

Contributions of the University of California Radiation Laboratory

Paper No. 3

ACCELERATION OF URANIUM SALES IN WATER SOLUTION

by

Ambrose R. Nichols, Jr.

CLASSIFICATION CANCELLED
BY AUTHORITY OF D.E.M.S.D.
BY *[Signature]*
DECLASSIFICATION BRANCH
[Signature]

For inclusion in the
National Nuclear Energy Series
Distribution Limited




ABSTRACT

In the autoxidation of aqueous uranyl chloride, there is an increase in hydrogen ion concentration and an oxygen uptake which is in agreement with the equation:



The rate of autoxidation in solutions containing 0.05 moles U^{4+} per liter is appreciably increased by the addition of as little as 0.0002 moles per liter of Cu^{2+} . At Cu^{2+} concentrations from 0.001 to 0.8 molar, the rate is proportional to the 0.68 power of the cupric ion concentration.

The autoxidation is first order with respect to oxygen, while in the presence of copper, the reaction is first order with respect to uranium. The rate is decreased by hydrogen ion, chloride ion, and sulfate ion, while cobaltous, chromic, ferric, and uranyl ions have little or no effect.



SECRET

AUTOXIDATION OF URANOUS SALTS IN WATER SOLUTION^(a)

By Ambrose R. Nichole, Jr.

1. Introduction

The fact that tetravalent uranium either in the form of solutions of its salts or, in some cases, in the dry state, is readily oxidized by gaseous oxygen, has been observed by various investigators. A quantitative study of this reaction appeared to be desirable as a means of learning more about the nature of the ionic species present in uranous solutions. It was also of potential value in determining the importance of autoxidation as an undesirable side reaction involved in the handling of uranous solutions, and, if necessary, in developing procedures for minimizing the reaction.

2. Apparatus

The measurements of autoxidation rate have been made with an apparatus similar to that described by Filson and Walton,^(a) A specially designed reaction flask is mounted in a thermostated shaker and connected by capillary tubing with a thermostated gas buret. An ampule containing an accurately measured volume of a stock uranous chloride solution is carefully placed in the flask along with sufficient water to bring the total volume to 50 ml. Part or all of the added water may be replaced by an equal volume of solution of whatever reagent is to be used as a buffer or tested for catalytic effect. The reaction flask is a 300 ml round bottom, long neck, Pyrex flask which has been grooved externally in such a way as to leave the interior divided roughly into quadrants separated

by ridges about one-half inch in height and extending from the bottom about half way up the side of the flask. The externally padded neck of the flask is clamped in the shaker which rotates the flask rapidly back and forth through an arc of about 90° about its own axis. The flask is fitted with a rubber stopper through which passes a capillary tube by which it is connected to the gas buret. The rate of shaking used was about 500 cycles per minute.

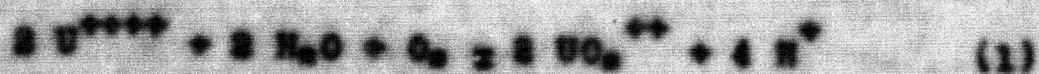
After the flask is clamped in position, but before the shaker is started, the entire system is evacuated by means of an aspirator. It is then filled with oxygen, re-evacuated, and again filled with oxygen at atmospheric pressure. After temperature equilibrium has been reached, the buret reading is recorded and the shaker started. The thermostat temperature ($25.0 \pm 0.1^\circ$ for the work reported) and the barometric pressure are recorded at the beginning of each trial. The starting of the shaker results in the immediate thorough mixing of the contents of the ampoule with the remainder of the solution. The vigorous shaking keeps the mixture saturated with oxygen. The apparatus used has duplicate flask holders and gas burets, permitting two trials to be made simultaneously. The oxygen uptake is followed by recording the buret readings at specified time intervals. Water is used as confining liquid, and corrections are made for the vapor pressure of water at 25°C . The levelling tube arrangement used permits readings to be made as frequently as every ten seconds if necessary.

Since it was of interest to follow the changes of pH with concentration, a different type of apparatus was devised

for this purpose. pH measurements were made on solutions identical with those autoxidized in the apparatus previously described. These solutions were contained in a 40 mm filter tube fitted with a coarse sintered glass disc. Nitrogen was supplied from beneath the disc, stirring the solution and preventing it from draining out. When the initial measurement had been made, the valves were quickly changed so as to supply oxygen in place of nitrogen. pH readings, made with a Beckman Laboratory Model pH meter, were recorded at specified time intervals as the autoxidation proceeded. In certain other experiments, the stream of nitrogen was maintained and the solutions were titrated with standard NaOH and the titration curves plotted.

5. Experimental Results

5.1 Hydrolysis and Autoxidation. Aqueous UCl_4 solutions in the concentration range studied are appreciably hydrolyzed, as indicated by the fact that a fresh solution whose uranous ion concentration is about 0.05 molar has a hydrogen ion concentration of about 0.05 molar. However, such solutions are not stable. On standing out of contact with air, a dark precipitate of hydrous UO_2 is formed and the green color of the solution disappears. This process is noticeable within a few hours, and is complete in a few days. In concentrated UCl_4 solutions, the hydrolysis is much less complete, and no precipitation occurs. Autoxidation of the fresh UCl_4 solution is accompanied by an increase in hydrogen ion concentration which is in accordance with the equation:



This is illustrated by Table 1.

Table 1

Trial number	I	II
Original U^{++++} concentration	0.048 molar	0.048 molar
Original H^+ concentration	0.029	0.029
H^+ concentration after autoxidation	0.098	0.098

Titration of dilute (0.05M) UO_2 solutions with 0.1M NaOH gave titration curves showing only the single inflection point at a ratio, $NaOH/U^{++++}$ equal to 4. There was no indication of such intermediate ions as UOH^{+++} , $U(OH)_2^{++}$, etc. However, calculation of hydrolysis constants on the basis of the single process:



Based on pH measurements, failed to give consistent K values over any appreciable concentration range. In view of the slow precipitation mentioned above, it is likely that no equilibrium measurements are possible by this method.

3.2 Autoxidation. The studies of the autoxidation rate have been represented by curves in which the concentration of uranous ion is plotted against time. The total volume of oxygen ultimately absorbed was in agreement with equation (1). For convenience, the concentration has been expressed in terms of equivalent milliliters of oxygen. For example, if the initial concentration was such that the 50 ml of solution

in the flask contained sufficient U^{4+} to take up 40 ml of oxygen, the initial concentration was plotted as 40. In this way the plots could be made directly from buret readings. Where necessary, these values were converted into molarity. In some cases, $\log C$, $1/C$, and \sqrt{C} have been plotted against time in order to establish the rate law.

When aqueous UCl_4 solutions alone are autoxidized, smooth C vs T curves are obtained, (Fig. 1), but no simple rate law is observed. The observation that the rate is influenced by the hydrogen ion concentration provides an explanation, since the autoxidation itself produces an accompanying increase in acidity. In order to minimize this effect, most of the experiments were carried out at hydrogen ion concentrations which were large in comparison with the stoichiometric quantities produced by the oxidation reaction. However, under such conditions the reaction is very slow. It was subsequently observed that cupric ion is a very effective accelerator. After this effect had been thoroughly investigated, the use of added $CuCl_2$ was made part of the operational procedure for the study of other effects, in order to decrease the time required for each determination.

