

6-1968

Radiation chemistry of aqueous chloroform solutions

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THE RADIATION CHEMISTRY OF AQUEOUS CHLOROFORM SOLUTIONS

by

Henry Douglas Kutz UC 1968

Submitted in partial fulfillment
of the requirements for
Honors in the Department of Chemistry

UNION COLLEGE

May, 1968



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ABSTRACT

Saturated aqueous chloroform solutions have been irradiated with gamma rays from a cobalt-60 source. G values for the formation of HCl in oxygenated and de-aerated solutions have been determined. Preliminary work involving the determination of hydrogen gas from the irradiated solutions is reported.

This Thesis

Submitted by

H. Douglas Kutz

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

John L. Festa

ACKNOWLEDGEMENT

I am grateful to Dr. John L. Festa for his guidance and friendly encouragement.

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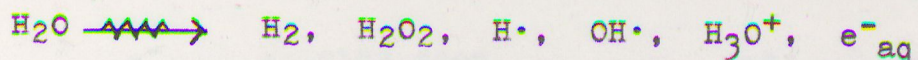
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INTRODUCTION

The interaction of ionizing radiation with aqueous chloroform has been studied by several individuals (1),(2). Teply must be credited with contributing most to our knowledge of the behavior of this system (3)-(7). That hydrochloric acid is the major product formed and that hydrogen peroxide and carbon dioxide are also produced are demonstrated by his experiments. After following the formation of these products for variations in dose rate, oxygen concentration, chloroform concentration, and for the addition of ferrous and thallos ions, Teply concludes that a free radical mechanism is occurring. He proposes a reaction mechanism and verifies it through kinetic analysis.

The radiation chemical study of aqueous chloroacetic acid, performed a few years later by Hayon and Allen (8), raises serious doubts whether ionizing radiation interacts with aqueous solutions purely by a free radical mechanism. It is shown in their work that neutral chloroacetic acid solutions yield the predominant product hydrochloric acid. At a pH of about two, however, the major product is hydrogen gas. This phenomenon is unexplainable solely in terms of a free radical mechanism, and Hayon and Allen suggested the following: two reactive species are present, both species react with chloroacetic acid, and the two species are interconvertible through the gain and loss of a hydrogen ion.

Recent work in the field of radiation chemistry (9)-(13) has shown that ionizing radiation produces six "intermediates" during the irradiation of water and aqueous systems.



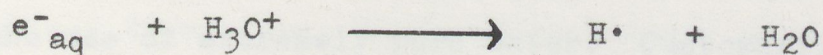
The formation of products takes place as these intermediates react with themselves and with the solute molecules. Of these six species the hydrated electron, e^-_{aq} , is presently of great importance in radiation chemistry.

For some time the dark blue color of solutions of sodium in liquid ammonia has been attributed to a solvated electron (14). Only until recently, however, has evidence for the hydrated electron been found in radiation chemistry (15). The hydrated electron, which may be considered the basic form of the hydrogen atom (16), has been found to react often similarly to the hydrogen atom but with a rate that is 3.4 times faster (8),(17). Its absorption spectrum resembles that of the solvated electron in metal-ammonia solutions (14), and many of its physical properties have been evaluated (18). It has been shown that the primary reacting intermediate for many radiation induced reactions in aqueous solutions is the hydrated electron (19).

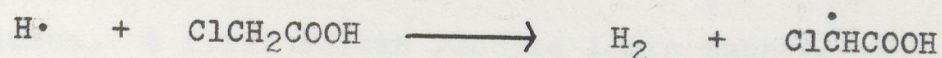
The observations of Hayon and Allen may now be interpreted in terms of competing reactions involving the hydrated electron. In neutral solutions the hydrated electron is the primary attacking species.



In acidic solutions hydronium ions compete with the chloroacetic acid for the hydrated electrons,



and because of the high concentration of hydrogen atoms, the chloroacetic acid is now attacked by hydrogen atoms.

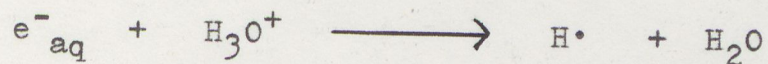


This study is a re-examination of the gamma-ray irradiation of saturated aqueous chloroform. Teply's experiments are repeated in part to afford some idea of reliability. A pH examination similar to that of Hayon and Allen is performed on aqueous chloroform. The following reactions are expected:

neutral conditions:



acidic conditions:



It is anticipated that under neutral conditions the major product of the gamma irradiation of saturated aqueous chloroform is hydrochloric acid and that under acidic conditions the principal yield is hydrogen gas.

EXPERIMENTAL

A. Materials

The study of aqueous solutions in radiation chemistry demands the use of extremely pure water. Customarily, to insure a sufficiently high degree of purity water is triply distilled. This procedure, however, is replaced in this study by passing ordinary distilled water through two resin columns. A first column removes ionic substances, a second, organic material; columns are Barnstead Hose Type Cartridges. Water prepared in this manner is stored in a ten gallon polyethylene bottle.

Hydrochloric acid, which is one of the products of the radiation induced decomposition of aqueous chloroform, is analysed titrimetrically. Brom-cresol purple serves as the indicator. Because hydrochloric acid is being determined in micro-mole quantities, the pH of the indicator is critical. After the indicator is prepared (20), its pH is adjusted to about two with 2N HCl.

Standard 0.2 Normal solutions of hydrochloric acid and sodium hydroxide are prepared. Ten- and one-hundred-fold dilutions of these solutions allow the titrimetric determination of the product hydrochloric acid.

