

THE CATALYTIC EFFECT OF SOME ORGANIC ACIDS ON THE OXIDATION OF URANIUM (IV) BY THALLIUM (III) IN PERCHLORIC ACID

> Thesis for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY Lawrence P. Quinn 1961

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Lawrence P. Quinn

A THESIS

Submitted to the School for Advanced Graduate Studies of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

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AN ABSTRACT

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Approved Carl H. Brubaker On

ABSTRACT

THE CATALYTIC EFFECT OF SOME ORGANIC ACIDS ON THE OXIDATION OF URANIUM (IV) BY THALLIUM (III) IN PERCHLORIC ACID

The reaction between uranium (IV) and thallium (III) in the presence of various organic acids was studied. Dibasic saturated acids studied were oxalic acid, malonic acid, and succinic acid. Oxalic acid and succinic were found to inhibit the reaction. Oxalic acid has only a slight effect on the system compared to succinic acid. Malonic acid has no effect on the rate of the system.

The unsaturated dibasic acids, fumaric acid and maleic acid, were investigated along with the hydroxy dibasic acids, malic acid and tartaric acid. Under the appropriate conditions these acids all catalyze the reaction. At low concentrations of fumaric or maleic acid, the reaction between uranium (IV) and thallium (III) is catalyzed, but as the concentration of the organic acid is increased, the effect is to inhibit the reaction. This is attributed to the formation of a one to one complex that catalyzes the reaction, followed successively by a one to two (uranium to organic acid) complex which inhibits the reaction. Tartaric acid appears to exhibit the same behavior, and although the evidence is scanty malic acid is believed to catalyze the reaction.

Most of the graphs of the rate equation

$$-\frac{d \left[U(IV) \right]}{dt} = k \left[U(IV) \right] \left[TI(III) \right]$$

were found to be linear over a large part of the reaction studied. Almost all curves, however, exhibited a peculiar deviation. The extrapolation of the linear curve to zero time did not pass

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through log Tl₀/U₀, which is required by theory. Rather, initial experimental points formed a curve which became linear only after several hundred seconds. Experiments at low temperatures showed that this curvature was due to two separate reactions, one occurring with a fast rate, and ending rather rapidly as it uses all of one reactant, and the other occurring simultaneously but with a slower rate.

The energy of activation was determined for this fast reaction and found to be 27.4 kilocalories when maleic acid was present as the catalyzing substance. The energies of activation were also determined for the reaction that occurred more slowly. The values obtained were 31.8 kilocalories and 22.1 kilocalories for concentrations of maleic acid that inhibit and that accelerate the reaction, respectively.

Partial rate laws were determined. The reaction is first order in uranium (IV) and thallium (III), and in the accelerated area the order of the maleic acid is 0.07, while in the inhibited area the maleic acid has an order of -0.84. The hydrogen ion was found to have an order of -1.17 in the inhibited area.

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1. INTRODUCTION

The question of the simultaneous transfer of two electrons as against two single electron transfers is still receiving much attention^{1,2}. Various systems, all having in common the fact that at least one of the reactants changes its oxidation state by two, have been studied. The oxidation of uranium (IV) to uranium (VI) is one such system. Several investigations have been made using oxygen gas³, iron (III)⁴, and thallium (III)⁵ as the oxidizing agent. The thallium (III) - uranium (IV) system is particularly interesting since both the oxidizing and reducing agents undergo an oxidation state change of two. A system such as this might then provide some information on the question of one or multielectron transfers.

Taube^{6,7} has shown that certain organic acids will catalyze the reaction between chromium (II) and cobalt (III). According to Taube the unsaturated acids act as a bridge between the two reacting species and provide a path for the transfer of the single electron.

Brubaker and Andrade⁸ have studied the effect of several organic acids on the thallium (I) - thallium (III) exchange. Acetic and succinic acids retard the exchange while the other acids studied all reduce the thallium (III) at a rate comparable to the exchange rate.

This study was undertaken with the following purpose in mind: to discover the nature and sequence, if more than one, of the elementary steps which comprise the overall reaction, to

* For a more complete list see table III.

determine the composition and configuration of the activated complex in the electron transfer step, to elucidate the atomic rearrangements accompaning the electron transfer process, and to discover whether multi-electron redox reaction occur in a single step or more than one successive electron steps.

It was decided, therefore, to study the oxidation of uranium (IV) by thallium (III) in the presence of various organic acids. Perchloric acid was chosen as the medium in order to reduce the possibilities of complexing by the acid anion. A general study of several acids was to be made and a detailed study of one of these, maleic acid, was also to be carried out.

2. HISTORICAL

A. OXIDATION - REDUCTION MECHANISMS

Introduction

Oxidation is defined many times as the loss of electrons. In elementary teaching of chemistry this definition serves a valuable purpose and is an efficient tool. It allows half cells of the form

$$Cr_2O_7^{-2} + 14H^+ + 6e^- = 2Cr^{+3} + 7H_2O$$
 1)

to be written.

With the use of such half cells, oxidation-reduction equations may be balanced and electrode processes may be written, both with some view towards what is actually occuring in solution. In reality these half cells, while very useful, do not represent accurately what is occuring. They simply represent the reactants and products of an oxidation reduction equation. The mechanisms may be quite different.

This field of inorganic mechanisms (or inorganic chemical kinetics) has received little attention until recently. Enough work had been reported prior to 1959 to be reviewed by Basolo and Pearson⁹ in their textbook. This book, while certainly a pioneer work in the field, allocates only one relatively short chapter to oxidation-reduction mechanisms¹⁰.

There are three generally accepted mechanisms by which oxidation-reduction may occur. They are atom transfer, electron transfer and the tunneling process.

The Tunneling Process

The tunneling hypothesis was first introduced by Marcus, Zwolinski and Eyring¹¹. This simply amounts to an extension of electronic orbitals to that point where transfer occurs at distances larger than one would suspect, and greater than corresponds to actual collision. This is merely saying that there is a possibility for an electron to leak through the potential barrier to a given reaction.

Atom Transfer

The second method of oxidation-reduction is atom transfer. Taube¹² has demonstrated several cases of atom transfer.

$$C_0(NH_3)_5 Cl^{+2} + Cr^{+2} = C_0(NH_3)_5^{+2} + CrCl^{+2}$$
 2)

This reaction requires that a chlorine atom, not an ion, be transferred. Since the chromium (III) is not labile, the chlorine must have transferred during the oxidative process. While this does not necessarily prove that chlorine atom transfer caused the oxidation, this certainly seems likely, although chloride ion transfer could have accompanied electron transfer. Taube has also shown atom or group transfer for several other ligands, among them thiocyanate, azide, phosphate, acetate, oxalate, and bromide. Oxygen atom transfer has been demonstrated in the oxidation of nitrite with hypochlorous acid and in the oxidation of sulfite with hypochlorite, chlorite, chlorate, and bromate ions.

Hydrogen Atom Transfer

Hydrogen atom transfer is a special case of atom transfer. There is good reason for this, although the fact that it is merely atom transfer should be remembered. Several facts all point to the importance of the hydrogen atom transfer¹⁴.

1) There are a surprising number of redox reactions between metal ions which have activation energies close to 10 kilocalories per mole and entropies close to -25 calories per mole degree suggesting that they proceed by a common mechanism.

2) In a number of redox reactions of metal complexes there seems to be the requirement that one of the inner shell ligands be a water molecule.

3) The rates of several exchange reactions are reduced by a factor of two on changing from water to deuterium oxide as a solvent. This is consistent with the isotope effect expected for breaking an oxygen to hydrogen bond. There are, however, reactions which give larger water to deuterium oxide isotope effects than this.

These facts, of course, suggest that the reactions all proceed by a common mechanism, which probably involves water. Dodson and coworkers^{15, 16} have made the suggestion that these facts point to the transfer of a hydrogen atom between hydration shells. The classic example which they studied is the iron (II) -(III) isotope exchange reaction.

At this point in the discussion it might be pertinent to point out that only in the case of the hydrogen atom can it be

determined whether the atom transfers in one direction or the electron transfers in that direction followed by a negative ion transfering in the opposite direction, since these two processes are formally equivalent.

Electron Transfer

The third method, electron transfer, is known to exist in the gas phase where the collision of an atom and an ion can bring about the transfer of an electron. However, in the liquid state a more complicated situation exists. The transfer of the electron here is hindered. For example, one cannot merely consider an ion but must also consider the hydration shells and the distortion of the electronic orbitals by the solvent. How close these entities can approach, and the influence of other substances also dissolved in solution must also be considered. Calculations must consider a much larger number of particles than in the gas phase. The possibility of an activated complex forming must be examined, and it must be remembered that since there are more configurations possible than in the gas phase there are now more energy levels available for the electron. No longer is a simple collision possible.

Rearrangement of coordinated groups must occur before the movement of electrons. This is due to the Franck-Condon principle. The Franck-Condon principle, in its simplest form, states that the motion of nuclei is so slow compared to that of electrons that an electron transfer occurs without any appreciable movement of nuclei. The situation can be made clear by considering a specific case, the electron exchange of iron (II) - iron (III).

$$Fe(H_20)_6^{+3} + Fe(H_20)_6^{+2} = Fe(H_20)_6^{+2} + Fe(H_20)_6^{+3}$$
 4)

$$F_{e}^{*}(H_{2}O)_{6}^{+2} + F_{e}^{*}(H_{2}O)_{6}^{+3} = F_{e}(H_{2}O)_{6}^{+2} + F_{e}(H_{2}O)_{6}^{+3} + heat 5)$$

The asterisk with the products of reaction 4) indicates that these iron atoms are in an energy rich state. It would, of course, be possible for them to deactivate giving up their excess energy to the solvent, and returning to the unexcited state that they were in as reactants. But this whole process is a violation of the law of conservation of energy in that heat energy is created. Thusth becomes necessary to rearrange the hydrations shells of the ions to some intermediate position before the electron transfer can occur. This rearrangement to form an activated complex will require energy from the solution, but when the products revert to their average state an equivalent amount of energy will be released. However, this enables the electron transfer to take place without the creation of products in an excited state.

The least amount of energy will be required to form an activated complex consisting of identical configurations for both iron ions so that electron transfer probably involves a symmetrical transition state, intermediate between the iron (II) and the iron (III) arrangements.

If one considers electron transfer taking place between two ions not the same, then exothermic reactions are favored. Since heat is to be evolved, the lack of energy conservation shown in the iron (II) - iron (III) reaction is no longer necessarily a factor. Nonetheless rearrangement of the ligands of the two reacting species is still necessary so that the actual transfer of the electron is not hindered. The reactants must assume a configuration which will allow the electron to transfer without changing its energy state. For the electron transfer will occur many times before the activated complex breaks up.

One other important restriction is that during the transfer of one electron from one atom to another no overall change of electron spin should occur. The spins of the other electrons in the system should be undisturbed by the electron that transfers. This can be important for a metal ion in a complexing environment.

Two Equivalent Redox Reactions

There are certain reactions in inorganic chemistry which require the transfer of two electrons. Transition metals generally exhibit oxidation state differing by one electron and consequently react with each other by one equivalent steps. Several of the posttransition elements have oxidation state differing by two electrons: thallium (I) - thallium (III), tin (II) - tin (IV), etc. Naturally the question arises as to whether the electrons transfer in one electron steps or whether they transfer simultaneously. Michaelis¹⁷ has produced the principle of compulsory univalent oxidation steps. This has evolved from the consideration of a restricted field of redox reactions, and is generally considered no longer vaild. Shaffer's¹⁸ principle of equivalence change states that complimentary reactions are fast compared to noncomplimentary ones. A complimentary reaction is one in which the oxidant and reductant undergo the same

amount of change. Higgenson¹⁹ has suggested three rules. 1) Species derived from the transition elements will react with

each other by a series of univalent changes.

2) Species derived from the nontransition elements will react with each other in a series of bivalent changes unless at least one of the reactants is a free radical, in which case univalent change occurs.

3) Species derived from a transition and a nontransition element will react with each other by either univalent or bivalent changes, univalent changes being more common. Thus while it is impossible to predict accurately what will occur in a given situation, the preceeding rules make it possible for reasonable predictions to be made.

The Effect of Anions

The anions present during an oxidation-reduction reaction can vastly change the rate of that reaction. There are several reasons for this. Most oxidation-reduction reactions occur between ions bearing a positive charge. It is easier for these ions to approach each other, and less energy is required if a negative ion interposes itself between the positive ions in an activated complex. Anions can also stabilize one of the reacting ions or product ions by complexing. Cobalt (III) for example is not stable in aqueous solution unless it is complexed by some ligand. It is also possible for the anions to form a bridge between the reacting species thus making the electron transfer more likely, and secondly this bridge may be an easier pathway for electron transfer than other pathways

available to the electron. Finally sharing one ligand may symmetrize the transition state, again making the transfer of an electron more probable. Thus the anion which has many times in the past been relegated to the position of a spectator ion is assuming more and more importance in oxidation-reduction reactions. Consequently the effect of the anion on the rate of oxidation-reduction reactions is being examined more closely.

B. URANIUM CHEMISTRY

Uranium was discovered in a pitchblende sample from Czechoslovakia in 1789 by M. H. Klaproth, who named it after the then recently discovered planet Uranus. It was over one hundred years later that Becquerel discovered that uranium undergoes radioavtive decay. It was an additional forty years before the crucial importance of uranium was discovered. Hahn and Strassman showed in 1938 that uranium undergoes fission. Shortly thereafter a crash program was instituted in the United State to produce a bomb based on the fissionability of uranium. It was during this program that uranium chemistry underwent a more careful scrutiny than any element had ever been subjected to before.

Of major interest to the bomb program were the gaseous compounds of uranium, and consequently the aqueous chemistry was somewhat neglected. A rather complete record of binary compounds and the chemistry of uranium is found in Katz and Rabinowitch²⁰, while Seaborg and Katz²¹ provide a general record of uranium chemistry.

There are four common oxidation states of uranium. Each is listed along with its color and formula in table I.

Table I

Uranium Ions In Aqueous Solution²²

Oxidation State	Formula	Color
+3	υ ⁺³	Red
+4	v ⁺⁴	Green
+5	002 ⁺¹	
+6	vo ₂ +2	Yellow

Two outstanding properties that uranium ions possess are their ease of hydrolysis and with the exception of uranyl ion, their instability. Considerable hydrolysis is expected because of the relatively high charge that the ions possess, and in order to maintain monomeric species in solution a high hydrogen ion concentration is necessary. With decreasing hydrogen ion concentration, hydrolysis occurs, then polymerization of the hydrolysis products and finally precipitation of hydroxides. The order of increasing hydrolysis is U(IV) < U(VI) < U(III).

As has been mentioned uranyl ion is the only stable species in solution. All other species react with water, oxygen or themselves to produce a more stable species. Consequently special techniques are necessary to produce and preserve these ions. The order of stability of the uranium ions is U(VI) > U(IV) >U(III) > U(V).

All uranium species can be produced by electrolysis or by dissolving the appropriate chloride in water.

Uranium in the plus three oxidation state can be produced by dissolving uranium trichloride in water or by electrolysis. It is unstable, reacting readily with air, and reducing water to produce hydrogen.

The uranium in the plus four oxidation state is most easily produced by electrolysis or solution of uranium tetrachloride in water. It is unstable and reacts slowly with the oxygen in the air, consequently it must be protected with some form of inert gas. If this is done, the uranium (IV) solution can be maintained in the laboratory indefinately.

Uranium (V) is very unstable and disproportionates according to the equation that follows.

$$2 \text{ uo}_2^{+1} + 4 \text{ H}^+ = \text{ u}^{+4} + \text{ uo}_2^{+2} + 2 \text{ H}_2 \text{ 0}$$
 6)

The equilibrium constant for this reaction is reported by Nelson and Krause²³ to be 1.7 \times 10⁶. Thus in any solution containing uranium in the oxidation states of four and six, there will be a small amount of uranium (V).

In a recent paper Gordon and Taube²⁴ report several methods of producing uranium (V). Chromium (II), europium (II), and uranium (III) all reacting with uranium (VI) will produce uranium (V) in solution. Krause and Nelson²⁵ report that the dissolution of uranium pentachloride in water first forms a solution of uranium (IV) and (VI) which then reacts to form uranium (V).

Uranium (VI) is the familiar stable oxidation state of uranium. It is easily prepared and is completely stable under all normal conditions. The oxidation potentials for the various oxidation states of uranium are shown in table II.

Table II

Oxidation Potentials of Uranium Ions²⁶



Formal potential in 1 M Perchloric Acid at 25° C. C. URANIUM OXIDATION-REDUCTION MECHANISMS

Even though uranium has received much careful attention recently, there is a dearth of quantitative data. The oxidation reduction reactions which have been studied are tabulated in table III. The thermodynamic information that is available is listed in table IV.

The isotopic exchange between uranium (IV) and uranium (VI) was studied by Rona²⁷ in 1950. The reaction is second order in uranium (IV) and first order in uranium (VI). The activated complex postulated contains UOH^{+3} and UO_2^{+2} ions. It is very interesting to note that added chloride had no effect on the rate of the reaction.

Moore²⁸ studied some aspects of the reduction of uranium (VI) with tin (II) determining that the rate was first order in both uranium (VI) and tin (II). Qualitative effects of hydrochloric acid, chloride ion and hydrogen ion were noted. Increasing the hydrochloric acid concentration, increases the rate

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OXIDATION-REDUCTION REACTIONS OF URANIUM

Reducing Agent	Oxidizing Agent	Medium	Rate Law	Reference
U(IV)	Fe(III)	HCIO4	d (Fe ⁺²) / dt=2 [u(IV]] [Fe(III] *	t
U(IV)	(IN)N	HCL	$Rate = kk_1 \left[\overline{U}(IV) \right]^2 \left[UO_2^{+2} \right] / \left(\frac{H_+}{K_h} + 1 \right)^2 (H_+)^2$	27
U(IV)	02	HC104	$a \left[\overline{u(IV)} \right] / at = k \left[\overline{u(IV)} \right] \left[o_2 \right] / \left[\overline{H^+} \right]$	ĸ
Sn(II)	(IV)U	HCI	Rate = $k \left[u(vI) \right] \left[Sn(II) \right]$	28
U(IV)	Fe(III)	H ₃ PO ₄		29
U(IV)	(111)LT	нсто ₄	$a \left[u(IV) \right] / at = \left[u^{+t} \right] \left[T_{1}^{+2} \right] (k_{1} \left[T_{1}^{+} \right]^{-1} + k_{2} \left[T_{1}^{+} \right]^{-1}$	-2) 5
U(IV)	(VI)dN	[†] oton	$a \left[N_{p0}^{+} \right] / at = 2k \left[u^{++} \right] \left[N_{p0}^{-} \right]^{-2} / \left[H^{+} \right]$	34
U(IV)	Pu(VI)	HCI0 ⁴		30
U(IV)	U(VI)	H ₂ 0	ſ	31
		C ₂ H5oH Ethylene Glycol	* $\frac{\mathbf{k}^{*} (\mathbf{H}^{+}) + \mathbf{k}^{"}}{(\mathbf{H}^{+})^{2} + (\mathbf{k}_{1} + \mathbf{k}_{2})(\mathbf{H}^{+}) + \mathbf{k}_{1}\mathbf{k}_{2}}$	32

Reducing Agent	Oxidizing Agent	Activated Complex	∆ ^{∎∙}	۵s•	Reference
U(IV)	Fe(III)	UOHFe	22.5		4, 35
		UOFe	24.5	5 5 7	4, 35
U(IV)	(III)TL	UOHTI	24.6	16	Ŀ
		LTOU	21.7	2	5
U(IV)	(11)dN		18.2	7.4	34
U(IV)	Pu(VI)	н ₂ оионор _и о	17.6	3.4	30
		HOUOHOPuO	21.4	18.1	30
U(IV)	U(VI)	HOUOUO	32.8	25.8	27
U(IV)	Ce(IV)	CeOHU	13.9	6.2	35
Sn(II)	(II)U		17.4	1	28

THERMODYNAMIC DATA FOR URANIUM OXIDATION-REDUCTION REACTIONS

Table IV

tremendously, while the addition of either hydrogen ion or chloride ion, keeping the other ion concentration constant, only increases the rate slightly.