(1) Effect of Cupric Ion. Figures 2 and 3 show the powerful accelerating effect of cupric ion. The uranous concentration in the trial with copper absent was 0.0595, while in all other cases the initial concentration was 0.0627 moles. The hydrochloric acid concentration was 3 molar in all cases. Since the form of the curve, and thus the rate law, is not the same for all of these trials, it is not

possible to set up a comparison of rate constants. However, by arbitrarily defining the "rate" as the fraction reacting per minute at a specified concentration, (0.05 M in these cases) a comparable value is obtained. If the logarithm of this "rate" is plotted against the logarithm of the copper concentration, the curve shown in Figure 4 is obtained. It is to be noted that the curve is a straight line in regions where the cupric ion concentration is high, but deviates, as would be expected, in the region of low copper concentration, where the rate of the uncatalyzed reaction is an appreciable fraction of the overall rate. From the deviation of these experimental points from the extrapolated line, it is possible to calculate the rate of the uncatalyzed reaction. A value is obtained which checks fairly well with the value obtained by direct measurement in the absence of copper.

(2) Effect of other Metallic Ions. Cobalt chloride and chromic chloride were found to have no effect upon the rate when added at a concentration of 0.002 M, while ferric chloride had a very slight accelerating effect. Uranyl chloride has no appreciable effect.

(3) Effect of Hydrogen Ion. Since chloride ion has an independent effect, it was necessary to vary the concentration of hydrochloric acid and sodium chloride simultaneously so as to maintain constant chloride ion concentration. The results of these trials are shown in Figure 5. It is noted that increasing the hydrogen ion concentration from 1 to 3 molar appears to have no appreciable effect. The initial uranous

concentration was 0.0627 M in each of these trials. The concentrations of HCl and NaCl are given on the curves.

In a few trials it was observed that HCl concentrations of 4 to 6 molar resulted in rates slightly greater than those observed with 3 molar. This observation recalls the fact that HCl concentrations in that range produce a slight alteration in the absorption spectrum of UCl_4 solutions. (*)

In another series of trials, corresponding mixtures of acetic acid and sodium acetate were used. While there is the same tendency for increasing hydrogen ion concentration to cause a decrease in the rate of autoxidation, the situation is complicated by the fact that at the higher pH values there is a precipitate of hydrous UO_2 formed. The precipitate undergoes autoxidation at a practically constant rate, as indicated by the concentration vs. time curves. (Figure 6)

(4) Effect of Various Anions. Variation in the concentration of sodium chloride at constant hydrochloric acid concentration (0.18 M) produces the results shown in Figure 7. The uranic concentration in each of these trials was 0.0627 M . The specific nature of this inhibiting effect was shown further in the series of experiments represented by Figure 8. In these trials the ionic strength was kept at 3.15, and sulfate and chloride ions compared with perchlorate. The uranic concentration was 0.0627 and the hydrochloric acid 0.12 M . Comparison at constant anion concentration rather than at constant ionic strength indicate that the chloride has a slightly greater inhibiting effect than the sulfate. The marked difference shown by chloride and sulfate in comparison with perchlorate

strongly suggests the existence of uranous complexes with these two ions.

(5) Effect of Oxygen Partial Pressure. To check on the way in which oxygen enters into the reaction, a series of trials were made in which the space above the solution in the reaction flask was filled with air, but the connecting gas buret was filled with nitrogen. The concentration of uranous ion in the solution was large (0.5 M) so that the total capacity for oxygen uptake was large in comparison to the actual volume of oxygen in the system. Thus, the concentration of uranous ion was practically constant throughout the trial. However, the partial pressure of oxygen over the solution diminished in proportion to the decrease in volume registered in the buret. The results (Figure 9) indicate a reaction which is first order with respect to oxygen. The solutions used contained added copper chloride to diminish the time required for the determinations.

(6) Effect of Surface. The addition of up to 5 grams of finely powdered (300 mesh) pyrex glass to the reaction mixture was found to produce no significant change in the reaction rate.

(7) Effect of Illumination. Visible light appears to have no effect upon the rate, as indicated by trials in which a 60 watt incandescent lamp was placed in the thermostat a few inches from the flasks in which the trials were made. One flask was painted black while the other was left clear. The two trials checked as closely as any pair of duplicate runs.

4. Discussion

The copper catalyzed reaction appears to be first order with respect to uranous ion, as indicated the log concentration vs. time curve (Figure 10), although the agreement is not perfect in all cases.

As shown by Figure 4, the rate is a function of the cupric concentration. The slope of the linear portion of the curve is 0.82. That is, over the concentration range from about 0.001 to 0.2 molar cupric ion, the rate is proportional to the 0.82 power of the cupric ion concentration.

The marked catalytic effect of cupric ion is presumably due to the cupric-cuprous couple acting as a carrier. It is interesting that the same couple acts very effectively to catalyze the cathodic reduction of uranyl ion to uranous.

In the case of the uncatalyzed reaction in 3 M hydrochloric acid, a better agreement is obtained if the square root of concentration is plotted against time. (Figure 11) A possible mechanism to account for this rate would involve an association equilibrium of the type:



If only the unassociated form undergoes oxidation, and if the equilibrium greatly favors the associated form, a square root dependence on total uranous concentration would be expected. No assumption has been made as to the actual formula of either the single or the associated ion.

It is impossible to present a clear-cut picture of the autoxidation mechanism at present, because of the extreme

complexity of the solutions involved. It is likely that the tetravalent uranium in these solutions exists as an equilibrium mixture of two or more different ionic species, the proportions of which will vary depending upon the concentration of uranium, hydrogen ion, and the various negative ions present. The autoxidation reaction may directly involve only one of these species, or it may represent a summation of several simultaneous autoxidations. The ultimate clarification of the nature of these solutions must be consistent with the present observations as to the retarding effect of hydrogen ion, chloride ion and sulfate ion.

6. SUMMARY

- (1) The rate of autoxidation of aqueous uranous chloride has been measured under various conditions.
- (2) The autoxidation reaction is accompanied by an increase in hydrogen ion concentration and an oxygen uptake which is in agreement with the equation:

$$2 U^{++++} + 2 H_2O + O_2 = 2 UO_2^{++} + 4 H^+$$
- (3) The rate of autoxidation in solutions containing 0.06 moles U^{++++} per liter is appreciably increased by the addition of as little as 0.00002 moles per liter of Cu^{++} . At Cu^{++} concentrations from 0.001 to 0.2 molar, the rate is proportional to the 0.62 power of the cupric ion concentration.
- (4) Cobaltous, chromic, ferric, and uranyl ions have little or no effect upon the rate of autoxidation.
- (5) The rate decreases with increasing hydrogen ion concentration.

(6) In comparisons at constant total ionic strength, chloride ion and sulfate ion retard the reaction very much more than does perchlorate ion, suggesting the existence of chloride and sulfate complexes with uranous ion.

(7) The autoxidation reaction is first order with respect to oxygen.

(8) Added surface, in the form of powdered Pyrex glass, and visible illumination have no effect upon the autoxidation rate.

