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# An Investigation of the Isotopic Exchange of Arsenic Atoms Between Arsenic(III) And Arsenic(V) In Aqueous Hydrochloric Acid Solutions

Lewis L. Anderson

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THE ISOTOPIC  
EXCHANGE OF  
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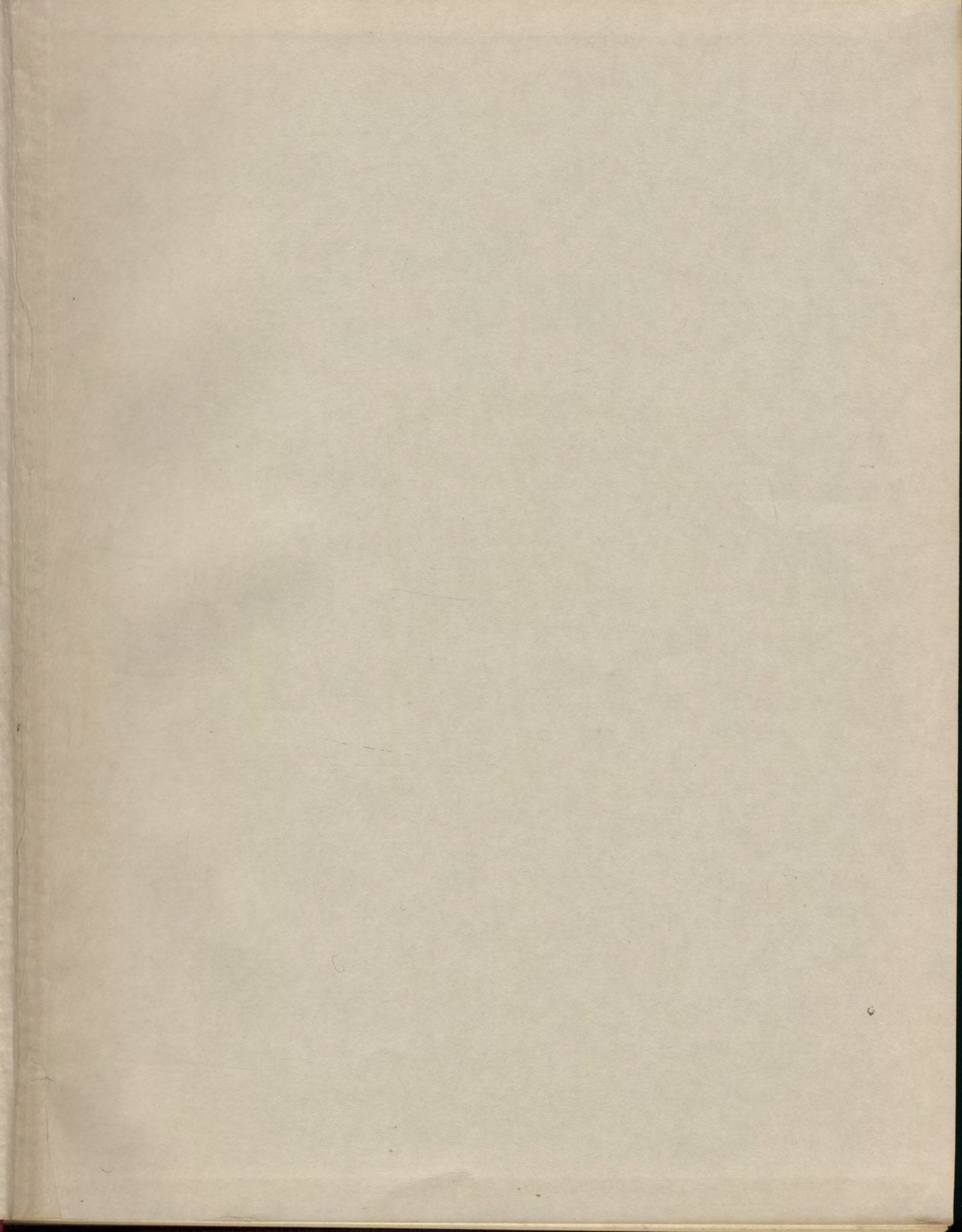


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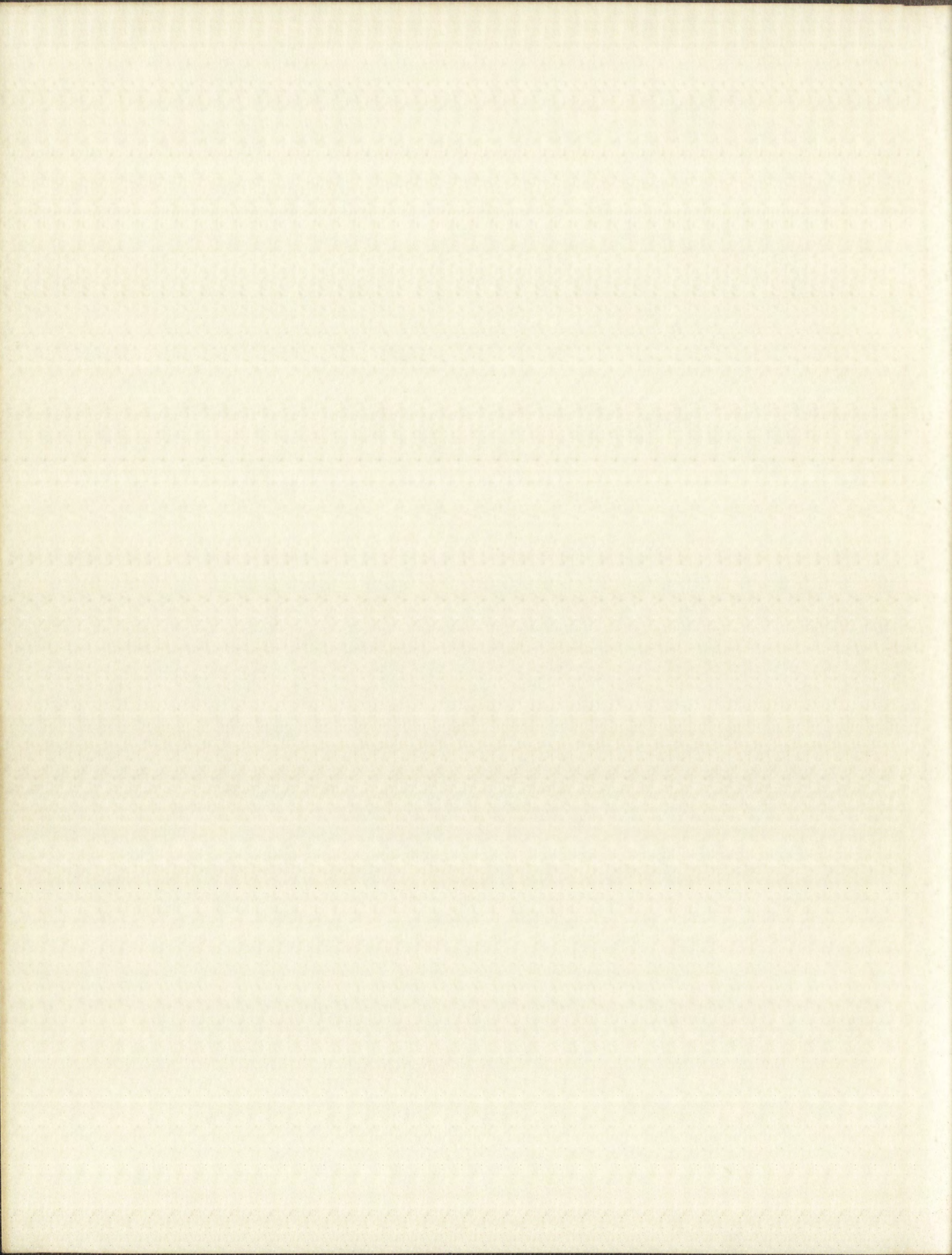


















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AN INVESTIGATION OF THE ISOTOPIC  
EXCHANGE OF ARSENIC ATOMS BETWEEN ARSENIC(III)  
AND ARSENIC(V) IN AQUEOUS HYDROCHLORIC ACID SOLUTIONS

By

Lewis L. Anderson

A Dissertation

Submitted in Partial Fulfillment of the  
Requirements for the Degree of  
Doctor of Philosophy in Chemistry

The University of New Mexico

1961





*W. H. Miller*

*W. H. Miller*



This dissertation, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

E. H. Castetter  
DEAN

June 20, 1961  
DATE

Committee

Walter Kahn  
J. D. Knight

CHAIRMAN

E. L. Martin

Raymond C. Cantel  
Donald Ward Dubois  
J. L. Reelzoner



This dissertation, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

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[Signature]  
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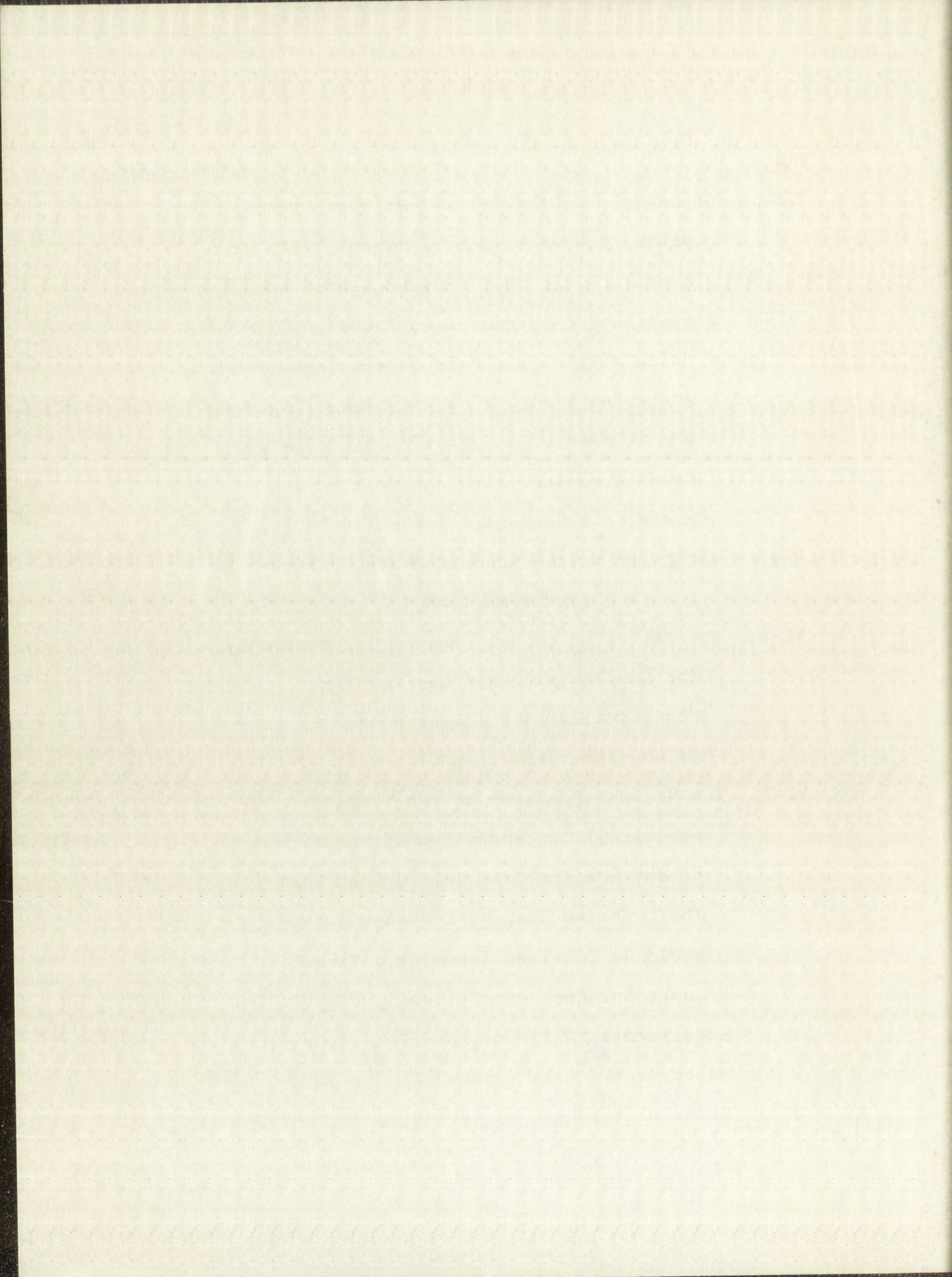


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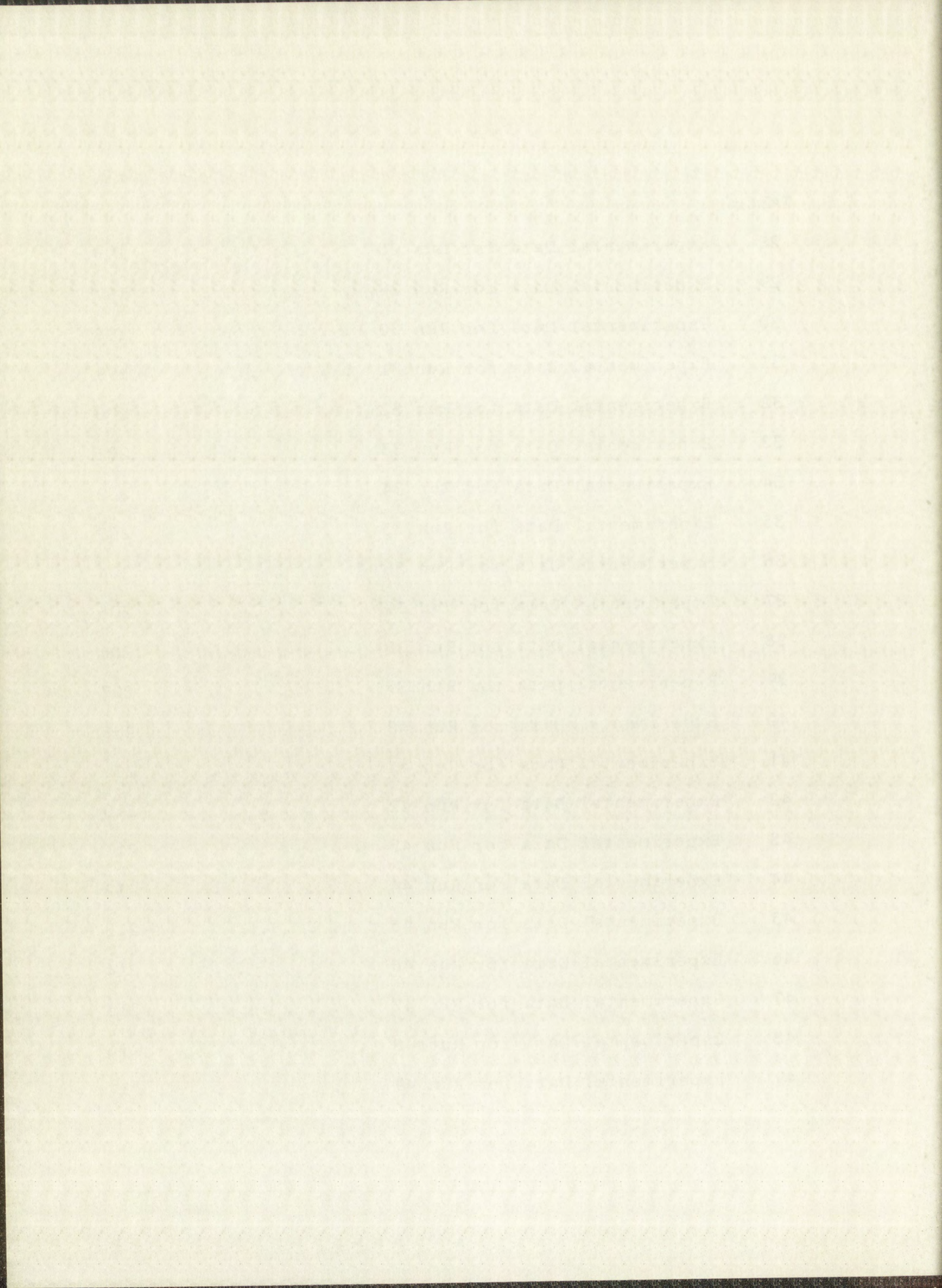


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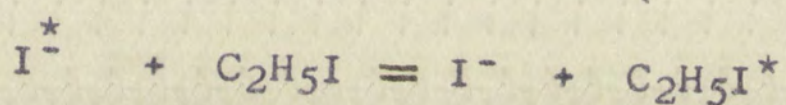




## I. INTRODUCTION

### A. Isotopic Exchange in a Homogeneous Stable System

An isotopic exchange reaction is a chemical reaction in which atoms of a given element interchange between two or more chemical forms of the element.<sup>1</sup> A homogeneous stable system<sup>1</sup> is one in which all reactants are in chemical equilibrium and distributed uniformly throughout a single phase. An example of isotopic exchange is the interchange of iodine atoms between iodide ions and ethyl iodide, where the asterisk indicates radioactive atoms of iodine.



Because the chemical properties of isotopes of an element are very similar, the enthalpy change of an isotopic exchange reaction is essentially zero. Hence the driving force of the reaction is to be attributed, in the main, to the entropy of mixing associated with the redistribution of isotopes among the reactants.

### B. Isotope Effect

Isotopic molecules\*\* differ slightly in chemical behavior because of difference in mass. Heavier molecules

---

\*\*Isotopic molecules are molecules differing in isotopic composition but identical in chemical composition and structure.







nearly always react more slowly than light ones. This difference is due in part to the lower velocity of the heavier molecule and in part to the additional energy needed to dissociate the heavier molecule. The maximum difference in reaction rates should be observed when the tracer atom is tightly bound in the reactant and free in the transition state. Bigeleisen<sup>2</sup> has estimated the magnitude of this maximum isotope effect for various tracers. Because conditions for a maximum effect are rarely met, the effect is usually less than a few per cent and may be neglected in most investigations except those involving the lightest elements.

C. Simple Isotopic Exchange in a Homogeneous Stable System

A simple isotopic exchange reaction is one in which chemically equivalent atoms in one molecular species interchange with chemically equivalent isotopic atoms in a second molecular species. The rate of appearance of radioactive atoms in the initially inactive reactant follows a simple exponential law. A form of this law was first derived by McKay.<sup>3</sup> Other workers have since given more general derivations showing that the exponential law is followed regardless of the mechanism of exchange, the number of equivalent exchangeable atoms, or the concentration of the radioactive atoms.<sup>1</sup> The law can be expressed by the equation







$$(I-1) \quad \log_e(1-F) = - \frac{[(A) + (B)]Rt}{(A)(B)}$$

where

$F$  = fraction exchange at time  $t$

$$= \frac{S_A - S_{A_0}}{S_{A_\infty} - S_{A_0}} = \frac{S_B - S_{B_0}}{S_{B_\infty} - S_{B_0}}$$

$S_A$  = specific activity (fraction of the atoms in the A form that are radioactive) of the A form at time  $t$

$S_{A_0}$  = specific activity of the A form at  $t=0$

$S_{A_\infty}$  = specific activity of the A form at  $t=\infty$

$S_B$  = specific activity of the B form at time  $t$

$S_{B_0}$  = specific activity of the B form at  $t=0$

$S_{B_\infty}$  = specific activity of the B form at  $t=\infty$

$(A)$  = total concentration of the A form in terms of gram-atoms of the exchanging element

$(B)$  = total concentration of the B form in terms of gram-atoms of the exchanging element

$R$  = constant rate of exchange

$t$  = elapsed time since start of the reaction

A convenient concept is that of the half-time of exchange,  $t_{\frac{1}{2}}$ , which is defined as that time required for  $1-F$  to decrease by a factor of one-half. This quantity may be obtained from a semi-logarithmic plot of  $1-F$  against time. The rate of exchange,  $R$ , for a given set of experimental conditions,







may then be obtained from the equation

$$(I-2) \quad R = \frac{(A)(B)0.693}{[(A) + (B)] t_{\frac{1}{2}}}$$

In simple isotopic exchange studies, the two chemical forms of an element, one of which has been tagged, are mixed and maintained at constant temperature. At various times a sample is removed, the two forms separated, and the specific activity of one of the forms determined. The fraction exchange,  $F$ , the half-time of exchange,  $t_{\frac{1}{2}}$ , and the rate of exchange,  $R$ , are evaluated from these data.

If a reproducible fraction of exchange is induced by the procedure used to separate the forms, or if some exchange has taken place prior to the start of the measurements, the plot of  $\log_{10}(1-F)$  vs. time will give a straight line with the same slope as indicated by equation (I-1) but not passing through the origin.<sup>1</sup> The half-time of exchange is determined only from the slope of the line and is independent of the intercept.

The rate of exchange is generally a function of the concentration of the reactants and a function of temperature. The rate law for the reaction at a given temperature is determined empirically by correlating rates of exchange with concentrations of reactants. Investigation at other temperatures allows the determination of activation energies of the individual paths of reaction. The experimentally determined rate law allows one to deduce one or more mechanisms consistent

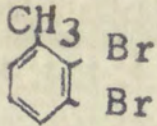






with the known chemistry of the reactants.

D. Complex Isotopic Exchange in a Homogeneous Stable System

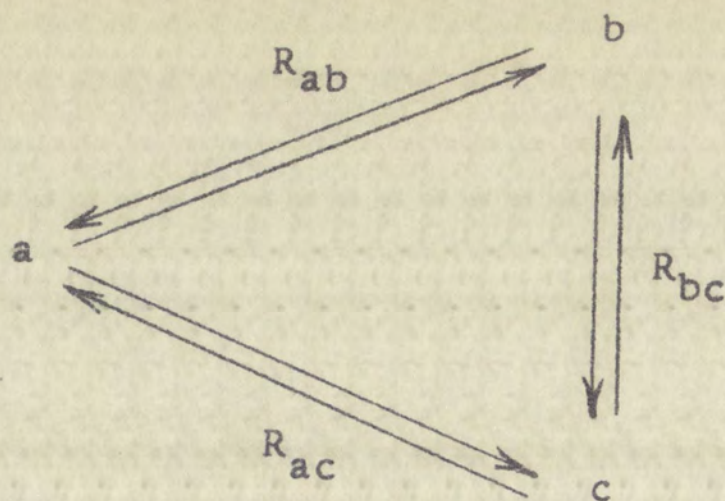
Isotopic exchange between three or more chemically nonequivalent forms of an element is called complex exchange. Examples of nonequivalence of atoms in a reactant are (a) 2,3-dibromotoluene, , and (b) antimony(V) species in hydrochloric acid solution<sup>4</sup> which, for instance, might be represented as  $\text{SbCl}_6^-$ ,  $\text{SbCl}_4(\text{OH})_2^-$ , etc. In the first example, the bromine atoms are not chemically equivalent because of nonequivalent bonding to the aromatic ring. In the second example, the antimony(V) atoms are not chemically equivalent because the interconversion of hydrolyzed forms is slow compared with the exchange between antimony(V) species and antimony(III).<sup>4</sup>

Complex isotopic exchange between three chemically non-equivalent forms follows a law which is the sum of two exponential terms. Limiting cases of this law are derived by Myers and Prestwood<sup>1</sup> and by Darbee, Jenkins, and Harris.<sup>5</sup> The following general derivation is given by Abell, Bonner, and Goishi.<sup>6</sup> The exchange reaction is represented by a reaction between three molecular species a, b, and c at three constant rates,  $R_{ab}$ ,  $R_{ac}$ , and  $R_{bc}$  (gram-atoms per liter per second):









The complex exchange law is expressed by the equations

$$(I-3) \quad 1 - F_a = Q_1 e^{-(q+p)t} + Q_2 e^{-(q-p)t}$$

where

$F_a$  = fraction exchange of the 'a' form at time  $t$

$$= \frac{S_a - S_a^0}{S_a^\infty - S_a^0}$$

$S_a$  = specific activity of the a form at time  $t$

$S_a^0$  = specific activity of the a form at  $t=0$

$S_a^\infty$  = specific activity of the a form at  $t=\infty$

$$(I-4) \quad Q_1 = \frac{1}{2pA} \left[ -A(q-p) + \frac{(R_{ab} + R_{ac})S_a^0 - R_{ab}S_b^0 - R_{ac}S_c^0}{S_a^0 - S_a^\infty} \right]$$

$$(I-5) \quad Q_2 = \frac{1}{2pA} \left[ A(q+p) - \frac{(R_{ab} + R_{ac})S_a^0 - R_{ab}S_b^0 - R_{ac}S_c^0}{S_a^0 - S_a^\infty} \right]$$

Note that  $Q_1 + Q_2 = 1$  provided  $F_a = 0$  at  $t=0$ .

$$(I-6) \quad 2q = \frac{(A+B)R_{ab}}{AB} + \frac{(A+C)R_{ac}}{AC} + \frac{(B+C)R_{bc}}{BC}$$

$$(I-7) \quad (q^2 - p^2) = \frac{(A+B+C)}{ABC} (R_{ab}R_{ac} + R_{ab}R_{bc} + R_{ac}R_{bc})$$







A = concentration of the a species

B = concentration of the b species

C = concentration of the c species

A semi-logarithmic plot of  $1-F_a$  vs. time is usually a curve composed of the sum of two straight lines. The value of  $1-F_a$  at the intersection of the straight line which has the greater slope with the  $t=0$  axis is  $Q_1$ . The value of  $1-F_a$  at the intersection of the other straight line with the  $t=0$  axis is  $Q_2$ . The slopes of the lines are  $-(q+p)$  and  $-(q-p)$ , respectively. The line which has the greater slope is referred to as the first component of exchange; the other line is referred to as the second component of exchange. For each component of exchange, a half-time,  $t_{\frac{1}{2}}$ , can be defined as the time required for  $1-F_a$  to decrease by a factor of one-half. The slopes of the two components of exchange are related to the half-times by the equations:

$$(I-8) \quad q + p = \frac{0.693}{(t_{\frac{1}{2}})_1}$$

$$(I-9) \quad q - p = \frac{0.693}{(t_{\frac{1}{2}})_2}$$

The subscripts refer to the first and second components of exchange.

The complex exchange curve is resolved into two straight lines as follows. A straight line is drawn tangent to the lower end of the curve and is extended back to zero time.







This line represents approximately\* the second component of exchange. The straight line is subtracted from the original curve point by point; that is, at a given time the value of  $\log_{10}(1-F)$  read from the straight line is subtracted from the value of  $\log_{10}(1-F_a)$  read from the curve and the difference is marked on the graph at that time. The locus of points obtained should be a straight line representing approximately the first component of exchange provided that the tangent is a reasonable representation of the longer-lived component and the experimental exchange curve is reliable.

The slopes  $-(q+p)$  and  $-(q-p)$  are calculated from half-times of exchange which may be read directly from a graph or calculated by the formula,

$$(I-10) \quad t_{\frac{1}{2}} = \frac{0.693t}{\log_e(1-F)_0 - \log_e(1-F)_t}$$

where the values of  $(1-F)$  read from a component of an exchange curve at time zero and at time  $t$  are denoted by  $(1-F)_0$  and  $(1-F)_t$ , respectively.

The values of the parameters  $q$ ,  $p$ , and  $Q_1$  along with the concentrations  $A$ ,  $B$ , and  $C$  are substituted into equations I-4, I-6, and I-7. The equations can then be solved simultaneously for  $R_{ab}$ ,  $R_{ac}$ , and  $R_{bc}$ .

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\*The line correctly representing the second component of exchange would be asymptotic to the complex curve.







A special case of complex exchange is that in which one species can be separated from the other two, which cannot be further separated. For example, if species a is arsenic(III) and species b and c are two nonequivalent forms of arsenic(V), it is easy to separate arsenic(III) from arsenic(V), but impractical to separate the b and c forms of arsenic(V) from each other. The expression for  $(1-F_a)$  remains essentially the same except that  $Q_1$  and  $Q_2$  are simplified by the fact that  $S_b^0 = S_c^0$  :

$$(I-11) \quad Q_1 = \frac{1}{2pA} \left[ -A(q-p) + \frac{(R_{ab} + R_{ac})(S_a^0 - S_b^0)}{S_a^0 - S_a^{\infty}} \right]$$

$$(I-12) \quad Q_2 = \frac{1}{2pA} \left[ A(q+p) - \frac{(R_{ab} + R_{ac})(S_a^0 - S_b^0)}{S_a^0 - S_a^{\infty}} \right]$$

In this case the fraction exchange for the a species is always equal to the fraction exchange for the b and c species together; and it is no longer necessary to identify the species being considered. Therefore, the complex isotopic exchange reaction is carried out in the same manner as a simple isotopic exchange reaction and  $\log_{10}(1-F_a)$  is plotted against time. The complex exchange curve is resolved into two straight lines and the parameters  $q$ ,  $p$ ,  $Q_1$ , and  $Q_2$  evaluated by the methods indicated previously. The parameters and concentrations of a and b+c are substituted in equations I-6, I-7, and I-9 or I-10. One obtains three equations containing four







unknowns,  $R_{ab}$ ,  $R_{ac}$ ,  $R_{bc}$ , and the concentration of one of the species b or c. Further information is necessary for explicit solution of the equations. The relative amounts of species b and c might be determined from solvent extraction data or spectrophotometric data as was done for antimony(V) by Bonner and Goishi.<sup>4</sup>

#### E. Isotopic Exchange Involving Arsenic Compounds

The following isotopic exchange reactions involving arsenic compounds have been reported in the literature. Investigations of the exchange of arsenic atoms between arsenic compounds are summarized in Table I-1. Other exchange investigations with arsenic compounds involve the exchange of halogen atoms between an arsenic halide and some other halide.

Muetteterties and Phillips<sup>7</sup> observed that compounds of the type  $MAsF_4$ , where M is potassium, rubidium, cesium, or thallium, dissociate to a large extent in the fused state and rapidly exchange fluorine atoms with  $AsF_3$  in molten  $AsF_3$ .

Clusius and Haimerl<sup>8</sup> studied the exchange of chlorine atoms between hydrogen chloride and arsenic trichloride; the reaction was found to be rapid. Their findings were confirmed by Lewis and Sowerby<sup>9</sup> many years later. Lewis and Sowerby<sup>10</sup> also found that exchange of chlorine atoms between arsenic trichloride and solvent nitrosyl chloride,  $NOCl$ , was complete in the length of time necessary to separate the two chemicals.







Table I-1

## Investigations Involving Isotopic Exchange of Arsenic Atoms

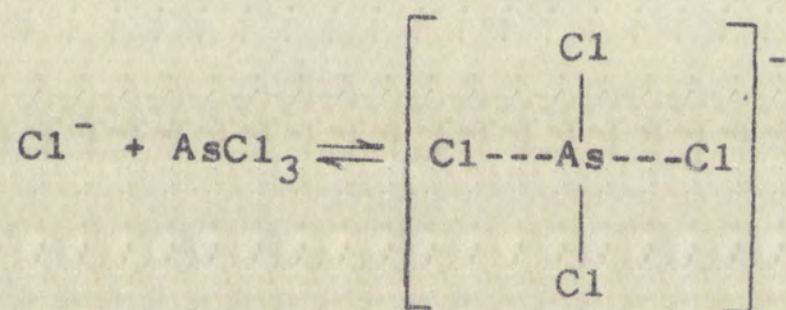
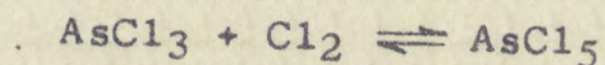
Reactants	Temp., °C.	Other Conditions	Extent of Exchange	Reference
$\text{Ag}_3\text{AsO}_3(\text{s})-\text{AsO}_3^{\equiv}$	Room temp.	---	9% in 2 hrs.	17
$\text{AsO}_3^{\equiv}-\text{AsO}_4^{\equiv}$	100°	0.1 f HCl	none in 3 hrs.	14
$\text{AsO}_3^{\equiv}-\text{AsO}_4^{\equiv}$	100°	1 f NaOH	none in 3 hrs.	14
$\text{AsO}_3^{\equiv}-\text{AsO}_4^{\equiv}$	---	---	nil	18
$\text{AsO}_3^{\equiv}-\text{AsO}_4^{\equiv}$	100°	aqueous	nil	15
$\text{AsO}_3^{\equiv}-\text{AsO}_4^{\equiv}$	100°	conc. HCl	complete in 90 min.	16
$\text{AsS}_4^{\equiv}-\text{AsO}_4^{\equiv}$	---	aqueous	nil in 20 min.	19
$\text{AsS}_3^{\equiv}-\text{AsO}_4^{\equiv}$	---	aqueous	nil in 20 min.	19
$\text{AsS}_4^{\equiv}-\text{As}_2\text{S}_5(\text{s})$	---	aqueous	5% in 114 hrs.	19
$\text{AsS}_4^{\equiv}-\text{As}_2\text{S}_3(\text{s})$	---	aqueous	10% in 112 hrs.	19
$(\text{NH}_4)_3\text{AsO}_4(\text{s})-$ $\text{As}_2\text{S}_5$ in $\text{NH}_3(1)$	---	---	50% in 40 min.	19
$(\text{NH}_4)_3\text{AsO}_4(\text{s})-$ $\text{As}_2\text{S}_3$ in $\text{NH}_3(1)$	---	---	50% in 40 min.	19
$\text{AsS}_4^{\equiv}-\text{Cd}_3(\text{AsS}_4)_2(\text{s})$	---	aqueous	complete in 2 min.	19
$\text{AsS}_3^{\equiv}-\text{Cd}_3(\text{AsS}_4)_2(\text{s})$	---	aqueous	complete in 2 min.	19
$\text{AsO}_3^{\equiv}-\text{Ag}_3\text{AsO}_3(\text{s})$	---	aqueous	9% in 2 hrs.	19
$\text{K}_3\text{As}(\text{S}_2\text{O}_3)_3(\text{aq.})-$ $\text{As}_2\text{O}_3(\text{aq.})$	3°	2 f HCl	50-72% in 10-12 min.	20
$\text{AsCl}_3(1)-\text{AsBr}_3$	132°	The $\text{AsCl}_3$ served as a solvent	complete within separation time	21







They stated that the exchange could take place through the formation of either  $\text{AsCl}_2^+$  or  $\text{AsCl}_4^-$ . The intermediate  $\text{HAsCl}_4$  was suggested by Owen and Johnson's<sup>11</sup> work on the exchange between chlorine and arsenic trichloride in carbon tetrachloride solution at room temperature. They discovered that the exchange was measurable but markedly catalyzed by hydrogen chloride which vitiated a thorough study of the mechanism. They were, however, able to determine that the reaction was not first order in  $\text{AsCl}_3$  or  $\text{Cl}_2$  and concluded that the mechanism cannot involve either of the reactions:



In the course of their investigation they also found that the exchange between hydrogen chloride and arsenic trichloride in carbon tetrachloride solution at room temperature is very rapid; exchange is complete in less than six minutes.

Fairbrother<sup>12</sup> studied exchange of bromine atoms between arsenic tribromide and ethyl bromide at  $15^\circ\text{C}$ . He reported no exchange in ten minutes.

Fialkov and Nazarenko<sup>13</sup> studied exchange of iodine atoms between arsenic triiodide and both iodine and potassium iodide. With molten iodine in a sealed tube at  $150^\circ\text{C}$ , and

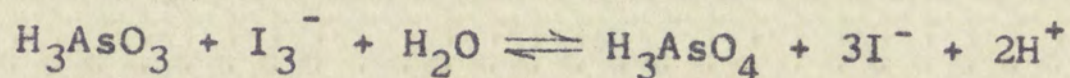






with iodine vapor, exchange was complete in one to two hours. With potassium iodide at the boiling point of arsenic triiodide, exchange was insignificant in ten minutes.

The exchange of arsenic atoms between arsenic compounds was first studied in 1937 by Wilson and Dickinson.<sup>14</sup> Their determination of the reaction rates at equilibrium for the system



required a knowledge of any direct exchange between arsenate and arsenite. They discovered there was no significant exchange between arsenate and arsenite in aqueous alkali solution (ca. 1 formal NaOH) or in dilute acid solution (ca. 0.1 formal hydrochloric acid) at temperatures up to 100°C. In 1950, Muller and Broda<sup>15</sup> verified that no exchange occurred between arsenate and arsenite in aqueous solution at 100°C. But in 1955, Malý and Šimánová<sup>16</sup> discovered that in boiling concentrated hydrochloric acid a rapid exchange reaction between arsenic(III) and arsenic(V) takes place. The reaction itself was not studied further.

The investigations of the exchange of arsenic atoms which are reported in the literature are summarized in Table I-1, p. 11.







F. Scope of the Investigation

The kinetics of isotopic exchange of arsenic atoms between arsenic(III) and arsenic(V) species in aqueous hydrochloric acid, particularly 10.9 f hydrochloric acid, has been investigated at 29.6°C, 48.6°C, and 67.3°C. The rate of exchange was found to depend on the age of the arsenic(V) solutions.

A spectrophotometric investigation was initiated in order to provide additional evidence for the existence of chemically nonequivalent species of arsenic(V) in 10.9 f hydrochloric acid solution.







## II. REAGENTS AND SOLUTIONS

### A. Stock Solutions

#### 1. Hydrochloric Acid

Hydrochloric acid solutions were made by dilution of Mallinckrodt Analytical grade 37% hydrochloric acid or Baker and Adamson C.P. 37% hydrochloric acid with doubly-distilled water.\* The maximum amounts of chlorine and arsenic impurities were 0.0001% and 0.000001%, respectively.

#### 2. Arsenic(III)

Arsenic(III) solutions were prepared by dissolving Fisher Scientific Company C.P. arsenious acid anhydride in hydrochloric acid. Whenever an exact amount of arsenic trioxide was desired, it was dried several hours at 110°C and cooled in a dessicator before weighing.

The preparation of arsenic(III) "tracer" solutions is described in Section III.D.

#### 3. Arsenic(V)

Fisher Scientific Company C.P. arsenic acid

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\*All solutions used in this investigation were prepared from doubly-distilled water. Tap water was first distilled from a metal still and tested for chloride with silver nitrate. If no turbidity appeared in a few minutes, the distilled water was redistilled from an alkaline permanganate solution in an all glass apparatus.







anhydride which is 99.6% pure and contains 0.1% arsenic trioxide impurity was used without further purification. Arsenic pentoxide was difficultly soluble in fairly concentrated hydrochloric acid. A small fraction of the oxide usually remained undissolved in 7 f to 11 f hydrochloric acid even after weeks of shaking the solutions frequently. This residue was removed from the solutions by filtration through a medium-pore fritted-glass disc.

For spectrophotometric studies, an attempt was made to remove the arsenic trioxide impurity by oxidation with nitric acid. Several grams of arsenic pentoxide was dissolved in 10 ml. of concentrated nitric acid and the solution gently boiled down to a few milliliters, whereupon the oxide precipitated. The residue was taken up with doubly-distilled water, gently boiled down to a few milliliters, and the process repeated. The final residue was dried several hours at 110°C. It is believed the product obtained is similar to the material reported as  $H_5As_3O_{10}$  or  $3As_2O_5 \cdot 5H_2O$  by Menzies and Potter in 1912 and described elsewhere by Partington.<sup>22</sup>

This "purified" arsenic pentoxide dissolved readily in concentrated hydrochloric acid. For instance, 0.1 g. of "purified" arsenic pentoxide completely dissolved in 100 ml. of concentrated hydrochloric acid in thirty minutes provided the solution was shaken frequently. Several solutions were prepared with the "purified" arsenic pentoxide. Whenever







these solutions are mentioned, it will be noted that "purified" arsenic pentoxide was used in the preparation.

The preparation of arsenic(V) "tracer" solutions is described in Section III.E.

## B. Gases

Nitrogen was washed with distilled water to remove foreign particles. Anhydrous gases hydrogen chloride, chlorine, hydrogen sulfide, and sulfur dioxide were obtained from Matheson Company and were used without further purification.

## C. Analytical Reagents

### 1. Magnesia Mixture

Magnesia mixture for the precipitation of magnesium ammonium arsenate was prepared as described by Hillebrand and Lundell.<sup>23</sup> About 50 g. of Baker and Adamson reagent grade magnesium chloride hexahydrate and about 100 g. of Baker's Analysed reagent grade ammonium chloride was dissolved in 500 ml. of water. The solution was made slightly alkaline with ammonium hydroxide, allowed to stand overnight, and filtered. The filtrate was made slightly acid with hydrochloric acid and diluted to one liter with water.

### 2. Standard Solutions

All standard solutions were prepared according to methods given by Kolthoff and Sandell.<sup>24</sup> Silver nitrate and potassium thiocyanate, dried according to methods given



These results are summarized in Table I. The results show that the reaction of the ester with the base is a reversible process. The equilibrium constant for the reaction is 1.0. The reaction is first order in the ester and first order in the base. The rate of reaction is independent of the concentration of the catalyst.

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by Kolthoff and Sandell,<sup>24</sup> were used as primary standards without further purification. Both solutions were stored in dark brown bottles. Potassium bromate and potassium dichromate were used as primary standards after recrystallization from water. Sodium thiosulfate solutions were standardized against potassium dichromate.

### 3. Indicators

The indicators consisted of a 0.1% aqueous methyl orange solution for bromate titrations, a saturated solution of ferric ammonium sulfate for Volhard determinations, and a 0.2% starch solution containing 0.001% mercuric iodide for use in iodometric titrations.







### III. RADIOACTIVITY

#### A. High Specific Activity Arsenic

The radioactive isotope of arsenic which was used in this investigation was 17.5-day  $\text{As}^{74}$ . It was obtained in the form of a solution of high specific activity sodium arsenate from Abbott Laboratories at Oak Ridge, Tennessee. Other isotopes of arsenic present in lesser amounts were 2.5-day  $\text{As}^{71}$ , 26-hour  $\text{As}^{72}$ , and 76-day  $\text{As}^{73}$ . Relative amounts of the isotopes were reported by Abbott Laboratories. A typical assay listed:

$\text{As}^{71}$	-----0.139	mc./cc.
$\text{As}^{72}$	-----0.778	mc./cc.
$\text{As}^{73}$	-----0.229	mc./cc.
$\text{As}^{74}$	-----3.079	mc./cc.

The decay schemes for  $\text{As}^{74}$ ,  $\text{As}^{73}$ ,  $\text{As}^{72}$ , and  $\text{As}^{71}$  and its daughter,  $\text{Ge}^{71}$ , are shown in Figures III-1, III-2, III-3, and III-4.

#### B. Measurement of Radioactivity

All activities were determined by gamma counting of liquid samples contained in selected pyrex test tubes filled to a standard height and placed in a reproducible geometry with respect to a scintillation detector. All solutions counted to furnish exchange data were of the same density. Arsenic(III) solutions which were counted to determine an







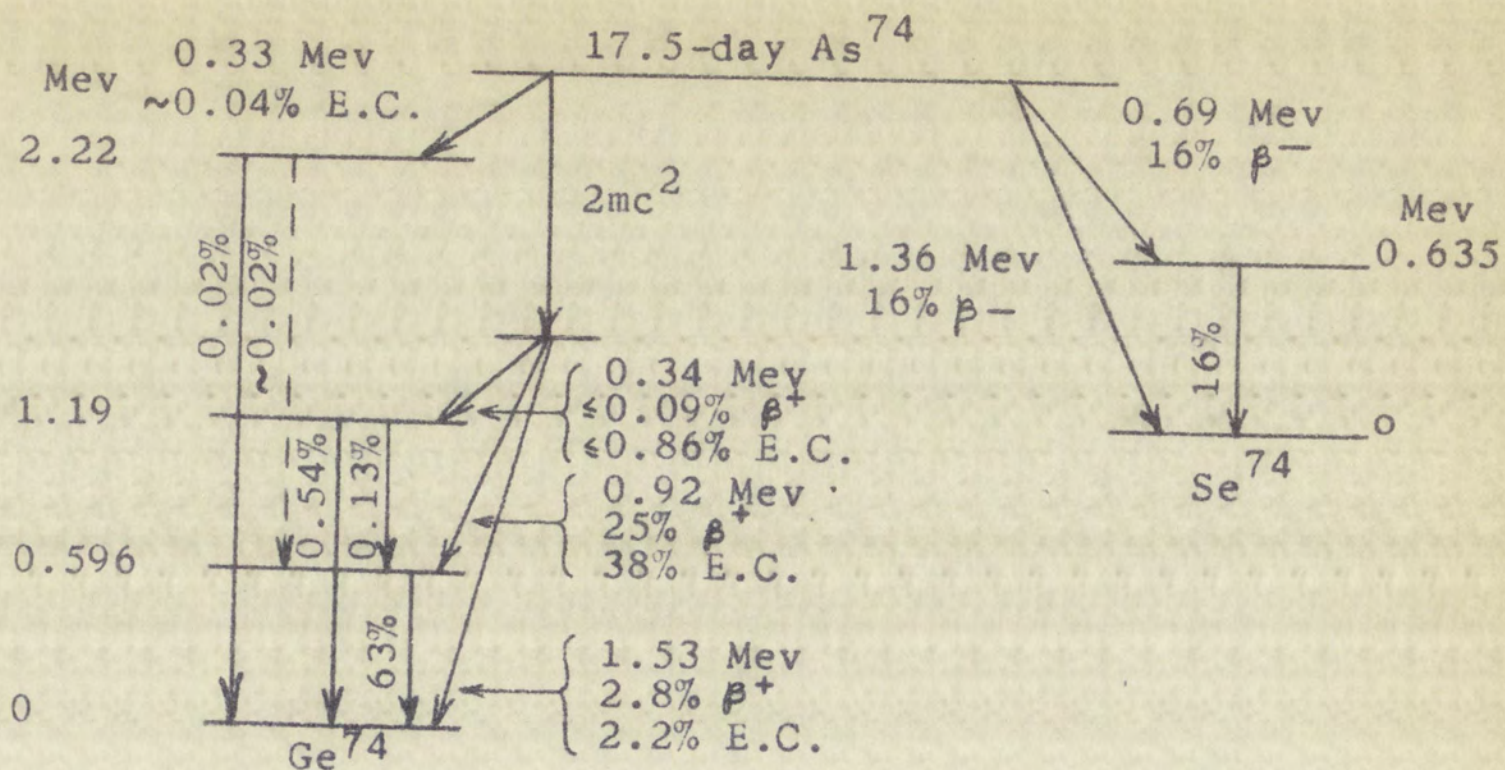


Figure III-1  
Decay Scheme<sup>25</sup> for  $^{74}\text{As}$

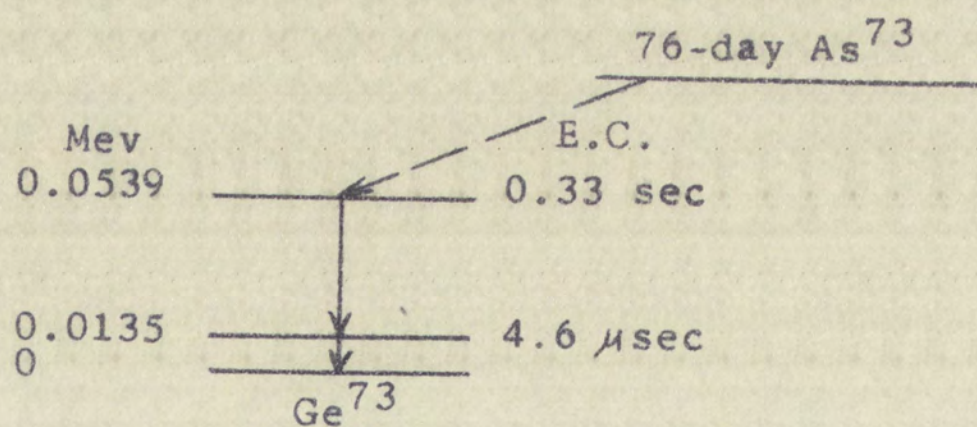
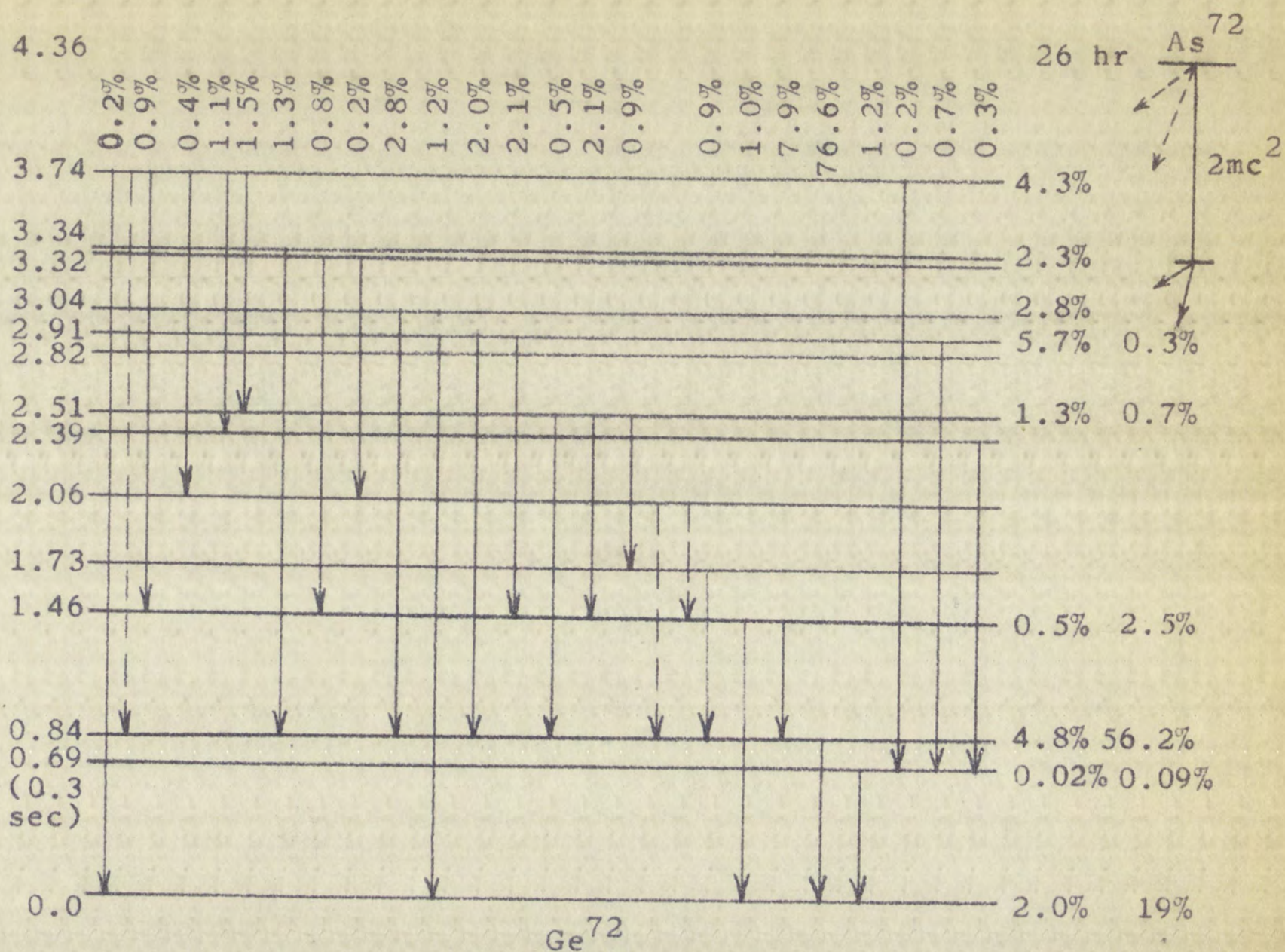


Figure III-2  
Decay Scheme<sup>26, 27</sup> for  $^{73}\text{As}$









Energy scale  
in Mev.

Percentages across the top of the diagram  
are the intensities of the  $\gamma$ -radiation.  
Errors in these intensities range  
from  $\pm 0.1\%$  to  $\pm 0.9\%$ .

E. C. Intensity

$\beta^+$  Intensity

Figure III-3

Decay Scheme<sup>28</sup> for  $As^{72}$







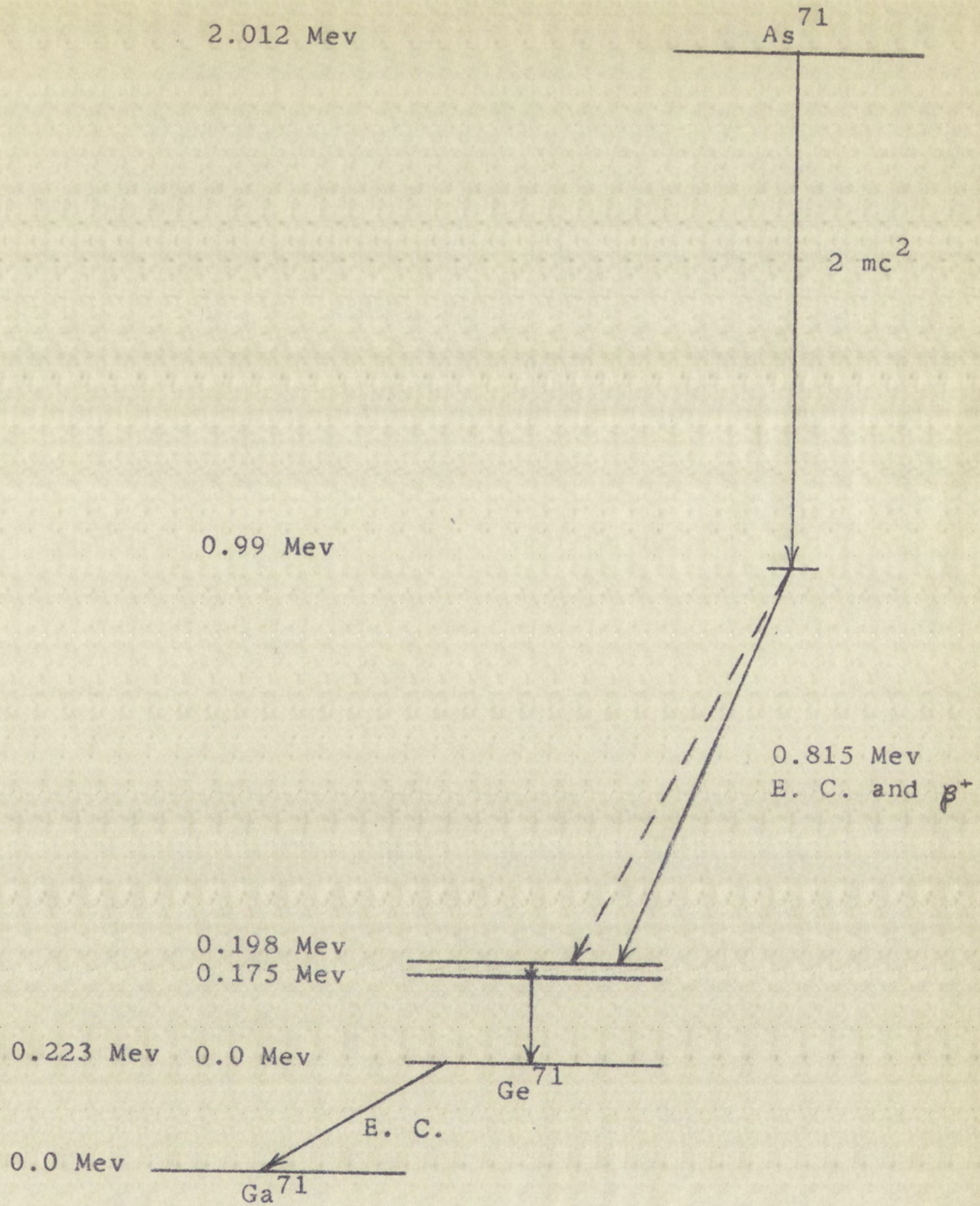


Figure III-4  
Decay Scheme<sup>29, 30</sup> for  $\text{As}^{71}$  and  $\text{Ge}^{71}$







activity balance were about 10% less dense than other solutions which were counted.

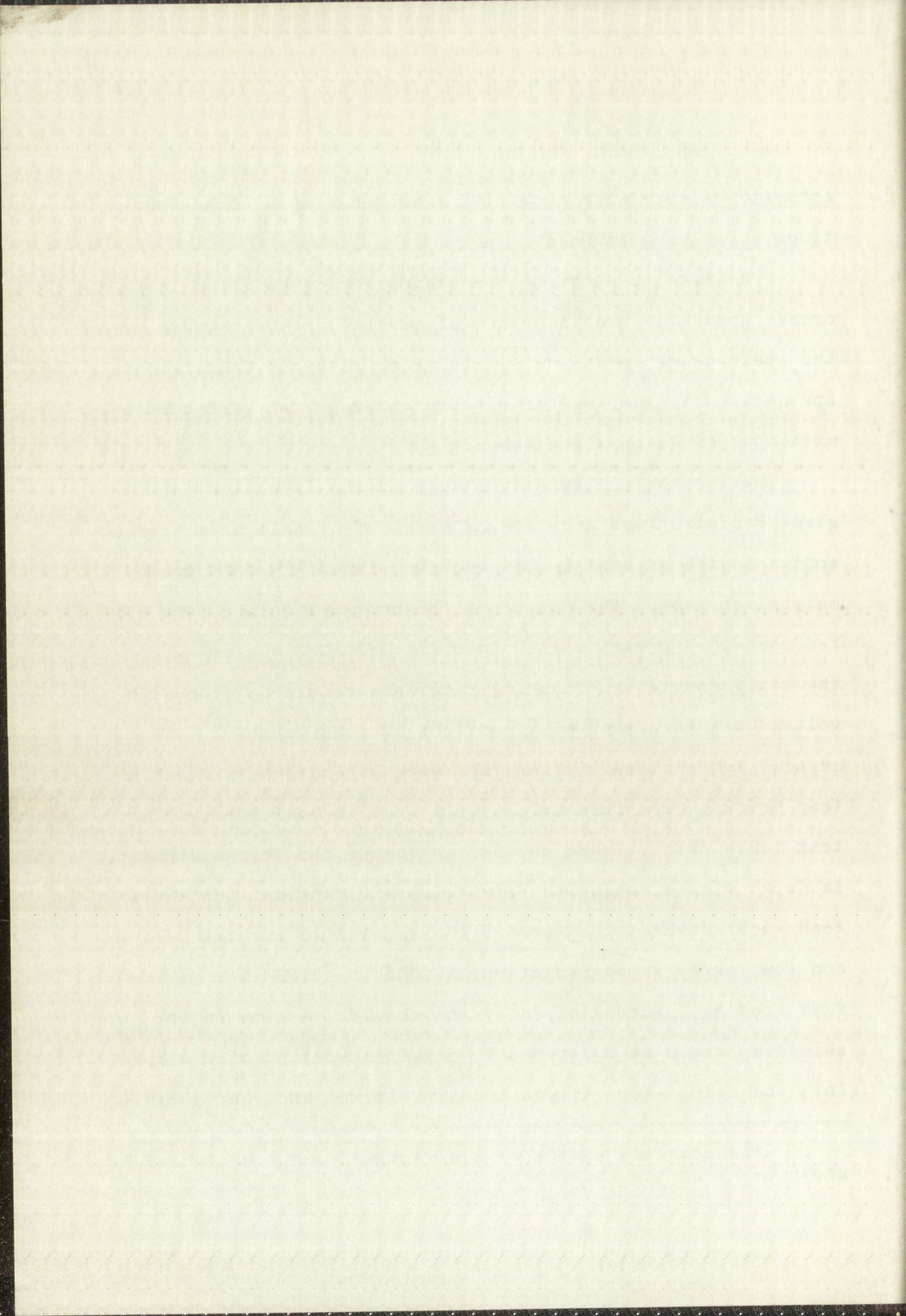
The rate of decay of the radioarsenic was found to decrease gradually over a period of several months because of the presence of 76-day  $\text{As}^{73}$ . In order to avoid corrections for decay, all samples for a given exchange run were counted within a period of a few hours.

During the preliminary stages of the investigation, gamma radiation was detected by means of a thallium-activated sodium iodide crystal in conjunction with a RCA 5819 photomultiplier tube. The output of the photomultiplier tube was fed through a preamplifier\* into a model SC-3 scaler\* where the total counts and counting time were recorded. The high voltage was furnished by a Model PS-12 power supply.\* The crystal and photomultiplier tube were shielded by a stack of lead bricks. Two fuse clips, of a size to hold 18mm.x150mm. test tubes firmly, were mounted on one of the bricks directly in front of and facing the crystal. A 0.0447 mm. thickness lead sheet covered the face of the crystal to cut out X-rays and low energy gamma radiation; 97% of the 0.054 Mev gamma rays from  $\text{As}^{73}$  were stopped by the shield. A slot in the shielding could be uncovered to permit insertion of a sample into the clips where it was held in a fixed and reproducible

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\*The counting equipment was designed and constructed by group CMR-7 of the Los Alamos Scientific Laboratory.







geometry.

Radioactivity used in all exchange experiments except runs 1-4 was counted with a Nuclear Chicago Model 132 single-channel analyzer in conjunction with a well-type scintillation detector (Nuclear Chicago Model DS5-5). The lower discriminator voltage was set at 12.5 volts in order to cut out X-rays and low energy gamma radiation.

The counting tubes used with the well-type counter were selected 15mm. x 125mm. pyrex test tubes. The inner diameter of the tubes was not less than 12.8mm. and the outer diameter of the tubes did not exceed 15.0mm. This method of selection was tested by counting the same amount of activity in each of twenty of the selected tubes chosen at random.

#### C. Purification of High Specific Activity Arsenic

Purification of high specific activity arsenic was based on several properties of arsenic. In hydrochloric acid solution, arsenic(V) is not volatile whereas arsenic(III) is volatile. Therefore, volatile impurities such as germanium tetrachloride and tin tetrachloride are removed from arsenic by distillation from hydrochloric acid solution in the presence of chlorine. The arsenic(V) is subsequently reduced by fuming hydrochloric acid (generally in the presence of ferrous chloride) and the arsenic(III) is distilled away from all remaining impurities.







Each shipment of radioactive arsenic was purified by distillation according to the procedure described below.

Figure III-5a shows a sketch of the distillation apparatus.

The high specific activity arsenic solution from Abbott Laboratories was added to about 20 ml. concentrated hydrochloric acid and chlorine was bubbled through the solution for a few minutes in order to make certain that all of the arsenic was pentavalent. The solution was then distilled in a stream of chlorine to one-fourth its original volume over fifteen to thirty minutes. Less than 1% of the radioactivity distilled over.

The residue was cooled to 0°C in an ice bath and maintained at that temperature until it was distilled again. Chlorine was removed from the solution either by bubbling nitrogen rapidly through the cold solution several minutes or by adding 1 g. of powdered  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}^*$ . This solution was saturated with hydrogen chloride by passing a stream of the gas into the cold solution for thirty minutes. A new condenser and a set of receivers (shown in Figure III-5b) were connected to the distilling flask. The first receiver contained 5 ml. of concentrated hydrochloric acid maintained at

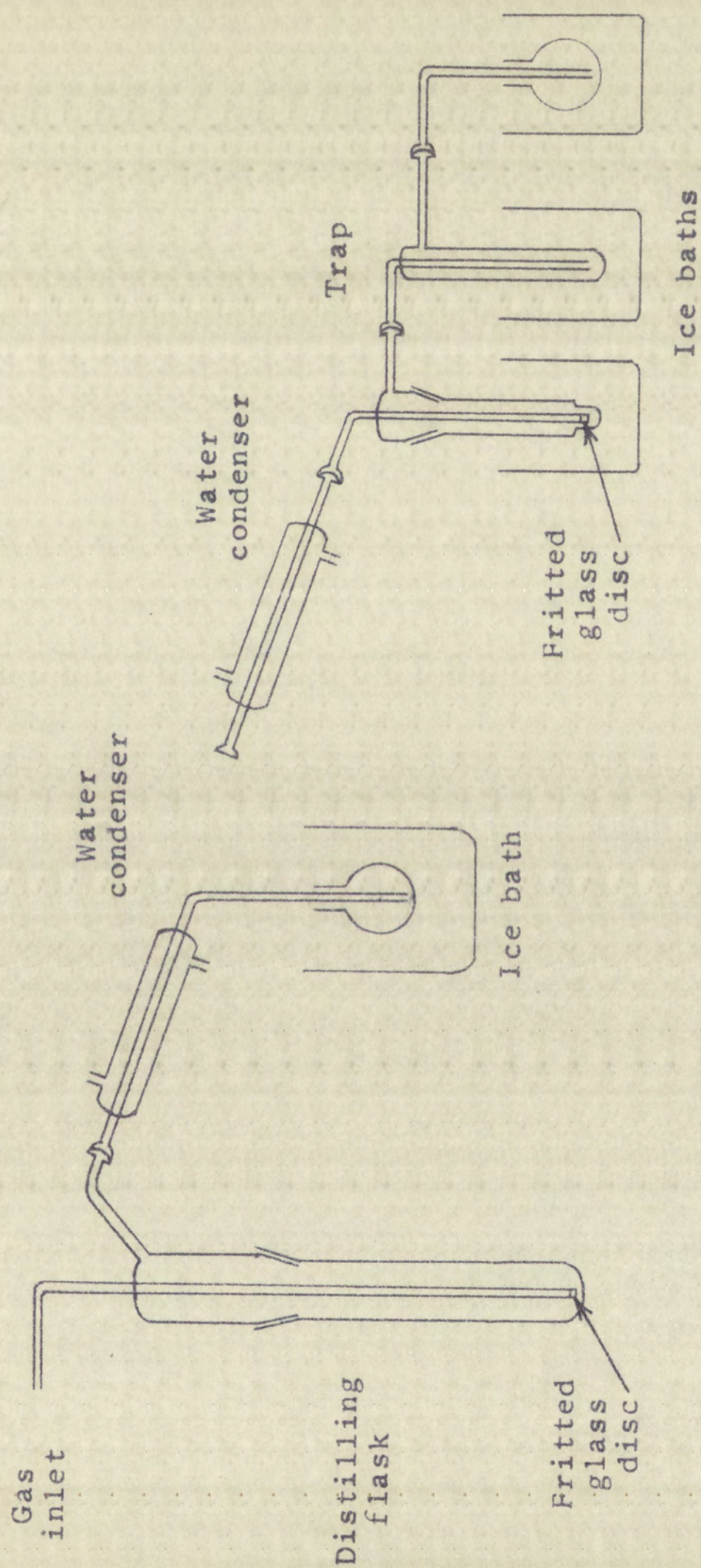
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\*It was found that reduction of the extremely small quantity of arsenic(V) present in the high specific activity arsenic solutions was accomplished efficiently by fuming hydrochloric acid without ferrous chloride.









a

Figure III-5

Distillation Apparatus

b





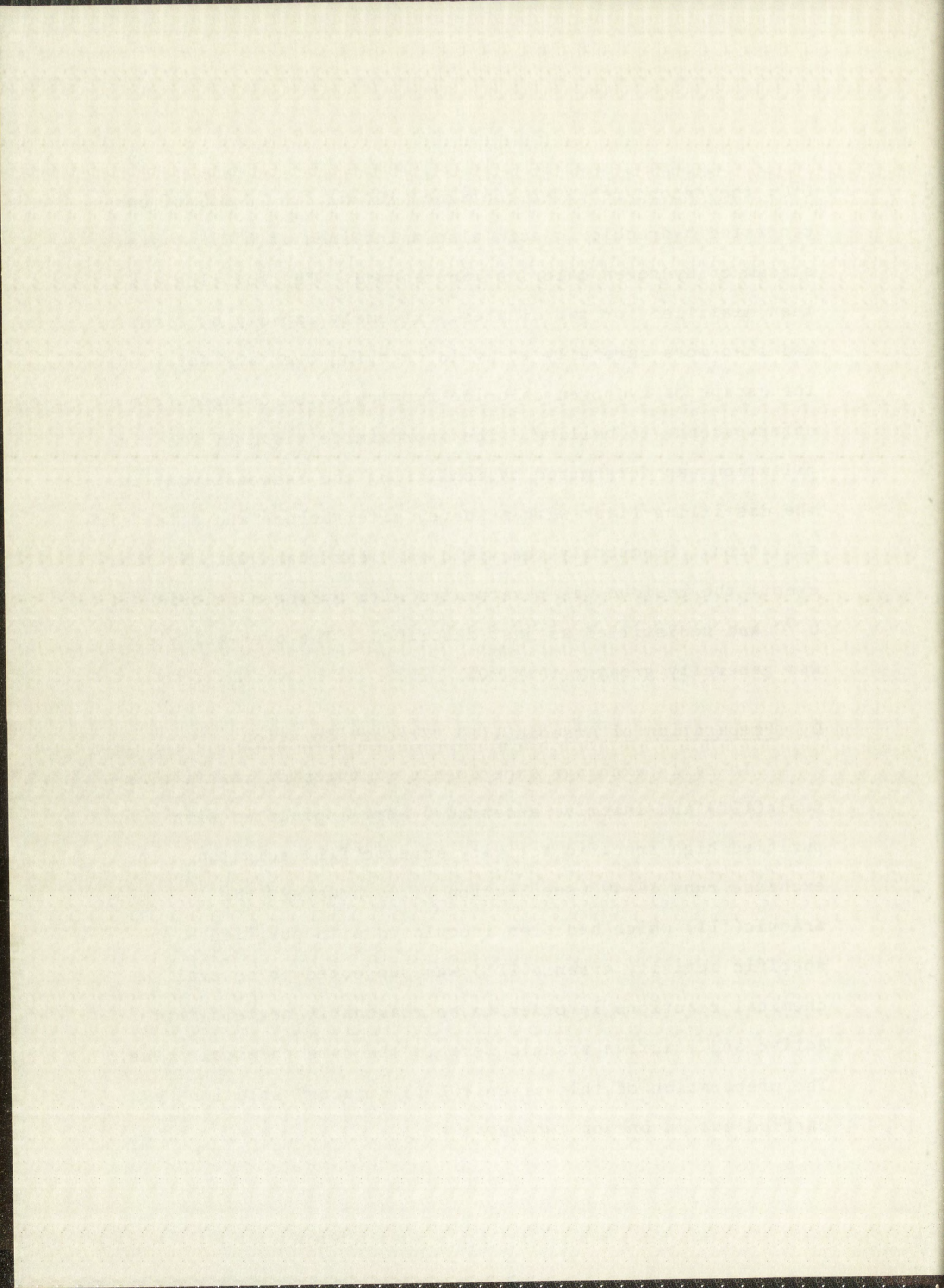


0°C; the second receiver contained 10. ml. to 20 ml. of concentrated hydrochloric acid also maintained at 0°C. A slow stream of hydrogen chloride was resumed. The solution was then distilled for two minutes, extremely rapidly at first and then more carefully to avoid carrying over any spray when the escape of hydrogen chloride from solution changed from effervescence to boiling. The approximate yield of the distillation was determined by monitoring the radioactivity in the distilling flask with a survey meter before and after distillation. Frequently the yield was less than 90%. In that event, the residue was resaturated with hydrogen chloride at 0°C and redistilled as just described. The over-all yield was generally greater than 90%.

#### D. Preparation of Arsenic(III) "Tracer" Solution

In early exchange experiments mixtures of inactive arsenic(III) and inactive arsenic(V) were inoculated with purified high specific activity arsenic(III) solution. In exchange runs 19-49 (see Section VI.), however, the arsenic(III) which had been inoculated with purified high specific activity arsenic(III) was subjected to several chemical reactions in order to be reasonably certain that active and inactive arsenic were in the same chemical forms. The preparation of this arsenic(III) "tracer" solution was carried out in one of two ways:







(1) Arsenic trioxide was dissolved in about 5 ml. of concentrated hydrochloric acid and inoculated with purified high specific activity arsenic(III). The solution was oxidized with chlorine in the following manner:

Chlorine gas was led into the solution. In about five minutes, the solution was yellow with excess chlorine. After standing five or ten minutes, the solution was heated gently until most of the free chlorine was removed; then the solution was cooled and more chlorine gas dissolved in it. The process of heating the solution, cooling it, and dissolving more chlorine in it was repeated.

Finally the solution was distilled for about five minutes while chlorine bubbled through it. The distillation apparatus is shown in Figure III-5a, p. 26. The arsenic was then reduced with fuming hydrochloric acid in the presence of ferrous chloride and distilled according to the procedure used for the purification of radioactive arsenic described in Section III.C.

(2) Five or ten milliliters of 0.1 f arsenic(III) in 10.9 f hydrochloric acid was inoculated with purified high specific activity arsenic(III) and the solution made about 8 f in hydrochloric acid. Dissolved oxygen was removed from the solution with a stream of nitrogen and 2 to 5 ml. of "Oxsorbent"\*

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\*"Oxsorbent" is the commercial name for a solution of chromous chloride sold by Burrell Corporation.







was added as nitrogen stirred the solution. Then, the solution, contained in a loosely stoppered tube, was heated ten minutes in a boiling water-bath. The suspension was immediately filtered through a glass filter pad and the metal was washed with 4 f hydrochloric acid and dried with acetone. The precipitate and supporting filter pad was added to 5 ml. of concentrated hydrochloric acid in a distilling flask. The solution was stirred rapidly with a stream of chlorine; the arsenic metal usually dissolved completely within ten minutes forming arsenic(III), which in turn was at least partially oxidized to arsenic(V). The arsenic(V) was then reduced with fuming hydrochloric acid in the presence of ferrous chloride and distilled according to the procedure used for the purification of radioactive arsenic described in Section III.C.

The distillate of arsenic(III) from either preparation (1) or (2) lost hydrogen chloride for sixty to ninety minutes while it warmed up to room temperature, yielding a solution about 13.5 f in hydrochloric acid. This solution was adjusted to a desired acidity and finally stored at the temperature at which the exchange reaction was to be studied. This final solution will be referred to as the arsenic(III) "tracer."

#### E. Preparation of Arsenic(V) "Tracer" Solution

Arsenic(V) "tracer" was prepared by exchange between inactive arsenic(V) and purified high specific activity arsenic(III) in 10.9 f hydrochloric acid at 95°C in a sealed







tube. It was found that exchange was essentially complete in three to four hours. The concentration ratio of arsenic(V) to arsenic(III) was approximately equal to 100.

F. Proof of Radiochemical Purity of the Arsenic Activity

The radiochemical purity of each shipment of radioactive arsenic was checked by two methods: the determination of the half-life and the constancy of the specific activity throughout oxidation, reduction, and distillation.

The half-life of purified high specific activity arsenic(III) sealed in a counting tube was determined over a period of five to seven half-lives of the  $\text{As}^{74}$ . The day-by-day variation in the operational characteristics of the counter was checked and corrected for by counting a  $\text{Co}^{60}$  standard or a  $\text{Cs}^{137}$  standard.

The half-life of activity used in exchange runs 1-4 was measured by the counting equipment designed by Los Alamos Laboratory. Figure III-6 shows a semi-logarithmic plot of activity versus time for arsenic activity two days after it was assayed by Abbott Laboratories. The initial portion of the curve was resolved into two components with 26-hour and 17.5-day half-lives corresponding to 26-hour  $\text{As}^{72}$  and 17.5-day  $\text{As}^{74}$ . The contribution of  $\text{As}^{72}$  was not observable after six days of counting. The half-life of arsenic activity from the one other shipment of activity which was measured by this particular counting equipment was found to be 17.4-days.







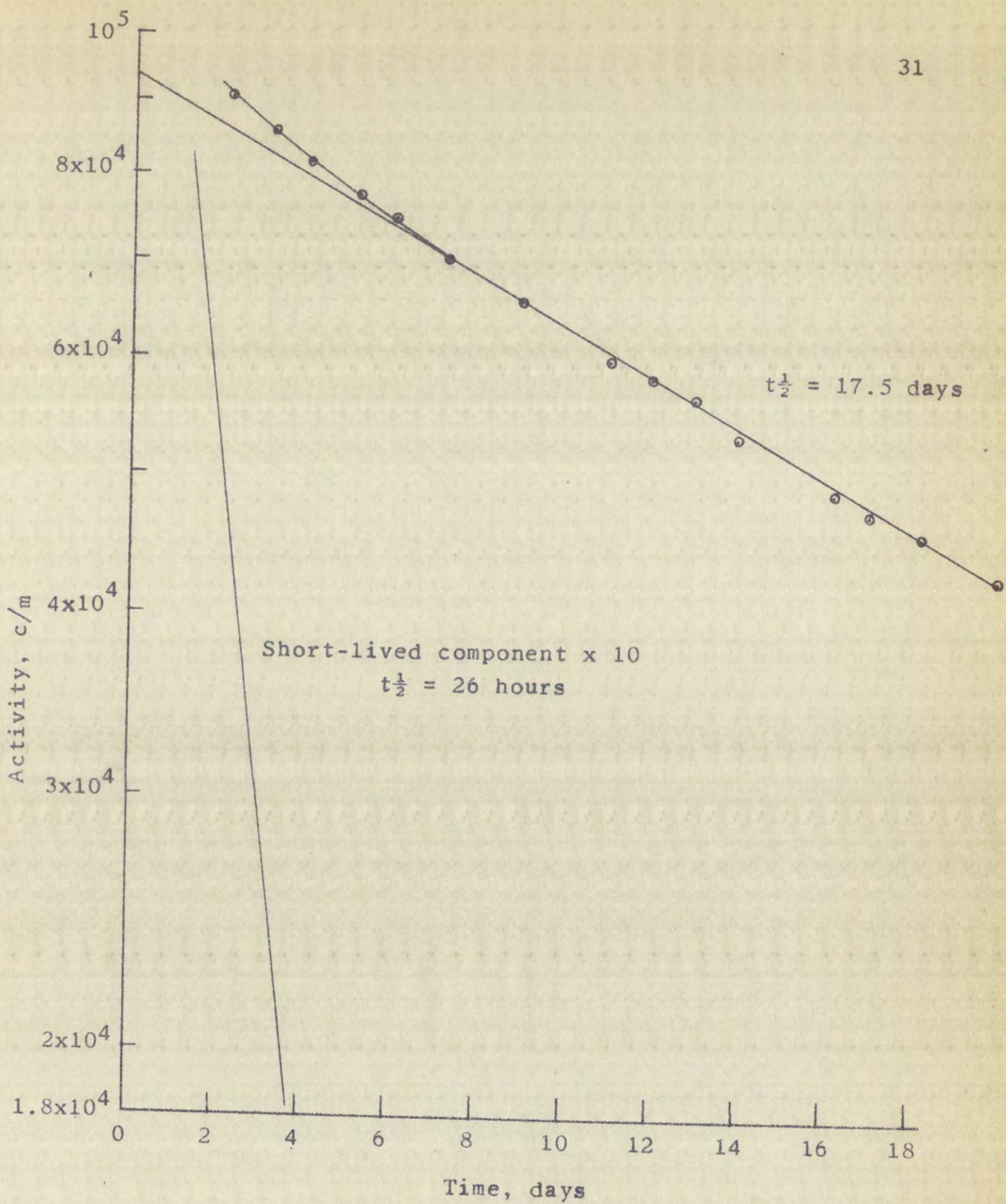


Figure III-6  
Experimental Decay Rate of Arsenic Activity







The half-life of activity used in exchange runs 5-49 was measured by the well-type scintillation counter. Figure III-7 shows a typical decay curve. For this particular half-life determination, counting was started seven days after assay by Abbott Laboratories. The curve was resolved into two components with 17.5-day and about 71-day half-lives corresponding to 17.5-day  $\text{As}^{74}$  and 76-day  $\text{As}^{73}$ .

The second method of testing the radiochemical purity of the radioactive arsenic was based on the premise that any activity which was not isotopic with stable arsenic would not entirely follow inactive arsenic through several chemical reactions. The radiochemical purity of the purified high specific activity prepared from each shipment of activity received from Abbott Laboratories was tested once by the following procedure. Prior to the preparation of arsenic(III) "tracer," several aliquots of the solution of inactive arsenic(III) inoculated with purified high specific activity arsenic(III) were counted and analyzed for arsenic(III) content. The arsenic(III) "tracer" was then prepared by procedure (2) in one instance and by procedure (1) in all other instances (see Section III.D). The specific activity of the arsenic(III) "tracer" was found to be within two per cent of the specific activity of the solution prior to the oxidation, reduction, and distillation.







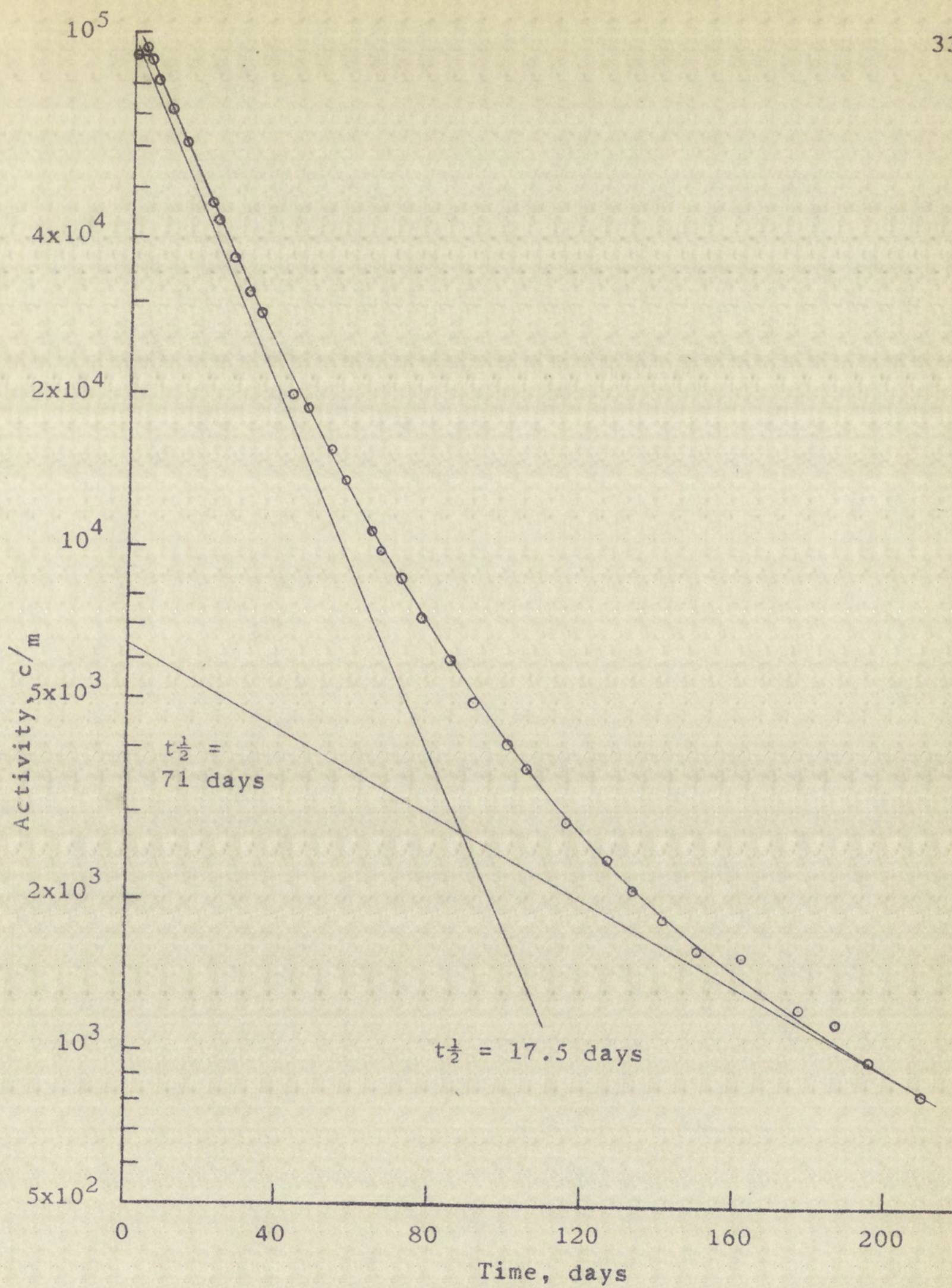


Figure III-7

Typical Experimental Decay Rate of Arsenic Activity







G. Proof of the Trivalence of Purified Radioactive  
Arsenic(III) and Arsenic(III) "Tracer"

Purified high specific activity arsenic(III) solution was stirred into a mixture of a known amount of inactive arsenic(III) and arsenic(V) at room temperature. Arsenic(V) was immediately separated from the mixture by precipitation of magnesium ammonium arsenate (see Sections VI.A.8. and VI.A.9.). The precipitate was dissolved in dilute hydrochloric acid, additional arsenic(III) was added, and the arsenic(V) was reprecipitated. This precipitate was dissolved, counted, and analyzed for arsenic(V). Less than 1% of the original activity followed the arsenic(V) (possibly due to adsorption). Thus, over 99% of the radioactive arsenic(III) was trivalent.

Arsenic(III) "tracer" solution was mixed with a known amount of inactive arsenic(V) and the arsenic(V) was immediately separated by the procedure just described. Less than 1% of the activity followed the arsenic(V); thus, over 99% of the "tracer" was trivalent.







#### IV. ANALYTICAL PROCEDURES

##### A. Analysis for Arsenic(III)

Arsenic(III) was determined by titration with potassium bromate solution according to the procedure given by Kolthoff and Sandell.<sup>24</sup> A 1 ml. - 10 ml. aliquot of arsenic(III) solution was diluted to about 50 ml. with enough water and hydrochloric acid to make the solution approximately 2.4 f in hydrochloric acid. Three drops of methyl orange indicator were added just before titration at room temperature with 0.0025 f potassium bromate solution. Since the reaction between arsenic(III) and potassium bromate is slow at room temperature, the titration was carried out dropwise using a 10 ml. or 25 ml. burette. The titration volume was usually between 3 ml. and 20 ml. There was a small and consistent correction of 0.06 ml. for the indicator blank.

##### B. Analysis for Arsenic(V)

Arsenic(V) was determined iodometrically according to a procedure given by Evdokimov.<sup>31</sup> An aliquot of arsenic(V) solution in an iodine flask was made 4 f in hydrochloric acid. One gram of potassium iodide was dissolved in the solution, the flask was stoppered, and the solution was allowed to stand six minutes. The solution was then diluted to 2 f hydrochloric acid with distilled water and the iodine titrated







immediately with standard sodium thiosulfate solution. Just before the end-point, about 1 ml. of starch solution was added and the titration continued.

### C. Analysis for Chloride

Chloride was determined by one of the modified Volhard methods described in Kolthoff and Sandell.<sup>24</sup> A 1 ml. aliquot was added to 25 ml. distilled water acidified with 5 ml. of 6 f nitric acid. A known volume of standard silver nitrate solution was added to the solution to precipitate silver chloride and leave an excess of silver nitrate. Then 3 ml. of pure nitrobenzene and 1 ml. saturated ferric alum indicator were added and the mixture shaken vigorously. The excess silver ion was titrated with standard potassium thiocyanate solution to a red-brown color which remained for several minutes.







## V. SPECTROPHOTOMETRIC INVESTIGATION

### A. Introduction

It has been found that isotopic exchange between arsenic(III) and arsenic(V) in 10.8 f to 12.6 f hydrochloric acid solution is, in general, not only complex but dependent on the age of the stock solutions (see Section VI.). This complex behavior implied the existence of chemically nonequivalent arsenic species in at least one of the valence states. Furthermore, the aging phenomenon indicated that several species were slowly approaching chemical equilibrium. Inasmuch as Bonner and Goishi<sup>32</sup> have successfully applied spectrophotometric techniques to the study of a similar aging effect of antimony(V) in hydrochloric acid solutions, an attempt was made to apply the same techniques to a study of the arsenic system.

This spectrophotometric investigation was not intended to be a detailed study of the equilibria and the rates of attainment of these equilibria among species of arsenic. Rather, the purpose was to get a qualitative picture of the nature of the aging process and identify the valence state which ages. No attempt was made to control the temperature of solutions; all spectra were taken at room temperature.

No spectrophotometric evidence was found which would







indicate that arsenic(III) solutions age. There was ample evidence, however, that the arsenic(V) solutions do age.

The investigation showed that more than two chemically nonequivalent species of arsenic(V) exist in  $10.4 \pm 0.5$  f hydrochloric acid solution, and that the species are in slow hydrolytic and polymeric equilibrium. A series of consecutive reactions has been proposed to explain most of the observations.

#### B. Experimental

All spectra were taken on a Cary Model PM 14 Recording Spectrophotometer at Sandia Corporation. The absorption of light was studied in the ultraviolet region (2100 Å to 3000 Å). The spectra were scanned at the rate of 2.5 Å/sec; for the purpose of rate studies, the time when a spectrum (from 2600 Å to 2200 Å) was taken was reckoned from the instant scanning was started at the longer wavelength.

Solutions were contained in 1 cm. glass-stoppered, fused silica cells. The cell compartment was not thermostated, and no attempt was made to regulate the temperature of the solutions; thus the spectra were taken at room temperature.

The absorption of light by hydrochloric acid was balanced out by using a reference cell which contained hydrochloric acid of the same concentration as the solution in the sample cell. Prior to each spectrophotometric measurement, the hydrochloric acid in the reference cell was replaced with fresh







hydrochloric acid solution in order to minimize the possibility of decomposition of the hydrochloric acid by action of ultraviolet light. For a similar reason, the sample cells were filled with solution just prior to each spectrophotometric measurement.

All solutions of arsenic(III) and arsenic(V) which are referred to as "aged" solutions were approximately nine months old. The preparation of these solutions is described in Section II.

A stock solution of 10.9 f hydrochloric acid was prepared at the beginning of the investigation and was used for dilution of arsenic solutions throughout most of the investigation. Small aliquots were withdrawn frequently from the stock solution over nearly two months. The concentration of hydrochloric acid apparently decreased gradually during this time, for analysis of the remaining solution showed that the concentration was 9.90f. This happenstance proved fortunate because it brought to light the sensitivity of the equilibria among arsenic(V) species to the concentration of hydrochloric acid. This hydrochloric acid which started out 10.9 f and decreased to 9.90f over two months will be referred to as 10.4±0.5 f hydrochloric acid.







C. Aging of Arsenic(III), Arsenic(V), and Mixtures of Arsenic(III) and Arsenic(V)

1. Arsenic(III)

The absorption bands of arsenic(III) in  $10.4 \pm 0.5$  f hydrochloric acid were observed at 2130 A and 2550 A. Typical spectra of arsenic(III) in  $10.9$  f hydrochloric acid are shown in Figure V-1.

The absorption at 2130 A was very strong; the maximum apparent\* extinction coefficient is  $12,000 \pm 600$  l. g.-at.<sup>-1</sup> cm.<sup>-1</sup>. This absorption band followed Beer's law and did not depend on the age of the solution or the method of preparation of the solution (see Table V-1, p. 42).

Because the absorption at 2550 A was weak, a relatively high concentration of arsenic(III) (about  $0.00393$  f) was necessary in order to produce a distinguishable peak on the edge of the 2130 A absorption band (compare the spectrum of  $0.00393$  f arsenic(III) with the spectrum of  $0.0197$  f arsenic(III) shown in Figure V-1). As a result of extremely high absorption and superposition of the two bands, measure-

---

\*An apparent extinction coefficient is defined as the ratio of absorbancy to the product of the total arsenic concentration and the light path. The absorbancy is defined as the common logarithm of the ratio of the intensity of incident light to the intensity of transmitted light. The apparent extinction coefficients are minimum values because the concentration of the species which absorbs light at a specified wavelength may be less than the total arsenic concentration.



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ARTICLE

The reaction of ethylmagnesium iodide with ethyl iodide in the presence of a catalyst

by J. H. Goldstein and R. M. Waymouth

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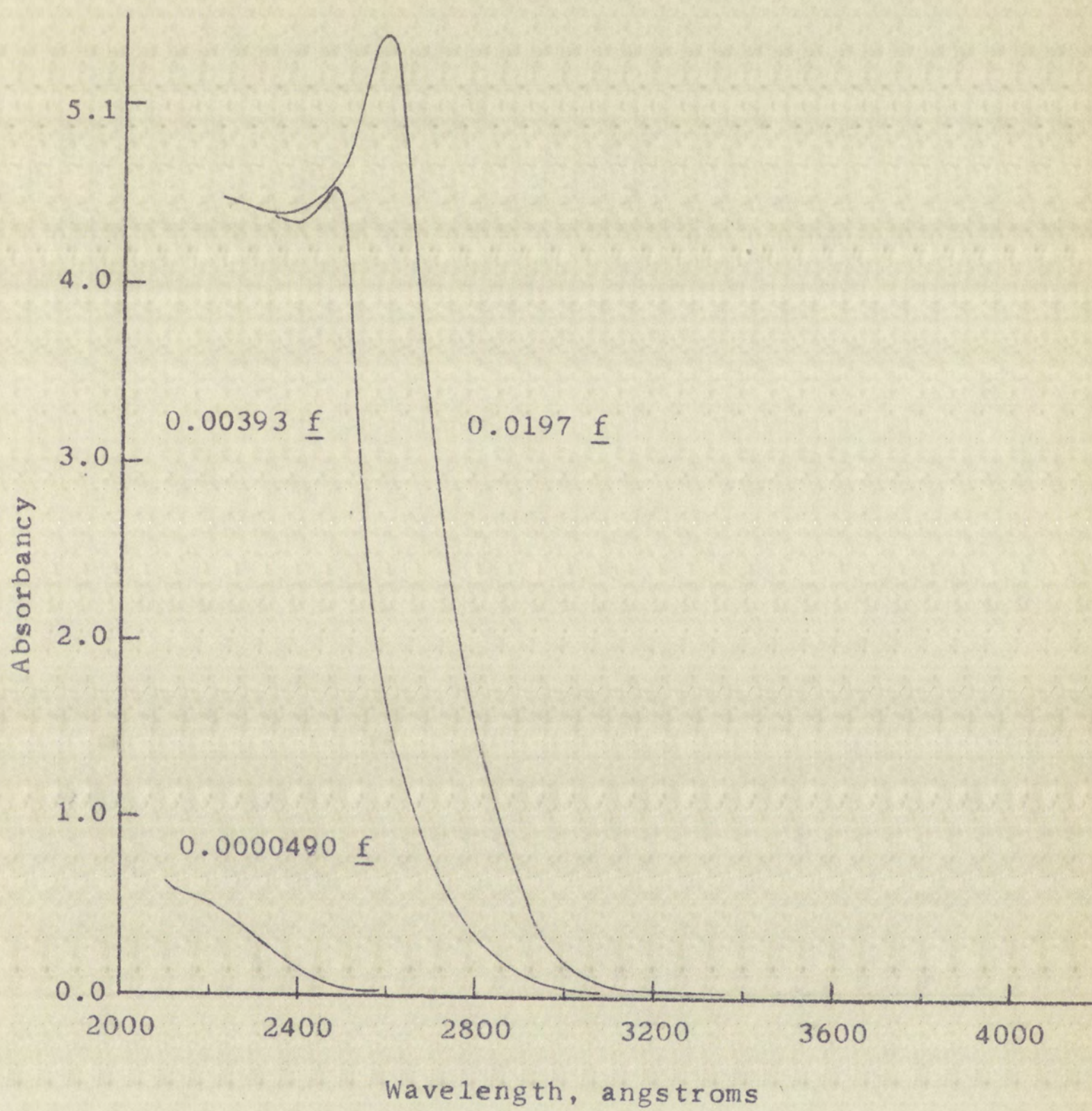


Figure V-1

Typical Ultraviolet Absorption Spectrum of  
Arsenic(III) in 10.9 f Hydrochloric Acid





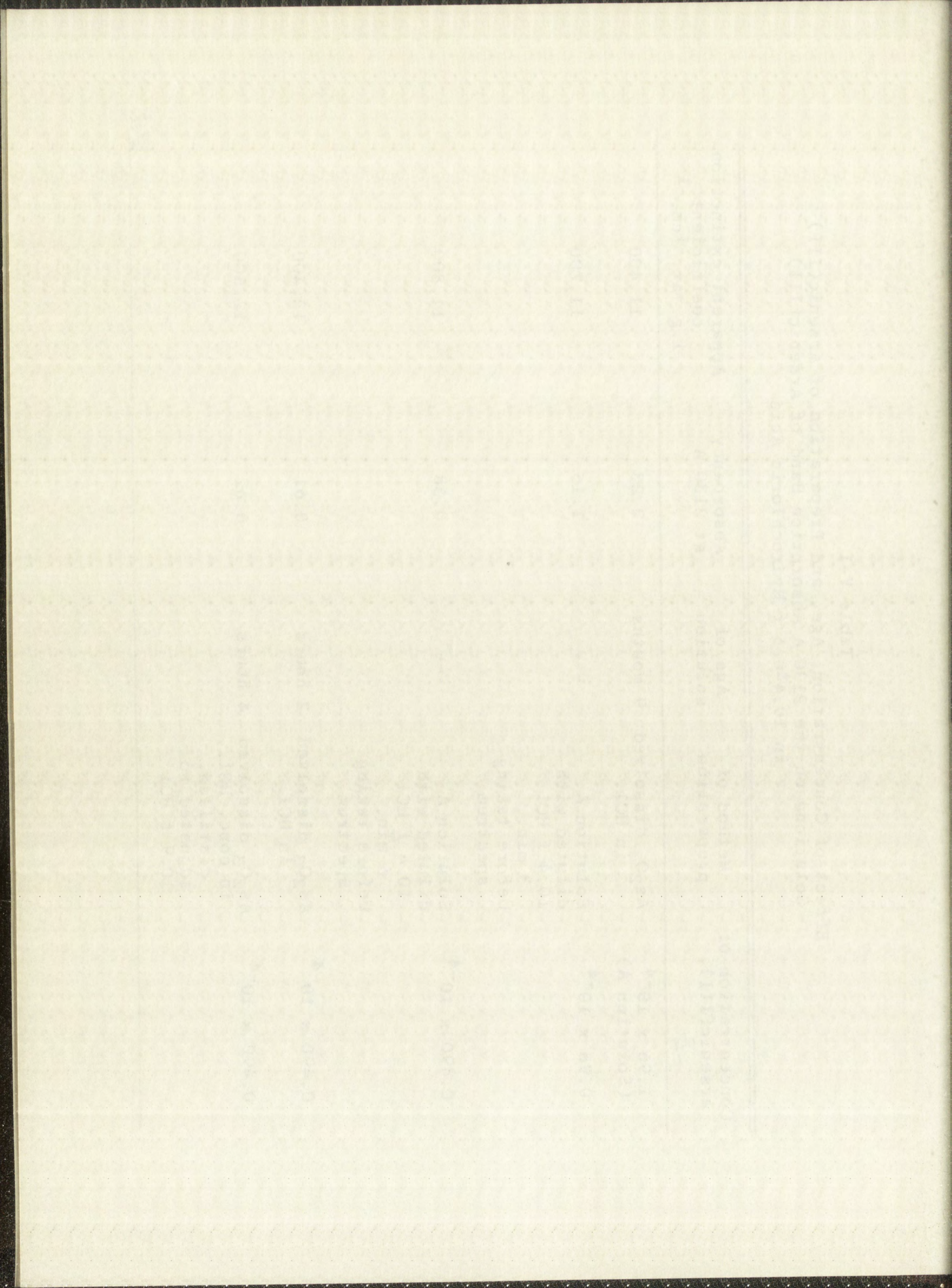


Table V-1

Effect of Concentration, Age, and Preparation of Arsenic(III)  
Solutions on the 2130 Å Absorption Band of Arsenic(III)  
in  $10.4 \pm 0.5$  f Hydrochloric Acid

Concentration of arsenic(III), f	Method of preparation	Age of solution	Absorbancy at 2130 Å	Apparent extinction coefficient, 1.g.-at.-1cm. <sup>-1</sup>
$1.96 \times 10^{-4}$ (Solution A)	As <sub>2</sub> O <sub>3</sub> dissolved in HCl.	9 months	2.23	11,400
$0.98 \times 10^{-4}$	Solution A diluted with 10.4 f HCl 3 min. before taking spectrum.	---	1.15	11,700
$0.490 \times 10^{-4}$	Solution A diluted with 10.4 f HCl 6 min. before taking spectrum.	---	0.58	11,800
$0.490 \times 10^{-4}$	As <sub>2</sub> O <sub>3</sub> dissolved in HCl.	2 hours	0.61	12,400
$0.490 \times 10^{-4}$	As <sub>2</sub> O <sub>3</sub> dissolved in conc. HCl., distilled, adjusted to 10.9 f HCl	4 hours	0.62	12,600







ments at 2550 A involve considerable error. The 2550 A absorption band does not appear to follow Beer's law, but neither does it depend on the age of the arsenic(III) solutions (see Table V-2).

There was no spectrophotometric evidence for the aging of arsenic(III).

## 2. Arsenic(V)

The absorption bands of arsenic(V) in 10.9 f hydrochloric acid were observed at 2300 A and 2700 A. Typical spectra of arsenic(V) are shown in Figure V-2, p. 45. Both absorption bands are weak or else due to species which represent only a small fraction of the arsenic(V).

The absorption band at 2700 A is superimposed on the side of the stronger absorption at shorter wavelength. Nevertheless, the absorption at 2700 A appears to adhere to Beer's law over an arsenic(V) concentration range of 0.0090 f to 0.126 f (see Table V-3, p. 46). The apparent extinction coefficient at 2700 A is about  $16 \pm 1$  l. g.-at.<sup>-1</sup> cm.<sup>-1</sup>. The minimum extinction coefficient which can be attributed to the 2700 A absorption band was calculated from the difference of the peak absorbancy (at 2700 A) and the minimum absorbancy (at about 2550 A) between the two bands and was found to be  $2 \pm 2$  l. g.-at.<sup>-1</sup> cm.<sup>-1</sup> over an arsenic(V) concentration range of 0.0090 f to 0.126 f.

The somewhat stronger absorption of aged arsenic(V) at







Table V-2

Effect of Concentration and Age of Arsenic(III) Solutions  
on the 2550 Å Absorption Band of Arsenic(III) in  
10.4<sup>±</sup>0.5 f Hydrochloric Acid

Concentration of arsenic(III), <u>f</u>	Age of solution <sup>a</sup>	Absorbancy at peak absorption	Apparent extinction coefficient, 1. g.-at. <sup>-1</sup> cm. <sup>-1</sup>
0.0197 (Solution B)	9 months	~ 5.2 @ ~2600 Å	260
0.0393	9 months	4.53 @ 2470 Å	1,150
0.0197	~ 2 hours	~ 5.4 @ 2590 Å	270
0.0099	~ 2 hours	4.62 @ 2520 Å	470
0.00393	~ 2 hours	4.35 @ 2470 Å	1,110
0.00393	Solution B diluted with 10.4 <u>f</u> HCl 7 min. before taking spectrum.	4.53 @ 2470 Å	1.150

<sup>a</sup>Solutions were prepared by dissolution of arsenic trioxide in hydrochloric acid.







