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THE UNIVERSITY OF MICHIGAN  
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THE EFFECT OF GAMMA RADIATION ON CHEMICAL REACTIONS

A collection of material originally presented as part of the Progress Reports of the Fission Products Laboratory from 1951 to 1955

Joseph J. Martin

Associate Professor, Department of Chemical and Metallurgical Engineering

Leigh C. Anderson

Professor and Chairman, Department of Chemistry

Project Supervisors

David E. Harmer

John G. Lewis

Bruce G. Bray

Senior Research Assistants

F. Bashore

R. A. Carstens

C. E. Eckfield

D. J. Goldsmith

J. R. Hallman

J. P. Holmes

R. L. Kinney

R. L. Klemm

R. R. Nissle

E. M. Rosen

W. M. Sergy

S. A. Stolton

H. H. Yang

Assistants in Research

Project M943-4

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## INTRODUCTION

A research team in the Engineering Research Institute of The University of Michigan has been investigating various uses of radiation for industrial applications. This investigation was conducted under the general title "Utilization of the Gross Fission Products." The effects of radiation on such things as combustion-engine performance, promotion of chemical reactions, and preservation of foods, were studied. Various cooperative programs with other departments of the University and with industrial concerns were instigated. The results of these investigations were collected and published semiannually as progress reports of the whole laboratory facility.

The demand for reprints for specific sections of these reports warranted this reproduction in a collected form. This volume is the collected work on "The Effect of Gamma Radiation on Chemical Reactions."

This study began in 1951 and has continued unbroken until the present time. Presented in this volume is all the work that was reported from August, 1951, until December, 1954, in Progress Reports 1 through 7 of the Fission Products Laboratory. A portion of this work may be found in the doctoral dissertations of D. E. Harmer and J. G. Lewis of The University of Michigan. A number of papers based on these reports were written and published in the technical literature from time to time. The page numbers, figure numbers, and table numbers are the same here as in the original reports. The contributors to the work are listed on the title page and each appears at the head of the section in which he was involved. A table of contents, list of figures, and list of tables appears before each individual section.

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PROGRESS REPORT NO. 1 (COO-86), "Utilization of the Gross Fission Products," by L. C. Anderson, J. J. Martin, L. E. Brownell, et al., Eng. Res. Inst. Project M943, Univ. of Mich., Ann Arbor, August 31, 1951, pp. 28-60.

A complete literature survey was made on the effects of radiation upon chemical reactions. Ninety-two references involving both experimental and theoretical work are listed.

PROGRESS REPORT NO. 2 (AECU-1889), "Utilization of the Gross Fission Products," by L. C. Anderson, J. J. Martin, L. E. Brownell, et al., Eng. Res. Inst. Project M943, Univ. of Mich., Ann Arbor, January 31, 1952, pp. 30-42.

A high-pressure stainless-steel reactor was designed for using high-pressure reactions under gamma radiation. Some preliminary experiments were conducted with the 1000-curie Co-60 source and with a palladium-109 source.

PROGRESS REPORT NO. 3 (COO-91), "Utilization of the Gross Fission Products," by L. C. Anderson, J. J. Martin, L. E. Brownell, et al., Eng. Res. Inst. Project M943, Univ. of Mich., Ann Arbor, June, 1952, pp. 31-39.

Experiments have been conducted on the polymerization of styrene and natural oils and additional information has been obtained on the ammonia synthesis reaction.

PROGRESS REPORT NO. 4 (COO-124), "Utilization of the Gross Fission Products," by L. C. Anderson, J. J. Martin, L. E. Brownell, et al., Eng. Res. Inst. Project M943, Univ. of Mich., Ann Arbor, March, 1953, pp. 24-36.

It has been found that gamma radiation readily promotes the chlorination of benzene by substitution to produce benzene hexachloride. Gamma radiation also promotes the chlorination of toluene. Ethylene can be polymerized under the influence of gamma radiation to produce a polymer having properties which differ from the conventional polymer produced by existing methods. Sulfurous acid can be converted to sulfuric acid by passing oxygen through sulfurous acid in the presence of gamma radiation.

PROGRESS REPORT NO. 5 (COO-196), "Utilization of the Gross Fission Products," by L. C. Anderson, J. J. Martin, L. E. Brownell, et al., Eng. Res. Inst., Project M943, Univ. of Mich., Ann Arbor, September, 1953, pp. 21-68.

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The study of the effect of radiation on the promotion of chemical reactions has been continued with studies on the polymerization of ethylene and the chlorination of benzene and toluene. Initial studies indicate that the chlorination of toluene gives the hexachloro addition product. A discussion of the thermodynamics and kinetics of reactions is included.

Dosimetry studies on both the 1-kc and 10-kc sources are reported, and the nominal activities and those determined from dosimetry measurements are compared. The actual activity of both the 1-kc and 10-kc sources is found to be considerably less than the reported activity. Personnel of Brookhaven National Laboratory have reached the same conclusion regarding the true activity of the 1-kc source, based on reactor computations.

PROGRESS REPORT NO. 6 (COO-198), "Utilization of the Gross Fission Products," by L. C. Anderson, J. J. Martin, L. E. Brownell, *et al.*, Eng. Res. Inst. Project M943, Univ. of Mich., Ann Arbor, March, 1954, pp. 12-48.

Ethylene was polymerized under gamma radiation at pressures of about 1000 psi and room temperature. Radiation dosages of 5 to 7 megarep produced a hard, tough polymer having a tensile strength up to 2300 psi with 79 percent elongation upon rupture, and a molecular weight of 37,300. Lesser dosages of radiation produced a soft, brittle, waxy polymer. Toluene was chlorinated under gamma radiation and produced the addition compound. This reaction is considered to be unique in that it is believed to be promoted only by gamma radiation. The product toluene "hexachloride" is being evaluated as an insecticide.

PROGRESS REPORT NO. 7 (AECU-2981), "Utilization of the Gross Fission Products," by L. C. Anderson, J. J. Martin, L. E. Brownell, *et al.*, Eng. Res. Inst. Project M943, Univ. of Mich., Ann Arbor, December, 1954, pp. 9-53.

Further studies on the polymerization of ethylene under gamma radiation were made using higher temperatures and slightly higher pressures. At 220°C an oily liquid was obtained whereas tough or waxy solids had been obtained at lower temperatures.

Toluene was chlorinated under gamma radiation. The products obtained by dehydrohalogenation and subsequent oxidation of the chlorinated toluene confirm the hypothesis that chlorine adds to the ring of toluene. New glass reaction equipment has been constructed to study the kinetics of the chlorination reaction and analytical procedures have been developed.

A design was developed for a chemical plant to chlorinate benzene under gamma radiation for the production of insecticides. Sources of cesium-137, 6-month-old mixed fission products, and cooling reactor-fuel elements were compared. Estimated prices of producing the addition product using gamma radiation compared favorably with existing prices of the product prepared under ultraviolet radiation.



Progress Report No. 1

UTILIZATION OF THE GROSS FISSION PRODUCTS

The Effect of Gamma Radiation on Chemical Reactions

L. C. Anderson  
J. J. Martin

D. E. Harmer  
J. G. Lewis





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Progress Report No. 1

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## B. PROJECT M943C — THE EFFECT OF RADIATION ON CHEMICAL REACTIONS

### 1. Introduction

It is the purpose of this project to study the promotion of chemical reactions by the use of radiation from waste fission products. Interest has been stimulated in this and other applications of waste radioactive materials by the availability of vast quantities of these materials as by-products from the operations of the nuclear reactors of the Atomic Energy Commission. Both from technical and economic considerations it is of interest to attempt to employ fission products for industrial purposes. If fission products should prove capable of promoting some chemical reactions to an extent which is attractive from a technical viewpoint, the processes which would be suggested by such reactions would still have to be examined to determine their economic feasibility.

This project is primarily concerned with radiation chemistry, which deals with the effects of high-energy photons and charged particles resulting from radioactivity. A study of the influence of radiation, consisting of these high-energy photons and particles, upon those chemical reactions which are thermodynamically feasible under the existing operating conditions seems to be a logical and appropriate starting point. Such reactions would be those which would yield a favorable ratio of desired product to reactant if brought to equilibrium under the conditions of the reaction. Judging from a study of the previous work done in the field of radiation chemistry, it appears to be debatable whether or not radiation may cause a displacement of the position of equilibrium in a chemical reaction. At any rate, the first studies of this project will be to determine the effect of radiation upon the reaction rates for selected systems. "Radiocatalysis" is the term which will be used to designate promotion of reactions in the manner just described. Thus "radiocatalysis" as used here and "catalysis" as generally used, have much the same basic significance, i.e., both terms are used to describe the changing of the rates of a chemical reaction without changing the composition of the reacting masses at equilibrium. Radiocatalysis simply indicates that some form of radiation is employed to change the reaction rates.

The radiation from fission products consists of beta and gamma rays. The gamma radiation, because of its great penetrating power, could be useful in commercial processes in which the chemical reactants are separated from the fission products by solid walls. On the other hand, the beta radiation, because of its small penetrating power, may be utilized if reactants can be brought into intimate contact with the fission products. In the course of this study gamma-ray and beta-ray sources and x-ray machines will be employed. Comparison of results using different sources of radiation may serve to indicate the relative efficiency of different kinds and different energies of radiation in promoting reactions.

Tests may be made of the relative effects upon chemical reactions of radiation alone and of radiation in combination with solid catalysts. It is thought that perhaps radiation may cause a catalyst ordinarily used for a given reaction to promote the reaction under less severe physical conditions (such as lower temperature and pressure) than are ordinarily required, or that the addition of radiation to the usual installations may increase the rates of reaction. There is the possibility that because of the low absorption of the gamma rays, little reaction might occur, especially in those cases where the reactants are not very dense. In order to utilize the energy of the gamma rays in the reacting masses, a chemically inert material might be added to the reactants in the form of a liquid or a gas, or else a solid packing might be placed in a reaction vessel. Such added materials might influence the rate of reaction by one or more of several mechanisms. Secondary emissions might be produced, such as softer gamma rays or electrons. Some gases or vapors might be added which would be more opaque to gamma radiation than the reactant molecules or which would be capable of absorbing and transferring energy to the reactant molecules without being permanently altered themselves.

Laboratory experiments determining the effect of radiation on chemical reactions are not new. However, the industrial application of these reactions has not been feasible until this time because of the lack of cheap sources of radiation. With the vast quantities of fission products available, it is worthwhile to review these experiments with the obvious intention of trying to find some reactions which might have great industrial promise. Although there are many papers on the general subject, the following review covers only those which are closely related to the objectives of this work.

## 2. Literature Review for Project M943C

a. Inorganic Reactions: There is some evidence in the literature that ammonia may be formed from the elements under the influence of charged particles. Lind and Bardwell (49) gave data for the flow method of producing ammonia from nitrogen and hydrogen activated by alpha radiation from radon. The resulting gas mixture was analyzed and showed the ratio of the molecules of ammonia formed to the ion pairs of reactants produced to be 0.2 to 0.3. According to these investigators the ratio of moles of ammonia decomposed to those ionized is one, and the equilibrium is reached when five times as much radiation falls on the hydrogen and nitrogen molecules as on the ammonia molecules. This is found to occur when there are 10 volumes of reactant ( $3\text{H}_2 + \text{N}_2$ ) gases to one volume of ammonia, or a mixture containing 9.09 per cent ammonia by volume. Results in which decomposition of ammonia proceeded to 73 per cent showed that the reaction-velocity constant falls steadily as the decomposition reaction proceeds, as if a reverse reaction were occurring.

Lind (44) discusses radiochemical equilibrium in the synthesis of ammonia. He designates "M" as the number of moles of ammonia that are formed and "N" as the number of ion pairs formed. Using  $M/N = 0.2$  and  $-M/N = 1.0$  (49), for the formation and decomposition of ammonia, respectively, Lind and Bardwell calculated equilibrium at 25° to be 83.3 per cent decomposition, or 9.09 per cent ammonia by volume.

Ponsaert (70) used 0.32 for  $M/N$ , and 1.03 for  $-M/N$  to calculate equilibrium at 13.5 per cent ammonia by volume. The actual equilibrium found by D'Alieslager and Jungers (21) was only 4.7 per cent ammonia by volume. In calculating it was assumed that the mechanisms of the two reactions were independent of each other in intermediate steps. Only 0.11 for  $M/N$  would be required to give an equilibrium concentration of 4.7 per cent ammonia by volume. Accordingly, Lind (44) maintains that the intermediate steps are not independent and that there must be an exchange of activation energy in the direction to produce decomposition. The shift of equilibrium is in the correct direction to be accounted for by an exchange of ionization from  $H_2^+$  (16 volts) or  $N_2^+$  (17 volts) to give  $NH_3^+$  (11 volts).\* This behavior favors decomposition at the expense of synthesis.

The type and direction of shift just described may be general in other similar reactions because a large molecule usually has a lower ionization potential than that of its components.

Bouille tested the effect of cathode rays from various metallic cathodes upon the ammonia synthesis. Methods and apparatus for the catalysis of  $N_2 + 3 H_2 = 2NH_3$  at about 3 mm pressure by the radiations from various metallic cathodes were described. Aluminum, antimony, silver, tin, platinum, lead, and silicon in various chemical and physical forms were tested as catalysts. Optimum currents, voltages, and pressures for the best yields per unit of power input were determined. A platinum coil was found best as a catalyst. Ammonia yields were comparable to those of a high-pressure reaction. The thermodynamic equilibrium of the reaction and the temperature of the cathode discharge were determined. No catalysis was found at the anode.

Williams and Essex (90) studied the ion yield in nitrous oxide bombarded by alpha rays at 10-20 cm absolute pressure. The ion yield increased with electric field strength above half saturation values because of electron acceleration.

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\* Later measurements show these values to be 15.4 volts for  $H_2^+$ , 15.5 volts for  $N_2^+$ , and 11.2 volts for  $NH_3^+$ . (Friedlander, G., and Kennedy, J., Introduction to Radiochemistry. New York: John Wiley and Sons, Inc., 1949.)

Lind (42) studied the kinetic behavior of the combination of oxygen and hydrogen under the influence of alpha rays. The velocity of the reaction was found to depend only upon the quantity of radiation and the pressure. A kinetic equation was given. Hydrogen and oxygen were both found to be activated. Varying proportions of reactants caused changes in the rate of reaction, due to the different specific ionizations of the reactants. The temperature coefficient of the reaction was found to be zero between 0 and 25°C.

Lind (43) investigated the rate of reaction of hydrogen with oxygen under the influence of alpha rays at small volumes and low pressures. Under the conditions mentioned the rate of reaction was observed to be abnormally high. This effect was attributed to the action of "recoil ions" resulting from the recoil of an atom from which an alpha particle had been ejected. The approximate statistical agreement between ionization and chemical action was cited for cathode rays, beta rays, alpha particles, and recoil atoms, with respective masses from 1/1700 to 220 times the mass of the hydrogen atom.

The catalytic influences of the ions of the inert gases during the bombardment of certain gases by alpha particles was studied by Lind and Bardwell (47). The effects were noted of alpha particles on acetylene, cyanogen, hydrogen cyanide, the oxidation of CO and H<sub>2</sub>, the decomposition of CO and the decomposition of NH<sub>3</sub>, as catalyzed by the inert gases nitrogen, helium, neon, argon, krypton, xenon, carbon dioxide, and hydrogen. The ions of the inert gases acting as catalysts were quantitatively equivalent to those of the reactants in producing chemical reaction. Nitrogen and carbon dioxide failed to autocatalyze the reactions in which they were generated. This behavior was exceptional. The catalyst may have had an ionization potential either higher or lower than that of the reactants. This possibility precluded a primary step consisting of an exchange of charges between the ionized catalyst and the neutral reactants. By observation, it was determined that for any fraction of ionization of the gaseous catalysts up to 0.50, the catalyst efficiency was 100 per cent.

Lind and Bardwell (46) have investigated the reactions of carbon dioxide and carbon monoxide. Carbon monoxide alone under alpha rays gave carbon dioxide, carbon, and an unknown suboxide of carbon. A mixture of carbon monoxide and oxygen was oxidized to carbon dioxide by alpha radiation. This reaction proceeded at the temperature of liquid air at about one-half the rate observed at room temperature. Carbon monoxide and hydrogen gave a white solid which was neither aldehyde nor sugar, was insoluble in water, and had the approximate composition of a polymer of formaldehyde. Carbon

dioxide and hydrogen gave a polymer of formaldehyde different from that mentioned above, water, and a small amount of carbon monoxide, but no methane. It was stated that there was no chain effect. Carbon dioxide alone was unaffected by alpha radiation.

Watson, Vanpee, and Lind (86) mixed carbon monoxide in an 8-cm-diameter glass flask with radon having an initial activity of 100 mc and allowed the mixture to stand for "more than a month". Carbon dioxide, graphite, and one additional solid were obtained as products. The graphite and the other solid were examined by x-ray powder patterns, by means of which the graphite was identified. Lines appeared which could not be identified and were attributed to a suboxide of carbon,  $C_3O_2$ , which was presumed to be the solid other than graphite. Examination of the solids by electron microscopy indicated the presence of hexagonal particles, supporting the identification of graphite by powder diffraction. The overall reaction was given as  $6CO = 2CO_2 + C + C_3O_2$ . This reaction, it was suggested, proceeds by two or more reactions of lower order, as a result of the ionization of the CO by the alpha particles.

Ammonium persulfate dissolved in anhydrous glycerine was irradiated with  $0.8 \text{ \AA}$  x-rays by Broda (7). The decomposition of the persulfate was measured iodometrically. The decomposition was proportional to the dosage of radiation and was of the first order with regard to persulfate concentration. Glycerine was used because it was unaffected by the x-rays.

Solutions of potassium dichromate were subjected to electron bombardment by Treiman (84). Acidic solutions were steadily reduced, while neutral solutions became alkaline and the rate of reduction became slower. Aerated solutions gave the same yields as deoxygenated ones.

Mund (65), assuming Geiger's law, gave formulas and numerical tables for the calculation of the number of ions which are produced in a spherical vessel by the alpha rays of a given amount of radon in equilibrium with RaA and RaC wholly deposited on the walls.

An evaluation was given by Snyder and Powell (77) of the usefulness of various formulas in calculating the efficiency of different materials in absorbing gamma radiation. Experimental values were given for the absorption coefficients of aluminum, iron, copper, silver, tin, tantalum, lead, and vanadium as functions of the mev of the radiation. Absorption data were also given for nitrogen, oxygen, carbon, water, air, and tissue.

b. Literature Review - Organic Reactions: It is indicated in the literature that the types of reactions which are most frequently promoted by radioactive discharge are those which involve polymerization and/or dehydrogenation. Saturated hydrocarbons have been observed to undergo both reactions, yielding an unsaturated product of higher molecular weight. Unsaturated hydrocarbons were found to polymerize.

A 20 cc ampule of monomeric styrene, pure or in solution, was placed 4.5 cm from 100-400 mc of radium wrapped in 1 mm lead foil (3). At 12°C the material polymerized at the rate of 0.015 per cent polymer per curie-hour exposure. For pure styrene less than 5 per cent polymerized, and for styrene in methanol less than 15 per cent polymerized the percentage converted was linear with exposure time and was proportional to the square root of the radiation intensity. The reaction was assumed to involve free radicals, since polymerization was blocked by 1 per cent benzoquinone. Styrene in solutions 20 mole per cent with primary or secondary amines, acetone, propionitrile, benzene, or cyclohexane was polymerized faster than when pure. When in solution in hydrocarbons, the rate of polymerization was reduced.

Coolidge (14) used hot-cathode, high-vacuum tubes, allowing cathode rays to pass out through a window of aluminum foil 0.00265 mm thick, and 1.7 mm in diameter. There was produced from acetylene a yellow compound resembling the product both from corona discharge in acetylene and from the use of radium emanation. Under the influence of the rays described, castor oil changed rapidly to a solid. Crystals of cane sugar turned white and evolved a gas upon subsequent heating. Aqueous solutions of cane sugar became acid to litmus.

The theory and experimental methods and procedure were discussed for the polymerization of acrylonitrile and methacrylonitrile by means of gamma rays and x-rays (15). The results were discussed, and many references were given.

Aqueous solutions of acrylonitrile of several concentrations were given various dosages of gamma radiation from radium (16). Polymerization occurred as a second-order reaction with respect to the concentration of monomer. The reaction was independent of the strength of the source. The induction period was dependent upon the strength of the source and upon the concentration of monomer. The induction period was thought to be caused by the presence of an inhibitor which was destroyed by the products of the primary process, as well as by reaction with growing polymer chains.

The action of radon upon various hydrocarbons was reported by Heisig (32). Compounds acted upon by radon were allene, methylacetylene, dimethylacetylene, 2-butene, and isoprene. Details of the experiments were given, with a short discussion pertaining to the structure of the compounds. The polymerization of allene and methylacetylene were similar, in that in the presence of radiation a fog formed, which in turn condensed to a light-colored liquid. The liquid became more viscous, and a light-colored solid formed. A fog formed immediately in dimethylacetylene and condensed to a moderately viscous liquid, resembling a medium lubricating oil in color and viscosity; no solid formed. A fog formed in butene-2, and after several hours the droplets settled. The liquid became darker and more viscous as the action progressed, but no solid formed. In isoprene, a fog formed immediately, droplets settled, and a heavy, colorless, viscous, rubbery mass collected.

Styrene (13), and acrylonitrile (15,16), were polymerized during radiation by gamma rays.