(9) In the presence of copper the reaction is first order with respect to uranium. A possible association equilibrium is mentioned as an explanation for the apparent one-half order rate law for the autoxidation in the absence of copper.

mem
4-20-46

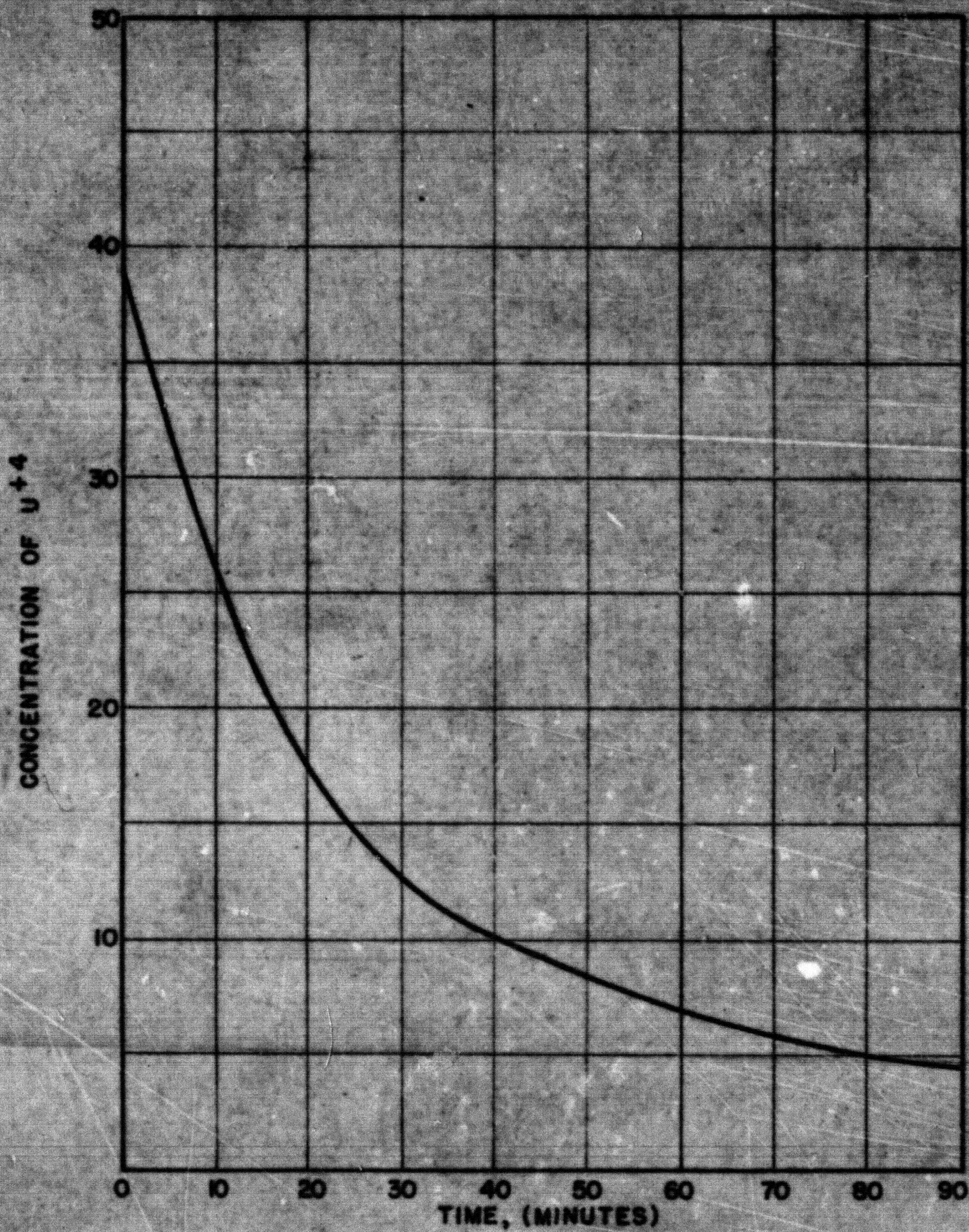


FIG. 1

AUTOXIDATION OF UCl_4

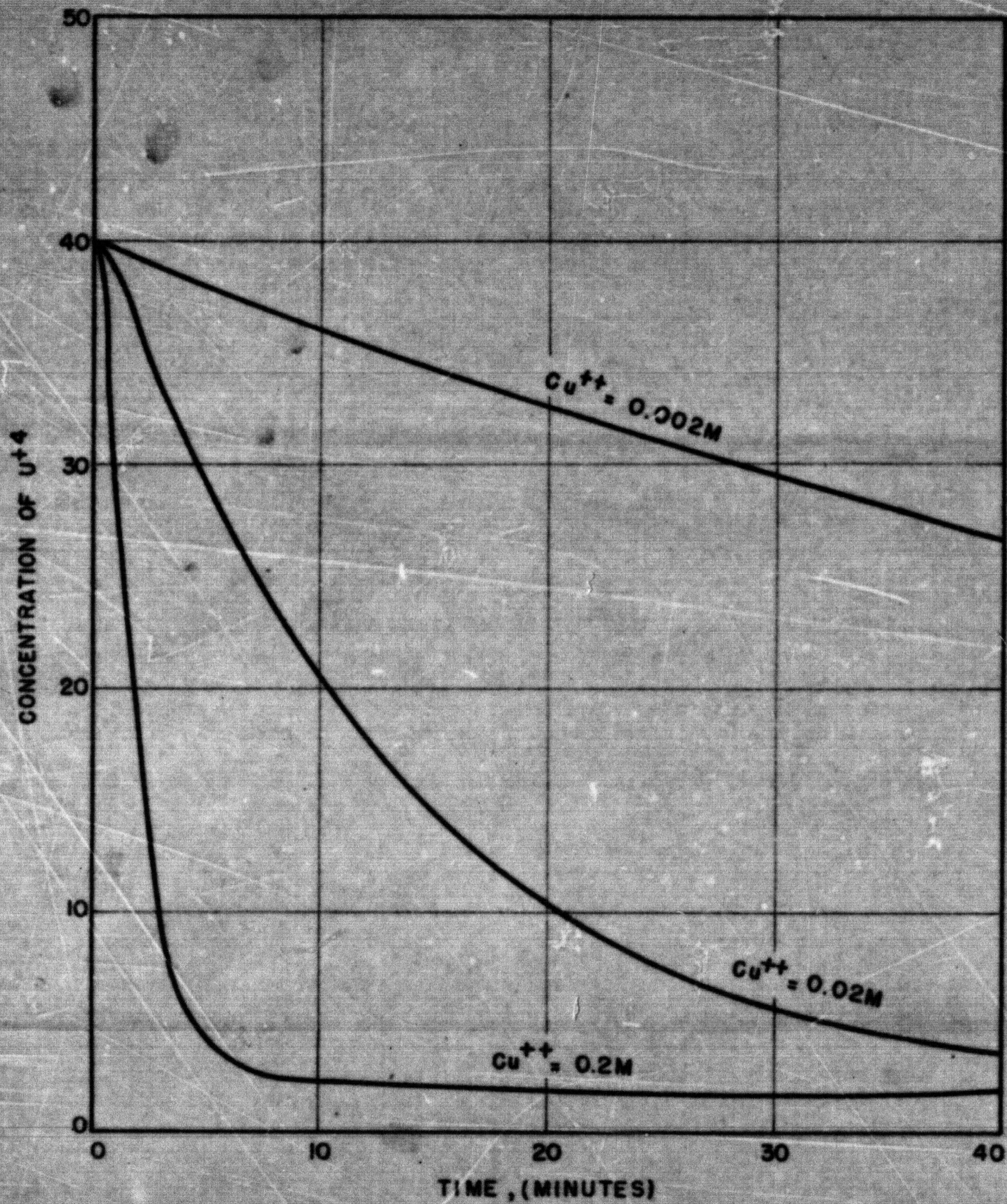
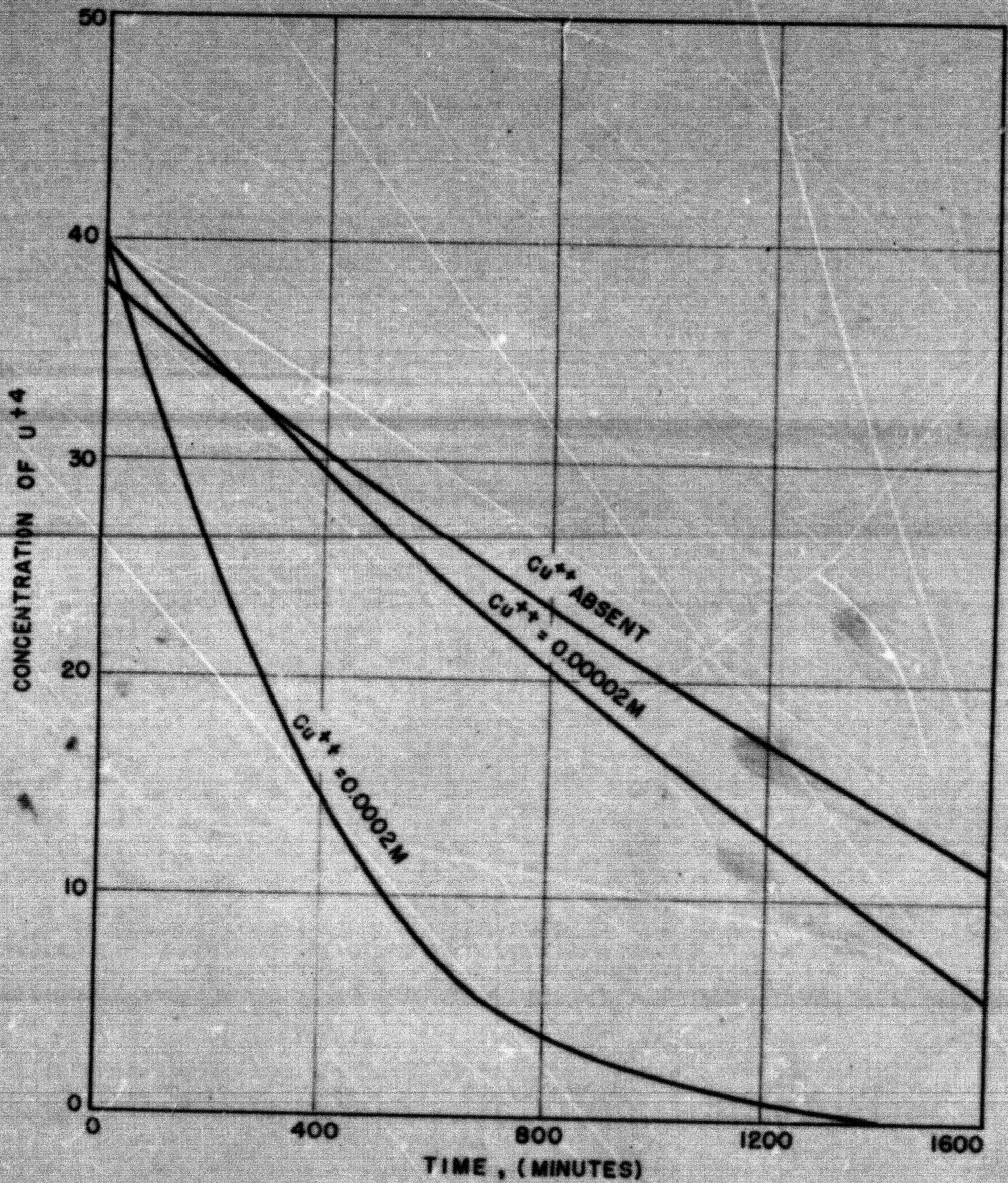