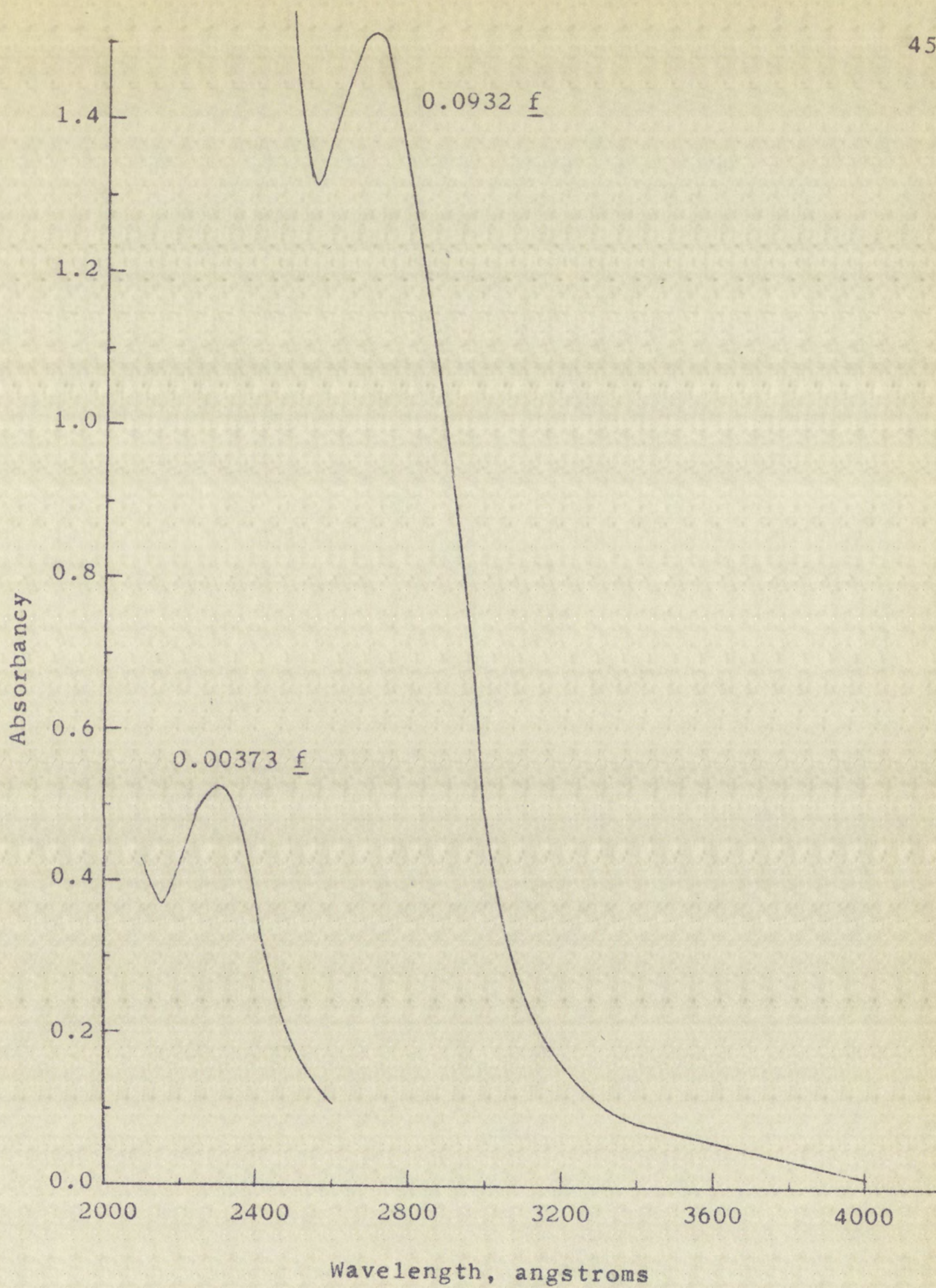


Figure V-2

Typical Ultraviolet Absorption Spectrum of Aged  
Arsenic(V) in 10.9  $\underline{f}$  Hydrochloric Acid







Table V-3

Effect of Concentration and Age of Arsenic(V) Solutions  
on the 2700 Å Absorption Band of Arsenic(V) in  
10.9  $\underline{f}$  Hydrochloric Acid

Concentration of arsenic(V), $\underline{f}$	Age of solution	Absorbancy	Apparent extinction coefficient, 1. g.-at. $^{-1}$ cm. $^{-1}$
0.126	3 months	2.11	16.8
0.093 (Solution C)	9 months	1.51	16.2
0.0186	9 months	$\sim 0.32$	$\sim 17.2$
0.0186	Solution C diluted with 10.4 $\pm$ 0.5 $\underline{f}$ HCl 3 min. before taking spectrum.	0.29	15.6
0.090	$\sim 2$ hours	1.46	16.2
0.045	$\sim 2$ hours	0.72	16.0
0.0180	$\sim 2$ hours	0.27	15.0
0.0090	$\sim 2$ hours	0.14	16.1

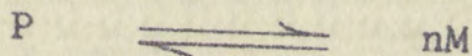






2300 A did not follow Beer's law (see Table V-4). The maximum apparent extinction coefficient increased from 52 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> to 378 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> with decreasing concentration of arsenic(V) (0.0186  $\underline{f}$  to 0.000745  $\underline{f}$ ).

This nonadherence of the 2300 A absorption band to Beer's law suggests that the absorbing species may be a dissociation product of polymeric species. If a simple, weak dissociation of a polymer, P, into identical monomers, M, is assumed, a relationship between the absorbancy and the total concentration of the polymer and monomer may be derived.



$$[M]^n/[P] = K, \text{ a constant}$$

$$[M] = K[P]^{1/n}$$

$$\text{Absorbancy, } A = k[M] = kK[P]^{1/n}, \quad k = \text{constant}$$

$$\text{If } [P] \approx [\text{As(V)}],$$

$$\text{then } \log [\text{As(V)}] = n \log A - \log kK$$

The logarithm of total arsenic(V) concentration was plotted against the logarithm of the absorbancy at a specified wavelength (see Figure V-3, p. 49). This plot was found to be linear at all wavelengths between 2200 A and 2600 A, but the slopes of the lines, tabulated below, varied from 1.46 to 2.66

Wavelength, angstroms	2200	2250	2300	2400	2500	2600
Slope(n)	1.73	2.28	2.66	2.63	2.17	1.46







Table V-4

Effect of Concentration of Aged Arsenic(V) on the 2300 A  
Absorption Band of Arsenic(V) in 10.9 f  
Hydrochloric Acid

Concentration of Arsenic(V), <u>f</u>	Absorbancy	Apparent extinction coefficient, 1. g.-at.- <sup>1</sup> cm. <sup>-1</sup>
0.0186	0.960	52
0.00373	0.524	141
0.000745	0.282	378



Table 1-1

Summary of 1980-1981  
Annual Report of the  
Department of the Interior

1. The Department of the Interior has been successful in its efforts to protect and manage the Nation's natural resources.

2. The Department has also been successful in its efforts to protect and manage the Nation's cultural resources.

3. The Department has also been successful in its efforts to protect and manage the Nation's historic resources.

4. The Department has also been successful in its efforts to protect and manage the Nation's scientific resources.

5. The Department has also been successful in its efforts to protect and manage the Nation's wildlife resources.

6. The Department has also been successful in its efforts to protect and manage the Nation's fisheries resources.

7. The Department has also been successful in its efforts to protect and manage the Nation's forests resources.

8. The Department has also been successful in its efforts to protect and manage the Nation's parks resources.

9. The Department has also been successful in its efforts to protect and manage the Nation's public lands resources.

10. The Department has also been successful in its efforts to protect and manage the Nation's mineral resources.

11. The Department has also been successful in its efforts to protect and manage the Nation's water resources.

12. The Department has also been successful in its efforts to protect and manage the Nation's energy resources.

13. The Department has also been successful in its efforts to protect and manage the Nation's transportation resources.

14. The Department has also been successful in its efforts to protect and manage the Nation's housing resources.

15. The Department has also been successful in its efforts to protect and manage the Nation's health resources.



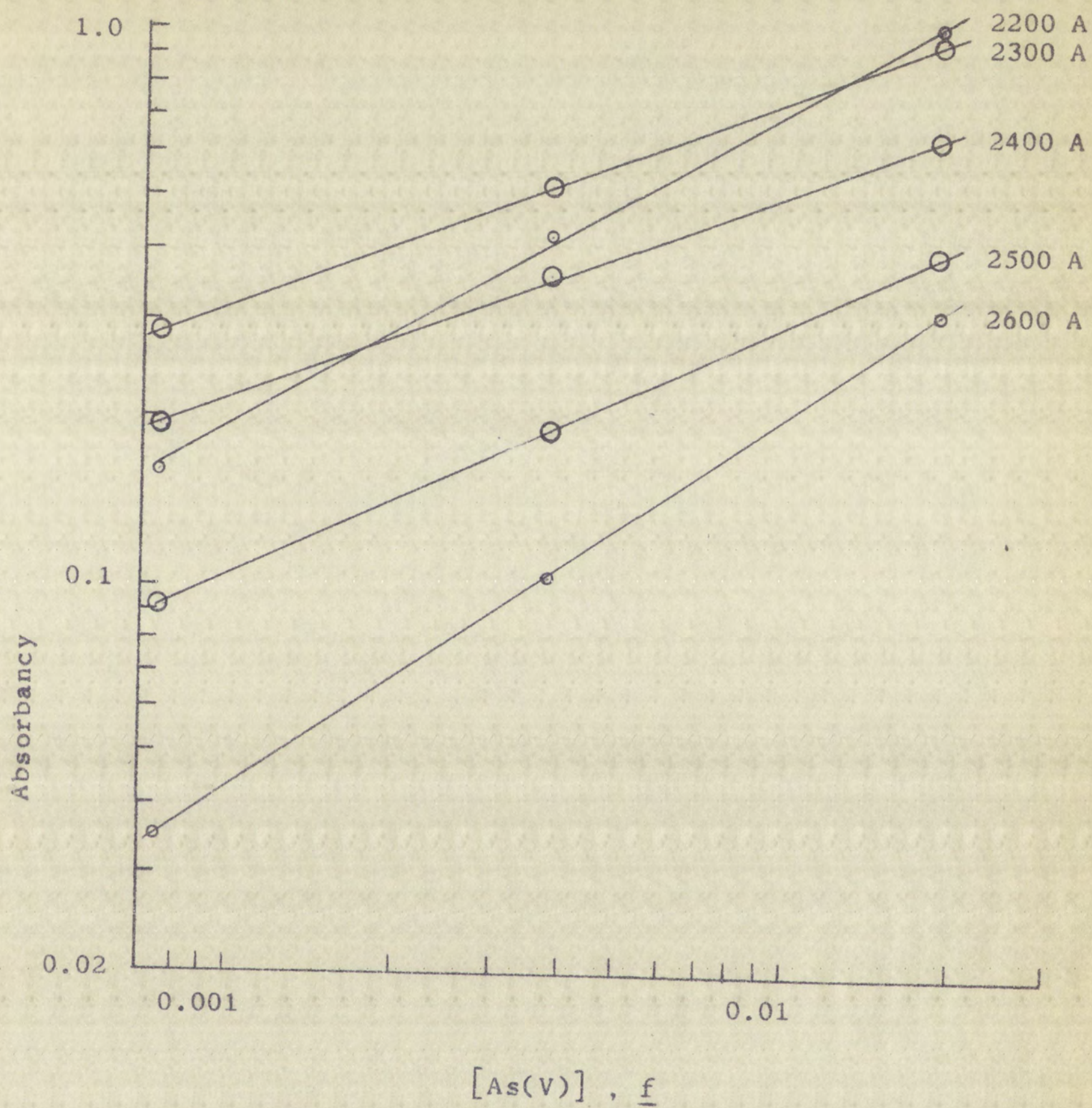


Figure V-3

Dependence of the 2300 A Absorption Band of Aged  
Arsenic(V) in 10.9 f Hydrochloric Acid  
on the Arsenic(V) Concentration







and were not integers, indicating complex equilibria which do indeed involve polymeric forms of As(V). No evidence which would indicate that polymers of arsenic(V) exist in acid solution has been previously reported<sup>33,34</sup>.

The aging of 0.00410 f arsenic(V)<sup>\*</sup> in 10.9 f. hydrochloric acid is shown in Table V-5. In most instances, the absorption spectra were not observed beyond 2600 A because of the small absorbancy in this region. The absorbancy of aged 0.00373 f arsenic(V) in 10.9 f hydrochloric acid solution is listed at the bottom of Table V-5. At 2300 A, the absorbancy of freshly prepared arsenic(V) increased gradually from about 5% to nearly 44% of the absorbancy of the aged arsenic(V) over nineteen days. The change was more rapid at shorter wavelengths, and less rapid at longer wavelengths up to 2600 A.

The variation of the spectrum with time indicates that there must be at least two species of arsenic(V) in slow equilibrium; indeed, it is reasonable to suspect that there are several species in slow equilibrium because of the variation in the rate of aging observed at different wavelengths.

It is possible that part of the increase in absorbancy at the shorter wavelengths ( $\sim 2200$  A) may be due to arsenic(III) formed by decomposition of arsenic(V). Although no decom-

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\*The 0.00410 f arsenic(V) solution was prepared from "purified" arsenic pentoxide.







Table V-5

Change in Absorbancy of 0.00410 f Arsenic(V) Solution, 10.9 f in Hydrochloric Acid, Freshly Prepared from "Purified" Arsenic Pentoxide

Time after preparation, min.	Absorbancy at specified wavelengths, wavelength in angstroms									
	2200	2300	2400	2500	2600	2700	2800	3000		
13	0.042	0.031	0.031	0.037	0.050	0.051	0.044	0.031		
24	0.050	0.038	0.037	0.040	0.050	0.054	0.049	0.034		
45	0.049	0.036	0.032	0.037	0.049	0.051	0.046	0.031		
63	0.056	0.040	0.037	0.040	0.050	0.052	0.046	0.031		
89	0.061	0.045	0.039	0.039	0.050	0.052	0.047	0.031		
119	0.070	0.051	0.045	0.042	0.053					
200	0.079	0.059	0.045	0.040	0.048					
362	0.086	0.062	0.047	0.040	0.048					
368	0.112	0.082	0.059	0.049	0.054					
402	0.113	0.082	0.059	0.049	0.051					
416*	0.120	0.087	0.059	0.048	0.051					
10,105 (7 days)	0.325	0.238	0.131	0.070	0.045	-0.003	-0.001	0.003		
27,761 (19 days)	0.378	0.260	0.142	0.078	0.058					
27,795* (19 days)	0.387	0.269	0.146	0.078	0.058					

Aged 0.00373 f  
As(V)

\* Solution was stored in the dark since immediately after preparation.







position could be detected by volumetric analysis, arsenic(III) could have been formed in quantities sufficient for spectrophotometric observation near 2130 Å.

The insensitivity of the aging process to the fluorescent light of the laboratory was demonstrated in the aging experiment just described. A portion of the 0.00410  $\text{f}$  arsenic(V) solution was stored in a blackened flask immediately after it had been prepared. The absorption spectra of the solution stored in the dark and the solution exposed to the light were essentially the same after the solutions had aged 416 minutes and 27,795 minutes. These data are marked with an asterisk in Table V-5, p. 51.

### 3. Mixtures of Arsenic(III) and Arsenic(V)

The absorption spectrum of mixtures of arsenic(III) and arsenic(V) in  $10.4 \pm 0.5 \text{ f}$  hydrochloric acid will be discussed in connection with the "Dilution effect" in Section V.D.3. It was found that the rate of change in the absorbancy of arsenic(V) was slightly faster when arsenic(III) was present. The hydrochloric acid concentration of the mixture, however, was slightly higher than that of the arsenic(V) alone, so the faster rate could be attributed to the higher acid concentration. It is concluded that the rate of aging of arsenic(V) is about the same whether or not a small quantity of arsenic(III) is present.







D. Dilution Effect in 11 f Hydrochloric Acid

1. Arsenic(V)

A striking phenomenon was observed in an attempt to determine whether the absorbancy at 2300 A of arsenic(V) in 10.9 f hydrochloric acid followed Beer's law. When arsenic(V) solutions were diluted with 10.4<sup>+</sup>0.5 f hydrochloric acid, the absorbancy of the diluted solution dropped to about one-third of the absorbancy of an equivalent nine-months-old solution; the absorbancy then increased to about 90% of that of the aged solution in the first few hours and then increased slowly for several weeks. This phenomenon is called the dilution effect.

The dilution effect is, indeed, puzzling, but it is not unprecedented. The absorbancy of hydrochloric acid solutions of antimony(V) has been found to be strongly dependent on the hydrochloric acid concentration<sup>32</sup>. The possibility that the dilution effect resulted in part from hydrolysis of arsenic(V) was not at first recognized because it was not realized that the acidity of the arsenic(V) solution had been lowered by dilution. After most of the dilution experiments were done, the hydrochloric acid used in the experiments was reanalyzed and found to be only 9.90 f whereas it was prepared 10.9 f in hydrochloric acid. It was obvious that dilution of the arsenic(V) solutions which were 10.9 f in hydrochloric acid







resulted in an appreciable decrease in acidity. This dilution effect, however, may well be due to the combined effects of the dissociation of polymers and the hydrolysis of less-hydrolyzed arsenic(V) species. A detailed description of the dilution experiments is given below.

Aged 0.00373  $\underline{f}$  arsenic(V), 10.9  $\underline{f}$  in hydrochloric acid, was diluted fivefold with  $10.4 \pm 0.5$   $\underline{f}$  hydrochloric acid (see Table V-6 for the results). Three minutes after dilution, the absorbancy at 2300 A was 16% of the absorbancy of the corresponding aged arsenic(V) solution at the same wavelength. The absorbancy of all wavelengths from 2200 A to 2600 A increased gradually. Four hours later, the absorbancy at 2300 A was 90% of the absorbancy of the corresponding aged arsenic(V) solution.

In a similar experiment, an aged 0.0186  $\underline{f}$  arsenic(V) solution, 10.9  $\underline{f}$  in hydrochloric acid, was diluted fivefold with  $10.4 \pm 0.5$   $\underline{f}$  hydrochloric acid to obtain 0.00373  $\underline{f}$  arsenic(V) solution. The absorption spectrum of the diluted arsenic(V) solution was compared with the spectrum of aged 0.00373  $\underline{f}$  arsenic(V) which was 10.9  $\underline{f}$  in hydrochloric acid (see Table V-6). At 2300 A, the absorbancy of the arsenic(V) six minutes after dilution was 36% of the absorbancy of aged 0.00373  $\underline{f}$  arsenic(V). The subsequent increase in absorbancy is shown graphically in Figure V-4, p. 56. Although the initial rise appears to be linear, it is felt that the data







Table V-6

Change in Absorbancy of Arsenic(V) in  $10.4 \pm 0.5$  f Hydrochloric Acid after Fivefold Dilution of Aged Solutions to 0.00373 f and 0.000745 f Compared with Aged 0.00373 f and 0.000745 f Arsenic(V) Solution, 10.9 f in Hydrochloric Acid

Solution	Time after dilution, min.	Absorbancy at specified wavelengths, wavelength in angstroms			
		2200	2300	2400	2500
Aged 0.000745 f As(V)	---	0.160	0.282	0.191	0.091
0.000745 f As(V), prepared by fivefold dilution of aged As(V) solution	3	0.050	0.045	0.027	0.009
	13	0.069	0.062	0.030	0.010
	23	0.084	0.070	0.035	0.011
	75	0.167	0.133	0.068	0.021
	214	0.324	0.253	0.132	0.043
Aged 0.00373 f As(V)	---	0.430	0.524	0.362	0.191
0.00373 f As(V), prepared by fivefold dilution of aged As(V) solution	6	0.252	0.191	0.108	0.060
	16	0.297	0.223	0.126	0.063
	96	0.570	0.471	0.279	0.131
	116	0.571	0.473	0.280	0.132
	3,135	0.592	0.483	0.260	0.115







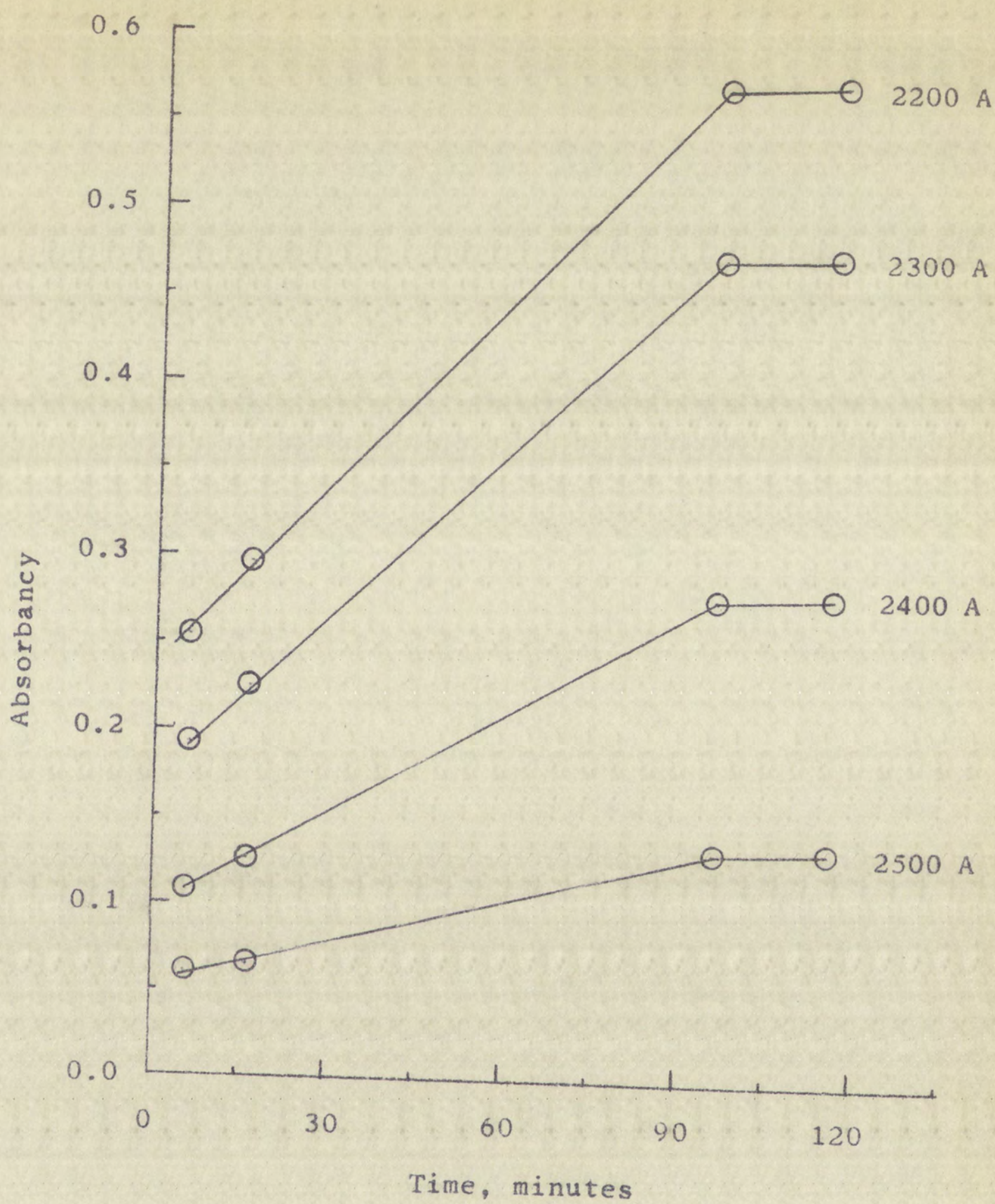
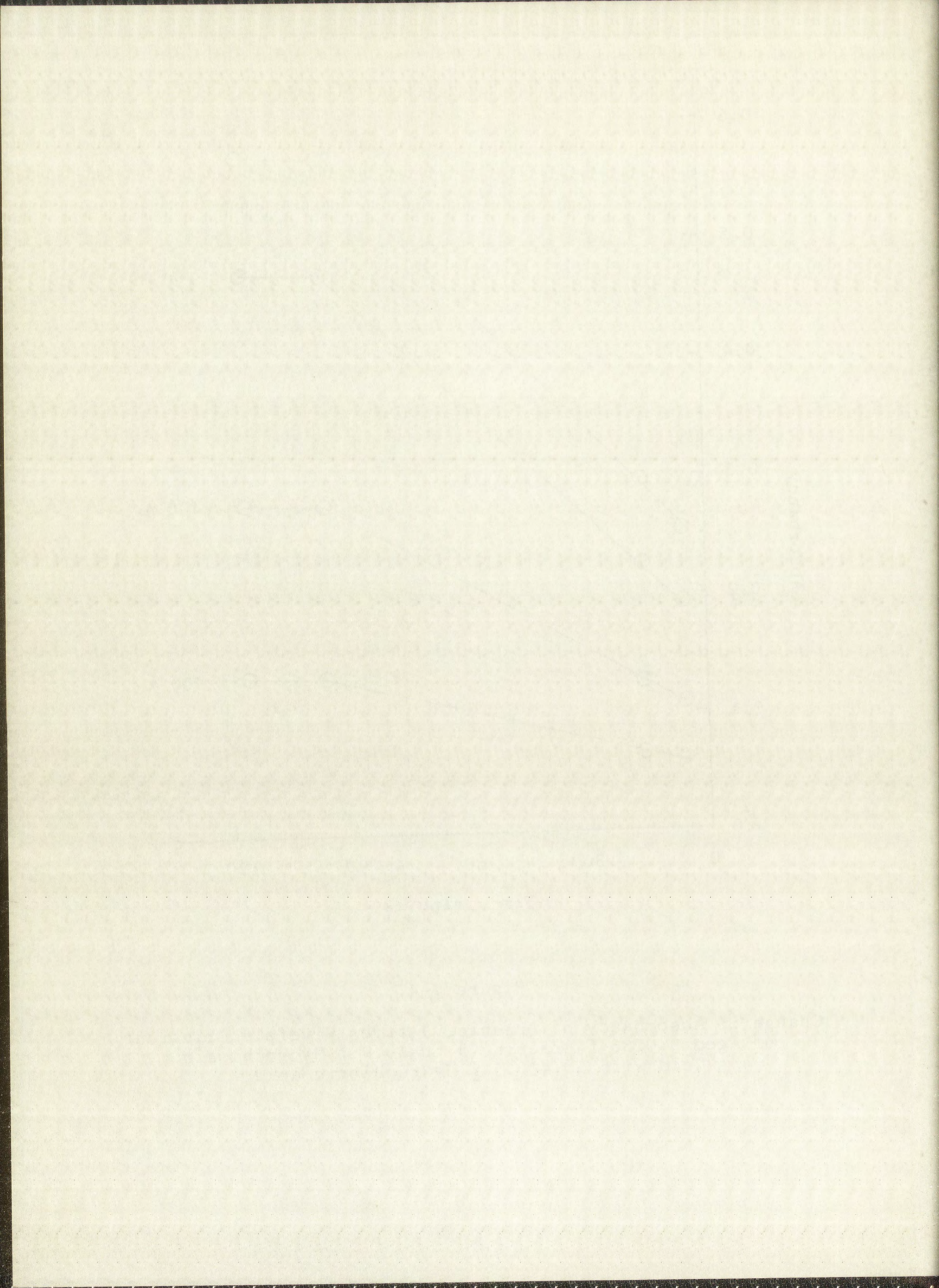


Figure V-4

Change in Absorbance of Arsenic(V) after Fivefold Dilution  
of Aged 0.0186 f Arsenic(V) in 10.9 f Hydrochloric  
Acid with  $10.4 \pm 0.5$  f Hydrochloric Acid







are insufficient to conclude that the growth is proportional to the time. For this reason the experiment was duplicated and the spectrum was scanned more frequently.

The results of the duplicate experiment are tabulated in Table V-7. Several spectra taken at different times are plotted in Figure V-5, p. 59, in order to compare the changing shapes of the absorption bands of diluted arsenic(V) with the shape of the absorption band of aged arsenic(V) of the same concentration. As in previous dilution experiments, a large initial drop in absorbancy (75%) was observed. Then there was a moderately slow increase in absorbancy for about 136 minutes (average rate of  $1.45 \times 10^{-3}$  absorbancy units per minute) followed by a very slow increase for twenty days (average rate of  $1.43 \times 10^{-6}$  absorbancy units per minute). It is obvious from Figure V-4 that the absorbancy increases more rapidly at the shorter wave lengths. The rate of increase in absorbancy is shown graphically in Figure V-6, p. 60. Two distinct components of growth are apparent. The kinetic order of the faster reaction, represented by the initial increase in absorbancy, was determined as follows. It was assumed that the reaction was essentially at equilibrium in 136 minutes because the initial increase in absorbancy leveled off at that time. The difference in absorbancy at equilibrium,  $A_{eq}$ , and the absorbancy at time  $t$ ,  $A_t$ , was plotted against time on semilogarithmic graph paper (see







Table V-7

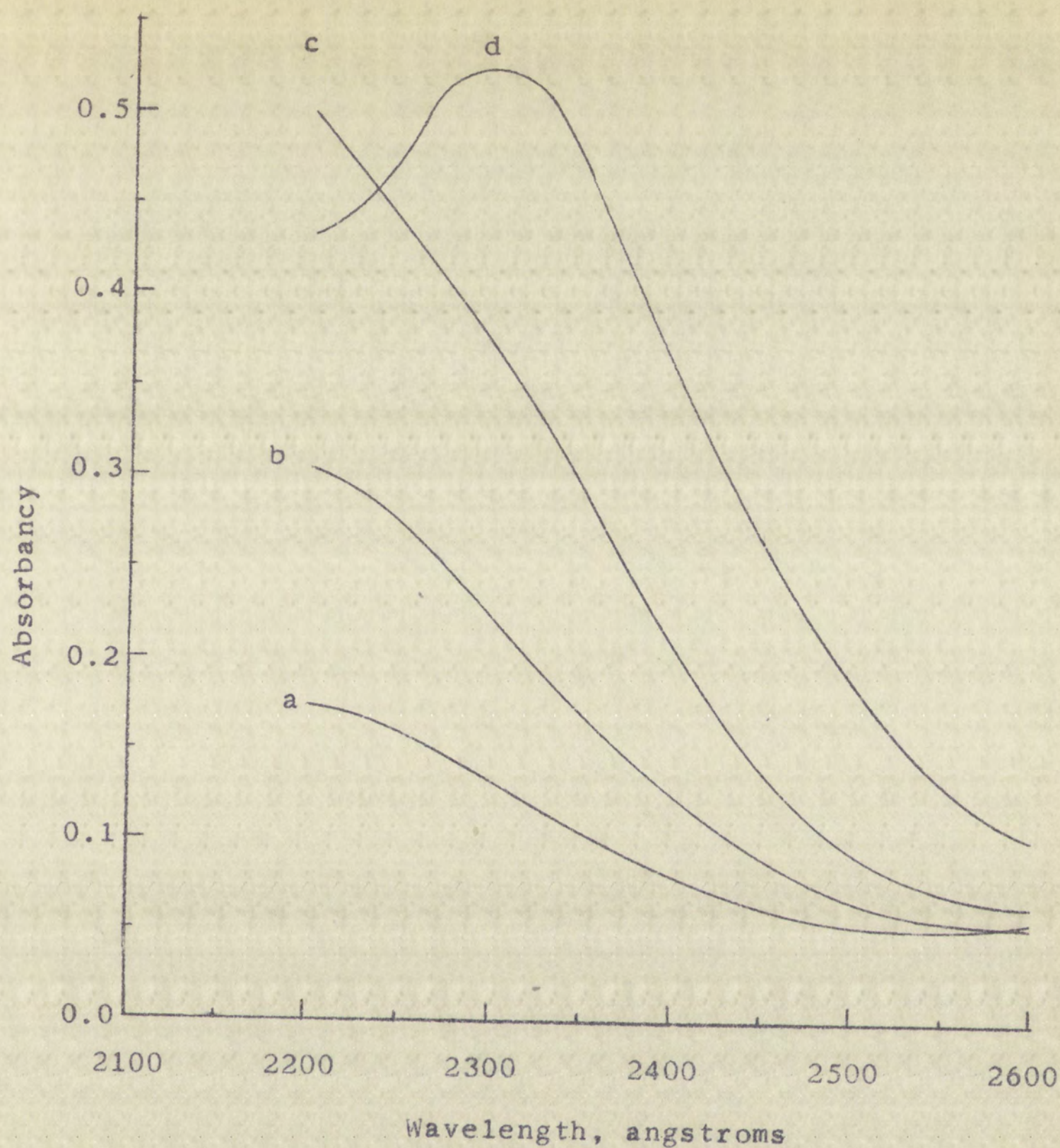
Change in Absorbancy of 0.0037 f Arsenic(V) After  
 Fivefold Dilution of Aged 0.0186 f Arsenic(V)  
 10.9 f in Hydrochloric Acid, with 10.4±0.5  
 Hydrochloric Acid

Time after dilution, min.	Absorbancy at specified wavelengths, wavelength in angstroms				
	2200	2300	2400	2500	2600
3.5	0.174	0.133	0.081	0.053	0.058
13	0.208	0.151	0.087	0.054	0.056
23	0.240	0.172	0.100	0.061	0.057
38	0.269	0.193	0.110	0.063	0.056
53	0.304	0.223	0.128	0.069	0.056
74	0.340	0.241	0.140	0.073	0.056
104	0.399	0.303	0.175	0.089	0.058
136	0.428	0.331	0.190	0.098	0.063
173	0.429	0.331	0.191	0.098	0.063
255	0.432	0.335	0.191	0.098	0.063
1,508 (1 day)	0.442	0.340	0.193	0.098	0.065
11,613 (8 days)	0.472	0.358	0.199	0.100	0.065
28,893 (20 days)	0.500	0.372	0.210	0.093	0.067
Aged 0.00373 f As(V)	0.432	0.524	0.362	0.191	0.102









- a. 3.5 min. after dilution  
b. 53 min. after dilution  
c. 28,893 min. after dilution  
d. Aged solution

Figure V-5

Absorption Spectrum of Arsenic(V) after Fivefold Dilution  
of Aged 0.0186 f Arsenic(V) in 10.9 f Hydrochloric Acid  
with  $10.4 \pm 0.5$  f Hydrochloric Acid





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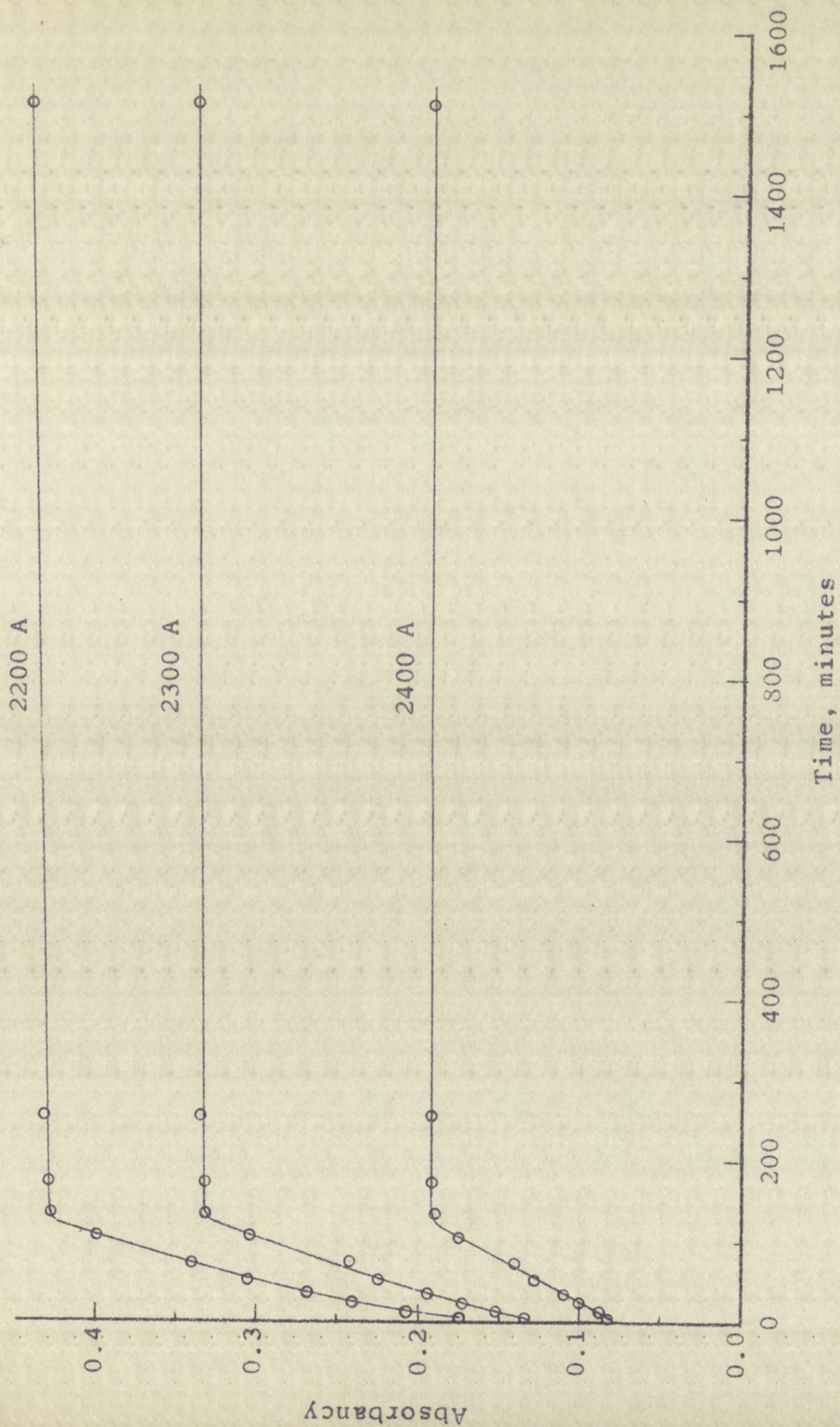


Figure V-6

Change in Absorbance of 0.00373 f Arsenic(V) After Fivefold Dilution  
 of Aged 0.0186 f Arsenic(V) in 10.9 f Hydrochloric Acid with  
 10.4±0.5 f Hydrochloric Acid







Figure V-7. The plot is linear at all wavelengths, indicating a pseudo-first order reaction, but the slope of the line is greater at the shorter wavelengths. The slopes in terms of half-times are:

48 minutes @ 2200 A

61 minutes @ 2300 A

59 minutes @ 2400 A

76 minutes @ 2500 A

The dilution effect is accounted for, in part, by assuming consecutive polymeric reactions followed by consecutive hydrolytic reactions (see Section V.I. for a detailed discussion).

When it was found that chlorine in hydrochloric acid solution has an absorption band at 2250 A, it was wondered if part of the absorbancy of arsenic(V) solutions at 2300 A could be due to chlorine. The 2300 A absorption band appeared only when a solution contained arsenic(V), so if chlorine were present, it resulted from the decomposition of arsenic(V). The smallest concentration of chlorine which can be detected at 2250 A was found to be tenfold larger than the concentration of arsenic(III) which can be detected at 2130 A. Equal amounts of chlorine and arsenic(III) would be formed by the decomposition of arsenic(V); therefore, a strong absorption at 2130 A due to arsenic(III) would be apparent long before the absorbancy of chlorine at 2250 A would be appreciable.



Figure 1. The effect of the concentration of the solution on the rate of the reaction. The rate of the reaction is measured at different concentrations of the solution. The rate of the reaction is measured at different concentrations of the solution.

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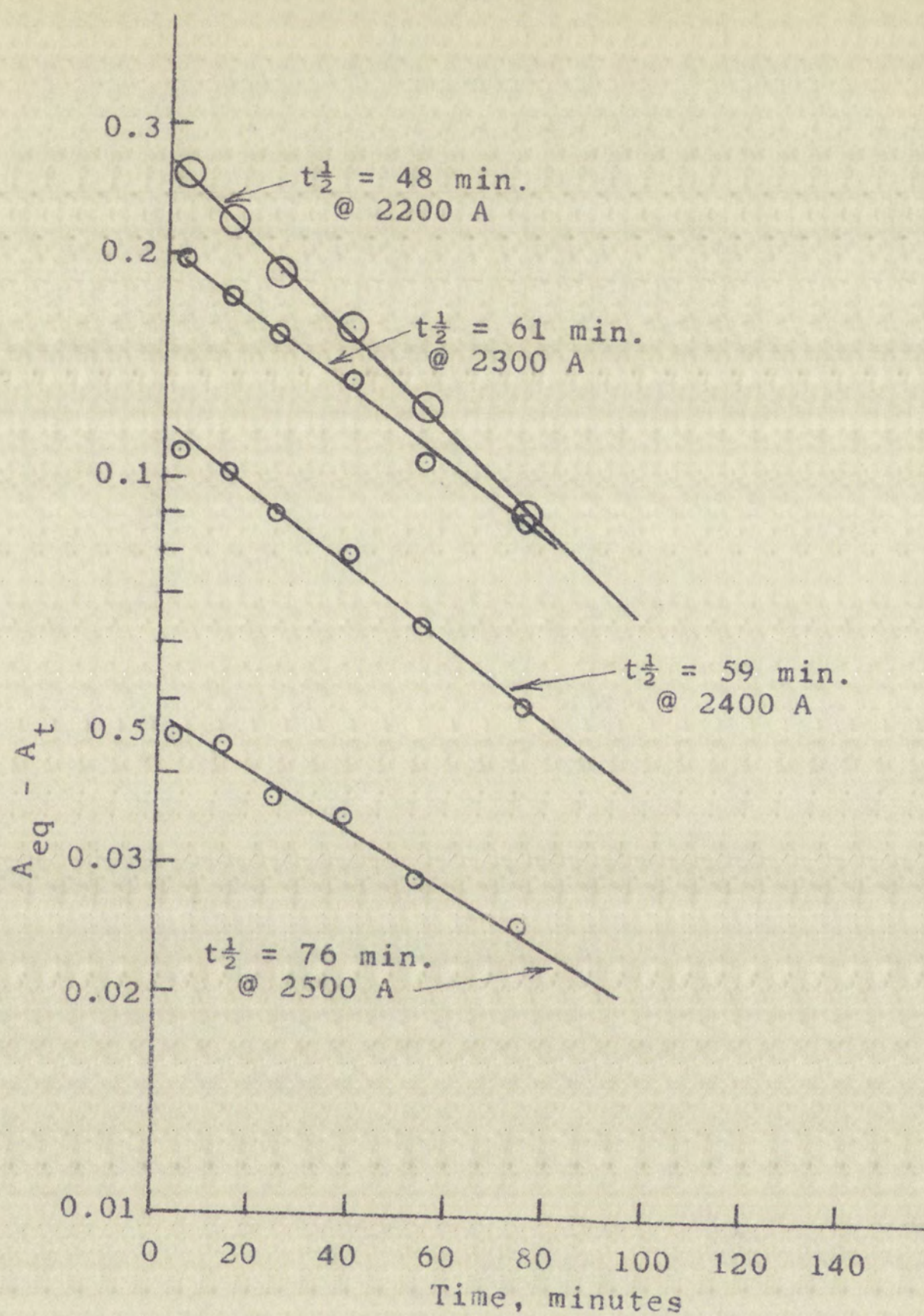
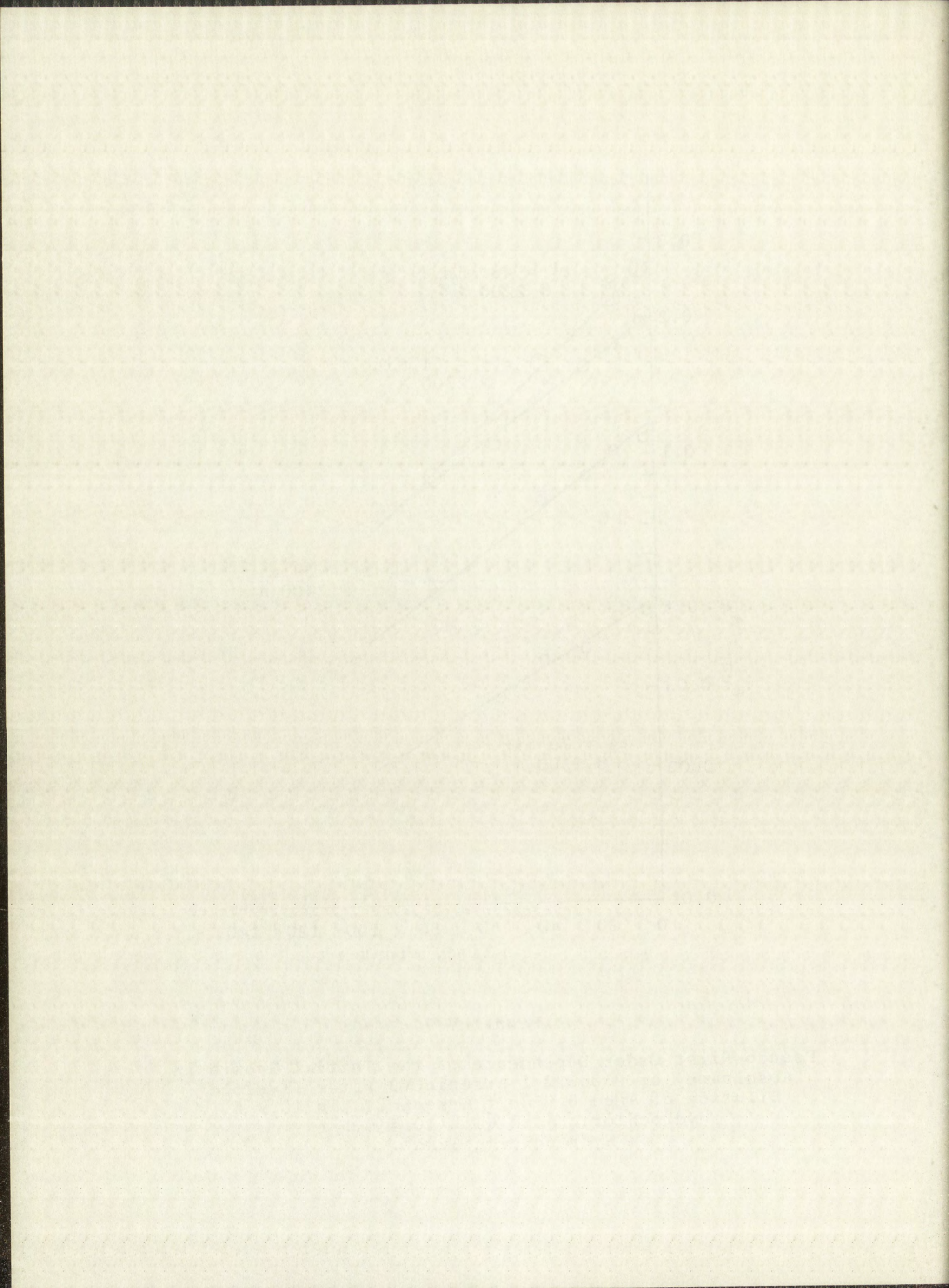


Figure V-7

Pseudo-First Order Dependence of the Initial Growth in Absorbance of 0.00373 f Arsenic(V) after Fivefold Dilution of Aged 0.0186 f Arsenic(V) in 10.9 f Hydrochloric Acid with 10.4 $\pm$ 0.5 f Hydrochloric Acid







Because arsenic(V) solutions show no such strong absorbancy at 2130 A, very little absorbancy at 2300 A is attributed to chlorine.

## 2. Arsenic(III)

Aged arsenic(III) solutions were diluted in order to determine whether the absorbancy of arsenic(III) followed Beer's law. The absorbancy obeyed Beer's law at 2130A but not at 2550 A (see Table V-1 and Table V-2, pp. 42 and 44). No other dilution effect was noticed. In all instances the absorbancy was independent of the preparation and the age of the solutions.

## 3. Mixtures of Arsenic(III) and Arsenic(V)

Mixtures of arsenic(III) and arsenic(V) were found to change after dilution in much the same manner as arsenic(V) solutions changed after dilution. In the following experiment, 10 ml. of an aged 0.00373 f arsenic(V) solution, 10.9 f in hydrochloric acid, was diluted with 12.5 ml. of aged 0.000196 f arsenic(III) solution, 10.9 f in hydrochloric acid, and the mixture was made up to 50 ml. with 10.4 $\pm$ 0.5 f hydrochloric acid. The final mixture was 0.000745 f in arsenic(V) and 0.0000490 f in arsenic(III). The absorbancy of 0.0000490 f arsenic(III) in 10.9 f hydrochloric acid was subtracted at each wavelength from the absorbancy of the mixture. The results are tabulated in Table V-8. The absorbancy at 2300 A dropped 90% and grew steadily at an average rate about 6%



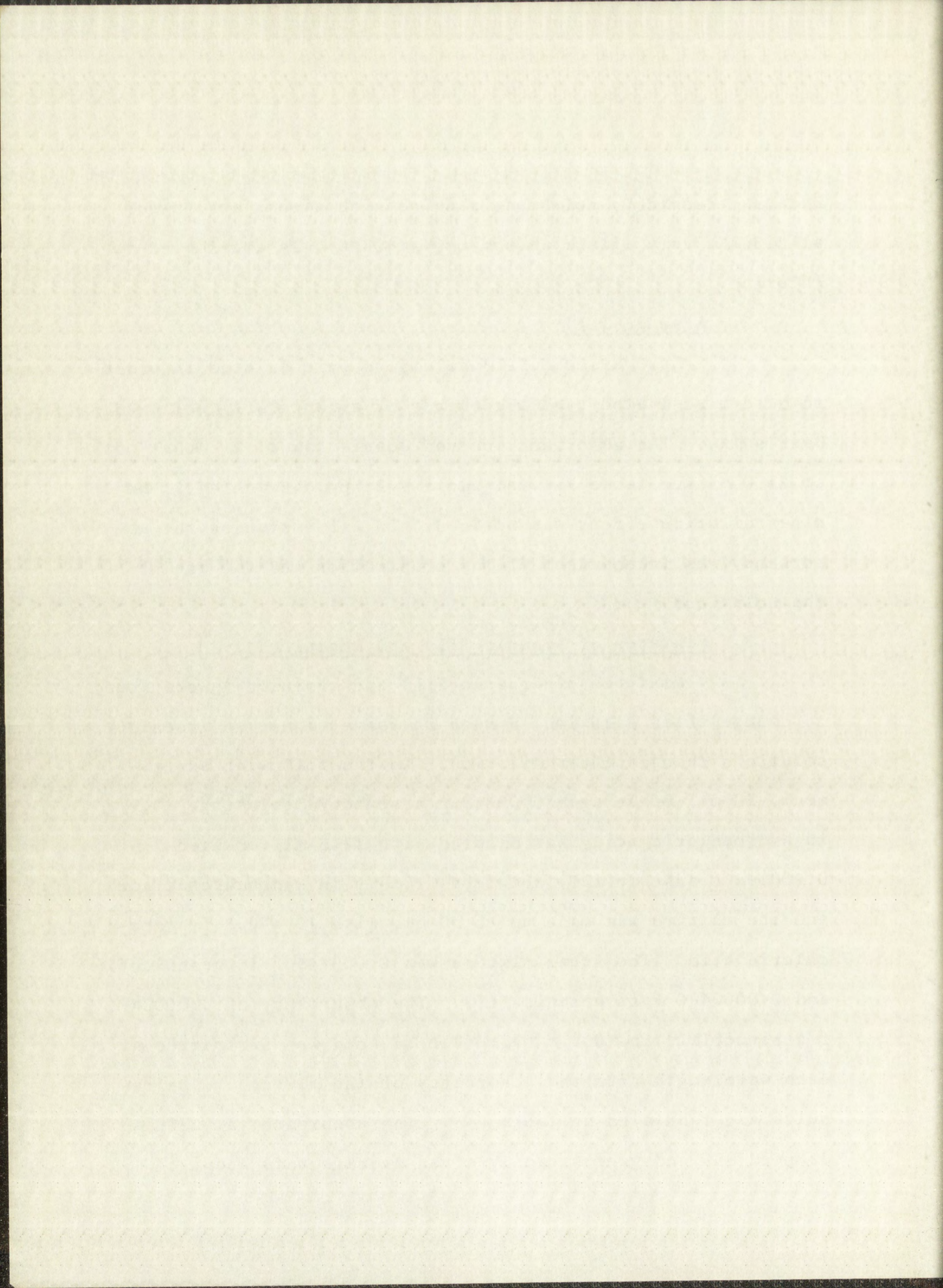


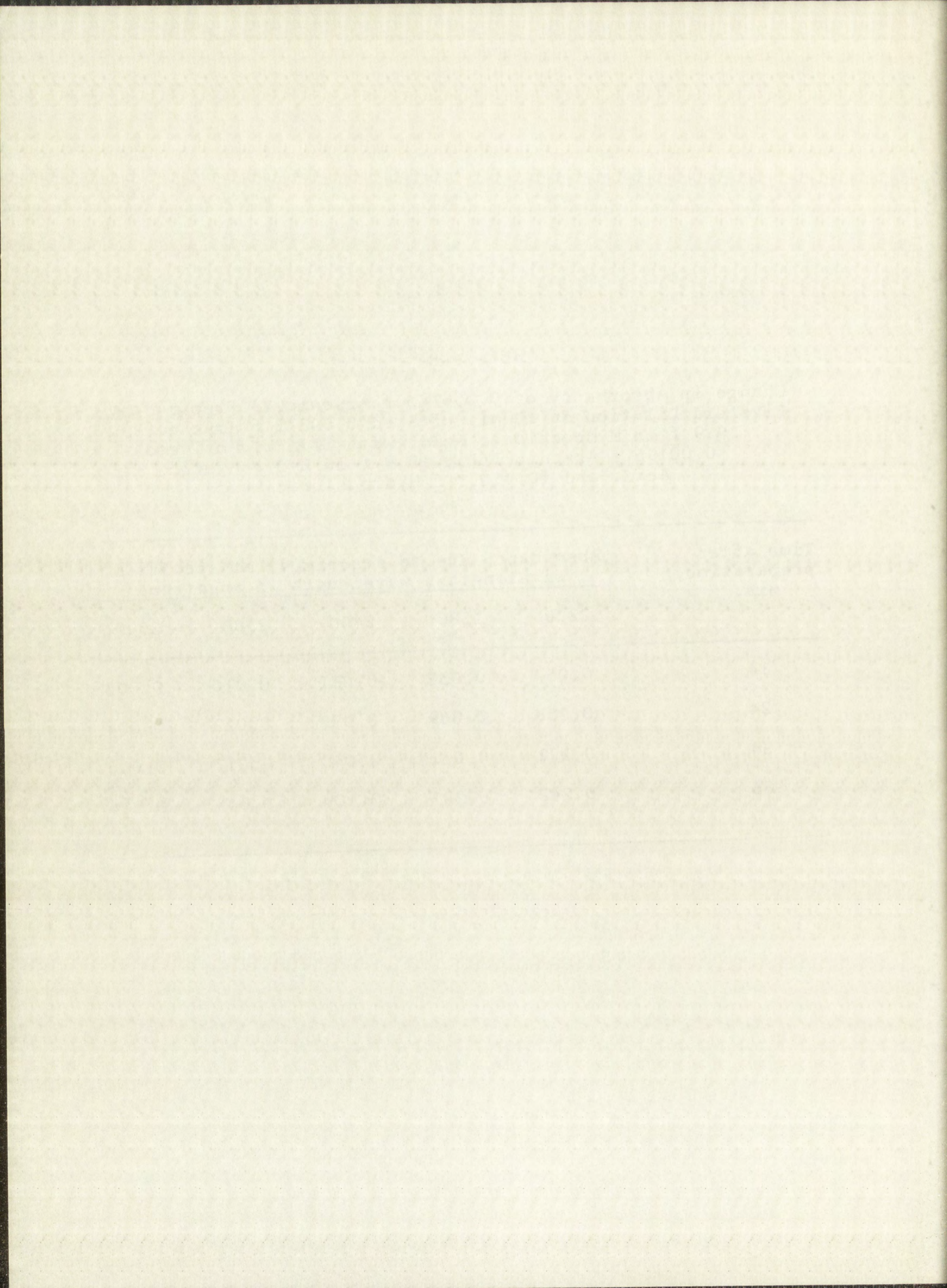


Table V-8

Change in Absorbancy of 0.000745  $\mu$ g Arsenic(V) Prepared by  
 Fivefold Dilution of 10 ml. of Aged 0.00373  $\mu$ g Arsenic(V),  
 10.9  $\mu$ g in Hydrochloric Acid, with 12.5 ml. of Aged  
 0.00196  $\mu$ g Arsenic(III), 10.9  $\mu$ g in Hydrochloric  
 Acid, and 10.4 $\pm$ 0.5  $\mu$ g Hydrochloric Acid

Time after preparation, min.	Absorbancy due to arsenic(V) at specified wavelengths, wavelength in angstroms				
	2200	2300	2400	2500	2600
14	0.057	0.052	0.031	0.010	0.002
24	0.083	0.069	0.033	0.012	0.004
34	0.102	0.081	0.040	0.017	0.006
86	0.242	0.201	0.109	0.047	0.014







faster than the average rate of increase in the absorbancy of 0.000745  $\underline{f}$  arsenic(V) without arsenic(III) present (compare Table V-6, p. 55).

It is difficult to say whether or not the arsenic(III) was responsible for the faster growth, because the acid concentration was not exactly the same in the two experiments due to the substitution of arsenic(III) solution for some of the hydrochloric acid. Nevertheless, the influence of arsenic(III) on the arsenic(V) was not very great. Because it is believed that the dilution effect and the aging of arsenic(V) involve the same reactions, it is concluded that arsenic(V) ages at about the same rate whether or not arsenic(III) is present.

#### E. Dilution Effect in 7 $\underline{f}$ Hydrochloric Acid

##### 1. Arsenic(V)

It was found that the absorption spectrum of arsenic(V) in 6.98  $\underline{f}$  hydrochloric acid underwent changes similar to those observed in 10.9  $\underline{f}$  hydrochloric acid. An aged 0.1011  $\underline{f}$  arsenic(V) solution, 6.98  $\underline{f}$  in hydrochloric acid, was diluted to 0.00373  $\underline{f}$  with 6.98  $\underline{f}$  hydrochloric acid. The results are listed in Table V-9.

The absorbancy near 2300 A increased slowly during twenty-seven days of observation; the average rate of increase was  $1.31 \times 10^{-5}$  absorbancy units per minute over the first three days and  $1.10 \times 10^{-6}$  absorbancy units per minute over





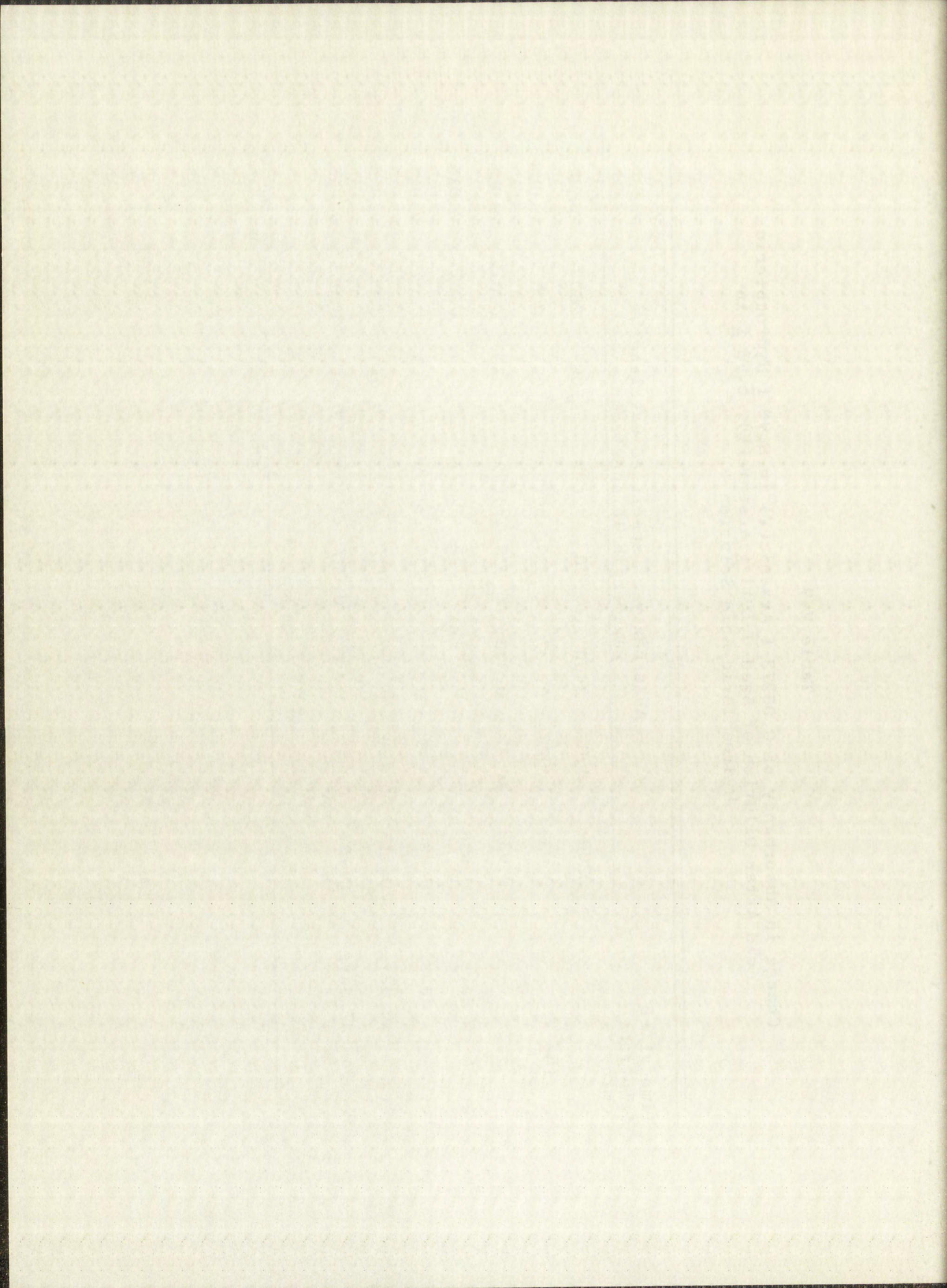


Table V-9

Change in Absorbancy of 0.00373 f Arsenic(V) in 6.98 f Hydrochloric  
 Acid After Dilution of Aged 0.1011 f Arsenic(V), 6.98 f in  
 Hydrochloric Acid Solution

Time after dilution, min.	Absorbancy at specified wavelengths, wavelength in angstroms									
	2200	2300	2400	2500	2600	2700	2800	3000		
10	0.033	0.038	0.037	0.039	0.029	0.023	0.017	0.008		
54	0.032	0.037	0.036	0.038	0.026	0.020	0.012	0.005		
4,486 (3 days)	0.088	0.097	0.085	0.068	0.042	0.026	0.017	0.013		
10,051 (7 days)	0.083	0.094	0.081	0.058	0.029	0.013	0.003	0.003		
14,525 (10 days)	0.117	0.120	0.096	0.067	0.032	0.015	0.004	0.005		
39,056 (27 days)	0.127	0.135	0.097	0.067	0.033	0.017	0.008	0.005		







the last twenty-four days. Both rates are slower than the corresponding average rates of growth after dilution in  $10.4 \pm 0.5$  f hydrochloric acid (see page 61). At all wavelengths the absorbancy of the arsenic(V) in  $6.98 \pm$  f hydrochloric acid was lower than the absorbancy of an equal concentration of arsenic(V) after dilution in  $10.4 \pm 0.5 \pm$  f hydrochloric acid.

The data suggest that arsenic(V) ages in  $7 \pm$  f hydrochloric acid as well as in  $11 \pm$  f hydrochloric acid.

## 2. Arsenic(III)

No slow hydrolysis of arsenic(III) in  $6.94 \pm$  f hydrochloric acid solution could be detected. An aged  $0.0985 \pm$  f arsenic(III) solution,  $6.94 \pm$  f hydrochloric acid, was diluted to  $0.0000490 \pm$  f with  $6.94 \pm$  f hydrochloric acid. The absorption spectrum between 2150 A and 2400 A did not change over twelve days.

## F. Dependence of the 2300 A Absorption Band of Arsenic(V) on Small Changes in Hydrochloric Acid Concentration

Small changes in the hydrochloric acid concentration of aged arsenic(V) solutions,  $10.9 \pm$  f in hydrochloric acid, were found to induce fairly large changes in the 2300 A absorption band of arsenic(V). These changes at 2300 A are summarized graphically in Figure V-12 on page 80. The hydrochloric acid concentration was increased about 1% by addition of hydrogen chloride to a solution; the acid concentration was



the following results were obtained:

1. The rate of reaction was found to be first order with respect to the concentration of the reactant.

2. The rate of reaction was found to be independent of the concentration of the catalyst.

3. The rate of reaction was found to be independent of the concentration of the solvent.

4. The rate of reaction was found to be independent of the concentration of the product.

5. The rate of reaction was found to be independent of the concentration of the reactant.

6. The rate of reaction was found to be independent of the concentration of the reactant.

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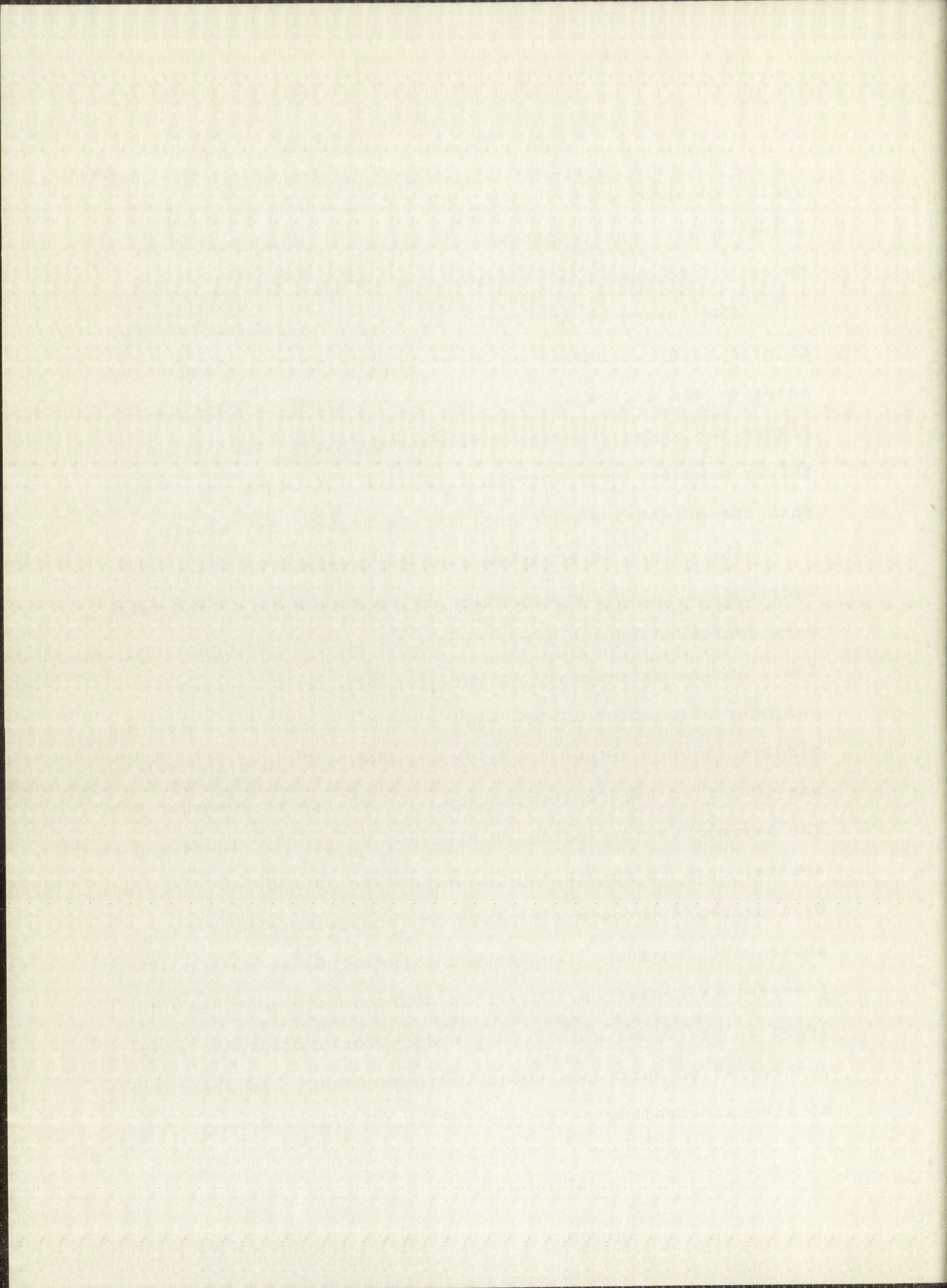


decreased about 1% by (1) removal of hydrogen chloride from solution with an air stream, (2) dilution with 9.90 f hydrochloric acid, and (3) dilution with water.

The change in absorbancy of arsenic(V) after the hydrochloric acid concentration of an aged 0.00373 f arsenic(V) solution was increased from 10.9 f to 11.0 f is plotted in Figure V-8. The absorbancy increased fairly rapidly for thirty minutes, went through a maximum 12% higher at 2300 A than the original absorption, and decreased very slowly.

The change in absorbancy of the arsenic(V) after the hydrochloric acid concentration of aged arsenic(V) solutions were decreased in the range from 0.9% to 2.3% is described below. In one experiment, the hydrochloric acid concentration was decreased about 1% by rapidly bubbling moist air for two minutes through an aged 0.00373 f arsenic(V) solution which was 10.9 f in hydrochloric acid. The change in absorbancy of the arsenic(V) is plotted in Figure V-9, p. 70. There was an initial drop in absorbancy (33% decrease at 2300 A) followed by a decrease through a minimum in about ninety minutes and a subsequent increase. In another experiment, an aged 0.00373 f arsenic(V) solution, 10.9 f in hydrochloric acid, was diluted 5% by volume with 9.90 f hydrochloric acid; the acid concentration decreased about 2.3%. The change in absorbancy at several wavelengths is plotted in Figure V-10, page 71.







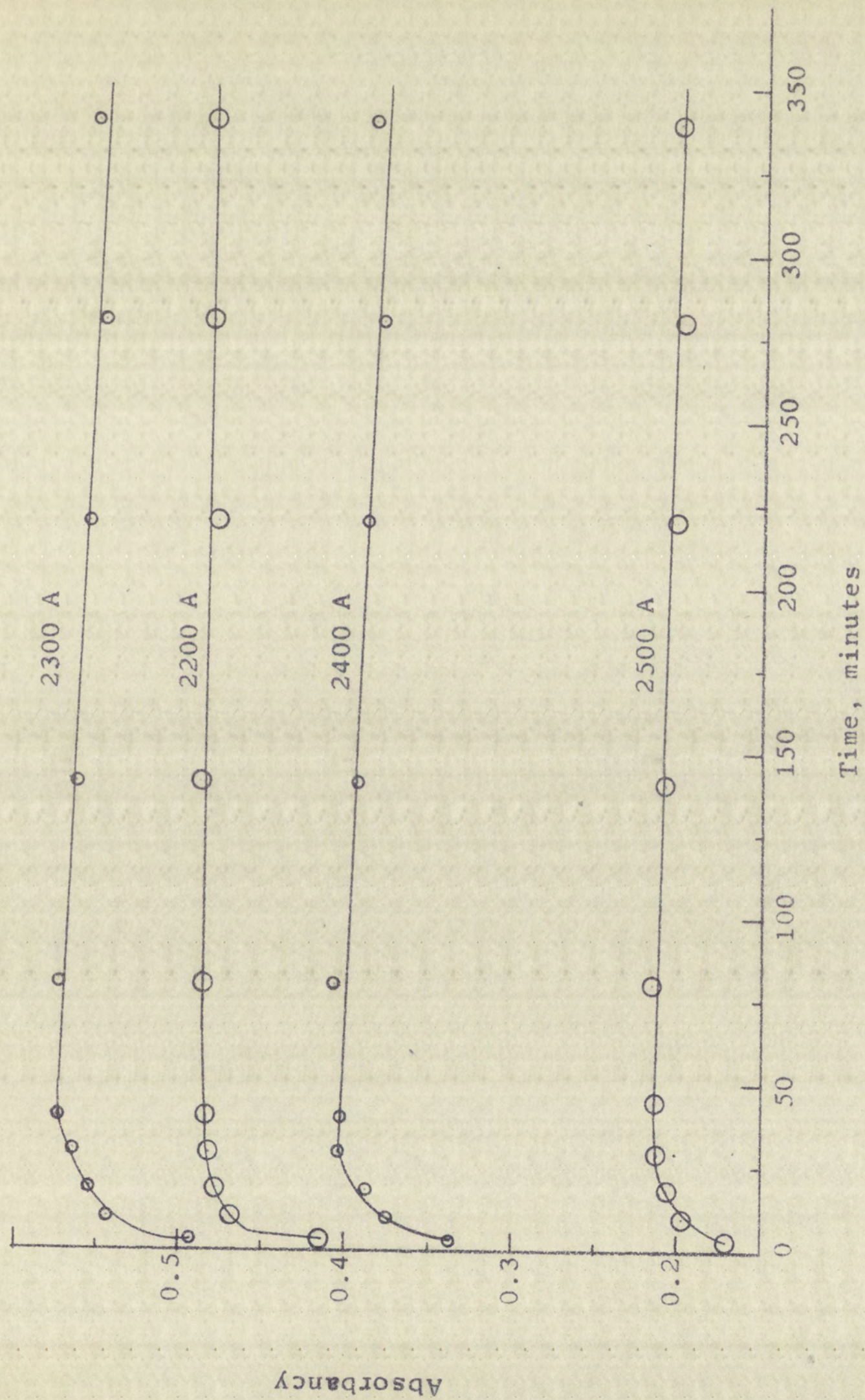
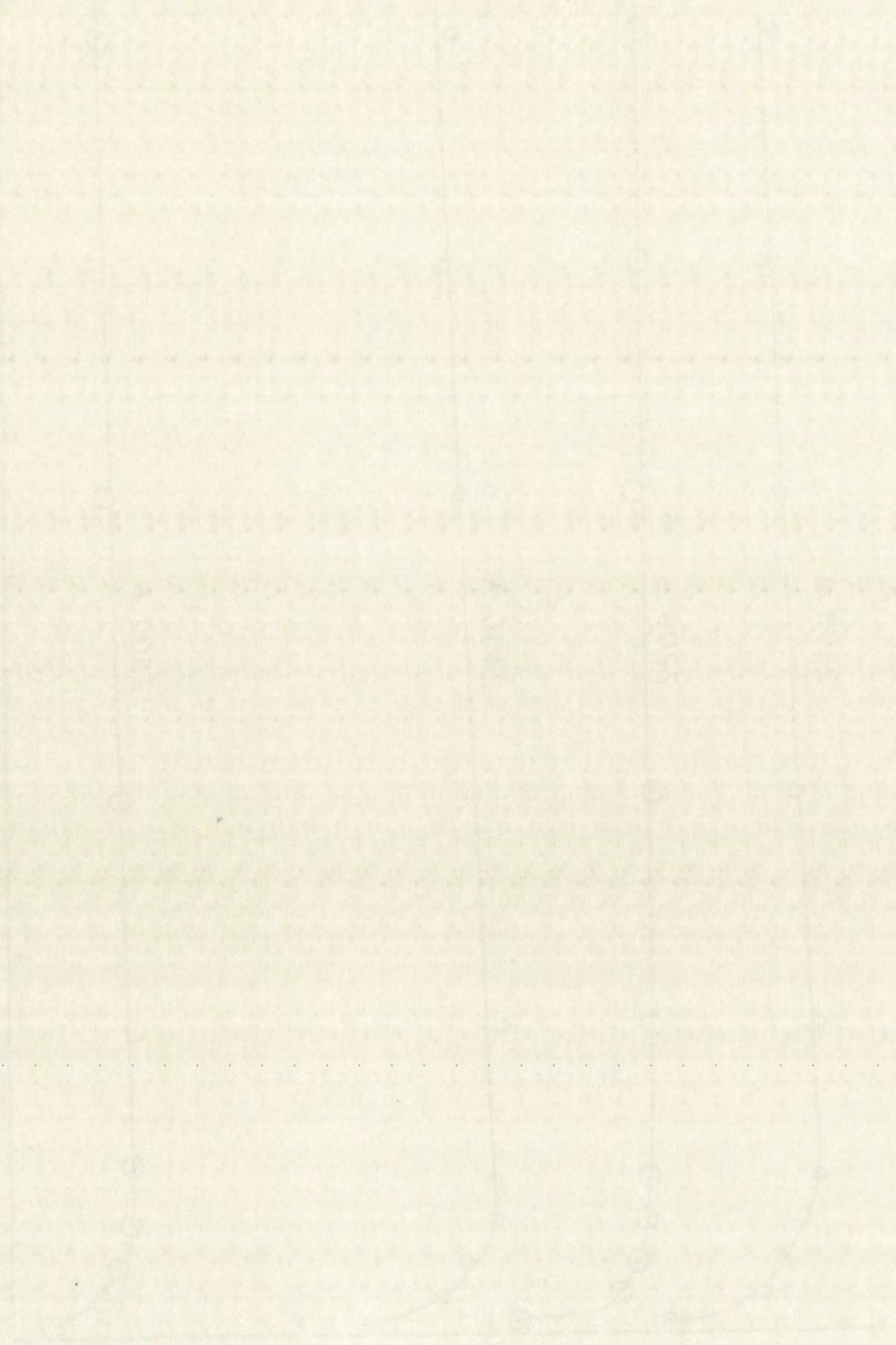


Figure V-8

Change in Absorbance of 0.00373 f Arsenic(V) after the Hydrochloric Acid Concentration of Aged 10.9 f Solution of Arsenic(V) Had Been Increased About 1% by Addition of Anhydrous Hydrogen Chloride







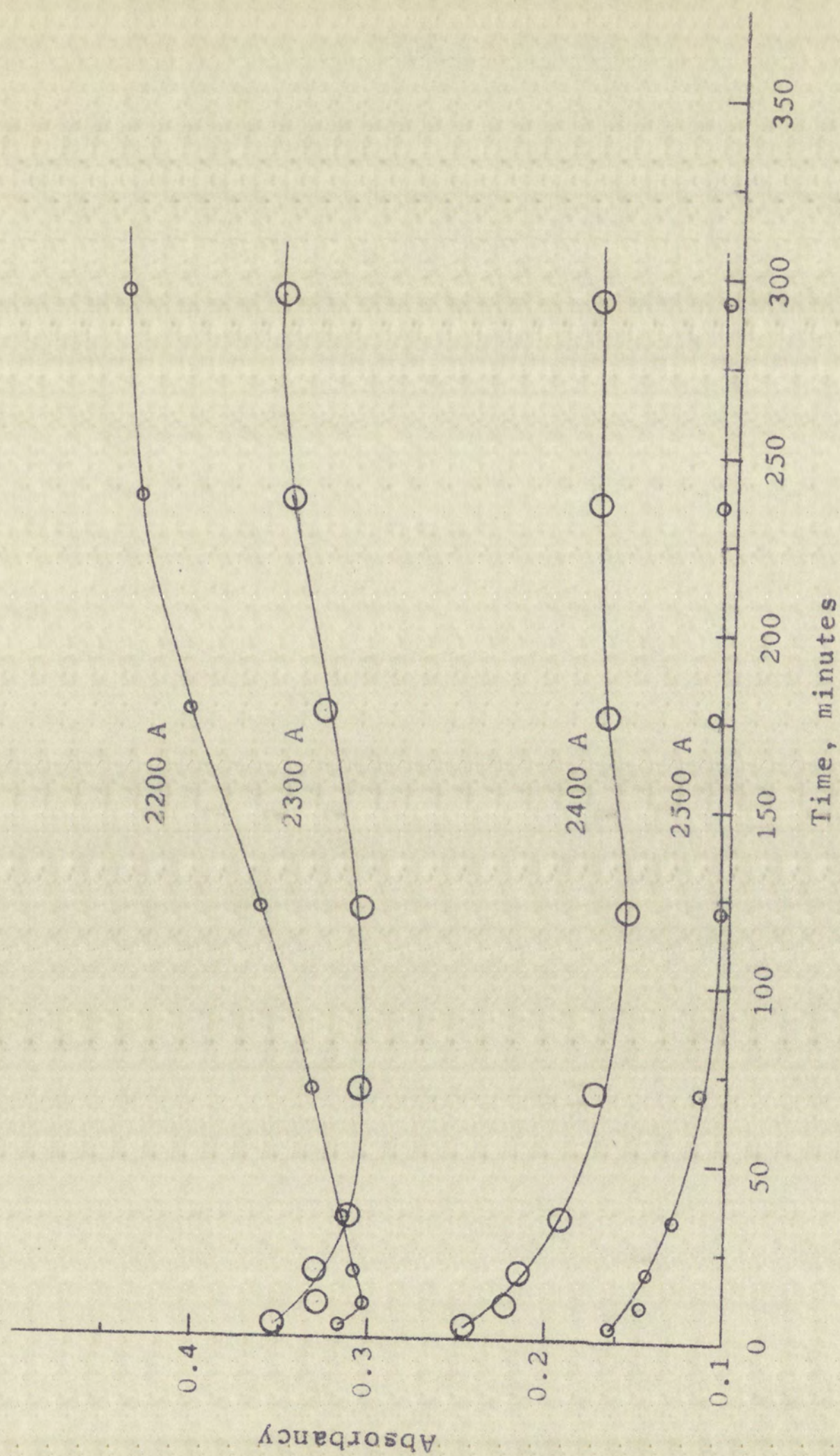
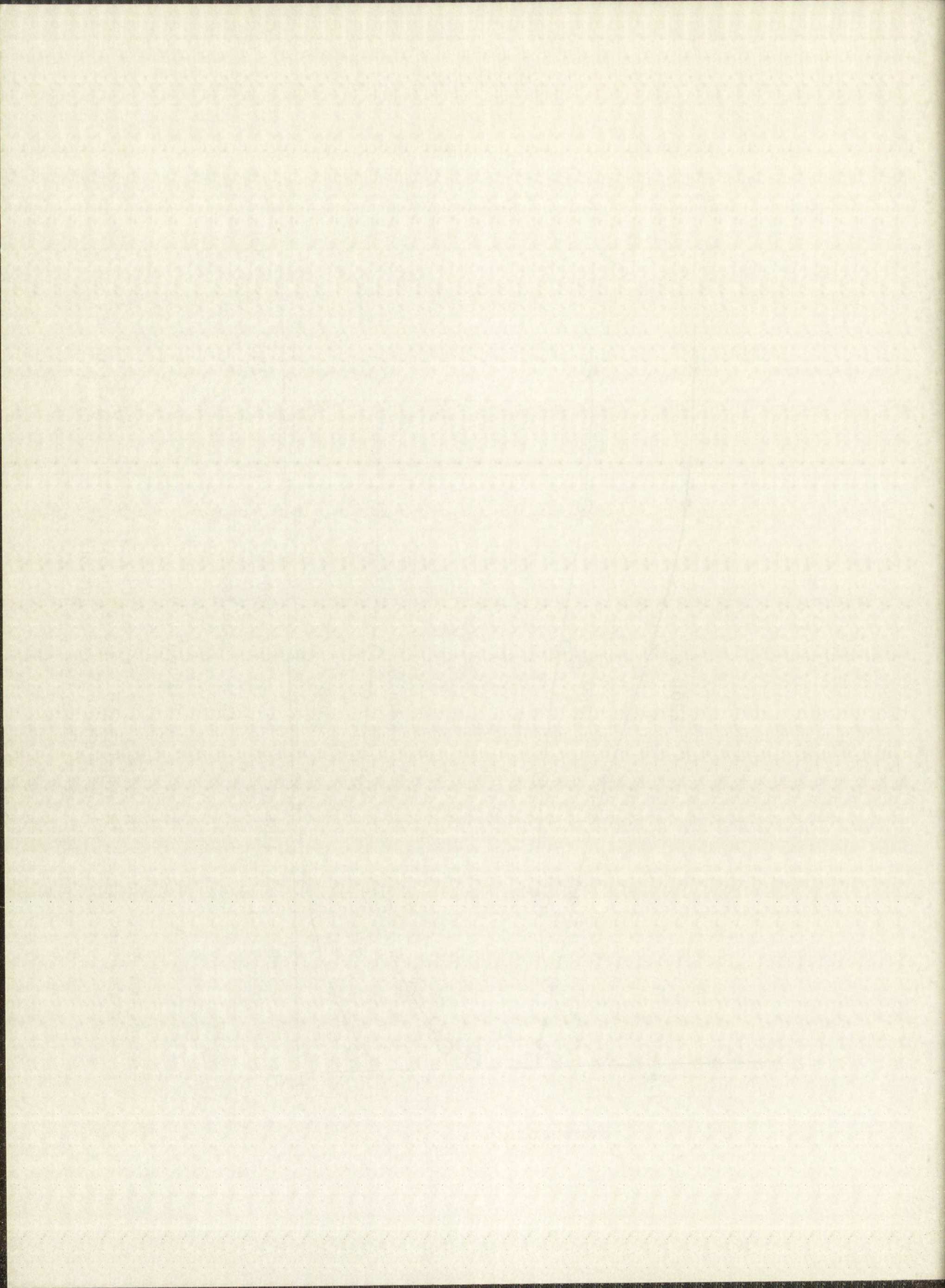


Figure V-9

Change in Absorbance of 0.00373 f Arsenic(V) after the Hydrochloric Acid Concentration of Aged 10.9 f Hydrochloric Acid Solution of Arsenic(V) had been Decreased about 1% by Removal of Hydrogen Chloride with an Air Stream







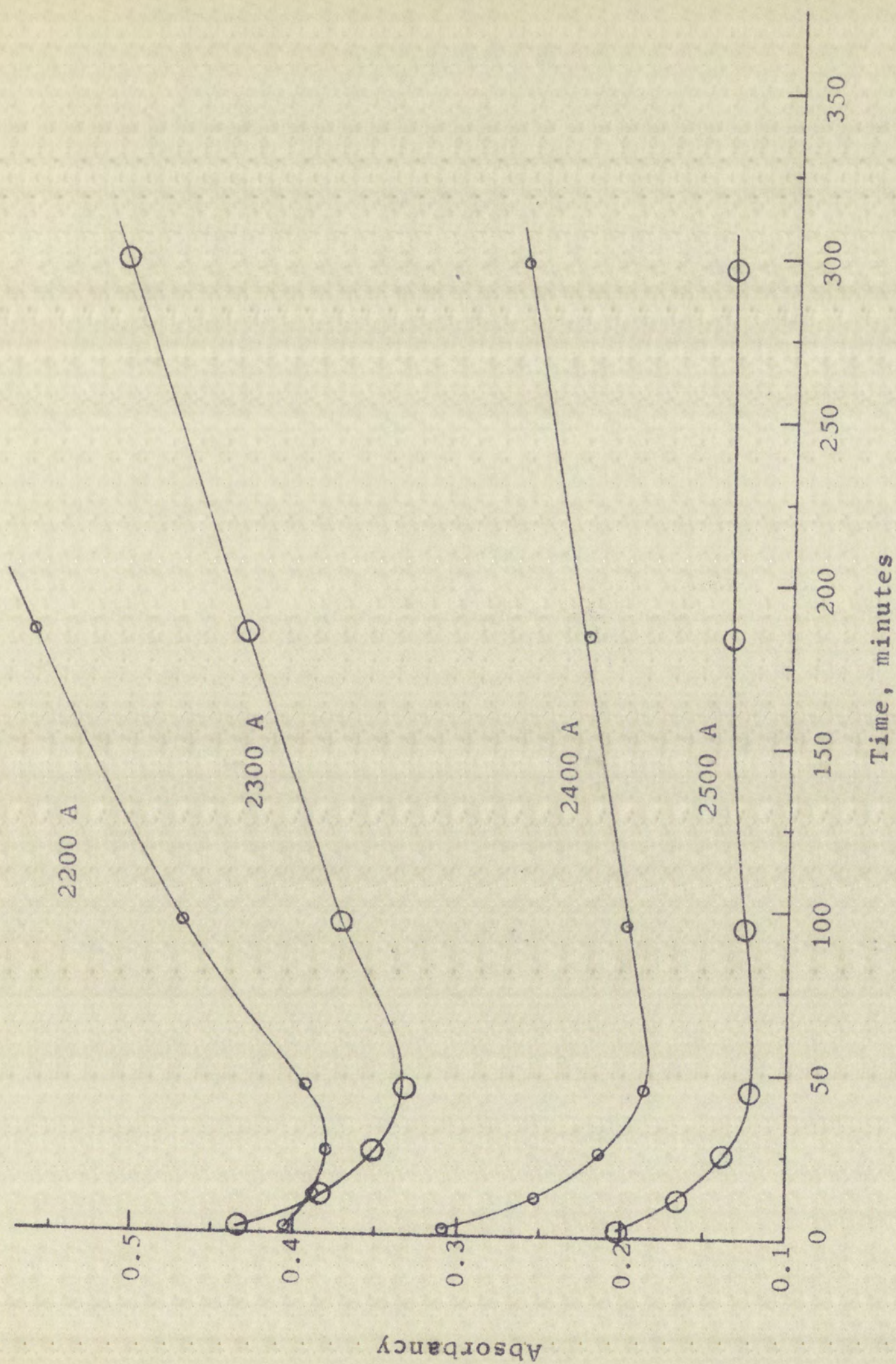


Figure V-10

Change in Absorbance of Arsenic(V) after 5% Dilution by Volume  
 (2.3% Decrease in Acid Concentration) of an Aged 10.9 f  
 Hydrochloric Acid Solution of 0.00373 f Arsenic(V)  
 with 9.90 f Hydrochloric Acid







At 2300 A, the absorbancy dropped 17% immediately after the change in acid concentration, then decreased through a minimum in forty-five minutes (37% below that of aged arsenic(V) at 2300 A), and returned to the original value in about five hours. In two other experiments, aged 0.0186  $\mu$  and aged 0.000745  $\mu$  arsenic(V) solutions, 10.9  $\mu$  in hydrochloric acid, were each diluted 0.5% by volume with water; the acid concentration decreased about 0.87%. The absorbancy dropped 5% and 12%, respectively, and remained approximately constant over ninety minutes.

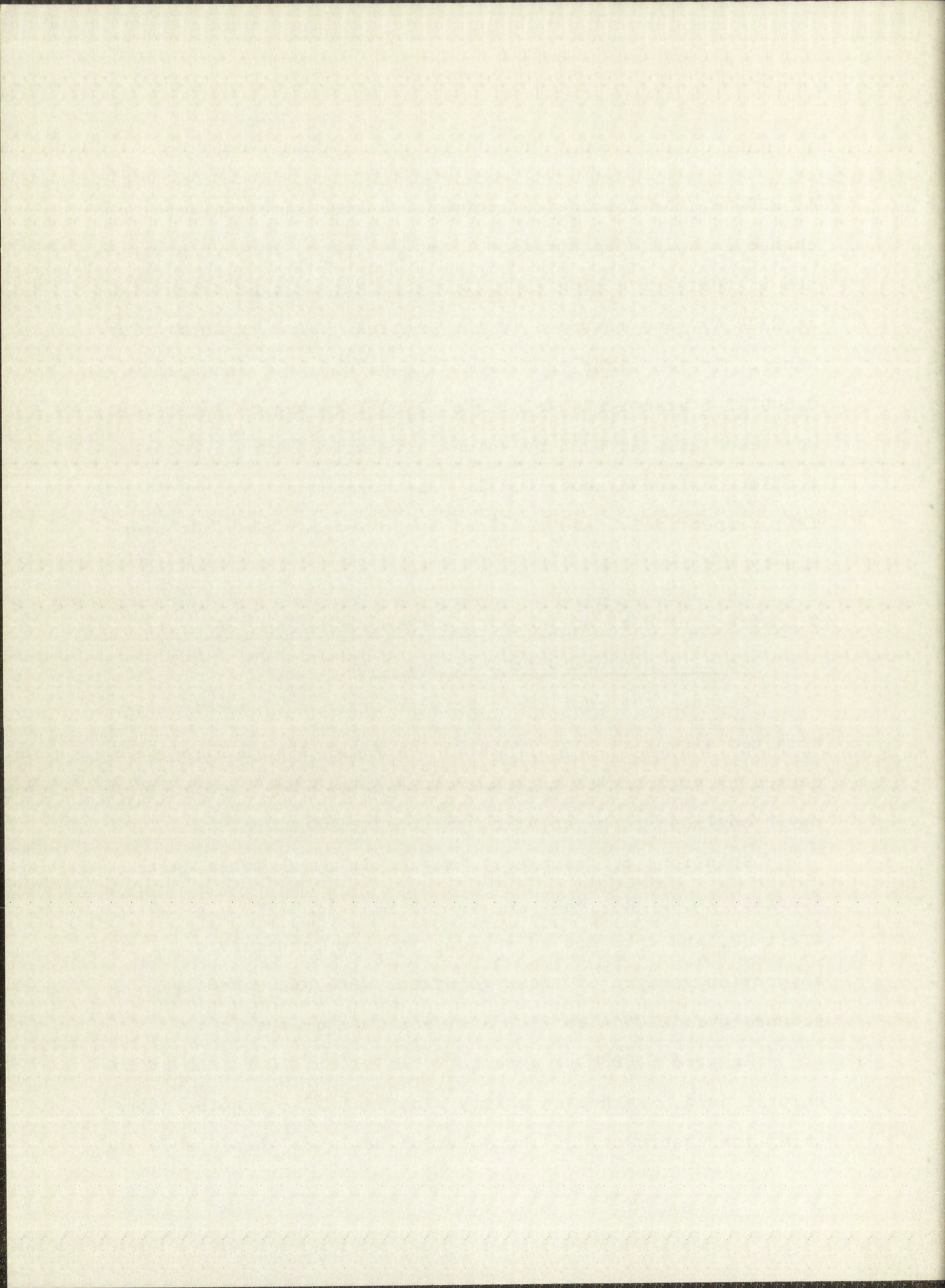
G. Effect of Heat on the 2300 A Absorption Band of Arsenic(V) in 11  $\mu$  Hydrochloric Acid Solution

Because the equilibria between arsenic(V) species are attained slowly at room temperature, any shift in equilibria caused by an increase in temperature should be "frozed in" by rapid cooling of the solution to room temperature.

Solutions of arsenic(V), sealed in pyrex tubes, were immersed in boiling water which was usually at 95°C at this altitude, and then cooled rapidly to room temperature. The absorption spectra of these solutions were subsequently scanned over 2200 A to 2600 A at room temperature.

An aged 0.00373  $\mu$  arsenic(V) solution, 10.9  $\mu$  in hydrochloric acid, was heated thirty minutes. Five minutes afterward, the absorbancy of the solution was more than double the







absorbancy of the unheated solution (see Table V-10). The absorbancy of the heated solution decreased at a moderate rate: after ninety-six minutes the absorbancy was only 7% higher than that of the unheated solution.

An aged 0.0186 f arsenic(V) solution, 10.9 f in hydrochloric acid, was diluted fivefold with 10.4 $\pm$ 0.5 f hydrochloric acid. Five minutes after dilution, a portion of the solution was heated twenty-five minutes at 95°C. For nearly two hours after the heated solution had been rapidly cooled, the absorbancy at 2300 A remained 0.283, whereas over the same period of time, the absorbancy of unheated solution increased from 0.109 to 0.142 at 2300 A. These values are to be compared with 0.524, which is the absorbancy at 2300 A of aged 0.00373 f arsenic(V) in 10.9 f hydrochloric acid (see Table V-10).

A portion of a freshly prepared 0.00410 f arsenic(V) solution, 10.9 f in hydrochloric acid, was heated one hour at 95°C. The absorbancy of the solution which was heated increased from 0.031 to 0.281 at 2300 A, whereas the absorbancy of the solution which was not heated increased from 0.031 to 0.051 at 2300 A over the same period of time. The absorbancy at 2300 A of aged 0.00373 f arsenic(V) in 10.9 f hydrochloric acid is 0.524 (see Table V-10).

It appears that not only are the equilibria among



the intensity of the absorption at the 2.13  $\mu$  band is a function of the concentration of the solution. The absorption at the 2.13  $\mu$  band is also a function of the temperature of the solution.

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Table V-10

Effect of Heat (30 minutes at 95°C) on the Absorbancy  
of Aged 0.00373  $\mu$  Arsenic(V), 10.9  $\mu$  in  
Hydrochloric Acid

	Absorbancy at specified wavelength, wavelength in angstroms				
	2200	2300	2400	2500	2600
Unheated solution	0.432	0.524	0.362	0.191	0.102
Heated Solution, time after heating:					
5 minutes	0.999	1.056	0.789	0.407	0.180
65 minutes	0.490	0.585	0.449	0.237	0.112
96 minutes	0.470	0.560	0.433	0.228	0.108







arsenic(V) species shifted by an increase in temperature toward the species which absorb light at 2300 A, but the rate of the aging process is speeded up.

#### H. Summary and Discussion of Spectrophotometric Observations

##### 1. Arsenic(III)

No spectrophotometric evidence was found which would indicate that arsenic(III) in  $10.4 \pm 0.5$  f or  $6.94$  f hydrochloric acid ages; the absorption bands of arsenic(III) did not change with time.

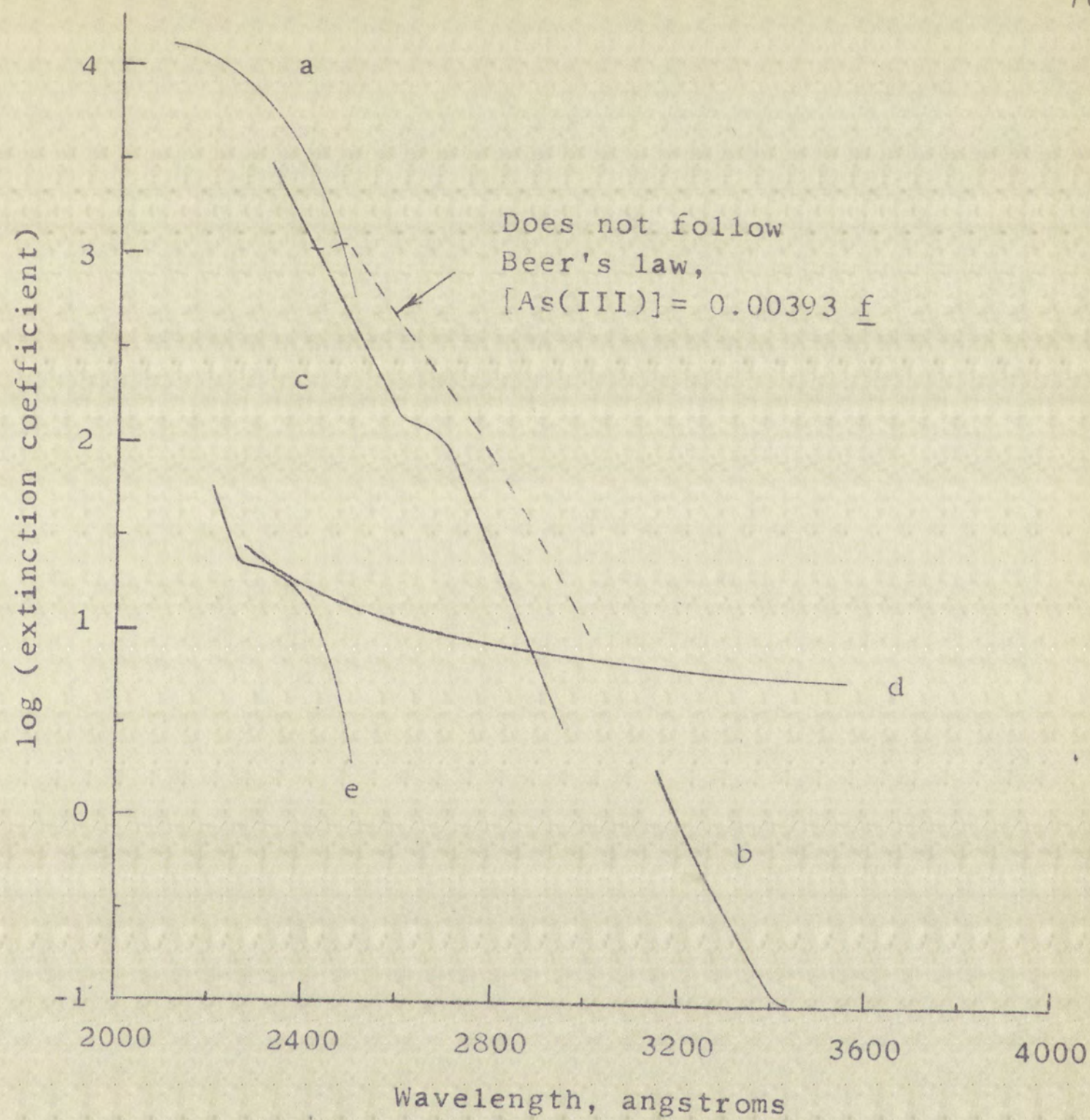
Beer's law is obeyed in the vicinity of the 2130 A absorption band; the maximum apparent extinction coefficient is  $12,000 \pm 600$  l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> (see Figure V-11). The other absorption band did not appear to follow Beer's law; the peak shifted from 2470 A to 2600 A with increase in the concentration of arsenic(III). The maximum apparent extinction coefficient of this band increased from 260 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> to 1,150 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> with decrease in concentration of arsenic(III) from  $1.97 \times 10^{-4}$  f to  $3.93 \times 10^{-5}$  f.

The equilibrium between arsenic(III) species in hydrochloric acid solution has been quantitatively studied by Arcand.<sup>34</sup> From his data one calculates that approximately 98% of the arsenic(III) in  $10.4$  f hydrochloric acid exists as arsenic trichloride. It follows, therefore, that the maximum extinction coefficient for arsenic trichloride is about









- a.  $As(III)$  in  $10.4 \pm 0.5 \text{ f HCl}$ , this dissertation
- b.  $As(III)$  in conc.  $HCl$ , Whitney and Davidson<sup>35</sup>
- c.  $AsCl_3$  in hexane, Mohler and Polya<sup>37</sup>
- d.  $AsCl_3$  in  $1 \text{ f HCl}$ , Macbeth and Maxwell<sup>40</sup>
- e.  $As(III)$  in  $\leq 0.1 \text{ f HCl}$ , Ghosh and Bisvas<sup>41</sup>

Figure V-11

Ultraviolet Absorption Spectra  
 of Arsenic(III)





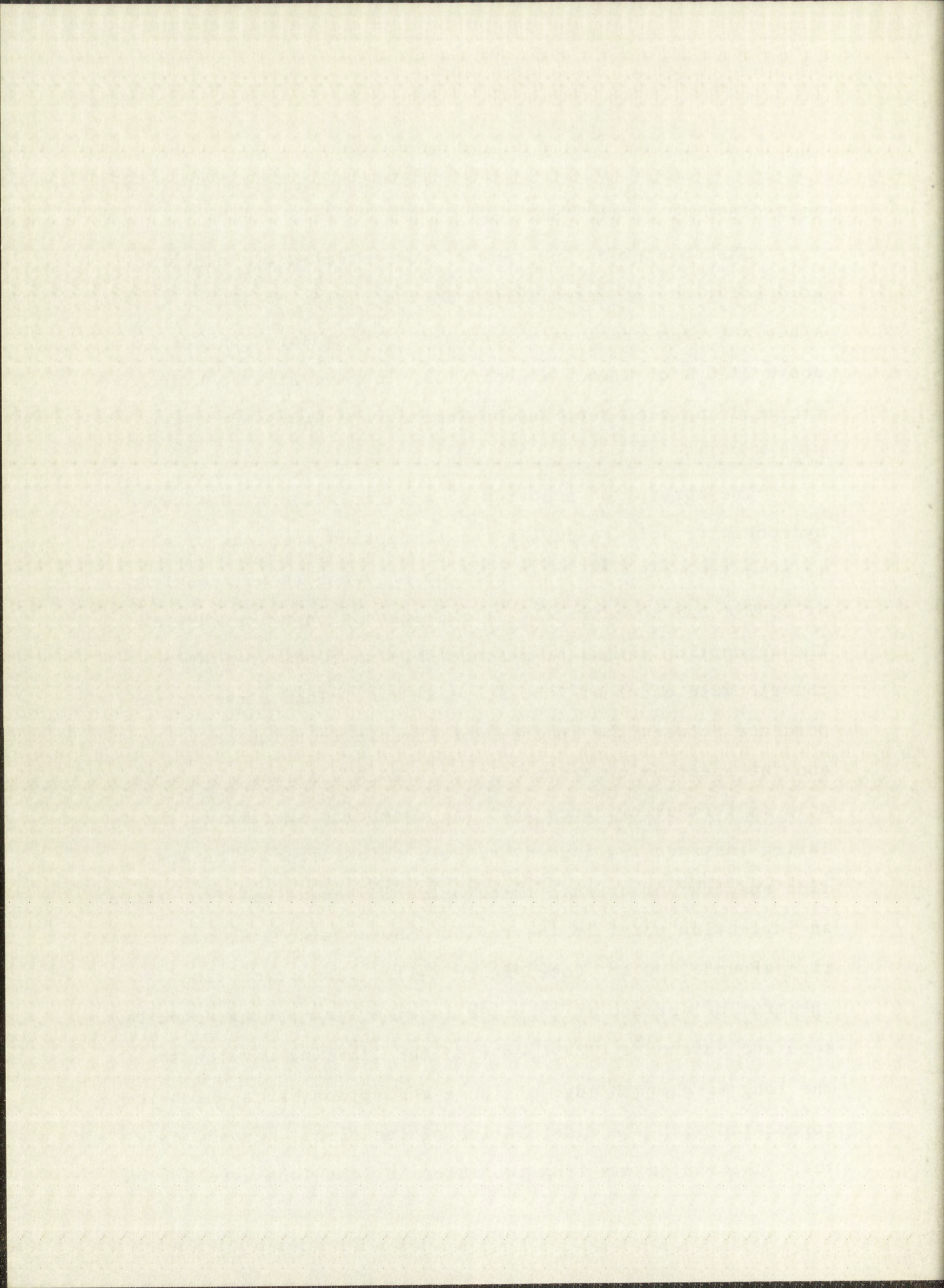


$11,760 \pm 600$  l. g.-at. $^{-1}$  cm. $^{-1}$  at 2130 A.