Saturated solutions of aqueous chloroform are prepared. Spectral grade chloroform is washed ten times with pure water to remove inhibitors. The washed chloroform is placed under a layer of pure water in a stoppered brown glass bottle. Saturation of the aqueous layer with chloroform occurs within a few days. Teply states that saturated aqueous chloroform is 7×10^{-2} molar in chloroform (7).

Because oxygen effects the formation of products, chloroform solutions are both oxygenated and nitrogen de-aerated. Preparation of the two solutions is accomplished by bubbling the appropriate gas into the brown glass storage bottle. The gas passes first through the chloroform layer and then through the aqueous layer. Bubbling continues for at least one-half hour. Allowing the solutions to stand overnight reduces the super-saturation of the aqueous layer. General Electric commercial grade tank oxygen and Matheson "Prep" nitrogen are used in these operations. To remove possible traces of oil the oxygen is first passed through a cotton filter.

B. Irradiations

Solutions are irradiated in pyrex ampules. The procedure for preparing and filling the ampules is illustrated in Figure I. The partially formed ampules are thoroughly washed and dried between steps two and three. Step four is performed in a glove bag containing the proper atmosphere, either oxygen or nitrogen. It is noted that air remains trapped inside the ampule because of the long capillary neck on the vessel. In order to remove this air, thus allowing the atmosphere of the glove bag to fill the ampule, a hose connected to a vacuum pump is placed inside the glove bag. The neck of the ampule is inserted briefly into the hose and then withdrawn. As the neck is withdrawn, the atmosphere of the glove bag rushes into the evacuated ampule; this procedure is repeated several times. Solutions are injected into the ampules by means of a hypodermic syringe. The ampules are removed from the bag, and the break seals are fashioned.

Solutions are irradiated with gamma rays from a 250 Curie cobalt-60 source. For irradiations, ampules are placed in an aluminum holding device and lowered into the source. The radiation source and holding device are shown in Figure II.

Figure I Ampule Formation

- Step 1: 15 cm length of 14 mm pyrex tubing is cut,
Step 2: tubing is sealed on one end,
vessel is washed, dried,
Step 3: capillary neck is formed,
Step 4: glove bag atmosphere is forced into ampule,
10 mls solution are injected into ampule,
Step 5: break seal is fashioned.

Step 1: Step 2: Step 3: Step 4: Step 5:

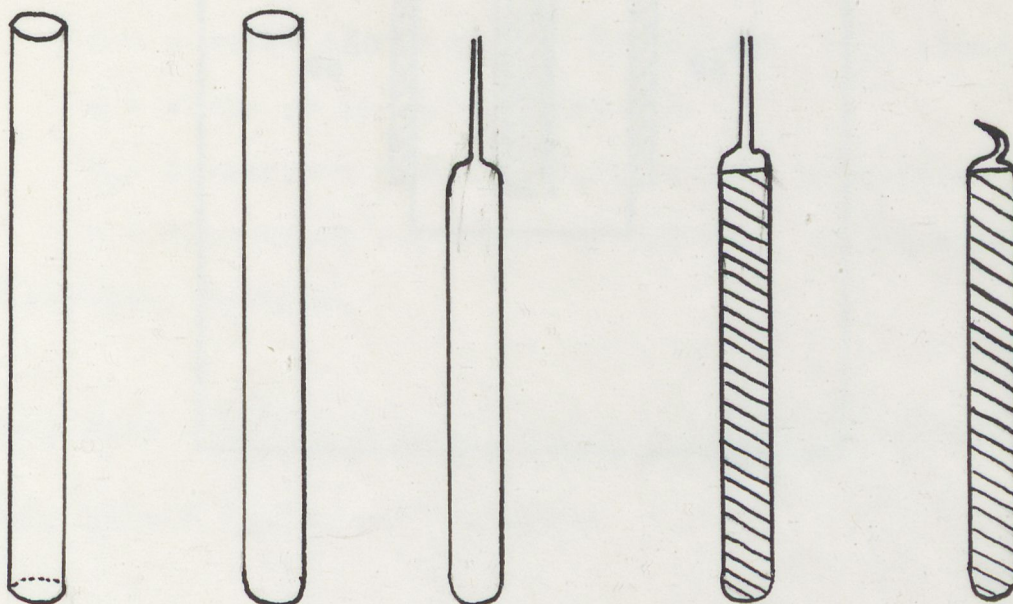
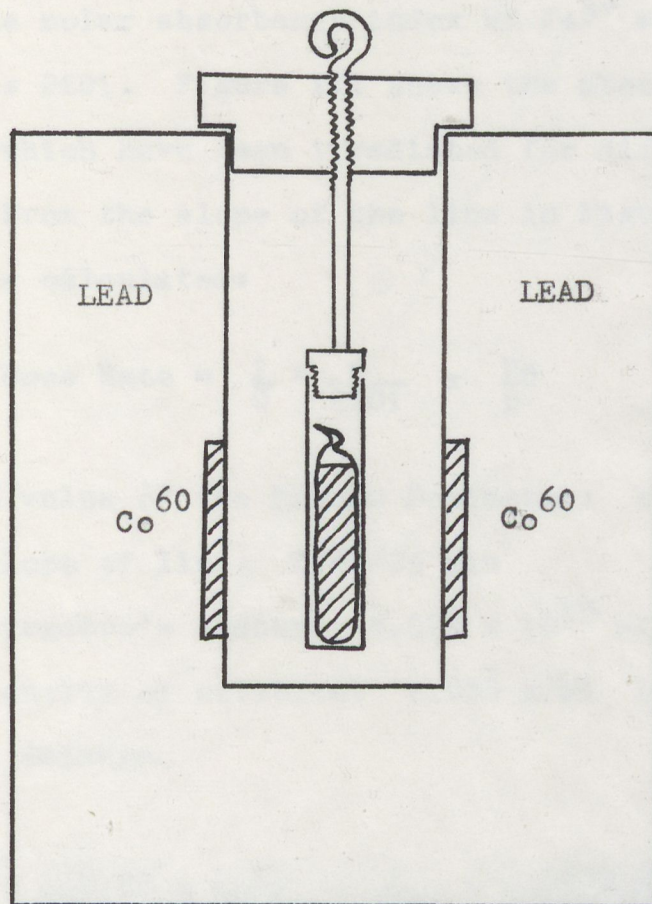