Baes²⁹ found the oxidation of uranium (IV) by iron (III) proceeds to completion. The reaction in the presence of phosphoric acid is not nearly as fast as in sulfate media.

In the same year Betts⁴ carried out a thorough study of the uranium (IV) - iron (III) reaction. Two paths were found, both first order in both uranium (IV) and iron (III). The hydrogen ion order was -1.48 suggesting mixed first and second order paths. Betts concludes that this indicates hydrolysis products and believes the species UOH⁺³ and U(OH)₂⁺² are the most probable reacting species.

Halpern and Smith ³ have reported a chain reaction mechanism for the oxidation of uranium (IV) with oxygen. The reaction is first order in both uranium (IV) and oxygen and negative first order in hydrogen ion. This again suggests that hydrolysis products are reacting. Catalysis by metal ions was also studied and among other things it was discovered that copper (II) catalyzed the reaction greatly.

The reaction between uranium (IV) and plutonium (VI) was shown by Newton³⁰ to be first order in uranium (IV) and plutonium (VI). In explaining the hydrogen ion dependence of the reaction, the idea of an inhibiting back reaction was presented. Newton states that this means that the system must cross two barriers (i.e. two activated complexes) consecutively rather than by parallel paths.

In one of the simplest reactions of this type encountered, Sullivan, Zielen, and Hindman³⁴ found that the reaction of uranium (IV) with neptunium (VI) was first order in uranium and neptunium, and negative first order in hydrogen ion. Thus the reaction has only one reaction path, through the hydrolyzed uranium neptunyl ion intermediate.

Harkness and Halpern⁵ found two parallel paths in their study of the thallium (III) - uranium (IV) reaction. The reaction is first order in uranium and thallium. Consideration of the hydrogen ion effect leads to the activated complexes UOHT1⁺⁶ and UOT1⁺⁵. The effect of several anions and cations on the rate was noted but no attempt was made to explain these effects quantitatively.

Mathews, Hefley and Amis³¹ have studied the rate of the uranium (IV) - (VI) exchange in water, ethanol, and water-ethanol mixtures. As the composition of the solvent changes from 0 per cent ethanol to 100 per cent ethand, all reacting substances change their reacting order radically.

Amis and coworkers^{32,33} have extended this study to ethylene glycol-water and acetone-water systems.

In all three of these systems the order of the reactants change with change in composition of solvent. Rate laws have been derived to explain the rate in certain solvent compositions, but as would be suspected, no rate law can be written to explain the rates in all solvent compositions.

One important fact should be noted. In almost all cases where uranium (IV) is oxidized, it is a hydrolysis product that reacts although most of the uranium (IV) is present as the +4 ion. No more than a few per cent of the uranium (IV) can be hydrolyzed under these conditions of high acidity.

3. THEORETICAL

All rate reactions were graphed as a second order reaction with two reactants. For the reaction

$$A + B = C + D$$
 7)

the change in the concentration of A per unit time is given by

$$-\frac{dA}{dt} = k [A] [B] \qquad 36,37 \qquad 8)$$

This, upon integration, yields

$$\frac{1}{B_{o}-A_{o}}\ln\frac{A_{o}B}{B_{o}A} = kt \qquad 9)$$

This may be plotted several ways. The first is simply to plot the quantities on the left hand side of the equation as a function of time. Then the slope of the line is equal to the constant, k.

An easier procedure, however, is to rearrange the equation into the following form.

$$\log \frac{B}{A} = \frac{B_0 - A_0}{2 \cdot 303} \text{ kt} - \log \frac{A_0}{B_0}$$
 10)

Here log B/A, a quantity more easily determined, may be plotted as a function of time. The slope of this line will equal $(B_0-A_0) k / 2.303$ and so k may be determined by solving the equation for k.

$$\mathbf{k} = \frac{2.303 \text{ X Slope}}{B_o - A_o} \qquad 11)$$

In equation 9) the intercept at time equals zero is zero since the logarithm term is equal to zero. In equation 10) this is no longer true. The intercept will be equal to $\log B_0/A_0$ when time is equal to zero.

Two other significant situations need to be discussed. It is obvious that at equal concentrations both of the previous equations give no solution due to the term $B_0 - A_0$ which appears in each equation. Using equal concentrations of two reactants is equivalent to the case of a second order reaction with one reactant. This condition of exactly equal concentrations is difficult to achieve experimentally, thus an equation for the case of very nearly equal concentrations is necessary.

This method is discussed in both of the kinetic texts pre-

$$\frac{1}{(d-x)} - \frac{1}{d} = kt$$
 12)

where d is the mean initial concentration. When the quantity 1 / (d - x) is plotted as a function of time, the graph will be a straight line with a slope equal to the constant k.

The second situation arises as a result of mathematical rearrangement of the equation. Assume that over the first part of the reaction, the concentration of B is a constant and that B is in excess over A. Then rearrange equation 10)

$$\log \frac{1}{A} = \frac{k(B_0 - A_0)t}{2.303} + \log \frac{B_0}{A_0B}$$
 13)

and substitute

$$K = \frac{k(B_0 - A_0)}{2.303}$$
 14)

and write the resulting equation in the exponential form.

$$\frac{1}{A} = \frac{B_0}{A_0 B} e^{Kt}$$
 15)

Now expand e^{Kt} as a series.

$$e^{Kt} = 1 + Kt + \frac{K^2 t^2}{2!} + \frac{K^3 t^3}{3!} + \cdots$$
 16)

and substitute into equation

$$\frac{1}{A} = \frac{B_0}{A_0B} (1 + Kt + \frac{K^2 t^2}{2!} + \frac{K^3 t^3}{3!} + \dots)$$
 17)

In the early part of the reaction, e^{Kt} may be approximated by (1 + Kt) to give the following equation.

$$\frac{1}{A} = \frac{B_0}{A_0 B} (1 + Kt)$$
 18)

This can be rearranged in to the linear form shown below.

$$\frac{1}{A} = \frac{B_{o}K}{A_{o}B} t + \frac{B_{o}}{BA_{o}}$$
 19)

Now a graph of the quantity 1/A as a function time should be linear, at least for the early part of the reaction. Figure 1 shows a graph of 1/U as a function of time for a typical reaction. It can be seen that the graph is linear for approximately the first sixteen hundred seconds.

In many reactions where catalysis was observed, the 1/U graphs do not yield a straight line. This is illustrated in figure 2. Here, as later discussion will show, there are two paths, both second order, occuring simultaneously, and resulting in curvature of the 1/U graph.





4. EXPERIMENTAL

A. **PREPARATION OF REAGENTS**

All reagents used were analytical grade or were purified by recrystallization before use.

Perchloric Acid

The perchloric acid used was Baker's Analyzed Reagent or Mallinckrodt 70% Analytical Reagent, both of which were used without further purification. No noticeable difference appeared in the kinetic runs as a result of using different brands of acid.

Thallium (III) Perchlorate

The thallium source was a thallium (I) sulphate stock solution previously prepared by Mickel³⁸. The original material was purchased from E. H. Sargent and Company. The thallium (I) sulphate was oxidized with 1 M potassium hexacyanoferrate (III) solution which was 3 M in sodium hydroxide. The oxidation went smoothly and a rich cocoa brown precipitate was produced. The precipitate and supernatant liquid were transferred to a large beaker. After standing, the supernatant liquid was removed with a fine fritted glass filter stick. The thallium (III) oxide was washed with boiling demineralized water until the supernatant liquid gave no detectable test for sulfate ion with barium nitrate, or for hexacyanoferrate (III) ion with ferrous ammonium sulfate, or for hexacyanoferrate (II) with ferric nitrate. The precipitate was then dissolved in hydrochloric acid. The thallium was reprecipitated with solid sodium hydroxide. Twenty-five milliliters

of the oxidizing solution were added to assure complete oxidation. The precipitate was washed with boiling water until it gave no test with silver nitrate.* The precipitate was then dissolved in a slight excess of perchloric acid, and diluted to one liter with demineralized water. The solution produced was about 2.5 N in hydrogen ion and 0.46 M in thallium (III) ion.

Uranium (IV) Perchlorate

Baker's C. P. Analyzed Reagent was used to prepare uranium (VI) perchlorate by a method modified from that found in Gmelin³⁹. About seventy-five grams of uranium (VI) nitrate hexahydrate was dissolved in water. Thirty per cent hydrogen peroxide was diluted to three per cent, and added with stirring to the uranium (VI) nitrate which had been heated to a temperature higher than seventy degrees centigrade on a steam bath. A coarse lemon yellow precipitate was formed. This was filtered and washed with conductance water.

Here again the importance of using a hot solution is seen. The precipitate formed under room temperature conditions is characterized by small particle size, poor filterability, etc. If the precipitation is carried out at 80° C., the precipitate is coarse, easy to filter, settles out rapidly, and generally has more desirable characteristics.

* It is essential that very hot water be used, otherwise the precipitate changes characteristics and becomes almost impossible to filter. The use of cold water also causes peptization. The use of boiling water was found to eliminate both problems.
The uranium (VI) peroxide thus prepared was mixed with four hundred milliliters of conductance water and sixty-four milliliters of concentrated perchloric acid, and heated on a steam bath. Solution generally took some hours depending on the hydrogen ion concentration, the higher concentration being the one in which solution took place more rapidly.

When complete solution was attained, the solution was filtered through a fine grade fritted glass filter and the process of precipitation repeated. After three precipitations had been made the solution of uranium (VI) perchlorate was kept hot for twenty-four hours and then boiled for one-half hour to remove any remaining traces of peroxide. Then the solution was poured into an electrolysis flask. The preparation of uranium (IV) perchlorate was carried out in a manner similiar to that described by Ahrland⁴⁰. The electrolysis flask was a modified one liter one neck flask. A small "L" shaped piece of tubing was added to the bottom of the flask to provide an external electrical connection to the mercury cathode. On the side of the flask was attached a fifteen millimeter "L" shaped tube containing a coarse fritted disk about three centimeters from the flask proper.

The closure consisted of a bent tube with stopcock passing through a 24/40 standard taper joint and reaching to the bottom of the flask. Two additional inlets to the joint were provided. The finished apparatus is shown in figure 3.

In operation the solution of uranium (VI) perchlorate was placed in the flask over a pool of mercury six centimeters in diameter. The side arm was filled with 0.5 N perchloric acid. A

platinum electrode was inserted in the side arm and a platinum wire in the mercury leveling bulb. Dry oxygen-free nitrogen was bubbled through the inlet (A) and then through the solution. It exited via (I), when the electrolysis was complete (I) was closed off by clamping the attached rubber tube, and nitrogen was admitted through (B). The pressure then forced the liquid out of the flask via (M), assuming appropriate adjustment of the stopcock at (M).

The pumping time had to be short so that the pressure would not force the solution out of tube (H).

When the electrolysis of the uranium (VI) perchlorate was begun the solution was about 0.5 <u>M</u> in perchloric acid and 0.13 <u>M</u> in uranium (VI) ion. As the electrolysis began the solution was yellow. A current of 0.7 amperes at 7 volts was passed into the solution and very rapidly a green coloration was produced above the mercury. Agitation of the solution was provided by a stream of dry nitrogen which was bubbled through the flask. The electrolysis was continued for several hours until the solution turned quite dark due to the production of uranium (III). When the uranium (III) appeared to be fairly well distributed through the flask, the electrolysis was discontinued. The excess uranium (III) was destroyed by bubbling oxygen through the flask. Oxygen reacts rapidly with uranium (III) but only slowly with uranium (IV).

The electrolysis was carried out at room temperature. Gordon⁴¹ notes that the electrolysis proceeds to completion if the solution is cooled to 0° C. No attempt was made to cool the solution, consequently the uranium (IV) solution always contained some uranium (VI), generally on the order of a few per cent.

This preparation was carried out at first in a different manner from the above. The wire dipping into the mercury was ordinary tinned copper, the hydrogen peroxide used was three per cent not diluted thirty per cent, and demineralized water was used. In these cases a small amount of unidentified very finely divided solid was found. This would make the solution appear cloudy, although it settled out after a day.

The first preparation was transferred immediately after electrolysis to the storage flask and thus the precipitate settled out in the storage flask. The second solution was allowed to stand in the electrolysis flask for two days until settling had occured. Then the solution was carefully transferred.

Additional preparations were carried out in the nammer first noted and no precipitates were produced.

The precipitate was isolated but never identified. A suggestion was made that the precipitate might be U_{304} since this is suspected to be formed in certain electrolyses⁴².

No evidence could be found that this precipitate interfered with the oxidation reaction as long as the precipitate was removed before the use of the uranium.

Two different materials were used for the anode in the electrolysis procedure. One was a platinum wire with a one centimeter platinum square attached to the end. This electrode produced no side reactions. The other was a gold wire coiled into a spring. This was used in two electrolyses and both times a black deposit appeared on the gold which could be removed by nitric acid but only with difficulty. Use of the gold was discontinued.

- B Nitrogen inlet
- C 24/40 standard

taper joint

- D Uranium solution
- E Heavy wall tygon

tubing

- F Coarse fritted disk
- G Platinum anode
- H Side arm (15MM)
- I Nitrogen outlet
- J Platinum wire to

mercury cathode

- K Mercury cathode
- L Leveling bulb
- M Solution outlet



Figure 3. Uranium (IV) Preparation Flask.

Finally it should be noted that the D. C. source was such that approximately a one volt ripple was imposed on the direct current. This was determined by viewing the current on a calibrated oscilloscope. The effect of this on the electrolysis is unknown.

Water

For the first part of the program demineralized water was used. The demineralized water was produced by passing distilled water through a mixed bed of anion and cation ion exchange resins. This water contained less than 0.5 parts per million impurities. It is possible that this water contained some organic impurity introduced by the resin.

However difficulty was experienced in preparing the uranium (IV) perchlorate solution and in reproducing the same rate constant values as reported by Harkness and Halpern⁵. In an effort to improve this situation conductance water was substituted for the demineralized water. This water was prepared by taking demineralized water and distilling it out of alkaline potassium permanganate solution. Conductance water was used exclusively from February 9, 1961. In the appendix all reactions using conductance water are noted by an asterisk after the uranium concentration.

Nitrogen

Prepurified nitrogen which had been further treated to remove the last traces of oxygen was used to protect the uranium (IV) perchlorate from atmospheric oxidation, and to remove the uranium solution from the storage flask. For a description of the

nitrogen purification train see the special apparatus section below.

Sodium Perchlorate

Anhydrous sodium perchlorate was obtained from the G. Frederick Smith Chemical Company. This was dissolved in demineralized water, filtered and placed on a hot plate to reduce the solution volume. As the solution was heated a pale reddish gelatinous material precipitated out of solution. The solution was filtered and the precipitate tested for ferric ion by adding thiocyanate ion in a solution made acidic with hydrochloric acid. The test was positive. The evaporation procedure was continued until no further precipitate was produced. The solution was filtered and put back on the hot plate. It was cooled after further reduction of the volume. When the production of crystals had ceased the solution was filtered and the crystals so obtained were washed and redissolved, and the process repeated to produce a new crop of crystals. After filtration the crystals were washed, dried, and stored in a vacuum desiccator.

Maleic Acid

Maleic acid was obtained from Eastman Kodak Company. This was dissolved in ninety-five per cent ethanol until a saturated solution was formed at room temperature. The solution was cooled with stirring in an isopropanol-dry ice bath. Crystallization occured as the solution cooled. When crystallization was complete the crystals were filtered in a Buchner funnel which had been cooled with dry ice and then the crystals were washed with

ethanol which had also been cooled with dry ice. The crystals, when dry, were stored in a vacuum desiccator. The melting point of the crystals was determined as $129-132^{\circ}C$. The literature value is given as $130-130.5^{\circ}C.^{43}$

Tartaric Acid

Mallinckrodt Analytical Reagent was used without further purification.

Succinic Acid

Baker's C. P. Analyzed crystals were used without further purification.

Oxalic Acid

Baker Analyzed Reagent was used without further purification.

Fumaric Acid

Fumaric acid used was obtained as the practical grade from the Eastman Kodak Company. It was recrystallized from boiling water.

Malonic Acid

The malonic acid was the practical grade from Distillation Products Industries. An unsuccessful attempt was made to recrystallize the acid from water. A sample was then purified two times via sublimation at 130°C. under a pressure of less than ten milliliters of mercury. A sample melted at 134-135.5°C. The melting point found in the literature is 135.6°C.⁴³

Malic Acid

Practical dl-malic acid from Eastman Kodak Company was recrystallized from a mixture of absolute ethyl alcohol and trichloroethane. A three to two mixture of alcohol to trichloroethane was used and a saturated solution at the boiling point was formed. An additional four parts of trichloroethane was then added and the solution allowed to cool. Crystallization occurs slowly as the cooling proceeds. It was found necessary to cool the solution with dry ice-isopropanol mixture to initiate crystallization on occasion. The malic acid was recrystallized three times in the above manner.

Monomethyl Ester of Maleic Acid

Several attempts were made to produce the methyl half ester of maleic acid, but all were unsuccessful.* In one preparation maleic anhydride was reacted with methyl alcohol in ethyl ether. The maleic anhydride was recovered unreacted.

Maleic anhydride was also reacted with sodium methoxide in ethyl ether. On removal of the ether a thick syrup was obtained. This crystallized after a day and much stirring. Maleic acid was recovered after filtering and recrystallizing from ethyl ether.

^{*} The author would like to thank Mr. James D. Hoeschele and Mr. Calvin M. Love for their work in attempting these preparations.

Finally maleic anhydride was reacted with sodium methoxide in methyl alcohol. A crystalline product proved to be maleic acid under analysis.

Siegel and Moran⁴⁴ claim to have produced the methyl half ester in acetone by reacting equimolar amounts of maleic anhydride and methyl alcohol. The ester was never isolated. Their proof of its existance rests mainly on the value of the neutralization equivalent determined by titrating the acetone solution with standard hydroxide solution.

When these solutions of the ester in acetone are titrated with aqueous sodium hydroxide, the neutralization equivalent so determined is that of maleic acid. Any attempt to isolate a solid by removal of the acetone results in the production of a white solid with a neutralization equivalent equal to that of maleic acid. Solutions of the recrystallized ester in methyl alcohol were titrated with standard alcoholic sodium hydroxide. The neutralization equivalent obtained was again that of maleic acid. Therefore it must be concluded that while the methyl half ester apparently exists under anhydrous conditions, any attempt to isolate or purify the substance introduces enough water to hydrolyze it.

B. SPECIAL APPARATUS

The several pieces of special apparatus used in this research are illustrated in the figures that follow. A short description of each appears below.

Circles are used to designate the stopcocks, the solid line (s) in the circles showing the holes bored in the stopcock. All joints are either 24/40 standard taper if they are connected to

flasks or ball and socket joints if they appear in transfer lines. No joints or stopcocks that contacted the solution were greased.