The absorption spectrum of concentrated hydrochloric acid solutions of arsenic(III) in the region of 2200 A to 3000 A has not been previously reported. The absorption spectrum above 3150 A of 0.76 f arsenic(III) in concentrated hydrochloric acid has been reported by Whitney and Davidson<sup>35</sup> (see Figure V-11).

The absorption spectrum of arsenic(III) in  $10.4 \pm 0.5$  f hydrochloric acid resembles the absorption spectrum of arsenic trichloride vapor.<sup>36</sup> The spectrum of vapor shows a maximum at 2547 A and an extremely strong absorption below 2390 A. The absorption maxima of arsenic(III) in  $10.4 \pm 0.5$  f hydrochloric acid occur at 2550 A and 2130 A. This close correspondence between the spectrum of arsenic trichloride vapor and the spectrum of arsenic(III) in  $10.4 \pm 0.5$  f hydrochloric acid is further evidence that the absorbing species in the latter instance is, indeed, arsenic trichloride. The absorption spectrum of arsenic trichloride in hexane solution shows an inflection point in the region 2550 A to 2650 A, and a steep rise around 2400 A<sup>37</sup> (see Figure V-11). The absorption spectrum of arsenic trichloride in ether was photographed by Kato and Someno<sup>38</sup>. They reported the limiting wavelength of the long wavelength edge of three absorption bands which they correlated with the dissociation of the first, second, and third chlorine atoms from the molecule; the long wavelengths







limits were 2760 A, 2590 A, and 2439 A, respectively. Long wavelength limits of the absorption bands of arsenic trichloride vapor were reported by Jan-Khan and Samuel<sup>36</sup> to be 2687 A and 2475 A. They referred to an investigation by Trivedi<sup>39</sup> wherein a long wavelength limit of an absorption band of arsenic trichloride was found to be 3466 A.

Macbeth and Maxwell<sup>40</sup> studied the absorption spectrum of 0.01 f arsenic trichloride in 1 f hydrochloric acid solution. They observed the absorbancy to increase fairly rapidly near 2270 A (see Figure V-11, p. 76). The extinction coefficient increased from 5 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> to 30 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> with decreasing wavelength between 3570 A and 2270 A. No doubt the arsenic trichloride was hydrolyzed considerably in 1 f hydrochloric acid. It can be calculated from the equilibrium constants determined by Arcand<sup>34</sup> that  $10^{-7}\%$  of the arsenic was present as arsenic trichloride. The absorption of arsenic trichloride in 1 f hydrochloric acid resembles that of an aqueous arsenious acid solution. Ghosh and Bisvas<sup>41</sup> investigated the ultraviolet absorption spectrum of various acids and their salts in aqueous solution  $\leq 0.1$  f in hydrochloric acid. The maximum extinction coefficient of arsenious acid was about 5.2 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> at about 2450 A (see Figure V-11). Their investigation followed the work of Wright<sup>42,43</sup> and other investigators who showed that the absorption



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spectrum of a weak acid generally differs from that of its salt. Wright<sup>42</sup> found that aqueous 0.1 f arsenious acid solution absorbed light at shorter wavelengths than aqueous 0.1 f sodium arsenite solution. The absorption spectrum of aqueous 1 f arsenious acid was studied by Goldfinger and von Schweinitz<sup>44</sup>; the long wavelength limit of the spectrum was found to be 2680 Å for  $\text{H}_2\text{AsO}_3^-$  and 2800 Å for  $\text{HAsO}_3^{=}$ .

## 2. Arsenic(V)

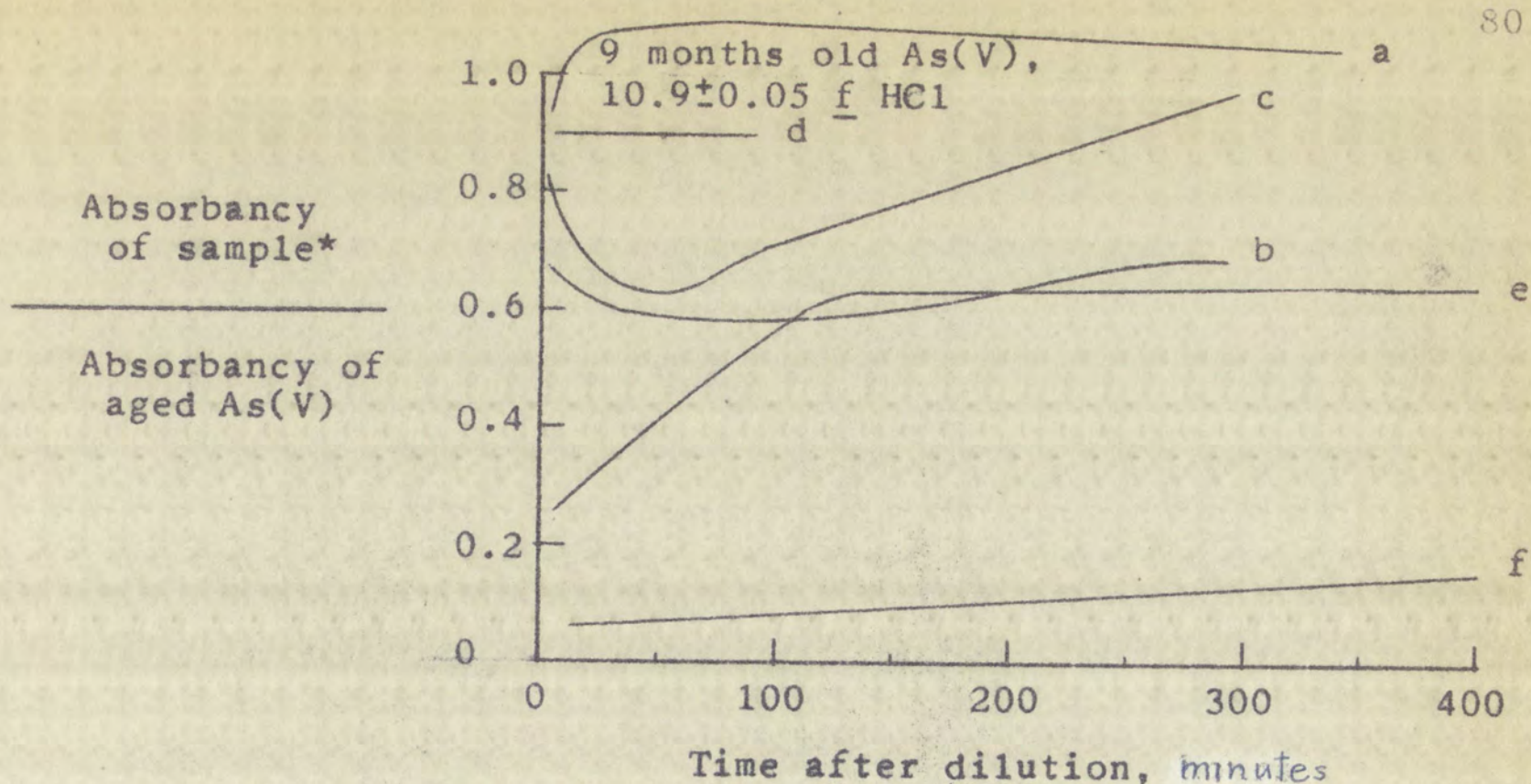
Aging of arsenic(V) in  $10.4 \pm 0.5$  f hydrochloric acid was evidenced by the slow growth of the 2300 Å absorption band. At room temperature, based upon the absorbancy of nine-months-old arsenic(V) solutions, the absorbancy of freshly prepared 0.00410 f arsenic(V) increased from 6%, in thirteen minutes, to 51%, in nineteen days (see curve f in Figure V-12). The 2700 Å absorption band showed no indication of aging.

A comparison of nine-months-old arsenic(V) solutions revealed that the 2700 Å absorption band obeyed Beer's law. The maximum apparent extinction coefficient was about 2 to 16 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> over a concentration range of 0.0090 f to 0.126 f arsenic(V) (see page 43). The 2300 Å absorption band of nine-months-old arsenic(V) solution did not follow Beer's law. The maximum apparent extinction coefficient at 2300 Å increased from 52 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> to 378 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> with decreasing concentration of arsenic(V) from  $1.86 \times 10^{-2}$









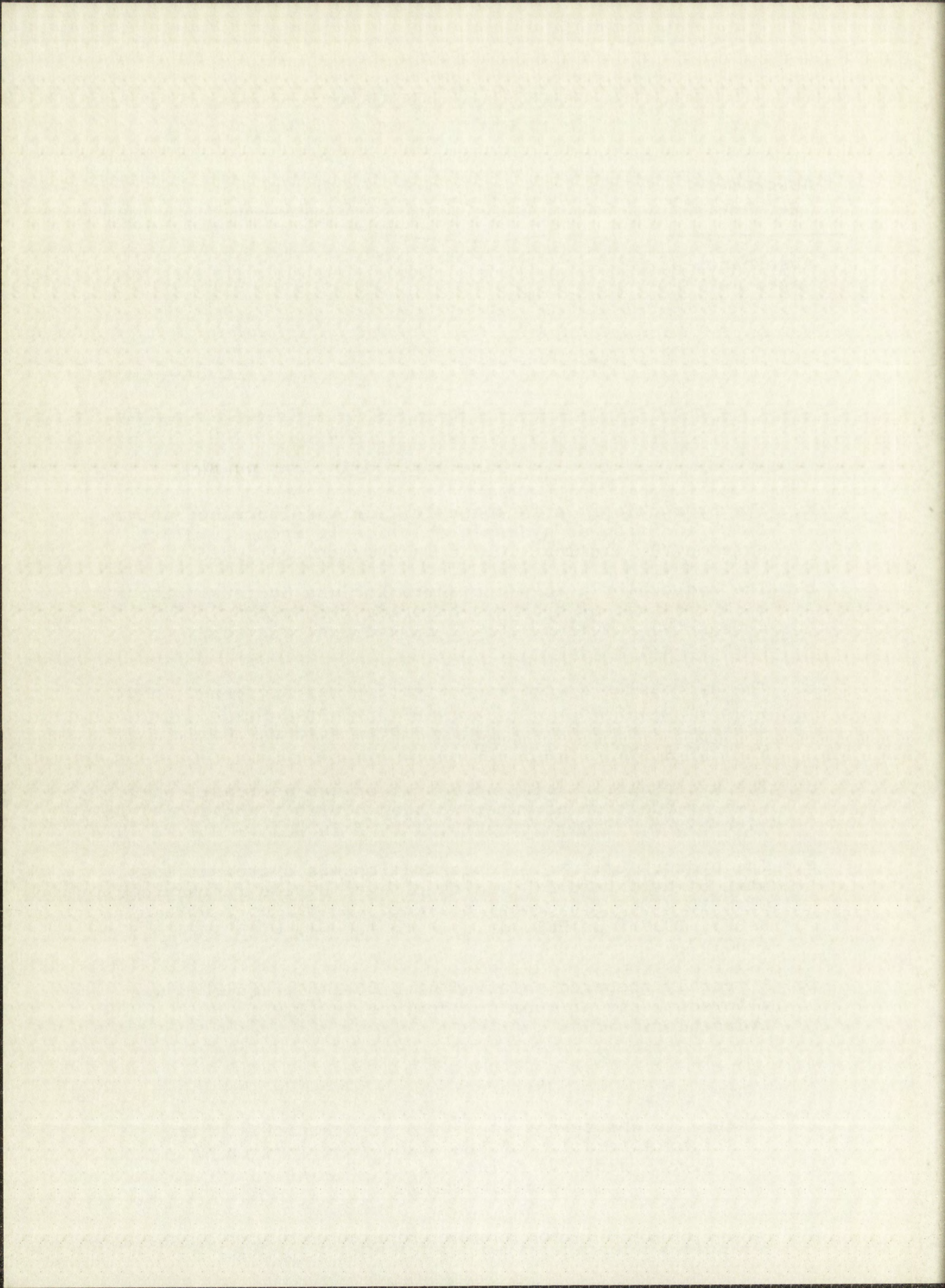
- a. The hydrochloric acid concentration was increased about 1% by addition of hydrogen chloride to aged 0.00373  $\bar{f}$  arsenic(V) solution, 10.9  $\bar{f}$  in hydrochloric acid.
- b. The hydrochloric acid concentration was decreased about 1% by removal of hydrogen chloride from aged 0.00373  $\bar{f}$  arsenic(V) solution, 10.9  $\bar{f}$  in hydrochloric acid, with an air stream.
- c. The hydrochloric acid concentration was decreased about 2.3% by dilution ( 5% by volume) of aged 0.00373  $\bar{f}$  arsenic(V) with 9.90  $\bar{f}$  hydrochloric acid (20 ml. 0.00373  $\bar{f}$  As(V) + 1 ml. HCl).
- d. The hydrochloric acid concentration was decreased about 0.9% by addition of water to aged 0.0186  $\bar{f}$  arsenic(V) solution (20 ml. 0.0186  $\bar{f}$  As(V), 10.9  $\bar{f}$  in HCl, + 0.1 ml. H<sub>2</sub>O).
- e. The hydrochloric acid concentration was decreased less than 8% by fivefold dilution of aged 0.0186  $\bar{f}$  arsenic(V) with 10.4±0.5  $\bar{f}$  hydrochloric acid (20 ml. of 0.0186  $\bar{f}$  As(V), 10.9  $\bar{f}$  in HCl, diluted to 100 ml. with 10.4±0.5  $\bar{f}$  HCl).
- f. A freshly prepared solution of 0.00410  $\bar{f}$  arsenic(V) was allowed to age at room temperature in 10.9  $\bar{f}$  hydrochloric acid.

Figure V-12

Change in Absorbance at 2300 Å of Arsenic(V) after  
Slight Alteration of the Acid Concentration of  
Aged Arsenic(V) Solutions, 10.9  $\bar{f}$  in  
Hydrochloric Acid

\* Ratio calculated for sample and aged solution of the same arsenic(V) concentration.



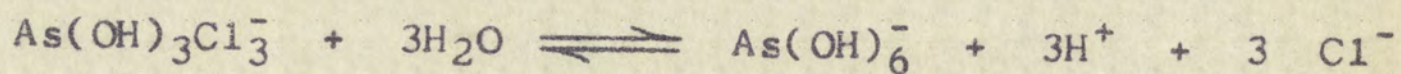




$\underline{f}$  to  $7.45 \times 10^{-4} \underline{f}$ .

The 2300 A absorption band of aged arsenic(V) solutions proved to be extremely sensitive to hydrochloric acid concentration. A small decrease (about 1%) in the acid concentration generally caused a rapid drop in absorbancy (up to 33% at 2300 A) followed by a slow change over several hours. An increase of 1% in the acid concentration caused a gradual increase in absorbancy (12% at 2300 A) for a short time and a subsequent slow decrease over several hours. These changes are summarized in Figure V-12 (see curves a, b, and c). Small dilution of aged arsenic(V) solutions with water, however, caused a rapid drop in absorbancy but no subsequent changes over ninety minutes (see curve d). Fivefold dilution of aged arsenic(V), such that the hydrochloric acid concentration decreased no more than 8% of its original value, resulted in a rapid drop in absorbancy followed by a gradual increase which was moderately fast for a few hours and then very slow for weeks (see curve e).

The extreme sensitivity of this system to the concentration of hydrochloric acid may be explained by assuming that the reactions are hydrolytic in nature. For example, consider the hypothetical reaction:





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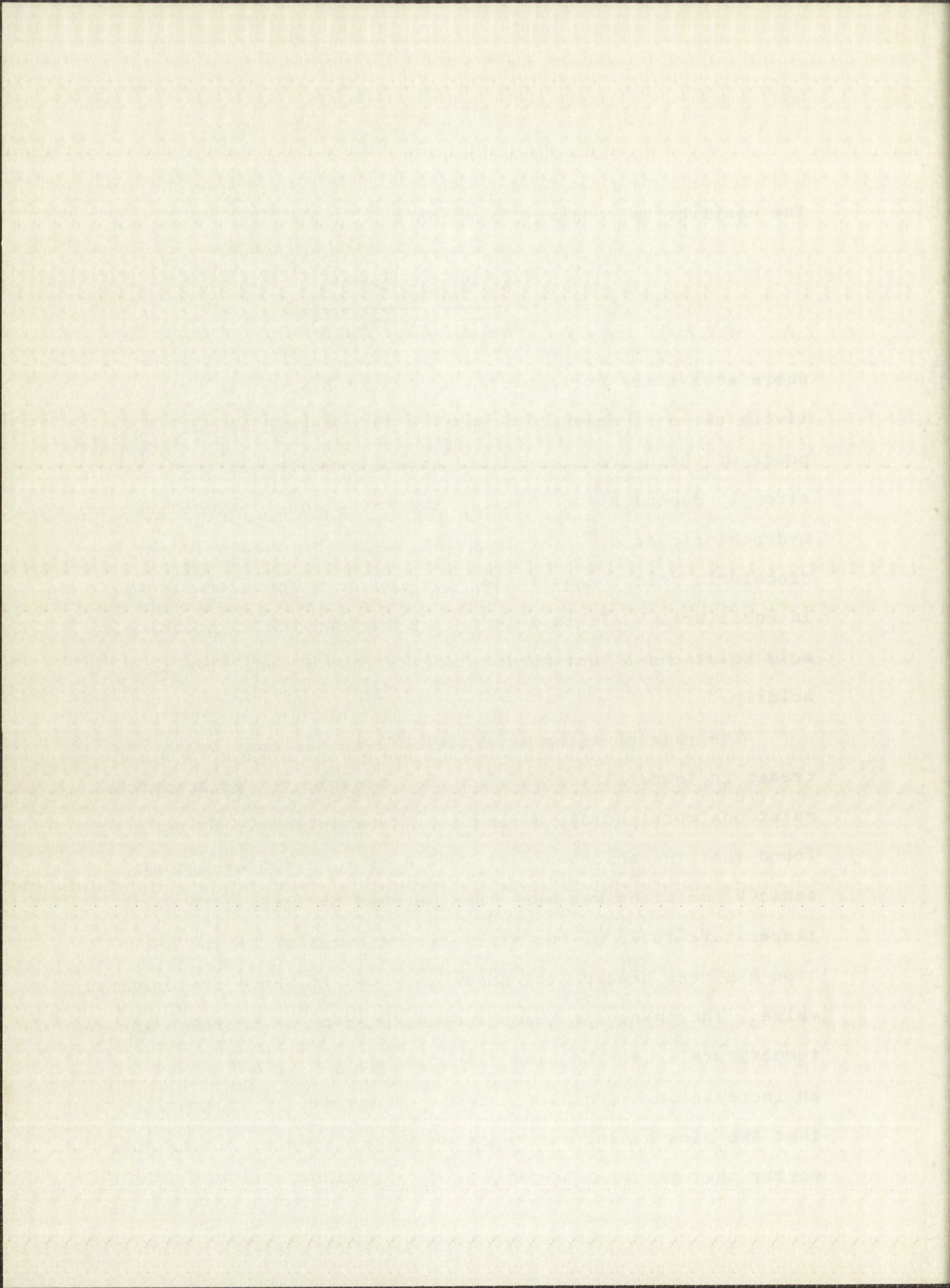
The equilibrium constant is given by

$$K = \frac{(a_{\text{As}(\text{OH})_6^-})(a_{\text{HCl}})^6}{(a_{\text{As}(\text{OH})_3\text{Cl}_3^-})(a_{\text{H}_2\text{O}})^3}$$

where activities are represented by the symbol "a". The activity ratio of arsenic(V) species is governed by the sixth power of the hydrochloric acid activity which, in turn, is strongly dependent on the acid concentration in concentrated hydrochloric acid.<sup>45</sup> As a result, a slight change in the hydrochloric acid concentration can induce a considerable shift in equilibrium. It is interesting to note that hydrochloric acid solutions of antimony(V) are extremely sensitive to acidity.<sup>4</sup>

The rate of aging of arsenic(V) is hastened by an increase in temperature; it might be possible to age arsenic(V) solutions more rapidly by heating the solutions. It was found that the absorbancy at 2300 Å of nine-months-old arsenic(V) solution was more than doubled by increasing the temperature to 95°C, but sixty-five minutes after the solution had been heated, the absorbancy was 7% above its original value. The change in absorbancy induced by an increase in temperature is in the same direction as the change caused by an increase in hydrochloric acid concentration, indicating that the slow hydrolysis reaction is exothermic. It is noteworthy that the slow hydrolysis of antimony(V) in hydrochloric





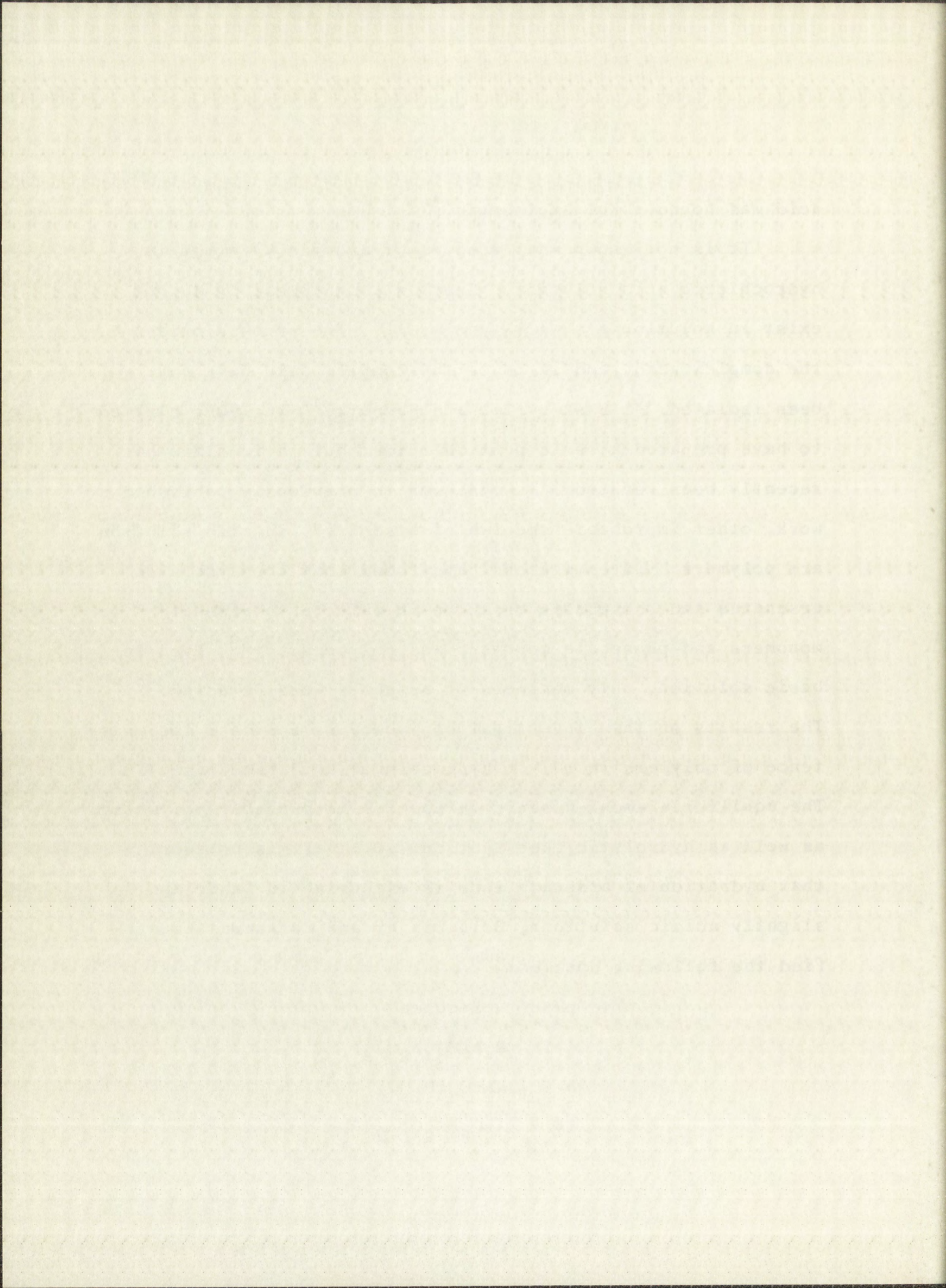


acid was found to be exothermic.<sup>4</sup>

It is not known what species of arsenic(V) exist in hydrochloric acid solution. Species which probably do not exist in solution are  $\text{AsCl}_5$  and  $\text{AsCl}_6^-$ . The pentachloride, the complex acid, and salts of the complex acid have never been isolated.<sup>46</sup> Baskerville and Bennett,<sup>47</sup> in 1902, claimed to have prepared arsenic pentachloride, but their claim has recently been refuted.<sup>11</sup> According to previously published work, other improbable species of arsenic(V) in acid solution are polymers. Investigators have found that copolymers of arsenates and phosphates break up in water into arsenate monomers and phosphate monomers and polymers.<sup>32,33</sup> Even in basic solution, only monomers of arsenate were detected.<sup>48,49</sup> The results of this investigation, however, indicate the existence of polymers in 10.9  $\text{f}$  hydrochloric acid (see page 47). The equilibria among arsenic(V) species is probably polymeric as well as hydrolytic (see Section V.I.). It is noteworthy that hydration of arsenate ions is extensive in basic and slightly acidic solutions; Brintzinger and Ratanarat identified the following species:<sup>49</sup>

pH	Species
4-5	$\text{H}_2\text{AsO}_4(\text{H}_2\text{O})_2^-$
8-10	$\text{HAsO}_4(\text{H}_2\text{O})_6^-$
14	$\text{AsO}_4(\text{H}_2\text{O})_{12}^{3-}$





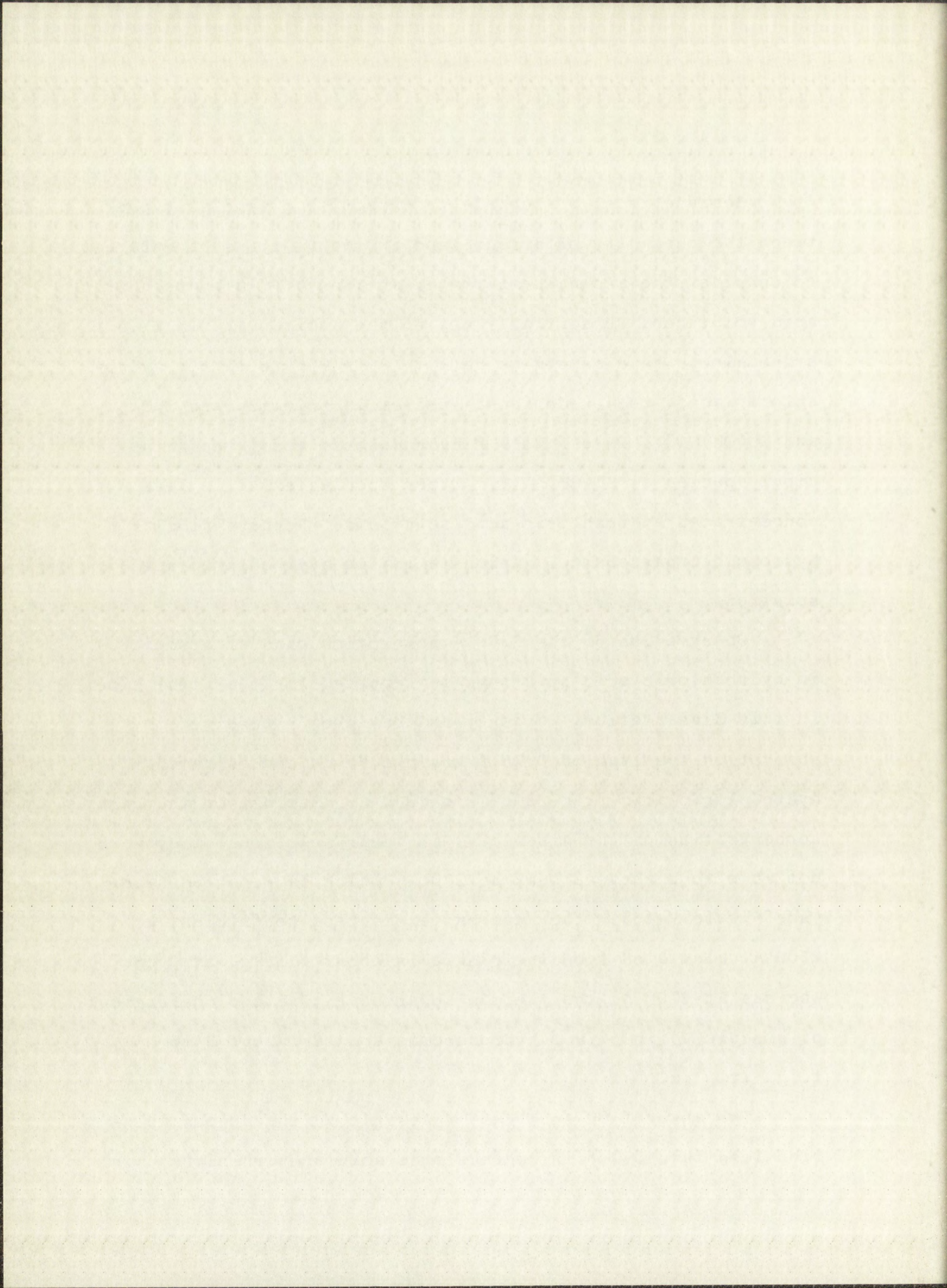


Because it is reasonable to expect some similarity between the chemistry of arsenic and antimony, it is of interest to consider the known chemistry of antimony(V) in hydrochloric acid solutions. Essentially all of the antimony(V) in 11.5 f hydrochloric acid exists as  $\text{SbCl}_6^-$ .<sup>50</sup> In 9 f to 11.5 f hydrochloric acid, the predominant species in solution are  $\text{SbCl}_6^-$  and  $\text{Sb(OH)Cl}_5^-$ . In 6 f to 9 f hydrochloric acid, the principal species is  $\text{Sb(OH)}_2\text{Cl}_4^-$ . Other species exist in less concentrated hydrochloric acid solutions. Perhaps similar hydroxochloroarsenate(V) anions exist in hydrochloric acid solutions.

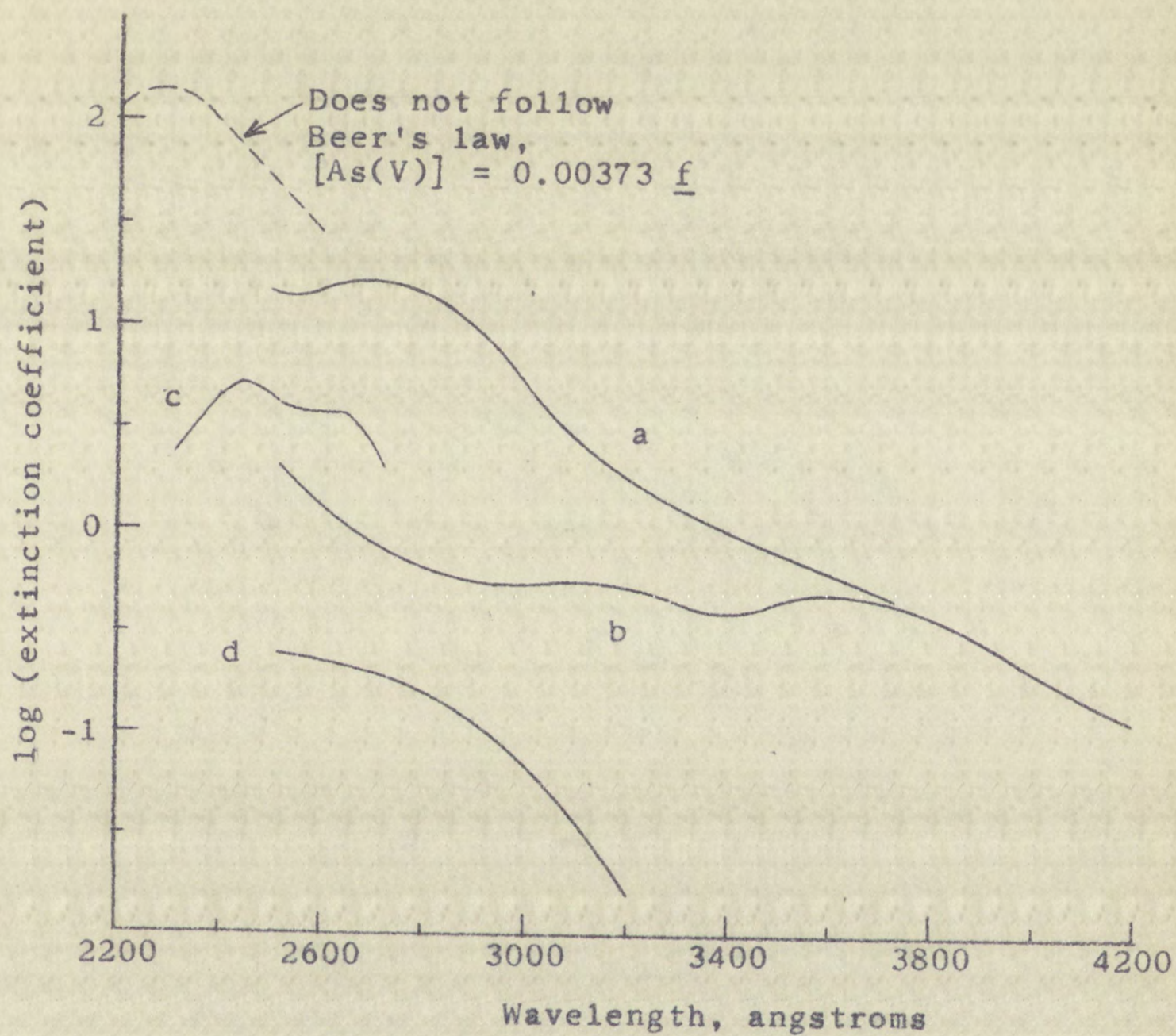
Observation of the 2300 A absorption band of arsenic(V) in hydrochloric acid solutions is reported for the first time in this dissertation. Whitney and Davidson<sup>35</sup> observed the absorption spectrum of 0.76 f arsenic(V) in concentrated hydrochloric acid from 2500 A to 4300 A. Because of the high concentration of the arsenic(V) in their solutions, they were not able to observe a peak at 2700 A which is reported here (see Figure V-13). The apparent extinction coefficient at 2700 A calculated from their data is about 1 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup>; whereas at 2700 A, the maximum apparent extinction coefficient of arsenic(V) in 10.9 f hydrochloric acid is about 2 to 16 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup>.

The absorption spectrum of arsenic(V) in aqueous solution less than 0.1 f in hydrochloric acid and arsenic(V) was





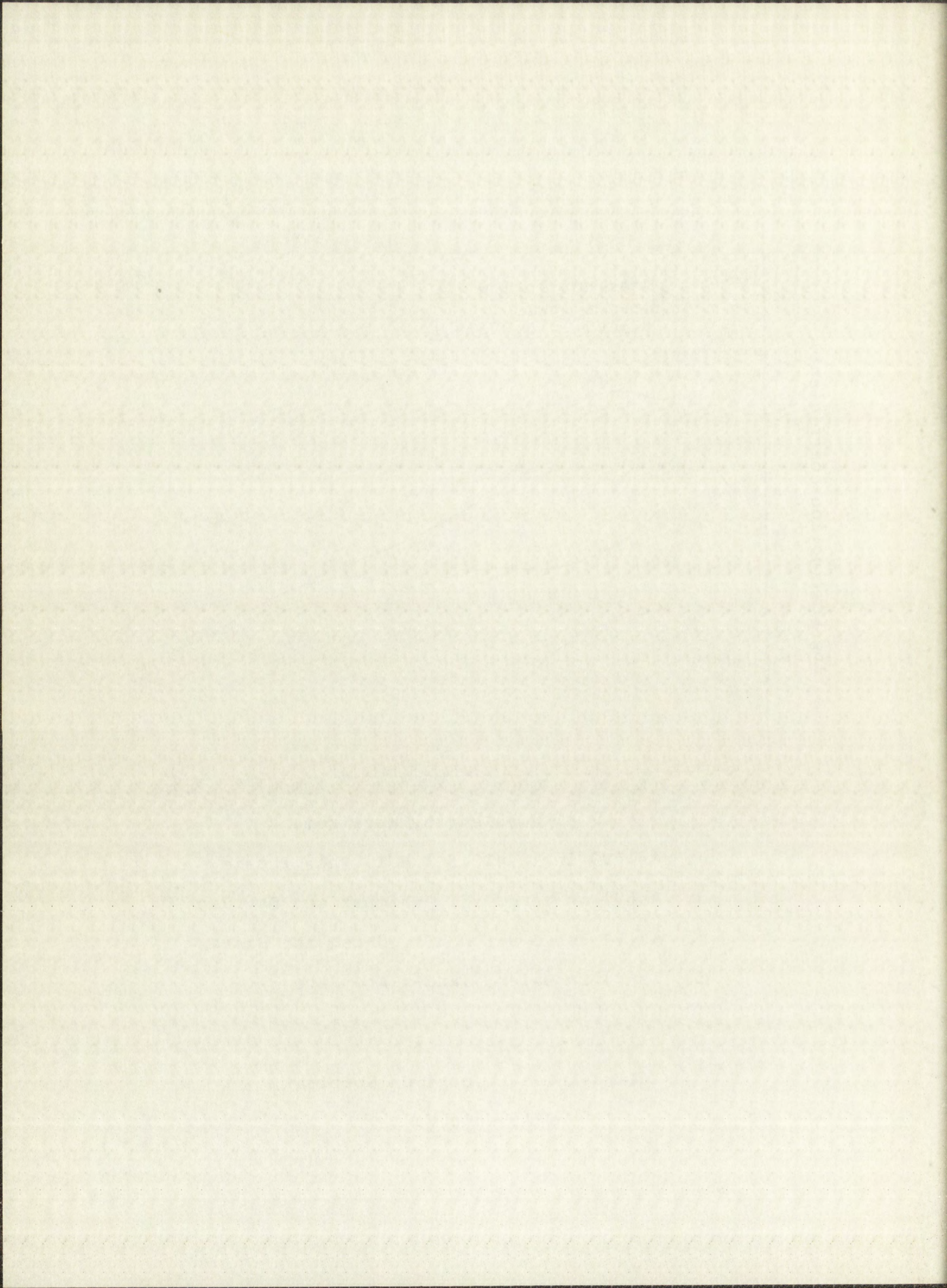




- a. As (V) in  $10.4 \pm 0.5 \underline{f}$  HCl, this thesis
- b. As(V) in conc. HCl, Whitney and Davidson<sup>35</sup>
- c. As(V) in  $\leq 0.1 \underline{f}$  HCl, Ghosh and Bisvas<sup>41</sup>
- d. As(V) in water, Jander and Jahr<sup>51</sup>

Figure V-13  
 Ultraviolet Absorption Spectra  
 of Arsenic(V)







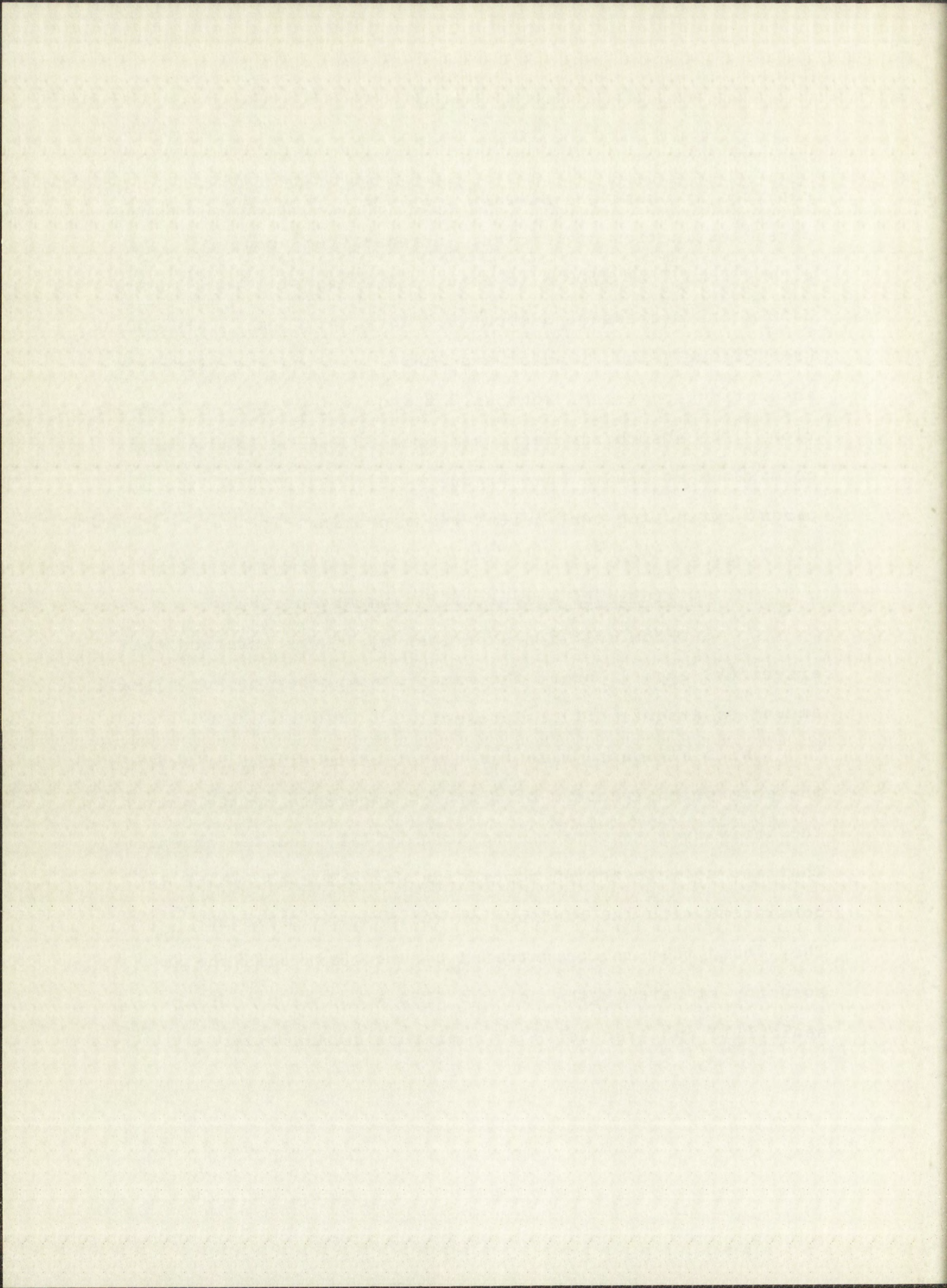
reported by Ghosh and Bisvas<sup>41</sup> in 1924. They found the apparent extinction coefficient increased from about 2.2 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> at 2700 Å to about 5.2 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> near 2450 Å and decreased to about 2.2 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup> at 2300 Å (see Figure V-13). Jander and Jahr<sup>51</sup> studied the ultraviolet absorption spectra of aqueous 2 f and 10 f arsenic acid solution. The absorbancy increased from 3300 Å to 2400 Å with no maximum at 2700 Å (see Figure V-13). At 2700 Å, the apparent extinction coefficient was approximately 0.2 l. g.-at.<sup>-1</sup>cm.<sup>-1</sup>.

### 3. Mixtures of Arsenic(III) and Arsenic(V)

From dilution experiments, it was inferred that arsenic(V) ages at about the same rate whether or not a small amount of arsenic(III) is present.

With allowance made for the dilution effect of arsenic(V), the absorption spectrum of mixtures appears to be the sum of the individual spectra of the arsenic(III) and the arsenic(V). That is, no interaction absorption was observed, which is consistent with the findings of Whitney and Davidson.<sup>35</sup> They found that in concentrated hydrochloric acid the absorbancy at wavelengths between 3150 Å and 4300 Å of arsenic(III) and arsenic(V) in a mixture is additive.

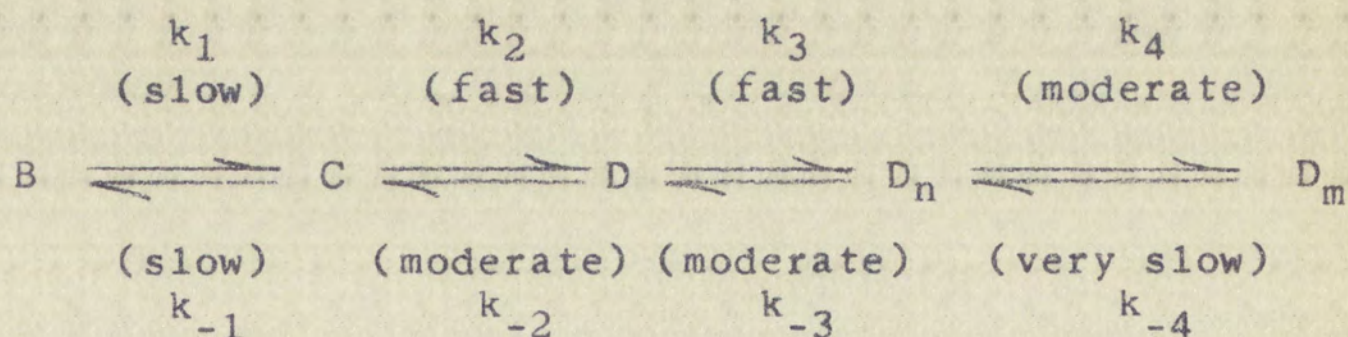






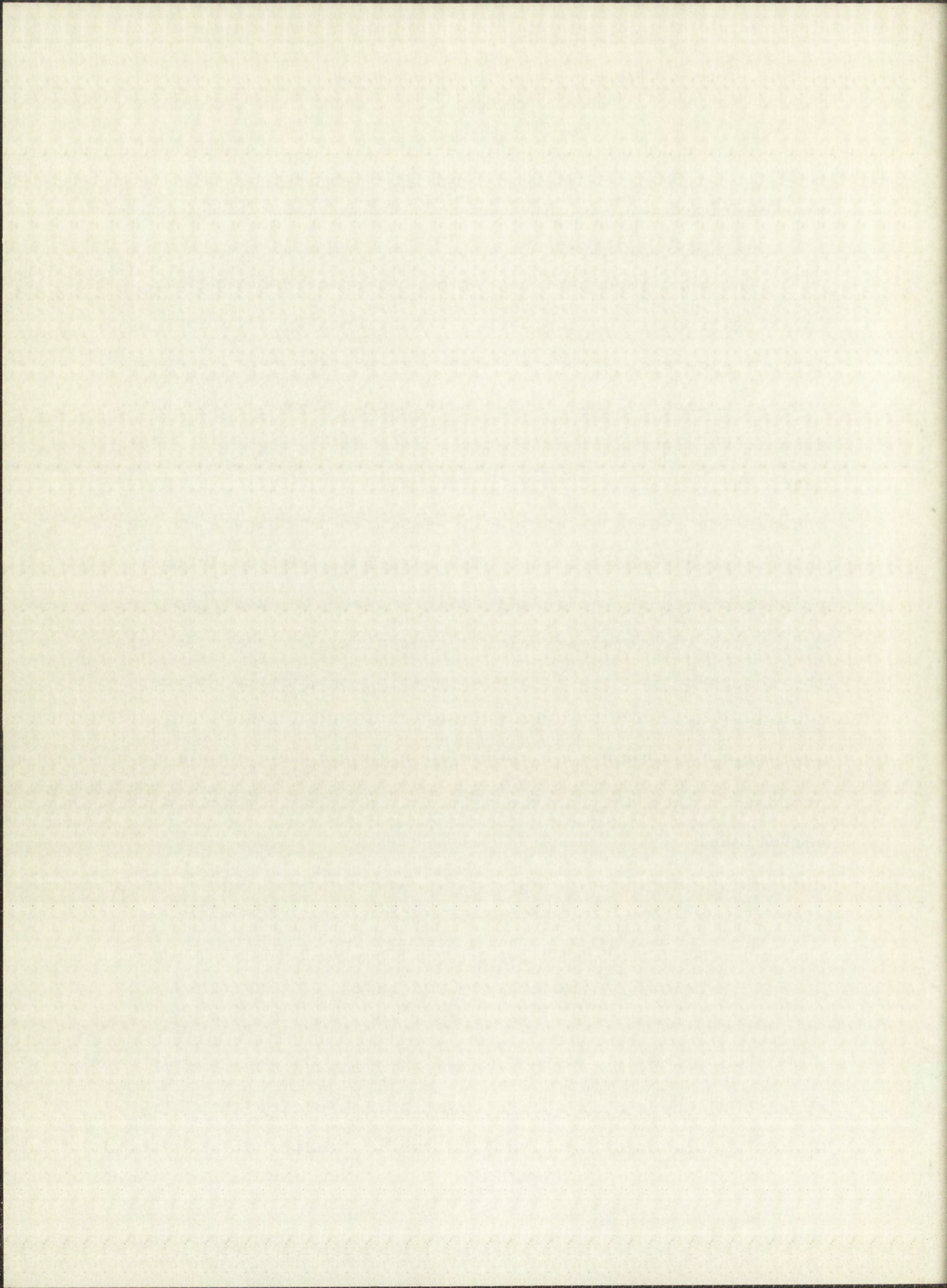
# I. Discussion of the Nature of the Equilibria among Arsenic(V) Species

The most important result of the spectrophotometric investigation is the discovery that arsenic(V) solutions undergo a slow aging process. The mere existence of an aging process indicates that in the attainment of equilibria among arsenic(V) species at least one slow step is involved. The reactions are assumed to be principally hydrolytic in nature because the system is extremely sensitive to changes in hydrochloric acid concentration. The reactions must be in part polymeric because the relationship between the absorbancy at 2300 A and the total arsenic(V) concentration indicates that the absorbing species is a dissociation product of polymers (see section V.C.2.). The following reaction scheme which embodies reversible hydrolytic and polymeric equilibria is proposed to account for the principal spectrophotometric observations.



Species B, C, and D are less-hydrolyzed monomers of arsenic(V) where B is a more chlorinated species than D;  $D_n$  and  $D_m$  are more-hydrolyzed polymeric species of arsenic(V).







The indicated rates are specific reaction rates which are related as follows:

$$\begin{array}{lll} k_1 \approx k_{-1} & k_3 > k_{-3} & k_1 \ll k_2 \approx k_3 > k_4 \\ k_2 > k_{-2} & k_4 \gg k_{-4} & \end{array}$$

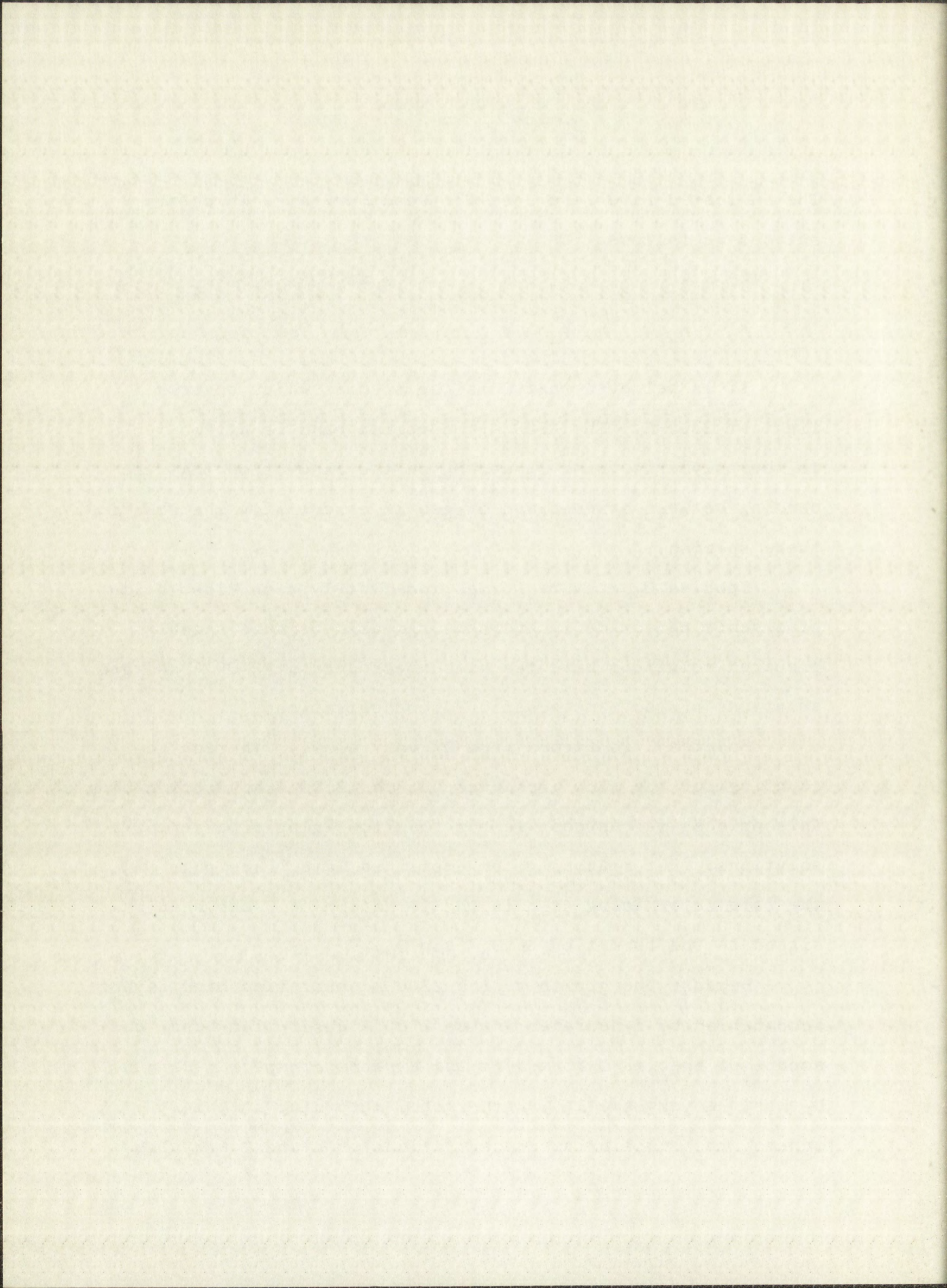
It is believed that C is the species which absorbs light at 2300 A. The 2700 A absorption band is attributed to the polymeric forms  $D_m$  and  $D_n$  on the assumption that the bonding between arsenic and oxygen is essentially the same in these species.

Species  $D_m$  must be formed immediately upon dissolution of arsenic pentoxide in hydrochloric acid because freshly prepared solutions have the same absorbancy at 2700 A as aged solutions of the same arsenic(V) concentration.

Species C is formed from  $D_m$  very slowly, thereby accounting for the slow appearance of the 2300 A absorption band. This process is responsible for the slow aging of arsenic(V) solutions. For reasons to be explained later (see page 90), the rate determining step in the formation of C has been assigned to the formation of  $D_n$  from  $D_m$ .

Because the growth of the 2300 A absorption band is not accompanied by a decrease in the 2700 A absorption band, the amount of species C formed at the expense of species  $D_m$  and  $D_n$  must be very small. Furthermore, according to this scheme, the equilibrium concentrations of B and D are also





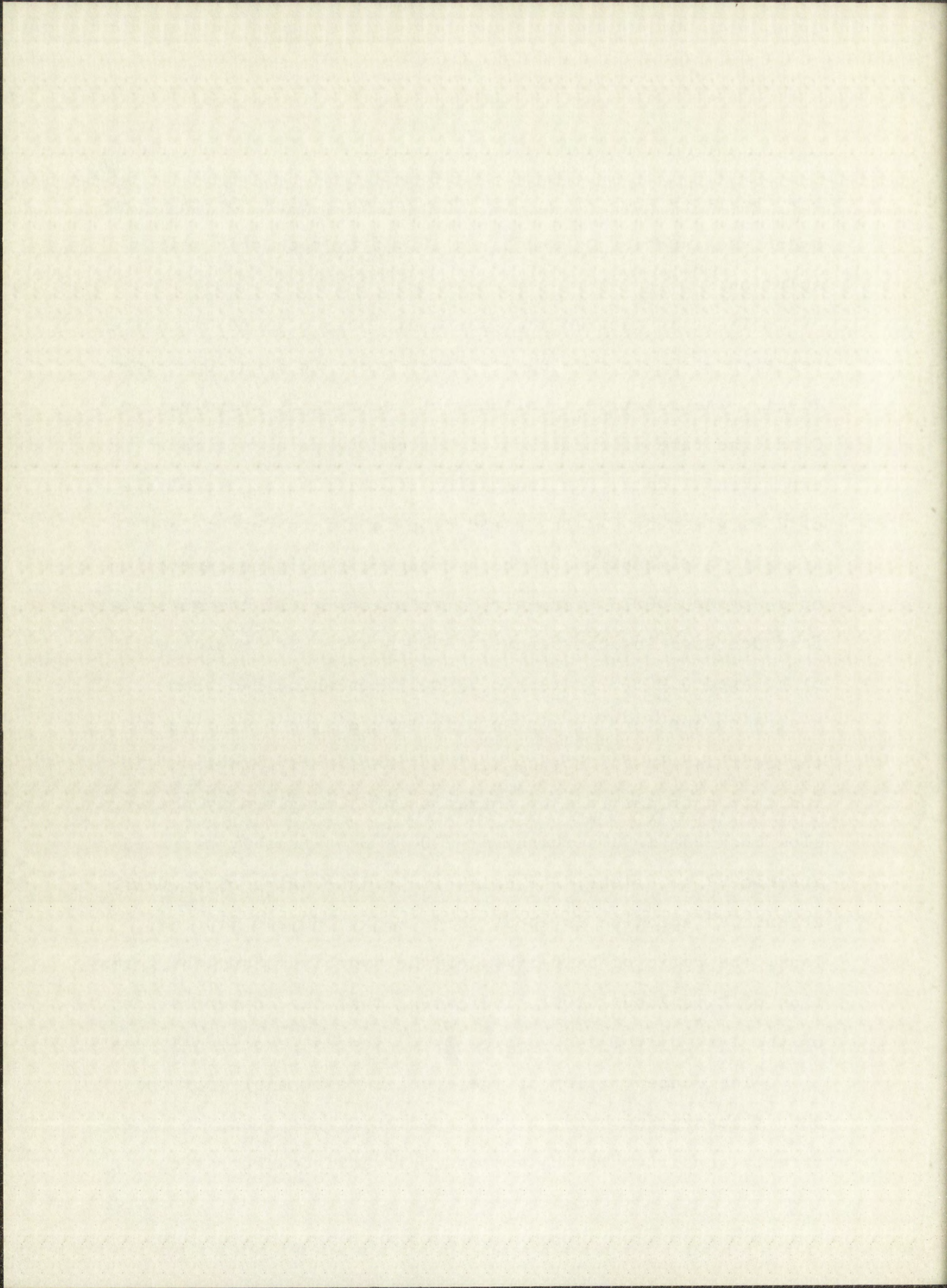


very small in comparison with the concentrations of the more-hydrolyzed species  $D_m$  and  $D_n$  in 10.9  $\underline{f}$  hydrochloric acid solution.

If it is assumed that the hydrolysis of C to D and the reaction of  $D_m$  to form  $D_n$  are first order in C and  $D_m$  respectively, the relative magnitudes of the rate of hydrolysis of C and the rate of formation of C from  $D_m$  can be estimated from experimental data. An indication of the rate of hydrolysis of C is given by (1) the rapid drop in absorbancy at 2300 A after a 1% diminution of the hydrochloric acid concentration of an aged 0.00373  $\underline{f}$  arsenic(V) solution or (2) the moderately fast decrease in absorbancy at 2300 A after the rapid cooling of an aged 0.00373  $\underline{f}$  arsenic(V) solution which had been heated to about 95°C. In both instances, the half-time of the decrease in absorbancy is less than thirty minutes. An indication of the rate of formation of C is given by the very slow increase in absorbancy at 2300 A of a freshly prepared arsenic(V) solution. The half-time of the aging of 0.00410  $\underline{f}$  arsenic(V) solution is about three weeks (30,240 minutes). Thus, the ratio of half-times of the hydrolysis and the formation of C is about 0.001, indicating that the concentration of the less-hydrolyzed species C is, indeed, exceedingly small.

The concentration of the species responsible for the 2300 A absorption band, namely species C, was found to be extremely sensitive to the hydrochloric acid concentration.





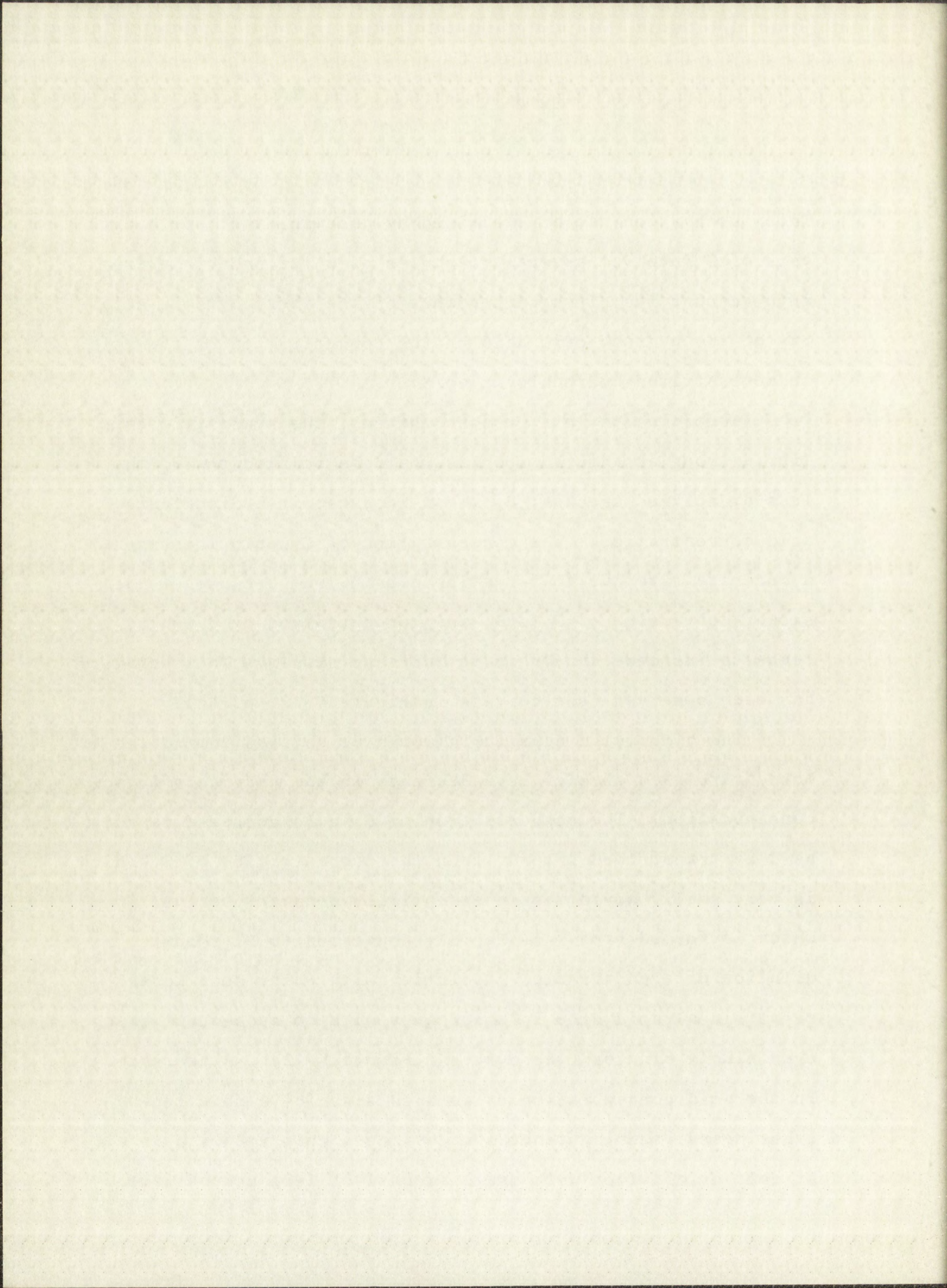


This observation can be explained by assuming that the hydrolysis of C involved several molecules of water and by taking into account the strong dependence of the thermodynamic activity of the hydrochloric acid on the concentration of the acid in concentrated hydrochloric acid.

According to this proposed scheme, the hydrolytic equilibria among arsenic(V) species would be shifted toward the less-hydrolyzed species, B, by an increase in hydrochloric acid concentration. The concentration of C would increase at a moderate rate due to formation from D, but because of the slower conversion of C to B, the concentration of C would cease to increase and begin to decrease slowly. This behavior has been observed (see curve a in Figure V-12, p. 80).

The hydrolytic equilibria would be shifted toward the more-hydrolyzed species by a decrease in the hydrochloric acid concentration. The concentration of C would decrease rapidly as C is transformed into D, then the concentration of C (which is very small) would remain essentially constant because C which is formed from B is rapidly converted to D. Minute dilution of aged arsenic(V) solution with water does indeed result in a rapid drop in absorbancy with no subsequent change over ninety minutes (see curve d, Figure V-12). A decrease in the acid concentration of an aged arsenic(V) solution by other means, such as removal of hydrogen chloride with an air stream, or dilution with small amounts of less concentrated







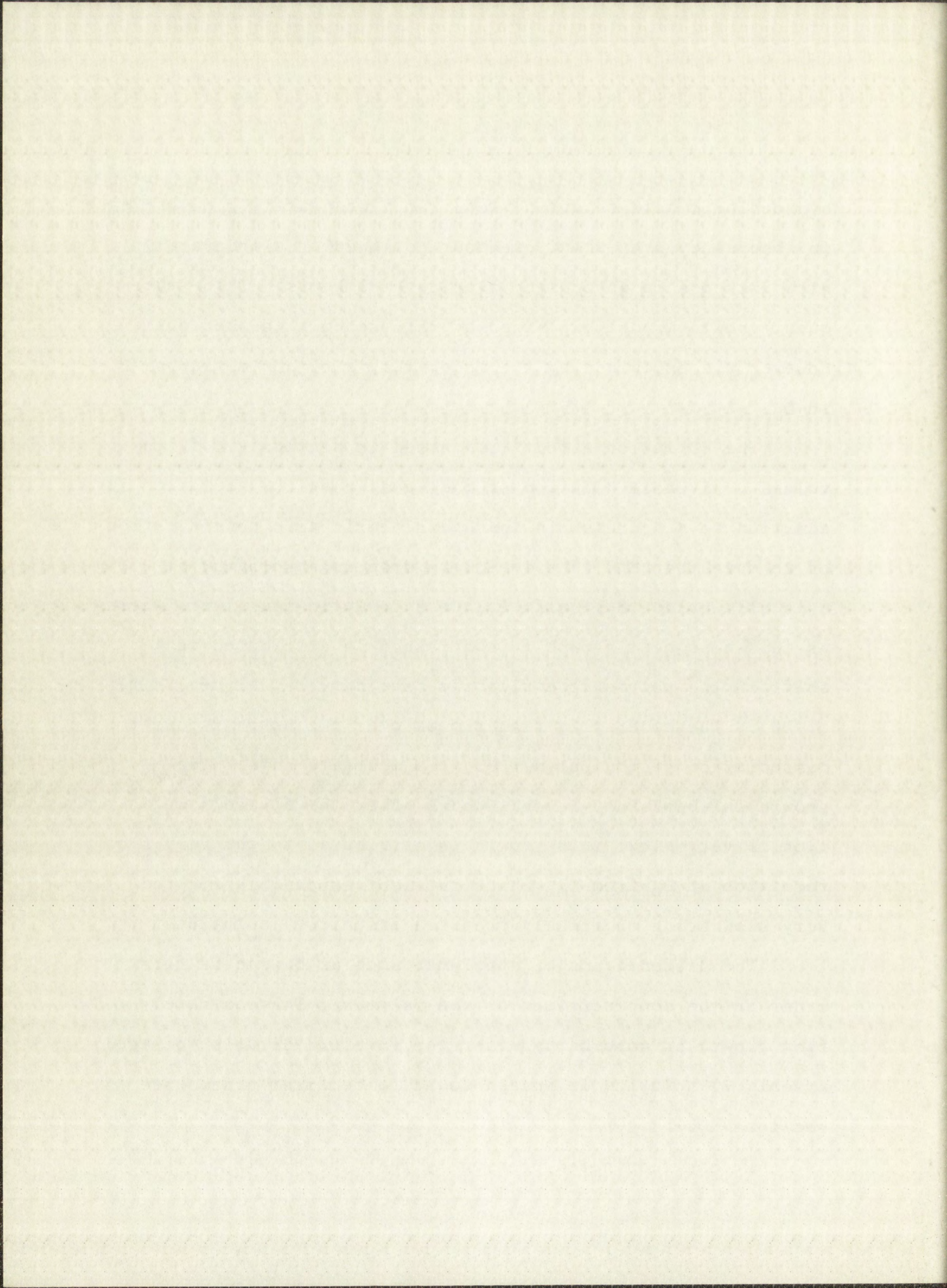
hydrochloric acid solution, leads to a moderately slow decrease in absorbancy over about one hour followed by a moderately slow increase in absorbancy over several hours. This subsequent growth is not explained by this scheme; the decrease, however, is explained by the moderately slow conversion of  $D_n$  to  $D_m$ .

The "Dilution effect" discussed in section V.D.1. involved a fivefold dilution of the aged arsenic(V) solution in addition to a decrease in the hydrochloric acid concentration of no more than 8%. The immediate drop in absorbancy at 2300 A is attributed to a shift in the hydrolytic equilibria whereas the subsequent growth in absorbancy is attributed to a shift in the polymeric equilibria (see curve e, Figure V-12, p. 80). The moderately fast growth over two hours is due to dissociation of the polymer  $D_n$  at a moderate rate. The growth in absorbancy several hours after the fivefold dilution is very slow; this growth is attributed to the very slow formation of  $D_n$  from  $D_m$ , which is also responsible for the very slow aging of freshly prepared arsenic(V) solutions.

The dissociation of a polymer such as  $D_n$  can be first order in the concentration of the polymer. The moderately fast growth in absorbancy after the fivefold dilution of aged arsenic(V) solution is indeed found to be first order (see section V.D.1.).

It has been noted previously that the growth of the

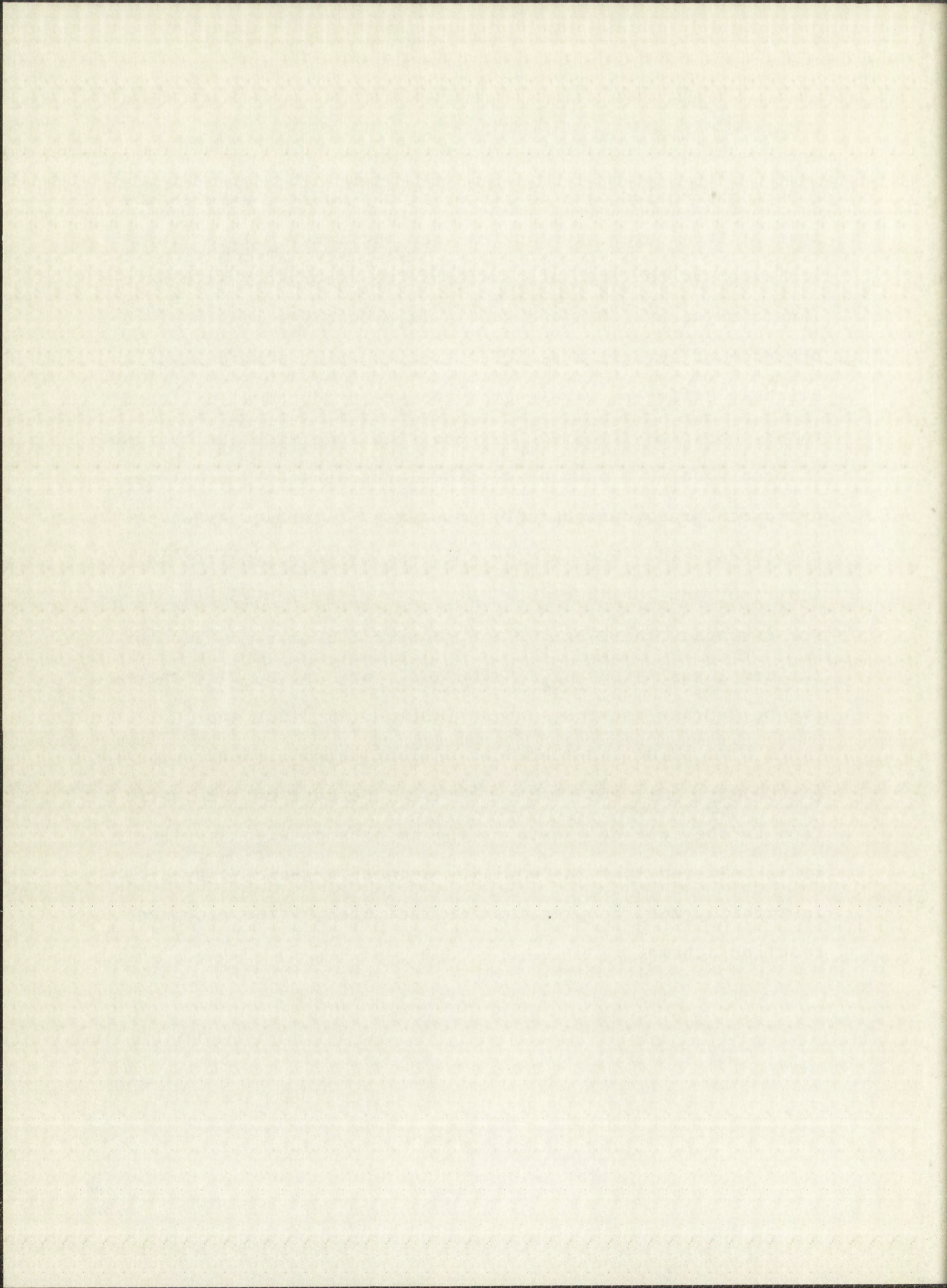






2300 Å absorption band is faster at the shorter wavelengths than at the longer wavelengths (see Section V.D.1.). This variation in the rate of growth of the absorbancy with wavelength between 2200 Å and 2600 Å is probably a result of the presence of several arsenic(V) species which absorb light at slightly different wavelengths and are produced at different rates. Species involved in these reactions might be hydroxochloroarsenate(V) complexes, oxochloroarsenate(V) complexes, hydroxochloroaquoarsenate(V) complexes, chloroaquoarsenate(V) complexes, etc. Some of the species may be polymeric; in addition, some of these complexes may exist in isomeric forms. For instance, there can be two geometric isomers of each of the complexes  $\text{As}(\text{OH})_2\text{Cl}_4^-$ ,  $\text{As}(\text{OH})_3\text{Cl}_3^-$ , and  $\text{As}(\text{OH})_4\text{Cl}_2^-$ ; there can be hydrate isomers such as  $[\text{As}(\text{H}_2\text{O})_2\text{Cl}_4]^+\text{Cl}^-$  and  $[\text{As}(\text{H}_2\text{O})\text{Cl}_5]\text{H}_2\text{O}$ ; and there can be ionization isomers such as  $[\text{As}(\text{OH})\text{Cl}_3]^+\text{Cl}^-$  and  $[\text{AsCl}_4]^+(\text{OH})^-$ . Because of this variation in the rate of growth of the absorbancy with wavelength, it is believed that the equilibria among arsenic(V) species is actually more complex than is indicated by the proposed reaction scheme.







## VI. ISOTOPIC EXCHANGE

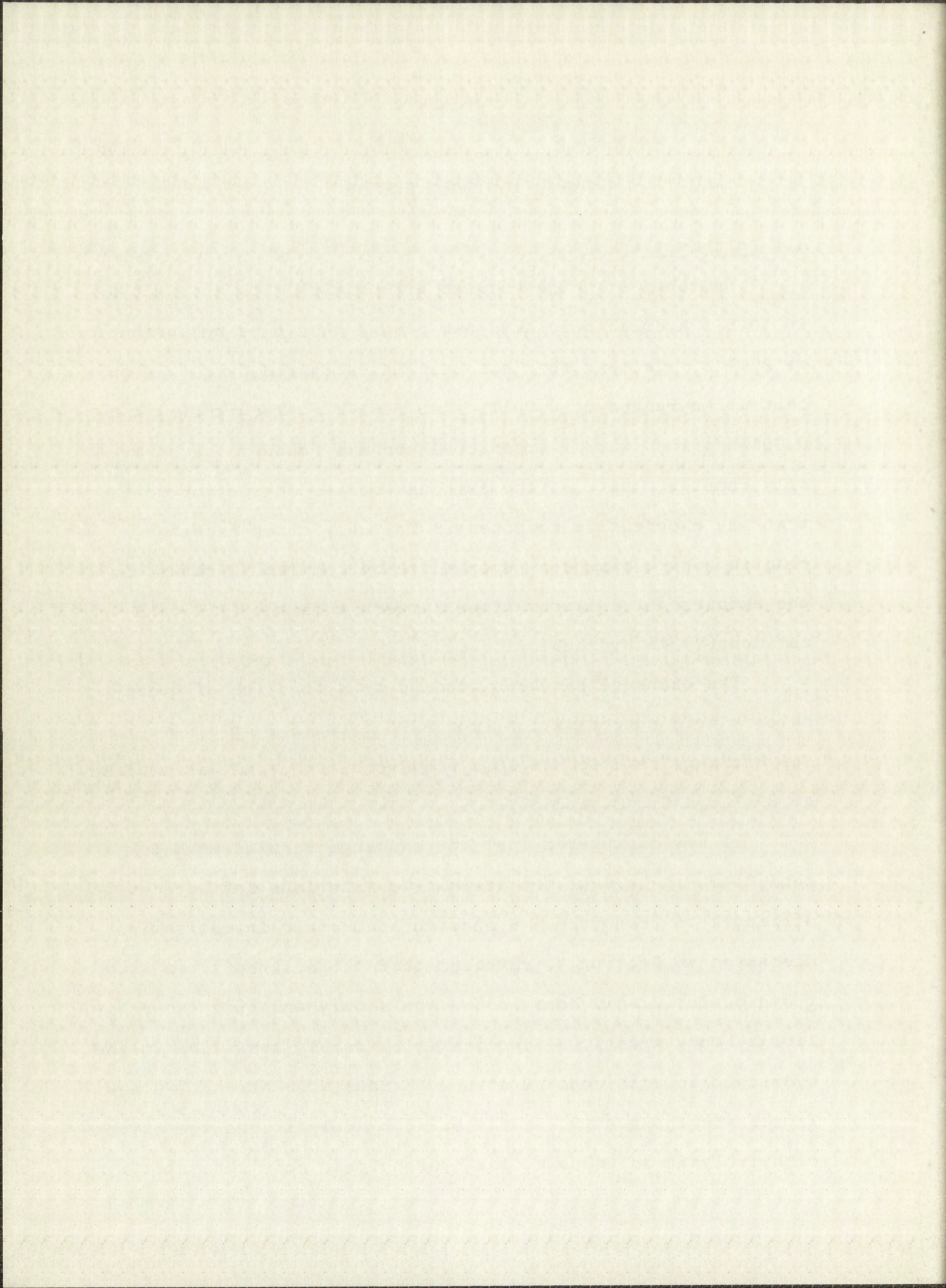
A. Introduction

Isotopic exchange between arsenic(III) and arsenic(V) in 10.8  $\underline{f}$  hydrochloric acid has been found to be measurable at 29.7°C. The exchange has been investigated over the concentration ranges of 0.00111  $\underline{f}$  to 0.0474  $\underline{f}$  arsenic(III) and 0.00446  $\underline{f}$  to 0.0837  $\underline{f}$  arsenic(V) and was found to be generally complex; that is, the exchange curves consist of more than one exponential component. The only other exchange reaction which has been reported to be complex in nature is the exchange of antimony atoms between antimony (III) and antimony(V) in hydrochloric acid.<sup>4</sup>

The exchange has been studied as a function of hydrochloric acid concentration from 6.98  $\underline{f}$  to 12.6  $\underline{f}$  at 29.7°C. The exchange reaction in 10.9  $\underline{f}$  hydrochloric acid was studied at 29.7°C, 48.6°C, and 67.3°C.

It was discovered that the exchange results were dependent on the age of the arsenic(V) solutions and were quite difficult to reproduce. A spectrophotometric investigation, discussed in Section V, revealed that the arsenic(V) in 10.9  $\underline{f}$  hydrochloric acid does indeed age slowly and that the equilibria among arsenic(V) species is extremely sensitive to the hydrochloric acid concentration. Because the arsenic(V) equilibria are apparently, in the main, hydrolytic and the extent of hydrolysis is unknown, the hydrochloric acid concentration,



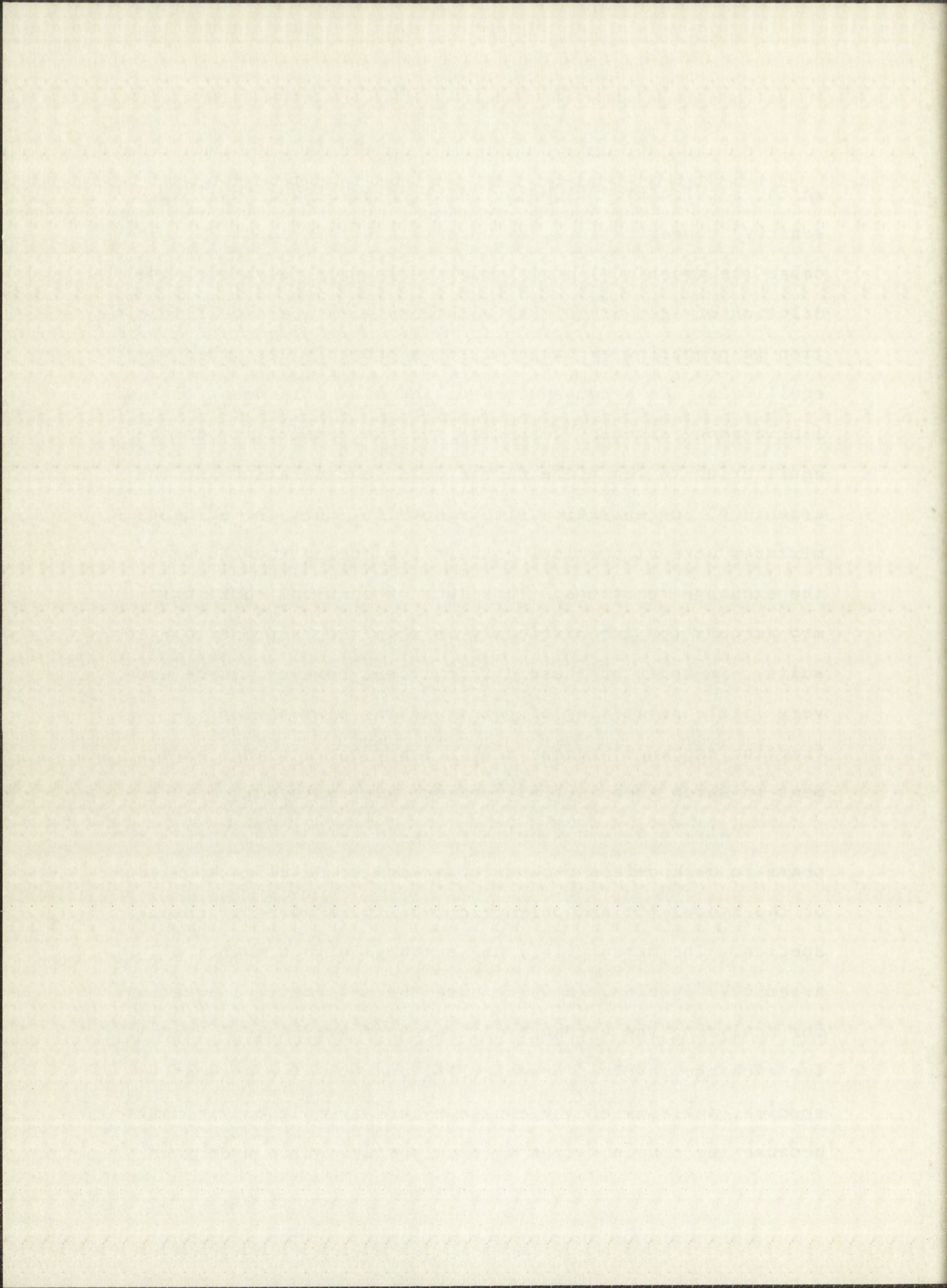




which is calculated from the total chloride and total arsenic(V) concentrations, is uncertain within about 2%. Because the arsenic(V) equilibria are in part polymeric, the dilution of aged arsenic(V) solutions with arsenic(III) solution in preparing exchange mixtures probably disturbed the equilibria. As a consequence of the slow attainment of equilibria among arsenic(V) species and the sensitivity of the equilibrium to the hydrochloric acid concentration and the arsenic(V) concentration, it is doubtful that the exchange mixtures were at chemical equilibrium during the course of the exchange reactions. This lack of chemical equilibrium may account for the difficulty in obtaining reproducible results. In spite of these difficulties, however, there was very little scattering of points in the plot of  $\log(1 - \text{fraction exchange})$  versus time for any one exchange experiment in which arsenic(III) "tracer" was employed.

Analysis of the complex exchange curves at present appears to be hopeless because of a lack of detailed knowledge of the hydrolytic and polymeric equilibria among arsenic(V) species. The arsenic(III) may exchange with a number of arsenic(V) species, in which case the mathematical equations for analyzing the exchange data are not available. Even if the exchange involved arsenic(III) and only two arsenic(V) species, analysis of the exchange curves would be difficult because the concentration of each species which undergoes







exchange is unknown.

The initial portion of the exchange curves was analyzed by employing the simple exchange law. The initial rate of exchange in 10.9 f hydrochloric acid at 29.7°C is well represented by rate expressions such as  $R = k_1[\text{As(III)}]^n$  and  $R = k_2[\text{As(V)}]^m$  for a constant arsenic(V) concentration and a constant arsenic(III) concentration, respectively. For a given concentration range of arsenic(III), the exponent  $n$  is a function of the arsenic(V) concentration; similarly, for a given concentration range of arsenic(V), the exponent  $m$  is a function of the arsenic(III) concentration. At 48.6°C, the initial rate of exchange in 10.9 f hydrochloric acid is well represented by

$$R = 6.71 \times 10^{-5} [\text{As(III)}]^{0.91} [\text{As(V)}]^{0.38} \text{ l. g.-at.}^{-1} \text{sec.}^{-1}$$

over the concentration ranges of 0.00132 f to 0.00660 f arsenic(III) and 0.00777 f to 0.0388 f arsenic(V). At 67.3°C, the initial rate of exchange in 10.9 f hydrochloric acid is well represented by

$$R = 8.72 \times 10^{-5} [\text{As(III)}]^{0.37} [\text{As(V)}]^{0.76} \text{ l. g.-at.}^{-1} \text{sec.}^{-1}$$

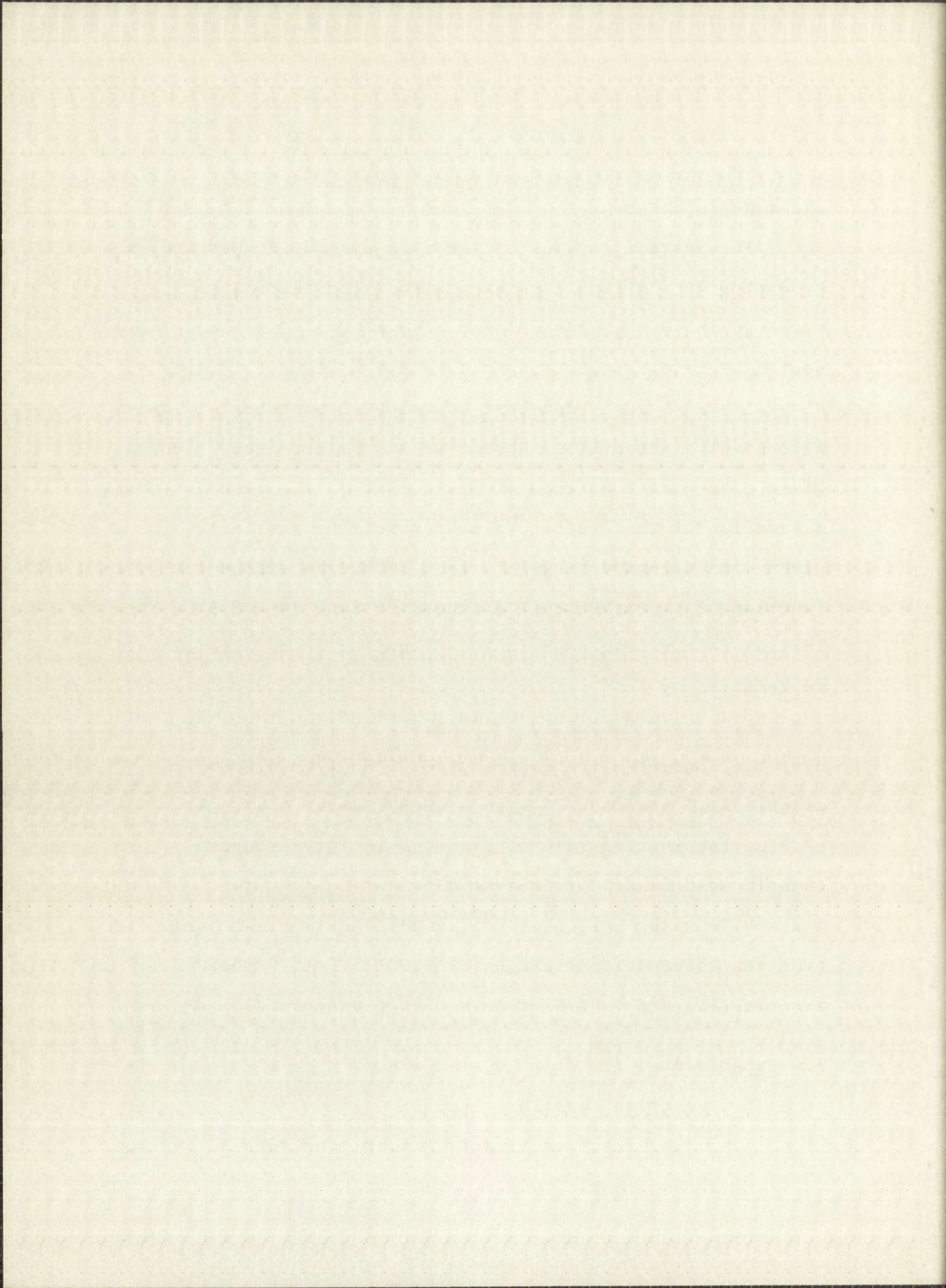
over the concentration ranges of 0.00132 f to 0.00660 f arsenic(III) and 0.00777 f to 0.0388 f arsenic(V).

## B. Experimental

### 1. Reaction Vessels

The reaction vessels, except for runs 33 and 36,







were blackened in order to exclude light from the reaction mixture.

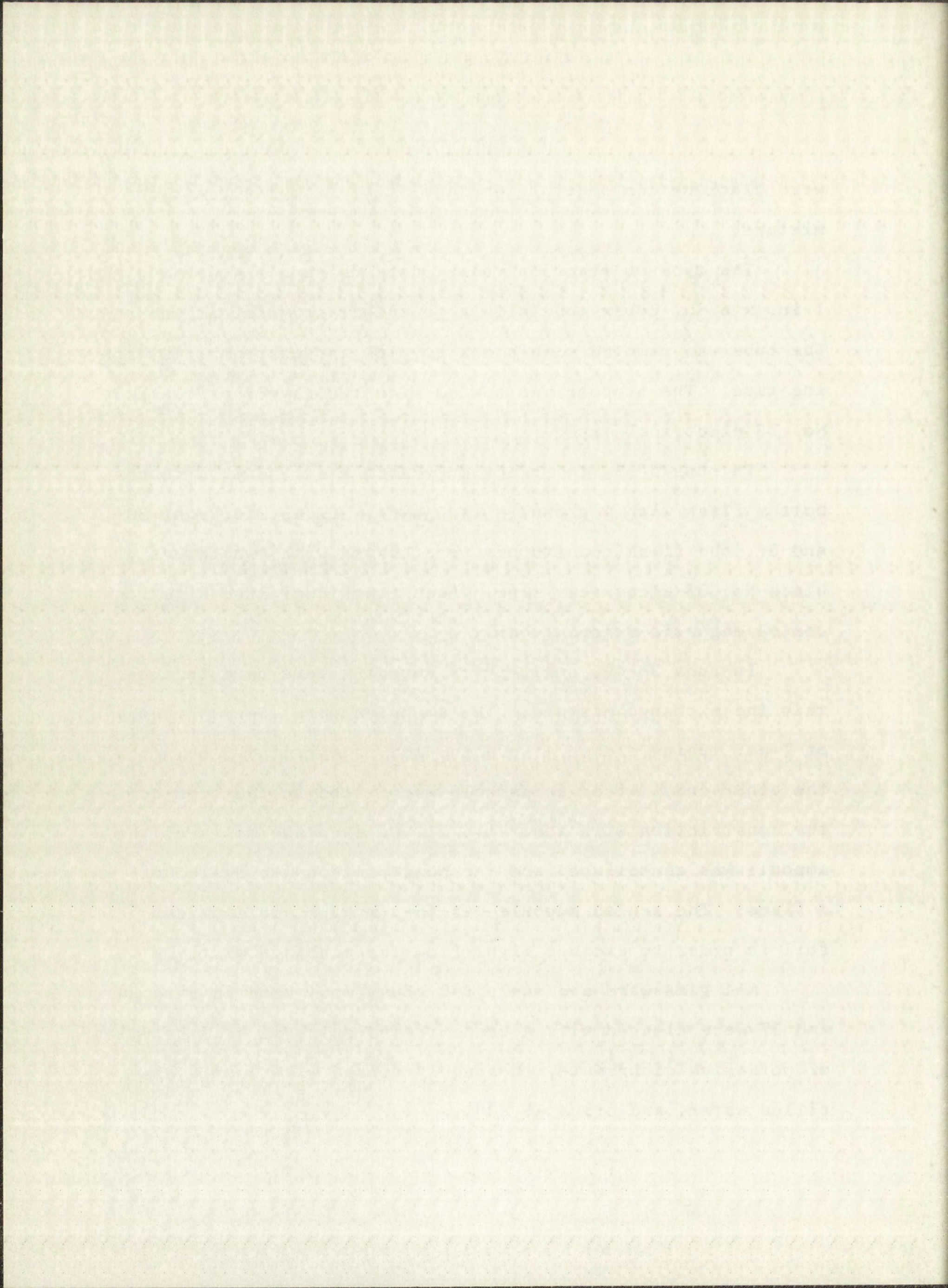
The type of reaction vessel used in runs 1-4 was a 1 in. x 6 in. pyrex tube with a ground-glass joint at one end. The tube was painted with black glyptal and wrapped with masking tape. The stopper was coated with two layers of black No. 33 electrical tape.

In runs 5-37, the reaction vessel was a 50 ml., round-bottom flask with a ground-glass joint. Except for runs 33 and 36, the flask and stopper were coated with two layers of black No. 33 electrical tape. Each flask contained a teflon-coated magnetic stirring bar.

In runs 38-49, small pyrex ampoules were used to contain the exchange mixture. The ampoules were 12-cm. lengths of 7-mm. tubing closed at one end and constricted 3 cm. from the other end. After an ampoule was filled to the base of the constriction with about 1.6 ml. of exchange mixture, the ampoule was centrifuged and the constriction was sealed off in a flame. The sealed ampoule was then wrapped in aluminum foil in order to exclude light from the exchange mixture.

All glassware and the pyrex glass wool used in runs 34 and 37 were cleaned with a concentrated sulfuric acid solution of potassium dichromate, thoroughly rinsed with doubly distilled water, and dried at 80°C.



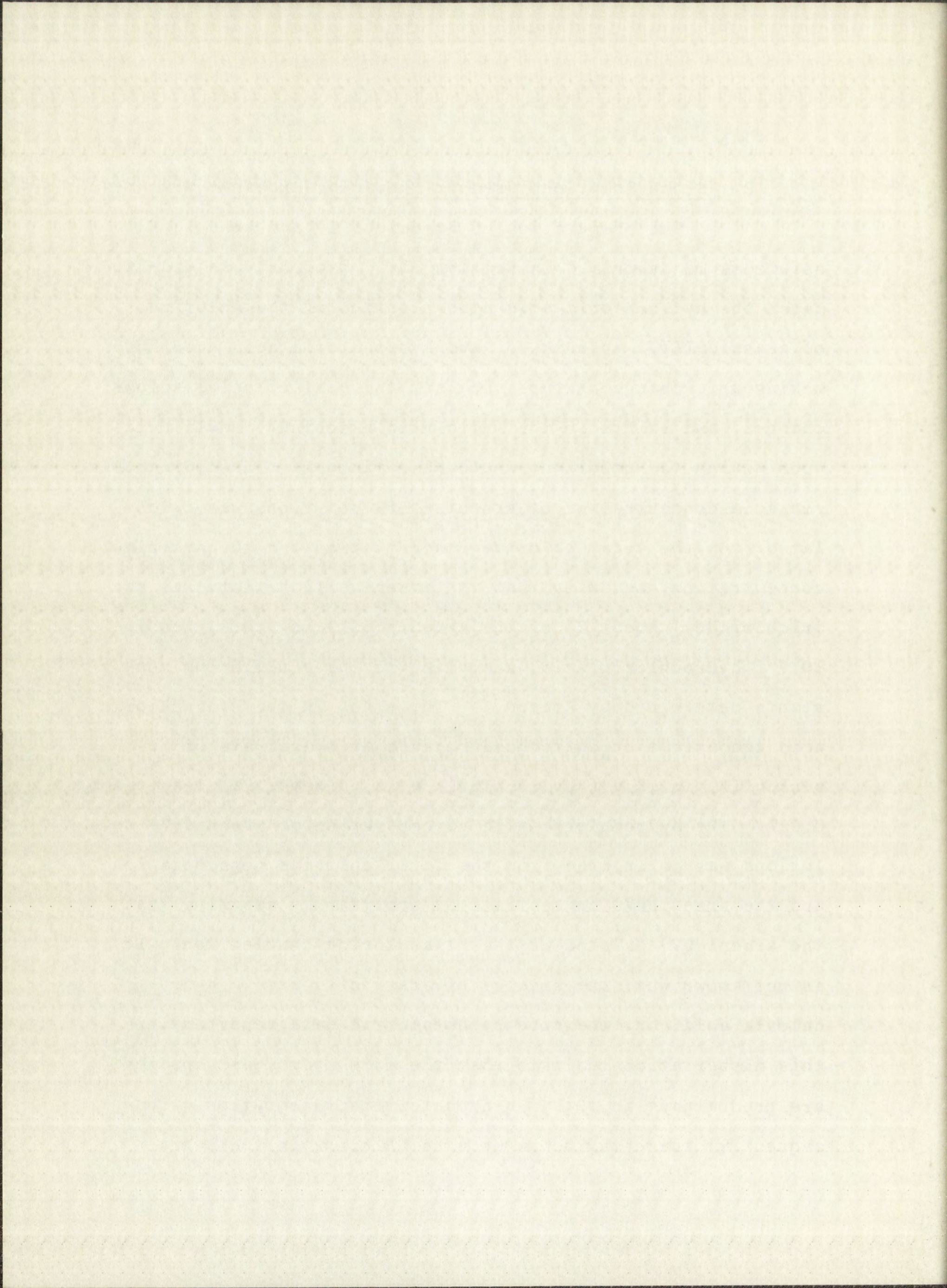




## 2. Stock Solutions Used in Preparing Exchange Mixtures

The preparation of arsenic(III) and arsenic(V) solutions is described in Section II. An effort was made to match the hydrochloric acid concentration of the solutions of arsenic(III), arsenic(V), and hydrochloric acid used for making up exchange mixtures so that the heat effects, volume changes, and shifts in the hydrolytic arsenic(V) equilibria upon mixing the solutions would be a minimum. The hydrochloric acid concentration of arsenic(III) solutions was calculated from the total chloride concentration and the arsenic(III) concentration, assuming that the arsenic(III) existed as the trichloride. About 2% of the arsenic(III) is hydrolyzed in 10.9  $\underline{f}$  hydrochloric acid, according to the equilibrium constants determined by Arcand.<sup>35</sup> The error in the hydrochloric acid concentration introduced because of hydrolysis of arsenic(III) in 10.9  $\underline{f}$  hydrochloric acid, however, is less than 0.02%. The hydrochloric acid concentration of arsenic(V) solutions was calculated from the total chloride concentration and the arsenic(V) concentration, arbitrarily assuming that the arsenic(V) existed as the hexachloride complex ion. It is not known what the species of arsenic(V) are in hydrochloric acid, but the spectrophotometric data reported in this dissertation indicate that the more-hydrolyzed species are predominant in 10.9  $\underline{f}$  hydrochloric acid solution. Consequently, there may be as much as 2% error in the hydro-







chloric acid concentration because of hydrolysis.

### 3. Thermostating of Solutions

Constant temperature baths maintained at  $29.7 \pm 0.05^\circ\text{C}$ ,  $48.6 \pm 0.05^\circ\text{C}$ , and  $67.3 \pm 0.1^\circ\text{C}$  were controlled by a "Metastatic" mercury thermoregulator connected to an electronic relay circuit. The temperature of each bath was measured with an Anschutz thermometer calibrated by the National Bureau of Standards.

Solutions to be used in the preparation of an exchange mixture at  $29.7^\circ\text{C}$  were immersed in the  $29.7^\circ\text{C}$  constant-temperature bath at least two hours before use. Exchange flasks were immersed up to the neck at least one-half hour before a reaction was started.