Figure II Radiation Source and Holding Device



C. Dosimetry

The exact rate at which solutions are absorbing energy during irradiations is determined by means of the Fricke Dosimeter (21). For every 100 electron-volts of energy that the Fricke Solution, aqueous Fe^{2+} , absorbs, 15.6 ions of Fe^{3+} are formed. The concentration of Fe^{3+} is determined spectrophotometrically on a Beckman Model DU spectrophotometer. The molar absorptivity index of Fe^{3+} at 305 millimicrons is taken as 2201. Figure III shows the absorptivity of Fricke solutions which have been irradiated for different lengths of time. From the slope of the line in Figure III the dose rate can be calculated:

$$\text{Dose Rate} = \frac{1}{G} \times \frac{m}{2201} \times \frac{N_0}{p}$$

G = G value of the Fricke Dosimeter: 15.6 atoms/100 ev

m = slope of line: 1.67/25 min

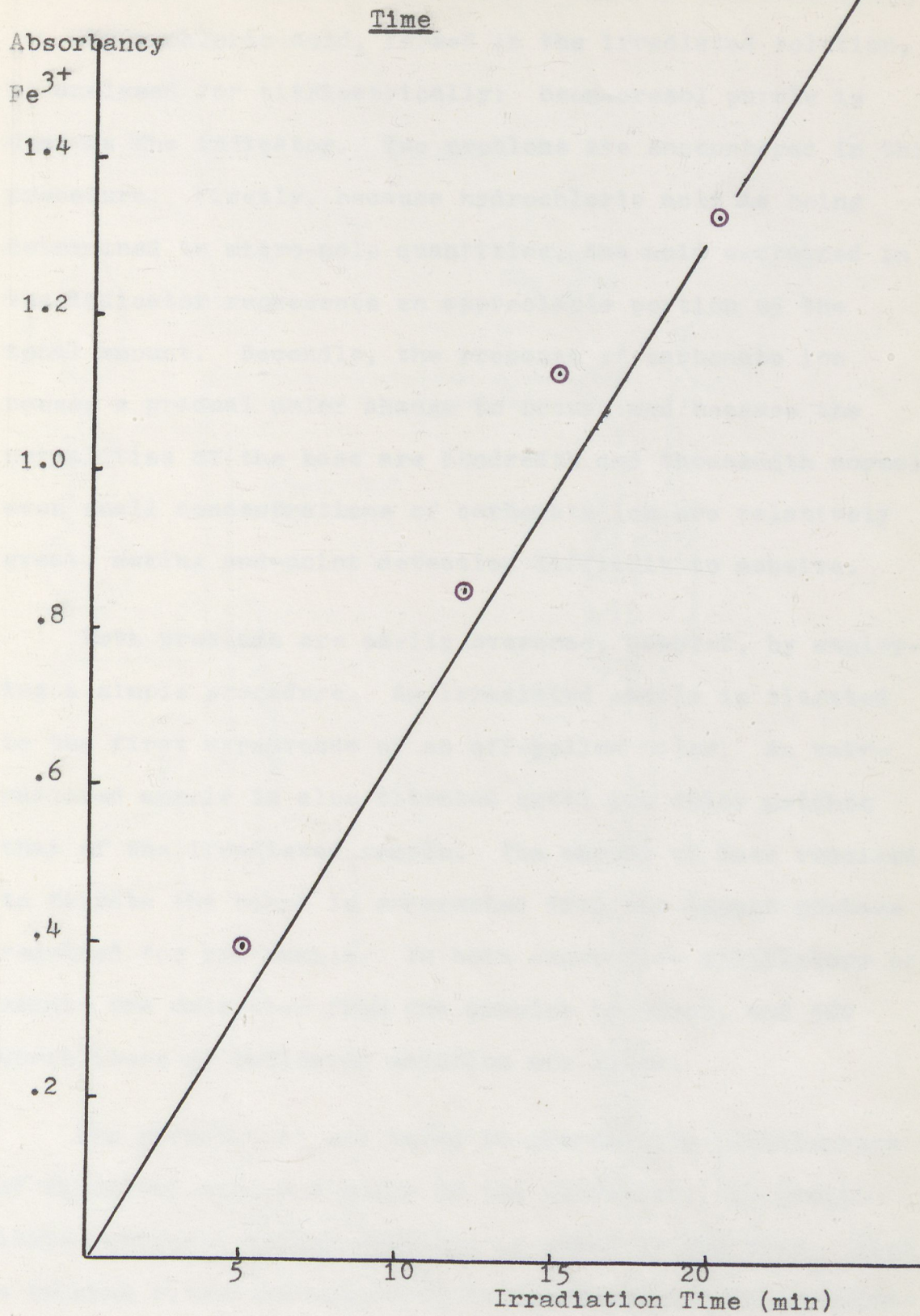
N_0 = Avogadro's number: 6.023×10^{23} atoms/mole

p = density of solution: 1.038 g/ml as measured on a Westphal Balance.

