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# Exchange Reactions of the Transuranium Elements Section 1. Am(III)-Am(V)-Am(VI), Am(III)- Am(V), and Am(V)-Am(VI)

Thomas K. Keenan

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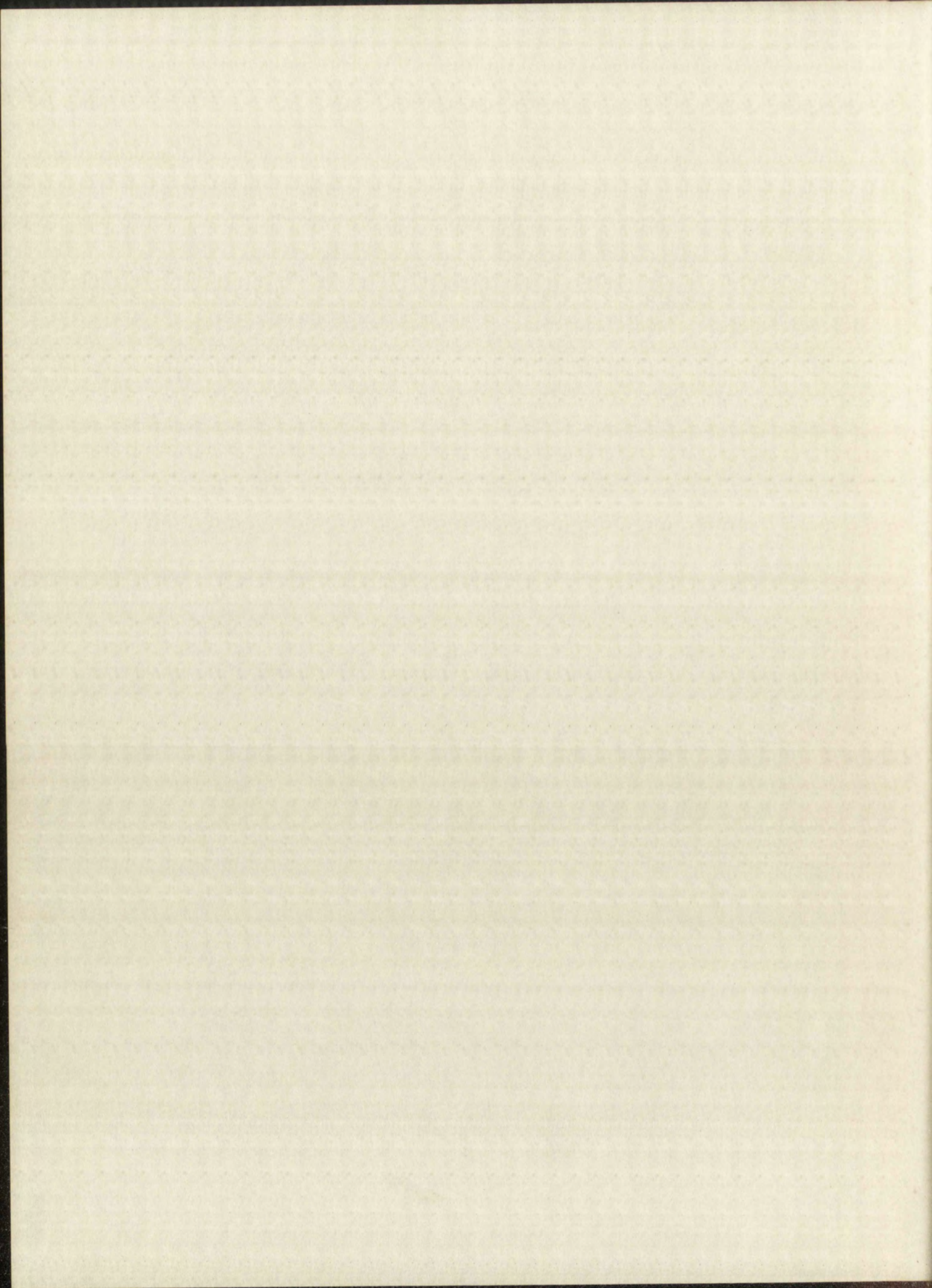


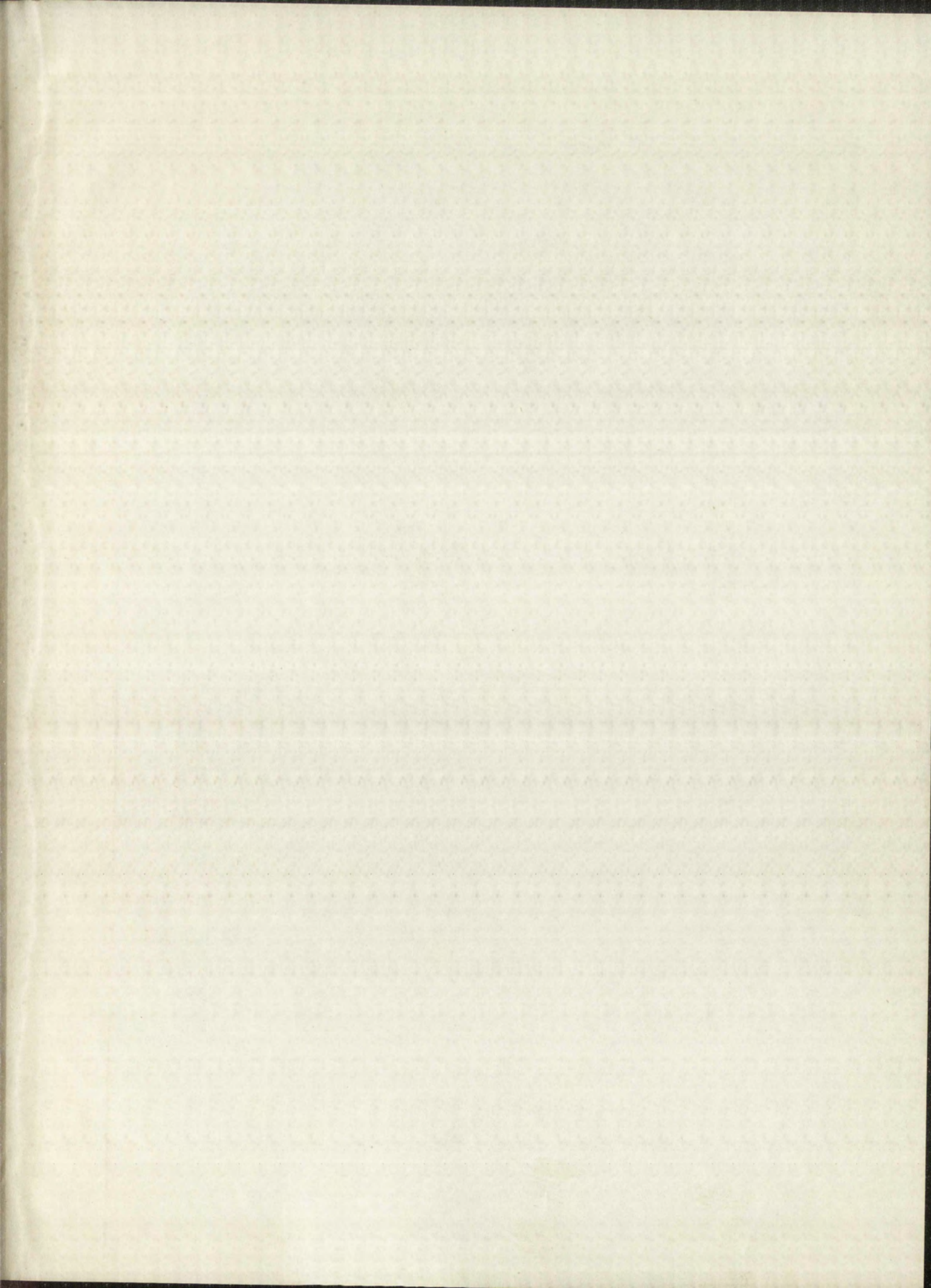
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EXCHANGE REACTIONS OF THE TRANSURANIUM ELEMENTS

SECTION I.

Am(III)-Am(V)-Am(VI), Am(III)-Am(V), AND Am(V)-Am(VI)

By

Thomas K. Keenan

A Dissertation

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

The University of New Mexico  
1954



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. J. Casteller*

DEAN

*January 26, 1954*

DATE

EXCHANGE REACTIONS OF THE TRANSURANIUM ELEMENTS

SECTION I.

Am(III)-Am(V)-Am(VI), Am(III)-Am(V) AND Am(V)-Am(VI)

(This dissertation is divided into two sections. Section I is unclassified, Section II contains classified material and is on file in the Los Alamos Scientific Laboratory)

Committee

*John F. Suttis*

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*Richard L. Ferm*

*Milton Kahn*

This is a copy of the report prepared by the committee on the subject of the University of California, Berkeley, California, 1954.

REPORT OF THE COMMITTEE

*James R. ...*

EXCHANGE REACTION OF THE ...

SECTION I

As(III)-As(V)-As(VI), As(III)-As(V), and As(V)-As(VI)

(This classification is a final one, and Section I is unclassified, Section II contains classified material and is on the list of Los Alamos Scientific Laboratory)

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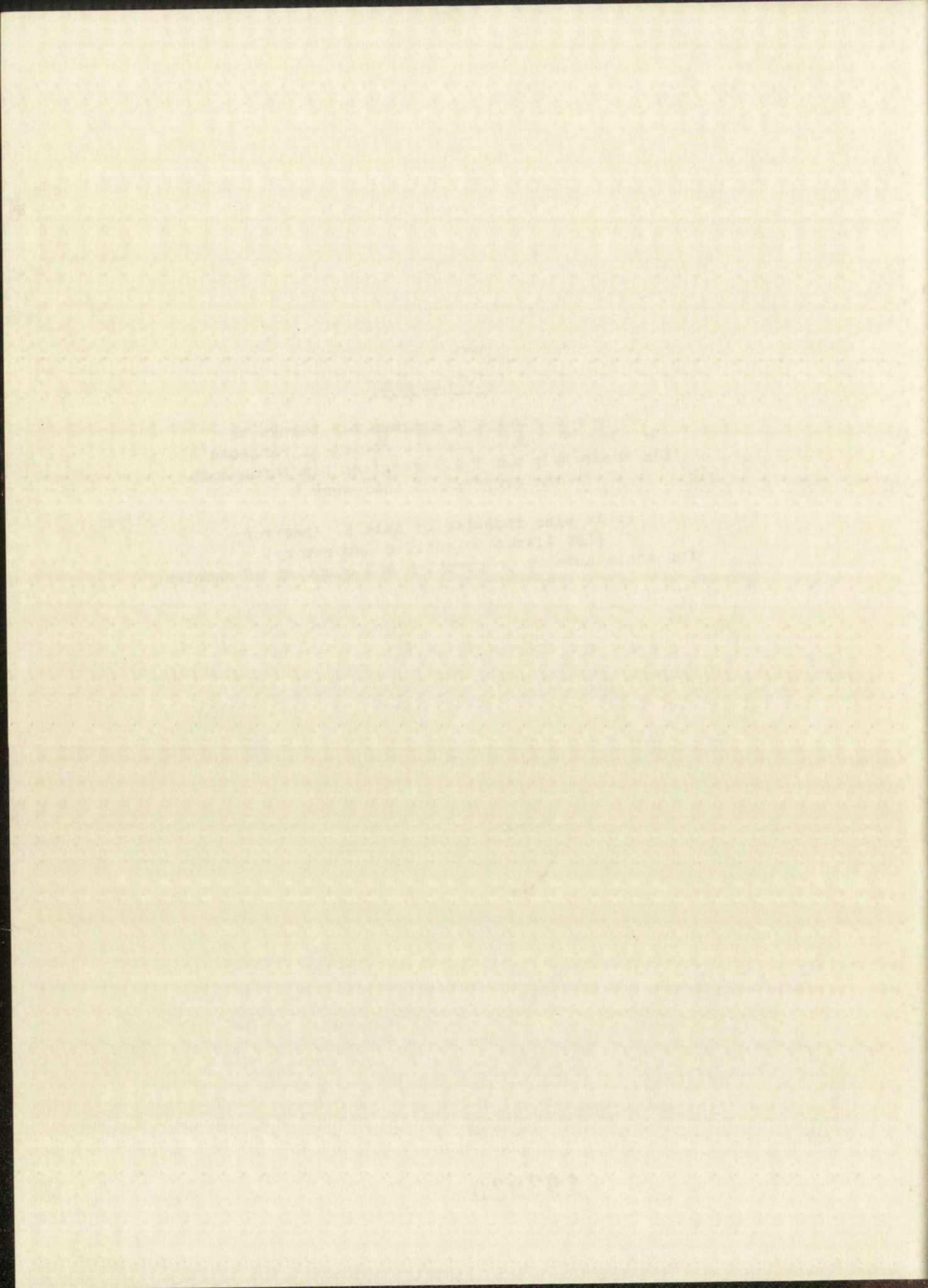
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(Los Alamos Scientific Laboratory)  
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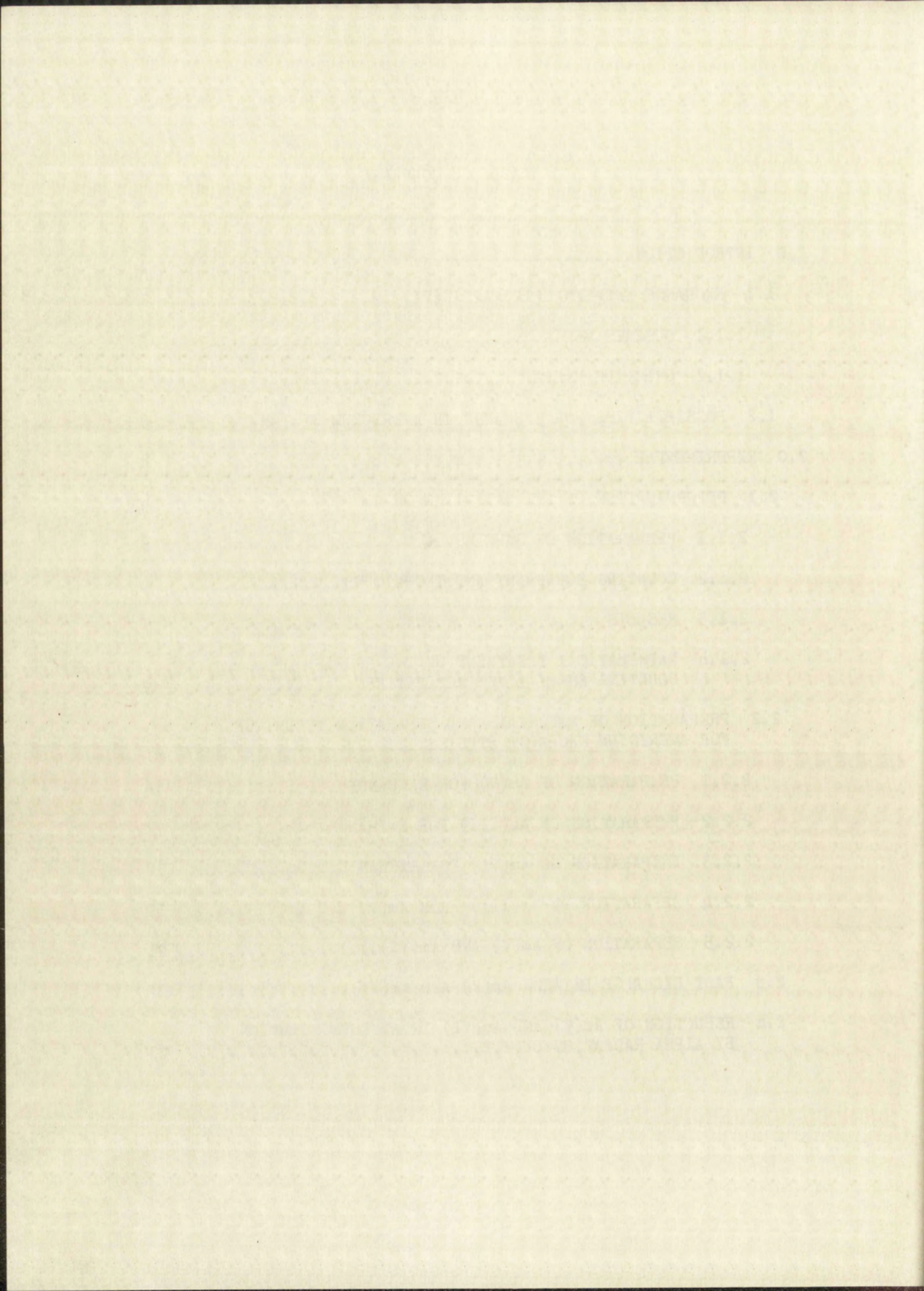
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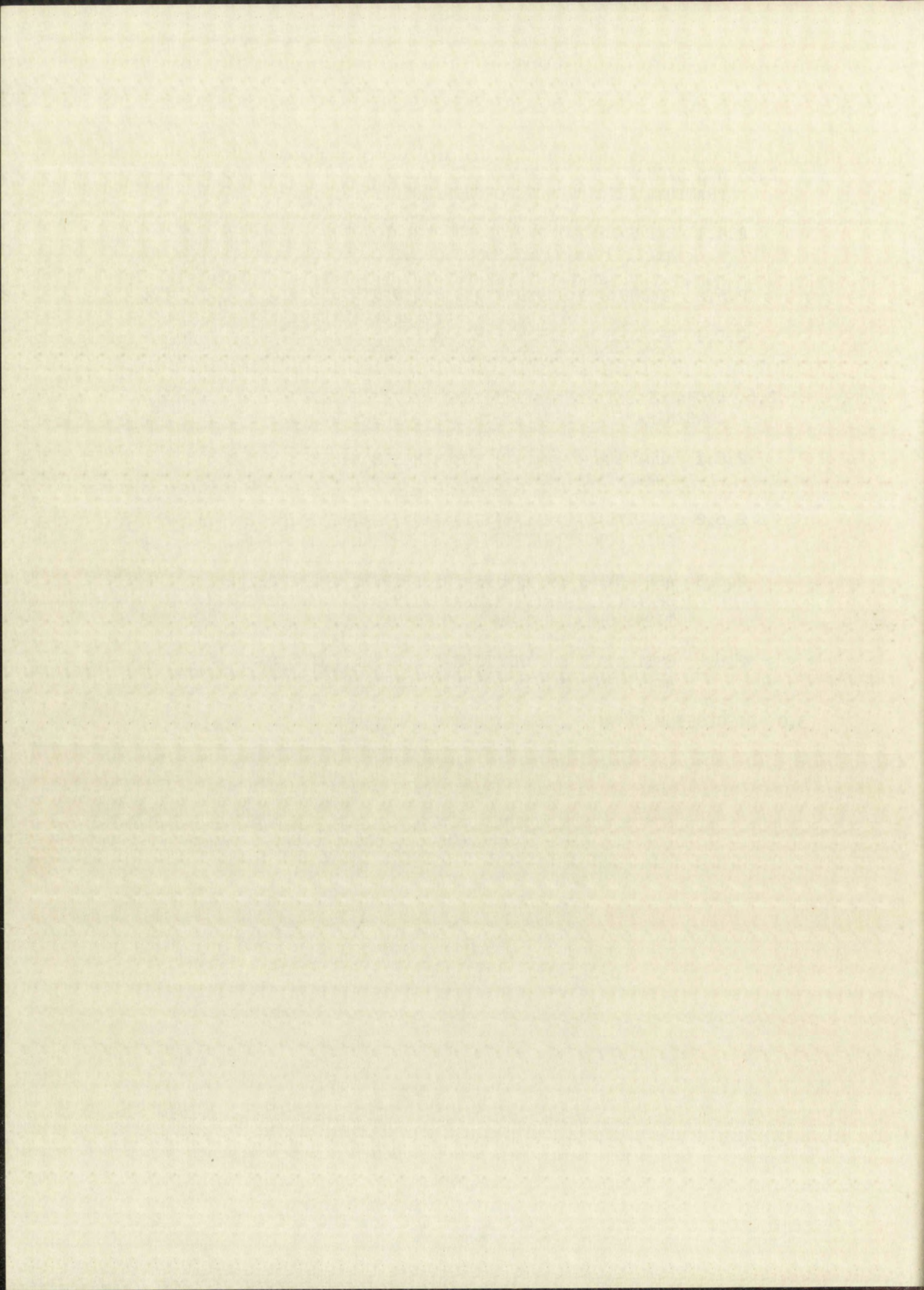


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## 1.0 INTRODUCTION

No exchange work prior to this dissertation has been reported on the americium system. Neptunium exchange is presently being studied by J. C. Hindman and co-workers<sup>(1)</sup> at the Argonne National Laboratory,

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(1) J. Hindman, D. Cohen, and J. Sullivan, ANL-5042 (1953).

---

but has not been completely reported. Study of uranium exchange, which is still in an unsatisfactory state, has been limited to the U(IV)-(VI) exchange<sup>(2-4)</sup>.

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(2) R. Betts, Can. J. Research 26B, 702 (1948).

(3) A. Grosse, MDDC-1644 (1948).

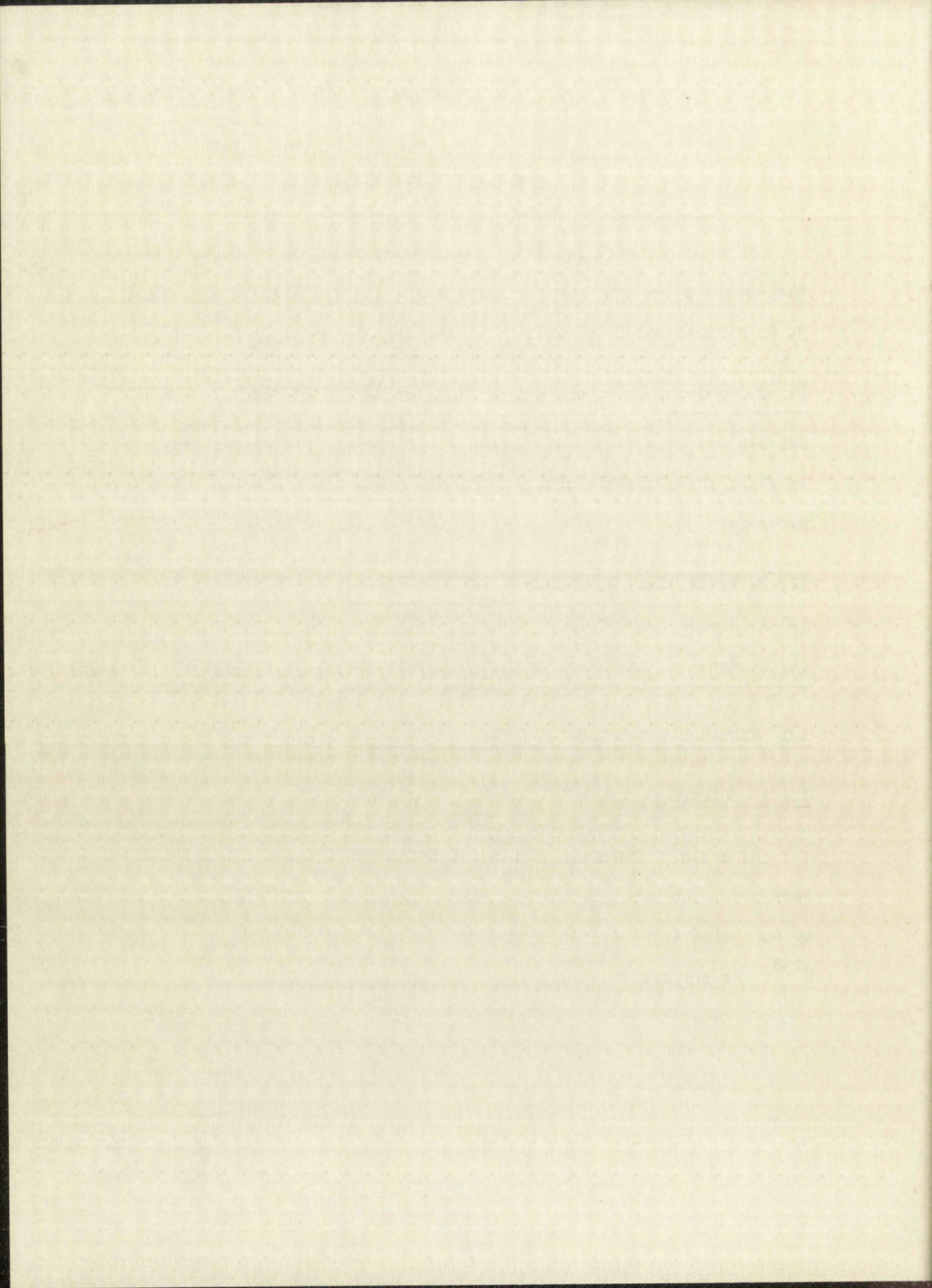
(4) E. Rona, J. Am. Chem. Soc. 72, 4339 (1950).

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### 1.1 EXCHANGE BETWEEN U(IV) AND U(VI).

#### 1.1.1 SULFATE MEDIA.

R. Betts<sup>(2)</sup> determined that the U(IV)-U(VI) exchange was light-sensitive, the exchange being markedly catalyzed by incandescent light by approximately a factor of 20. The tracer was  $U^{233}$  in solutions of  $U^{238}$ . He proposed the following rate law in the presence of  $SO_4^{--}$ :



$R = 1.5 \times 10^{-4} (IV)^{0.5} (VI)^{0.5} (H^+)^{-3}$ . No mechanism was postulated to explain the rather unexpected half-order dependencies of the exchanging species. This exchange was investigated over a concentration range of 0.01-0.02 f U(IV); 0.01-0.02 f U(VI); 2.79 f  $H^+$  and in solutions of constant ( $HSO_4^- + SO_4^{--}$ ) concentrations of 1.91 f. All of these experiments were carried out under the illumination of a 300 watt tungsten light bulb 4 cm. from the reaction vessel. The temperature range studied was 24°-36°C. The kinetics of the dark reaction were not investigated.

A. Grosse<sup>(3)</sup> carried out one run with U(IV) = 0.043 f; U(VI) = 0.060 f;  $H_2SO_4$  = 0.186 f. He reports a half-time for these conditions as 43 hours.

### 1.1.2 CHLORIDE MEDIA.

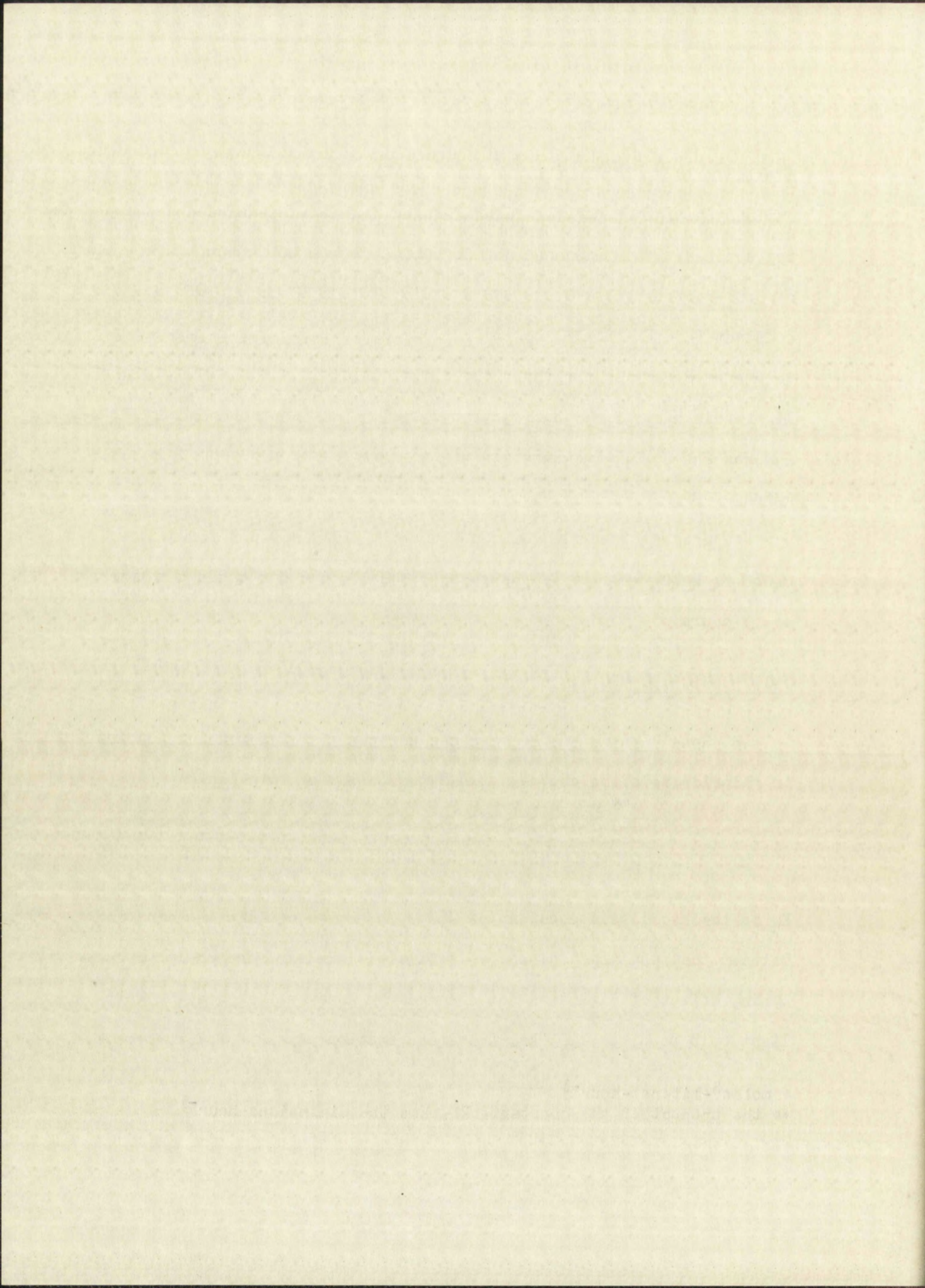
E. Rona<sup>(4)</sup> studied the exchange between the same uranium species in chloride solution and determined the following rate law:

$$R = k K_1 \frac{[U(IV)]^2 [U(VI)]}{\left[ \frac{H^+}{K_h} + 1 \right] [H^+]^2}$$

$K_h$  is the hydrolysis constant of U(IV),  $K_1$  is an equilibrium constant between the reacting ions and an activated complex. The positive catalyzing effect of light was not observed by Rona, although a 100 watt light bulb used was 100 cms. from the reaction vessel. All runs made

\* moles<sup>3</sup>-liters<sup>1</sup>-hour<sup>-1</sup>

\*\* the product of the constants  $kK_1$  has the dimensions hour<sup>-1</sup>





by Rona were in chloride solution, some being run in high ionic environments of NaCl or NaClO<sub>4</sub> to study the effect of increased ionic strength. No change in the rate of exchange was noted. The numerical values of the equilibrium constant  $K_1$  and the specific rate constant  $k$  were not given.