Exchange mixtures to be studied at  $48.6^\circ\text{C}$  and  $67.3^\circ\text{C}$  were prepared at room temperature, sealed in ampoules, and the ampoules immersed in the appropriate temperature bath. It was found, with the aid of a thermocouple, that the reaction mixtures attained thermal equilibrium within one minute.

### 4. Preparation of Exchange Mixtures at $29.7^\circ\text{C}$ .

Although there is no reason to believe that the order of mixing arsenic(III) and arsenic(V) solutions influences the exchange results, the solutions were generally mixed in the same order in each experiment. Except for runs 7, 11, and 18 (in which the tracer was pentavalent) and runs 27-31,







the solutions were mixed in the order: hydrochloric acid, arsenic(V), and arsenic(III). Otherwise, the order of mixing the arsenic(III) and arsenic(V) was reversed. The last solution was added under the light of a red safe-light; in exchange runs 1-4, however, the arsenic solutions were never exposed to the fluorescent light in the laboratory.

The instant that the arsenic(III) solution and the arsenic(V) solution first came in contact was taken to be the zero time for the exchange reaction.

5. Preparation of Exchange Mixtures for Reaction at 48.6°C or 67.3°C.

Solutions of hydrochloric acid, arsenic(V), and arsenic(III) tracer were mixed in that order at room temperature under normal fluorescent laboratory light. The mixture was immediately transferred with a capillary tube to pyrex ampoules which were then centrifuged, sealed, and wrapped in aluminum foil. The ampoules were then immersed in a temperature bath. The zero time of reaction was reckoned from the time of immersion in the temperature bath.

6. "Tracer" Used to Prepare Exchange Mixtures

The "tracer" was generally introduced into the exchange mixture in the form of arsenic(III). In runs 1-6, 8-10, and 12-17, inactive arsenic(III) was inoculated with







purified high specific activity arsenic(III) according to the following schedule:

Run 1-4: A stock solution of arsenic(III) was prepared and inoculated one day prior to run 1. The tracer solution was stored in the dark at room temperature.

Runs 5, 6, 8, 9, 10, and 12-17: A stock solution of arsenic(III) was prepared and inoculated three days prior to run 5. This tracer solution was stored under normal laboratory light at  $29.7^{\circ}\text{C}$ .

The arsenic(V) "tracer" was prepared according to the procedure in Section III (see page 24) three days prior to run 5 and was stored under normal laboratory light at  $29.7^{\circ}\text{C}$ .

In all experiments subsequent to run 18, the "tracer" was prepared by oxidation, reduction, and distillation of arsenic(III) which had been inoculated with purified high specific activity arsenic(III) according to the procedures described in Section III. Only for runs 27-31 and 35-37, 40, and 42 was the inoculated arsenic(III) reduced to the metal, dissolved in chlorine solution, and distilled (see Section III). Otherwise, the arsenic(III) tracer was prepared by oxidation to arsenic(V) followed by reduction to arsenic(III) and distillation. In runs 19-37 and 44-48 the "tracer" solution was distilled one day prior to the exchange experiments. The







arsenic(III) "tracer" solution was two days old for runs 38-42 and fifteen days old for runs 43 and 49.

7. Age of the Arsenic(V) Solutions Used to Prepare Exchange Mixtures

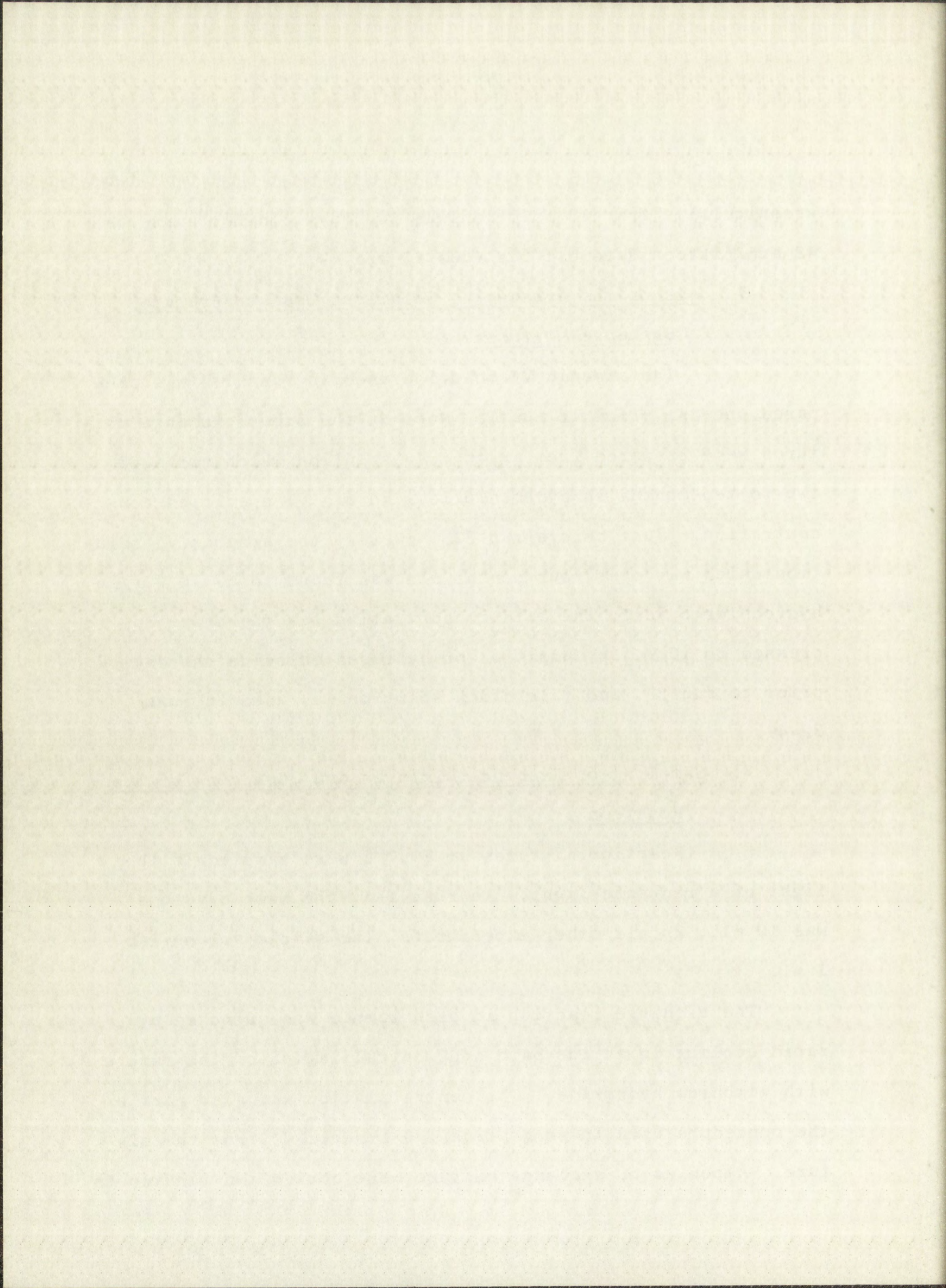
The arsenic(V) solution used in runs 1-4 was prepared one day prior to run 1. Most of the other exchange mixtures were prepared from arsenic(V) solution which had aged two to ten months in hydrochloric acid of the specified concentration. Just before run 32, however, the arsenic(V) solution which was over four months old was found to be 10.7  $\mu$  in hydrochloric acid; the acid concentration was therefore increased to 10.9  $\mu$  by addition of hydrogen chloride one day prior to run 32, and this stock solution was used in runs 32-49.

8. Sampling of Exchange Mixtures and Quenching of the Reaction

Reaction mixtures at 29.7°C were sampled in the light of a red safe-light. In runs 1-4, the sample volume was 10 ml.; in all other experiments, the sample volume was 1 ml.

The exchange reaction in each sample was quenched by rapid cooling in an ice bath and neutralization of the sample with ammonium hydroxide. The neutralization was also part of the procedure used in separating the arsenic(V) from the mixture. Ampoules of exchange mixture were cooled two minutes in







an ice bath before they were opened to withdraw a 1 ml. sample. Except for runs 1-4, every sample was delivered into 1 ml. of an ice-cold concentrated hydrochloric acid solution which was about 0.05  $\mu$  in arsenic(III) and about 0.05  $\mu$  in arsenic(V); the solution was simultaneously stirred with a teflon-coated magnetic stirring bar. The solution was then diluted with 2 ml. of ice-cold water and nearly neutralized with 1.5 ml. of ice-cold concentrated ammonium hydroxide. In runs 1-4, the 10 ml. samples were mixed with 5 ml. of an ice-cold concentrated hydrochloric acid solution which was about 0.05  $\mu$  arsenic(V); the solution was simultaneously stirred with a teflon-coated magnetic stirring bar. The solution was then diluted with 20 ml. of ice-cold water and nearly neutralized with 14 ml. of ice-cold concentrated ammonium hydroxide.

The time at which a sample of exchange mixture was immersed in an ice bath was taken to be the end of the reaction for that sample.

#### 9. Separation of Arsenic(V) from Exchange Mixtures

Arsenic(V) was separated from the exchange mixture by precipitation of magnesium ammonium arsenate.<sup>23</sup> A similar method of separation was used successfully by Wilson and Dickinson.<sup>14</sup> The following procedure was used in all exchange experiments, excluding runs 1-4. A drop of phenolphthalein indicator and 10 ml. of magnesia mixture (see page 17) were







added to the ice-cold quenched sample of exchange mixture. The solution was neutralized with a few drops of concentrated ammonium hydroxide and then 1 ml. of concentrated ammonium hydroxide was added. In order to facilitate precipitation, the solution was kept in an ice bath for ten to twenty minutes. The slurry of magnesium ammonium arsenate was filtered with suction through Whatman #50 paper mounted on a sawed-off Hirsch funnel with a glass chimney as shown in Figure VI-1. The precipitate was rinsed from the precipitation flask into the glass chimney with 2 f ammonium hydroxide and then washed at least three times with 2 f ammonium hydroxide; the sides of the chimney were rinsed with acetone.

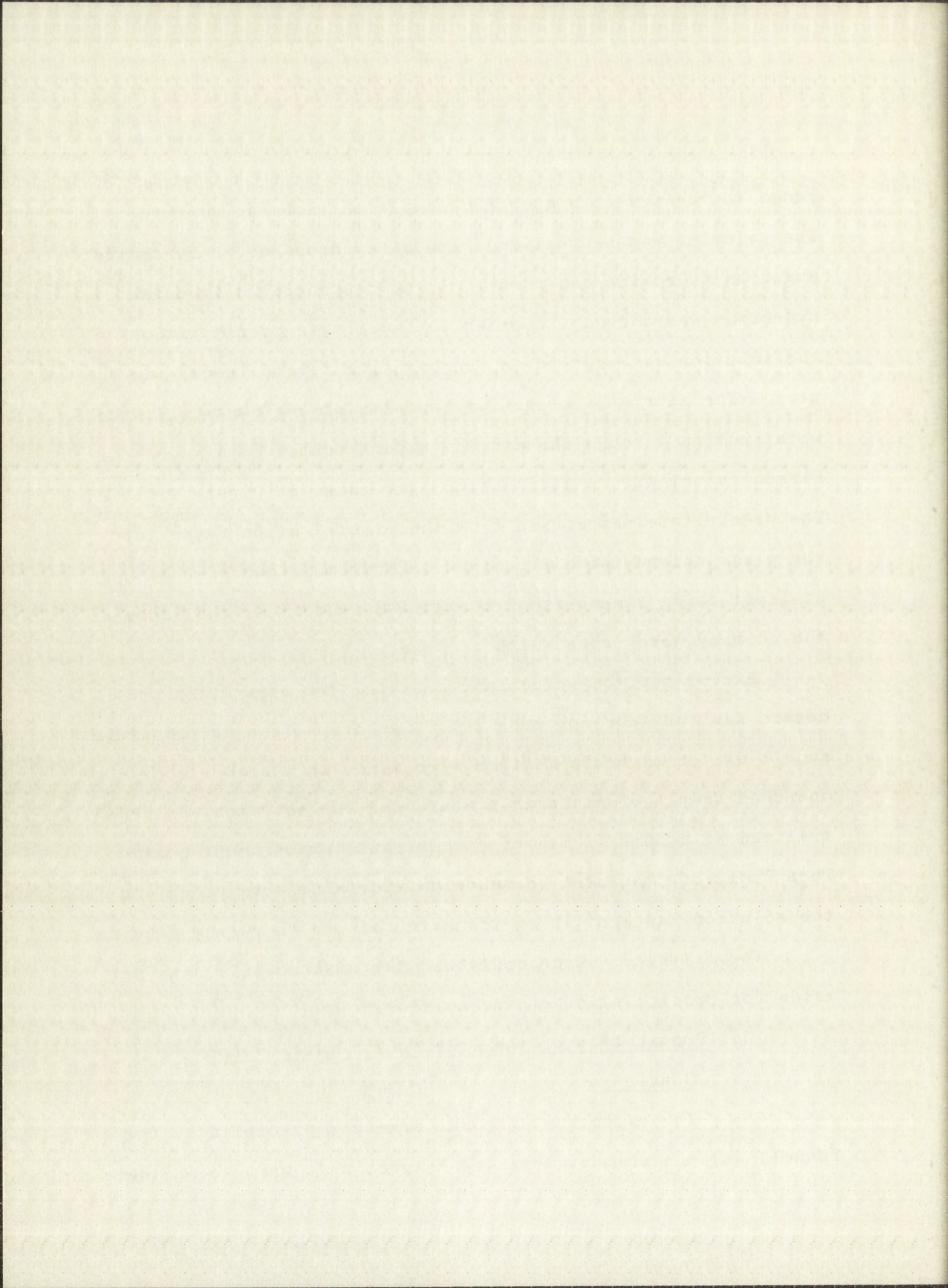
Except for the volume of reagents, the separation procedure was the same for runs 1-4. One drop of phenolphthalein and 13 ml. of magnesia mixture were added to the ice-cold quenched sample of exchange mixture and the solution was neutralized with about 1 ml. of concentrated ammonium hydroxide. Then 3 ml. of concentrated ammonium hydroxide were added and the solution was kept in an ice bath for ten to twenty minutes.

The filtrate, which contained the arsenic(III), was set aside for precipitation of the sulfide.

#### 10. Preparation of the Arsenic(V) Fraction for Counting

The magnesium ammonium arsenate precipitate, the funnel, and the chimney were transferred as a unit to another







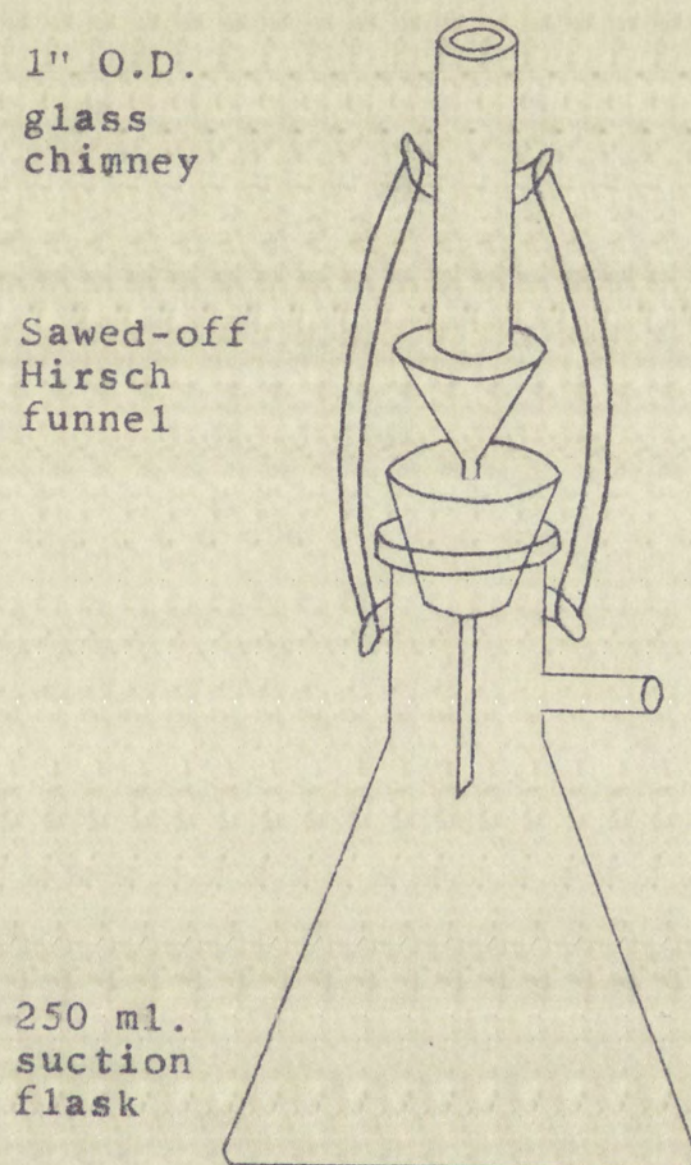
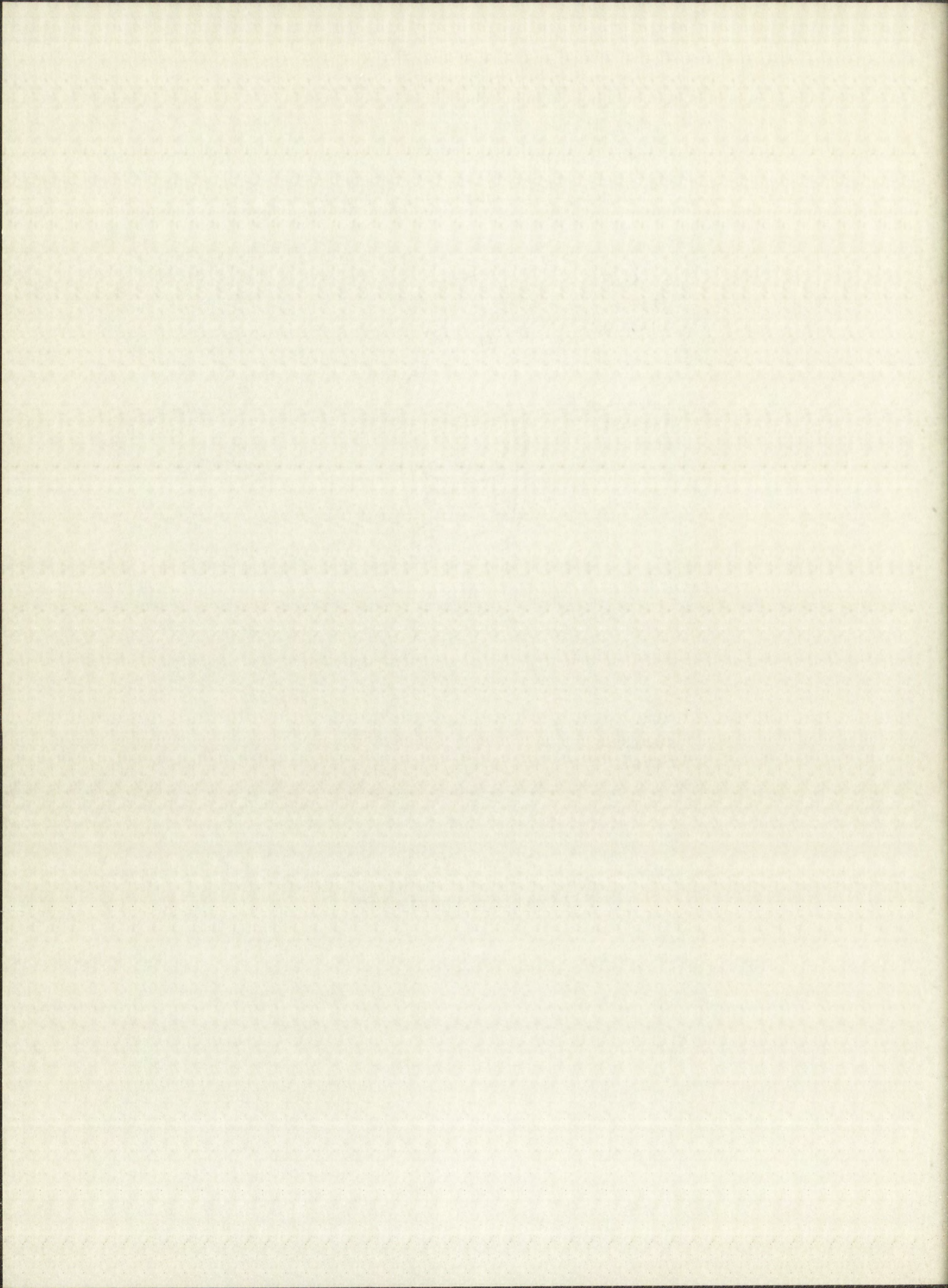


Figure VI-1  
Filtration Apparatus







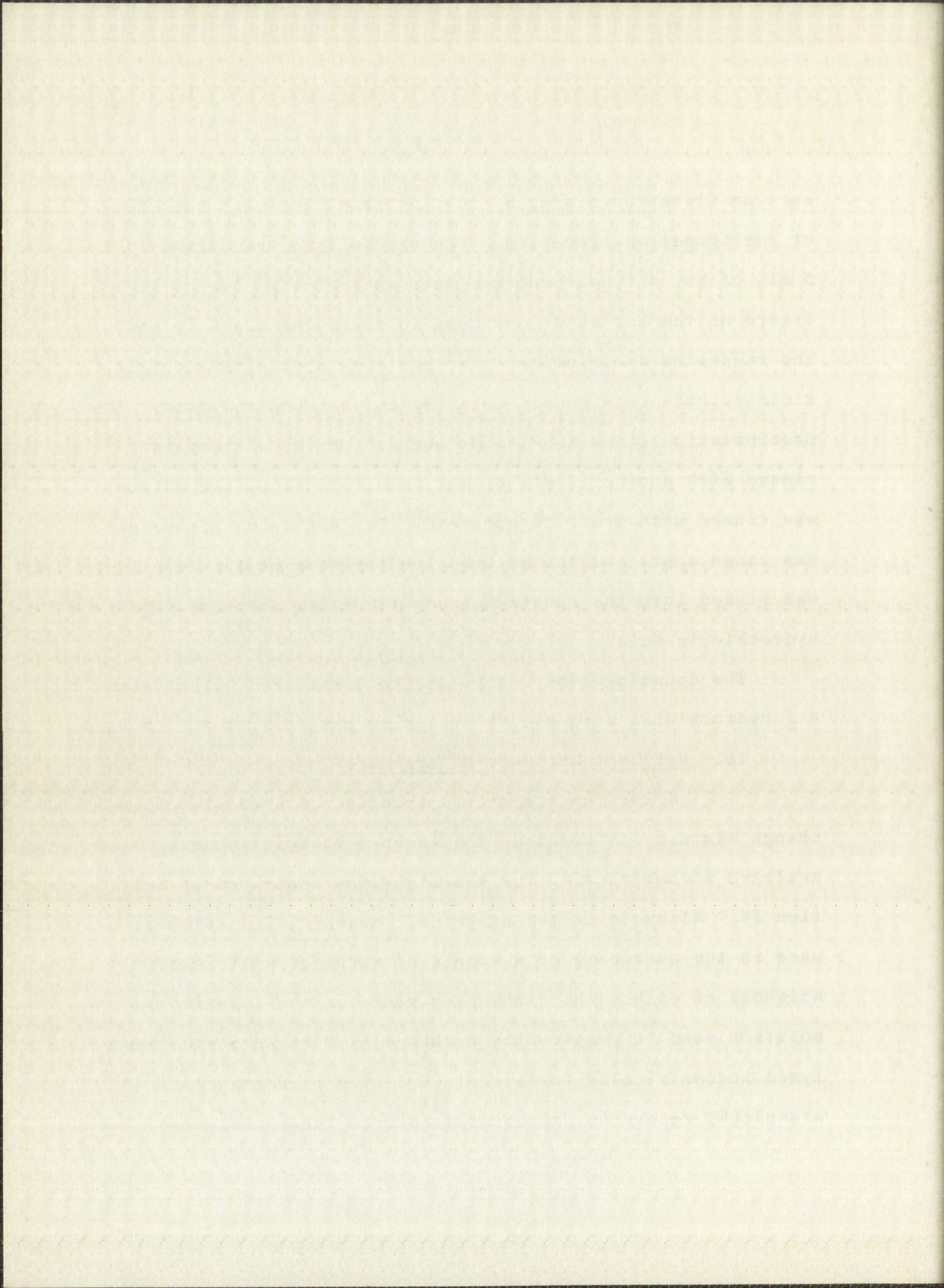
suction flask containing a counting tube into which the stem of the funnel was inserted. The precipitate was dissolved in 5 ml. of hot 4 f hydrochloric acid as follows: two milliliters of the hot acid was used to rinse the flask in which the magnesium ammonium arsenate had been precipitated; this rinse solution was poured into the chimney and filtered. The precipitation flask and inside surface of the chimney were rinsed with another 2 ml. of hot acid. Finally, the chimney was rinsed with 1 ml. of hot acid. The filtering apparatus was taken apart and the solution on the stem of the funnel was rinsed into the counting tube with a few drops of 4 f hydrochloric acid.

The counting tube was filled to a standard height with 4 f hydrochloric acid and the solution was stirred and counted.

#### 11. Per Cent Recovery of Arsenic(V)

After the arsenic(V) fraction of a sample of exchange mixture was counted, the arsenic(V) solution was analyzed iodometrically for arsenic(V) as described in Section IV. Aliquots of the arsenic(V)-arsenic(III) solution used in the quenching of a sample of exchange mixture and aliquots of either the exchange mixture or the arsenic(V) solution used to prepare the exchange mixture were also analyzed iodometrically for arsenic(V). The percentage of arsenic(V) recovered, as determined from these analyses,







generally ranged from 92% to 100%.

12. Preparation of the Arsenic(III) Fraction for  
Counting

The filtrate from the magnesium ammonium arsenate precipitation was made about 9 f in hydrochloric acid with 100 ml. of concentrated hydrochloric acid. Approximately 1 ml. of a concentrated hydrochloric acid solution, which was about 0.05 f in arsenic(III) and about 0.05 f in arsenic(V), was added to the filtrate. One or two drops of an aerosol solution was stirred into the filtrate, then hydrogen sulfide was bubbled through the solution for fifteen minutes. This slurry was heated in a steam bath for five to ten minutes and immediately filtered through a glass-fiber filter in an apparatus similar to the one pictured in Figure VI-1, p. 103. The last traces of precipitate were washed into the chimney with 4 f hydrochloric acid and the chimney was rinsed with 95% ethanol.

The chimney was carefully removed while the precipitate was still under suction. The filter disc was then folded in half and inserted in a counting tube. The precipitate clinging to the bottom edge of the chimney was then rinsed into the counting tube with 7.5 f ammonium hydroxide which also dissolved the arsenic sulfides. The counting tube was filled to a standard height with water and the solution was stirred and counted.







### 13. Activity Balance

Two or three aliquots of exchange mixture were diluted to a standard height in a counting tube, stirred, and counted. The sum of the activities of the arsenic(III) and the arsenic(V) fractions of each sample of exchange mixture was generally within 3% of the activity of an equivalent aliquot of the exchange mixture.

### 14. Experimental Difficulties

The 50 ml. round-bottom exchange flasks were always immersed in the temperature bath up to the neck of the flask. During runs 33 and 36, in which the flasks were not covered with tape, it was discovered that condensate slowly collected in the neck of the flask. The effect was investigated and it was determined that the concentration of 10.69 f hydrochloric acid in the bulb of an exchange flask maintained at 29.7°C for seven hours decreased about 1.2%. The decrease in concentration of hydrochloric acid was the same for 15 ml. and 5 ml. of solution in the flask. Because of this condensation, the concentration of hydrochloric acid and the concentration of arsenic changed slightly during every exchange experiment conducted at 29.7°C. This difficulty was eliminated in runs 38-49 by completely immersing sealed ampoules of exchange mixture in a temperature bath at 48.6°C or 67.3°C.

The problem of matching the concentration of hydrochloric







acid of arsenic(III) and arsenic(V) solutions is dependent on the species of arsenic in solution and the sensitivity of the technique used in the matching process. It is apparent from spectrophotometric data that matching hydrochloric acid concentrations by titration is not adequate. Perhaps a spectrophotometric method of matching similar to the one used in the antimony system by Bonner and Goishi<sup>4</sup> could be developed.

Because the equilibria among arsenic(V) species is shifted by heat, the stock solutions of arsenic(V) should be aged at the temperature of the exchange reaction prior to preparation of the reaction mixture.

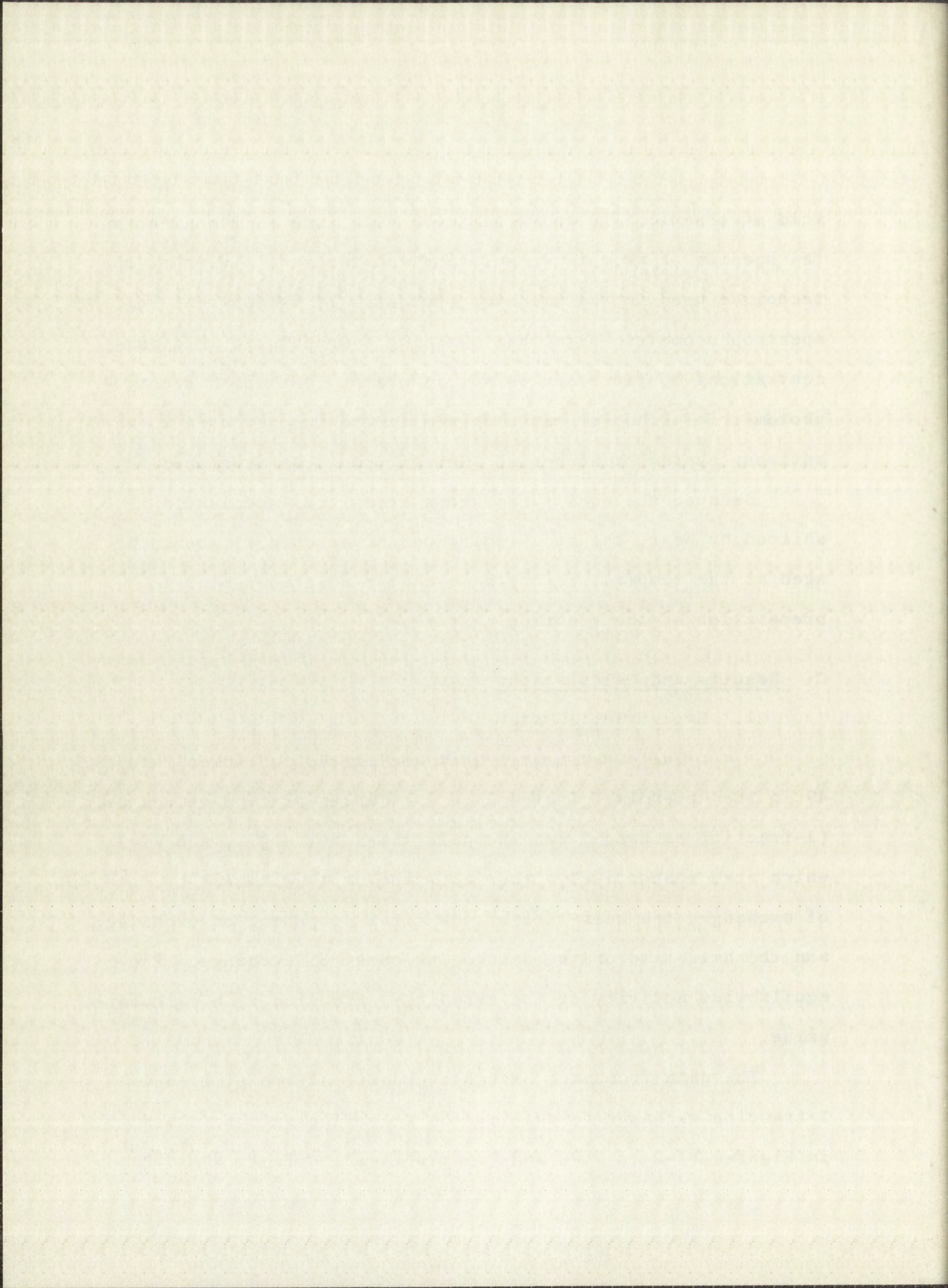
### C. Results and Calculations

#### 1. Experimental Data

The experimental data are listed in Tables 1 to 49 in the Appendix. Included in the Tables are the values of (1-fraction exchange) and the half-times  $t_{\frac{1}{2}}$ ,  $(t_{\frac{1}{2}})_1$ , and  $(t_{\frac{1}{2}})_2$  which are, respectively, the half-time of the initial portion of exchange, the half-time of the first component of exchange, and the half-time of the second component of exchange. The equilibrium activity of the arsenic(V) fraction is a calculated value.

The data from each exchange experiment are plotted as 1-fraction exchange versus time on a semilogarithmic scale in Figures VI-2 to VI-6 and Figures VI-12 to VI-15 in this







Section and Figures 1 to 11 in the Appendix. The curves were fitted to the points visually.

The temperature, concentrations of arsenic(III), arsenic(V), and hydrochloric acid, the half-times, and the intercept of the second component of exchange for each exchange experiment are summarized in Table VI-1. The concentrations listed in the Table are those of the exchange mixtures at the beginning of the reaction. The hydrochloric acid concentration decreased one or two per cent during the course of the reaction at 29.7°C.

## 2. Nature of the Isotopic Exchange

The exchange reaction was generally complex in 10.8 f to 12.6 f hydrochloric acid at 29.7°C; typical complex curves are shown in Figures VI-2, VI-3, and VI-4, pages 113, 114, and 115. The complex nature of exchange was not apparent at 9.98 f hydrochloric acid at 29.7°C (see run 29). In 8.88 f and 6.91 f hydrochloric acid solution at 29.7°C, no exchange was detected in five days (see runs 27 and 28).

Isotopic exchange in 10.9 f hydrochloric acid is also complex at 48.6°C (runs 38-43) and 67.3°C (runs 44-49).

## 3. Aging

The results of runs 1-4 indicate an aging process which was essentially complete in three weeks; the exchange mixtures were identical except for the age of the arsenic(III) and arsenic(V) solutions (see Figure VI-5, p. 116). Although







Table VI-1

## Summary of Exchange Data

Run	[As(III)] $\times 10^2, \underline{f}$	[As(V)] $\times 10^2, \underline{f}$	[HCl], $\underline{f}$	Temp., $^{\circ}\text{C}$	$t_{\frac{1}{2}},$ min.	$(t_{\frac{1}{2}})_1,$ min.	$(t_{\frac{1}{2}})_2,$ min.	$Q_2$		
1	0.490*	(1) <sup>a</sup>	1.16	(1) <sup>a</sup>	11.2	29.7	216	109	17,650	0.44
2	0.490*	(7)	1.16	(7)	11.2	29.7	210	140	600	0.35
3	0.490*	(22)	1.16	(22)	11.2	29.7	176	140	490	0.21
4	0.490*	(42)	1.16	(42)	11.2	29.7	176	141	491	0.21
5	0.111*	(3)	3.24	(184)	10.9	29.7	211	211	---	---
6	0.691*	(4)	3.24	(185)	10.9	29.7	470	198	960	0.71
7	0.691	(4)	3.24*	(185)	10.9	29.7	$\sim 450$	$\sim 140$	$\sim 780$	
8	0.276*	(11)	1.61	(192)	10.9	29.7	485	231	930	0.67
9	0.111*	(11)	1.61	(192)	10.9	29.7	265	135	449	0.67
10	0.691*	(12)	1.61	(193)	10.9	29.7	710	265	1,440	0.80
11	0.691	(12)	1.61*	(193)	10.9	29.7	$\sim 630$	$\sim 200$	$\sim 1,160$	
12	0.276*	(18)	3.24	(199)	10.9	29.7	300	132	455	0.74

\* Indicates traced species in hydrochloric acid solution.

a The age in days of the solution used to prepare the exchange mixture is indicated in parentheses.



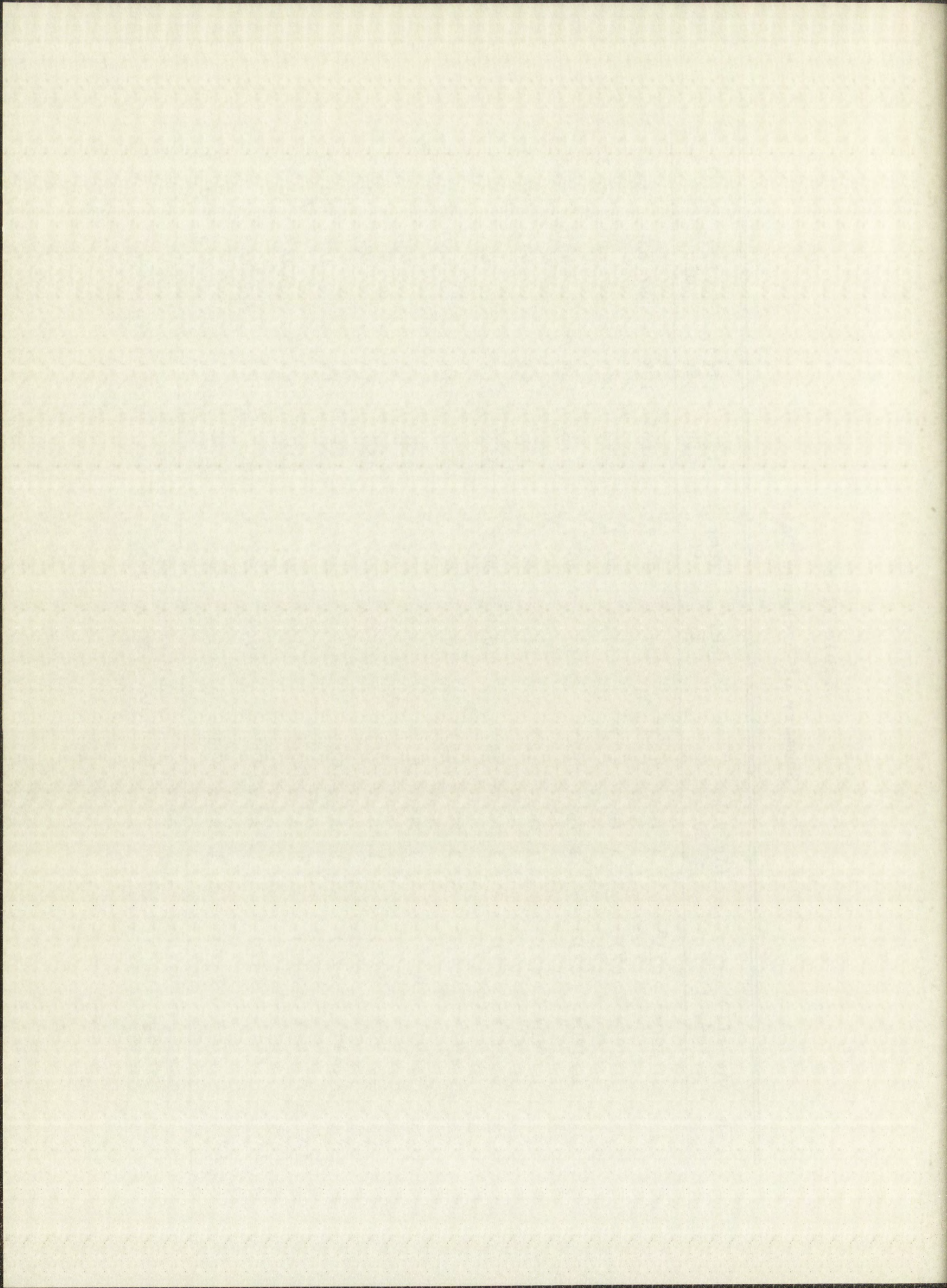




Table VI-1--Continued

Run	[As(III)] $\times 10^2$ , $\underline{f}$	[As(V)] $\times 10^2$ , $\underline{f}$	[HCl], $\underline{f}$	Temp., $^{\circ}\text{C}$	$t_{\frac{1}{2}}$ , min.	$(t_{\frac{1}{2}})_1$ , min.	$(t_{\frac{1}{2}})_2$ , min.	$Q_2$
13	0.111*	(18) <sup>a</sup>	3.24 (199) <sup>a</sup>	29.7	213	88	265	0.85
14	0.691*	(19)	3.24 (200)	29.7	510	193	1,100	0.74
15	0.276*	(25)	1.61 (206)	29.7	465	222	926	0.65
16	0.111*	(25)	1.61 (206)	29.7	285	127	409	0.78
17	0.691*	(26)	1.61 (207)	29.7	790	290	1,380	0.78
18	0.691	(26)	1.61* (207)	29.7	$\sim 700$	$\sim 200$	$\sim 1,260$	
19	4.74*	(1)	4.18 (56)	29.7	250	131	358	0.69
20	1.42*	(1)	4.18 (56)	29.7	295	152	495	0.65
21	0.474*	(1)	4.18 (56)	29.7	360	210	2,863	0.42
22	0.420*	(1)	0.837 (62)	29.7	860	418	3,568	0.52
23	0.420*	(1)	8.37 (62)	29.7	240	115	558	0.57
24	0.420*	(1)	2.51 (62)	29.7	440	176	1,426	0.59
25	1.26*	(1)	2.51 (62)	29.7	360	260	1,860	0.40

\* Indicates traced species in hydrochloric acid solution.

a The age in days of the solution used to prepare the exchange mixture is indicated in parentheses.







Table VI-1--Continued

Run	[As(III)] $\times 10^2, \underline{f}$	[As(V)] $\times 10^2, \underline{f}$	[HCl], $\underline{f}$	Temp., $^{\circ}\text{C}$	$t_{\frac{1}{2}}$ , min.	$(t_{\frac{1}{2}})_1$ , min.	$(t_{\frac{1}{2}})_2$ , min.	$Q_2$
26	4.20*	(1) <sup>a</sup>	2.51 (62) <sup>a</sup>	10.9	29.7	240	---	---
27	0.231*	(1)	0.446 (319)	6.91	29.7	negligible exchange in 5 days		
28	0.231*	(1)	0.448 (319)	8.88	29.7	negligible exchange in 5 days		
29	0.235*	(1)	0.450 (319)	9.98	29.7	56,640	---	---
30	0.233*	(1)	0.453 (319)	10.8	29.7	9,900	47,600	0.93
31	0.230*	(1)	0.453 (319)	12.6	29.7	790	22,350	0.49
32	0.416*	(1)	0.829 (133)	10.9	29.7	~100	554,000	0.95
33 <sup>b</sup>	0.416*	(1)	0.829 (133)	10.9	29.7	---	185,000	0.96
34 <sup>c</sup>	0.416*	(1)	0.829 (133)	10.9	29.7	---	>185,000	0.96
35	0.416*	(1)	0.829 (133)	10.9	29.7	~80	320,000	0.94
36 <sup>b</sup>	0.416*	(1)	0.829 (133)	10.9	29.7	---	320,000	0.94
37 <sup>c</sup>	0.416*	(1)	0.829 (133)	10.9	29.7	---	320,000	0.94

\* Indicates traced species in hydrochloric acid solution. <sup>a</sup>The age in days of the solution used to prepare the exchange mixture is indicated in parentheses. <sup>b</sup>Exchange reaction was conducted under fluorescent light. <sup>c</sup>Exchange mixture was in contact with 0.21 g. pyrex glass wool.



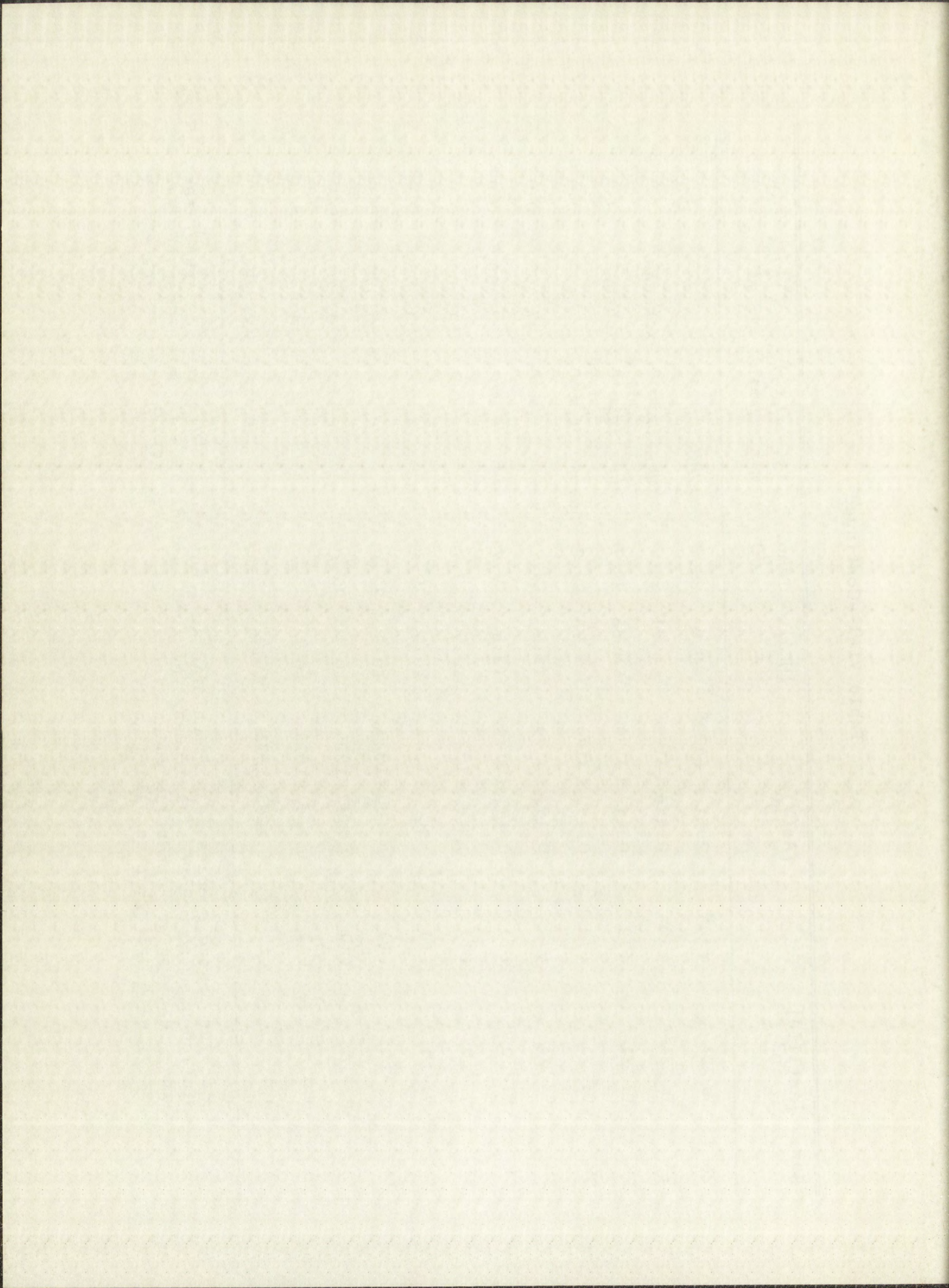


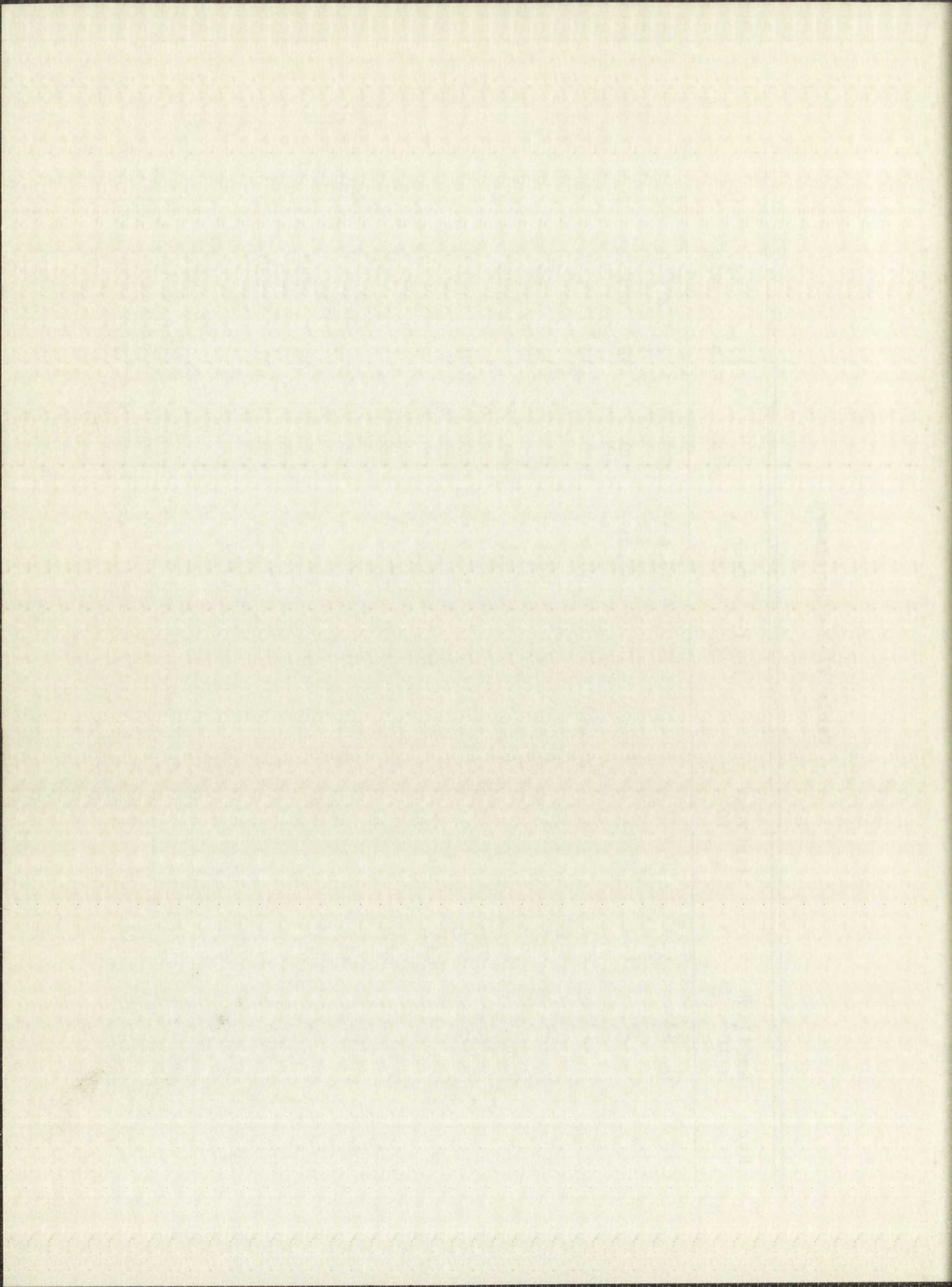


Table VI-1--Continued

Run	[As(III)] x 10 <sup>2</sup> , f	[As(V)] <sub>2</sub> x 10 <sup>2</sup> , f	[HCl], f	Temp., °C	t <sub>1/2</sub> , min.	(t <sub>1/2</sub> ) <sub>1</sub> , min.	(t <sub>1/2</sub> ) <sub>2</sub> , min.	Q <sub>2</sub>
38	0.132*	(2) <sup>a</sup>	(171) <sup>a</sup>	48.6	475	142	2,900	0.73
39	0.132*	(2)	(179)	48.6	430	88	1,160	0.81
40	0.132*	(2)	(179)	48.6	320	320	---	---
41	0.264*	(2)	(179)	48.6	435	307	1,450	0.67
42	0.660*	(2)	(179)	48.6	380	?	2,220	0.96
43 <sup>d</sup>	0.132*	(15)	(192)	48.6	660	240	1,265	0.74
44	0.132*	(1)	(178)	67.3	69	---	---	---
45	0.132*	(1)	(178)	67.3	45	---	---	---
46	0.132*	(1)	(178)	67.3	23	---	---	---
47	0.264*	(1)	(178)	67.3	62	40	130	0.47
48	0.660*	(1)	(178)	67.3	95	43	196	0.70
49 <sup>d</sup>	0.132*	(15)	(192)	67.3	81	---	---	---

\* Indicates traced species in hydrochloric acid solution. a The age in days of the solution used to prepare the exchange mixture is indicated in parentheses.  
d Arsenic(III) and arsenic(V) solutions were aged 13 days at the temperature of the reaction.







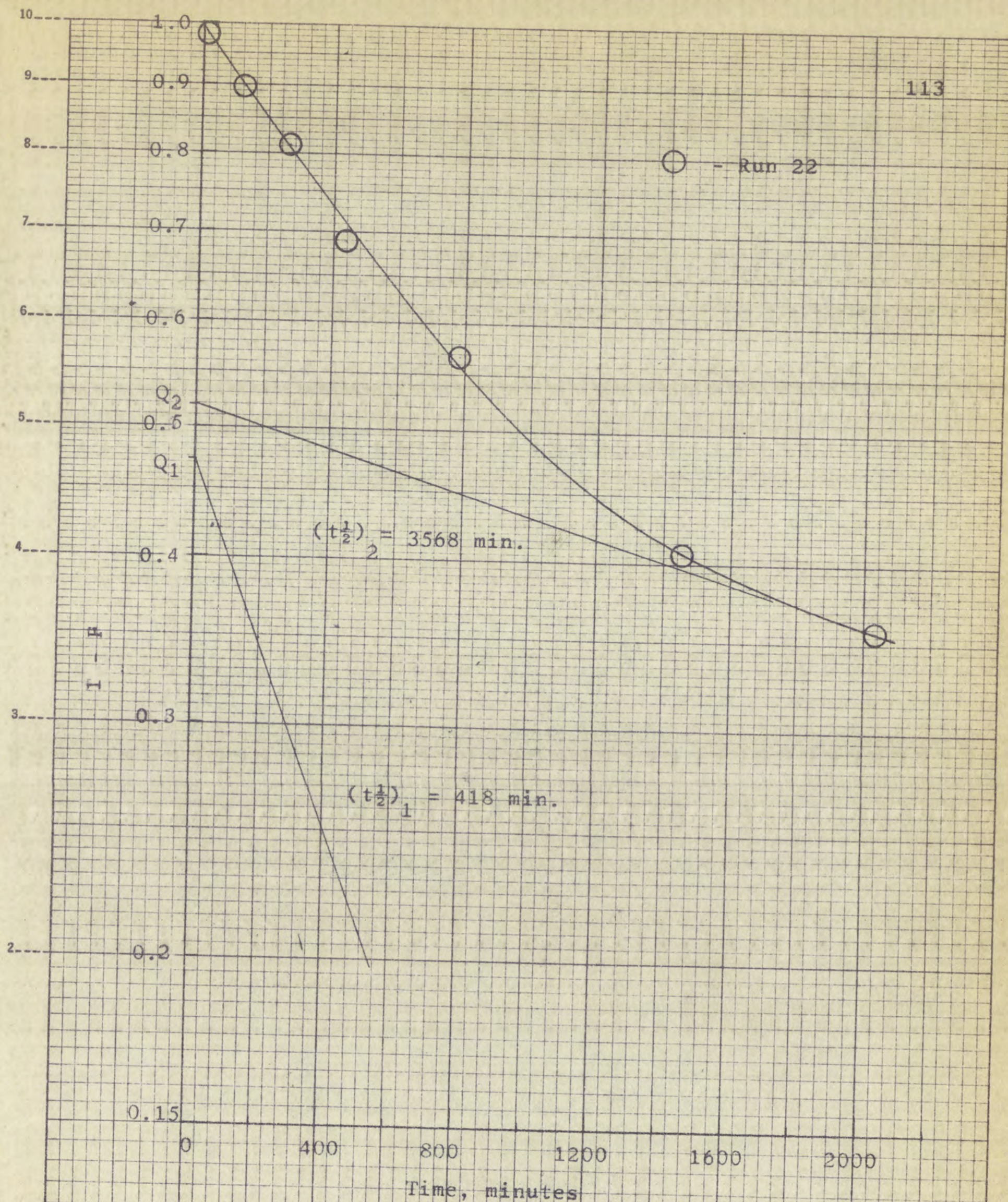
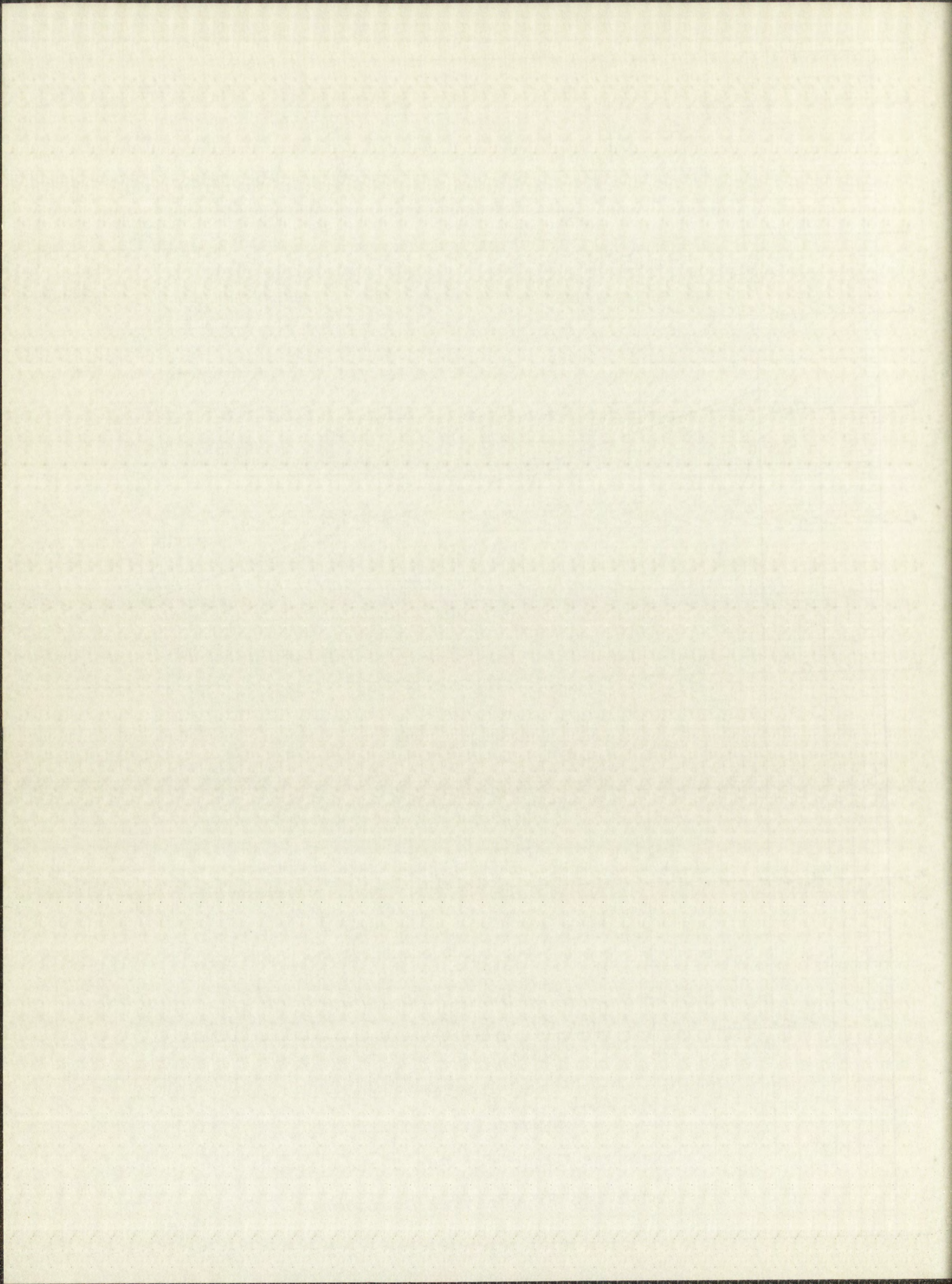


Figure VI-2  
Exchange Curve for Run 22 Resolved  
Into Two Exponential Components







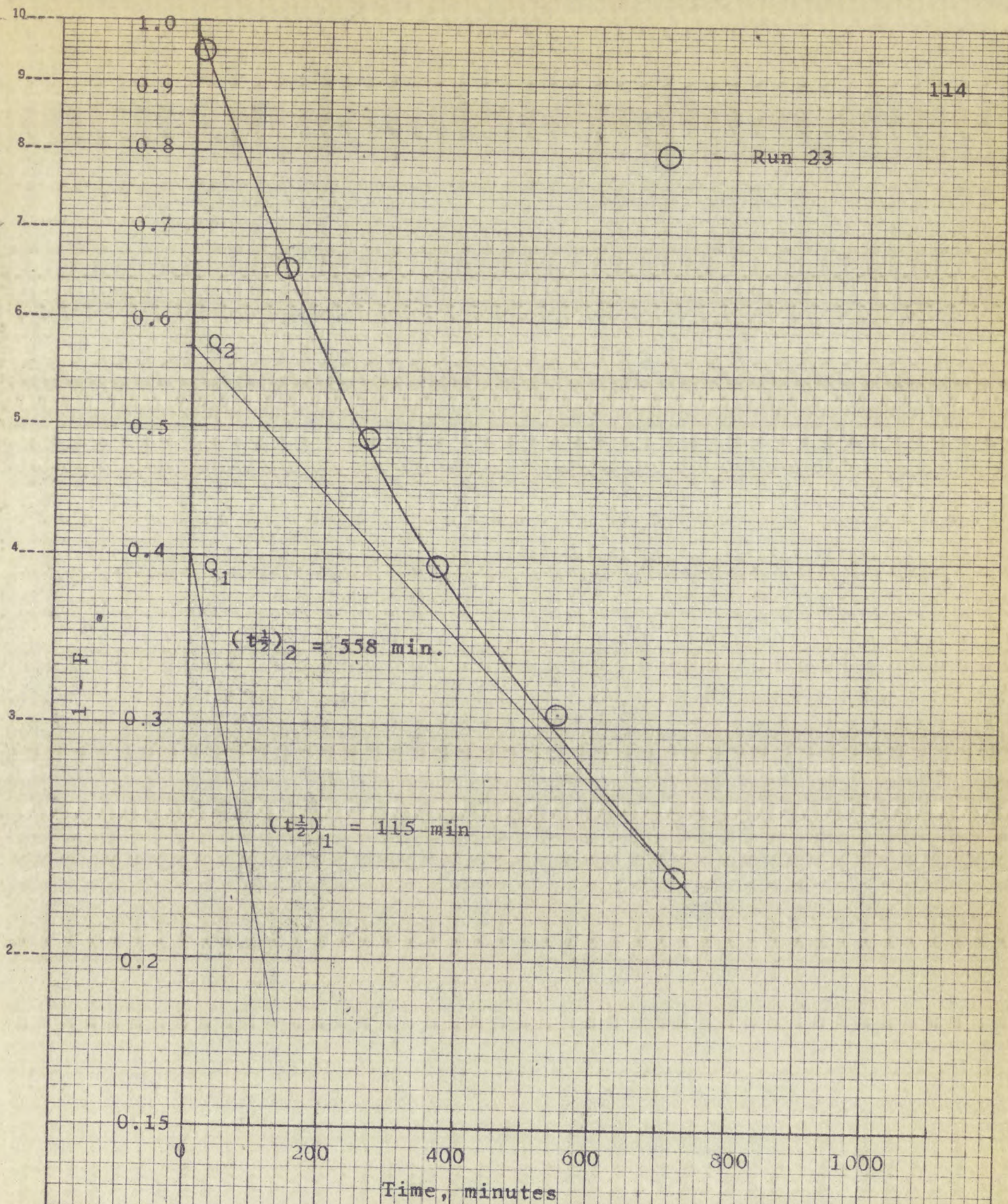


Figure VI-3

Exchange Curve for Run 23 Resolved  
Into Two Exponential Components







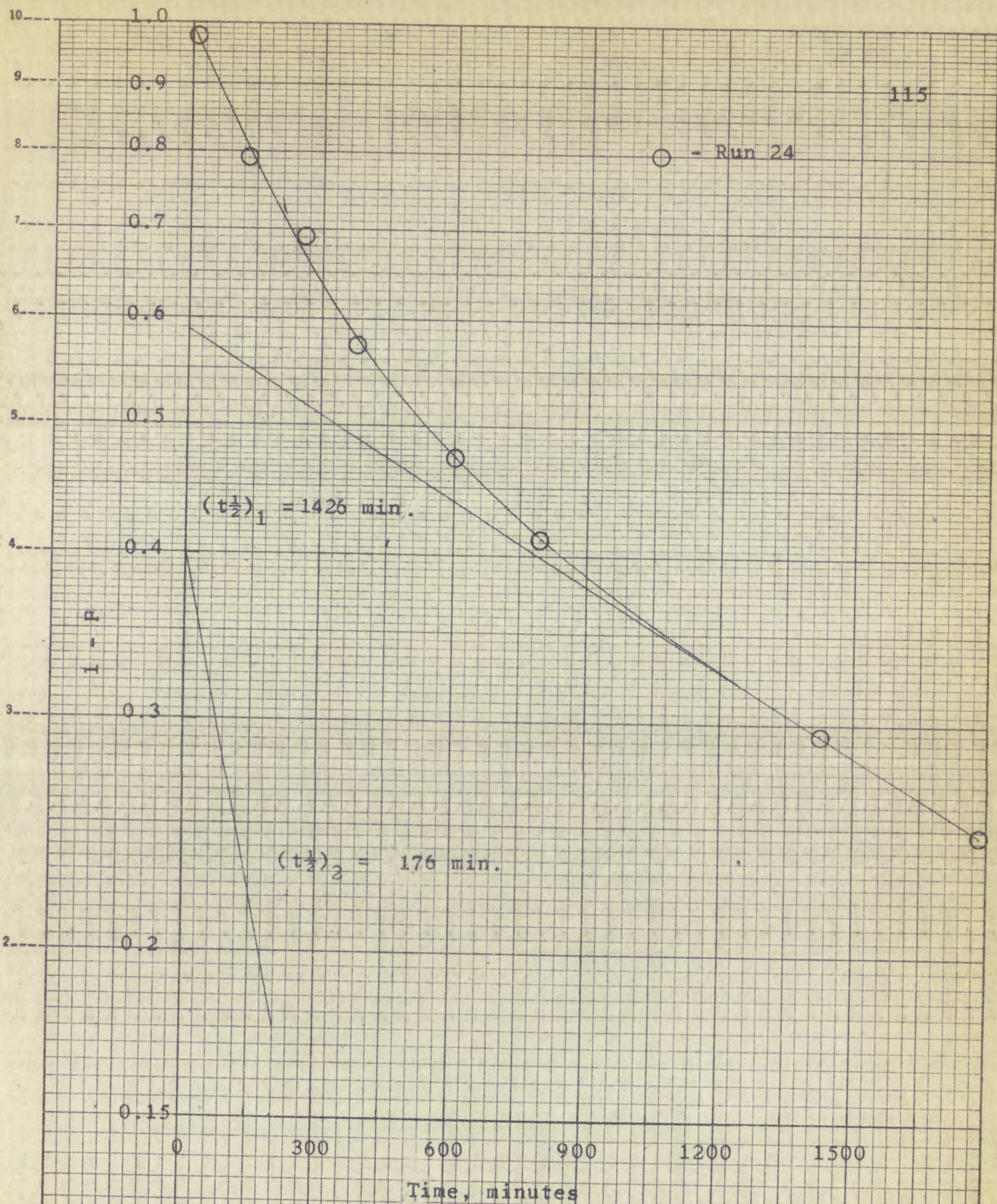


Figure VI-4

Exchange Curve for Run 24 Resolved  
Into Two Exponential Components







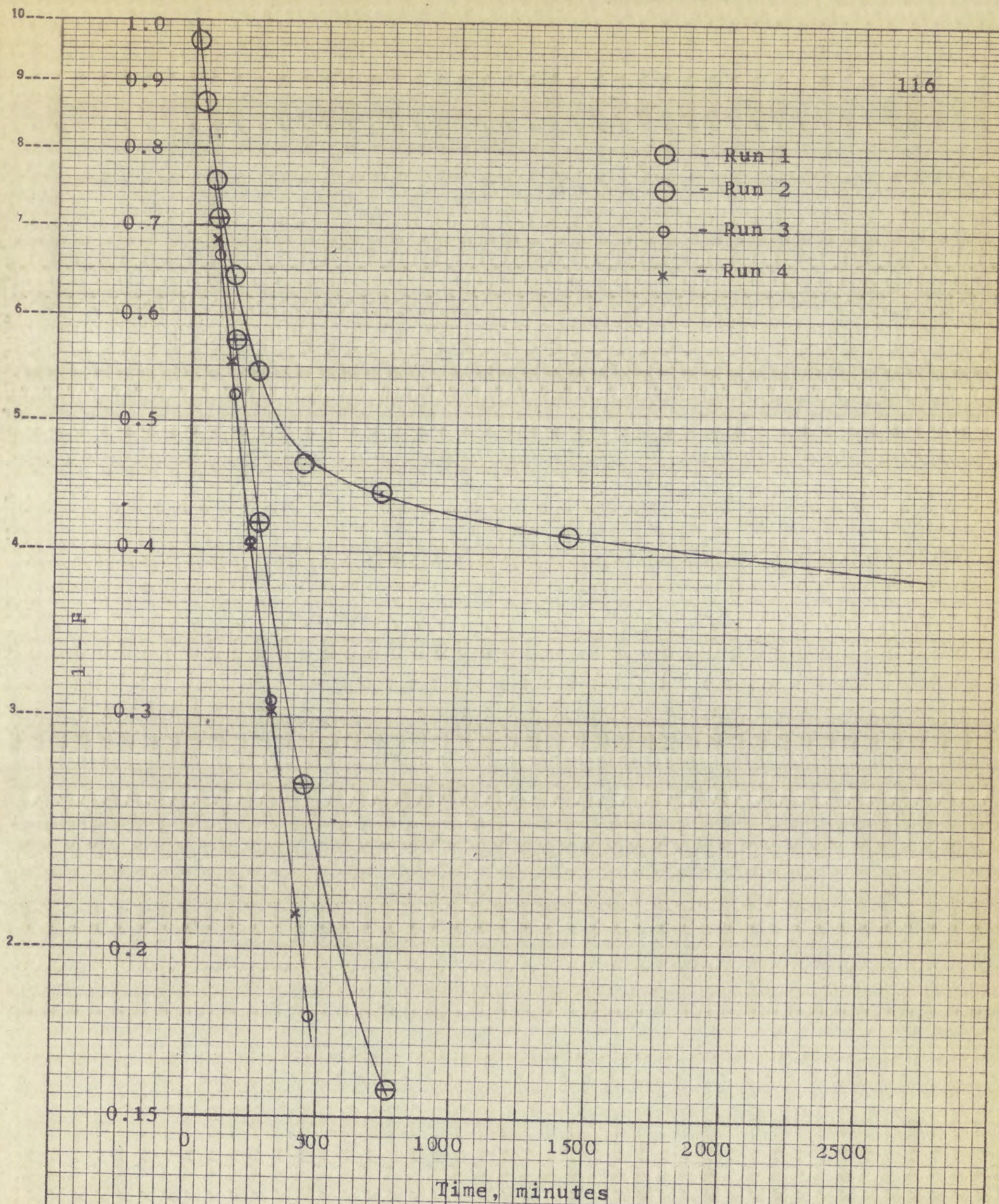
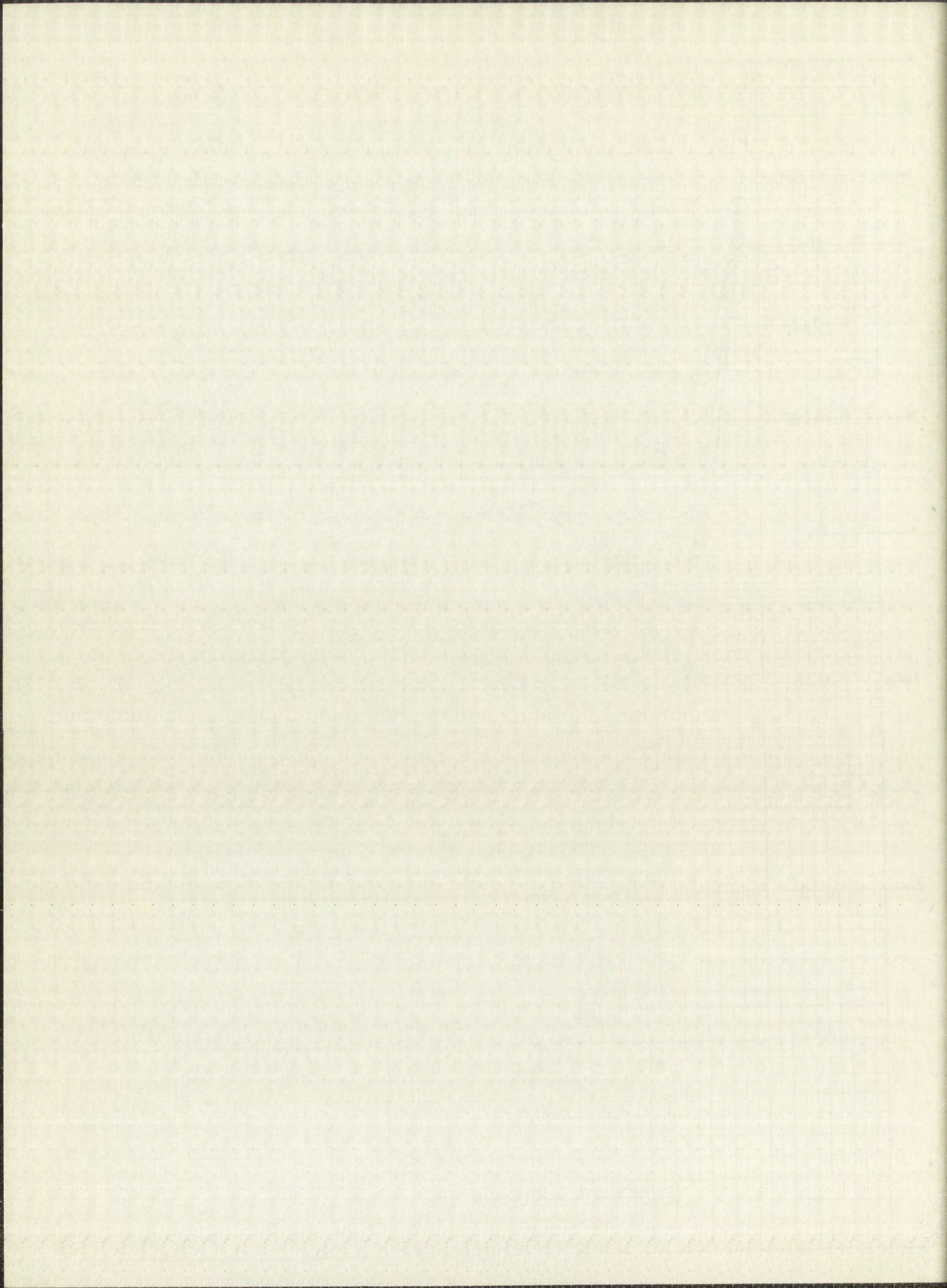


Figure VI-5

Exchange Curves for Runs 1, 2, 3, and  
4 Resolved into Two Exponential  
Components







$(t_{\frac{1}{2}})_1$  did not change very much with age of the solutions,  $(t_{\frac{1}{2}})_2$  and  $Q_2$  changed considerably over three weeks; six-weeks-old solutions gave the same exchange results as three-weeks-old solutions.

The results of exchange experiments duplicated after fourteen to fifteen days are summarized in Table VI-2. Considering the difficulty in reproducing the exchange curves, it is concluded from the results listed in Table VI- that the arsenic(III) solutions do not age (see Section VI.C.4 for a discussion of the reproducibility). Thus only the arsenic(V) solutions age. A comparison of runs 3 and 4 in Table VI-1, page 109, reveals that the relatively rapid aging of arsenic(V) apparently has been completed in three weeks (see Figure VI-5, p. 116). These observations are in accord with the spectrophotometric data.

#### 4. Reproducibility

The data from several exchange runs which were duplicated after 14 to 15 days are summarized in Table VI-2. The variation in the half-times of exchange runs which were carried out under identical conditions except for the age of the solutions is attributed to a slight difference in the hydrochloric acid concentration of the reaction mixtures.

It appears to be important that the arsenic(V) be aged in hydrochloric acid of the same concentration as that of the exchange mixture. Run 32 was supposed to be a duplicate of



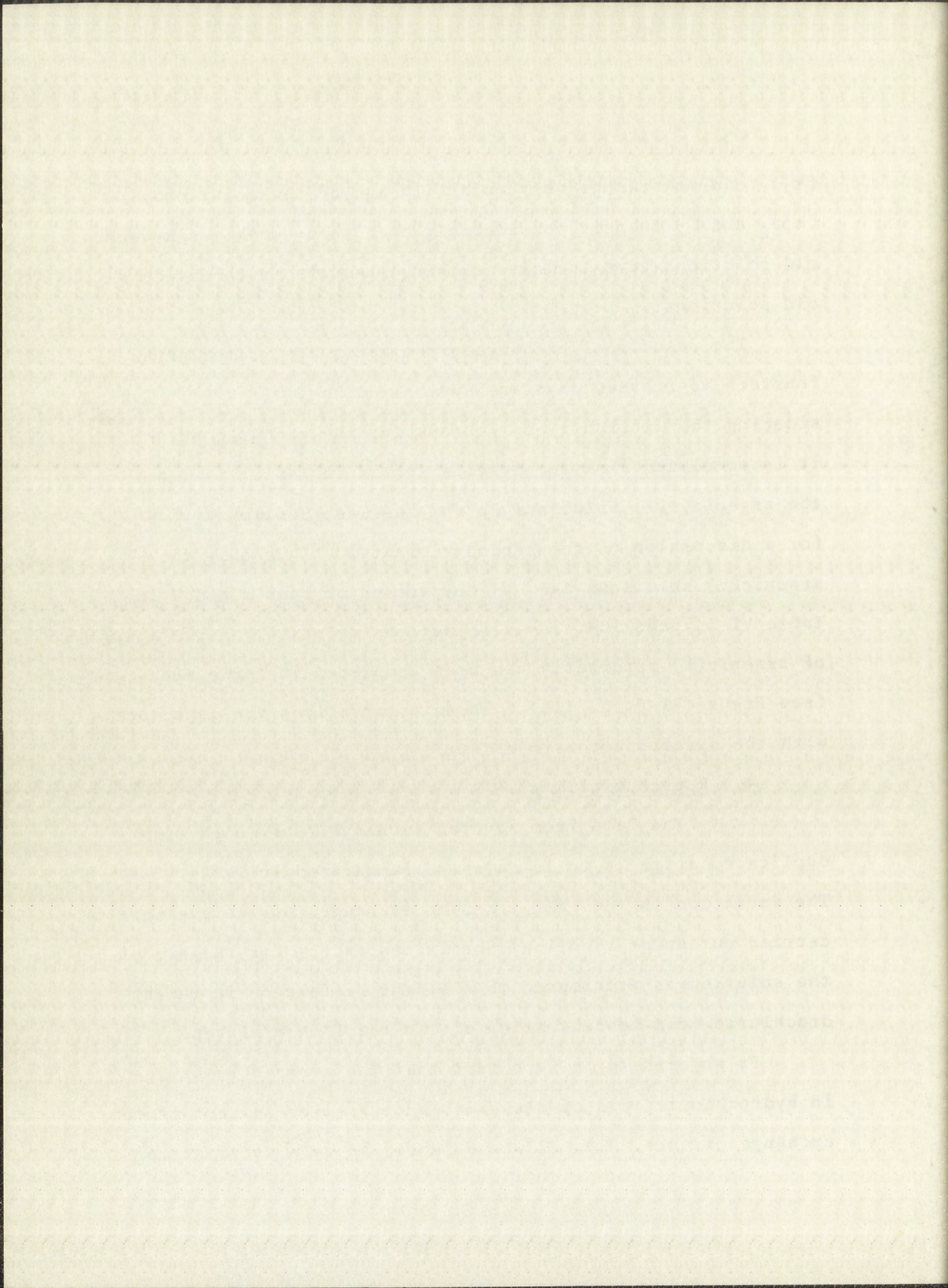




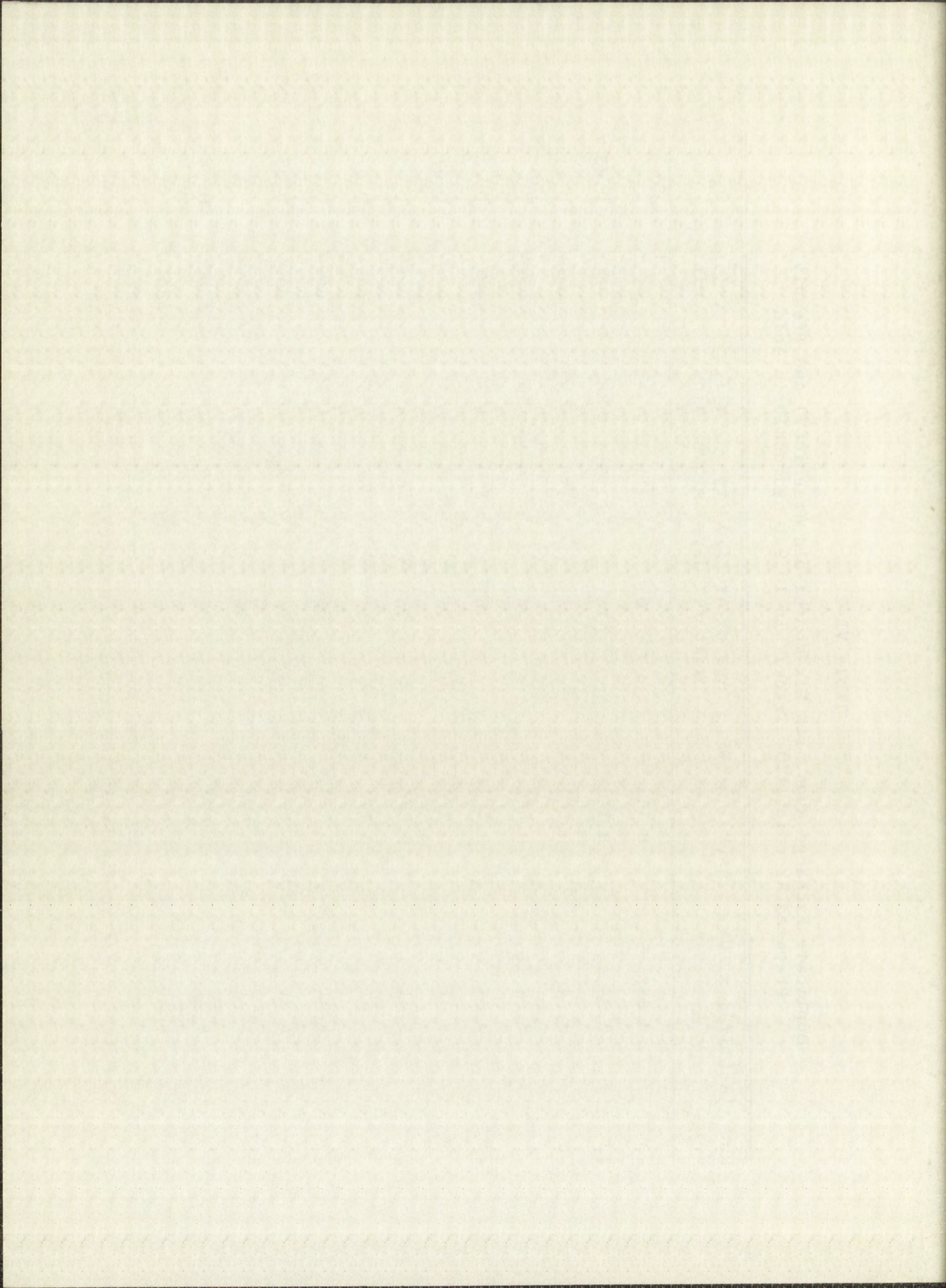
Table VI-2

Duplicate Exchange Runs with Six-months-old Arsenic(V) and Freshly  
Prepared Arsenic(III) "Tracer" in 10.9 f Hydrochloric Acid

Run No.	$[\text{As(III)}] \times 10^2, \text{ f}$	$[\text{As(V)}] \times 10^2, \text{ f}$	Age of As(III) "tracer," days	$t_{\frac{1}{2}}, \text{ min.}$	$(t_{\frac{1}{2}})_1, \text{ min.}$	$(t_{\frac{1}{2}})_2, \text{ min.}$	$Q_2$
5	3.24	0.111	3	211	---	---	---
13	3.24	0.111	18	213	88	265	0.85
6	3.24	0.691	4	470	198	960	0.71
7*	3.24	0.691	4	~450	~140	~780	
14	3.24	0.691	19	510	193	1100	0.74
8	1.61	0.276	11	485	231	930	0.67
15	1.61	0.276	25	465	222	926	0.65
9	1.61	0.111	11	265	135	449	0.67
16	1.61	0.111	25	285	127	409	0.78
10	1.61	0.691	12	710	265	1440	0.80
11*	1.61	0.691	12	~630	~200	~1160	
17	1.61	0.691	26	790	290	1380	0.78
18*	1.61	0.691	26	~700	~200	~1260	

\* The tracer was initially in the form of arsenic(V).







run 22 about three months after run 22 was conducted (see Table VI-1, p. 109). The arsenic(V) solution which had been 10.9  $\underline{f}$  in hydrochloric acid when it was used in run 22 was found to be 10.7  $\underline{f}$  in hydrochloric acid the day before run 32 was performed. Therefore, one day prior to run 32, the acid concentration of the arsenic(V) stock solution was increased to 10.9  $\underline{f}$  by dissolving hydrogen chloride in the solution. The results of runs 22 and 32 are quite different (see Table VI-1, p. 109); the only resemblance of run 32 to run 22 is the moderately fast initial exchange.

#### 5. Effect of Hydrochloric Acid Concentration

The effect of the hydrochloric acid concentration on the exchange reaction at 29.7°C is shown by the results of runs 27-31 which are summarized in Table VI-1 and Figure VI-6. Exchange in 6.91  $\underline{f}$  and 8.88  $\underline{f}$  hydrochloric acid is negligible over five days. In 9.98  $\underline{f}$  hydrochloric acid, the exchange is very slow ( $t_{\frac{1}{2}} = 3.94$  days) and appears simple. With increasing hydrochloric acid concentration the first component of the complex exchange becomes more prominent and the initial half-time decreases. For example, the initial half-times for exchange in 10.9  $\underline{f}$  and 12.6  $\underline{f}$  hydrochloric acid (runs 30 and 31) are 9,900 minutes and 790 minutes, respectively.

#### 6. Effect of Temperature

The isotopic exchange reaction proceeds at a faster







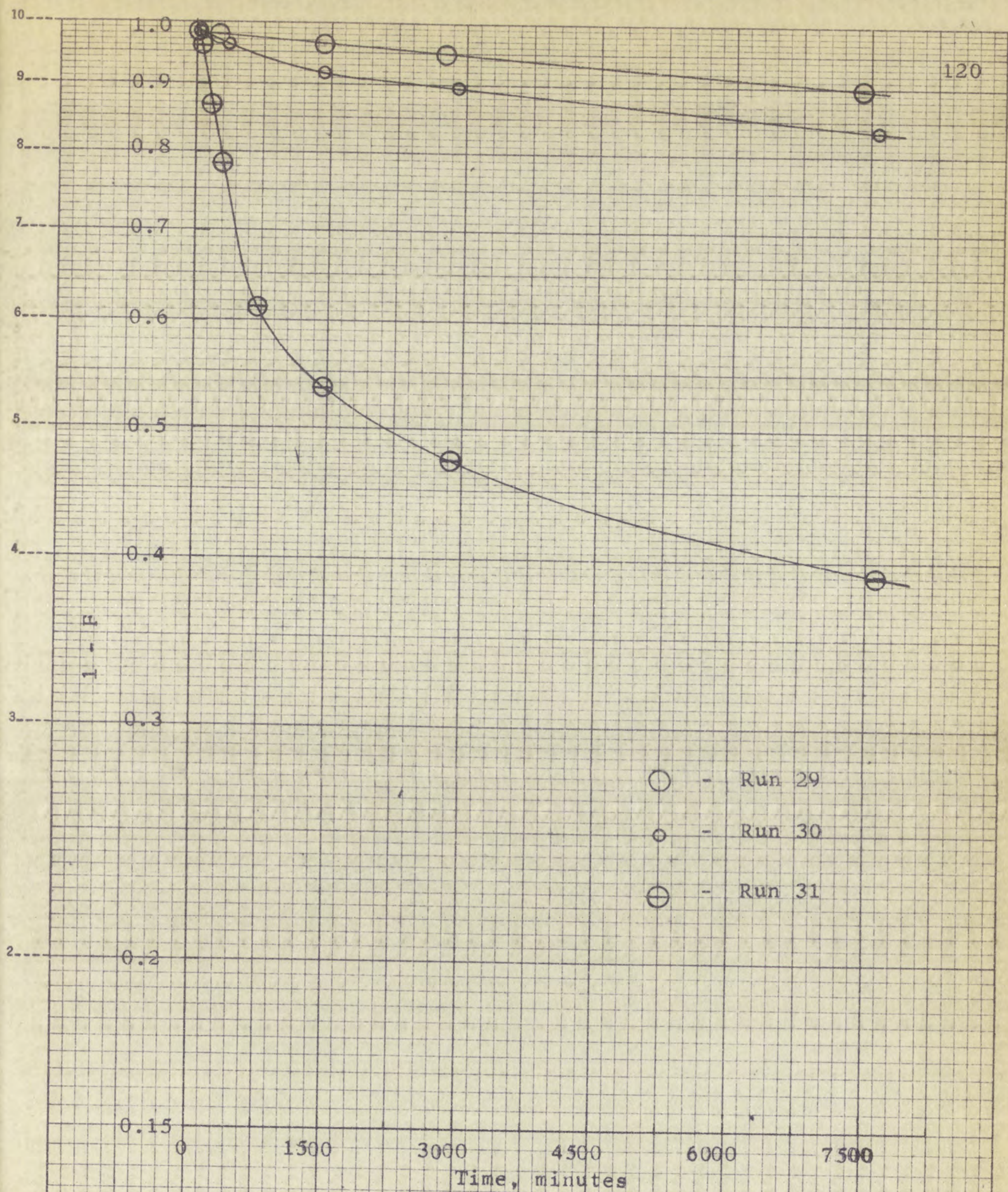
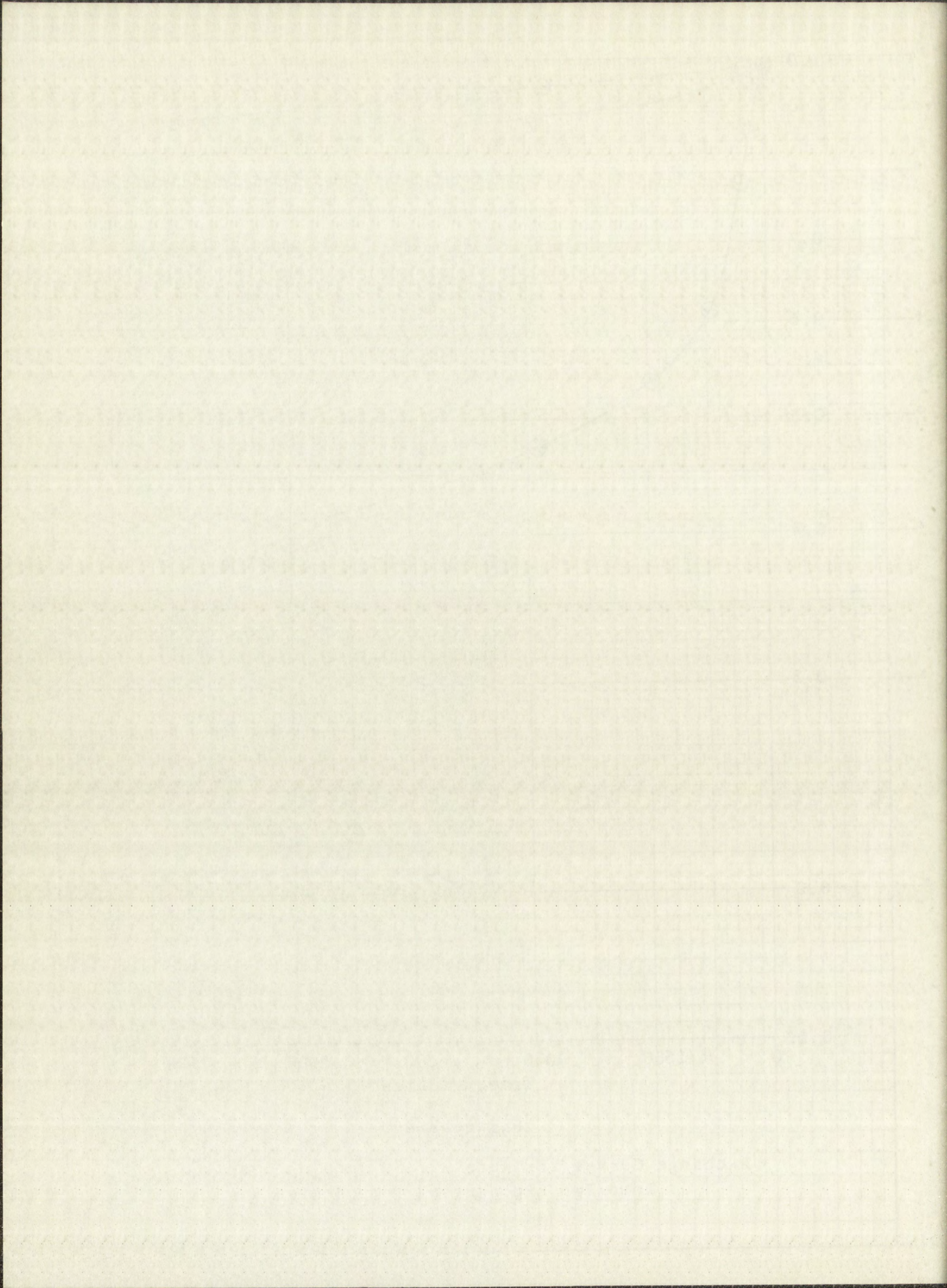


Figure VI-6

Exchange Curves for Runs 29, 30, and 31 Resolved  
Into Two Exponential Components







rate at elevated temperatures. The data from the exchange at  $48.6^{\circ}\text{C}$  and  $67.3^{\circ}\text{C}$  are summarized in Table VI-1, runs 38-49 (see page 109).

One of the experiments at  $48.6^{\circ}\text{C}$  and one at  $67.3^{\circ}\text{C}$  were duplicated after the two-days-old arsenic(III) and the five-months-old arsenic(V) solutions were aged at the respective temperatures for thirteen days (runs 43 and 49 respectively). The results are shown in Table VI-1. The half-time increased with aging at both  $48.6^{\circ}\text{C}$  and  $67.3^{\circ}\text{C}$ . Inasmuch as the hydrolytic equilibria among arsenic(V) species are bound to be affected by the temperature, it is concluded that the exchange reactions performed at elevated temperatures were not conducted under equilibrium conditions.

7. Dependence of the Initial Rate of Exchange at  $29.7^{\circ}\text{C}$ ,  $48.6^{\circ}\text{C}$ , and  $67.3^{\circ}\text{C}$  on the Concentrations of Arsenic(III) and Arsenic(V)

The initial rate of exchange was calculated from the initial slope of the exchange curves employing the simple exchange law. In spite of the likelihood that arsenic(V) species in the exchange mixtures were not at equilibrium because of the dilution effect (see Section V.D.1.), the initial rate of exchange was correlated with the concentration of arsenic(III) and the concentration of Arsenic(V) in four







series of experiments, namely runs 5-17 at 29.7°C, runs 19-26 also at 29.7°C, runs 38-42 at 48.6°C, and runs 44-48 at 67.3°C. The preparation of the arsenic(III) "tracer" used to make up the reaction mixtures in runs 5-17 differed from the preparation of the arsenic(III) "tracer" used to make up the reaction mixtures in runs 19-26 (see Section VI.B.6).

The dependence of the initial rate of exchange on the arsenic(III) concentration was determined from the slope of a log-log plot of the rate versus the concentration of the arsenic(III) for a constant arsenic(V) concentration (see Figures VI-7 to VI-11 following). The dependence of the initial rate of exchange on the arsenic(V) concentration was determined from the slope of a log-log plot of the rate versus the concentration of the arsenic(V) for a constant arsenic(III) concentration (see Figures VI-7 to VI-11). The results are summarized in Table VI-3, pages 128-129.

