a modification of the method of Masters and Schwartz.[28] Since the ^{233}U is in secular equilibrium[36] with its daughter, $^{229}_{90}Th$, and the succeeding products of radioactive decay are all very short lived compared to the two nuclides mentioned, the problem reduces to obtaining a good separation of thorium from

uranium. The ^{233}U oxide powder was dissolved with 11 ml of concentrated nitric acid in a 50 ml beaker. The residue in the shipping bottle was washed with 6 M nitric acid and the two solutions combined. When heating on a hot plate had reduced the volume to about 50 ml, an equal volume of concentrated hydrochloric acid was added. When further heating had reduced the volume to 30 ml, 10 ml of concentrated hydrochloric acid was added and the heating repeated until near dryness. This process was repeated until the addition of hydrochloric acid to the concentrated solution gave no evolution of nitrogen dioxide.

The resulting 10 ml of a chloride solution was then passed through an anion exchange column (Dowex 1X-10, 200-400 mesh, chloride form, Baker Analyzed Reagent) where a chloro complex of uranium was retained while the thorium passed directly through. The column was washed with two 10 ml portions of 1:1 hydrochloric acid to remove the thorium and then the uranium was eluted with demineralized water. The solution containing the uranium was repeatedly heated nearly to dryness with 10 ml portions of concentrated perchloric acid to drive off the remaining hydrochloric acid. When this process was completed, the remaining solution was diluted to 100 ml in a volumetric flask and stored in the water bath.

This procedure was previously tested using 0.53 g of natural uranium oxide to which 0.1 g of thorium nitrate was added. Tests of the effluent from the ion exchange column indicated excellent separation was obtained.

The starting material used in preparing both the U(IV) and U(VI) stock solutions was Baker Analyzed Reagent uranyl nitrate hexahydrate. Three different purifications were carried out using a modification of

of an established method.[37] One pound of uranyl nitrate hexahydrate was dissolved in approximately 700 ml of demineralized water and then filtered through a medium fritted funnel. The filtrate was then placed on the hot plate and kept at approximately seventy-five degrees centigrade. Thirty per cent hydrogen peroxide (Baker's Analyzed Reagent) was slowly and carefully added, with rapid stirring, to the above solution. A coarse lemon yellow precipitate of uranium (VI) peroxide soon formed. This was filtered on a coarse fritted funnel and washed with demineralized water.

For convenient handling one-half of the uranium (VI) peroxide thus obtained was placed in a beaker, 500 ml of demineralized water was added, and then 50 ml of concentrated perchloric acid was added with vigorous stirring. The beaker and contents were then left on the hot plate until the peroxide dissolved. If solution did not occur within twenty-four hours, another 10 ml of concentrated perchloric acid was added and the beaker was again left on the hot plate. This process was repeated until a clear yellow solution resulted. The remaining uranium peroxide obtained was treated in a like manner.

The uranium (VI) perchlorate solutions thus obtained were carried through the precipitation process two more times to yield a purified uranium (VI) peroxide product which was air dried and then used to make up all uranium (IV) and (VI) stock solutions.

The handling quality of the uranium (VI) peroxide precipitates obtained was variable at first. The ability to get coarse precipitates which filter easily apparently is an acquired art. Particular attention must be paid to the amount of perchloric acid used to dissolve the precipitate for the peroxide is difficult, if not impossible, to reprecipitate

from solutions that are too acidic.

Various stock solutions of uranium (VI) perchlorate were prepared by dissolving the purified uranium peroxide in perchloric acid. In earlier experiments, such as are described in Appendix A, care was taken to use as little perchloric acid as possible so that the free hydrogen ion concentration was kept as low as possible. In later experiments more acid conditions were used and so low acidity in the stock solutions was not required. Originally attempts were made to prepare solutions approximately 0.1 M in uranium (VI), based on the assumption that the uranium peroxide was $UO_4 \cdot 2H_2O$. These solutions had to be made more concentrated before standardization since the peroxide invariably contained more water than the above formula indicated. After the peroxide had all dissolved, the solution was boiled for one-half hour to insure that all of the hydrogen peroxide present had been destroyed. The solution was then transferred to a one liter volumetric flask and enough water was added to bring the volume to between 900 and 1000 ml. Then ten milliliters of the ^{233}U stock solution was pipetted out of the storage flask and added to the solution. The solution when made up to the one liter mark was ready for standardization.

Uranium (IV) perchlorate was prepared by an electrolytic procedure similar to that of Ahrland[38] using an apparatus modified from that described earlier by Quinn.[39]

The apparatus for the electrolysis of uranium (VI) and the storage of uranium (IV) is shown in Figure 1. The electrolysis flask (A) is a modified one-liter single-neck flask. On one side of the flask is attached a bent 15 mm "L" shaped tube (B) containing a coarse fritted disc

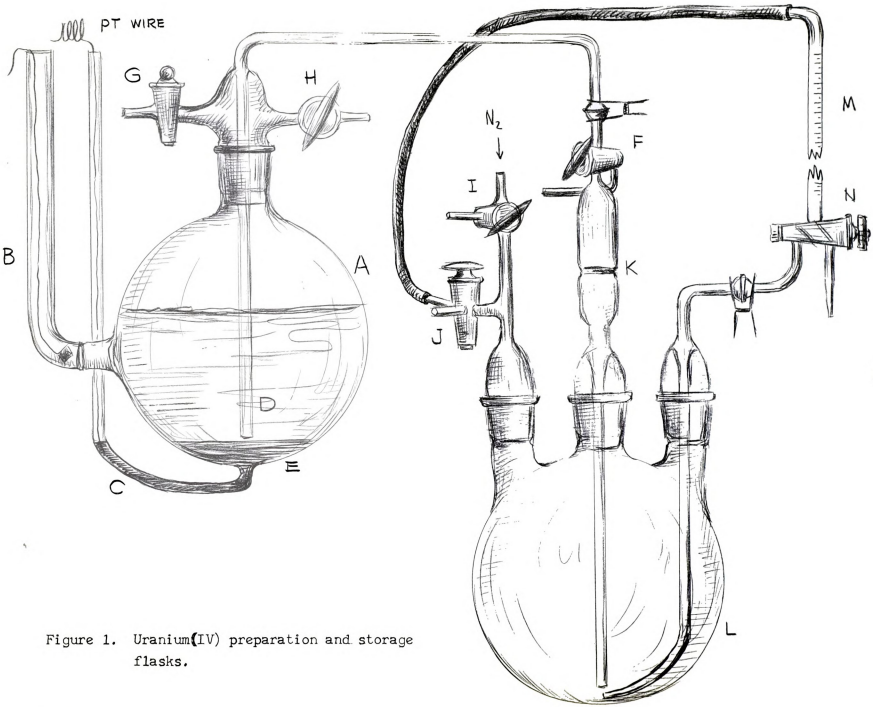

Figure 1. Uranium(IV) preparation and storage flasks.

3 cm from the main body of the flask. This tube forms the anode compartment in an electrolysis. A curved piece of 7 mm tubing (C) which extends up to the neck is attached to the bottom of the flask. It enables an external connection to be made to the cathode.

Since uranium (IV) solutions are oxidized by the atmosphere, all preparations were carried out in an atmosphere of specially pruified nitrogen. A drawing of the apparatus used to purify nitrogen is shown in Figure 2.

Prepurified nitrogen (The Matheson Co., Inc., 8 ppm of oxygen) was used as a cover gas for all experiments as well as in the electrolytic production of uranium (IV). The train shown in Figure 2 was used to insure complete removal of oxygen. The nitrogen passes successively through copper gauze in a tube furnace (A) at 450°C, active copper (B) deposited on kieselguhr at 175°C,[40] and through an approximately 0.4 M solution of chromous sulfate[41] (C,D). After these treatments the gas is scrubbed in a gas washing bottle (E) containing water and then passes through a 2.0 M solution of sodium perchlorate (F) maintained at the temperature of the experiment. The sodium perchlorate maintains constant water vapor pressure in the gas phase. Manipulation of stopcock (G) enables the nitrogen flow to be directed into the preparation apparatus or into the flasks for the kinetic runs.

The copper gauze and the copper on kieselguhr were activated by passing hydrogen through them until all evidence of the oxide was gone. The hydrogen was conveniently passed through this apparatus by utilizing stopcocks (H) and (I). The chromous sulfate solutions had to be replaced approximately every three months when gummy deposits of hydrous chromium (III) oxide eventually plugged the fritted discs.

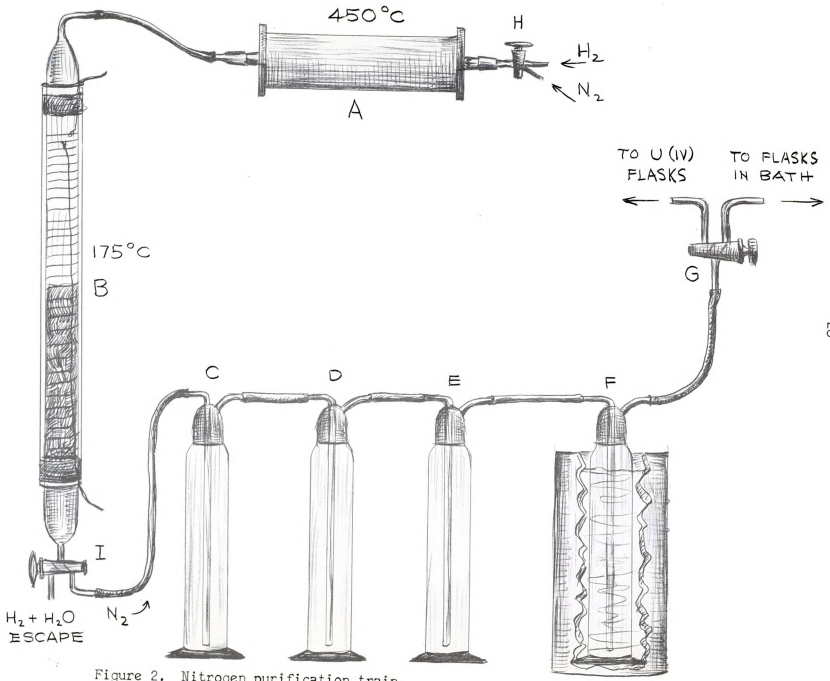

Figure 2. Nitrogen purification train.

A pool of mercury (E) 6 cm in diameter was next placed on the bottom of flask (A) and the uranium (VI) solution was added through the 24/40 standard taper joint. The apparatus was then assembled as shown in Figure 1 and flushed out thoroughly with a rapid flow of nitrogen before the electrolysis was begun. The flow was reduced to about one bubble per second at the exit tube (D) when electrolysis was begun.

Because it has been shown[42] that complete reduction of uranium (VI) to uranium (IV) can be obtained only at 0°C., all reductions were begun only after the electrolysis flask had been immersed in an ice-salt mixture for about one-half hour. The temperature of the bath was thus able to be kept near 0°C.

The cathode for the reduction process was the 6 cm pool of mercury (E) on the bottom of the electrolysis flask. This was connected to the outside circuit by a platinum wire which dipped into the mercury in the tube (C). The anode was a one centimeter square piece of platinum fastened to a platinum wire which was suspended in the anode compartment (B). During electrolysis the anode compartment was filled with a perchloric acid solution of the same concentration as the solution in the cathode compartment.

The electroyses were carried out by passing a current of 0.7 ampere through the uranium (VI) while it was being stirred by the slow passage of purified nitrogen through tube (D). The direct current source was an Electro Products Laboratories, Model D-612 T Filtered D.C. Power Supply. The voltage required for a current of 0.7 amperes varied with the solution used and usually ranged between 10 and 18 volts. The length of time required for the electrolysis varied depending on the

uranium (VI) and hydrogen ion concentrations, increasing with increasing uranium (VI) concentration and decreasing with increasing hydrogen ion concentration.

The reduction was complete when uranium (III) began to be produced. Uranium (III) was easily detected since the green solution of uranium (IV) turned dark when red uranium (III) was produced. The red color could easily be detected if the electrolysis was allowed to proceed too long. Any uranium (III) produced was removed by passing a stream of oxygen in the outlet of stopcock (F) and bubbling it through the solution. When all of the uranium (III) had been removed, a fast flow of nitrogen through the electrolysis flask was maintained for another half hour.

When the preparation of the uranium (IV) was complete, stopcock (G) or (H) was closed and stopcock (I) opened to the atmosphere. A piece of rubber tubing was then attached to the exit tube of stopcock (I). Corks were then tightly fitted in the two sidearms of the electrolysis flask. The solution was then transferred through the fritted disc (K) to the storage flask (L) by passing a very rapid nitrogen flow through stopcocks (I) and (H) into the electrolysis flask and exiting at stopcock (J). The transfer process could normally be completed in about ten minutes. When the transfer was complete, stopcocks (I) and (F) were closed. The electrolysis apparatus was then removed for cleaning and storage. The uranium (IV) stock solutions were normally stored in this manner with all stopcocks closed and with no nitrogen flow. Samples could be forced into the buret (M) by admitting nitrogen in stopcock (I). They were delivered out the Teflon stopcock (N) by allowing nitrogen to flow through both stopcocks (I) and (J).

Analytical reagent grade tartaric acid (Mallinckrodt Chemical Works) was used without further purification. The melting point of the acid was 168-170°C, corresponding to pure d-tartaric acid.

The other organic acids used were those previously purified by Quinn[39] and stored in a dessicator. They were used without further purification. Table II indicates the melting points of the acids.

Table II. Melting points of organic acids

Acid	M.P. (43)	Observed Melting Point (uncorrected)
maleic	138°C	Began subliming at 136°C
malic	128-129°C (dl)	127-129°C
malonic	130-135°C	135-136°C

Analytical Determinations

A 0.44 N sodium hydroxide solution was prepared as described by Kolthoff and Sandell[44] and stored in a large polyethylene bottle protected from the carbon dioxide in the atmosphere by an Ascarite guard tube. It was standardized against potassium acid phthalate (Mallinckrodt Analytical Reagent - primary standard) using phenolphthalein as the indicator. The potassium acid phthalate was dried at 110°C before use. No carbonate precipitate appeared in the standard base and no change in titer occurred in a period of over one year.

Solutions of perchloric acid were prepared by diluting the 70% reagent (Baker's Analyzed Reagent) to the appropriate concentration

with deionized water. Solutions of approximately 6 M were made up and acidity was determined by titration with the standard base.

The concentrated stock solutions of sodium perchlorate were analyzed by the method described by Masters and Schwartz.[28] One milliliter aliquots were delivered into previously dried and weighed platinum crucibles and the solutions evaporated to dryness in an oven held at 155-160°C. The crucibles containing the anhydrous salt were then reweighed and the concentration was determined.

Cerium (IV) in sulfuric acid was used to determine uranium (IV). The solutions were prepared from ammonium hexanitratocerate (IV) (G. Frederick Smith Chemical Co. - Reagent Grade) and analyzed as described by Leininger and Stone.[45] The standarization utilized arsenic (III) oxide as the primary standard. Osmium (VIII) oxide was the catalyst for the reaction and the endpoint was indicated by Ferroin (G. Frederick Smith Chemical Company). No change in the titer of the standard cerium (IV) solution was noted during an interval of one year.