Direct Current Supply

Figure 4 illustrates the direct current supply. The diagram is self-explanatory. The component parts for the supply were mounted on a piece of plywood. A one volt alternating current ripple was shown to be present by means of an oscilloscope.

Nitrogen Purification Train

The nitrogen purification train is shown in figure 5. The method followed was that of Gordon⁴⁵. Prepurified nitrogen from the Matheson Company was passed over copper turnings kept at 450°C. in a tube furnace (A). Then the gas passed over copper deposited on Kieselguhr also heated to 450°C. (B). From there it passed successively through four gas washing bottles equipped with glass The first two towers (C,D) contain alkaline pyrogallol frits. (fifty grams of sodium hydroxide and thirty grams of pyrogallol in three hundred milliliters of water). The final two towers (E,F) contain water and aqueous perchloric acid, respectively. The perchloric acid is adjusted to the same acidity as that present in the uranium storage flask. The purified nitrogen was then bubbled through the uranium solution. A hydrogen outlet, (G), is used when the copper is regenerated. This also serves to remove the water formed during the process.



Figure 4. Direct Current Supply

Uranium Storage Flask

This is a three neck flask shown in figure 6, two necks of which (B,C) are fitted with tubes that lead to the bottom of the flask. The third neck (A) has a bent tube with stopcock fitted into it. This serves as an exit tube for the nitrogen. The center tube (B) serves not only as a delivery tube for the uranium solution but also as a gas inlet tube for the nitrogen. The remaining tube (C) serves also as an inlet for nitrogen as well as an outlet for the uranium solution.

During storage a slow stream of nitrogen is admitted through tube (C). Stopcock (F) is turned to allow nitrogen to flow through the "tygon" tube (E). To provide for an exit for the nitrogen, tube (A) is open. To allow for removal of uranium solution exit (A) is closed and nitrogen inlet (B) is used to admit nitrogen. This requires adjusting stopcocks (F) and (H) to allow nitrogen to flow through tube (I). Finally stopcock (D) is turned so that the uranium solution will flow out the lower of the two connections. In normal removal the tube (C) is filled with uranium solution twice (allowing a little to flow out exit (J)) before removing a sample.

C. ANALYTICAL DETERMINATIONS

Sodium Hydroxide

A sodium hydroxide solution that was 0.5 \underline{N} was prepared as described by Kolthoff and Sandell⁴⁶ and stored in polyethylene bottles, protected from the atmosphere by "Ascarite" carbon dioxide absorbent. It was standardized against potassium acid phthalate (Mallinckrodt Analytical Reagent - primary standard) Which had been







dried at 125°C. and stored in a desiccator.

Perchloric Acid

The 5 \underline{N} perchloric acid was standardized against the standard sodium hydroxide in the normal way using phenolphthalein as the indicator.

Potassium Permanganate

Standard O.1 <u>N</u> potassium Permanganate was prepared according to Kolthoff and Sandell⁴⁷. It was standardized against sodium oxalate (Mallinckrodt Analytical Reagent - primary standard) which had been dried at 110°C.

Uranium

Solutions of uranium perchlorate were analyzed for both uranium (IV) and uranium (VI), as well as for hydrogen ion.

To determine the uranium (IV) content, (C_4) , the solution was simply diluted with conductance water and titrated with standard potassium permanganate to the first pink coloration.⁴⁸

The total uranium, (C_t) was determined by reduction of a sample in a Jones reductor thus reducing any uranium (VI) to uranium (IV). The solution was then titrated to a pink color with standard potassium permanganate. If the same size sample was used in both analyses, the uranium (VI) concentration, (C_6) , can be calculated from the difference in the two titrations.

$$c_6 = c_t - c_4$$
 20)

The total hydrogen ion was determined by replacing the uranium ions on a column of Dowex $50x \times 12$ (Bio-Rad Analytical Grade - 100-200 mesh - hydrogen form). The resulting solution was titrated with standard sodium hydroxide to a phenolphthalein endpoint. The free hydrogen ion then can be calculated from the equation below

$$H_{o} = H_{t} - 4C_{4} - 2C_{6}$$
 21)

In this equation H_t equals the total amount of hydrogen ion in the titrated solution, and H_o equals the amount of free hydrogen ion in the original solution. Concentrations were in units of molarity.

It was found that a pH titration did not give accurate results in the determination of H⁺ ion. Difficulty was caused in these titrations by the precipitation of the uranium hydroxides, so the ion exchange method, which was much simpler and more accurate was adopted.

The fact was soon discovered that the uranium solutions change titer with time. This is really to be expected but it was hoped that this could be cut to a minimum by the precautions taken to keep oxygen out of the flask. However, the titer did change and so the uranium (IV) analysis was repeated every few days and the points graphed.

The uranium concentration my given day was determined to the nearest quarter day. After each uranium (IV) determination the method of least squares was applied to obtain the best line through the points. Figure 7 shows a typical graph that was obtained in this way. Uranium (IV) perchlorate solutions were prepared four times during the course of the project. For the final solution several changes were made to minimize any time dependent change of uranium concentration.

First, extreme precautions were taken to prepare and keep the uranium solution pure. And secondly the solution storage flask was wrapped with aluminum foil to bring to a minimum the amount of light entering. It was impossible to cut off the light completely since tubings lead from the flask and these cannot be completely wrapped. The protection from light did not provide any reduction in rate of change of titer. For example, the uranium solution molarity changed by 0.0140 moles per liter in one hundred and twenty-five days in the third uranium (IV) perchlorate preparation. The fourth preparation changed its molarity by 0.0123 moles per liter in one hundred and twenty days.

Thus even with the utmost precautions it was impossible to stop the uranium (IV) solution from changing titer. In order to know the uranium (IV) concentration at any time, it was necessary to constantly analyze the uranium (IV) solution.

In addition to this it appeared from several reactions that the amount of uranium (IV) supplied to the reaction flask, was not equal to the amount of uranium (IV) present when the reaction is initiated. Since some of the uranium (IV) had reacted in the interval between preparation of the solution and initiation of the reaction, it was important that a method of determining the concentration of the uranium (IV) at the beginning of the reaction be developed.





In the section on theory, the reasons were given why a graph of the reciprocal uranium concentration as a function of time should be linear. Such a graph can then be used to determine the uranium concentration by extrapolating the line time to zero and determining the value of 1/U at that point. This method gives the uranium concentration most consistent with the reaction data.

By the use of this method, the initial concentration of uranium could be determined rather accurately from the reaction data. At this point a rather interesting discrepancy was noted. In reactions where the amount of maleic acid present was varied, it was noticed that the initial concentration of the uranium (IV) varied also. Table VI shows the variation of the absorbance of maleic acid as a function of the temperature and concentration of maleic acid. The variation could be caused by several factors. One possible source of error is the normal operative and instrumental errors associated with quantitative analysis. A second cause might be reaction of the uranium (IV) with the oxygen of the air. A complex with a different molar absorption coefficient might slowly form causing a third source of error. Fourth the uranium could react with the organic acid present reducing it.

The first error can be eliminated by considering the data listed in table VI. The changes with temperature and concentration are too regular to be due to random error.

In order to determine whether complexing of the organic acid by the uranium might cause any change in the absorbance, the molar extinction coefficient was determined for several acids using the Beckman Model DK-2 spectrophotometer. The results are shown in

Table VI

Initial Absorbance of Uranium Solutions

Sodium perchlorate - 1.06 M, Perchloric Acid - 1.76 M, Thallium (III) Perchlorate - $9.00 \times 10^{-2} \text{ M}$, Uranium (IV) Perchlorate - The starting concentration of the uranium varied. All solutions contained 0.70 milliliters of stock solution.

Temperature °C	Maleic Acid <u>M</u> x 10 ²	Total Volume Added ml.	Initial Absorbance at 100 Sec.*
35	900.	7.69	0.156
35	90.0	7.69	0.162
35	9.00	7.69	0.166
25	900.	7.69	0.172
25	90.0	7.69	0.183
25	9.00	7.69	0.181
15	900.	7.69	0.192
15	90.0	7.69	0.195
15	9.00	7.69	0.198

Absorbance determined at 650 mμ.

table VII. The data indicate that within the limits of error there is no change in color due to complexing. There might be some questions in the case of tartaric, but in a later study by Job's method in an attempt to show complexing of the tartaric acid with the uranium, all solutions prepared were within 0.02 absorbance units of the standard. This is well within the limits of error in using the Beckman spectrophotometer. It can be concluded that the change in absorbance is not due to the organic acid complexing with the uranium (IV) ion.

Table VII

Molar Extinction Coefficient of Uranium (IV)-Organic Acid Solutions

Organic Acid	Concentration of Org. Acid <u>M</u>	Uranium Concentra- ion <u>M</u>	Molar extinction Coefficient*
None		0.0155	55.8
Succinic	0.0170	0.0154	56 .6
Malic	0.0170	0.0154	56.1
Tartaric	0.0170	0.0154	54 •5
Fumaric	0.0170	0.0154	55 •9

* Determined at 650 m μ .

Thus while it certainly is possible that the uranium could be reducing the organic acid, it seems more likely that it is reacting with the oxygen of the air. The carboxyl group is rather resistant to reduction either by chemical or catalytic means⁵⁰. It would appear that the change in initial absorbance is due to reaction of the U(IV) with the air, the reaction being catalyzed by the organic acid present.

Uranium Standards

To interpret the data from the kinetic reactions a relationship was needed between the concentration of a uranium (IV) solution and the absorbance of that solution. All absorbance readings were made at 6500 angstroms. The necessary data were provided by making up a series of solutions varying in uranium concentration but constant in hydrogen ion and ionic strength. When the absorbance for the solutions was plotted against the concentration a straight line was obtained. The method of least squares was applied to the data and the equation obtained was used to calculate concentrations corresponding to any absorbance reading. The equation is reproduced below.

$$Y = 17.6 X + 0.0176$$
 22)

In this equation X = the absorbance of the U(IV) solution and Y = the concentration of uranium (IV) x 10³. Table VIII lists the absorbance and the concentration of the uranium standard solution.

Table VIII

Uranium (IV) Standards

Sodium Perchlorate	=	1.06 <u>M</u> ,	Perchloric Acid	=	1.76]	<u>Μ</u> , μ	=	2.	, 9
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<u>M</u> x 10 ³	Absorbance
1.06	0.059
2.12	0.119
3.18	0.180
4.24	0.242
5.30	0.297

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While no study was carried out to determine the effect of hydrogen ion concentration on the molar absorption coefficient, information from two reactions indicates that this can be neglected. In these two reactions the hydrogen ion concentration varied from 0.88 M to 2.50 M. The same volume of uranium was added to each solution and the initial concentration was determined experimentally to be $3.50 \times 10^{-3} \text{ M}$. If the hydrogen ion affects the molar absorption coefficient, then the initial concentration should be different. The initial concentrations were determined by the 1/Umethod.

Krause and Nelson⁵¹ also report that the variation of molar absorption coefficient with hydrogen ion is negligible at this high acidity.

Thallium

Both oxidation states as well as total hydrogen ion were determined for solutions of thallium (III) perchlorate.

Total thallium, (C_t) , was obtained by reducing a sample of the thallium (III) perchlorate solution with sulfur dioxide to the thallium (I) state. The thallium was then precipitated as the chromate⁵², dried and weighed.

Thallium (III), (C_3) , was determined by making the solution basic, thus precipitating thallium (III) oxide⁵². This was filtered in Gooch crucibles, dried and weighed. Thallium (I), (C_1) , can then be calculated from the following equation, if the sample volumes are identical.

$$C_1 = C_t - C_3$$
 23)

Total hydrogen ion, (H_t) , was determined as in the uranium solution. The thallium ions were exchanged for hydrogen ions on Dowex 50 ion exchange resin, and the resulting solution was titrated with standard sodium hydroxide. Potentiometric titrations were attempted, but thallium oxide precipitates as sodium hydroxide is added, and the results cannot be reproduced. The free hydrogen ion could be determined more easily and accurately using the ion exchange technique. The free hydrogen ion was calculated from the equation that follows.

$$H_{o} = H_{t} - 3C_{3} - C_{1}$$
 24)

Again the concentrations are expressed as molarity. D. THE OXIDATION-REDUCTION REACTION

A reaction was initiated by mixing equal amounts of two solutions, one containing the thallium and the other containing the uranium. Both solutions were as similiar as possible to minimize dilution effects, slow hydrolyses, etc. Obviously the thallium and uranium were kept separated, but in all other aspects the solutions were identical.

Normally the organic acid was added only to one solution, usually the uranium solution, but reactions were examined out where both the thallium and the uranium solutions contained equal amounts of the organic acid. Reactions were also studied in which the organic acid was added to the thallium. Table IX gives the normal concentrations of substances used in a reaction. In most reactions only the organic acid was varied. It was necessary to vary other substituents, in a few cases. The preparation of the solutions was usually divided into two sections, the dividing point being the removal of the uranium from the storage flask. Up to this point the initiation of reactions could be delayed any length of time, but once the solution of uranium is removed from the storage flask the reaction had to be carried out in the next few hours. To minimize errors the time, from removal of the uranium solution from the storage flask until the reaction was initiated, was kept constant. No precautions were taken to protect the uranium solution after it was removed from the storage flask, thus the reaction had to be completed before deterioration of the uranium solution had taken place.

Table IX

	Uranium Solution <u>M</u>	Thallium solution <u>M</u>
U (IV)	3.50×10^{-3}	
Tl (III)		9.00×10^{-3}
HC104	1.76	1.76
NaClO4	1.06	1.06
Maleic Acid	4.50×10^{-3}	

Concentration of Reactants for a Typical Oxidation-Reduction Reaction

Reactions were executed in one of three different ways. The catalyzing substance was added either to the uranium, the thallium or to both solutions. Normally the reaction was carried out with the catalyzing substance mixed in with the uranium. Therefore this procedure will be discussed in detail and only the difference between this and the other procedures noted.

Reactions were carried out in sets of three. Two of these would be catalyzing reactions and the third a standard reaction containing no catalyzing substance. Solutions with the exception of the uranium stock were stored in a water bath maintained at 25.0° C. The necessary amounts of sodium perchlorate and perchloric acid were pipetted into one ten milliliter volumetric flask, while thallium perchlorate, sodium perchlorate and perchloric acid were pipetted into a second flask. Pipettes were given a two second drain time. Various types of pipettes were used at different times and no difference was noted in the results.

All pipettes were cleaned in the same manner. After an immersion in aqua regia they were rinsed several times with distilled water and then ten times with deionized water. The pipettes were dried in an oven.

Extreme care was taken to keep the glass equipment clean and free from possible contamination. The volumetric flasks were also cleaned in aqua regia and rinsed several times with both distilled and demineralized water.

Once the flasks had received all the reactants except the uranium and the catalyzing solution, they could be stored until needed, providing they were sealed against dust, etc. To complete the experiment the organic acid along with the uranium solution was added to the partially filled flask. Then the liquid level in the flasks was adjusted to the mark on the neck of the flask with

conductance water. If the runs were carried out at a temperature different from 25°C., the liquid level was not adjusted until the solution had equilibrated in an appropriate bath for one hour.

The amount of reaction was followed by noting the disappearance of the uranium (IV) peak at 6500 angstoms. A Beckman model DU spectrophotometer was used. This was kept at constant temperature by means of the bath in which the reactant solutions were stored. When the solution were put into the bath the spectophotometer was turned on and allowed to warm up. Also at this time a cell holder containing four cells, one of which was filled with demineralized water, was inserted in the spectrophotometer. Demineralized water was used as the reference solution for all reactions.

After the solutions had been stored in the constant temperature bath for the prescribed time, four milliliters of the thallium solution was measured into a thirty milliliter Erlenmeyer flask. Immediately thereafter four milliliters of uranium solution was added and the timing was begun. The uranium and the thallium were both measured with class A pipettes so there would be no drain time. Timing commenced when the pipette containing the uranium was half drained. After the addition of the uranium the contents of the flask were mixed well, a cell filled and the first measurement made when one hundred seconds had elapsed.

Additional reactions to a total of three were started at two hundred second intervals. This has the result of staggering the reading time of the solutions. If the absorbancy of each solution is read every three hundred seconds, then staggering

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of the times allows the reading of one solution every one hundred seconds.

Unless there was a specific reason, reactions were concluded at 2500 seconds. Some of the slower reactions were studied for as long as 10,000 seconds. When as much data as desired were gathered, the cells were rinsed with water and stored in 3 <u>M</u> hydrochloric acid. The 3 <u>M</u> acid served two purposes. It kept growths from forming in the water and also removed any thallium (III) oxide deposited on the cell walls during the rinsing process. The reaction residues were saved so that they might be reclaimed for uranium and thallium later.

E. MISCELLANEOUS EXPERIMENTS

Spectra

The spectrum of uranium (IV) perchlorate was determined and found to agree with that reported in the literature^{51,53}. The spectrum is shown in figure 8 and the absorption peaks are noted in table X.

Growths In Acids

One unusual problem occurred in connection with the organic acids. Several of the acids repeatedly developed growths that appeared to fungi on long standing. Because of this all organic acid solutions used in this project were freshly prepared.

Job's Method

Attempts were made in two cases to determine the composition of several complexes by Job's method of continous variations.





Table X

Absorption Peaks of Uranium (IV) Perchlorate

Uranium (IV) Perchlorate - 0.0154 <u>M</u>, Perchloric Acid - 1.76 <u>M</u>, Sodium Perchlorate - 1.06 <u>M</u>, Ionic Strength - 2.9, Temperature 24.9°C.

Principle Absorption Bands	Molar Extinction Coefficients
680	20.3
655	55.8
555	18.1
498	26.0
488	21.9
431	16.0

The first attempt, that of tartaric acid and uranium, has already been mentioned. A slight difference was noted between the molar extinction coefficient of a tartaric acid-uranium solution and a uranium standard. To check this, several solutions containing varying amounts of uranium (IV) perchlorate and tartaric acid were compared with uranium (IV) standards. In all cases the difference in absorbance between the mixtures and the standards was less than or equal to 0.002 absorbance units. This is well within the limits of error of determining the uranium concentration. Thus it must be concluded that if differences in absorbance do exist, they are too small to detect with existing equipment. An attempt was also made to carry out Job's method to determine uranium-tartaric acid complexes by the change in rotation that the tartaric acid undergoes on complexing. This method has been successfully used to determine thorium complexes⁵⁴. Unfortunately no rotation could be detected with the existing equipment and solutions.

This method may be practical with this system, but it will require a more concentrated uranium solution as well as a very sensitive polarimeter.

Extraction Experiments

Several extractions were carried out on the reaction products of the uranium-thallium system as catalyzed by maleic acid.

The extraction was carried out in a liquid-liquid extractor designed for use with an extracting liquid lighter than water. The extracting liquid was ethyl ether. This was removed by evaporation. Due to the slight solubility of water in ether, a small amount of water solution was obtained from the ether. This solution was initially purple but over a period of days the color changes to light brown. The extracted species were not identified.

Infra-Red Spectra

In connection with this study the infra-red spectra of maleic acid and fumaric acid were determined. The spectra are shown in graphical form in figures 9 and 10. The main absorption peaks are listed in table XI.