It is interesting to note that the rate expressions at 29.7°C are consistent with one another. For example, the initial rate of exchange between 0.00420  $\mu$  arsenic(III) and 0.0161  $\mu$  arsenic(V) and the initial rate of exchange between 0.00420  $\mu$  arsenic(III) and 0.0324  $\mu$  arsenic(V) can be calculated by the rate expression  $R = 1.18 \times 10^{-6} [\text{As(V)}]^{0.71} \text{ l. g.-at.}^{-1} \text{ sec.}^{-1}$ . The former initial rate can also be calculated from the expression  $R = 3.34 \times 10^{-7} [\text{As(III)}]^{0.30} \text{ l. g.-at.}^{-1} \text{ sec.}^{-1}$ , and the latter initial rate can be calculated







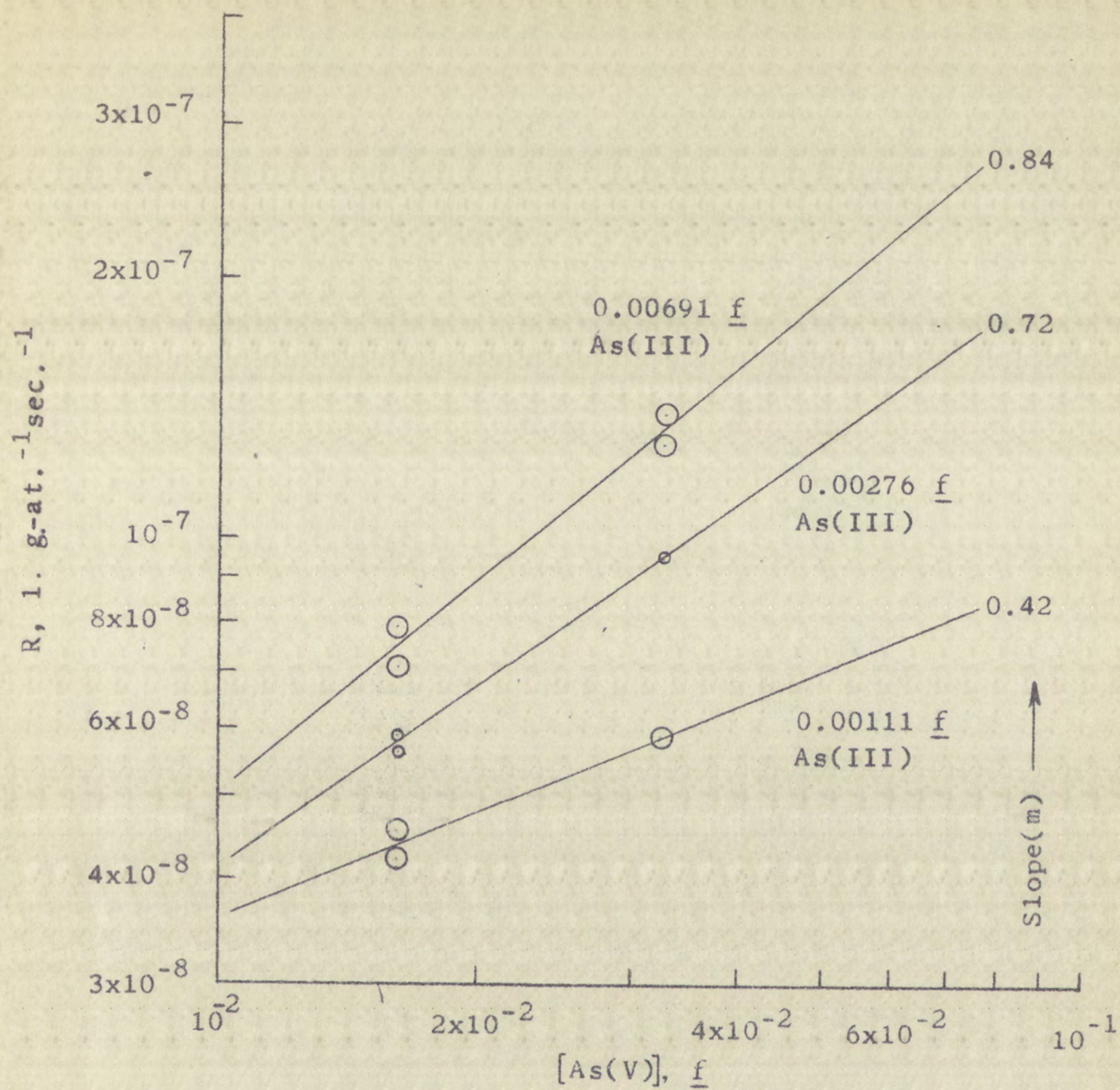


Figure VI-7

Dependence of the Initial Rate of Exchange on the Arsenic(V) Concentration at Constant Arsenic(III) Concentrations for Runs 5-17 at 29.7°C







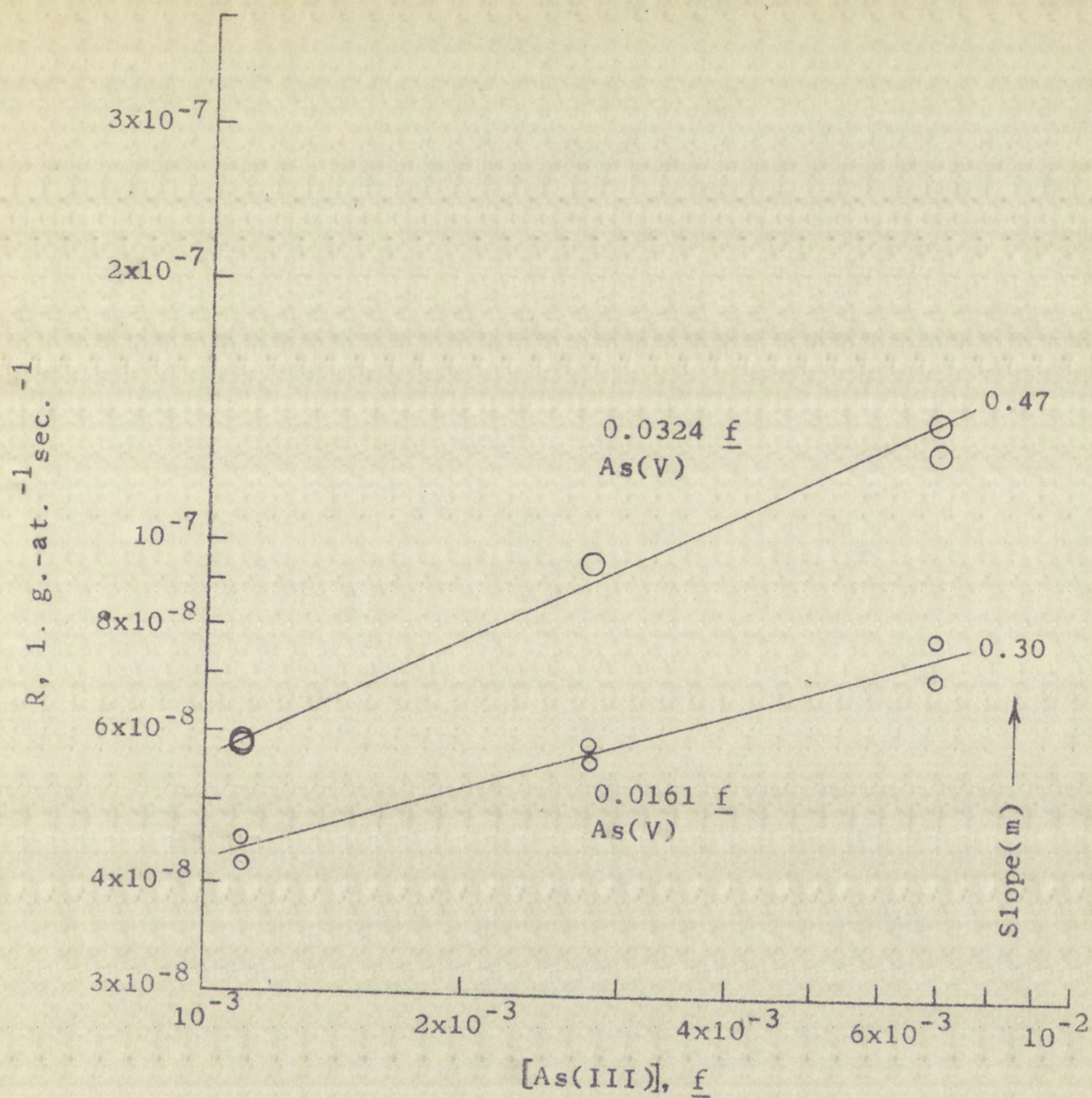
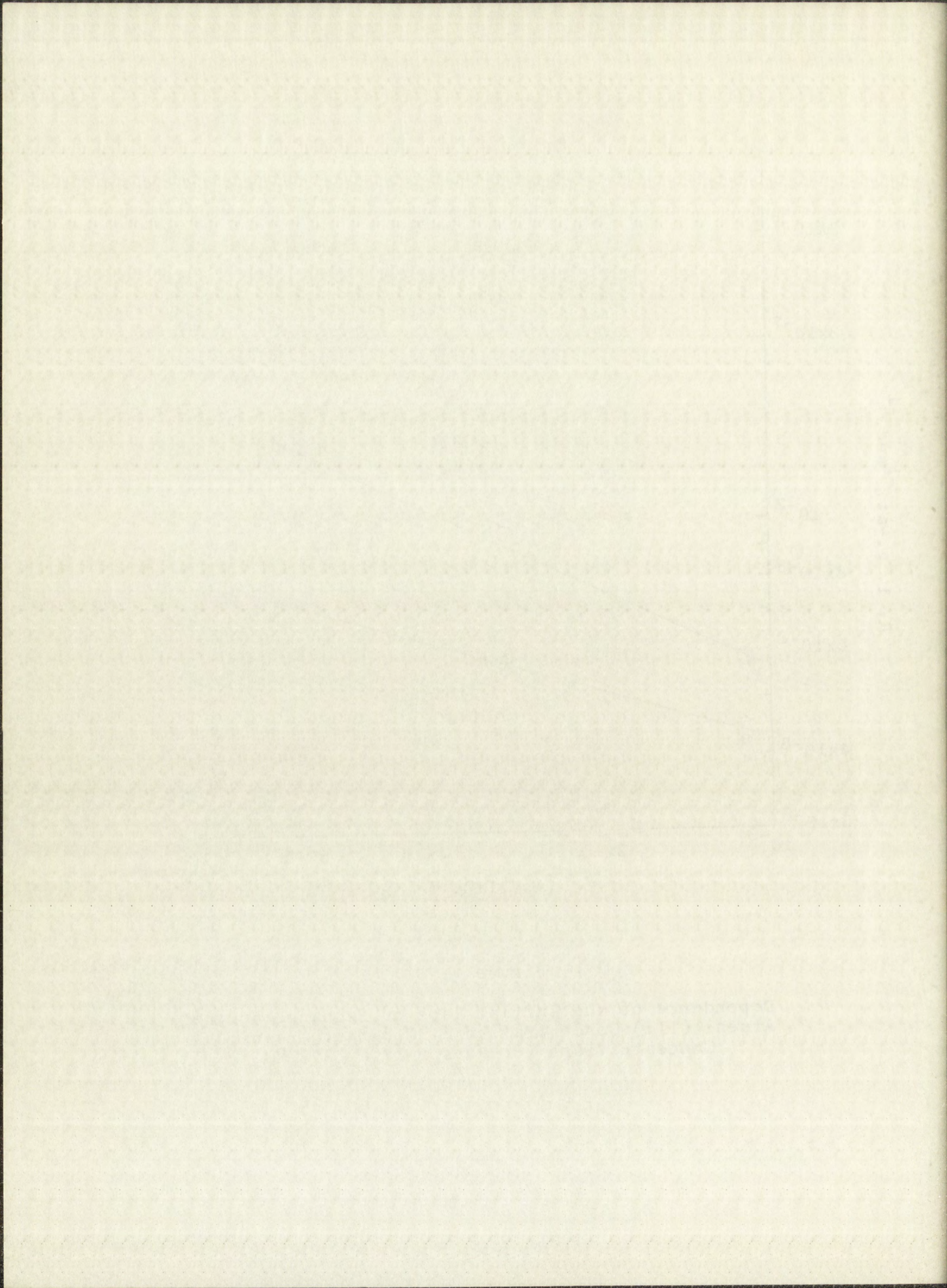


Figure VI-8

Dependence of the Initial Rate of Exchange on the Arsenic(III) Concentration at Constant Arsenic(V) Concentrations for Runs 5-17 at 29.7°C







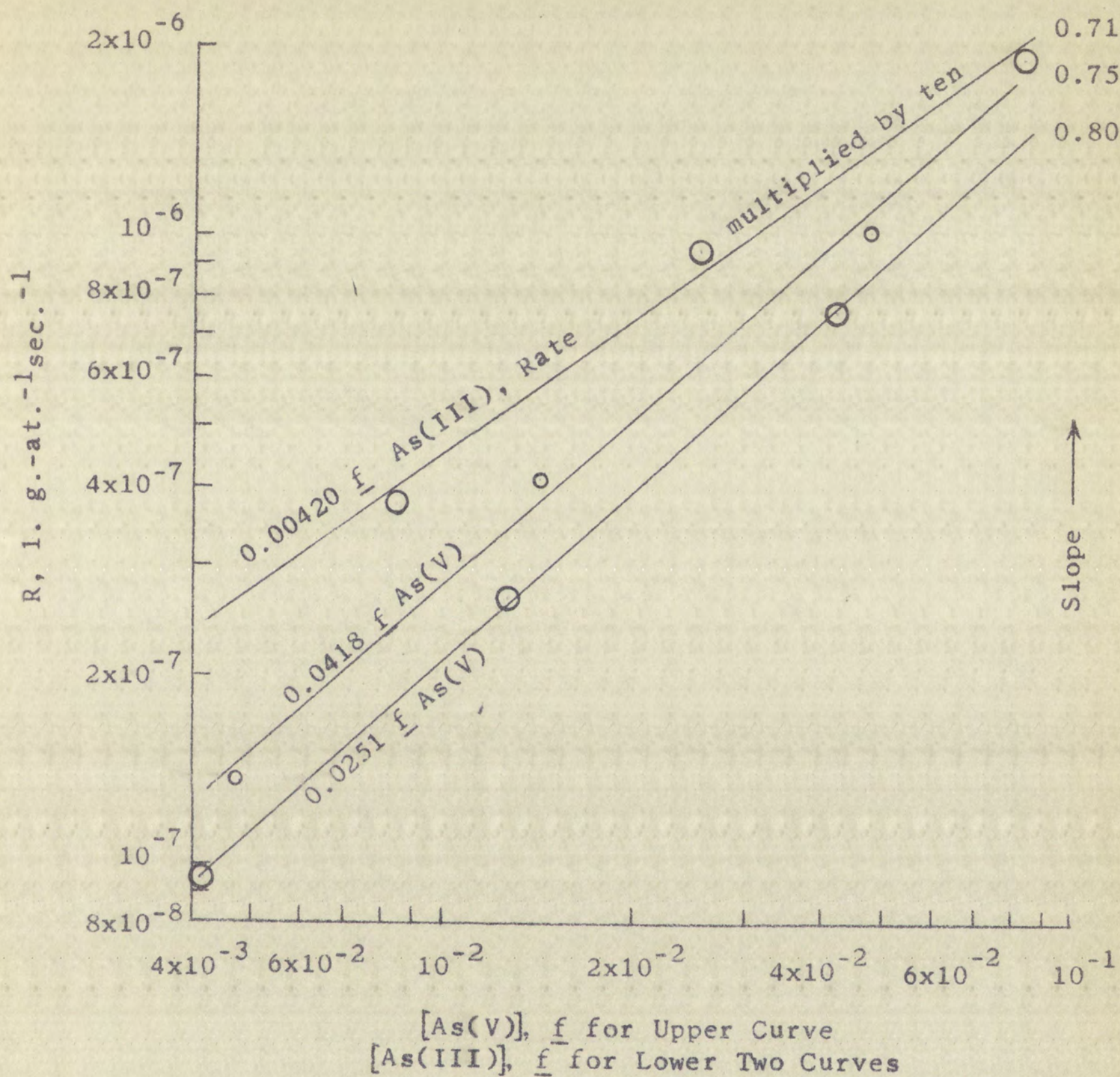


Figure VI-9

Dependence of the Initial Rate of Exchange on the Arsenic(V) Concentration at Constant Arsenic(III) Concentration and Dependence of the Initial Rate of Exchange on the Arsenic(III) Concentration at Constant Arsenic(V) Concentration for Runs 19-26 at 29.7°C.







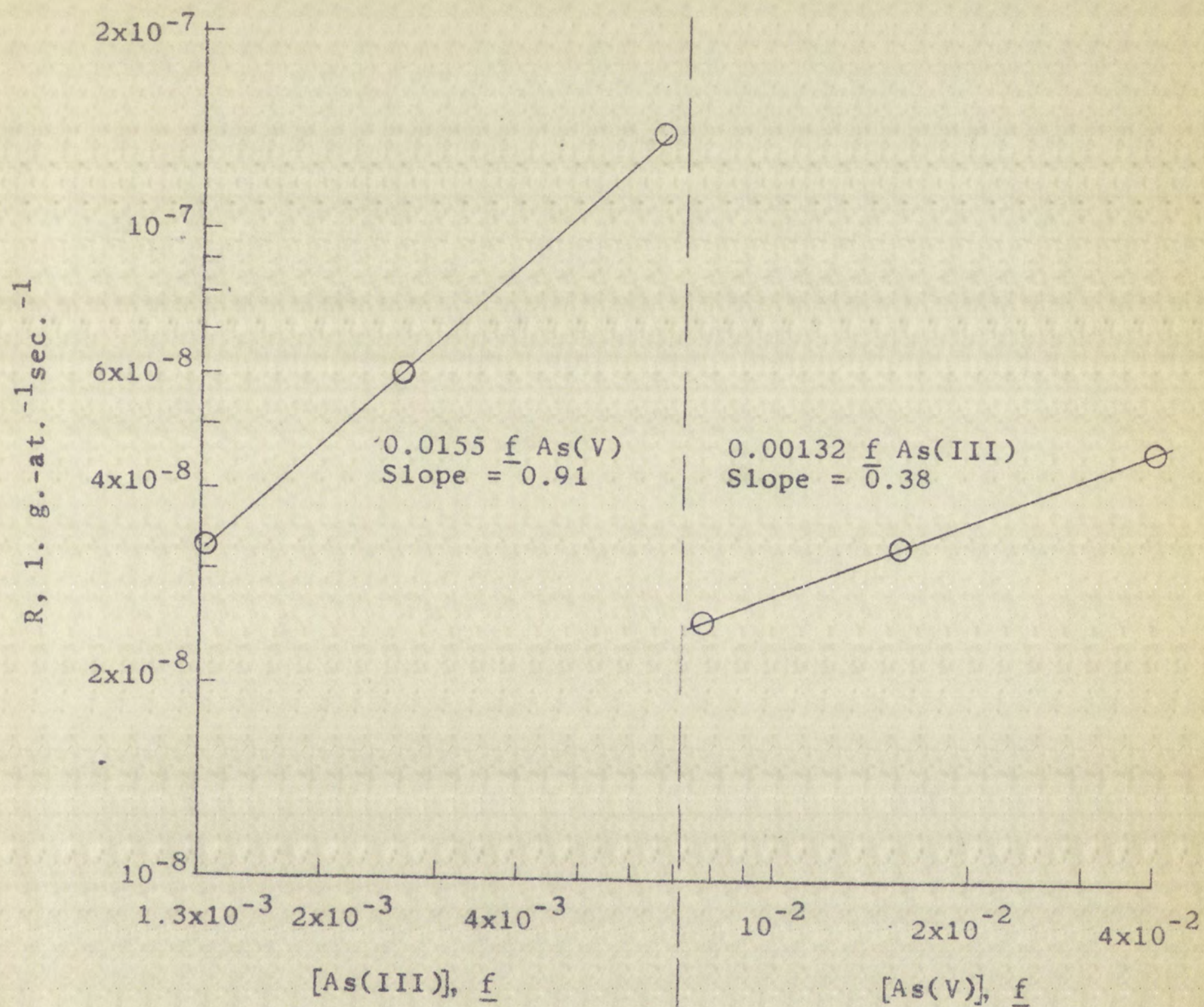


Figure VI-10

Dependence of the Initial Rate of Exchange on the Arsenic(III) Concentration at 0.0155 f Arsenic(V) and Dependence of the Initial Rate of Exchange on the Arsenic(V) Concentration at 0.00132 f Arsenic(III) for Runs 38-42 at 48.6°C







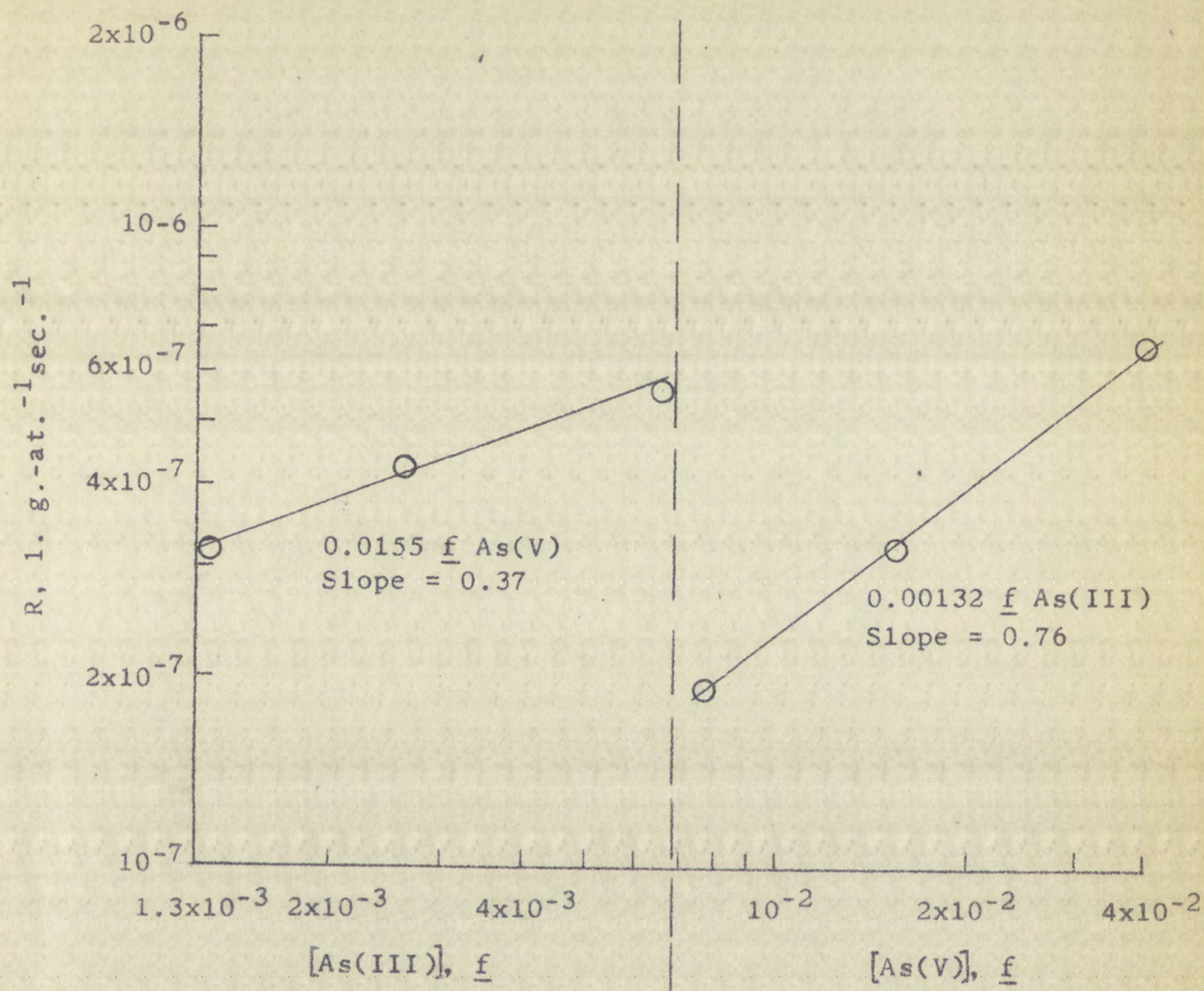


Figure VI-11

Dependence of the Initial Rate of Exchange on the Arsenic(III) Concentration at 0.0155 f Arsenic(V) and Dependence of the Initial Rate of Exchange on the Arsenic(V) Concentration at 0.00132 f Arsenic(III) for Runs 38-42 at 67.3°C



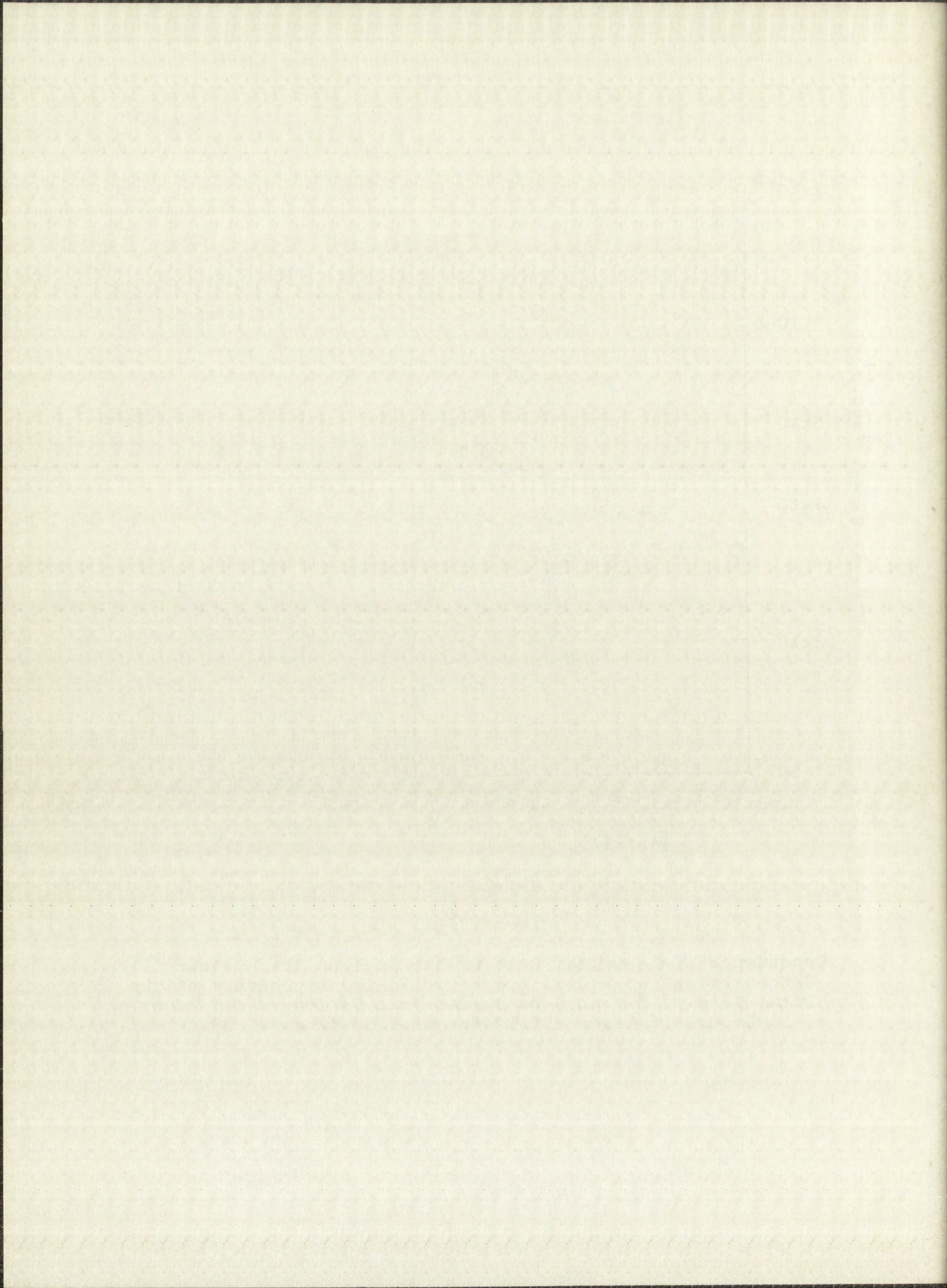




Table VI-3

Dependence of the Initial Rate of Exchange on the Concentration of Arsenic(III) or Arsenic(V) in 10.9  $\underline{f}$  Hydrochloric Acid

$R = k[\text{As(III)}]^n$		$1. \text{ g.-at.}^{-1} \text{ sec.}^{-1}$	$R = k[\text{As(V)}]^m$		$1. \text{ g.-at.}^{-1} \text{ sec.}^{-1}$
Runs	Temp., $^{\circ}\text{C}$	$k \times 10^{-5}$	n	m	$[\text{As(III)}]_{\underline{f}} \times 10^2, \quad [\text{As(V)}]_{\underline{f}} \times 10^2,$
a8, 9, 10 15, 16, 17	29.7°	0.0334	0.30	---	0.111 to 0.691      1.61
a5, 6, 12, 13, 14	29.7°	0.146	0.47	---	0.111 to 0.691      3.24
a5, 9, 13, 16	29.7°	0.0247	---	0.42	0.111      1.61 to 3.24
a8, 12, 15,	29.7°	0.112	---	0.72	0.276      1.61 to 3.24
a6, 10, 14, 17	29.7°	0.237	---	0.84	0.691      1.61 to 3.24

<sup>a</sup>The arsenic(V) solution used to prepare the exchange mixtures was 184 days to 207 days old.



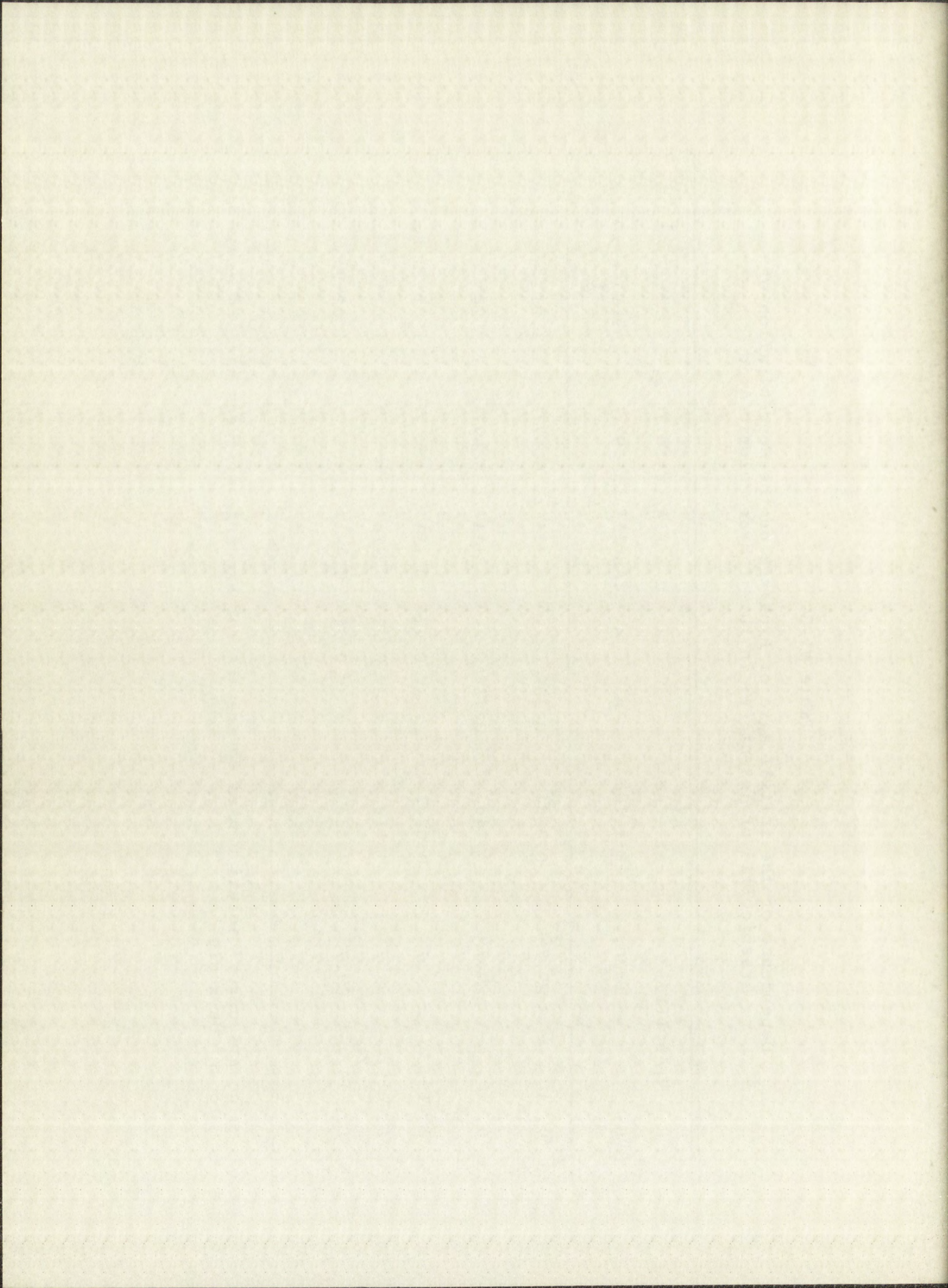




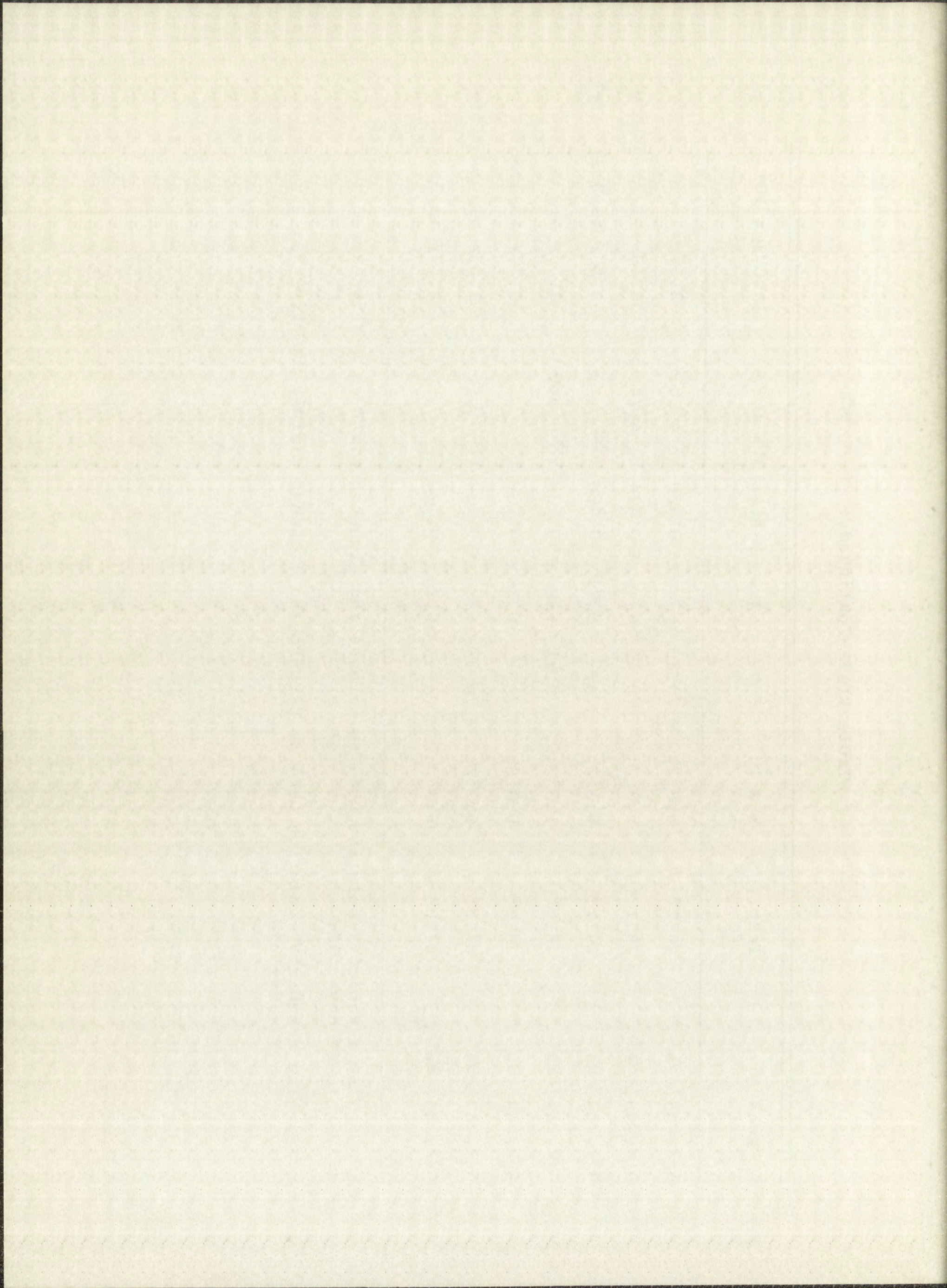
Table VI-3--Continued

Runs	Temp., °C	$k \times 10^{-5}$	n	m	$[\text{As(III)}] \times 10^2,$ $\bar{f}$	$[\text{As(V)}] \times 10^2,$ $\bar{f}$
b24, 25, 26	29.7°	0.835	0.80	---	0.420 to 4.20	2.51
b19, 20, 21	29.7°	0.885	0.75	---	0.474 to 4.74	4.18
b22, 23, 24	29.7°	0.118	---	0.71	0.420	0.837 to 8.37
c39, 41, 42	48.6°	1.33	0.91	---	0.132 to 0.660	1.55
c38, 39, 40	48.6°	0.0158	---	0.38	0.132	0.777 to 3.88
c45, 47, 48	67.3°	0.159	0.37	---	0.132 to 0.660	1.55
c44, 45, 46	67.3°	0.760	---	0.76	0.132	0.777 to 3.88

<sup>b</sup>The arsenic(V) solution used to prepare the exchange mixtures was 56 days to 62 days old.

<sup>c</sup>The arsenic(V) solution used to prepare the exchange mixture was 178 days to 179 days old.







from the expression  $R = 1.46 \times 10^{-6} [\text{As(III)}]^{0.47} \text{ l. g.-at.}^{-1} \text{ sec.}^{-1}$ . The rate calculated for each set of concentrations is the same within seven per cent by either rate expression used (see Table VI-4, p. 131). The initial rate of exchange between 0.00691 f arsenic(III) and 0.0251 f arsenic(V) can also be calculated from two different rate expressions, and the rate is about the same by either calculation (see Table VI-4). This consistency among rate expressions is an indication that the initial rate of exchange is reproducible. Consequently, the initial rate of exchange must be relatively independent of the dilution effect (see Section V.D.1.), and of the small changes in hydrochloric acid concentration which accompany the preparation of exchange mixtures.

The exchange mixtures in runs 38-42 and runs 44-48 which were studied at elevated temperatures were prepared from arsenic(V) solution which had been aged five months at room temperature and had not been heated to the temperature of the reaction prior to each exchange run. Because of the effect of aging five-months-old arsenic(V) solution at the elevated temperatures (see Section VI.C.6), it is likely that the exchange mixtures studied at the elevated temperatures were not at equilibrium. Nevertheless, over a concentration range of 0.00132 f to 0.00660 f arsenic(III) and 0.00777 f to 0.0388 f arsenic(V), the initial rate of exchange in 10.9 f hydrochloric acid is







Table VI-4

Comparison of the Rates of Exchange Calculated by the Rate Expressions\*  $R = k_1 [\text{As(III)}]^n$  1. g.-at.<sup>-1</sup>sec.<sup>-1</sup> and  $R = k_2 [\text{As(V)}]^m$  1. g.-at.<sup>-1</sup>sec.<sup>-1</sup> for a Given Arsenic(III) Concentration and Arsenic(V) Concentration at 29.7°C

---


$$[\text{As(III)}] = 0.00420 \text{ f}$$

$$[\text{As(V)}] = 0.0161 \text{ f}$$

$$R = 3.34 \times 10^{-7} [\text{As(III)}]^{0.30} = 6.46 \times 10^{-8} \text{ 1. g.-at.}^{-1}\text{sec.}^{-1}$$

$$R = 1.18 \times 10^{-6} [\text{As(V)}]^{0.71} = 6.29 \times 10^{-8} \text{ 1. g.-at.}^{-1}\text{sec.}^{-1}$$


---

$$[\text{As(III)}] = 0.00420 \text{ f}$$

$$[\text{As(V)}] = 0.0324 \text{ f}$$

$$R = 1.46 \times 10^{-6} [\text{As(III)}]^{0.47} = 1.11 \times 10^{-7} \text{ 1. g.-at.}^{-1}\text{sec.}^{-1}$$

$$R = 1.18 \times 10^{-6} [\text{As(V)}]^{0.71} = 1.04 \times 10^{-7} \text{ 1. g.-at.}^{-1}\text{sec.}^{-1}$$


---

$$[\text{As(III)}] = 0.00691 \text{ f}$$

$$[\text{As(V)}] = 0.0251 \text{ f}$$

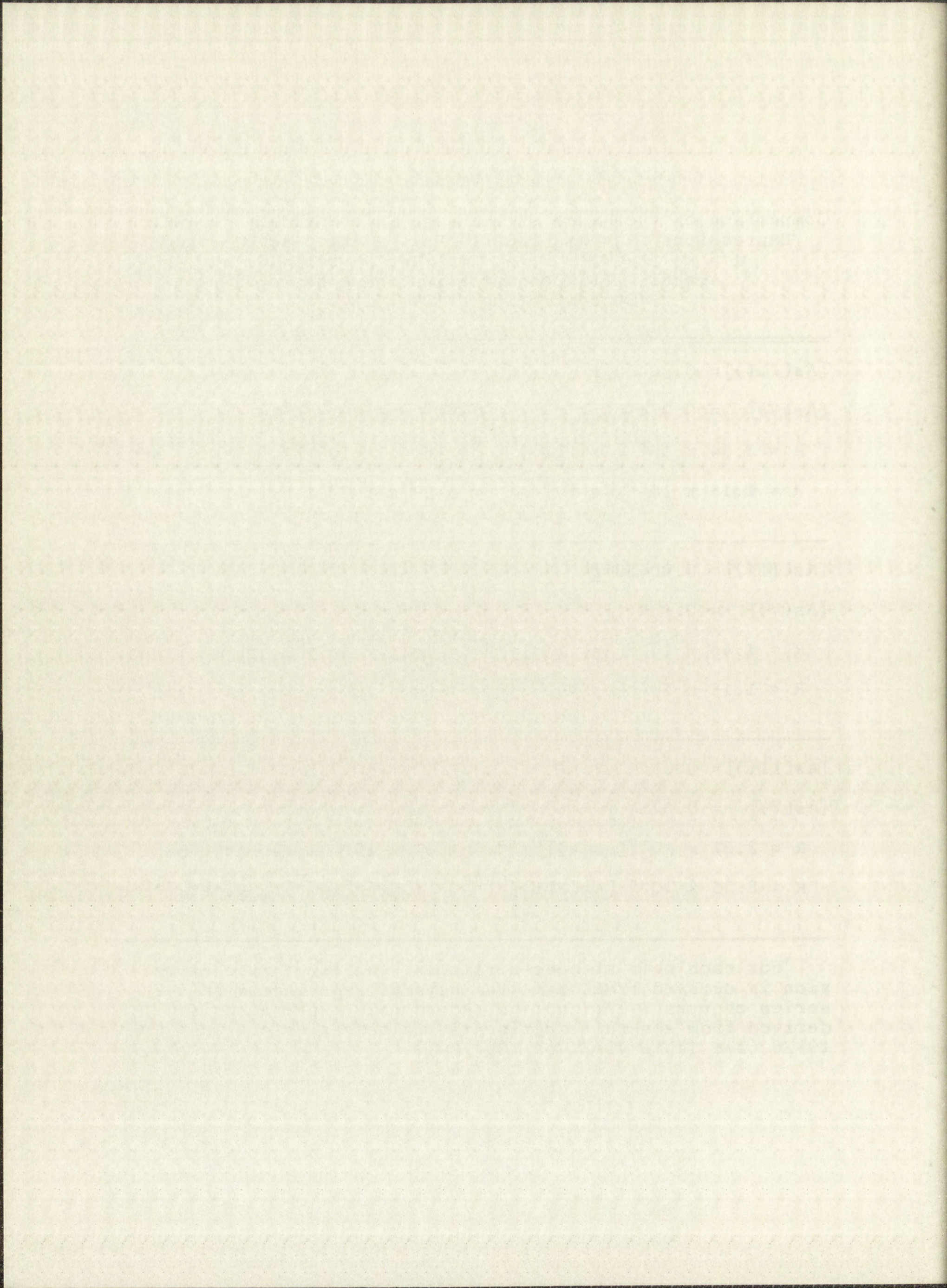
$$R = 2.37 \times 10^{-6} [\text{As(V)}]^{0.84} = 1.07 \times 10^{-7} \text{ 1. g.-at.}^{-1}\text{sec.}^{-1}$$

$$R = 8.35 \times 10^{-6} [\text{As(III)}]^{0.80} = 1.56 \times 10^{-7} \text{ 1. g.-at.}^{-1}\text{sec.}^{-1}$$


---

\*For each pair of concentrations, the first rate expression is derived from data from several experiments in the series of runs 5-17, and the second rate expression is derived from several experiments in the series of runs 19-26 (see Table VI-3, pp. 128-129).







well represented by the rate law

$$R = 6.71 \times 10^{-5} [\text{As(III)}]^{0.91} [\text{As(V)}]^{0.38} \text{ l. g.-at.}^{-1} \text{sec.}^{-1}$$

at 48.6°C and

$$R = 8.72 \times 10^{-5} [\text{As(III)}]^{0.37} [\text{As(V)}]^{0.76} \text{ l. g.-at.}^{-1} \text{sec.}^{-1}$$

at 67.3°C, respectively. The probable error in the specific rate constants, which are listed in Table VI-5, is 2.7% at 48.6°C and 1.3% at 67.3°C.

#### 8. Effect of the Method of Preparation of Arsenic(III)

##### "Tracer"

The initial rate of exchange in 10.9 f hydrochloric acid solution at 29.7°C does not appear to be affected by the method of preparation of the arsenic(III) "tracer." The arsenic(III) "tracer" used in runs 5-17 was prepared by inoculation of an arsenic(III) solution with purified high specific activity arsenic(III) (see page 24), whereas the "tracer" used in runs 19-26 was prepared by oxidation of an inoculated arsenic(III) solution followed by reduction and distillation (see page 27). The initial rate of exchange which is calculated for given arsenic(III) and arsenic(V) concentrations with the appropriate rate expression derived from several experiments in the series of runs 5-17 is compared in Table VI-4 (see p.131) with the initial rate of exchange which is calculated for the same arsenic(III) and arsenic(V) concentrations with the appropriate rate expression derived from several experiments in the series of runs 19-26.







Table VI-5

Variation in the Specific Rate Constants for  
the Rate Laws at 48.6°C and 67.3°C

Run no.	Temp., °C	[As(III)] x 10 <sup>2</sup> , <u>f</u>	[As(V)] x 10 <sup>2</sup> , <u>f</u>	Specific rate constant x 10 <sup>5</sup>
38	48.6°	0.132	0.777	7.25
39	48.6°	0.132	1.55	6.64
40	48.6°	0.132	3.88	6.61
41	48.6°	0.264	1.55	6.48
42	48.6°	0.660	1.55	6.60
44	67.3°	0.132	0.777	8.81
45	67.3°	0.132	1.55	8.55
46	67.3°	0.132	3.88	8.81
47	67.3°	0.264	1.55	8.92
48	67.3°	0.660	1.55	8.50







The rates are approximately equal for three different sets of concentrations of arsenic(III) and arsenic(V), whether or not the arsenic(III) "tracer" was subjected to oxidation, reduction, and distillation subsequent to preparation by inoculation with high specific activity arsenic(III).

Exchange runs 32 and 35 are duplicate experiments except for the preparation of the arsenic(III) "tracer." The "tracer" used in run 32 was prepared by oxidation of inoculated arsenic(III) followed by reduction and distillation whereas the "tracer" used in run 35 was prepared by reduction to the metal and subsequent oxidation prior to distillation. The exchange curves for runs 32 and 35 shown in Figure VI-12 are similar; the half-times of the second component are 384 days and 222 days respectively, and the intercepts,  $Q_2$ , are 0.955 and 0.938 respectively. In view of the difficulty in reproducing exchange experiments, it is concluded that the results of the exchange experiments are affected little, if at all, by the order of the chemical reactions employed in the preparation of arsenic(III) "tracer."

#### 9. Effect of the Valence of the "Tracer"

The results of runs 7, 11, and 18, in which the "tracer" was initially pentavalent, are shown in Figures VI-13, VI-14, and VI-15, pages 136, 137, and 138. Except for the valence of the "tracer," these runs are duplicates of runs 6, 10, and 17, respectively. The points on the plots of







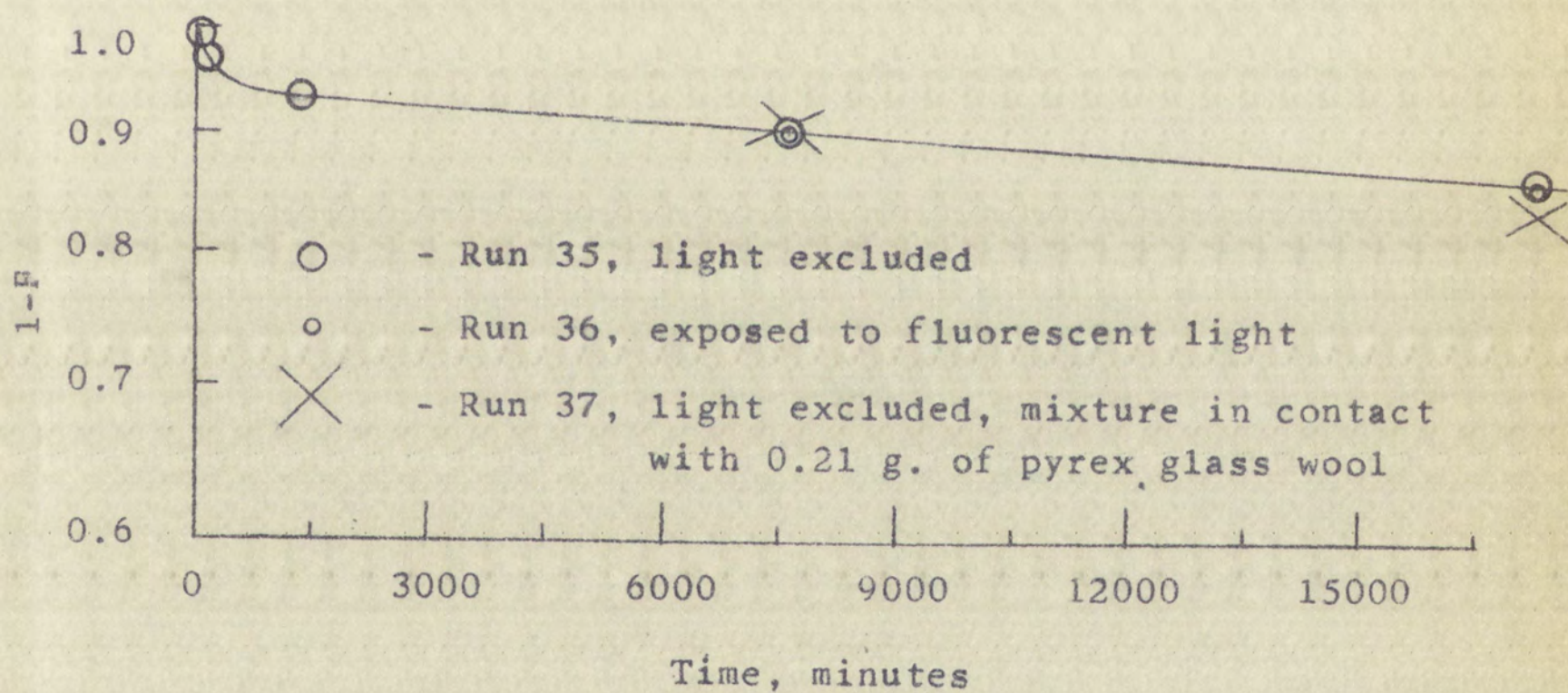
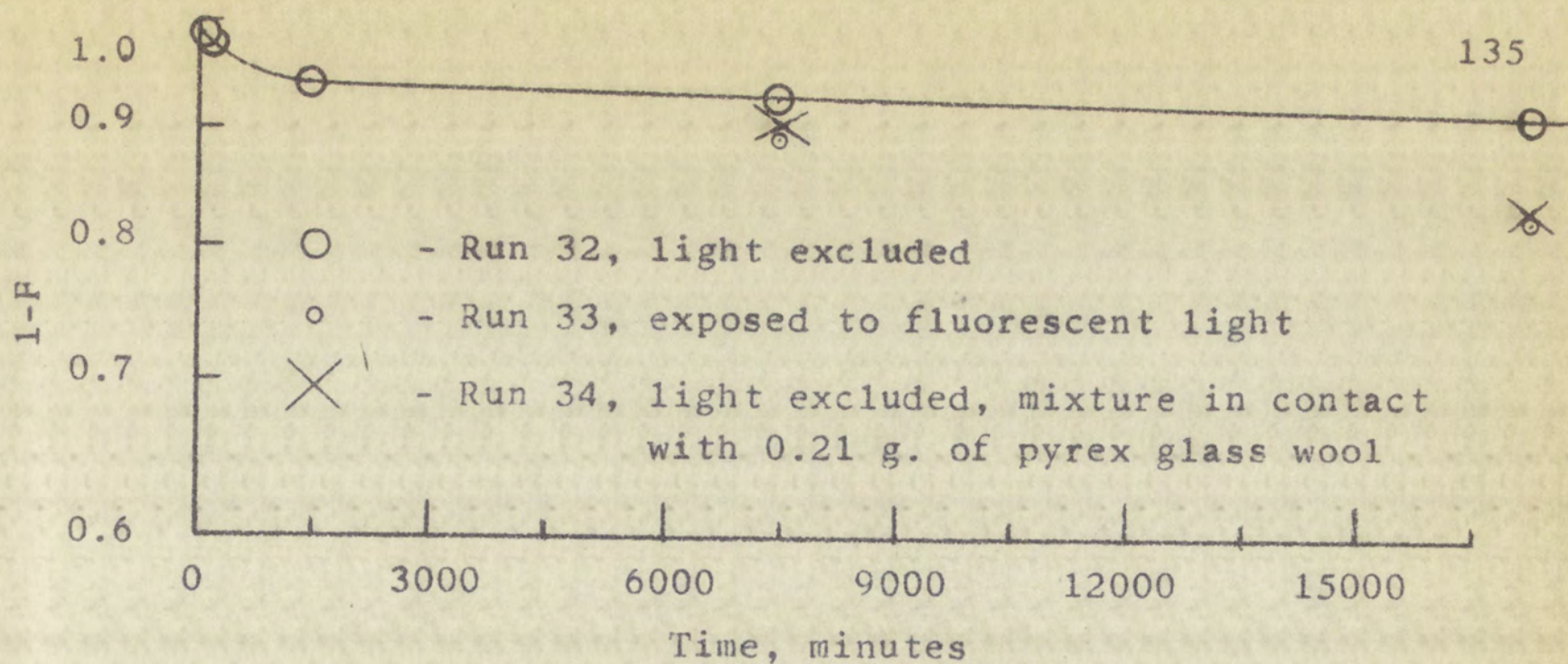


Figure VI-12

Exchange Curves for Runs 32-37







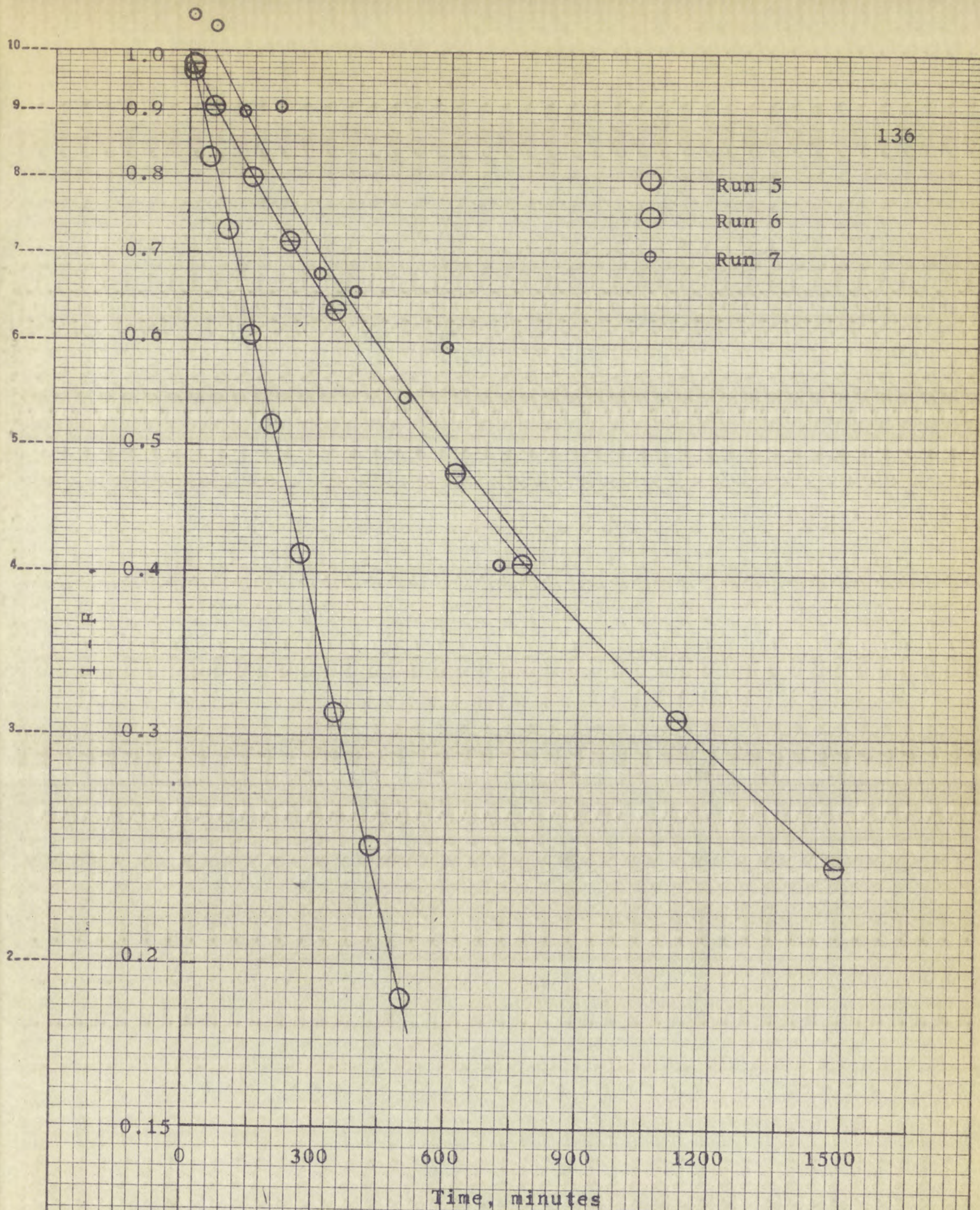
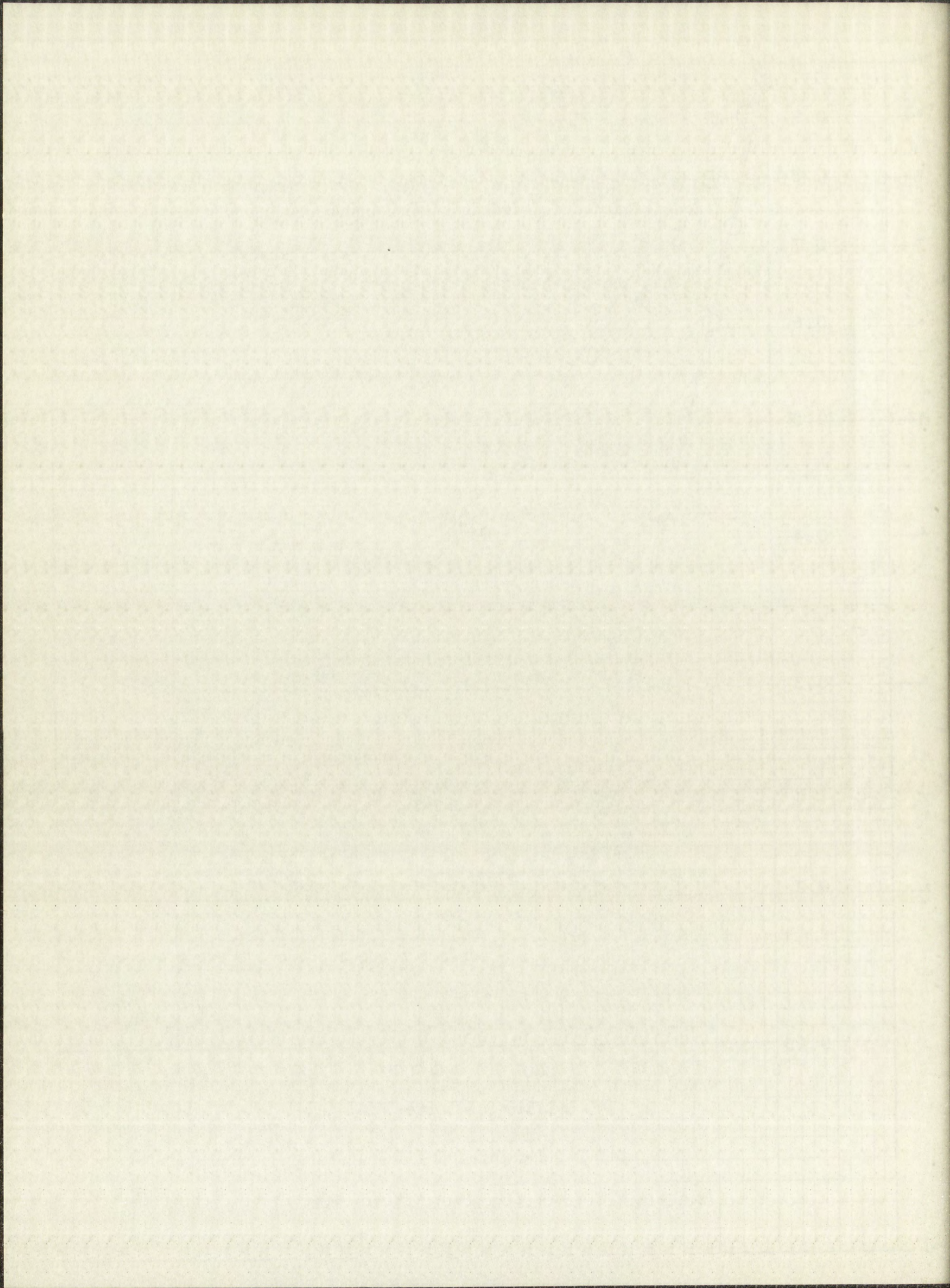


Figure VI-13

Exchange Curves for Runs 5, 6, and 7







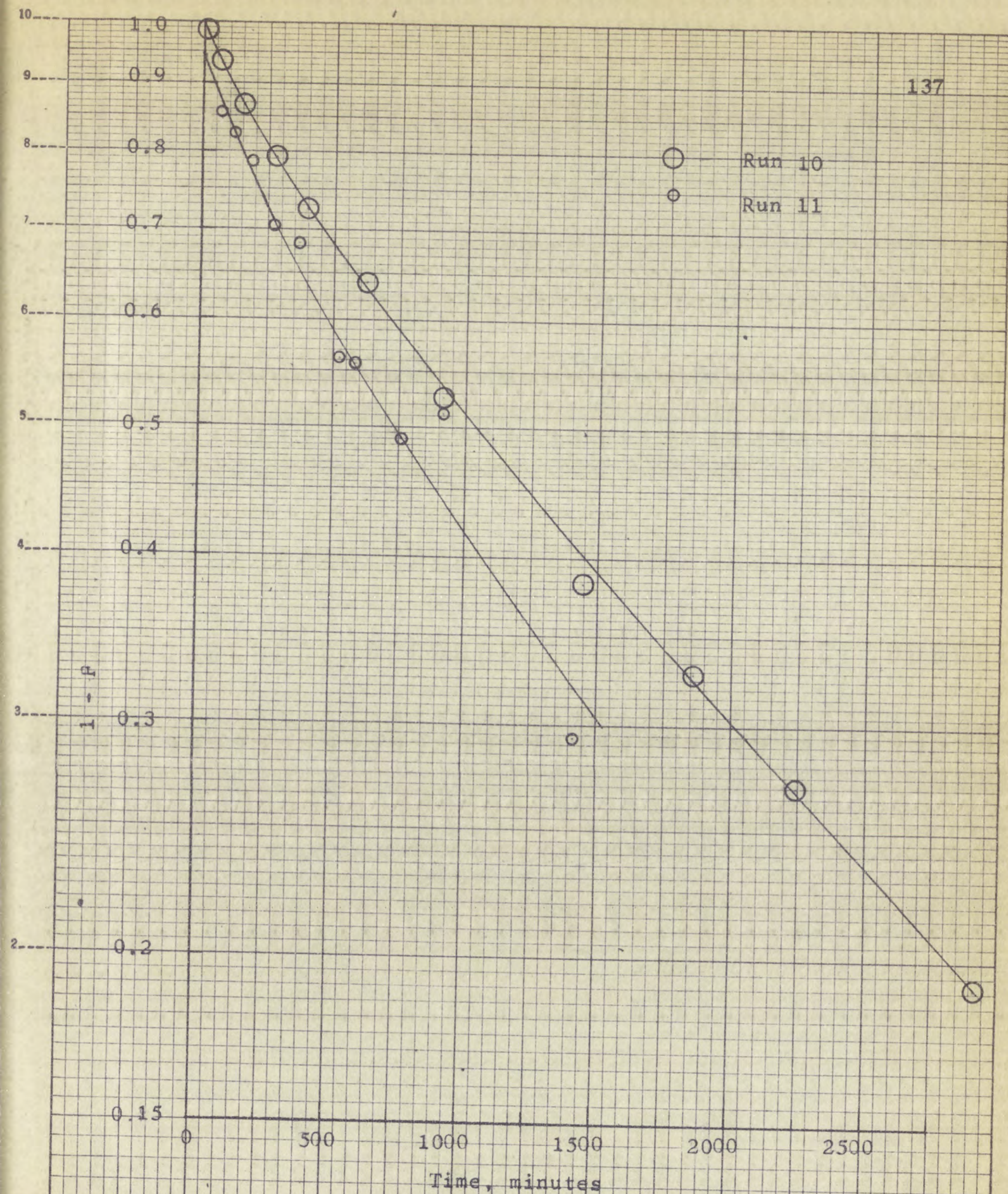
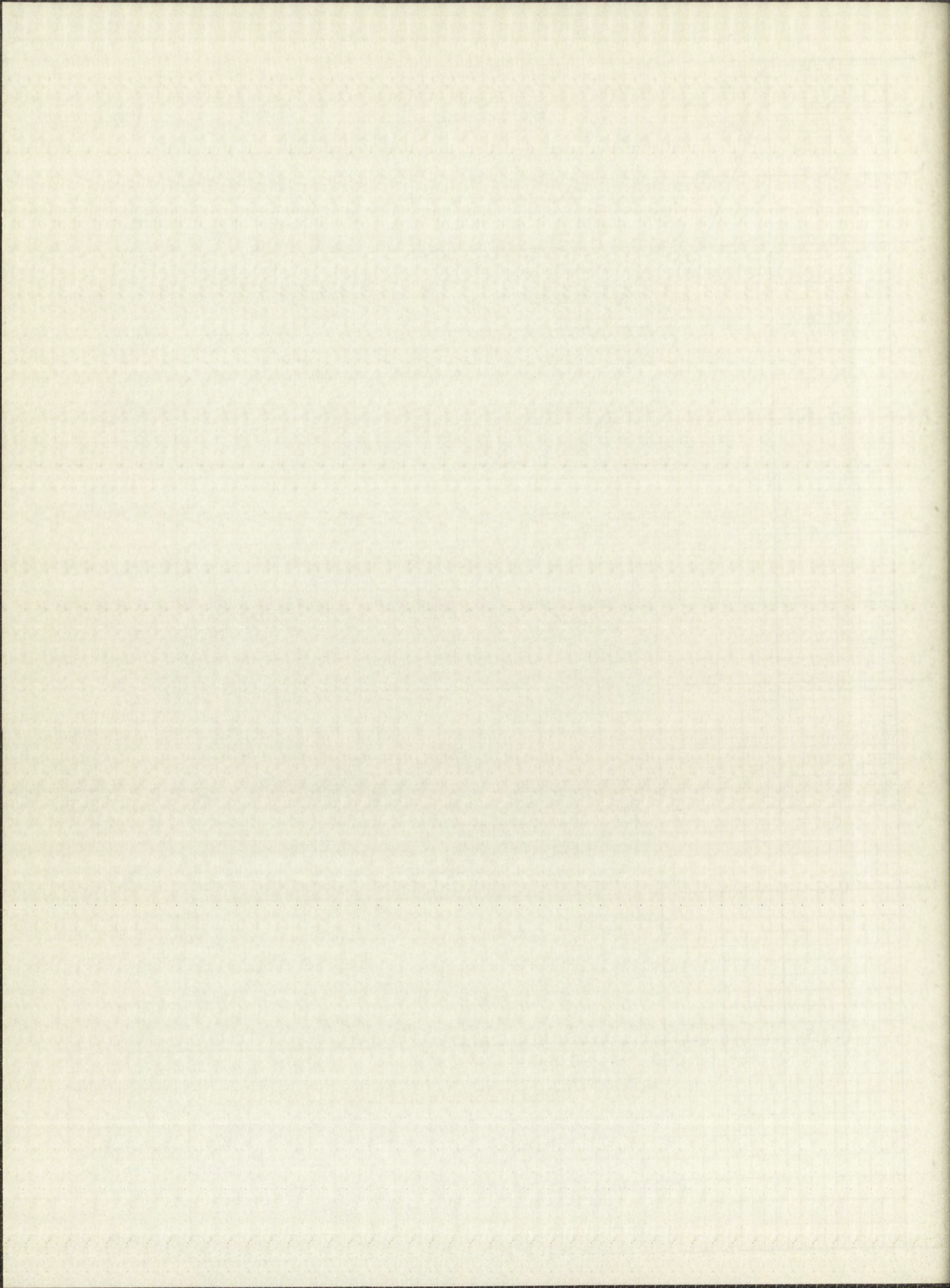


Figure VI-14

Exchange Curves for Runs 10 and 11







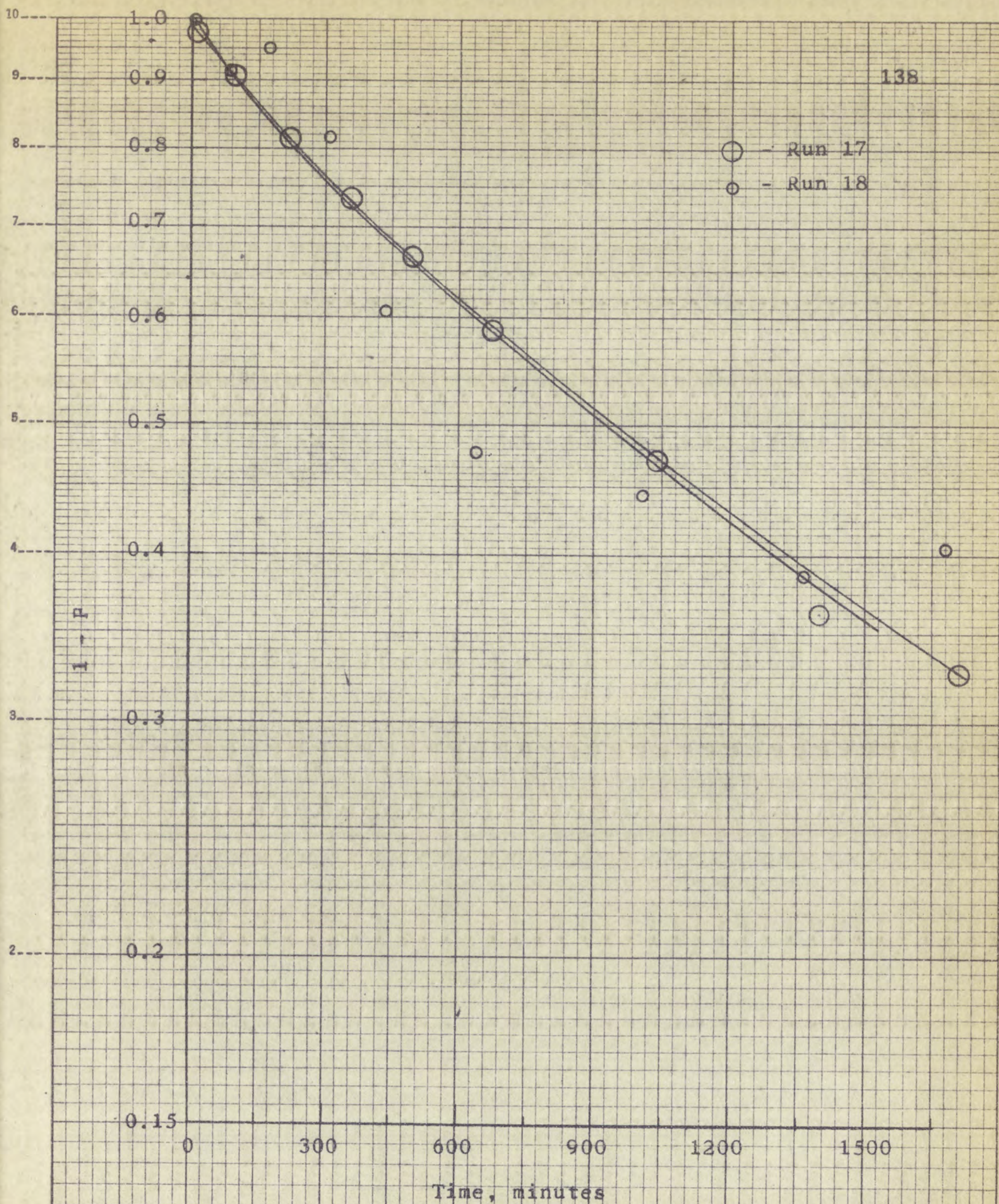


Figure VI-15

Exchange Curves for Runs 17 and 18







$\log (1-F)$  versus time for runs 7, 11, and 17 are so widely scattered that it is difficult to know where to place a curve among the points. Nevertheless, a reasonable curve can be drawn among the points for each run in such a way that each of the exchange curves in runs 7, 11, and 18 is similar to the exchange curves of runs 6, 10, and 17, respectively. The approximate half-times of the exchange reactions are compared in Table VI-2, page 118.

The reason for the scattering of points only when the "tracer" is initially pentavalent is not understood. The largest errors should occur at the beginning of the reaction because the difference between two large numbers, namely the activity of the arsenic(V) fraction and the initial activity of the arsenic(V), enters into the calculation of  $1-F$ .

#### 10. Effect of Light and Surface Area

Three exchange experiments were carried out with identical solutions, one in a 50 ml. blackened flask, one in a transparent 50 ml. flask, and one in a 50 ml. blackened flask containing 0.21 g. of pyrex glass wool. The exchange mixture in the transparent flask was exposed to the fluorescent light in the laboratory during the course of the reaction. These three experiments were carried out once with the arsenic(III) "tracer" prepared by the oxidation of inoculated arsenic(III) to arsenic(V), reduction to arsenic(III), and distillation (runs 32-34 respectively). These three





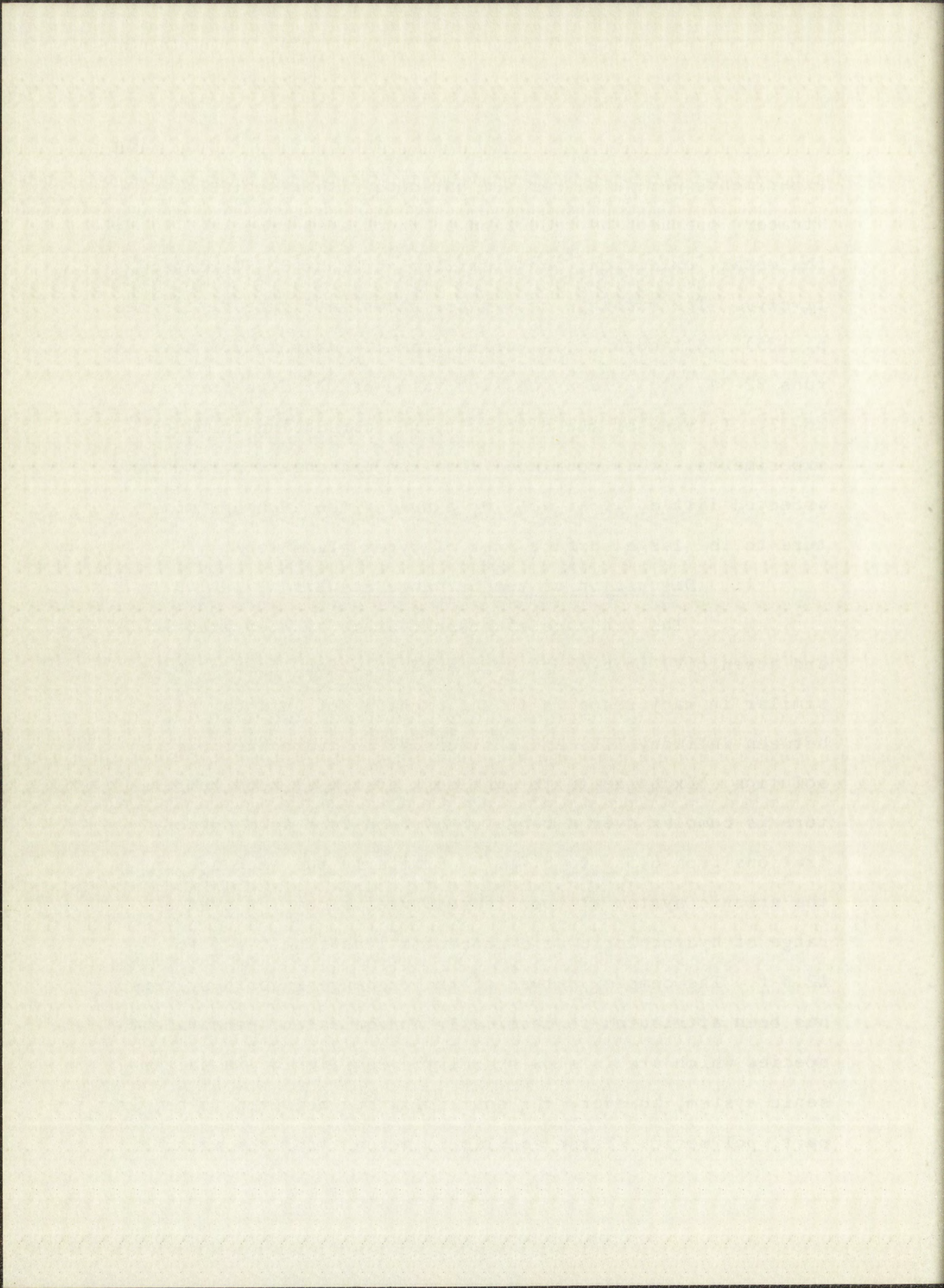


experiments were also carried out once with arsenic(III) "tracer" prepared by reduction of inoculated arsenic(III) to the metal, oxidation, and distillation (runs 35-37 respectively). The exchange curves are shown in Figure VI-12 (see p. 135). Although  $(t_{\frac{1}{2}})_2$  varies from 114 days to 384 days in runs 32-34,  $(t_{\frac{1}{2}})_2$  is a constant value of 222 days for runs 35-37. In view of the difficulty in reproducing exchange experiments, it is concluded that the exchange reaction is affected little, if at all, by exposing the exchange mixture to the large surface area of pyrex glass wool.

#### 11. Discussion of the Exchange Results

The exchange of arsenic atoms between arsenic(III) and arsenic(V) in hydrochloric acid solution appears to be similar in many respects to the exchange of antimony atoms between antimony(III) and antimony(V) in hydrochloric acid solution. Exchange in the antimony system at room temperature is complex over a range of hydrochloric acid concentrations from 6.5 f to 8. f.<sup>52</sup> Similarly the exchange in the arsenic system at room temperature is complex over a range of hydrochloric acid concentrations from 10.9 f to 12.6 f. The complex nature of the exchange in both systems has been attributed to chemically nonequivalent pentavalent species which are in slow hydrolytic equilibria; in the arsenic system, however, the equilibria are believed to be, in part, polymeric. These equilibria account for the aging of



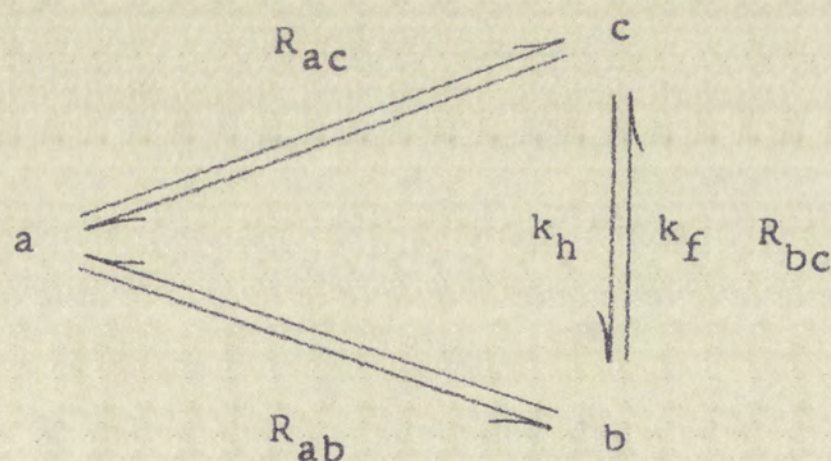




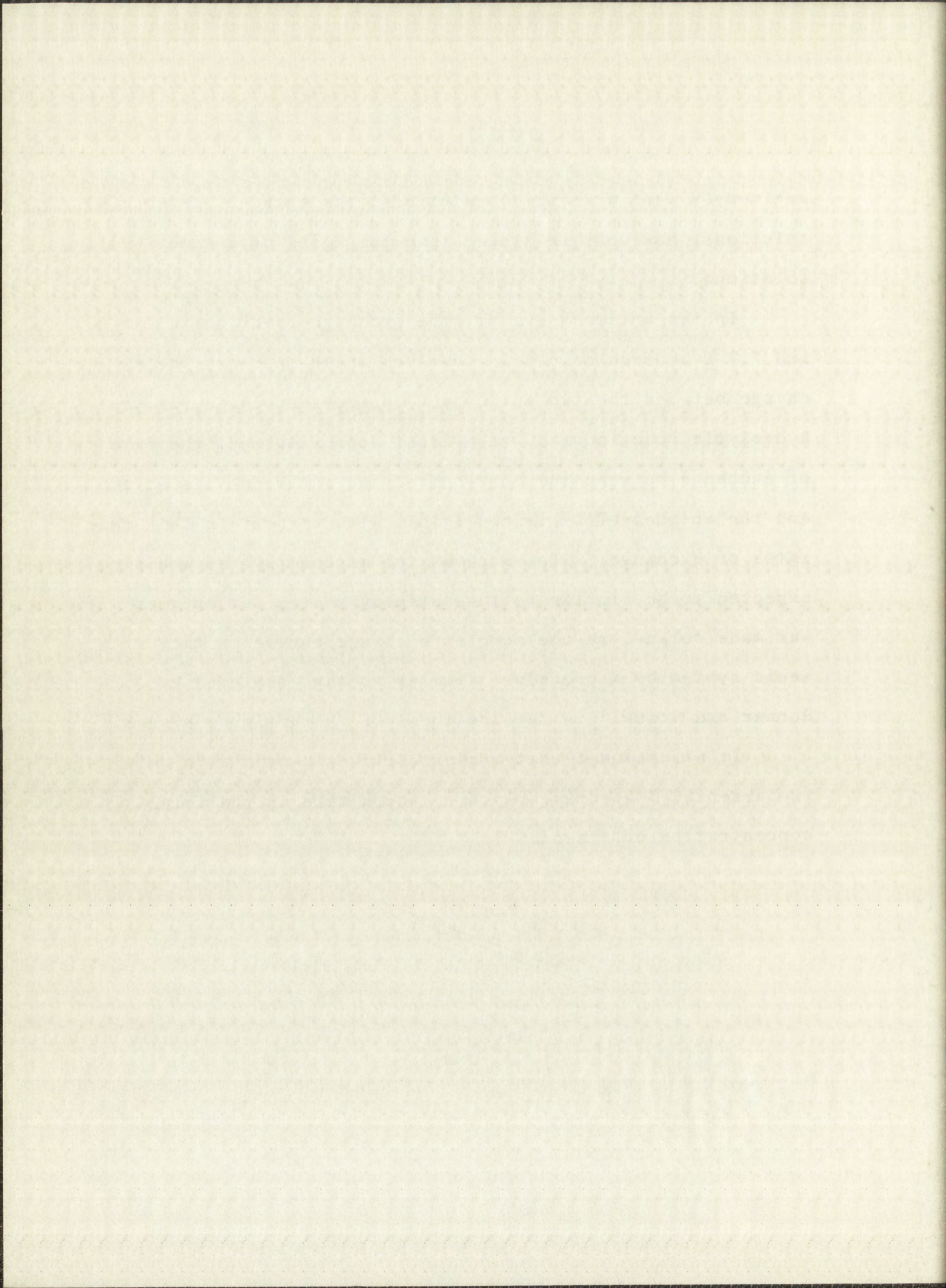
antimony(V) and arsenic(V) solutions; the aging of arsenic(V) solutions, however, is slower than the aging of antimony(V) solutions.

In the antimony system, the exchange reaction in 7 f and 7.7 f hydrochloric acid involves three species; the exchange between the two antimony(V) species proceeds via the hydrolytic reaction and, to a first approximation, the rate of exchange between the more-hydrolyzed antimony(V) species and the antimony(III) is negligible with respect to the other rates of exchange.<sup>4</sup> Inasmuch as the arsenic system would be expected to be similar to the antimony system, an attempt was made to analyze the complex exchange curves of the arsenic system by a procedure similar to that employed by Bonner and Goishi<sup>4</sup> in the treatment of the antimony system.

It was assumed that arsenic(III) exchanges with only two arsenic(V) species, b and c, which make up the total concentration of arsenic(V):









The ratio of the concentration of the c species (the less-hydrolyzed species) of arsenic(V) to the total arsenic(V) concentration is denoted by the symbol  $\phi$ . The symbols  $R_{ab}$  and  $R_{ac}$  represent the rate of exchange between arsenic(III) and the b species and the c species of arsenic(V), respectively. It is assumed that  $R_{ab} = 0$ . The symbol  $R_{bc}$  represents the rate of exchange between the two arsenic(V) species. If it is assumed that exchange between arsenic(V) species proceeds via the hydrolytic reaction and that the hydrolytic reaction is first order, then the specific rate of hydrolysis  $k_h$  and the specific rate of formation  $k_f$  can be calculated from the rate  $R_{bc}$  by the method employed in the antimony system.<sup>4</sup>

These calculations require the resolution of the exchange curves into exponential components; the majority of the curves were difficult to resolve with much certainty because the lower portion of the curves generally did not become linear. Therefore, there may be considerable error in the half-time of the second component and the intercept  $Q_2$ .

The calculated values for  $\phi$ ,  $k_h$ , and  $k_f$  are listed in Table VI-6. Whereas in the antimony system  $\phi$  is a constant for a given hydrochloric acid concentration at a given temperature, the value of  $\phi$  for arsenic(V) in 10.9 f hydrochloric acid at 29.7°C varies from 0.082 to 0.661. Even for a constant arsenic(V) concentration of 0.0418 f,  $\phi$  increases







Table VI-6

The Value of  $\phi$ ,  $k_h$ , and  $k_f$  Calculated by the Complex Exchange Law  
for Three Nonequivalent Species with the Assumption that  $R_{ab}=0$

Run No.	Temp., °C	[HCl], $\underline{f}$	[As(III)], $\underline{f}$ $\times 10^2$	[As(V)], $\underline{f}$ $\times 10^2$	$\phi$	$k_h \times 10^5$ , sec. <sup>-1</sup>	$k_f \times 10^{-5}$ , sec. <sup>-1</sup>
19	29.7	10.9	4.74	4.18	0.661	1.97	3.84
20	29.7	10.9	1.42	4.18	0.408	2.54	1.75
21	29.7	10.9	0.474	4.18	0.149	0.57	0.10
22	29.7	10.9	0.420	0.837	0.334	0.40	0.20
23	29.7	10.9	0.420	8.37	0.082	3.58	0.32
24	29.7	10.9	0.420	2.51	0.149	1.46	0.26
25	29.7	10.9	1.26	2.51	0.440	0.54	0.42
38	48.6	10.9	0.132	0.777	0.071	1.21	0.092
39	48.6	10.9	0.132	1.55	0.036	3.83	0.14
41	48.6	10.9	0.264	1.55	0.191	1.37	0.32







from 0.149 to 0.661 with an increase in the arsenic(III) concentration from 0.00474  $\underline{f}$  to 0.0474  $\underline{f}$ . The value of  $\varphi$  decreases with an increase in arsenic(V) concentration. Furthermore, these values of  $\varphi$  are larger than are consistent with the spectrophotometric evidence (see Section V.I.). The specific rate constants  $k_h$  and  $k_f$  were also calculated for the reaction in 10.9  $\underline{f}$  hydrochloric acid at 29.7°C; both rates varied by at least a factor of ten.

The values of  $\varphi$  for arsenic(V) in 10.9  $\underline{f}$  hydrochloric acid were smaller at 48.6°C than at 29.7°C and varied from 0.036 to 0.191 for a constant arsenic(V) concentration. The specific rates at 48.6°C vary by a factor of less than four. Increasing the temperature from 29.7°C to 48.6°C should have resulted in a larger value for  $\varphi$  because the hydrolysis reaction is exothermic according to the spectrophotometric evidence (see Section V.).

It is apparent that either the basic assumption of a three component exchange system or the assumption that  $R_{ab} = 0$  is not correct. The possibility that  $R_{ac} = 0$  might be a better approximation than  $R_{ab} = 0$  was investigated. It was found that this interchange of  $R_{ab}$  and  $R_{ac}$  resulted in merely an interchange of  $\varphi$  and  $1-\varphi$  and an interchange of  $k_h$  and  $k_f$ . Therefore at 29.7°C, the values of  $\varphi$  varied from 0.339 to 0.918; at 48.6°C,  $\varphi$  varied from 0.809 to 0.964. These values are much higher than are consistent with the



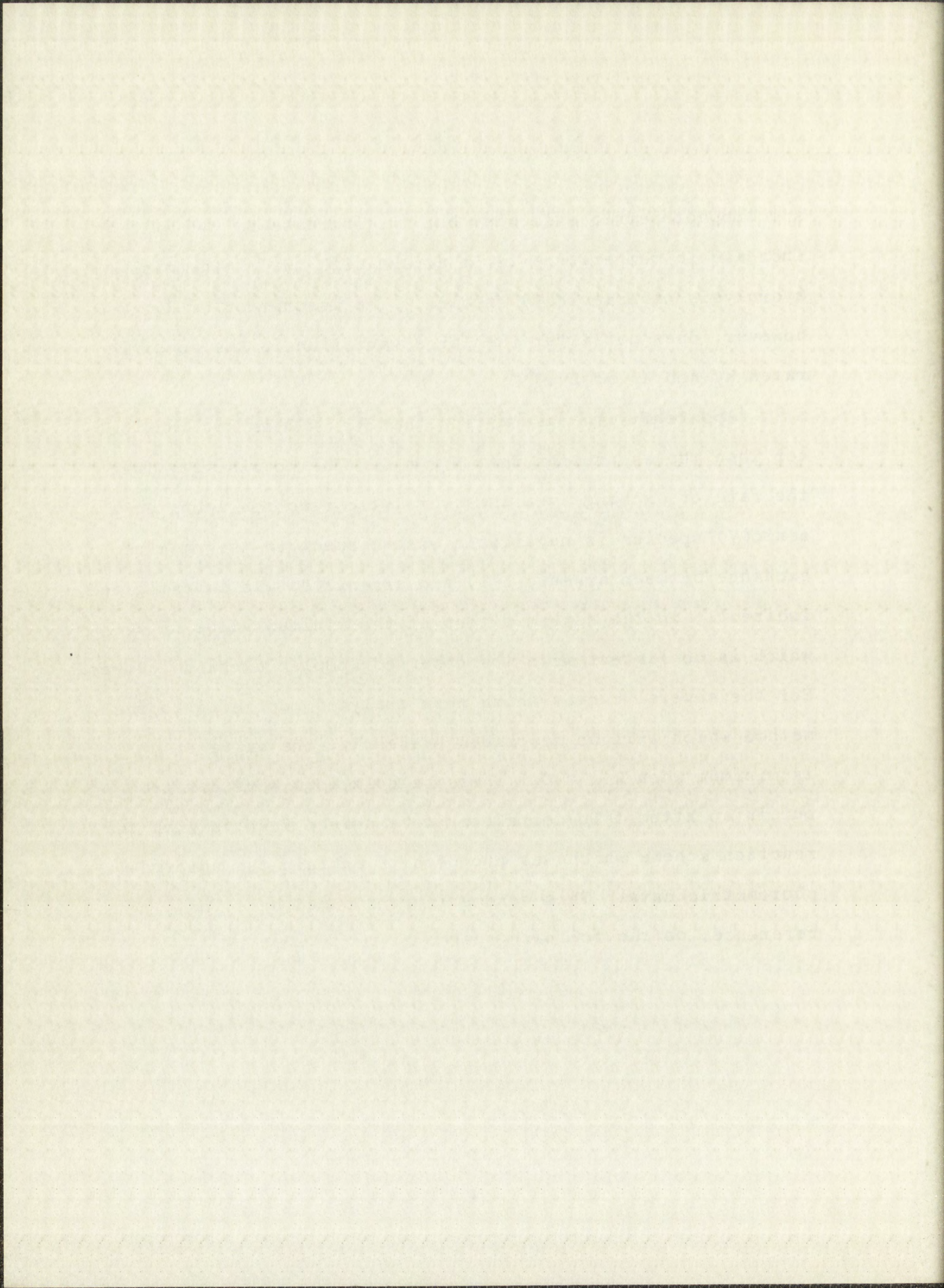




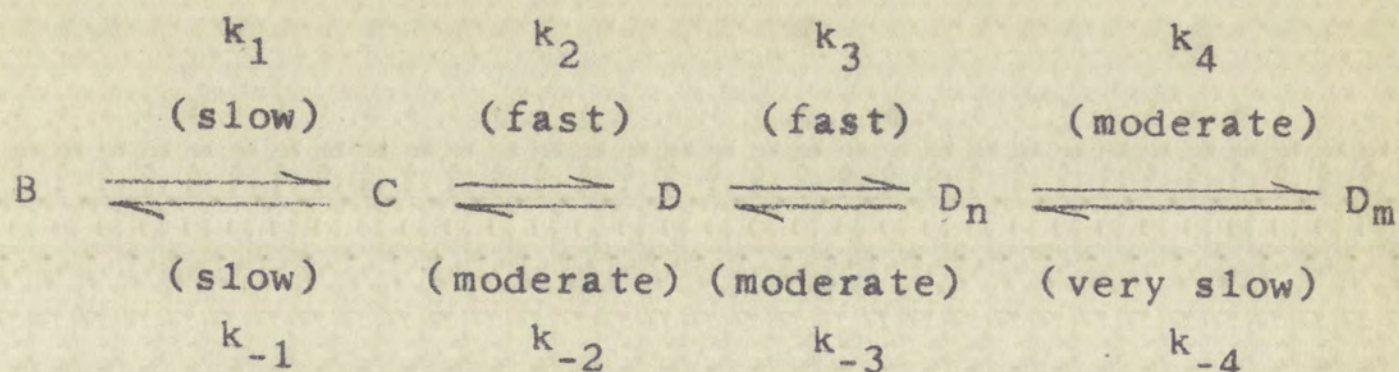
spectrophotometric evidence; but the increase in  $\varphi$  with an increase in temperature is in accord with the exothermic hydrolysis of arsenic(V) species. The assumption of  $R_{ac} = 0$ , however, does not alter the large variation in the specific rates  $k_h$  and  $k_f$  at 29.7°C.

Apparently the assumption that  $R_{ac} = 0$  is not much better than the assumption that  $R_{ab} = 0$ . The possibility that the rate of exchange via the hydrolytic reaction among arsenic(V) species is negligible with respect to the rate of exchange between arsenic(III) and arsenic(V) was investigated indirectly in the determination of the minimum value of  $\varphi$  which is consistent with the observed complex exchange curves. For the several curves which were analyzed according to the method which will be described presently, the value of  $\varphi$  is minimum when  $R_{bc} = 0$ . These calculations were carried out in an attempt to correlate the exchange results with the reaction scheme which was proposed to explain the spectrophotometric data. This scheme is reproduced here for reference, on the following page.









$$k_1 \approx k_{-1}$$

$$k_3 > k_{-3}$$

$$k_1 \ll k_2 \approx k_3 > k_4$$

$$k_2 > k_{-2}$$

$$k_4 \gg k_{-4}$$

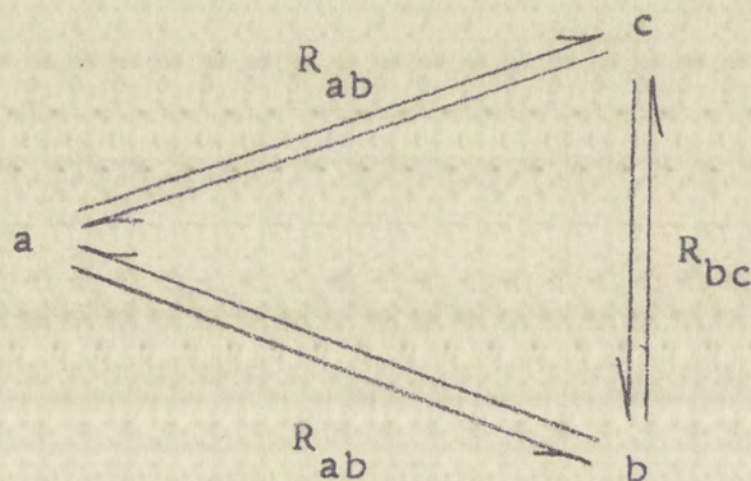
According to this scheme, there are more than two chemically nonequivalent arsenic(V) species which might partake in exchange with arsenic(III). If the exchange does indeed involve more than two arsenic(V) species, the analysis of the exchange data at the present time would not be possible because the mathematical equations for exchange among more than three species have not been developed. Furthermore, resolution of the complex exchange curves, which would consist of more than two exponential components, would be very difficult. Nevertheless, the results of several exchange runs were analyzed with the complex exchange law for three species on the assumption that there is exchange among only the arsenic(III), the arsenic(V) species  $D_m$ , and the arsenic(V) species  $D_n$ . This system is represented as follows:



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DEPARTMENT OF CHEMISTRY  
CHICAGO, ILLINOIS 60637

According to this scheme, there are two main  
types of compounds which are known to be  
formed in the reaction of the alkyl  
halides with the organotin compounds. The  
first type is the organotin compound which  
contains the organotin atom in the  
molecule. The second type is the  
organotin compound which contains the  
organotin atom in the side chain.  
The organotin compound which contains the  
organotin atom in the side chain is  
formed in the reaction of the alkyl  
halides with the organotin compounds.  
The organotin compound which contains the  
organotin atom in the molecule is  
formed in the reaction of the alkyl  
halides with the organotin compounds.





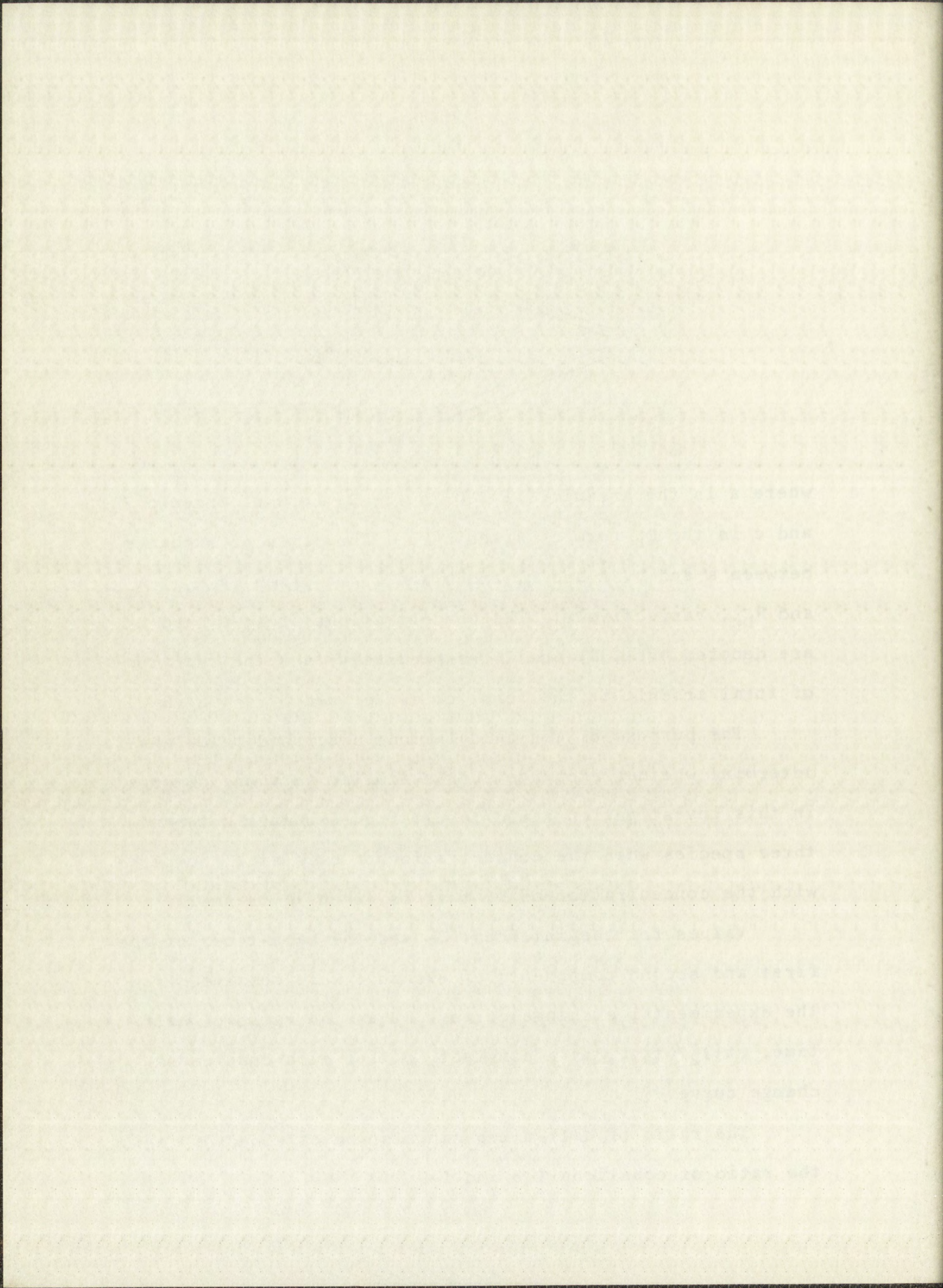
where  $a$  is the arsenic(III),  $b$  is the  $D_m$  form of arsenic(V), and  $c$  is the  $D_n$  form of arsenic(V). The rates of exchange between  $a$  and  $b$ ,  $a$  and  $c$ , and  $b$  and  $c$  are given by  $R_{ab}$ ,  $R_{ac}$ , and  $R_{bc}$ , respectively. The concentrations of  $a$ ,  $b$ , and  $c$  are denoted by  $A$ ,  $B$ , and  $C$ , respectively; and the fraction of total arsenic in the form,  $c$ , is defined by  $\phi = C/(B+C)$ .

The purpose of the calculations described below was to determine whether exchange curves similar to those observed in this investigation could result from exchange between three species when the concentration of  $c$  is small compared with the concentration of  $b$ , that is, when  $\phi$  is small.

Values for the intercept  $Q_1$  and the half-times of the first and second components of exchange were obtained from the experimental exchange curves. Thus the ratio of half-time,  $(t_{\frac{1}{2}})_2/(t_{\frac{1}{2}})_1$ , is a constant,  $n$ , for each complex exchange curve.

The ratio of half-times can also be obtained by taking the ratio of equations I-8 and I-9:







$$(q+p) / (q-p) = (t_{\frac{1}{2}})_2 / (t_{\frac{1}{2}})_1 = n$$

It follows that

$$(VI-1) \quad p = \frac{n-1}{n+1} q$$

The parameter  $p$  in equation I-11 is eliminated by substitution of  $q(n-1)/(n+1)$  and the equation is solved for  $2q$  in terms of the variables  $R_{ab}$  and  $R_{ac}$  :

$$(VI-2) \quad 2q = \frac{n+1}{1+(n-1)Q_1} \frac{S_a^0 - S_b^0}{S_a^0 - S_a^\infty} \frac{1}{A} (R_{ab} + R_{ac}) = \frac{N}{A} (R_{ab} + R_{ac})$$

For simplicity, let the number  $\frac{n+1}{1+(n-1)Q_1} \frac{S_a^0 - S_b^0}{S_a^0 - S_a^\infty}$

be represented by  $N$ .

The parameter  $q$  in equation I-6 is then eliminated between equations I-6 and VI-2; the resulting equation is solved for  $R_{bc}$  in terms of the variables  $R_{ab}$ ,  $R_{ac}$ , the concentration of the arsenic(V) species  $b$ , and the concentration of the arsenic(V) species  $c$ .

(VI-3)

$$R_{bc} = \frac{BC}{A(B+C)} \left[ \left( N - \frac{A+B}{B} \right) R_{ab} + \left( N - \frac{A+C}{C} \right) R_{ac} \right]$$

The parameters in equation I-7 are related to the







variables  $R_{ab}$  and  $R_{ac}$  by use of equations VI-1 and VI-2:

$$\begin{aligned}
 q^2 - p^2 &= q^2 - \left( \frac{n-1}{n+1} q \right)^2 \\
 &= \left[ 1 - \left( \frac{n-1}{n+1} \right)^2 \right] \frac{N^2}{4A^2} (R_{ab} + R_{ac})^2 \\
 &= \frac{nN^2}{(n+1)^2 A^2} (R_{ab} + R_{ac})^2
 \end{aligned}$$

For simplicity, let the number  $\frac{nN^2}{(n+1)^2}$  be represented by  $M$ ;

therefore, according to equation I-7,

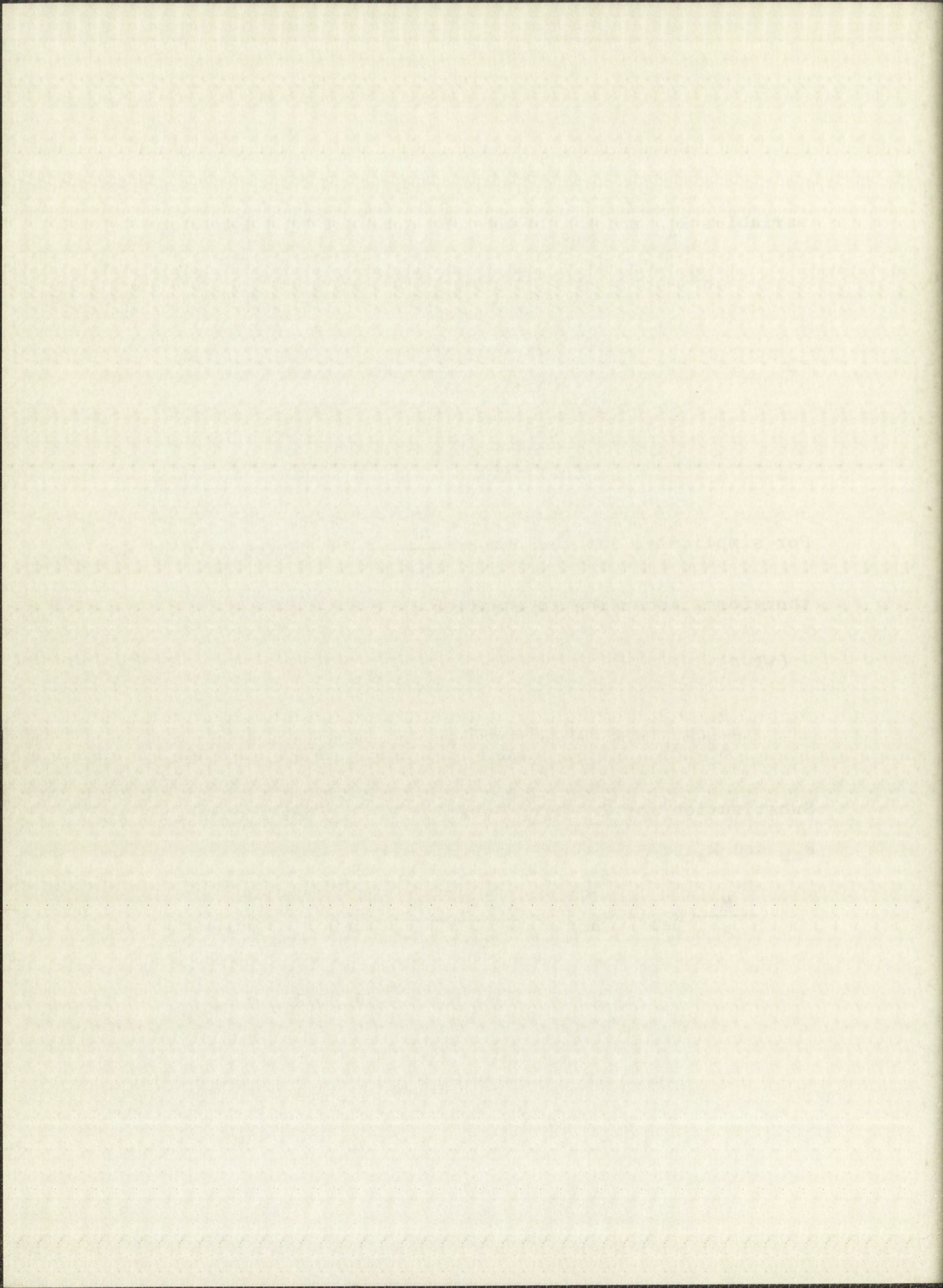
(VI-4)

$$\frac{M}{A^2} (R_{ab} + R_{ac})^2 = \frac{A+B+C}{ABC} \left[ R_{bc} (R_{ab} + R_{ac}) + R_{ab} R_{ac} \right]$$

Substitution for  $R_{bc}$  from equation VI-3 gives a quadratic in  $R_{ab}$  and  $R_{ac}$  :

$$\begin{aligned}
 \frac{M}{A} (R_{ab} + R_{ac})^2 &= \frac{A+B+C}{BC} \left[ \frac{BC}{A(B+C)} \left\{ \left( N - \frac{A+B}{B} \right) R_{ab} \right. \right. \\
 &\quad \left. \left. + \left( N - \frac{A+C}{C} \right) R_{ac} \right\} (R_{ab} + R_{ac}) \right. \\
 &\quad \left. + R_{ab} R_{ac} \right]
 \end{aligned}$$







$$\begin{aligned}
& \left[ M - \frac{A+B+C}{B+C} \left( N - \frac{A+B}{B} \right) \right] R_{ab}^2 \\
& + \left[ 2M - \frac{A+B+C}{B+C} \left( 2N - \frac{A+B}{B} - \frac{A+C}{C} + \frac{A(B+C)}{BC} \right) \right] R_{ab} R_{ac} \\
& + \left[ M - \frac{A+B+C}{B+C} \left( N - \frac{A+C}{C} \right) \right] R_{ac}^2 = 0
\end{aligned}$$

(VI-5)

$$\begin{aligned}
& \left[ M - \frac{A+B+C}{B+C} \left( N - \frac{A+B}{B} \right) \right] R_{ab}^2 \\
& + 2 \left[ M - \frac{A+B+C}{B+C} (N-1) \right] R_{ab} R_{ac} \\
& + \left[ M - \frac{A+B+C}{B+C} \left( N - \frac{A+C}{C} \right) \right] R_{ac}^2 = 0
\end{aligned}$$

For each value of  $\varphi$  which is assumed, the quadratic can be solved for  $R_{ab}$  in terms of  $R_{ac}$ . The ratio of  $R_{ab}/R_{ac}$  is substituted in equation VI-3 which is then solved for  $R_{bc}$  in terms of  $R_{ac}$ .