Uranium (IV) analyses were originally attempted using the method of Willard and Young[46] but unsatisfactory results were obtained. The reaction between cerium (IV) and uranium (IV) is slow and solutions must be heated for the titration. However, since the reaction between cerium (IV) and iron (II) is rapid[47] and uranium (IV) is quickly oxidized by iron (III) according to the following equation

$$(50) \quad U^{+4} + 2Fe^{+3} + 2H_2O \longrightarrow UO_2^{++} + 2Fe^{++} + 4H^+$$

with one equivalent of iron (II) produced for each equivalent of uranium (IV) oxidized, the iron (II) released in the reaction can then be titrated with the standard cerium (IV).

The procedure used was as follows. Samples of uranium (IV) ranging from 0.5 ml to 2.0 ml, depending on the concentration of the stock solution, were treated with 1.0 or 2.0 ml of a 2% solution of iron (III) chloride (depending on the concentration of the uranium (IV)). To this was added 2 ml of a solution made by diluting 25 ml of concentrated sulfuric acid with 100 ml of deionized water. This step is taken to make certain the cerium (IV) will remain in a sulfate solution since the potential for the reduction of cerium (IV) to cerium (III) depends on the medium.[48] The solution was next diluted with 20 ml of water and two drops of the iron (II)-o-phenathroline complex (Ferroin) added. The solution was now titrated at room temperature with the standard cerium (IV), the endpoint being indicated by the color change from red-orange to pale blue which occurs when the Ferroin is oxidized to a complex containing iron (III). An indicator blank was run.

Uranium (VI) was the only other oxidation state present in the uranium (IV) stock solutions. Any uranium (III) formed was removed immediately after the electrolysis and any uranium (V) disproportionated[49] under these conditions.

The total uranium content was determined by pouring the same size sample through a Jones reductor[50] with 5 ml of a 1:9 concentrated sulfuric acid-water solution and washing with two 10 ml portions of deionized water. Air was bubbled through this solution for two minutes to oxidize any uranium (III) formed to uranium (IV). The reduced solution was then titrated as before except no dilution was necessary. The uranium (VI) concentration in the stock can be found by difference.

The total hydrogen ion content, (H_t^+), of the stock solutions was determined by passing an aliquot (usually 0.5 to 1.0 ml) through a

column of Dowex 50W-X12 ion exchange resin (Baker's Analyzed Reagent, 100-200 mesh, hydrogen form). Uranium (IV) attaches itself to the column, releasing four moles of hydrogen ion for each mole of uranium (IV).[38] The column is eluted with fifteen milliliters of deionized water and the eluant titrated with standard base. The free hydrogen ion concentration, (H_0^+), in the stock solution can be calculated by the equation:

$$(51) \qquad H_0^+ = H_t^+ - 4C_4 - 2C_6$$

where C_4 is the concentration of uranium (IV) and C_6 is the concentration of uranium (VI) in moles per liter.

It should be noted here that although all of the uranium (VI) was reduced in the electrolysis to produce uranium (IV) and the uranium (IV) was stored in a closed flask under an inert atmosphere, small amounts of the uranium (IV) appeared to be oxidized over a period of time, as illustrated in Table III.

Table III. Oxidation of uranium stock solutions

Date	Elapsed Time	$[H^+]$	U(IV)	U(VI)
5/24/63	-------	0.842 N	0.368_6 N	0.000 N
6/3/63	10 days	-------	0.364_2 N	0.002_5 N
6/27/63	34 days	0.892 N	0.353_3 N	0.016_0 N
7/11/63	48 days	0.910 N	0.341_2 N	0.027_8 N
8/25/63	93 days	1.123 N	0.233_4 N	0.135_6 N

Since the half-reaction for the oxidation of uranium (IV) is

$$(52) \qquad U^{+4} + 2H_2O \rightleftharpoons UO_2^{++} + 4H^+ + 2\,e^-$$

it can be seen that the hydrogen ion concentration will increase more rapidly than the uranium (VI) concentration. Because of these changes in titer all uranium (IV) solutions were restandardized before a series of runs was made, if more than four days had elapsed since the last restandardization.

Stock solutions of uranium (VI) were analyzed for uranium in the same manner as the total uranium content of the uranium (IV) stocks was determined. The free hydrogen ion content was also determined in the same manner.

Kinetic Studies

This section describes the steps involved in following an exchange reaction using the normal procedure. Earlier work utilizing another method is presented in Appendix A.

The exchange experiments were carried out at a molar ionic strength of 2.00 in 100 ml flasks which had been blackened by dipping them first in X-I-M bonding material (H. Forsberg Company) and then in black enamel paint. The flasks were cleaned by allowing aqua regia to stand in them overnight after which they were thoroughly rinsed and dried. The rinsing process included a minimum of six washings with distilled water followed by a minimum of six more with deionized water. Since the reactions are very slow, the solutions were protected from the atmosphere by nitrogen.

A 14/35 standard taper joint was fitted with 6 mm inlet and outlet tubes as shown in Figure 3. The vertical tubing served as the nitrogen inlet and the horizontal tubing acted as the outlet to the next inlet

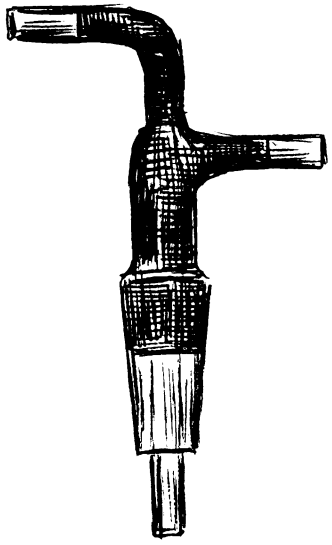

Figure 3

tube. Eleven flasks were mounted in a constant temperature bath with these special adapters in series as tops. The flasks were flushed before use by maintaining a rapid nitrogen flow overnight. Experiments carried out with a positive nitrogen pressure above the solutions were studied for a period of four weeks without detectable loss of uranium (IV).

The exchange solutions were prepared by combining the required amounts of water, sodium perchlorate, perchloric acid, tartaric acid and uranium (VI) perchlorate in that order in a 150 ml beaker. Then the proper amount of uranium (IV) perchlorate stock was added, the resulting solution mixed with a stirring rod, and then poured into one of the previously flushed flasks while a slow flow of nitrogen was maintained.

Earlier results indicated that the experiments would have to be carried out at conditions where the hydrogen ion concentration would be 1.0 M. Although the amount of hydrolysis of both uranium species is low at these conditions, stock solutions of uranium (IV) and uranium (VI) were made up with free hydrogen ion concentrations near 1.0 M. This minimized any change from the calculated hydrogen ion concentration by hydrolysis changes which might occur when the stock solutions were mixed.

The total mixing process required a maximum of fifteen minutes. Of this time the uranium (IV) was exposed to the atmosphere for a maximum of two minutes although Lundell and Knowles[51] note that solutions of uranium (IV) undergo no change in titer on exposure to the atmosphere

for one half hour.

For reactions carried out above room temperature the procedure was altered in the following manner. The uranium (IV) was withdrawn and added directly to the reaction flask. The solution made up of the other reagents was stored in a clean flask in another part of the bath. After a lapse of four hours to allow the contents of each flask to attain the bath temperature, the contents of the flask containing the uranium (VI) were poured into the reaction flask, the protective top replaced, and the flask agitated vigorously to complete mixing.

Separation Procedure

The separation procedure used was adapted from that described by Masters and Schwartz.[28] Five milliliter aliquots of the reaction solution were withdrawn from the reaction flask and delivered into five milliliters of a 0.1 M solution of 4,4,4-trifluoro-1, (2 thienyl) -1,3-butanedione (hereafter called thenoyltrifluoroacetone) in benzene contained in a 25 ml separatory funnel. The separatory funnel was shaken vigorously for one and one half minutes and the lower layer drawn off. The uranium (IV) was extracted into the benzene layer as a complex containing four moles of the thenoyltrifluoroacetonate anion.

$$(53) \qquad U^{+4} + 4\,HTTA \rightleftharpoons U(TTA)_4 + 4H^+$$

Five milliliters of a 0.5 M perchloric acid solution was added and the funnel shaken vigorously for another one half minute. The lower layer was drawn off again and discarded. The uranium (IV) was then re-extracted into the aqueous phase by shaking it vigorously with 5 ml of 3.0 M hydrochloric acid for one and a half minutes. The uranium (IV)

is extracted as a chloro complex into the acid solution. The five milliliters of aqueous solution was drawn off into a twenty milliliter beaker for sampling.

The thenoyltrifluoroacetone (Columbia Southern Chemical Company) was purified by sublimation in a vacuum of approximately one millimeter at room temperature. The purified product was dissolved in benzene (C.P. grade) to prepare the solution used for the extraction. One molar perchloric acid, 0.5 M perchloric acid, and 3.0 M hydrochloric acid were prepared by adding the calculated amount of the concentrated reagent (perchloric acid - Baker's Analyzed Reagent and G. Frederick Smith Chemical Company Reagent; hydrochloric acid - Baker's Analyzed Reagent and E.I. Du Pont de Nemours Reagent) to deionized water.

The time of each separation was taken as the time when the sample was delivered into the separatory funnel. Since the reactions were slow, the time was read to the nearest minute from an electric clock. For convenience, zero time for a reaction was taken as the time when the first sample was removed.

Handling of the Sample

Three 0.5 ml aliquots of the uranium (IV) in 3.0 M hydrochloric acid were withdrawn and were placed on three separate 25 mm watchglasses. Since this was near the capacity of the watch glasses, the edge of each watchglass was ringed with a line drawn with a grease pencil that prevented the solution from creeping over the edge of the watchglass.

Each set of three samples was heated to dryness under an infrared

lamp and transferred to a muffle furnace. When the samples had been heated to a temperature of 500 to 550°C, they were cooled and removed from the oven. This treatment converted the samples to orange uranium (VI) oxide.

The above preparation of the triplicate counting samples gave a uniform deposit of uranium (VI) oxide over the surface of the watchglass since evaporation was rapid. This prevented a large build-up of sample in the center of the watchglass and thus helped to lower the amount of self absorption of the α-rays emitted. The triplicate samples were always very similar in appearance. Since there were only small variations in the amount of uranium (IV) extracted for each separation during a run, the difference in self-absorption from separation to separation was negligible.

The samples were counted for alpha activity in the proportional region using a windowless preflush flow counter (Radiation Instrument Development Laboratory - Model 2-7) with external pre-amplifier and a glow tube scaler (Baird-Atomic, Inc. - Model 131A). A 90% argon and 10% methane gas mixture (The Matheson Company) was used. If the observation time, t, is short compared to the half-life of the isotope,[52] then the standard deviation is given by

$$(54) \qquad s = \sqrt{M}$$

where M is the average number of atoms disintegrating in the time, t. If a reasonably large number, m, of counts has been obtained, that number, m, may be used in the place of M for the purpose of evaluating s. The counting rate R is given by

$$(55) \qquad R = m/t$$

and the standard deviation of the rate is given by

$$(56) \qquad s_R = (m)^{1/2}/t$$

Five or ten minute intervals were usually sufficient to reduce s_R to about 2% of the rate, R.

The uranium (IV) in hydrochloric acid solution that remained after the counting samples were withdrawn was used to determine the concentration of the solution. The sample was placed in a one centimeter quartz cell and the absorbance measured at a wavelength of 650 mμ, using a Beckmann DU spectrophotometer. Solutions of uranium (IV) in hydrochloric acid obey Beer's law and have a molar absorptivity of about 58 $M^{-1}cm^{-1}$. Therefore, the concentration of the solution can be determined from the following relationship:

$$(57) \qquad C = A/\epsilon 1$$

Where A is the measured absorbance, ϵ is the molar absorptivity, C is the concentration of the solution in moles per liter, and 1 is the path length of the cell used.

Infinite time or complete exchange samples were prepared by taking advantage of the fact that the specific activity is the same in both oxidation states when the exchange is complete.[53] An "H" cell was prepared by connecting two six inch test tubes by a length of ten millimeter tubing that contained a coarse frit. Into one side of the cell was placed an appropriate amount of concentrated perchloric acid and deionized water to make 6 or 7 ml of a solution that was 2.5 to 3.0 M in hydrogen ion. One milliliter of concentrated perchloric acid was placed in the other side of the cell and to this was added a 5.0 ml aliquot of

the exchange solution. Electrolyses were carried out at one half ampere for 60-75 minutes using a platinum square for the anode and a carbon rod for the cathode. The solution produced, which contained all of the uranium as uranium (IV), was separated and treated as above.

Miscellaneous Experiments

Initially the attempt was made to study the exchange reaction using a separation technique described by Rona.[26] This technique separated uranium (IV) from uranium (VI) by precipitating it as uranium (IV) fluoride.

It was soon discovered that a separation by this means gave erratic and unreproducible results. Attempts were made to improve the results using thorium (IV) as a carrier in the precipitation since the solutions were not very concentrated in uranium (IV). This gave no increase in the efficiency of the separation and still gave erratic results as well.

In addition the hydrofluoric acid used attacked the volumetric ware and thus required the use of constant calibrations. The extraction method of separation was successful.

The geometry of the flow counter was determined by doing a standard separation on a known sample which contained only natural uranium (IV) and counting aliquots from this separation. Calculations indicated that the geometry was 85.6%. This high value is probably due to a large amount of back-scattering.

The spectra of the uranium (IV) and uranium (VI) stocks were determined on the Beckmann DK-2 spectrophotometer and were found to agree with those reported in the literature.[54] Samples from several kinetic

runs where the tartaric acid concentration was varied were also measured, but no evidence for any complex formation could be observed.

It was observed that solutions made up for kinetic studies would often form a white to pale gray precipitate if tartaric acid was present. The stability of such solutions depended on the relative concentrations of the uranium (IV), free acid, and tartaric acid present. For example, when $[U^{+4}]$ = 0.025 M, $[UO_2^{++}]$ = 0.0274 M, $[H_2Tar]$ = 0.260 M, $[H^+]$ = 1.00 M, and I = 2.00, a stable solution results. If the concentration of uranium (IV) or tartaric acid is increased or the amount of free acid decreased, precipitation occurs immediately. The precipitate slowly dissolves on the addition of perchloric acid to give a stable solution.

With maleic, malonic, or malic acids, it is found that when other conditions are as above the $[H^+]$ can be lowered to 0.27 M without any precipitation occurring.

Two experiments were carried out in which solutions in clear flasks at 25°C were subjected to the light emitted from a 250 W ultraviolet lamp (Kenmore; Sears, Roebuck, and Company). It was found that a solution containing $[U^{+4}]$ = 0.025 M, $[UO_2^{++}]$ = 0.0274 M, and $[H^+]$ = 1.00 M with I = 2.00 exhibited a half-time for exchange of only 750 minutes while a similar solution without light would be expected to have a half-time of exchange of 7.8×10^5 min. A similar solution 0.130 M in tartaric acid was found to have a shorter half-time of 100 minutes compared to 2.4×10^4 minutes without the influence of light.

RESULTS

From the triplicate counting samples and their corresponding absorbance values, specific activity values (hereafter designated by the symbol S) were obtained. These were corrected for the radioactive ^{238}U present by subtracting the specific activity of a sample made up without any added ^{233}U. This simple correction was valid since the maximum amount of ^{233}U present was 2% of the total uranium and the half-life of ^{238}U is 28,000 times that of ^{233}U.