FIG. 2

AUTOXIDATION IN PRESENCE OF Cu^{++}



-15-

FIG. 3
EFFECT OF LOW CONCENTRATIONS OF Cu^{++}

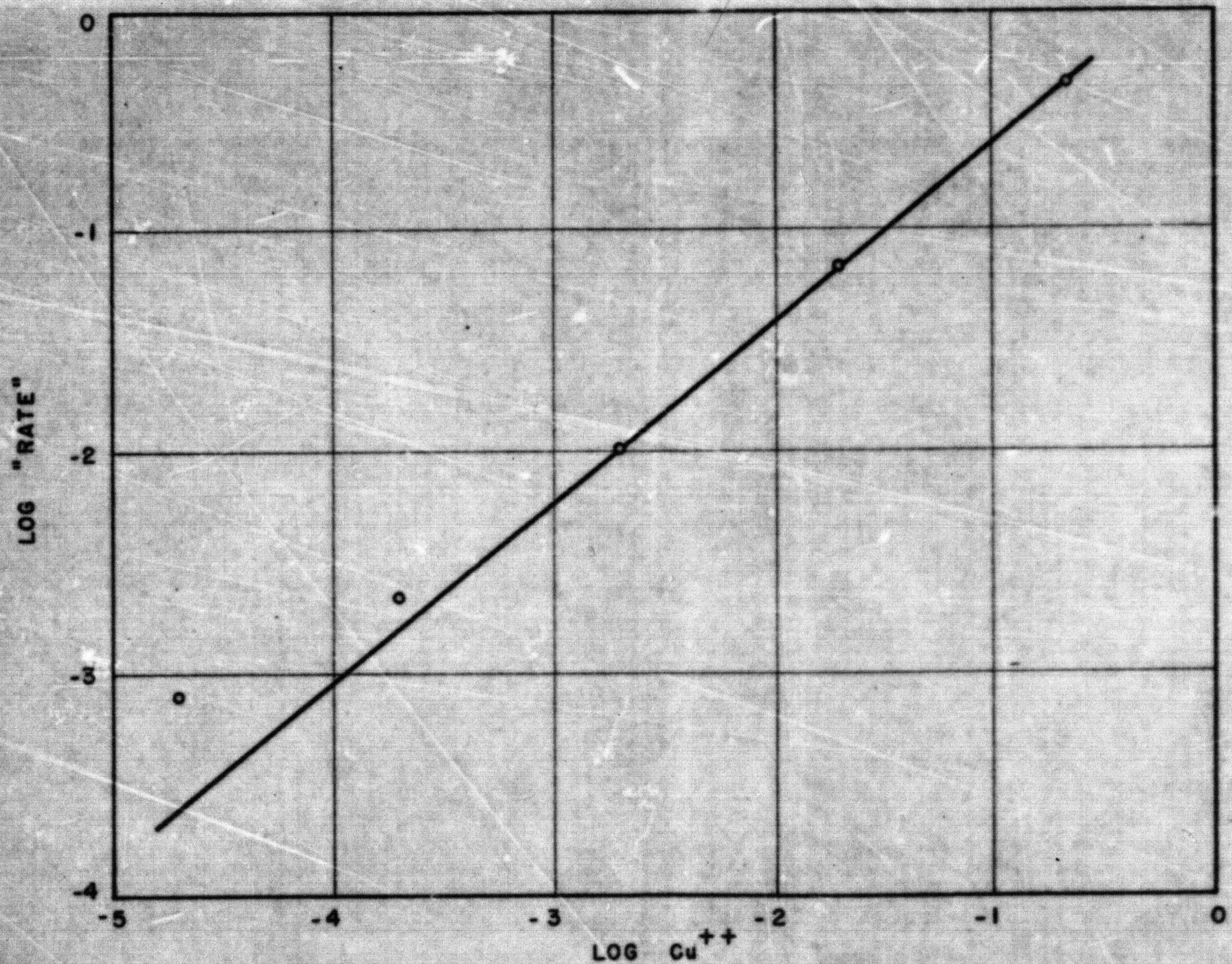


FIG. 4. AUTOXIDATION RATE VS Cu^{++} CONCENTRATION

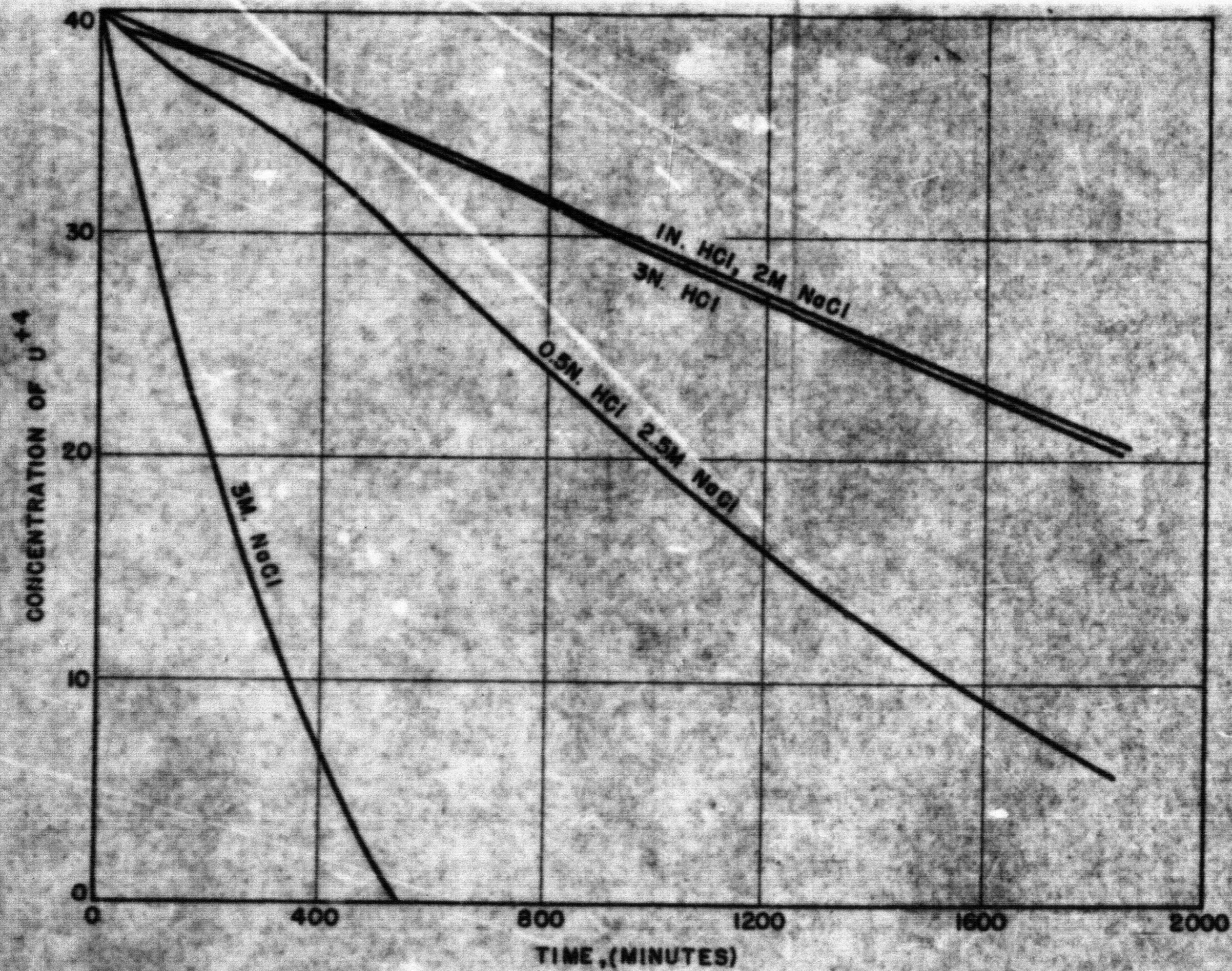
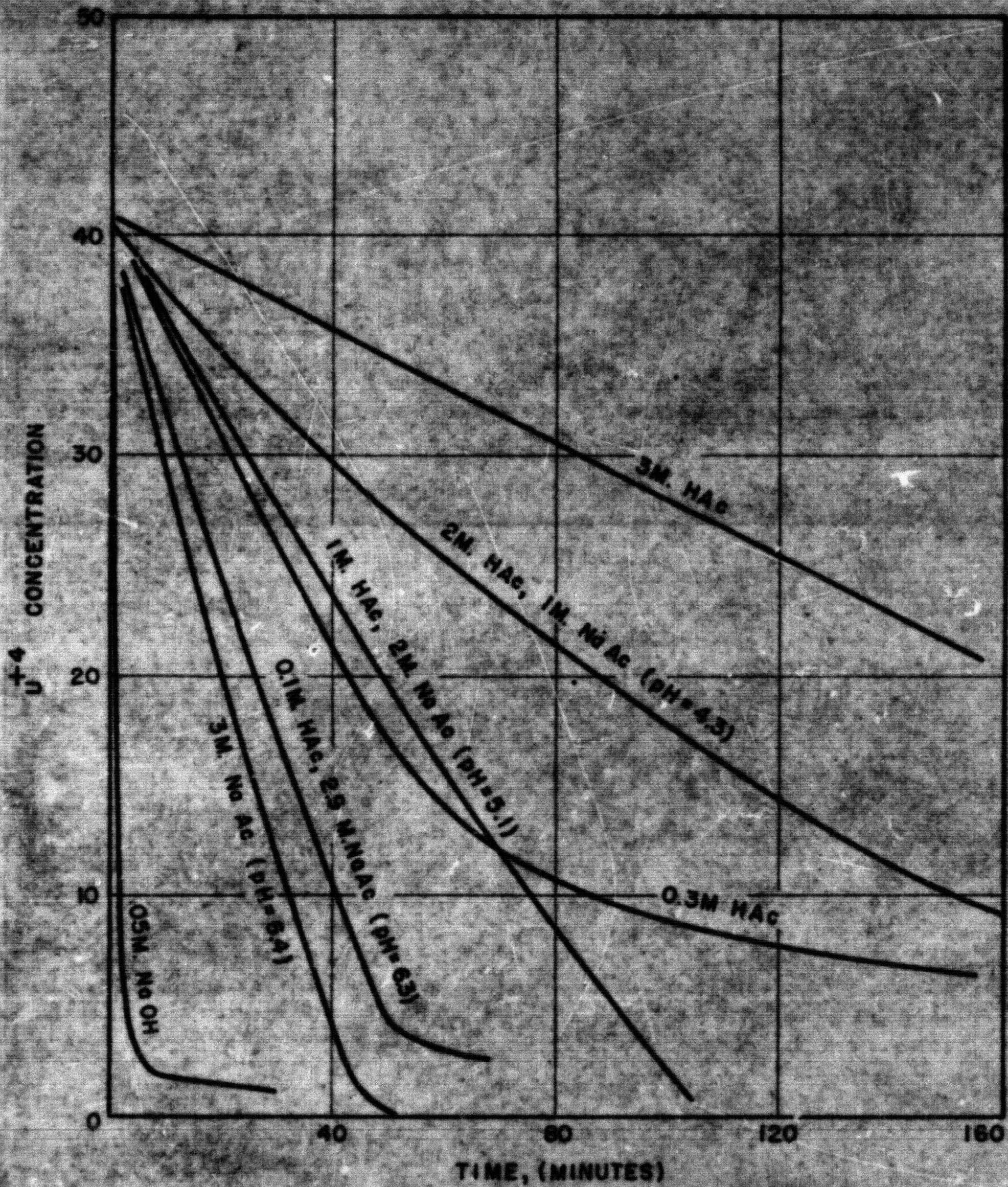