It was found that there is a minimum value of  $\varphi$  for which the ratio of rates  $R_{bc}/R_{ac}$  becomes negative. Because a negative rate has no physical significance, this minimum value of  $\varphi$  was taken to be the smallest value consistent with the observed complex exchange. The minimum value of  $\varphi$  for several exchange reactions is listed in Table VI-7.

The minimum value of  $\varphi$  for run 24 was found to be 0.026, that is, the concentration of  $D_n$  can indeed be small





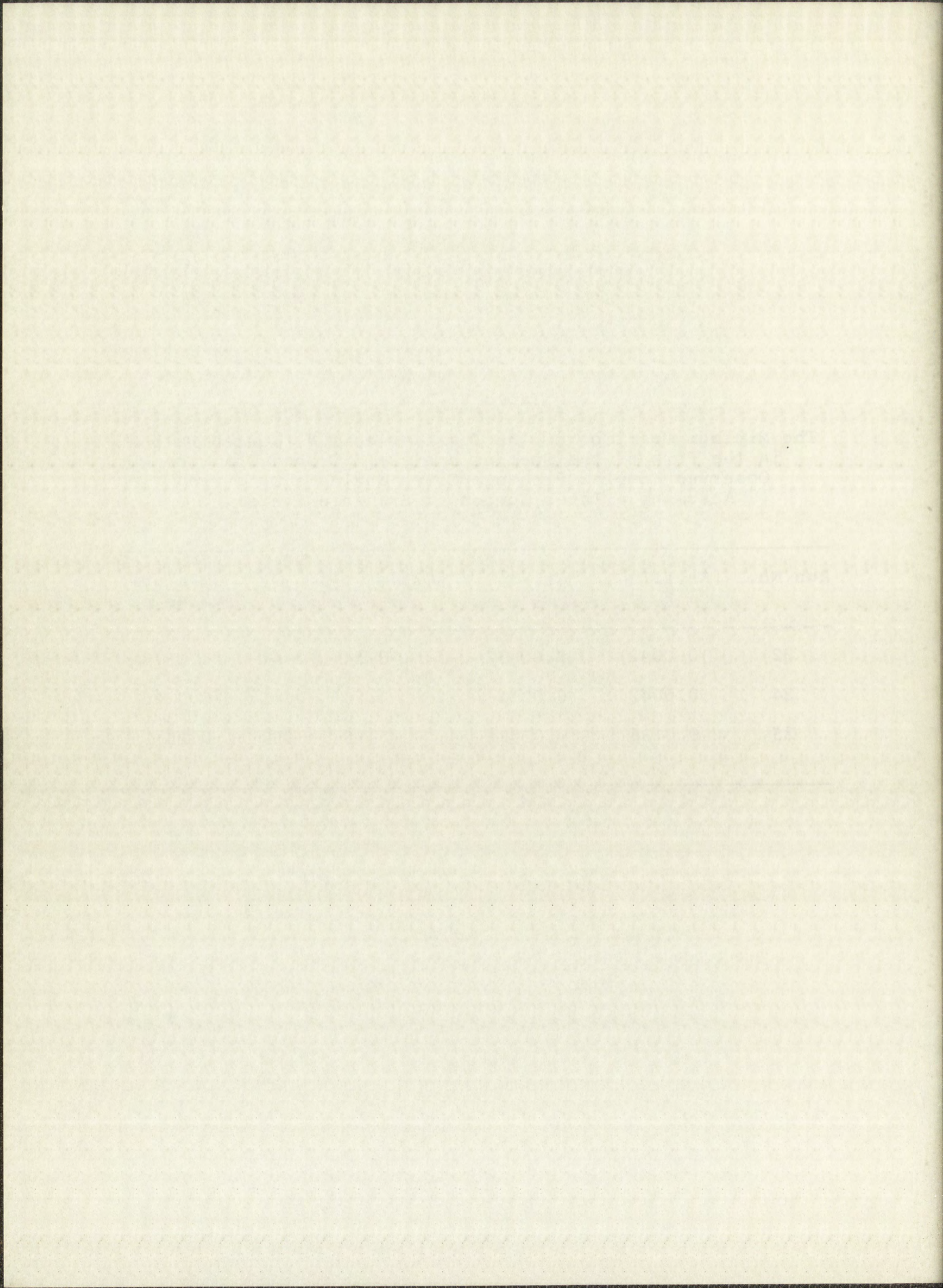


Table VI-7

The Minimum Fraction of the Total Arsenic(V) Concentration  
in the Form of the Species  $c$  at  $29.7^{\circ}\text{C}$  Such That the  
Observed Complex Exchange Curve Would Be Obtained  
Assuming a Three Component Exchange System

Run No.	$[\text{As(III)}]_{\underline{f}}$	$[\text{As(V)}]_{\underline{f}}$	$(t_{\frac{1}{2}})_2 / (t_{\frac{1}{2}})_1$	$Q_1$	Minimum value of $\phi$
22	0.0042	0.00837	8.54	0.47	0.189
24	0.0042	0.0251	2.50	0.41	0.0263
25	0.0126	0.0251	7.15	0.59	0.251







in comparison with the concentration of  $D_m$  and still give rise to the complex exchange curve which is observed. It is noted for this run that, because the minimum concentration of  $D_n$  is 14% of the arsenic(III) concentration, a measurable fraction of the radioactivity may transfer from the arsenic(III) to the species  $D_n$  provided the rate of appearance of radioactivity in  $D_m$  is slow compared with the rate of appearance of radioactivity in  $D_n$ .

The minimum values of  $\phi$  for runs 22 and 24 were found to be 0.19 and 0.25 respectively (see Table VI-7). These results require the concentration of  $D_n$  to be higher than is consistent with the reaction scheme.

There is an additional observation which is not explained by the reaction scheme. The first component of exchange in 11.2  $\underline{f}$  hydrochloric acid (runs 1-4) is moderately rapid ( $t_{\frac{1}{2}} = 109$  min. to 141 min.) and contributes 40% to 60% of the total exchange regardless of the age of the arsenic(V) solution over one day to six weeks. The aging of the arsenic(V), however, continues over at least three weeks. These observations indicate that the exchange involves at least two arsenic(V) species which are both present in appreciable concentrations in freshly prepared solutions.

According to the preceding discussion, the arsenic(V) equilibria are not adequately described by the reaction scheme which accounts reasonably well for the spectrophoto-







metric observations. Until more is known about the actual chemistry of arsenic(V) species in hydrochloric acid solution, it is improbable that the complex exchange data can be analyzed.

#### D. Summary

Isotopic exchange between arsenic(III) and arsenic(V) in 10.9  $\underline{f}$  hydrochloric acid has been found to be measurable at 29.7°C. The exchange has been investigated over the concentration ranges of 0.00111  $\underline{f}$  to 0.0474  $\underline{f}$  arsenic(III) and 0.00446  $\underline{f}$  to 0.0837  $\underline{f}$  arsenic(V) and was found to be complex in general; that is, the exchange curves consist of more than one exponential component. The exchange results are dependent on the age of the arsenic(V) solution, but independent of the age of the arsenic(III) "tracer" solution. The exchange results appear to be largely independent of the method of preparation of the arsenic(III) "tracer" (see Section VI.C.8.). Elevation of the reaction temperature increases the rate of exchange. Exposure of the exchange reaction mixture to the normal fluorescent laboratory light or to the large surface area of pyrex glass wool caused noticeable changes in the observed results but because of the difficulties in reproducing the exchange experiments, one could not definitely attribute these changes to the fluorescent light or the increased surface area.







The initial rate of exchange was calculated with the simple exchange law and correlated with the concentration of arsenic(III) and arsenic(V). Although the initial rate of exchange in 10.9 f hydrochloric acid at 29.7°C cannot be expressed by a rate law involving one path, rate expressions of the form  $R = k_1[\text{As(III)}]^n$  and  $R = k_2[\text{As(V)}]^m$  are derived (see Table VI-3). The initial rate of exchange in 10.9 f hydrochloric acid over a concentration range of 0.00132 f to 0.00660 f arsenic(III) and 0.00777 f to 0.0388 f arsenic(V) is well represented by

$$R = 6.71 \times 10^{-5} [\text{As(III)}]^{0.91} [\text{As(V)}]^{0.38} \text{ l. g.-at.}^{-1} \text{sec.}^{-1}$$

at 48.6°C and

$$R = 8.72 \times 10^{-5} [\text{As(III)}]^{0.37} [\text{As(V)}]^{0.76} \text{ l. g.-at.}^{-1} \text{sec.}^{-1}$$

at 67.3°C, respectively.







VII. DISCUSSION OF EXPERIMENTAL DIFFICULTIES,  
SUGGESTED IMPROVEMENTS IN EXPERIMENTAL TECHNIQUES,  
AND PROPOSALS FOR FUTURE WORK

A. Introduction

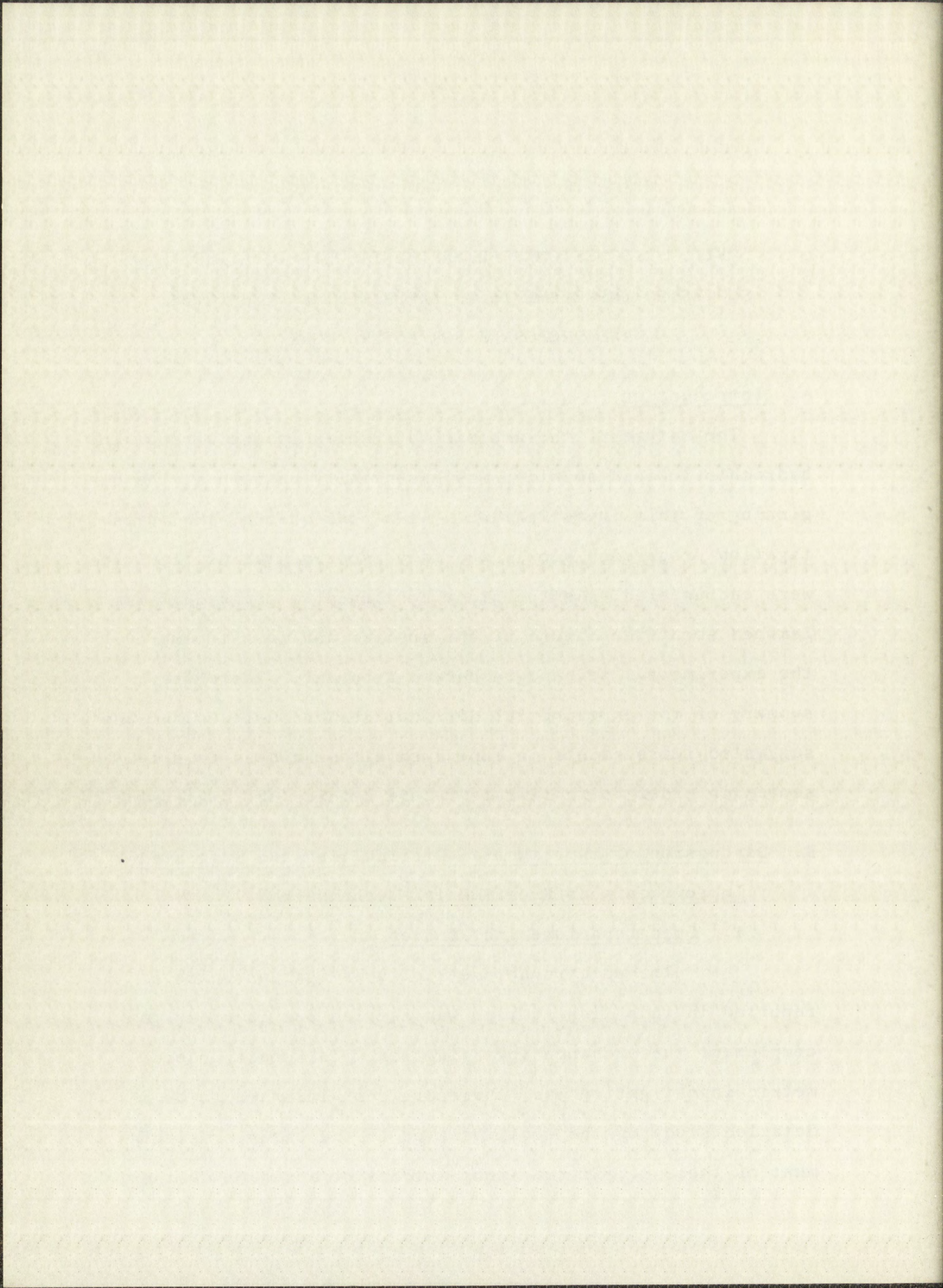
The nature of the arsenic(V) species in equilibrium in hydrochloric acid solution was essentially unknown at the beginning of this investigation. As a consequence, the investigation progressed slowly and many experimental difficulties were encountered. As the study continued, a great deal was learned about the nature of the species and ways to improve the experimental techniques became apparent. Therefore a summary of the experimental difficulties encountered and the suggested improvements in experimental techniques is presented in order to facilitate future studies of this system.

B. Discussion of Experimental Difficulties and Suggested Improvements in Experimental Techniques

1. Spectrophotometric Studies

The spectrophotometric investigation which is reported in this dissertation was carried out in order to complement the exchange investigation. The spectrophotometric investigation was, therefore, not intended to be a detailed study of the equilibria or of the rates of attainment of these equilibria among species of arsenic. Rather,







the purpose was to obtain a qualitative picture of the nature of the aging process and identify the valence state which ages. Therefore, no attempt was made to control the temperature of the solutions and no special techniques were employed to prevent small changes in the hydrochloric acid concentration or to precisely match the acid concentration of solutions which were mixed.

It was found that the equilibria among arsenic(V) species is strongly dependent on the temperature. Therefore, in future studies, the solutions should be stored and observed at a constant temperature.

The equilibria among arsenic(V) species were found to be extremely sensitive to the hydrochloric acid concentration. Consequently, all solutions should be prepared from the same large stock solution of hydrochloric acid and aliquots of these solutions should be stored in sealed glass tubes in order to avoid loss of hydrogen chloride through volatilization. Aliquots of the same hydrochloric acid stock solution to be used in the reference absorption cell should also be stored in sealed tubes.

The solutions to be studied at elevated temperatures should be stored in sealed absorption cells which can be observed directly in the spectrophotometer at constant temperature. All sealed tubes or cells should contain the minimum air space necessary to accommodate expansion of the solution







at the higher temperatures.

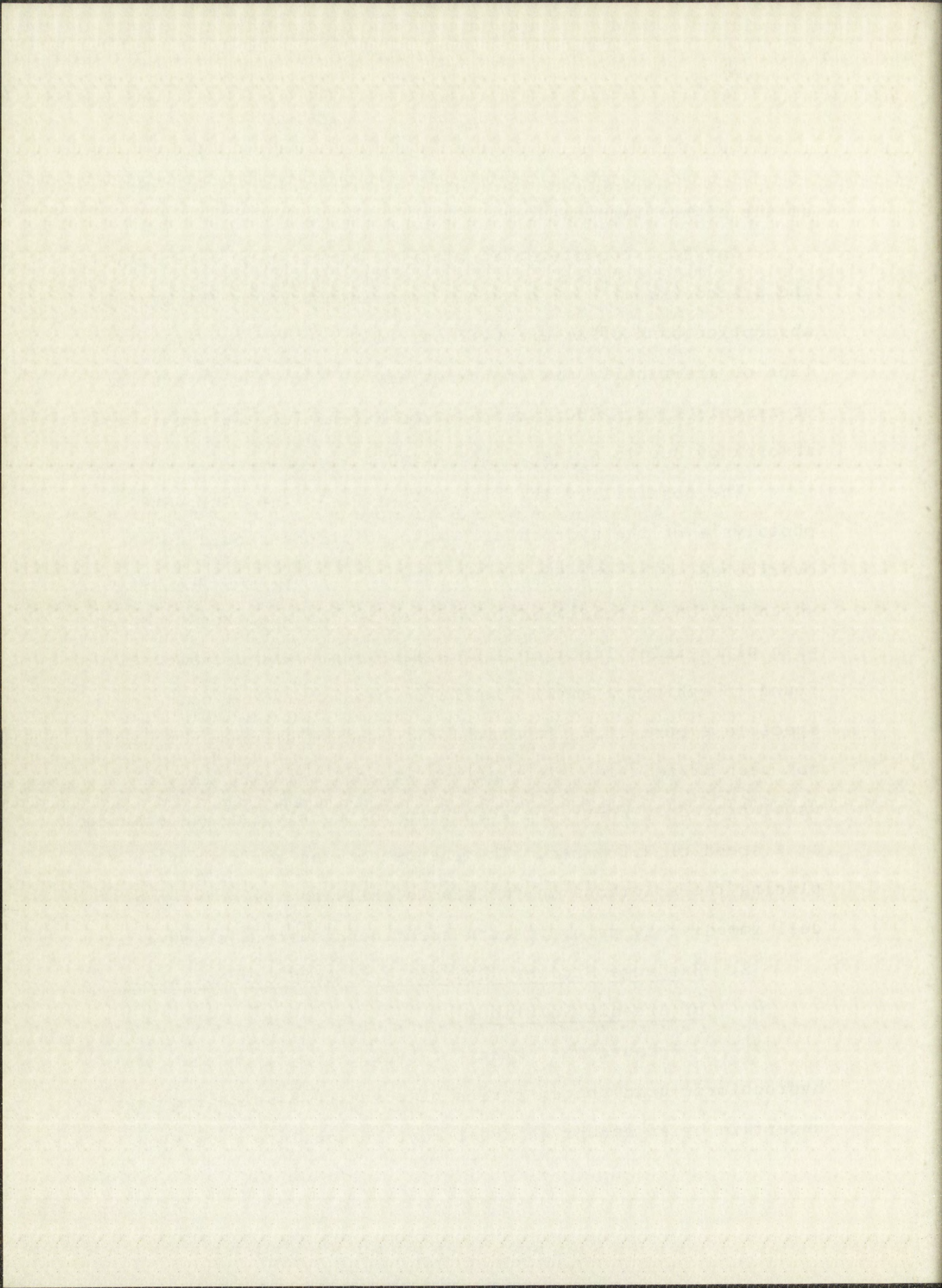
Any spectrophotometric study of mixtures of arsenic(III) and arsenic(V) at 2300 Å should take into account the strong absorption band of arsenic(III) at 2130 Å. If the concentration of arsenic(III) is approximately  $10^{-4}$   $\underline{f}$ , the absorbancy of arsenic(V) at 2300 Å is obscured except for the growth in absorbancy due to aging of the arsenic(V).

The possibility that the ultraviolet light may cause photolysis of the hydrochloric acid solutions should not be overlooked. The absorbancy of pure 10.9  $\underline{f}$  hydrochloric acid which had been irradiated 15 minutes in the spectrophotometer with ultraviolet light of 2700 Å wavelength was occasionally found to exhibit a small absorption band at 2700 Å with respect to a pure 10.9  $\underline{f}$  hydrochloric acid solution which had not been irradiated. This effect was not detected in the usual procedure where the absorbancy of a solution was scanned at a speed of 2.5 Å/sec. The phenomenon was avoided by replacing the solutions in the sample cell and the reference cell immediately prior to each spectrophotometric observation.

## 2. Exchange Studies, Hydrochloric Acid Concentration of Arsenic Solutions

Because the extent of hydrolysis is unknown, the hydrochloric acid concentration of arsenic(V) solutions is uncertain by an amount which at most is equal to five times



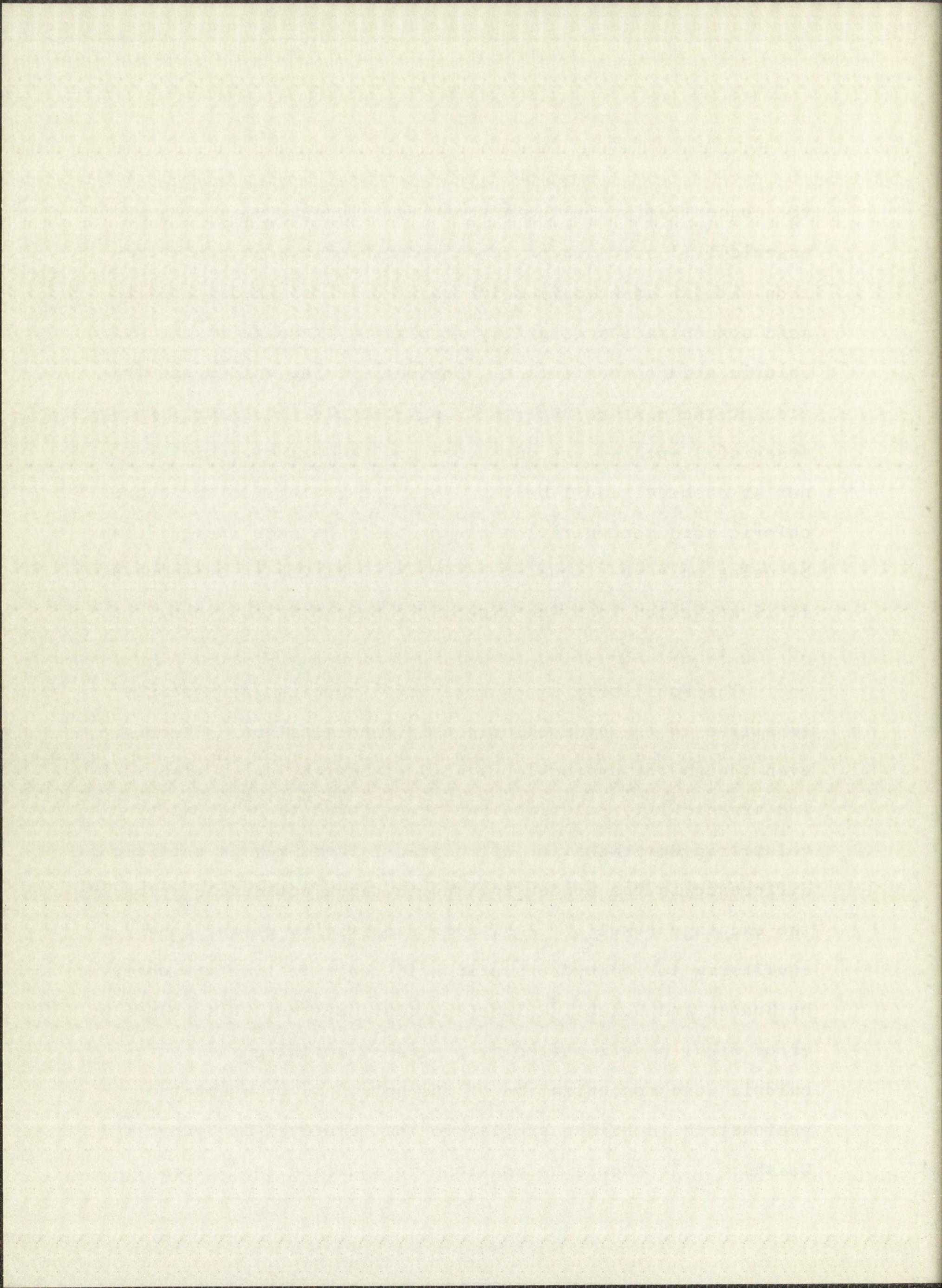




the concentration of the arsenic(V). Therefore, mixing an arsenic(III) solution of known hydrochloric acid concentration with an arsenic(V) solution of uncertain hydrochloric acid concentration generally results in a change in the hydrochloric acid concentration. Not only is the acid concentration of the mixture uncertain, but the slow equilibria among arsenic(V) species are disturbed and the exchange mixture is not at chemical equilibrium. This uncertainty in the hydrochloric acid concentration can probably be made insignificant by using only solutions which are very dilute in arsenic(V); it is suggested that the arsenic(V) concentration should be  $10^{-2}$  f to  $10^{-4}$  f.

The equilibria among arsenic(V) species is extremely sensitive to the hydrochloric acid concentration. Therefore, even though the hydrochloric acid concentration of arsenic(V) and arsenic(III) solutions have been found to be equal by volumetric determination of chloride, there may be sufficient difference in the concentrations to cause noticeable error in the exchange results. A similar sensitivity of antimony(V) equilibria to the hydrochloric acid concentration was observed by Bonner and Goishi.<sup>4</sup> In the arsenic system, this source of error might be eliminated by precisely matching the hydrochloric acid concentration of the solutions by a spectrophotometric technique similar to that employed by Bonner and Goishi.<sup>4</sup> It should be possible to minimize the error



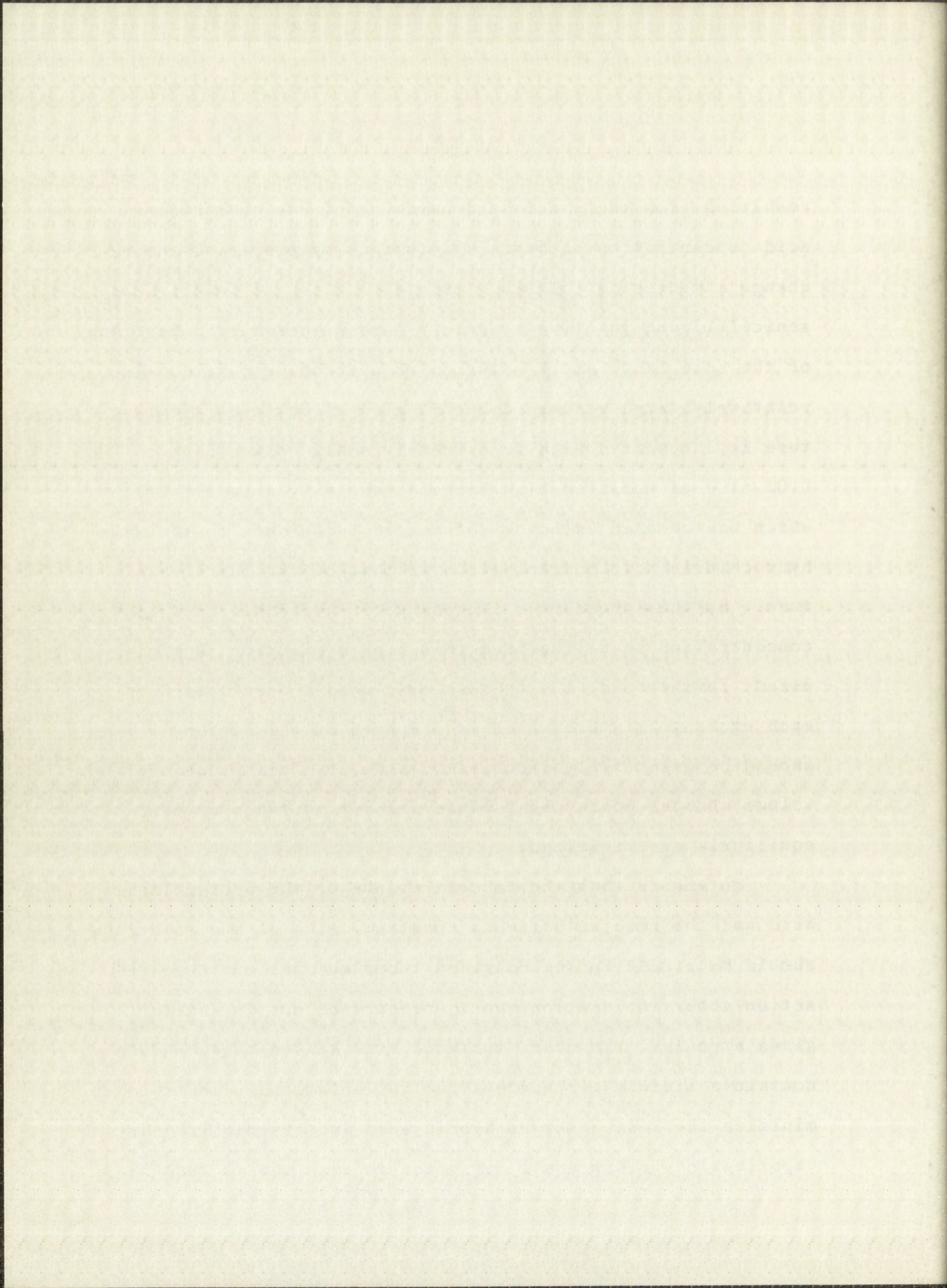




resulting from the inadequate matching of the hydrochloric acid concentration of arsenic solutions by preparing the exchange mixtures as follows. Dilute mixtures of inactive arsenic(III) and inactive arsenic(V) are prepared from portions of the same large stock solution of hydrochloric acid. A relatively large volume (about 25 ml.) of an inactive mixture is inoculated with an extremely small volume (about 0.01 ml.) of purified high specific activity arsenic(III) which has been adjusted by volumetric techniques to the same hydrochloric acid concentration as that of the inactive mixture. By this procedure, the change in hydrochloric acid concentration resulting from this minute dilution is minimized; furthermore, the hydrochloric acid concentration of each exchange mixture which is prepared by this method should be essentially identical. Also, by this procedure, volume changes which might cause a shift in the polymeric equilibria are minimized.

To ensure that the concentrations of the hydrochloric acid and the reactants remain constant, each of the solutions should be stored in sealed glass tubes and the exchange reaction after inoculation should be carried out in sealed glass ampoules. In every instance, the sealed tubes should contain a minimum air space above the solution in order to minimize the loss of hydrochloric acid and arsenic(III) by vaporization. This small air space in each sealed tube is







necessary to accommodate the expansion of the liquid at elevated temperatures.

There should be no difficulties associated with the inoculation of inactive mixtures with purified high specific activity arsenic(III) because the species in the high specific activity arsenic(III) appear to be equivalent to the species present in inactive arsenic(III) solutions (see Section VI). This point, however, may deserve further investigation.

### 3. Exchange Studies. Aging of the Arsenic Solutions

It was discovered in this investigation that the arsenic(V) solutions aged over several weeks at room temperature. Because the rate of aging is dependent on the hydrochloric acid concentration, aging of hydrochloric acid solutions of arsenic(V) should be carried out in sealed glass tubes in order to maintain a certain acid concentration.

According to the spectrophotometric data, the equilibria among arsenic(V) species is dependent on the temperature. Furthermore, exchange data indicate that the shift in equilibrium induced by increasing the temperature of arsenic(V) solution which was aged at the lower temperature is relatively slow. Therefore, arsenic(V) solutions should be aged at the temperature at which the exchange reaction is to be studied.

A special problem is encountered when the aging is





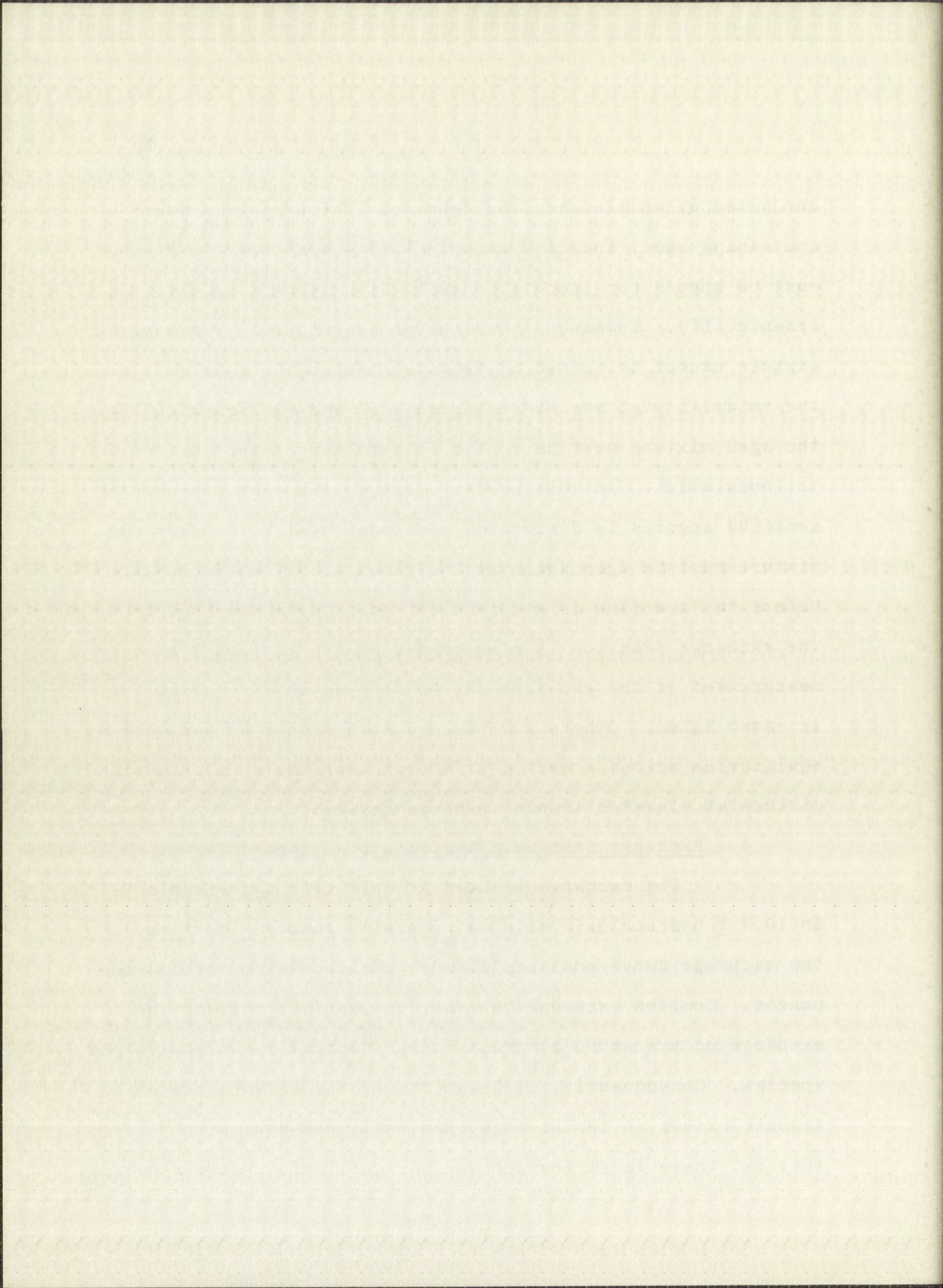


conducted at an elevated temperature. The storage vessels containing aged, inactive arsenic(III) - arsenic(V) mixture must be opened for inoculation with high specific activity arsenic(III). Inasmuch as a tube of arsenic(III) - arsenic(V) mixture cannot be opened at elevated temperatures because of the volatility of the hydrochloric acid and the arsenic(III), the aged mixture must be cooled to room temperature prior to inoculation. In this process, the equilibrium among arsenic(V) species is disturbed, and consequently the exchange mixture must be aged again at the given elevated temperature before the reaction is studied. If conditions are such that the exchange reaction is slow compared with the aging process, measurement of the exchange can be delayed until equilibrium is established. Otherwise, the exchange cannot be measured at equilibrium unless a method of inoculating the aged, inactive mixture at elevated temperatures is devised.

#### 4. Exchange Studies. Analysis of Exchange Curves

The exchange between arsenic(III) and arsenic(V) in 10.9  $\%$  hydrochloric acid is generally complex; that is, the exchange curve consists of more than one exponential component. Complex exchange behavior is possible only if the exchange occurs among at least three chemically non-equivalent species. Consequently, at least one of the valence states of arsenic exists in two or more chemically non-equivalent forms; that is, there is at least one slow equilibrium between species







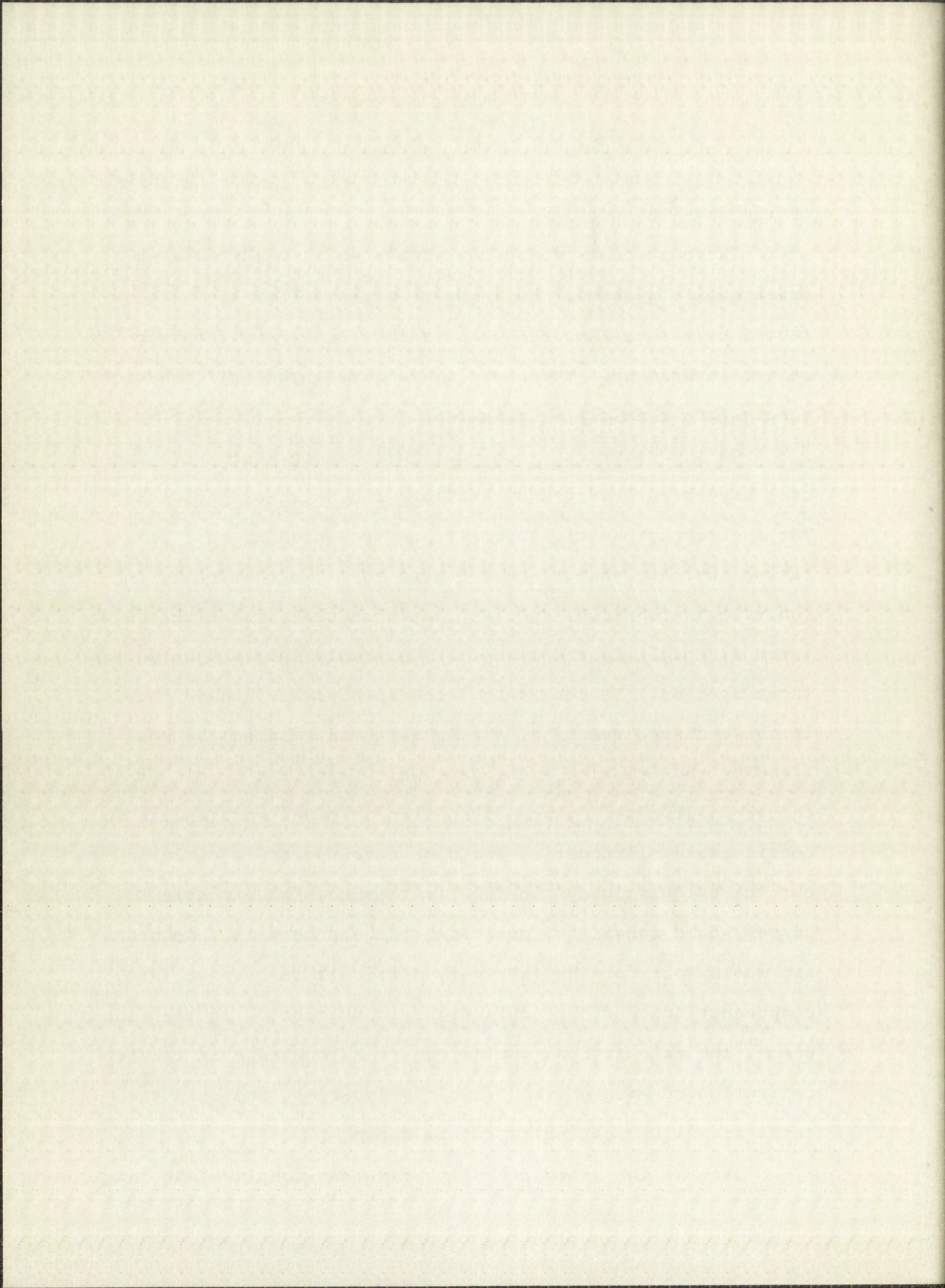
of the same valence.

There is no evidence for a slow equilibrium between arsenic(III) species. No aging of arsenic(III) has been detected by either exchange measurements or by spectrophotometric techniques. Therefore it is likely that all arsenic(III) species are chemically equivalent.

On the contrary, slow equilibria among arsenic(V) species have been observed by exchange and by spectrophotometry. The spectrophotometric observations presented in this dissertation indicate that there are more than two chemically non-equivalent arsenic(V) species, in which case, the exchange between arsenic(III) and arsenic(V) probably involves more than three species. If more than three species are indeed involved in the exchange reaction, the exchange data cannot be analyzed by the existing exchange laws. Even if a complex exchange law for the number of species involved were available, considerable difficulties would be encountered in carrying out the calculations. In the first place, the exchange curves would consist of more than two exponential components and would therefore be extremely difficult to resolve into components under the most favorable conditions. In the second place, the calculations would require a knowledge of the concentration of each of the arsenic(V) species, and only the total arsenic(V) concentration is known.

Even if the arsenic system were less complex than has







been suggested in this dissertation and the exchange is a result of reaction among only two arsenic(V) species and one arsenic(III) species, the analysis of the exchange curves would be difficult because the concentration of each arsenic(V) species is unknown.

The preceding discussion leads one to believe that it would be hopeless to attempt further investigation of the exchange between arsenic(III) and arsenic(V). On the contrary, exchange studies at elevated temperatures may prove fruitful because the attainment of equilibria among arsenic(V) species may become rapid and consequently the exchange may become simple in nature.

### C. Future Work

#### 1. Spectrophotometry

It is advisable to learn more about the arsenic system by spectrophotometry before proceeding with further exchange experiments which, to be sure, are more time consuming than the spectrophotometric measurements. The primary object of the investigation would be to elucidate the equilibria among arsenic(V) species in hydrochloric acid solution and the rates of attainment of these equilibria. Both the equilibria and the rates of attainment of these equilibria should be studied as a function of the concentration of hydrochloric acid, the concentration of arsenic(V), the concentration of arsenic(III) in arsenic(III) - arsenic(V) mixtures,



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and the temperature. It would also be of interest to study the effect of varying the chloride concentration at constant acidity. Such studies, in addition to providing intrinsic information regarding the chemistry of arsenic(V), should serve as a basis for the planning and interpretation of exchange experiments.

A spectrophotometric study of the preparation of arsenic(V) solutions might lead to a method of preparing hydrochloric acid solutions of arsenic(V) which require a relatively short time to reach equilibrium. The aging over several weeks at room temperature of arsenic(V) solution prepared by dissolution of arsenic pentoxide in hydrochloric acid is believed to be a result of the slow formation of chloride complexes. The hydrolysis of at least some of the chloride complexes, however, appears to be complete in several hours (see Section V.9.). Thus, if the chloride complexes could be formed directly by a process such as the oxidation of arsenic trichloride in hydrochloric acid solution by chlorine, the subsequent aging of the arsenic(V) solution would probably require only a few hours. Therefore, the arsenic(V) produced by chlorine oxidation of arsenic(III) in hydrochloric acid solution should be studied spectrophotometrically.

It would be worthwhile to study spectrophotometrically the polymeric equilibria among arsenic(V) species without







disturbing the hydrolytic equilibria. This study would involve investigation of the "Dilution effect" (see Section V. D.1.) as a function of arsenic(V) concentration and volume changes at constant hydrochloric acid concentration.

## 2. Separation of Arsenic(V) Species

It would be of interest to attempt to separate the arsenic(V) species by solvent extraction or ion-exchange; the disposition of the arsenic(V) species between phases could be determined by spectrophotometry. Solvents which might be used in the solvent extraction studies include isopropyl ether, benzene, and carbon tetrachloride. Ion-exchange resins used in the ion-exchange studies should include cation-exchange resins as well as anion-exchange resins; cationic species such as  $\text{As}(\text{OH})_4^+$ ,  $\text{As}(\text{OH})_3\text{Cl}^+$ , etc., as well as anionic species might exist in solution.

## 3. Exchange Studies

The first component of exchange in 10.9 f hydrochloric acid becomes more prominent at 67.3°C. Therefore, it is suggested that future experiments be conducted at elevated temperatures (above 70°C) in order to avoid the mathematical analysis of complex exchange curves. Other problems, such as aging and inoculation, arise and must be coped with. The improvements in experimental techniques suggested in Section VII.A. should help to obtain reproducible and reliable results.





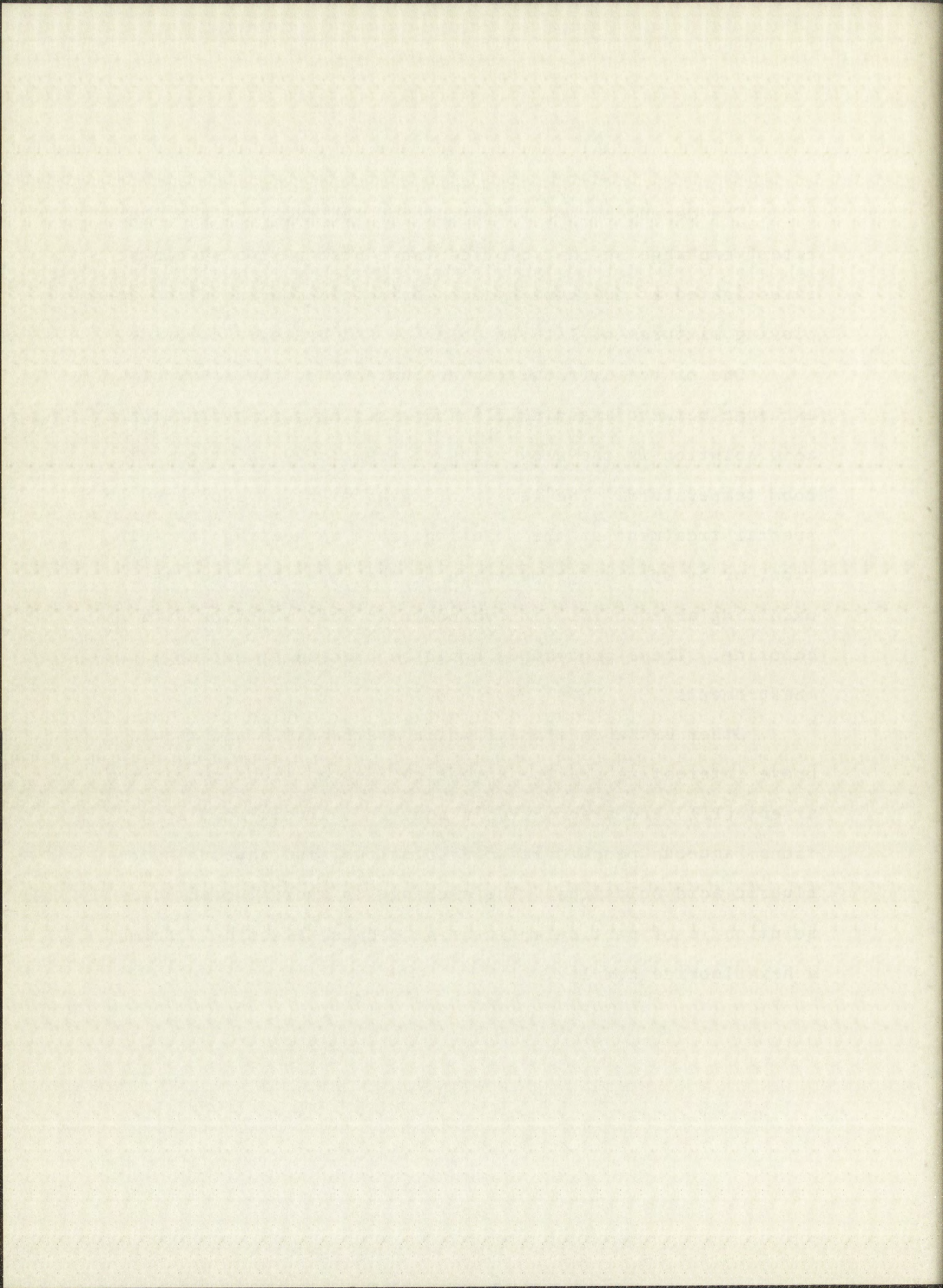


The dependence of the nature of the exchange and the rate of exchange on the chloride ion concentration should be investigated at constant hydrochloric acid concentration employing mixtures of lithium chloride and hydrogen chloride.

One of the difficulties encountered in the study of exchange between arsenic(III) and arsenic(V) in hydrochloric acid solution is the slow aging of arsenic(V) solutions at room temperature. The length of aging might be shortened by special treatment of the solution, such as heating the solution, or by special preparation of the solution, such as oxidizing arsenic(III) in hydrochloric acid solution with chlorine. These procedures could be checked by exchange measurements.

Other exchange studies which are feasible and should prove interesting are the investigations of exchange between arsenic(III) and arsenic(V) in aqueous sulfuric acid solutions, aqueous perchloric acid solutions, and aqueous hydrofluoric acid solutions. The exchange in hydrofluoric acid solution is of particular interest because arsenic(V) forms a hexafluoride complex.

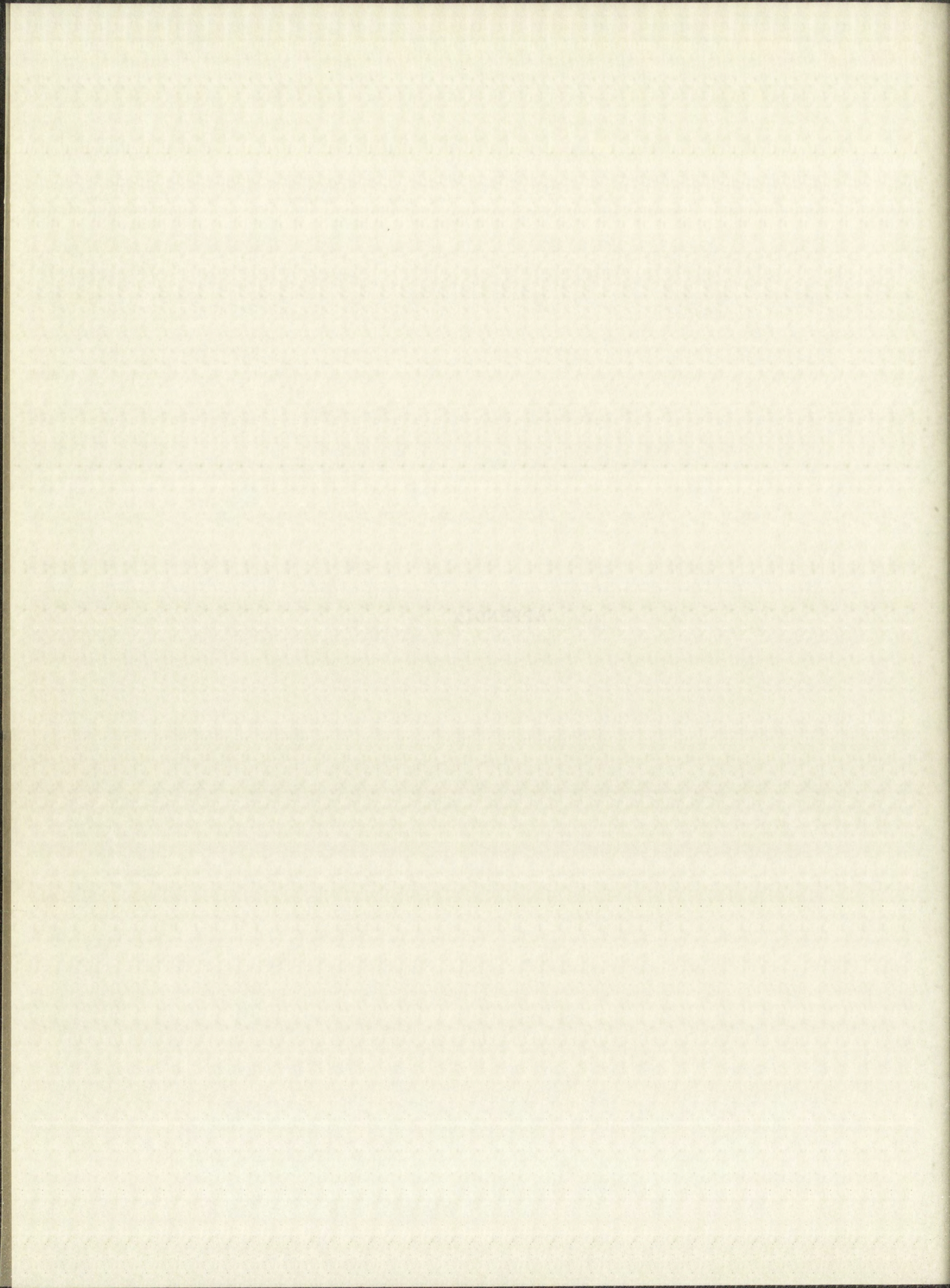






## APPENDIX







## EXPLANATION OF TABLES IN APPENDIX

In the following Tables, the asterisk is used to indicate the "tracer" solution with which the exchange mixtures were prepared. The equilibrium activity of the arsenic(V) listed at the bottom of each Table is a calculated value. The half-time symbols are defined as follows:

$t_{\frac{1}{2}}$  = half-time of the initial portion of the exchange curve

$(t_{\frac{1}{2}})_1$  = half-time of the first component of exchange

$(t_{\frac{1}{2}})_2$  = half-time of the second component of exchange



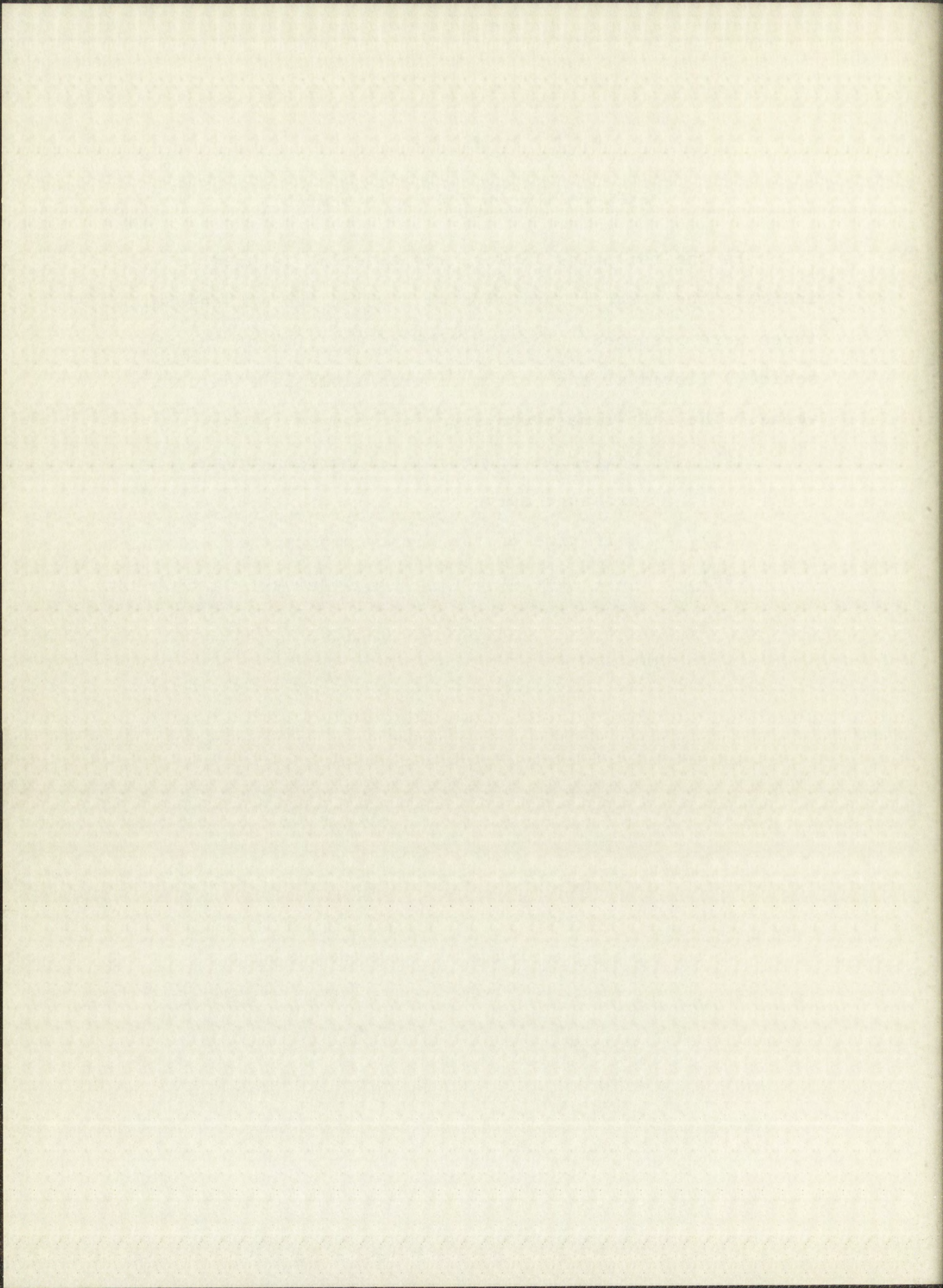




Table 1  
Experimental Data for Run 1

29.7°C

0.0117  $\underline{f}$  As(V), 0.00505  $\underline{f}$  As(III)\*, 11.2  $\underline{f}$  HCl

Reaction mixture prepared from 65 ml. of 1-day-old As(V) and 65 ml. of 1-day-old As(III)\*.

$t_{\frac{1}{2}} = 216$  min.  $(t_{\frac{1}{2}})_1 = 109$  min.  $(t_{\frac{1}{2}})_2 = 17,650$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
3	309	0.963
37	1,109	0.868
80	2,022	0.758
152	3,007	0.641
248	3,810	0.545
423	4,488	0.465
711	4,659	0.444
1,420	4,912	0.413
4,278	5,338	0.363
8,542	5,740	0.315
$\infty$	8,440	0.000



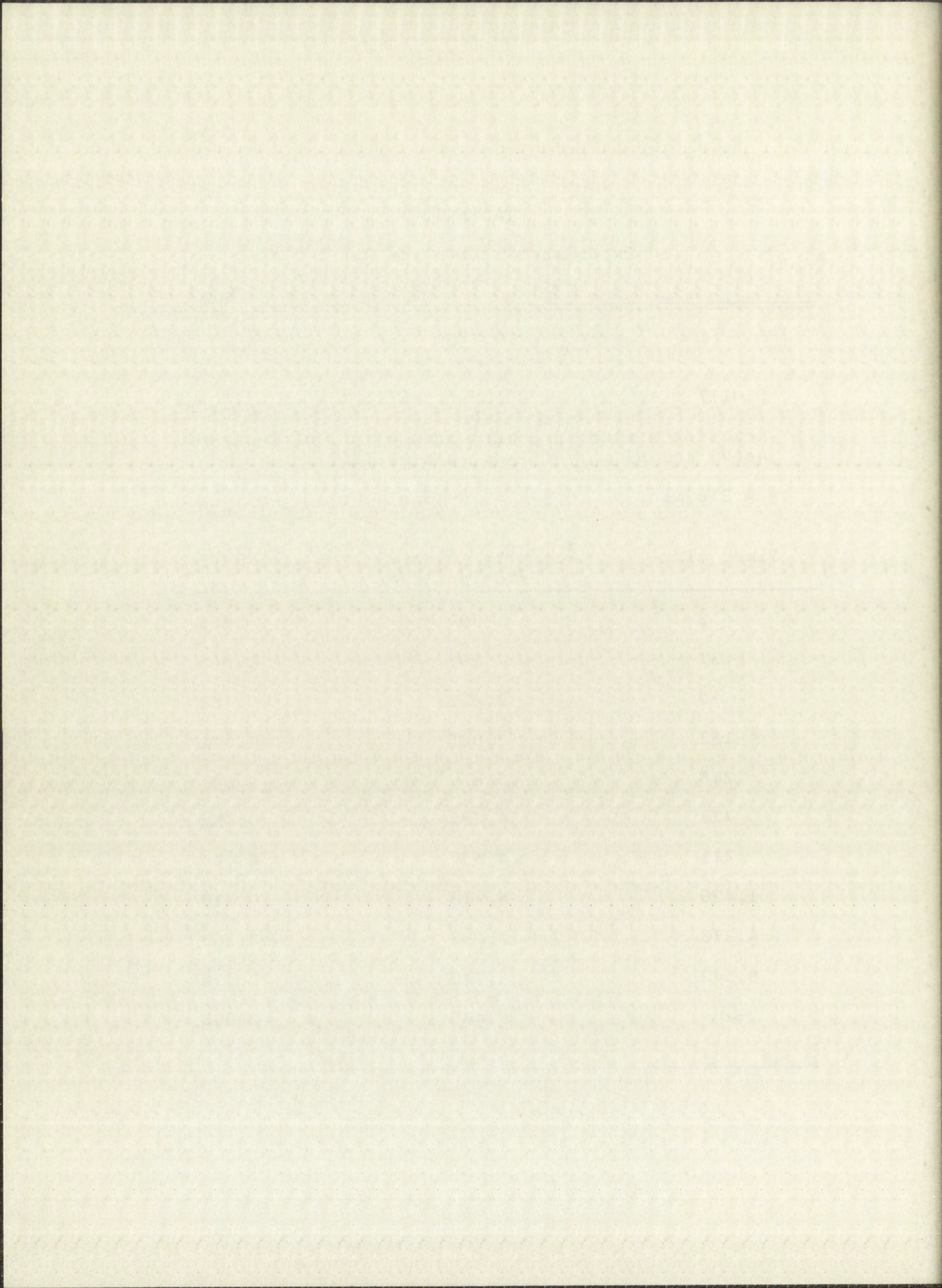




Table 2  
Experimental Data for Run 2

29.7°C

0.0117  $\underline{f}$  As(V), 0.00505  $\underline{f}$  As(III)\*, 11.2  $\underline{f}$  HCl

Reaction mixture prepared from 65 ml. of 7-days-old As(V) and 65 ml. of 7-days-old As(III)\*.

$t_{\frac{1}{2}} = 210$  min.  $(t_{\frac{1}{2}})_1 = 140$  min.  $(t_{\frac{1}{2}})_2 = 600$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
2	208	0.969
42	1,090	0.837
91	1,942	0.709
158	2,838	0.575
253	3,871	0.420
443	4,900	0.266
758	5,634	0.157
$\infty$	6,680	0.000



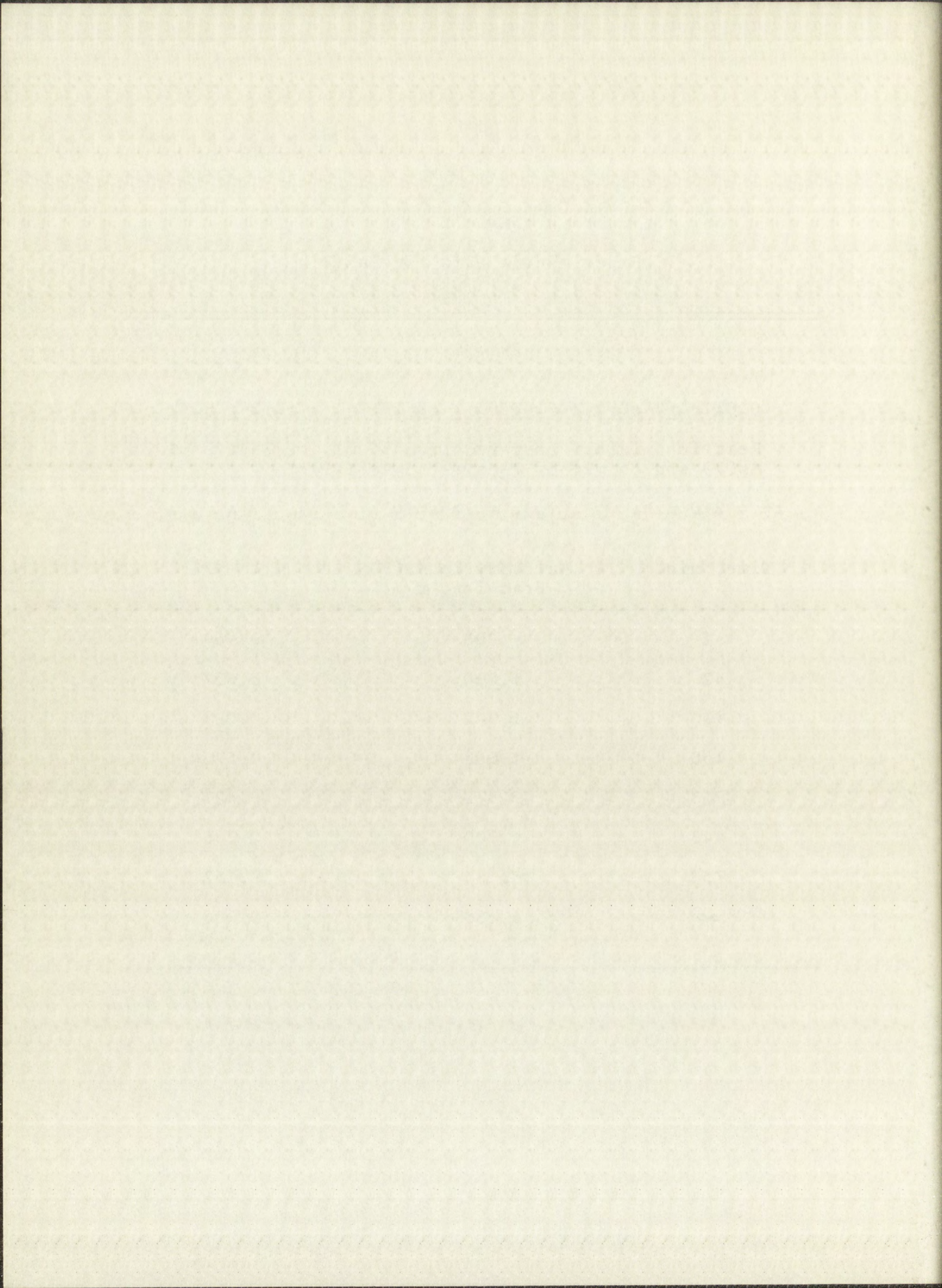




Table 3  
Experimental Data for Run 3

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29.7°C		
0.0114 $\underline{f}$ As(V), 0.00505 $\underline{f}$ As(III)*, 11.2 $\underline{f}$ HCl		
Reaction mixture prepared from 65 ml. of 22-days-old As(V) and 65 ml. of 22-days-old As(III)*.		
$t_{\frac{1}{2}} = 176$ min. $(t_{\frac{1}{2}})_1 = 140$ min. $(t_{\frac{1}{2}})_2 = 490$ min.		
Time, min.	Activity in As(V) Fraction, c/m	1 - F
2	155	0.960
41	664	0.827
97	1,289	0.665
156	1,834	0.523
228	2,290	0.405
316	2,662	0.308
470	3,159	0.178
$\infty$	3,845	0.000

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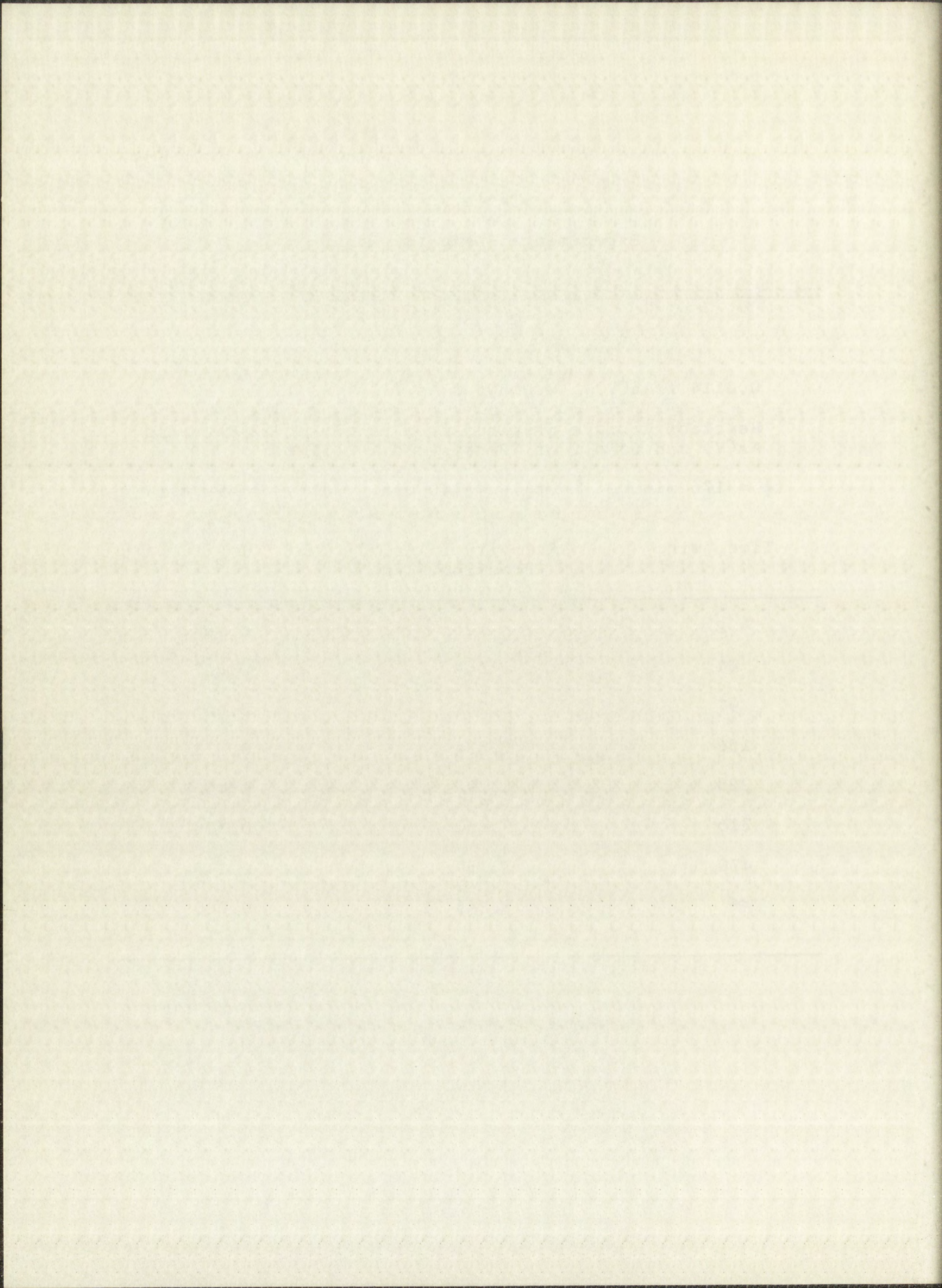




Table 4  
Experimental Data for Run 4

29.7°C		
0.0117 $\underline{f}$ As(V), 0.00505 $\underline{f}$ As(III)*, 11.2 $\underline{f}$ HCl		
Reaction mixture prepared from 65 ml. of 42-days-old As(V) and 65 ml. of 42-days-old As(III)*.		
$t_{\frac{1}{2}} = 176$ min. $(t_{\frac{1}{2}})_1 = 141$ min. $(t_{\frac{1}{2}})_2 = 491$ min.		
Time, min.	Activity in As(V) Fraction, c/m	1 - F
3	107	0.940
37	350	0.804
84	561	0.685
147	828	0.556
227	1,065	0.403
317	1,241	0.304
411	1,403	0.213
562	1,545	0.133
$\infty$	1,783	0.000



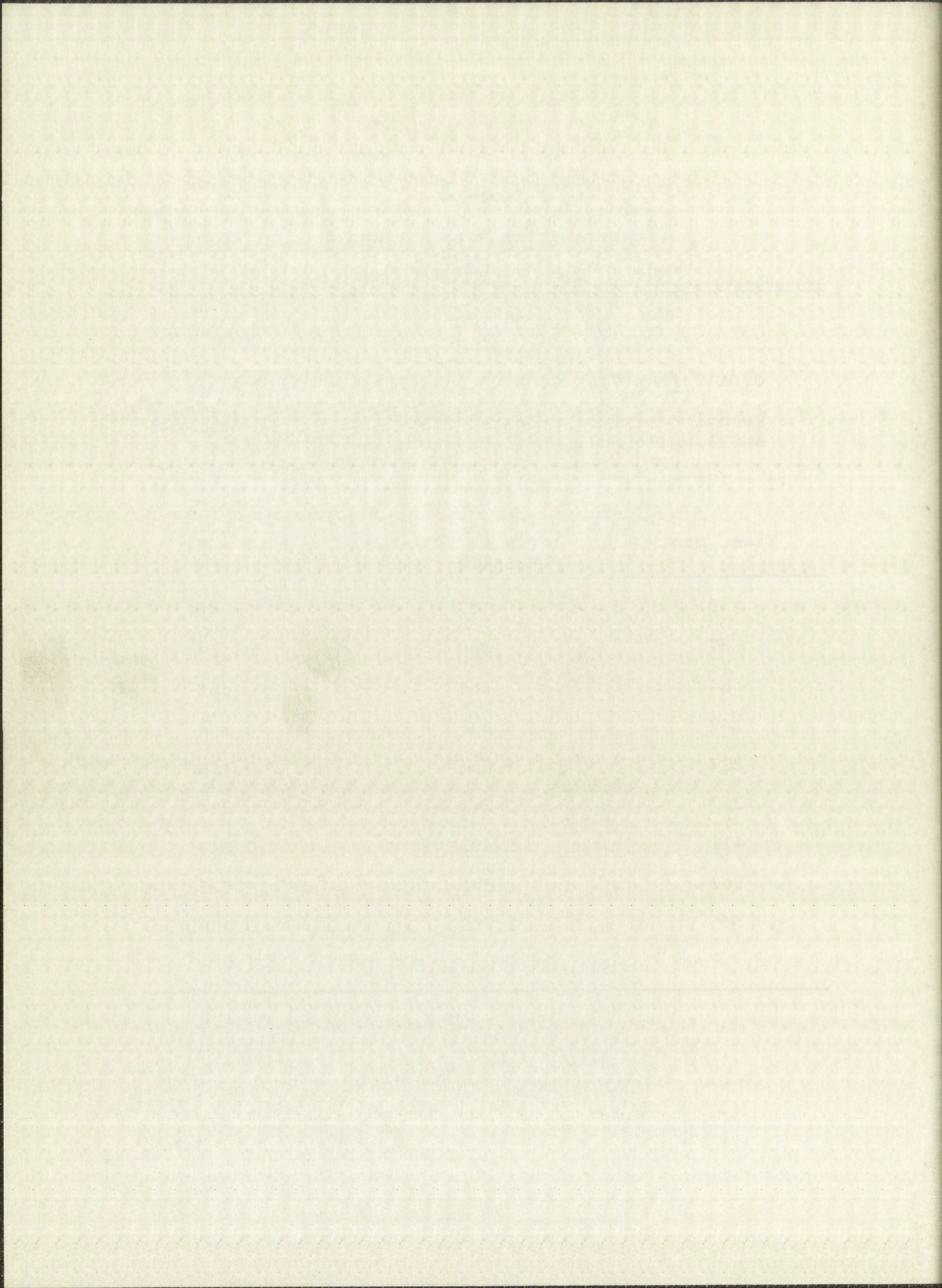




Table 5  
Experimental Data for Run 5

29.7°C		
0.0324 $\underline{f}$ As(V), 0.00111 $\underline{f}$ As(III)*, 10.9 $\underline{f}$ HCl		
Reaction mixture prepared from 15 ml. of 184-days-old As(V), 15 ml. of 3-days-old As(III)*, and 10 ml. of HCl.		
$t_{\frac{1}{2}} = 211$ min.		
Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	1,761	0.966
48	8,887	0.829
90	14,095	0.729
143	20,419	0.607
190	25,017	0.519
264	30,452	0.414
345	35,817	0.312
427	39,234	0.246
502	42,255	0.188
$\infty$	52,000	0.000



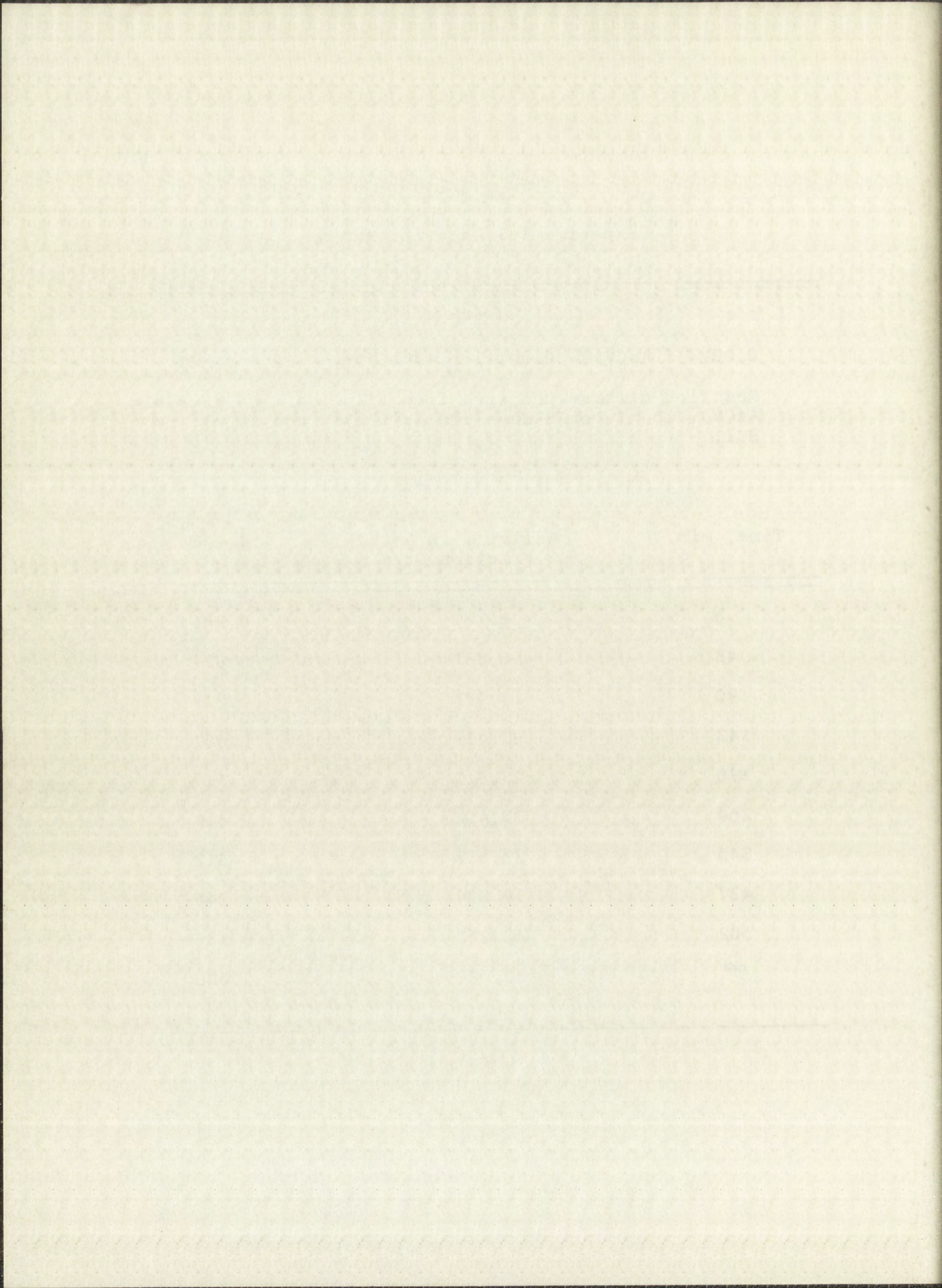




Table 6  
Experimental Data for Run 6

29.7°C		
0.0324 f As(V), 0.00691 f As(III)*, 10.9 f HCl		
Reaction mixture prepared from 15 ml. of 185-days-old As(V), 15 ml. of 4-days-old As(III)*, and 10 ml. of HCl.		
$t_{\frac{1}{2}} = 470$ min. $(t_{\frac{1}{2}})_1 = 198$ min. $(t_{\frac{1}{2}})_2 = 960$ min.		
Time, min.	Activity in As(V) Fraction, c/m	1 - F
5	1,019	0.977
57	4,239	0.906
147	9,077	0.800
233	12,941	0.714
341	16,679	0.632
461	19,919	0.560
615	23,697	0.477
773	26,870	0.407
1,120	31,236	0.310
1,479	34,442	0.239
1,875	38,307	0.154
$\infty$	45,277	0.000



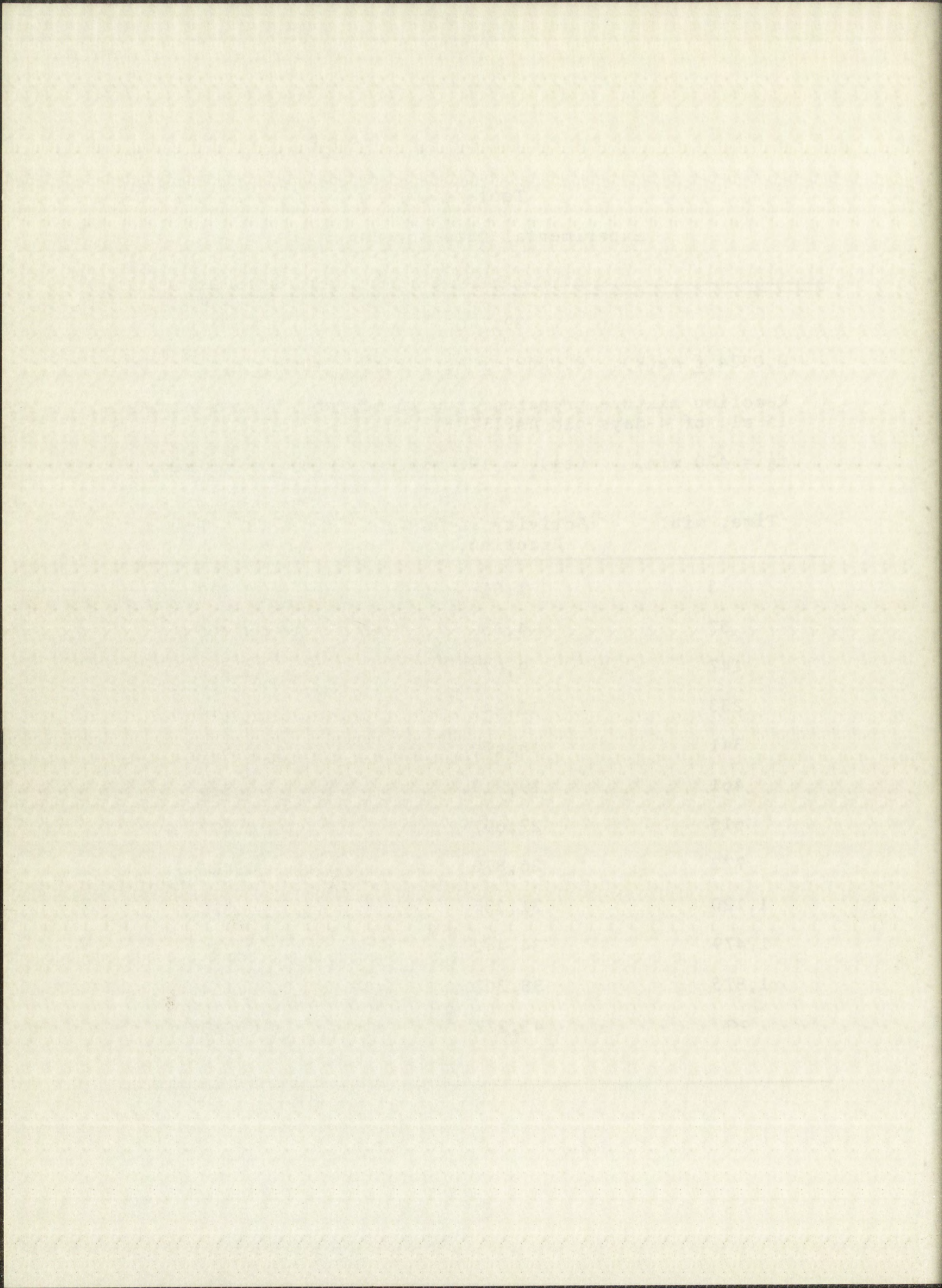




Table 7  
Experimental Data for Run 7

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29.7°C		
0.0324 $\underline{f}$ As(V)*, 0.00691 $\underline{f}$ As(III), 10.9 $\underline{f}$ HCl		
Reaction mixture prepared from 15 ml. of 185-days-old As(V)*, 15 ml. of 4-days-old As(III), and 10 ml. of HCl.		
$t_{\frac{1}{2}} \approx 450$ min.	$(t_{\frac{1}{2}})_1 \approx 140$ min.	$(t_{\frac{1}{2}})_2 \approx 780$ min.
Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	55,488	1.074
60	55,243	1.048
124	53,811	0.899
209	53,869	0.905
299	51,682	0.676
384	51,476	0.655
487	50,398	0.542
591	50,893	0.594
719	49,093	0.406
$\infty$	45,200	0.000

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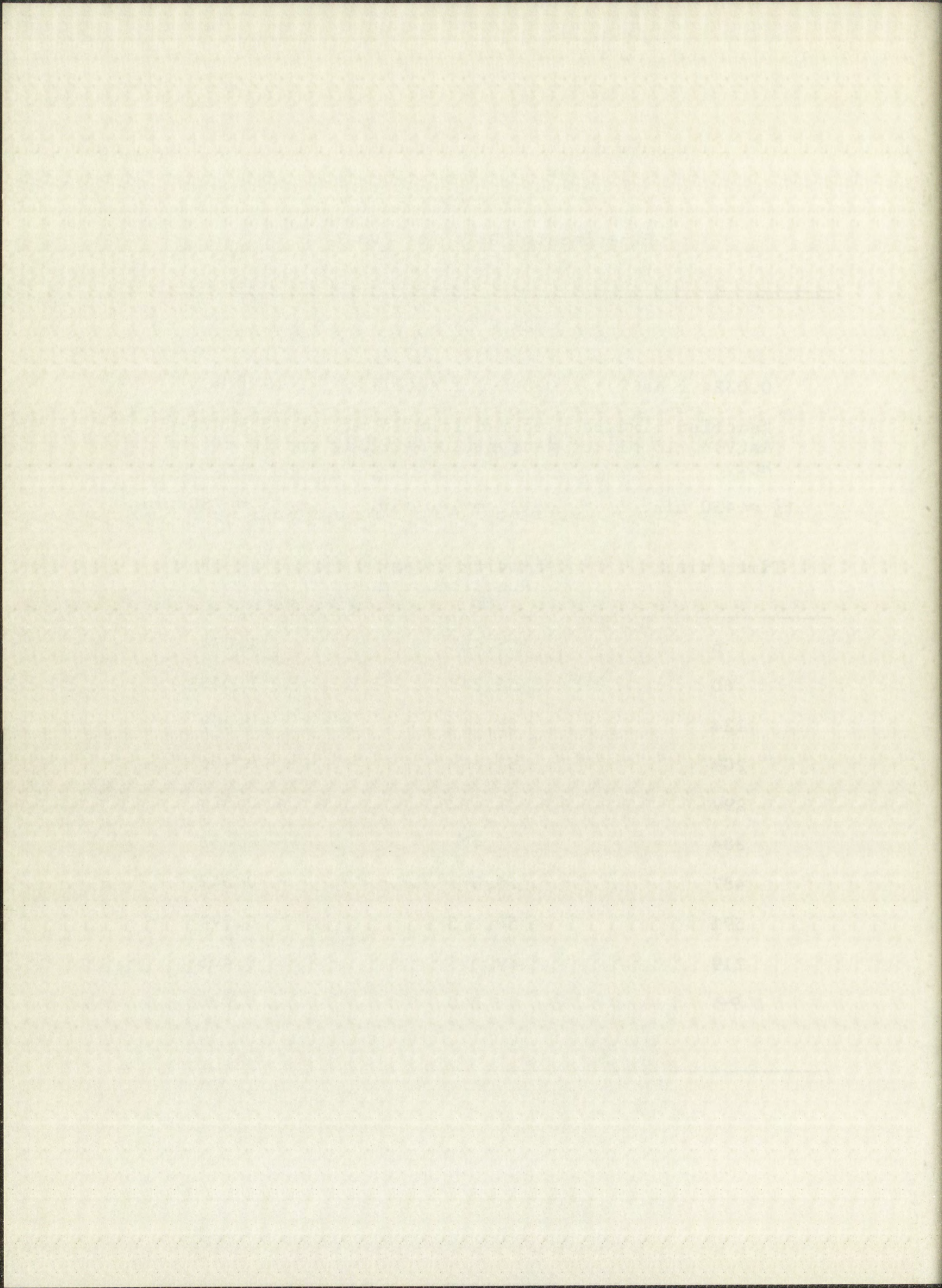




Table 8  
Experimental Data for Run 8

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29.7°C		
0.0161 $\underline{f}$ As(V), 0.00276 $\underline{f}$ As(III)*, 10.9 $\underline{f}$ HCl		
Reaction mixture prepared from 15 ml. of 192-days-old As(V), 15 ml. of 11-days-old As(III)*, and 10 ml. of HCl.		
$t_{\frac{1}{2}} = 485$ min.	$(t_{\frac{1}{2}})_1 = 231$ min.	$(t_{\frac{1}{2}})_2 = 930$ min.
Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	907	0.974
67	3,733	0.895
149	7,110	0.799
247	10,485	0.704
359	13,491	0.619
496	16,559	0.533
652	19,469	0.450
850	22,702	0.359
1,138	25,038	0.293
1,547	28,161	0.205
1,799	29,304	0.173
2,061	29,847	0.157
$\infty$	35,424	0.000

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# TABLE 1

Summary of the results of the tests conducted on the specimens of the material under investigation.

The tests were conducted in accordance with the requirements of the standard.

The results of the tests are presented in the following table.

The table shows the values of the parameters measured during the tests.

The values are given in the units specified in the standard.

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Table 9

## Experimental Data for Run 9

29.7°C

0.0161  $\underline{f}$  As(V), 0.00111  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 15 ml. of 192-  
days-old As(V), 15 ml. of 11-days-old As(III)\*,  
and 10 ml. of HCl.

 $t_{\frac{1}{2}} = 265 \text{ min.}$        $(t_{\frac{1}{2}})_1 = 135 \text{ min.}$        $(t_{\frac{1}{2}})_2 = 449 \text{ min.}$ 

Time, min.	Activity in As(V) Fraction, c/m	1 - F
5	1,167	0.970
61	6,280	0.836
118	10,216	0.734
185	14,533	0.622
240	17,265	0.550
328	21,110	0.450
430	24,254	0.368
549	27,046	0.296
667	29,308	0.237
817	31,175	0.188
$\infty$	38,394	0.000



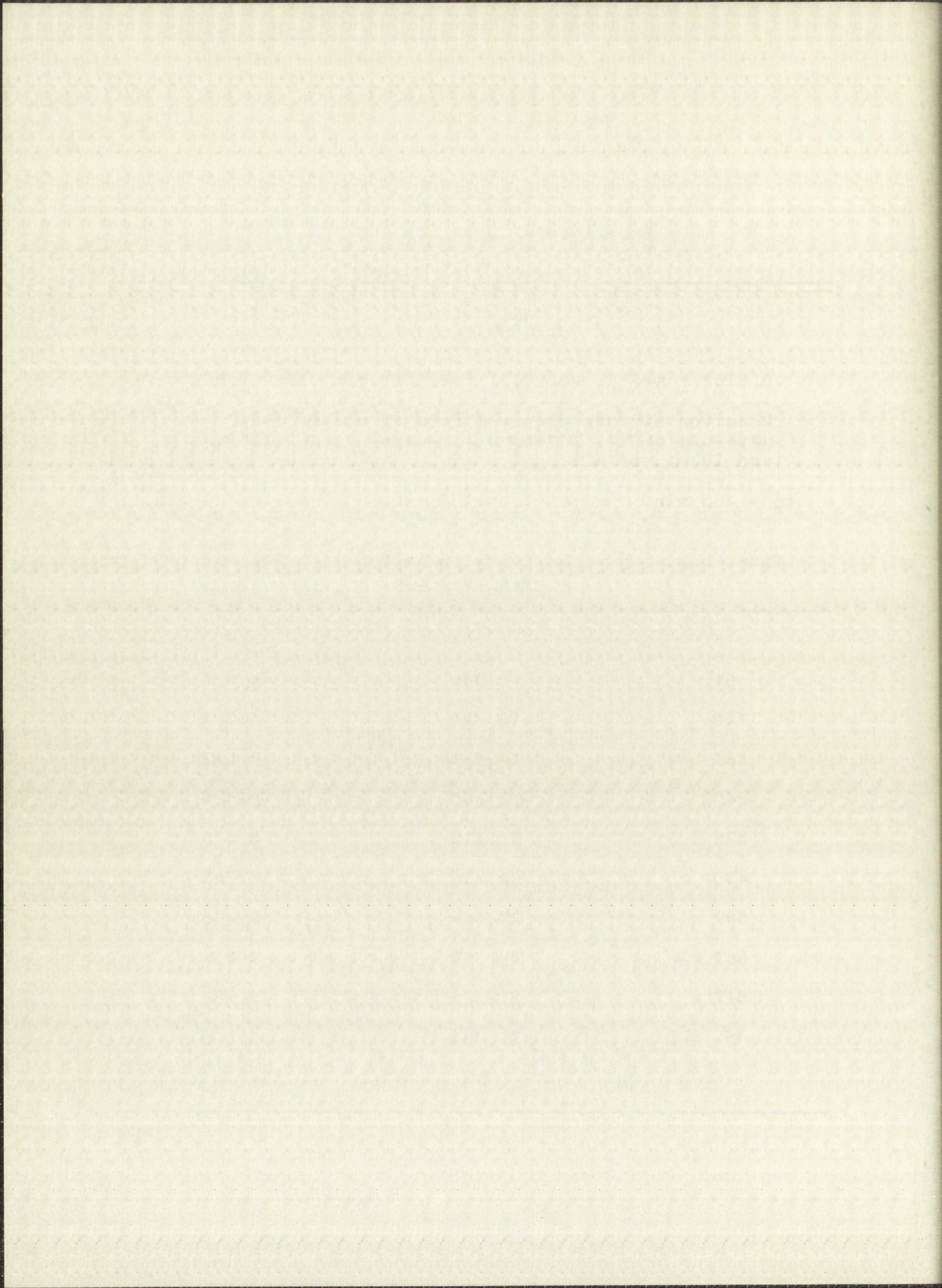




Table 10  
Experimental Data for Run 10

29.7°C		
0.0161 $\underline{f}$ As(V), 0.00691 $\underline{f}$ As(III)*, 10.9 $\underline{f}$ HCl		
Reaction mixture prepared from 15 ml. of 193 days-old As(V), 15 ml. of 12-days-old As(III)*, and 10 ml. of HCl.		
$t_{\frac{1}{2}} = 710$ min. $(t_{\frac{1}{2}})_1 = 265$ min. $(t_{\frac{1}{2}})_2 = 1,440$ min.		
Time, min.	Activity in As(V) Fraction, c/m	1 - F
7	397	0.986
66	1,954	0.933
153	3,837	0.868
277	6,101	0.791
399	8,019	0.725
622	10,492	0.640
915	13,784	0.527
1,447	17,984	0.383
1,856	19,599	0.328
2,244	21,294	0.270
2,911	23,603	0.191
$\infty$	29,170	0.000



Experiment 1

Experimental Data

Time (min)	Temperature (°C)	Pressure (atm)	Volume (L)
0	25.0	1.00	0.00
10	25.5	1.02	0.10
20	26.0	1.04	0.20
30	26.5	1.06	0.30
40	27.0	1.08	0.40
50	27.5	1.10	0.50
60	28.0	1.12	0.60
70	28.5	1.14	0.70
80	29.0	1.16	0.80
90	29.5	1.18	0.90
100	30.0	1.20	1.00
110	30.5	1.22	1.10
120	31.0	1.24	1.20
130	31.5	1.26	1.30
140	32.0	1.28	1.40
150	32.5	1.30	1.50
160	33.0	1.32	1.60
170	33.5	1.34	1.70
180	34.0	1.36	1.80
190	34.5	1.38	1.90
200	35.0	1.40	2.00



Table 11  
Experimental Data for Run 11

29.7°C

0.0161  $\underline{f}$  As(V)\*, 0.00691  $\underline{f}$  As(III), 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 15 ml. of 193-days-old As(V)\*, 15 ml. of 12-days-old As(III), and 10 ml. of HCl.

$t_{\frac{1}{2}} \approx 630$  min.  $(t_{\frac{1}{2}})_1 \approx 200$  min.  $(t_{\frac{1}{2}}) \approx 1,160$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
7	42,219	0.943
63	41,111	0.855
117	40,740	0.825
193	40,253	0.786
270	39,210	0.703
368	38,941	0.682
522	37,426	0.561
589	37,390	0.558
754	36,539	0.490
914	36,803	0.511
1,417	34,070	0.293
$\infty$	30,393	0.000



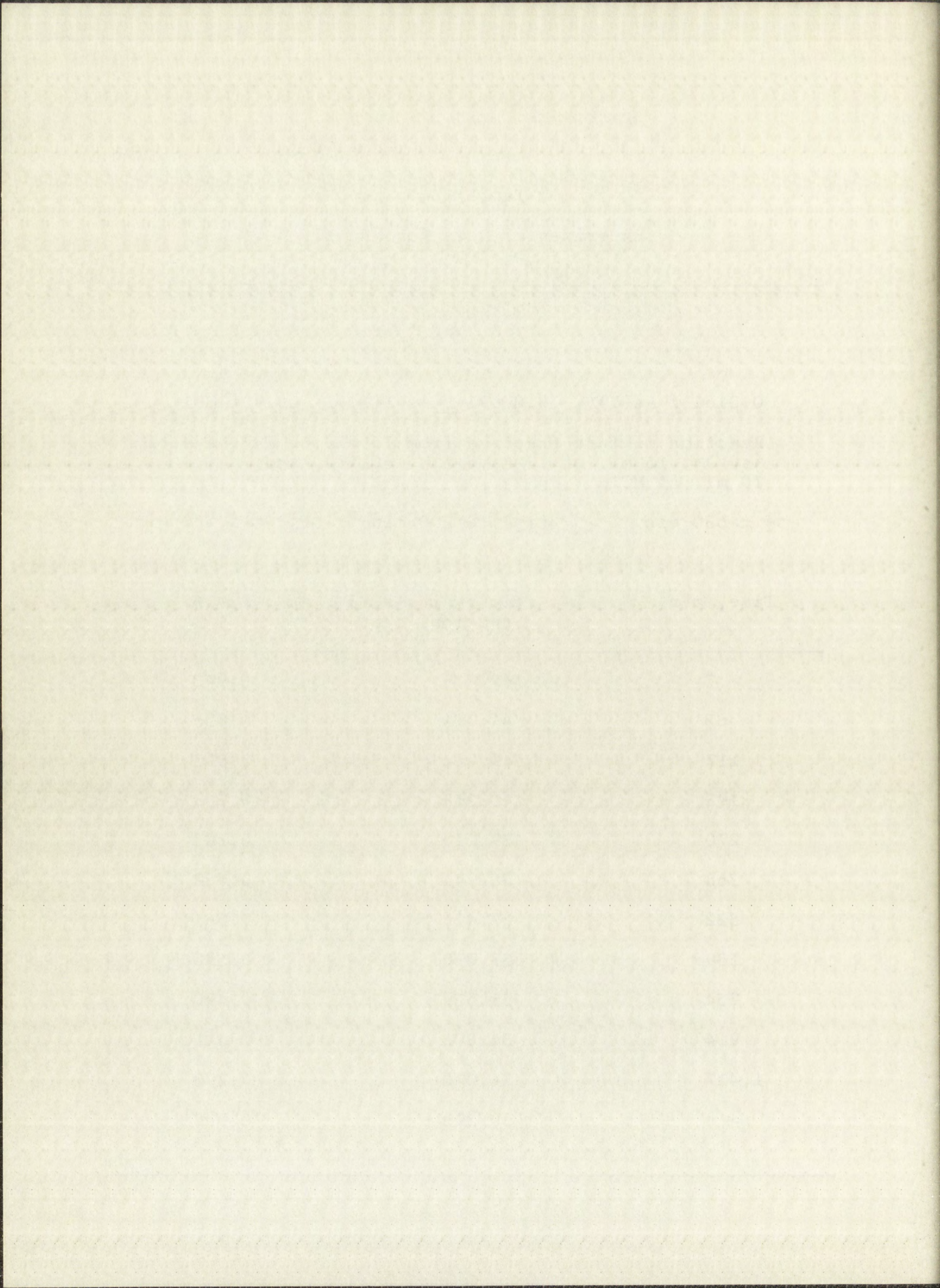




Table 12

## Experimental Data for Run 12

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29.7°C		
0.0324 $\underline{f}$ As(V), 0.00276 $\underline{f}$ As(III)*, 10.9 $\underline{f}$ HCl		
Reaction mixture prepared from 15 ml. of 199-days-old As(V), 15 ml. of 18-days-old As(III)*, and 10 ml. of HCl.		
$t_{\frac{1}{2}} = 300$ min.	$(t_{\frac{1}{2}})_1 = 132$ min.	$(t_{\frac{1}{2}})_2 = 455$ min.
Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	1,001	0.967
66	4,686	0.847
147	8,977	0.706
234	12,555	0.589
362	16,863	0.448
492	19,258	0.370
670	23,171	0.242
856	24,585	0.196
$\infty$	30,558	0.000

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Table 13  
Experimental Data for Run 13

29.7°C

0.0324  $\underline{f}$  As(V), 0.00111  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 15 ml. of 199-days-old As(V), 15 ml. of 18-days-old As(III)\*, and 10 ml. of HCl.