Calculations were carried out by means of a program written for and executed by a Control Data Corporation 160-A computer. A print-out of the program, including the input for an experiment, is shown in Appendix B. In addition a reproduction of the results from the calculations performed on the data is duplicated on the next page of Appendix B.

The fraction of exchange (F) was calculated from the following relation

$$F = \frac{S - S_0}{S_\infty - S_0} \tag{34}$$

For convenience the first sample was taken as the zero time sample and its activity was used for S_0. The specific activity of a sample that had been electrolyzed for an hour was taken as S_∞, which is possible because the specific activity of either oxidation state is the same at infinite time. The samples which determine S are taken as a function of time.

The McKay equation is written in the form of the equation of a straight line

$$(58) \qquad Y = K' x + P$$

where K', the slope, has the value -R/ab (a+b), P, the intercept, is given by ln 100, y is the value of ln (100-100F) and x is the elapsed time, t. Since the most probable slope of such a straight line is given by a least squares treatment,[57] this calculation was performed on all data using the equations

$$(59) \qquad K' = \frac{n\sum xy - \sum x \sum y}{n\sum x^2 - (\sum x)^2}$$

$$(60) \qquad P = \frac{\sum x^2 \sum y - \sum x \sum xy}{n\sum x^2 - (\sum x)^2}$$

where n is the number of values of x and y.

The standard deviations of the results were then calculated by the treatment in Youden.[58] In this treatment it has been assumed that the values of x are known with negligible error compared with the values of y, a valid assumption, because the reactions are slow, and thus there is relatively little error in measuring time.

If this treatment is used, an estimate of the standard deviation of a single y measurement (s) is given by

$$(61) \qquad (n-2)s^2 = y^2 - \frac{(\sum y)^2}{n} - \frac{1}{n}\frac{(n\sum xy - \sum xy)^2}{n\sum x^2 - (\sum x)^2}$$

The quantity (n-2) is used instead of (n-1) since the data were used to estimate K' as well as least squared values of y.

The data were tested for the rejection of points in the following manner. Least squared values of y (labelled Y) were calculated for each value of x. The absolute value of the difference between this value and the experimental value (y) was then determined. Any

experimental value which did not fit the following test

$$(62) \qquad \left|Y - y\right| \leq 3s$$

was rejected.

The standard deviations of the slope ($s_{K'}$) and the intercept (s_P) were then calculated by means of the following equations:

$$(63) \qquad s^2_{K'} = \frac{ns^2}{n\sum x^2 - (\sum x)^2}$$

and

$$(64) \qquad s^2_P = \frac{s^2\sum x^2}{n\sum x^2 - (\sum x)^2}$$

The standard deviation of the intercept showed that there was no evidence of induced exchange by the separation method, since all values for the intercept from the least squares treatment were within ± 2% of the theoretical value. The standard deviation in the slope is used in determining the standard deviation of the rate. Since

$$(65) \qquad R = (-K') \frac{ab}{a+b}$$

then

$$(66) \qquad s_R = s_{K'} \frac{ab}{a+b}$$

A survey of the effects of several organic acids on the exchange reaction was carried out. Figure 4 shows some typical graphs of ln(100-100F) against t for different acids. Since the rate of the reaction at these conditions without any added organic acid was too slow to measure conveniently, it was estimated by extrapolation of Rona's data. It can be seen that tartaric acid has the greatest accelerative effect on the reaction. Maleic and malic acids have a similar

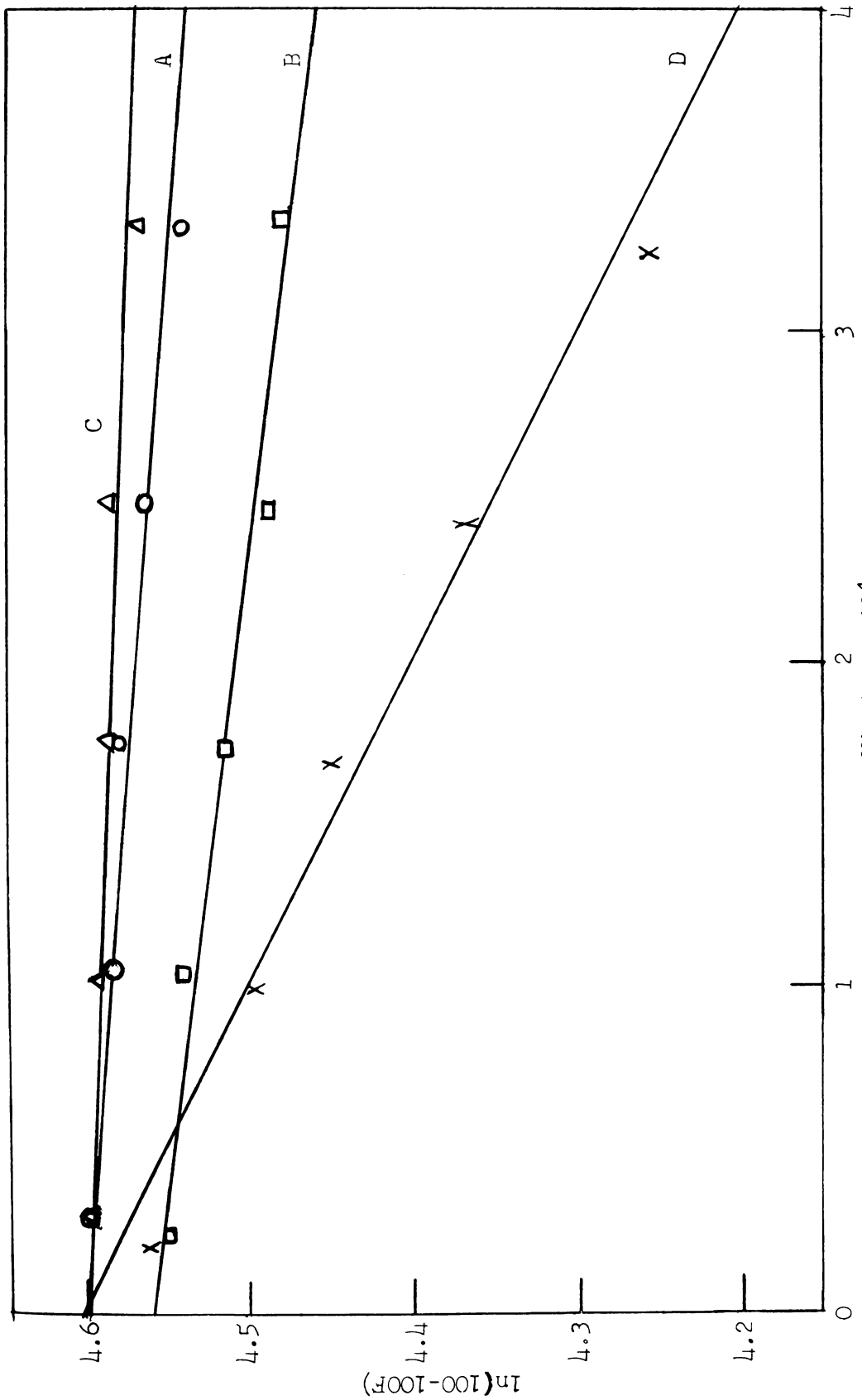

Figure 4. Typical rate data for different organic acids.
0.0250 M U(IV), 0.0274 M U(VI), 1.76 M H^+, I = 2.00, T = 25.0°C
(A) 0.130 M Maleic acid
(B) 0.130 M Malic acid
(C) 0.130 M Malonic acid
(D) 0.130 M Tartaric acid

effect on the rate while malonic acid has little effect on the reaction. Table IV shows the calculated half-times for these reactions.

The stability of the solutions containing the organic acids was studied further. It was found that solutions that were 0.0250 M in U(IV), 0.0274 M in U(VI), and 0.013 M in organic acid were stable down to hydrogen ion concentrations of 0.708 M for tartaric acid and to 0.270 M for the others. At these limits the effect due to tartaric acid was still greater than the others. Therefore, a more detailed study of the reaction in the presence of tartaric acid was carried out. These studies were conducted at a hydrogen ion concentration of 1.00 M so that the tartaric acid concentration could be studied over a moderate range.

Table IV. Effect of various organic acids on the exchange rate.

Uranium (IV) perchlorate = 0.0250 M, Uranium (VI) perchlorate = 0.0274 M, Perchloric acid = 1.76 M, Organic acid = 0.130 M, Ionic strength = 2.00, Temperature = 25.0°C.

Organic Acid	Rate $M\ min^{-1}$	$T_{1/2}$ min
None*	1.93×10^{-9}	4.68×10^{6}
malonic	8.46×10^{-9}	1.07×10^{6}
maleic	2.24×10^{-8}	4.05×10^{5}
malic	3.32×10^{-8}	2.72×10^{5}
tartaric	1.29×10^{-7}	7.01×10^{4}

*Estimated value.

A log-log plot of the gross rate of exchange, from independent variation of uranium (IV) and uranium (VI) concentrations, exhibits the expected linear relationship in Figure 5. When the uranium (IV) concentration was varied while the uranium (VI) concentration was held constant, it was found that the order with respect to uranium (IV) was 1.3 ± 0.1. The maximum concentration of uranium (IV) that could be used in these studies was 0.040 M; above that concentration precipitation occurred in a short time. The lower limit was governed by the slowness of the reaction at reduced uranium (IV) concentrations. Constant values of uranium (IV) concentration and variation of uranium (VI) concentration resulted in an order with respect to uranium (VI) of 0.47 ± 0.07. These data are summarized in Table V.

The effect of hydrogen ion on the exchange was evaluated over the range from 0.80 M to 1.25 M. These data, summarized in Table VI and graphed in Figure 6, show that the order with respect to hydrogen ion is -2.9 ± 0.2. Here again, the narrow range of the investigation was dictated by the precipitation that occurred in solutions with hydrogen ion concentrations less than 0.80 M. Because of the higher order dependence on hydrogen ion concentration, the rate becomes too slow to measure conveniently above 1.25 M.

Two different investigations of the effect of varying the concentration of tartaric acid on the rate were carried out. One investigation was carried out using solutions made up in the normal manner as described in the experimental section. These data gave an order with respect to tartaric acid concentration of 0.89 ± 0.11. They are reported in Table VII. Another series of experiments carried out with

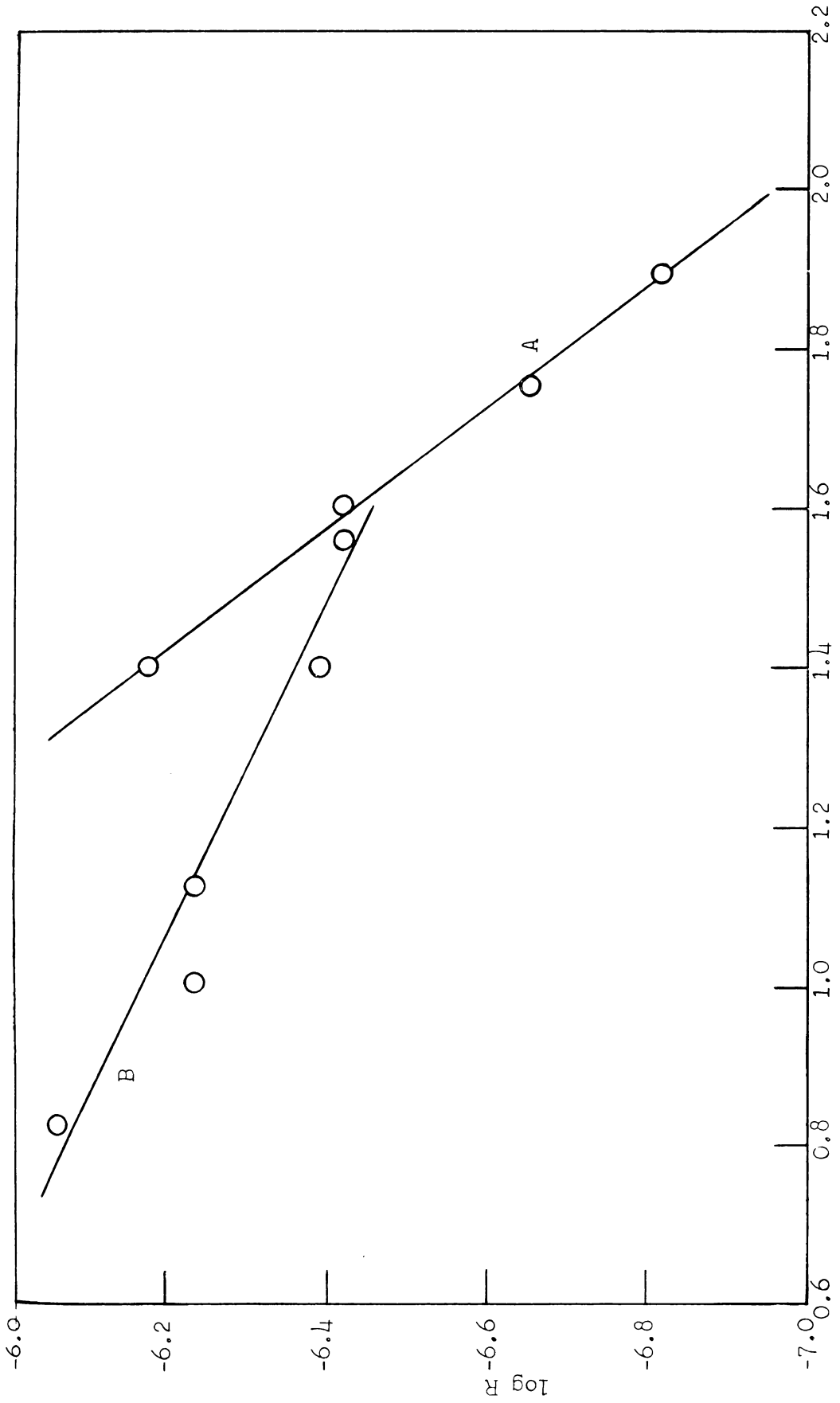

Figure 5. Log R vs log of concentration of U(IV) and U(VI).
1.00 M H^+, 0.130 M Tartaric acid, I = 2.00, T = 25.0°C
(A) U(IV) varied; 0.0274 M U(VI)
(B) 0.0250 M U(IV); U(VI) varied

Table V. Dependence of exchange rate on concentration of uranium (IV) and uranium (VI).

Perchloric acid = 1.00 M, Tartaric acid = 0.130 M, Ionic strength = 2.00, Temperature = 25.0°C.

[U(IV)] M	[U(VI)] M	$R \times 10^7$ (calc) M min^{-1}	$R \times 10^7$ (obs) M min^{-1}
0.0120	0.0274	1.68	1.51
0.0178	0.0274	2.51	2.13
0.0250	0.0274	3.55	3.82
0.0400	0.0274	5.77	6.68
0.0250	0.0274	3.55	3.82
0.0250	0.0400	4.08	4.07
0.0250	0.0750	5.58	5.93
0.0250	0.100	6.65	5.90
0.0250	0.150	8.80	8.79

Table VI. Dependence of exchange rate on the concentration of hydrogen ion.

Uranium (IV) = 0.0250 M, Uranium (VI) = 0.0274 M, Tartaric acid = 0.130 M, Ionic strength = 2.00, Temperature = 25.0°C.