1.2 POSSIBILITIES FOR EXCHANGE STUDY IN THE AMERICIUM SYSTEM.

Although the uranium case seems far from completely elucidated as yet, it would seem of interest to extend these exchange studies to the element americium. Reasonable quantities of this element are available, and it exhibits three well-defined valence states in solution. It is fortunate that for this element, a tracer exists which emits an entirely different type of radiation. This may be summarized as follows:

TABLE I

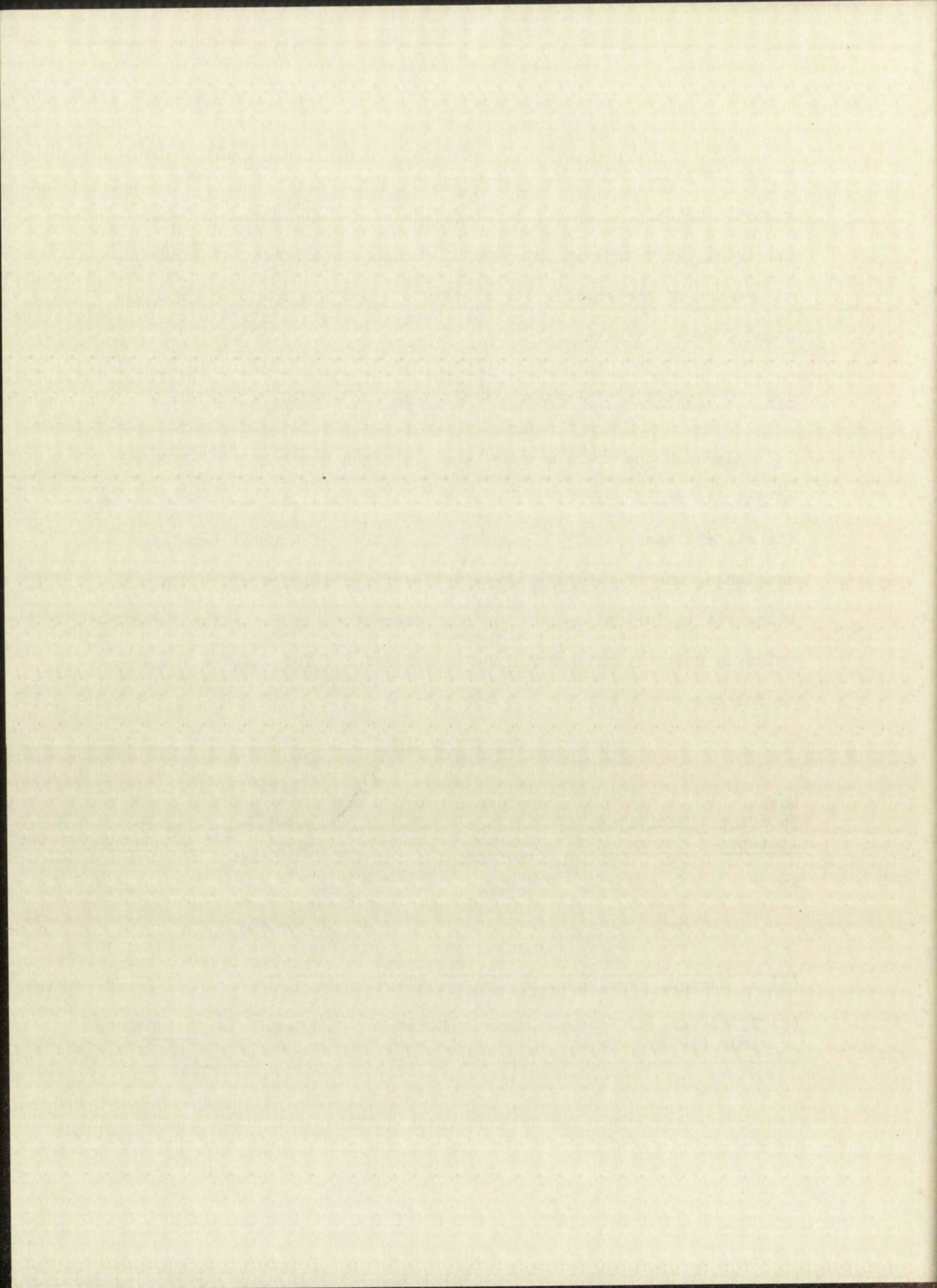
<u>Most Abundant Isotope</u>	<u>Radiation, Energy</u>	<u>Solution Valence States</u>	<u>Tracer Isotope</u>	<u>Radiation, Energy</u>	<u>Tracer Production</u>
Am <sup>241</sup>	(5) α, 470 yr., E <sub>α</sub> = 5.47 Mev	(III), (V), (VI)	Am <sup>242m</sup>	(6) β, 16.0 hr., E <sub>β</sub> = 0.628 Mev	Irradiation of Am <sup>241</sup>

---

(5) B. Harvey, Phys. Rev. 85, 482 (1952).

(6) T. Keenan, R. Penneman, and B. McInteer, J. Chem. Phys. 21(10), 1802 (1953).

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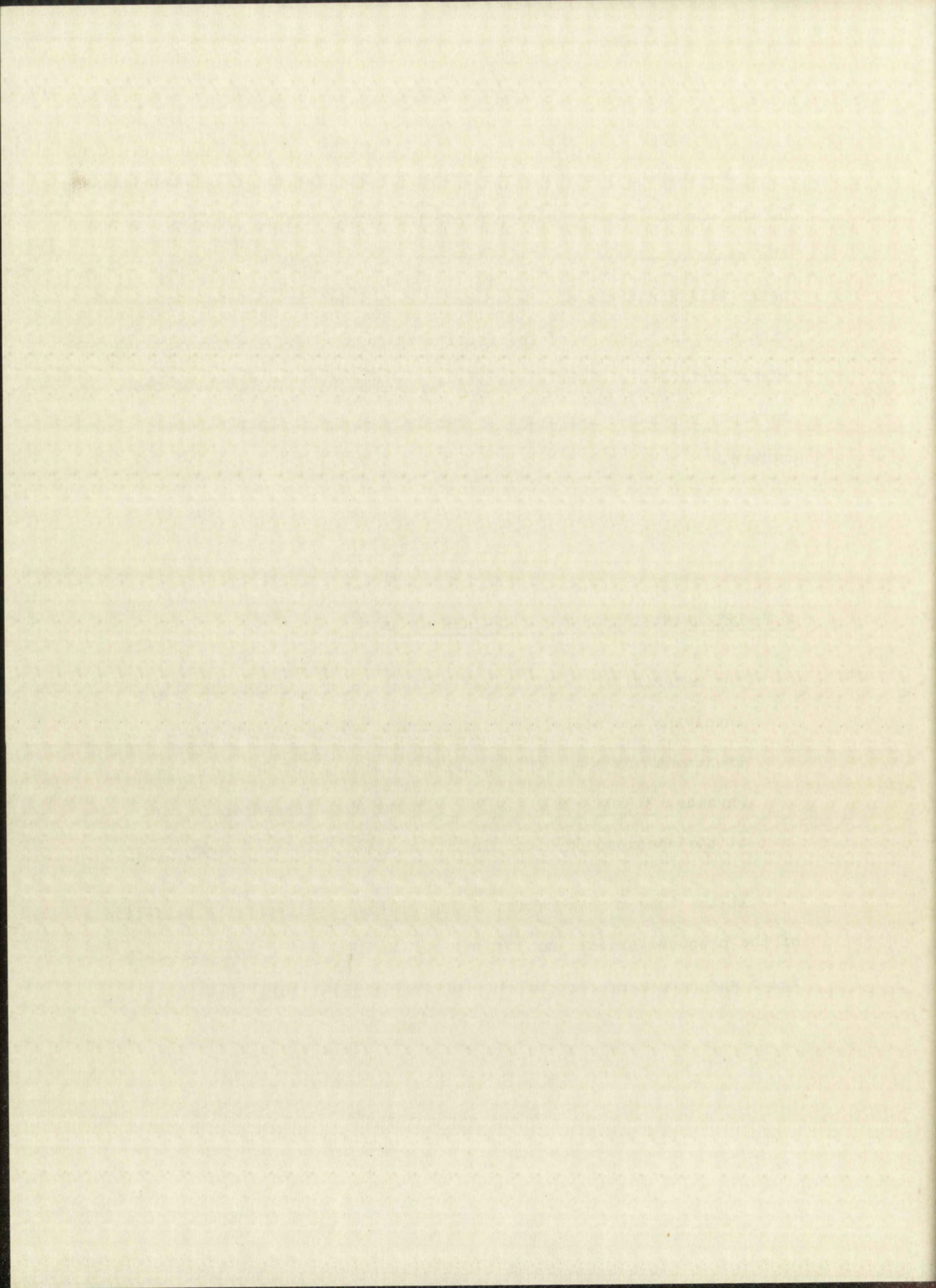
Determining the amount of tracer in the presence of a large excess of the common isotope is simple for the beta-emitting isotope. Because the range of alphas is only a few mgs./cm<sup>2</sup> in aluminum while energetic betas will penetrate of the order of a gm./cm<sup>2</sup>, a very thin aluminum window on the chamber of the usual beta counter will completely absorb alpha particles without seriously affecting the beta counting rate. An alpha counting instrument is insensitive to 10<sup>9</sup> beta disintegrations/minute.

## 2.0 EXPERIMENTAL

### 2.1 DETERMINATION OF THE HALF-LIFE OF Am<sup>242m</sup>.

(The material to be described in Sections 2.1.1 through 2.1.4, involving the half-life measurements and the mathematical treatment has been published in the Journal of Chemical Physics, 21(10), 1802 (1953). It was also presented in part at the American Physical Society meeting, May 1-3, 1952.)

At the time this work was begun, an exact value of the half-life of the proposed tracer, Am<sup>242m</sup>, was not available. A more accurate value was necessary for the study of the exchange rate between various



americium aqueous ions.

The americium isotope of mass 241 undergoes neutron capture to form  $\text{Am}^{242\text{m}}$ , which decays 64%<sup>(7)</sup> by beta-particle emission to form

---

(7) G. Hanna, B. Harvey, and N. Moss, Phys. Rev. 81, 486 (1951).

---

$\text{Cm}^{242}$ . The half-life of  $\text{Am}^{242\text{m}}$  has been previously reported as  $16 \pm 3$  hrs.<sup>(8)</sup> and  $15.75 \pm 0.25$  hrs.<sup>(9)</sup>

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(8) L. Asprey and W. Manning, "The Transuranium Elements", NNES-IV-14B, McGraw-Hill Book Co., New York (1949), p. 1595.

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(9) B. Harvey, Chalk River, private communication.

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#### 2.1.1 PREPARATION OF SAMPLES

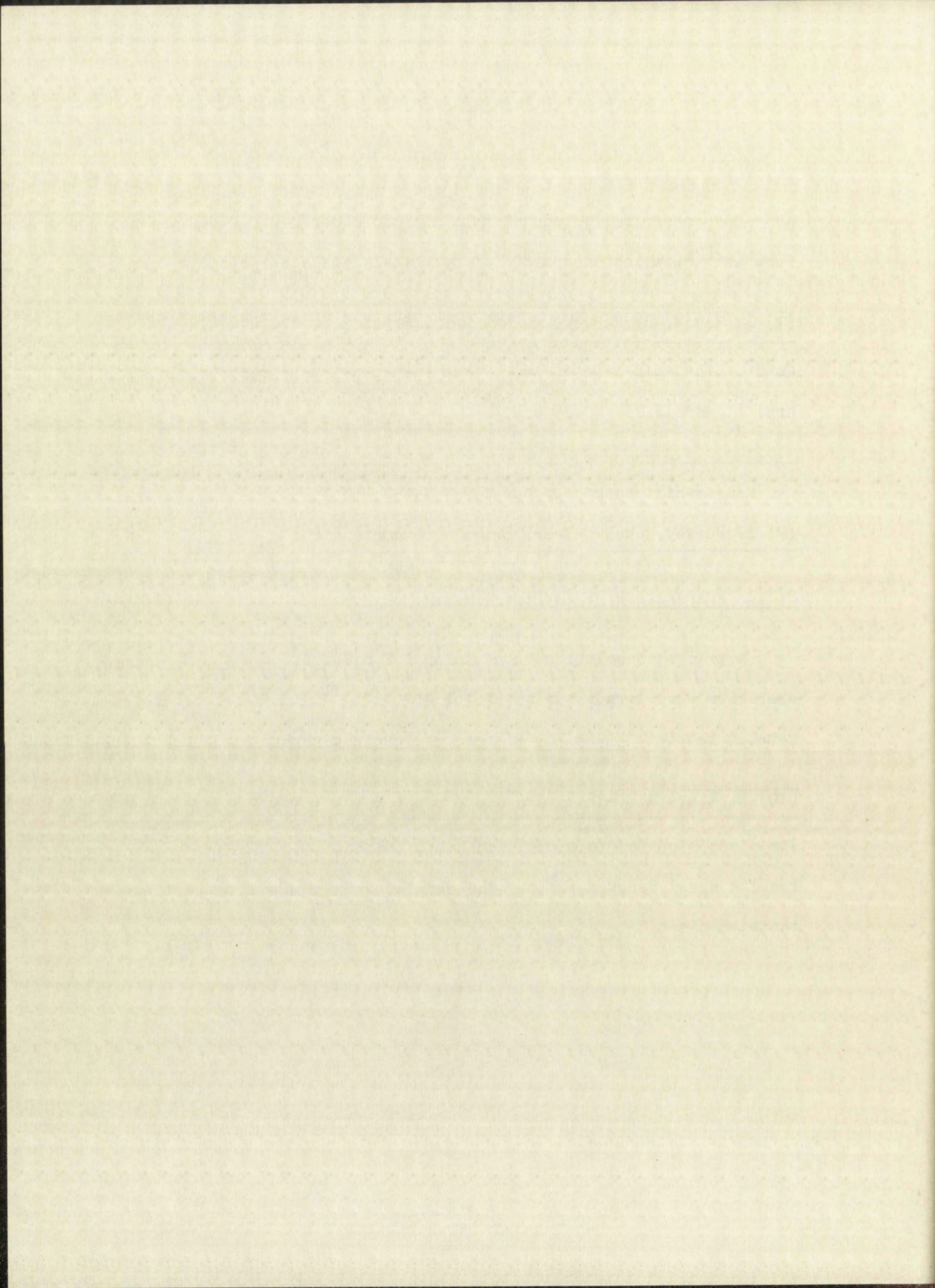
Nitric acid solutions containing 1-2  $\mu\text{gms}$ . of pure (>99% purity) americium were irradiated at a flux of  $5 \times 10^{11}$  n/cm<sup>2</sup>/sec. in the homogeneous reactor<sup>(10)</sup> at Los Alamos. Aliquots were pipetted onto tanta-

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(10) L. King, AECD-3287 (1951).

---

lum discs, ignited to a dull red heat, and counted. Duplicate counting results were observed whether the samples were prepared on platinum or tantalum discs.



2.1.2 COUNTING EQUIPMENT AND TECHNIQUE.

The beta-particles were collected in a methane-flow external chamber which was fitted with a 7.8 mg./cm<sup>2</sup> aluminum window to block out the alpha particles resulting from unconverted Am<sup>241</sup> or Cm<sup>242</sup> daughter. These alpha particles have energies of 5.48 Mev and 6.08 Mev, respectively. The curium alpha particles have a range in aluminum of 7.13 or 7.65 mgs./cm<sup>2</sup> using the two values given for the stopping power of aluminum vs. air quoted in the review article by Livingston and Bethe<sup>(11)</sup>.

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(11) M. Livingston and H. Bethe, Rev. Mod. Phys. 9, 272 (1937).

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The pulses were fed into a PA-2<sup>(12)</sup> pulse amplifier and recorded

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(12) V. Rexroth, LA-1239 (1951).

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on an SC-3<sup>(13)</sup> binary scaler which had a factor of 1024. Careful exper-

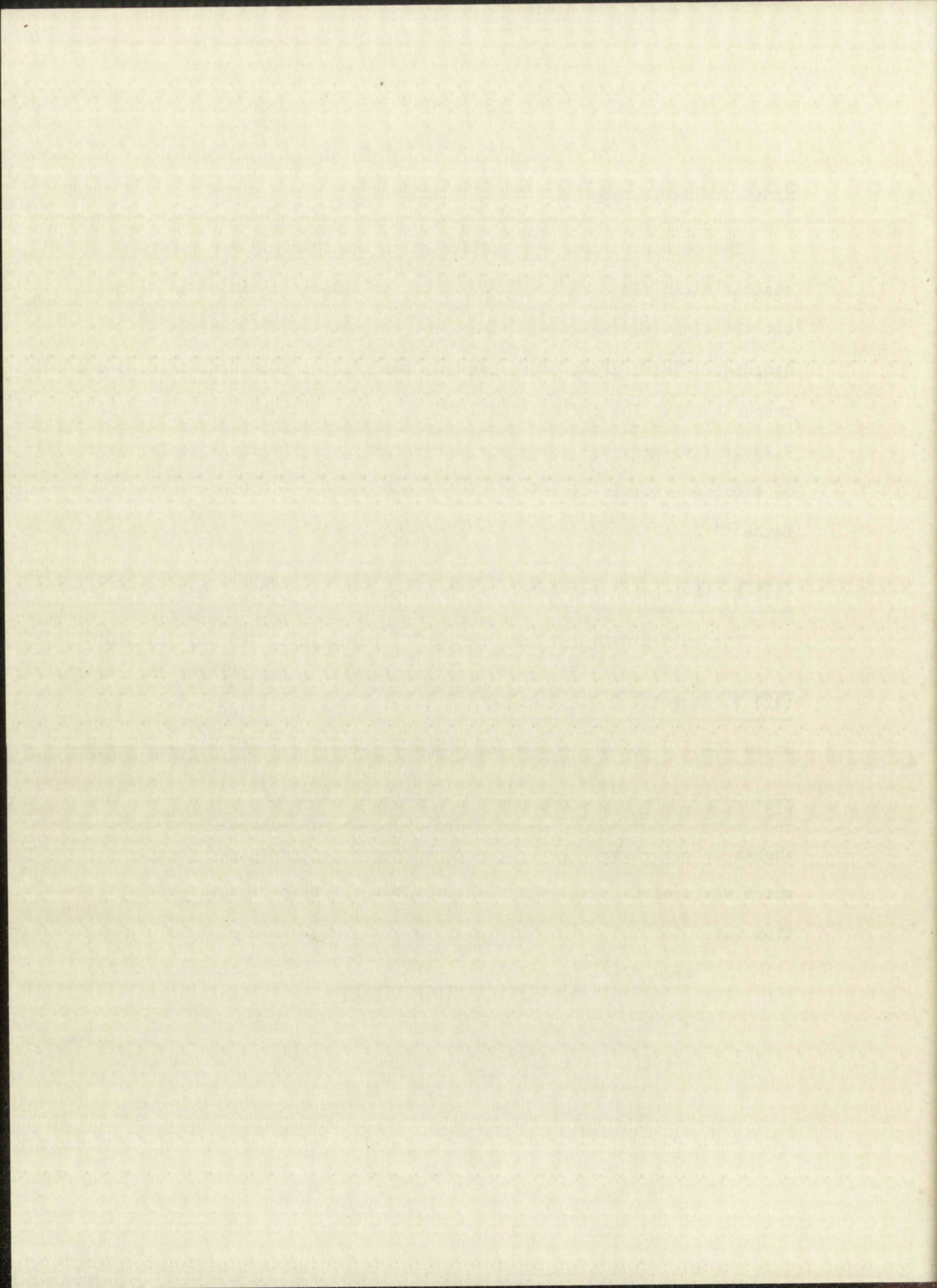
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(13) E. Kemp, LA-1207 (1950).

---

iments on coincidence loss in this counter resulted in an equation which was used to correct all counts exceeding 54,000 c/m. This equation was:

$$\text{true c/m} = \frac{(\text{obs. c/m})^2}{0.9564 (\text{obs. c/m}) + 2381}$$





During each counting period, time was determined to the nearest second by standardizing a clock with WWV.

### 2.1.3. RESULTS.

The decay of ten samples was followed over a total time of 7 1/2 to 8 half-lives (>100 hours). A constant background is present because of the gammas from unconverted Am<sup>241(14)</sup>. The samples were allowed to

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(14) F. Asaro, F. Reynolds, and I. Perlman, UCRL-1681 (1952). See also J. Beling, et al, Phys. Rev. 86, 797 (1952); 87, 670 (1952).

---

decay until this gamma background gave agreement within 0.1% in two counts taken 24 hrs. apart. This background was then subtracted from all previous counts, the resulting data yielding a straight line when plotted against time on semi-log paper. Figure I is a sample plot of such data.

The best slope for this straight line was determined by the method of least squares and the half-life evaluated from the equation:

$$t_{1/2} = - \frac{\ln 2}{(\text{slope})(2.303)}$$

The data obtained from this equation are shown in Table II.

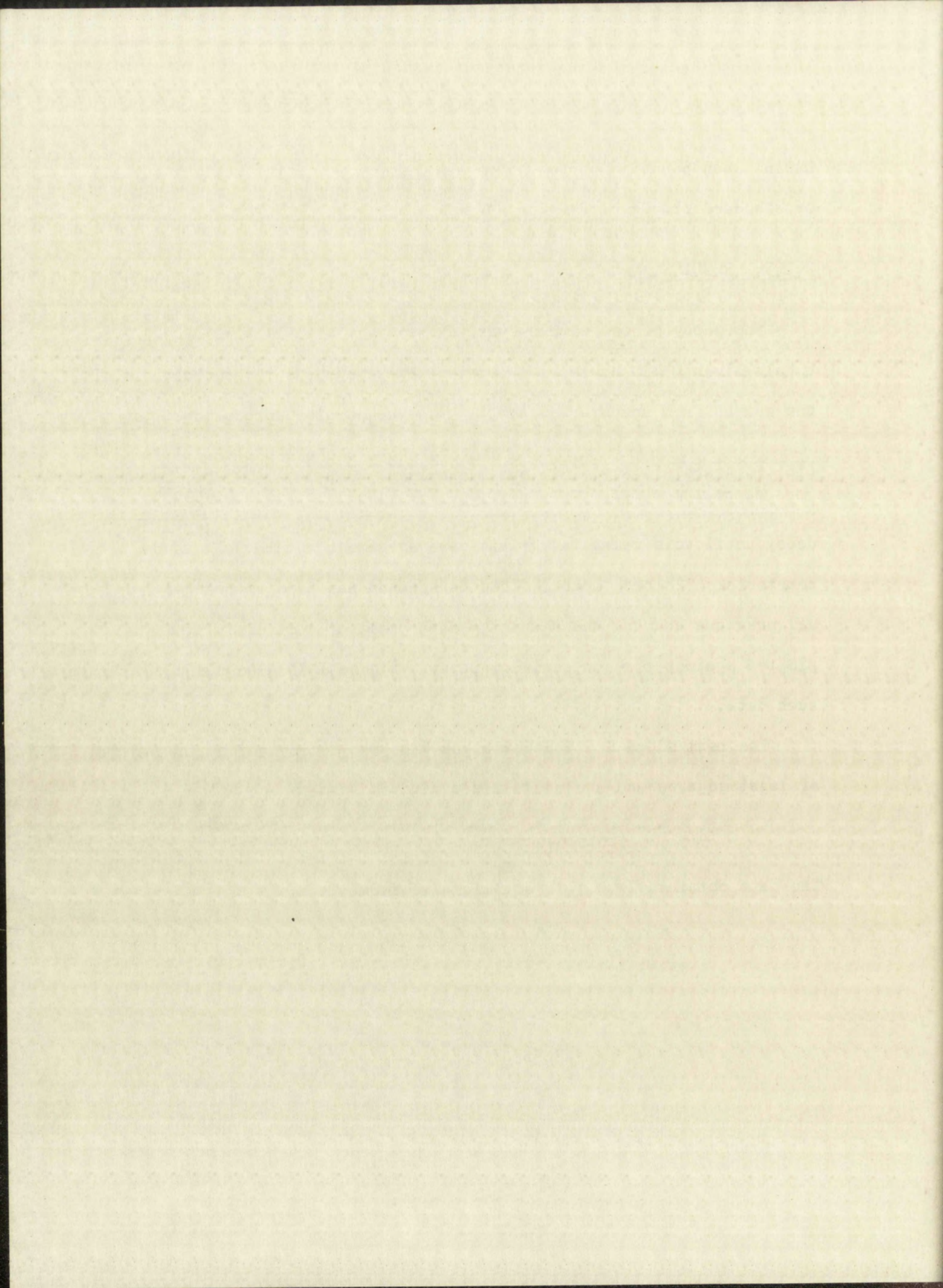
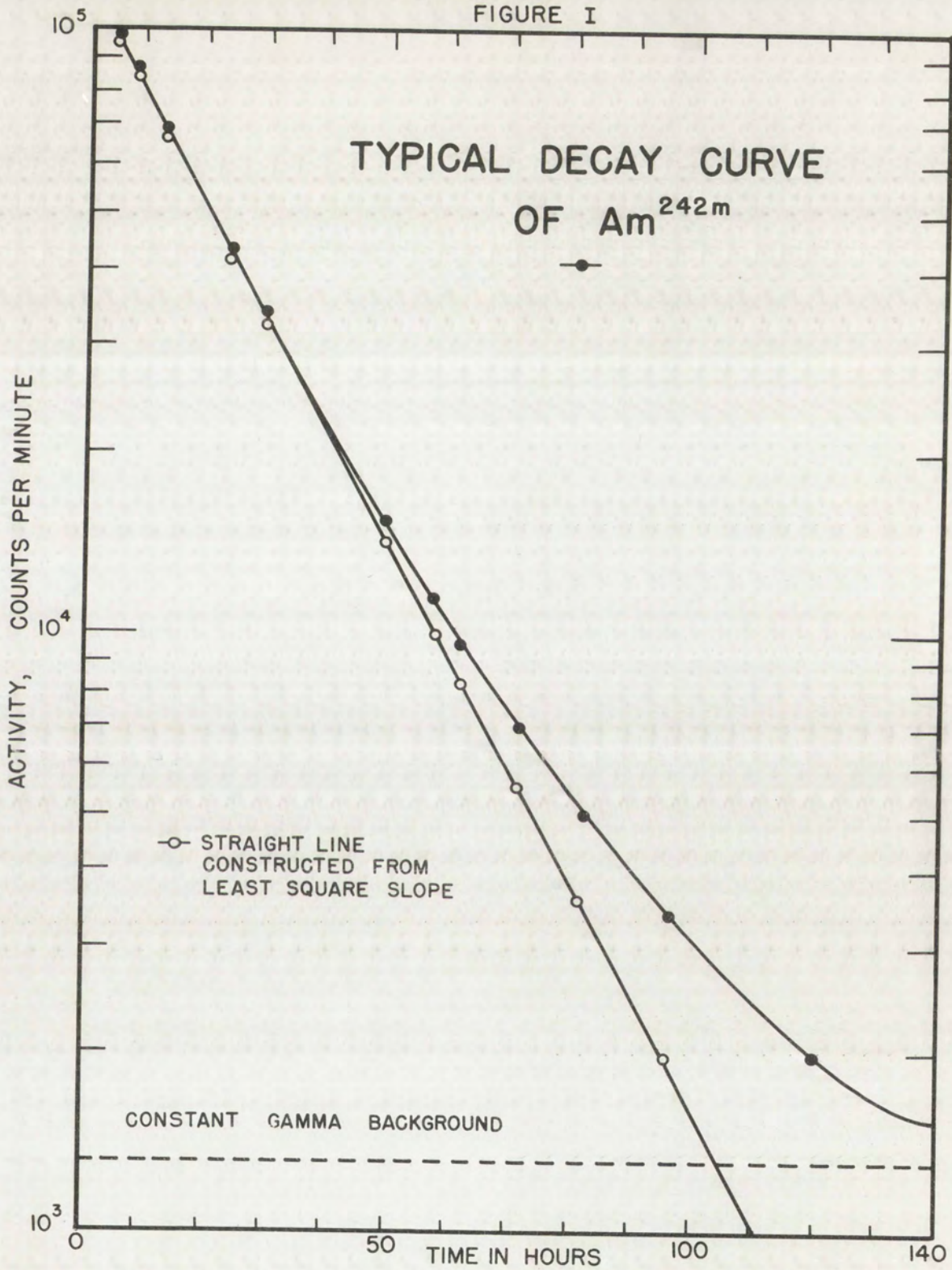


FIGURE I



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TABLE II

<u>Sample</u>	<u>Half-Life in Hours</u>
1	16.00
2	15.98
3	15.99
4	16.02
5	16.01
6	16.02
7	16.02
8	16.04
9	15.97
10	<u>16.02</u>

Mean:  $16.01 \pm 0.015$  hrs.  
(99% confidence limits)

The limits  $\pm 0.015$  hours represent the confidence limits obtained from the standard deviation, using the "range"<sup>(15)</sup> method of determining reliability.

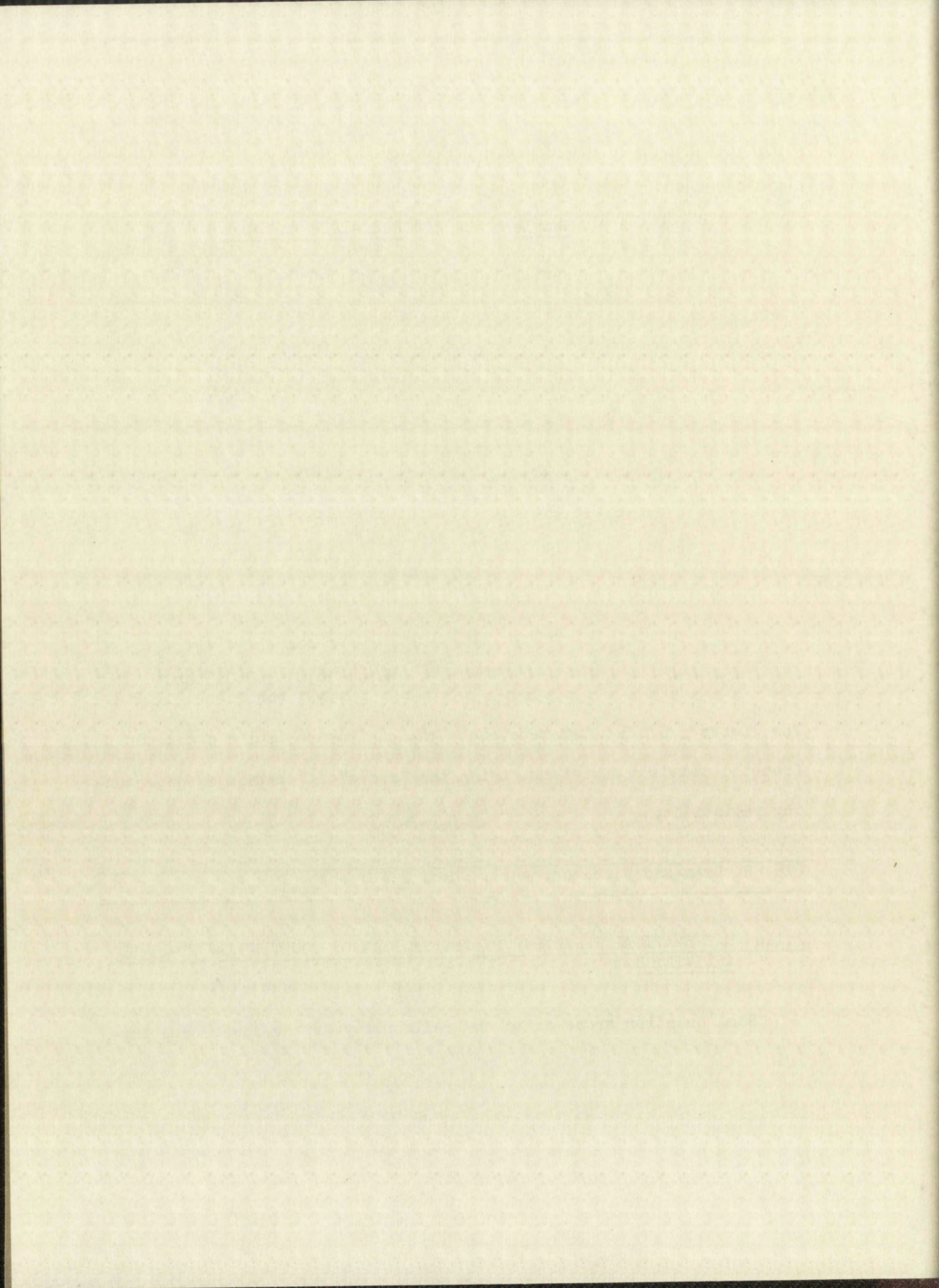
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(15) R. Dean and W. Nixon, Anal. Chem. 23(4), 636 (1951).

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2.1.4 MATHEMATICAL TREATMENT OF THE PROBLEM OF COUNTING SHORT-LIVED ACTIVITIES.

Some question arose as to the reliability of the lower counting-



rate portion of the curve shown in Figure I. At least  $10^5$  total counts were collected for each point. It was necessary to know whether  $\Delta N/\Delta t$  was an accurate measure of  $dN/dt$  at mid-time ( $\Delta t/2$ ) when counting periods of 20 minutes were necessary to collect 100,000 total counts. The following treatment was derived to clarify this situation:\*

---

\*The author is indebted to B. McInteer, Los Alamos Scientific Laboratory, for his kind assistance in setting up the mathematical relationships.