$t_{\frac{1}{2}} = 213$  min.       $(t_{\frac{1}{2}})_1 = 88$  min.       $(t_{\frac{1}{2}})_2 = 265$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
5	1,072	0.967
60	6,329	0.804
115	10,593	0.671
183	14,307	0.556
257	17,880	0.445
333	21,370	0.337
388	22,465	0.303
485	24,649	0.235
585	26,274	0.184
685	27,914	0.134
$\infty$	32,211	0.000



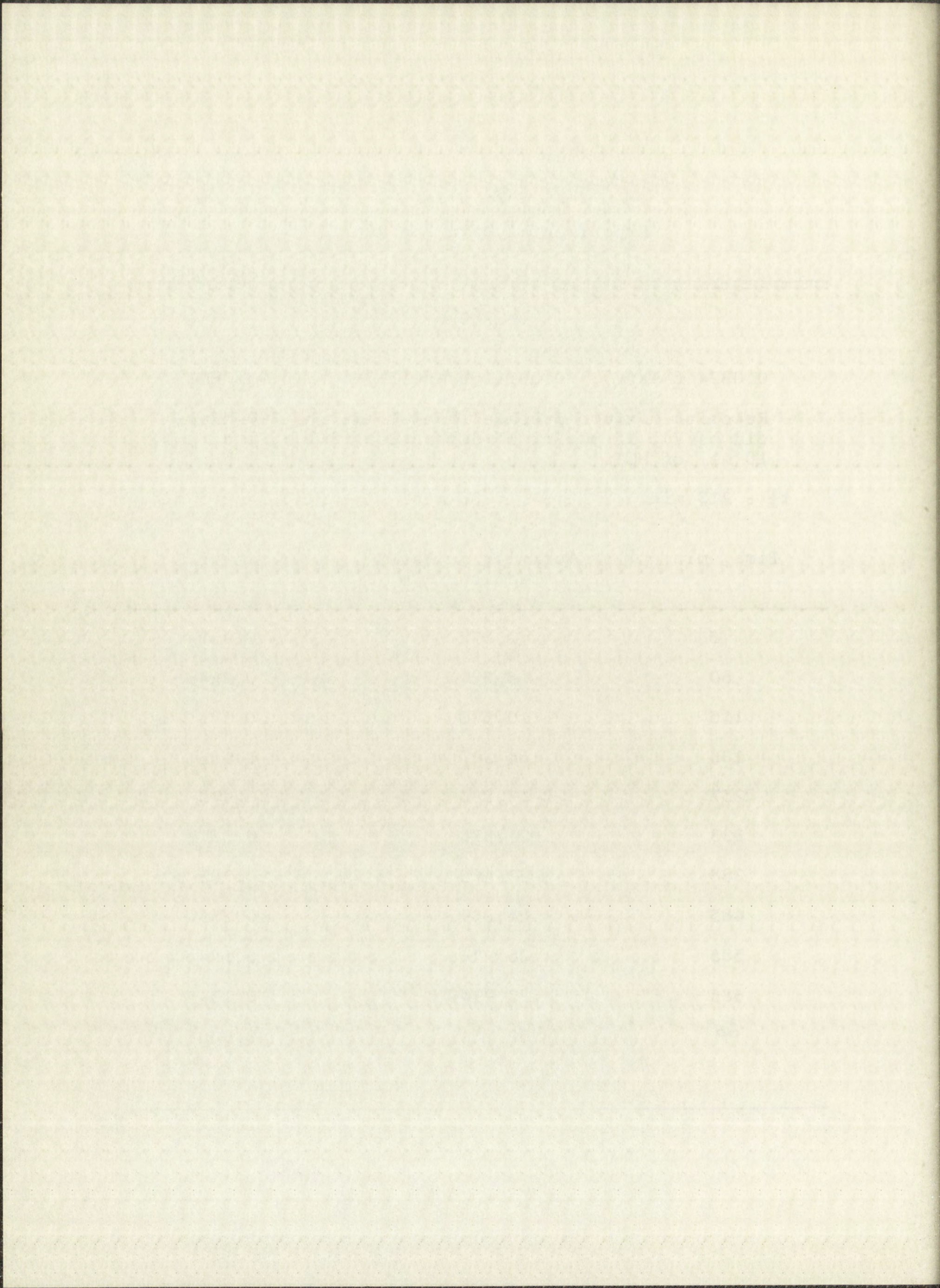




Table 14  
Experimental Data for Run 14

29.7°C

0.0324 f As(V), 0.00691 f As(III)\*, 10.9 f HCl

Reaction mixture prepared from 15 ml. of 200-days-old As(V), 15 ml. of 19-days-old As(III)\*, and 10 ml. of HCl.

$t_{\frac{1}{2}} = 510$  min.       $(t_{\frac{1}{2}})_1 = 193$  min.       $(t_{\frac{1}{2}})_2 = 1,100$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
5	580	0.978
60	2,343	0.913
137	4,588	0.830
225	6,780	0.749
345	8,904	0.670
526	12,062	0.553
735	14,027	0.480
1,065	16,897	0.373
1,400	18,847	0.301
1,725	19,895	0.262
1,871	21,268	0.211
2,025	21,354	0.208
2,846	21,627	0.198
$\infty$	26,968	0.000



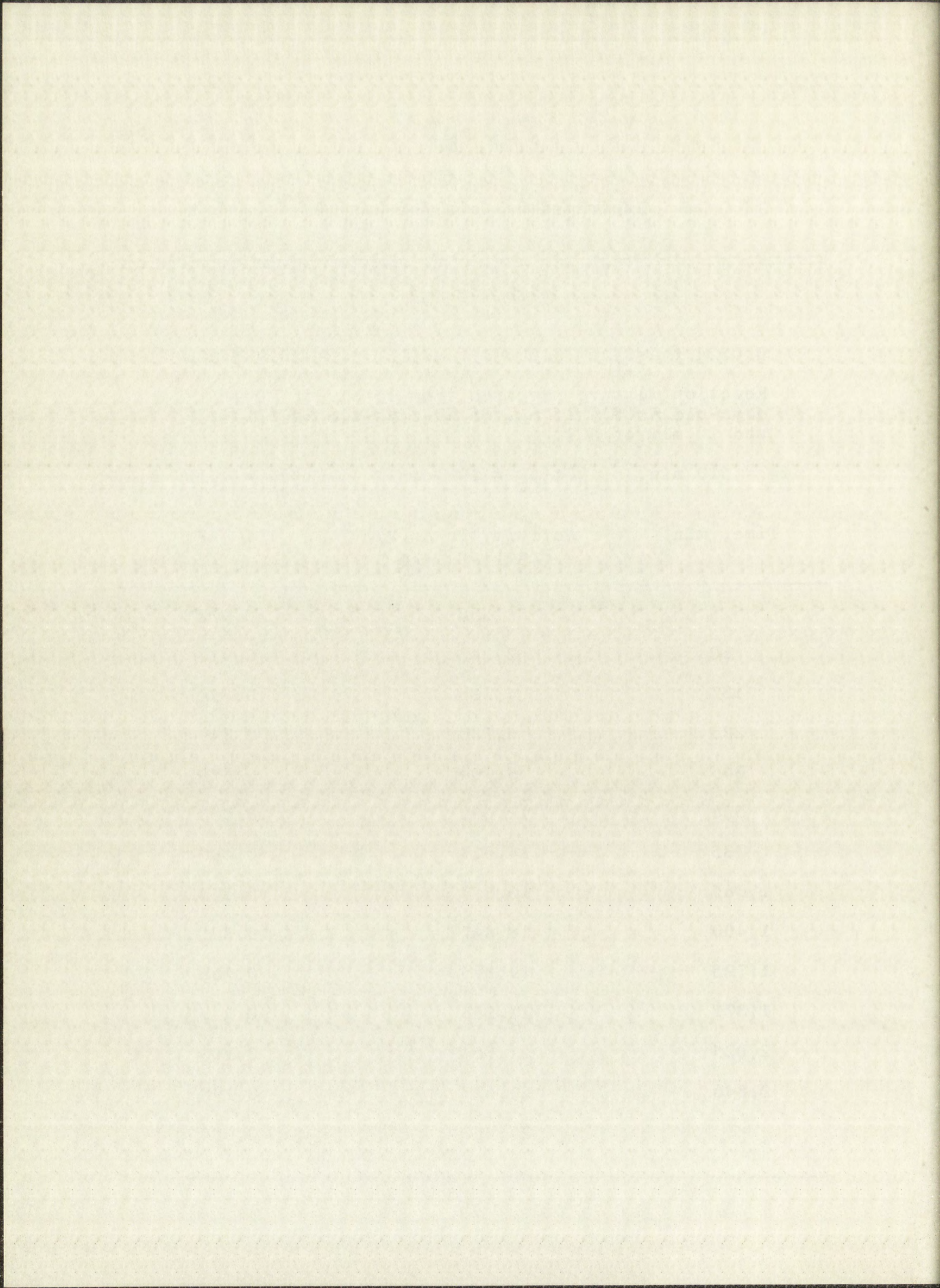




Table 15  
Experimental Data for Run 15

29.7°C

0.0161  $\underline{f}$  As(V), 0.00276  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 15 ml. of 206-days-old As(V), 15 ml. of 25-days-old As(III)\*, and 10 ml. of HCl.

$t_{\frac{1}{2}} = 465$  min.       $(t_{\frac{1}{2}})_1 = 222$  min.       $(t_{\frac{1}{2}})_2 = 926$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	574	0.975
72	2,599	0.888
134	4,324	0.813
207	6,028	0.739
300	8,074	0.651
426	10,627	0.540
550	11,903	0.485
700	13,379	0.421
881	15,226	0.341
1,095	16,495	0.286
1,437	18,266	0.209
1,753	18,678	0.182
$\infty$	23,104	0.000







Table 16  
Experimental Data for Run 16

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$29.7^{\circ}\text{C}$		
0.0161 $\underline{f}$ As(V), 0.00111 $\underline{f}$ As(III)*, 10.9 $\underline{f}$ HCl		
Reaction mixture prepared from 15 ml. of 206-days-old As(V), 15 ml. of 25-days-old As(III)*, and 10 ml. of HCl.		
$t_{\frac{1}{2}} = 285 \text{ min.}$ $(t_{\frac{1}{2}})_1 = 127 \text{ min.}$ $(t_{\frac{1}{2}})_2 = 409 \text{ min.}$		
Time, min.	Activity in As(V) Fraction, c/m	1 - F
8	634	0.971
70	3,549	0.836
132	6,030	0.722
201	8,263	0.619
298	10,923	0.496
399	12,719	0.413
505	14,282	0.341
674	16,208	0.252
855	18,594	0.142
1,067	18,919	0.127
$\infty$	21,673	0.000

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Table 17  
Experimental Data for Run 17

29.7°C		
0.0161 $\underline{f}$ As(V), 0.00691 $\underline{f}$ As(III)*, 10.9 $\underline{f}$ HCl		
Reaction mixture prepared from 15 ml. of 207-days-old As(V), 15 ml. of 26-days-old As(III)*, and 10 ml. of HCl.		
$t_{\frac{1}{2}} = 790$ min.	$(t_{\frac{1}{2}})_1 = 290$ min.	$(t_{\frac{1}{2}})_2 = 1,380$ min.
Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	403	0.975
95	1,537	0.906
218	3,055	0.814
359	4,339	0.735
493	5,450	0.667
671	6,741	0.589
1,041	8,662	0.471
1,400	10,444	0.362
1,711	11,023	0.327
$\infty$	16,382	0.000



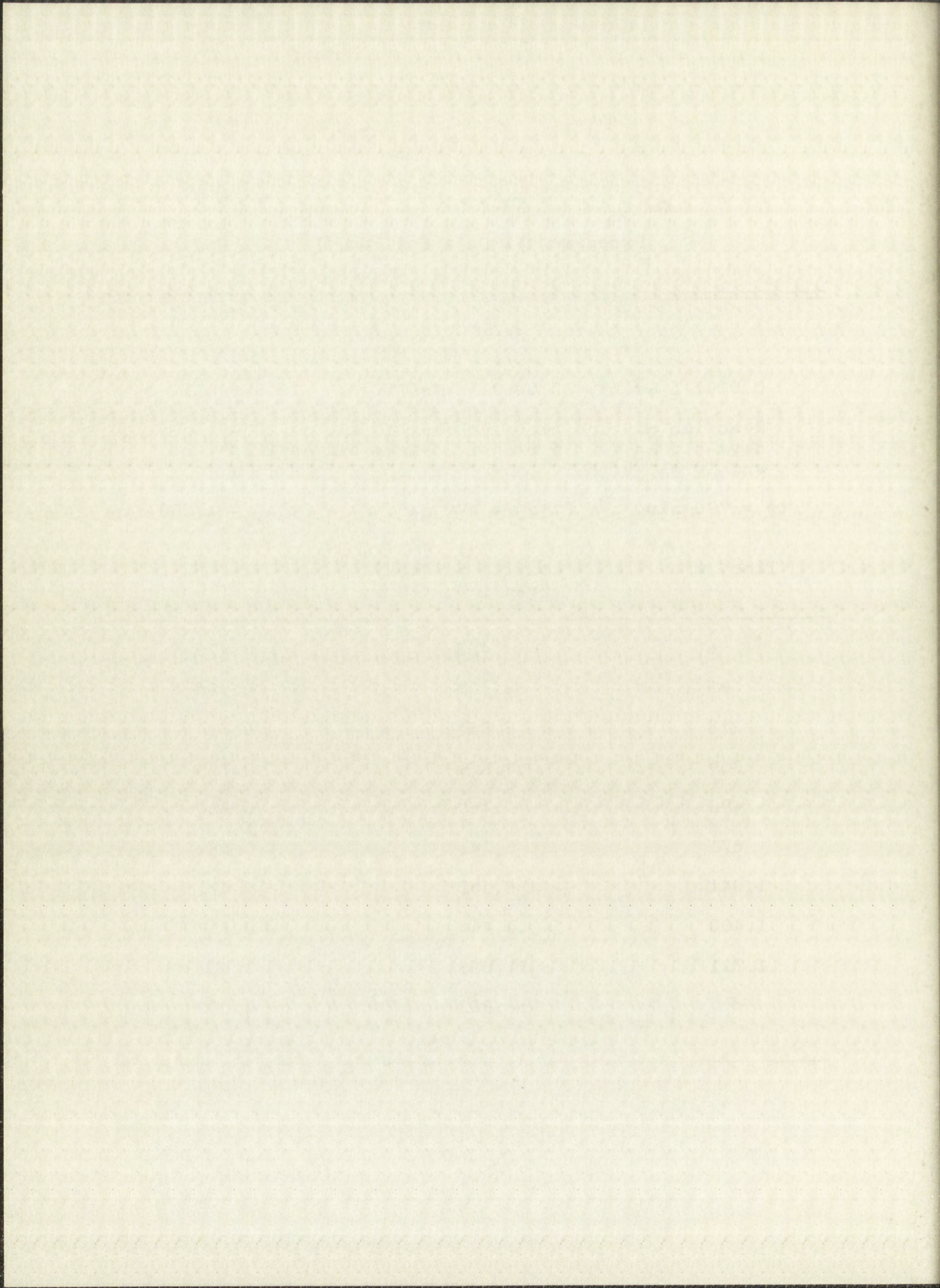




Table 18  
Experimental Data for Run 18

29.7°C		
0.0161 $\underline{f}$ As(V)*, 0.00691 $\underline{f}$ As(III), 10.9 $\underline{f}$ HCl		
Reaction mixture prepared from 15 ml. of 207-days-old As(V)*, 15 ml. of 26-days-old As(III), and 10 ml. of HCl.		
$t_{\frac{1}{2}} \approx 700$ min.	$(t_{\frac{1}{2}})_1 \approx 200$ min.	$(t_{\frac{1}{2}})_2 \approx 1260$ min.
Time, min.	Activity in As(V) Fraction, c/m	1 - F
5	24,020	0.998
89	23,404	0.911
173	23,678	0.950
307	22,743	0.817
437	21,268	0.607
637	20,349	0.477
1,007	20,116	0.444
1,362	19,712	0.386
1,679	19,843	0.405
$\infty$	16,991	0.000



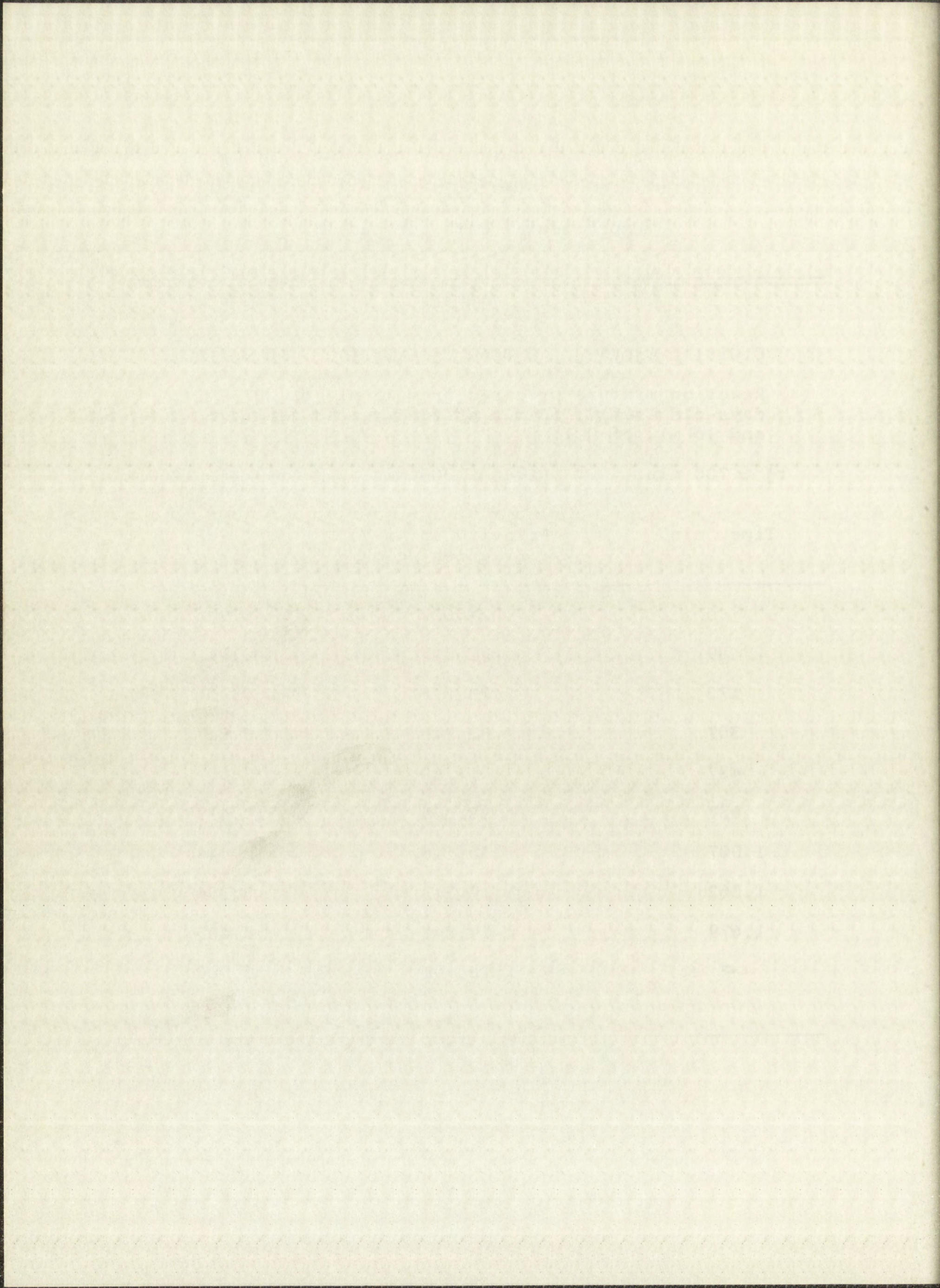




Table 19  
Experimental Data for Run 19

29.7°C

0.0418  $\underline{f}$  As(V), 0.0474  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 5 ml. of 56-days-old As(V) and 10 ml. of 1-day-old As(III)\*.

$t_{\frac{1}{2}} = 250$  min.  $(t_{\frac{1}{2}})_1 = 131$  min.  $(t_{\frac{1}{2}})_2 = 358$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
9	775	0.962
100	5,200	0.747
209	9,013	0.562
317	11,396	0.446
469	14,508	0.294
625	15,931	0.225
836	17,855	0.131
$\infty$	20,555	0.000







Table 20  
Experimental Data for Run 20

29.7°C

0.0418  $\underline{f}$  As(V), 0.0142  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 5 ml. of 56-days-old As(V), 3 ml. of 1-day-old As(III)\*, and 7 ml. of HCl.

$t_{\frac{1}{2}} = 295$  min.  $(t_{\frac{1}{2}})_1 = 152$  min.  $(t_{\frac{1}{2}})_2 = 495$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
8	366	0.962
73	1,660	0.827
180	3,293	0.658
309	4,837	0.497
460	6,117	0.364
618	6,855	0.287
860	7,745	0.195
$\infty$	9,621	0.000



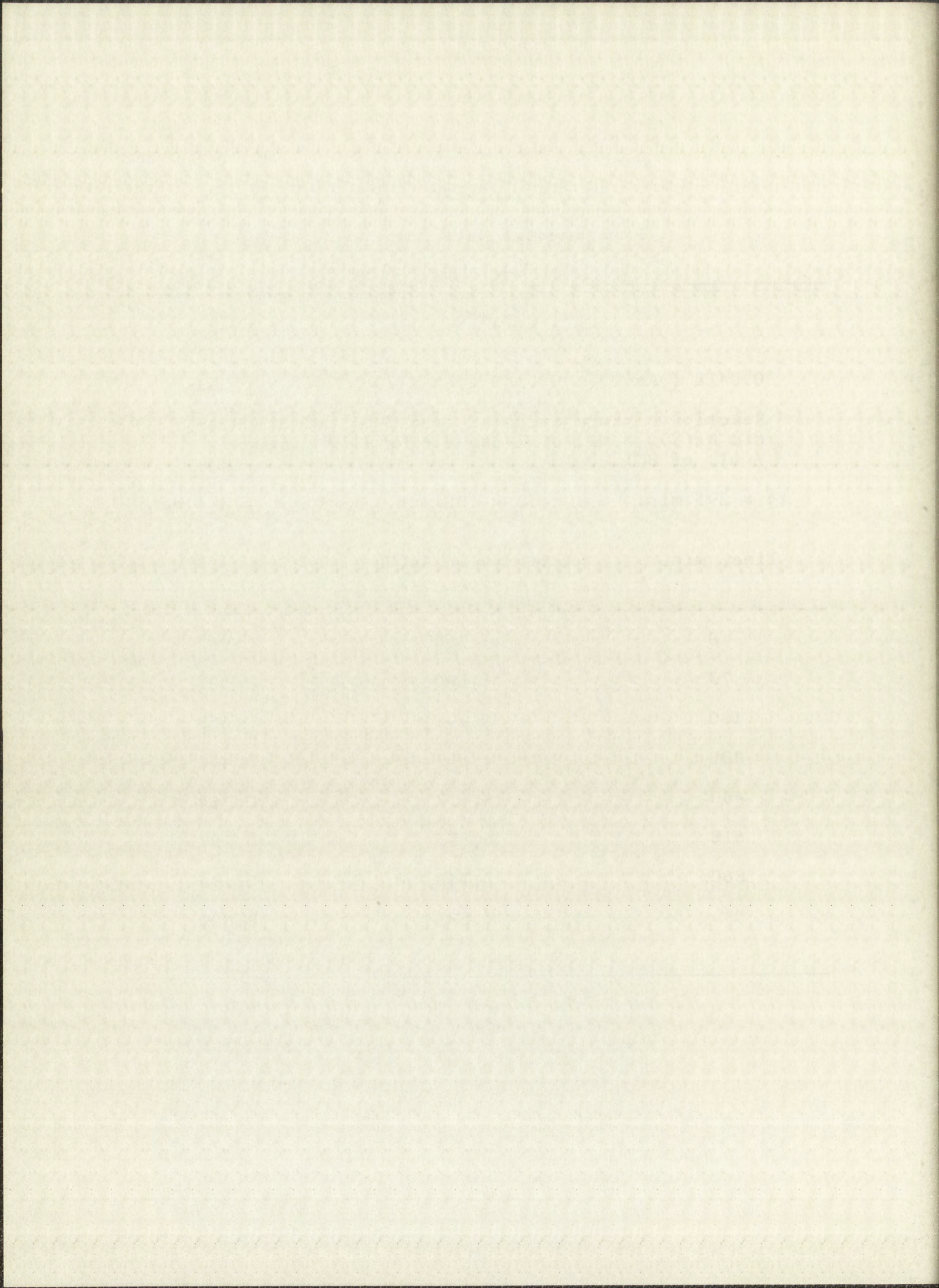




Table 21  
Experimental Data for Run 21

29.7°C

0.0418  $\underline{f}$  As(V), 0.00474  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 5 ml. of 56-day-old As(V), 1 ml. of 1-day-old As(III)\*, and 9 ml. of HCl.

$t_{\frac{1}{2}} = 360$  min.  $(t_{\frac{1}{2}})_1 = 210$  min.  $(t_{\frac{1}{2}})_2 = 2,863$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
7	125	0.968
120	905	0.769
240	1,384	0.646
364	1,808	0.538
492	1,918	0.509
750	2,304	0.411
1,350	2,686	0.313
2,028	2,913	0.255
$\infty$	3,910	0.000







Table 22  
Experimental Data for Run 22

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29.7°C		
0.00837 $\underline{f}$ As(V), 0.00420 $\underline{f}$ As(III)*, 10.9 $\underline{f}$ HCl		
Reaction mixture prepared from 1 ml. of 62-days-old As(V), 1 ml. of 1-day-old As(III)*, and 13 ml. of HCl.		
$t_{\frac{1}{2}} = 860$ min.	$(t_{\frac{1}{2}})_1 = 418$ min.	$(t_{\frac{1}{2}})_2 = 3,568$ min.
Time, min.	Activity in As(V) Fraction, c/m	1 - F
7	44	0.980
122	225	0.897
264	411	0.811
438	677	0.689
783	941	0.568
1,453	1,291	0.407
2,035	1,400	0.357
$\infty$	2,177	0.000

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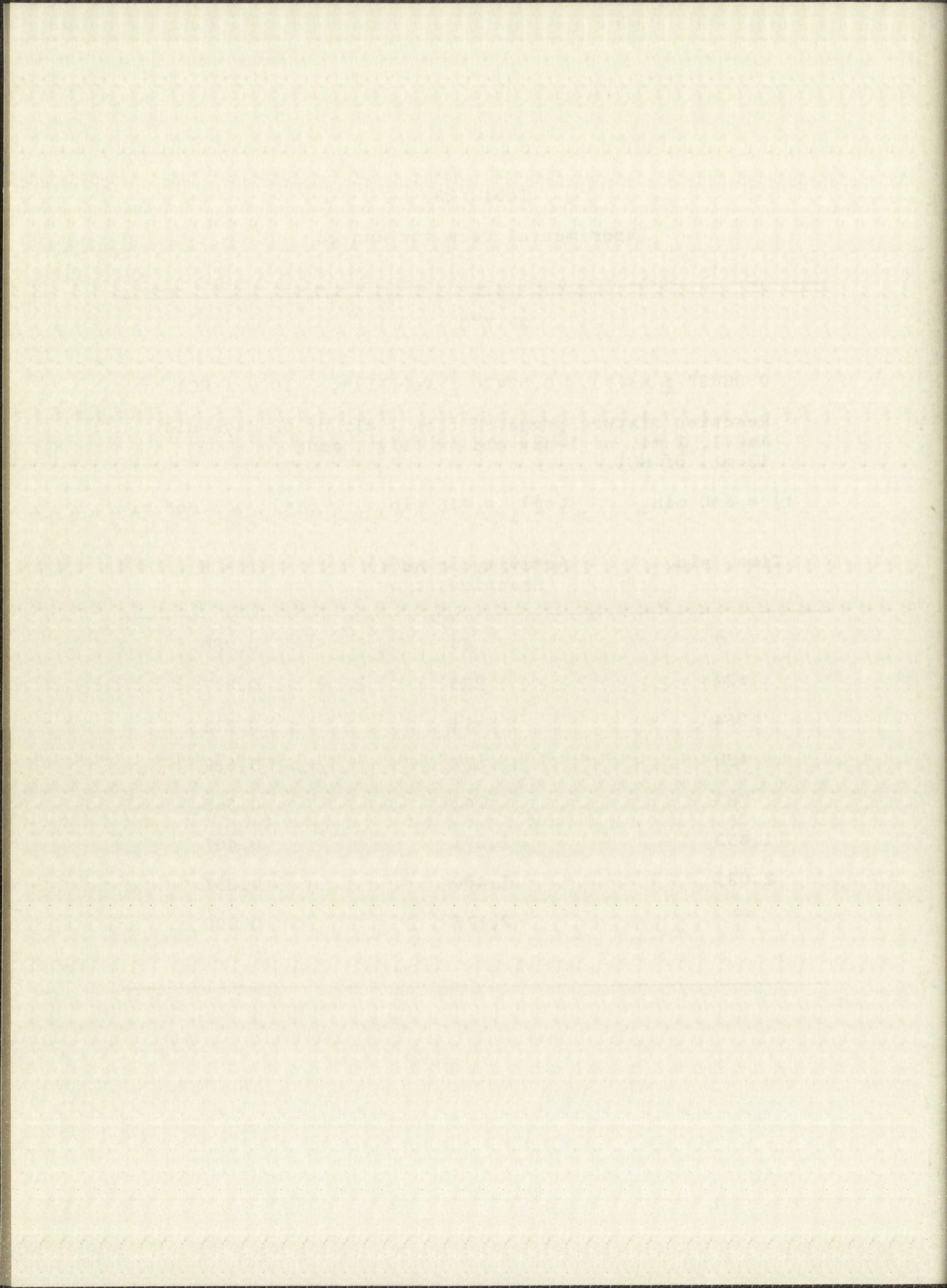




Table 23

## Experimental Data for Run 23

29.7°C

0.0837  $\underline{f}$  As(V), 0.00420  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 10 ml. of 62-days-old As(V), 1 ml. of 1-day-old As(III)\*, and 4 ml. of HCl.

 $t_{\frac{1}{2}} = 240$  min. $(t_{\frac{1}{2}})_1 = 115$  min. $(t_{\frac{1}{2}})_2 = 558$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
9	168	0.950
139	1,164	0.653
262	1,711	0.490
364	2,034	0.394
547	2,329	0.306
722	2,578	0.232
$\infty$	3,358	0.000



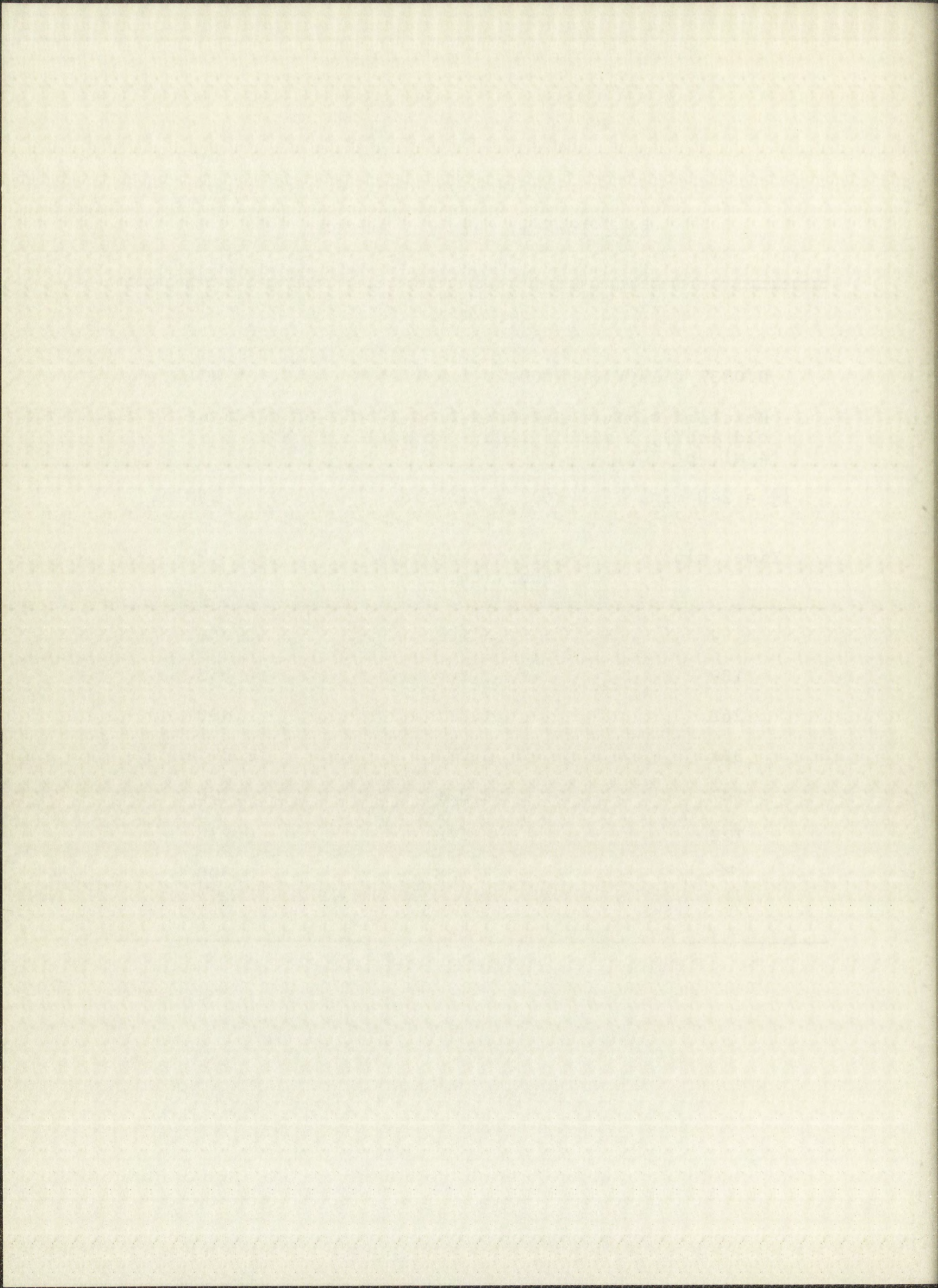




Table 24  
Experimental Data for Run 24

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29.7°C		
0.0251 $\underline{f}$ As(V), 0.00420 $\underline{f}$ As(III)*, 10.9 $\underline{f}$ HCl		
Reaction mixture prepared from 3 ml. of 62-days-old As(V), 1 ml. of 1-day-old As(III)*, and 11 ml. of HCl.		
$t_{\frac{1}{2}} = 440$ min. $(t_{\frac{1}{2}})_1 = 176$ min. $(t_{\frac{1}{2}})_2 = 1,426$ min.		
Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	70	0.976
128	613	0.791
259	938	0.680
383	1,254	0.572
604	1,542	0.473
797	1,724	0.411
1,426	2,068	0.294
1,780	2,204	0.247
$\infty$	2,928	0.000

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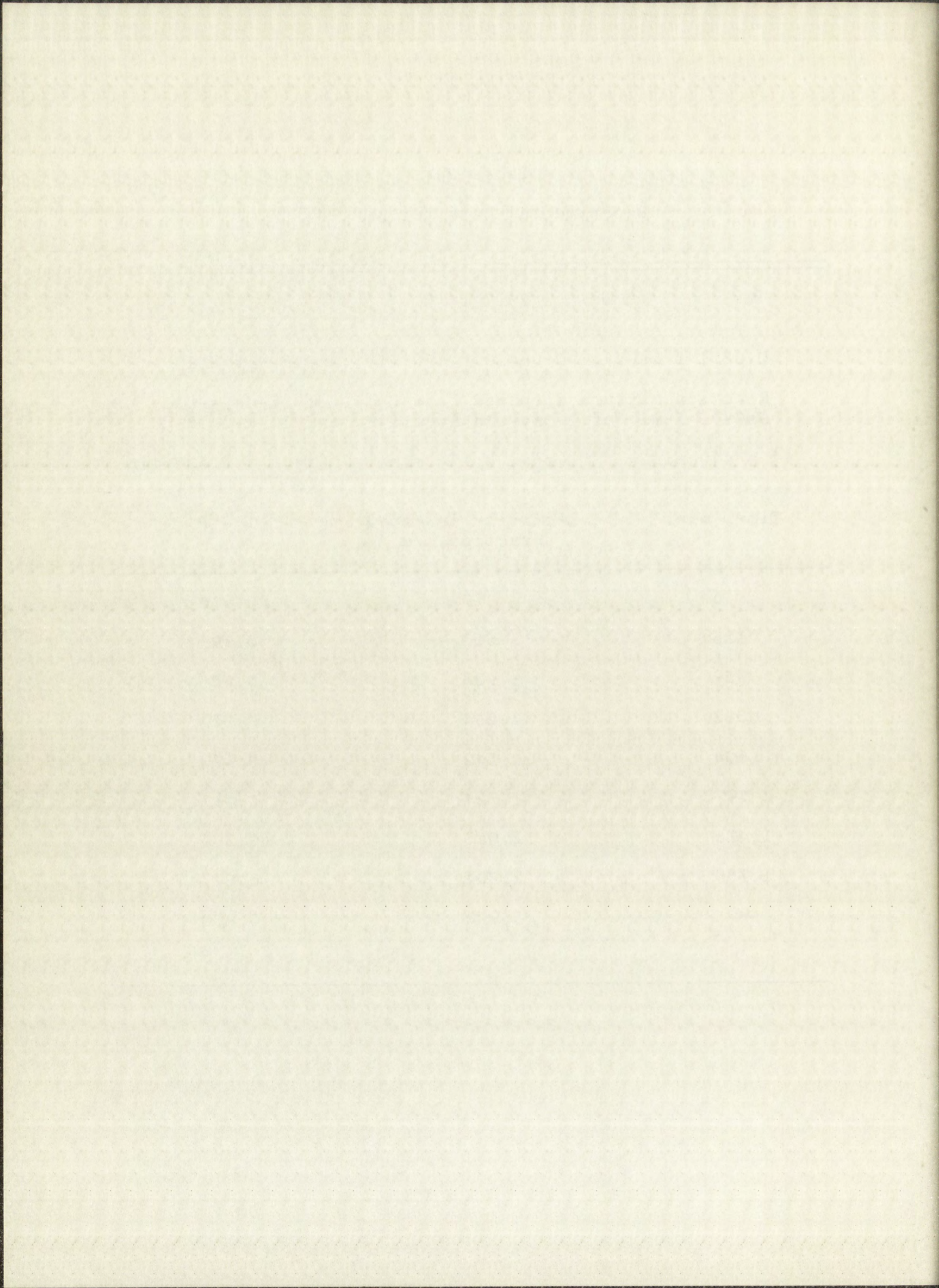




Table 25  
Experimental Data for Run 25

29.7°C

0.0251  $\underline{f}$  As(V), 0.0126  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 3 ml. of 62-days-old As(V), 3 ml. of 1-day-old As(III)\*, and 9 ml. of HCl.

$t_{\frac{1}{2}} = 360$  min.  $(t_{\frac{1}{2}})_1 = 260$  min.  $(t_{\frac{1}{2}})_2 = 1,860$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	178	0.971
115	1,201	0.804
235	1,990	0.675
359	2,623	0.571
558	3,342	0.454
747	4,236	0.308
1,357	4,577	0.252
1,837	4,770	0.220
$\infty$	6,117	0.000



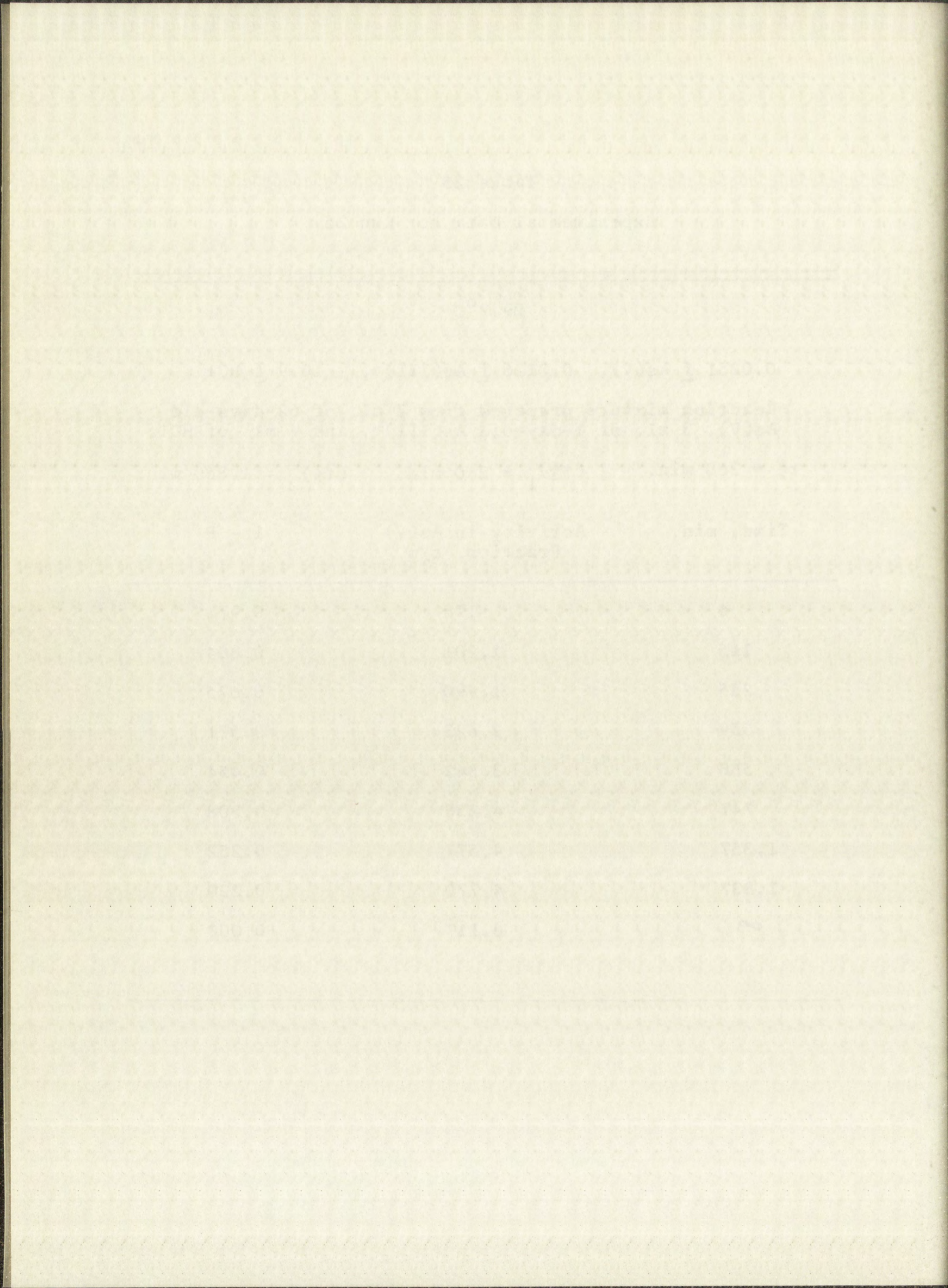




Table 26  
Experimental Data for Run 26

29.7°C

0.0251  $\underline{f}$  As(V), 0.0420  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 3 ml. of 62-days-old As(V), 10 ml. of 1-day-old As(III)\*, and 2 ml. of HCl

$t_{\frac{1}{2}} = 240$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
7	524	0.955
130	3,981	0.657
246	6,219	0.464
355	7,644	0.341
481	8,716	0.249
659	9,931	0.144
$\infty$	11,607	0.000



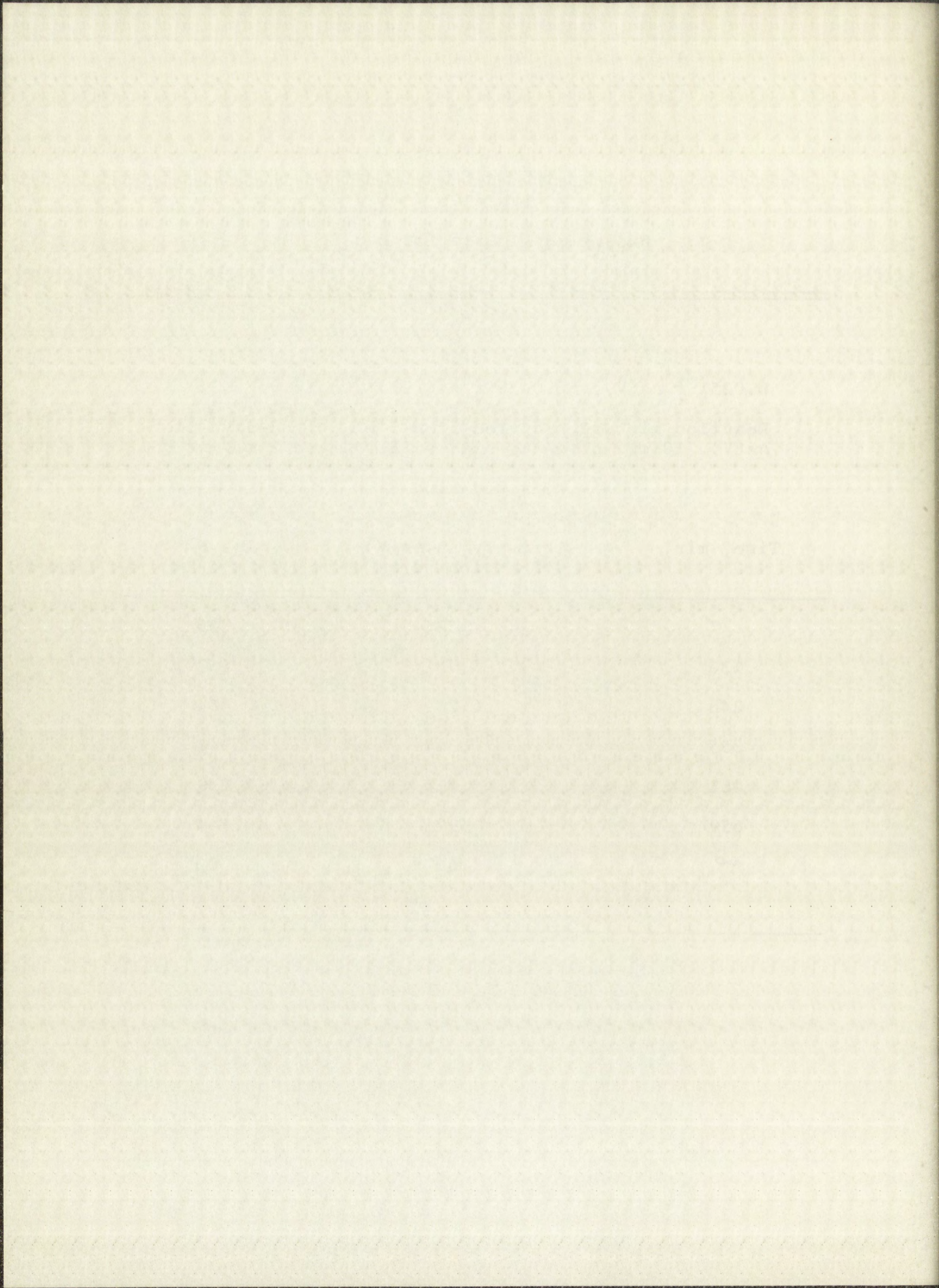




Table 27

## Experimental Data for Run 27

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 29.7°C

 0.00446  $\underline{f}$  As(V),    0.00231  $\underline{f}$  As(III)\*,    6.91  $\underline{f}$  HCl

 Reaction mixture prepared from 1 ml. of 319-days-old  
 As(V) and 20 ml. of 1-day-old As(III)\*.

Negligible exchange in 5 days.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	70	0.986
115	61	0.988
403	67	0.987
2,958	70	0.986
7,510	74	0.985
$\infty$	5,058	0.000

---







Table 28  
Experimental Data for Run 28

29.7°

0.00448  $\mu$  As(V), 0.00231  $\mu$  As(III)\*, 8.88  $\mu$  HCl

Reaction mixture prepared from 1 ml. of 319-days-old As(V) and 20 ml. of 1-day-old As(III)\*.

Negligible exchange in 5 days.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
4	133	0.974
111	92	0.982
360	109	0.978
1,514	66	0.987
2,914	60	0.988
7,482	105	0.979
$\infty$	5,045	0.000



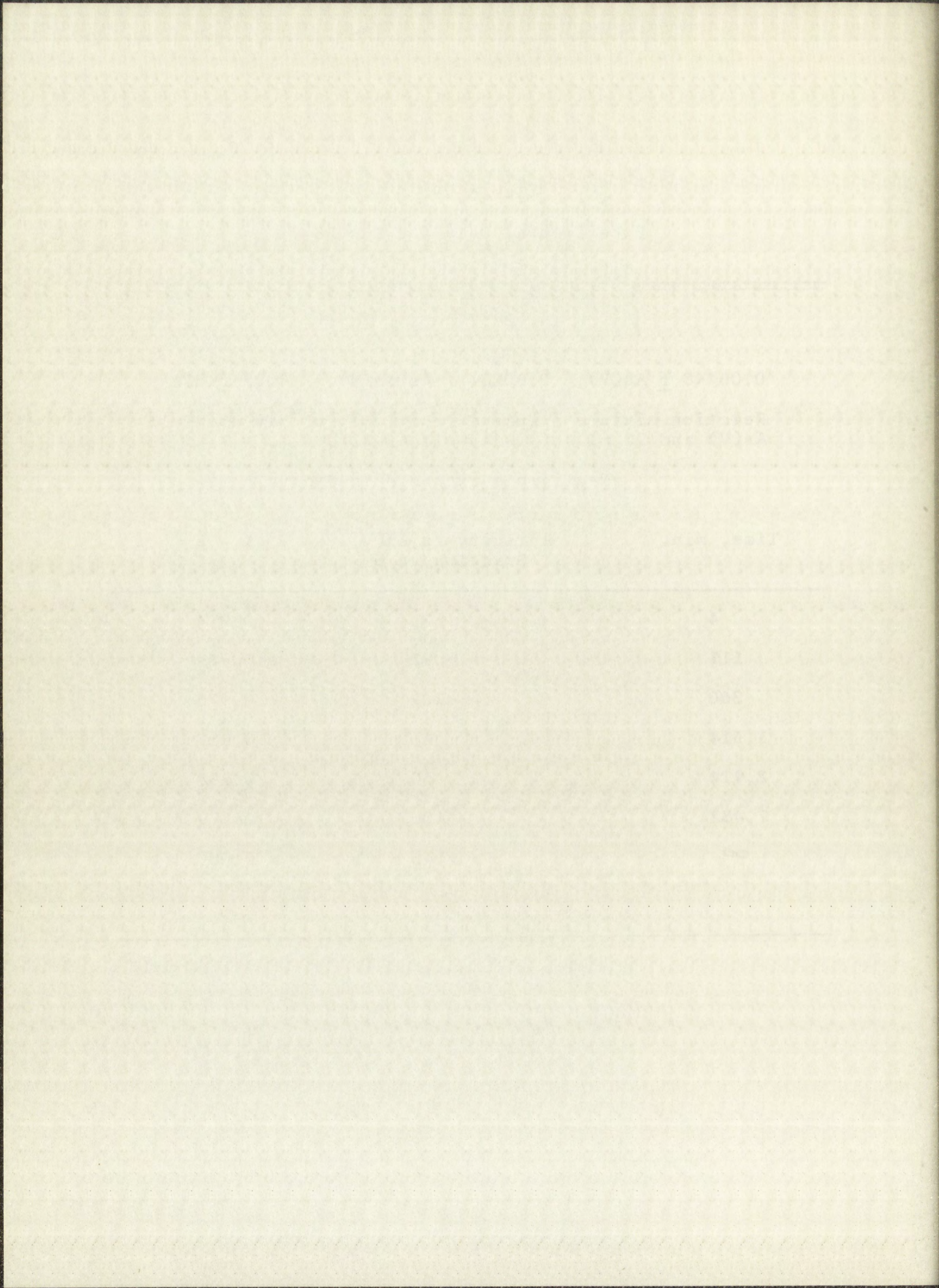




Table 29  
Experimental Data for Run 29

29.7°C

0.00450  $\underline{f}$  As(V), 0.00235  $\underline{f}$  As(III)\*, 9.98  $\underline{f}$  HCl

Reaction mixture prepared from 1 ml. of 319-days-old As(V) and 20 ml. of 1-day-old As(III)\*.

$t_{\frac{1}{2}} = 56,640$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
8	85	0.983
261	113	0.978
1,410	193	0.962
2,765	262	0.949
7,392	524	0.898
$\infty$	5,129	0.000



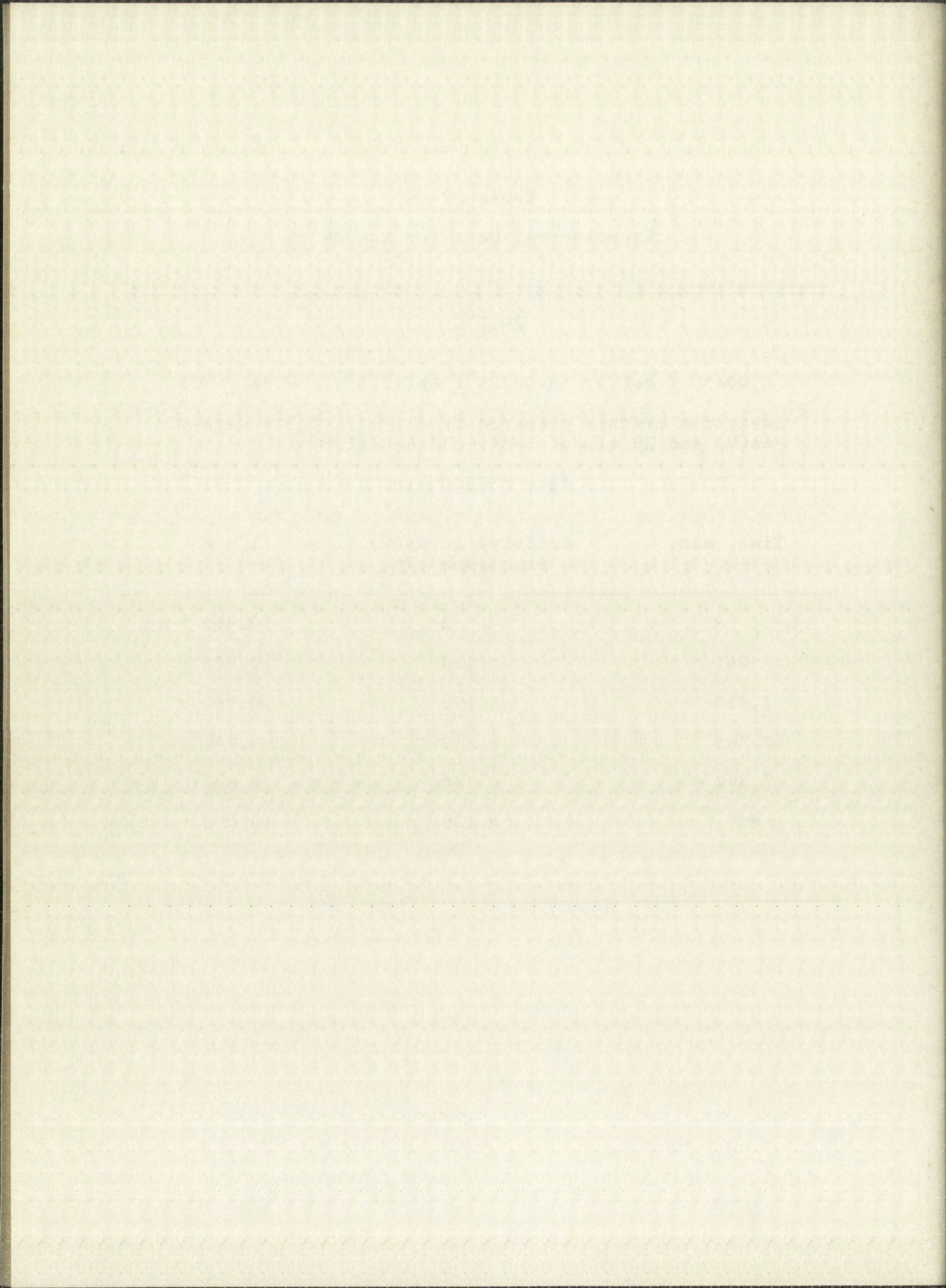




Table 30

## Experimental Data for Run 30

29.7°C

0.00453  $\underline{f}$  As(V), 0.00233  $\underline{f}$  As(III)\*, 10.8  $\underline{f}$  HCl

Reaction mixture prepared from 1 ml. of 319-days-old As(V) and 20 ml. of 1-day-old As(III)\*.

 $t_{\frac{1}{2}} = 9,900$  min.  $(t_{\frac{1}{2}})_1 = 450$  min.  $(t_{\frac{1}{2}})_2 = 47,600$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	92	0.981
52	82	0.983
326	193	0.961
1,415	408	0.917
2,883	524	0.893
7,571	820	0.833
$\infty$	4,898	0.000



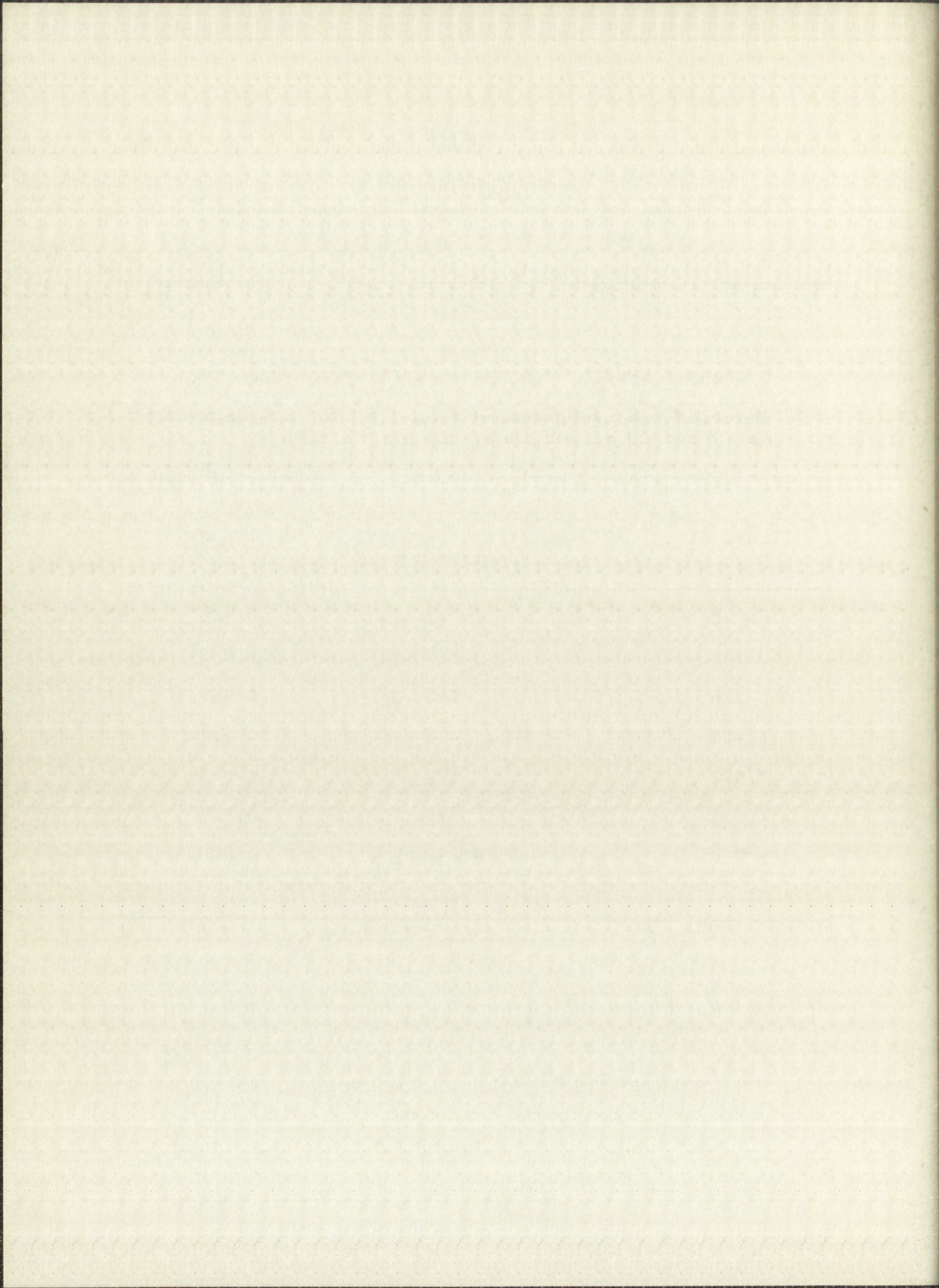




Table 31

## Experimental Data for Run 31

29.7°C

0.00453  $\underline{f}$  As(V), 0.00230  $\underline{f}$  As(III)\*, 12.6  $\underline{f}$  HCl

Reaction mixture prepared from 1 ml. of 319-days-old As(V) and 20 ml. of 1-day-old As(III)\*.

 $t_{\frac{1}{2}} = 790$  min. $(t_{\frac{1}{2}})_1 = 372$  min. $(t_{\frac{1}{2}})_2 = 22,350$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
5	60	0.988
57	191	0.960
156	634	0.868
300	1,046	0.782
720	1,864	0.612
1,440	2,237	0.534
2,857	2,533	0.473
7,624	2,932	0.390
$\infty$	4,803	0.000







Table 32  
Experimental Data for Run 32

29.7°C

0.00829  $\underline{f}$  As(V), 0.00416  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 2 ml. of 133-days-old As(V), 2 ml. of 1-day-old As(III)\*, and 26 ml. of HCl.

$(t_{\frac{1}{2}})_1 \approx 100$  min.

$(t_{\frac{1}{2}})_2 = 554,000$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
13	34	0.989
162	71	0.976
1,384	177	0.940
7,475	220	0.926
17,226	255	0.914
$\infty$	2,971	0.000



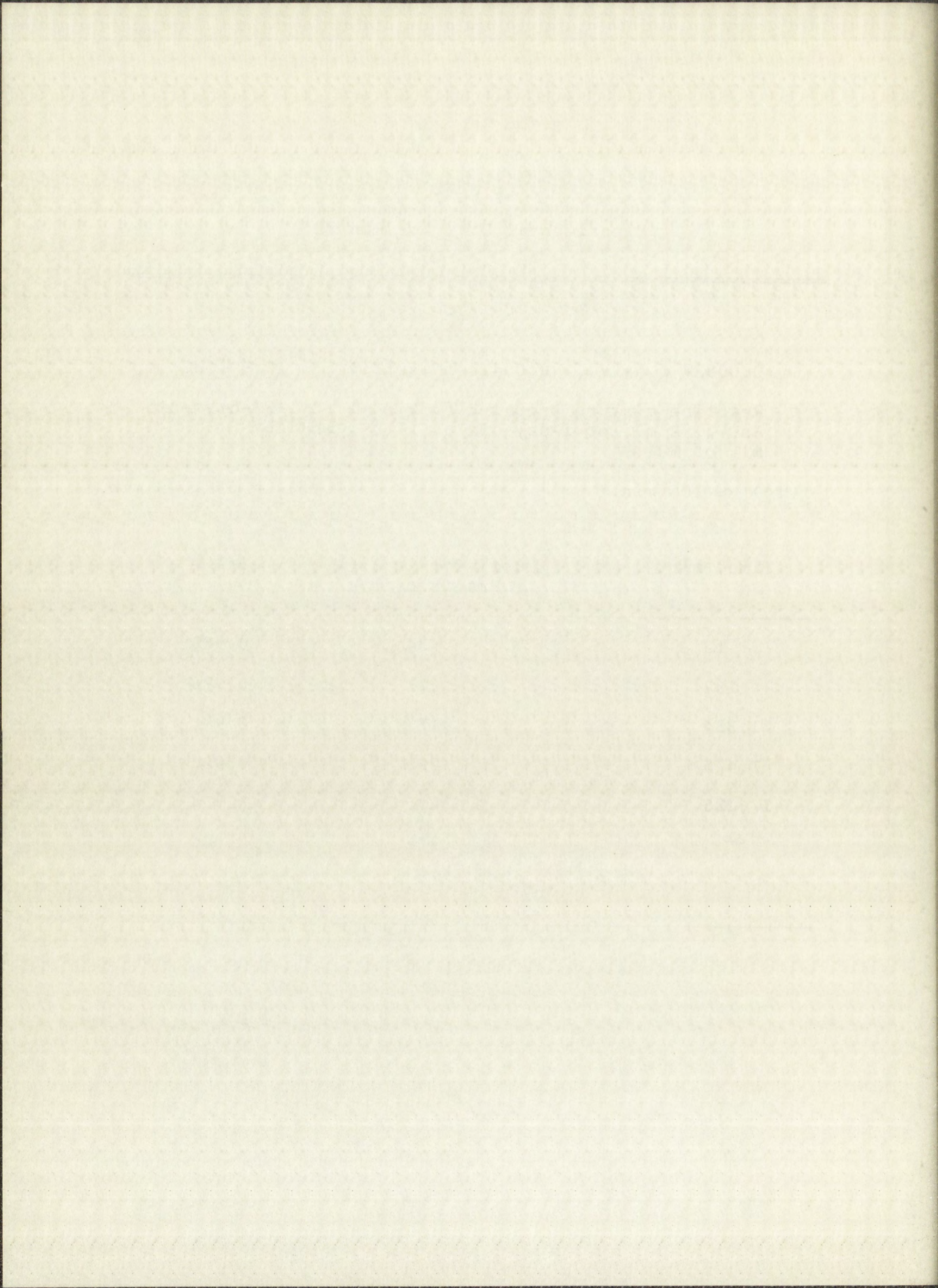




Table 33

## Experimental Data for Run 33

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 29.7°C

 0.00829  $\underline{f}$  As(V), 0.00416  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 5 ml. of exchange mixture from run 32; solution exposed to normal laboratory light.

 $(t_{\frac{1}{2}})_2 = 185,000 \text{ min.}$ 

Time, min.	Activity in As(V) Fraction, c/m	1 - F
7,484	325	0.891
17,233	524	0.824
$\infty$	2,971	0.000

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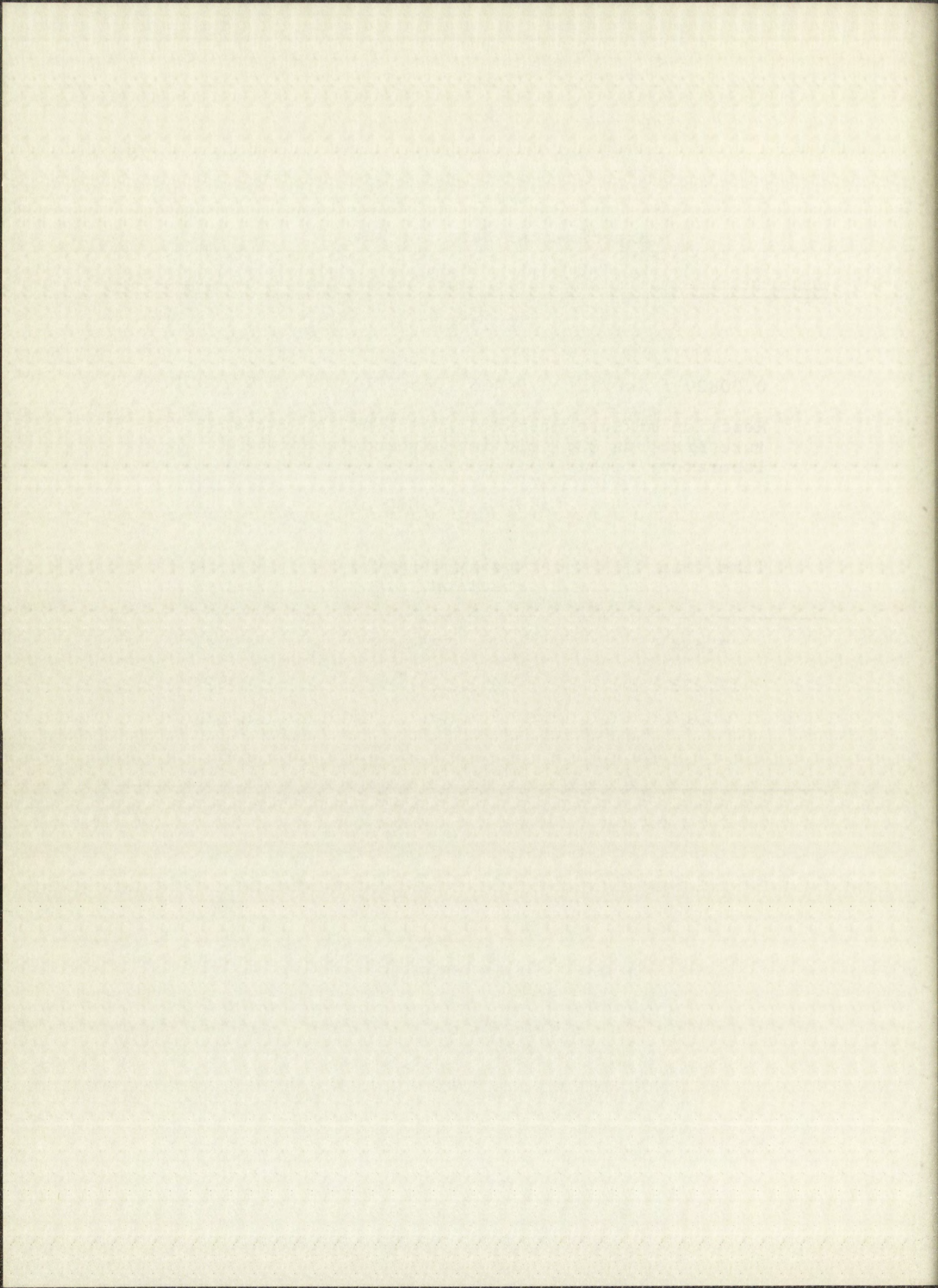




Table 34

## Experimental Data for Run 34

29.7°C

0.00829  $\underline{f}$  As(V), 0.00416  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 10 ml. of exchange  
mixture from run 32 plus 0.21 g. of pyrex glass  
wool.

 $(t_{\frac{1}{2}})_2 > 185,000$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
7,492	289	0.903
17,239	501	0.831
$\infty$	2,971	0.000



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Table 35  
Experimental Data for Run 35

29.7°C

0.00829  $\underline{f}$  As(V), 0.00416  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 2 ml. of 133-days-old As(V), 2 ml. of 1-day-old As(III)\*, and 26 ml. of HCl.

$(t_{\frac{1}{2}})_1 \approx 80$  min.

$(t_{\frac{1}{2}})_2 = 320,000$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
11	31	0.990
138	96	0.968
1,355	209	0.931
7,531	299	0.901
17,259	422	0.860
$\infty$	3,012	0.000



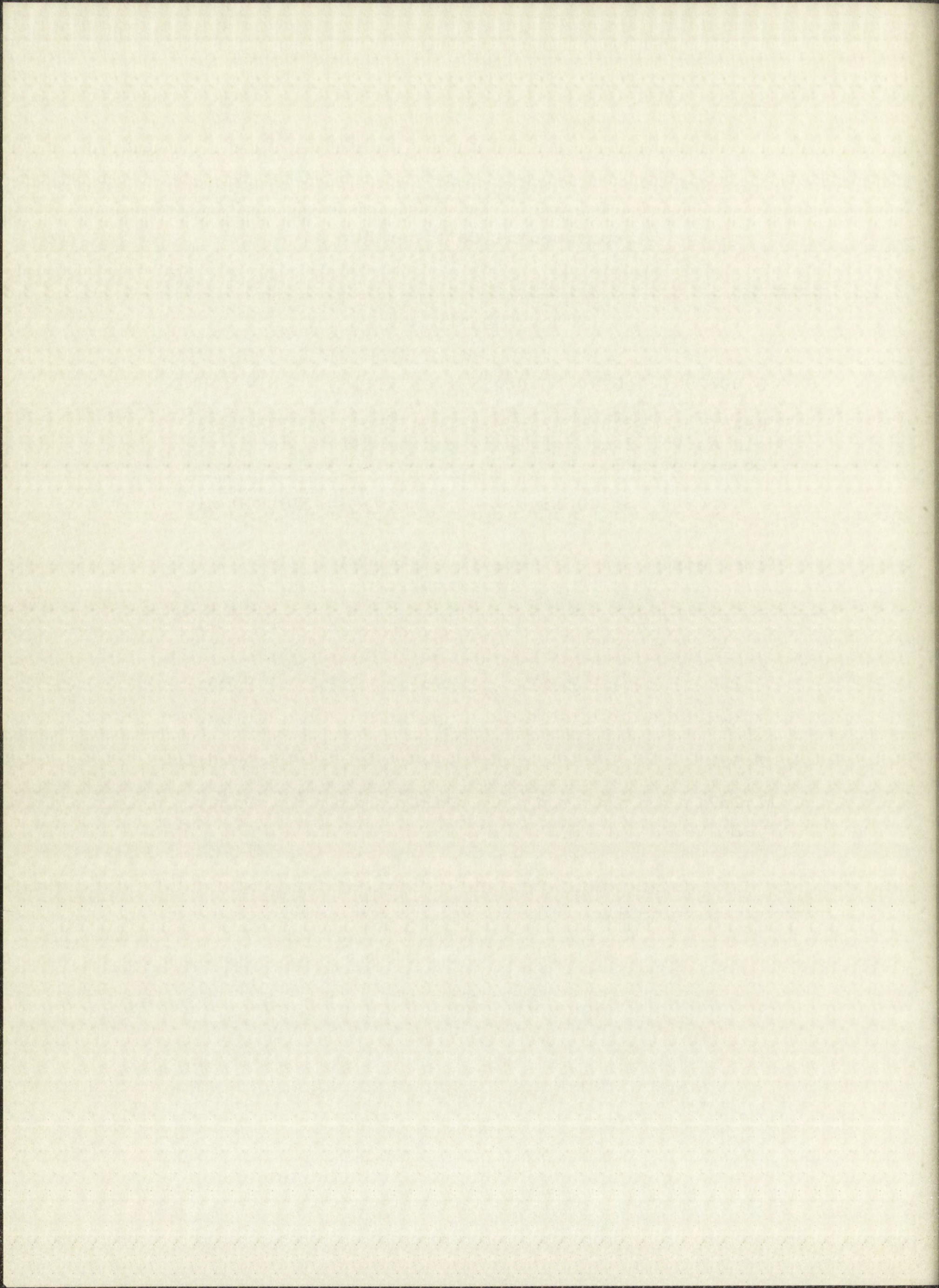




Table 36

## Experimental Data for Run 36

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 29.7°C
0.00829  $\underline{f}$  As(V), 0.00416  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 5 ml. of exchange mixture from run 35; solution exposed to normal laboratory light.

 $(t_{\frac{1}{2}})_2 = 320,000 \text{ min.}$ 

Time, min.	Activity in As(V) Fraction, c/m	1 - F
7,537	290	0.904
17,264	439	0.854
$\infty$	3,012	0.000

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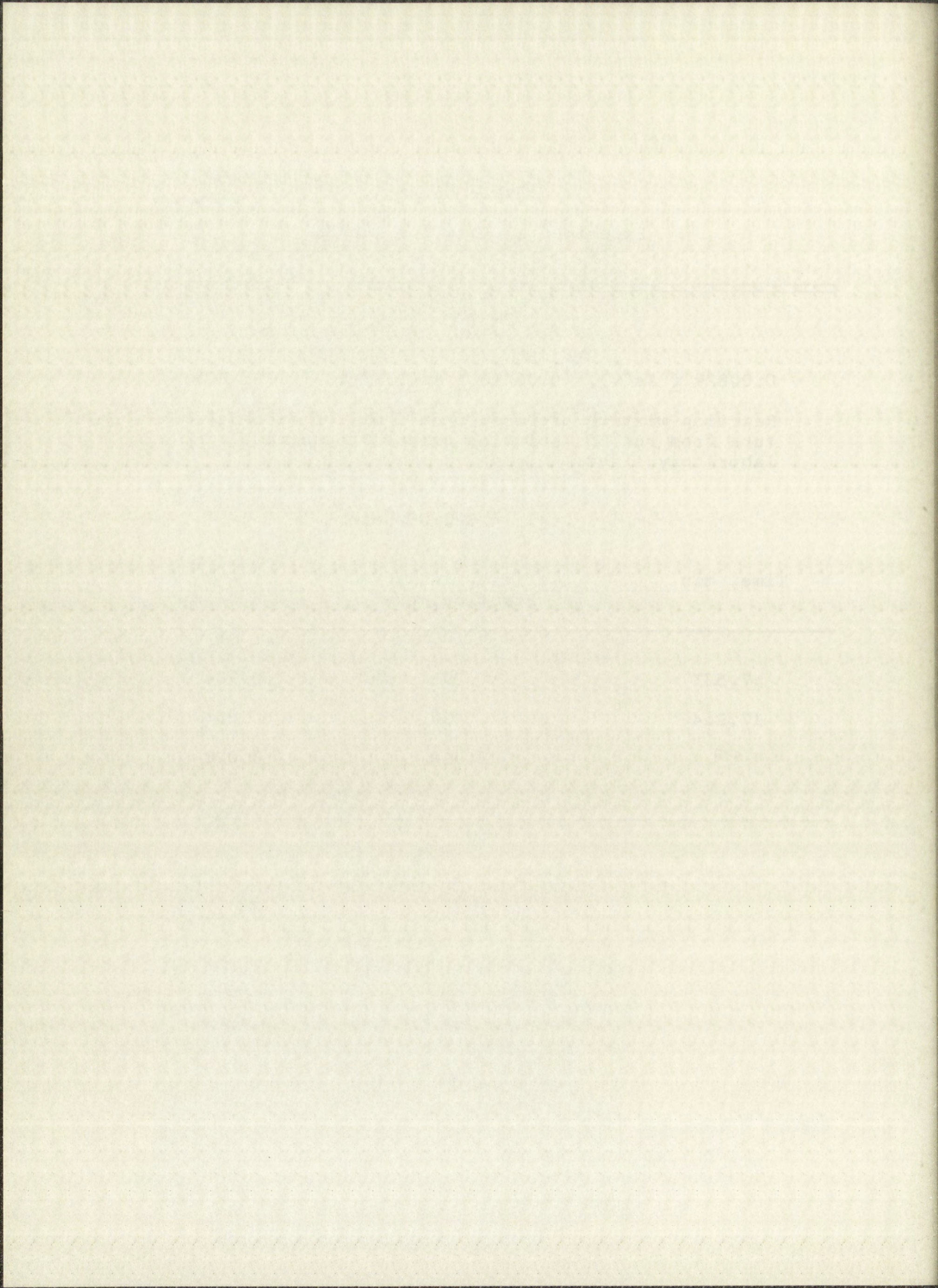




Table 37

## Experimental Data for Run 37

29.7°C

0.00829  $\underline{f}$  As(V), 0.00416  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 10 ml. of exchange  
mixture from run 35 plus 0.21 g. of pyrex glass  
wool.

 $(t_{\frac{1}{2}})_2 = 320,000 \text{ min.}$ 

Time, min.	Activity in As(V) Fraction, c/m	1 - F
7,551	275	0.909
17,270	491	0.833
$\infty$	3,012	0.000



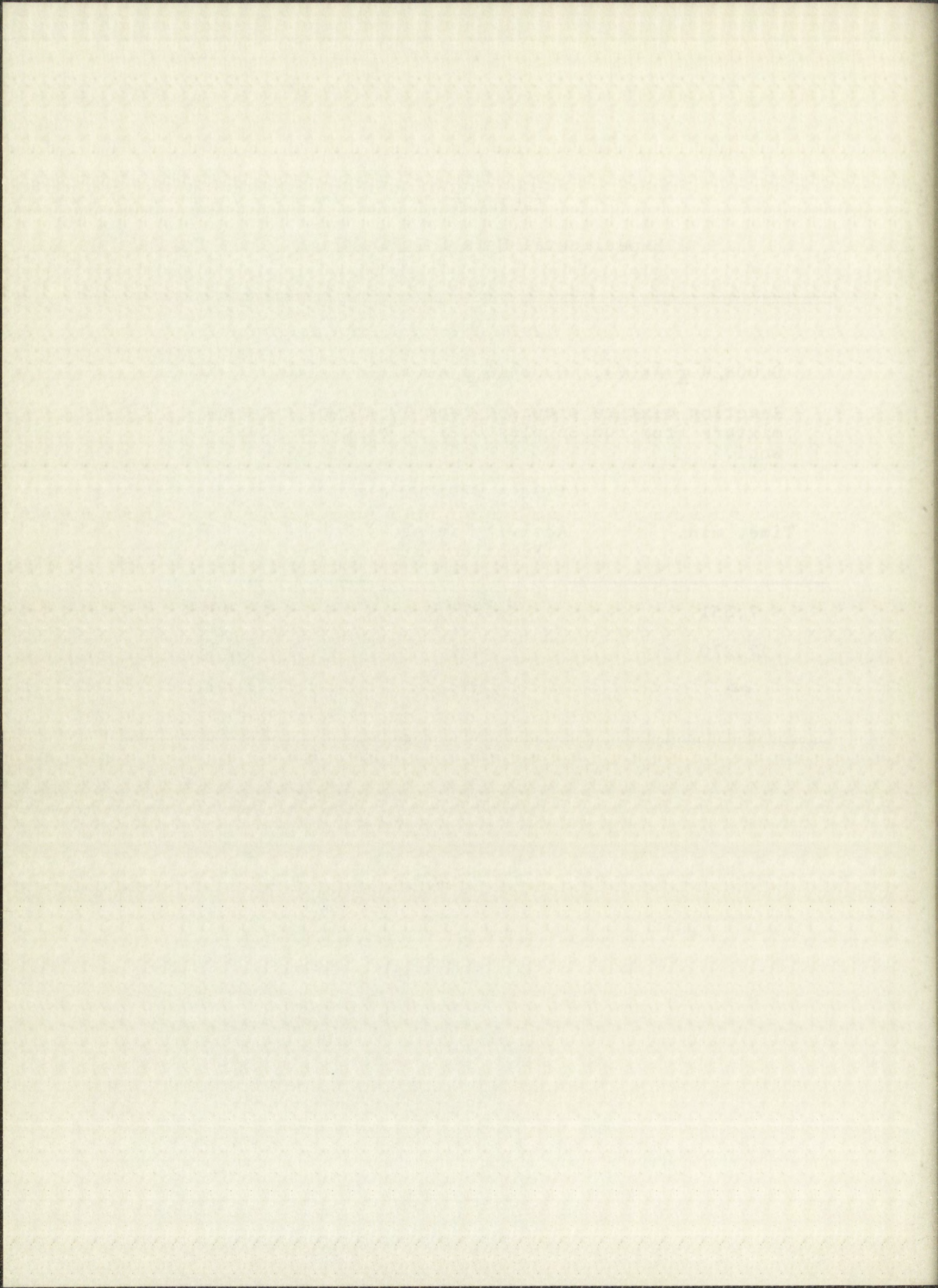




Table 38  
Experimental Data for Run 38

48.6°C

0.00777  $\underline{f}$  As(V) 0.00132  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 1 ml. of 179-days-old As(V), 1 ml. of 2-days-old As(III)\*, and 14 ml. of HCl.

$t_{\frac{1}{2}} = 475$  min.  $(t_{\frac{1}{2}})_1 = 142$  min.  $(t_{\frac{1}{2}})_2 = 2,900$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	57	0.981
71	322	0.893
311	775	0.744
669	1,097	0.637
1,441	1,472	0.513
2,830	1,898	0.372
4,347	2,267	0.250
$\infty$	3,023	0.000







Table 39

## Experimental Data for Run 39

48.6°C

0.0155  $\mu$  As(V), 0.00132  $\mu$  As(III)\*, 10.9  $\mu$  HCl

Reaction mixture prepared from 2 ml. of 179-days-old As(V), 1 ml. of 2-days-old As(III)\*, and 13 ml. of HCl.

 $t_{\frac{1}{2}} = 430$  min.  $(t_{\frac{1}{2}})_1 = 88$  min.  $(t_{\frac{1}{2}})_2 = 1,160$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
5	166	0.946
64	394	0.871
304	960	0.685
661	1,398	0.542
1,350	1,949	0.361
1,594	2,051	0.327
2,804	2,437	0.202
$\infty$	3,057	0.000



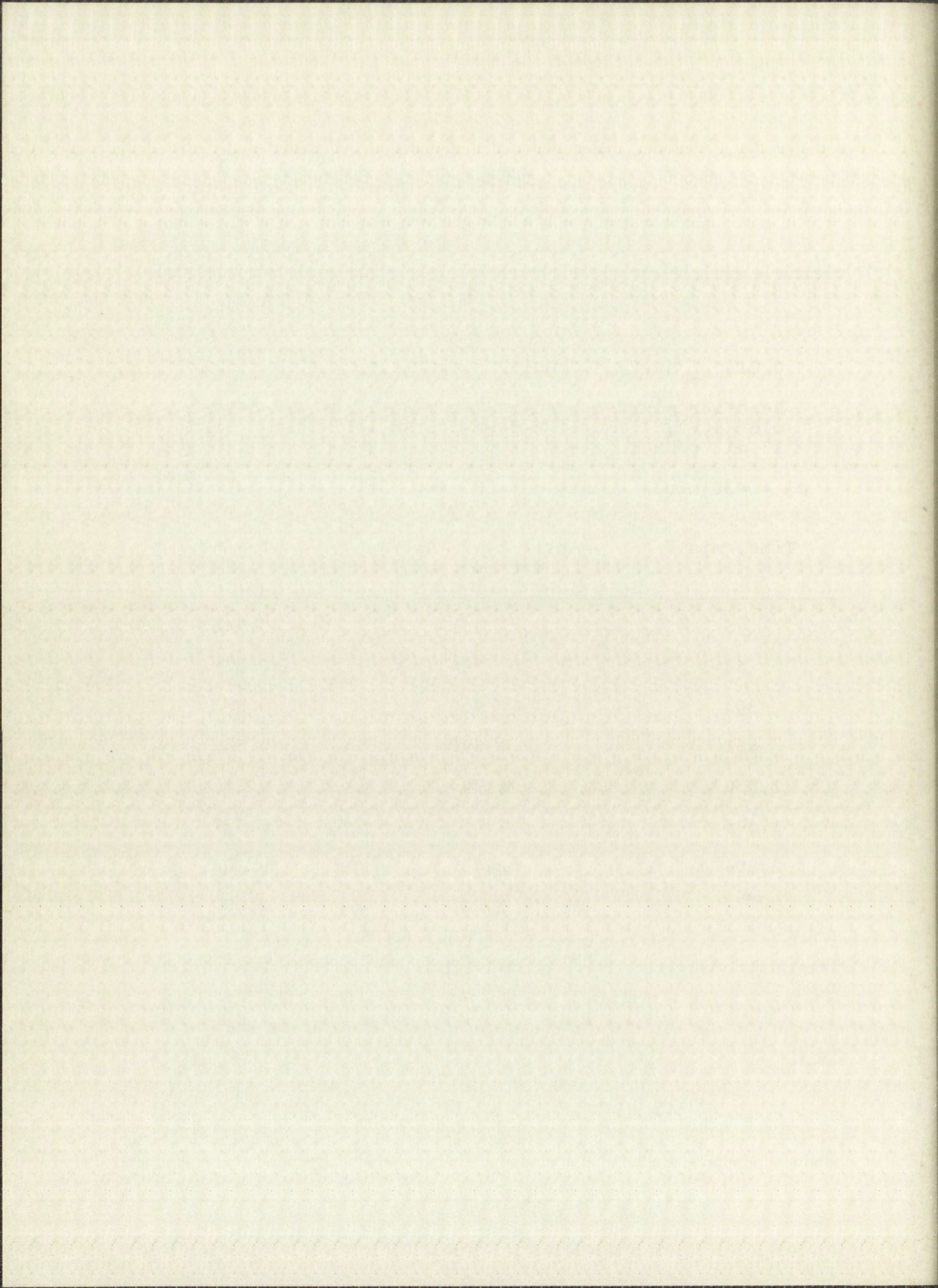




Table 40

## Experimental Data for Run 40

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 48.6°C

 0.0388  $\underline{f}$  As(V), 0.00132  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

 Reaction mixture prepared from 5 ml. of 179-days-old  
 As(V), 1 ml. of 2-days-old As(III)\*, and 10 ml. of HCl.

 $t_{\frac{1}{2}} = 320 \text{ min.}$ 

Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	240	0.925
203	1,130	0.652
660	2,530	0.221
$\infty$	3,247	0.000

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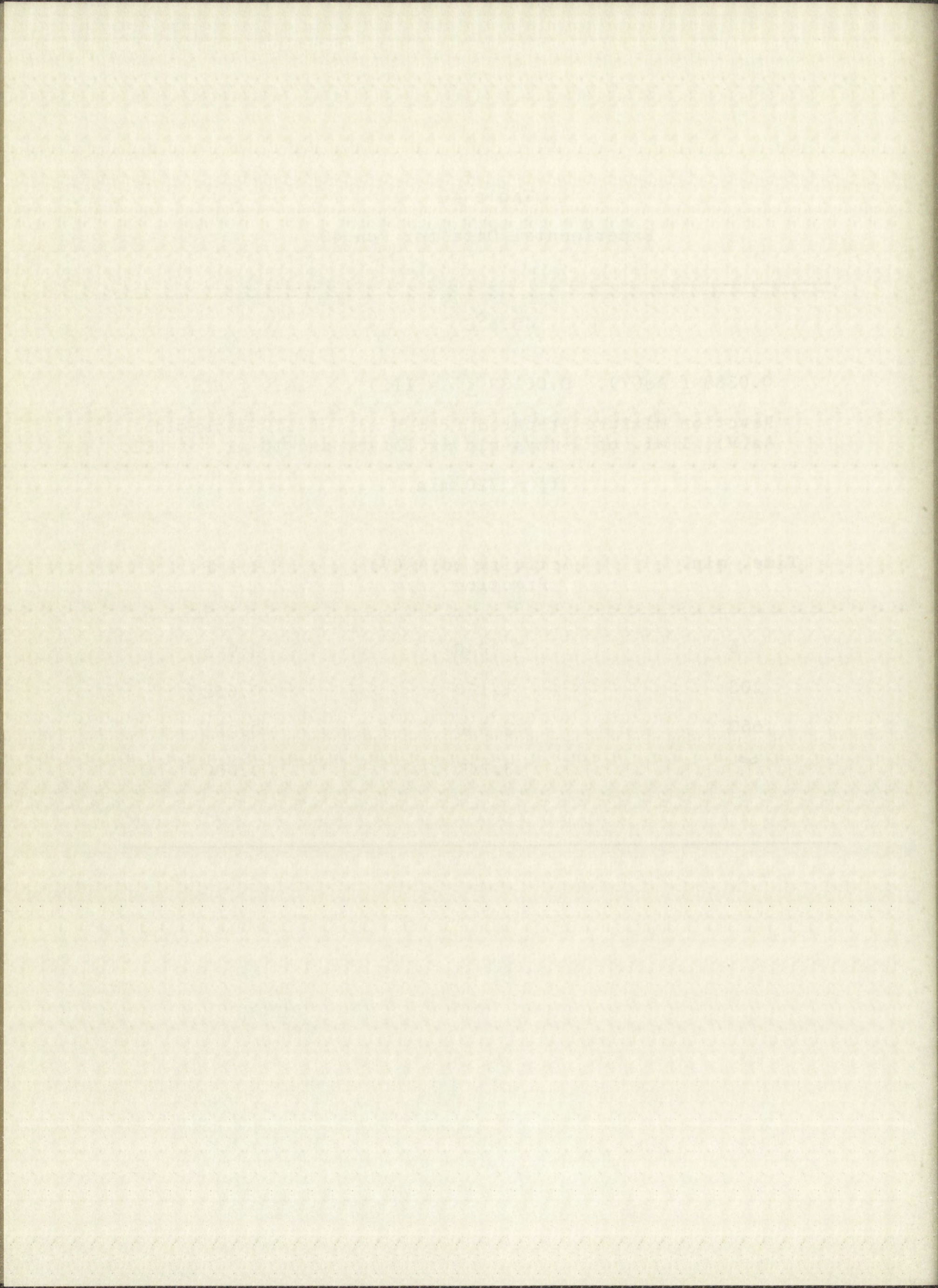




Table 41

## Experimental Data for Run 41

48.6°C

0.0155  $\underline{f}$  As(V), 0.00264  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 2 ml. of 179-days-old As(V), 2 ml. of 2-days-old As(III)\*, and 12 ml. of HCl.

 $t_{\frac{1}{2}} = 435$  min.  $(t_{\frac{1}{2}})_1 = 307$  min.  $(t_{\frac{1}{2}})_2 = 1,450$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	199	0.965
202	1,190	0.790
696	2,581	0.545
1,404	3,621	0.361
2,836	4,684	0.173
4,267	5,025	0.113
$\infty$	5,667	0.000



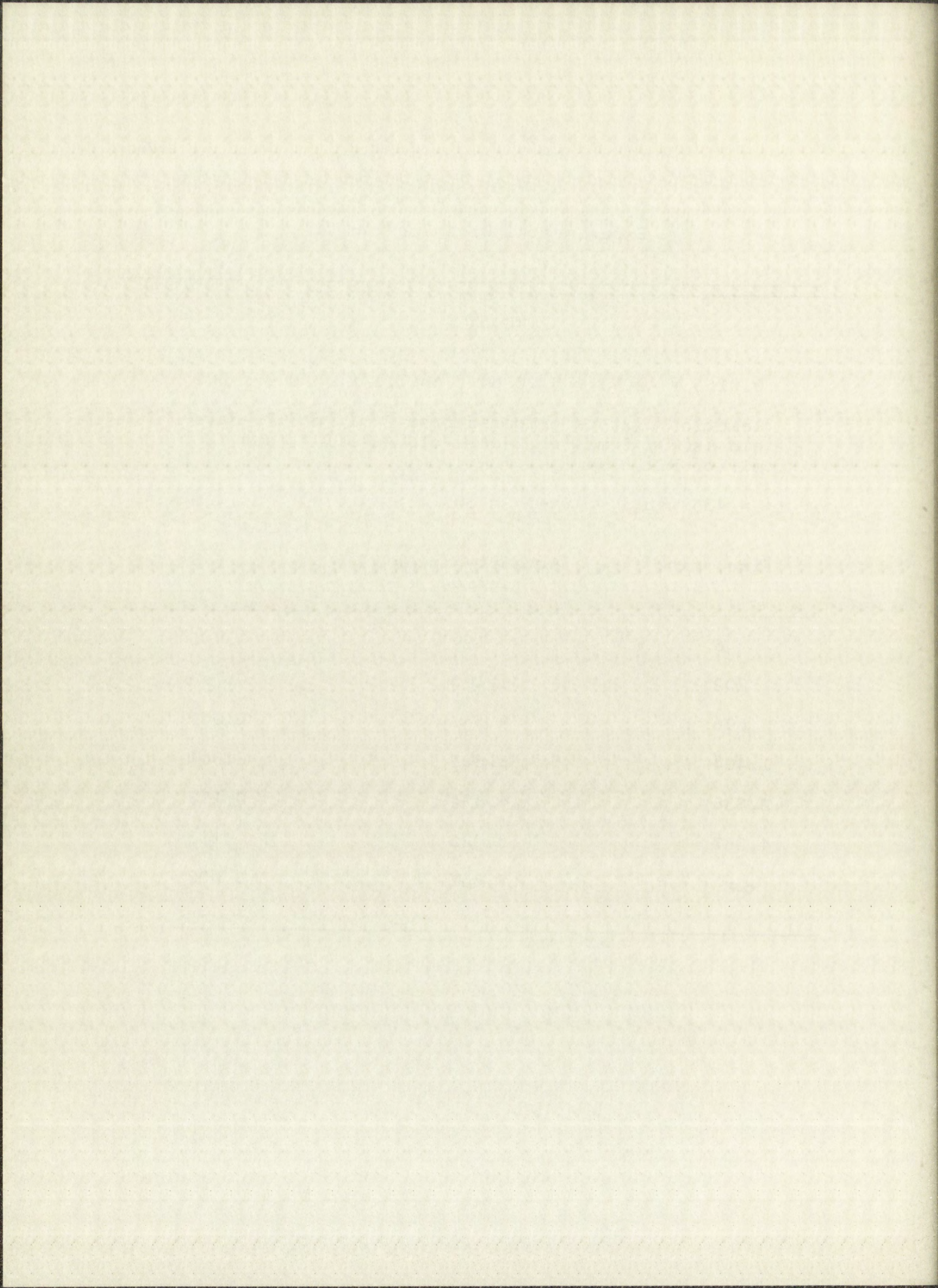




Table 42  
Experimental Data for Run 42

48.6°C

0.0155  $\underline{f}$  As(V), 0.00660  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 2 ml. of 179-days-old As(V), 5 ml. of 2-days-old As(III)\*, and 9 ml. of HCl.

$t_{\frac{1}{2}} = 380$  min.  $(t_{\frac{1}{2}})_1 = ?$   $(t_{\frac{1}{2}})_2 = 2,220$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
7	275	0.979
238	1,477	0.885
655	2,821	0.781
1,365	4,784	0.629
2,797	7,695	0.402
4,266	9,620	0.253
$\infty$	12,878	0.000







Table 43

## Experimental Data for Run 43

48.6°C

0.0155  $\bar{f}$  As(V), 0.00132  $\bar{f}$  As(III)\*, 10.9  $\bar{f}$  HCl

Reaction mixture prepared from 1 ml. of 192-days-old As(V), 0.5 ml. of 15-days-old As(III)\*, and 65 ml. of HCl.

$t_{\frac{1}{2}} = 660$  min.       $(t_{\frac{1}{2}})_1 = 240$  min.       $(t_{\frac{1}{2}})_2 = 1,265$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
9	98	0.959
234	558	0.765
754	1,144	0.518
1,577	1,631	0.313
$\infty$	2,380	0.000



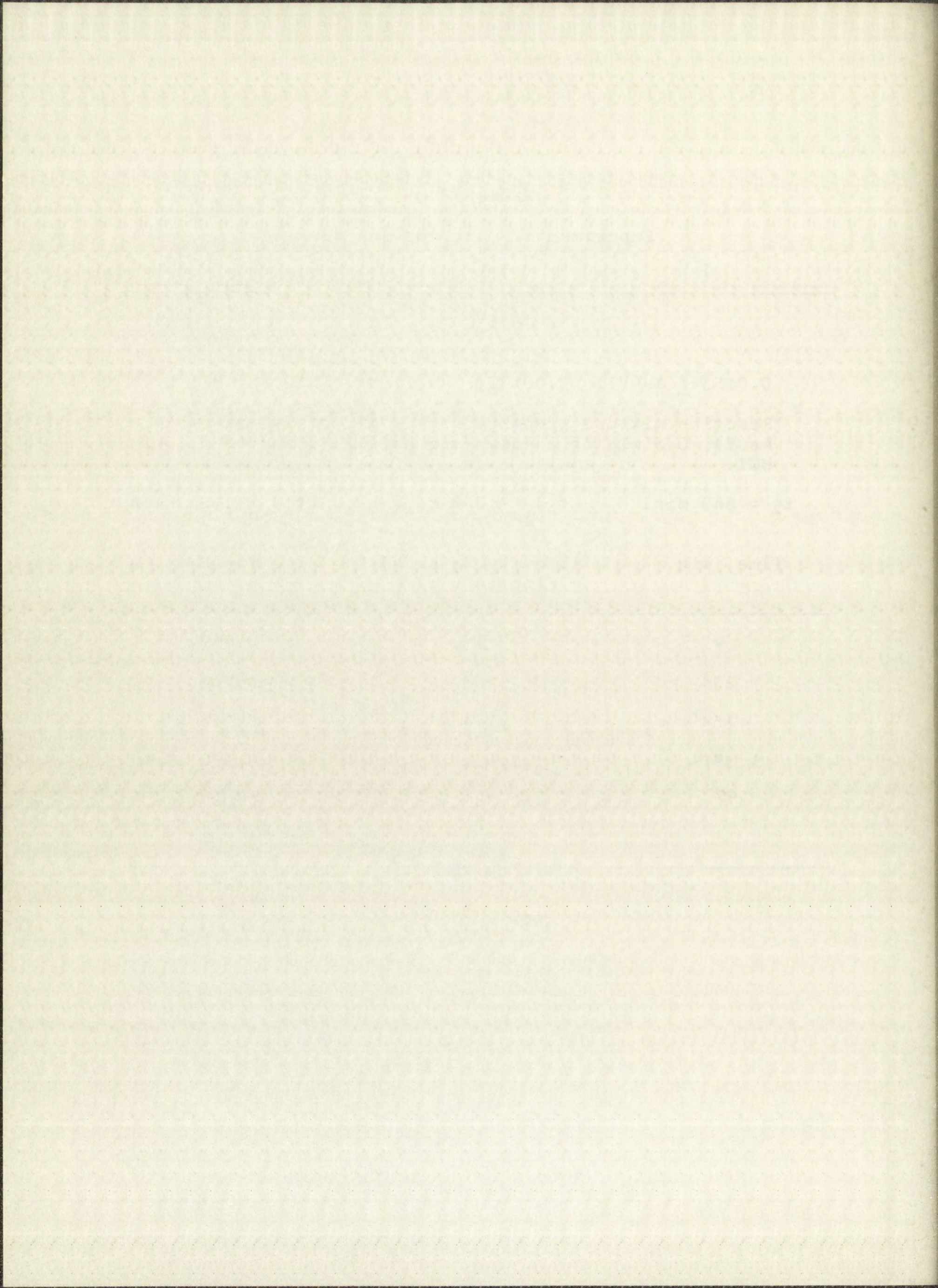




Table 44  
Experimental Data for Run 44

67.3°C

0.00777  $\underline{f}$  As(V), 0.00132  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 1 ml. of 178-days-old As(V), 1 ml. of 1-day-old As(III)\*, and 14 ml. of HCl.

$t_{\frac{1}{2}} = 69$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
5	232	0.933
30	871	0.749
68	1,748	0.496
105	2,311	0.333
138	2,488	0.282
198	2,992	0.137
$\infty$	3,467	0.000







Table 45  
Experimental Data for Run 45

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67.3°C

0.0155  $\underline{f}$  As(V), 0.00132  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 2 ml. of 178-days-old As(V), 1 ml. of 1-day-old As(III)\*, and 13 ml. of HCl.