The polymerization of methyl methacrylate at room temperature under the action of a radium preparation was determined (71). Polymerization occurred not only during but after irradiation. In both periods the reaction was autocatalytic, though much less rapid in the latter.

Hopwood and Phillips (37) used a volume dilatometer to study the rate of polymerization of methyl methacrylate with neutrons, beta rays, and gamma rays. The rate of polymerization was somewhat higher using both gamma rays and neutrons than when using gamma rays alone. The sources of radiation were: for gamma rays, 78 mg  $\text{Ra}(\text{SO}_4)$  in platinum needles; for gamma rays plus neutrons, 78 mg  $\text{Ra}(\text{SO}_4)$  plus beryllium in Monel tubes.

Data and discussion were presented by Burr and Garrison (8) for some investigations of the changes of physical properties of 25 different plastics and synthetic rubbers. Samples were irradiated with beta and gamma rays, and then the specific electrical resistance, the hardness, and the tensile strength were determined. Beta and gamma rays gave about the same change in tensile strength for the total energy absorbed, evidently because of heating within the material. The presence of polar impurities and polar groups alike within a plastic appeared to cause temporary reduction of the electrical resistance under irradiation.

Tests were made by Davidson and Geib (22) to determine the possibility of vulcanizing uncured natural rubber and a butyl stock by means of pile radiations. It was also desired to test the possibility



of introducing unsaturation into materials such as polyisobutylene, polyvinylchloride, acrylates, and others not mentioned, in order to make these materials vulcanizable. The effect of introducing a boron salt into the materials was also checked to determine the results of the reaction  $B^{10} (n,\alpha) Li^7$ . No procedure was reported to yield a cure of natural rubber at all comparable to sulfur vulcanization. No unsaturation was introduced into polyisobutylene. The butyl stock was permanently degraded by pile radiation. Natural rubber showed some radioactivity for days after irradiation, possibly because of its mineral content.

Heisig (33) reported experiments in which propylene and cyclopropane were radiated by alpha particles from radon. In the propylene, a fog appeared shortly after mixing, and collected as a mobile, colorless oil. It was not identified. In the cyclopropane, a fog appeared after five minutes, and after six hours, a small pool of a mobile, colorless liquid condensate had formed.

A preliminary report was made of a study of the effect of radon on methane, ethane, propane, butane, ethylene, acetylene, cyanogen, hydrogen cyanide, and ammonia (45). The reactions observed were as follows: oxidation of the foregoing except ethylene and hydrogen cyanide; hydrogenation of acetylene, ethylene, and cyanogen; polymerization of acetylene, of cyanogen, and of hydrogen cyanide. The effect on methane, propane, and butane was the production of liquid and, on further radiation, some light-yellow solid. Methane and hydrogen were produced in these reactions. Cyanogen yielded a brownish-black solid with the elimination of 5 per cent of nitrogen. Ethylene yielded a liquid and much free hydrogen. Acetylene yielded a yellow solid similar to cuprene and 2 per cent hydrogen. The oxidation of methane and ethane (under radiation) proceeded completely; with propane and butane, less completely. The oxidation of acetylene gave a clear, colorless liquid and no solid. The product combined with oxygen in the ratio 1:1, with slight formation of carbon dioxide. The oxidation of cyanogen gave a white powder thought to be  $(CNO)_x$ , with some nitrogen and carbon dioxide. A 1:1 mixture of nitrogen and acetylene gave a yellow product, as with acetylene alone, but proceeded at a faster rate, which increased during the reaction. The nitrogen did not combine and was referred to as an ionic catalyst, i.e., the  $N_2^+$  was believed to furnish additional clustering and polymerizing centers. Carbon dioxide, hydrogen, and methane did not affect the rate. Twenty acetylene molecules polymerized for each  $N_2^+$  ion, the same as for the  $C_2H_2^+$  ion. The  $N_2^+$  had the same influence on the polymerization of cyanogen and hydrogen cyanide.

Gibbs and Lockenvitz (27) studied the relative molecular stopping power of n-butane, isobutane, and butene-1, butene-2, and isobutene. The specific ionization method, with the apparatus of Colby and Hatfield, was used to determine the extrapolated ionization range.

Honig and Sheppard (36) compared the effects of deuterons and alpha particles on methane and n-butane. The products from the two types of bombardments were found to be quite similar. The liquid obtained from the butane under deuterons, showed a wide range of molecular weights with evidence of the presence of both olefin and ring structures.

According to Viallard and Magat (85), the impact of electrons with energies of tens to hundreds of ev on polyatomic molecules produced ionized fragments and free neutral radicals in addition to ions of those molecules. In a homologous series, the percentage of ionized fragments produced with simple C-H bond rupture diminished with increasing chain length. The presence of multiple bonds increases this proportion. In fluorinated C chains, the formation of ions of free radicals is more probable than formation of ions of molecules. Simultaneous rupture of two C-C bonds is practically nonexistent. The percentage of  $\text{CH}_3^+$  and  $\text{CH}_2^+$  does not increase with an increase in chain length. The ratios of  $\text{CH}_2^+/\text{CH}_3^+$  and  $\text{C}_2\text{H}_4^+/\text{C}_2\text{H}_5^+$  approach limiting values for long chains. The rupture of the ends of saturated chains was infrequent. A double bond in the 1-2 position lessens the relative number of fragments obtained by cutting this bond and neighboring bonds. A double bond in the middle of the chain augments the number of fragments.

The relative ionization probabilities of ten hydrocarbons and carbon dioxide, carbon monoxide, nitrogen, oxygen, nitrous oxide, helium, neon, and argon have been determined by Otvos (68) for beta particles from  $\text{C}^{14}\text{O}$  and  $\text{C}^{14}\text{O}_2$ . For a hydrocarbon series, the ionization probability increases linearly with the number of valence electrons; for periodic neighbors carbon, nitrogen, and oxygen, the ionization probability showed simple additive relationships based on valence electrons: methane and neon are isoelectronic, but the ionization probability for methane is higher, due to the lack of centralization of the nuclear charge. Ionization probabilities at high energies of  $\text{C}^{14}$  beta particles bear no relation to ionization potentials or chemical properties, but seem to be governed by quasi-geometrical factors, such as molecular volume. The interpolation of ionization probabilities for high electron energies should be possible on the basis of valence electrons, distribution of nuclear charge, and the position in the periodic table, with values for He, Ne, Ar relating the first three rows.

Lind and Bardwell (48) reported work done on the radiation of saturated hydrocarbons by alpha particles. Hydrogen was liberated with the production of a liquid, which then continued to react under the irradiation. The liquid phase was unsaturated. For all saturated hydrocarbons except methane, one-fifth as much methane was liberated as hydrogen. The gaseous products contained only saturated compounds, which were either higher or lower homologs. A mixture of methane and carbon dioxide produced a wax-like solid under alpha rays.

Lind, Bardwell, and Perry (50) reported considerable information on the chemical action of gaseous ions produced by alpha particles on unsaturated carbon compounds. Acetylene was polymerized by the radiation to give a light-yellow powder, with 20 molecules reacting for each ion pair which was calculated to be formed. The molecular weight of the resulting powder could not be found because of its insolubility. Further radiation of the powder liberated more hydrogen, probably as a result of further condensation of the solid. No methane was found. Radiation of cyanogen produced a black powder which gave off increasing amounts of nitrogen gas. It was concluded that the nitrogen formed had a catalytic effect on the reaction. Hydrogen cyanide was found to polymerize similarly to cyanogen. A dark solid with a reddish cast not apparent in the cyanogen polymer was formed, with the evolution of nitrogen and hydrogen. Ethylene condensed with the liberation of hydrogen and methane. The liquid which first formed became a solid under further radiation with increasing evolution of hydrogen and methane. Attempts at the hydrogenation of ethylene gave no evidence of such a reaction. In fact, hydrogen appeared to act as a center for reaction without actually reacting. In the attempted hydrogenation of acetylene, a solid formed, as it did with only acetylene present. The hydrogen was shown to act as an ionic catalyst and also to combine in some way. Hydrogen and cyanogen combined under alpha radiation in the ratio of 3:2 to form a dark reddish solid. Oxygen combined with cyanogen to give a yellow powder of formula  $(\text{CNO})_x$ , with no trace of the black powder which was formed by the radiation of the cyanogen alone. Carbon dioxide, nitrogen, and some carbon monoxide were also liberated during the radiation. The oxidation of acetylene gave a colorless liquid and no solid. The products were  $(\text{C}_2\text{H}_3)_x$  and carbon dioxide, a fact which contradicted the former statements that a  $(\text{CHO})_x$  polymer resulted from this reaction.

Lind and Schiflett (56) have reported on the oxidation of cuprene produced by alpha rays. Acetylene was polymerized by alpha particles from radon and the resulting polymer was analyzed. In an acetylene atmosphere, this polymer was insoluble in water, ethanol, ether, acetone, carbon disulfide, carbon tetrachloride, and benzene. The gases resulting from

the rapid oxidation of the polymer (the oxidation was followed manometrically) indicated 7.13 per cent CO and 92.85 per cent O<sub>2</sub>, with traces of CO<sub>2</sub> and H<sub>2</sub>O. The carbon-to-hydrogen ratio of the remaining solid was 11.65 and 12.08. The amount of O<sub>2</sub> which reacted was 5-1/2 times the CO formed. This ratio suggested an oxidation solid of C<sub>39</sub>H<sub>40</sub>O<sub>10</sub>, or an original polymer of (C<sub>2</sub>H<sub>2</sub>)<sub>20</sub>. The heat of polymerization was calculated as 47 kcal per gram-mole of C<sub>2</sub>H<sub>2</sub> reacted.

Mund and Koch (66) have investigated the rate of polymerization of acetylene under alpha radiation, and have also investigated the influence upon the rate of oxygen, pressure, and temperature. They concluded that these influences had no effect on the number of molecules of acetylene that were polymerized per ion pair produced. It was also found that 20 molecules of acetylene reacted per ion pair formed.

Rosenblum (72) has given a short review of the identification of benzene in acetylene radiated by alpha rays from radon. Approximately one fifth of the reacting acetylene was utilized for benzene formation. A small amount of benzene was believed to react further. The probable reason that benzene was missed by earlier workers was that 50 to 100 fold higher radiation was used formerly, and this accelerated the further reaction of benzene. The theory was presented that the reaction proceeded by successive bimolecular reactions between normal acetylene molecules and excited molecules or polymers. It was suggested that benzene forms from a cyclization of the activated trimer. It was also concluded that benzene is formed in the polymerization of acetylene by beta and gamma rays.

Fricke, Hart, and Smith (25) irradiated gas-free aqueous solutions of CO, alcohols, aldehydes, ketones, and acids in the concentration range 10 micromolar to 1 M, between pH of 1 to 13, and studied the reactions principally by gas analysis and potentiometric acid analysis. Oxidation and condensation reactions with the evolution of gaseous hydrogen were observed. CO<sub>2</sub> was produced from certain acids, especially from those having an oxygen-containing group in the alpha position. No liberation of CO, hydrocarbons, or O<sub>2</sub> was found. The pH of the solutions affected both the rate and the nature of the reactions.

Newton (67) subjected a number of alcohols, in the liquid state, to high-energy alpha particles. Various oxidized and reduced products resulted, as well as methane and hydrogen. As the alcohols became more branched, the methane yield increased, while the hydrogen yield decreased, the latter seeming to indicate that the hydrogens on the carbon to which the hydroxyl is attached were especially subject to attack. No evidence of polymerization was noticed. The mechanism involved was thought to be excitation and ionization with the formation of free radicals.

The effects of radioactivity on fatty acids has been reported by Shepard and V. Burton (75). They tested the hypothesis that radioactivity might be a factor in the production of petroleum from gaseous paraffins. Several fatty acids which included acetic, caprylic, lauric, and palmitic acids, were bombarded with alpha particles from radon. The production of a gas which consisted of  $H_2$ ,  $CO$ ,  $CO_2$ ,  $H_2O$ ,  $CH_4$ , and higher hydrocarbons was proportional in the initial stages to the fraction of radon decayed. Under radiation, lauric acid and palmitic acid yielded n-undecane and n-pentadecane, respectively, as products, indicating decarboxylation to be predominant. The experimental procedure and results of the radiation were discussed. The processes resulting from the bombardment can be summarized as follows: dehydrogenation, decarboxylation, the formation of low-molecular-weight water-soluble acids, the formation of methane and other hydrocarbons, and the formation of  $CO$  and  $H_2O$ .

The effects of the bombardment of oleic acid with deuterons was discussed by V. Burton (12). Of the original acid 31 per cent was unreacted. Of the converted material, 10 per cent was non-saponifiable material, 52.5 per cent was a polymerized acid, and about 1.7 per cent was stearic acid. The presence of the stearic acid in the products indicated that hydrogen produced under the influence of radioactivity could be removed from the gas phase by reaction with the unsaturated components produced during the bombardment.

Hart (31) has recently studied the mechanism of formic acid oxidation by gamma rays in air-free aqueous solutions. It was concluded that the oxidation occurs as a result of a reaction between formic acid and the H and OH free radicals produced by the action of the gamma radiations on the solvent water. The effect could be varied by the addition of hydrogen peroxide, and it was suggested that the reactions proceed by a chain mechanism.

Work done by Penneman (69) on the effects of radiation on aqueous carboxylic acid solutions shows that for various amounts of x-, electron, and deuteron radiation, both the reducing and acid equivalents of oxalic and formic acids are decreased. Quantitative data are given.

Some types of electrical discharges have been found to exert influences upon saturated hydrocarbons similar to the effects produced by alpha particles. Cathode rays also were capable of polymerizing acetylene.

Gaseous and liquid reaction products were obtained by Lind and Glockler (51) from the action of a 12,000-volt silent discharge upon gaseous ethane. The composition of the gas and liquid produced corresponded to  $C_nH_{1.8n}$  and agreed rather closely with the composition of the products obtained by irradiating ethane with alpha rays. About 10 kwh of electricity was used to produce 5 grams of oil.

The effect of electric discharge on ethane and the subsequent control of the liquid hydrocarbons produced have been reported by Lind and Glockler (52). Silent, corona, and high-frequency discharges caused condensation of the ethane to liquid with the liberation of various gases. In semicorona and corona discharges, cracking was apparent, resulting in the formation of free carbon. In corona discharge a solid film deposited on the wall. Variation in the molecular weight of the liquid products appeared to be dependent upon the time the earlier products had remained in the discharge subject to further ionization. The average molecular weight was regulated between 467 and 105 by controlling the time of reaction. Evidence of a delayed condensation was attributed to "open bonds," which react slowly to form liquid without repeated ionization.

Methane, ethane, propane, butane, and ethylene were condensed to liquid and solid hydrocarbons in a semicorona discharge (53). Hydrogen and methane were eliminated, as with alpha rays. The liquid products from different hydrocarbons or from the same hydrocarbon in different tubes, were similar in physical properties and were complex. The solid products were gummy, resinous, and inert toward solvents and reagents except strong oxidizing agents. The extent of the reaction was found to be dependent upon time.

Paraffins, cycloparaffins, olefins, cyclo-olefins, and aromatics were irradiated by Schoepfle and Fellows (73) with cathode rays at 170,000 volts and 0.3 ma. The total quantity of gas released from the hydrocarbons was largest in the case of paraffins and decreased in the order in which the compounds are named. In general, as the molecular weight of a given series increased, the percentage of hydrogen in the gas given off increased, and the percentage of methane decreased. The branched-chain compounds gave higher percentages of methane and of gaseous saturated hydrocarbons than the straight-chain compounds.

Ozonizers were used to pass an electrical discharge through butane (54). The experimental procedure was given for the preparation of about one liter of liquid. The liquid was fractionated into three fractions. The light fraction I was fractionated into eleven subfractions. Light fraction I-6 (the largest) was refractionated. Light fraction I-6-2 was examined. The properties resembled those of 2,4-dimethylhexane and 2-methyl-3-ethylpentane. The density, C-H ratio, molecular weight, halogenation number, and freezing point -- all indicated unsaturation. Presumably the products were octylenes. It was not yet possible to identify the isomers.

The condensation of hydrocarbons in ozonizers was compared with the condensation by alpha particles (55). The similarity of these processes was confirmed by the following: the analogy of pressure changes during reaction; the amount of free hydrogen produced is of the same order for both; the similar percentage of hydrogen in the hydrogen-methane gas phase for both types; the similar percentages of liquid conversion; the similar composition of the liquids approximating  $C_nH_{2n}$ , as calculated from the analysis of the gas phases; and the similarity of the amounts of total hydrocarbon reacted in both types of processes. Unsaturated hydrocarbons were suspected in the gas phase produced by stopping the condensation of butane at the point of maximum pressure.

Loiseleur, Latarjet, and Crevisier (60) have carried out work on oxygen containing organic compounds. Hydrogen peroxide and organic peroxides were formed when 0.01 - 0.00001 M solutions of crotonic, succinic, fumaric, acetic, and benzoic acids, formaldehyde, methanol, and ethanol were irradiated with x-rays.

Stein and Weiss (74) investigated the effects of ionizing radiations upon aromatic organic compounds. Benzene suspended in oxygen-free water was radiated with  $10^6$  roentgens of x-rays. Analysis showed formation of a trace of phenol. Diphenyl was also isolated. Benzoic acid solution treated similarly formed 0.1 millimole of hydroxybenzoic acids, and salicylic acid was isolated. Similar experiments using a neutron-alpha ray source (radium and beryllium powder) resulted in the products mentioned above and catechol, together with products from opening of the ring. The total yield was stated to depend upon pH. The formation of diphenyl suggested free phenyl radicals in the reaction.

It might be noted here that the free-energy change for the reaction resulting in phenol from benzene is a positive quantity, indicating that additional energy must have been supplied from the x-rays in order to cause the reaction. The polymerizations which were reported served to substantiate the idea that gamma rays may be used to produce the same reactions which are found as a result of alpha and beta radiation.

Breger and Burton (6) have studied the effect of alpha particles and deuterons on a naphthenic acid. Cyclohexanecarboxylic acid was used to determine whether anticipated decarboxylation would lead to formation of ring compounds or whether ring cleavage would lead to formation of straight-chain hydrocarbons. Analysis of material subjected to alpha particles showed decarboxylation with some dehydrogenation. The results showed little or no difference between the chemical effects of alpha particles and deuterons. The experimental data given dealt with the bombardment and with the analysis of the resulting mixtures. It is presumed that cyclohexane and cyclopentane rings were not opened by the bombardment.

Radiation of nitrogenous compounds by x-rays has been found to produce deamination (20). The ion yield for the reaction increased approximately exponentially with increasing concentration of the aqueous solution.

Aqueous solutions of L-serine of varying concentrations were given x-radiation (18). Because of the greater solubility of this compound, higher concentrations were possible than had been previously obtainable. It was found that ionic yield increased with increasing concentration and then, at highest concentrations, "leveled-off."

Solutions of glycine were deaminated by alpha radiation (19). However, the ionic yields for this reaction using alpha radiation, were only 15 to 19 per cent of that produced by x-radiation. This lower ion yield for alpha rays than for x-rays is an unusual circumstance.

The rates of reaction were measured by Alyea (4) in a solution of chlorine in benzene and in a solution of oxygen in sodium sulfite solution, both with and without radon present. Earlier work was cited regarding similar treatment of mixtures of  $H_2$  and  $Cl_2$  and of CO and  $Cl_2$ . The ratio M/N varied from 700 to 200,000, depending upon the purity of the materials and the intensity of the radiation. The data could be explained more readily in terms of a chain mechanism rather than in terms of the "ion cluster" theory.

The rate of decomposition of chloroform by radon was found by Harker (30) to be greatly influenced by the presence of the products of decomposition ( $Cl_2$  and HCl). The presence of iodine in a potassium bisulphite solution increased the rate of oxidation of the latter under gamma radiation.

A series of articles on chemical actions of ionizing radiations on aqueous solutions is currently being published in the Journal of the Chemical Society (British). The purpose of this series is to study the action of the radiations, to study the reactions of the free radicals formed by the radiation in the absence of interfering reagents, and to study the products of those reactions which are similar to those in biological systems (24). X-rays, neutrons, and alpha rays are used in these studies.

Solutions of benzene and benzoic acid in water were irradiated by x-rays. Phenol, diphenyl, and terphenyl were produced from the benzene (79) (cf. Stein and Weis (74)). Salicylic acid and p-hydroxybenzoic acid



were the main products isolated from the benzoic acid solution. Results of varying the atmosphere above the solution and comparison of energies involved in alternative reaction paths led to the conclusion of a free radical mechanism for these reactions.

When benzene was subjected to bombardment of alpha particles and neutrons, it was found that in addition to phenol and diphenyl, which had also been produced by gamma and x-radiation, polyphenols and a straight-chain dialdehyde were formed (80). This additional reaction could be attributed to further reaction of the phenol molecules due to the intensity of ionization, hence free radicals, along the tracks of the bombarding particles.

Aqueous solutions of glycine, alanine, and serine were irradiated by x-rays, under various conditions (81). Deamination occurred, giving ammonia, molecular hydrogen, and aldehydes. It was concluded that both the atomic hydrogen and hydroxyl radicals produced by the x-radiation attack the amino acid, and an oxidative and reductive mechanism are operative in the deamination.

Saturated solutions of nitrobenzene in air-saturated water were irradiated with  $3.5 \times 10^4$  energy units of X-rays (58). Each 200 ml of this solution yielded about  $10^{-6}$  moles of the mixed phenols of nitrobenzene.