$$\text{Dose Rate} = \frac{100 \text{ ev}}{15.6 \text{ at}} \times \frac{1.67}{25 \text{ min}} \times \frac{1}{2201} \times \frac{6.023 \times 10^{23} \text{ at/mole}}{1.038 \text{ g/ml}}$$

$$\text{Dose Rate} = 1.17 \times 10^{17} \text{ ev/g-min}$$

Figure III Absorbancy Fe³⁺ versus Irradiation



D. Hydrochloric Acid Analysis

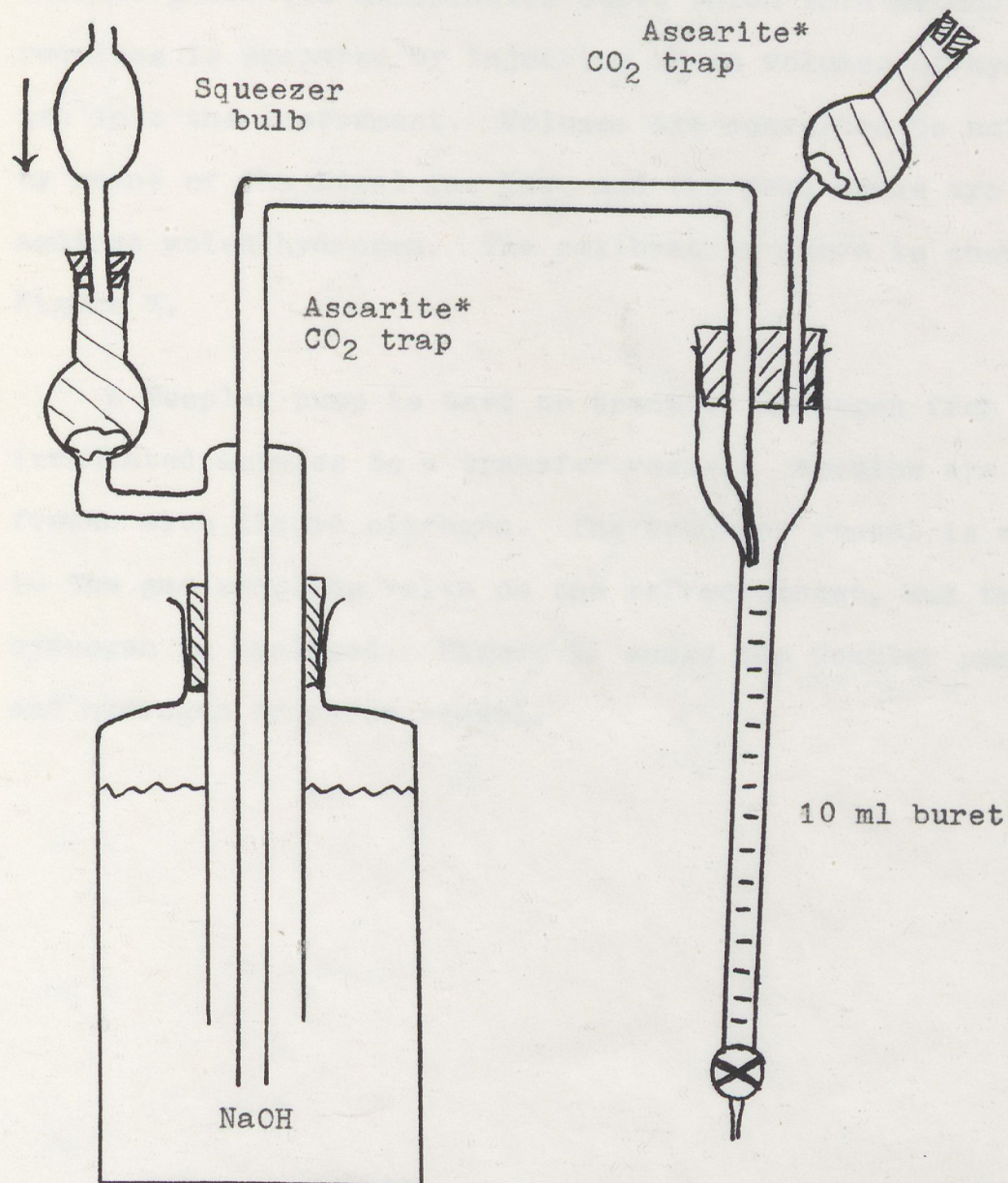
Hydrochloric acid, formed in the irradiated solution, is analysed for titrimetrically; brom-cresol purple is used as the indicator. Two problems are encountered in this procedure. Firstly, because hydrochloric acid is being determined in micro-mole quantities, the acid contained in the indicator represents an appreciable portion of the total amount. Secondly, the presence of carbonate ion causes a gradual color change to occur, and because the normalities of the base are hundredth and thousandth normal, even small concentrations of carbonate ion are relatively great, making end-point detection difficult to achieve.

Both problems are easily overcome, however, by employing a simple procedure. An irradiated sample is titrated to the first appearance of an off-yellow color. An unirradiated ampule is also titrated until its color matches that of the irradiated sample. The amount of base required to titrate the blank is subtracted from the amount of base required for the sample. In both cases five milliliters of sample are extracted from the ampules by pipet, and 500 microliters of indicator solution are added.

Two precautions are taken to prevent the interference of dissolved carbon dioxide on the titration. To precipitate carbonate barium chloride is added to the base. Also, a special titration apparatus is constructed. This appara-

tus, which prevents the exposure of base to the atmosphere, is shown in Figure IV.

Figure IV Titration Apparatus



* Obtained from the Arthur H. Thomas Co., Philadelphia.

E. Hydrogen Gas Analysis

Hydrogen gas is determined by gas chromatography using a Perkin Elmer Model 154 vapor refractometer. Molecular sieve 5A column packing is used with nitrogen as the carrier gas. The calibration curve which this method requires is prepared by injecting known volumes of hydrogen into the instrument. Volumes are converted to moles by means of the ideal gas law, and the peak areas are plotted against moles hydrogen. The calibration curve is shown in Figure V.