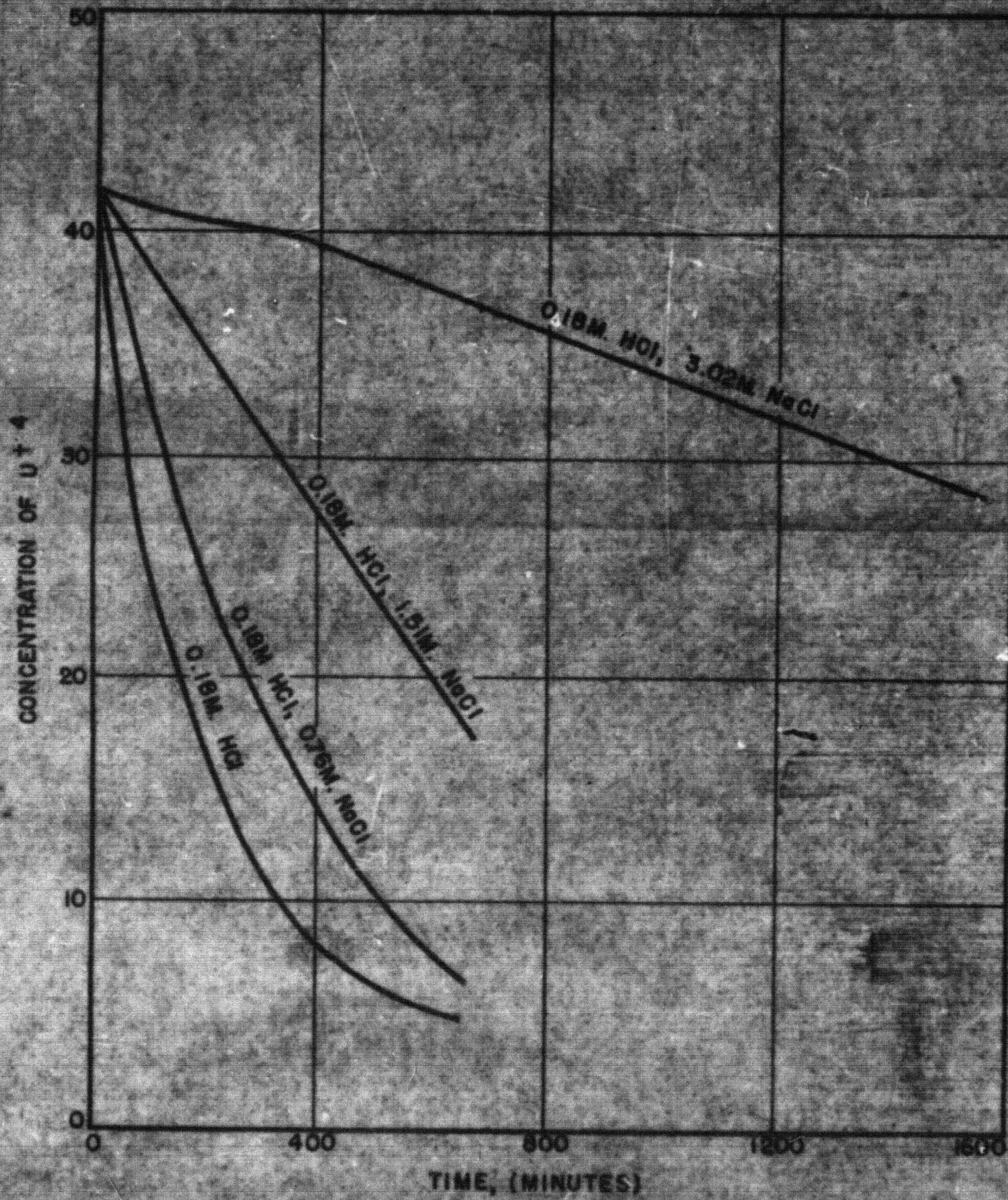
FIG. 5 EFFECT OF H^+ CONCENTRATION



- 81 -

FIG. 6

AUTOXIDATION IN ACETIC ACID



-19-

FIG. 7