Solutions of cholesterol and 3- $\beta$ -hydroxypregn-5-en-20-one, which are both naturally occurring steroids, were irradiated with  $10^6$  r of x-rays (38). The isolated double bond in the sterol ring was attacked by hydroxyl groups, resulting in adjacent OH groups in the ring. The labile hydrogens adjacent to the double bond in the cholesterol were also attacked, leaving a ketone group in this position. The mechanism for this change may also involve free radicals.

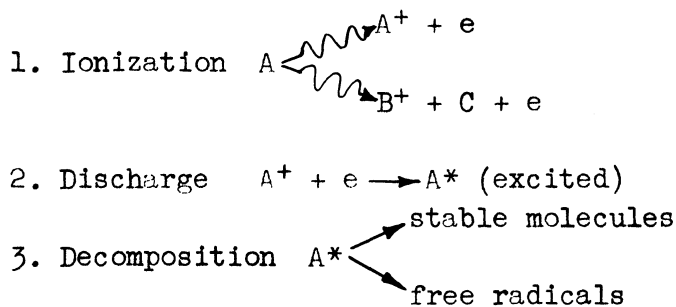
Solutions of the sodium salt of cholic acid in water were subjected to x-radiation (39). The product which was isolated was 3 $\alpha$ :12 $\alpha$ -dihydroxy-7-keto cholanic acid. This reaction represents the change of the hydroxy group in the 7-position to a keto group. The 7-position in cholesterol was similarly attacked (39). Both these reactions can be explained by attack of OH radicals which are produced by the radiations and subsequent elimination of water to leave the keto group in that position.

Radiation of 0.2 per cent aqueous oxygen-containing benzoic acid solutions produced a yield of the mixed isomers of salicylic acid (59). Up to a dose of  $5 \times 10^4$  energy units, the formation of salicylic acid, in the presence of oxygen, is a linear function of the dosage. The yield for 200 ml of solution given  $5 \times 10^4$  energy units was approximately 1.2 mg.

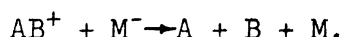
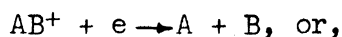
Both alkaline and acid solutions of (+) - œstrone-b were irradiated by x-rays (40). The resulting compounds from both were identical. This compound was apparently a lactone similar to that produced by hydrogen peroxide or other oxidation methods. In effect, the carbon-to-carbon bond at the 17-position in the five-membered steroid ring is broken, and a six-membered lactone ring is formed. If attack by OH radicals on a double bond formed by enolization is assumed, it is most probable that the ring is broken between the carbons of 16- and 17-positions.

c. Literature Review - Theoretical: In the earlier experimental work done in the field of radiation chemistry, and especially in that done by Lind and his associates, large yields per ion pair and polymerization were often explained by a "cluster theory", which assumed the grouping of molecules around the central ion as being responsible for these effects. Later work has, in general, disproved this original theory.

Eyring, Hirschfelder, and Taylor (23) regarded clustering as playing a very minor role. They proposed a mechanism of ionization involving formation of excited molecules, ions, and radicals. This mechanism may be summarized by equations for three steps (as reviewed by Burton (10)):



Burton (9) has given a unified picture of the theory involved in radiation chemistry. He differentiates radiation chemistry from photochemistry in terms of the energy involved. In the primary acts (in radiation chemistry), electrons are released and trapped at some remote point. The succeeding processes depend upon the nature of the ions involved and their stability in their environment. The significant reaction, where solvation does not occur is given as,



(cf. Eyring, Hirschfelder, and Taylor (23)). According to the Franck-Condon principle, the electron moves to the positive ion in such a short

time that the constituent atoms are left in positions whose energy states are above those necessary for dissociation of the bond concerned. This state leads to the reaction given above. As the size of the molecule increases, the ionic configuration is more nearly like that of the unchanged molecule, so the energy of neutralization may not be localized enough for bond rupture to occur within one vibration period. As a result, the process of relocation of potential energy of the molecule may lead to decomposition to ultimate molecules before rupture can occur. This process may be important in many cases where free-radical decomposition had been assumed. In the liquid state, the energy could leak from the excited molecule before decomposition can occur, thus lowering the decomposition yield. In photochemistry, it is often possible to choose wave lengths which promote a reaction in one direction, and therefore do not aid the reverse reaction. However, in radiation chemistry, this does not appear to be the case; hence a steady state may be attained in which the forward and reverse reactions take place at equal rates. Alpha particles, deuterons, and protons rarely make direct nuclear impact, but rather, cause a large degree of ionization along their paths. An energetic electron, or beta particle produces a much smaller degree of ionization, which is also more diffuse and homogeneous. Gamma and x-rays interact with molecules to produce ions and energetic electrons, which in turn, are responsible for much of the observed effects. Fast neutrons scatter the nuclei with which they collide, and for sufficiently high velocities, any ejected nucleus may leave one or more electrons behind it. Fast neutrons were found to cause displacement of atoms of solids from their lattice positions. This was called the "discomposition" effect. Coloration of ionic crystals was explained on the basis of electrons trapped in negative ion vacancies. Effects of radiation on water may be represented by the reactions given previously. Tables of data for the effect of 170-kv cathode rays on various hydrocarbon compounds show that the methane yield increases with the number of methyl groups. Unsaturation tends to decrease hydrogen yields, and increase polymerization. The hydrogen yield decreases with increasing complexity of structure in accordance with the principle of increased probability of internal conversion with increased molecular complexity.

Burton has also discussed the effects of radiation on organic compounds in a paper presented before the Symposium on Radiation Chemistry at the 110th Meeting of the American Chemical Society at Chicago, Illinois, in September, 1946 (11). He states his views in the summary of the paper: "All the processes which occur in photochemical reactions of organic compounds occur also in radiation-chemical processes. In addition, there are

reactions resultant from the peculiar sequence characteristic of radiation chemistry: i.e., ionization, discharge, and decomposition. In general, any electron in the molecule is equally susceptible to ionization in the initial act; this fact must be constantly recalled in any interpretation of radiation-chemical mechanisms.

"Since, in general, the excitation energy lies in any part of the molecule, the yield of a particular product is closely related to the number of parent groups in the molecule. Gas production, particularly in unsaturated compounds, is an inadequate criterion of the resistance of a compound to high-energy radiation. In the liquid state, the excessive excitation energy tends to minimize the Franck-Rabinowitch effect (i.e., decrease in yield due to collisional deactivation and cage effect). Factors which increase resistance of organic compounds to radiation (and ratio of ultimate molecules to free-radical processes) are molecular complexity, resonance in the molecule, and all properties of the molecule which tend to increase the correspondence between ionic and molecular configurations. Among the latter are molecular symmetry (cf. benzene) and molecular size (cf. palmitic acid). Apparently, increase of molecular size tends to channel the decomposition along a particular path rather than to diversify the products."

Dainton, in 1948, gave a report on radiation chemistry in the British Annual Reports on the Progress of Chemistry (17). He defines "radiation chemistry" as chemical effects produced by the absorption of all types of rays whose energy is above 50 ev which result from radioactive processes or by the absorption of electrons or positive ions of similar energy. The sources of various radiations were discussed, as well as the dosimetry. Positively charged particles lose their energy by elastic impacts with particles in their path. The average energy dissipated per ion pair is about 30 ev. Electrons, being of low mass, are easily deflected, giving badly defined tracks. They lose energy by elastic impact and by the production of bremsstrahlung. Photons must be absorbed in a single elementary act. Those of high energy have three modes of absorption: ejection of a photoelectron usually from the K-orbit, Compton scattering, and positron-electron pair production when the energy is high enough. In the primary act, the charged particle leaves a path of positive ions, surrounded by a more distant field of the electrons which have been knocked out by the particles. The positive ion may or may not dissociate. The free electrons may be captured by neutral atoms to produce negative ions. Production of new, uncharged species may occur by a charge-neutralization process, or directly, when the molecules can be excited to nonionic repulsive levels. The "cluster" theory, which was formerly proposed, was discarded in favor of the "atom-radical" theory

(cf. Eyring, Hirschfelder, and Taylor (23)). Several reaction systems are discussed. In many of the single inorganic substances, the yield is so large as to suggest that more than one radical is formed per ion pair. A discussion of the theory and kinetics of the effect of radiation on water is given in this report by Dainton.

Burton, in one section of his report for the Notre Dame Symposium (10) has summarized the effects of the types of particles. Energetic heavy particles produce one ion for every 5-10 molecules of path, while electrons with the same velocity produce one ion in every 500 molecules of path.

In the theoretical discussion of their work, Sheppard and Honig (76) show why the alpha particles and deuterons should produce similar chemical effects. They also point out that the amount of change is proportional to the number of ion pairs formed, because for every ion pair formed, a given amount of energy is absorbed and a given amount made available for each electronic process. This rule implies that the total amount of reaction should be proportional to the amount of radiation, which in turn produces the ion pairs.

The number of molecules which condense per ion pair formed ( $-M/N$  ratio) is stated by Heisig (34) to be highest for the substances having negative heats of formation from the elements in their standard states. The condensation process for saturated hydrocarbons is nearly isothermal, having small  $-M/N$  values. For unsaturated hydrocarbons,  $-M/N$  values vary with their negative heats of formation. Their condensation is exothermic.

Experimental results and theoretical interpretations were given by Toulis (83) for the decomposition of water by radiation. He concurs with the hypothesis that the primary process in water is the creation of H-atoms and OH free radicals. The decomposition of water was found to depend upon the rate of energy loss of the radiation. X-rays, gamma rays, electrons, and extreme ultraviolet light and particles losing energy at a rate less than 70 mev/gm/cm<sup>2</sup> of water showed little effect. The outstanding property of a given reaction was thought to be the probability of the capture of a free radical while in a solvent cage. Emphasis was placed upon this concept rather than upon the usual rate constant for a chemical reaction. The probability of capture is independent, to a first approximation, of a solute and depends only upon the type of radical with which the radical in question reacts. The types of reactions possible are: radical-radical, H-radical-molecule, and OH radical-molecule. Studies were made of the rate of decomposition of both pure (conductivity) water and of aqueous solutions of H<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> under the influence of

x-rays. Most data were evidently deleted from the text. X-rays were used in preference to particles because the x-rays gave a more nearly uniformly distributed effect throughout the solution, and simplified calculations resulted thereby. The dissolved impurities were found to influence the equilibrium compositions and rates of reaction, apparently by capturing free radicals. A further comment worthy of note was that in the case of ionizing radiation (whether photon or particle, was not stated) the free radicals formed were segregated into two coaxial cylindrical regions about the track of the radiation. The H were in the outer cylinder, of 150 Å diameter, and the OH, in the inner cylinder, of 8 Å diameter. Thus, back-reaction to H<sub>2</sub>O was hindered in preference to other reactions.

Allen (1) in a review of existing data indicates that covalent compounds are decomposed by ionizing radiations. The change of rate of reaction with progressive conversion is discussed. A mechanism involving free radicals is proposed for the decomposition of water. This proposed presence of free radicals is used to explain the great effect of dissolved solutes upon the behavior of irradiated aqueous solutions.

Another article by the same author (2) has a discussion of the effects of ionizing radiations upon chemical compounds in various physical states of aggregation. Several possible theories were discussed for the mechanism by which a chemical reaction proceeds as a result of irradiation of the reactants. The effects of excited and ionized molecules, positive ions, energy absorption by inert gases present, decomposition of ions, reactions of ions with molecules, reaction of an electron with a molecule having electron affinity, breaking of bonds before neutralization of an ion, formation of "clusters", significance of ion yield, and production of chain reactions were all discussed in their relation to reaction mechanism. The reversibility of reactions induced by radiation was discussed, as was the effect upon equilibrium of certain "promoters" or "inhibitors". Some basic differences were pointed out in the behavior of covalent, ionic, and metallic solids under irradiation.

A general theoretical discussion was tendered by Steacie (78), showing similarities between photochemistry and radiation chemistry and posing questions resulting from their differences. The discussion included the primary process, the secondary process in respect to ions and in respect to excited molecules, and the application of the knowledge of thermal reactions to the investigation of the secondary processes. Many references to experimental data were cited.

It was pointed out by Garrison (26) that several alternative hypotheses are available to explain the polymerization of acetylene by ionizing radiations. The ion cluster theory of Lind was mentioned. Alternative to this theory were suggested the following mechanisms: the action of  $C_2H_2^+$  ions as acid catalysts by combining with the negative carbon atom of the ionic-resonance-form of acetylene; and the polymerization via a free radical mechanism because of the unshared electron in  $C_2H_2^+$ .

A discussion of radiochemistry, a comparison with photochemistry, and the ion-excitation theory (Eyring, Hirschfelder, and Taylor (23)), are given in an article by Wildschut (89). He also gives a mechanism for polymerization of hydrocarbons starting with the ion produced in the primary act, which is similar to that given by Garrison above.

The mechanism of the radiochemical reactions in aqueous solutions was discussed by Weiss (87). An attempt was made to interpret the facts of the radiochemistry of solutions on the basis of known photochemical and chemical reactions in solutions. It was stated that the products to be obtained from the irradiation of solutions depend upon the nature of the solute and the pH of the solution. The pH and nature of the solute both determine the oxidizing properties of the solute. A reducing solute would react with OH radicals, and free  $H_2$  would be produced. An oxidizing solute would permit oxygen to be freed by combining with H radicals.

The general principles involved in the chemical and biological action of radiation are examined by Weiss (88). An important difference between photochemistry and radiation chemistry is that in the latter, the absorption of radiation energy is not specific and is approximately proportional to the mass but almost independent of the chemical linkage. Therefore, in dilute solutions, most of the energy is absorbed by the solvent, so that most of the primary changes must take place in that medium. The direct or indirect action of the radiation may, however, lead to the same qualitative result. It was found that the recombination process following primary formation of radicals is of considerable importance. If recombination can be neglected, then the effects are approximately independent of the nature and wave length of the radiation and depend only on the total dosage.

Lind and Vanpee (57) studied the effect of xenon ions in the chemical action of alpha particles. Xenon has a higher ionization potential than acetylene. Hence ionization passes from Xe to acetylene by collision. Therefore these two gases can not be used to prove that the nature of an ion is indifferent in causing the polymerization of

acetylene to cuprene. Both  $H_2$  and  $O_2$  have ionization potentials higher than Xe, so that the reaction  $2H_2 + O_2 = 2H_2O$  can be used to test the effect of added  $Xe^+$  ions. The  $Xe^+$  ions constituting 70-95 per cent of the total ionization caused the reaction to proceed 12 times as fast as in their absence.  $Xe^+$  ions added to  $2CO + O_2 = 2CO_2$  gave a slight positive effect. The presence of  $Xe^+$  ions in the reaction of CO to a carbon suboxide had no effect.

Zimmer (91) has stated that there is no indication of a transfer of energy from solvent to solute. His experimental data seem to indicate the questionability of the hypothesis of activated solvent molecules and point to a possibility that the energy transfer takes place by diffusing molecules.

However, a paper which was submitted by Manion and Burton (64) at the Symposium on Radiation Chemistry at the 119th Meeting of the American Chemical Society in April, 1951, reemphasizes the significance of ionization transfer in radiation chemistry, especially in the liquid state. Studies of hydrocarbon mixtures radiated with 1.5 mev electrons show results which are explained in terms of ionization and excitation transfer, as well as removal of free radicals through attack on unsaturated bonds.

In a recent article (61), Magee has outlined a model of a system being radiated with particles, from which an equation is set up which allows mathematical treatment of the effects arising from the variation of ionization density due to the lack of homogeneity caused by the tracks of the charged particles. Most former considerations had assumed that all intermediates are created homogeneously in space.

In a further discussion (63), Magee and Burton have considered the negative ion formation by electron capture. When its energy is sufficiently low, an electron may be captured by a neutral molecule to form a negative ion. If a thermal electron is to be captured in a dissociative process, the electron affinity of the ion produced must exceed the strength of the bond which is ruptured.

Magee and Burton have published a theoretical discussion (62) of the mechanism by which the electron is captured in the process of discharging the positive ion produced by an ionizing radiation. Capture of the electron most probably leads to formation by dissociation of two particles, one of which is excited. Dissociation into radicals is favored over dissociation into molecules. However, in the liquid state, the production of ultimate molecules increases in importance.



In the preceding review only those papers were discussed which are closely related to the objectives of this work. For a comprehensive list of references related to radiocatalysis, one may turn to the A.C.S. Monograph by Lind (41) which lists 508 references, Dainton's review (17) which lists 149, the symposium in J. of Phys. and Colloid. Chem. (82) with 339 references, and the section on ammonia in Gmelins Handbuch (28), with 131 references.

### 3. Proposed Research on Selected Reactions

a. Proposed Research - Inorganic Reactions: It is proposed to study the formation of ammonia from the elements under the influence of x-, beta, and gamma radiation.

It appears that if ammonia can be synthesized in commercially attractive yields by this process, an important supplement can thereby be provided to facilities for the production of ammonia. The reason for this statement is that evidently the reaction can be made to proceed at ordinary temperatures. Considerable savings in ammonia-plant maintenance and construction should result if the conversion step can be carried out at considerably decreased temperatures. In addition, of course, the use of lower temperatures would favor the presence of ammonia in the equilibrium mixture.

There are indications from thermodynamic data, as is well known, that nitric acid can be formed directly from its elements. It is possible that the reaction forming water may predominate; however, it is proposed to test the possibility of producing  $\text{HNO}_3$  from  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{O}_2$ .

It is proposed to conduct preliminary studies on the oxidation of sulfur dioxide by means of radiation. If this reaction were to take place at ordinary temperatures or above, it should prove interesting in sulfuric-acid manufacture. A single stage of adiabatic reaction might prove feasible in the conversion step, with the final temperature still low enough to produce near-quantitative yields. This might prove attractive, especially if it were necessary to use recovered sulfur dioxide from smelter operations, etc., for raw material. A careful economic study of plant performance, freight rates, etc., would be necessary to determine the commercial importance of this reaction, should the reaction prove possible.

Various means have been proposed for the recovery of elemental sulfur from hydrogen sulfide. It is proposed to study the direct oxidation of hydrogen sulfide under the influence of radiation in order to determine the extent to which oxidation would proceed under the influence of radiation.

Elemental sulfur may also be recovered from stack gases. A mixture of sulfur dioxide, carbon monoxide, and water has free-energy relationships such that it should be completely converted to carbon dioxide and hydrogen sulfide if at equilibrium at 25°C and one atmosphere pressure. If equilibrium could be partially attained under irradiation, the resulting hydrogen sulfide and unreacted sulfur dioxide would react in the presence of moisture to yield elemental sulfur. This reaction would facilitate tremendously the processing of power-plant, smelter, and other waste gases to avoid atmospheric pollution. At the same time the recovery of elemental sulfur should permit attractive pay-off times for the installations, while adding to the national supply of elemental sulfur.

Carbon monoxide might be oxidized to carbon dioxide by the use of radiation as a catalyst. An important purpose of this reaction could be to supplement existing methods for purifying the exhaust gases from internal-combustion engines.

b. Proposed Research — Organic Reactions: Since polymerization and/or dehydrogenation have previously been reported under the influence of radiation, these types of reactions will be attempted first. Success in simple reactions would lead to the trial of more complex reactions. Acetylene can be polymerized to benzene within a wide range of temperatures if the reaction can be activated. Radiocatalysis may bring about the desired activation. More interesting is the fact that at certain temperatures the free-energy change for the conversion of ethylene or ethane to acetylene or benzene becomes negative, indicating a possible reaction. The formation of acetylene from methane by dehydrogenation is thermodynamically possible at elevated temperatures.

An alternative method for attempting to produce acetylene from methane might be the partial oxidation of the methane, with an accompanying polymerization to the higher hydrocarbon. Since radiation may produce polymerization reactions, it is conceivable that the desired oxidation and polymerization might be promoted by a radiocatalyst. According to free-energy data, the reaction involving the partial oxidation of methane should yield a favorable proportion of acetylene at room temperature.

At sufficiently high temperatures the conversion of methane or natural gas to benzene has been accomplished (29); however, the yields reported were small and considerable coking occurred. It is hoped that under the influence of radiation, suitable yields of benzene might be obtained from methane. The commercial importance of this conversion can hardly be overestimated. A process which could convert natural gas to benzene or its derivatives would be of great importance to the chemical industry.

It may be worthwhile to attempt the hydrogenation of hydrocarbons, although the literature seems to indicate that the reverse reaction is predominant under radiation.

Three reactions which resemble hydrogenation are the Fischer-Tropsch, methyl alcohol, and "Oxo" syntheses. All three of these involve the hydrogenation or partial reduction of carbon monoxide with hydrogen. Special catalysts and conditions are needed for all three syntheses. The conditions and thermodynamics of the methyl alcohol synthesis are very similar to those for the production of ammonia. Since the literature has reported ammonia syntheses effected by means of radiation, the synthesis of methyl alcohol may be worth studying. In the Fischer-Tropsch process carbon monoxide and hydrogen are used to produce hydrocarbons containing varying numbers of carbon atoms. Therefore, some sort of polymerization is involved. Since radiation has often been shown to produce polymerization, this reaction appears to merit some study. The "Oxo" process, producing, as a final product, aldehydes and primary alcohols, also involves polymerization.

A type of reaction which possesses interesting industrial possibilities is the hydration of unsaturated hydrocarbons to alcohols. This reaction normally does not proceed easily, but under the influence of radiation it might be caused to proceed fairly rapidly.