A Toepler pump is used to transfer hydrogen from irradiated ampules to a transfer vessel. Ampules are first frozen with liquid nitrogen. The transfer vessel is attached to the gas sampling valve on the refractometer, and the hydrogen is analysed. Figure VI shows the Toepler pump and hydrogen transfer vessel.

Figure V Hydrogen Calibration Curve

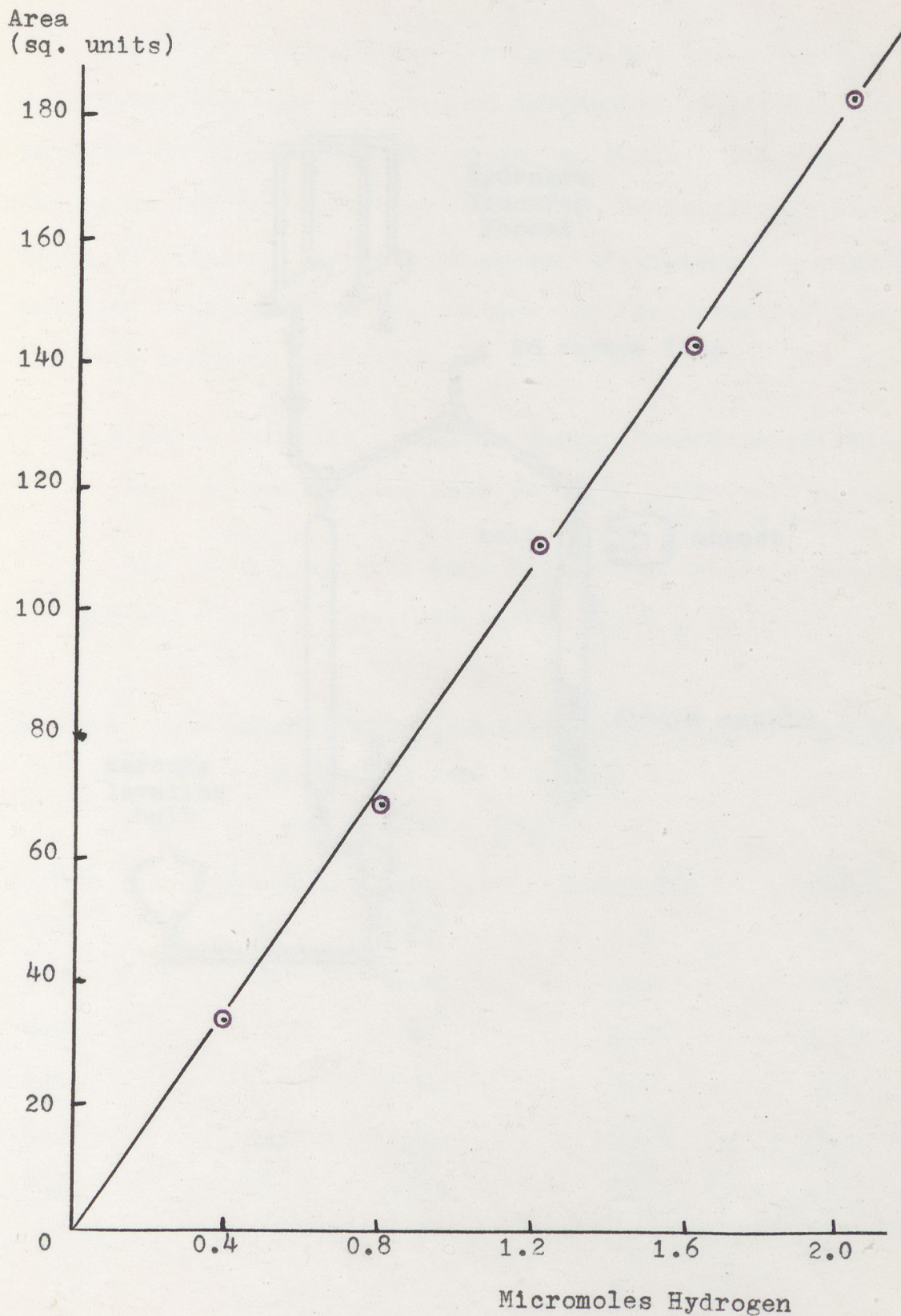
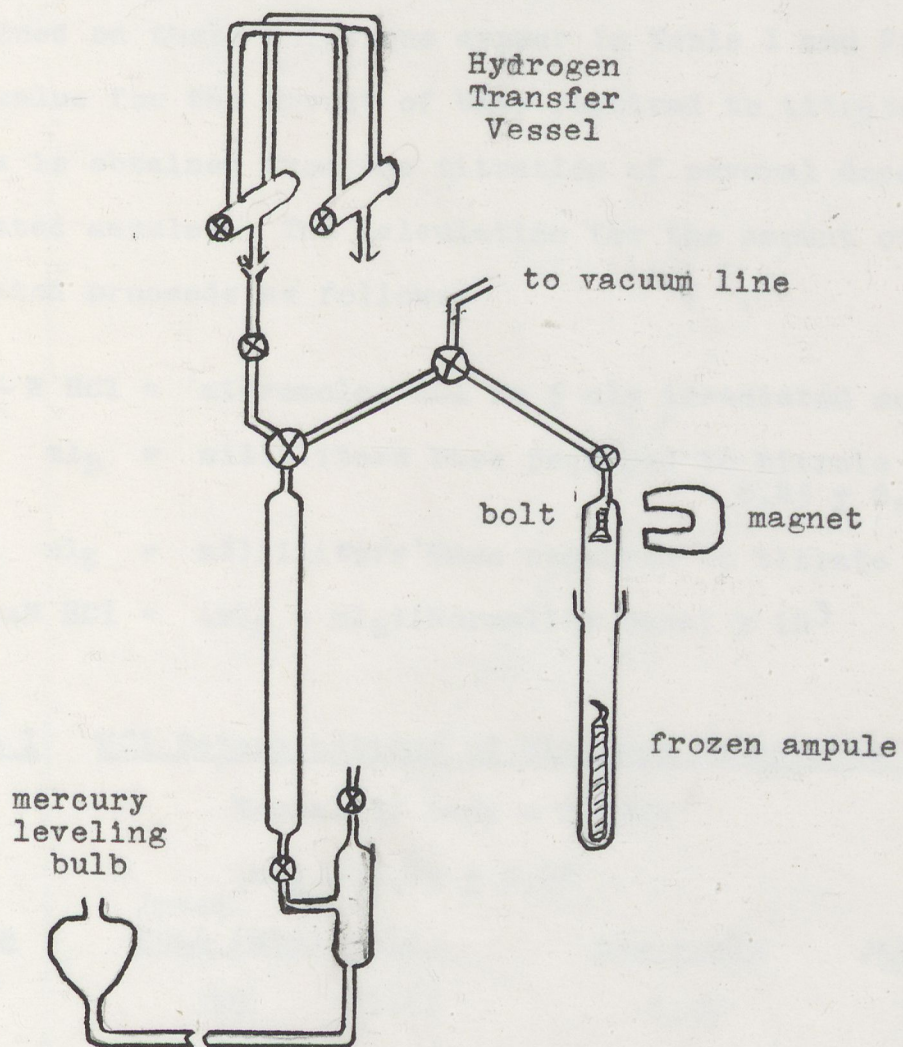