EFFECT OF Cl^- CONCENTRATION

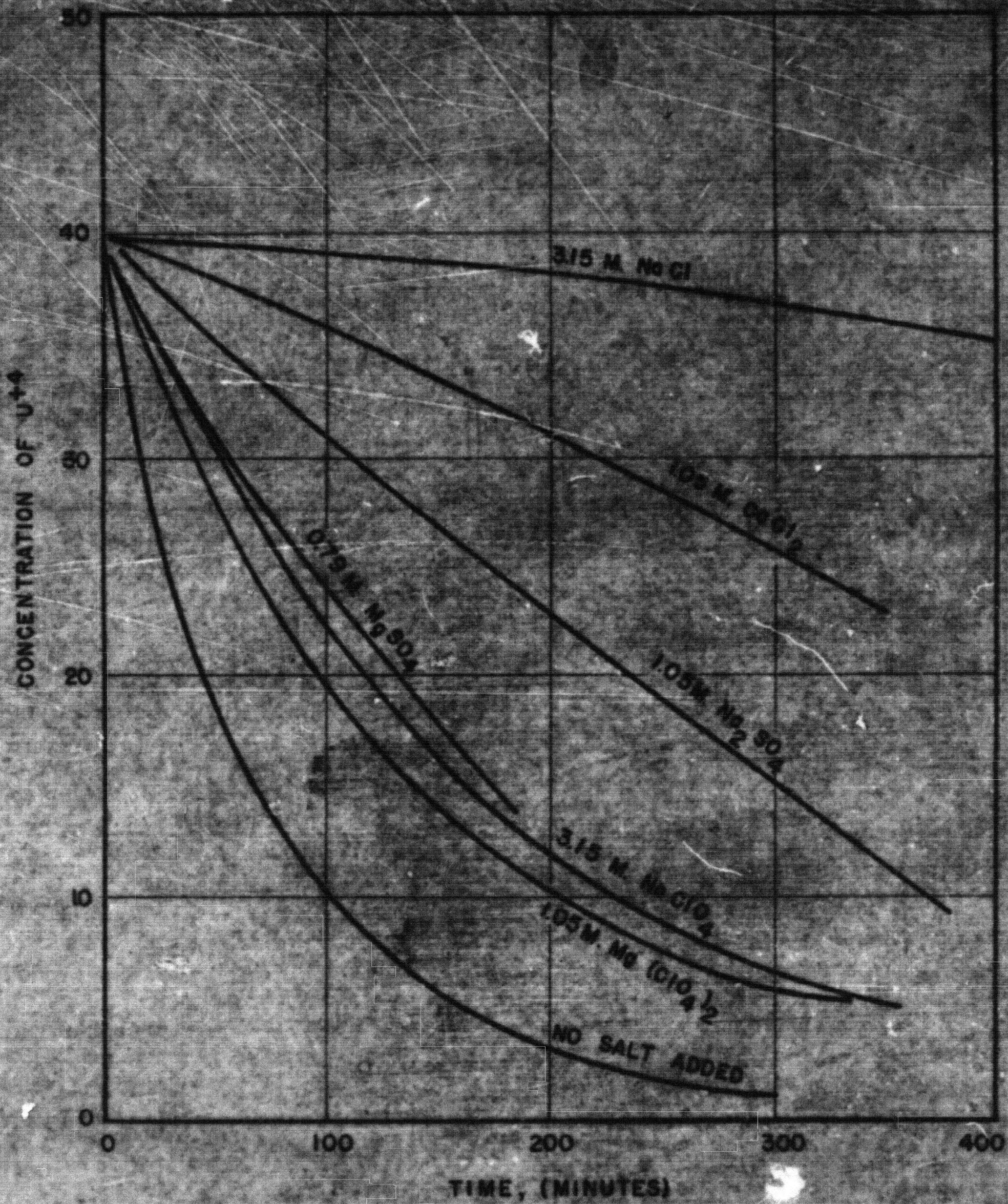
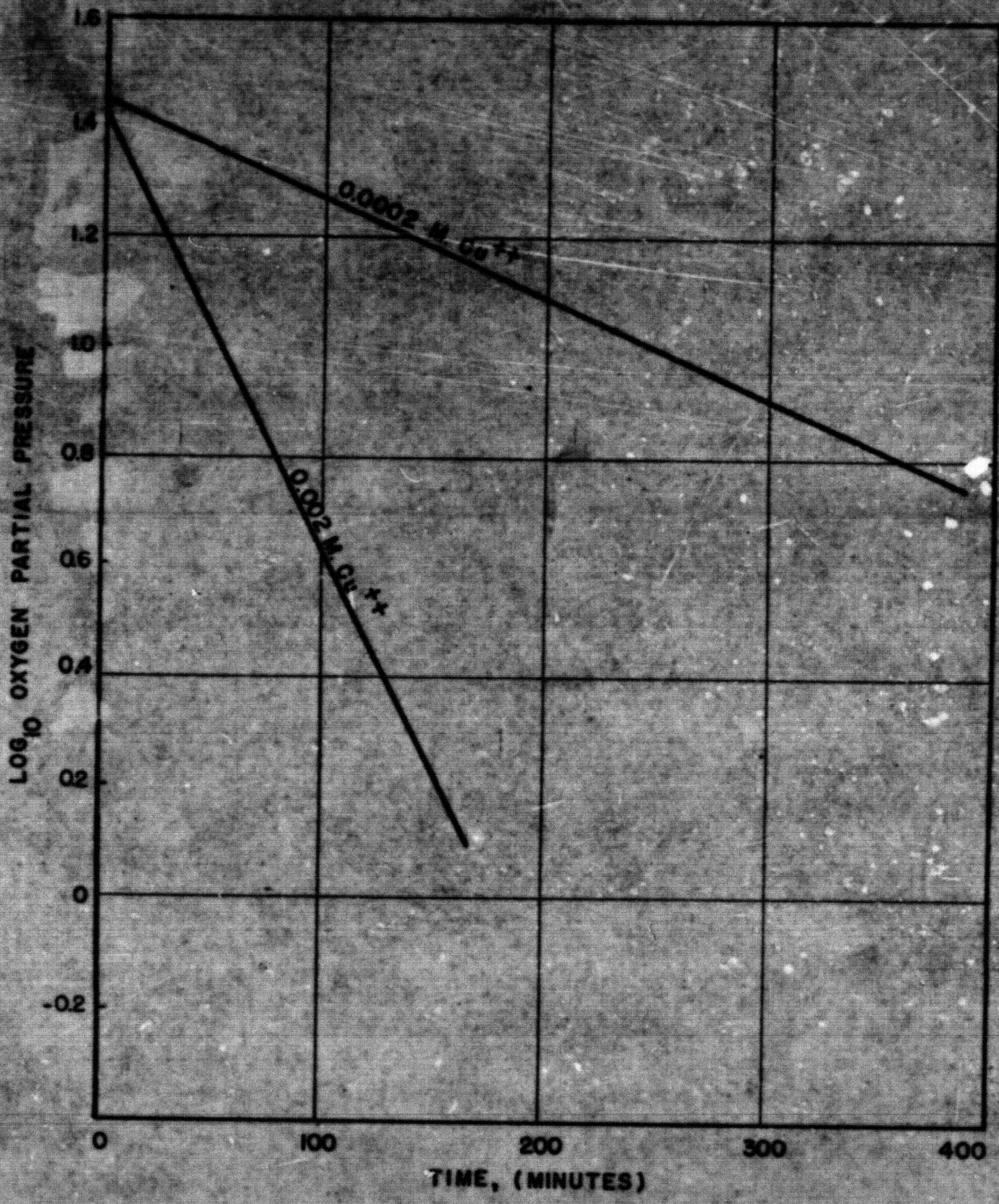
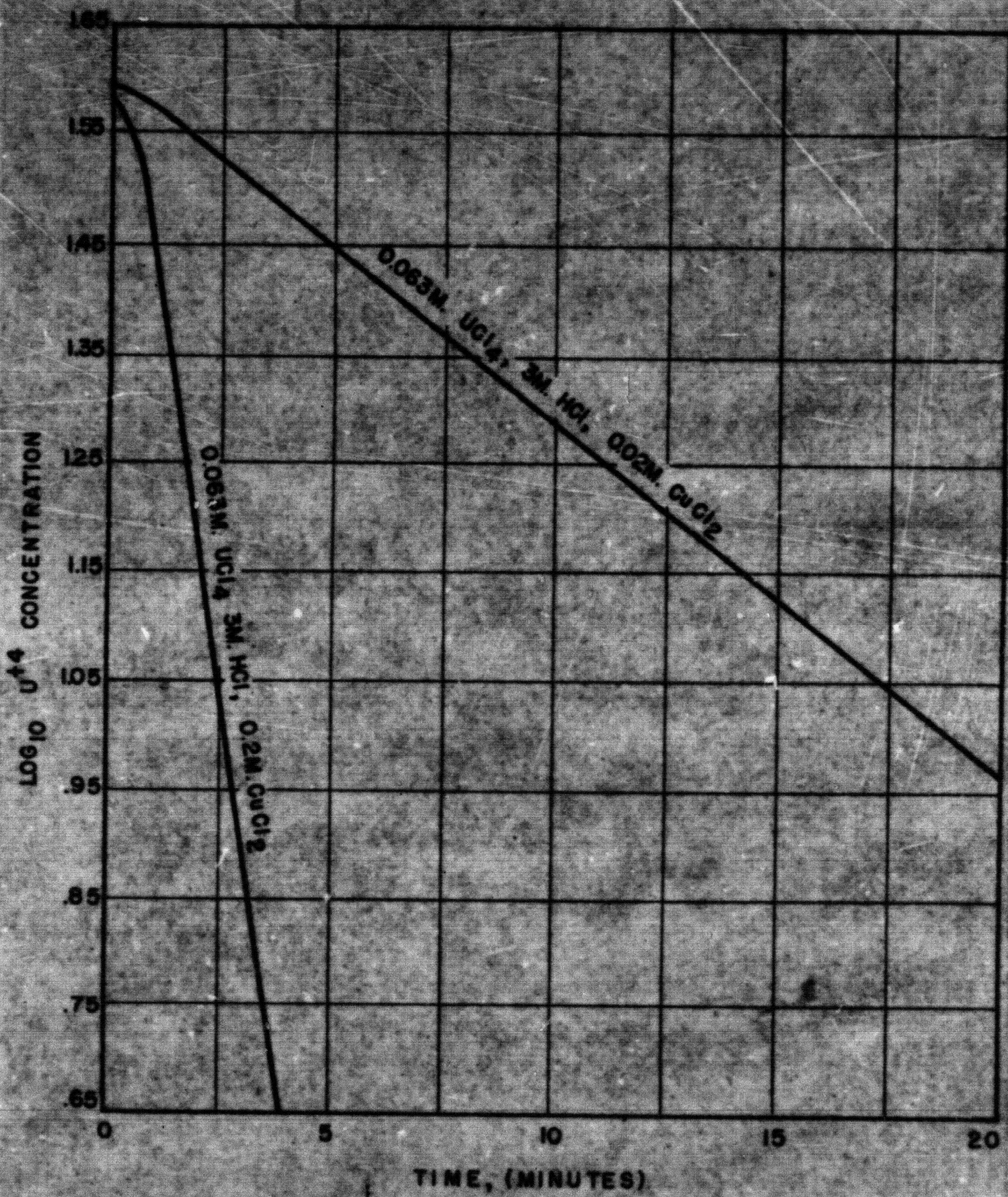