$[H^+]$ M	a_{H^+} M	$R \times 10^7$ (calc) M min^{-1}	$R \times 10^7$ (obs) M min^{-1}
0.800	0.846	5.62	8.22
0.900	0.964	4.40	4.94
1.00	1.08	3.55	3.82
1.12	1.23	2.79	2.84
1.25	1.38	2.25	2.19

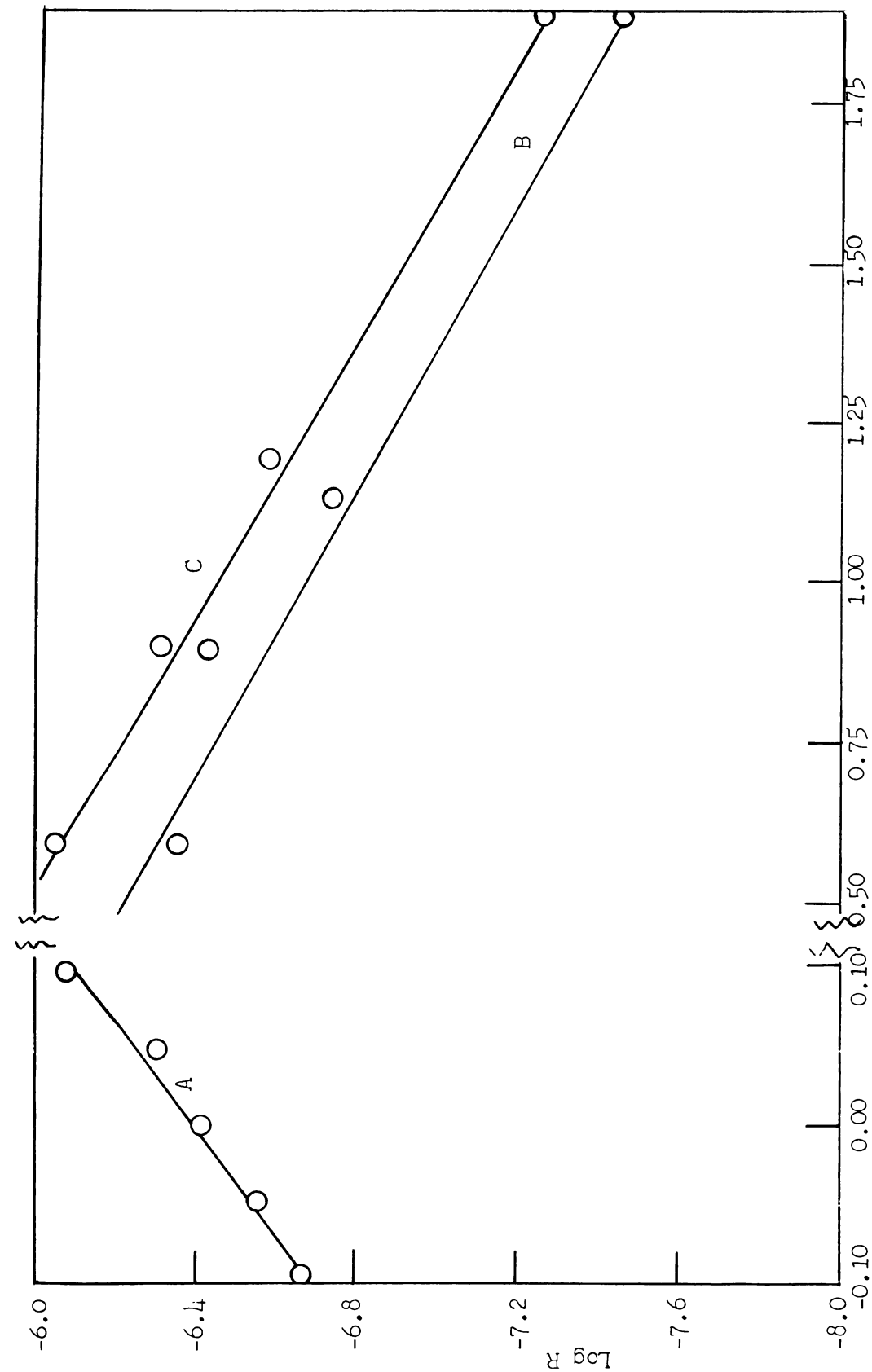

Figure 6. Log R vs log of concentration of hydrogen ion and tartaric acid.
0.0250 M U(IV), 0.0274 M U(VI), I = 2.00, T = 25.0°C
(A) H^+ varied; 0.130 M Tartaric acid
(B) and (C) 1.00 M H^+; Tartaric acid varied

solutions made up in the manner described in Appendix A gave an order of 0.90. Graphs of these data are also shown in Figure 6.

Table VII. Dependence of the exchange rate on the concentration of tartaric acid.

Uranium (IV) = 0.0250 M, Uranium (VI) = 0.0274 M, Perchloric acid = 1.00 M, Ionic strength = 2.00, Temperature = 25.0°C.

Tartaric Acid M	$R \times 10^7$ (calc) M min^{-1}	$R \times 10^7$ (obs) M min^{-1}
0.0130	0.442	0.364
0.0750	2.09	1.86
0.130	3.55	3.82
0.260	6.99	4.44

The effect of varying the ionic strength, I, is seen in the data reported in Table VIII. The data could not be extended to lower values of ionic strength at the conditions used.

Experiments were also carried out to measure the effect of temperature on the rate of the reaction. The data in Table IX indicate the marked increase of the rate with increasing temperature. Analysis of these data to determine activation energies could not be carried out due to the complexity of the reaction.

Table VIII. Dependence of exchange rate on the ionic strength.

Uranium (IV) = 0.0250 M, Uranium (VI) = 0.0274 M, Perchloric acid = 1.00 M, Tartaric acid = 0.130 M, Temperature = 25.0°C.

Ionic Strength	$R \times 10^7$ (obs) M min^{-1}
1.33	2.87
1.67	3.19
2.00	3.82

Table IX. Dependence of the exchange rate on temperature.

Uranium (IV) = 0.0250 M, Uranium (VI) = 0.0274 M, Perchloric acid = 1.00 M, Tartaric acid = 0.130 M, Ionic strength = 2.00

Temperature	$R \times 10^7$ (obs) M min^{-1}
25.0°C	3.82
32.0°C	8.40
39.8°C	25.7

DISCUSSION

Several experiments were first carried out on the uncatalyzed system in order to repeat some of the work of Rona.[26] In experiments where hydrogen ion was varied, the order was found to be -3.5 compared with Rona's value of -3.0. This difference may be reconciled partially by briefly examining the mechanism she reports. One of the important preliminary steps is the hydrolysis of uranium (IV). As equations (12) to (15) show, incorporation of this step in the mechanism predicts a negative second order dependence on hydrogen ion at low acidities and a negative fourth order at conditions of high acidity. Since the acid concentrations used in this work extended beyond the high acid end of the range used by Rona, a larger negative order might be expected.

In addition it should be noted that experiments carried out at conditions that were supposedly identical with Rona's gave rates higher than those she found. This increase in rate can be attributed to a difference between the hydrogen ion concentrations calculated from her pH measurements and the true hydrogen ion concentrations of her solutions.

Rona reported that pH measurements were made at the beginning and the end of each of her experiments. However, the pH measured probably varied from experiment to experiment since no attempt was made to control ionic strength during her studies. A calibration described in Appendix A and illustrated in Figure 7 shows the linear relation between true hydrogen ion concentration and measured pH at a high ionic

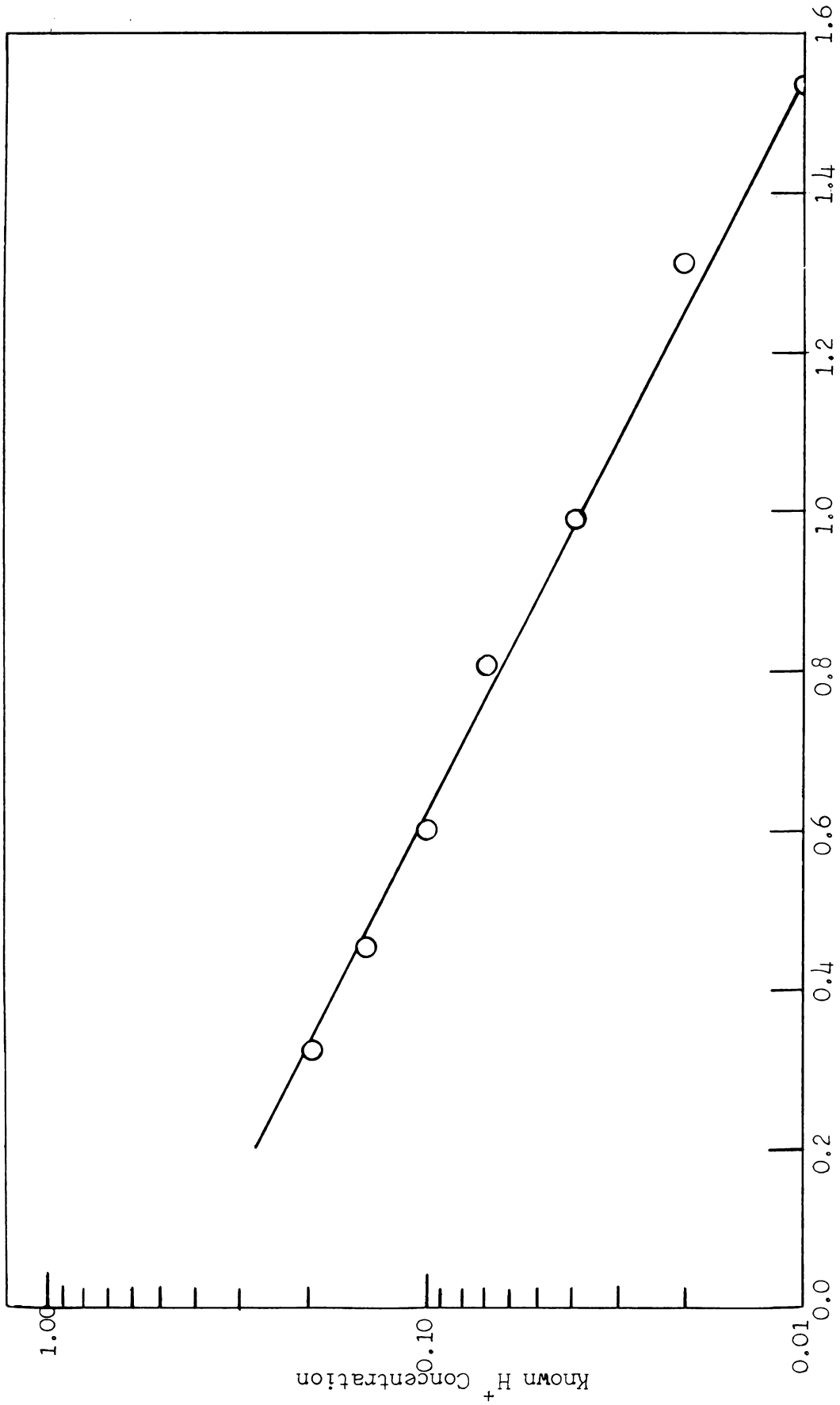

Figure 7. Known hydrogen ion concentration as a function of measured pH.

strength. The correction factor thus obtained will be a function of ionic strength.

The results of the two series of experiments, in which the tartaric acid concentration was varied, show the same disagreement in the value of the estimated hydrogen ion concentration. Line C of Figure 6 shows a log-log plot for exchange solutions made up by the method described in Appendix A. Graph B exhibits a similar result for a series of solutions made up in the standard manner. It can be seen that, although the order of the reaction with respect to tartaric acid concentration is the same, the absolute values of the slopes (K'), and therefore the rates, for reactions supposedly made up to the same conditions differ by a constant amount. This difference is undoubtedly due to the method used in making up the solutions. The method used in Appendix A is suspect since it involves a large increase in the hydrogen ion concentration after the pH measurement has been made. Dissociation of the tartaric acid which had occurred prior to this measurement would now be repressed. However, the primary effect is probably a decrease in the amount of hydrolysis of U^{+4}. These discrepancies support the idea that the solutions made up as described in the experimental section are close to the desired hydrogen ion concentration.

From the experimental results, the following rate law is established

$$(67) \qquad R = \frac{k' \, [U(IV)]^{1.3} \, [U(VI)]^{0.47} [H_2Tar]^{0.90}}{[H^+]^{2.9}}$$

The appearance of fractional orders in the expression suggests that more than one principal path is contributing to the overall observed rate.

The large, negative order for hydrogen ion concentration may be interpreted as a result of hydrolysis or ionization reactions.

A knowledge of the principal species in solution is necessary before a mechanism can be proposed. Since perchlorate is a very weak complexing anion,[59] its use as the anion in solution reduces the possibilities for complex species. Therefore, the main species in the solutions would be U^{+4}, UO_2^{++}, and undissociated tartaric acid.

There have been several studies on the hydrolysis of UO_2^{++} ion.[60, 61, 62, 63] Calculations from equilibria presented in these studies indicate that the main species found in the present experiments is UO_2^{++} with no more than 0.03% of the uranium(VI) present as the dimer, $(UO_2)_2(OH)_2^{+2}$.

Studies have also been made on the hydrolysis of U(IV).[30, 64, 65] Consideration of the equilibria presented show that U^{+4} is the principal species in the present studies. Less than 3% of the uranium(IV) is present as the hydrolyzed species, UOH^{+3}.

The other species present in the experimental rate law is tartaric acid. Consideration of its stepwise ionization constants show that unionized tartaric acid was the main species present in the exchange solutions with an upper limit of 0.3% of the tartaric acid present as the bitartrate ion.

A rate law which will fit the data obtained for this reaction will probably contain at least two terms since there are fractional orders observed. It seems quite likely that some contribution due to the uncatalyzed path postulated by Rona[26] will be present although the high acidity of the solutions relegate it to a minor contribution to the rate, since the concentration of the intermediate UOH^{+3} is minimal.

Extrapolation of Rona's data allows evaluation of the rate at $[H^+]$ = 1.00 M. Calculations based on her rate law at conditions of high acidity

$$(68) \qquad R = \frac{k_1[U^{+4}]^2[UO_2^{++}]}{[H^+]^4}$$

give a value of 5.7×10^{-4} moles^2 /l^2 - min. for k_1.

If a two term rate law such as

$$(69) \qquad R = \frac{k_1[U^{+4}]^2[UO_2^{++}]}{[H^+]^4} + \frac{k_2[U^{+4}][H_2Tar]}{[H^+]^2}$$

is fitted using the data from the experiments in which the concentration of tartaric acid is varied, then the rate law can be written as

$$(70) \qquad R = F + k_2C$$

and values of the constant k_2 determined. When k_2 is substituted in this equation, using the rest of the data, a poor fit is obtained when the data involving the variation of UO_2^{++} is tested. This indicated there is a path that is operative which involves both uranium(VI) and tartaric acid.