Figure VI Toepler Pump and Hydrogen Transfer Vessel



RESULTS

A. Hydrochloric Acid Analysis of Nitrogen De-aerated Solutions

The first analyses that are performed are hydrochloric acid determinations of nitrogen de-aerated solutions. Data obtained on these solutions appear in Table I and Figure VII. The value for the amount of base required to titrate the blank is obtained from the titration of several dozen unirradiated ampules. The calculation for the amount of acid titrated proceeds as follows:

μ M HCl = micromoles HCl in 5 mls irradiated solution

ml_B = milliliters base required to titrate blank:
0.45 ± 0.08

ml_S = milliliters base required to titrate sample

μ M HCl = (ml_S - ml_B)(Normality base) x 10³

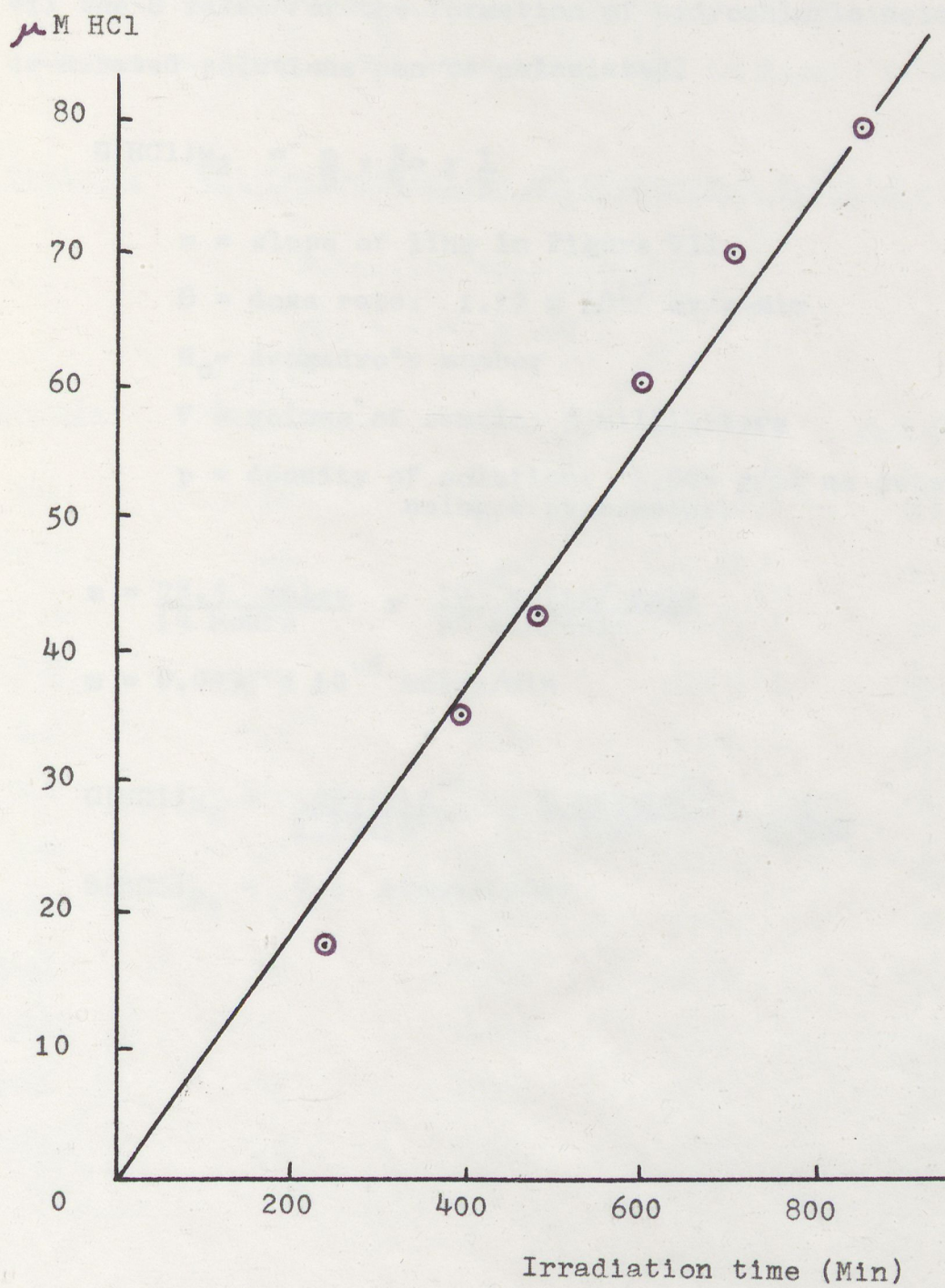
Table I HCl Determinations of Nitrogen De-aerated Solutions