Absorption Peaks of Maleic and Fumaric Acids

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-	Maleic Acid		Fumaric Acid	
	Wavelength M	Intensity	Wavelength M	Intensity
-	2.37	6.2	2.39	1.6
	4.65	Sh	6.01	10.0
	4.92	Sh	7.61	2.50
	5.33	4.1	7.88	7.50
	5.88	9.41	8.18	5.0
	6.14	3.2	8.27	Sh
	6.31	5.0	9.91	2.50
	6.42	5•3	10.85-11.15	2.2
	7•97	4.7	12.89	< 1
	8.28	2 .6	13.90	1.6
	10.26	<٦		
	10 .6 10.89	3.2		
	11.44	Sh		
	11.61	10.0		
	12.76	7.6		
	13.84	4.4		

5. RESULTS

All rate constants reported in this section are the apparent second order rate constants from the equation

$$- \frac{dU(IV)}{dt} = k[U(IV)][T1(III)]$$
 25)

A. SUCCINIC ACID

Several reactions were carried out with various amounts of added succinic acid. The range of succinic acid concentrations covered was 4.5×10^{-2} <u>M</u> to 1.12×10^{-3} <u>M</u>. The rate constants for these reactions are listed in table XII. The graph of the rate equation for the first reaction listed in the table appears in figure 11. The other rate plots are similar to this one. It should be noted that the first few points do not fit the straight line. This is quite common and occurs in almost all reactions studied.

If the straight line is extrapolated to zero time, for the second order plot it should pass through the point, $\log Tl_0/U_0$. However, the extrapolated line does not pass through this point. This will be discussed fully below.

The results of this series of reactions can be seen best by examining table XII. When the succinic acid concentration is low enough, then the system has a rate constant equal to the rate constant of the system in the absence of succinic acid. As the succinic acid concentration increases, the rate constant for the reaction decreases to a minimum. From that point on additional succinic acid has no effect. The last two reactions, where the succinic acid concentration increase by a factor of two caused no



Table XII

Rate Constants for Reactions Containing Succinic Acid

Temperature = $24.9^{\circ}C_{\bullet}$		
Succinic Acid <u>M</u> x 10 ²	Uranium (IV) <u>M</u> x 10 ²	M ^k l ^x 10 ² M ^{sec}
1.12	3.46	24.7
3.38	3.46	1.73
6.75	3.46	1.23
13.5	3.47	8.2
22.5	3.47	7•4

3.47

Thallium (III) perchlorate = 9.00×10^{-3} M, Perchloric Acid = 1.76 M, Sodium perchlorate = 1.06 M, Ionic strength = 2.9 Temperature = 24.9° C.

corresponding decrease in the rate constant.

For all succinic acid reactions, the first few points deviated from the straight line. Most reactions had only the first point deviating, thus the reaction illustrated is worse than usual in this respect.

5.4

B. OXALIC ACID

45.0

The results of several reactions carried out with varying amounts of oxalic acid present are listed in table XIII. The oxalic acid concentration was varied from 2.25 x 10^{-4} <u>M</u> to 2.25 x 10^{-3} <u>M</u>. When attempts were made to increase the oxalic acid concentration above this level, a pale green-white solid precipitated in the reaction flask. Presumably the precipitate is a reaction product between oxalic acid and uranium (IV). The graphs of the rate equations all yield excellent straight lines for reactions containing oxalic acid. In all reactions the first point deviated from the straight line provided by the rest of the points. In addition the straight line failed to pass through the log Tl_0/U_0 point. In the higher concentrations of oxalic acid, the plotted lines approach the zero time intercept (log Tl_0/U_0).

The relation between oxalic acid and the rate constant is an inverse one. As oxalic acid increases, the rate constant decreases. The change in rate constant is not very large and no minimum is reached; due, perhaps, to the fact that the oxalic acid concentration cannot be very large or precipitation occurs.

Table XIII

Rate Constants for Reactions Containing Oxalic Acid

Thallium (III) perchlorate = 9.00×10^{-3} M, Perchloric Acid = 1.76 M, Sodium perchlorate = 1.06 M, Ionic strength = 2.9, Temperature = 24.9° C.

Oxalic Acid <u>M</u> x 10 ³	Uranium (IV) <u>M</u> x10 ³	k x 10 ² M ⁻¹ sec ⁻¹
2.25	3,48	2.23
4.50	3.48	2.21
11.2	3.47	1.92
22.5	3.48	1.87
22.5	3.47	1.69

C. MALONIC ACID

The reactions containing malonic acid are tabulated in table XIV. The malonic acid concentration range covered is $9 \times 10^{-4} \text{ M}$ to $9.00 \times 10^{-3} \text{ M}$. When the data from these reactions is graphed two facts are noted. One is that all experimental points occur on a line, and secondly this line includes the point $\log Tl_0/V_0$. In the two acids discussed previously neither of these two facts was true.

The first reaction in table XIV is plotted as a second order reaction in figure 12.

There is no catalysis of the uranium-thallium reaction by malonic acid. The table shows that there is only scatter in the rate constant, k, and no relationship between malonic acid and the rate constant is seen when the malonic acid varies by a factor of ten.

Table XIV

Rate Constants for Reactions Containing Malonic Acid Thallium (III) perchlorate = 9.00×10^{-3} <u>M</u>, Perchloric Acid = 1.76 <u>M</u>, Sodium perchlorate = 1.06 <u>M</u>, Ionic Strength = 2.9, Temperature = 24.9° C.

Malonic Acid <u>M</u> x 10 ⁴	Uranium (IV) <u>M</u> x 10 ³	k x 10 ² <u>M</u> ⁻¹ sec ⁻¹
9.00	3.53	2.13
22.5	3.26	2.19
45.0	3.26	2.30
67.5	3.62	2.29
90.0	3.62	2.38



D. MALIC ACID

Four reactions were carried out with malic acid included as the catalyzing agent. The range of malic acid concentrations studied was from 2.25 x 10^{-3} <u>M</u> to 9.00 x 10^{-3} <u>M</u>. The graphs of the rate equations for two of the reactions are pictured in figure thirteen.

All reactions gave a curve when plotted as a second order reaction. A gradation can be noticed in the curves with the final half of one of the reactions assuming a straight line. This reaction, the only one that gave any semblance of linearity on the rate plots was the one with the lowest malic acid concentration, 2.25 x 10^{-3} M.

The slope of this line was determined as noted in table XV. While it is dangerous to use one reaction to decide, it appears that malic acid catalyzes the reactions. First the rate constant is fifty per cent higher than the standard rate constant,* and secondly this curvature occurs in all cases where catalysis occurs.

The features of the rate plots to be noted are the linearity occuring only with low concentration and the non-linearity occurring in the range where the ratio of organic acid to uranium (IV) is one.

The rate constant in reactions containing no catalyzing agent is referred to as the standard rate constant.



Table XV

Rate Constants for Reactions Containing Malic Acid

Thallium (III) perchlorate = 9.00×10^{-3} M, Sodium perchlorate = 1.06 M, Perchloric acid = 1.76 M, Ionic strength = 2.9, Temperature = 24.9° C.

Malic Acid <u>M</u> x 10 ³	Uranium (IV) <u>M</u> x 10 ³	k x 10 ² M ⁻¹ sec ⁻¹
2.25	3.50	3.18
4.50	3.50	Curve
6.75	3.58	Curve
9.00	3.58	Curve

E. FUMARIC ACID

Table XVI lists a series of reactions carried out with varying amounts of fumaric acid. The range of fumaric acid concentrations studied were 2.50 x 10^{-4} <u>M</u> to 5.00 x 10^{-3} <u>M</u>. The data from table XVI is presently graphically in figure 14. Catalysis is very definitely present.

The curve shows that at low concentrations the system acts as though no fumaric acid is present. As the concentrations of fumaric acid increases so does the rate constant to a maximum which occurs at apporximately 3.00×10^{-3} M.

From this point on the value of the rate constant decreases with increasing fumaric acid concentration so that by the time the concentration of the fumaric acid reaches 5.00×10^{-2} the rate constant has decreased to below that of the standard uranium-thallium reaction.

Table XVI

Rate Constants for Reactions Containing Fumaric Acid

Thallium (III) perchlorate = 9.00×10^{-3} M, Sodium perchlorate = 1.06 M, Perchloric acid = 1.76 M, Ionic strength = 2.9, Temperature = 24.9° C.

Fumaric Acid <u>M</u> x 10 ³	Uranium (IV) <u>M</u> x 10 ³	k x 10 ² M ⁻¹ sec ⁻¹
5.00	3.45	1.88
4.38	3.43	2.24
3.75	3.43	2.66
3.12	3.43	3.16
3.12	3.41	2.65
3.12	3.41	3.00
2.50	3.45	2.91
2.50	3.41	2 •77
1.88	3.41	3.36
1.88	3.41	3.44
1.25	3.45	2.62
1.25	3.45	2.78
0.625	3.45	2.44
0.250	3.45	2.28





F. SODIUM PERCHLORATE

Harkness and Halpern⁵ studied the effect of ionic strength on the oxidation of uranium by thallium. These data were checked in the present study and since small differences appear this work is presented here. The data gathered are reported in table XVII, and presented graphically in figure 15.

All of the points determined by both authors fall in the same region of the graph, but the present study gave a line with a higher slope than the data gathered by Harkness and Halpern.

G. TARTARIC ACID

Over twenty-five reactions were studied in an attempt to elucidate information on the effect of tartaric acid on the uranium-thallium oxidation reaction. The range of tartaric acid studied was from 9.00×10^{-3} to 2.25×10^{-3} . The apparent rate constants for these reactions are listed in table XVIII. In the first group of reactions shown, the tartaric acid was varied while the uranium concentration was held as constant as possible. The results, at best, are poor. In the range of tartaric acid studied there appears to be a strong catalysis, with the catalysis decreasing with decreasing acid concentration.

Great difficulty was encountered in this range of tartaric acid concentration. Graphs of the second order rate equation in this range of tartaric acid are very frequently not linear or linear only after a certain amount of reaction has occurred. Figure 14 illustrates this same property for malic acid.

In the first set of reactions only three produced

Table XVII

Rate Constants for Reactions Containing Sodium Perchlorate Uranium (IV) perchlorate = $3.48 \times 10^{-3} M$, Thallium (III) perchlorate = $9.00 \times 10^{-3} M$, Perchloric Acid = 1.76 M, Temperature = $24.9^{\circ}C$.

Sodium perchlorate <u>M</u>	k x 10 ² M ⁻¹ sec ⁻¹ Harkness & Halpern	k x 10 ² M ⁻¹ sec ⁻¹ This work
0.000	1.08	
0.424		1.78
0.84	1.55	
0.949		2.00
1.06		2.21
1.29	2.00	
1.48		2.47
2.12		3.00
2.58	3.24	
2.96	3.83	





straight lines based on all points. Three reactions produced nonlinear graphs. Three more yield six or fewer straight lines based on points. One reaction is very interesting in that when the data are plotted the points group themselves into two distinct lines. The graph of the rate law for this reaction is reproduced in figure 16.

The first two reactions of the second set show again the effect of varying tartaric acid. These were run at a different uranium (IV) concentration than those above. With the lower uranium concentration the graph of the rate equation had very little curvature. In the final three reactions of this set the effect of decreasing uranium while keeping tartaric acid constant is seen in the increasing rate constant.

In the reaction previously discussed the tartaric acid was mixed with the uranium solution. In the third set of reactions the tartaric acid was mixed with the thallium solution, and in the last set the tartaric acid was split equally between the uranium and thallium solutions. In both of these cases, the apparent second order rate constant increases as the concentration of the uranium decreases.

Table XVIII

Rate Constants for Reactions Containing Tartaric Acid Thallium (III) perchlorate = 9.00×10^{-3} M, Perchloric acid = 1.76 M, Sodium perchlorate = 1.06 M, Ionic strength = 2.9, Temperature = 24.9° C.

Tartaric Acid <u>M</u> x 10 ³	Uranium (IV) <u>M</u> x 10 ³	k x 10 ² M ⁻¹ sec ⁻¹
9.00	3.41	4.93
9.00	3.50	4.48*
8.75	3.64	5.42
6.75	3.50	Curve
6.75	3.64	2.27
4.50	3.41	Curve
4.50	3.50	Curve
3.50	3.64	3.35*
2.25	3.41	2 lines
2.25	3.62	1.14
9.00	1.96	5.89
4.50	1.96	4.39
6.75	2.60	3.24
6.75	1.82	6.70
6.75	1.04	6.85

* Not treated by the method of least squares.

Tartaric Acid <u>M</u> x 10 ³	Uranium (IV) <u>M</u> x 10 ³	k x 10 ² M ⁻¹ sec ⁻¹
6.75*	3.64	2.56
6.75*	3.64	1.94
6.75*	2.60	4.84
6.75*	1.82	4.79
6.75*	1.04	5.60
6.75**	3.62	3.95
6.75**	2.60	4.02
6.75**	1.79	5.52
6.75**	1.02	6.34
35.0 **	3.48	3.96
17.5 **	3.48	Curve

Table XVIII (Continued)

* In this group of reactions the tartaric acid was added to the thallium solution, not the uranium solution as usual.

** In these reactions the uranium was divided equally between and mixed with both the uranium and the thallium solution.



Maleic Acid

Maleic acid was investigated rather completely and in more detail than the preceeding acids. Consequently the data concerning it is presented in several tables. The first of these, table XIX shows the variation of the rate constant with the hydrogen ion.

Table XIX

Rate Constant as a Function of Hydrogen Ion **Thallium** perchlorate = $9.00 \times 10^{-3} M$, Maleic acid = $4.50 \times 10^{-3} M$; Ionic strength = 2.9, Temperature = $24.9^{\circ}C$.

Hydrogen ion <u>M</u>	Sodium perchlorate <u>M</u>	Uranium (IV) <u>M</u> x 10 ³	k x 10 ² M ⁻¹ sec ⁻¹	
2.50	0,32	3.33	1.88	
1.76	1.06	3.29	2.66	
0.88	1.94	3.14	6.37	

The maleic acid was divided equally between the uranium and thallium solutions.

One of the most common ways of determining the order of a **Bubstitutent** is to carry out a series of reactions where only the concentration of the substitutent under consideration is varied. This has been done in the case of the hydrogen ion for the maleic aicd catalyzed reaction. To determine the order of the substitutent then, a graph is made of the logarithm of the initial concentration for the varied substance as a function of the logarithm of the initial rate for the reaction. The slope of this line is equal to the order of the substitutent. Figure 17 shows



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The Rate Constant as a Function of Maleic Acid Thallium (III) perchlorate = 9.00×10^{-3} M, Perchloric Acid = 1.76 M, Sodium perchlorate = 1.06 M, Ionic strength = 2.9, Temperature = 24.9° C.

Maleic Acid	Uranium (IV)	k x 10
$\underline{M} \times 10^{2}$	<u>M</u> x 10 ²	
35.0	3.48	0.425
9.00	3.53	0.998
6.75	3.62	0.684
4.50	3.62	1.83
4.50	3.40	1.51
3.50	3.48	2.28
2.25	3.60	3.76
0.900	3.60	2.94
0.350	3.51	2.64
0.0350	3.51	2.12
4.50	3.40	1 .79*
4.50	3.47	0.905**
4.50	3.52	1.05**

* In this reaction the malic acid was added to the thallium solution.

** In the reactions the uranium was divided equally between and mixed with both the uranium and the thallium solution.

such a graph for the variation of hydrogen ion in maleic acid catalyzed reactions. The slope of the line is -1.17.

Table XX shows the rates as a variation of maleic acid concentration. Since there is large variations in the data this has also been presented in graphical form in figure 18. There is great similarity between this curve and the one already seen in the section on fumaric acid. Beginning with low concentrations of maleic acid, the system reacts as though no organic acid were present. As the concentration of the maleic acid increases, the rate of the reaction increases, with a maximum occurring at 9.00 x 10^{-4} <u>M</u> maleic acid. As the maleic acid concentration increases still further, the rate of the reaction suddenly drops to levels below that which the system would possess if no maleic acid were present.

The initial rates were determined as a function of initial concentration of maleic acid so that the order for the maleic acid might be determined. The results are presented in figures 19 and 20. Figure 19 shows the points calculated from the reactions representing maleic acid concentrations between 3.50 x 10^{-2} M and $9.00 \text{ x} 10^{-3} \text{ M}$. Thus this curve represents those concentrations in which an increase of maleic acid results in a decrease in the apparent rate constant. Figure 20 covers the area where an increase in maleic acid concentration results in an increase in the apparent rate constant. The maleic acid concentrations for figure 20 are between $9.00 \text{ x} 10^{-4} \text{ M}$ and 3.50 x 10^{-5} M . The slope obtained from figure 19 after a least squares treatment is $0.84 \pm .025$. Figure 20 yields a slope of 0.072 ± 0.25 .







Table XXI presents the variation in the apparent rate constant with temperature for three different concentrations of maleic acid.

These data are presented graphically in figures 21 and 23. Represented in figure 21 are the data from two of the concentrations. Excellent lines are obtained in each case and the slope is the same for each line within experimental error. The data for these curves was treated by the method of least squares so that the best slope and intercept might be obtained. The data Obtained in this manner are listed in table XXII.

The data presented in figure 21 are from concentrations of maleic acid where the relation between k and maleic acid is direct. The graphs obtained in this area are distinctly different from the graph obtained at other concentrations. The points Obtained deviate only a little from a straight line, and the intercept is much closer to the theoretical than has been found to be normal for these systems.

Also presented in table XVII is a set of data gathered at a maleic acid concentration where the relation between k and the maleic acid concentration is an inverse one. Data collected in this area are similar to the data collected on the other acids. The first few points taken deviate greatly from a straight line, and the intercepts for these reactions deviate from the theoretical by a large magnitude. However, a very interesting pheonomenon was noted as these reactions were subjected to a decrease in temperature. The graph of the rate equation for the reaction at five degrees centigrade and a maleic acid concentration of 9.00 x 10^{-3} <u>M</u> is shown in figure 22. Here it is obvious that the points are related

Variation of the Rate Constant with Temperature Thallium(III) perchlorate = $9.00 \times 10^{-3} M$, Sodium perchlorate = 1.06 M, Perchloric acid = 1.76 M, Ionic strength = 2.9.

Temperature °C.	Uranium (IV) <u>M</u> x 10 ³	k x 10 ² M ⁻¹ sec ⁻¹	$\frac{k \times 10^2}{\underline{M}^{-1} \text{ sec}^{-1}}$
35.0	2.81	1.74	
24.9	3.09	1.11	1.77
15.0	3.53	0.240	3.86
5.0	4.24	0.0261	0.643
Maleic Acid =	9.00×10^{-3}		
35.0	3.17	8.61	
24.9	3.33	2.98	
15.0	3.45	0.821	
5.0	3.78	0.223	
Maleic Acid =	9.00×10^{-4}		
35.0	3.14	6.80	
24.9	3.31	2.37	
15.0	3.49	0.685	
15.0	3.72	0.651	
5.0	3.52	0.175	
Maleic Acid =	9.00 x 10 ⁻⁵		







FOG F

to one of two lines with a few points falling in a curved area between the two lines. A similiar situation occured with all runs at this concentration. Rather than a curve which became linear, there were two linear sections with a curve between them.

The deviation from linearity of the first line increased with a increase in temperature until it was impossible to tell that a straight line existed in the first portion of the rate plot. Graphs of the Arrhenius equation have been prepared and are presented in figure 23.