---

I. From radioactive decay laws:  $dN/dt = -\lambda N$

where  $N$  is the number of atoms present at time  $t$ .

1) Integrating the above:

$$N = N_0 e^{-\lambda \Delta t}$$

where  $N_0$  = the number of atoms present at  $t = 0$  and  $\Delta t$  is the time elapsed between  $t = 0$  and the present.

2) Subtract both sides of I-1. from  $N_0$ :

$$N_0 - N = N_0 - N_0 e^{-\lambda \Delta t}$$

$$N_0 - N = N_0(1 - e^{-\lambda \Delta t})$$

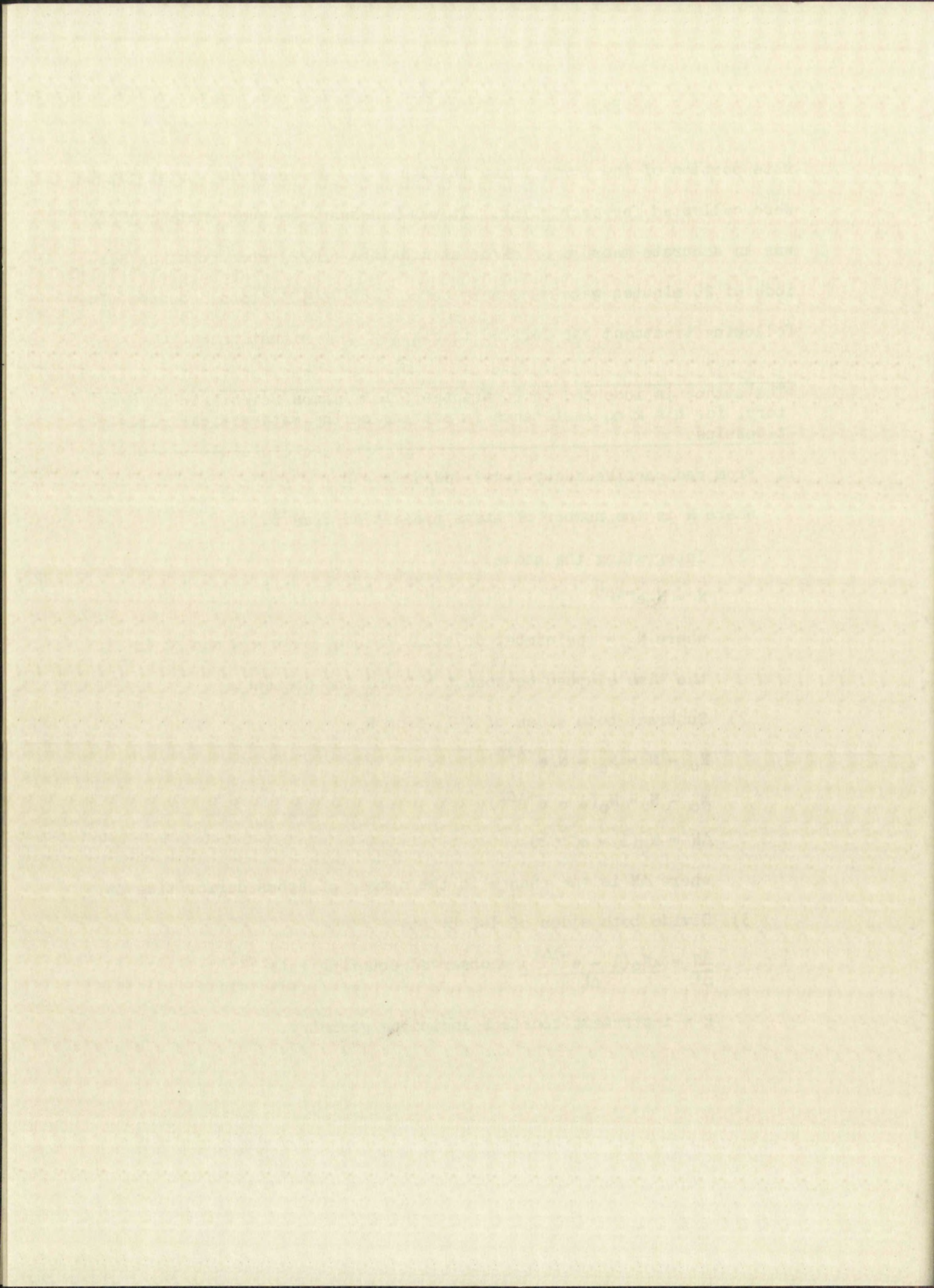
$$\Delta N = N_0(1 - e^{-\lambda \Delta t})$$

where  $\Delta N$  is the change in the number of atoms during time  $\Delta t$ .

3) Divide both sides of I-2 by  $\Delta t$ :

$$\frac{\Delta N}{\Delta t} = \frac{k N_0(1 - e^{-\lambda \Delta t})}{\Delta t} = \text{observed counting rate}$$

$k$  = instrument constant including geometry.





4) Actual disintegration rate at the mid-time or  $\Delta t/2$ :

$$- dN/dt = \lambda N_{\Delta t/2}$$

where  $N_{\Delta t/2}$  = number of atoms actually present at this time

5) But  $N_{\Delta t/2} = N_0 e^{-\lambda \Delta t/2}$  from I-1.

$$- dN/dt = \lambda N_0 e^{-\lambda \Delta t/2} = \text{actual counting rate at mid-point of counting period } \Delta t.$$

II. To compare the counting rates, set up the ratio:

$$\begin{aligned} 1) \frac{\text{average counting rate}}{\text{actual counting rate (at } \Delta t/2)} &= \frac{(1 - e^{-\lambda \Delta t})}{\lambda \Delta t \left[ (e^{-\lambda \Delta t/2}) \right]} \\ &= \frac{1}{\lambda \Delta t} (e^{\lambda \Delta t/2} - e^{-\lambda \Delta t/2}) \end{aligned}$$

2) The right-hand side of II-1 will be found to be the same form as the sinh function:  $\sinh x = 1/2(e^x - e^{-x})$ .

Substituting the terms from II-1:

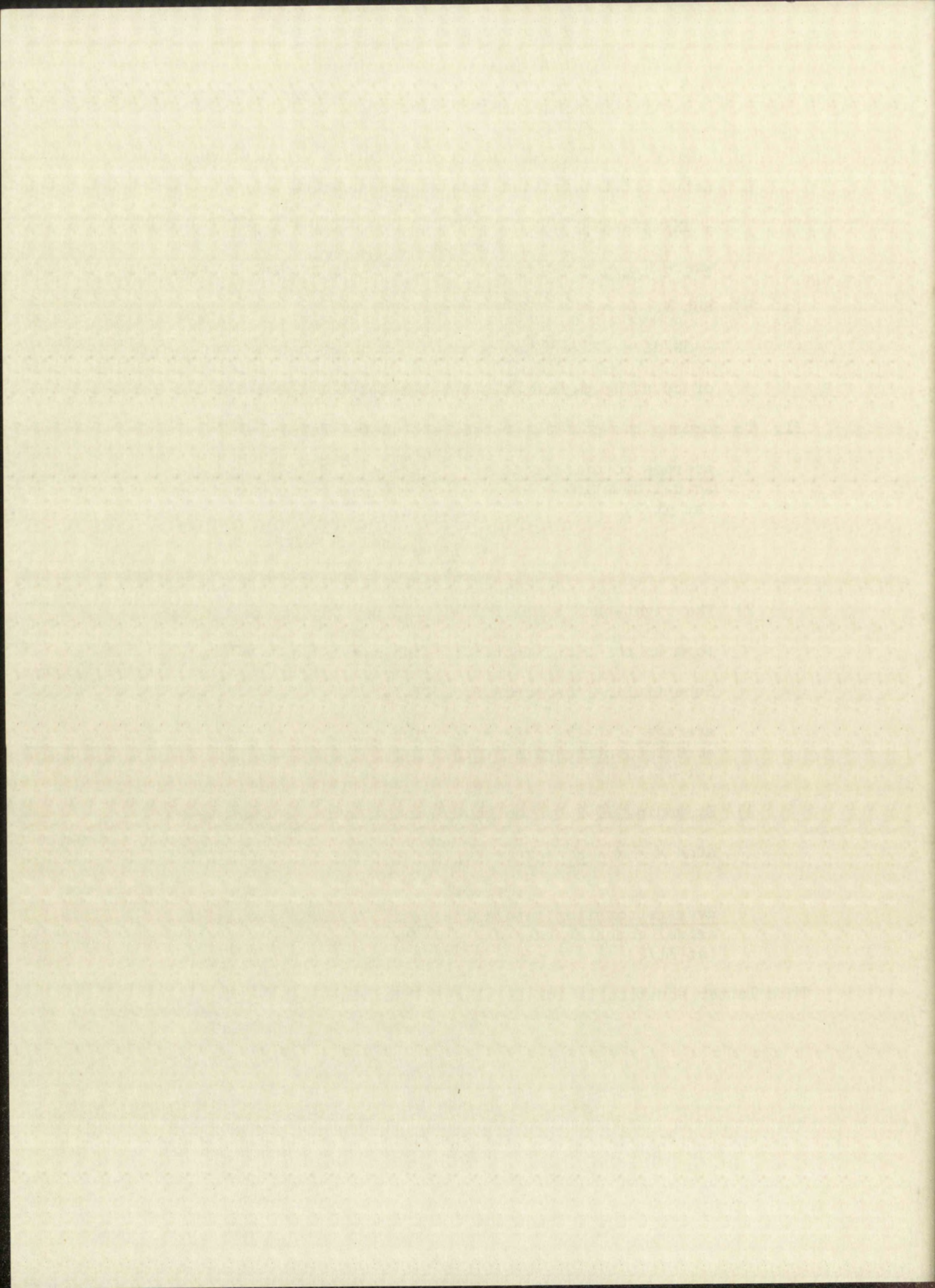
$$\frac{\text{average counting rate}}{\text{actual counting rate (at } \Delta t/2)} = \frac{2}{\lambda \Delta t} \sinh (\lambda \Delta t/2)$$

3) Expanding II-2 by the known expansion for a sinh function:

$$\sinh x = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \dots$$

$$\frac{\text{average counting rate}}{\text{actual counting rate (at } \Delta t/2)} = 1 + \frac{(\lambda \Delta t)^2}{24} + \frac{(\lambda \Delta t)^4}{1920} + \dots$$

This latter equation is identical with that reported in 1952 by



Schuler<sup>(16)</sup>, and was developed independently by Keenan and Penneman

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(16) R. Schuler, Nucleonics 10, 96 (1952).

---

in the fall of 1951.

Thus, for  $t_{1/2} = 16$  hours,  $\lambda = 0.000722 \text{ min.}^{-1}$ ,  $t = 20$  min.:

$$\frac{\text{average counting rate}}{\text{actual counting rate}} = 1.0000087 \text{ or agreement to } 10^{-3}\%,$$

(at  $\Delta t/2$ )

between average disintegration rate and actual disintegration rate at the mid-time of a 20-minute counting period.

Therefore, no error was introduced using 20-minute counting intervals at the lower portion of the curve in Figure I. In fact, for a 16-hour half-life, a counting time of 214 minutes can be used, and the agreement between the average counting rate and the actual counting rate at the mid-point of this counting period will be 0.1%.

III. The problem may be approached by considering that there is some fraction,  $\phi$ , of the counting time ( $\Delta t$ ) at which the actual counting rate is equal to the observed average counting rate. By the same type of treatment as followed in I:

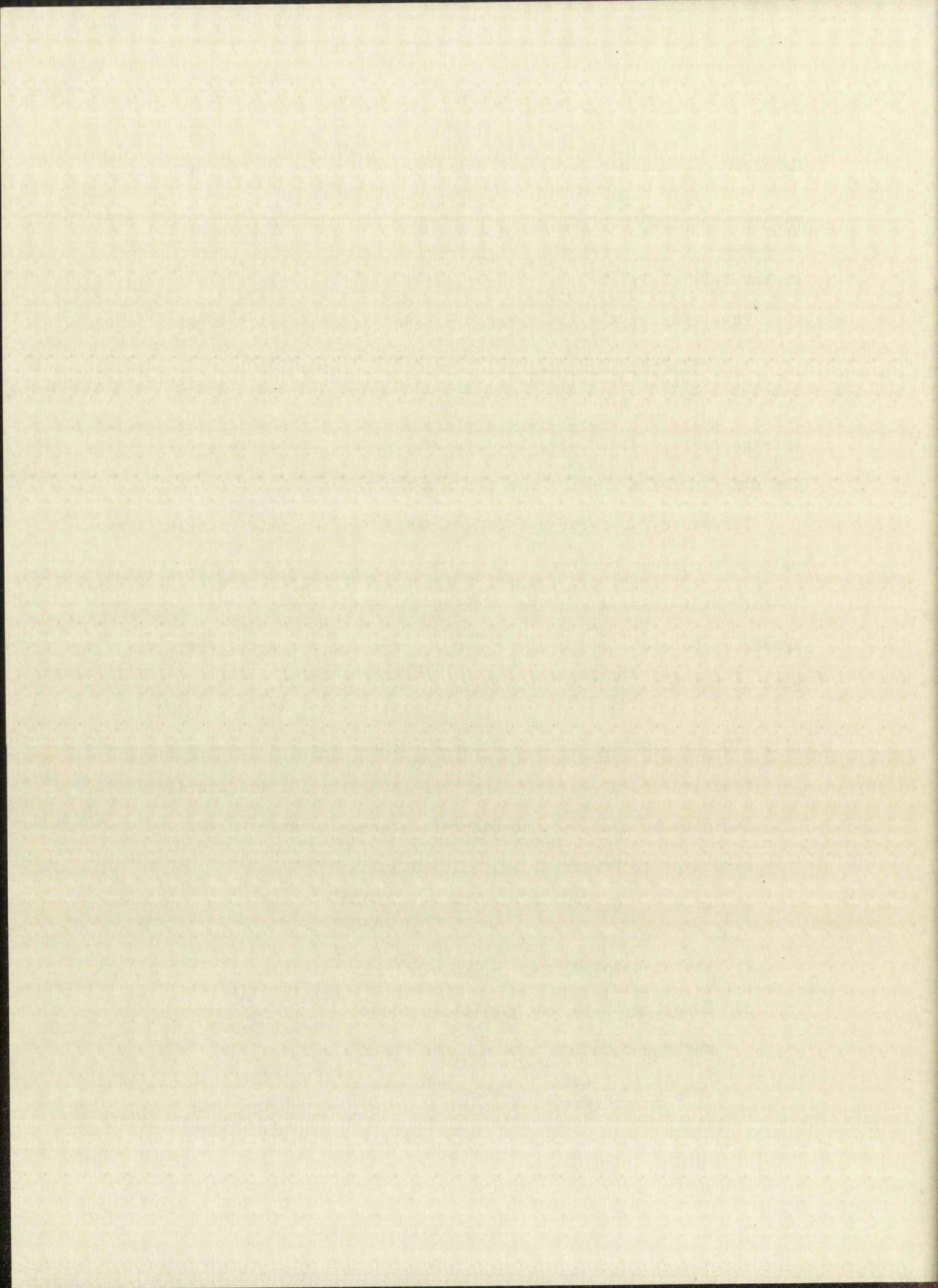
1) average counting rate =  $\frac{kN_0(1 - e^{-\lambda\Delta t})}{\Delta t}$

2) actual counting rate =  $\lambda kN_0 e^{-\lambda\phi\Delta t}$

3) Equating these two quantities then:

average counting rate = actual counting rate

$$kN_0 \frac{(1 - e^{-\lambda\Delta t})}{\Delta t} = \lambda kN_0 e^{-\lambda\phi\Delta t}$$



4) Dividing both sides of III-3 by  $kN_0$  and taking logarithms:

$$\phi = \frac{1}{\lambda \Delta t} \ln \left[ \frac{\lambda \Delta t}{1 - e^{-\lambda \Delta t}} \right]$$

5) For convenience, let  $\lambda \Delta t = x$  and multiply both numerator and denominator of the logarithm term by  $e^{x/2}$ :

$$\phi = \frac{1}{x} \ln \left[ \frac{x e^{x/2}}{e^{x/2} - e^{-x/2}} \right]$$

$$\phi = \frac{1}{x} \ln e^{x/2} + \frac{1}{x} \ln \left[ \frac{x}{e^{x/2} - e^{-x/2}} \right]$$

6) Taking antilogarithms in the first and inverting the second term yields:

$$\phi = 1/2 - \frac{1}{x} \ln \left[ \frac{e^{x/2} - e^{-x/2}}{x} \right]$$

7) The numerator of the term within the bracket will be recognized as having the same form to a sinh function similar to II-1. Rewriting and substituting the sinh function:

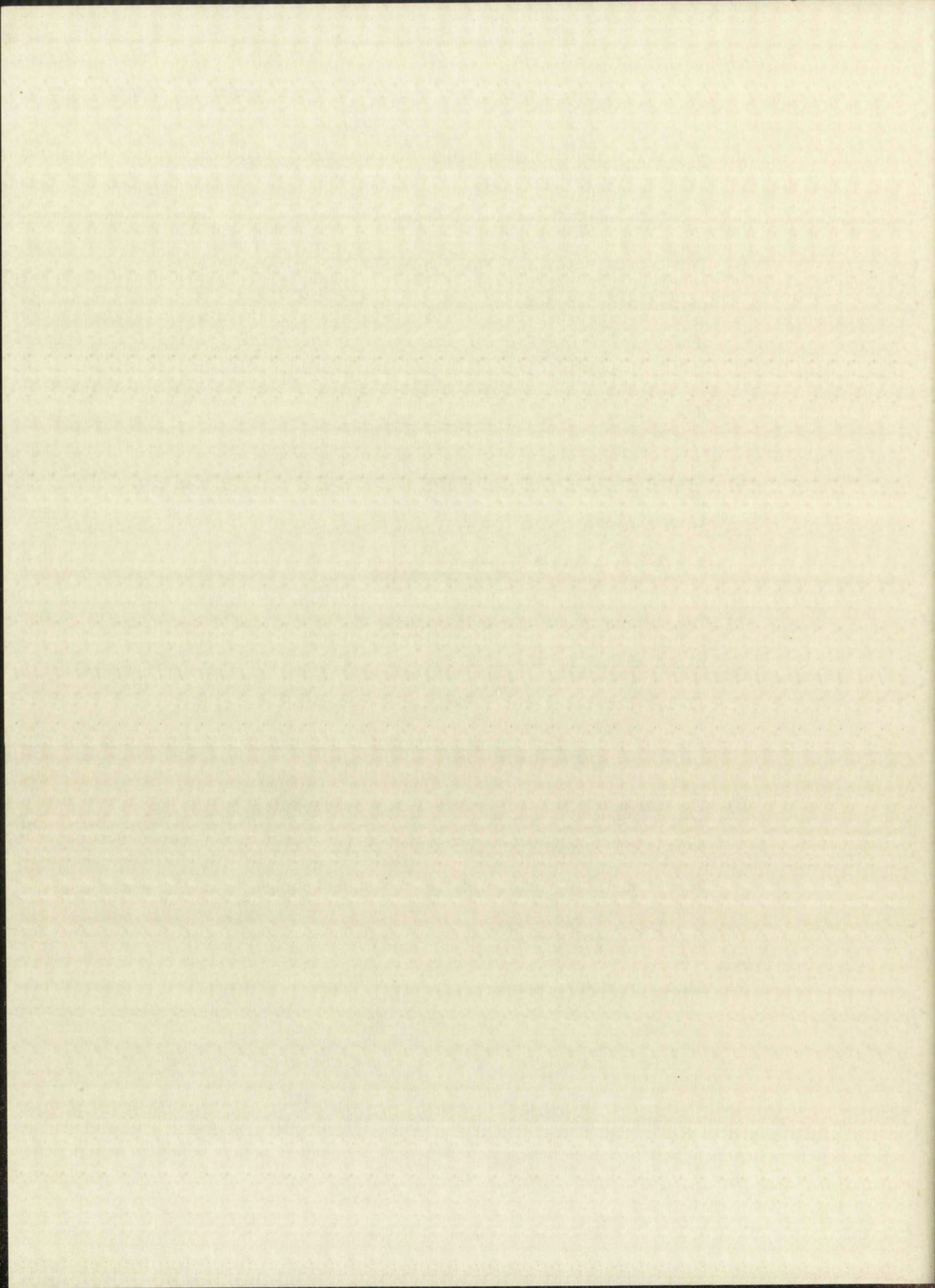
$$\phi = 1/2 - \frac{1}{\lambda \Delta t} \ln \left[ \frac{2 \sinh \lambda \Delta t / 2}{\lambda \Delta t} \right]$$

8) The terms within the brackets may be expanded by the known expansion series for  $\sinh x$  and  $\ln(1+x)$ .

Rewriting III-7 again making the substitution that  $\lambda \Delta t = x$ :

$$\phi = 1/2 - \frac{1}{x} \ln \left[ \frac{2 \sinh x}{x} \right]$$

9)  $\sinh x = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \dots$



$$\phi = 1/2 - \frac{1}{x} \ln \left[ \frac{2}{x} \left( \frac{x}{2} + \frac{x^3}{2.31} + \frac{x^5}{2.51} \right) \right]$$

$$\phi = 1/2 - \frac{1}{x} \ln \left[ 1 + \frac{x^2}{24} + \frac{x^4}{1920} \right]$$

- 10) Let the quantity  $\left[ \frac{x^2}{24} + \frac{x^4}{1920} \right] = y$  and rewrite III-9:

$$\phi = 1/2 - \frac{1}{x} \ln (1 + y)$$

- 11) Expand the term within brackets in III-10 by the known expansion for the  $\ln (1 + y) = y - \frac{y^2}{2} + \frac{y^3}{3} + \dots$

$$\phi = 1/2 - \frac{1}{x} \left[ \frac{x^2}{24} + \frac{x^4}{1920} \right] + \frac{1}{2x} \left[ \frac{x^2}{24} \right]^2$$

(Note that the second part of the term  $\left[ \frac{x^2}{24} + \frac{x^4}{1920} \right]$  is not carried in the squared term of the logarithm expansion.)

- 12) Clearing fractions:

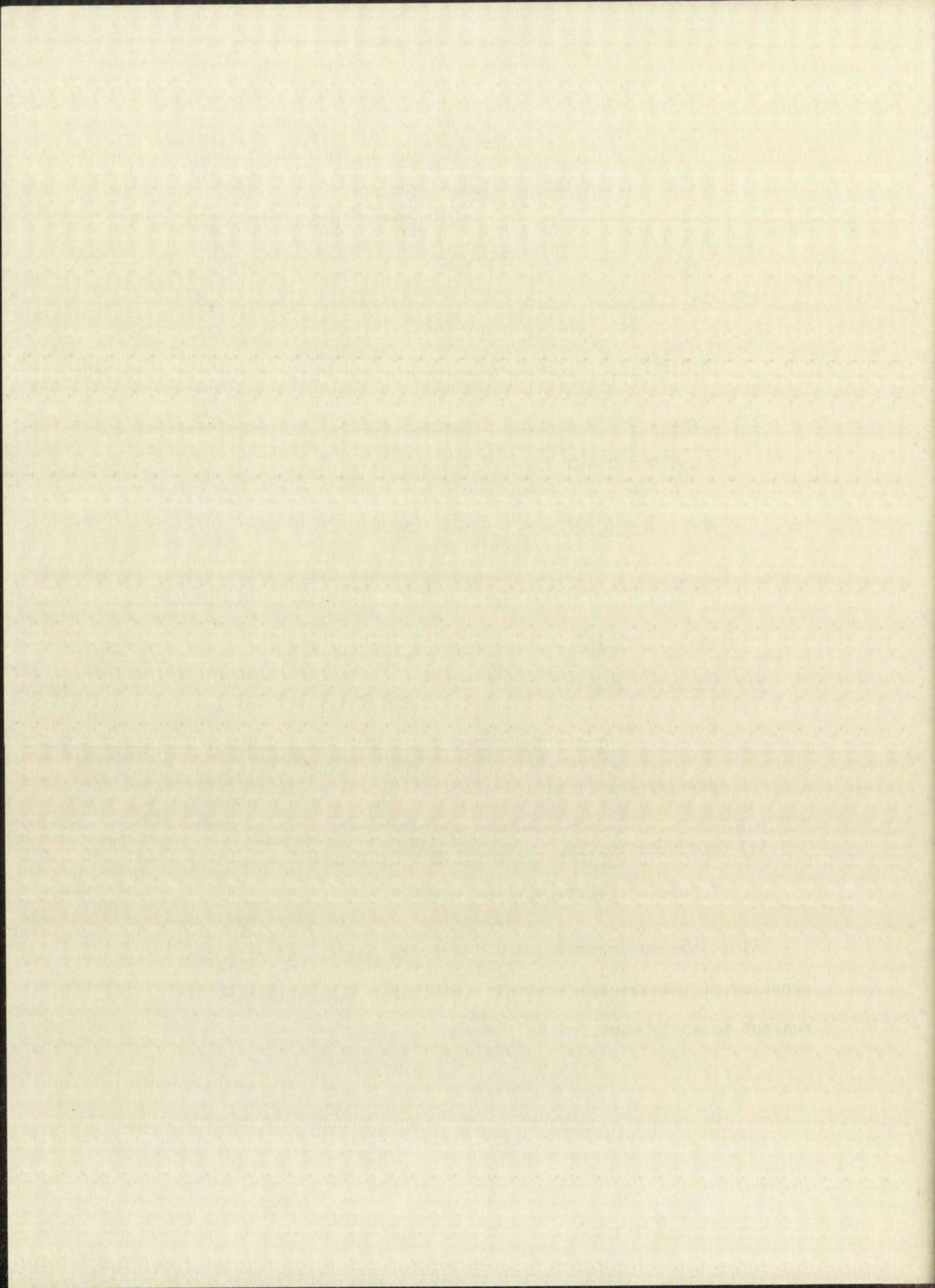
$$\phi = 1/2 - \frac{x}{24} - \frac{x^3}{1920} + \frac{x^3}{1152}$$

$$\phi = 1/2 - \frac{x}{24} + \frac{x^3}{2880}$$

- 13) And substituting the value  $\lambda \Delta t$  for  $x$ :

$$\phi = 1/2 - \frac{\lambda \Delta t}{24} + \frac{(\lambda \Delta t)^3}{2880}$$

Since the major experimental error is associated with the determination of the average counting rate rather than with time, it is convenient to apply equation II-3 rather equation III-13. Indeed, experi-





mental counting data do not generally warrant application of the correction terms of equation III-13 when  $\lambda \Delta t$  is  $\leq 0.1549$  (or when  $\Delta t$  is  $< 22.35\%$  of  $t_{1/2}$ ). A NEW, CONVENIENT RULE OF THUMB MAY BE STATED: "ONE MAY COUNT A DECAYING SAMPLE FOR 20% (i.e., 1/5th) OF A HALF-LIFE; ASSIGN THE DETERMINED AVERAGE COUNTING RATE TO THE MIDPOINT OF THIS COUNTING PERIOD, AND STILL BE ACCURATE TO  $< 0.1\%$ ".

IV. The half-life problem may be formulated as follows for two counting periods:

Let  $N_0$  = atoms initially present

$N_1$  = atoms present after time  $t_1$

$N_2$  = atoms present after time  $t_2$

$N_3$  = atoms present after time  $t_3$

1) Then:

$$N_0 - N_1 = \delta N_1 \text{ in time } (t_1 - t_0)$$

$$N_2 - N_3 = \delta N_2 \text{ in time } (t_3 - t_2)$$

$$N_1 = N_0 e^{-\lambda t_1}$$

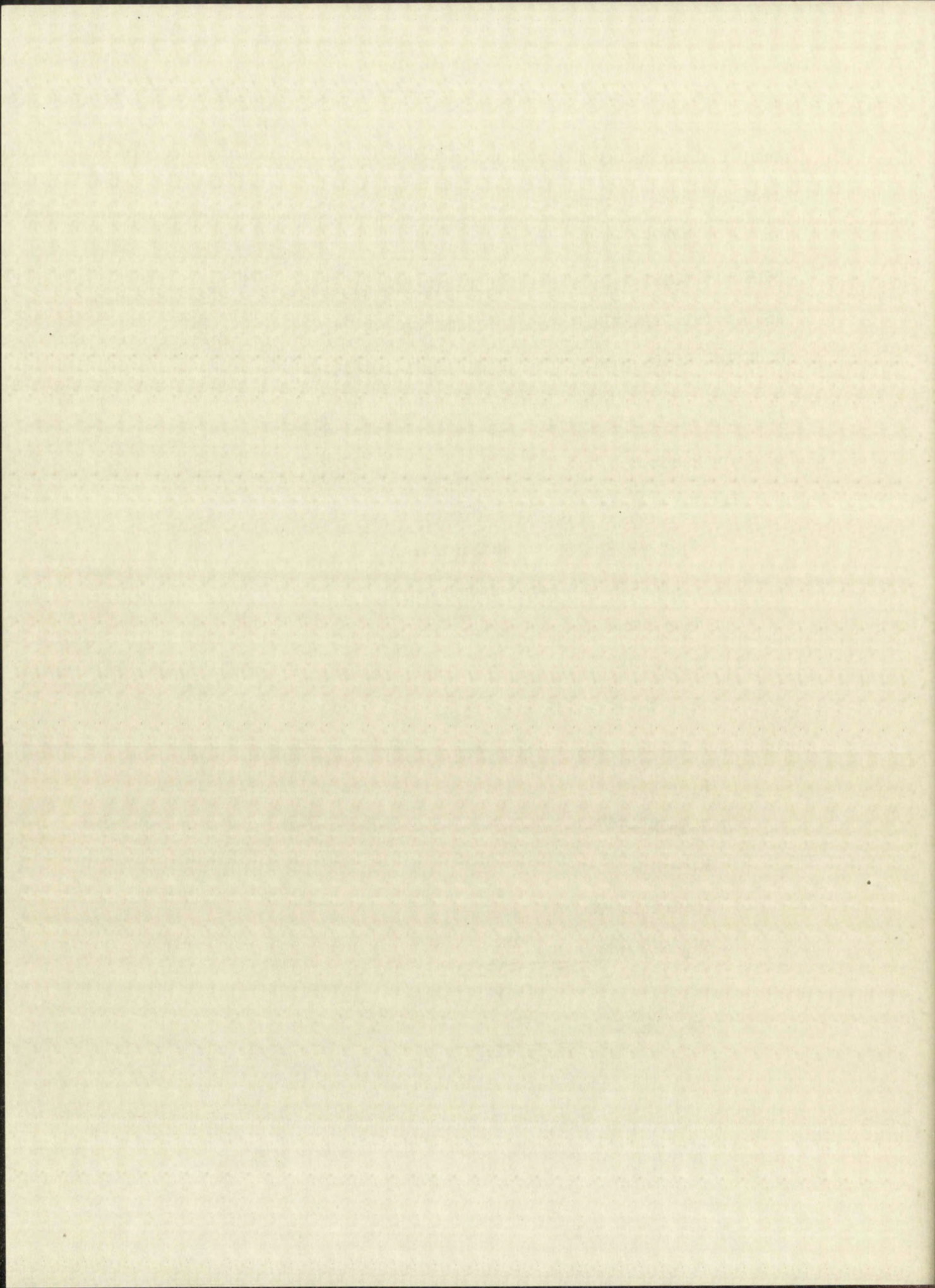
$$N_2 = N_0 e^{-\lambda t_2}$$

$$N_3 = N_0 e^{-\lambda t_3}$$

2) The ratio  $\delta N_1 / \delta N_2$  is equal to:

$$\frac{\delta N_1}{\delta N_2} = \frac{N_0 - N_0 e^{-\lambda t_1}}{N_0 e^{-\lambda t_2} - N_0 e^{-\lambda t_3}}$$

$$\frac{\delta N_1}{\delta N_2} = \frac{(1 - e^{-\lambda t_1})}{(e^{-\lambda t_2} - e^{-\lambda t_3})}$$



This expression represents an exact solution for the specific decay constant,  $\lambda$ . In general, equation IV-2 cannot be solved for  $\lambda$  explicitly. However, if time intervals are chosen so that  $t_3 - t_2 = t_1 - t_0$  then equation IV-2 becomes simplified to the form:

$$3) \quad \delta N_1 / \delta N_2 = \frac{1}{e^{-\lambda t_2}}$$

$$4) \quad \lambda = \frac{\ln (\delta N_1 / \delta N_2)}{t_2}$$

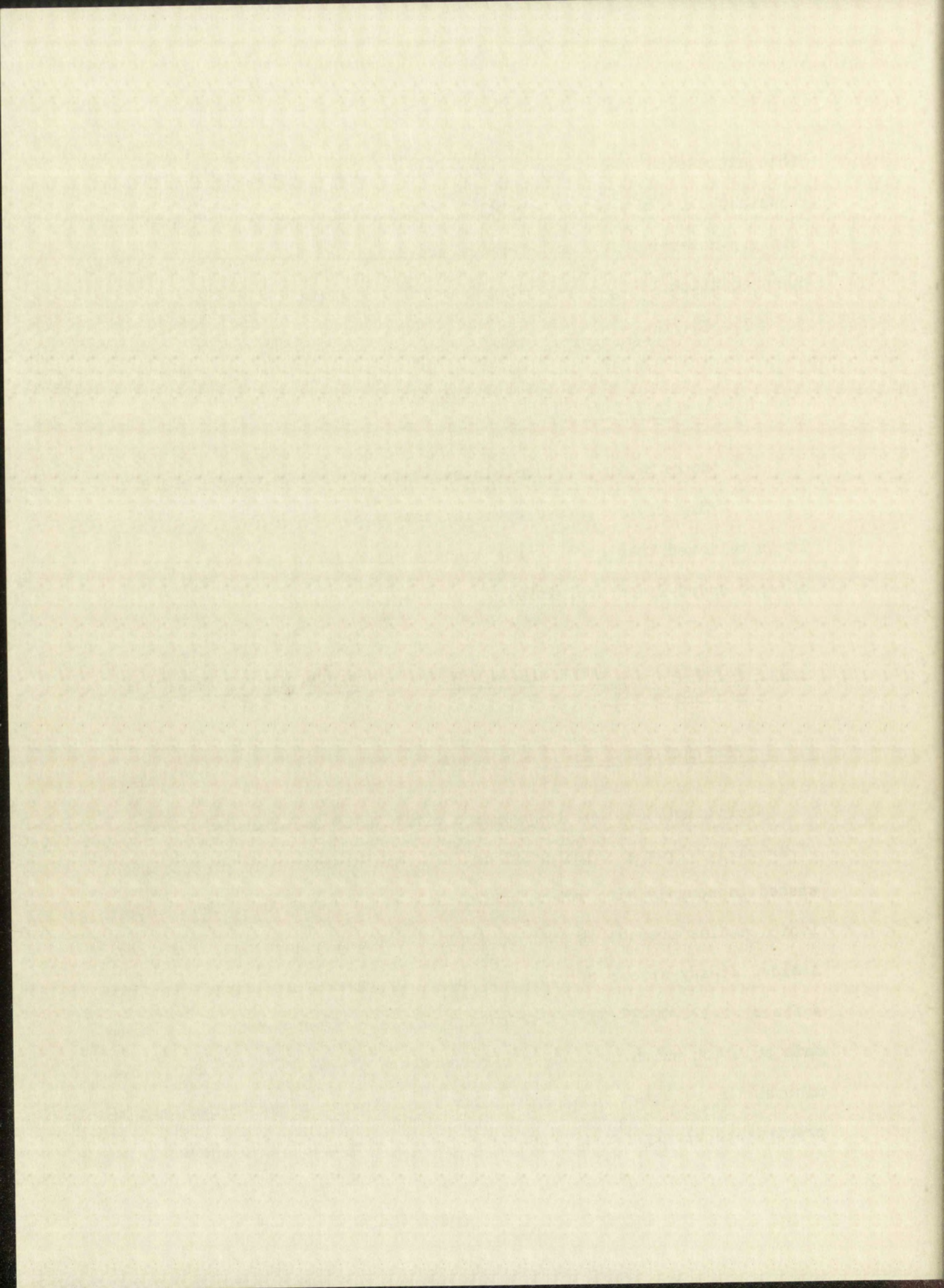
where  $t_2$  is the time elapsed between time zero and the beginning of the second counting interval.