FIG. 8
EFFECT OF VARIOUS ANIONS



-21-

FIG. 9
EFFECT OF OXYGEN PARTIAL PRESSURE



- 22 -

FIG. 10
 AUTOXIDATION IN PRESENCE OF CU^{++}

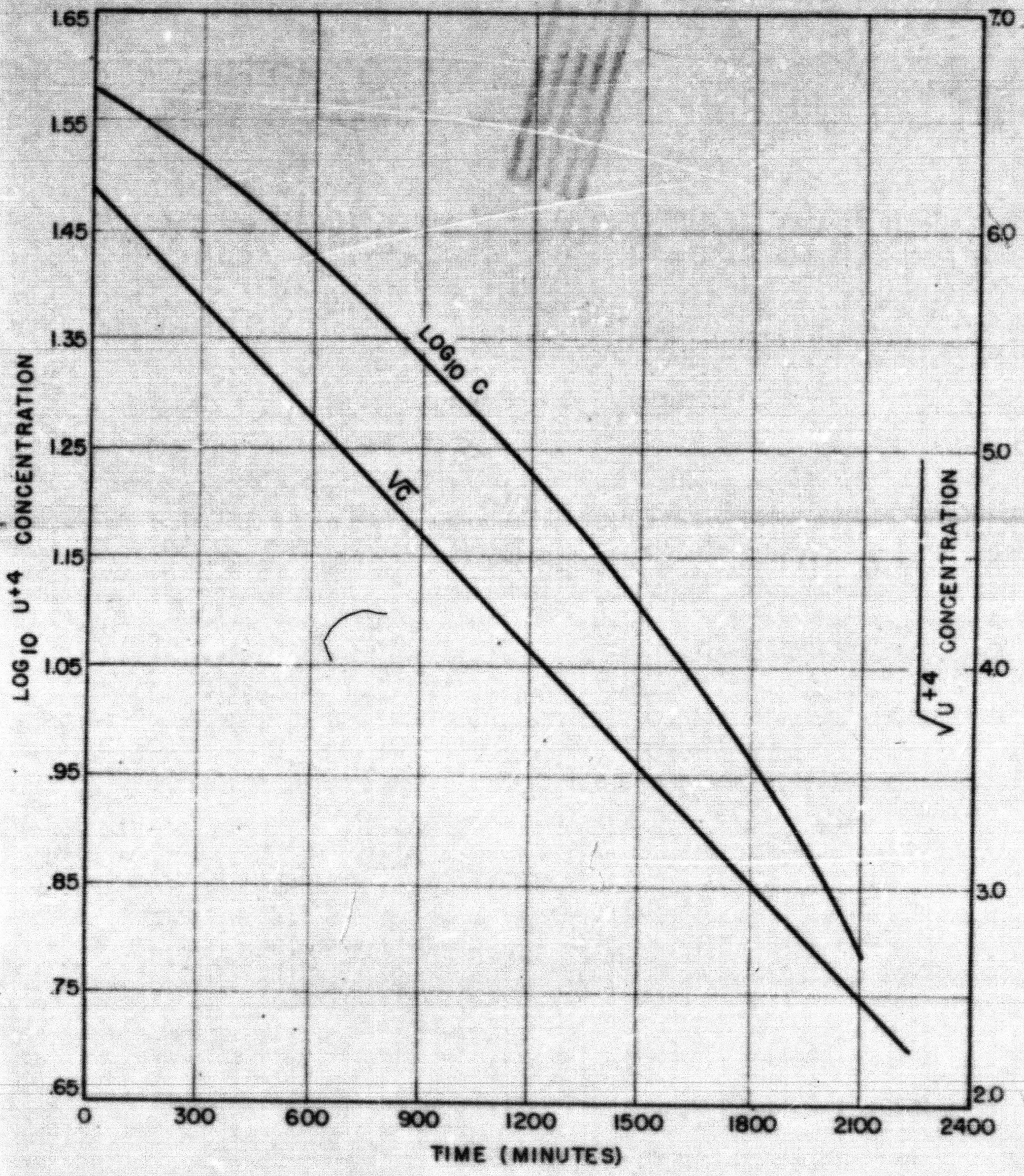


FIG. II
 UNCATALYZED AUTOXIDATION

REFERENCES

- (1) Ambrose R. Nichols, Jr., "Autoxidation of Uranoous Salts in Water Solution", Report Chem S-268 (UCRL), July 13, 1944.
Ambrose R. Nichols, Jr., "The Autoxidation of Uranoous Solutions", Part II, Report RL 4.6.930, August 25, 1945.
- (2) Filson and Walton, J. Phys. Chem. 16, 740 (1932)
- (3) Ambrose R. Nichols, Jr., Clare Gropp, "Absorption Spectra of Uranium Compounds in Aqueous Solution", Report RL 4.6.927, August 22, 1945.