The production of small amounts of phenol from benzene and water was reported in the literature (74). Apparently, under the conditions reported the free-energy change was positive. If conditions could be found to give a negative free-energy change, the promotion of this reaction by radiation might be industrially feasible. It might also be possible to conduct this reaction as a partial oxidation, similar to the production of acetylene from methane.

Many other organic reactions such as cracking, condensation, isomerization, cyclization, esterification, and nitration, may be studied at a later date. The reactions which have been chosen for the initial work are those which seem to have the greatest promise, judging from the experiments reported above in the literature survey.

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Progress Report No. 2

UTILIZATION OF THE GROSS FISSION PRODUCTS

The Effect of Gamma Radiation on Chemical Reactions

J. J. Martin

L. C. Anderson

D. E. Harmer

J. G. Lewis



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## PART II

### THE EFFECT OF RADIATION ON CHEMICAL REACTIONS (SUBPROJECT M943-C)

#### Personnel

Subproject Supervisors: J. J. Martin, Associate Professor of Chemical Engineering; L. C. Anderson, Professor of Chemistry and Chairman of Department. D. E. Harmer, Research Assistant; J. G. Lewis, Research Assistant.

#### A. Introduction

The basic objective of this work was stated in Progress Report I; namely, to study the promotion of chemical reactions by the use of radioactive fission products. In the course of the study answers to two questions are being sought: When does radiation accelerate the rate of approach to thermodynamic equilibrium in a chemical reaction or cause a displacement of the equilibrium point, and how does the extent of the reaction vary with the quantity of radiation? When the answers to these questions have been found, it is believed it will be merely an application or developmental procedure to determine whether radiation from fission products can be effectively and economically utilized in the promotion of reactions of industrial importance.

Among the reactions which have been shown by previous investigators to be affected by radioactivity are the synthesis of ammonia, polymerization of some liquids, and dehydrogenation of some hydrocarbon gases. These reactions have, for the most part, been carried out under the influence of alpha and beta radiation. Comparatively little has been published about the effect of gamma radiation. Since fission products yield considerable amounts of gamma radiation and since the project has had available for the past several months a 1000-curie, cobalt-60 gamma source prepared at Brookhaven National Laboratory, a number of experiments have been conducted using this source of radiation. Also as this report is being written, a small piece of palladium foil containing 3 curies of Pd-109 has been received after irradiation at Chalk River, and some reactions have been studied under the influence of the 1 Mev beta radiation from this source.

## B. Experimental Results

The first reactions to be studied under the influence of gamma radiation were conducted in small 9 mm by 20 cm pyrex tubes. The procedure was simply to seal the chemical reactants in the tubes and place them in the cobalt-60 vault for approximately 24 hours. At the end of this period the tubes were removed for observation and tested for any changes that might have taken place.

In the case of a number of hydrocarbon gases, including isobutane, butene-2, ethylene, butane, isobutylene and acetylene, the analysis involved breaking the sealed tubes in a closed system and observing the pressure change which resulted. It was found that none of these hydrocarbon gases originally sealed at atmospheric pressure and room temperature underwent any appreciable change in pressure, and this fact has been interpreted to mean that no reaction occurred.

In the case of a tube of liquid butane which was examined after 24 hours of gamma radiation, an appreciable amount of unsaturated gas was found by absorption in sulfuric acid and the presence of hydrogen was confirmed by combustion with copper oxide. This result indicated that significant decomposition had occurred. Since gaseous butane gave no reaction, it appears that the ability of the material to absorb and utilize radiation depends upon the density of the material, as would be expected.

Stoichiometric mixtures of nitrogen and hydrogen charged to the small tubes showed no measurable change after being exposed to the cobalt-60 source for 24 hours. However, in this case, as well as in the case of the hydrocarbon gases, the amount of reactant charged was very small and detection of any reaction was not considered very accurate. Therefore, large pyrex tubes of approximately 100 ml capacity were fitted with stopcocks and charged with nitrogen and hydrogen for further studies. Some of these samples were subjected to 24 hours of gamma radiation from the cobalt-60, and some of them were placed 6 inches from the target of a 200 KVP X-ray machine operating at 20 ma and 155 KVP for 3 hours. After radiation the gases in these large tubes were drawn through Nessler's test reagent for ammonia, which is capable of detecting a small fraction of one per cent of ammonia in the sample. In no case was any appreciable amount of ammonia formed. These experiments included tests in which nitrogen and hydrogen were dried before charging and also tests in which these gases were saturated with water vapor before charging.

In the next set of experiments sample tubes were constructed which had glass stopcocks at one end and ground-glass-joint caps at the other end. The caps permitted charging solid catalyst, or any other solid, into the tubes (see Fig. 26, page 33). A doubly promoted ammonia catalyst was obtained from the Pennsylvania Salt Mfg. Co. and prepared by reduction in hydrogen at 450° to

500°C. This reduced catalyst was transferred under nitrogen to the reaction tubes which were then evacuated and filled with a stoichiometric mixture of nitrogen and hydrogen. Using both dry and wet reactant gases, no appreciable amount of ammonia was detected by Nessler's test after these samples had the usual 24 hours in the cobalt-60 vault. It was noted in these experiments that the catalyst tended to adsorb gases very readily since it was quite porous. It is conceivable that very small amounts of ammonia might have remained on the catalyst, though the consistently negative results seem to indicate absence of ammonia. Because of the necessity of using stopcock grease on the ground-glass joints, the reaction tube with the catalyst could not be heated to very high temperatures after radiation to assure the liberation of minute amounts of ammonia.

In an attempt to determine whether gamma radiation might be favoring the decomposition of ammonia rather than its synthesis, a sample tube was charged with pure ammonia. Analysis was made on an Orsat-type gas analyzer using 10 per cent sulfuric acid as the absorber for ammonia gas. After 24 hours of gamma radiation no appreciable amount of unabsorbed gas remained, indicating no decomposition of ammonia. Experiments are now in progress to determine whether the presence of a catalyst might have any effect on the decomposition of ammonia when irradiated with gamma rays at room conditions.

It might be pointed out that the results of thermodynamic calculations for the system nitrogen, hydrogen, and ammonia at room temperature and atmospheric pressure, as given later in this report, show that equilibrium in the absence of radiation greatly favors ammonia. Therefore, if any appreciable decomposition is to be found, the equilibrium point must change. Furthermore, it seems probable that if decomposition does take place, it will vary directly with the quantity of radiation supplied, because the radiation must satisfy the positive free-energy-change requirement of the reaction. On the other hand, the extent of the synthesis reaction to make ammonia might well be independent of the quantity of radiation once the reaction is started, for the negative free-energy change forms an ideal setting for the initiation of a chain reaction.

In another experiment on the radiation of a liquid with gamma rays, it was found that a sample of acrylonitrile (practical grade) in a sealed tube formed many small nuclei of solid polymer during the first part of the irradiation; and at the end of 24 hours of irradiation, a hard white solid was obtained.

Monomeric styrene showed evidence of polymerization by a gradual increase in viscosity during irradiation. The viscosity continued to increase after the irradiated styrene was removed for the cobalt-60 vault while unirradiated check samples remained unchanged. Results obtained up to the time of this writing have not been consistent enough to warrant any general conclusions, although the viscosity increase after radiation seems to indicate that the long induction period usually found in thermal polymerization of plastics may be shortened in the presence of gamma radiation. Further experiments have been planned.



Since it is known from the literature that beta particle energy is more readily absorbed than high energy photon radiation, an investigation was started to find out whether the electrons produced by the Compton effect might be used as a means of imparting energy to chemical reactants. An increase in count was observed with Geiger counters when thin metal sheets were placed in front of the counter windows and gamma radiation passed parallel to the surface of the window. As an application of these observations, nitrogen and hydrogen were charged to reaction tubes containing copper gauze or brass sheets or aluminum dust. Although no ammonia was detected after the usual 24-hour gamma radiation from cobalt-60, it is felt that the possibility of using these secondary emissions should be investigated further, especially at higher pressures where absorption of the emitted electrons would be nearly complete. It is also planned to investigate other types of secondary radiation, particularly that which emanates from materials which fluoresce or phosphoresce when activated by beta or gamma rays.

More recent experiments involving beta radiation directly have not given any positive results. In one experiment nitrogen and hydrogen were charged to a two-liter flask (Fig. 27) along with a piece of palladium foil containing

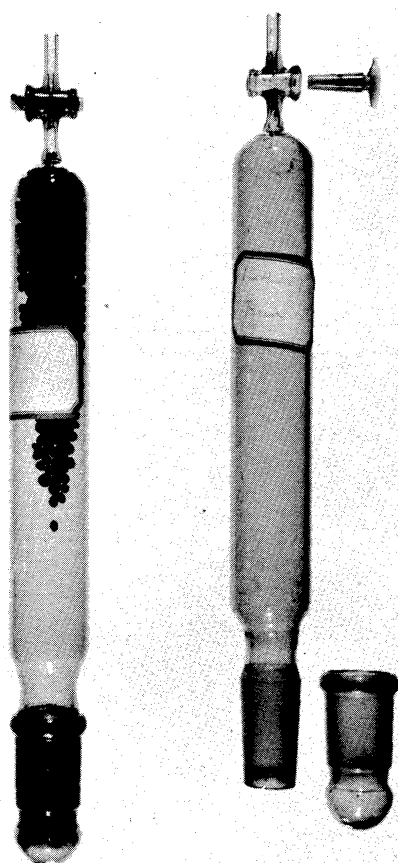


Fig. 26. Pyrex Glass Tubes for Irradiation of Gases at Low Pressure. Tube on the left is charged with a solid ammonia catalyst.

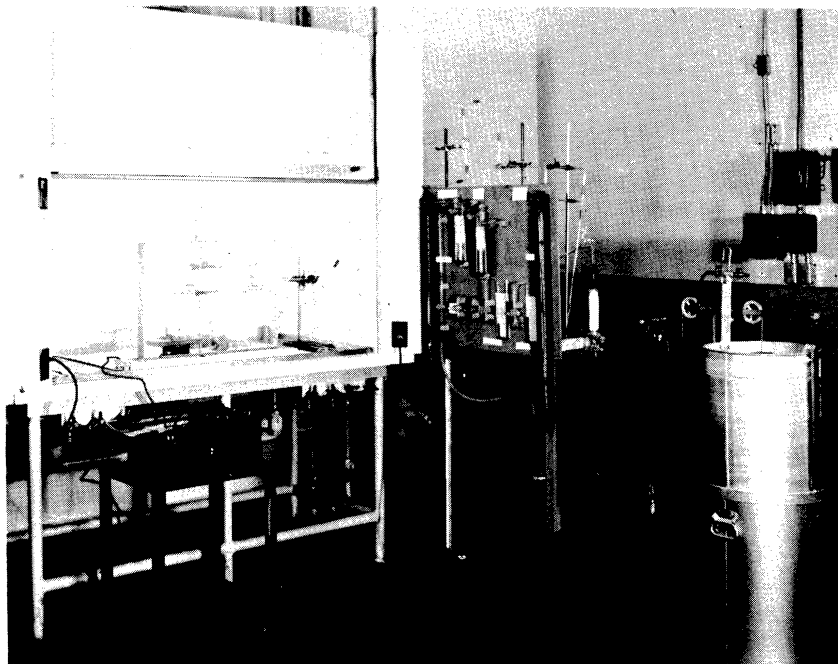


Fig. 27. Low-Pressure System for Gases in the Presence of Radioactive Catalysts. Flask behind lucite shield contains palladium foil with a small percent of Pd-109.

some palladium-109, whose total activity was about 3 curies. At the end of about 12 hours no ammonia could be detected by Nessler's test. In another experiment a stainless steel reactor tube (Fig. 28) was charged with the palladium foil

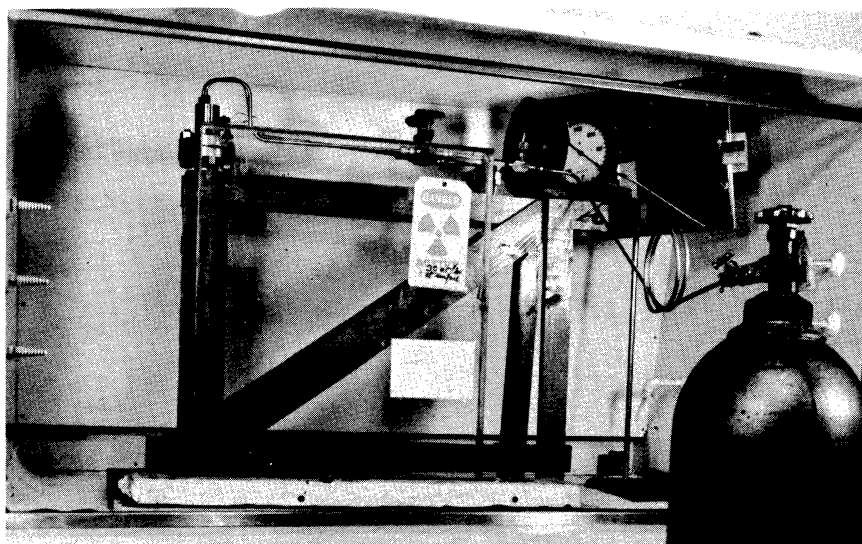


Fig. 28. Batch Reaction System Utilizing High-Pressure Reactor.

whose activity was now approximately 1 curie, and a stoichiometric mixture of nitrogen and hydrogen was added at a pressure of about 55 atmospheres. At the end of about 11 hours the Nessler test indicated that no appreciable amount of ammonia had been produced at room temperature by the beta radiation. This is the first experiment to be conducted at a pressure higher than atmospheric, and considerable confirmation and extension of this work remains to be done.

### C. Design and Construction of New Equipment

The preliminary experiments to date indicate that high density of the chemical reactants is most favorable to the promotion of a reaction by radiation. This means that, in the case of gases, high pressures appear to give the greatest promise, both because of greater absorption of radiation and because of the increased conversion at equilibrium in many systems.

As an example of a reaction in which elevated pressure increases the normal equilibrium percentage of desired product, the ammonia synthesis is considered in detail. The equilibrium molar percentages of ammonia present in a reaction mass originally consisting of nitrogen and hydrogen in the stoichiometric ratio are given in Table IV.

TABLE IV

THEORETICAL PERCENTAGES OF AMMONIA IN A SYSTEM INITIALLY  
CONSISTING OF A STOICHIOMETRIC MIXTURE OF NITROGEN AND HYDROGEN  
(Results of Thermodynamic Calculations)

	Temperature (°F)	Pressure (psia)	Percentage of Ammonia at Equilibrium
1	70	147	100-
2	70	1500	100-
3	450	14.7	35.9
4	450	1500	72.1
5	932	4400	26.4

(Data from Curtis,<sup>1</sup> Dodge,<sup>2</sup> and Hougen and Watson<sup>3</sup>).

Lines 1 through 4 represent conditions of temperature and pressure attainable in the apparatus which will soon be available in this laboratory. Line 5 represents conditions approximating those in industrial ammonia reactors. It is evident from Line 2 that it is desirable to operate an ammonia reactor at as high a pressure and low a temperature as possible in order to obtain the maximum conversion to desired product at equilibrium. However, if the usual catalysts are employed for the reaction, the rate of reaction decreases with

<sup>1</sup> Curtis, H. A., Fixed Nitrogen. New York, Reinhold (1932).

<sup>2</sup> Dodge, B. F., Chemical Engineering Thermodynamics. New York, McGraw-Hill (1944)

<sup>3</sup> Hougen, O. A., and Watson, K. M., Chemical Process Principles. New York, Wiley (1947).

temperature decrease in such a way that at room temperature there is no conversion whatsoever. Now it seems possible that radiation may speed up the reaction and permit lower operating temperatures either with or without catalyst. Similar remarks could be made for the methanol synthesis and for some other reactions of commercial importance.

By constructing a reaction system in which both temperature and pressure can be varied over considerable ranges, it is thought that much more information can be secured concerning the kinetics and equilibria of the systems to be investigated. In addition, it is possible that some reactions which would escape detection if carried out under milder conditions may be detected by operation under severe conditions.

The experimental reaction system being constructed is centered around a high temperature, high pressure reaction vessel. Fig. 29 is a photograph of the completed vessel, and Fig. 30 is a working drawing for the construction of the

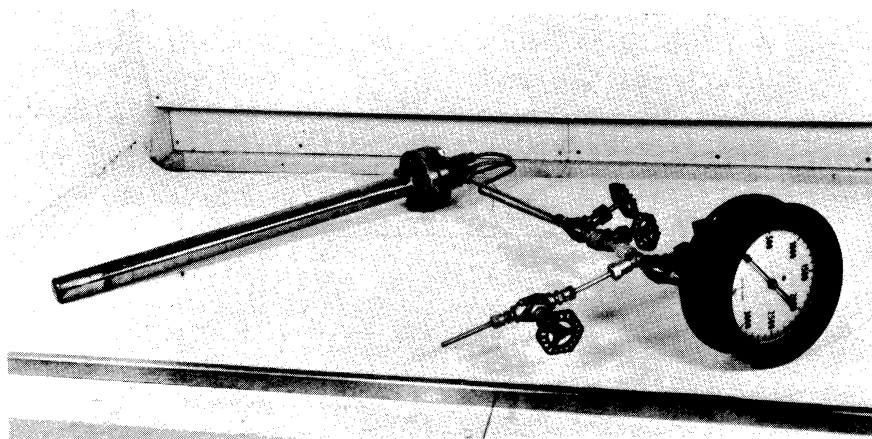


Fig. 29. Stainless-Steel Reactor and Auxiliary Fittings for Use with Gases at High Pressure.

vessel. Accessory equipment will be provided to permit the reactor to be operated either batch-wise or as a part of a continuous-flow reaction system, as shown on the flow sheet in Fig. 31. The reactor itself was designed according to the ASME code to operate at maximum conditions of 2000 psi and 650°F and was given a hydrostatic test at 2800 psi and room temperature. The reactor is constructed of stainless steel, and fits snugly into the 1-1/2-inch diameter access opening in the cobalt-60 vault. It will be necessary to limit the temperature of the outside of the reactor to approximately 350°F in order to avoid damage to the vault. It is thought that higher temperatures might cause warping of the aluminum case enclosing the cobalt or warping of the stainless-steel inner shell of the vault, or might even cause softening of the lead shielding. Provisions must be made for cooling the chemicals coming from the reactor since the accessory supply and control tubing will be of aluminum. The accessory equipment may be operated at 2000