It is believed that such a treatment is valuable in the particular case of very short-lived activities.

## 2.2 PREPARATION OF MATERIALS AND SEPARATION TECHNIQUE FOR AMERICIUM EXCHANGE STUDIES

### 2.2.1 PREPARATION OF Am(V) FOR EXCHANGE.

Americium(V) cannot be prepared directly in solution by oxidation of Am(III). From a solution of Am(III), the hydroxide is precipitated, washed thoroughly with water, and dissolved in 3 f  $K_2CO_3$ . The exact ionic species present in such an Am(III)-carbonate solution is unknown. A slow, steady stream of ozone (prepared by passing dry oxygen through a field of 12,000-15,000 volts potential) is bubbled through this carbonate solution which is held at a temperature of 90°-95°C. Within a few minutes the solution changes in color from pink to a deep brown, and a precipitate slowly forms. The oxidation is complete in one hour at the



temperatures stated above. The formula of the Am(V) compound precipitated at high pH has not been uniquely characterized but is believed to be between  $\text{KAmO}_2\text{CO}_3$ <sup>(17)</sup> and  $(\text{K}_2\text{CO}_3)_2(\text{AmO}_2)_2\text{CO}_3$ . The precipitate is

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(17) J. Nigon, R. Penneman, E. Staritzky, T. Keenan, and L. Asprey, J. Am. Chem. Soc., submitted.

---

separated from the carbonate supernatant by centrifugation, and it is washed twice with dilute (0.01 f)  $\text{K}_2\text{CO}_3$ . Washing with water results in peptization of the precipitate. The precipitate can then be dissolved in any desired acid. Ammonium persulfate<sup>(18)</sup> or alkali hypochlorite<sup>(19)</sup>

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(18) S. Stephanou, J. Nigon, and R. Penneman, J. Chem. Phys. 21(1), 42, (1953).

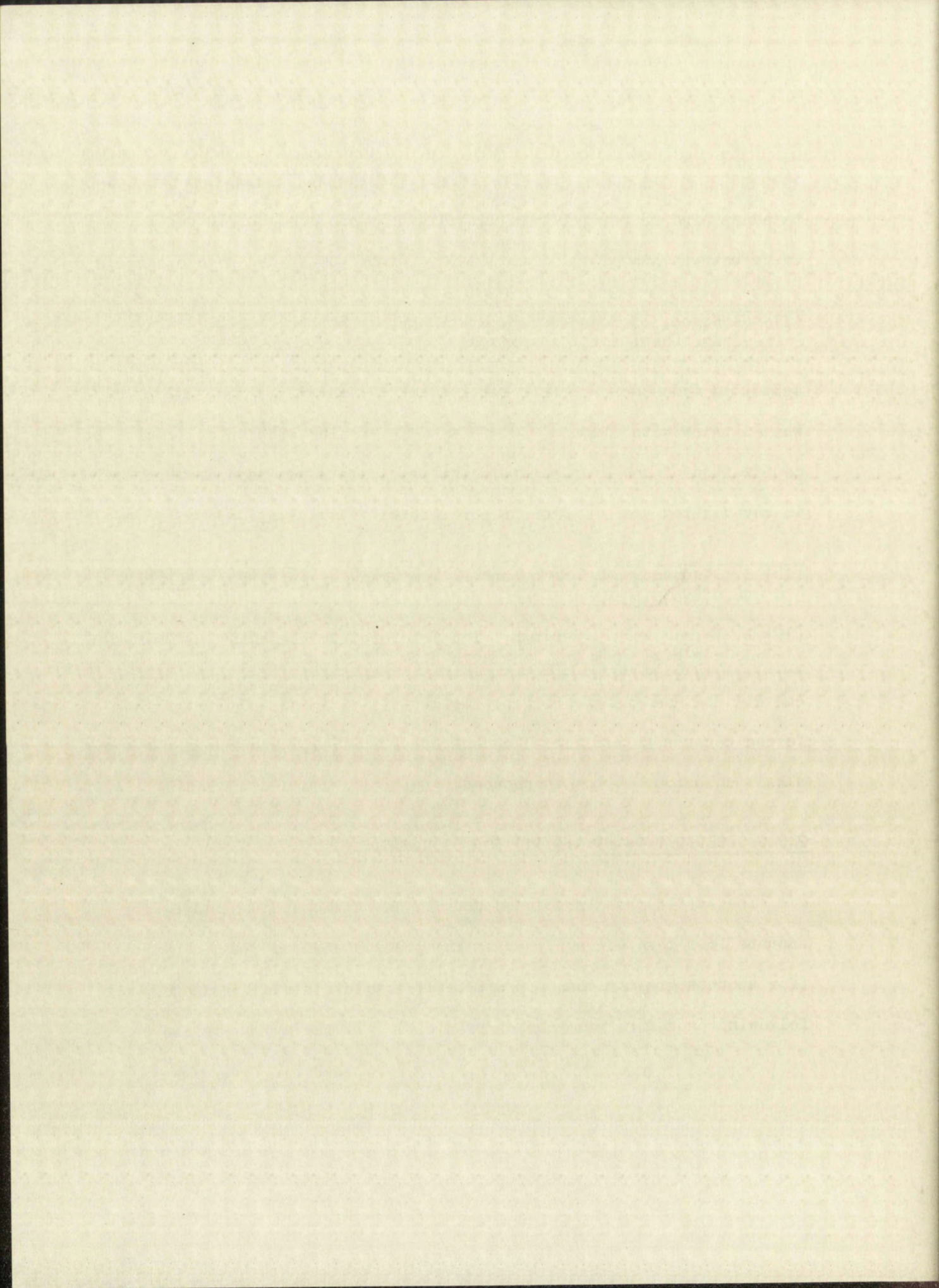
(19) L. Werner and I. Perlman, "The Transuranium Elements", NNES-IV-14B, McGraw-Hill Book Co., New York City (1949) p. 1586.

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can also be used as the oxidant for Am(III) to Am(V). Ozone is preferred because an additional amount of salt, i.e., ammonium sulfate or alkali chloride, is not introduced.

#### 2.2.2 PREPARATION OF Am(III) FOR EXCHANGE.

The Am(III) was irradiated usually in nitric acid solution (for amounts less than 0.5 mg.), or as the precipitated and washed hydroxide (for amounts greater than 0.5 mg.). If a solution was irradiated, the following procedure was then carried out: (1) The hydroxide was preci-



pitated and washed with water to neutrality. This hydroxide precipitation was necessary to remove peroxide produced by the neutron irradiation of the acidic medium. Often the initial precipitation of Am(III) hydroxide was brownish in color because of the peroxide present. Washing with water, followed by a second hydroxide precipitation with washing, restored the compound to its usual bright pink color. (2) The washed hydroxide could then be dissolved in any desired acid.

If the hydroxide itself was irradiated, the compound was dissolved in a mixture of 1.0 f  $\text{HNO}_3$  satd.  $\text{H}_3\text{BO}_3$ . This mixture proved the most effective in dissolving the dried hydroxide. From this solution, the hydroxide was precipitated with gaseous  $\text{NH}_3$  and the same procedure followed as shown under step (1) above.

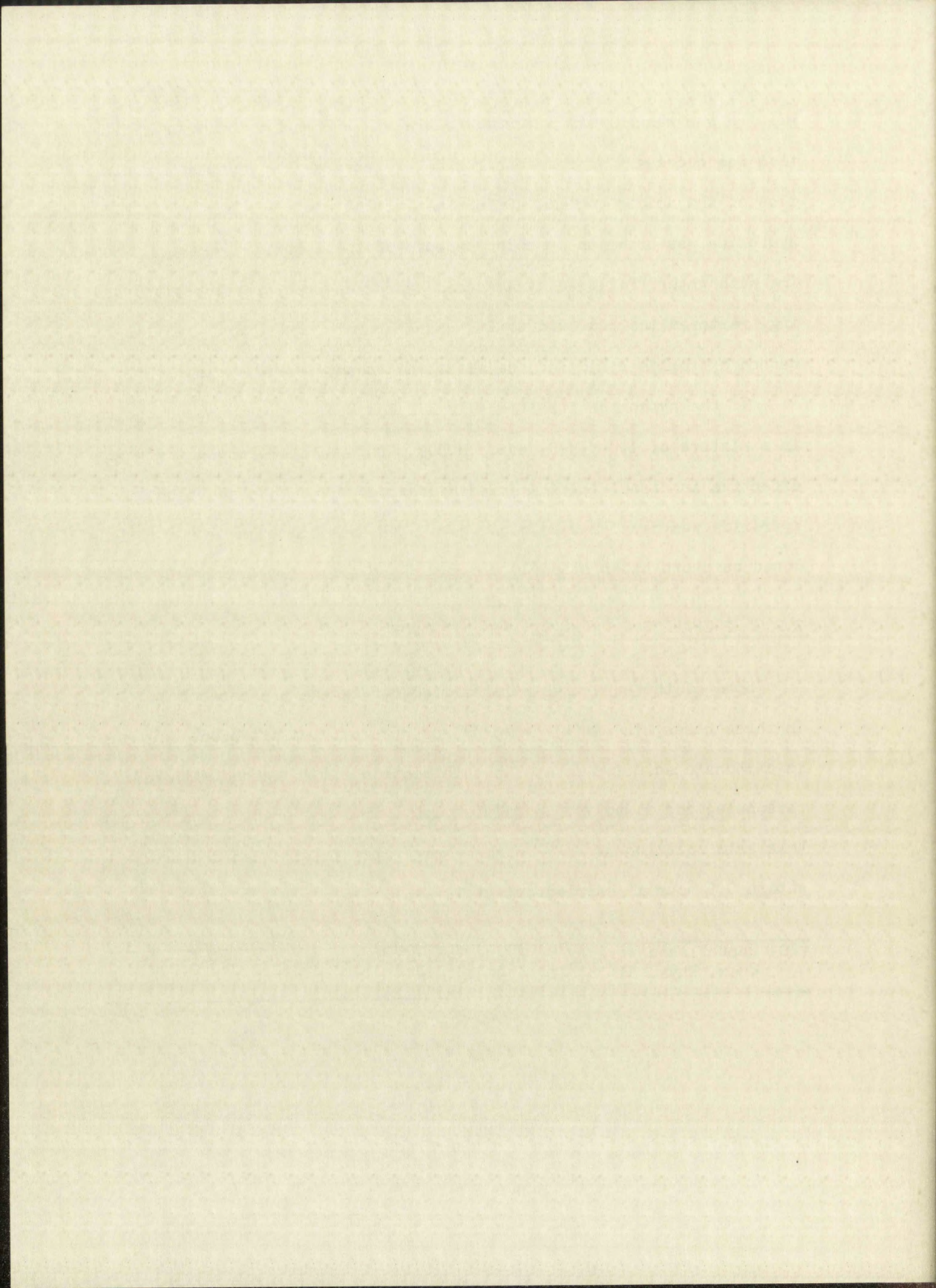
### 2.2.3 PREPARATION OF Am(VI) FOR EXCHANGE.

Some of the exchanges were carried out in the presence of Am(VI). In these cases, the Am(V) compound was precipitated via ozone oxidation in carbonate solution as outlined in Section 2.2.2, washed with dilute carbonate, and dissolved in dilute (1.0 f or less) acid. Treatment of this acid solution of Am(V) with ozone yields Am(VI) quantitatively within 0.5 hour if carried out at  $90^\circ\text{-}95^\circ\text{C}$  (20).

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(20) Unpublished work by T. Keenan and S. Stephanou described in J. Chem. Phys. 21(3), 542 (1953).

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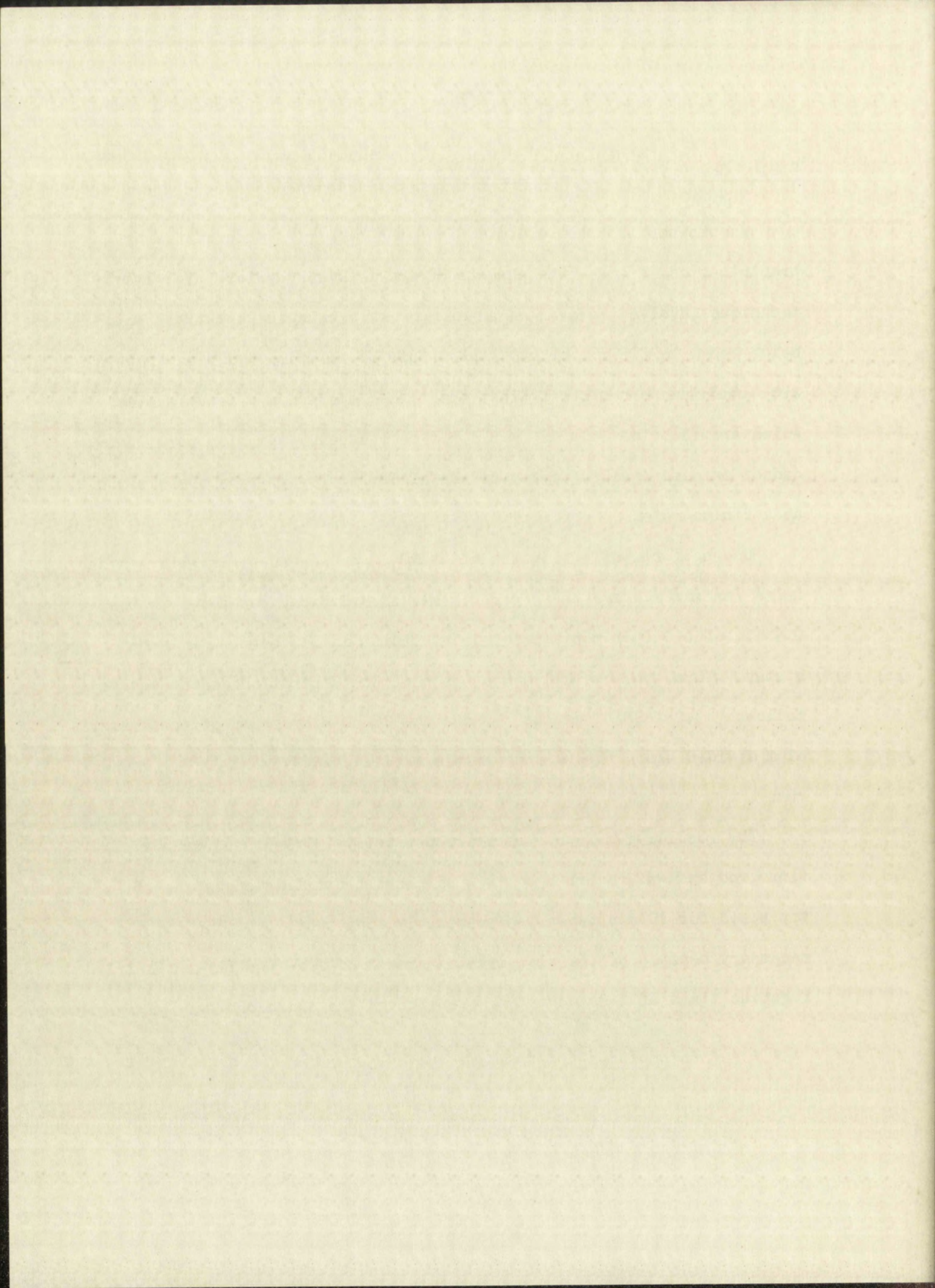


2.2.4 SEPARATION OF Am(III) FROM Am(V) AND Am(VI).

Americium(III) was separated from the higher valence states by precipitation of  $\text{AmF}_3$  with aqueous HF and La(III) carrier. The exact technique involved removal of an aliquot of exchanging solution, this being added to 0.5 ml. of 6.0 f HF. This HF solution had been treated with ammonium persulfate so that the higher americium valence states, which are fluoride soluble, would not be reduced. Ammonium persulfate cannot oxidize Am(III) to any of the higher states at room temperature at a finite rate.

One-half ml. of a solution of  $\text{La}(\text{NO}_3)_3$  or  $\text{La}_2(\text{SO}_4)_3$  in water, made up to contain 2.0 mg.  $\text{La}^{+++}$  per 0.5 ml. of solution, was added to the 0.5 ml. of 6.0 f HF containing the americium in its several valence states. Thus, the overall composition of the separation medium was as follows: 3.0 f HF, 2 mg.  $\text{La}^{+++}$ , and the 20-30 micrograms of total americium divided among the valence states Am(III), Am(V), and Am(VI)(in some runs).

The resulting mixture was stirred briefly (30 seconds) with a platinum rod and was centrifuged in a clinical centrifuge operating at top speed for 10 minutes. The reasonably long centrifugation time is necessary because of the slow crystal growth of  $\text{AmF}_3$  and  $\text{LaF}_3$ . Centrifugation times of less duration, even though the solutions were allowed



to digest at 90°-95°C for five minutes prior to centrifugation, were found to be not effective in complete removal of AmF<sub>3</sub>.

Repeated experiments showed that such a separation technique allowed 85-90% of the higher valence states, (V) or (VI), to remain in the supernatant while removing 99.5-99.8% of the initial amount of Am(III). The separation of Am(VI) from Am(III)<sup>(21)</sup> and of Am(VI) from

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(21) L. Asprey, S. Stephanou, and R. Penneman, J. Am. Chem. Soc. 73, 5715 (1951).

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Cm(III)<sup>(22)</sup> has already been reported. Since Am(V) and Np(V) have simi-

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(22) S. Stephanou and R. Penneman, J. Am. Chem. Soc. 74, 3701 (1952).

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lar infrared absorption and structure<sup>(23)</sup>, similar gross fluoride solu-

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(23) L. Jones and R. Penneman, J. Chem. Phys. 21(3), 542 (1953).

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bilities are anticipated. No precipitate of Np(V) fluoride forms in the presence of HF<sup>(24,25)</sup>.

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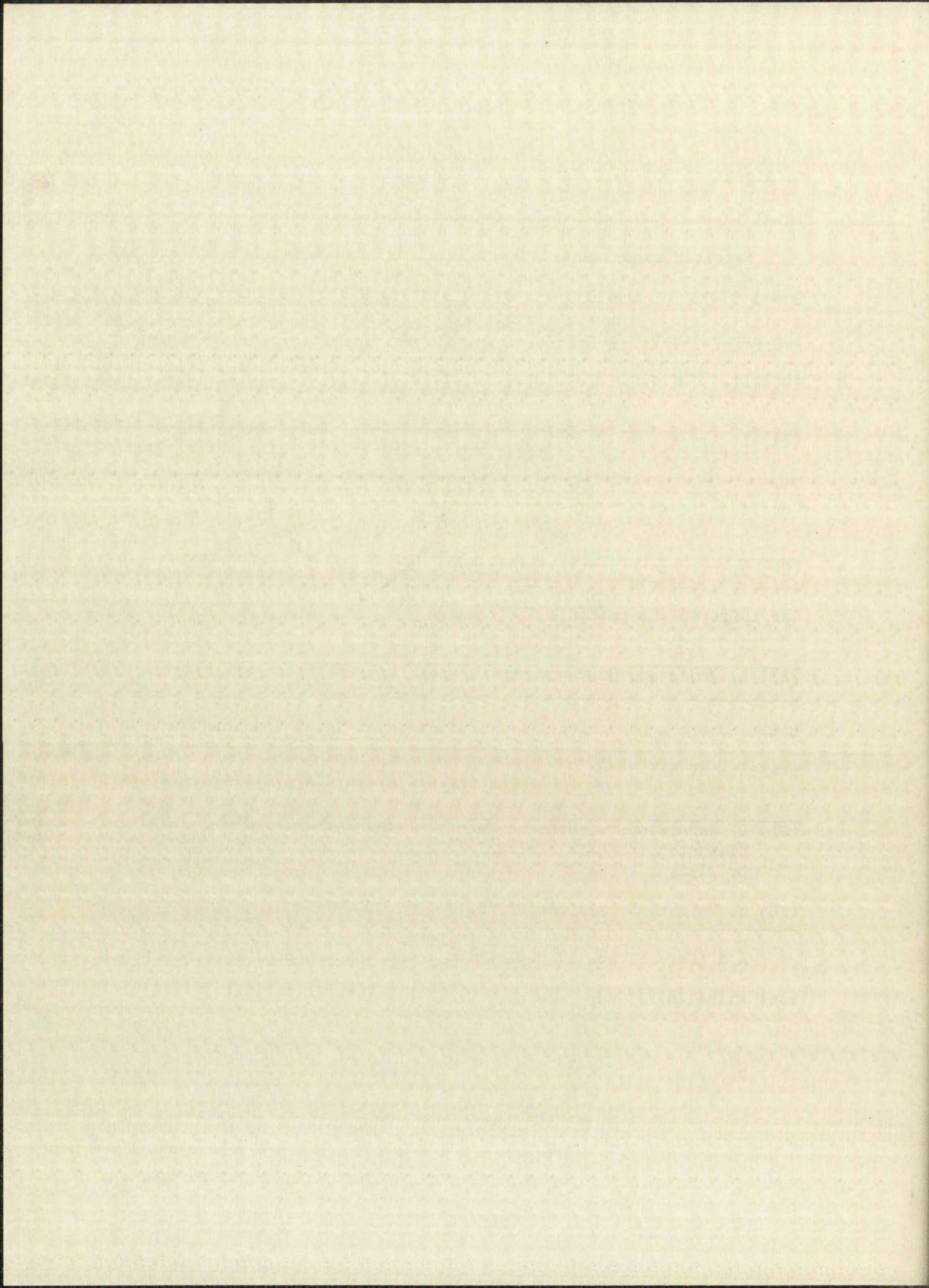
(24) L. Magnusson, J. Hindman, and T. LaChappelle, "The Transuranium Elements", NNS-IV-14B, McGraw-Hill Book Co., New York City (1949), p. 1134.

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(25) A. Voight, N. Sleight, R. Hein, and J. Wright, *ibid.*, p. 1119.

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A different type of separation technique was used in some of the runs where Am(VI) was present. It is possible to extract Am(VI) and



some Am(V) essentially free of Am(III) into diethyl ether from a solution 10.0 f HNO<sub>3</sub>-satd. La(NO<sub>3</sub>)<sub>3</sub>. The extraction of Am(VI) into diethyl ether from aqueous solutions has been reported<sup>(21)</sup>. In the runs where this technique was used, an aliquot of the exchanging mixture was added to 1.0 ml. of the 10.0 f HNO<sub>3</sub>-satd. La(NO<sub>3</sub>)<sub>3</sub> solution. One-half ml. portions of Mallinckrodt's ether (anhydrous) was added. The mixture was shaken vigorously for 5 seconds and then centrifuged briefly (30 seconds) to completely separate the two phases. An aliquot was then taken of the ether phase for counting. Table III shows the results.

TABLE III

$$K_D = \frac{[\text{Conc. org.}]}{[\text{Conc. aq.}]}, \text{ 10 f HNO}_3\text{-satd. La(NO}_3)_3; \text{ ether}$$

<u>Initial Am</u>	<u>Valence</u>	<u>K<sub>D</sub></u>
2 x 10 <sup>-4</sup> f	III	0.00175
3.1 x 10 <sup>-4</sup> f	VI	0.191

2.2.5 SEPARATION OF Am(V) AND Am(VI).

It was found that Am(VI) was preferentially extracted into ether from a solution 1.0 f HNO<sub>3</sub>-satd. NH<sub>4</sub>NO<sub>3</sub><sup>(21)</sup>. If K<sub>D</sub> is defined as  $\frac{[\text{conc. org.}]}{[\text{conc. aq.}]}$ , the following values were determined:

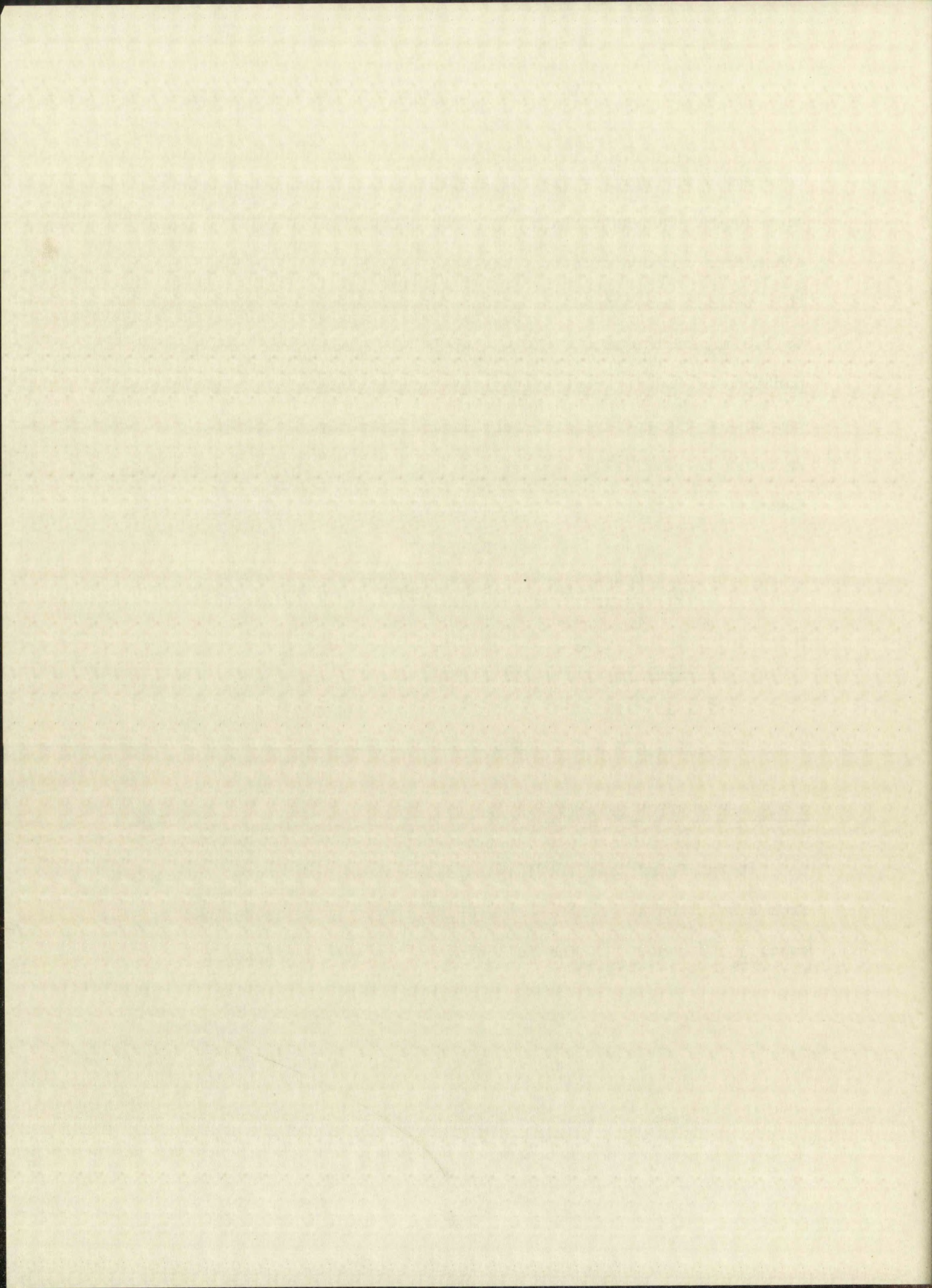


TABLE IV

<u>Conc. Am</u>	<u>Valence Am</u>	<u>K<sub>D</sub></u>	<u>Equilibration Time</u>
10 <sup>-4</sup> f	V	0.007	5 seconds
10 <sup>-4</sup> f	VI	0.54	5 seconds

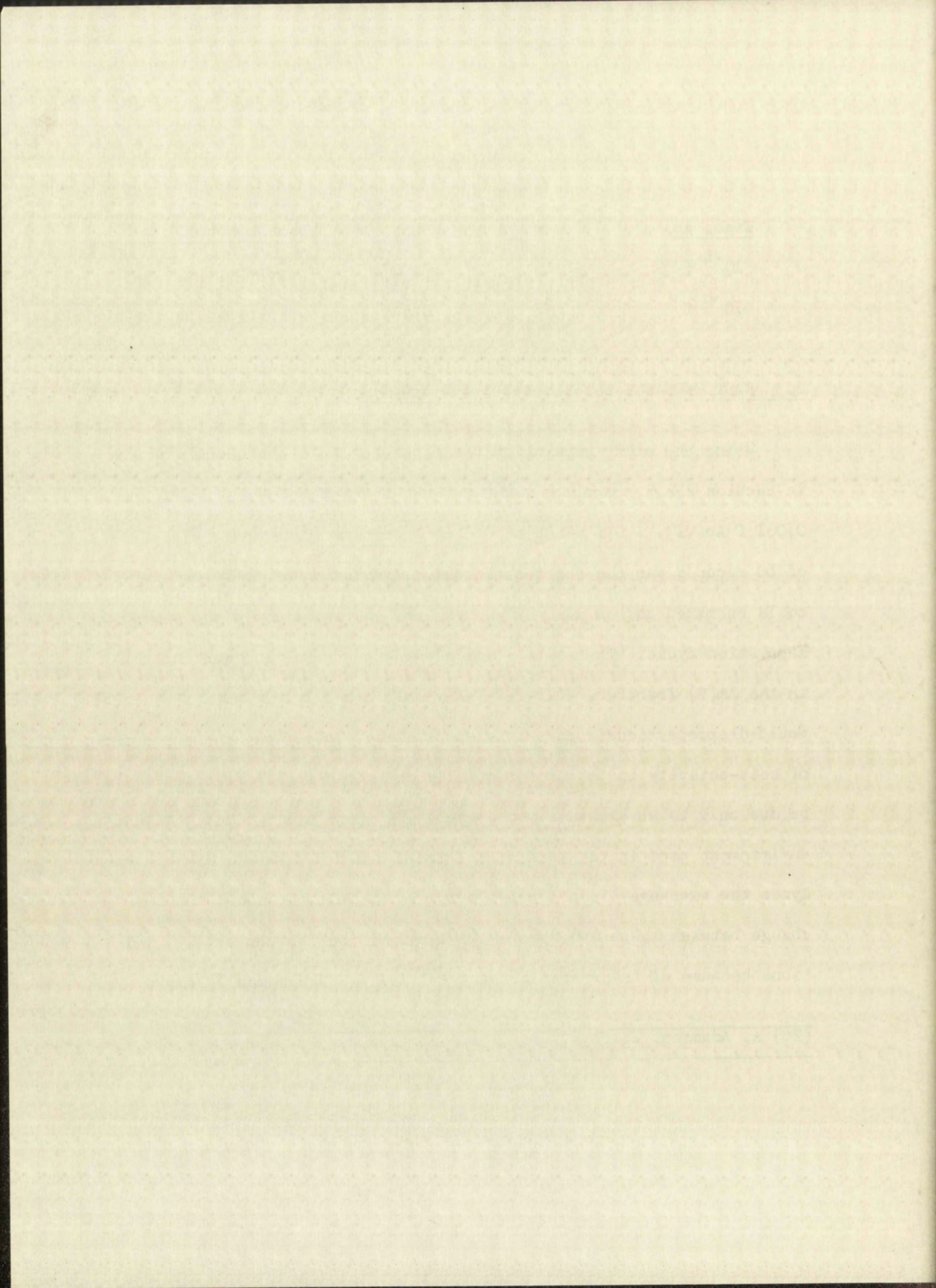
### 2.3 FAST EXCHANGE BETWEEN Am(V) AND Am(VI).