Normality base = 0.0224

ml_B = 0.45 ± 0.08

<u>Sample</u>	<u>Irrad.</u> <u>time (min)</u>	<u>ml_S</u>	<u>ml_S - ml_B</u>	<u>μ M HCl</u>
8-1	390	2.02	1.57	35.2
8-2	607	3.16	2.71	60.7
8-3	240	1.26	0.81	18.2
8-4	710	3.55	3.10	69.5
8-5	850	4.00	3.55	79.5
8-6	480	2.33	1.88	42.1

Figure VII HCl Determinations of Nitrogen De-aerated Solutions



A term describing the formation of a particular product in a radiation chemical reaction is "G value". The G value represents the number of atoms of product formed for every one hundred electron volts of energy absorbed. From Figure VII the G value for the formation of hydrochloric acid in de-aerated solutions can be calculated.

$$G(\text{HCl})_{\text{N}_2} = \frac{m}{D} \times \frac{N_0}{V} \times \frac{1}{p}$$

m = slope of line in Figure VII

D = dose rate: 1.17×10^{17} ev/g-min

N_0 = Avogadro's number

V = volume of sample: 5 milliliters

p = density of solution: 1.004 g/ml as determined using a pycnometer.

$$m = \frac{78.5 \text{ moles}}{14 \text{ hours}} \times \frac{10^{-6} \text{ moles/mole}}{60 \text{ min/hour}}$$

$$m = 0.0935 \times 10^{-6} \text{ moles/min}$$

$$G(\text{HCl})_{\text{N}_2} = \frac{.0935 \times 10^{-6}}{1.17 \times 10^{17}} \times \frac{6.023 \times 10^{23}}{5.00} \times \frac{1}{1.004}$$

$$G(\text{HCl})_{\text{N}_2} = 9.6 \text{ atoms/100ev}$$

B. Hydrochloric acid analysis of oxygenated solutions

Aqueous chloroform solutions saturated with oxygen are also studied. Table II lists data from which are calculated the amounts of hydrochloric acid formed during various irradiation times. The data is plotted in Figure VIII.

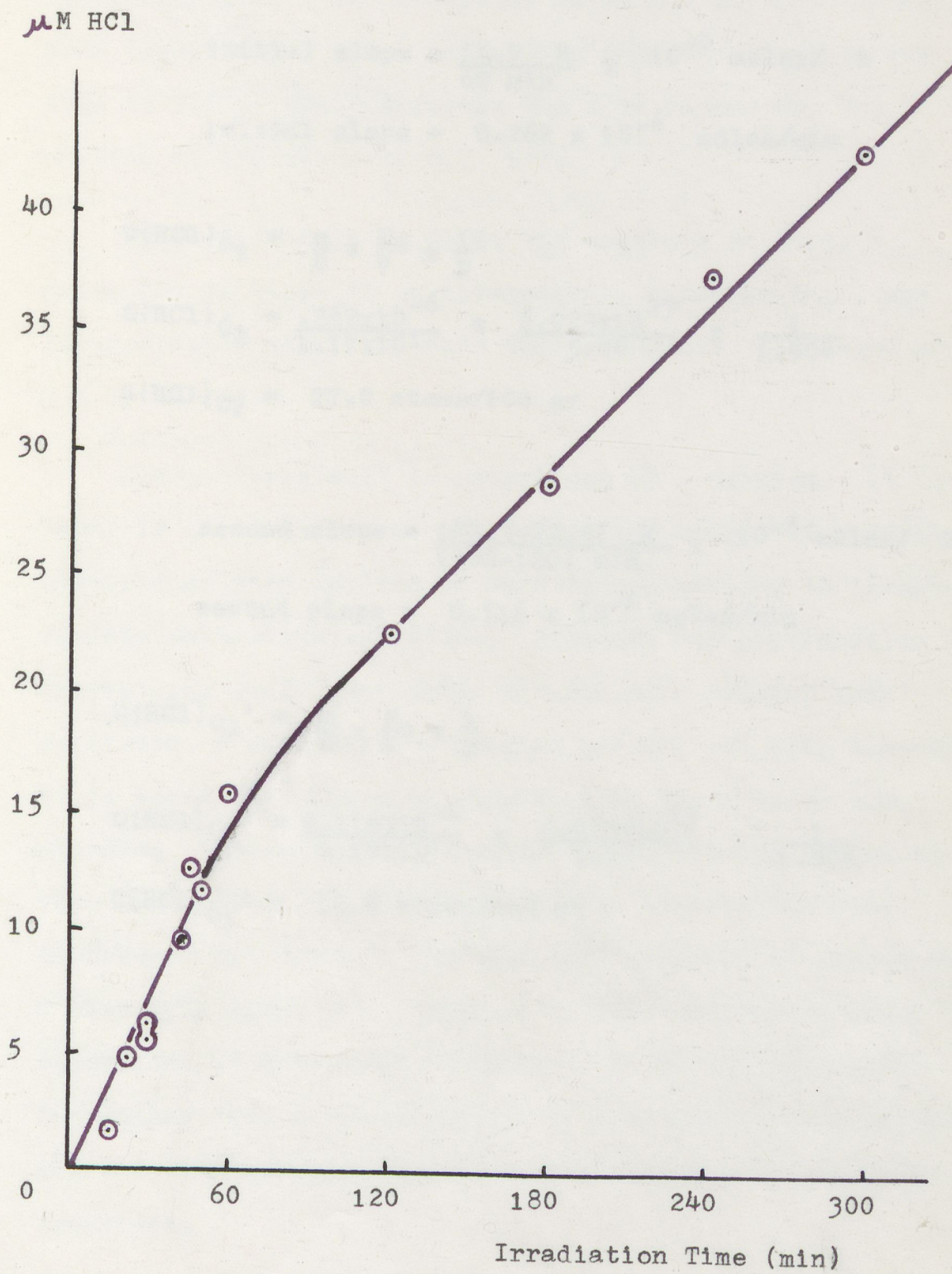
Table II HCl Determinations of Oxygenated Solutions