Table XXII

Thermodynamic Quantities for the Maleic Acid Catalyzed Reaction

Maleic Acid <u>M</u>	Δ H kilocalories	Δ S calories/degree C.
9.00 x 10 ⁻³ <u>M</u> (A)	27.40	35.42
9.00 x 10 ⁻³ <u>M</u> (B)	31.8	44,98
9.00 x 10^{-4}	22.32	14.87
9.00×10^{-5}	21.9	12.77

6. DISCUSSION

The temperature dependence studies show rather well that the curvature often appearing in maleic acid catalyzed reactions is due to two second order reactions. The first one is fast at 25° C. One of two situations could exist here. The first reaction could go to completion so that the first reaction stops, allowing the second to be seen. Another possibility, and perhaps the more likely one, is that one of the reactants is slowly formed, and this reactant is used up rapidly until the concentration is reduced to a level determined by the equilibrium constant of the reaction. At this point the speed of the reaction depends on the rate of production of that reactant.

If at certain concentrations, the rate of production of the desired reactant, and the rate at which uranium is used up in the second reaction are comparable, then the graph of the rate equation could be curved for the major part of the reaction. These reactions whose graphs of the second order rate equation are nonlinear, have been recalculated and graphed according to all common rate laws. No linear relationship was discovered.

The energy of activation for this reaction has been determined. Unfortunately, these data, as all data regarding this reaction are subject to great error. The energy and entropy of activation have been determined from a line which is dependent on only two points. It should be noted that information on this reaction is subject to more error, than other reactions considered.

Finally it should be noted that all information gathered on this fast reaction, was gathered from reactions where the con-

centration of maleic acid was 9.00×10^{-3} M, that range where an increase in maleic acid concentration results in a reduction of rate. No curvature resulted in the other two reactions, also observed at 5° C. Both of these reactions with concentrations of 9.00×10^{-4} M and 9.00×10^{-5} M maleic acid occur in that range where the catalysis is positive, that is where an increase in maleic acid results in an increase in the rate.

It is unfortunate that a single rate equation cannot be written for the system uranium (IV) perchlorate, thallium (III) perchlorate and maleic acid. It should be evident from the evidence presented in the results that this system is complicated. However, this is not to say that the system is undefineable. It does mean that there are areas where more research is necessary if the system is to be defined in detail at all.

If one considers the uranium-thallium reaction alone, an expression can be written for the disappearance of uranium (IV).

$$\frac{d[U(IV)]}{dt} = k[U(IV)][T1(III)]$$
 26)

Here all other variables such as temperature, hydrogen ion concentration, etc. are kept constant, and the U(IV) and Tl(III) expressions are used so that exact species need not be specified. Likewise, it is possible to write a similiar equation for the system uranium, thallium, maleic acid.

Before this can be done, it is necessary to make some definition so that the area of validity for the equation is known. The first equation that is presented covers the area of maleic acid concentration where the reaction is catalyzed by maleic acid.

That is the region between 3.5 x 10^{-5} <u>M</u> and 2.25 x 10^{-3} <u>M</u>. The expression that can be written for this area is:

$$\frac{d[U(IV)]}{dt} = k[U(IV)][T1(III)][Maleic]^{0.075} 27)$$

The second expression covers the area of maleic acid concentrations from 2.25 x 10^{-3} <u>M</u> to 3.5 x 10^{-2} <u>M</u>. Here the maleic acid retards the reaction. Consequently the maleic acid term now appears in the denominator.

$$-\frac{d[U(IV)]}{dt} = k [U(IV)] [T1(III)] [Maleic Acid] -1.16 28)$$

It should be noted at this point that the equations presented are valid only over the linear region of graph of the rate equation for any reaction.

The effect of hydrogen ion was determined in the region where the first equation is valid. The graph of initial rate versus initial concentration for hydrogen ion had a slope of -1.17 indicating a hydrogen order of the same value. The essential point is that the previously important second order path in hydrogen ion found by Harkness and Halpern is now almost non-existent. It would appear that only a slight amount of reaction occurs by this path. Energies and entropies of activation have been determined. These are for the overall reaction and do not account for the fact that there may be two paths present, as has been suggested for the uranium-thallium system.

The energy of activation for that part of the curve where positive catalysis occurs is slightly lower, 22.1 kilocalories, than the energy of activation found in the uranium-thallium reaction for the path that is first order in hydrogen ion, 24.6 kilocalories. The energy of activation for the reaction taking place in the region of negative catalysis is much larger, 31.8 kilocalories, presumably indicating an intermediate that is more difficult to form. Thus it appears that there are two paths initially, the normal hydrolysis path and a path that may be the one to one complex of uranium and maleic acid. The latter reacts slightly faster with the thallium than the hydrolysis product, thus causing a slight amount of catalysis. As the amount of one to one complex increases so does the catalysis. However, as the amount of maleic acid increases, larger and larger portions of the two to one complex of maleic acid and uranium, respectively, form, and this does not react with thallium at any significant rate, thus rapidly slowing the reaction.

It appears from all available evidence that all acids studied can be placed in one of three classes: those which increase the rate of the reaction, those which slow down the reaction, and those which do not affect the system at all. In this latter case there is one acid, malonic. It has been suggested that this might be due to the reaction in acid to produce carbon dioxide and acetic acid. The acetic acid would not be expected to affect the system much at all. The addition of catalytic amounts of the acid was found to have no effect on the rate. This may also indicate that no strong complex is formed between malonic acid and the thallium or uranium, and thus no effect on the reaction.

In the second group there appear two acids, succinic and oxalic acids, which reduce the rate of the reaction. The most likely explanation for this behavior is that both oxalic and
succinic acids form complexes that are less reactive than the hydrolyzed species that normally react. But if one considers the series, oxalic, malonic, and succinic, it is immediately noticed that the three carbon dibasic acid has no effect on the rate, while the two and the four carbon dibasic acids inhibit the rate. This may be due to the fact that succinic and oxalic acids form strong complexes while malonic acid does not, perhaps due to steric considerations. The simple act of complex formation should destroy the ability of the uranium and thallium to react unless the ligand provides a lower energy path for the electron than is normally available.

Three acids catalyze the reaction between uranium and thallium, and there is strong indication that the same is true for a fourth acid. The fourth acid is malic acid, the one acid on which almost no data could be gathered because of the non-linearity of most of the graphs of the rate equation. One of the graphs was linear and indicated catalysis. The fact that the graphs were nonlinear is in itself suggestive of positive catalysis for these acids, since nonlinearity occurred only in cases of positive catalysis and never with cases where the reaction was slowed down. The other three acids, tartaric, fumaric, and maleic acid, all definately catalyze the reaction. Their graphs of rate versus concentration of catalyzing acid have similar shape. That is they first catalyze the reaction and with increasing acid concentration, the acids then inhibit it. The case of maleic acid has already been discussed in some detail.

Rather great difficulty was experienced with tartaric

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acid. The similarity between malic and tartaric should be noted. It was impossible to obtain linear graphs of the rate equation for many reactions. All orders of reaction were checked and none were found to be linear whether considering uranium, thallium, or some appropriate combination of these. It would seem logical therefore, on the basis of the information gained from maleic acid, that in these reactions there are at least two reactions occuring with different rates. These rates are such that they do not produce a linear graph when plotted according to any common rate equation.

In order to elucidate completely any one of these reactions more detailed research is necessary. Malic, fumaric, and tartaric should all be studied in more depth. Certainly the work on maleic acid indicated in which direction the future work should proceed. A whole series of reaction should be carried out at 5° C. so that the initial reaction taking place can be studied in detail. It is quite possible that the information gained here will aid greatly in explaining the slower reaction that is occurring.

Quantitative information should be determined on the complexes of the acid being considered. Ion exchange might be used for this since the colorless acid do not present the normal means. Then too, this method is more adaptable to low concentrations than many of the other methods.

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7. SUMMARY

The reaction between uranium (IV) and thallium (III) in the presence of various organic acids was studied. Dibasic saturated acids studied were oxalic acid, malonic acid, and succinic acid. Oxalic acid and succinic acid were found to inhibit the reaction. Oxalic acid has only a slight effect on the system compared to succinic acid. Malonic acid has no effect on the rate of the system.

The unsaturated dibasic acids, fumaric acid and maleic acid, were investigated along with the hydroxy dibasic acids, malic acid and tartaric acids. Under the appropriate conditions these acids all catalyze the reaction. At low concentrations of fumaric or maleic acid, the reaction between uranium (IV) and thallium (III) is catalyzed, but as the concentration of the organic acid is increased, the effect is to inhibit the reaction. This is attributed to the formation first of a one to one complex that catalyzes the reaction, followed by the formation of a one to two (uranium to maleic or fumaric acid) complex which inhibits the reaction. Tartaric acid appears to exhibit the same behavior, and although the evidence is scanty, malic acid is believed to catalyze the reaction.

Most of the graphs of the rate equation

$$-\frac{dU(IV)}{dt} = k[U(IV)][T1(III)]$$
 29)

were found to be linear over a large part of the reaction studied. Almost all curves exhibited a particular deviation from the expected. The extrapolation of the linear curve to zero time did not pass

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through log Tl_0/U_0 , which is required by theory. Rather, initial experimental points formed a curve which became linear only after several hundred seconds. Experiments at low temperatures showed that this curvature was due to two separate reactions, one occurring with a fast rate, and ending rather rapidly as it uses all of one reactant, and the other occurring simultaneously but with a slower rate.

The energy of activation was determined for this fast reaction and found to be 27.4 kilocalories when maleic acid was present as the catalyzing substance. The energies of activation were also determined for the reaction that occurred more slowly. The values obtained were 31.8 kilocalories and 22.1 kilocalories for concentrations of maleic acid that inhibit and that accelerate the reaction, respectively.

Partial rate laws were determined. The reaction is first order in uranium (IV) and thallium (III), and in the accelerated area the order of the maleic acid is 0.07, while in the inhibited area the maleic acid has an order of -0.84. The hydrogen ion was found to have an order of -1.17 in the inhibited area.

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APPENDIX

ORIGINAL KINETIC DATA

These data are organized in the same manner as they appear in the results section. To locate the original data it is only necessary to note the position of the desired reaction in its table. For example, if in the table discussing succinic acid, the original data are desired for the fourth reaction listed; this will be the fourth set of data in the group containing succinic acid in this appendix.

(Pa	.ge 61)		
	Time	A	log T1/U
3.46 x 10 ⁻³ <u>M</u> U(IV)	100	.188	•4255
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.169	•4553
1.76 <u>м</u> н ⁺	700	.156	.4781
1.06 <u>M</u> NaClO _L	1000	.145	•4991
2.9	1300	.138	•5134
1.125 x 10 ⁻³ <u>M</u> Succinic Acid	1600	.131	• 5299
	1900	.125	•5434
	2200	.119	• 5594
	2500	.113	•5747
3.46 x 10 ⁻³ M U(IV)	100	.189	•424 7
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.170	•4535
1.76 <u>м</u> н ⁺	700	.163	.4649
1.06 <u>M</u> NaClO _L	1000	.155	•4793
2.9	130 0	.150	•4890
3.38 x 10 ⁻³ <u>M</u> Succinic Acid	1600	.140	• 509 7
	1900	.142	• 5049
	2200	.131	•5299
	2500	.132	• 5274
3.46 x 10 ⁻³ <u>M</u> U(IV)	100	.186	. 428 8
9.00 x 10 ⁻³ <u>M</u> T1(III)	400		
1.76 <u>M</u> H ⁺	700	.167	• 4582
1.06 <u>M</u> NaClO ₄	1000	.163	•4649
2.9	1300	•159	•4720
6.75 x 10 ⁻³ <u>M</u> Succinic Acid	1600	•154	.4813
	1900	.150	. 4890
	2200	•14 7	•4957
	2500	•143	• 5038

ORIGINAL DATA FROM TABLE XII (Page 61)

		Time	A	log Tl/U
$3.47 \times 10^{-3} M$	U(IV)	100	.190	. 422 6
9.00 x 10^{-3} M	Tl(III)	400	.181	•4358
1.76 <u>M</u> H ⁺		700	.177	•4420
1.06 M NaClO4		1000	.173	.4482
2.9		1300	.169	•454 7
$1.35 \times 10^{-2} M$	Succinic Acid	1600	.167	•4576
		1900	.164	• 46 34
		2 20 0	.161	•4684
		2500	.158	•4735
$3.47 \times 10^{-3} M$	U(IV)	115	.192	.4193
$9.00 \times 10^{-3} M$	Tl(III)	400	.185	.4299
1.76 <u>м</u> н ⁺		700	,180	•4368
1.06 <u>M</u> NaClO ₄		1000	.177	.4420
2.9		1300	.175	• 4447
2.25 x 10^{-3} M	Succinic Acid	1600	.171	.4510
		1900	.168	•456 7
		2200	.166	•4595
		2500	.163	•4643
$3.47 \times 10^{-3} M$	U(IV)	100	.192	. 422 6
$9.00 \times 10^{-3} M$	Tl(III)	400	.185	•4299
1.76 <u>M</u> H ⁺		7 05	.181	•4358
1.06 <u>M</u> NaClO _L		1015	.178	•4403
2.9		1300	.175	• 4447
4.50 x 10^{-2} M	Succinic Acid	1615	•174	•4464
		1910	.170	•4529
		220 0	.168	•456 7
		2505	•171	.4510

Original Data from Table XII - Continued

	Time	A	log Tl/U
3.48 x 10 ⁻³ <u>M</u> U(IV)	110	.188	•424 5
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.173	•4478
1.76 <u>м</u> н ⁺	700	.163	•4639
1.06 <u>M</u> NaClO ₄	1000	.154	.4803
2.9	1300	.146	•4957
2.25 x 10^{-4} M Oxalic Acid	1600	.140	• 508 7
	1900	.132	• 5262
	2200	.125	•5423
	2500	.120	• 5553
3.48 x 10 ⁻³ M U(IV)	100	.179	•4379
$9.00 \times 10^{-3} \text{ M}$ T1(III)	410	.165	•4609
1.76 <u>M</u> H ⁺	700	.155	.4781
1.06 <u>M</u> NaClO _L	1000	.146	+495 7
2.9	1300	.140	• 5087
$450 \times 10^{-4} M$ Oxalic Acid	1610	•132	• 5262
	1900	.125	•5423
	2200	.121	•5523
	2515	.115	•5689
3.47 x 10 ⁻³ <u>M</u> U(IV)	100	.190	•4473
9.52 x 10 ⁻³ <u>M</u> T1(III)	400	•177	•4673
1.76 <u>M</u> H ⁺	700	.167	•4834
1.06 <u>M</u> NaClO _L	1000	•159	•4976
2.9	1300	.150	•5151
1.12 x 10 ⁻³ <u>M</u> Oxalic Acid	160 0	•144	•5280
	1900	.138	•5402
	2200	•131	•557 3
	2500	.125	•571 1

ORIGINAL DATA FROM TABLE XIII

(Page 62)

		Time	A	log T1/U
3.48 x 10 ⁻³ <u>M</u>	U(IV)	100	.192	•4434
9.52 x 10 ⁻³ <u>M</u>	Tl(III)	400	•177	•4669
1.76 <u>м</u> н ⁺		700	.167	•4830
1.06 <u>M</u> NaClO	+	1000	.160	.4961
2.9	•	1300	•152	•5112
2.25 x 10 ⁻³ <u>M</u>	Oxalic Acid	1600	.145	•52 50
		1900	.140	•5359
		2200	.133	•551 3
		2500	.127	•5669
5.47 x 10 ⁻³ M	U(IV)	100	.195	•4400
9.52 x 10 ^{−3} <u>M</u>	Tl(III)	400	.183	• 45 74
.76 <u>м</u> н ⁺		700	.174	•4719
.06 <u>M</u> NaClo	L	1000	.167	•4834
2.9	•	1300	.160	•4966
2.25 x 10 ⁻³ M	Oxalic Acid	1600	. 152	•4834
		1900	.145	•5256
		2200	.141	•5340
		2500	•134	•5492

Original Data from Table XIII - Continued

ORIGINAL DATA FROM TABLE XIV

(Page 63)

	Time	A	log Tl/U
3.53 x 10 ⁻³ M U(IV)*	100	.197	•4103
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.185	•4270
1.76 <u>M</u> H ⁺	700	.175	•441 7
1.06 <u>M</u> NaClO ₄	1000	.165	•458 3
2•9	1300	.156	• 4745
9.00 x 10 ⁻⁴ <u>M</u> Malonic Acid	1600	.148	•4897
	1900	.141	•5035
	2200	•134	•5182
	2500	.127	•5354

••••••••••••••••••••••••••••••••••••••	Time	A	log Tl/U
3.26 x 10 ⁻³ M U(IV)+	100	.181	•4462
9.00 x 10 ⁻³ M T1(III)	400	.169	•4654
1.76 <u>M</u> H ⁺	700	.160	.4812
1.06 <u>M</u> NaClO ⁴	1000	.150	•4994
2.9	1300	.144	•5120
2.25 x 10 ⁻³ M Malonic Acid	1600	.137	•52 66
	1900	.129	• 5449
	2200	.123	• 5603
	2500	•117	•5752
3.26 x 10 ⁻³ M U(IV) *	100	.182	•4445
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.168	•4673
1.76 <u>м</u> н ⁺	700	.160	.4812
1.06 <u>M</u> NaClO _L	1000	.150	•4994
2.9	1300	.143	•5144
4.5 x 10 ⁻³ <u>M</u> Malonic Acid	1600	.135	•5317
	1900	.128	•5476
	2210	.121	• 5647
	2500	•115	•5814
3.62 x 10 ⁻³ M U(IV)*	100	.200	.4014
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.185	•4224
1.76 <u>м</u> н ⁺	700	•175	•4370
1.06 <u>M</u> NaClO ₄	1000	•166	•4518
2.9	1300	.157	. 46 76
6.75 x 10 ⁻³ <u>M</u> Malonic Acid	1600	. 148	•484 7
	1900	•141	•4986
	2200	•133	•5159
	2500	•125	•5344
	3600	•104	•5920

Original Data from Table XIV - Continued

	Time	A	log Tl/U
3.62 x 10 ⁻³ <u>M</u> U(IV)*	100	•197	•4059
9.00 x 10 ^{-3<u>M</u> T1(III)}	400	. 184	•4232
1.76 <u>M</u> H ⁺	700	•173	•4406
1.06 <u>M</u> NaClO _L	1000	.164	•4556
2.9	1300	.155	•470 7
9.00 x 10 ⁻³ <u>M</u> Malonic Acid	1600	•145	•4904
	1930	.136	•50 95
	2 20 0	.129	•524 9
	2500	•123	•5401
	3200	.107	•5834

Original Data from Table XIV - Continued

ORIGINAL DATA FROM TABLE XV

(Page 67)

		Time	A	log Tl/U
$3.50 \times 10^{-3} M$	U(IV) *	100	.163	•4628
9.00 x 10^{-3} M	Tl(III)	400	•134	•5200
1.76 <u>M</u> H ⁺		700	.120	•5541
1.06 <u>M</u> NaClo _L	L	1000	.107	•5905
2.9	r	1300	•098	. 6192
2.25 x 10^{-3} M	Malic Acid	1610	.091	•6430
		1900	•086	•6623
		2200	•080	. 6854
		2500	•075	•7079
3.50 x 10 ⁻³ M	n(IA).	100	. 153	•4314
$9.00 \times 10^{-3} M$	Tl(III)	405	.125	•5412
1.76 <u>M</u> H ⁺		700	.108	•5870
1.06 <u>M</u> NaClo ₁	L	1000	•098	. 6192
2.9	r	1300	•089	• 6514
$4.50 \times 10^{-3} M$	Malic Acid	1600	.081	•6830
		1900	•076	• 7 028
		2200	•072	•7240
		2500	.066	•7529