Using the ether separation technique for Am(V) and Am(VI) outlined in Section 2.2.5, complete exchange was observed between 0.001 f Am(V), 0.001 f Am(VI), 1.0 f HClO<sub>4</sub> at 0°C in less than 60 seconds. The time of 60 seconds was the shortest in which a solution of Am(V) and Am(VI) could be mixed and an aliquot removed and carried through the ether separation cycle. The isotope Am<sup>242m</sup> was the tracer and was initially in the Am(V) fraction. (In 1.0 f H<sup>+</sup>, only a negligible amount of Am(V) would disproportionate in such a short time. Therefore, the appearance of beta-activity in the preferentially extracted Am(VI) fraction could be due only to an exchange mechanism.) The possibility that the ionic environment used in the separation, i.e., 1.0 f HNO<sub>3</sub>-satd. NH<sub>4</sub>NO<sub>3</sub>, catalyzes the exchange, is not ruled out. It is felt, however, that exchange between these two species is likely to be fast under any conditions because of their similar nature<sup>(26)</sup>. J. C. Hindman<sup>(1)</sup> and co-

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(26) A. Adamson, J. Phys. Chem. 56, 858 (1952).

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workers state that the Np(V)-Np(VI) exchange is complete in less than 60 seconds.

#### 2.4 REDUCTION OF Am(V) AND Am(VI) IN AQUEOUS SOLUTION BY ALPHA RADIATION EFFECTS.

The choice of americium exchange reactions is rather limited, since there are only three solution valence states, Am(III), Am(V), and Am(VI), and the exchange between Am(V) and Am(VI), as shown in Section 2.3, is too fast to measure with present techniques. This would leave Am(III) and either Am(V) or Am(VI) as remaining possibilities for exchange studies.

Both of the higher solution valence states of americium undergo auto-reduction<sup>(27)</sup>, and Am(V) also can disproportionate<sup>(28)</sup>, although

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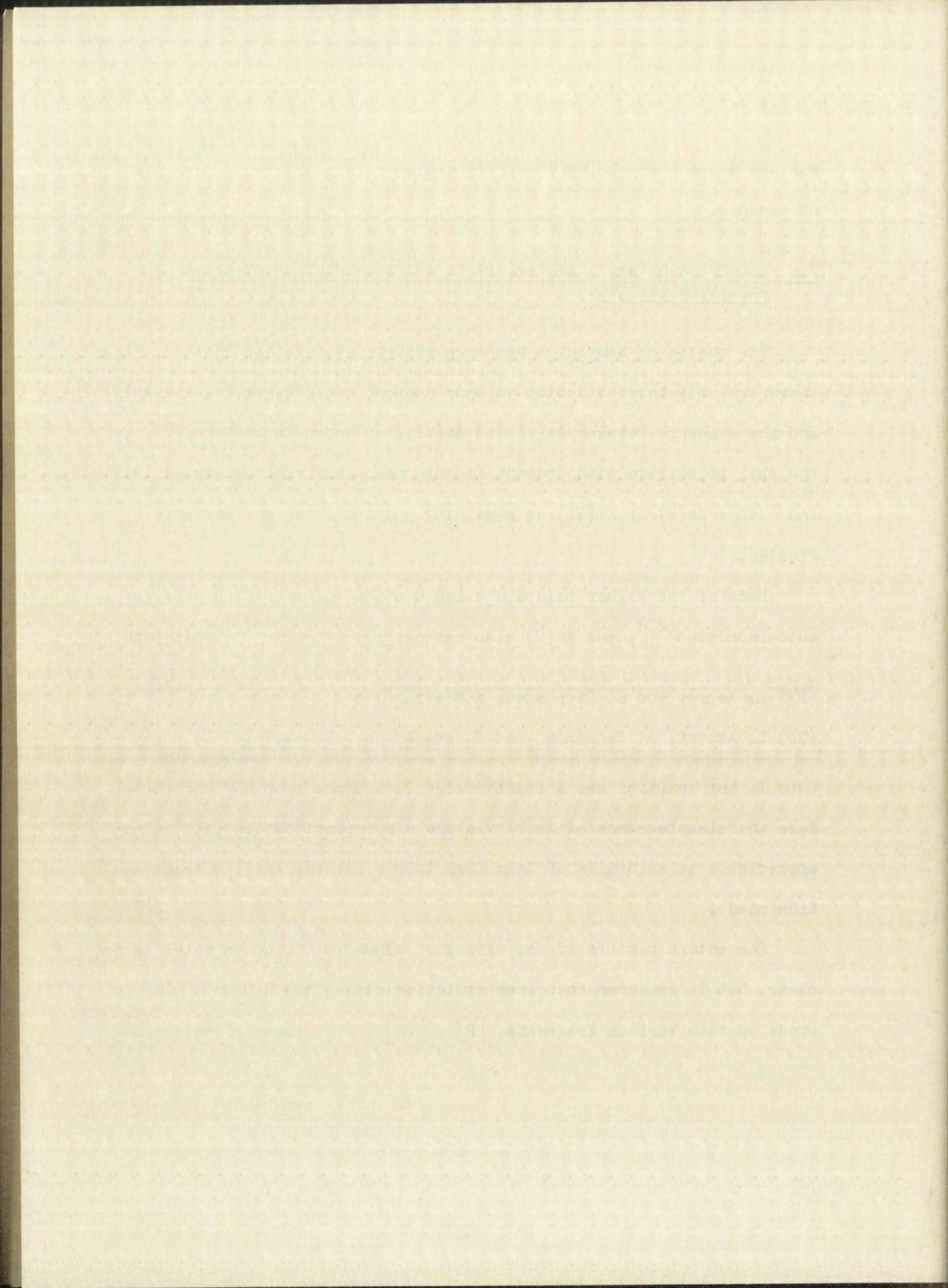
(27) L. Asprey and S. Stephanou, AECU-924 (1950).

(28) L. Asprey, R. Penneman, and S. Stephanou, AECU-925 (1950).

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this latter reaction has a fourth order dependence upon  $H^+$ , and therefore the disappearance of Am(V) via the disproportionation path is not appreciable at acidities of less than 1.00 f (at the Am(V) concentration used).

The entire picture of the effect of alpha radiation on water is not clear, but it is known that such radiation causes the  $H_2O$  molecules to break up into various fragments,  $[H]$ ,  $[OH]$ , etc., some of which com-



bine to yield  $H_2O_2$ <sup>(29)</sup>. The higher valence states of americium can

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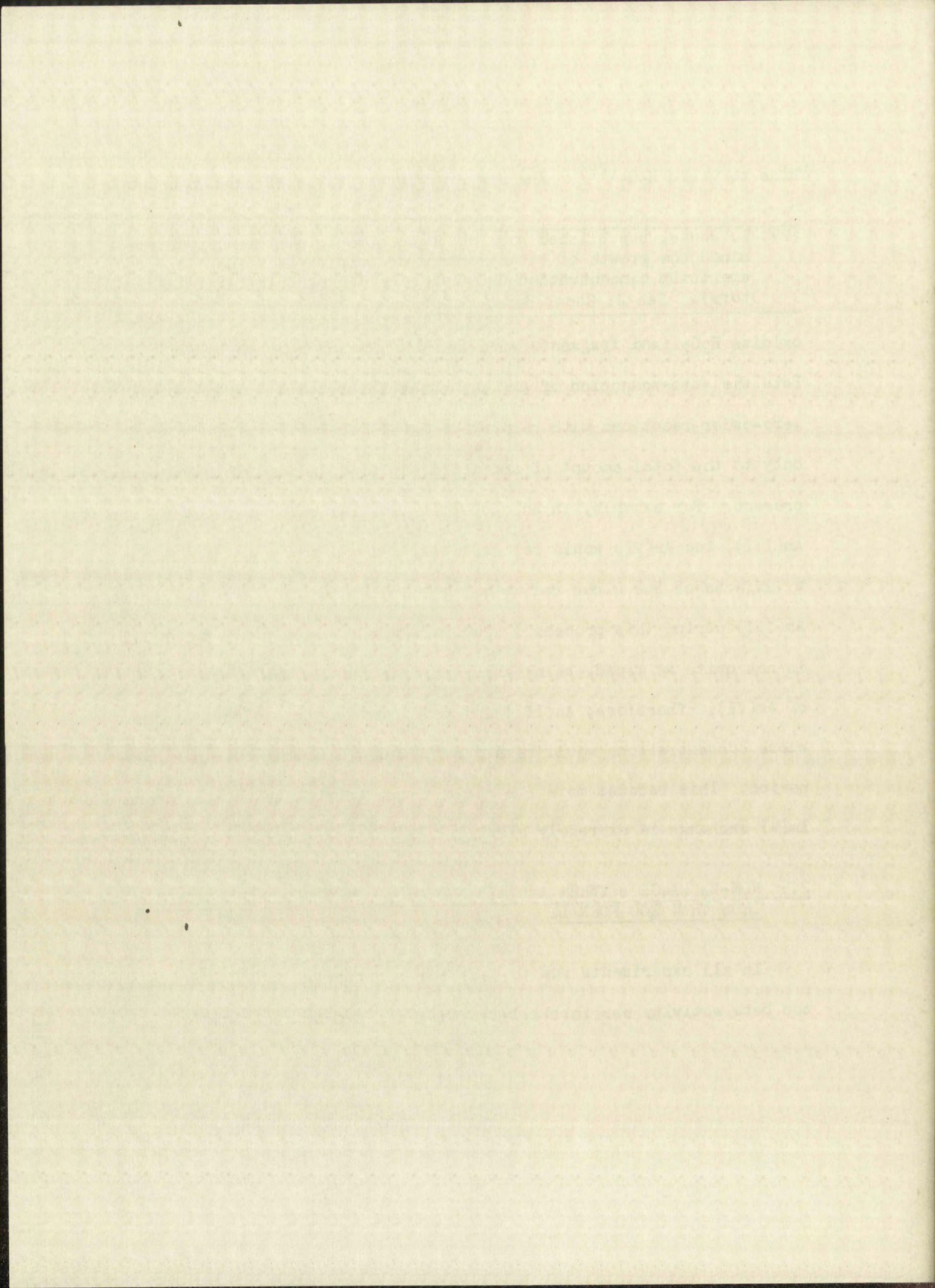
(29) L. Jones, unpublished work which spectrophotometrically determined the growth of titanyl peroxide complex as a function of americium concentration and time (Los Alamos Scientific Laboratory). See J. Chem. Phys. 21(1), 42 (1953).

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oxidize  $H_2O_2$  (and fragments such as  $[H]$ ), being reduced to Am(III). Both the auto-reduction of Am(VI) and Am(V) are to a good approximation zero-order reactions with respect to Am(VI) or Am(V), being proportional only to the total amount of americium (or total amount of alpha-emitter) present. For example, in an equi-molar initial mixture of Am(VI) and Am(III), the Am(VI) would be completely reduced to Am(V) in  $\sim 1/2$  day by effects of its alpha radiation. (There is negligible reduction to Am(III) during this process.) The self-reduction of Am(V) to Am(III) is not quite as rapid, being about half as fast as the rate of reduction of Am(VI). Therefore, Am(III) and Am(V) are the two valence states whose concentrations would remain most nearly constant over a longer period. This becomes more important since, as will be shown, the Am(III)-Am(V) exchange is extremely slow.

#### 2.5 NON-EXCHANGE BETWEEN Am(III) AND Am(V) IN ACID CONCENTRATIONS LESS THAN 200 FORMAL.

In all experiments run to test the exchange of Am(III) and Am(V), the beta activity was initially in the (III) oxidation state only. If



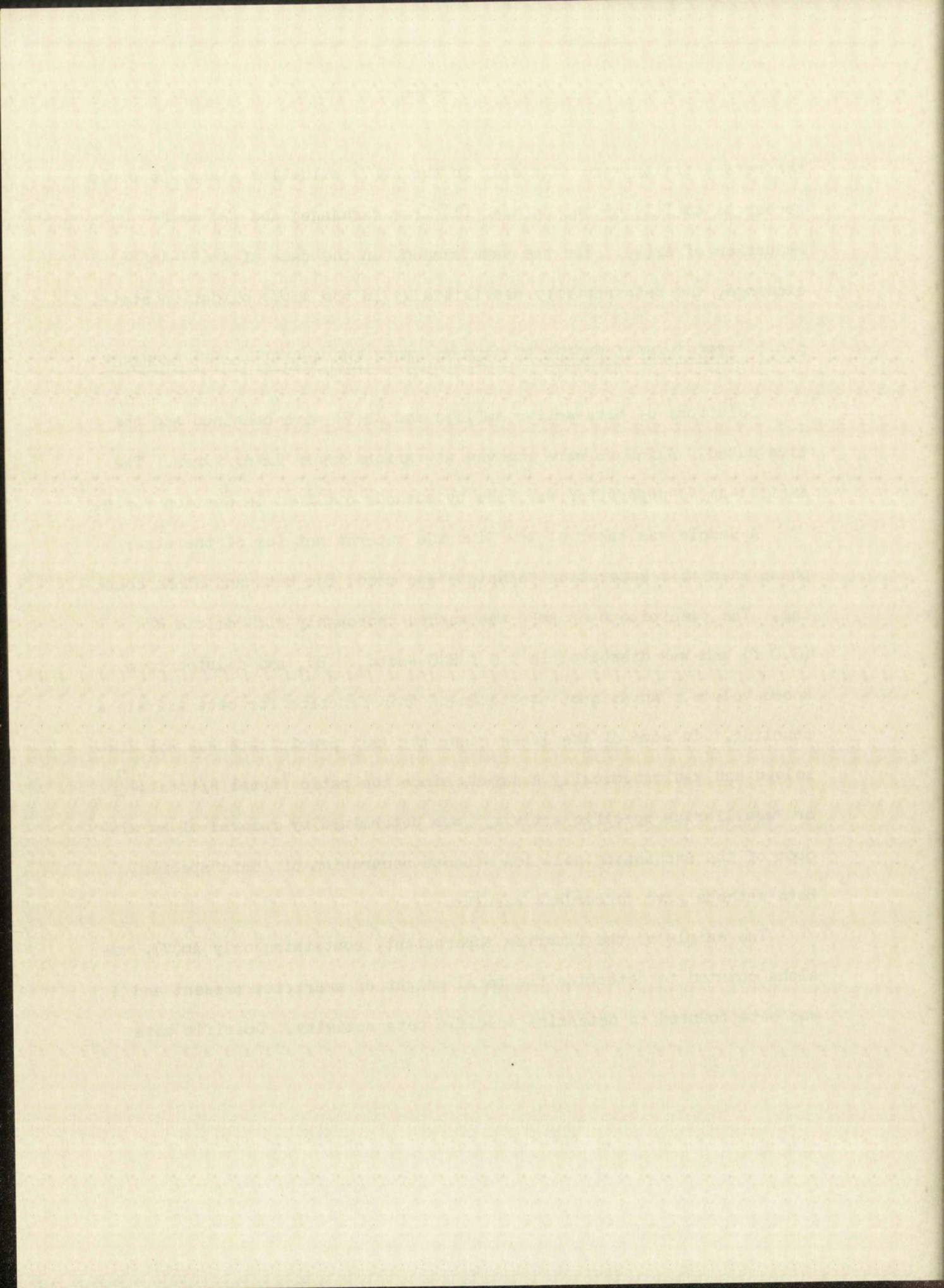
the beta activity were initially in the Am(V) oxidation state, it could appear as Am(III) by two paths: (1) true exchange; and (2) self-reduction of Am(V). For the same reason, in the case of Am(V)-Am(VI) exchange, the beta activity was initially in the Am(V) oxidation state.

#### 2.5.1 EXPERIMENTAL PROCEDURE USED TO STUDY THE Am(III)-Am(V) EXCHANGE.

Solutions of beta-active Am(III) and Am(V) were combined and the time noted. Aliquots were removed at various known later times. The Am(III)-Am(V) separation was made by methods outlined in Section 2.2.4.

A sample was taken of the fluoride supernatant (or of the ether phase when this separation technique was used) for beta and alpha counting. The precipitate of  $\text{AmF}_3$  was washed thoroughly with dilute HF (3.0 f) and was dissolved in 1.0 f  $\text{HNO}_3$ -satd.  $\text{H}_3\text{BO}_3$  and diluted to a known volume. An aliquot was taken of this fraction for beta and alpha counting. In some of the later runs, the  $\text{AmF}_3$  precipitate was not dissolved and radiochemically assayed, since the ratio  $[\text{total } \beta / \text{total } \alpha]$  or "equilibrium specific activity" was determined by removal of an aliquot of the exchanging solution without separation of ionic species. Both methods gave concordant results.

The sample of the fluoride supernatant, containing only Am(V), was alpha counted to determine the total weight of americium present and was beta counted to determine specific beta activity. Specific beta

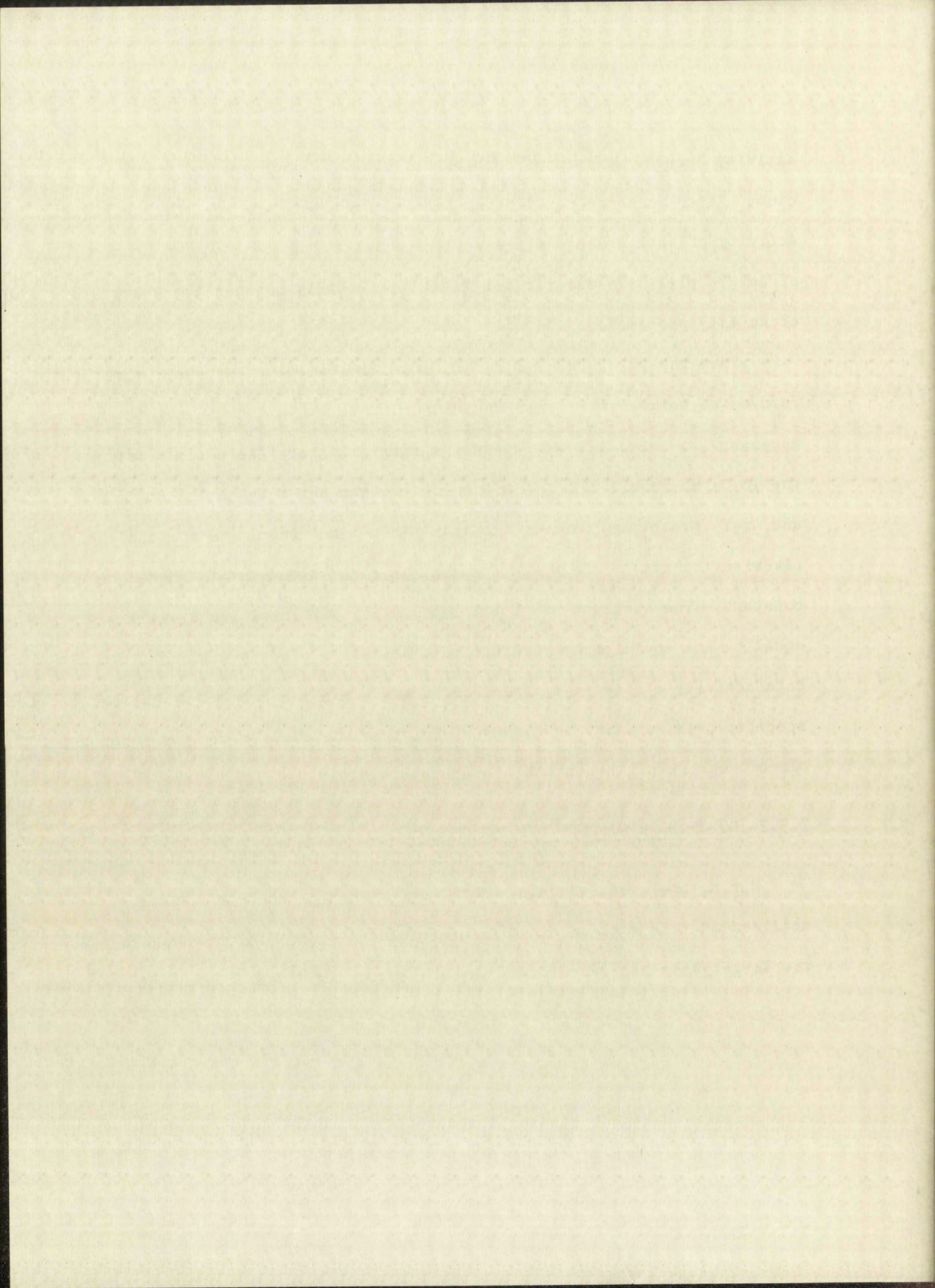


activity here is defined as beta counts/min. per microgram of americium. After exchange equilibrium has been reached, the specific beta activity of each valence state will be equal, as the beta-active atoms of  $\text{Am}^{241m}$  will have distributed themselves equally between the atoms of  $\text{Am(III)}$  and  $\text{Am(V)}$ .

Since the aliquots used to determine the extent of exchange were removed at various times and therefore counted at various times, it was necessary to refer all beta counts to some arbitrary "zero-time" using the 16.01 hour half-life. The sum of the beta activity in the  $\text{Am(III)}$  and  $\text{Am(V)}$  fractions, referred to this "zero-time" should be constant. Likewise the sum of the weight present in each valence state should be constant. The quotient of  $[\text{Total Beta Activity}] / [\text{Total Weight}]$  will be equal to the equilibrium specific beta activity. The initial specific beta activity of the  $\text{Am(V)}$  fraction is zero, and the rate at which the specific beta activity in the  $\text{Am(V)}$  fraction increases with time is a direct measure of the extent of exchange.

#### 2.5.2 COUNTING EQUIPMENT AND TECHNIQUES.

During the great majority of the experiments, the beta counter utilized in this work was that as described on p. 6. The presence of the large gamma background associated with the  $\text{Am}^{241}$  was a constant





disadvantage in that the true beta activity must be of an appreciable level to be accurately counted. For example, a sample containing 1.00 micrograms of  $\text{Am}^{241}$  alone gave rise to 4,881 "recorded" beta counts/minute in the instrument. In the later runs, the beta activity was measured on a scintillation counter<sup>(30)</sup> which was especially suitable for

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(30) This counter was of a special design, constructed by D. Hull and H. Eberline (Los Alamos Scientific Laboratory). It utilized a transtilbine crystal and an RCA-5819 photomultiplier tube. While the 0.628 Mev beta and the 0.05 Mev gamma both gave rise to scintillations in the crystal, the produced voltages in the photomultiplier tube were greatly different. A voltage "gate" was installed prior to the scaler input which blocked out the lower energy gammas and allowed only the betas to be recorded.

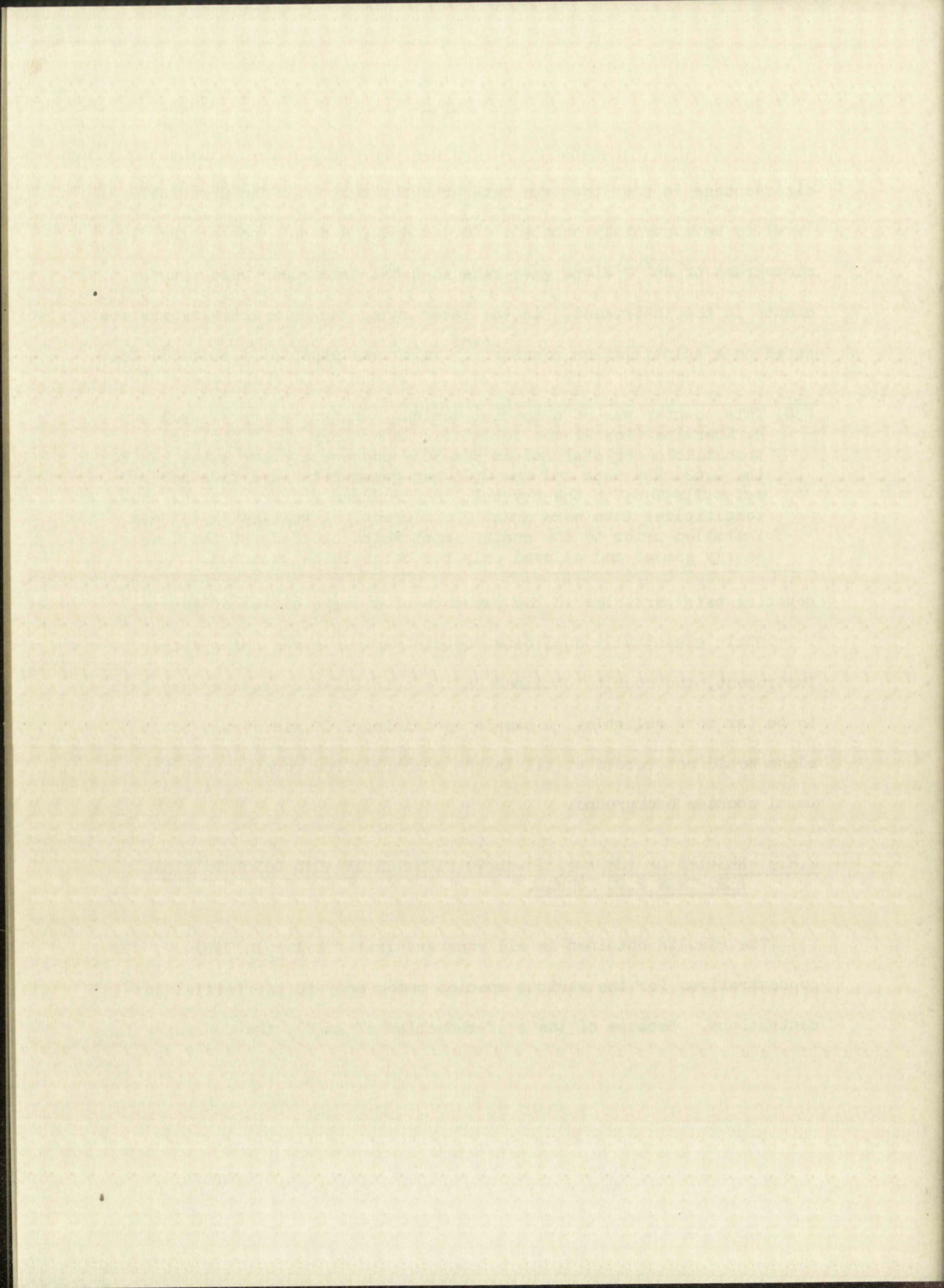
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counting beta particles in the presence of a large excess of gammas.

While essentially duplicate results were observed using either instrument, the results obtained on the scintillation counter are felt to be far more reliable. A sample containing 2.00 micrograms of  $\text{Am}^{241}$  alone would not record at all in the scintillation counter over the usual counter background.

### 2.5.3 RESULTS OF THE $\text{Am(III)}$ - $\text{Am(V)}$ EXCHANGE IN ACID CONCENTRATIONS LESS THAN 2.00 FORMAL.

The results obtained in all runs are listed below in Table V. The concentrations for the various species refer only to the initial concentrations. Because of the self-reduction of  $\text{Am(V)}$ , the concentrations



of Am(V) and Am(III) were not constant during any one run.

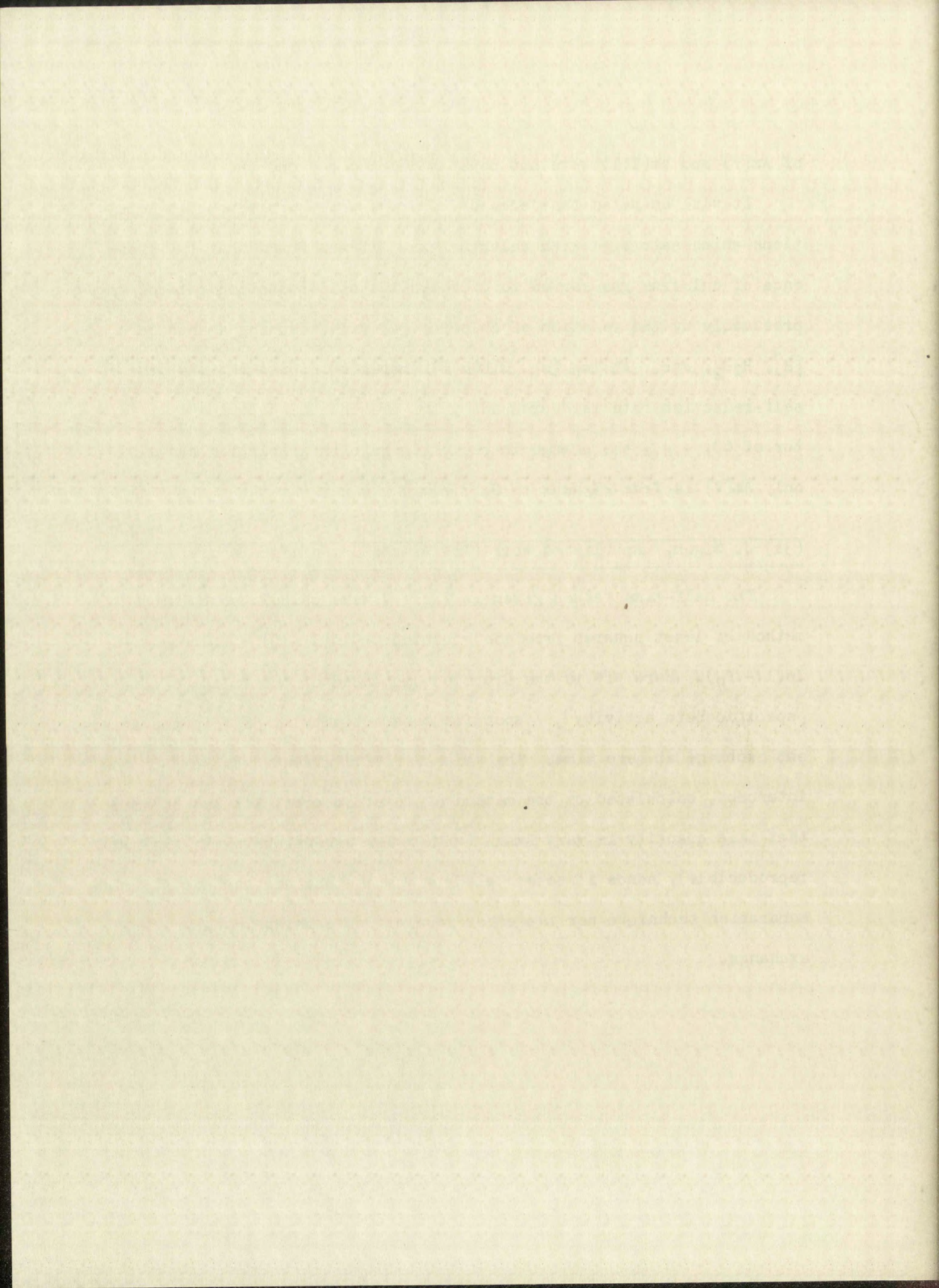
It will be noted that some of the runs were carried out in solutions which saturated with chlorine gas. It was found that the presence of chlorine gas served to decrease the self-reduction rate of Am(V) presumably by the reaction of chlorine gas with reducing agents such as [H], H<sub>2</sub>O<sub>2</sub>, etc. At low (ca. 0.001 f) americium concentrations, the self-reduction rate is decreased by the presence of chlorine by a factor of 60, e.g., the change in reduction rate in a solution containing only Am(V) is from 2%/hour to 0.87%/day<sup>(31)</sup>.