Normality base = 0.0231

ml_B = 0.45 ± .08

<u>Sample</u>	<u>Irrad. Time(min)</u>	<u>ml_S</u>	<u>ml_S-ml_B</u>	<u>μ M HCl</u>
G-1	180	1.69	1.24	28.6
G-2	60	1.13	0.68	15.7
G-4	240	2.08	1.63	37.6
G-5	120	1.42	0.97	22.4
G-7	295	2.29	1.84	42.5
G-8	20	0.66	0.21	4.9
G-9	30	0.70	0.25	5.8
G-10	15	0.53	0.08	1.8
G-11	40	0.86	0.41	9.5
G-13	50	0.96	0.51	11.8
G-14	30	0.69	0.25	5.5
G-15	45	0.95	0.54	12.5

Figure VIII HCl Determinations of Oxygenated Solutions



The plot of Figure VIII is seen to consist of two linear segments, and two G values are calculated.

$$\text{initial slope} = \frac{15.7 \text{ M}}{60 \text{ min}} \times 10^{-6} \text{ moles/ M}$$

$$\text{initial slope} = 0.262 \times 10^{-6} \text{ moles/min}$$

$$G(\text{HCl})_{\text{O}_2} = \frac{m}{D} \times \frac{N_0}{V} \times \frac{1}{p}$$

$$G(\text{HCl})_{\text{O}_2} = \frac{.262 \times 10^{-6}}{1.17 \times 10^{17}} \times \frac{6.023 \times 10^{23}}{5.00} \times \frac{1}{1.004}$$

$$G(\text{HCl})_{\text{O}_2} = 27.0 \text{ atoms/100 ev}$$

$$\text{second slope} = \frac{(43.3-22.5) \text{ M}}{(300-120) \text{ min}} \times 10^{-6} \text{ moles/ M}$$

$$\text{second slope} = 0.116 \times 10^{-6} \text{ moles/min}$$

$$G(\text{HCl})_{\text{O}_2}' = \frac{m}{D} \times \frac{N_0}{V} \times \frac{1}{p}$$

$$G(\text{HCl})_{\text{O}_2}' = \frac{0.116 \times 10^{-6}}{1.17 \times 10^{17}} \times \frac{6.023 \times 10^{23}}{5.00} \times \frac{1}{1.004}$$

$$G(\text{HCl})_{\text{O}_2}' = 12.0 \text{ atoms/100 ev}$$

DISCUSSION

A. $G(\text{HCl})_{\text{N}_2}$

It is shown in Figure VII that the formation of hydrochloric acid in de-aerated solutions depends linearly with time. The G value calculated from the slope of the line is 9.6. Teply observes the same dependence but arrives at a G value of 6.3 (7).

It is difficult to doubt the accuracy of Teply's value for he bases it on titrimetric, nephelometric, and polarographic studies. More understandably, the value of 9.6 is in error.

Hydrochloric acid is determined by titration. It is found in this study that this classical method of analysis breaks down when applied to acid determinations in irradiated aqueous chloroform solutions. Although the difficulties of determining small quantities of acid have already been mentioned, a more serious problem has not yet been described. It is noted that titrated samples lose their color upon standing, indicating that reaction products are interacting with the indicator. Woods and Spinks observe the same occurrence and suggest that hydrogen peroxide is acting as a bleaching agent (2). Because of this occurrence color comparison is extremely difficult. It is the opinion of the author that a better method of acid analysis is needed and that the present method has led to a G value which is incorrect.

B. $G(\text{HCl})_{\text{O}_2}$

Figure VIII, which describes oxygenated solutions, is seen to consist of two linear segments. The change in slope at higher doses is due to consumption of oxygen in the irradiated solution. The G value calculated from the initial slope is 27, which is the same value obtained by Teply. The G value at higher doses is only one third of the initial G value. It is clear from this work and from Teply's work that dissolved oxygen greatly enhances the yield of products.

C. Hydrogen Analysis

Preliminary work on hydrogen analysis has been done. Although several de-aerated solutions have been analyzed, insufficient data have been collected to determine a G value. It is expected that this work will be continued.

SUGGESTIONS FOR FURTHER WORK

A reliable method of hydrochloric acid analysis is needed. The shortcomings of the indicator titration method have already been mentioned. Methods involving the potentiometric analysis of H^+ look especially appealing. One might also try to follow the formation of Cl^- ion, possibly using polarography, which Teply mentions. These few sugges-

tions should show that the study of the cobalt-60 gamma irradiation of aqueous chloroform is far from complete and that further work would be most productive.

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