$3.58 \times 10^{-3} \underline{M} U(IV) * 100 0.185 .424$ 9.00 x 10 ⁻³ $\underline{M} T1(III) 400 0.160 .464$ 1.76 $\underline{M} H^{+} 700 .143 .497$ 1.06 $\underline{M} NaClo_{4} 1000 .130 .524$ 2.9 $1315 .121 .546$ 6.75 x 10 ⁻³ $\underline{M} Malic Acid 1600 .116 .560$ 1900 $.110 .577$ 2200 $.105 .590$ 2500 $.100 .606$ 3.58 x 10 ⁻³ $\underline{M} U(IV) * 100 0.183 .427$ 9.00 x 10 ⁻³ $\underline{M} T1(III) 400 0.156 .471$	c 10 ⁻³ <u>M</u> U(IV)* c 10 ⁻³ <u>M</u> T1(III) <u>4</u> H ⁺ <u>4</u> NaClo ₄	100 1) 400 700 1000	0.185 0.160 .143	•4244 •4646 •4972
9.00 x 10^{-3} M T1(III) 400 0.160 .464 1.76 M H ⁺ 700 .143 .497 1.06 M NaClo ₄ 2.9 1315 .121 .546 6.75 x 10^{-3} M Malic Acid 1600 .116 .560 1900 .110 .577 2200 .105 .590 2500 .100 .666 3.58 x 10^{-3} M U(IV) * 100 0.183 .427 9.00 x 10^{-3} M T1(III) 400 0.156 .471 1.00 0.156 .471	x 10 ⁻³ <u>M</u> T1(III) 4 H ⁺ 4 NaClo ₄	I) 400 700 1000	0.160 .143	•4646 •4972
1.76 \underline{M} \underline{H}^{+} 1.06 \underline{M} NaClO ₄ 2.9 6.75 x 10 ⁻³ \underline{M} Malic Acid 1600 110 100 110 100 110 100 10	<u>4</u> н ⁺ <u>4</u> NaClO ₄	700 1000	•143	•4972
$1.06 \ \underline{M} \ NaClo_{4} $ $2.9 $ $6.75 \ x \ 10^{-3} \ \underline{M} \ Malic \ Acid $ $1600 \ .116 \ .560 $ $1900 \ .110 \ .577 $ $2200 \ .105 \ .590 $ $2500 \ .100 \ .606 $ $3.58 \ x \ 10^{-3} \ \underline{M} \ U(IV) \ \cdot \ 100 \ 0.183 \ .427 $ $9.00 \ x \ 10^{-3} \ \underline{M} \ Tl(III) \ 400 \ 0.156 \ .471 $	MaClO4	1000	170	
2.9 6.75×10^{-3} M Malic Acid 1600 1900 100 100 100 100 100 100	•		•150	•524 5
$6.75 \times 10^{-3} \underline{M} \text{ Malic Acid} 1600 .116 .560 1900 .110 .577 2200 .105 .590 2500 .100 .606 3.58 \times 10^{-3} \underline{M} U(IV) * 100 0.183 .427 9.00 \times 10^{-3} \underline{M} T1(III) 400 0.156 .471 200 0.156 .471 200 0.156 .471 200 0.156 .471 200 0.156 .507 200 0.156 .471 200 0.156 .507 200 0.156 .507 200 0.156 .577 200 0.100 .577 200 0.100 .577 200 0.100 .577 200 0.100 .577 200 0.100 .577 200 0.100 .577 200 0.100 .577 200 0.105 .590 2500 0.100 .577 2500 0.577 2500 0.000 .577 2500 0.000 .5777 2500 0.$		1315	.121	•5467
1900 .110 .577 2200 .105 .590 2500 .100 .606 3.58 x 10-3 M U(IV) * 100 0.183 .427 9.00 x 10-3 M T1(III) 400 0.156 .471 200 .100 .100 .100 .100 .100 .100 .100 .100 .100 .100 .577 .100 .590 .100	K 10 ⁻³ <u>M</u> Malic Aci	Acid 1600	•116	•5600
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1900	.110	•5774
$2500 .100 .606$ $3.58 10^{-3} M U(IV) 100 0.183 .427$ $9.00 10^{-3} M T1(III) 400 0.156 .471$ $2500 0.156 .471$		2200	.105	•5908
$3.58 \times 10^{-3} \underline{M} U(IV) * 100 0.183 .427$ $9.00 \times 10^{-3} \underline{M} T1(III) 400 0.156 .471$		2500	.100	•6069
9.00 x 10^{-3} M T1(III) 400 0.156 .471	κ 10 ^{−3} <u>Μ</u> U(IV) *	• 100	0.183	•4270
	ε 10 ⁻³ <u>Μ</u> T1(III)	I) 400	0.156	•4719
Т• 76 <u>м</u> н 700 0•140 •505	<u>1</u> H ⁺	700	0.140	•5031
1.06 <u>M</u> NaClo _L 1000 0.128 .529	<u>1</u> NaClO _L	1000	0.128	•529 9
2.9 1300 0.121 .546	•	1300	0.121	•546 7
9.00 x 10 ⁻³ M Malic Acid 1600 0.115 .563	c 10 ⁻³ <u>M</u> Malic Acio	Acid 1600	0.115	•5631
1900 0.110 .577		1900	0.110	•5 77 4
2200 0 .107 . 585		2200	0.107	•5858
2500 0.104 .59 ^L		2500	0.104	•5944

Original Data from Table XV - Continued

ORIGINAL DATA FROM TABLE XVI

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	Time	A	log Tl/U
$3.45 \times 10^{-3} M U(IV)$	100	.182	•4395
9.00 x 10 ⁻³ <u>M</u> T1(III)	405	. 160	•4765
1.76 <u>M</u> H ⁺	700	.146	•5031
1.06 M NaClO _L	1000	.140	•5164
2.9	1300	•133	•531 7
5 x 10 ⁻³ <u>M</u> Fumaric Acid	1600	.128	•5441
	1900	•123	•5570
	2200	.118	• 5705
	2500	•113	•5834

		Time	A	log Tl/U
3 43 × 10 ⁻³ M		100		
$-3 \times 10^{-3} \times$		100	101.	• + + 22
$\frac{1}{2} = \frac{1}{2} = \frac{1}$	11(111)	400	•159 245	•4797
		700	•145	• 5077
$1.06 \underline{M}$ Nacio ₄		1000	•138	•5224
2.9		1300	•132	•5369
$4.38 \times 10^{-5} M$	Fumaric Acid	1600	.125	•5538
		2200	•112	•5895
		2500	.107	.6050
3.43 x 10 ⁻³ <u>M</u>	U(IV)	100	.183	•4387
$9.00 \times 10^{-3} M$	Tl(III)	400	. 158	•4819
1.76 <u>м</u> н ⁺		700	. 144	•5001
1.06 <u>M</u> NaClO ₁		1000	.132	•5369
- 4 2.9		1300	.128	•5465
$3.75 \times 10^{-3} M$	Fumaric Acid	1600	.122	•5625
_		1900	. 115	•5813
		2200	.108	.6015
		2500	.102	.6215
$3.43 \times 10^{-3} M$	U(IV)	100		4379
$9.00 \times 10^{-3} M$	Tl(III)	400	.165	• · <i>5</i> 7 5
1.76 м н ⁺		700	150	• 1009 4072
		1000	.138	• - > / -
2.9		1200	•⊥90 1 ⊃2	• JCCT
-• <i>2</i> z z z z z -3 Μ	Rumania Asid	1600	05T•	• 7407 FC17
\mathbf{M}	rumaric Aclo	TOOO	•141	• 5041
		1900	•115	•5813
		2200	•105	•6122
		2500	.100	. 6272

Original Data from Table XVI - Continued

		Time	A	log Tl/U
3.41 x 10 ⁻³ M	U(IV)	100	.170	.4616
9.00 x 10^{-3} M	Tl(III)	400	.146	•5064
1.76 <u>м</u> н ⁺		700	.133	•5353
1.06 <u>M</u> NaClO _L		1000	.126	•550 5
2.9		1300	.119	•5714
$3.12 \times 10^{-3} M$	Fumaric Acie	1600	•111	•5941
		1900	. 105	. 6115
		2200	.100	. 6284
		2500	•094	. 6505
3.41 x 10 ⁻³ M	U(IV)	125	.180	•4450
$9.00 \times 10^{-3} M$	Tl(III)	400	.163	•4735
1.76 <u>M</u> H ⁺		700	. 148	• 5030
1.06 <u>M</u> NaClO ₁		1000	•138	•5236
2.9		1300	.127	•5491
$3.12 \times 10^{-3} M$	Fumaric Acid	1600	. 120	•5682
		1900	.112	•5906
		2200	.105	. 6115
		2500	.100	. 6284
$3.45 \times 10^{-3} M$	N(IN)	100	.182	•4395
9.00 x 10^{-3} M	Tl(III)	400	•163	•4704
1.76 <u>M</u> H ⁺		700	. 148	•4984
1.06 M NaCloh		1000	•138	• 5201
2.9		1300	.127	•5469
2.50 x 10^{-3} M	Fumaric Acid	1600	.120	•5644
_		1900	.112	•5867
		2200	.106	• 6038
		2500	.100	. 6260

Original Data from Table XVI - Continued

		Time	A	log Tl/U
3.41 x 10 ⁻³ M	U(IV)	110	.171	•459 7
9.00 x 10^{-3} M	Tl(III)	400	.150	•4983
1.76 <u>м</u> н+		700	.138	•5236
1.06 <u>M</u> NaClO ₄		1000	.127	•5491
2.9		1300	.119	•5714
2.50 x 10^{-3} M	Fumaric Acid	1600	•111	•5941
		1900	.105	.6115
		2200	•099	•6322
		2500	•093	•652 6
3.41 x 10 ⁻³ M	U(IV)	100	.180	• 4450
$9.00 \times 10^{-3} M$	Tl(III)	400	.163	•4735
1.76 <u>M</u> H ⁺		700	. 148	•5030
1.06 <u>M</u> NaClO _L		1000	.138	•5236
2.9		1300	.128	•5476
$1.88 \times 10^{-3} M$	Fumaric Acid	1600	.119	•5714
		1900	.109	•5991
		2200	.103	. 6189
		2500	•095	•6463
3.41 x 10 ⁻³ M	U(IV)	100	.183	•4396
$9.00 \times 10^{-3} M$	Tl(III)	400	. 165	•4695
1.76 <u>M</u> H ⁺		700	.151	•4961
1.06 <u>M</u> NaClO,		1000	.140	•5198
2.9		1300	•129	•5449
1.88 x 10 ⁻³ <u>M</u>	Fumaric Acid	1900	•111	•5941
-		2200	.103	. 6189
		2500	•095	. 6463

Original Data from Table XVI - Continued

3.45 x 10^{-3} M	U(IV)	110	.183	•4378
9.00 x 10^{-3} M	Tl(III)	400	.162	•4725
1.76 <u>м</u> н ⁺		705	•147	•5008
1.06 M NaClo ₄		1000	.136	•5279
2.9		1300	.127	•5469
$1.25 \times 10^{-3} M$	Fumaric Acid	1600	.122	•55 ⁸ 5
		1905	.115	•5785
		2200	.110	•5934
		2500	.103	•614 7
3.45 x 10 ⁻³ M	U(IV)	100	.185	•4342
$9.00 \times 10^{-3} M$	Tl(III)	700	•155	•4852
1.76 <u>M</u> H ⁺		1000	.145	•5060
1.06 <u>M</u> NaClO,		1300	.136	•5253
2.9		1600	.128	•5441
1.25 x 10 ⁻³ M	Fumaric Acid	1900	.120	•5644
		2215	.112	•5867
		2500	.106	.6056
$3.45 \times 10^{-3} M$	U(IV)	100	.187	•4317
9.00 x 10^{-3} M	Tl(III)	400	•169	•4606
1.76 <u>M</u> H ⁺		700	. 158	•4797
1.06 <u>M</u> NaClO ₄		1000	. 148	•4984
2.9		1300	. 140	•5164
6.25 x 10^{-4} M	Fumaric Acid	1600	•132	•5345
		1900	.125	•5512
		2200	•118	•5705
		2500	.112	•5867

	Time	A	log Tl/U
3.45 x 10 ⁻³ M U(IV)	100	.186	•4334
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.170	• 4586
1.76 <u>м</u> н ⁺	700	.160	•4765
1.06 <u>M</u> NaClO _L	1000	.150	•4962
2.9	1300	.143	•5091
2.50 x 10 ⁻⁴ <u>M</u> Fumaric Acid	1600	.135	•5266
	2200	.122	• 5585
	2500	.116	•5753

Original Data from Table XVI - Continued

ORIGINAL DATA FROM TABLE XVII

(Page 71)

	Time	A	log T1/U
3.32 x 10 ⁻³ M U(IV)	100	.189	•4315
9.00 x 10 ⁻³ M T1(III)	400	•175	•4521
1.76 <u>M</u> H ⁺	700	. 166	•4672
0.424 <u>M</u> NaClO ₄	1000	.159	•4791
·	1300	.151	•4940
	1600	•145	•5065
	1900	. 140	•5172
	2200	•134	•5298
	2500	. 128	•5443
3.41 x 10 ⁻³ M U(IV)	100	•192	•422 3
$9.00 \times 10^{-3} M$ Tl(III)	400	•177	•4450
1.76 <u>м</u> н ⁺	710	.166	•4626
0.848 M NaClOL	1000	.158	•4765
Ŧ	1310	. 150	•4916
	1600	•143	• 5064
	1900	•136	•5211
	2200	.130	•5340
	2500	. 124	•5491

			
	Time	A	log TL/U
3.33 x 10 ⁻³ M U(IV)	100	. 184	•4376
$9.00 \times 10^{-3} M$ Tl(III)	400	.169	. 4618
1.76 <u>M</u> H ⁺	700	.160	•4770
1.06 <u>M</u> NaClO _L	1000	.149	•4980
'	1300	•143	•510 7
	1600	. 135	•527 9
	1900	.128	•5438
	2200	.122	•559 3
	2500	•116	•5743
3.42 x 10 ⁻³ M U(IV)	100	•192	•4218
$9.00 \times 10^{-3} M$ Tl(III)	400	.175	•4472
1. 76 <u>м</u> н ⁺	700	.164	•4660
1.484 <u>M</u> NaClO,	1000	•153	• 4856
- 4	1300	.1 45	• 5012
	1600	•137	•5180
	1900	.129	•5362
	220 0	.122	•5542
	2500	•115	•5723
3.38 x 10 ⁻³ <u>M</u> U(IV)	100	.185	•4344
$9.00 \times 10^{-3} \text{ M}$ Tl(III)	400	.169	• 4594
1.76 <u>M</u> H ⁺	700	•154	. 4856
2.12 <u>M</u> NaClO ₁	1000	•14 4	• 5070
- +	1300	•135	•5252
	1600	.125	•5480
	1900	.117	•5684
	2200	.109	•5907
	2500	.103	•609 7

Original Data from Table XVII - Continued

	Time	A	log Tl/U
3.41 x 10 ⁻³ M U(IV)	100	.165	•4288
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	. 135	. 4850
1.76 <u>м</u> н ⁺	700	.118	•5249
1.06 <u>M</u> NaClO _L	1000	.104	•5653
2.9	1300	•093	.6007
9.00 x 10 ⁻³ <u>M</u> Tartaric Acid	1600	.085	•6303
	1900	•078	.6612
	2200	•073	. 6839
	2500	•0 70	•6984
3.46 x 10 ⁻³ M U(IV)	100	.164	•4741
$9.00 \times 10^{-3} \text{ M}$ T1(III)	400	.138	•5232
	700	.122	•5610
 1.06 M NaClO,	1000	.108	.6003
– 4 2•9	1300	•099	.6291
9.00 x 10^{-3} M Tartaric Acid	1600	•091	.6550
-	1900	.082	•6906
	2200	•078	•7077
	2500	•074	•7258
3.46 x 10 ⁻³ M U(IV)*	100	•155	•4697
$9.00 \times 10^{-3} \text{ M}$ T1(III)	400	.126	• 5306
1.76 <u>м</u> н ⁺	700	.110	•5739
- 1.06 M NaClO,	1000	•09 9	•6069
- 4 2•9	1300	•088	•6448
8.75 x 10 ⁻³ <u>M</u> Tartaric Acid	1605	•077	. 6913
-	1900	•070	•7233
	2200	.064	•7560
	2505	050	

ORIGINAL DATA FROM TABLE XVIII (Page 74)

	Time	A	log Tl/U
3.62 x 10 ⁻³ M U(IV) *	100	.173	•4406
9.00 x 10 ⁻³ M T1(III)	400	.147	•4804
1.76 <u>M</u> H ⁺	7 00	•134	•5132
1.06 <u>M</u> NaClO _L	1010	.123	•5401
2.9	1300	.115	•5607
6.75 x 10 ⁻³ <u>M</u> Tartaric Acid	1600	.109	•576 7
	1900	.103	•5955
	2200	.100	•6044
	2500	•095	. 621 5
	2800	•092	•6314
	3125	•090	•6397
	3400	.088	•6461
	3720	•083	. 6660
	4000	•082	•6707
	4500	.081	•6754
	5010	•080	•6778
	6200	.081	. 6754
3.64 x 10 ⁻³ M U(IV) *	115	.173	. 4864
9.00 x $10^{-3} \frac{M}{M}$ T1(III)	400	.149	•5307
1.76 <u>M</u> H ⁺	700	•135	•5616
1.06 M NaClO ₁	1010	.125	•5851
2.9	1300	.116	• 6094
6.75 x 10 ⁻³ <u>M</u> Tartaric Acid	1600	.110	. 6275
—	1920	.105	. 6415
	2200	.100	.6580
	2500	•097	. 6697
	-		

	Time	A	log Tl/U
3.41 x 10 ⁻³ M U(IV)	105	.169	•4223
$9.00 \times 10^{-3} \text{ M}$ T1(III)	400	.144	.4666
1.76 M H ⁺	700	.129	•498 3
1.06 M NaClO,	1000	.119	•5223
- 4 2.9	1300	.110	•5463
4.50 x 10 ⁻³ M Tartaric Acid	1600	.105	•5622
-	1900	.100	•5792
	2200	•096	•5906
	250 0	•094	•5975
$3.30 \times 10^{-3} M U(IV)$	100	.168	.4672
$9.00 \times 10^{-3} \text{ M}$ T1(III)	700	•132	• 537 3
1.76 M H ⁺	1000	.123	•5581
1.06 M NaClO,	1300	.115	•5791
- 4 2.9	1600	.108	.6003
4.50 x 10 ⁻³ <u>M</u> Tartaric Acie	1900	.105	.6091
-	2200	.101	. 6216
	2500	•098	•6310
$3.64 \times 10^{-3} \text{ M U(IV)}^*$	100	. 165	•4527
$9.00 \times 10^{-3} \text{ M} \text{ Tl(III)}$	400	•137	• 5060
1.76 M H ⁺	710	.120	•5460
- 1.06 M NaClO,	1000	.109	•5755
- 4 2.9	1306	.100	•6032
3.50 x 10 ⁻³ M Tartaric Acid	1600	•095	•6203
-	1900	•087	•6491
	2200	•082	. 6694
	2511	•076	•6938