If this third path is taken into account, the rate law then becomes

$$(71) \qquad R = \frac{k_1[U^{+4}]^2[UO_2^{++}]}{[H^+]^4} + \frac{k_2[U^{+4}][H_2Tar]}{[H^+]^2} + \frac{k_3[U^{+4}][H_2Tar][UO_2^{++}]}{[H^+]^2}$$

which can be written

$$(72) \qquad R = F + k_2C + k_3C\,[UO_2^{++}]$$

where

$$(73) \qquad C = \frac{[U^{+4}][H_2Tar]}{[H^+]^2}$$

This can be rearranged to the form

$$(74) \qquad \frac{R-F}{C} = k_2 + k_3 [UO_2^{++}]$$

A graph of (R-F)/C vs $[UO_2^{++}]$ for the experiments where the UO_2^{++} concentration was varied should give a straight line if this equation is followed. The result is shown in Figure 8. From the graph k_2 is estimated to be 7.3×10^{-5} and k_3 to be 1.21×10^{-3}. Rates calculated from this rate law show good agreement except for the one obtained at the lowest hydrogen ion concentration.

The second term of the proposed rate law is consistent with the mechanism

$$(75) \qquad U^{+4} + H_2Tar + 2H_2O \rightleftharpoons (A.C.)_{21}^{+2} + 2H^+$$

with a rate constant k_{21} for the forward step. The quantity $(A.C.)_{21}^{+2}$ represents the activated complex in the theory of absolute reaction rates[24] for the first mechanism proposed for the second term of the rate law. This step is followed by a rapid reaction with UO_2^{++}

$$(76) \qquad (A.C.)_{21}^{+2} + UO_2^{++} \longrightarrow \text{products}$$

In this case the rate is given by

$$(77) \qquad R'' = \frac{k_{21}[U^{+4}][H_2Tar]}{[H^+]^2}$$

Identical results are obtained by considering the following mechanism for the second term. The two equilibria

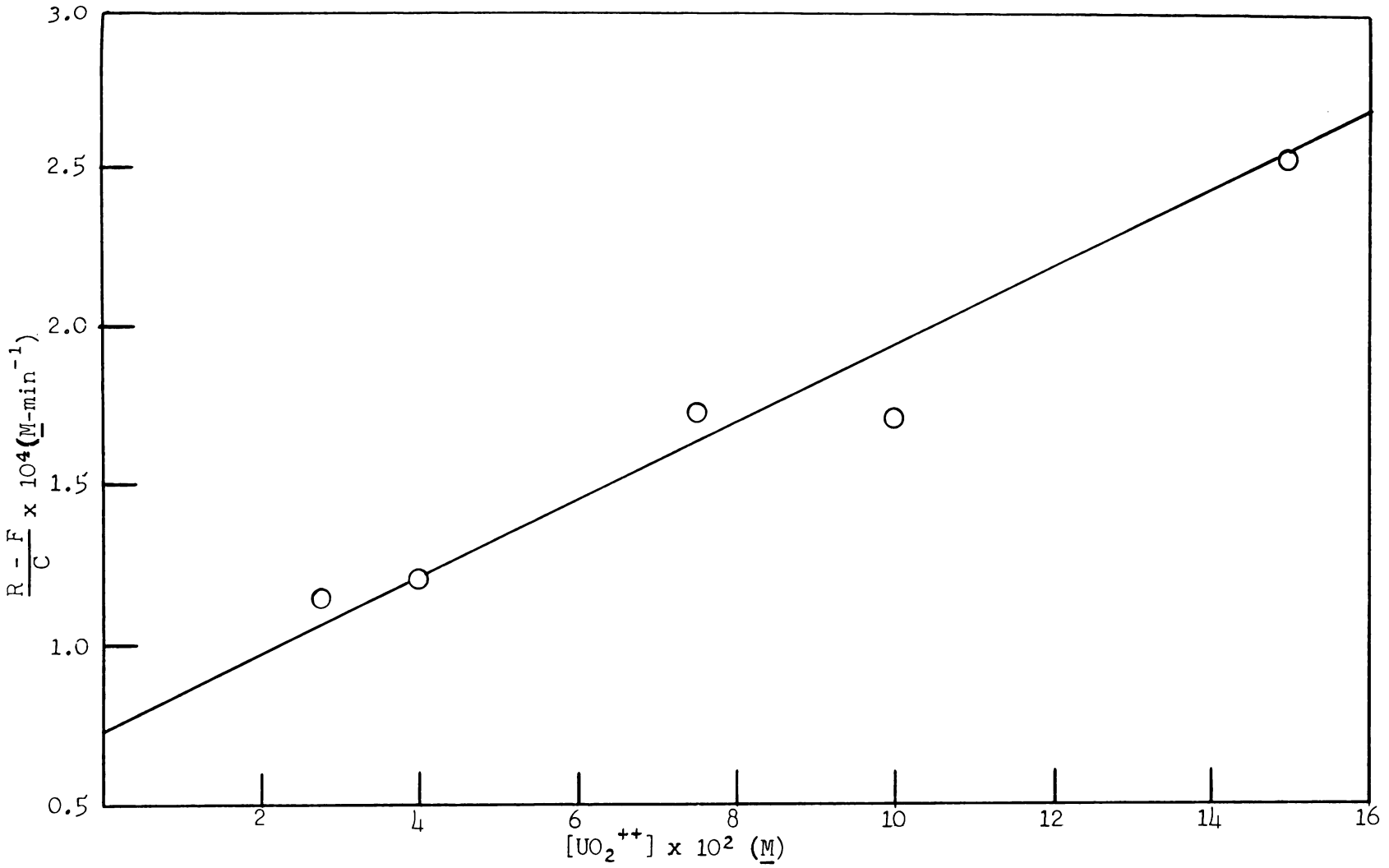

Figure 8. A function of R vs uranium(VI) concentration.

(12) $U^{+4} + H_2O \rightleftharpoons UOH^{+3} + H^+$

(78) $H_2Tar \rightleftharpoons HTar^- + H^+$

with equilibrium constants K_h and K_1 respectively would be present in the exchange solutions. The species formed in these equilibria would then react to form the activated complex

(79) $UOH^{+3} + HTar^- \longrightarrow (A.C.)_{22}^{+2}$

in the rate determining step with a rate constant k_{22} followed by a rapid reaction with UO_2^{++}

(80) $(A.C.)_{22}^{+2} + UO_2^{++} \longrightarrow$ products

Here the rate is given by

(81) $$R'' = \frac{k_{22}K_hK_1[U^{+4}][H_2Tar]}{[H^+]^2}$$

where the group of constants, $k_{22}K_hK_1$, is identical with k_2 of the equation (71)

A path also can be envisioned in which tartaric acid dissociates completely to form the tartrate ion

(82) $H_2Tar \rightleftharpoons HTar^- + H^+$

(83) $HTar^- \rightleftharpoons Tar^= + H^+$

with an equilibrium constant K_2 for reaction (83). The tartrate subsequently reacts with U^{+4} in a rate determining step

(84) $U^{+4} + Tar^= \longrightarrow (A.C.)_{23}^{+2}$

with a rate constant k_{23}, followed by a rapid reaction with UO_2^{++} to give products

(85) $(A.C.)_{23}^{+2} + UO_2^{++} \longrightarrow$ products

For this series of steps the rate would be given by

(86) $R'' = k_{23}\,[U^{+4}][Tar^{=}]$

which on inclusion of the two equilibria (78) and (83) gives for the rate expression

(87) $$R'' = \frac{k_{23}K_1K_2[U^{+4}][H_2Tar]}{[H^+]^2}$$

The third term could consist of the following sequence of reactions: First would be the formation of a uranium(IV) - tartaric acid (H_2Tar) complex

(88) $U^{+4} + H_2Tar \rightleftharpoons (U\cdot H_2Tar)^{+4}$

with an equilibrium constant K_{31}, followed by a rate determining step which forms the activated complex

(89) $(U\cdot H_2Tar)^{+4} + UO_2^{++} + 2H_2O \rightleftharpoons (A.C.)_{31}^{+4} + 2H^+$

which has a rate constant k_{31} for the forward reaction. The activated complex formed then rapidly breaks down into products

(90) $(A.C.)_{31}^{+4} \longrightarrow$ products

The rate for this mechanism is given by

(91) $$R''' = \frac{k_{31}[(U\cdot H_2Tar)^{+4}][UO_2^{++}]}{[H^+]^2}$$

If the equilibrium (88) is included, the expression becomes

(92) $$R''' = \frac{k_{31}K_{31}[U^{+4}][H_2Tar][UO_2^{++}]}{[H^+]^2}$$

Alternatively the third term could be formulated by the consideration of the equilibria shown in equations (12) and (78) followed by the reaction

$$(93) \qquad UOH^{+3} + HTar^{-} \rightleftharpoons [(UOH)\cdot(HTar)]^{+2}$$

with an equilibrium constant K_{32}. This step would be followed by reaction with UO_2^{++} in a rate determining step

$$(94) \qquad [(UOH)\cdot(HTar)]^{+2} + UO_2^{++} \longrightarrow (A.C.)_{32}^{+4}$$

with a rate constant k_{32} to give the activated complex which would rapidly break up into products.

The overall rate law given by this sequence of reactions would be

$$(95) \qquad R''' = \frac{k_{32}K_{32}K_hK_1[U^{+4}][H_2Tar][UO_2^{++}]}{[H^+]^2}$$

Here again a third path which involves the tartrate anion is possible. An equilibrium forming an uranium(IV) - tartrate complex

$$(96) \qquad U^{+4} + Tar^{=} \rightleftharpoons [U\cdot Tar]^{+2}$$

with an equilibrium constant K_{33} can occur. This complex reacts with UO_2^{++} in a rate determining step

$$(97) \qquad [U\cdot Tar]^{+2} + UO_2^{++} \longrightarrow (A.C.)_{33}^{+4}$$

with a rate constant k_{33}. This activated complex then breaks down to form products. Incorporating the preliminary steps gives as a rate expression for this path

$$(98) \qquad R''' = \frac{k_{33}K_1K_2K_{33}[U^{+4}][H_2Tar][UO_2^{++}]}{[H^+]^2}$$

The overall rate is then given by the sum of the rate for the uncatalyzed path (F) and the rates calculated from the mechanism chosen for the two separate paths which involve tartaric acid

$$R = F + R'' + R''' \qquad (99)$$

The three alternative mechanisms presented for each path are kinetically indistinguishable and thus it is difficult to choose one over the others.

There is some qualitative evidence that the first mechanism for both paths is favored from the data on dependence of the rate on ionic strength. The Bronsted equation[68]

$$\log k = G + 1.018\, z_A z_B\, I^{1/2} \qquad (100)$$

with G a constant, z_A and z_B the ionic charges of the species forming the activated complex, and I the ionic strength, predicts the rate constant, k, will increase with increasing ionic strength, if the species A and B combining to form the activated complex have a charge of the same sign. Although each rate constant postulated was not determined at different ionic strengths, the increase of the overall rate of exchange with increasing ionic strength as shown in Table VIII does suggest a positive primary salt effect. However, at the high ionic strengths employed, it is also doubtful that (100) applies.

There is an objection to the first mechanism presented for both steps involving tartaric acid. Rather than a slow, rate determining step followed by fast breakup into products, the mechanism must account for the inverse hydrogen ion dependence by use of an equilibrium in the rate determining step for formation of the activated complex. For the reverse of this step to occur requires a termolecular step. Since no

prior equilibria occur, this reverse step must be of some importance since a low rate is observed. Such a reaction in solution is not too likely.

The mechanism involving the tartrate anion is less likely than one involving only bitartrate because of the strongly acidic solutions used. While only a small amount of bitartrate may be present, there will be even less tartrate since formation of the bitartrate must occur first. The small quantities of these reactive species could lead to the overall slowness of the rate. Even so, a path involving tartrate could still be kinetically important.

The mechanism involving a hydrolysis step seems most likely. Although the equilibria shown in equations (12) and (78) are suppressed to some extent by the acidity of the solutions, the other steps leading to the activated complexes occur readily.

The calculated rates of exchange fit well with the observed rates in all but a few cases. It should be noted that the three values which fit the least closely are for the three points where the data was obtained near the limit of the experimental range. These are the points obtained with high tartaric acid concentration, high uranium(IV) concentration, and low hydrogen ion concentration. In all experiments where attempts were made to extend the range studied, some precipitation occurred. There is, then, the possibility that the solutions at these conditions were not truly stable but were slowly transforming to some other metastable condition prior to precipitation.

Because the rate law did not fit the experimental rate exactly, for the experiment where the hydrogen ion concentration was the lowest,

an attempt was made to calculate the rate using estimated hydrogen ion activities since the activity coefficient for perchloric acid could vary even though the ionic strength is kept constant. Activity coefficients for perchloric acid in sodium perchlorate were estimated using Harned's rule[68] which states the logarithm of the activity coefficient of one electrolyte in a mixture of constant total molality is directly proportional to the molality of the other component. This estimation was made using Guggenheim's treatment,[69] and variations in activity coefficients were seen to be small. It was found that rate constants calculated using those "activities" fit no better than those determined from concentrations. It is probable that the calculated "activities" are no better a measure of the actual activities than are the concentrations.

In addition to the mechanism proposed one might expect a path involving UO_2^+ as an intermediate species. In the absence of light this is not likely, since solutions having a moderate concentration of UO_2^+ are only obtained near pH 2.0-2.5. The rate constant, k_3, for disproportionation of UO_2^+ has been measured by Kern and Orleman[70] at a_{H^+} = 1.0 and I = 0.4

$$(101) \qquad 2UO_2^+ + 4H^+ \underset{k_4}{\overset{k_3}{\rightleftharpoons}} U^{+4} + UO_2^{++} + 2H_2O$$

k_3 was found to be 7.3×10^3 1 mole^{-1} min^{-1} indicating little UO_2^+ would be found.

The tremendous effect of light on the system is difficult to explain. Rona observed no effect due to light and one would expect the same result in perchlorate solutions. At the present one can only explain this observation in terms of a more favored path involving UO_2^+ even though acid conditions are used. When solutions containing tartaric

acid are irradiated the rate is even higher, indicating that some activated species containing UO_2^{++} and tartaric acid may be formed which greatly accelerates the reaction. Uranium(VI) is known to be photochemically active in the presence of many organic acids.[71]

SUMMARY

The effect of several organic acids on the exchange reaction between uranium(IV) and uranium(VI) in aqueous perchloric acid was studied. The catalytic effect of these acids was found to increase in the order malonic acid < maleic acid< malic acid << tartaric acid.

More detailed studies of the reaction in the presence of tartaric acid revealed that the order of the reaction is 1.3 with respect to uranium (IV) and 0.47 with respect to uranium(VI). The exchange is 0.90 order with respect to tartaric acid and hydrogen ion has an order of -2.9.