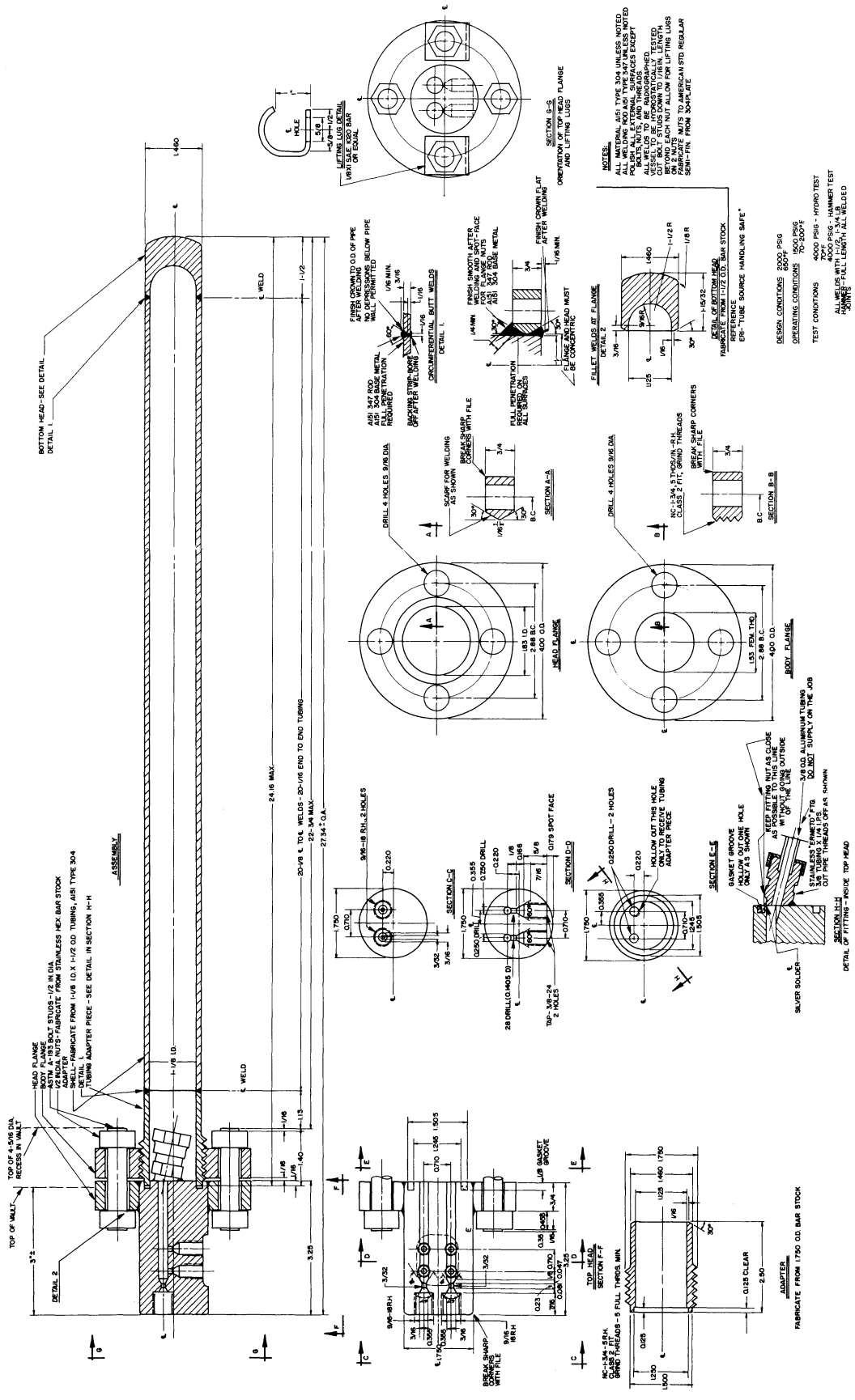
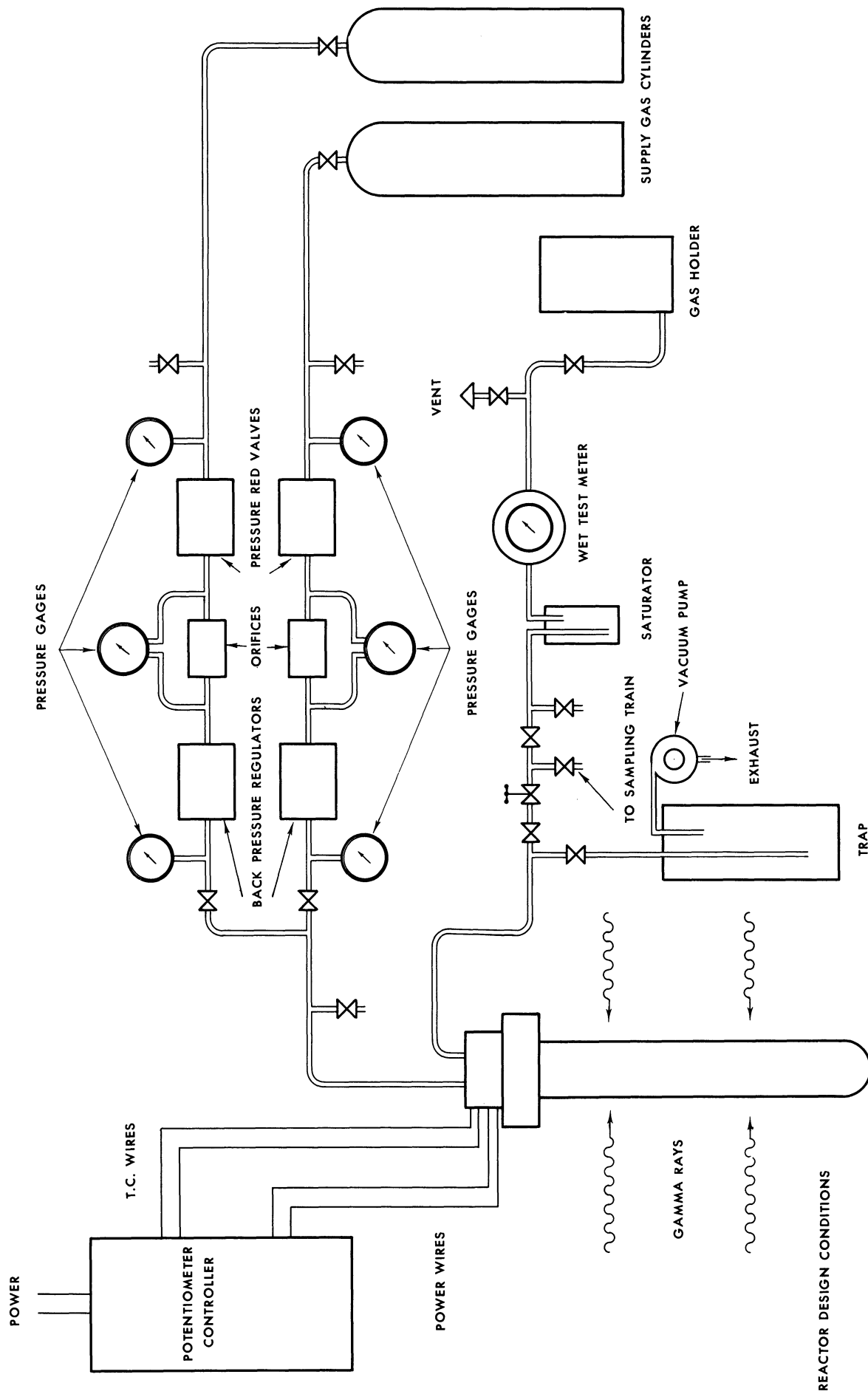


Fig. 30. Working Drawing for the Construction of the Reactor



FLOW SHEET PILOT PLANT FOR  
RADIATION CHEMISTRY STUDIES

REACTOR 2000PSI 650°F.

Fig. 31. Flow Diagram for a Continuous System Employing the High-Pressure Stainless-Steel Reactor

psi at room temperature, with the exception of the sampling, analytical and low-pressure metering apparatus. These three types of equipment will be operated at atmospheric pressure.

Fig. 32 shows the internal fittings for the reactor, which are patterned after some types of commercial reactors. The apparatus is designed in such a way that it may readily be removed from the reaction vessel shown in Fig. 30. Internal heat exchangers are provided in the form of baffles, so that incoming gases may cool the walls of the pressure vessel. A thermal radiation shield may be added if necessary in order to maintain the desired temperature in the interior and in order to prevent thermal radiation from the electric heater element from overheating the wall of the reactor. The heating element will be wrapped around the constriction just above the catalyst holder. Spiral countercurrent heat exchangers are provided to exchange the heat between the incoming and outgoing streams.

It may be discovered that the systems being investigated are so transparent to gamma radiation that little use is made of the energy of the radiation even at higher pressures. Since electrons in passing through a given thickness of material will lose a much higher percentage of their energy than will gamma rays, it may prove desirable to cause the gamma rays to eject electrons from a suitable material placed in the reacting system. If the rate of chemical reaction depends upon the rate of ionization, the rate of reaction should be increased by this secondary emission.

Fig. 33 is a drawing of a special packing which may be readily installed in or removed from the reactor vessel. This special packing consists of a series of washers placed parallel to the maximum component of the gamma radiation from the surrounding cylindrical source of cobalt-60. This packing should cause electrons produced in the washers by Compton-scattering of gamma rays to be dispersed in the reacting medium. The arrangement of the packing in washers was governed by the thought that a preferred orientation of the scattered electrons may exist and that this orientation may be different from the direction of the incident gamma radiation.

Although the reaction system described above was designed to fit into the arrangement of the existing cobalt-60 vault for studies using gamma radiation, it will be equally possible to use the entire system for studies in which a source of radioactivity is placed inside the reaction vessel itself. The latter arrangement would be particularly desirable when beta sources are used. The reaction vessel has now been completed and batch tests at room temperature will probably be conducted in this apparatus while construction on its internal fittings and the necessary equipment needed to study flow reactions is proceeding.

The greatest share of the materials needed to complete the construction of the experimental unit is now on hand, while most of the remainder of the materials should be secured within three months.

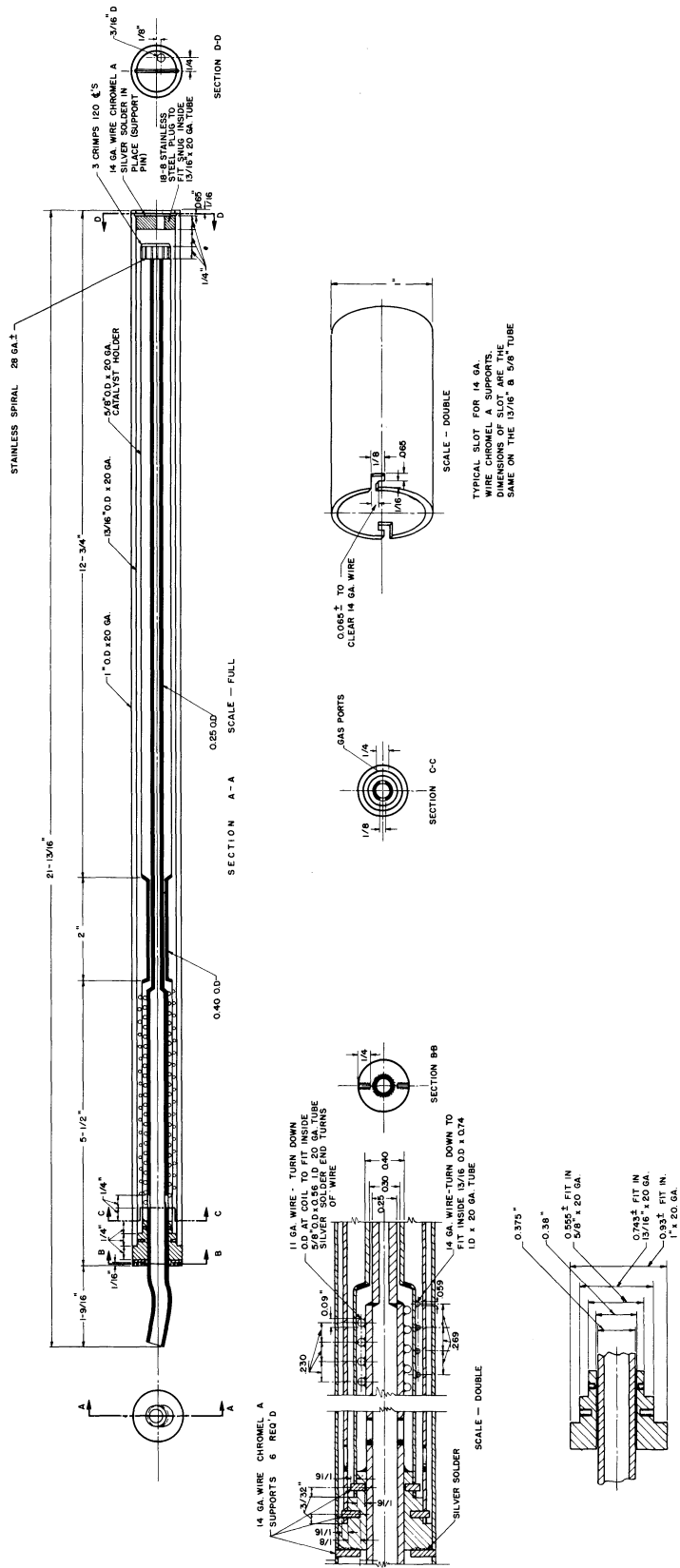
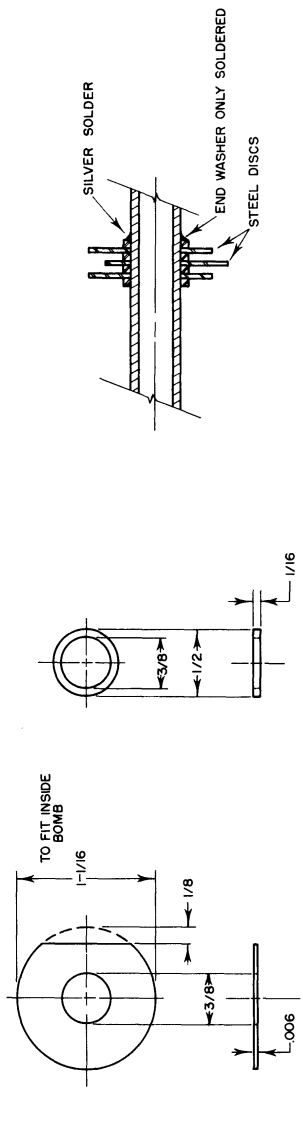
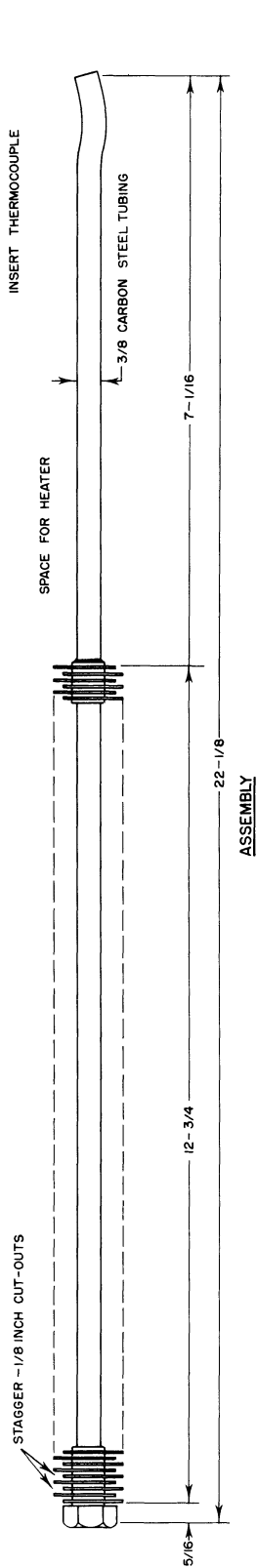


Fig. 32. Catalyst Holder for Reactor





A DETAIL WASHER ASSEMBLY

B DETAIL - WASHER ASSEMBLY

C SPACING WASHER DETAIL

D STEEL WASHER DETAIL

NOTE: FLATTEN WASHERS BEFORE ASSEMBLY

ELECTRON SCATTERING DEVICE  
 ONE REQ'D AS SHOWN  
 DWG. No. M943C-S3

**Fig. 33. Washer Packing for High-Pressure Reactor**

#### D. Future Program

It is planned to continue the studies on the ammonia synthesis reaction, varying the temperature and pressure over wide ranges and using the new stainless-steel reactor. Since many commercial reactors operate at 4400 psia and 500°C, it is quite reasonable that no positive results were found at room temperature and atmospheric pressure. It is expected that studies at higher temperatures and pressures will prove more enlightening and will indicate the range of usefulness of beta and gamma radiation in promoting the ammonia synthesis, as well as other reactions, such as the methanol synthesis and Fischer-Tropsch reactions.

While the higher-pressure gas reactions are being studied, further work will be carried on with liquids at lower pressures. It is planned to study some systems in which chain reactions have been postulated or might be possible. The polymerization of liquids such as styrene and acrylonitrile are worthy of further study. Also some reactions between different liquids and solids, such as the Diels-Alder reaction will be investigated in this program.

Gamma radiation will continue to be tried for all reactions studied, and an increasing amount of beta radiation will be utilized. It is planned to try some P-32 as the beta source, as well as Pd-109. Both of these will be charged inside the reacting system, as their penetrating power is quite low. Secondary particle and photon radiation will also be studied thoroughly.

Progress Report No. 3

UTILIZATION OF THE GROSS FISSION PRODUCTS

The Effect of Gamma Radiation on Chemical Reactions

J. J. Martin  
L. C. Anderson  
D. E. Harmer

J. G. Lewis  
J. R. Hallman  
S. A. Stolton

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PART II. SUBPROJECT M943-C, THE EFFECT OF RADIATION ON CHEMICAL REACTIONS

Personnel:

Subproject Supervisors: J. J. Martin, Associate Professor of Chemical Engineering; L. C. Anderson, Chairman of the Department of Chemistry.

Research Assistants: D. E. Harmer, J. G. Lewis, J. R. Hallman, S. A. Stolton.

A. INTRODUCTION

The objective of this work is indicated by the title of this subproject and has been discussed in earlier reports. Recently, the work has been concentrated on more nearly quantitative determinations of some effects of radiation, but studies are also being continued with the objective of finding which reactions are affected by radiation. The effects of gamma rays from the cobalt-60 source have been receiving the most attention. More work will probably be done on beta radiation in the future.

1. Styrene

In the last progress report made for this project<sup>1</sup>, it was reported that the viscosity of samples of monomeric styrene after irradiation in the cobalt-60 gamma source continued to increase after the samples were withdrawn from the source, while unirradiated check samples remained unchanged. This effect has been investigated more fully.

Others working in this field have produced a high degree of polymerization of styrene at room temperature with radiation<sup>2</sup>. The concern of this project, however, has been to study the effects of radiation on the progress of the conventional thermal polymerization of styrene. It is thought that industrial applications for radioactive materials may be more quickly realized by these methods.

In original experimental runs, relative viscosity was used as a qualitative measure of the degree of polymerization of unstabilized styrene which had been heated at 125°C. Samples of styrene were given 24 hours of

radiation in the kilocurie cobalt-60 gamma source. They were then subjected to thermal polymerization at 125°C. Viscosities of these samples were measured by observing the time required for stainless-steel ball bearings to fall through a given layer of the material. The viscosities of irradiated samples were found to be two to three times as great as the viscosities of corresponding unirradiated control samples. This relationship appeared to hold over the entire range of viscosities which could be measured by the method described.

The diameters of the glass tubes containing the styrene and falling ball were somewhat variable, since ordinary Pyrex tubing was employed, so a large variation in results was obtained. However, the data were regarded as being good evidence that radiation had produced a noticeable effect on the polymerization rate. When 12 or 48 hours of radiation were given, the viscosity increase of the irradiated sample was correspondingly less or more than that of the 24-hour runs, as would be expected. Runs made on styrene stabilized with tertiary butylcatechol also showed an increase in reaction of the irradiated sample over the unirradiated control. The samples used for this particular series of experiments were irradiated and polymerized under their own vapor pressure.

Since the experiments just described indicated that the irradiation of the monomeric styrene was giving a noticeable radiocatalysis to the subsequent thermal polymerization, data were sought to determine more quantitatively the effect of the prepolymerization irradiation period on the percentage conversion at various times of thermal polymerization.

A standard method for the purification of the styrene monomer has been developed. All glassware which would be used to handle the dried monomer was first heated to remove moisture and volatile impurities. The monomer (E. K. Co. No. 1465 stabilized with tertiary butylcatechol) was then run through a 10 x 400-mm tube packed with fresh Ascarite to act as a drying agent and to remove as much as possible of the phenolic inhibitor by salt formation. The dried styrene was placed in an all-glass distillation apparatus (see Fig. 17), after which the inlet tube was sealed with a torch. A stopcock was provided for evacuation of the apparatus, and was placed so that the liquid styrene did not come in contact with it or with the stopcock grease. The system was evacuated and the stopcock was closed. The distillation was carried out by a process of evaporation from the surface of the styrene, rather than by ebullition with the accompanying danger of spray being carried over through the Vigreux column into the receiver. It was found that such a distillation could be carried out by immersing the boiling flask in hot water, while cooling the receiver in a dry-ice, chloroform, carbon tetrachloride bath. Under these conditions the vapor came over at a temperature of 60°-75°C, and was frozen immediately in the receiver. When



Fig. 17. Glass apparatus for vacuum distillation of styrene, and glass-stoppered tube for irradiation and polymerization of styrene.

about three-fourths of the material had been distilled, air was admitted to the system, and the frozen distillate was brought to room temperature.

The sealed ends of the glass apparatus were broken open in order to pour the purified monomer, under air, into cleaned and dried glass-stoppered sample tubes, (See Fig. 17). The design of the distillation apparatus allowed the monomer to be poured out through the exit tube without coming into contact with the vacuum stopcock, while the undistilled material was retained by the shoulder of the boiling flask.

When the tubes of samples could not be used immediately, they were stored either in ice or in a dry-ice bath to prevent appreciable polymerization. In runs made up to the time of this report, the irradiated samples were given 24 hours in the cobalt-60 gamma source, corresponding to about 1,920,000 rep in air. During the irradiation, the samples were stoppered in an air atmosphere, and were at room temperature. Polymerization of control and irradiated samples was carried out in an oil bath maintained at  $125^{\circ} \pm 2^{\circ}\text{C}$ .

At the end of the polymerization period, the sample tubes were cooled to room temperature in a water bath, wiped clean, and weighed. The polymer solution was poured into absolute ethyl alcohol, and the tube, with the small amount of solution that remained in the tube, was weighed again. The known weight of polymer mixture was determined by the difference in weight of the original and emptied tube. This known weight of solution was allowed to remain in the alcohol for a few minutes. The resulting precipitate was then placed in a weighed Gooch crucible and extracted in a Soxhlet extractor with absolute alcohol for about 24 hours. The crucible and polymer were then placed in a vacuum dessicator at 68-75°C for 24 hours. At the end of this procedure, the cooled crucibles were weighed again with the remaining polymer. It is felt that by this process, the significant part of the unpolymerized styrene and the absorbed alcohol was removed, so that the percentage which had polymerized could be ascertained.