Original Data from Table XIII - Continued

	Time	A	log Tl/U
3.41 x 10 ⁻³ M U(IV)	100	•174	
$9.00 \times 10^{-3} M$ T1(III)	400	.160	•4371
1.76 <u>м</u> н ⁺	700	•153	•4495
1.06 M NaClO _L	1000	. 146	•4626
2.9	1300	•143	. 4685
2.25 x 10^{-3} <u>M</u> Tartaric Acid	1600	.139	•4765
	1900	•136	•4829
	2200	•132	•4916
	2500	.129	•4983
3.62 x 10 ^{−3} M U(IV)*	110	.180	•4293
$9.00 \times 10^{-3} \text{ M}$ T1(III)	400	•167	•4499
L.76 <u>м</u> н ⁺	700	.162	•4586
$L_{\bullet}06 \underline{M}$ NaClO _L	1000	•156	. 4697
2.9	1350	.152	•4771
2.25 x 10 ⁻³ <u>M</u> Tartaric Acid	1600	.149	•4826
	1900	.145	•4904
	2200	.143	•4950
	250 0	.140	•5009
	280 0	•137	• 5070
	3100	•135	•5120
	3400	•131	•5210
	3700	.130	•5223
	4000	.128	•5276
	4500	.126	•5317
	5000	.125	•5344

Original Data from Table XIII - Continued

		Time	A	log Tl/U
1.58 x 10 ⁻³ M	U(IV)*	100	•082	•7840
$9.00 \times 10^{-3} M$	Tl(III)	415	.065	. 8691
1.76 <u>M</u> H ⁺		700	.055	•9307
1.06 <u>M</u> NaClO _L		1000	.048	•9826
2.9		1315	•040	1.0423
9.00 x 10^{-3} M	Tartaric Acid	1600	•035	1.1038
		1930	.031	1.1517
		2 20 0	•02 7	1.2055
		250 0	.024	1.2519
		2805	.021	1.3047
		3100	•02 0	1.3232
		3400	•018	1.3659
		3700	.016	1.4120
		4000	.014	1.4640
		4300	.012	1.5238
1.52 x 10 ⁻³ M	U(IV)*	400	•06 8	.8562
$9.00 \times 10^{-3} M$	Tl(III)	700	•059	•9062
1.76 <u>M</u> H ⁺		1000	.053	•9481
1.06 <u>M</u> NaClO,		1325	.048	•9857
2.9		1625	.043	1.0278
4.50 x 10 ⁻³ <u>M</u>	Tartaric Acid	1900	•039	1.0652
		2200	.036	1.0966
		2555	.033	1.1307
		2805	.030	1.1673
		3125	.028	1.1951
		3410	.026	1.2240
		3710	•024	1.2553
		4005	.0225	1.2813
		4300	•021	1.3081

Original Data from Table XIII - Continued

		Time	A	log Tl/U
1.91 x 10 ⁻³ M U(IV)*	100	.120	. 6026
9.00 x 10 ⁻³ <u>M</u> T1	(III)	400	•098	.6701
1.76 <u>M</u> H ⁺		7 50	•085	•7192
1.06 <u>M</u> NaClO _L		1000	.076	•7563
2.9		1300	•070	• 7868
6.75 x 10 ⁻³ <u>M</u> Ta	rtaric Acid	1600	.065	.8140
		1910	.061	.8371
		2200	•055	. 8745
		2500	•053	. 8886
1.60 x 10 ⁻³ M U(IV)*	100	•082	•7722
9.00 x 10 ⁻³ M T1	(III)	400	•065	•856 7
1.76 м н ⁺		700	•055	•9181
1.06 M NaClO,		1000	.048	•9698
- 4 2.9		1300	•040	1.039
6.75 x 10 ⁻³ M Ta	rtaric Acid	1600	•035	1.091
-		1900	•032	1.126
		2200	•028	1.178
		2500	•024	1.239
.901 x 10 ⁻³ M U(IV)*	100	•044	1.043
9.00 x 10 ⁻³ M T1	(III)	400	•033	1.156
1.76 <u>м</u> н ⁺		700	.025	1.264
1.06 <u>M</u> NaClO,		1000	.022	1.315
2.9		1300	.020	1.352
6.75 x 10 ⁻³ <u>M</u> Ta	rtaric Acid	1600	.016	1.441
_		1900	.013	1.523
		2200	.011	1.588
		2500	.010	1.624

Original Data from Table XIII - Continued

	a dalam yana yana yana ang kana ang ka	Time	A	log Tl/U
3.62 x 10 ⁻³ M	J(IV)*	100	•172	•4425
$9.00 \times 10^{-3} M$	T1(III)	400	.146	.4881
1.76 <u>M</u> H ⁺		700	•131	•5210
1.06 <u>M</u> NaClO _L		1000	.120	•54 73
2.9		1300	.110	•5751
6.75 x 10 ⁻³ M □	^r artaric Acid	1600	.101	.6009
		1900	•095	. 628 3
		2200	•090	. 6397
		2500	•088	.6461
2.60 x 10 ⁻³ M	u(IV)*	100	.120	.6026
$9.00 \times 10^{-3} M$	Fl(III)	400	•099	. 6661
1.76 <u>M</u> H ⁺		700	•086	•7146
1.06 <u>M</u> NaClO _L		1000	•075	•7616
2.9		1300	•068	• 7986
6.75 x 10 ^{−3} M	Fartaric Acid	1600	.061	.8371
		1900	.056	.8692
		2200	.051	•9028
		2500	•047	•9332
1.79 x 10 ⁻³ <u>M</u>	J(IV)*	100	•082	• 77 36
9.00 x 10^{-3} M	Tl(III)	400	.065	. 8583
1.76 <u>M</u> H ⁺		700	•055	•9197
1.06 <u>M</u> NaClO _L		1000	•047	•9533
2.9		1300	.040	1.0410
6.75 x 10 ⁻³ M	Fartaric Acid	1600	•035	1.0924
		1900	•032	1.1274
		2200	.028	1.1801
		2500	.025	1.2238

Original Data from Table XIII - Continued

		Time	A	log Tl/U
1.02 x 10 ⁻³ M U	(IV)*	115	• 043	1.0535
$9.00 \times 10^{-3} \text{ M}$ T	1(III)	405	.033	1.1566
1.76 M H ⁺	/	710	.027	1,2353
1.06 M NaClO,		1000	.023	1.2991
- 4 2.9		1305	.019	1.3742
6.75 x 10 ⁻³ M T	artaric Acid	1600	.016	1.4423
_		1900	.014	1.4946
		2200	.012	1.5545
		2500	.010	1.6246
	·(TV)*	100	165	<u> </u>
$9.00 \times 10^{-3} \text{ m}$	(<u>-</u> ,	400	140	5087
1.76 м н ⁺	1(111)	700	•170 125	• J00 7 5423
1.06 M NaClo.		1000	115	•J+2J 5689
2.9		1300	106	• J00 J
3 50 v 10 ⁻² M T	antania Acid	1600	005	• <i>JJJ</i> 1
	artaric Aciu	1000	.090	•0900 6484
		2208	•090 081	-0+0+ 68/12
		2500	070	6015
		2,00	•079	•091)
3.48 x 10 ⁻³ M U	(IV)*	100	•147	•4946
9.00 x 10 ⁻³ M T	1 (I II)	407	.118	• 53 92
1.76 <u>м</u> н ⁺		700	.103	. 6038
1.06 <u>M</u> NaClO _L		1000	•090	• 6484
2.9		1310	.080	. 6866
1.75 x 10 ⁻² <u>M</u> T	artaric Acid	1650	.071	•7280
		1900	•068	•7452
		2200	.063	•7698
		2500	•06 0	.7895

Original Data from Table XIII - Continued

ORIGINAL DATA FROM TABLE XIX

(Page	77)
Tage	

		Time	A	log Tl/U
3.33 x 10 ⁻³ <u>M</u>	U(IV)*	100	.185	•4368
9.00 x 10^{-3} M	Tl(III)	400	.174	•4535
2.50 <u>M</u> H ⁺		700	.165	•4686
0.32 <u>M</u> NaClO ₄		1000	.157	•4829
2.9		1300	.150	•4958
$4.50 \times 10^{-4} M$	Maleic Acid	1600	•144	• 5084
		1900	.137	• 5228
		2200	.130	•5384
		2500	.125	•550 7
$3.29 \times 10^{-3} M$	U(IV)*	100	.180	•4456
$9.00 \times 10^{-3} M$	Tl(III)	400	.165	•4706
1.76 <u>M</u> H ⁺		715	. 155	. 4880
1.06 <u>M</u> NaClO _h		1000	.145	• 5081
2.9		1300	•135	•5301
$4.50 \times 10^{-4} M$	Maleic Acid	1600	.127	• 5488
		1900	.120	•5660
		2200	.112	•5876
		2500	.105	.6078
$3.14 \times 10^{-3} M$	U(IV)*	100	.165	•4781
$9.00 \times 10^{-3} M$	Tl(III)	400	.139	•5292
0.88 <u>м</u> н ⁺		700	.119	•5772
1.94 <u>M</u> NaClO _L		1000	.103	. 6235
2.9		1300	•089	•6729
$4.50 \times 10^{-4} M$	Maleic Acid	1600	•077	•7224
		1900	.067	•7696
		2200	•059	•8148
		2500	.051	. 8695

ORIGINAL DATA FROM TABLE XX

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	Time	A	log Tl/U
3.48 x 10 ⁻³ <u>M</u> U(IV)*	100	•184	•4302
$9.00 \times 10^{-3} \text{ M}$ T1(III)	450	.182	•4336
1.76 <u>м</u> н ⁺	700	.180	•4362
1.06 <u>M</u> NaClO _L	1000	.178	•439 7
2.9	1300	.176	•4423
3.5×10^{-2} <u>M</u> Maleic Acid	1600	•173	•4478
	1905	.172	•4496
	2200	.171	•4506
	2500	.169	•4542
3.53 x 10 ⁻³ <u>M</u> U(IV)*	105	.187	•4237
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.173	• 4453
1.76 <u>M</u> H ⁺	700	.170	•4498
1.06 <u>M</u> NaClO _L	1000	.165	•4583
2.9	1300	.164	•4603
9.00 x 10^{-3} <u>M</u> Maleic Acid	1 60 0	. 157	•4725
	1900	•154	•4777
	2200	. 150	•4852
	2500	•145	• 4953
3.62 x 10 ⁻³ M U(IV) *	100	.191	•41 <i>3</i> ć
$9.00 \times 10^{-3} \frac{1}{M}$ T1(III)	400	.170	•4451
1.76 <u>м</u> н ⁺	7 00	. 165	•4536
1.06 \underline{M} NaClO _L	1000	.163	•4567
2.9	1200	.161	•4606
$6.75 \times 10^{-3} M$ Maleic Acid	1320	.160	•4626
	1605	. 158	•46 <u>5</u> 5
	1900	. 155	•470 7
	2200	•151	.4781
	2500	.150	•4804

	Time	A	log Tl/U
3.62 x 10 ⁻³ M U(IV)*	105	.195	.4081
9.00 x 10^{-3} M T1(III)	400	.168	•4489
1.76 <u>M</u> H ⁺	700	.155	• 470 7
1.06 <u>M</u> NaClO _L	1000	.148	•4847
2.9	1300	•144	•4928
4.50 x 10 ⁻³ <u>M</u> Maleic Acid	1600	.138	• 5046
	1900	.132	•5184
	220 0	.126	•531 7
	2500	.122	• 5430
3.40 x 10 ⁻³ M U(IV)*	100	.182	•4376
$9.00 \times 10^{-3} \text{ M}$ T1(III)	400	.155	•4823
1.76 <u>м</u> . н ⁺	7 00	•145	• 5023
1.06 M NaClO,	1000	.140	•5130
2.9	1300	.135	•5241
4.50×10^{-3} <u>M</u> Maleic Acid	1600	.130	• 5345
_	1900	.126	•5441
	2200	.120	• 5598
	2500	.117	•5673
3.48 x 10 ⁻³ M U(IV)*	100	.187	•4262
$9.00 \times 10^{-3} \text{ M}$ T1(III)	400	.165	•4609
1.76 <u>M</u> H ⁺	700	.146	•4957
$1.06 \underline{M}$ NaClO ₁	1005	•134	•5210
2.9	1300	.128	• 5356
3.5 x 10 ⁻³ <u>M</u> Maleic Acid	1600	.123	• 5480
	1900	.116	• 56 58
	2200	.110	•5833
	2500	.105	•5968

Original Data from Table XX - Continued

	Time	A	log Tl/U
3.60 x 10 ⁻³ M U(IV)*	100	•194	.4106
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.175	.4381
1.76 <u>м</u> н ⁺	700	.159	•4646
1.06 <u>M</u> NaClO _L	1000	. 144	•4939
2.9	1300	.132	•5196
2.25 x 10^{-3} <u>M</u> Maleic Acid	1600	.123	•5412
	1900	.115	•5619
	2200	.110	•5762
	2500	.104	•5932
3.60 x 10 ⁻³ M U(IV)*	100	•194	.4106
$9.00 \times 10^{-3} \text{ M}$ T1(III)	400	.180	•4302
1.76 <u>м</u> н ⁺	700	.167	•450 9
- 1.06 <u>M</u> NaClO _L	1000	.155	•4719
- + 2,9	1300	•145	•4915
9.00 x 10 ⁻⁴ <u>M</u> Maleic Acid	1600	. 135	•5131
_	1910	,126	•5329
	2200	.118	•5544
	2500	.110	•5762
3.51 x 10 ⁻³ M U(IV)*	100	.189	•4223
$9.00 \times 10^{-3} M$ T1(III)	400	.174	• 4444
1.76 <u>м</u> н ⁺	700	.163	•4624
$1.06 \underline{M}$ NaClO _L	1000	.151	•4840
2.9	1300	•143	•501 1
3.5 x 10 ⁻⁴ <u>M</u> Maleic Acid	1605	•135	•518 1
	1900	.125	•540 7
	2215	.119	•556 5
	2500	.112	•5751

Original Data from Table XX - Continued

	Time	A	log Tl/U
3.51 x 10 ⁻³ <u>M</u> U(IV)+	100	.190	.4206
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.178	•4382
1.76 <u>M</u> H ⁺	700	.168	•4545
1.06 \underline{M} NaClO ₄	1000	.160	. 4684
2.9	1300	.150	•4863
3.5×10^{-5} <u>M</u> Maleic Acid	1600	•144	•4987
	1905	.137	•5131
	2200	.130	•5285
	2505	.124	•5434
3.40 x 10 ⁻³ M U(IV)*	100	.183	• 4358
9.00 x 10^{-3} M TI(III)	400	.158	.4771
1.76 <u>м</u> н ⁺	700	.145	•502 3
1.06 \underline{M} NaClO _L	1000	.138	•516 7
2.9	1300	.133	•5280
4.50 x 10^{-3} <u>M</u> Maleic Acid	1600	.126	•54 41
	1900	.122	•5555
	2200	.117	•5673
	2500	.112	•5814
3.47 x 10 ⁻³ <u>M</u> U(IV)*	100	.183	•4325
9.00 X 10 ⁻³ M T1(III)	400	•155	•4787
1.76 <u>M</u> H ⁺	700	•147	•4951
1.06 <u>M</u> NaClO _L	1000	.142	• 5043
2.9	1300	.140	•5092
4.50 x 10^{-3} <u>M</u> Maleic Acid	1600	.136	•5179
	1900	•133	•5241
	2200	•130	•530 7
	2500	.129	•5334

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Original Data from Table XX - Continued

	Time	A	log Tl/U
3.52 x 10 ⁻³ <u>M</u> U(IV)*	100	.189	.4218
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.162	•4637
1.76 <u>м</u> н ⁺	700	.151	•4836
1.06 <u>M</u> NaClO _L	1000	.146	•4936
2.9	1300	.1 42	• 5017
4.50 x 10 ⁻³ <u>M</u> Maleic Acid	1600	.138	•510 1
	1900	•135	•5176
	2205	•132	•5240
	2500	.130	•527 9

Original Data from Table XX - Continued

ORIGINAL DATA FROM TABLE XXI

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	Time	A	log Tl/U
2.81 x 10 ⁻³ <u>M</u> U(IV) *	100	. 156	•5109
$9.00 \times 10^{-3} \text{ M}$ T1(III)	400	. 148	•526 7
1.76 <u>M</u> H ⁺	700	.142	•5386
1.06 <u>M</u> NaClO _L	1000	.136	•5524
2.9	1300	.129	•5686
9.00 x 10^{-3} <u>M</u> Maleic Acid	1600	.124	•5814
35.0°C. Temperature	1910	.119	•5948
	2200	•114	•6090
	2500	.110	•620 6
3.09 x 10 ⁻³ M U(IV)*	110	.172	•4689
$9.00 \times 10^{-3} \frac{1}{M}$ T1(III)	400	.164	•4826
1.76 <u>M</u> H ⁺	720	. 160	•4897
1.06 M NaClO _L	1000	. 155	•4982
2.9	1306	.150	• 5081
9.00 x 10^{-3} <u>M</u> Maleic Acid	1600	.147	•5150
24.9 [°] C. Temperature	1900	.145	•5185
	2200	.141	•5269
	2500	.137	• 5356
	Time	A	log Tl/U
--	-------	--------------	----------------
3.53 x 10 ⁻³ <u>M</u> U(IV)*	100	.192	•4165
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.174	•4434
1.76 <u>м</u> н ⁺	700	.167	•4545
1.06 <u>M</u> NaClO ₄	1000	.165	•4583
2.9	1300	.164	.4603
9.00 x 10^{-3} <u>M</u> Maleic Acid	1600	.163	. 4614
15.0°C. Temperature	1900	.162	•4633
	2200	.161	•4652
	2500	.160	•4673
4.24 x 10 ⁻³ <u>M</u> U(IV)*	135	•237	• 3296
9.00 x 10 ⁻³ <u>M</u> T1(III)	560	•232	•3346
1.76 <u>M</u> H ⁺	1000	.226	• 3404
1.06 <u>M</u> NaClO ₄	1500	.220	•3471
2.9	2000	.214	• 3539
9.00 x 10^{-3} <u>M</u> Maleic Acid	3000	. 205	•3638
5.0°C. Temperature	4000	.198	•3729
	5000	•195	• 3766
	6000	•192	• 3802
	7000	.190	• 3833
	8000	.190	• 3833
	9000	.189	• 3847
	10000	•189	• 3847
3.17 x 10 ⁻³ <u>M</u> U(IV)*	105	.162	.4816
9.00 x 10 ⁻³ <u>M</u> T1(III)	400	.129	•5497
1.76 <u>M</u> H ⁺	700	.104	.6182
1.06 <u>M</u> NaClO ₄	1000	•084	. 6890
2.9	1300	•069	•7589
9.00 x 10 ⁻⁴ <u>M</u> Maleic Acid	1600	•058	.8199
35.0°C. Temperature	1900	•050	• 3746
	2200	.042	• 9 296
	2500	•036	•9980