The predominant uranium species in solution are U^{+4} and UO_2^{++}. The following three paths for exchange

$$U^{+4} + H_2O \rightleftharpoons UOH^{+3} + H^+ \qquad \text{(fast)}$$

$$UOH^{+3} + UO_2^{+2} \rightleftharpoons Y^{+3} + 2H^+ \qquad \text{(fast)}$$

$$Y^{+3} + UOH^{+3} \rightleftharpoons Z^{+6} \qquad \text{(rate-determining)}$$

and

$$U^{+4} + H_2O \rightleftharpoons UOH^{+3} + H^+ \qquad \text{(fast)}$$

$$H_2Tar \rightleftharpoons HTar^- + H^+ \qquad \text{(fast)}$$

$$UOH^{+3} + HTar^- \longrightarrow (A.C.)_{22}^{+2} \qquad \text{(rate-determining)}$$

$$(A.C.)_{22}^{+2} + UO_2^{++} \longrightarrow \text{products} \qquad \text{(fast)}$$

and

$$U^{+4} + H_2O \rightleftharpoons UOH^{+3} + H^+ \qquad \text{(fast)}$$

$$H_2Tar \rightleftharpoons HTar^- + H^+ \qquad \text{(fast)}$$

$$UOH^{+3} + HTar^- \rightleftharpoons [(UOH)\cdot(HTar)]^{+2} \qquad \text{(fast)}$$

$$[(UOH)\cdot(HTar)]^{+2} + UO_2^{++} \longrightarrow (A.C.)_{32}^{+4} \qquad \text{(rate-determining)}$$

$$(A.C.)_{32}^{+4} \longrightarrow \text{products} \qquad \text{(fast)}$$

combine to give an expression for the overall rate

$$R = \frac{5.7 \times 10^{-4}[U^{+4}]^2[UO_2^{++}]}{[H^+]^4} + \frac{7.3 \times 10^{-5}[U^{+4}][H_2Tar]}{[H^+]^2}$$

$$+ \frac{1.2 \times 10^{-3}[U^{+4}][H_2Tar][UO_2^{++}]}{[H^+]^2}$$

Rates calculated using this expression agree well with rates obtained experimentally.

The rate of the reaction increased with increasing ionic strength and was markedly accelerated by temperature increases. Irradiation with an ultraviolet lamp caused a very large increase in the rate of the reaction.

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APPENDIX A

PREPARATION OF EXCHANGE SOLUTIONS USING A pH METER

When work was first begun on the system, attempts were made to duplicate the work of Rona.[26] Because hydrolysis was important at these conditions, the pH of the solutions was determined as the stock solutions were mixed.

pH measurements were carried out with a Beckman Model G pH Meter using a glass electrode and a calomel reference electrode. Since erratic readings were obtained using a standard calomel reference electrode with a saturated potassium chloride electrolyte in the perchlorate solutions due to precipitation of potassium perchlorate at the fiber junction, a saturated sodium chloride solution was substituted as the electrolyte. It was also noted that there is an error in the hydrogen ion concentration of the solution calculated from the pH measurements made at high ionic strength. The pH's of a series of solutions of known hydrogen ion concentration at I = 2.00 were measured to be 0.39 pH units lower than the true pH. This correction factor was added to all measurements made.

All solutions for this series of runs were combined in a 150 ml beaker in which was fitted the electrodes for the pH meter and a glass tip drawn to a small opening through which passed a stream of nitrogen.

Uranyl perchlorate and sodium perchlorate were first added to the beaker. The pH of this solution was checked. The uranium(IV) was next added while the nitrogen flow continued. The pH was measured and recorded. The pH reading was corrected and the hydrogen ion concentration determined. The number of moles of hydrogen ion needed to give the required acidity was then calculated and the proper amount of stock

solution added. The solution was next diluted to the desired volume and the tartaric acid added. Upon completion of this final step the solution was poured into a darkened flask.

The chief disadvantages of this method are that solutions with a pH lower than 0.4 cannot be directly measured and the system is subject to error because of the great changes in hydrogen ion concentration it undergoes after the pH measurement is recorded. Once experiments were begun at 1.00 M in hydrogen ion this method was abandoned for the one described in the body of the thesis.

APPENDIX B

COMPUTER PROGRAM

```
*     PHILLIP BENSON   PROBLEM NUMBER 21-946T   214 KEDZIE CHEM LAB   MSU     G
C     MAIN PROGRAM
      COMMON N,T,S,TIME,ABSORB,COUNTS,BKGND,BKGRAT,CORAT,CAVRAT,CONC,
     1CRSPA,ACTNET,ENFACT,F,F100,FINVAL,SLOPE,A,THALF,RATE,U,U02,
     2ACID,ORG,TEMP,C,D,SA,SB,SR
      DIMENSION TIME(25),ABSORB(25),COUNTS(25,3),BKGND(3),BKGRAT(3),
     1COURAT(3,25),CORAT(3,25),CRSPA(25),FINVAL(25),C(3,25),D(3,25)
   10 READ 11,PGR,N,T,S,(BKGND(J),J=1,3)
   11 FORMAT(I2,3X,I2,3X,F3.0,3X,F3.0,3X,3(F5.0,3X))
   12 FORMAT(1H1,24HTHIS IS KINETIC RUN PGR-, I2  )
   13 FORMAT(F8.4,3X,F8.4,3X,F8.4,3X,F8.4,3X,F6.2 )
   14 FORMAT(1H0,2HU=, F8.4,3X,4HU02=, F8.4,3X,5HACID=, F8.4,3X,
     1  4HORG=,  F8.4,3X,5HTEMP=,F6.2  )
      PRINT 12,PGR
      READ 13,U,U02,ACID,ORG,TEMP
      PRINT 14,U,U02,ACID,ORG,TEMP
      DO 15 J=1,3
      BKGRAT(J)=BKGND(J)/T
   15 CONTINUE
      CALL REFINE
      CALL SLSTSQ
      RATE=((-SLOPE)*U*U02)/(U+U02)
      THALF=0.69315/(-SLOPE)
      PRINT 16, THALF, RATE
   16 FORMAT(1H0,6HTHALF=, E12.6,4X,5HRATE=, E12.6 )
      SR=(SB*U*U02)/(U+U02)
      PRINT 17, SR
   17 FORMAT(1H0,22HSTD DEVIATION IN RATE=, E14.8  )
      GO TO 10
      STOP
      END
C     SUBROUTINE FOR REFINING DATA
      SUBROUTINE REFINE
      COMMON N,T,S,TIME,ABSORB,COUNTS,BKGND,BKGRAT,CORAT,CAVRAT,CONC,
     1CRSPA,ACTNET,ENFACT,F,F100,FINVAL,SLOPE,A,THALF,RATE,U,U02,
     2ACID,ORG,TEMP,C,D,SA,SB,SR
      DIMENSION TIME(25),ABSORB(25),COUNTS(25,3),BKGND(3),BKGRAT(3),
     1COURAT(3,25),CORAT(3,25),CRSPA(25),FINVAL(25),C(3,25),D(3,25)
      PRINT 21
   21 FORMAT(1H0,40HVALUES OF CORRECTED SPECIFIC ACTIVITY    )
      READ 22, (TIME(I), ABSORB(I), COUNTS(I,1), COUNTS(I,2),
     1COUNTS(I,3),I=1,N)
   22 FORMAT(F8.0,3X,F6.3,3X,3(F8.0,3X))
      DO 25 I=1,N
      SUM=0.
      DO 23 J=1,3
      COURAT(I,J)=COUNTS(I,J)/S
      CORAT(I,J)=COURAT(I,J)-BKGRAT(J)
   23 SUM=SUM+CORAT(I,J)
```

```
      CAVRAT=SUM/3.
      CONC=ABSORB(I)*2052.
      SPECAC=CAVRAT/CONC
      CRSPA(I)=SPECAC-0.623
      PRINT 24, CRSPA(I)
   24 FORMAT(1H2,11X,E12.6 )
   25 CONTINUE
      M=N
      ENFACT=CRSPA(M)-CRSPA(1)
      PRINT 200, ENFACT,N
  200 FORMAT(1H0,7HENFACT=, E10.4,5X,2HN=, I2 )
   26 FORMAT(1H0,13HLOG(100-100F),5X,13HELAPSED TIME )
      PRINT 26
      K=N-1
      DO 28 I=2,K
      ACTNET=CRSPA(I)-CRSPA(1)
      F=ACTNET/ENFACT
      F100=100.00-100.00*F
      FINVAL(I)=LOGF(F100)
      PRINT 27, FINVAL(I),TIME(I)
   27 FORMAT(1H2,E12.6,6X,E12.6 )
   28 CONTINUE
      RETURN
      END
      LEAST SQUARES SUBROUTINE
      SUBROUTINE SLSTSQ
      COMMON N,T,S,X,ABSORB,COUNTS,BKGND,BKGRAT,CORAT,CAVRAT,CONC,
     1CRSPA,ACTNET,ENFACT,F,F100,Y,B,A,THALF,RATE,U,U02,
     2ACID,ORG,TEMP,C,D,SA,SB,SR
      DIMENSION X(25),ABSORB(25),COUNTS(25,3),BKGND(3),BKGRAT(3),
     1COURAT(3,25),CORAT(3,25),CRSPA(25),Y(25),C(3,25),D(3,25)
      SUMX=0.
      SUMY=0.
      SUMW=0.
      SUMU=0.
      SUMZ=0.
      K=N-1
      DO 31 I=2,K
      SUMX=SUMX+X(I)
      SUMY=SUMY+Y(I)
      SUMW=SUMW+X(I)*Y(I)
      SUMU=SUMU+Y(I)**2
   31 SUMZ=SUMZ+X(I)**2
      FK=N-2
      B=(FK*SUMW-SUMX*SUMY)/(FK*SUMZ-SUMX**2)
      A=(SUMY*SUMZ-SUMW*SUMX)/(FK*SUMZ-SUMX**2)
      PRINT 32, B, A
   32 FORMAT(1H0,6HSLOPE=, E12.6, 5X, 10HINTERCEPT=, E12.6 )
      L=N-2
```

```
      M=N-4
      FRACT=(((SUMW)-(SUMX*SUMY/L))**2)/((SUMZ)-(SUMX**2/L)))
      E=(SUMU)-(SUMY**2/L)-(FRACT)
      V=E/M
      SB2=(L*V)/((L*SUMZ)-(SUMX**2))
      SB=SQRTF(SB2)
      SA2=(V*SUMZ)/((L*SUMZ)-(SUMX**2))
      SA=SQRTF(SA2)
      PRINT 33, SB
   33 FORMAT(1H0,23HSTD DEVIATION OF SLOPE=, E14.8 )
   34 FORMAT(1H0,27HSTD DEVIATION OF INTERCEPT=, E14.8 )
      PRINT 34, SA
      PRINT 35
   35 FORMAT(1H0,50HDIFFERENCE BETWEEN CALCULATED AND EXPERIMENTAL Y    )
      DO 37 I=2,K
      C(1,I)=ABSF(Y(I)-(B*X(I)+A))
      PRINT 36,C(1,I)
   36 FORMAT(1H2,12X, E14.8 )
   37 CONTINUE
      DEV=SQRTF(V)
      D3=3.0*DEV
      PRINT 38, DEV, D3
   38 FORMAT(1H0,4HDEV=, E14.8, 4X, 3HD3=, E14.8 )
      RETURN
      END

27    14    15.     5.     306.     443.     362.
   .025         .0274     1.00         .13       24.96
               .465      4127.       4074.       3456.
    433.       .467      4575.       4362.       4384.
   1222.       .460      4965.       4955.       4788.
   1956.       .455      5748.       5634.       5856.
   3247.       .447      5612.       5563.       5324.
   4218.       .457      6838.       7003.       6596.
   4891.       .433      6411.       6137.       6111.
   5608.       .435      7167.       7513.       7373.
   6969.       .450      5886.       6497.       6287.
   7657.       .455      7418.       7462.       7677.
   8217.       .450      8420.       8146.       8228.
   9132.       .457      8586.       8498.       8676.
   9820.       .438      8315.       8364.       8655.
               .315     15046.      15042.      14878.
```

THIS IS KINETIC RUN PGR-27

U= .0250 UO2= .0274 ACID= 1.0000 ORG= .1300 TEMP= 24.96

VALUES OF CORRECTED SPECIFIC ACTIVITY

.165576E 00
.277962E 00
.389632E 00
.581411E 00
.549255E 00
.803561E 00
.749225E 00
.996402E 00
.698180E 00
.961207E 00
.114031E 01
.118197E 01
.122867E 01
.397653E 01

ENFACT= .3810E 01 N=14

LOG(100-100F)	ELAPSED TIME
.457523E 01	.433000E 03
.454457E 01	.122200E 04
.448962E 01	.195600E 04
.449905E 01	.324700E 04
.442195E 01	.421800E 04
.443893E 01	.489100E 04
.435925E 01	.560800E 04
.445463E 01	.696900E 04
.437099E 01	.765700E 04
.430976E 01	.821700E 04
.429496E 01	.913200E 04
.427811E 01	.982000E 04

SLOPE=-.292104E-04 INTERCEPT= .457401E 01

STD DEVIATION OF SLOPE= .34769172E-05

STD DEVIATION OF INTERCEPT= .21143408E-01

DIFFERENCE BETWEEN CALCULATED AND EXPERIMENTAL Y

.138692C0E-01
.62581000E-02
.27250300E-01
.19887100E-01
.28847100E-01
.77911000E-02
.50946200E-01
.84183400E-01
.20646900E-01
.24231500E-01
.12303100E-01
.90585000E-02

DEV= .36318038E-01 D3= .10895411E 00

THALF= .237295E 05 RATE= .381854E-06

STD DEVIATION IN RATE= .45452064E-07

APPENDIX C

ORIGINAL KINETIC DATA

Table X. Study of the effect of variations in hydrogen ion concentrations on the rate of exchange in the absence of organic acids.

	S	ln(100-100F)	t(min.)
E-73			
	-0.016	--	0
0.0250 M U(IV)	0.224	4.453	27
	0.195	4.473	52
0.0274 M U(VI)	0.215	4.459	75
	0.456	4.280	101
0.110 M H^+	0.595	4.160	130
	0.460	4.277	172
0.000 M Tartaric acid	0.530	4.218	201
	0.694	4.064	230
I = 2.00	0.727	4.031	258
T = 25.0°C	0.928	3.796	295
	1.685	--	∞
R = 2.89 ± 0.40 x 10^{-5} moles $l^{-1}min^{-1}$			
F-21			
0.0250 M U(IV)	0.118	--	0
	0.956	4.403	165
0.0274 M U(VI)	1.457	4.260	280
	2.227	3.989	420
0.141 M H^+	2.439	3.900	579
	2.579	3.836	748
0.000 M Tartaric acid	3.699	3.088	1311
	4.156	2.482	1432
I = 2.00	4.261	2.269	1589
T = 25.0°C	4.327	2.108	1663
	4.135	2.520	1758
R = 1.83 ± 0.14 x 10^{-5} moles $l^{-1}min^{-1}$	4.705	--	∞
F-23			
0.0250 M U(IV)	0.146	--	0
	0.214	4.590	247
0.0274 M U(VI)	0.649	4.486	1259
	0.787	4.450	1997
0.282 M H^+	1.068	4.374	2562
	1.403	4.275	3468
0.000 M Tartaric acid	1.708	4.175	4180
	1.880	4.114	4908
I = 2.00	1.858	4.122	5677
T = 25.0°C	2.183	3.996	6374
	2.361	3.920	7049
R = 1.25 ± 0.05 x 10^{-6} moles $l^{-1}min^{-1}$	2.281	3.955	7859
	2.622	3.797	8576
	2.964	3.608	10045
	4.611	--	∞

Table XI. Study of the effect of various organic acids on the rate of exchange.