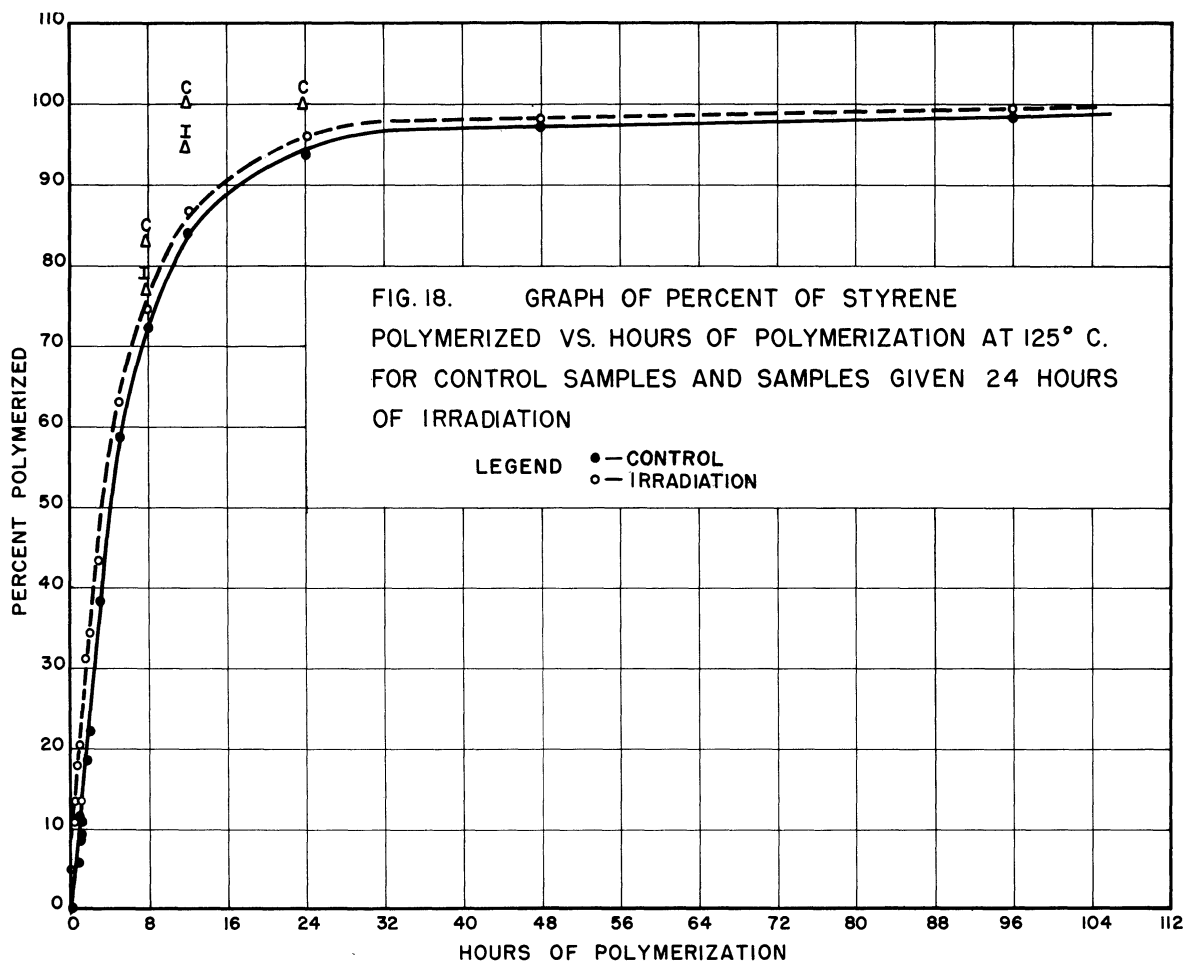
Some samples were polymerized to such an extent that they could no longer be poured into the alcohol. A slight modification of the above procedure was employed for these samples. The glass sample tube was broken, so that the solidified polymer mixture could be removed. The rod of polymer mixture was then crushed, weighed, and dissolved in benzene. The benzene solution could then be poured into alcohol, and the polymer precipitated as before.

From data thus obtained for a series of different times, a graph of per cent conversion versus time of polymerization at 125°C for irradiated (24 hours in the cobalt-60 gamma source) and the unirradiated samples was drawn (Fig. 18). Examination of this plot shows that some amount of polymerization has taken place during the irradiation process. The amount which was polymerized during irradiation is somewhat greater than that obtained by other investigators<sup>2</sup>. This difference may be attributed to the fact that the styrene used in the data for this report was polymerized in an air atmosphere. The upper line of the graph, representing the irradiated styrene, shows that such samples are always polymerized to a greater extent than the corresponding unirradiated samples. This fact is especially important in the highest percentages polymerized, since it is here that the reaction rate is the slowest. This graph does not correspond exactly to data published by the Dow Chemical Company<sup>3</sup>, but the slightly slower rate of polymerization of the control samples may be attributed to traces of inhibiting impurities, or to a different amount of dissolved air in the samples.

## 2. Exploratory Investigation of Reactions Influenced by Radiation

A considerable proportion of the work of this laboratory has been devoted to the search for chemical reactions which may be promoted to an





industrially important extent by radiation. Several different reactions have been investigated, using macro methods of chemical analysis in attempts to detect changes produced by radiation. From the data included in this report it can be seen that some reactions have given much more promising results than have others. Below are described some experiments which were conducted in order to find easily detectable effects of radiation on chemical systems.

Acetylene was irradiated with  $1.9 \times 10^6$  rep in air of cobalt-60 gamma radiation. The acetylene was dissolved in acetone which had first been absorbed in a dried portland cement, asbestos mixture. The cakes of cement were placed in a stainless-steel pressure vessel designed to hold 2000 psig and fitted with an aluminum rupture disc designed to burst at 150 psig. This assembly was known as the "bomb". (The pressure vessel is that described on p. 37 of Progress Report 2<sup>1</sup> of this laboratory.) The bomb was evacuated with the cement in place, flushed with nitrogen, and evacuated again. Then 105 grams of acetone was added and acetylene introduced until an equilibrium pressure of 5 psig was reached. The bomb thus charged was irradiated for 24 hours, after which the volatile contents of the bomb were recovered by immersing the bomb in hot water and heating the discharge pipes with infrared lamps. Subsequently, the bomb was evacuated while being heated in the manner just described. During the heating period all effluent material was passed through dry-ice traps.

The condensed liquid was distilled in a Podbielniak column, where it was observed that the overhead temperature was not significantly different from that of acetone during the distillation. About 0.2 gram of a brownish, waxy solid was recovered from the pot of the column. This material was insoluble in acetone.

Some natural oils, donated by the Wyandotte, Michigan, plant of the Archer-Daniels-Midland Company, of Minneapolis, Minnesota, were subjected to radiation by beta rays from palladium-109. Watch glasses were arranged on a wire frame. One drop of each oil to be observed was weighed on a separate watch glass. A thin polyethylene film was placed over the watch glasses, and the palladium-109 foil, encased in manila paper, was placed over the film of polyethylene. The oils were allowed to stand at ambient room temperature for one week in the apparatus described above. Control samples were run on the same oils. The control samples received no radiation, but were treated the same as the test samples in other respects. A summary of the results is given in Table I.

TABLE I

IRRADIATION OF NATURAL OILS WITH PALLADIUM-109 BETA RAYS

Material	Percentage Gain in Weight		Remarks	
	<u>Test</u>	<u>Control</u>	<u>Test</u>	<u>Control</u>
raw linseed	+7.8	+0.53	tough, rough film	no change
boiled linseed	+5.7	+7.0	tough, rough film	tough, rough film
degummed soya	+5.8	+0.39	tough, smooth film	no change
castor	+1.3	-0.58	no change	no change
refined menhaden	+9.3	+4.5	tough, smooth film	no change
cotton- seed pitch	-0.36	-0.19	no change	no change

Some of the gains in weight observed may have been caused by oxidation in the air. It is interesting to note that on the irradiated samples of raw linseed, degummed soya, and refined menhaden, hard, tough films appeared while on the unirradiated samples of these same oils, no films appeared.

A preliminary investigation was conducted on the effect of radiation on the increase in viscosity of dry, refined, degummed soya oil. Samples of the oil were placed in sealed containers and irradiated for 24 hours by gamma rays from cobalt-60. Immediately after a sample was removed from the cobalt-60 vault, it was placed in an apparatus designed to maintain the temperature and pressure of the sample at some fixed values. Nearly all runs reported were conducted at 1 mm absolute pressure. One set of runs was conducted at 575°F, and one set was conducted at 600°F. The results are tabulated in Table II, as follows:

TABLE II

CHANGES IN VISCOSITY OF SOYA OIL AFTER IRRADIATION AND SUBSEQUENT HEATING

The starting material used in each run was dry, refined, degummed soya oil.

Run No.	Irradiation	Temperature, °C	Time of Heating, Hr	Viscosity		Pressure, mm mercury, absolute
				G-H	Poises	
11	24 hr, Co <sup>60</sup>	300	6	N+1/3	3.5	1
12	--	300	6	J	2.5	1
13	24 hr, Co <sup>60</sup>	300	6	L	3.0	1
14	24 hr, Co <sup>60</sup>	300	6	L	3.0	1
15	--	300	NG-air leak	--	---	> 12
16	24, hr, Co <sup>60</sup>	300	6	L	3.0	1
17	--	300	6.3	L	3.0	1
18	--	300	6.2	J	2.5	1
19	--	300	6	J	2.5	1
26	24 hr, Co <sup>60</sup>	316	6	Z4	63.4	1
27	--	316	NG-air leak	--	----	> 10
28	24 hr, Co <sup>60</sup>	316	6	Z4+1/4Z5	69.4	1
29	--	316	NG-boiled over	--	----	1
30	--	316	6	Z1+2/3Z2	33.0	3
31	--	316	6	Z3+1/2Z4	54.8	3-4

The samples heated at 300°C after irradiation had viscosities of 3.0 to 3.5 poises, whereas those not irradiated but otherwise treated in the same way had viscosities of 2.5 to 3.0 poises. This difference in viscosities was approximately 20 per cent of the lower value. The samples heated at 316°C after irradiation were generally more viscous than those not irradiated but otherwise treated in the same manner. Some relatively mobile liquid distilled off the samples tested at 316°C. Because of the difficulties experienced in controlling the material balances at this temperature, further work under these conditions is indicated and planned.

Equipment has been constructed and is now being tested for the study of the kinetics of the ammonia synthesis at approximately 930°F. These tests will be conducted both in the presence and in the absence of gamma radiation from cobalt-60. Construction is also proceeding on equipment to test gaseous reactions in the presence of cobalt-60 gamma radiation at 2000 psig and temperatures up to 930°F. It is expected that operation at conditions of temperature and pressure approaching those used in the industrial processes for the manufacture of ammonia and methanol may provide useful additional information regarding the influence of radiation on these reactions.

## B. FUTURE WORK

### 1. Experimental Studies

Future work being planned with styrene includes investigations of the variables of polymerization temperature, irradiation time, and length of time elapsed between irradiation and thermal polymerization. Apparatus has now been constructed to permit thermal polymerization and irradiation of the styrene simultaneously in the gamma source. With this new arrangement, it may be possible to ascertain whether the effects of temperature and of radiation on this reaction may be combined to give a reaction rate greater than the combined individual effects, or whether the two effects will operate independently.

The use of impure samples of styrene, in which an induction period for the reaction is to be expected, may yield information about the usefulness of radiation to shorten this induction period. When sufficient data have been obtained in the case of styrene, those effects which appear to increase the rate of reaction will be investigated in other vinyl systems, and for other olefins.

It is planned to conduct additional tests on the oxidation and/or polymerization of natural oils under the influence of gamma radiation. More information regarding the changes taking place could be secured by subjecting

the treated samples to some of the tests ordinarily used in testing natural oils, such as iodine number, unsaponifiable material, free fatty acids, and melting point.

The work on the kinetics of gaseous reactions at high temperatures will be continued. The influence of radiation will be studied in the presence of catalysts ordinarily used for the reactions in question.

## 2. Need for Modified Gamma Source

The available space within the shielding of the present source of gamma radiation is so limited that the introduction of chemical equipment into the radiation field is severely handicapped. The demand for use of the present source is great, and only one small sample at a time can be accommodated. As a consequence, the work on chemical reactions is retarded, particularly by the necessity of designing and constructing highly specialized equipment needed to conduct the usual operations of chemistry within a space 1-1/2 inches in diameter by 13 inches long. If the working space within the shielding of the present source were to be increased, the flux density in the resulting volume would be reduced materially below the level now available.

The productive effort of this laboratory would be measurably increased if more working space were available. However, in order to maintain the intensity of gamma radiation in the working space at some value approximating that now available, a source of greater intensity would be needed. Such an arrangement would permit more frequent scheduling of experiments, each of which would require less time to prepare. In addition, experiments needed to explore the maximum effects of radiation upon given reactions could be scheduled for the long, continuous exposures required without interfering with other experiments.

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3. Polymerization of Styrene. Plastics Technical Service Bulletin, The Dow Chemical Company, Midland, Michigan.



Progress Report No. 4

UTILIZATION OF THE GROSS FISSION PRODUCTS

The Effect of Gamma Radiation on Chemical Reactions

J. J. Martin

L. C. Anderson

D. E. Harmer

J. G. Lewis

D. J. Goldsmith

J. R. Hallman

R. L. Kinney

E. M. Rosen





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PART II. SUBPROJECT M943-4 (FORMERLY M943-C),  
THE EFFECT OF RADIATION ON CHEMICAL REACTIONS

Personnel:

Subproject Supervisors: J. J. Martin, Associate Professor of Chemical Engineering, L. C. Anderson, Chairman of the Department of Chemistry.

Senior Research Assistants: D. E. Harmer, J. G. Lewis.

Assistants in Research: D. J. Goldsmith, J. R. Hallman, R. L. Kinney, E. M. Rosen.

A. INTRODUCTION

In the investigation of the effect of radiation on chemical reactions, two types of reactions are being studied: (1) chemical reactions of commercial, or possible commercial, importance that may be influenced by radiation, and (2) chemical reactions of a general kind which aid in explaining the mechanism of radiation effects.

B. EXPERIMENTAL WORK

In choosing chemical reactions for study of the effect of radiation, two different avenues of approach may be followed: A single reaction which has been found to be affected by radiation may be studied in detail, determining quantitatively the effect of all variables involved: or a large number of reactions may be tried in a preliminary sort of investigation to determine which reactions are affected appreciably by radiation. In general it is the latter approach which has been more closely followed so far. Of the reactions considered below, only the chlorination of benzene has received special attention.

1. Halogenation

As used in this work, the term halogenation (chlorination, bromination, or iodination) refers to the reaction of an organic compound with a halogen. The products may be the result of addition or substitution processes or combination thereof.

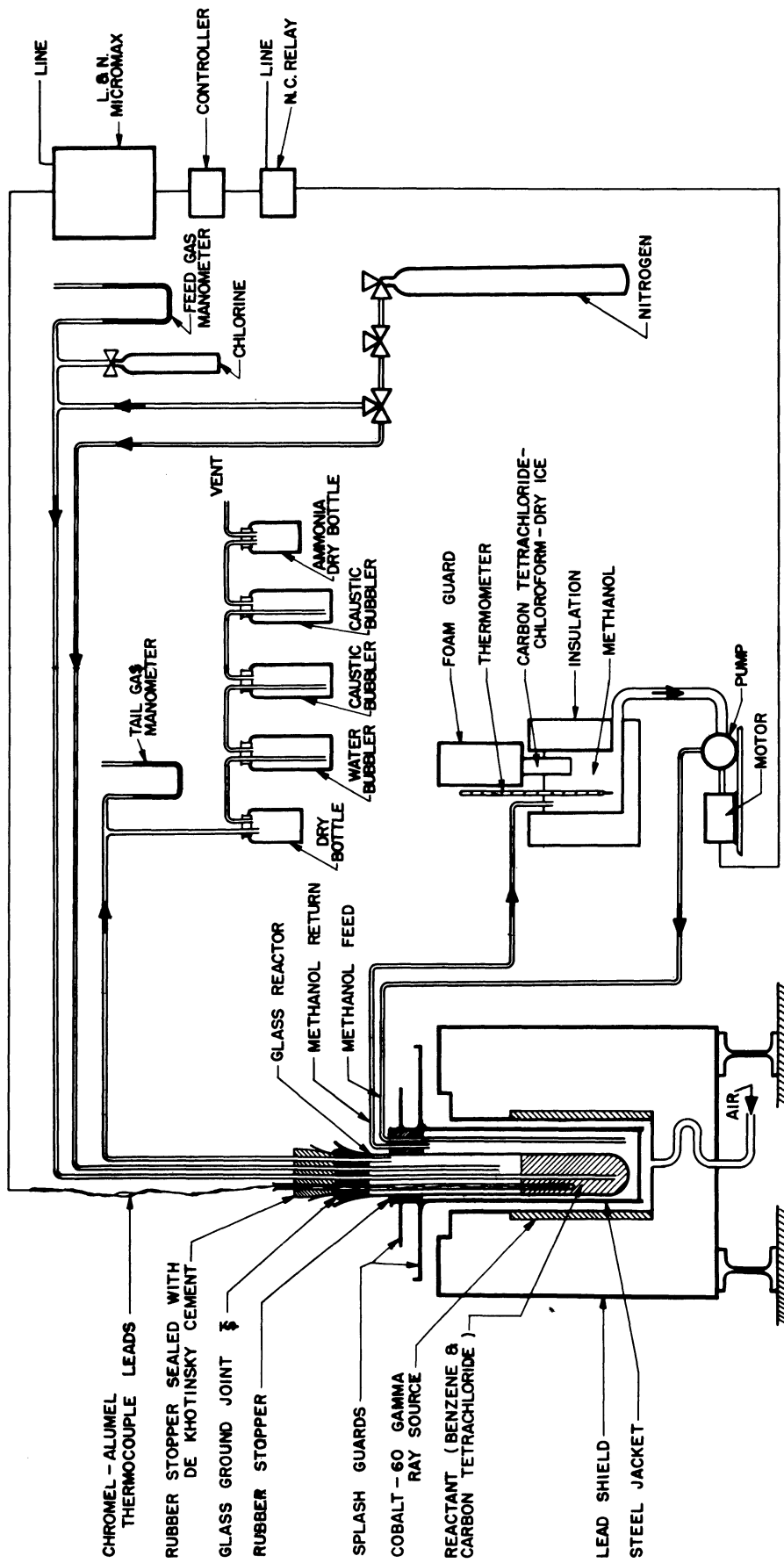


Fig. 13. Flow sheet for additive chlorination of benzene in cobalt-60 gamma ray source.

a. Chlorination of Benzene. It is well known that ultraviolet radiation promotes the addition of chlorine to the benzene ring, Slator<sup>12</sup> having demonstrated this fifty years ago. Alyea<sup>1</sup> showed that alpha radiation produces a similar effect. Therefore, an experiment was undertaken to determine whether this reaction could be promoted by gamma radiation.

When chlorine is bubbled through benzene, an addition reaction takes place at a very rapid rate. In view of the importance of the product, benzene hexachloride, it was decided to make a more intensive study of this reaction. After preliminary runs had been made, apparatus was constructed and assembled in which the reaction could be carried out under controlled conditions. A schematic diagram of this system is presented as Fig. 13. For convenience of operation in the Fission Products Laboratory, most of the controls for the experimental work were located on the second floor, adjacent to the opening over the kilocurie cobalt-60 source. (See laboratory plan on page 14 of Progress Report 1<sup>4</sup>.) Thus the gas cylinders, manometers, tail-gas absorption train, and temperature recorder-controller were located on the second floor (Fig. 14), while the kilocurie cobalt-60 source, glass reactor with its steel jacket, and the cooling system were located on the first floor. Glass tubing was used

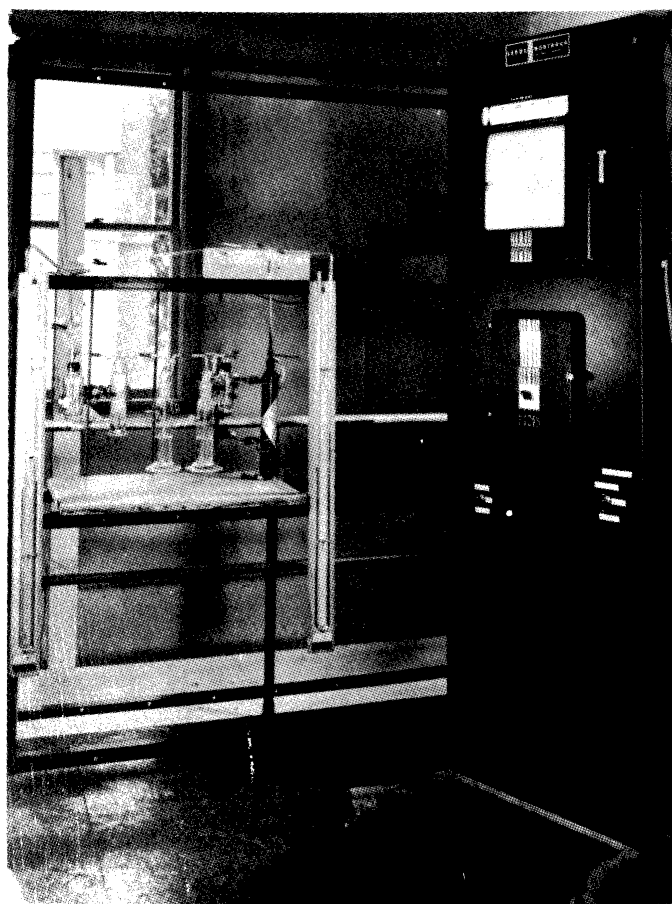


Fig. 14. Control equipment for chlorinations (Second floor, Fission Products Laboratory).

to carry gases between the reactor and the supply cylinders and absorption train.

The glass reactor consisted of a 25-mm glass tube long enough to extend completely out of the cobalt-60 source. The lower end of the glass reactor was closed, while the upper end was fitted with a standard ground joint. Four tubes, a chlorine inlet, a nitrogen inlet above the liquid level, a tail-gas exit, and a thermocouple well, were held in place in the inner ground joint by means of a rubber stopper sealed with resin cement (see Fig. 15). The assembled reactor (Fig. 16) was inserted in a steel jacket through a rubber stopper which also contained feed lines for the coolant liquid (Fig. 17). Splash guards were affixed to the steel jacket and compressed air was circulated through the vent hole at the bottom of the source container in order to prevent any possible damage to the cobalt-60 source in event of a spill or a chlorine leak. The tail gases from the reaction were absorbed in sodium hydroxide solution for analysis at the end of the experimental run (Fig. 18).