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(31) J. Nigon, unpublished work (Los Alamos Scientific Laboratory).

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The half-time values given in Table V were calculated by the method of least squares from the equation:  $-\ln(1 - f) = (\text{slope}) t - \ln(1 - f_0)$ . Here "f" is the fraction exchanged or the ratio:  $[\text{specific beta activity}]_t / [\text{specific beta activity}]_0$ , "f<sub>0</sub>" is the apparent exchange at zero time. The value for "f<sub>0</sub>" given in Table V is the intercept, calculated by the method of least squares. It can be seen that this quantity is very small (with a few exceptions which are non-reproducible), hence it seems valid to assume that neither the fluoride separation technique nor the ether separation technique catalyze the exchange.



The small solubility of the  $\text{AmF}_3$  in the supernatant contributes some beta activity to the supernatant. Using the known efficiency for the HF separation technique and the known initial concentrations of  $\text{Am(III)}$  and  $\text{Am(V)}$ , it can be shown that the small solubility of  $\text{AmF}_3$  in the supernatant can show  $\sim 1.0\%$  apparent exchange even when  $\text{Am(III)} \approx \text{Am(V)}$ . This solubility, however, undoubtedly accounts for a major fraction of the apparent "induced" exchange or the value of " $f_0$ " in Table V.

It can be noted from Table V that Run 50 gave a fairly short ( $< 50$  hours) half-time, but valid reasons exist for disregarding this result. In Run 50, rapid reduction of  $\text{Am(V)}$  was noted so that the  $\text{Am(III)} \gg \text{Am(V)}$  during the time of determinations. The reason for this reduction is unknown and is ascribed to some reducing impurity. However, in this run, the small solubility of the  $\text{AmF}_3$  in the supernatant becomes a major fraction of the beta activity in the supernatant. If the specific beta activity of the supernatant is ascribed totally to  $\text{Am(V)}$ , a large, erroneous apparent exchange is calculated.

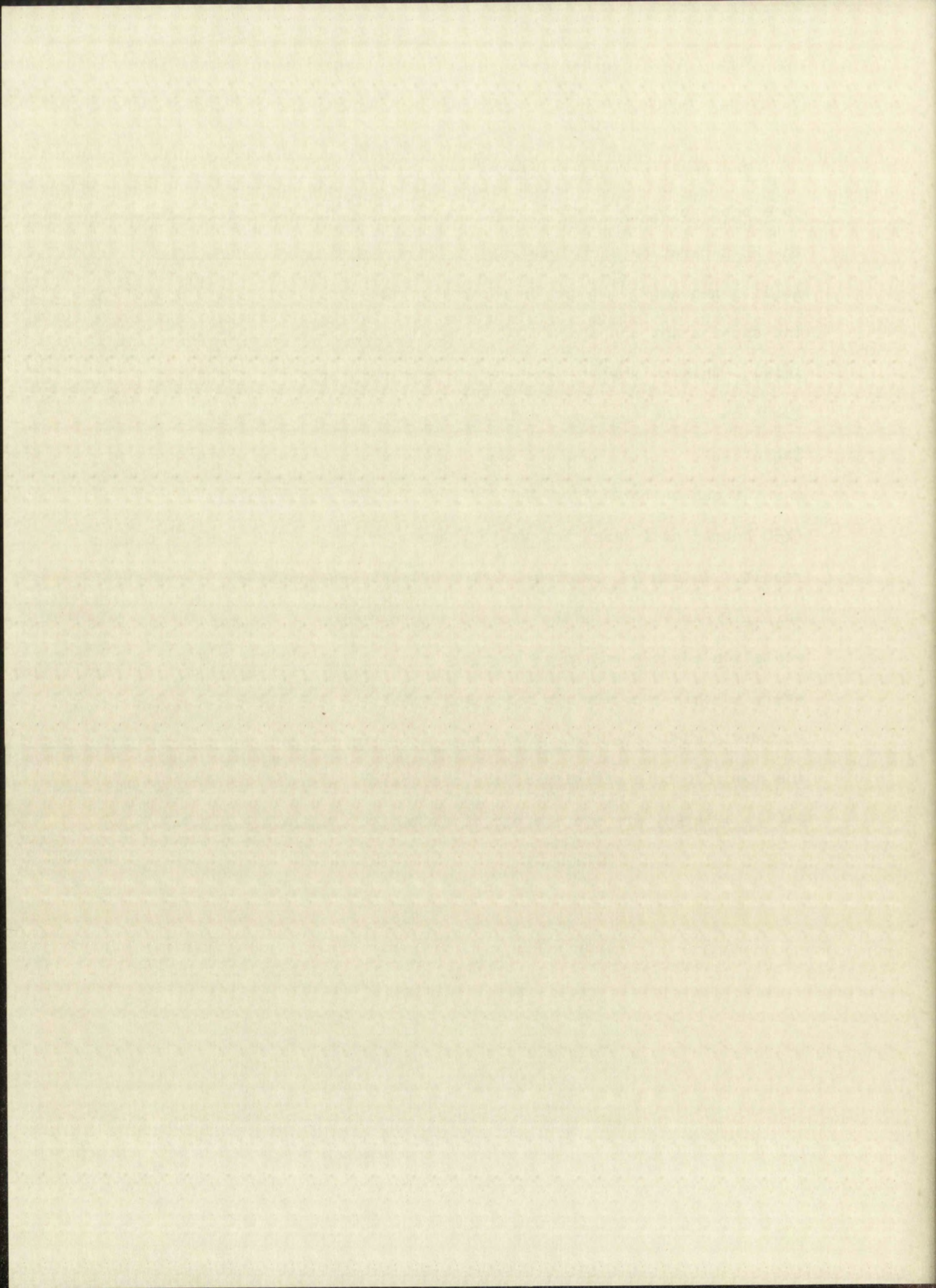


TABLE V

<u>Run No.</u>	<u>Am(III) Initial Conc. f.</u>	<u>Am(V) Initial Conc. f.</u>	<u>Calc'd. Half-Time in Hours</u>	<u>Calc'd. "f<sub>o</sub>"</u>	<u>Maximum Time Followed in Hours</u>	<u>Temp. °C</u>
22	0.0003	0.002	639	1.5%	37.8	70
34	0.0005	0.002	238	0.0%	25.2	70
44	0.0005	0.002	289	1.4%	18.1	70
50	0.0005	0.002	(42.2)	2.6%	5.38	70
56	0.001	0.003	872	1.2%	17.2	75
122	0.001	0.003	1100	1.0%	61.6	22
134	0.001	0.01	2650	0.0%	84.5	22
8	0.009	0.014	1100	1.1%	66.4	40
56	0.015	0.015	417	1.0%	22.4	22
65	0.001	0.0005	652	5.9%	57.7	22
73	0.013	0.018	1942	1.3%	45.2	22
138	0.018	0.019	>2000	1.0%	12.6	80

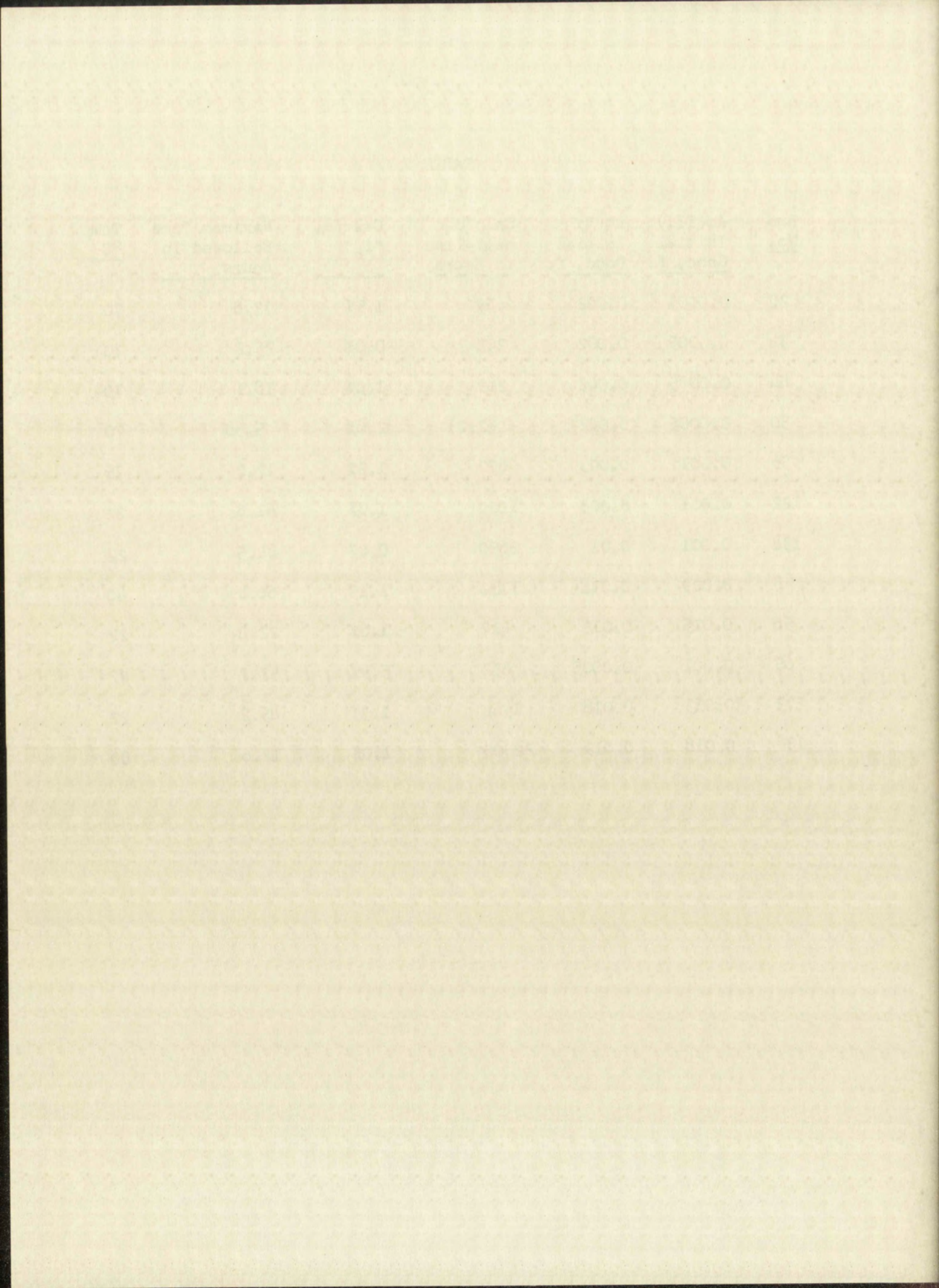
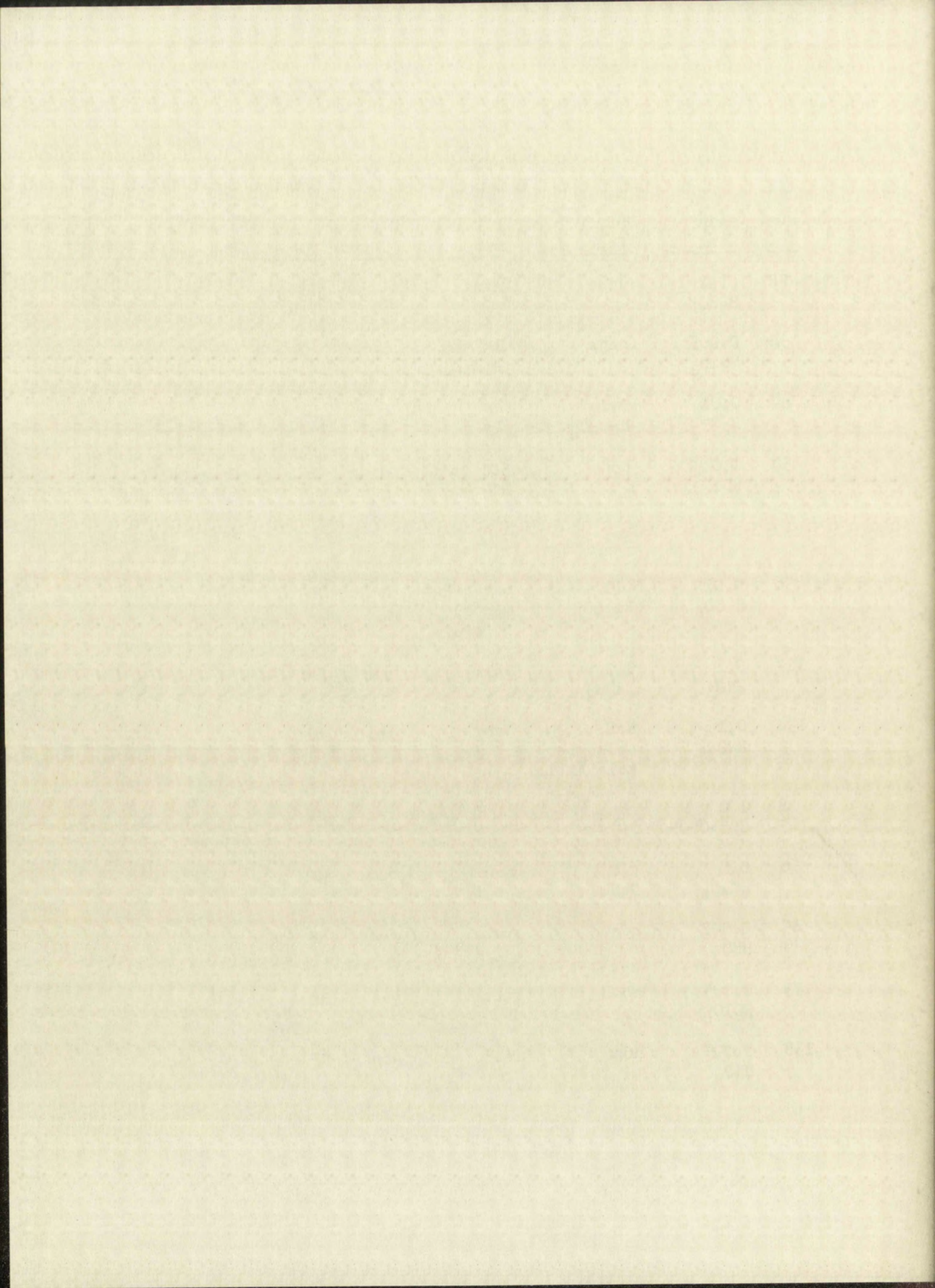




TABLE V, contd.

<u>Run No.</u>	<u>Acid Conc. f.</u>	<u>Salt Conc. f.</u>	<u>Illumi- nation</u>	<u>Cl<sub>2</sub> Gas</u>	<u>Sepn. Agent</u>	<u>Remarks</u>
22	0.12 HClO <sub>4</sub>	none	room	none	HF	
34	0.005 HClO <sub>4</sub>	none	100 watt 4" away	none	HF	
44	0.01 H <sub>2</sub> SO <sub>4</sub>	0.1 Na <sub>2</sub> SO <sub>4</sub>	"	none	HF	
50	1.0 HCl	none	500 watt 4" away	none	HF	Short half-time probably not valid because of rapid reduction of Am(V).
56	0.01 H <sub>2</sub> SO <sub>4</sub>	0.1 Na <sub>2</sub> SO <sub>4</sub>	u.v. (Hg- vapor) 4" away	none	HF	
122	0.1 HNO <sub>3</sub>	1.0 LiNO <sub>3</sub>	dark	yes	HF	
134	0.1 HNO <sub>3</sub>	NaF; 1.2 moles per mole Am(III)	dark	yes	HF	
8	1.0 CCl <sub>3</sub> COOH	none	dark	yes	HF	
56	0.5 HClO <sub>4</sub>	6.0 NaNO <sub>3</sub>	room	none	HF	
65	0.002 HNO <sub>3</sub>	none	room	yes	HF	
73	0.005 HClO <sub>4</sub>	none	room	yes	HF	
138	0.005 HNO <sub>3</sub>	none	room	none	HF	

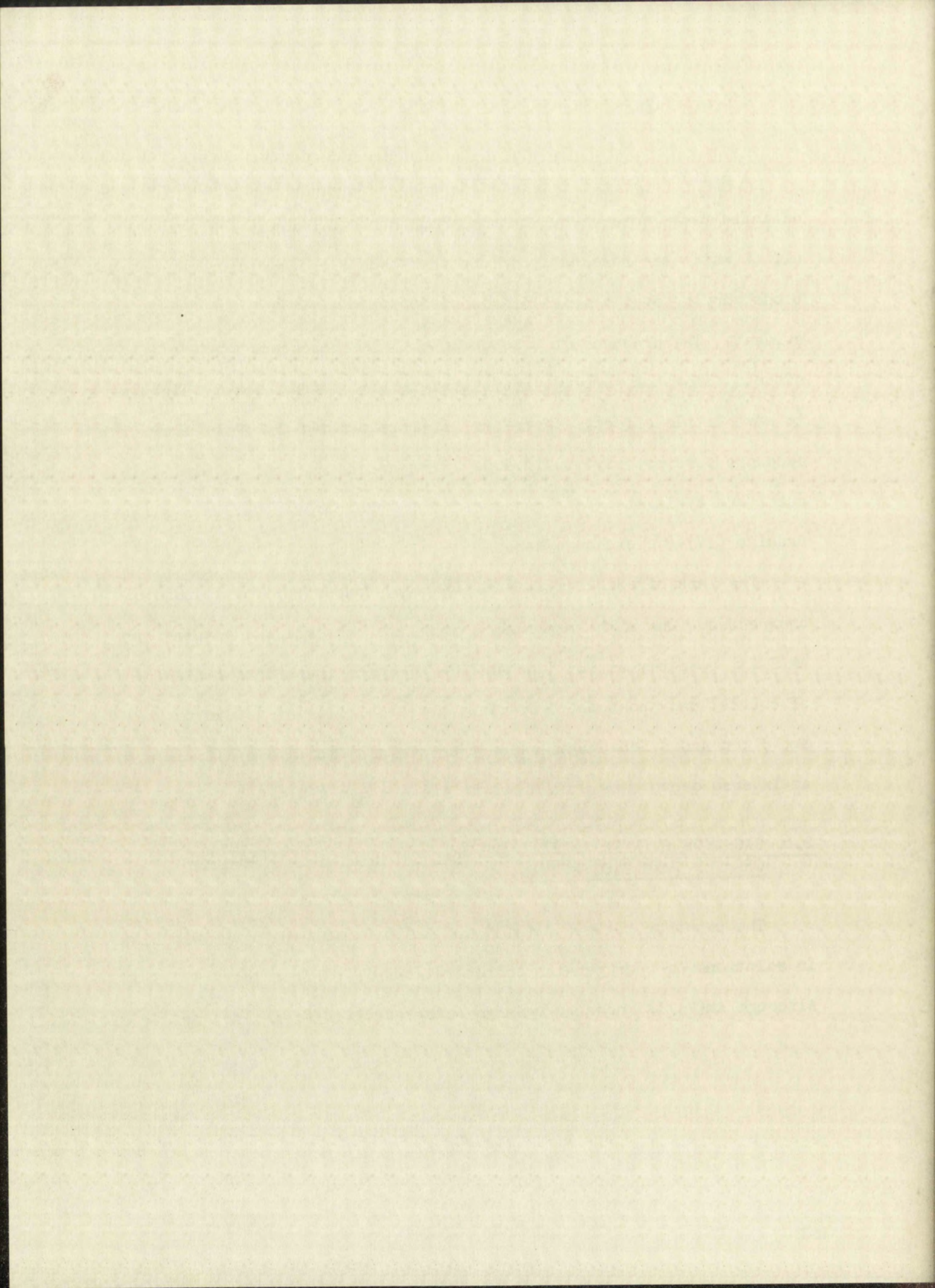


A critical comparison of several of the above runs brings several definite facts into view. In comparing Runs 34, 44, 65, 73, and 138, all of which are reasonably dilute in  $H^+$  but with americium concentrations varying over a range of almost 10-fold, very little exchange is evident. The presence or absence of chlorine gas seems to have little effect. Elevated temperatures, ultra-violet or incandescent light seem to have little effect. Therefore, it seems evident that the americium exchange does not have an inverse hydrogen-ion dependence; nor is it catalyzed by light. Both conclusions are at complete variance with the uranium (IV)-(VI) exchange case.

The lack of exchange at such low acid concentrations is somewhat unexpected. One might reasonably postulate a hydrolyzed species of Am(III), possibly  $Am(OH)^{++}$  or  $Am(OH)_2^+$ . Since these ions (which are, of course, only postulated species) have a similar structure to the Am(V) ion  $AmO_2^+$ , one might suspect an overall exchange mechanism with an inverse dependence upon  $H^+$  as in the uranium (IV)-(VI) exchange.

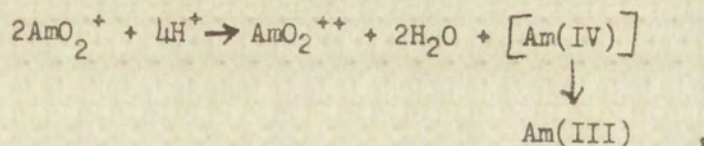
#### 2.6 EXCHANGE BETWEEN Am(III) AND Am(V) IN ACID CONCENTRATIONS GREATER THAN 2.00 FORMAL.

The exchange between Am(III) and Am(V) was shown to be very slow in solutions of hydrogen-ion concentrations  $< 2.00$  f in Section 2.5. Although Am(V) is known to undergo auto-reduction to Am(III) by a zero-



order reaction with the products of alpha radiation, the reverse kinetic path is evidently not available for an exchange mechanism.

In the disproportionation of Am(V), i.e.:<sup>(28)</sup>



Am(IV) is postulated as an intermediate in the formation of Am(III).

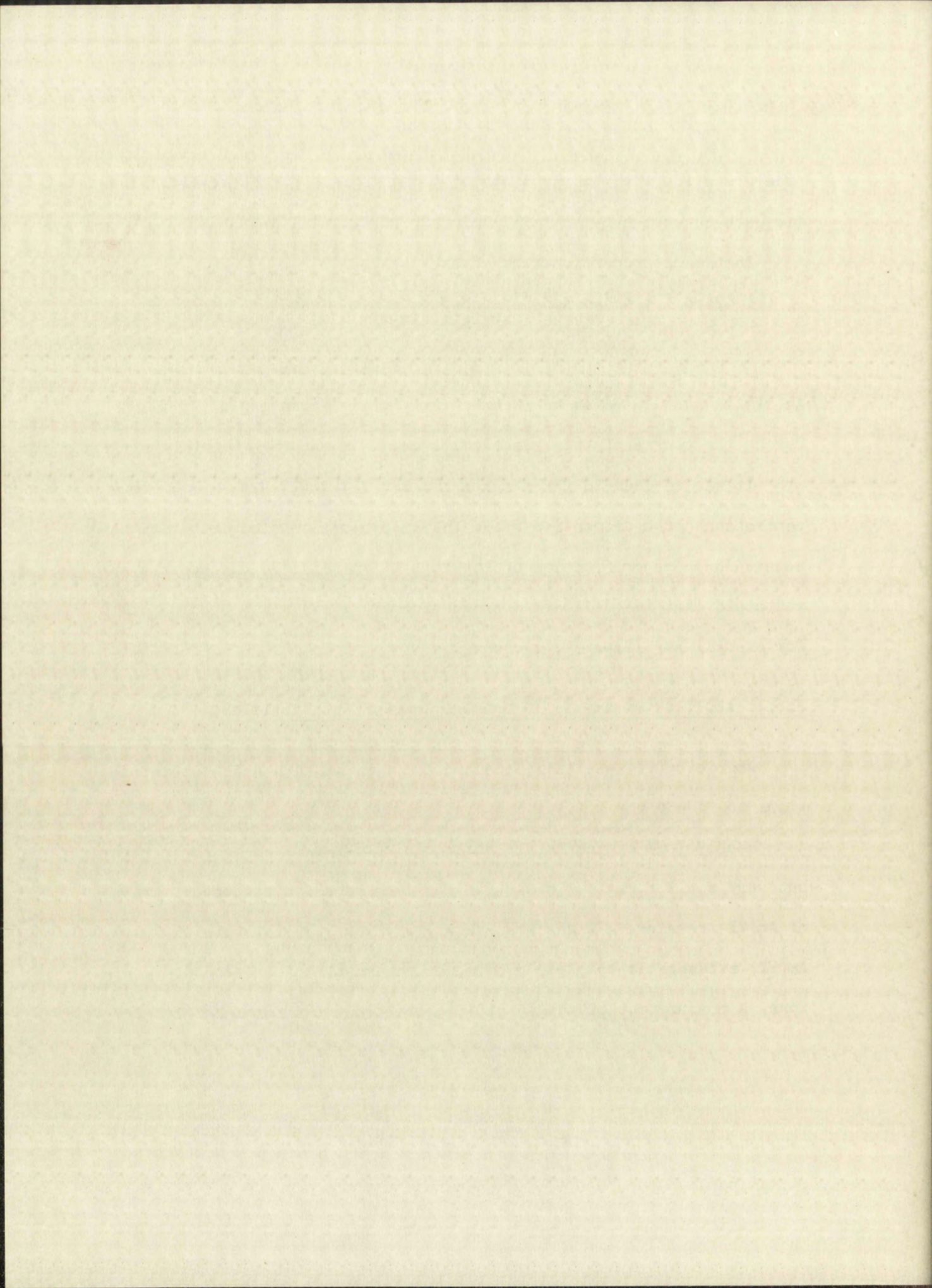
During the course of this reaction, a path for exchange might be opened.

It was decided to investigate the Am(III)-Am(V) exchange in concentrations of hydrogen-ion where the disproportionation mechanism accounts for a major fraction of the rate at which Am(V) disappears. It was hoped that the deliberate production of Am(IV) might open a path for overall Am(III)-Am(V) exchange.

#### 2.6.1 ADDITION OF Am(VI) TO MAINTAIN Am(V) CONCENTRATIONS.

Americium(VI) was introduced in the runs at high acid concentrations to "feed" the Am(V).

Nearly 100% of the Am(VI) undergoes auto-reduction to Am(V) with but very small formation of Am(III) as long as a finite concentration of Am(VI) remains. It has been shown (Section 2.3) that the Am(V)-Am(VI) exchange is complete within, at the most, a few seconds. Therefore, a measurement of the specific activity of the combined fluoride



soluble states, Am(V) and Am(VI), will be a direct measure of the rate of the Am(III)-Am(V) exchange as long as the Am(III)-Am(V) exchange is of the order of hours.

2.6.2 RESULTS OF THE Am(III)-Am(V) EXCHANGE IN ACID CONCENTRATIONS GREATER THAN 2.00 FORMAL.

The data collected in runs made in solutions where the hydrogen-ion concentration was  $>2.00$  f are shown in Table VI. As in Table V, the half-times indicated are the least square values, and the values of "f<sub>0</sub>" are the least-square intercepts and have the same significance as in Table V.

TABLE VI

Run No.	Am(III) Initial Conc. f.	Am(V) Initial Conc. f.	Am(VI) Initial Conc. f.	Calc'd. Half-Time in Hours	Calc'd. "f <sub>0</sub> "	Max. Time Followed in Hours	Temp. °C
70	0.02	0.02	0.000	36.2	10.1%	46.0	22
146	0.001	0.000	0.001	59.5	1.1%	15.8	22
4(b)	0.017	0.017	0.017	117	0.0%	10.2	22
27	0.010	0.010	0.010	444	0.3%	72.3	22
135	0.011	0.010	0.007	17.9-26.1	6.0%	17.9	80
145	0.021	0.027	0.014	39.0-40.4	3.7%	34.3	80
3	0.032	0.033	0.016	15.8-23.4	15.3%	4.87	78
4(a)	0.020	0.021	0.010	35.0-67.5	6.5%	5.45	78
56	0.088	0.132	0.068	11.6-17.4	6.3%	6.30	84

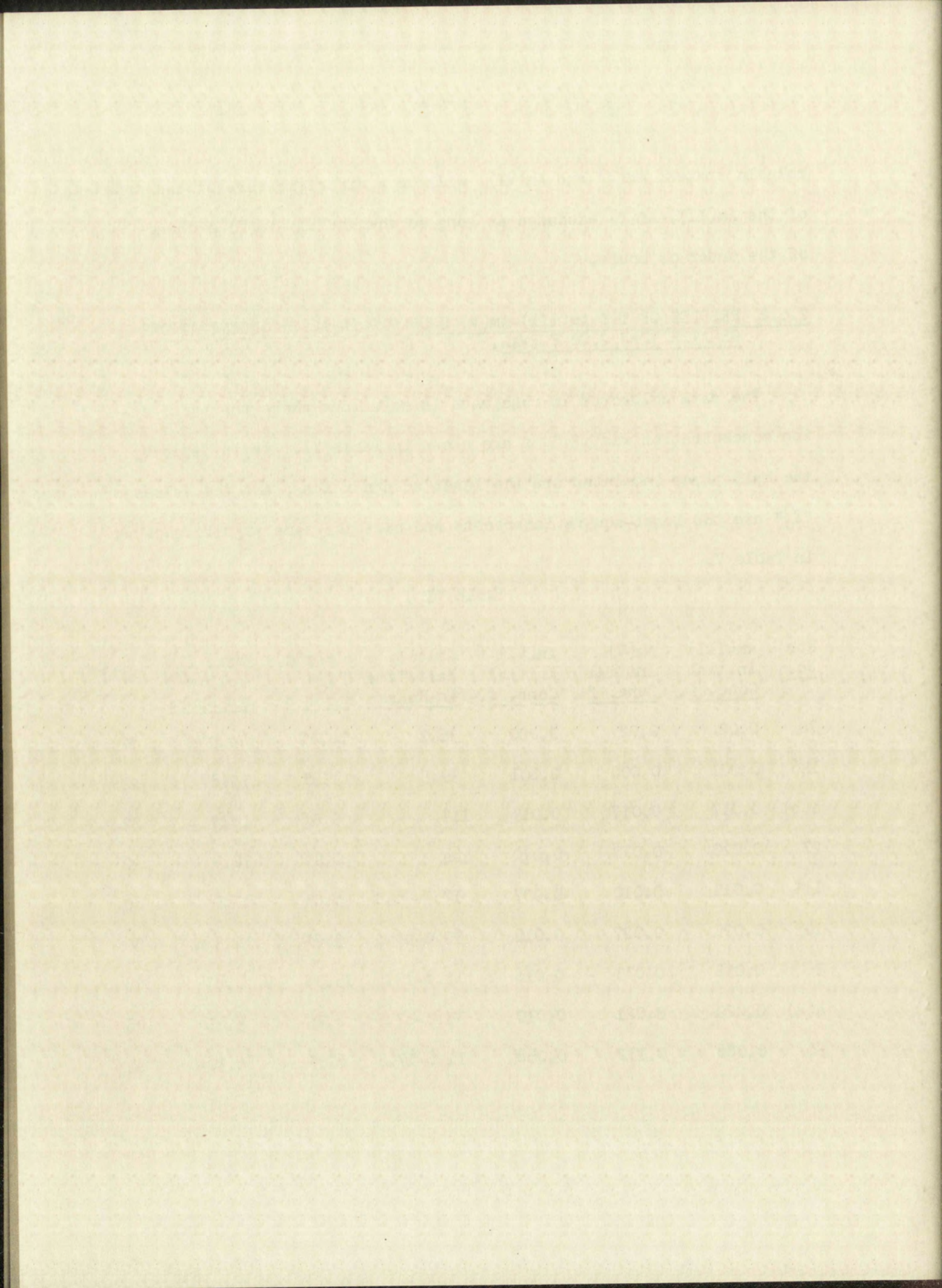




TABLE VI, contd.