Original Data from Table XXI - Continued

	Time	A	log Tl/U
3.33 x 10 ⁻³ <u>M</u> U(IV)*	100	.183	•4393
$9.00 \times 10^{-3} \text{ M}$ T1(III)	415	.167	• 4648
1.76 <u>м</u> н ⁺	700	.155	. 4860
$1.06 \underline{M}$ NaClO _L	1020	•145	•5060
2.9	1300	•136	•5254
9.00 x 10 ⁻⁴ <u>M</u> Maleic Acid	1600	.125	•550 7
24.9 [°] C. Temperature	1900	.118	•5697
	2200	.109	•5936
	2500	.109	•5936
3.45 x 10 ⁻³ M U(IV)*	105	.195	•4165
$9.00 \times 10^{-3} \text{ M}$ T1(III)	400	.189	•4252
1.76 <u>м</u> н ⁺	705	.185	•4309
$L_006 M$ NaClO,	1000	.180	•4378
2.9	1300	•177	•4430
9.00 x 10 ⁻⁴ <u>M</u> Maleic Acid	1900	•170	•4539
15.0°C. Temperature	2200	. 166	. 4606
	2500	.162	•4675
3.78 x 10 ⁻³ M U(IV)*	130	.210	•3815
$9.00 \times 10^{-3} \text{ M}$ T1(III)	500	.212	•378 8
1.76 <u>м</u> н ⁺	1000	.210	• 3815
$1.06 M$ NaClO $_{L}$	1500	. 208	• 3 835
2.9	2000	•205	• 3870
9.00 x 10 ⁻⁴ <u>M</u> Maleic Acid	3000	.202	•3913
5.0°C. Temperature	4000	.197	•3979
	5000	•194	.4018
	6100	.190	•4072
	7000	188	•4096
	8000	.185	•4143
	9 00 0	.183	.4168
	10010	•179	•4228

Original Data from Table XXI - Continued

	Time	Δ	log Tl /U
3.14 x 10 ⁻³ M U(IV)*	100	. 166	.4761
9.00 x 10 ⁻³ <u>M</u> T1(III)	465	.135	•5381
1.76 <u>M</u> H ⁺	700	•119	•5772
1.06 <u>M</u> NaClO ₄	1000	.102	. 6272
2.9	1300	.088	.6750
9.00 x 10^{-5} <u>M</u> Maleic Acid	1620	•073	•7410
35.0°C. Temperature	1900	•064	•7882
	2200	.056	•8363
	2500	•048	.8920
3.31 x 10 ⁻³ <u>M</u> U(IV)*	150	.181	•4437
$9.00 \times 10^{-3} \text{ M}$ T1(III)	420	.172	•4582
1.76 <u>м</u> н ⁺	700	.163	•4726
$1.06 \underline{M}$ NaClO,	1000	•154	•4891
2.9	1300	•146	•5047
9.00 x 10 ⁻⁵ <u>M</u> Maleic Acid	1630	.138	•5214
24.9 [°] C. Temperature	1900	•130	•5395
	2240	.124	•5546
	2500	.118	• 5708
3.49 x 10 ⁻³ M U(IV)*	100	•198	•4106
$9.00 \times 10^{-3} \text{ M}$ T1(III)	500	•191	•4200
1.76 м н ⁺	700	.188	•4241
1.06 M NaClO ₁	1000	.185	• 4289
2.9	1300	.181	•4349
9.00 x 10 ⁻⁵ <u>M</u> Maleic Acid	1605	•179	•4374
15.0°C. Temperature	1900	•175	•4436
	2200	•173	• 4473
	2505	.169	•4538

Original Data from Table XXI - Continued

	Time	A	log Tl/U
3.72 x 10 ⁻³ <u>M</u> U(IV)*	165	•209	• 3851
9.00 x 10 ⁻³ M T1(III)	500	•20 7	•3 ⁸ 79
1.76 <u>M</u> H ⁺	1000	.204	•3915
1.06 <u>M</u> NaClO ₄	1500	.201	•3950
2.9	2000	.200	•3966
9.00 x 10 ⁻⁵ <u>M</u> Maleic Acid	2500	.198	• 3995
5.0°C. Temperature	3000	.196	.4018
	4000	.193	•4062
	5000	.191	• 4086
	6000	.188	•4126
	7000	.185	•4175
	8000	.182	•4216
	9000	.180	•4241
	10000	•179	•4259
3.52 x 10 ⁻³ M U(IV) *	100	•200	•4062
9.00 x 10 ⁻³ M T1(III)	405	•194	•4145
1.76 <u>M</u> H ⁺	700	.191	. 4185
1.06 <u>M</u> NaClO _L	1000	.187	•4242
2.9	1300	.184	•4283
9.00 x 10 ⁻⁵ <u>M</u> Maleic Acid	1655	.181	•4333
15.0°C. Temperature	1900	.178	•4378
	2200	.175	•4422
	2500	.173	• 4458

Original Data from Table XXI - Continued

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APPENDIX

METHOD OF LEAST SQUARES

When the data from kinetic runs are graphed in the normal manner for a second order reaction with two reactants, one of two situations prevails. Either the data yield a straight line or a curve which becomes straight after x seconds. In either case the method of least squares⁵⁵ was applied to the straight portion of the line so that the best possible fit of points to a line might be obtained. The MISTIC digital computer of Michigan State University was used to carry out the necessary computations.

Essentially MISTIC⁵⁶ is a binary computer. However it is not necessary to provide MISTIC with binary data. Rather a decimal order input is programmed and the computer itself does the computations necessary to change the data from a decimal base to a binary base. It is also possible to build in a decimal readout program. All the programs used with the least squaring required a decimal data input and the answers were provided in decimal form.

MISTIC can compute only with fractions. Thus it is necessary to introduce one or more scaling factors so that the data will be presented to the computer in proper fractional form. After the answer is obtained the scaling factor is reintroduced to obtain the output in proper form.

The MISTIC can store only 1024 words of 40 bits each. Therefore care must be taken in some programs to be sure that more information is not provided to the computer than it can store. This is soon to be changed with the introduction of a core memory. For example space limitations require that no more than fifty

problems be presented to program 7. There simply is no more room to store any more information.

For a collection of points the method of least squares is essentially the determination of the equation of the straight line which has the property that the sum of the squares of the distances from the points to the line will be a mininum. The equation obtained is of the form:

$$y = mx + b$$

where m is the slope of the line, and b is the intercept of the line on the ordinate axis. The slope and the intercept of a line can be obtained by the solution of the two equations following.

$$\mathbf{m} = \frac{n \sum \mathbf{x}_{i} \mathbf{y}_{i} - \sum \mathbf{x}_{i} \sum \mathbf{y}_{i}}{n \sum \mathbf{x}_{i}^{2} - (\sum \mathbf{x}_{i})^{2}}$$
 1)

$$b = \frac{\sum \mathbf{x_i}^2 \sum \mathbf{y_i} - \sum \mathbf{x_i} \mathbf{y_i} \sum \mathbf{x_i}}{n \sum \mathbf{x_i}^2 - (\sum \mathbf{x_i})^2}$$
 2)

In these equations n is the number of points being operated upon, x_i , and y_i are the coordinates of point, p_i .

There are three programs involved in the least squares method. They are denoted as the 6N, Ranes' L2 and 7 programs: The first program6N, takes the data provided and produces matrix equations which is the equivalent of equations 1 and 2. The

* Many thanks are due to Dr. R. L. Schwendeman who developed these programs for the computer and who so generously loaned them to the author.

Table XXIII

The 6N Program

8002840001	-5F468L	3241 92708F	43020 F-5 000F
8002840002	L44L4211L	265L92644F	26000100000F
1902626000	814FL025L	19F L6F	0020+
8002840000	2210L402F	40F 003322	L5042F50000L
L400140001	L5F661F	0000000J	26072F41043F
8002840 3F6	lolf-JF	00F 503F	41042FF5044F
-500026316	40FL1F	002F 7J6L	40044FL0040F
81004263FJ	401FL52F	0020F 465L	36028FL5012F
4000122000	40FL58L	92133F L58L	L0041F40012F
7 J3LFL 4001	L44L468L	221014F 227L	41043F26012F
40001263 1 8	L52F427L	261 N	
L4002263F-	L023L32F	40F 1963-3	0028+
423FFL5001	L524L401F	50F 40F	92770FF5045F
L 4000 L 4000	41F814F	7512L 0036F	40045 FL00 40F
263F -lo3ll	L025L402F	824F 1040F	32004 LL 5037F
703LL-53F7	326 LL 424L	L5F L4F	46012 F 41044F
4000081004	40F814F	327L 22F	26012 F 92706F
50000L43LL	501F402F	OOF OOLOF	92551F24999F
323FLL43LO	L025L323L		
423L5L5001	7525L-5F	005+	0035+
1 40002600 0	401F5025L	50100F50000L	OFFOFF
40002L03L4	75F0039F	26046FL5037F	001F001F
423L8233L9	L42F2616L	42012F46012F	00100F00100F
5000140000	000F002F	41042F41043F	OOFOOlf
L13F9L43L4	00 F 005 F	41044FL5038F	
423F9L43L8	000F0010F	40045F26012F	201019 N
4231800027	003+00F0011F		
800080000N		0012+	
40001273L1	0072+	50000F74000F	
465 F 6604 -8		L4042F40042F	
7LLLLLLL6	40 F +5F	L5000LI40 36F	
223L-00001	4211L 92131F	40000lf5043f	
0046+	92515F L5F	40043FL0041F	

Table XXIV

	The Ran	es' L2 Program	
8002840001	00F00160F	L522L425L	7JF40F
8002840002	OOFOOF	492F41F	L536LL 467L
1902626000	OOFOOF	L51L4222L	40361L068L
8002840000	00F00200F	4227LL522L	3677LL54F
L400140001	00F0030F	4214L4216L	
8002 8 403 F6	00F0021F	4218LL54F	L471L464F
-5000263 16	l56f4290f	L42L4615L	L03F327L
81004263 FJ	40-35010F	4616L4619L	L53FL467L
4000122000	2630FL511-7	4621L4625L	403FL072L
7J3LFL4001	46136F46138F	L567L4221L	362LL565L
4000126318	1020F42136F	4623LL3F	42-415221
l4002263F -	4228FL5136F	l6f3680l	4250LL524L
423FFL5001	L0135F42121F	L5F66F	4673L4662L
L4000L4000	46113FL0135F	4321L2620L	L568L4650L
263 F- L43LL	4692FL 020F	5066 l75 F	2776L - 5F
743LL-53F7	46140F42140F	66 F 4723L	50 F7 4F
4000081004	413F2271F		L4F40F
50000L23LL	0 0159F 00159F	-121L405F	L42F3254L
323FLL43L0	814F0020F	L5F40F	506517J-4
4231515001	4624 F9213 5F	505FL5F	2645LL550L
L400026000		401F7J1F	L067L4050L
40002L03L4	92 131FL5-3	501023-4L4F	l073l3678l
42 <u>3</u> 1823319	50 F 524 F	40 FL 42 F	L550L 4258L
5000140000	2651FL523F	3627L4715L	4260LL3F
L13F9L43L4	L4135F4223F	L51F40F	l6 f36 53l
423 F9L 43L8	l028f3623f	L522LL066L	L5F66F
423 18 00027	12132FL5F	4222L4227L	l62F-162L
80008000N	26350F0FF	L525LL467L	40F1562L
40001273L1	0068+	4625L4621L	1075136-8
465F6604-8	413FL51L	L070L3621L	L474L2647L
80000000+	4222150 - 6	L515LL061L	00F0010000
223L-00001	40-3502L	3239LL569L	000000J7
003+	26 -7 414F	4036L5065L	L4095FLL4095F

	Table	XXIV (con't)
OOlfOOlf	41F236L	40 - 41590F
LJ1-4401-4	80 F00 10F	921 31FL5- 3
7J-340-3	00F0012F	
NO1-4L42F	OOFOOlOF	00350+
801F00F	0051+	L5300F 403F
80-500-5	40 FL 116L	L5301F404F
50 FL 6 F	-4L461L	40 5FL5 302 F
N01023-316F	4214L366L	406 FL 5303F
NO-316F	L5F365L	407 FL 5304 F
0040F2351L	92706F225L	408 FL5 305 F
0027F2235L	92642F002F	40138 FL5306F
-5F401F	J08 L7 J17L	4091FL5307F
2 279L 2249L	428L228L	40136FL5308F
	0 063F19F	4052 FL 5309 F
L516L4681L	L6F1039F	4121 FL5310F
50 F-3F	7515L0036F	4023 F 249F
3219L2618L	824F1040F	249 N
0030+	L51LL0 16L	
-5F4611L	46113610L	
L410L4214L	92965F22 F	
814F2213L	OOFOOlOF	
751F0039F	-41F001023F	
401 F 5020L	001F+91000F	
L52F74F		
- 5 F 40 F	00300+	
_ 814F5020L	00F00160F	
402FL018L	OOFOOF	
363LL5F	00F00200F	
661F - 51F	00F0030F	
40FL511L	00F0021F	
L4L4611L	NO1-4L42F	
L52FL0194	401F7J1F	
401 F 32F	LJ1-4401-4	
0039F3216L	-451F4652F	
2 36L1938F	50133 F7J- 4	

Table XXV

	The	7 Program	
8002840001	26999 F0 0000 F	0031+	-5F468L
8002840002	26230N00232+	OOFOOF	L44L4211L
1902626000	50070F50000L	OOlfoof	814FL025L
8002840000	26236F24999F	00F00280F	2210L402F
L400140001		OOFOOlF	L5F661F
80028403 F6	005+		101F-JF
- 500026316	41037F92535F	0043+	40FL1F
8100426 3FJ	92139F92515F	50031F41036F	401FL52F
4000122000	L5033F42013F	41037FL5000F	40FL58L
7J3LFL4001	42014F42044F	40038 FL 4039F	L44L468L
40001263 18	50280F50004L	40039FL5038F	L52F427L
l400226 3F-	26236F41039F	50006F50004L	L02 3L3 2F
42 3FFL 5001	26013F00000F	26262F92963F	L524L401F
L4000L4000		L5001LL4041F	41F814F
263F-L03LL	0013+	420011F5037F	L025L402F
703LL-53F7	41036F50000F	40037FL0040F	326LL424L
4000081004	75070F40000F	L4034F36055F	40F814F
50000L43LL	F5000L42000L	22001L00000F	501 F 402F
323FLL43L0	42001 lf 5036 f		L025L323L
423 151 5001	40036 F L0041F	0055+	7525L-5F
L 400026000	36020 F22 000L	92963FL5039F	
40002L03L4		50006 F 50001L	401 F5 025L
423L8233L9	0020+	26262F92963F	75F0039F
5000140000	L5014FL4032F	L5044F42004L	L42F26160
L1359L43L4	46014FF5037F	50031 FL 1000F	000F002F
423F9L43L8	40037FL0040F	500 06F 50005L	00F005F
4231800027	36043 FL 4034F	26262FF5036F	OOOFOOlOF
800080000 N	36005L26013F	40036FL0041F	00262+
40001273L1	L5014F46006L	34999F92131F	
465 F 6604 - 8	L5000F50031F	92515FL5033F	40 F+5 F
7LLLLLLL6	50011F50007L	l4036f42044f	426L4615L
223L-00001	26262 F 92135F	41039 F 26044F	367L5116L
00230+	92515F26013F		l6F1039F
92770F9257F5		00236+	L515LL013L

Table XXV (con't) 4615L3212L 92965F22F JO11L7J16L 4211LL5F 3210L92606F 2211L92642F 0031F19F 263L7517L 001F823F 223L00F 00F823F 001F+91000F 50F00F

OFFOFF

24232N

second program, Ranes' L2 then solves this matrix equation for the "best" slope and intercept. The final program 7 takes data from both of the previous programs and calculates mx_i , b_i and y_i and prints these along with the y_i obtained experimentally so that they may be compared. The programs are as follows.

As an example one reaction will be followed through the procedure. The data after the necessary calculations appears below.

Time	Log T1/U
100	0.4014
430	0.4193
700	0.4309
1000	0.4470
1305	0.4606
1600	0.4771
1900	0,4904
2200	0.5046
2500	0.5223

The data is supplied to the MISTIC on a punched data

tape. The data are presented as follows:

Table XXVI

Typical Data Supplied to MISTIC

0040+

00F003F

00F009F

26**5**N

+00100+00430+00700+01000+01305+01600+01900+02200+02500

+01+01+01+01+01+01+01+01

+04014+04193+04309+04470+04606+04771+04904+05046+05223N

Each problem consists of seven lines of data as shown above. Without going into great detail, the purpose of each line will be shown.

Line one gives a direction as to where lines two and three are stored in the computer memory. The sixth digit in line two is equal to one more than the number of variables in the equation being considered. For a straight line this is equal to three. The sixth number in line three is equal to the number of points in the data. This is the only number in the first four lines that will vary under normal circumstances. Finally line four is an order to the computer to transfer control to one of the programs in its memory.

In MISTIC a number is indicated by prefacing it by a + or a - sign. No spaces are necessary. Notice that in lines five, six and seven all numbers have been prefaced by a + sign. Line five contains the x coordinates for the points under consideration. Notice that all of the numbers have been multiplied by 10^{-5} the scaling factor for this portion of the data.

Line six is a line necessary to complete the matrix which will produce the linear equations. As many +Ol's are inserted as there are points being considered.

In line seven all numbers have been multiplied by 10^{-1} , the scaling factor for these data. These are the y coordinates of the points being considered. The last piece of data is followed by an N and at the end of all data sets, the number 2635N is inserted. The N is necessary since it indicates the end of a set

of data and the 2635N is nucessary to allow the computer to shut off.

Since the MISTIC operator is unfamiliar with the program, it is also necessary to furnish him with operating instructions. These are reproduced below.

Program	How Started	Stop Orde r	Comments
6 n	Bootstrap	20 1019	Insert input for 6N
Input	Black Switch	OFF>	If black switch set to
of 6N		>	"ignore". Retain input for
		>	6N for later use.
L2	Bootstrap		Insert output from 6N and
			black switch through
			problems. Do <u>not</u> remove
			output from L2 from punch
			until 7 is completely read in.
7	Bootstrap	24 232	Insert output from L2
Output	Black switch	24 999	Insert output from 6N
from L2			
Input	Black switch ()FF>	If the black switch see ∞
of 6N			"ignore".

After the 6N calculation has been made the output from 6N contains the following data. +00206479250 3)

+00117350000 4) +00564266000N 5) +00117350000 6)

+0009000000

+00412480000N-

This information is necessary only to the computer, consequently it is not normally printed. Written in matrix form it appears as

$$\begin{pmatrix} 00206479250 & 00117350000 \\ 00117350000 & 00090000000 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 00564266000 \\ 00412480000 \end{pmatrix}$$
 9)

If time is denoted as x and the log Tl/U readings as y, then the data as previously given represents summations of the various entries.

3)	Σ	\mathbf{x}_{i}^{2}	6)	Σ	× _i
4)	Σ	×. i	7)		n
5)	Σ	x _i y _i	8)	Σ	y _i

This information is then inserted into the computer after the Ranes' L2 program. The output of the program contains the following information.

The decimal point in the answer follows immediately the figure one in the scaling factor. Rewriting these they appear as follows.

-0.4944633615 13)

+1.000000000 15)

where 13) is the slope, 14) is the intercept and 15) is the

7)

8)

scaling factor. To correct these numbers for the scaling factors previously introduced, it is necessary to multiply 13) by 10^{-4} and 14) by 10^{-1} .

Now if the output from 6N is used as an input for program 7 along with the information from Ranes' L2, the following information is obtained.

Table XXVII

Output of Program 7.

+1000000000

-000049	-003938	-003988	-003985
-000213	-003938	-004151	-004161
-000346	-003938	-004284	-004278
-000494	-003938	-004433	-004439
-000645	-003938	-004584	-004574
-000791	-003938	-004730	-004739
-000939	-003938	-004878	-004871
-001088	-003938	-005026	-005012
-001236	-003938	-005175	-005189

Again a scaling factor for locating the decimal point is provided. The four columns from left to right are x_im , b, y_i (calculated), and y_i (experimental). Using this data a comparision of the experimental points and the calculated points can easily be made. CHEMISTRY LIBRARY

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