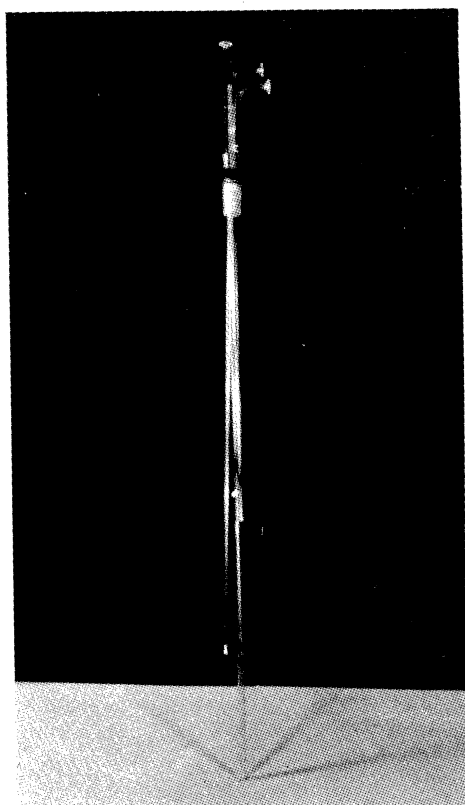


Fig. 15. Inner part of glass reactor tube, showing inlet and exit tubes and thermocouple well.

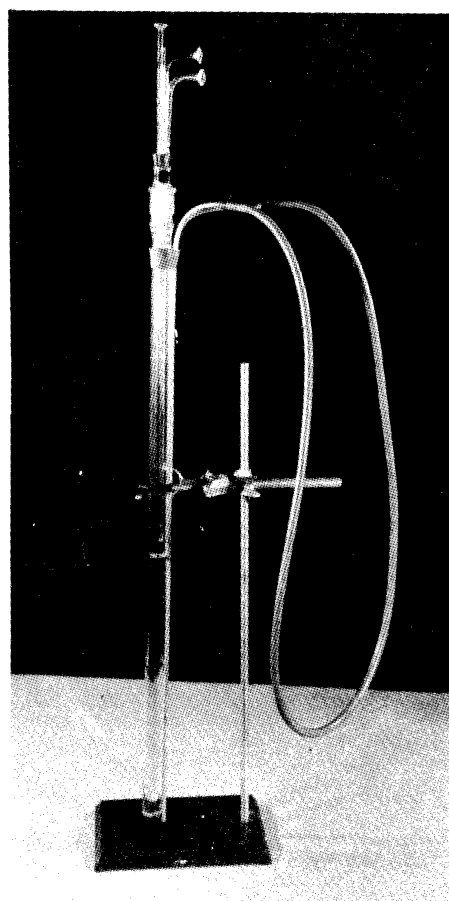


Fig. 16. Assembled glass reactor tube, containing liquid reactants.

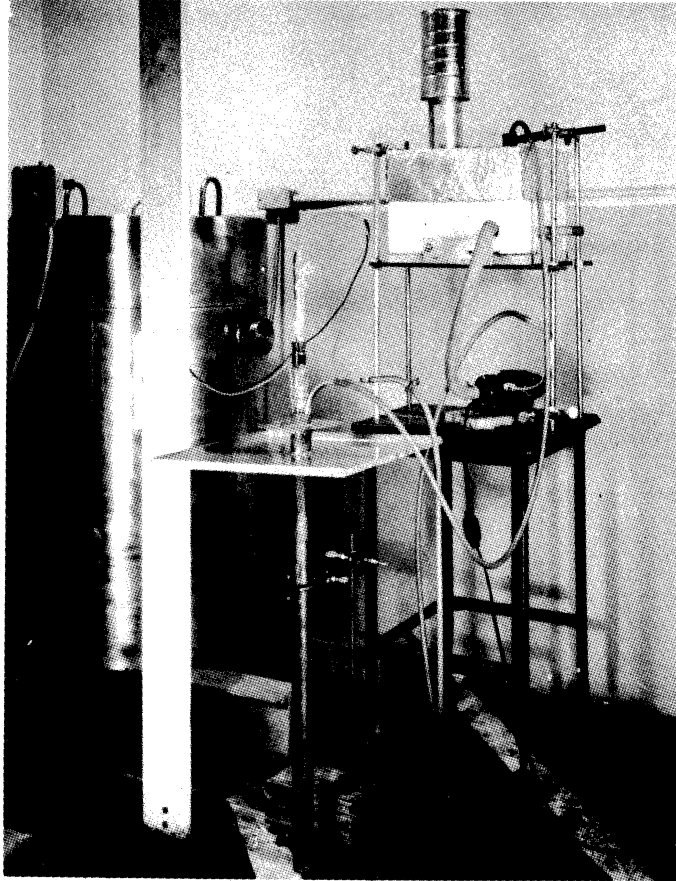


Fig. 17. Glass reactor tube in its steel jacket, connected to cooling system. Cobalt-60 vault is in the background.

The assembled glass reactor tube in its steel jacket was placed in the open kilocurie cobalt-60 gamma source and all glass connecting tubes were attached to the feed lines by extension tools fabricated for that purpose (Fig. 19). The design of the lead shielding of the kilocurie cobalt-60 gamma source at the University of Michigan is such that a high-intensity beam is located directly over the open source, but the radiation field at the sides of the container is low enough in intensity to allow loading operations in this area (see calibration of field around the open source, page 14 of Progress Report 1<sup>4</sup>).

Cooling of the reactor was accomplished by circulating methanol chilled by dry ice. When dry ice was added directly to the methanol, the centrifugal circulating pump became filled with carbon dioxide gas, causing the pump to lose its prime. Consequently, it was found necessary to chill the methanol indirectly by passing it around a can containing a mixture of carbon tetrachloride, chloroform, and dry ice. This part of the cooling system was

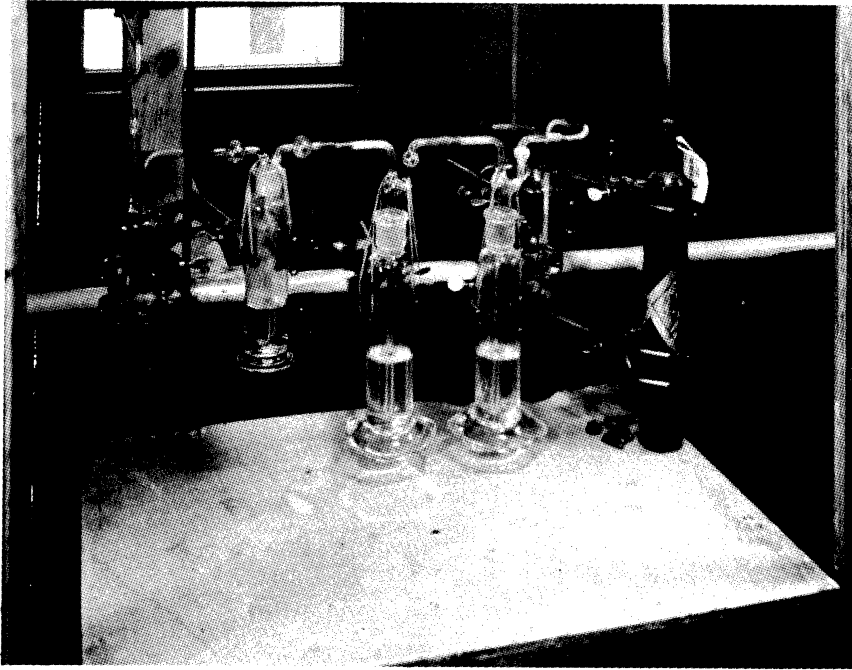


Fig. 18. Chlorine feed cylinder and tail-gas absorber bottles.

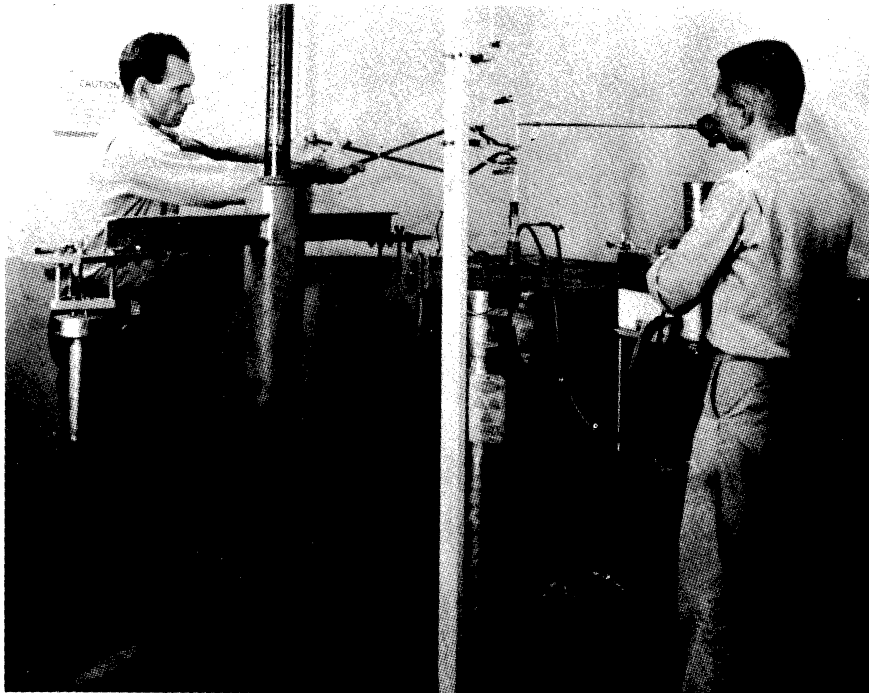


Fig. 19. When in place in the cobalt-60 gamma source, the glass reactor can be connected to feed lines by means of tools which allow the workers to stand in a field of low radiation intensity.

insulated with sections of polystyrene foam. The thermocouple of a Micromax temperature recorder-controller was placed inside the glass reactor tube. This controller alternately turned the pump on and off. The cold methanol was pumped into the steel jacket surrounding the reactor. The temperature control was greatly improved in later runs by circulating methanol continuously through the reactor cooling jacket. The temperature of the methanol was controlled by by-passing some of the methanol through the dry-ice chamber by means of a second pump. This pump was controlled by the Micromax regulator. The assembled apparatus was located on the first floor; its appearance from the second floor may be seen in Fig. 20.

Before each run, the entire system was purged with nitrogen in order to exclude all oxygen from the system. In early experiments, pure benzene was placed in the reactor. It was found, however, that the reaction then proceeded so rapidly that temperature control was virtually impossible, and the inlet lines soon became plugged with solid product. To prevent this complete solidification of the product, the reactant benzene was diluted with carbon tetrachloride. Mixtures containing as much as 30% benzene by volume produced

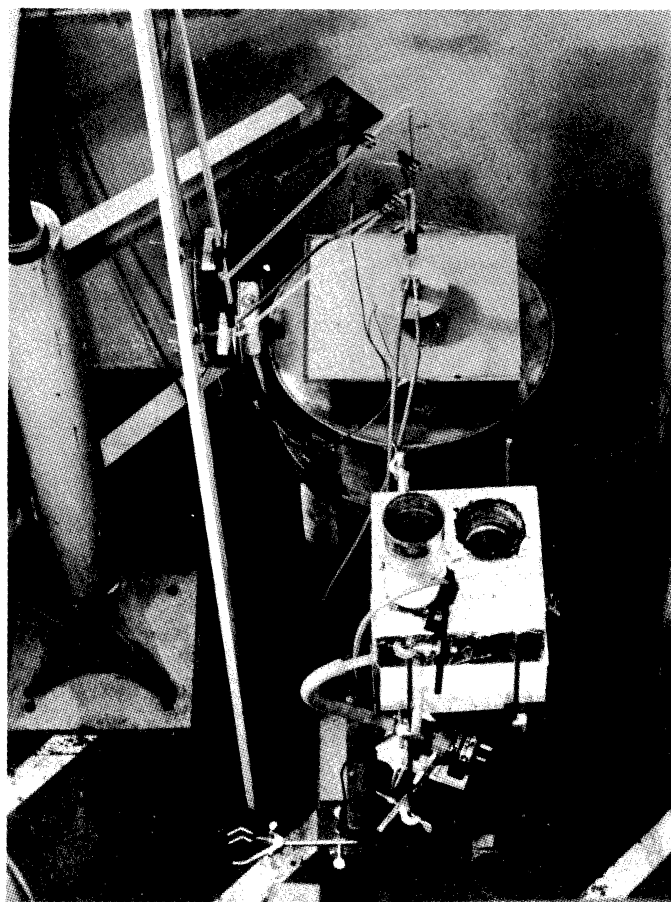


Fig. 20. Second-floor view of reactor and its glass feed lines and cooling system.



a semifluid slurry of solid product in the carbon tetrachloride. The reaction has been run to near completion in as little as 15 minutes when using benzene solution kept saturated with chlorine.

The solid product has been analyzed and was found to be nearly pure 1,2,3,4,5,6-hexachlorocyclohexane, or "benzene hexachloride".\* This compound is formed as a mixture of five stereoisomers, to which other investigators have assigned the first five letters of the Greek alphabet. The gamma isomer is known commercially as "Lindane" and possesses marked insecticidal properties which make it of considerable commercial value. The annual production of the mixed isomers in 1951 was about 125 million pounds<sup>7</sup>

Although the material may be used either as the unseparated mixture of isomers or in the purified gamma form, the insect-killing power is almost entirely dependent on the gamma isomer content. Table IV shows the gamma

TABLE IV \*\*

ANALYSIS OF SOME SAMPLES OF BENZENE HEXACHLORIDE

Approximate Temperature of Reaction, °C	% Benzene (by volume)	% CCl <sub>4</sub> (solvent) (by volume)	% Gamma Isomer in Benzene Hexachloride (from infra- red analysis)
20	10	90	11.3 (over chlorinated)
20	20	80	12.5
-10	10	90	12.3
-10	30	70	12.8

\* The authors are indebted to the Process Engineering Department of Wyandotte Chemicals Corporation and to Dr. L. E. Liggett of that company for an analytical method for total organic chlorides by the use of sodium diphenyl reagent.

\*\* The authors wish to express their gratitude to E. I. du Pont de Nemours and Company, Engineering Service Division, for furnishing the analyses for gamma isomer listed here.

Primary standard samples of the alpha, beta, gamma, and delta isomers were kindly supplied by the Hooker Electrochemical Company, Physical Chemical Laboratory. These samples were for the purpose of setting up analytical facilities in this laboratory.

isomer content of a few samples which were analyzed by infrared. It should be noted that the temperatures listed are only approximate. In each case the temperature went somewhat higher (as much as 5°C) at the height of the reaction. The continuous cooling system that was installed later brought this maximum temperature down several degrees. The percentages of gamma isomer are not significantly different from those obtained in processes from the addition of chlorine to benzene under the activation of ultraviolet light.

b. Chlorination of Toluene. Recently, work has been undertaken to chlorinate toluene under conditions similar to those used for benzene. Although both ultraviolet light and gamma radiation activated the addition of chlorine to the benzene nucleus, it is known that in toluene ultraviolet radiation activates substitution of chlorine for hydrogen in the methyl group. Therefore, it is of great interest to determine whether gamma radiation will activate the side-chain substitution or the nuclear-addition reaction. If it is the latter reaction which is predominantly promoted when toluene is chlorinated in the presence of gamma radiation, it is possible that gamma radiation may serve as a new tool to promote reactions that cannot be accomplished by other means. Preliminary results at the time of this writing indicate that both reactions, the addition and the substitution, are taking place under gamma irradiation; however, separation and analysis of reaction products is still in progress. The reaction between toluene and chlorine takes place at a rate comparable to that between benzene and chlorine under similar conditions.

c. Bromination and Iodination Reactions. Because of the success in the promotion of chlorine addition to benzene, experiments have been tried using bromine and iodine. Evaporation of a solution of bromine in benzene which had been given about 16 hours of gamma irradiation in the kilocurie cobalt-60 source left a residue of a small quantity of crystals in a liquid having noticeable lachrymatory properties. At the time of writing, this small yield of reaction product had not been identified. A solution of iodine in benzene which was given about 25 hours in the kilocurie cobalt-60 gamma source gave no noticeable residue on evaporation. No change in color of either the bromine or iodine solution could be observed during the irradiation. A solution of linseed oil, benzene, and iodine was found to become lighter in color when given about 21 hours of irradiation in the kilocurie cobalt-60 gamma source.

## 2. Oxidation

a. Using Elementary Oxygen. Sulfur dioxide and oxygen in a gaseous mixture of stoichiometric proportions were irradiated while under pressures of about 50 psig and temperatures of about 300°F. No sulfur trioxide was detected by iodometric-acidimetric titration procedures.<sup>3</sup>

Oxygen was bubbled through liquid sulfur dioxide held in the cobalt-60 vault at temperatures of about 250°F until the total pressure reached about 800 psig. No visible drop in total pressure was observed when introduction of oxygen was stopped. However, when the reaction products were absorbed in water, considerable amounts of sulfate were precipitated by the addition of barium chloride.

When sulfur dioxide and oxygen were agitated in aqueous solution at atmospheric pressure in the presence of gamma radiation, considerable amounts of sulfate were detected in the resulting solution. These results indicate the formation of sulfuric acid by the oxidation of sulfur dioxide dissolved in water. This can be compared with the results of Alyea<sup>1</sup> and Backstrom<sup>2</sup> on the oxidation of sodium sulfite in aqueous solution in the presence of ultraviolet radiation.

b. Using Other Oxidizing Agents. From time to time, when space has been available in the cobalt-60 source, single experiments were made on mixtures in which there was reason to believe, on the basis of other experience, that reaction might occur. In addition to investigating the possibility of brominating or iodinating benzene, as mentioned above, attempts have been made to react sulfur with benzene, pyridine, and naphthalene. Changes in odor after irradiation indicated that some reactions had apparently taken place, but these reactions have not been investigated further up to this time.

While other workers have also used elementary oxygen in reactions carried out in radiation fields, the use of other oxidizing agents has not been reported. Solutions of potassium permanganate in acetone and in an acetone-benzene mixture have been irradiated in the kilocurie cobalt-60 gamma source. The solutions containing benzene were decolorized and yielded a dark precipitate which appeared to be manganese dioxide. No change was apparent in irradiated solutions of permanganate in acetone.

Potassium iodide solutions were also irradiated in the cobalt-60 gamma source, using neutral solutions, some slightly acidic with acetic acid, and some 1 N with hydrochloric acid. Visible amounts of iodine were present in all samples irradiated for 30-40 hours. Titratable quantities of iodine (with 0.1 N thiosulfate) were present in the irradiated acidic samples. Irradiated aqueous acidic (acetic acid) potassium iodide solution displayed a measurable potential with respect to an unirradiated control solution, indicating a difference in concentration. Also, a measurable difference was detectable when each solution was measured separately with respect to a calomel half-cell.

### 3. Polymerization

Acetone has been reported to decompose into free methyl and acetyl radicals.<sup>13</sup> Acetone was therefore tried as a reaction initiator under gamma

irradiation. Irradiation appeared to change the odor of mixtures of acetone with ethanol and acetone with ethyl ether to some extent. It was consequently thought that some amount of ester may have been produced. However, distillation analysis on the Podbielniak column failed to yield any larger amount of any material other than the reactants. Mixtures of acetone and ethylene have been irradiated while under pressures of about 1000 psig. Yields of 1 to 5% by weight of white powder have resulted from these runs, and also with ethylene alone held at 900 psig and irradiated for about 50 hours with cobalt-60 gamma radiation.

Solutions of 1% glacial acetic acid in styrene have been irradiated, and viscosity measurements indicate that the acetic acid activates the polymerization of styrene under gamma irradiation. Liquid isobutylene was irradiated for some time under its own vapor pressure. A small amount of liquid residue was isolated. This material had a terpene-like odor. When a mixture of 50% (by volume) of styrene in linseed oil was irradiated for about 20 hours in the kilocurie cobalt-60 gamma source it showed slightly increased viscosity and a slightly bleached color. A similar mixture of linseed oil and acrylonitrile was given 39 hours in irradiation time, producing a thick, thixotropic paste. Odor indicated that some monomer was still present in this mixture.

#### 4. Other Reactions

Certain similarities in the electron configurations of the  $\text{Cl}_2$  molecule and the  $\text{H}_2\text{O}_2$  molecule led to the trial of hydrogen peroxide as a reactant with benzene. In some runs acetone was used as a mutual solvent. In one such run a crystalline product with a sharp melting point was obtained, but subsequent runs produced explosive products, which were probably organic peroxides. This work has been temporarily discontinued.