<u>Run No.</u>	<u>Acid Conc. f.</u>	<u>Salt Conc. f.</u>	<u>Illumination</u>	<u>Chlorine Gas</u>	<u>Separation Agent</u>
70	2.0 H <sub>2</sub> SO <sub>4</sub>	none	dark	yes	HF
146	10.0 HNO <sub>3</sub>	none	room	none	ether
4(b)	11.7 HNO <sub>3</sub>	none	room	none	ether
27	10.0 HNO <sub>3</sub>	none	room	none	ether
135	2.02 H <sub>2</sub> SO <sub>4</sub>	none	room	none	HF
145	3.46 H <sub>2</sub> SO <sub>4</sub>	none	room	none	HF
3	10.0 HNO <sub>3</sub>	none	room	none	HF
4(a)	5.00 HNO <sub>3</sub>	none	room	none	HF
56	10.0 HNO <sub>3</sub>	none	room	none	HF

It can be seen from Table VI that the majority of the runs which gave measurable exchange were made at elevated temperatures and at high acid concentrations. The data from these runs are listed again in condensed form in Table VII below.

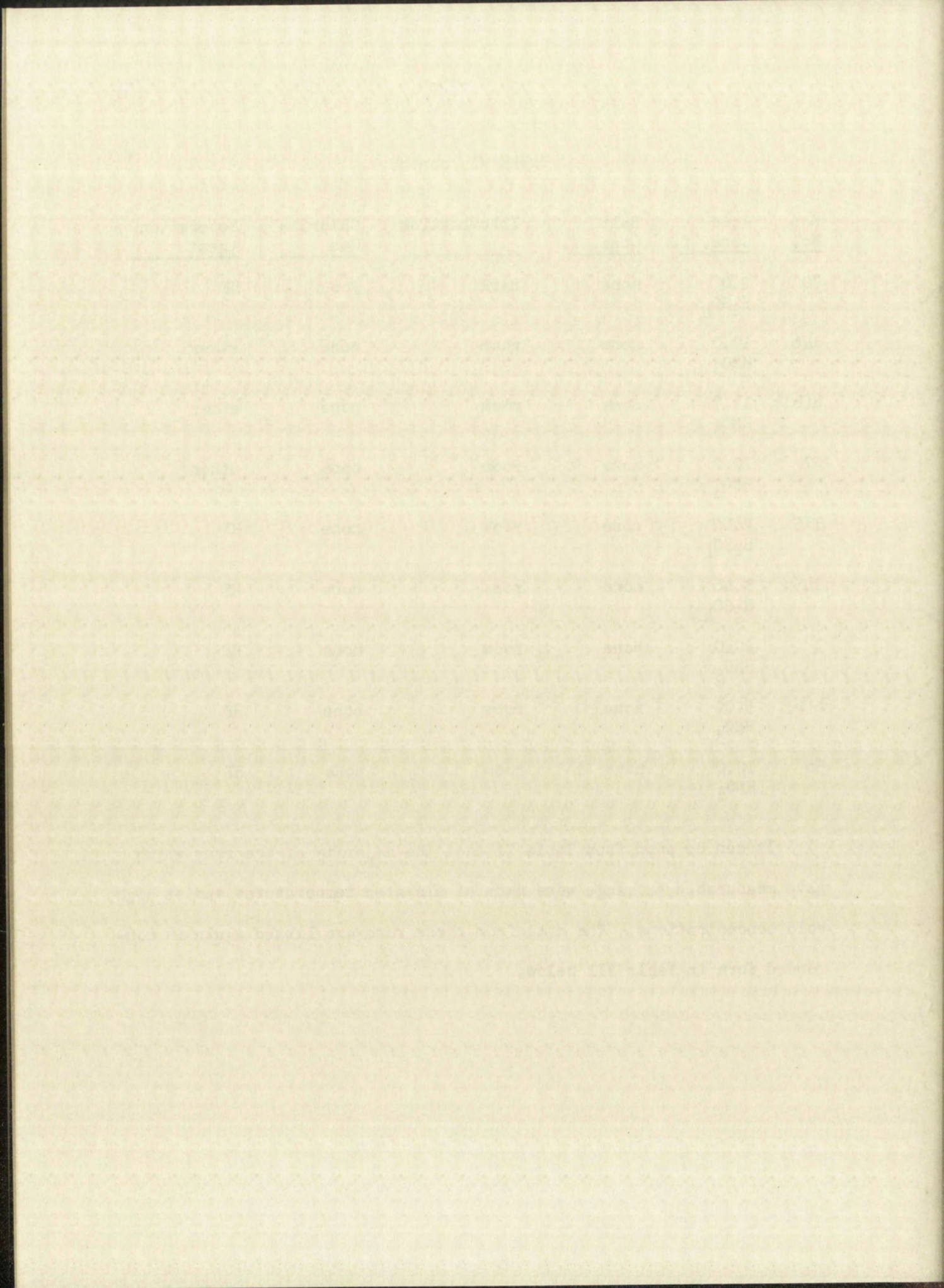


TABLE VII

<u>Run No.</u>	<u>Am(III) Initial Conc. f.</u>	<u>Am(V) Initial Conc. f.</u>	<u>Am(VI) Initial Conc. f.</u>	<u>Acid Conc. f.</u>	<u>Calc'd. Half-Time</u>	<u>Temp. °C</u>
135	0.011	0.010	0.007	2.02 H <sub>2</sub> SO <sub>4</sub>	17.9-26.1	80
145	0.021	0.027	0.014	3.46 H <sub>2</sub> SO <sub>4</sub>	39.0-40.4	80
3	0.032	0.033	0.016	10.0 HNO <sub>3</sub>	15.8-23.2	78
56	0.088	0.132	0.068	10.0 HNO <sub>3</sub>	11.6-17.4	84
4(a)	0.020	0.021	0.010	5.00 HNO <sub>3</sub>	35.0-67.5	78

The runs not listed in the condensed Table VII were disregarded because of rapid reduction of the Am(V) (Run 70) or longer half-times than 50 hours (Runs 146, 4(b), and 27; all of these were at low temperatures).

The data obtained from the runs listed in Table VII are shown graphically in Figure II. In these graphs,  $\ln(1-f)$  is plotted against time. It can be seen that, in all cases, there is considerable scatter of the experimental points. The two lines on the graphs represent upper and lower limits of the exchange half-time and are the least square lines constructed from the data in the manner treated in the following section.

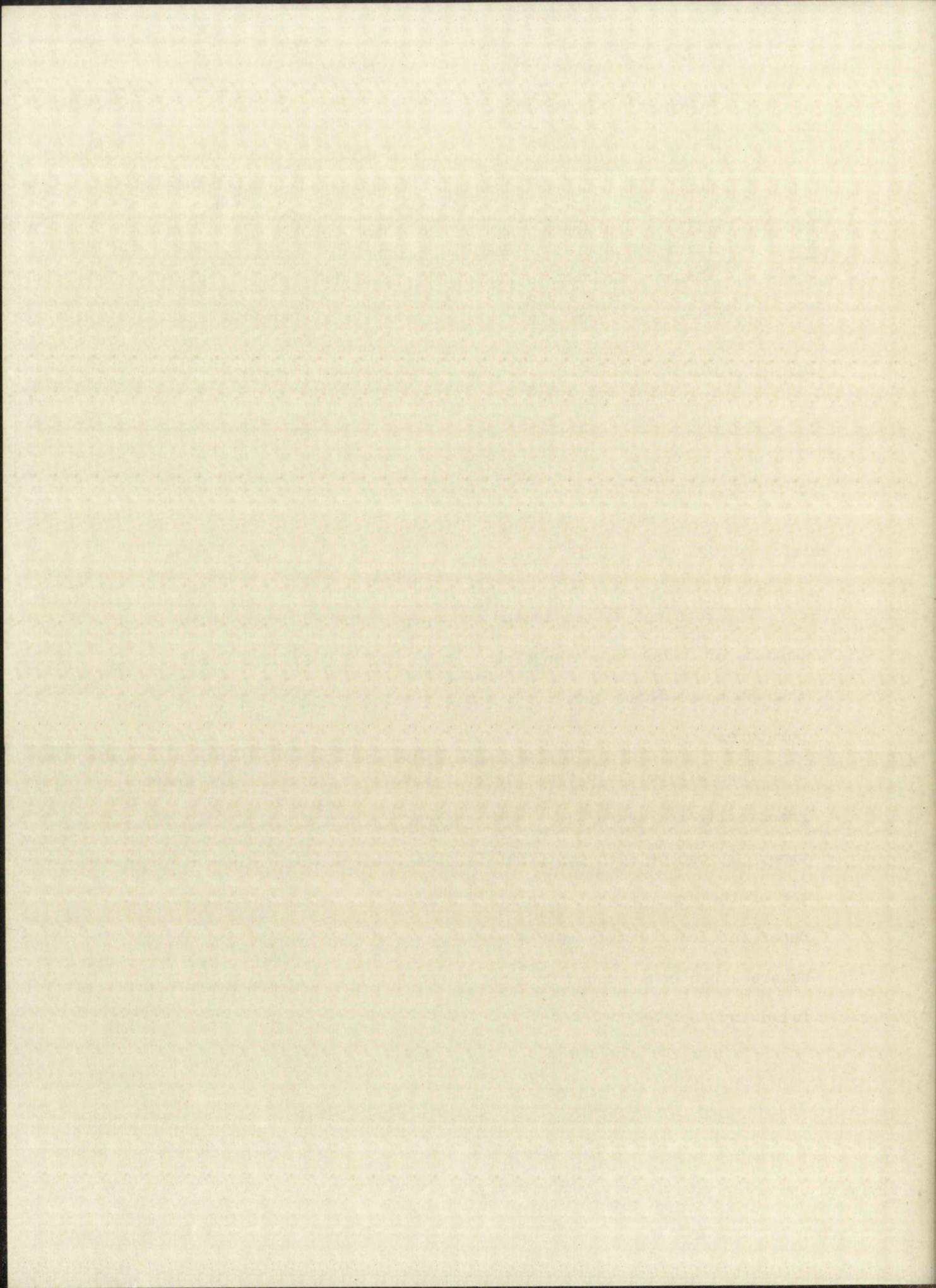
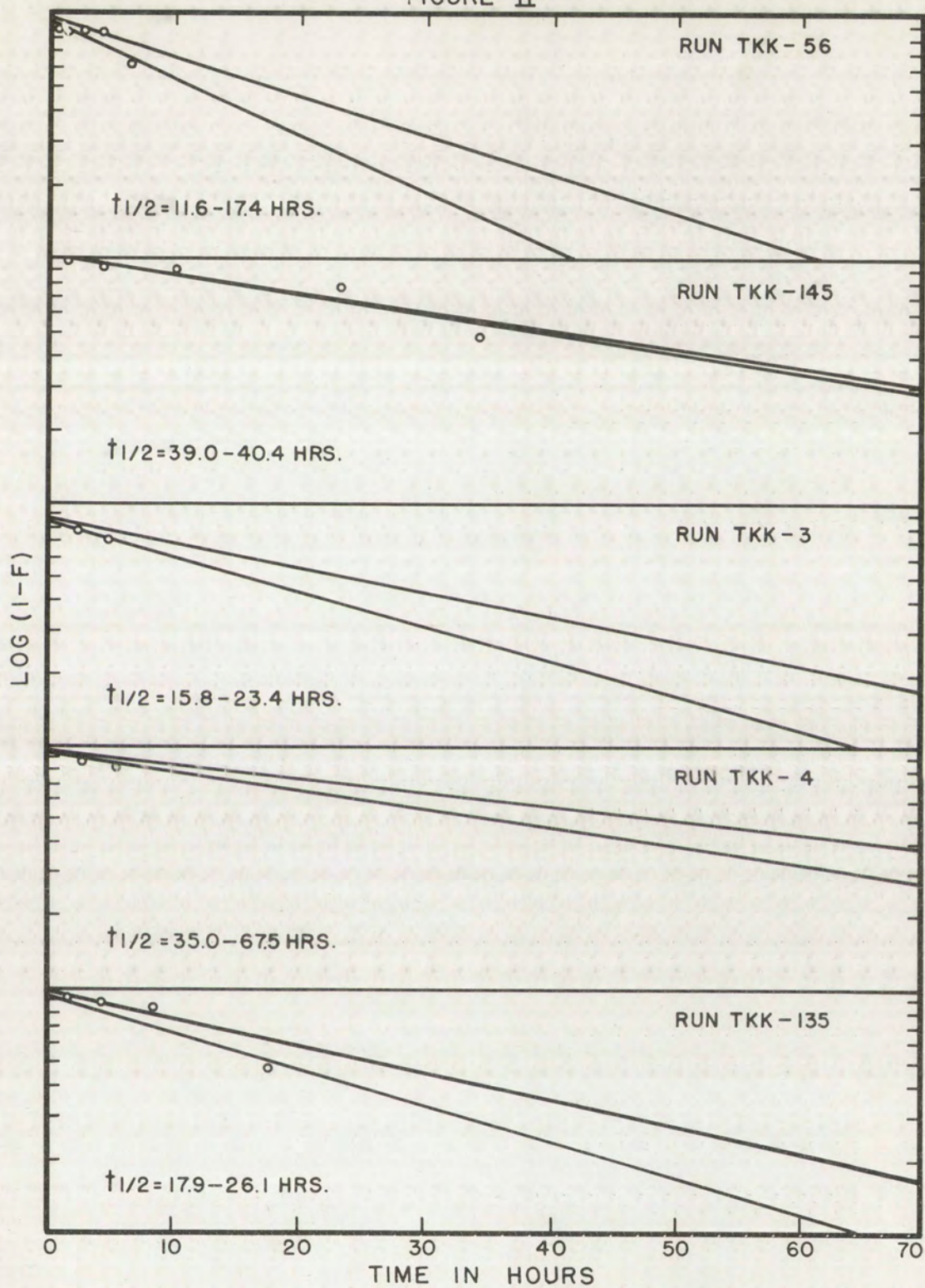


FIGURE II



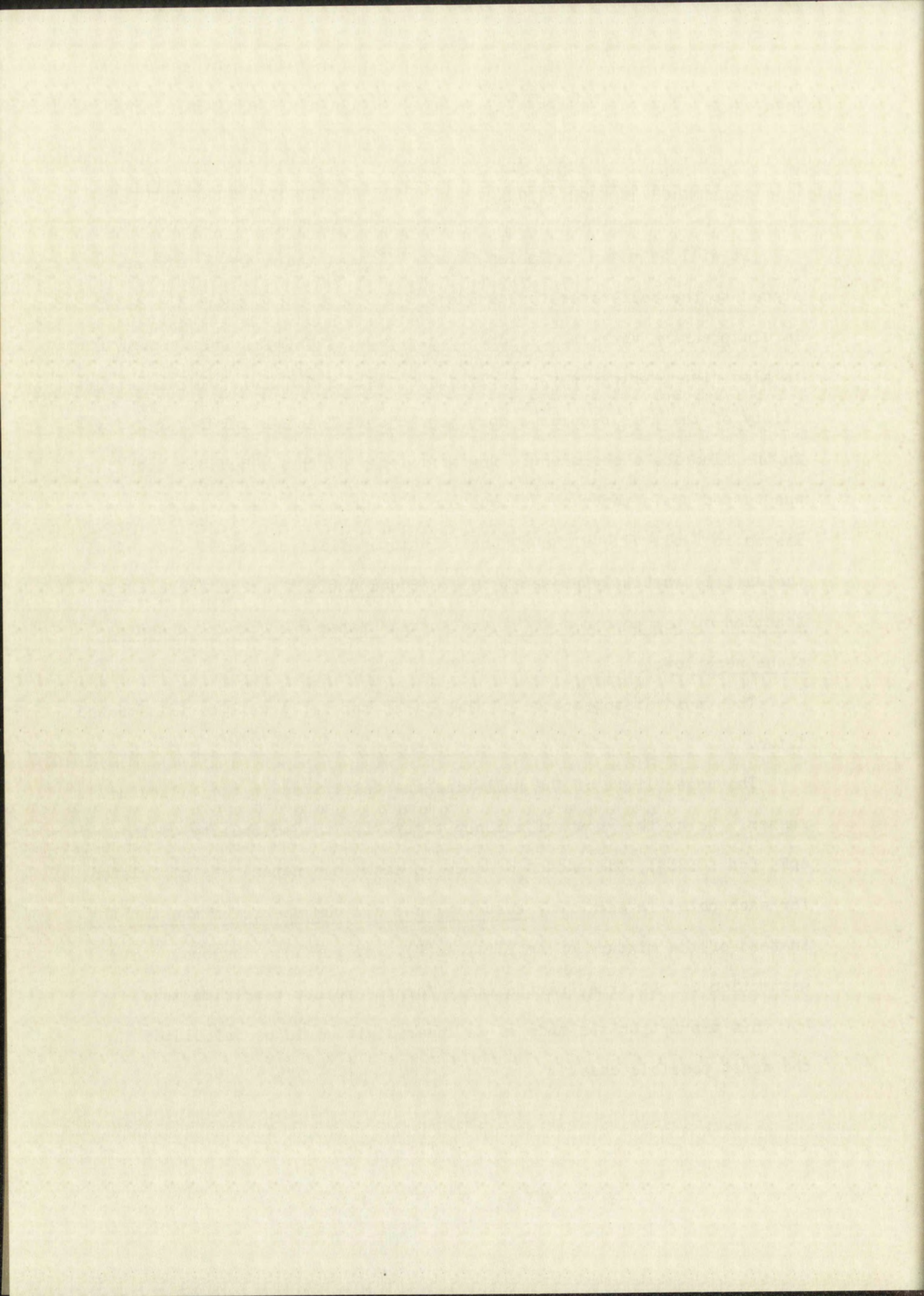
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2.6.3 ASSIGNMENT OF LIMITS TO OBSERVED HALF-TIME OF Am(III)-Am(V)  
EXCHANGE IN HIGH ACID.

It will be noted in Tables VI and VII that there are limits assigned to the half-times for exchange. In these runs, where the Am(V) is disappearing very rapidly due to disproportionation, and the Am(VI) is also disappearing very rapidly due to self-reduction, the small solubility of the  $\text{AmF}_3$  becomes a more appreciable fraction of the activity in the fluoride supernatant. The efficiency of the separation technique was tested again under conditions equal to those in the exchange runs listed in Table VII; although the technique still removed 99.6-99.9% of the Am(III) initially present, the residual Am(III) was an appreciable fraction of the combined Am(V) and Am(VI) states when their concentrations were low.

The rapid disappearance of the Am(VI) and Am(V) will be illustrated later.

The upper limit of the half-time was determined in the following manner. Using the known efficiency figure for the solubility of the  $\text{AmF}_3$  (ca. 0.28%), the amount of  $\text{AmF}_3$  in each supernatant was calculated for each point in each run, assuming that all the americium was Am(III) instead of the mixture of Am(III), Am(V), and Am(VI). Obviously this assumption is not true, particularly for the points near time zero, but this assumption was made so an upper limit could be calculated for the worst possible case.

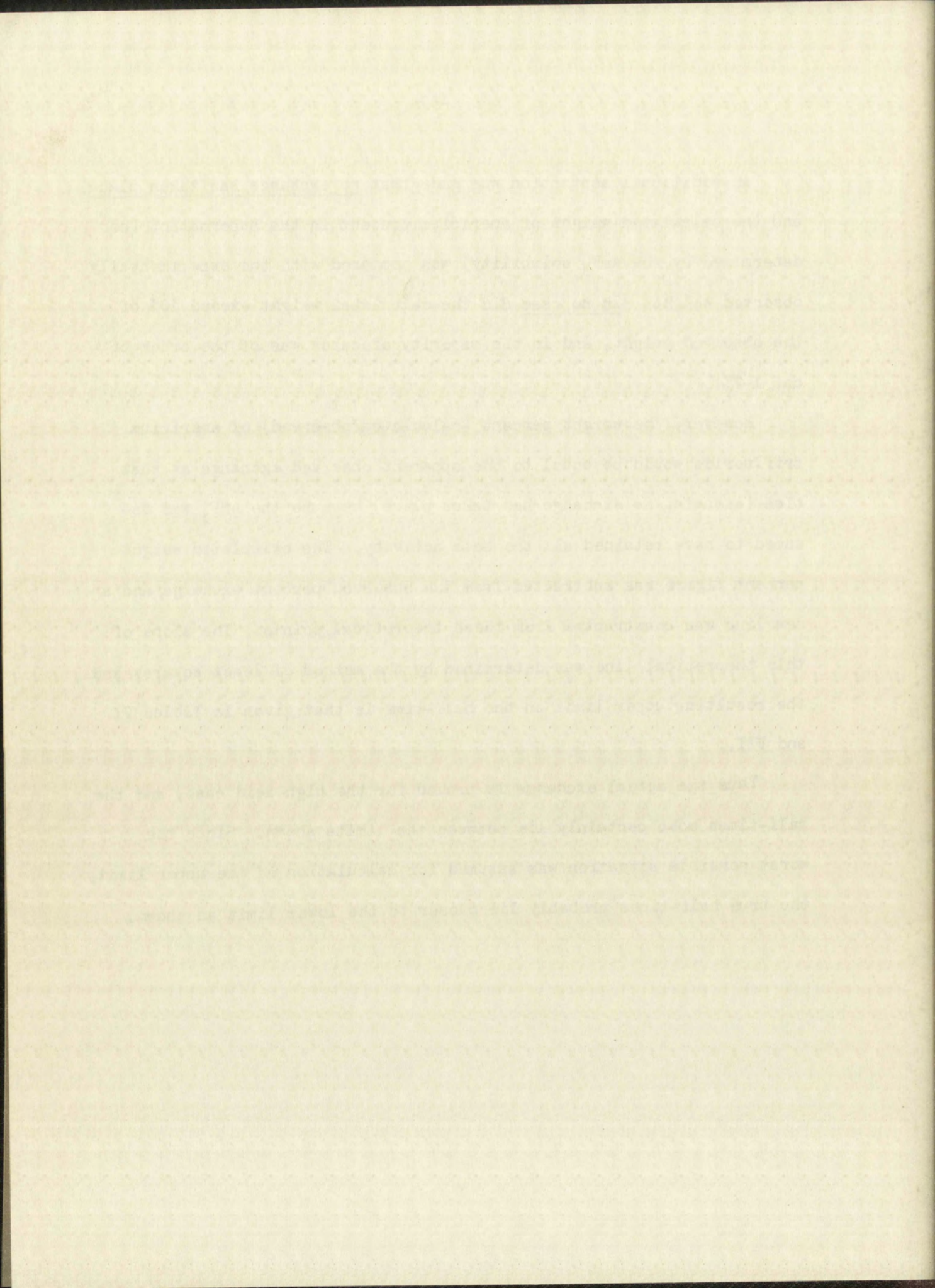




An additional assumption was made that no exchange had taken place and the calculated weight of americium present in the supernatant (as determined by the  $\text{AmF}_3$  solubility) was compared with the experimentally observed weight. In no case did the calculated weight exceed 10% of the observed weight, and in the majority of cases was of the order of ca. 1-2%.

However, the weight percent (calculated/observed) of americium trifluoride would be equal to the apparent observed exchange at that time (assuming no exchange had taken place) because the  $\text{AmF}_3$  was assumed to have retained all the beta activity. The calculated weight percent figure was subtracted from the observed percent exchange, and a new line was constructed from these theoretical points. The slope of this theoretical line was determined by the method of least squares, and the resulting upper limit on the half-time is that given in Tables VI and VII.

Thus the actual exchange is proved for the high acid case, and the half-times most certainly lie between the limits shown. Since the worst possible situation was assumed for calculation of the upper limit, the true half-times probably lie closer to the lower limit as shown.



2.6.4 ESTIMATION OF THE TIME-CONCENTRATION CHANGE OF Am(V) AND Am(VI) ASSUMING CERTAIN KINETICS.

Certain difficulties are inherent in a study of such americium systems at high hydrogen-ion concentration and reasonably high ( $\geq 0.02$  f) americium concentrations. These are the constantly changing concentrations of the americium species. Certain approximate equations (27, 28, 32)

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(32) S. Stephanou and T. Newton, unpublished work (Los Alamos Scientific Laboratory).

---

give an estimate of the magnitude of this change. These equations are based on the observed disproportionation rate of Am(V) and the observed self-reduction rates of Am(V) and Am(VI). However, an exact study of systems analogous to the exchange runs (containing initially high concentrations of Am(V) and Am(VI) has never been carried out.

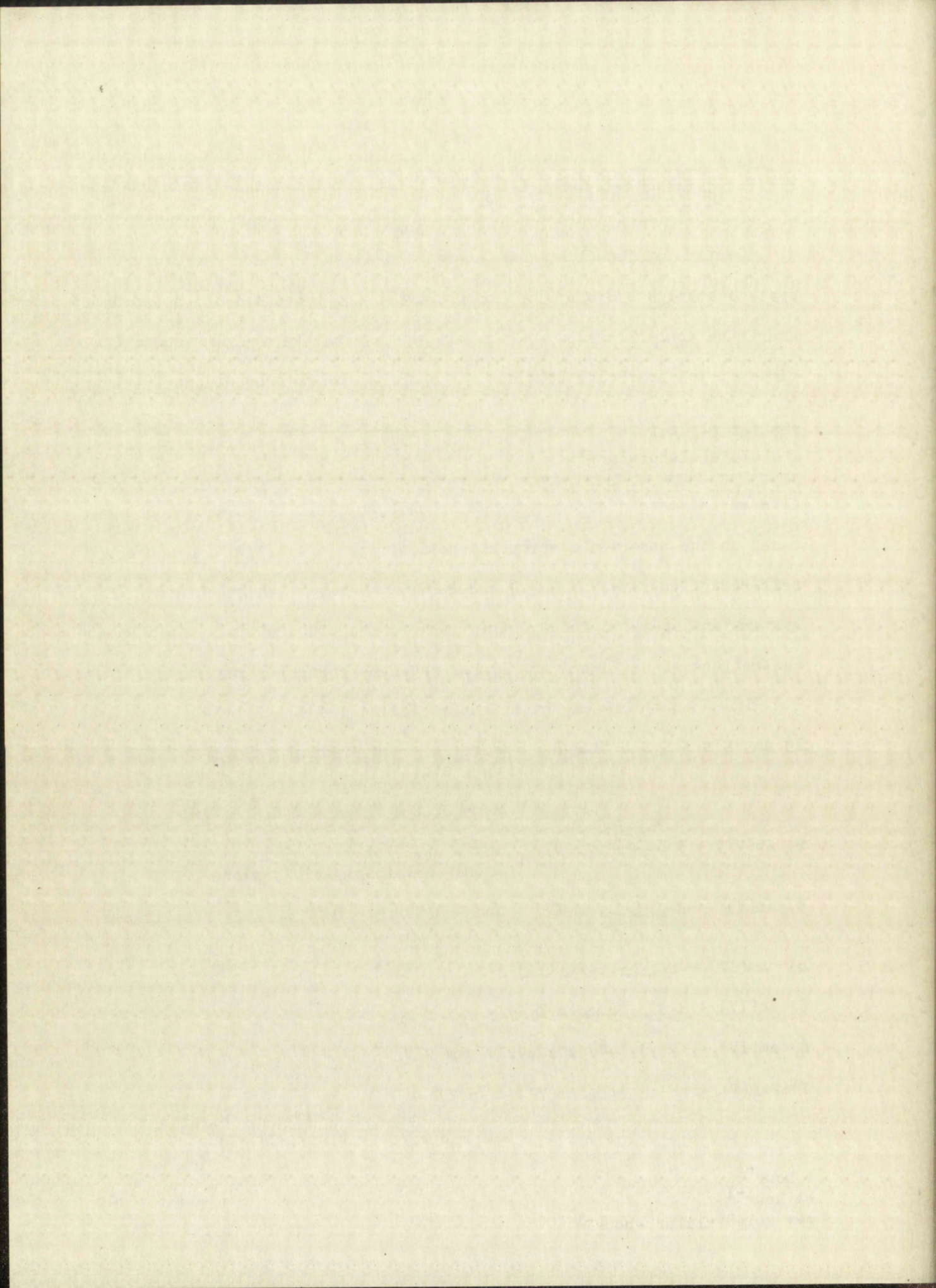
These equations may be set up as follows:

- 1)  $\text{Am } \alpha\text{'s} + \text{H}_2\text{O} \xrightarrow{k_1} \text{R}$  where "R" = any reducing fragment as [H], etc.  
 $k_1 = 0.045$ ;  $dR/dt = 0.045^* \sum (\text{Am})$  (27)
- 2)  $\text{Am(VI)} + \text{R} \xrightarrow{k_2} \text{Am(V)}$  and  $-d(\text{VI})/dt = 0.045 \sum (\text{Am})$  in solutions containing Am(VI) alone
- 3)  $\text{Am(V)} + \text{R} \xrightarrow{k_3} \text{Am(IV)}$  and  $-d(\text{V})/dt = 0.02^{**} \sum (\text{Am})$  in solutions containing Am(V) alone
- 4)  $\text{Am(IV)} + \text{R} \xrightarrow{k_4} \text{Am(III)}$
- 5)  $\text{Am(IV)} + \text{H}_2\text{O} \xrightarrow{k_5} \text{Am(III)} + \text{O}_2$
- 6)  $\text{Am(IV)} + \text{Am(V)} \xrightarrow{k_6} \text{Am(VI)} + \text{Am(III)}$
- 7)  $2\text{Am(V)} + 4\text{H}^+ \xrightarrow{k_7} \text{Am(VI)} + \text{Am(IV)} + 2\text{H}_2\text{O}$   
 $\text{and } -d(\text{V})/dt = 0.037(\text{H}^+)^4 (\text{V})^2$  (28) \*\*\*

\* hour<sup>-1</sup>

\*\* hour<sup>-1</sup>

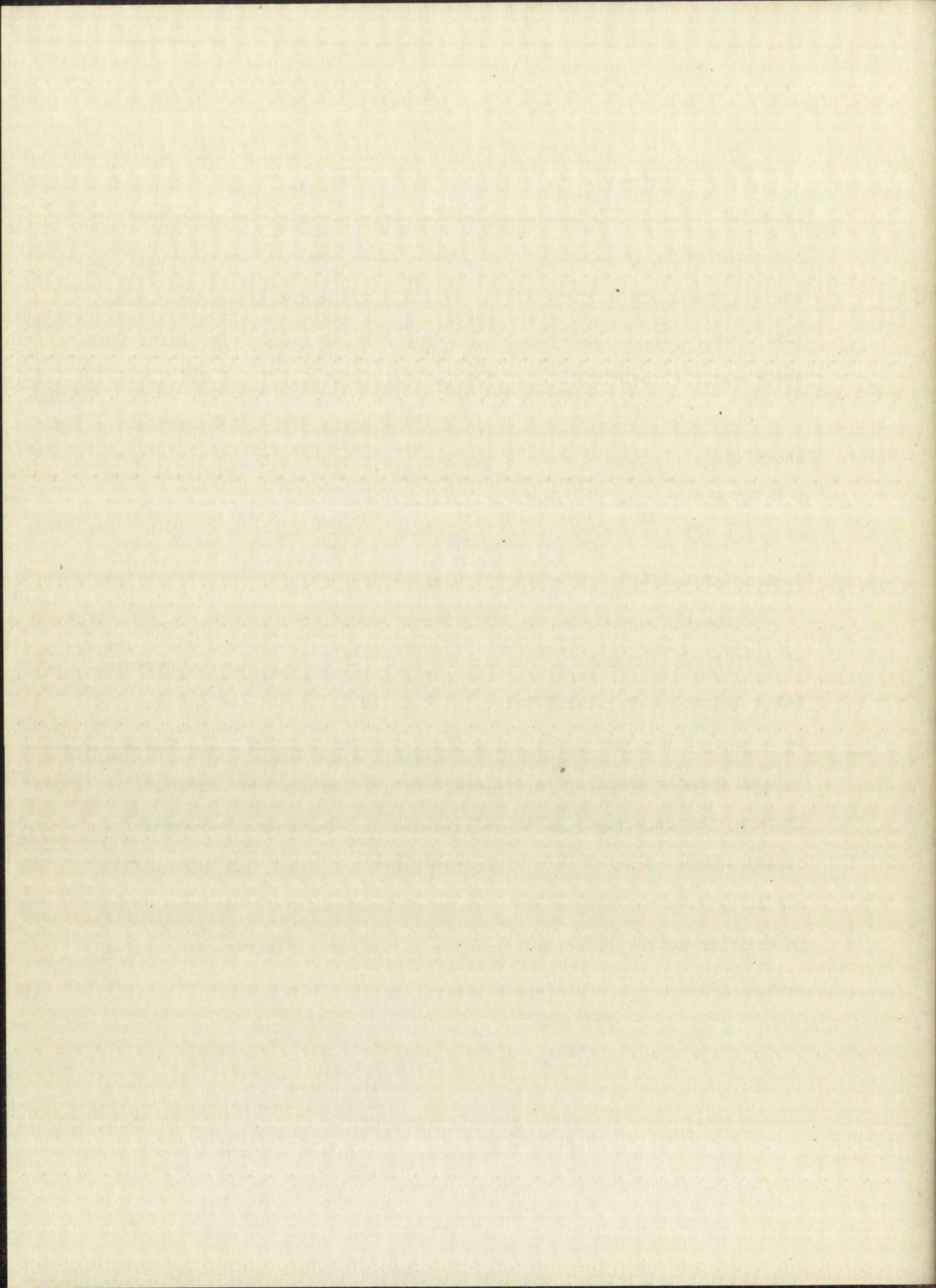
\*\*\* mole<sup>5</sup>-liter<sup>5</sup>-hour<sup>-1</sup>



The magnitude of the constants  $k_4$ ,  $k_5$ , and  $k_6$  has never been determined since Am(IV) has never been observed in solution. However, the constant  $k_4$  is assumed to be greater than the constant  $k_2$ ; that is, Am(IV) presumably reacts with the reducing fragments much more rapidly than does Am(VI). The Am(VI)-Am(V) potential is +1.60 volt, while the Am(IV)-Am(III) potential is of the order of +2.2 volt.