	S	ln(100-100F)	t(min.)
F-39			
0.0250 M U(IV)	0.005	--	0
	0.079	4.588	679
0.0274 M U(VI)	0.122	4.578	1426
	0.152	4.572	1943
0.562 M H^+	0.300	4.537	4364
	0.279	4.542	5083
0.0131 M maleic acid	0.378	4.519	5813
	0.388	4.516	6576
I = 2.00	0.605	4.468	10734
T = 25.0°C	0.740	4.427	18635
	1.110	4.325	27408
R = 1.32 x 10^{-7} moles $l^{-1}min^{-1}$	1.228	4.290	32274
	1.493	4.206	39645
	1.873	4.073	47553
	4.535	--	∞
F-43			
0.0250 M U(IV)	0.079	--	0
0.0274 M U(VI)	0.201	4.577	998
0.562 M H^+	0.345	4.543	4510
0.0131 M malic acid	0.841	4.416	15426
I = 2.00	1.009	4.369	20776
T = 25.0°C	1.145	4.330	28585
	1.440	4.238	36884
R = 1.22 ± 0.07 x 10^{-7} moles $l^{-1}min^{-1}$	4.506	--	∞
F-44			
0.0250 M U(IV)	0.085	--	0
0.0274 M U(VI)	0.122	4.593	999
0.562 M H^+	0.379	4.501	4503
0.0131 M malonic acid	0.786	4.335	15429
I = 2.00	0.865	4.300	21523
T = 25.0°C	1.172	4.148	29063
	1.559	3.917	37402
R = 2.23 ± 0.19 x 10^{-7} moles $l^{-1}min^{-1}$	3.048	--	∞
F-46			
0.0250 M U(IV)	0.092	--	0
0.0274 M U(VI)	0.163	4.590	1055
1.76 M H^+	0.091	4.605	4362
0.0262 M maleic acid	0.144	4.594	14546
I = 2.00	0.149	4.593	19672
T = 25.0°C	0.176	4.588	27253
	0.213	4.580	35547
R = 6.2 ± 2.9 x 10^{-9} moles $l^{-1}min^{-1}$	4.930	--	∞

Table XI (Cont.)

	S	ln(100-100F)	t(min.)
F-47			
0.0250 M U(IV)	0.139	--	0
0.0247 M U(VI)	0.142	4.604	1060
1.76 M H^+	0.091	4.619	4378
0.0262 M malic acid	0.227	4.579	14574
I = 2.00	0.269	4.567	19731
T = 25.0°C	0.165	4.598	27265
	0.214	4.583	35610
$R = 1.01 \pm 0.78 \times 10^{-8}$ moles $l^{-1}min^{-1}$	3.608	--	∞
F-48			
0.0250 M U(IV)	0.104	--	0
0.0274 M U(VI)	0.172	4.590	1057
1.76 M H^+	0.182	4.588	4381
0.0262 M malonic acid	0.203	4.584	14581
I = 2.00	0.198	4.585	19741
T = 25.0°C	0.131	4.599	27433
	0.211	4.582	35636
$R = 5.2 \pm 3.1 \times 10^{-10}$ moles $l^{-1}min^{-1}$	4.698	--	∞
F-49			
0.0250 M U(IV)	0.140	--	0
0.0274 M U(VI)	0.171	4.598	1061
1.76 M H^+	0.184	4.596	4395
0.0262 M tartaric acid	0.250	4.582	14583
I = 2.00	0.261	4.579	19750
T = 25.0°C	0.159	4.601	27448
	0.332	4.564	35658
$R = 8.7 \pm 5.6 \times 10^{-9}$ moles $l^{-1}min^{-1}$	4.877	--	∞
F-51			
0.0250 M U(IV)	0.097	--	0
0.0274 M U(VI)	0.143	4.594	2743
1.76 M H^+	0.192	4.583	11526
0.130 M maleic acid	0.150	4.593	17410
I = 2.00	0.248	4.569	24887
T = 25.0°C	0.371	4.539	33187
$R = 2.24 \pm 0.70 \times 10^{-8}$ moles $l^{-1}min^{-1}$	4.369	--	∞
F-52			
0.0250 M U(IV)	0.078	--	0
0.0274 M U(VI)	0.333	4.552	2735
1.76 M H^+	0.359	4.546	11374
0.130 M malic acid	0.484	4.518	17416
I = 2.00	0.616	4.489	24883
T = 25.0°C	0.637	4.484	33382
$R = 3.32 \pm 0.57 \times 10^{-8}$ moles $l^{-1}min^{-1}$	4.965	--	∞

Table XI (Cont.)

	S	ln(100-100F)	t(min.)
F-53			
0.0250 M U(IV)	0.077	--	0
0.0274 M U(VI)	0.129	4.595	2759
1.76 M H^+	0.124	4.596	11371
0.130 M malonic acid	0.165	4.588	17413
I = 2.00	0.130	4.595	24909
T = 25.0°C	0.244	4.572	33387
$R = 8.46 \pm 4.4 \times 10^{-9}$ molex $l^{-1}min^{-1}$	5.140	--	∞
F-54			
0.0250 M U(IV)	0.322	--	0
0.0274 M U(VI)	0.517	4.557	2450
1.76 M H^+	0.784	4.487	11076
0.130 M tartaric acid	0.861	4.466	17105
I = 2.00	1.138	4.387	24600
T = 25.0°C	1.590	4.241	33083
$R = 1.29 \pm 0.19 \times 10^{-7}$ moles $l^{-1}min^{-1}$	4.477	--	∞
F-69			
0.0250 M U(IV)	-0.012	--	0
	0.089	4.582	130
0.0274 M U(VI)	0.083	4.584	577
	0.078	4.585	869
0.708 M H^+	0.179	4.562	1169
	0.149	4.569	1565
0.013 M tartaric acid	0.277	4.539	2208
	0.281	4.537	2453
I = 2.00	0.224	4.551	2703
T = 25.0°C	0.331	4.526	3692
	0.231	4.549	4290
$R = 2.02 \pm 0.24 \times 10^{-7}$ moles $l^{-1}min^{-1}$	0.215	4.553	5516
	0.459	4.494	6801
	0.680	4.438	8246
	0.711	4.429	9621
	4.469	--	∞

Table XII. Study of the effect of variations in U(IV) on the rate of exchange.

	S	ln(100-100F)	t(min.)
G-19			
0.0400 M U(IV)	0.079	--	0
	0.278	4.528	282
0.0274 M U(VI)	0.228	4.548	599
	0.418	4.470	1377
1.00 M H^+	0.167	4.572	1837
	0.374	4.489	2094
0.130 M tartaric acid	0.228	4.548	2491
	0.494	4.437	3195
I = 2.00	0.605	4.387	4159
T = 25.0°C	0.579	4.399	4564
	0.702	4.341	4931
$R = 6.68 \pm 1.0 \times 10^{-7}$ moles $l^{-1}min^{-1}$	0.664	4.359	5590
	0.747	4.319	6006
	2.763	--	∞
G-27			
0.0250 M U(IV)	0.166	--	0
	0.278	4.575	433
0.0274 M U(VI)	0.390	4.544	1222
	0.581	4.490	1956
1.00 M H^+	0.549	4.499	3247
	0.804	4.422	4218
0.130 M tartaric acid	0.749	4.439	4891
	0.996	4.359	5608
I = 2.00	0.698	4.455	6969
T = 25.0°C	0.961	4.371	7657
	1.140	4.310	8217
$R = 3.82 \pm 0.45 \times 10^{-7}$ moles $l^{-1}min^{-1}$	1.182	4.295	9132
	1.229	4.278	9821
	3.976	--	∞

Table XII (Cont.).

	S	ln(100-100F)	t(min.)
G-33			
0.0120 M U(IV)	0.457	--	0
	0.844	4.568	565
0.0274 M U(VI)	0.898	4.563	983
	0.957	4.557	1311
1.00 M H^+	1.159	4.537	2072
	1.425	4.510	2861
0.130 M tartaric acid	1.635	4.488	4347
	2.013	4.447	5140
I = 2.00	2.254	4.420	6553
T = 25.0°C	2.496	4.393	7911
	2.638	4.376	11543
$R = 1.51 \pm 0.10 \times 10^{-7}$ moles $l^{-1}min^{-1}$	2.940	4.340	12665
	2.928	4.341	13566
	11.113	--	∞
G-67			
0.0178 M U(IV)	0.266	--	0
	0.886	4.530	1211
0.0274 M U(VI)	1.329	4.473	2869
	1.451	4.456	4271
1.00 M H^+	1.382	4.466	5857
0.130 M tartaric acid	2.052	4.371	7804
I = 2.00	2.038	4.373	8865
T = 25.0°C	2.088	4.366	9929
	2.592	4.288	11392
$R = 2.13 \pm 0.20 \times 10^{-7}$ moles $l^{-1}min^{-1}$	2.375	4.322	12987
	2.806	4.253	14333
	8.828	--	∞

Table XIII. Study of the effect of variations in U(VI) on the rate of exchange.

	S	ln(100-100F)	t(min.)
G-23			
0.0250 M U(IV)	0.282	--	0
	0.281	4.605	249
0.0750 M U(VI)	0.374	4.587	538
	0.467	4.568	1308
1.00 M H^+	0.722	4.514	1836
	0.669	4.526	2051
0.130 M tartaric acid	0.709	4.517	2566
	0.716	4.516	3203
I = 2.00	0.868	4.482	4217
T = 25.0°C	1.019	4.448	4622
	1.039	4.443	4989
$R = 5.93 \pm 0.38 \times 10^{-7}$ moles $l^{-1}min^{-1}$	1.096	4.430	5648
	1.209	4.403	6064
	5.347	--	∞
G-25			
0.0250 M U(IV)	0.608	--	0
	0.392	4.644	59
0.150 M U(VI)	0.315	4.658	249
	0.475	4.630	341
1.00 M H^+	0.556	4.615	538
	0.404	4.642	658
0.130 M tartaric acid	0.634	4.600	1308
	0.727	4.583	1436
I = 2.00	0.853	4.559	1836
T = 25.0°C	0.778	4.573	2051
	0.876	4.555	2566
$R = 8.79 \pm 0.67 \times 10^{-7}$ moles $l^{-1}min^{-1}$	0.877	4.554	3203
	1.129	4.504	4291
	1.379	4.452	4573
	1.525	4.421	4951
	6.048	--	∞

Table XIII (Cont.)

	S	ln(100-100F)	t(min.)
G-47			
0.0250 M U(IV)	0.780	--	0
	1.143	4.567	756
0.0500 M U(VI)	1.463	4.531	1576
	1.427	4.536	2294
1.00 M H^+	1.706	4.504	2501
	1.926	4.478	2996
0.130 M tartaric acid	1.732	4.501	3536
	2.323	4.430	5714
I = 2.00	2.302	4.433	6846
T = 25.0°C	2.435	4.416	8005
	2.376	4.424	9317
$R = 2.69 \pm 0.27 \times 10^{-7}$ moles $l^{-1}min^{-1}$	2.633	4.391	10038
	2.600	4.395	10692
	10.390	--	∞
G-57			
0.0250 M U(IV)	0.422	--	0
	0.847	4.554	1223
0.0400 M U(VI)	1.212	4.507	2616
	1.681	4.444	4331
1.00 M H^+	1.804	4.427	5680
	1.926	4.410	7262
0.130 M tartaric acid	2.424	4.336	9205
	2.652	4.300	10270
I = 2.00	2.873	4.264	11345
T = 25.0°C	3.097	4.226	12797
	3.161	4.215	14395
$R = 4.07 \pm 0.17 \times 10^{-7}$ moles $l^{-1}min^{-1}$	8.908	--	∞
G-59			
0.0250 M U(IV)	0.894	--	0
	0.980	4.597	1000
0.100 M U(VI)	1.697	4.530	2374
	1.978	4.502	4043
1.00 M H^+	2.220	4.477	5433
	2.832	4.412	7033
0.130 M tartaric acid	2.849	4.410	8972
	3.917	4.285	10034
I = 2.00	3.712	4.310	11097
T = 25.0°C	3.680	4.314	12555
	4.430	4.219	14158
$R = 5.90 \pm 0.50 \times 10^{-7}$ moles $l^{-1}min^{-1}$	5.227	4.107	15499
	11.936	--	∞

Table XIV. Study of the effect of variations in tartaric acid concentrations on the rate of exchange.

	S	ln(100-100F)	t(min.)
F-74			
0.0250 M U(IV)	0.069	--	0
	0.168	4.583	204
0.0274 M U(VI)	0.154	4.587	770
	0.369	4.538	1320
1.00 M H^+	0.287	4.556	1785
	0.291	4.556	2369
0.0650 M tartaric acid	0.288	4.556	3164
	0.376	4.536	3907
I = 2.00	0.622	4.477	5322
T = 25.0°C	0.773	4.439	8533
	1.308	4.292	13921
$R = 2.60 \pm 0.13 \times 10^{-7}$ moles $l^{-1}min^{-1}$	1.511	4.229	18891
	4.673	--	∞
F-75			
0.0250 M U(IV)	0.096	--	0
	0.161	4.592	204
0.0274 M U(VI)	0.160	4.592	792
	0.184	4.588	1370
1.00 M H^+	0.174	4.590	1806
	0.098	4.605	2390
0.0130 M tartaric acid	0.252	4.574	3185
	0.215	4.581	3928
I = 2.00	0.232	4.578	5343
T = 25.0°C	0.250	4.574	8554
	0.491	4.524	13942
$R = 5.46 \pm 0.68 \times 10^{-8}$ moles $l^{-1}min^{-1}$	0.489	4.524	18912
	5.135	--	∞

Table XIV (Cont.)

	S	ln(100-100F)	t(min.)
G-2			
0.0250 M U(IV)	0.203	--	0
	0.167	4.614	166
0.0274 M U(VI)	0.277	4.588	648
	0.316	4.578	920
1.00 M H^+	0.747	4.469	1545
	0.936	4.417	3876
0.130 M tartaric acid	1.277	4.316	6480
	1.798	4.139	8729
I = 2.00	1.857	4.116	10242
T = 25.0°C	2.048	4.041	12287
	1.909	4.096	14063
$R = 4.88 \pm 0.41 \times 10^{-7}$ moles $l^{-1}min^{-1}$	1.957	4.077	15934
	2.290	3.936	17283
	4.481	--	∞
G-3			
0.0250 M U(IV)	0.229	--	0
	0.329	4.583	166
0.0274 M U(VI)	0.485	4.548	648
	0.591	4.523	920
1.00 M H^+	1.168	4.376	1545
	1.358	4.323	3876
0.260 M tartaric acid	2.191	4.048	6480
	2.677	3.844	8729
I = 2.00	2.628	3.867	10242
T = 25.0°C	3.002	3.680	12287
	2.933	3.717	14063
$R = 8.62 \pm 0.48 \times 10^{-7}$ moles $l^{-1}min^{-1}$	3.148	3.597	15934
	3.510	3.354	17283
	4.825	--	∞

Table XIV (Cont.)