$t_{\frac{1}{2}} = 45$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
5	409	0.890
25	907	0.756
52	2,132	0.427
89	2,751	0.260
133	3,015	0.189
180	3,339	0.102
$\infty$	3,719	0.000

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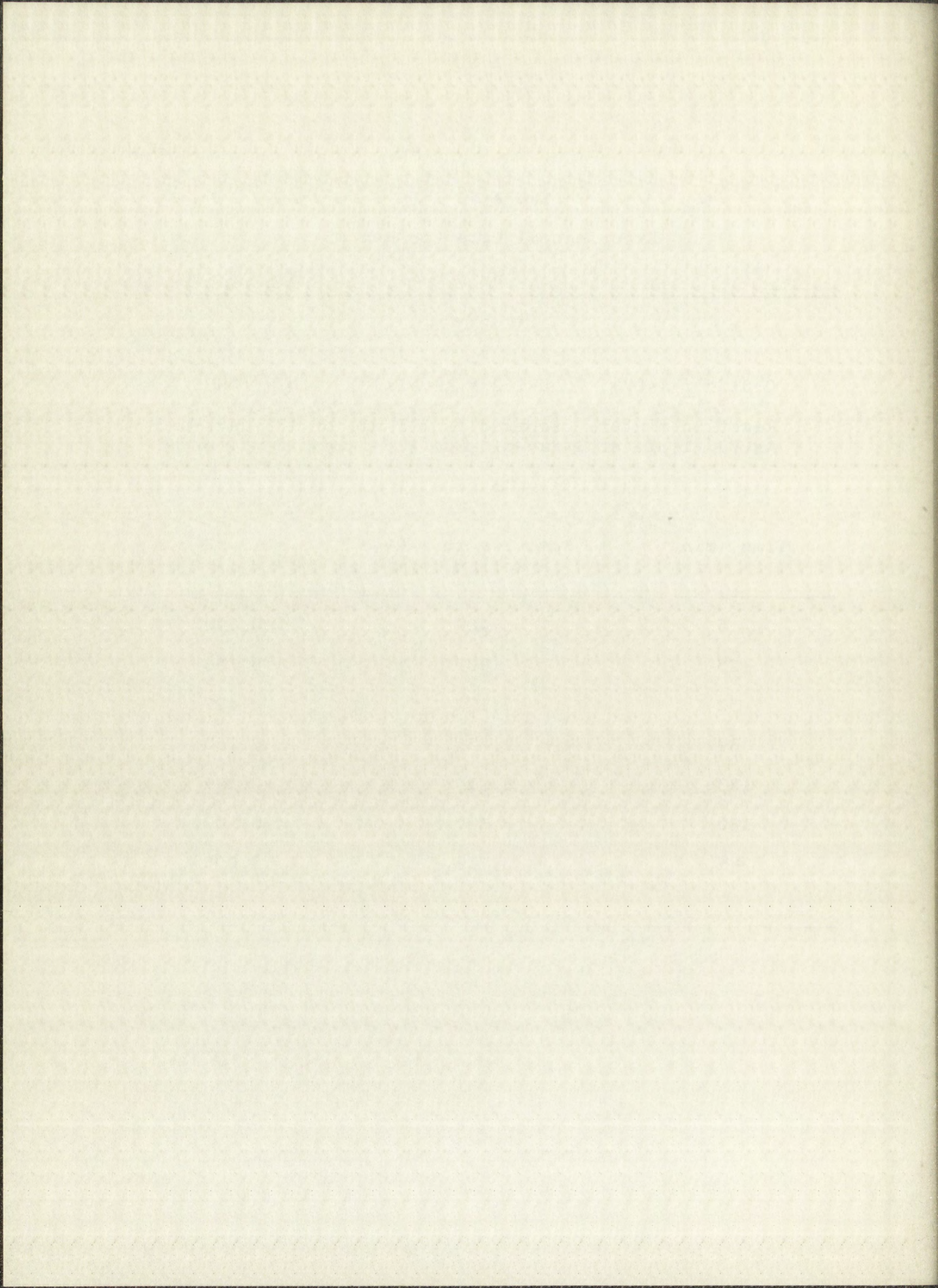




Table 46

## Experimental Data for Run 46

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 67.3°C

 0.0388  $\underline{f}$  As(V), 0.0132  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 5 ml. of 178-days-old As(V), 1 ml. of 1-day-old As(III)\*, and 10 ml. of HCl.

 $t_{\frac{1}{2}} = 23 \text{ min.}$ 

Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	704	0.820
30	2,401	0.388
63	3,328	0.151
$\infty$	3,920	0.000

---







Table 47

## Experimental Data for Run 47

67.3°C

0.0155  $\underline{f}$  As(V), 0.00264  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 2 ml. of 178-days-old As(V), 2 ml. of 1-day-old As(III)\*, and 14 ml. of HCl.

$t_{\frac{1}{2}} = 62$  min.       $(t_{\frac{1}{2}})_1 = 40$  min.       $(t_{\frac{1}{2}})_2 = 130$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
6	569	0.917
33	2,255	0.673
72	3,343	0.515
108	4,558	0.338
230	5,925	0.140
$\infty$	6,887	0.000



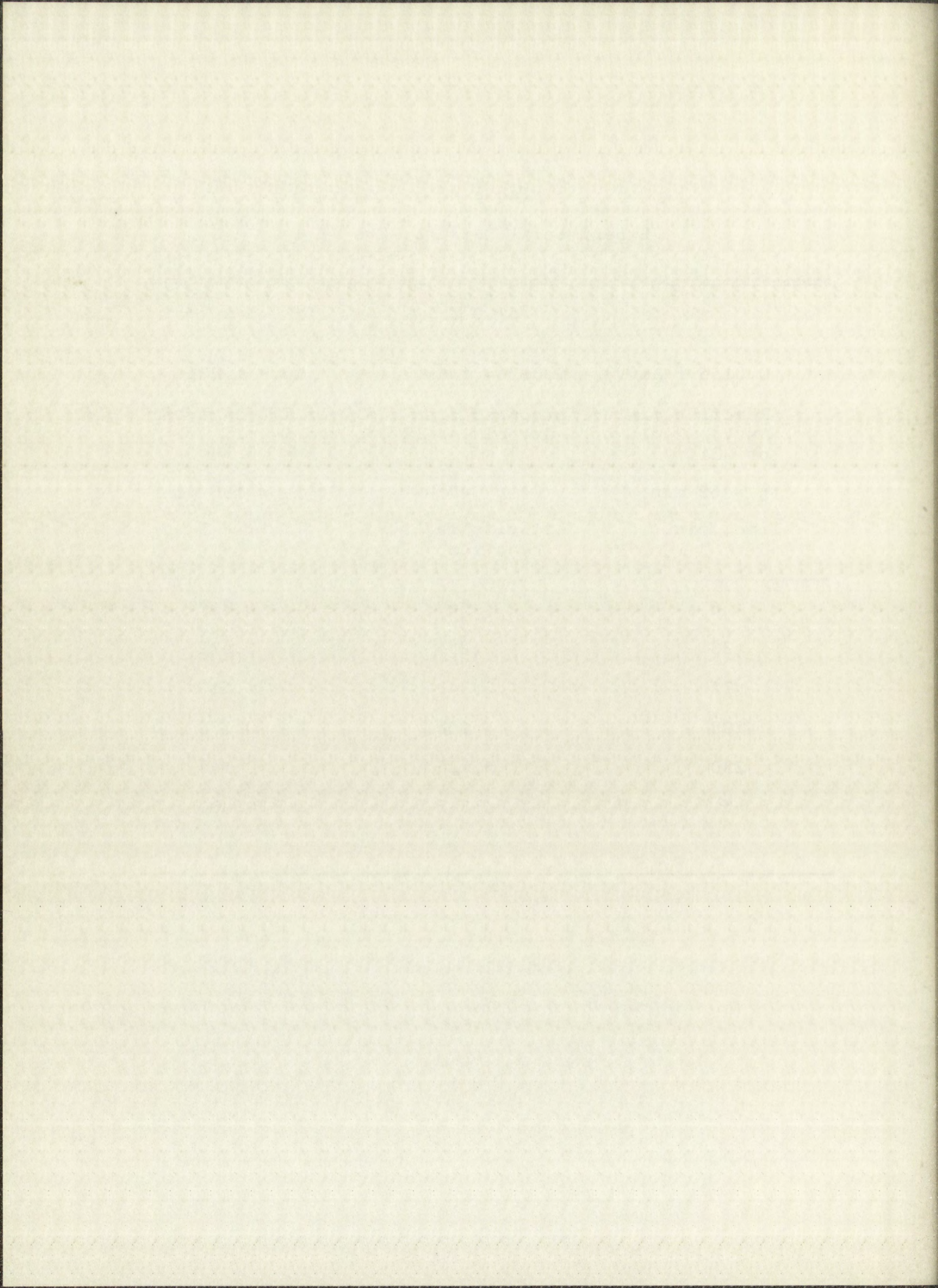




Table 48

## Experimental Data for Run 48

67.3°C

0.0155  $\underline{f}$  As(V), 0.00660  $\underline{f}$  As(III)\*, 10.9  $\underline{f}$  HCl

Reaction mixture prepared from 2 ml. of 178-days-old As(V), 5 ml. of 1-day-old As(III)\*, and 9 ml. of HCl.

 $t_{\frac{1}{2}} = 95$  min.  $(t_{\frac{1}{2}})_1 = 43$  min.  $(t_{\frac{1}{2}})_2 = 196$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
6.5	597	0.953
30	2,630	0.794
73	4,828	0.622
121	6,640	0.480
193	8,160	0.361
$\infty$	12,762	0.000



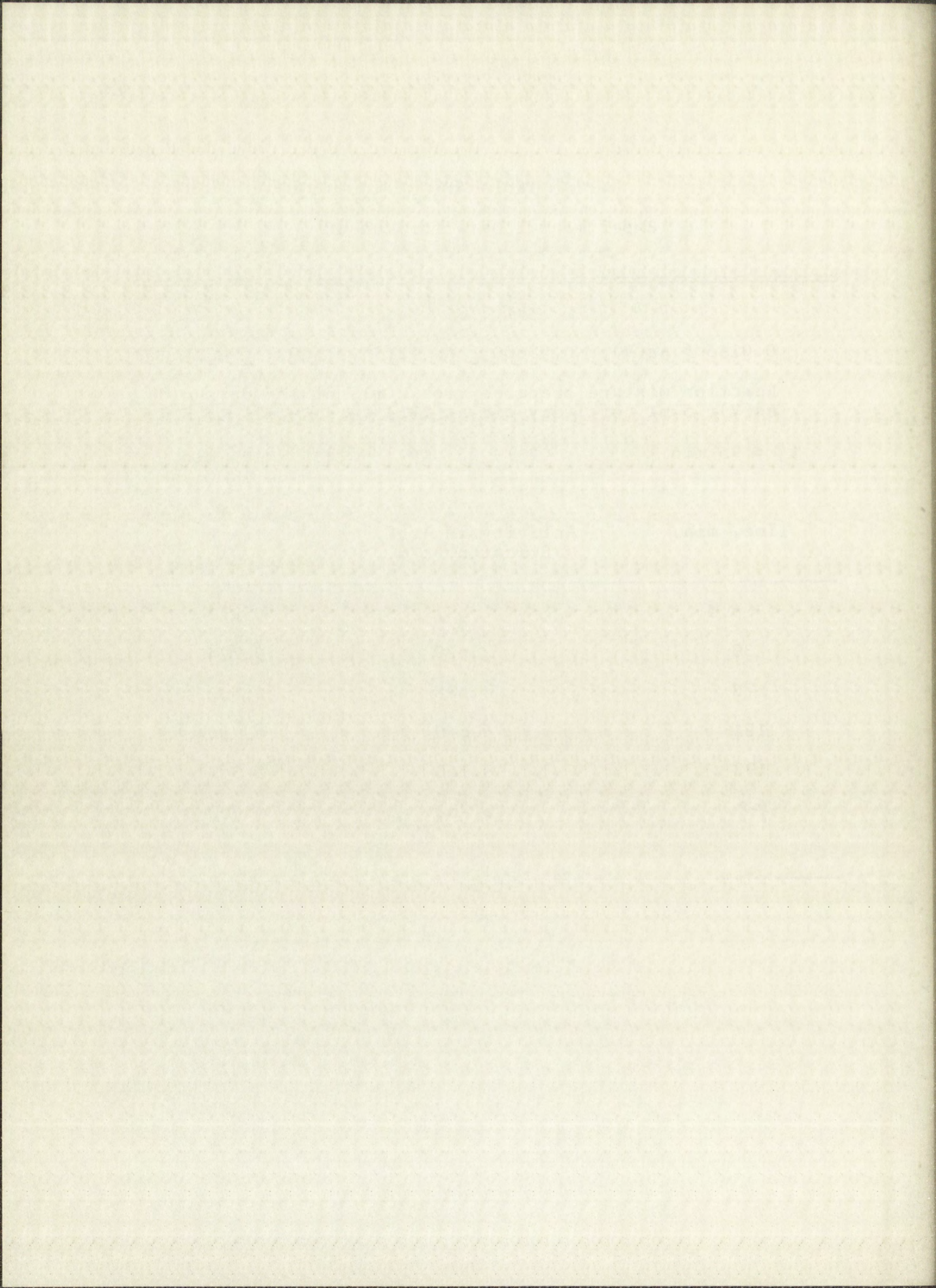




Table 49

## Experimental Data for Run 49

67.3°C

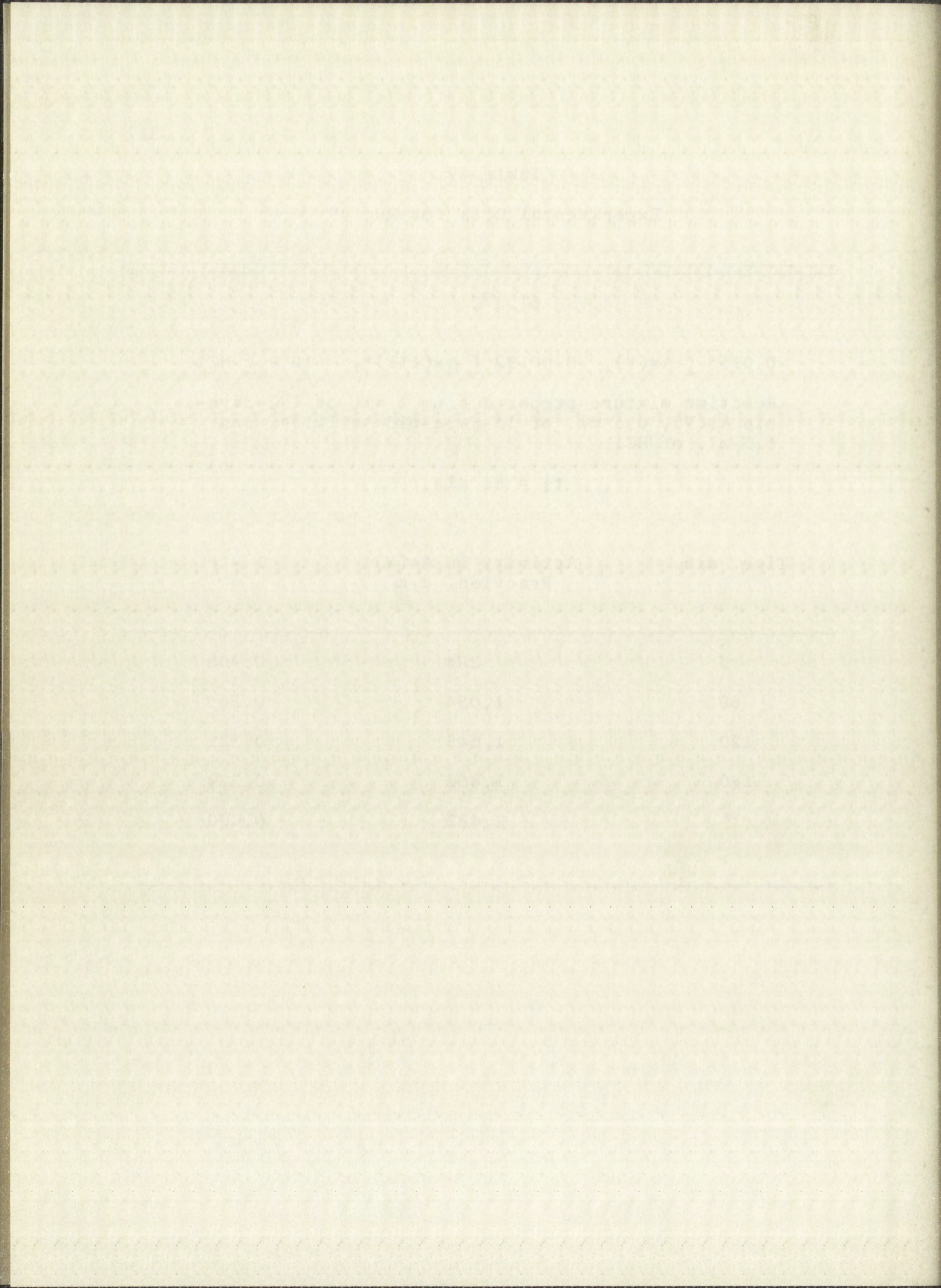
0.0155  $\mu$  As(V), 0.00132  $\mu$  As(III)\*, 10.9  $\mu$  HCl.

Reaction mixture prepared from 1 ml. of 192-days-old As(V), 0.5 ml. of 15-days-old As(III)\*, and 6.5 ml. of HCl.

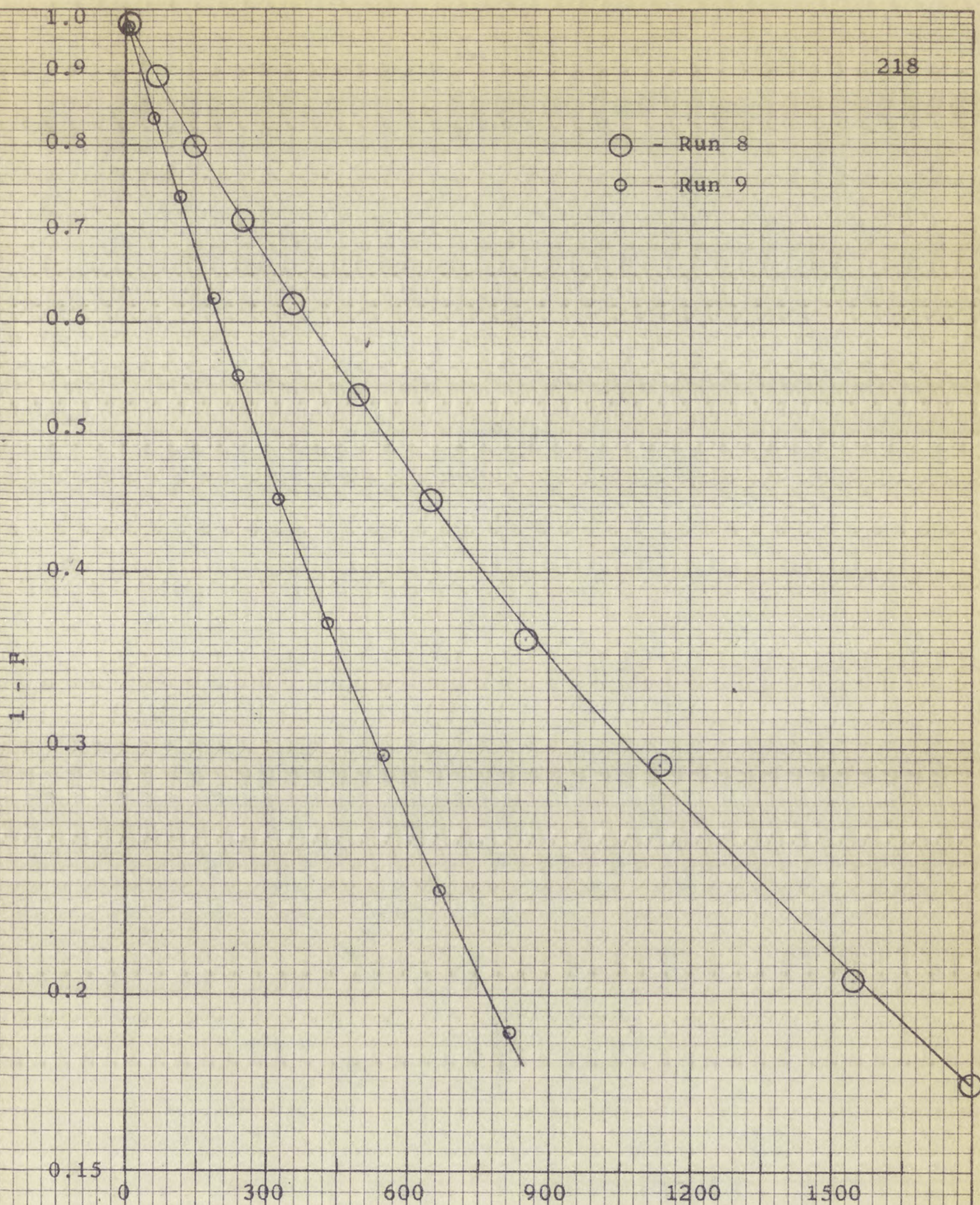
 $t_{\frac{1}{2}} = 81$  min.

Time, min.	Activity in As(V) Fraction, c/m	1 - F
5	224	0.908
60	1,054	0.565
120	1,645	0.321
180	1,868	0.229
$\infty$	2,422	0.000







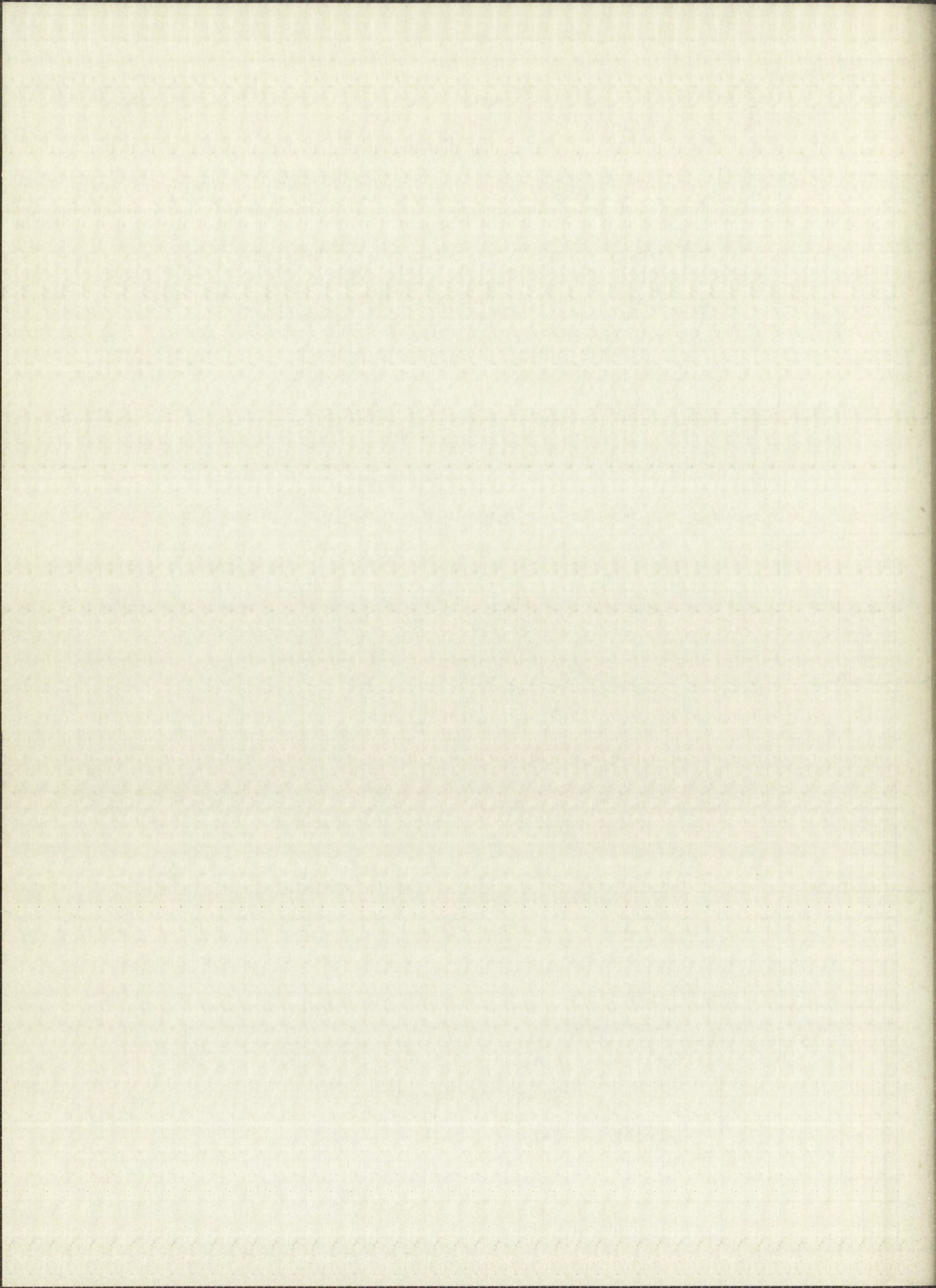


Time, minutes

Figure 1

Exchange Curves for Runs 8 and 9







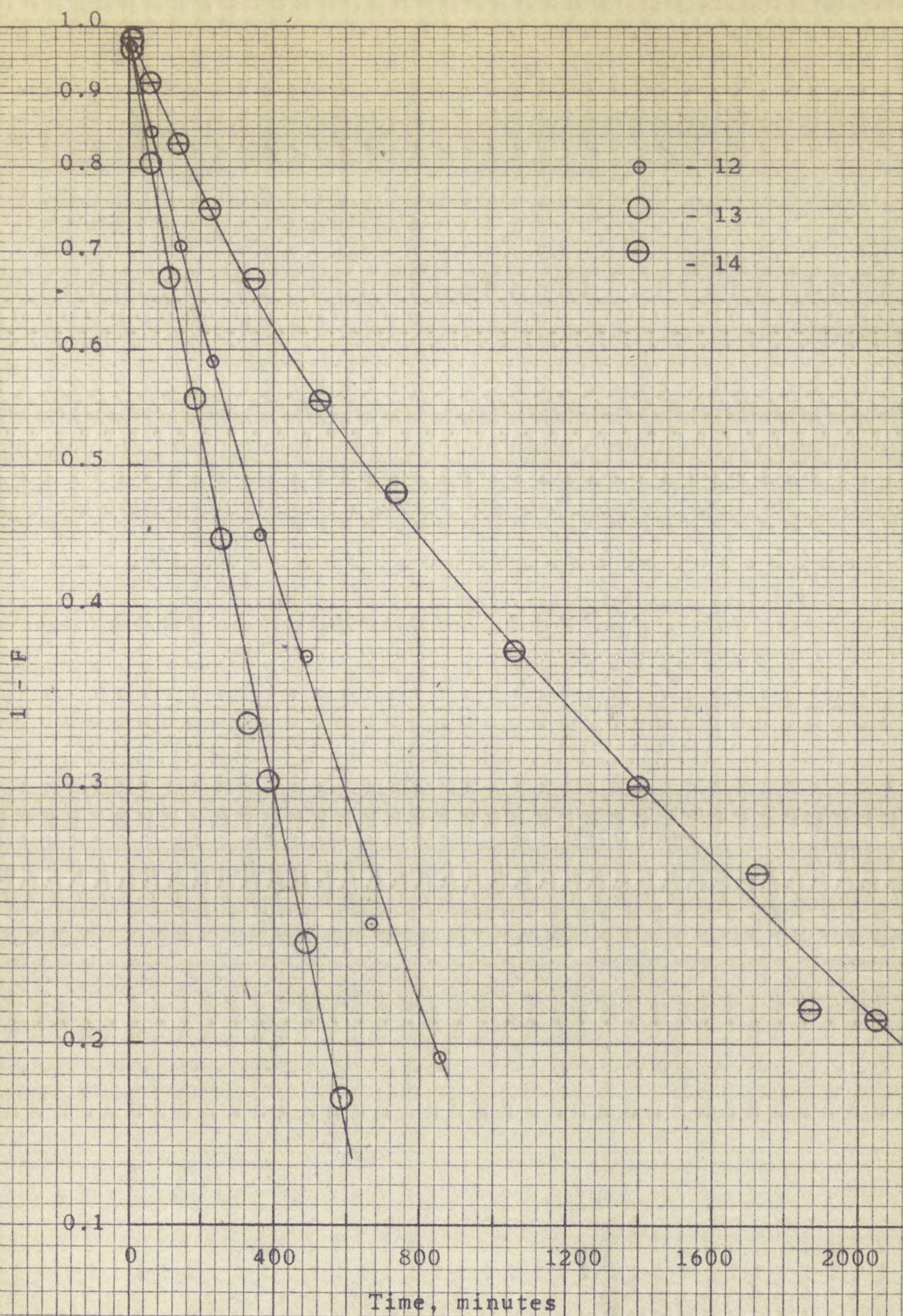
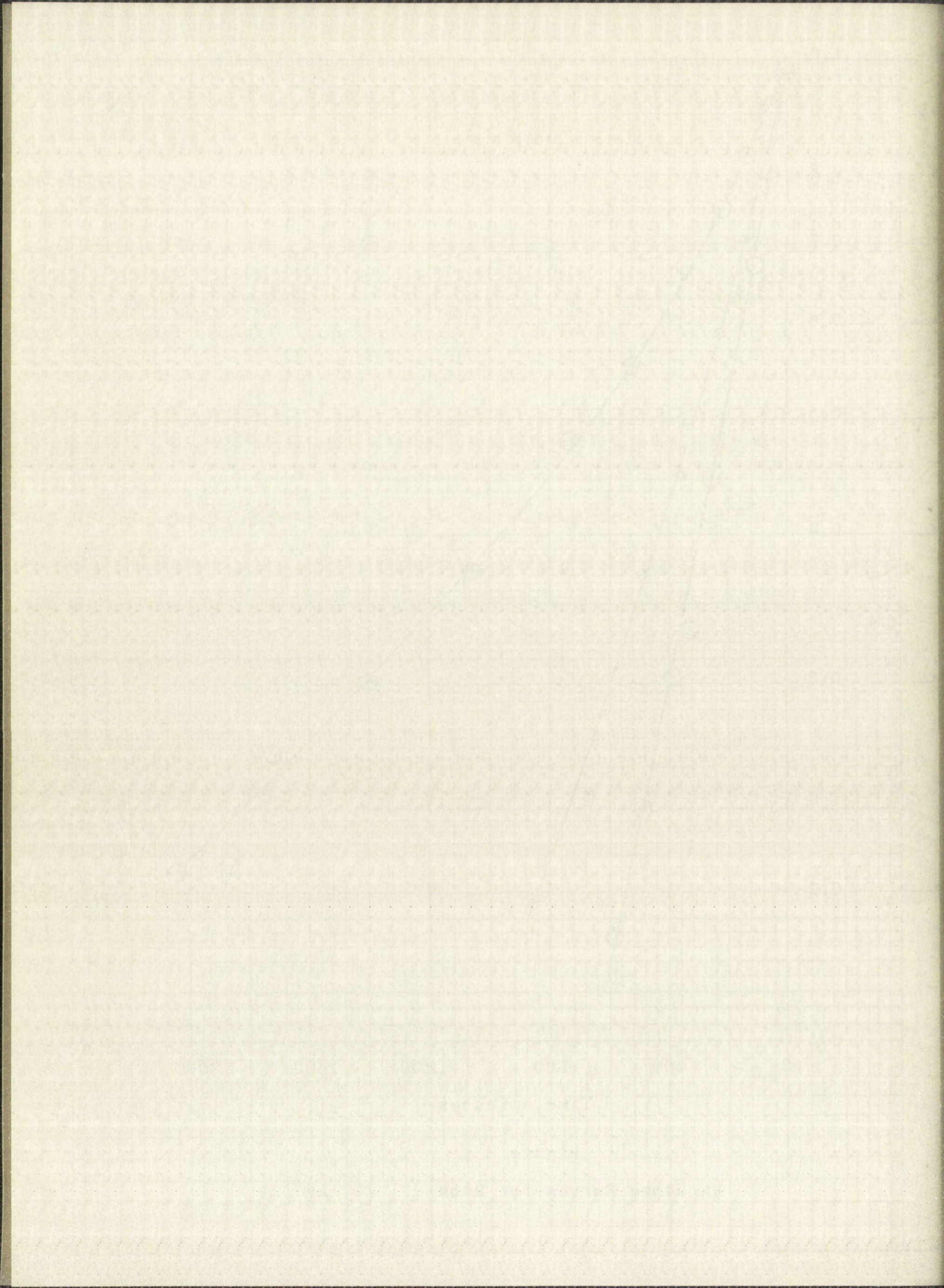


Figure 2

Exchange Curves for Runs 12, 13, and 14







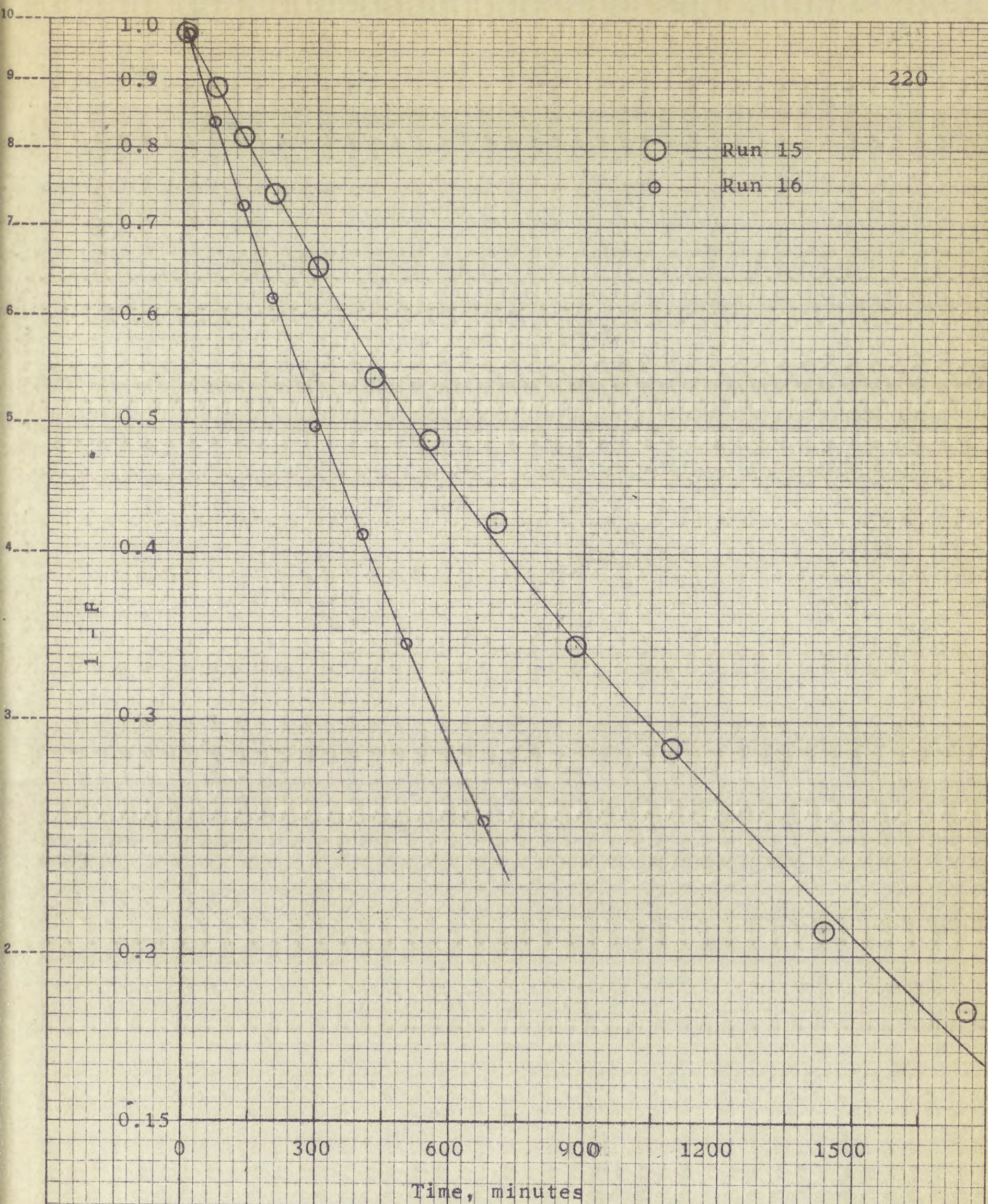
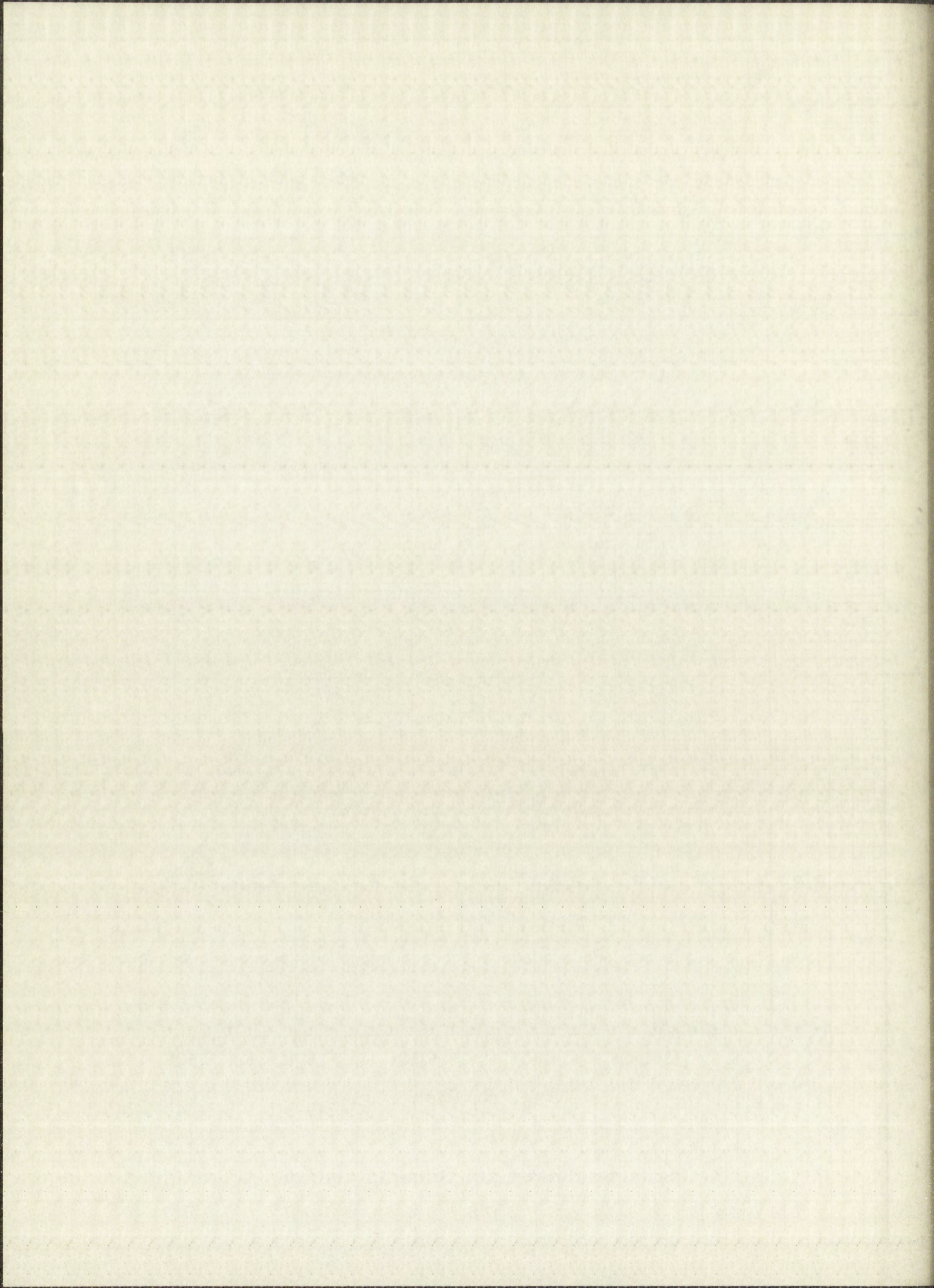


Figure 3  
Exchange Curves for Runs 15 and 16







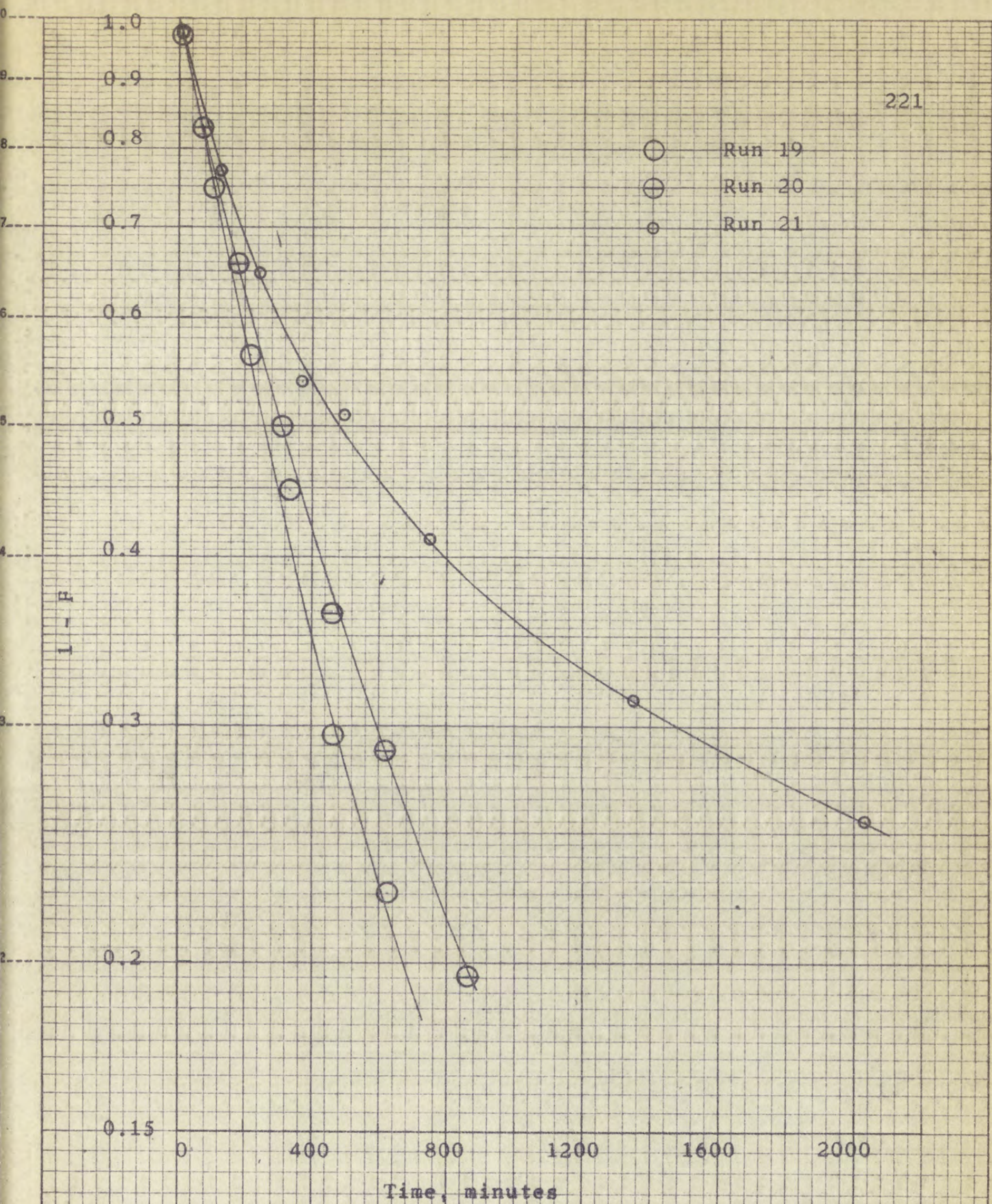
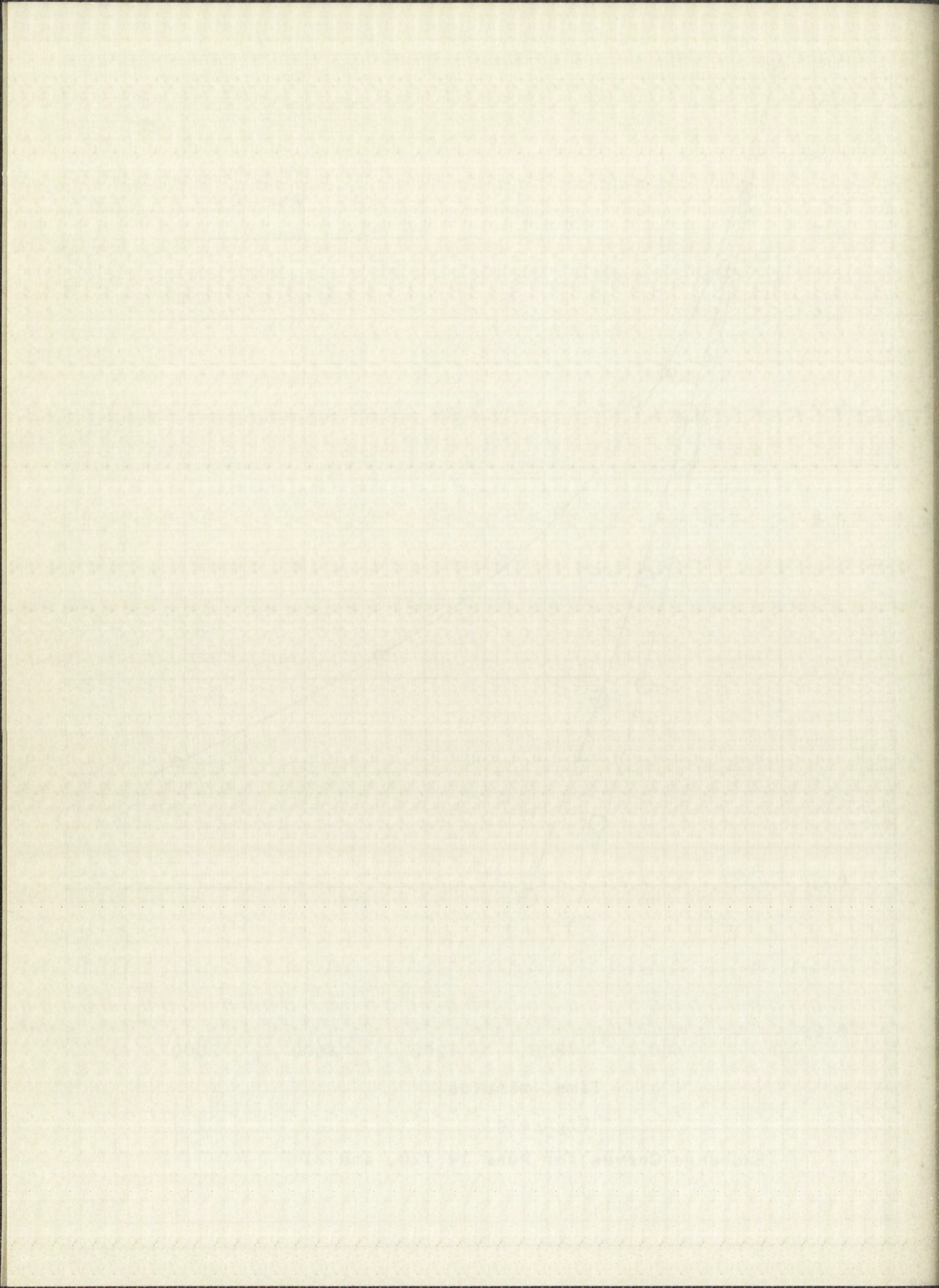


Figure 4

Exchange Curves for Runs 19, 20, and 21







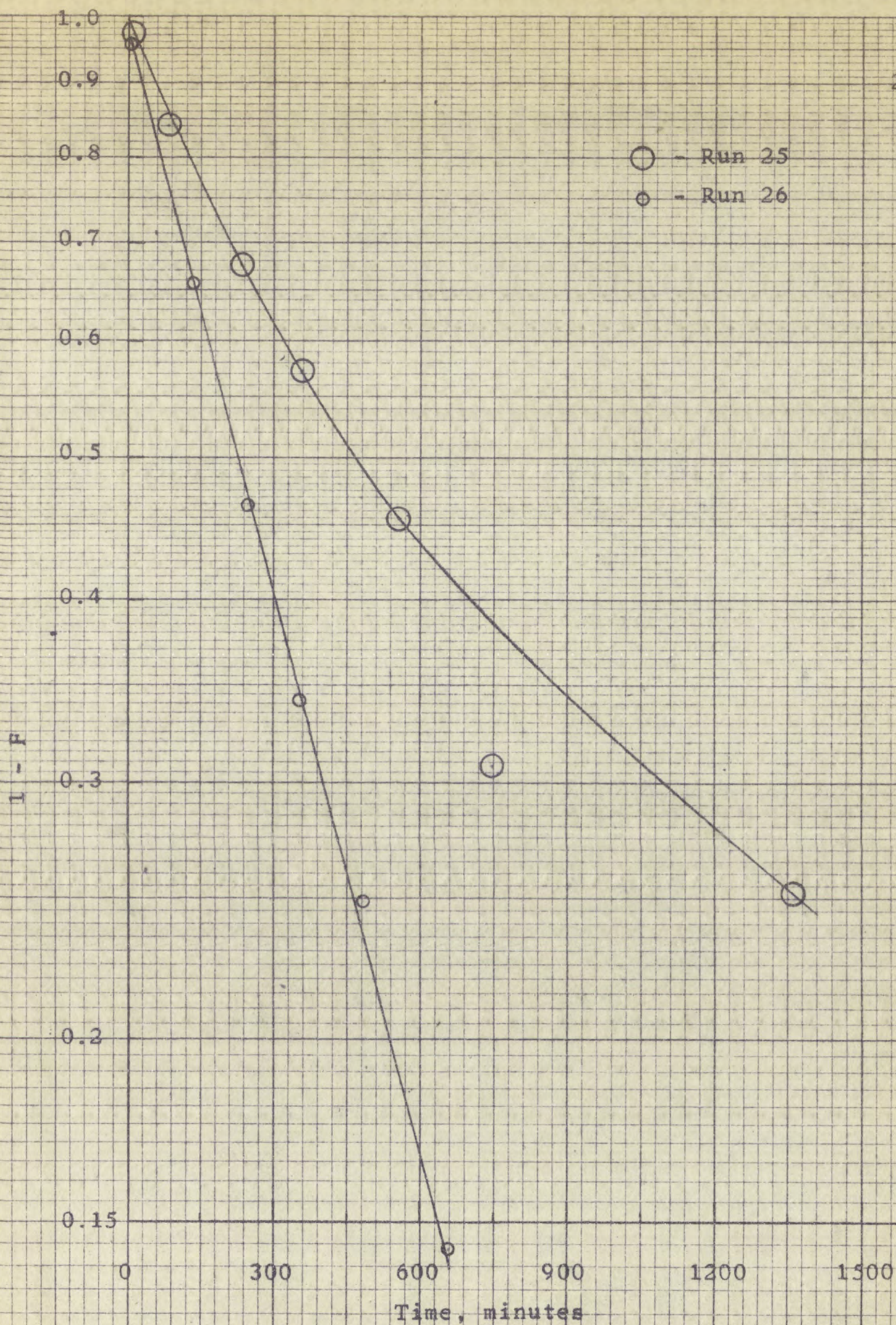
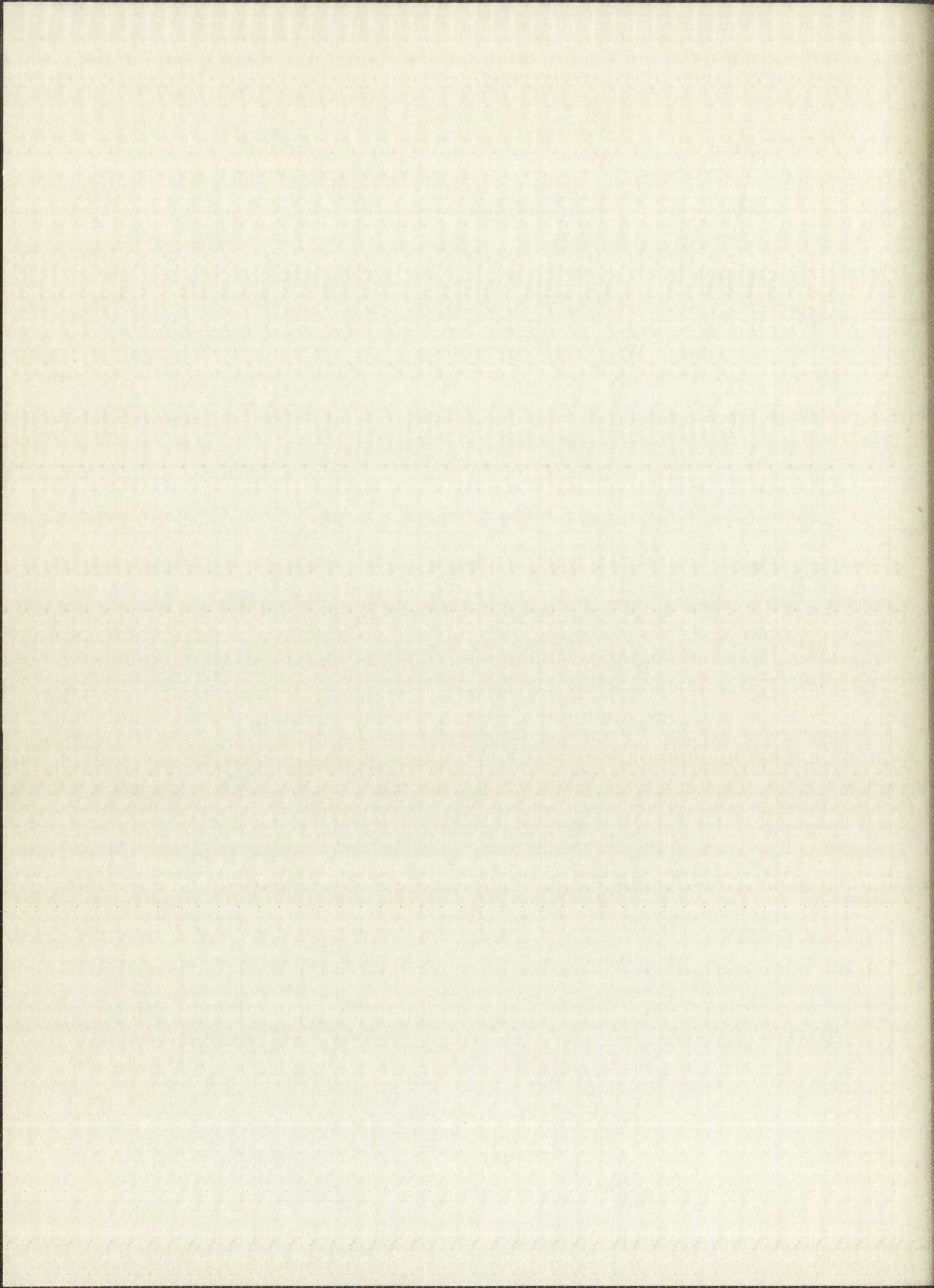


Figure 5

Exchange Curves for Runs 25 and 26







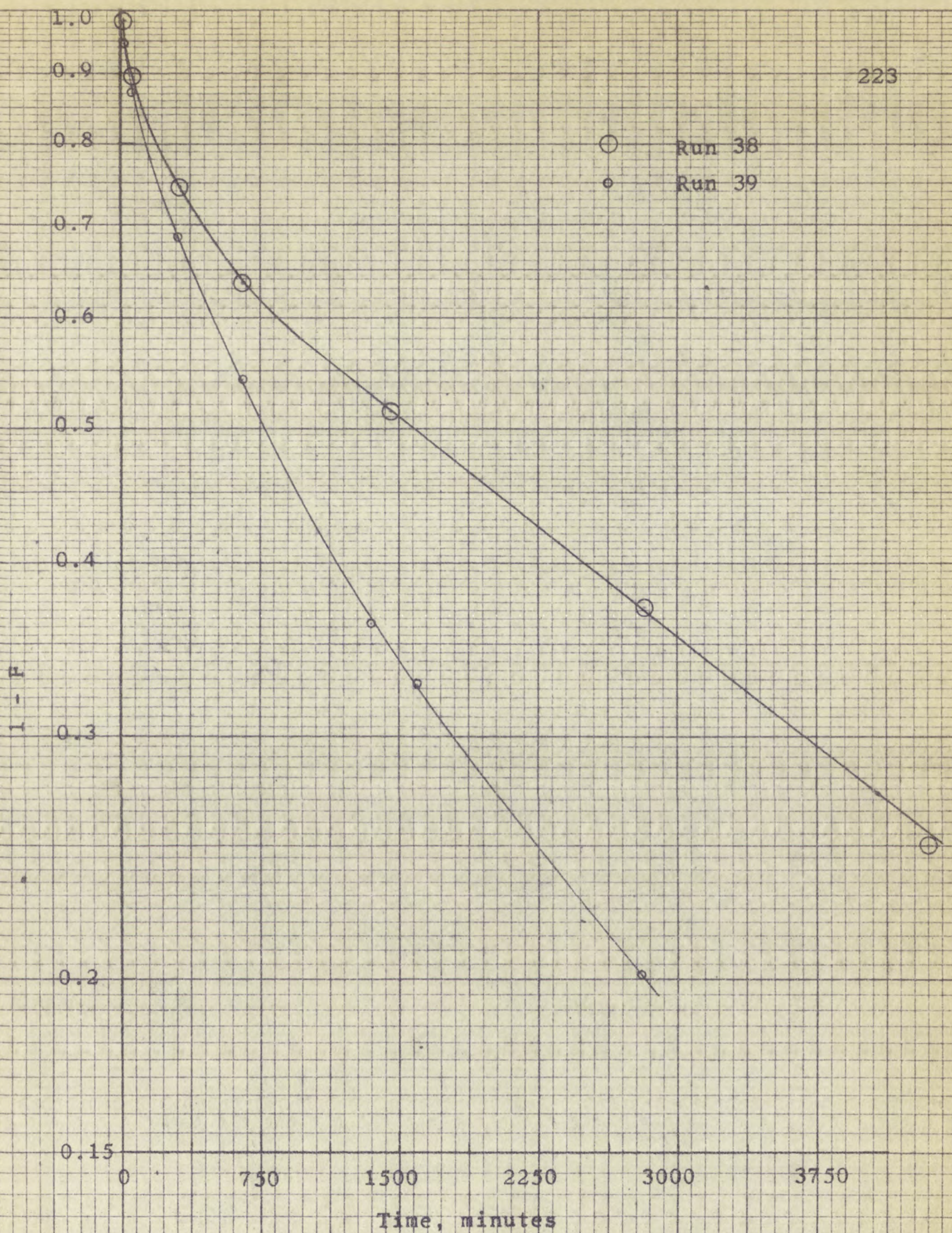


Figure 6

Exchange Curves for Runs 38 and 39







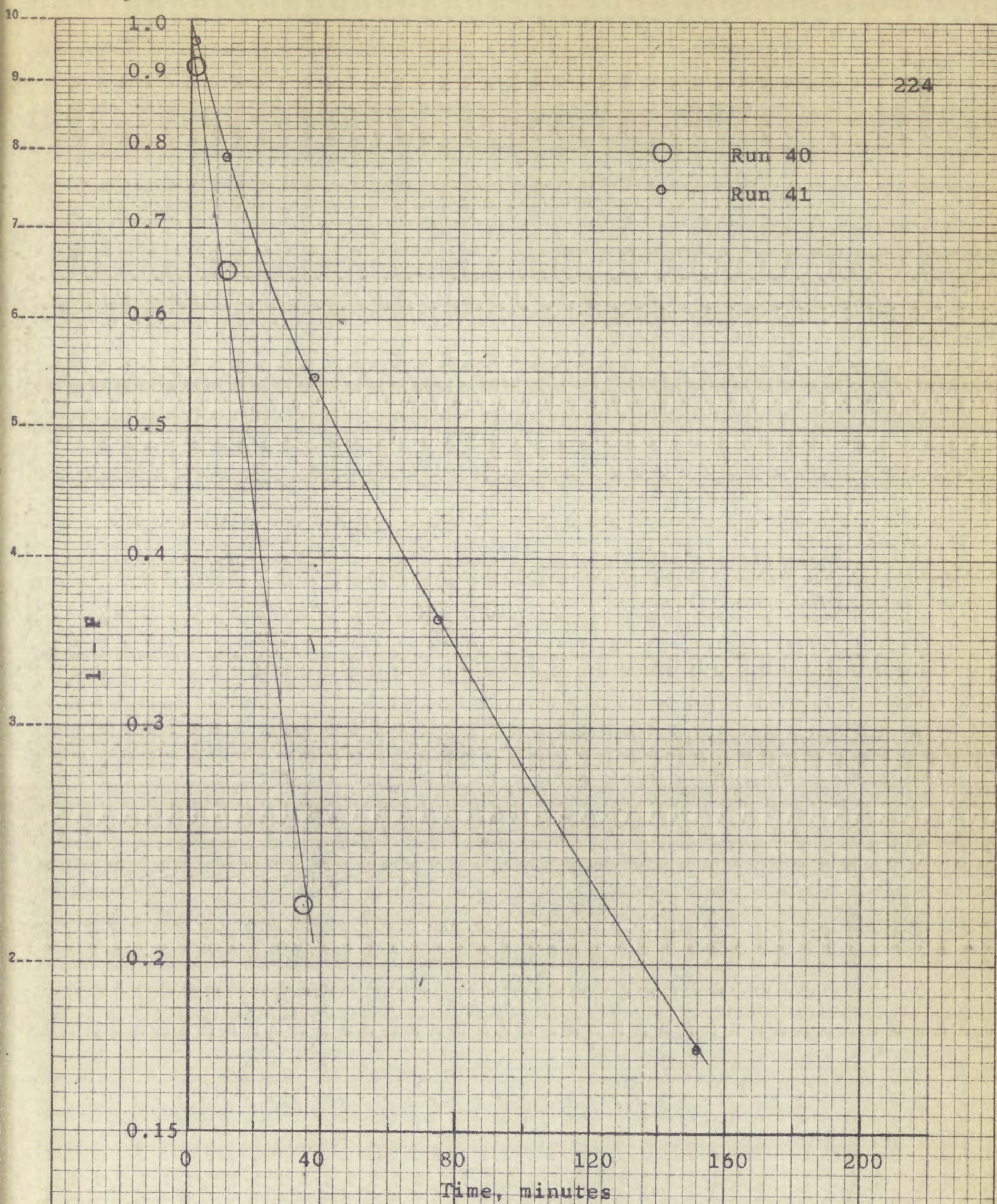
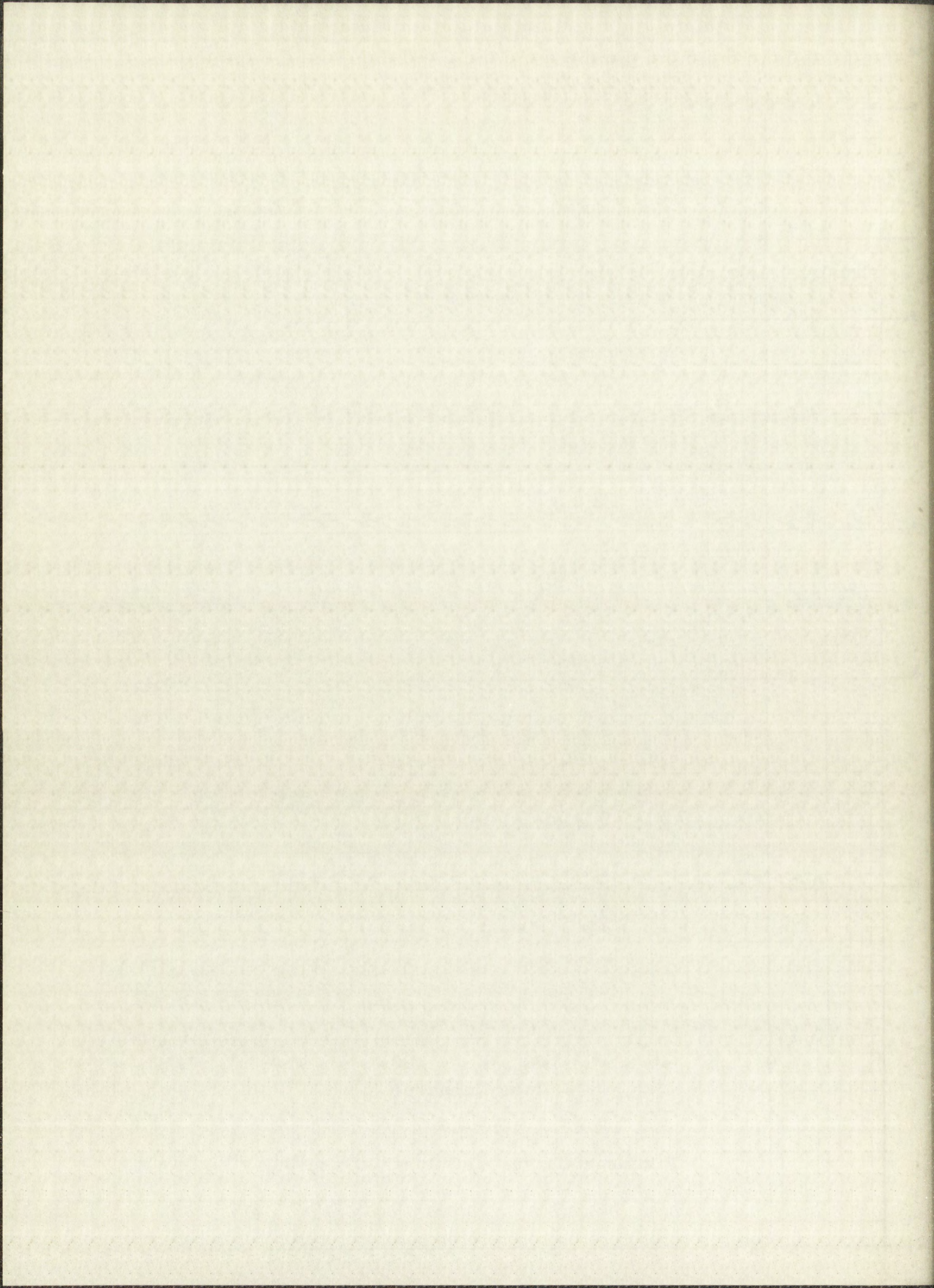


Figure 7

Exchange Curves for Runs 40 and 41







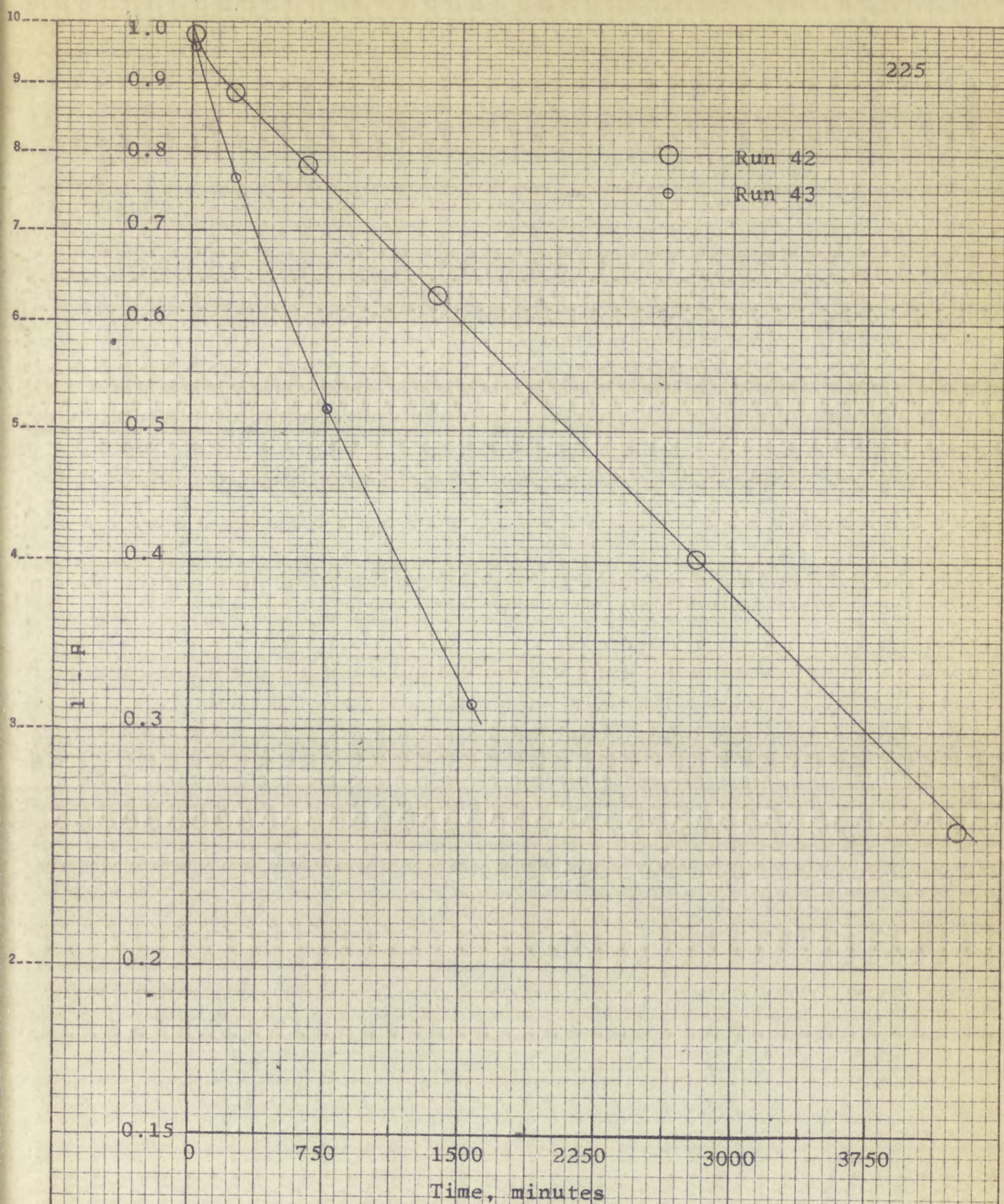
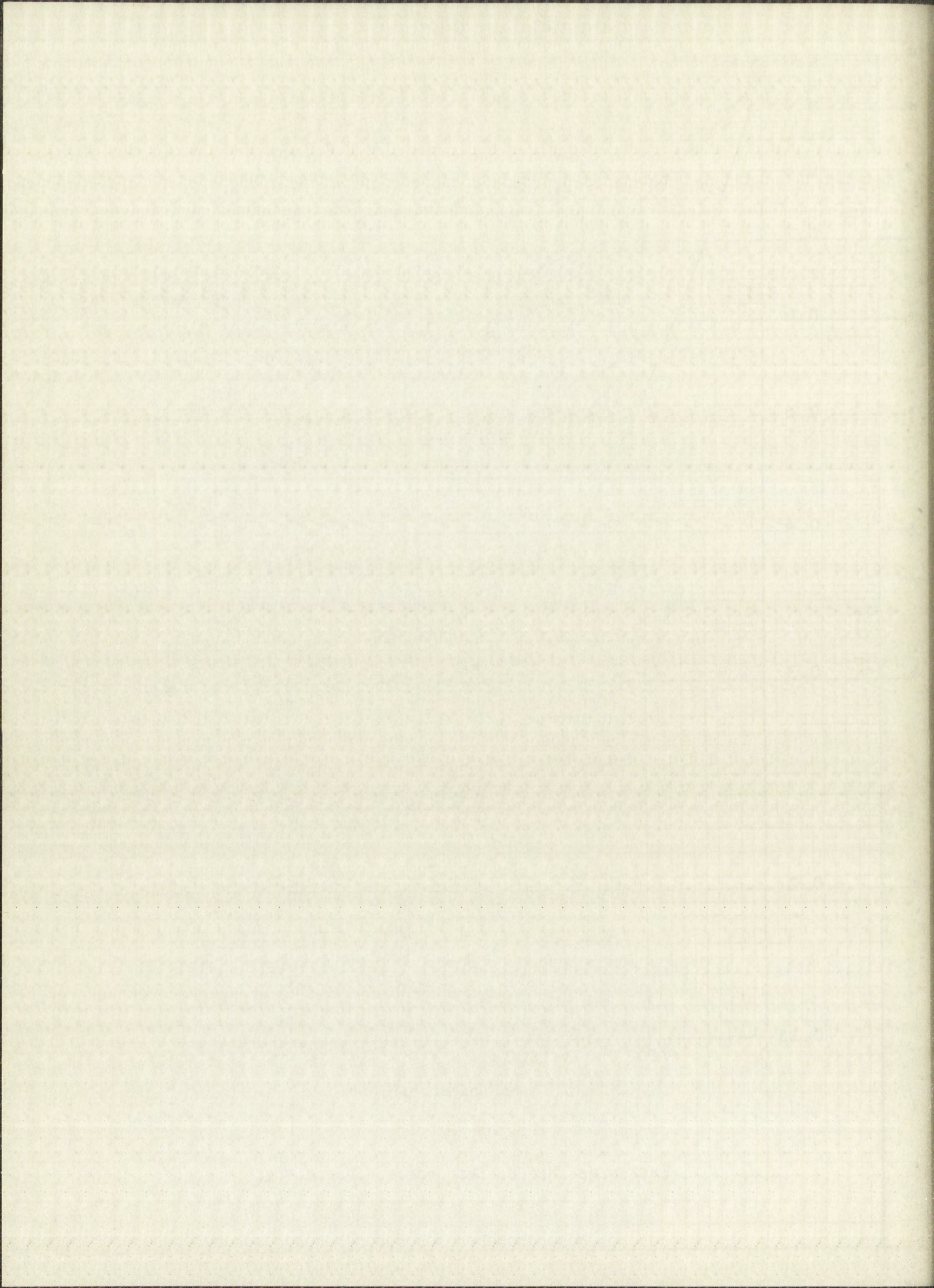


Figure 8

Exchange Curves for Runs 42 and 43







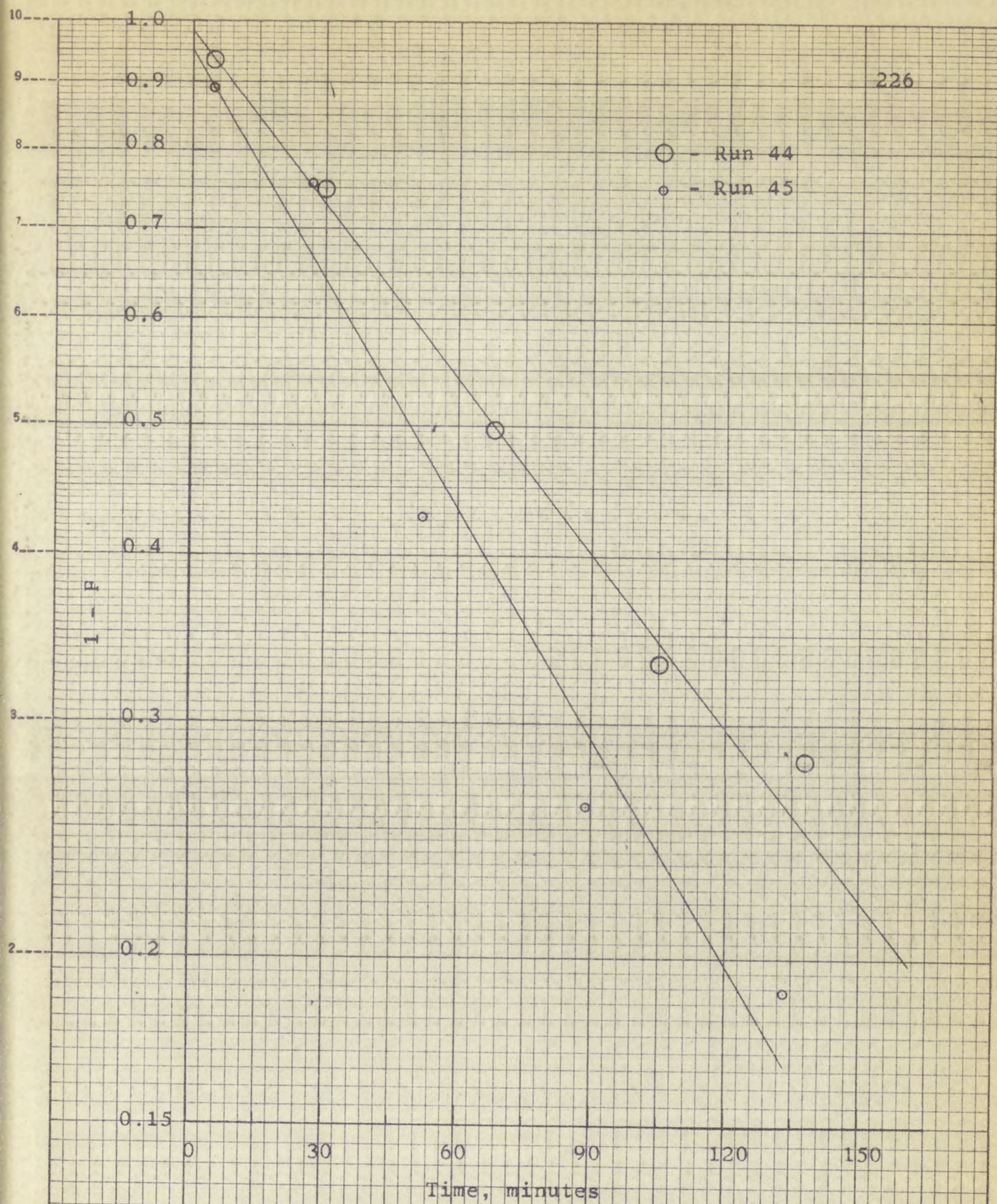


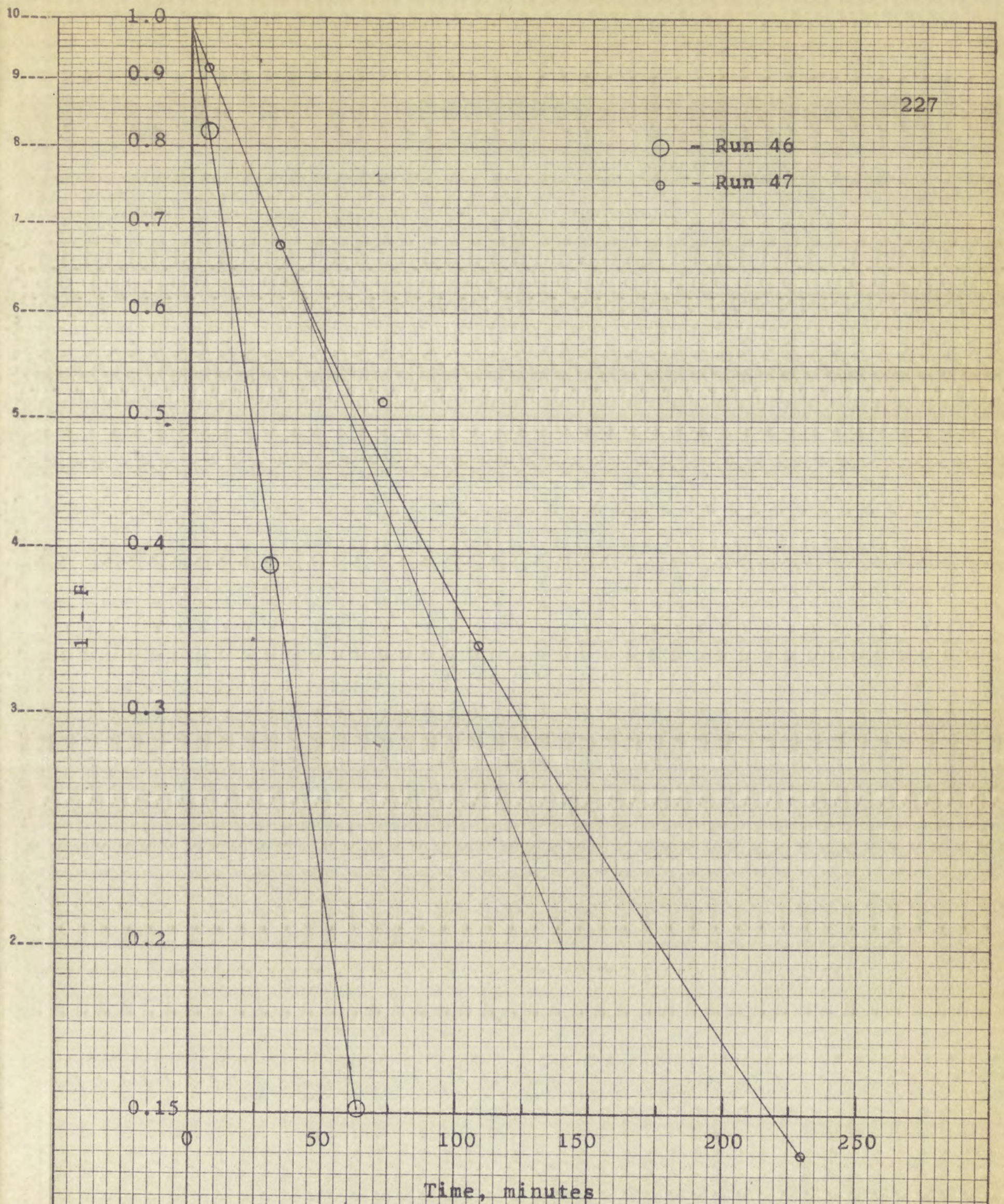
Figure 9

Exchange Curves for Runs 44 and 45







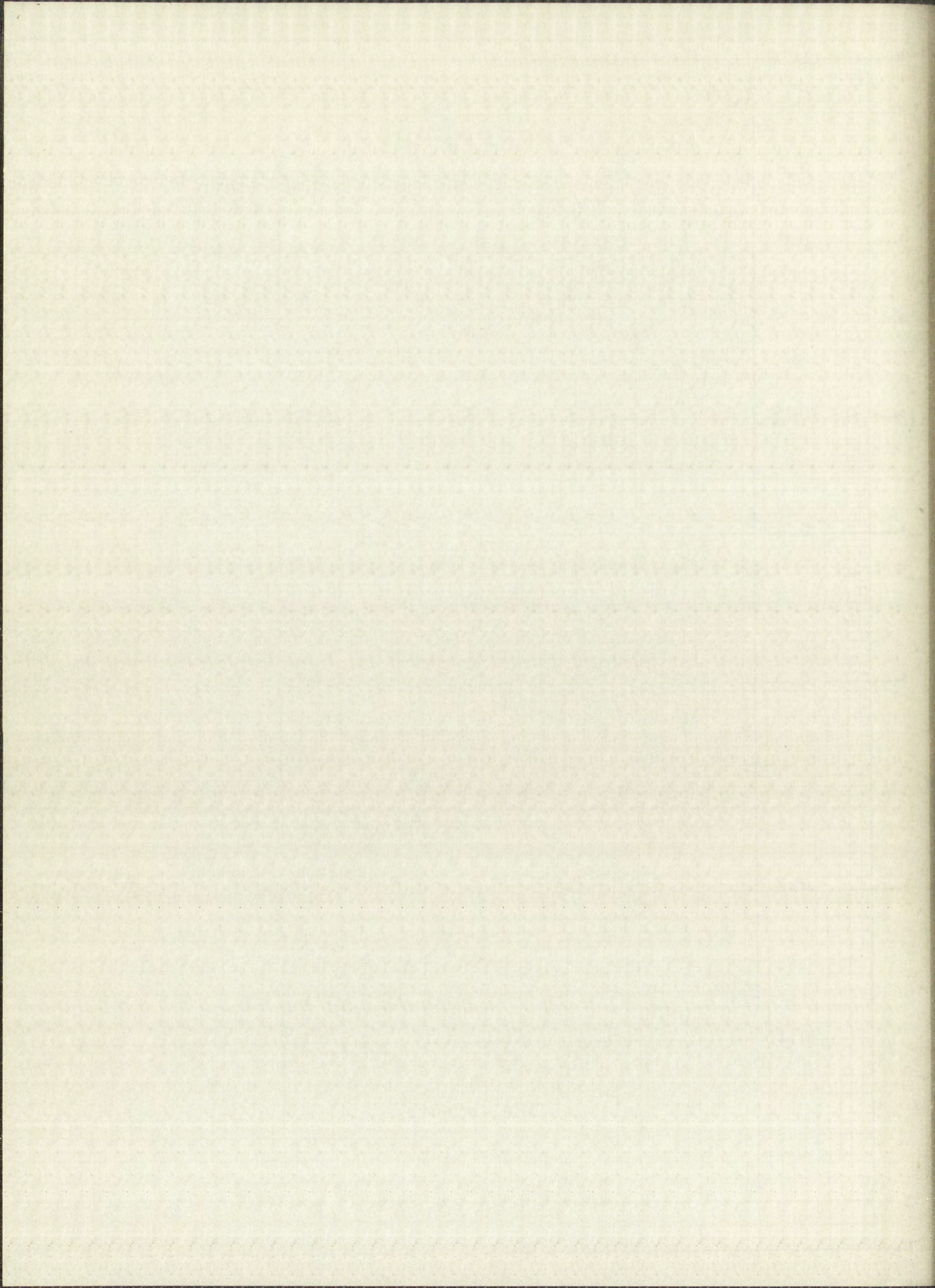


Time, minutes

Figure 10

Exchange Curves for Runs 46 and 47







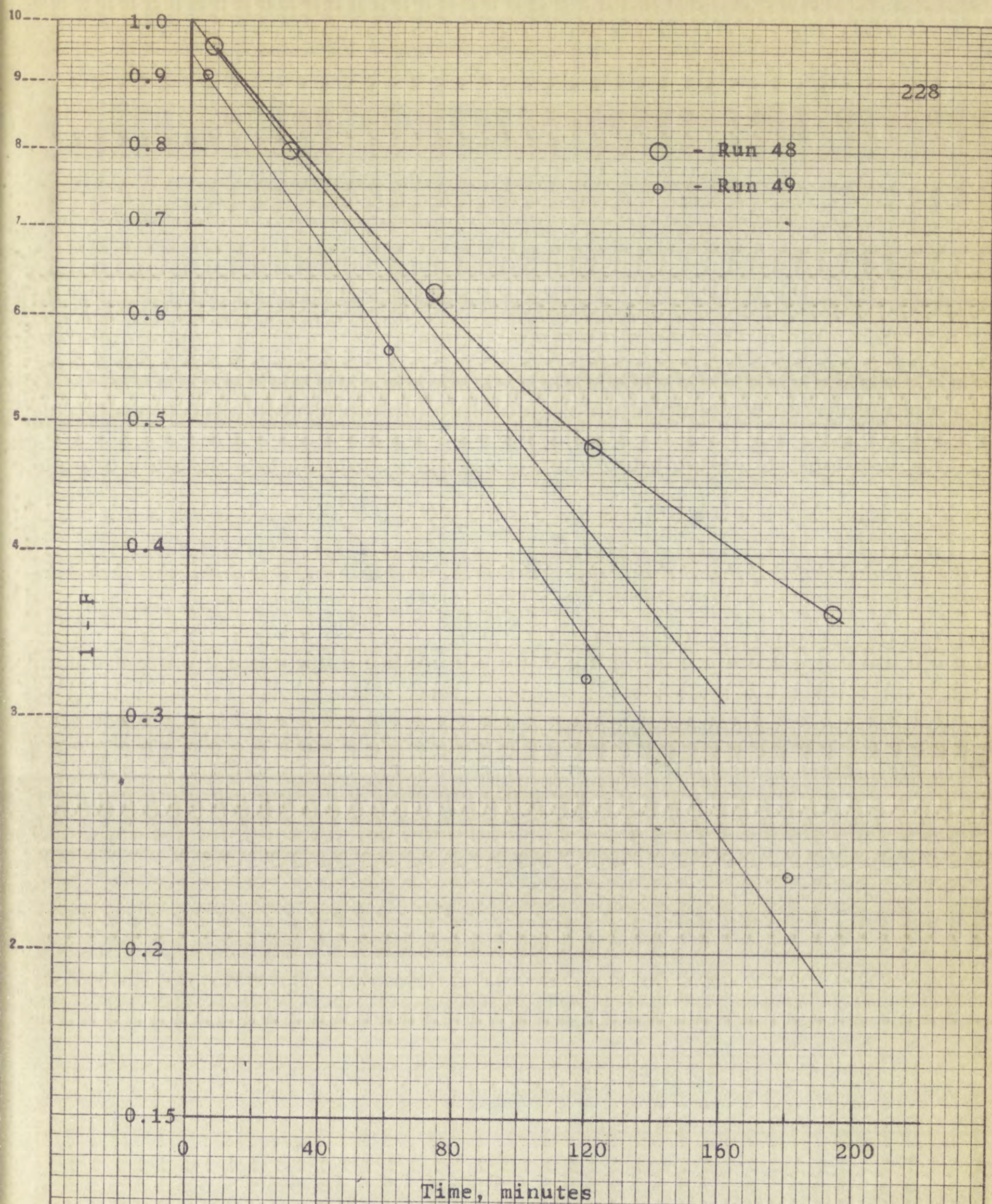


Figure 11

Exchange Curves for Runs 48 and 49

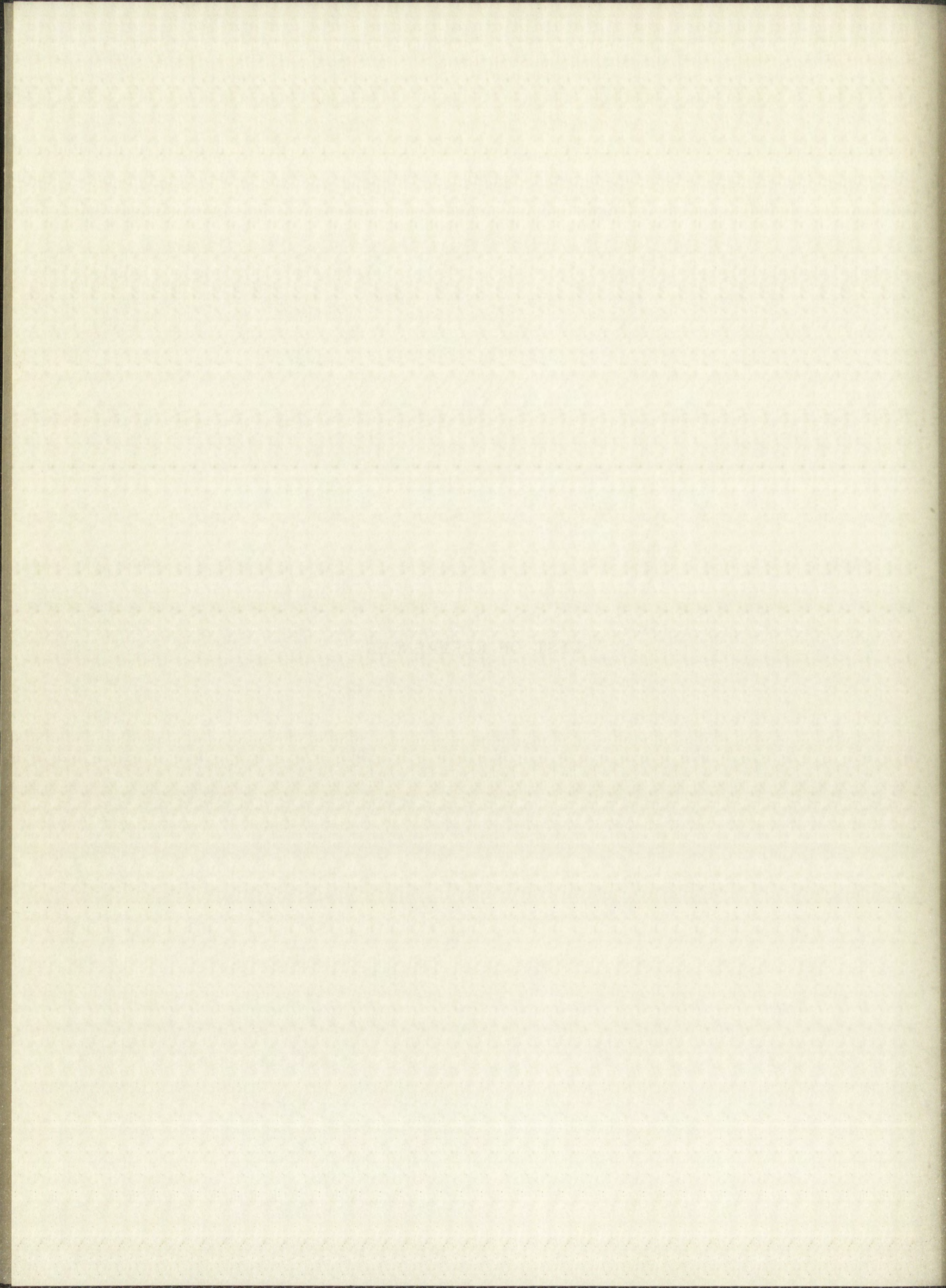






## LIST OF REFERENCES



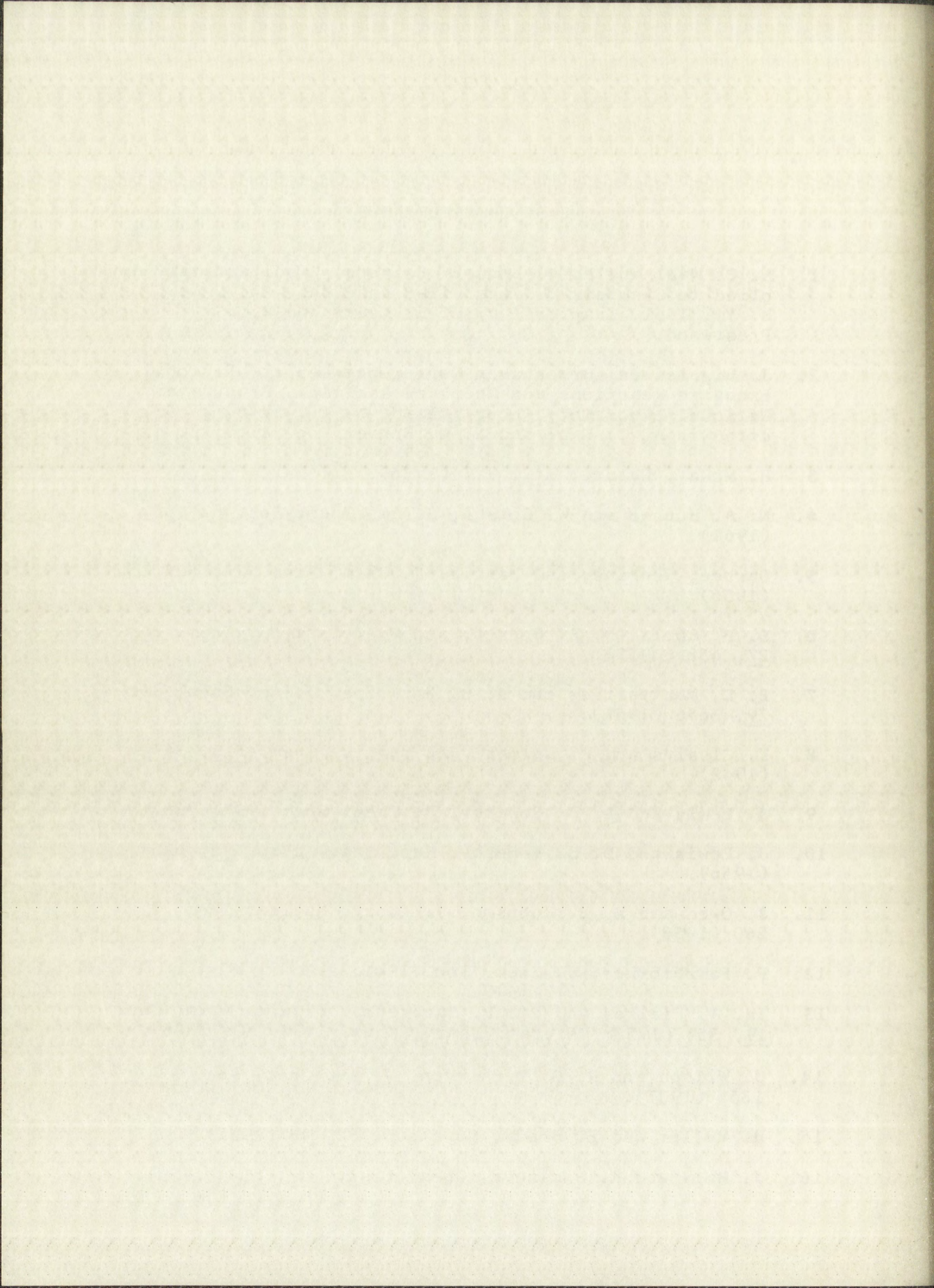




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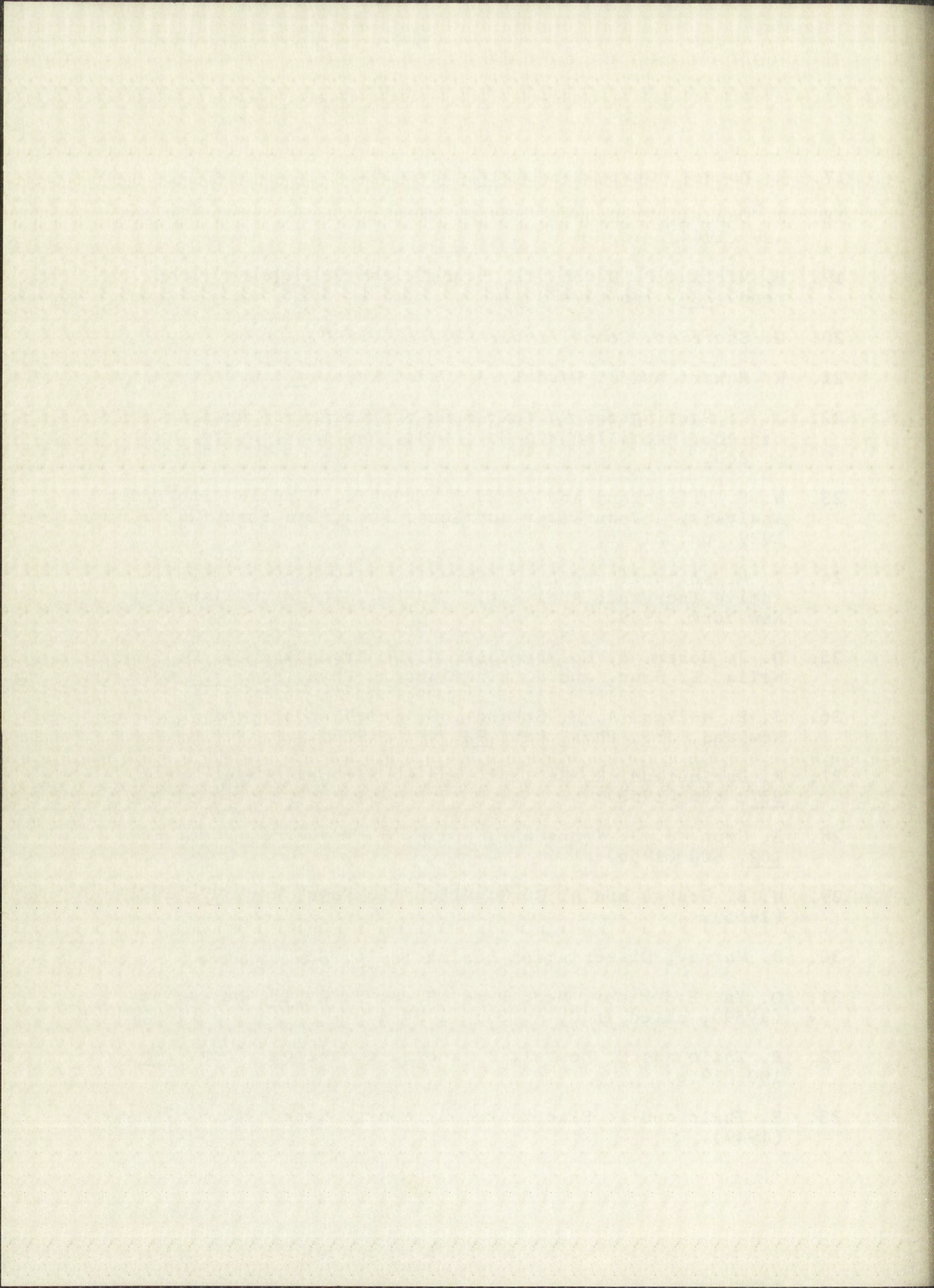






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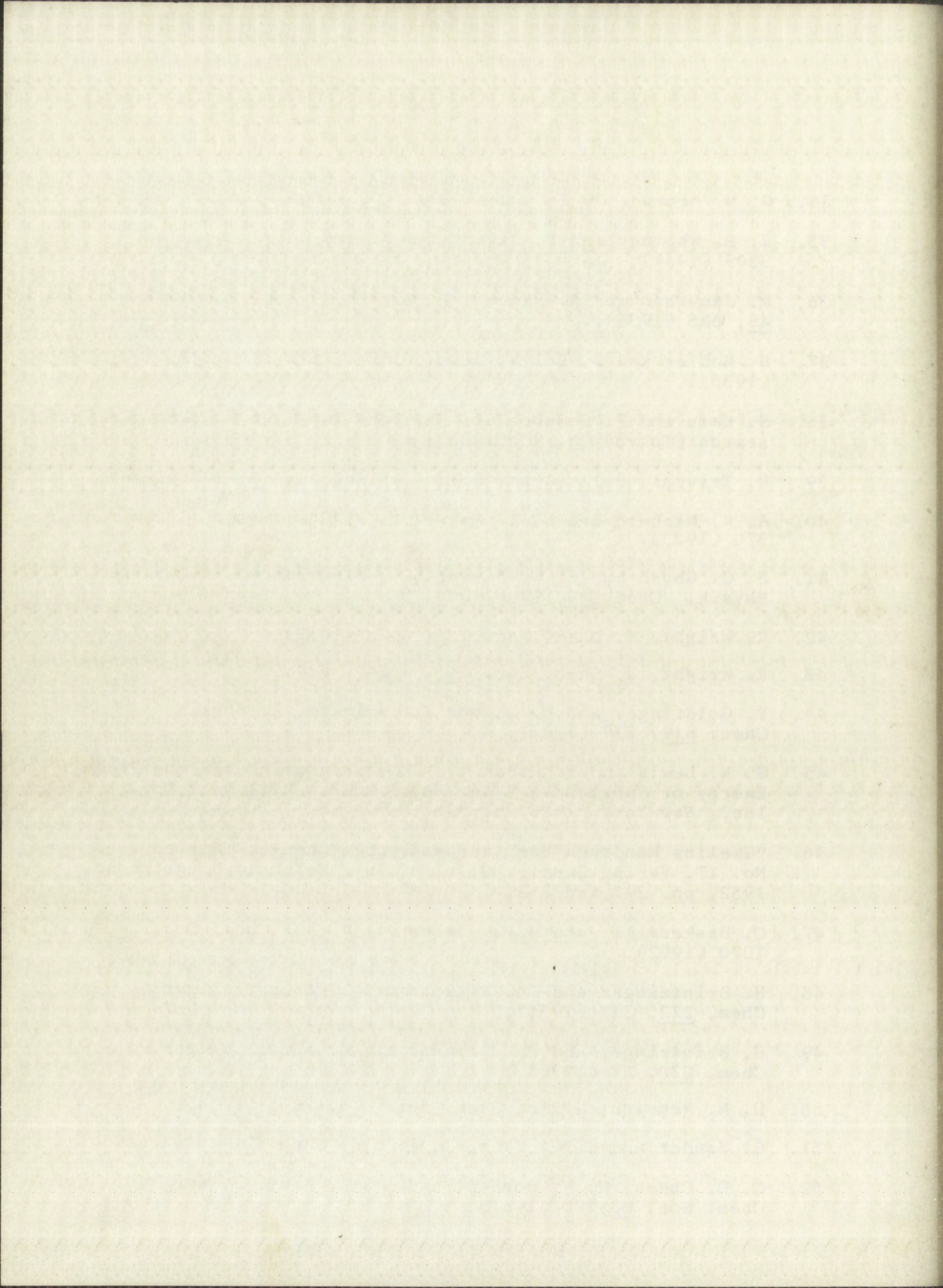






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INTRODUCTION

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