Since the limiting rate of production of reducing fragments is known, (Eq. 1), Am(IV) will be produced more rapidly than it can react with these reducing fragments in solutions where the Am(V) concentration and the hydrogen-ion concentration are high. This rate of production of Am(IV) is given by Eq. 7 above.

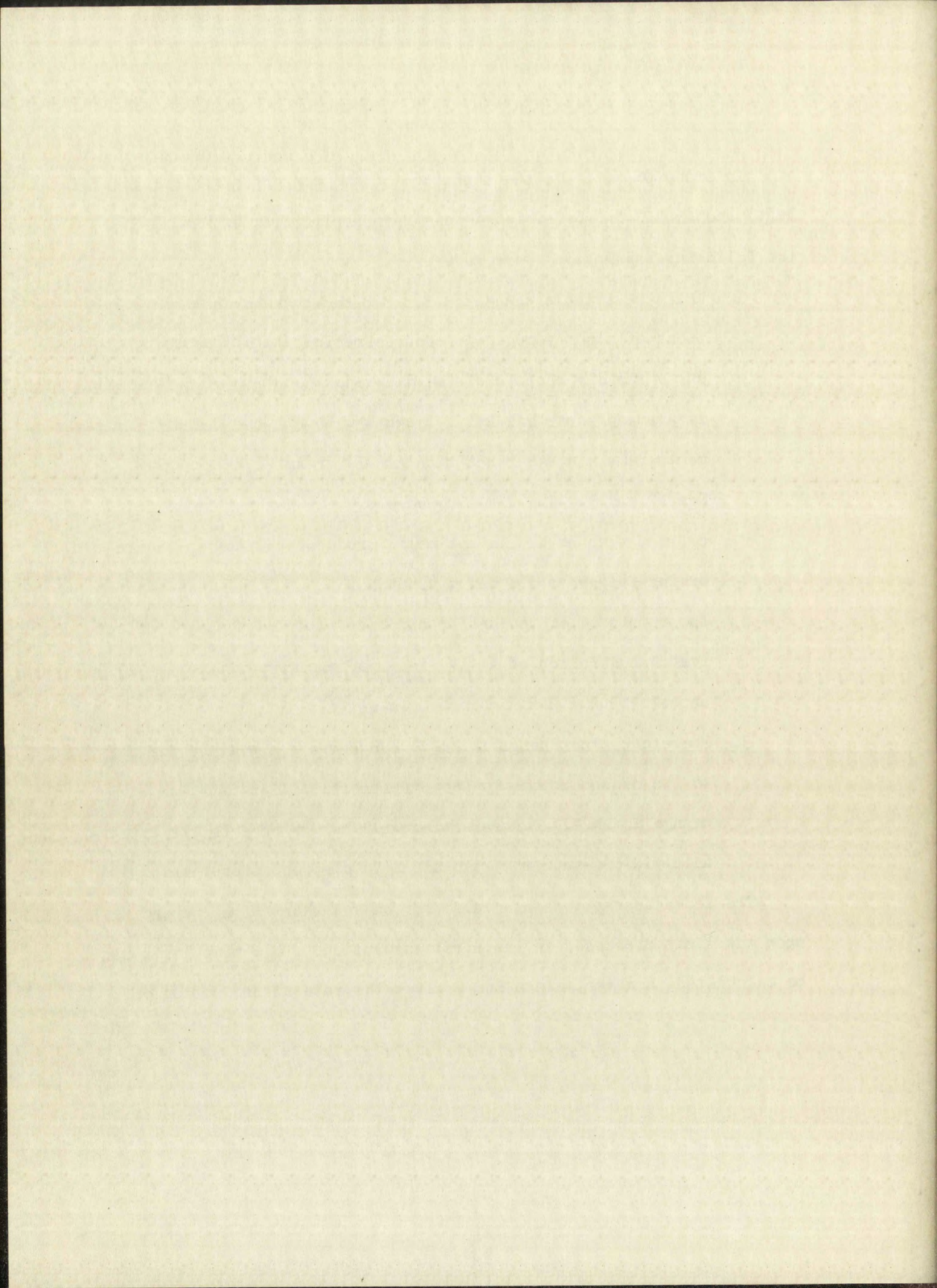
Since the appearance of Am(III) can result only from the reduction of Am(IV), the observed appearance of Am(III) in such an environment (high hydrogen-ion concentration and high Am(V) concentration) should be a test of the above postulate. The appearance of Am(III), however, is much greater than can be accounted for by the previous reasoning. In fact, the appearance of Am(III) is exactly the same as one-half the disappearance of Am(V)<sup>(28)</sup>. Therefore, it is assumed that the Am(IV) resulting from the disproportionation of Am(V) oxidizes water rapidly in addition to the reducing fragments so that the effective concentration of Am(IV) is essentially zero.



In order to estimate the magnitude of the concentration change of Am(V) and Am(VI) in the exchange runs from application of Eqs. 1-7, the following assumptions were made:

1. While reasonable concentrations of Am(V) are present in solutions of high hydrogen-ion concentration, Am(IV) is being produced rapidly because of the disproportionation of Am(V). It is assumed that this Am(IV) reacts with all the reducing fragments remaining to react with Am(VI) or Am(V) as shown in Eqs. 2 and 3. The limiting case of this assumption is, of course, when Am(IV) is not being produced as fast as the reducing fragments are being produced.
2. The remainder of the Am(IV) oxidizes water so that the effective concentration of Am(IV) is zero, and very little Am(VI) appears by the path indicated in Eq. 6.
3. Therefore, the change in Am(V) concentration will be due only to its disappearance by the disproportionation path, and the change in Am(VI) concentration will be due only to its appearance via one-half the rate of Am(V) disproportionation.

The above assumptions are valid for only a short time, depending upon the limit discussed in the first assumption. This time limit can be calculated, however, since Eq. 7 gives the rate of production of





Am(IV), and Eq. 1 gives the rate of production of the reducing fragments. Equating these quantities then:

$$8) \quad dR/dt = d(IV)/dt$$

$$0.045 \sum (Am) = 0.037/2 (H^+)^4 (V)^2$$

Using the known value of  $(H^+)$  for each run and the known value for  $\sum (Am)$ , Eq. 8 was solved for Am(V). This concentration of Am(V) was taken as the limit of the validity of the assumptions indicated on page 42. When Am(V) is lower than this limiting value, the production of Am(IV) is no longer sufficient to remove all the reducing fragments in the solutions, and the Am(VI) will begin to be reduced rapidly; and, as soon as it disappears, the Am(V) will begin to be reduced according to Eq. 3.

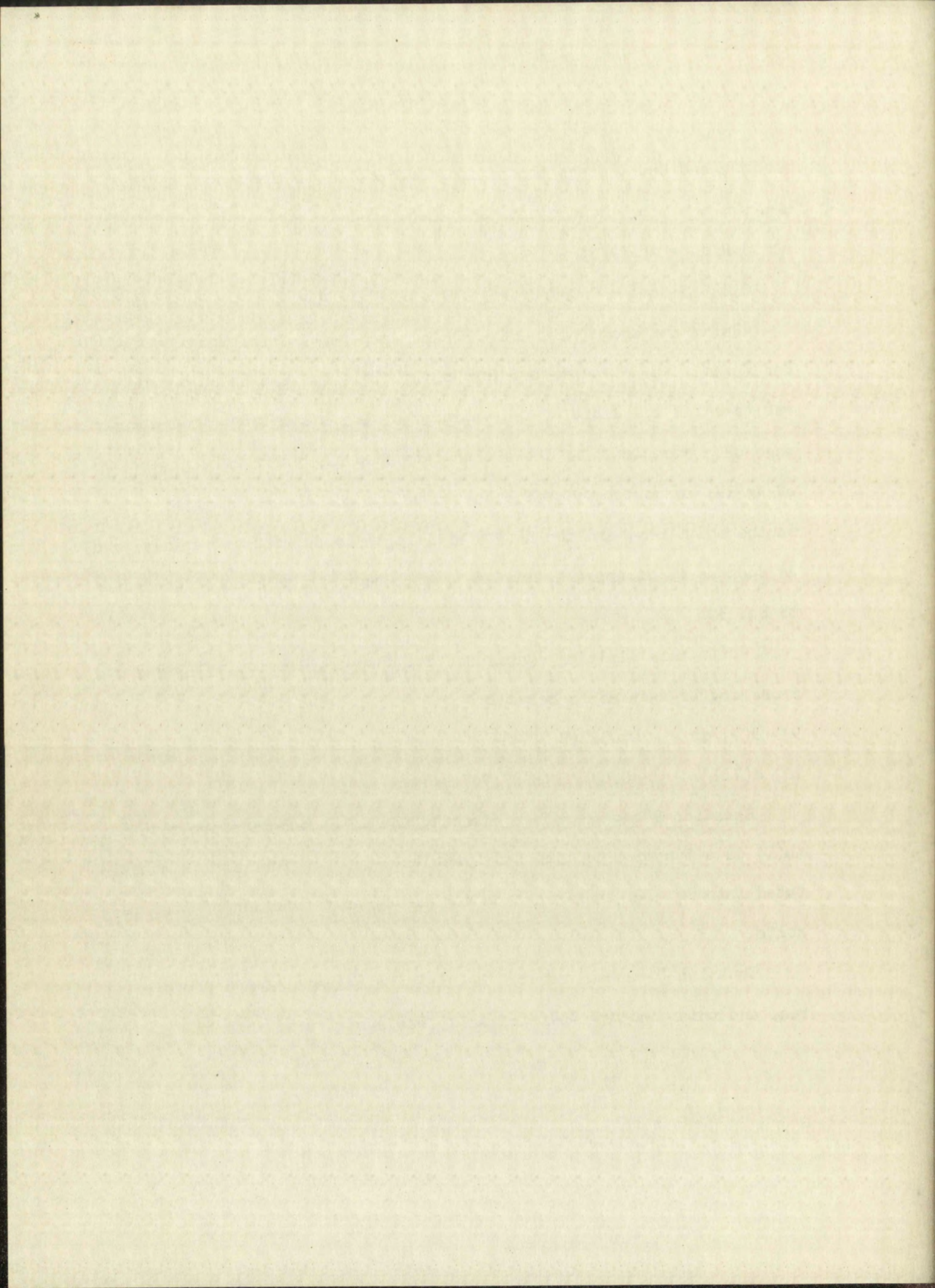
Up to this limiting concentration, however, the following equations may be assumed to be valid:

$$9) \quad d(V)/dt = - 0.037 (H^+)^4 (V)^2$$

$$10) \quad d(VI)/dt = + 0.037/2 (H^+)^4 (V)^2$$

Equation 9 may be solved directly for Am(V) and an expression for Am(V) as a function of time only results. If this function is substituted into Eq. 10, an expression for Am(VI) as a function of time results.

Equation 8 was solved for the limiting value of Am(V) for each run, and this limiting value of Am(V) was substituted into the integrated



form of Eq. 9 to evaluate the time at which Am(VI) and Am(V) will begin to disappear rapidly by their respective self-reduction paths.

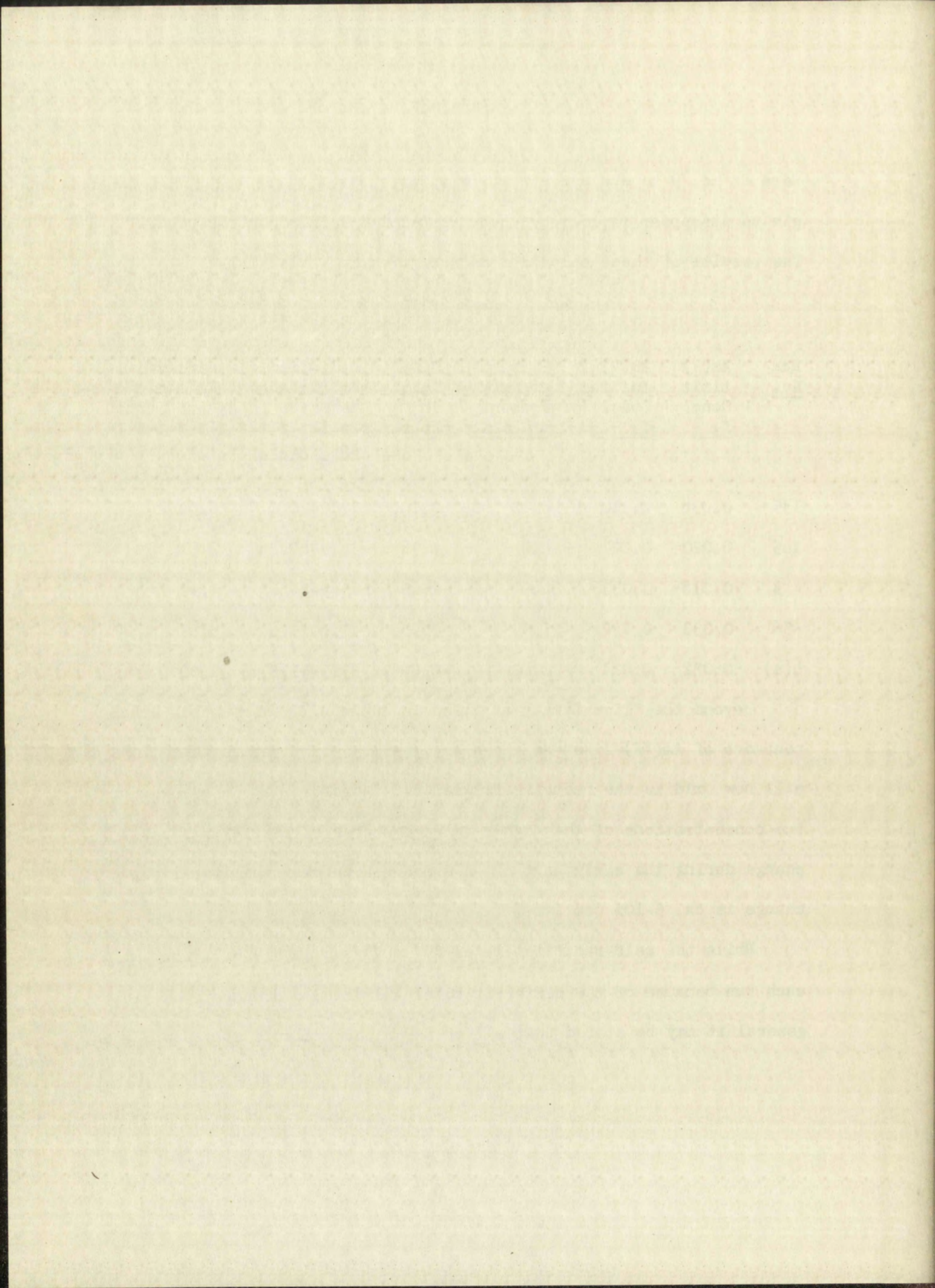
The results of these calculations are given in Table VIII.

TABLE VIII

<u>Run No.</u>	<u>Am(V) Limit Conc. f.</u>	<u>Am(V) Initial Conc. f.</u>	<u>Percent of Am(V) Present at Limit</u>	<u>Time Limit in Hours</u>	<u>Half-Time of Exchange as Given in Table VII in Hours</u>	<u>Percent of Exchange Half-Time beyond Which Am(VI) and Am(V) Disappear Rapidly</u>
135	0.038	0.010	0.00	0.00	17.9-26.1	0.00
145	0.020	0.027	74.0	0.98	39.0-40.4	2.51
3	0.018	0.033	54.5	1.10	15.9-23.4	6.92
56	0.033	0.132	25.0	0.98	11.6-17.4	8.45
4(a)	0.022	0.021	0.00	0.00	35.0-67.5	0.00

Beyond the "Time Limit" as given in Table VIII, very rapid disappearance of Am(VI) first and then Am(V) will occur because these ions will now oxidize the reducing fragments. Therefore, it is evident that the concentrations of the higher valence states of americium rapidly change during the early part of an exchange run when the overall exchange is ca. 5-10% complete.

While the self-reduction rates of Am(V) and Am(VI) will vary with each run because of the different total americium concentrations, in general it may be stated that all of the higher valence states are gone

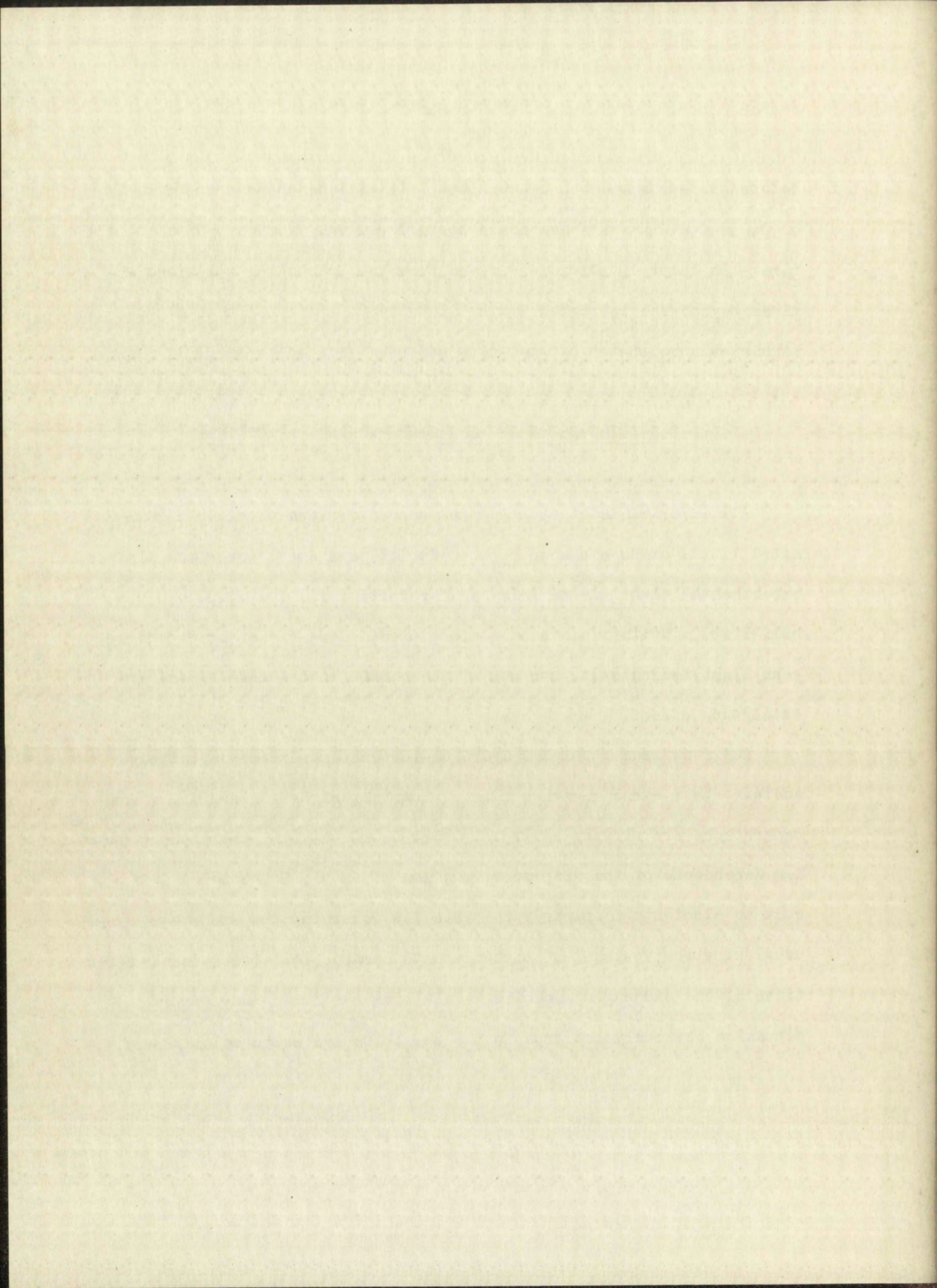


before the exchange is half complete. It will be noted from Table VI on p. 34 that the exchange could be followed only for ca. 50% of a half-time. In general, aliquots removed from the exchanging solutions at times beyond the indicated maxima in Table VI indicated that all the higher valence states of americium had been reduced to Am(III).

### 3.0 DISCUSSION OF AMERICIUM EXCHANGE REACTIONS

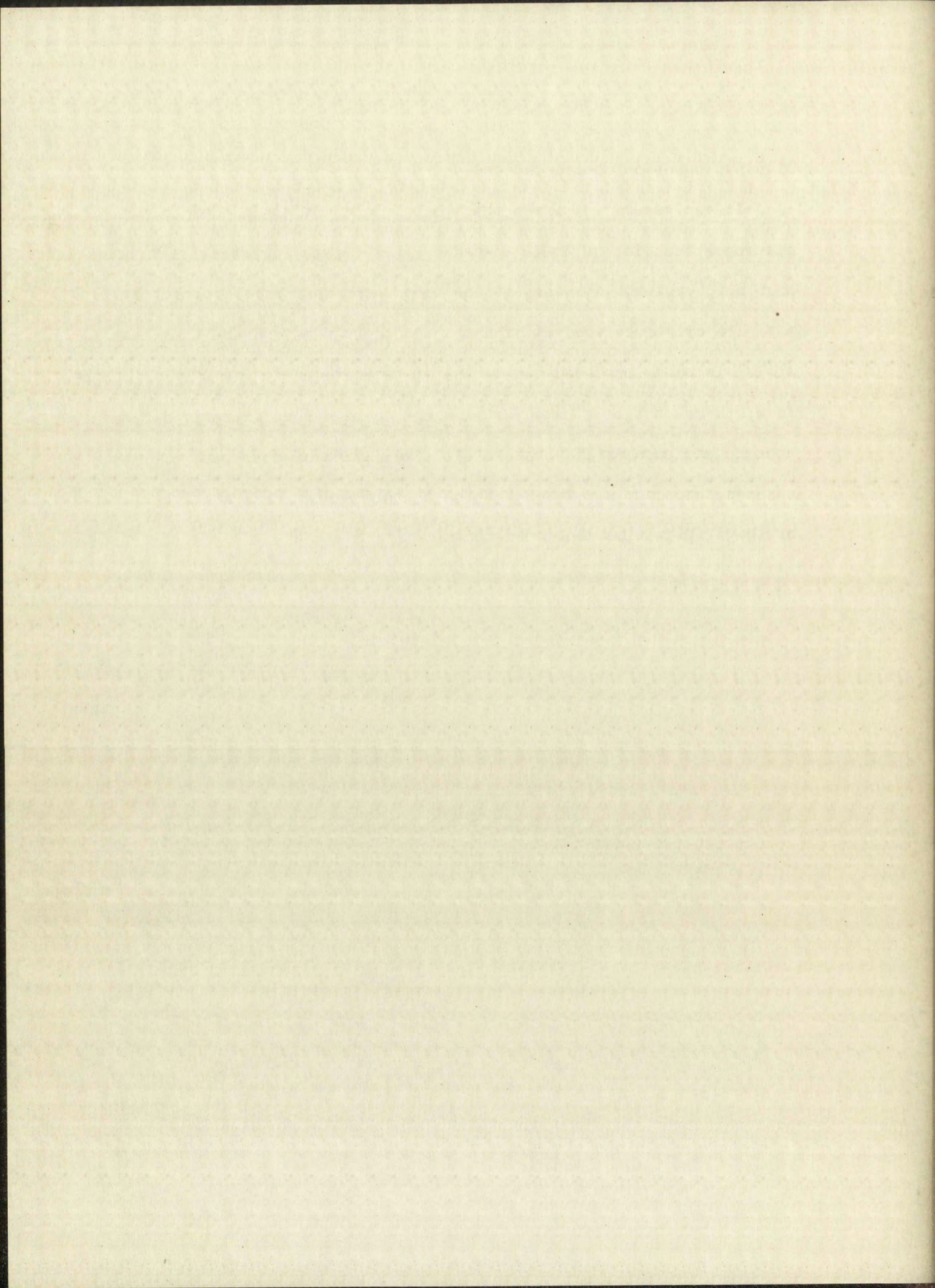
All experiments at hydrogen ion concentrations of  $<2.00$  f indicated little or no exchange between Am(III) and Am(V) (over the limited experimental times due to Am(V) self-reduction and the 16.01 hr. tracer half-life). Neither elevated temperatures, ultra-violet or incandescent light, added salt, nor any of the common anions have a positive catalyzing effect.

The runs made at higher hydrogen-ion concentrations definitely indicate that exchange takes place. However, since the americium concentrations are varying so rapidly because of the 4th power hydrogen-ion dependence of the disproportionation of Am(V), it would be difficult to elucidate completely the rate law governing the exchange. The usual kinetic treatment of exchange data demands that the concentrations of the exchanging species remain constant during any one run, a situation obviously not true in the americium system in solutions of



high hydrogen-ion concentrations.

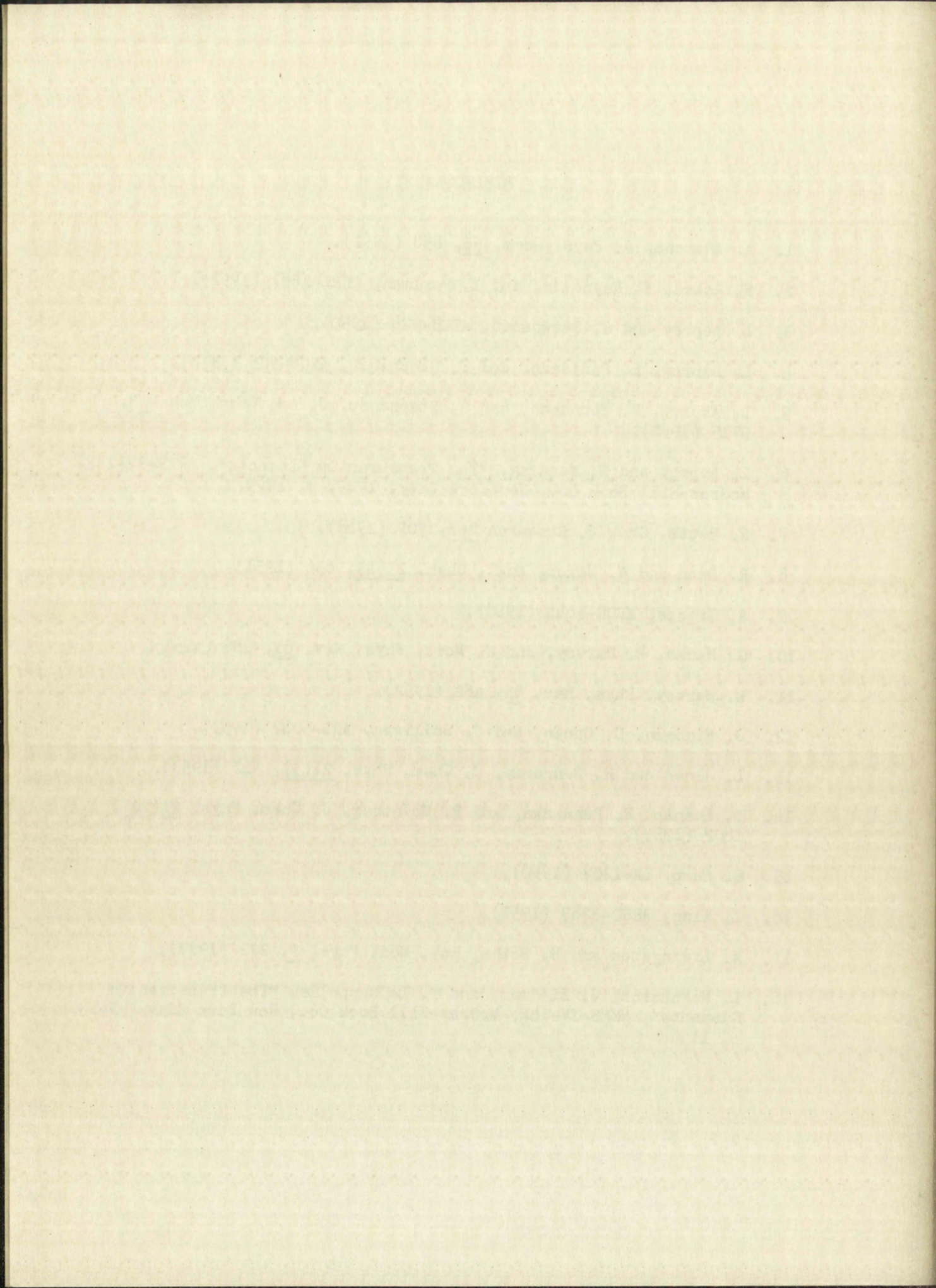
It was assumed at first that the presence of Am(IV) due to the disproportionation of Am(V) opened a kinetic path for exchange in the high acid system. However, it has been shown that Am(IV) cannot have a finite existence and yet exchange is observed beyond the time that Am(IV) is being produced due to the disproportionation of Am(V). Therefore, there must be a path for exchange in high acid directly dependent upon  $H^+$  and upon Am(III) and Am(V). The nature of this path is yet unknown, and complete investigation of this system will still be limited by the difficulties mentioned above.





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Note: All documents referred to in this bibliography are unclassified.