	S	ln(100-100F)	t(min.)
G-39			
0.0250 M U(IV)	0.094	--	0
	0.300	4.578	574
0.0274 M U(VI)	0.470	4.555	1043
	0.610	4.536	1316
1.00 M H^+	0.620	4.534	2044
	0.764	4.514	2808
0.0750 M tartaric acid	1.034	4.475	5716
I = 2.00	1.189	4.452	7671
T = 25.0°C	1.352	4.427	10765
	1.704	4.371	13449
$R = 1.86 \pm 0.12 \times 10^{-7}$ moles $l^{-1}min^{-1}$	7.792	--	∞
G-41			
0.0250 M U(IV)	0.198	--	0
0.0274 M U(VI)	0.164	4.609	761
1.00 M H^+	0.180	4.607	3550
0.0130 M tartaric acid	0.348	4.586	6917
I = 2.00	0.326	4.589	9642
T = 25.0°C	8.225	--	∞
$R = 3.64 \pm 1.3 \times 10^{-8}$ moles $l^{-1}min^{-1}$			
G-43			
0.0250 M U(IV)	0.744	--	0
0.0274 M U(VI)	0.727	4.607	761
1.00 M H^+	1.570	4.485	3550
0.130 M tartaric acid	1.990	4.418	6917
I = 2.00	2.278	4.370	8165
T = 25.0°C	2.382	4.351	9269
$R = 3.82 \pm 0.34 \times 10^{-7}$ moles $l^{-1}min^{-1}$	8.055	--	∞
G-45			
0.0250 M U(IV)	1.270	--	0
	1.861	4.520	756
0.0274 M U(VI)	2.294	4.453	1576
	2.383	4.438	2294
1.00 M H^+	2.416	4.433	2925
	3.158	4.303	3536
0.260 M tartaric acid	3.523	4.233	5714
	2.236	4.462	7296
I = 2.00	3.301	4.276	8064
T = 25.0°C	3.995	4.133	8597
	3.886	4.157	9441
$R = 4.44 \pm 1.24 \times 10^{-7}$ moles $l^{-1}min^{-1}$	8.515	--	∞

Table XV. Study of the effect of variation of hydrogen ion concentration on the rate of exchange in the presence of tartaric acid.

	S	ln(100-100F)	t(min.)
G-35			
0.0250 M U(IV)	0.235	--	0
	0.759	4.503	565
0.0274 M U(VI)	1.008	4.451	983
	1.042	4.444	1311
0.800 M H^+	1.428	4.356	2072
	1.711	4.287	2861
0.130 M tartaric acid	1.713	4.286	4347
	2.193	4.156	5140
I = 2.00	2.600	4.031	6553
T = 25.0°C	2.491	4.066	7129
	2.238	4.143	7911
$R = 8.22 \pm 0.43 \times 10^{-7}$ moles $l^{-1}min^{-1}$	3.044	3.874	10096
	3.382	3.735	11528
	3.465	3.698	12369
	3.555	3.656	14279
	5.649	--	∞
G-37			
0.0250 M U(IV)	0.277	--	0
	0.489	4.578	574
0.0274 M U(VI)	0.732	4.546	1043
	0.754	4.543	1316
1.25 M H^+	0.910	4.522	2044
	1.059	4.502	2808
0.130 M tartaric acid	1.421	4.450	5716
	1.606	4.423	7671
I = 2.00	1.761	4.400	10765
T = 25.0°C	2.138	4.340	13449
	8.265	--	∞
$R = 2.19 \pm 0.15 \times 10^{-7}$ moles $l^{-1}min^{-1}$			

Table XV (Cont.)

	S	ln(100-100F)	t(min.)
G-61			
0.0250 M U(IV)	0.386	--	0
	0.814	4.537	1086
0.0274 M U(VI)	1.109	4.488	2460
	1.778	4.366	4129
0.900 M H^+	1.674	4.386	5519
	1.920	4.338	7119
0.130 M tartaric acid	2.126	4.296	8338
	2.453	4.225	9400
I = 2.00	2.566	4.199	10463
T = 25.0°C	2.668	4.176	11921
	3.270	4.023	13511
$R = 4.94 \pm 0.31 \times 10^{-7}$ moles $l^{-1}min^{-1}$	3.331	4.006	14582
	6.922	--	∞
G-65			
0.0250 M U(IV)	0.263	--	0
	0.565	4.558	1211
0.0274 M U(VI)	0.890	4.506	2869
	1.122	4.466	4271
1.12 M H^+	1.089	4.472	5857
	1.607	4.378	7084
0.130 M tartaric acid	1.558	4.388	8865
	1.550	4.389	9929
I = 2.00	2.021	4.297	11392
T = 25.0°C	1.999	4.301	12987
	2.192	4.261	14333
$R = 2.84 \pm 0.24 \times 10^{-7}$ moles $l^{-1}min^{-1}$	6.891	--	∞

Table XVI. Study of the effect of varying ionic strength on the rate of exchange.

	S	ln(100-100F)	t(min.)
G-29			
0.0250 M U(IV)	0.211	--	0
	0.264	4.591	431
0.0274 M U(VI)	0.263	4.591	1222
	0.404	4.553	1956
1.00 M H^+	0.389	4.558	3247
	0.565	4.507	4218
0.130 M tartaric acid	0.497	4.527	4891
	0.692	4.471	5608
I = 1.33	0.602	4.497	6969
T = 25.0°C	0.713	4.464	7657
	0.827	4.429	8217
$R = 2.87 \pm 0.26 \times 10^{-7}$ moles $l^{-1}min^{-1}$	0.967	4.385	9132
	0.967	4.385	9820
	4.036	--	∞
G-49			
0.0250 M U(IV)	0.544	--	0
	0.840	4.566	763
0.0274 M U(VI)	1.339	4.495	2324
1.00 M H^+	1.628	4.452	3555
0.130 M tartaric acid	1.521	4.469	6290
I = 1.67	2.192	4.362	8144
T = 25.0°C	2.417	4.324	9397
$R = 3.19 \pm 0.58 \times 10^{-7}$ moles $l^{-1}min^{-1}$	8.192	--	∞
G-51			
0.0250 M U(IV)	0.404	--	0
0.0274 M U(VI)	0.534	4.588	763
1.00 M H^+	0.917	4.538	2324
0.130 M tartaric acid	1.108	4.512	3555
I = 1.33	1.386	4.472	6290
T = 25.0°C	1.908	4.394	8144
	1.884	4.398	9397
$R = 2.94 \pm 0.27 \times 10^{-7}$ moles $l^{-1}min^{-1}$	8.305	--	∞

Table XVII. Study of the effect of variation of temperature on the exchange reaction.

	S	ln(100-100F)	t(min.)
H-1			
0.0250 M U(IV)	0.549	--	0
	1.091	4.523	258
0.0274 M U(VI)	1.659	4.428	1073
	2.313	4.307	1474
1.00 M H^+	2.578	4.254	1835
	2.723	4.223	2510
0.130 M tartaric acid	3.677	3.994	3140
	4.322	3.804	4038
I = 2.00	4.409	3.775	4618
T = 39.8°C	5.044	3.536	5480
	5.377	3.383	6007
$R = 2.58 \pm 0.11 \times 10^{-6}$ moles $l^{-1}min^{-1}$	7.394	--	∞
H-5			
0.0250 M U(IV)	0.850	--	0
	1.041	4.584	258
0.0750 M U(VI)	2.291	4.436	1073
	2.790	4.370	1474
1.00 M H^+	3.369	4.228	1835
	4.174	4.161	2510
0.130 M tartaric acid	4.593	4.088	3145
	6.161	3.755	4038
I = 2.00	7.233	3.439	4618
T = 39.8°C	7.790	3.225	5480
	8.364	2.942	6007
$R = 5.31 \pm 0.36 \times 10^{-6}$ moles $l^{-1}min^{-1}$	10.121	--	∞
H-7			
0.0250 M U(IV)	0.493	--	0
	0.636	4.584	245
0.0274 M U(VI)	1.117	4.509	1056
	1.510	4.443	1463
1.25 M H^+	1.943	4.365	1814
	2.394	4.277	2498
0.130 M tartaric acid	2.423	4.271	3130
I = 2.00	2.520	4.251	4601
T = 39.8°C	3.741	3.956	5466
	3.700	3.967	6010
$R = 1.35 \pm 1.5 \times 10^{-6}$ moles $l^{-1}min^{-1}$	7.292	--	∞

Table XVII (Cont.)

	S	ln(100-100F)	t(min.)
H-9			
0.0250 M U(IV)	0.264	--	0
	0.508	4.570	245
0.0274 M U(VI)	0.937	4.505	1056
	1.015	4.493	1163
1.00 M H^+	1.327	4.442	1814
	1.735	4.372	2498
0.0650 M tartaric acid	1.874	4.346	3130
	3.026	4.109	4025
I = 2.00	1.517	4.410	4601
T = 39.8°C	2.895	4.139	5466
	3.053	4.103	6010
R = 1.02 ± 0.20 x 10^{-6} moles $l^{-1}min^{-1}$	7.328	--	∞
H-11			
0.0120 M U(IV)	0.795	--	0
	1.695	4.479	391
0.0274 M U(VI)	1.999	4.432	738
	2.390	4.369	1433
1.00 M H^+	3.284	4.207	1923
	3.674	4.128	2949
0.130 M tartaric acid	5.033	3.787	4401
I = 2.00	5.039	3.785	4877
T = 39.8°C	5.490	3.640	5692
	5.741	3.549	6183
R = 1.36 ± 0.05 x 10^{-6} moles $l^{-1}min^{-1}$	8.379	--	∞
H-13			
0.0250 M U(IV)	0.250	--	0
	0.350	4.588	290
0.0274 M U(VI)	1.207	4.424	1073
	1.232	4.419	1419
1.00 M H^+	1.395	4.385	1747
	1.487	4.365	2458
0.130 M tartaric acid	1.847	4.283	2836
	1.790	4.296	3162
I = 2.00	2.098	4.221	3947
T = 32.0°C	2.026	4.239	4490
	2.478	4.120	5385
R = 8.37 ± 1.2 x 10^{-7} moles $l^{-1}min^{-1}$	2.032	4.237	5988
	6.042	--	∞

Table XVII (Cont.)

	S	ln(100-100F)	t(min.)
H-14			
0.0250 M U(IV)	0.441	--	0
	0.619	4.588	290
0.0750 M U(VI)	1.503	4.497	1073
	1.350	4.514	1419
1.00 M H^+	0.923	4.558	1747
	2.028	4.439	2458
0.130 M tartaric acid	1.994	4.443	2836
	2.751	4.353	3162
I = 2.00	2.864	4.339	3947
T = 32.00°C	3.064	4.314	4490
	3.358	4.275	5477
R = 1.19 ± 0.13 x 10^{-6} moles $l^{-1}min^{-1}$	10.816	--	∞
H-15			
0.0250 M U(IV)	0.347	--	0
	0.525	4.582	290
0.0274 M U(VI)	0.935	4.525	1084
	0.904	4.529	1438
1.250 M H^+	0.989	4.517	1755
	1.059	4.507	2483
0.130 M tartaric acid	1.090	4.503	2853
	1.258	4.478	3162
I = 2.00	1.462	4.447	3863
T = 32.00°C	1.623	4.422	4401
	1.630	4.421	5405
R = 3.81 ± 0.32 x 10^{-7} moles $l^{-1}min^{-1}$	1.660	4.416	5885
	7.972	--	∞
H-16			
0.0250 M U(IV)	0.196	--	0
	0.265	4.594	290
0.0274 M U(VI)	0.652	4.530	1084
	0.713	4.520	1438
1.00 M H^+	0.541	4.549	1755
	0.831	4.499	2483
0.0650 M tartaric acid	0.754	4.512	2853
	0.841	4.497	3162
I = 2.00	0.922	4.483	3546
T = 32.00°C	1.092	4.452	4401
	0.872	4.492	5405
R = 2.30 ± 0.54 x 10^{-7} moles $l^{-1}min^{-1}$	0.940	4.479	5885
	6.493	--	∞

Table XVII (Cont.)

	S	ln(100-100F)	t(min.)
H-17			
0.0120 M U(IV)	0.428	--	0
	0.887	4.552	289
0.0274 M U(VI)	1.526	4.473	1093
	1.598	4.464	1455
1.00 M H^+	1.526	4.473	1761
	1.831	4.433	2529
0.130 M tartaric acid	1.972	4.414	2868
	2.238	4.377	3167
I = 2.00	2.520	4.336	3928
T = 32.00°C	2.428	4.349	4455
	2.522	4.336	5297
$R = 3.26 \pm 0.35 \times 10^{-7}$ moles $l^{-1}min^{-1}$	2.653	4.330	5900
	9.290	--	∞
H-18			
0.0250 M U(IV)	0.663	--	0
	1.032	4.554	217
0.0750 M U(VI)	1.606	4.468	392
	1.418	4.497	595
1.00 M H^+	1.810	4.436	724
	2.173	4.376	1199
0.130 M tartatic acid	2.410	4.335	1383
	3.054	4.213	1647
I = 2.00	3.284	4.166	2022
T = 39.8°C	4.514	3.866	2753
	4.004	4.001	3179
$R = 4.24 \pm 0.23 \times 10^{-6}$ moles $l^{-1}min^{-1}$	5.025	3.709	3665
	4.991	3.721	4229
	5.566	3.511	4675
	8.034	--	∞

Table XVII (Cont.)

	S	ln(100-100F)	t(min.)
H-20			
0.0250 M U(IV)	0.322	--	0
	0.562	4.549	217
0.0274 M U(VI)	0.727	4.508	392
	0.770	4.497	595
1.00 M H^+	0.792	4.491	724
	1.118	4.404	1199
0.130 M tartaric acid	0.938	4.453	1383
	1.376	4.329	1647
I = 2.00	1.278	4.358	2022
T = 39.8°C	1.844	4.177	2753
	1.848	4.176	3179
$R = 1.78 \pm 0.11 \times 10^{-6}$ moles $l^{-1}min^{-1}$	2.269	4.016	3665
	2.414	3.954	4229
	2.258	4.021	4675
	4.695	--	∞

Table XVIII. Study of the effect of irradiation on the exchange reaction.

	S	ln(100-100F)	t(min.)
H-21			
0.0250 M U(IV)	0.100	--	0
	0.010	4.627	5
0.0274 M U(VI)	0.110	4.603	10
	0.059	4.615	16
1.00 M H^+	0.097	4.606	22
	0.004	4.629	28
0.00 M tartaric acid	0.130	4.598	34
	0.152	4.592	42
I = 2.00	0.254	4.566	51
T = 25.0°C	0.191	4.582	59
	0.277	4.560	67
$R = 1.21 \pm 0.08 \times 10^{-5}$ moles $l^{-1}min^{-1}$	0.240	4.570	74
	0.539	4.489	143
	0.714	4.439	196
	1.34	4.234	317
	1.77	4.068	496
	1.75	4.075	706
	4.11	--	∞
H-22			
0.0250 M U(IV)	0.178	--	0
	0.453	4.534	6
0.0274 M U(VI)	0.672	4.474	10
	0.528	4.514	16
1.00 M H^+	1.14	4.332	22
	1.24	4.301	29
0.130 M tartaric acid	1.44	4.230	39
	1.61	4.167	50
I = 2.00	2.05	3.979	60
T = 25.0°C	2.30	3.860	72
	2.37	3.822	84
$R = 9.16 \pm 0.77 \times 10^{-5}$ moles $l^{-1}min^{-1}$	2.10	3.958	98
	2.31	3.852	112
	2.17	3.926	129
	3.18	3.237	142
	2.99	3.409	154
	3.09	3.322	168
	3.10	3.318	181
	4.21	--	∞

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