The reaction of benzene and chlorine is promoted by both ultraviolet and gamma radiation. It is therefore of some interest to compare the behavior of systems which have been subjected to known amounts of radiation from each of these two ranges of frequencies. For purposes of comparison, the benzophenone-isopropanol reaction was selected, since under certain conditions of concentration, sunlight, and geometrical arrangement of apparatus, this solution will show a visible precipitation of the bimolecular reduction product, benzopinacol, in about 5 hours.<sup>8</sup> A sample of this solution failed to show any such reaction after about 50 hours of gamma irradiation in the kilocurie cobalt-60 source. Apparently this reaction is not appreciably promoted by gamma radiation. The energy absorbed by this system in the kilocurie cobalt-60 gamma source was estimated to be 0.15 cal/ml-hr. This value is based in part on the calibration of the cobalt-60 gamma source as given in Progress Report 3.<sup>6</sup> In addition, the rate of energy absorption was calculated for this system when exposed to sunlight. The fraction of the solar constant in the range 3300Å to 3400Å was

estimated. The sun was assumed to be a black-body radiator, and the Planck radiation function was employed, as given by Jahnke and Emde.<sup>10</sup> It is further assumed that no absorption of incident solar radiation occurs in this frequency range, either by the atmosphere or by the glass container. When all radiation in the range of 3300Å to 3400Å was assumed to be absorbed by the reaction mixture, a value of 0.39 cal/ml-hr was found. It will be noted that the rates of energy absorption for this system in sunlight and in the source are of the same order of magnitude.

### C. FUTURE WORK

The investigations of this laboratory indicate that the reactions which are most likely to be accelerated by ionizing radiation are those which proceed by a free-radical chain mechanism. The evidence to date also indicates that dense phases (liquids or gases under very high pressures) are necessary to absorb appreciable amounts of gamma radiation to produce sufficient effects for the products to be measured by the usual macro-methods of chemical analysis. Future work will, therefore, follow lines consistent with these observations.

It is expected that reactions of liquids at atmospheric pressure and varying temperature, such as the benzene chlorination, will receive continued emphasis, as will reactions of gases under pressure such as the polymerization of olefins or the hydrogen-carbon monoxide reactions. Every effort is being made to control the temperature of the reactions more closely, since this is so important in comparing reactions with and without radiation. Reactions which normally take place at high temperature are especially important in this study; it is desirable to determine whether gamma radiation can cause them to proceed at a rapid rate at a lower temperature.

If other reactions are found to proceed as rapidly under gamma radiation as the chlorination of benzene, these reactions will probably be given special consideration and studied in some detail. However, the broad approach of trying a number of reactions is still very much in effect in the program at Michigan.

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Progress Report No. 5

UTILIZATION OF THE GROSS FISSION PRODUCTS

The Effect of Gamma Radiation on Chemical Reactions

J. J. Martin

L. C. Anderson

D. E. Harmer

J. G. Lewis

C. E. Eckfield

J. P. Holmes

R. L. Kinney

E. M. Rosen





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PART II. SUBPROJECT M943-4, THE EFFECT OF  
RADIATION ON CHEMICAL REACTIONS

Personnel:

Subproject Supervisors: Joseph J. Martin, Associate Professor of Chemical and Metallurgical Engineering; and Leigh C. Anderson, Professor of Chemistry and Chairman of Department.

Research Assistants: David E. Harmer and John G. Lewis Assistants in Research: C. Eckfield; J. Holmes; R. Kinney; and E. Rosen.

A. INTRODUCTION

Reference to previous progress reports will reveal the general nature of the studies being carried on at this laboratory. During the period covered by this report, the activities of the personnel of this subproject have not been confined strictly to determining experimentally, the effect of ionizing radiation on the promotion of chemical reactions. Consequently, the work is being reported under four major topic headings as follows: Chemical Reactions, Thermodynamics and Kinetics of Reactions, Dosimetry Problems, and Equipment Changes. These topics will now be considered in that order.

B. CHEMICAL REACTIONS

1. Polymerization

The polymerization of ethylene at pressures as high as 1600 psi and temperatures up to 400°F has received considerable attention. As shown in Table II, the early runs showed fairly high yields of a fluffy white powder. This was true for the runs in which the ethylene and a small amount of acetone were irradiated and for the runs in which ethylene alone was irradiated. The acetone was added with the idea that it would release free radicals on radiolysis and initiate chain polymerization of the ethylene. Later runs have

TABLE II

## IRRADIATION OF ETHYLENE WITH COBALT-60 GAMMA RAYS

Page	Starting Date	Pressure psig	Ave. Pres., psia	Ave. Temp., °F	Grams Polymer	Hours Irrad.	Grams Polymer Per Hr.	Other Reactants	Source	Position of Base of Reactor
132113	19 Dec 52	785-830	822	69	1.6+	69.7	0.02+	1 ml acetone	1-kc	-
132118	12 Jan 53	795-820	822	70	0.666	61	0.011	-	1-kc	-
132147	3 Mar 53	1330-1430	1395	230	0.292	17.2	0.017	-	10-kc	8" NE 9" UP
132149-II	7 Mar 53	{ 700-820 424-435	{ 775 445	50	0.004	{ 0.9 15. 15.9	0.0003	-	10-kc	8" NE 9" UP
132159	26 Nov 52	780-790	800	68	0.394	42	0.009	1 ml acetone	1-kc	-
132250	10 Mar 53	715-810	777	50	0.167	16.2	0.010	-	10-kc	9 on 9 at Base
132252	11 Mar 53	1330-1430	1395	200	1.04	16.1	0.06	-	10-kc	Do.
132253	12 Mar 53	692-698	710	45	1.48	87.7	0.017	-	10-kc	8" NE 9" UP
132254	17 Mar 53	655	670	45	-	23.3	-	{ 650 psi NA 15 psi Air Vent, Chg. C <sub>2</sub> H <sub>4</sub>	10-kc	8" NE 9" UP
132255	18 Mar 53	710-800	770	45	0.088	21.5	0.004	-	10-kc	8" NE 9" UP
132256	19 Mar 53	760-840	815	420	0.381	15.3	0.025	-	10-kc	8" NE 9" UP

132258	23 Mar 53	70-810	455	45	0.010	39.	0.0003	10 ml acetone	10-kc	-	
132259	26 Mar 53	183-788	485	61	-	15.3	-	-	10-kc	9 on 1 at Base	
132262-	4 May 53	1425-1600	1528	72	-	21.9	-	-	1-kc	-	
I											
132263-	5 May 53	595-620	623	72	0.022	23.	0.001	-	1-kc	-	
II											
132264	7 May 53	600-615	622	69	0.0001	20.7	0.000,005	100 ml O <sub>2</sub>	1-kc	-	
132265	8 May 53	608-620	631	67	0.0001	21.4	0.000,005	25 ml O <sub>2</sub>	1-kc	-	
132266	9 May 53	577-594	601	72	0.034	25.6	0.0013	5.0 ml O <sub>2</sub>	1-kc	-	
132267	10 May 53	595-600	603	75	0.001	17.0	0.000,05	2.0 ml O <sub>2</sub>	1-kc	-	
132268	11 May 53	597-617	622	70	0.017	22.3	0.0008	10.0 ml O <sub>2</sub>	1-kc	-	
132269	12 May 53	590-605	612	71	0.030	21.1	0.0014	10.0 ml O <sub>2</sub>	1-kc	-	
132270	13 May 53	629-637	638	66	0.016	14.8	0.0011	5.0 ml O <sub>2</sub>	1-kc	-	
132275	4 Jun 53	525-550	553	70	0.031	16.8	0.002	-	10-kc	8" sw 13-7/8" UP	

TABLE II (concluded)



produced very erratic results, and as noted in Table II, the yields have fallen considerably. At first it was thought this might be caused by the presence of oxygen in the system, and therefore a number of runs were made in which a known amount of oxygen was introduced. Although the results of these runs showed that the extent of reaction is dependent on the amount of oxygen, as shown in Fig. 28, the effect was far smaller than the decrease in reactivity from the early runs to the later runs. See Figs. 29 and 30. Therefore, it seemed unlikely that oxygen alone could be responsible for inhibiting the reaction. It should be noted that some uncertainty exists as to the slope of the curve of Fig. 28 for oxygen content near zero.

Other ideas which have been suggested are that the cylinder of ethylene contained impurities which acted either as promoters for the early runs or as inhibitors for the later runs. Alternative possibilities are that there might have been some polyethylene powder in the original cylinder of ethylene, that impurities might have been introduced by leakage during evacuation, that impurities might have been adsorbed on the packing or sealing washers, that acetone might have been present in the early runs even though it was not intentionally added except for three runs, and that some kind of separation reaction had taken place in the feed cylinder which resulted in different products over a period of time. These various ideas are being investigated and it is hoped to have a more definite information soon on just what causes ethylene to polymerize and what inhibits that polymerization in the system under investigation.

It should also be mentioned that the analysis for polymer after irradiation has been very crude. The procedure involves bleeding off all the gas, opening the reactor, and scraping out the fluffy powder. Analyses of the bleed-off gas are contemplated for future runs, as well as molecular-weight determinations on the polymer that is formed.

Liquid propylene was irradiated for 67.6 hours at a dose rate of about 25,000 rep/hr; the results are reported in Table III. A small quantity of a

TABLE III

IRRADIATION OF PROPYLENE IN 1-KC COBALT-60 GAMMA SOURCE

Date	Starting Date	Time	Hours Irrad.	Dose Rate, Rep/hr	Dose, Rep	Temp., °F	Pres., psia	Remarks
132140	6 Feb 53	1735	0.	65,000 ± 10%	0.	71.	147	2.8-in.-depth liq. propylene in bomb; 3000-lb gauge.
132140	9 Feb 53	1313	67.6	65,000 ± 10%	4,400,000.	65.5	145	Out of vault.
132140	18 Feb 53	1000	--	--	--	Room	25-30	0.2-0.3-in.-depth liquid in bottom, quickly evaporated.

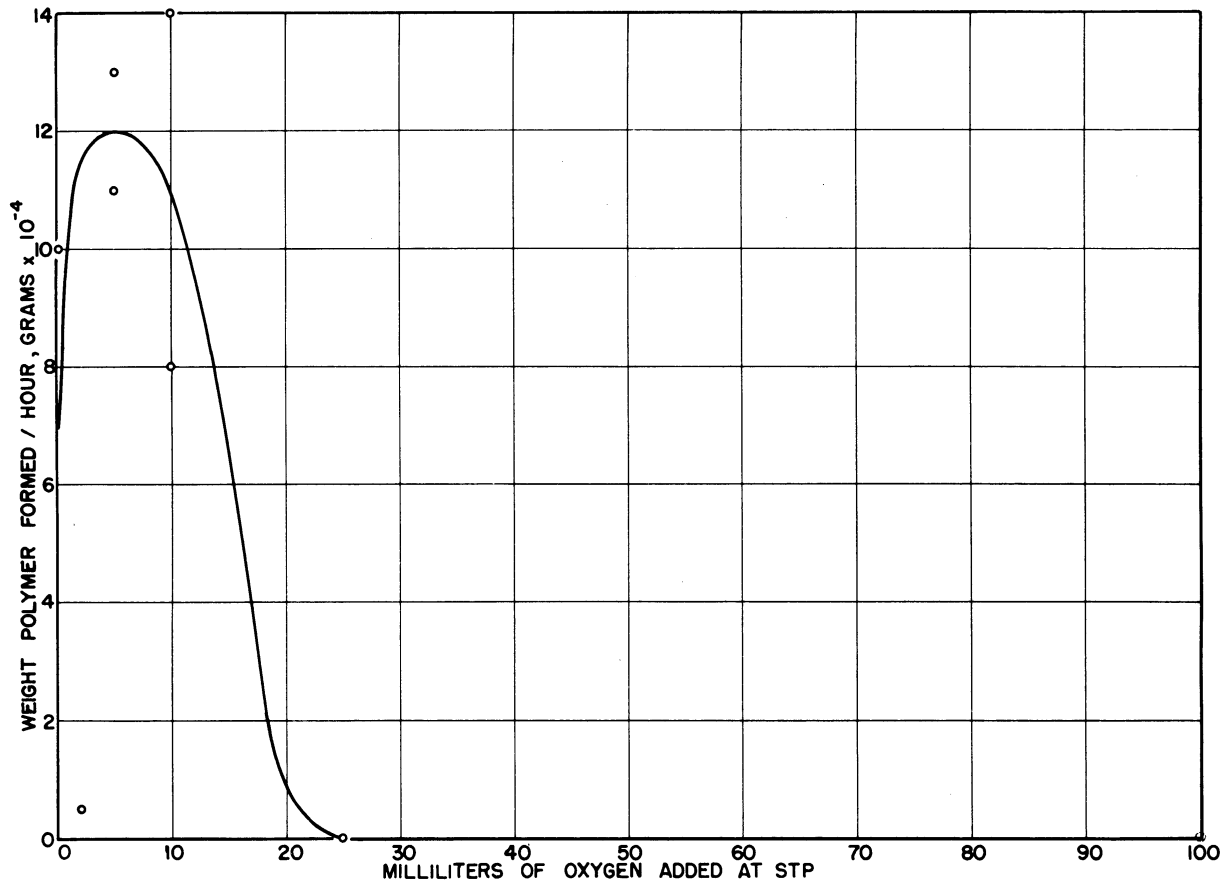


Fig. 28. Effect of Oxygen on Rate of Ethylene Polymerization.

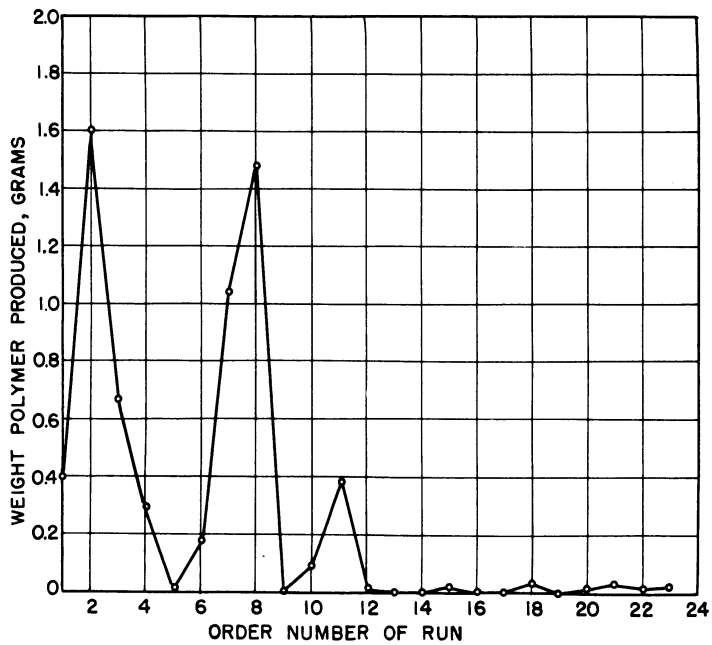


Fig. 29. Ethylene Yields for Successive Runs.

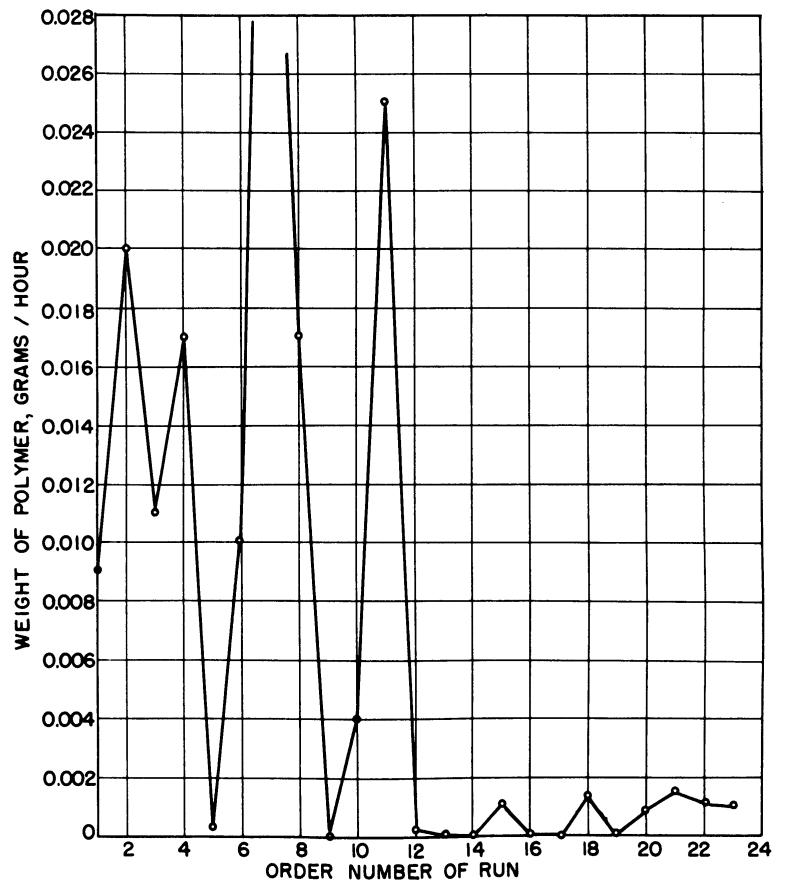


Fig. 30. Rate of Ethylene Production for Successive Runs.

volatile liquid was found in the reactor when it was vented and opened as in the ethylene runs. Undoubtedly some polymerization took place, although the quantitative amount has not yet been determined.

## 2. Chlorination

The addition of chlorine to benzene under gamma radiation to form the addition compound, benzenehexachloride, has been reported by this laboratory previously. The speed and extent of this reaction have led to investigations of the chlorination of other hydrocarbons such as toluene. Also, further work is anticipated on the kinetics of the benzene chlorination under gamma radiation to compare it with the reaction induced by ultraviolet radiation.

The reaction of chlorine with toluene has been carried out at 20°C. The experimental runs consisted of a 10-minute nitrogen purge through the toluene and the entire system, followed by passing an excess of chlorine gas through the toluene for 30 minutes during irradiation. After this, nitrogen was again passed into the system for 10 minutes, in order to allow the apparatus to be disconnected without escape of chlorine gas into the room. Equipment for the runs was identical to that used for benzene runs described in Progress Report 4<sup>1</sup>.

An attempt was made to separate the products of this reaction by distillation at atmospheric pressure. Fractions were obtained up to 225°C, but a vigorous decomposition began at 170°C with evolution of hydrogen chloride. About 30 per cent of the total chloride content of the sample was given off in this decomposition. When the original sample was extracted with water, it was found that less than 1 per cent of the total chloride passed into the aqueous layer, indicating that the chloride was not present in an active or ionic form.

A distillation of the products of another toluene chlorination run was carried out in a column packed with glass helices and operated at a pressure of 4.55 cm Hg. Table IV summarizes the fractions and some of their properties. The organic chloride analyses were carried out by the sodium diphenyl reagent method. Table IV shows that the largest single fraction (excepting the recovered starting material) is that boiling between 206 and 216°C (fraction X). This fraction has a chlorine content which is remarkably close to the theoretical percentage for a hexachloro addition product of toluene. Because of the possibilities which might be realized from the production of a new type of toluene derivative, further investigations are being made.

A control run was made on the reaction of chlorine and toluene in the absence of gamma radiation. All conditions were the same as for the runs previously described. Table V summarizes the fractions obtained from the distillation of the reaction product mixture at 4.50 cm Hg pressure. This control run

TABLE IV

DISTILLATION AT 4.55 CM HG PRESSURE OF THE PRODUCTS  
OF A TOLUENE CHLORINATION RUN WITH GAMMA IRRADIATION

Fraction	Volume, ml	Temperature Range, °C	Per Cent Chlorine	Comment
I	28.5	35-36°		Unreacted toluene
II and III	8.9	62-104°		
IV	5.6	95-96°	26.5	Mostly benzyl chloride (pure benzyl chloride is 28% Cl)
V to VII	6.2	96-127°		
VIII	2.8	142-157°	56.2	Mostly benzo trichloride (pure is 54.4% Cl)
IX	4.6	157-180°		
X	15.0	206-216°	68.8	Probably the hexachloro addition product. Theo- retical chlorine content is 69.8%.
XI	1.0	216-222°		Slight decomposition
Residue	12.0		70	

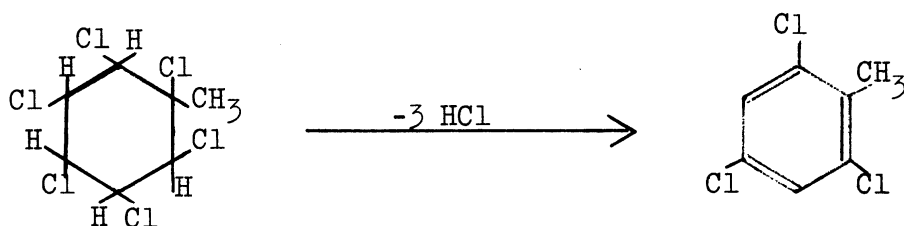
shows that very little reaction takes place in the absence of gamma radiation. Experiments which will allow comparison of the effectiveness and nature of products obtained under gamma irradiation and ultraviolet irradiation are contemplated.

TABLE V

 DISTILLATION AT 4.50 CM HG PRESSURE OF THE  
 PRODUCTS OF A TOLUENE CHLORINATION RUN WITHOUT IRRADIATION

Fraction	Volume	Temperature Range, °C	Per Cent Chlorine	Comment
I	85.5	34°		Toluene (identified by odor)
II	1.9	80-87°	25	Mostly benzyl chloride or chlorotoluene (theoretically 28% Cl)
Residue	4.1		68	High chlorine content, but dissimilar appearance to fraction X of Table IV.

Since fraction X of Table IV appeared to be somewhat unique, it was investigated further. If the structure is assumed to be the hexachloro addition compound of toluene, it should be possible to remove three molecules of hydrogen chloride and obtain 2,4,6-trichlorotoluene, or some corresponding isomer, by procedures similar to those which yield trichlorobenzene from hexachlorocyclohexane.



The thermal decompositions observed during distillation might lead to this type of compound in addition to other products. A sample of fraction X from Table IV was refluxed with pyridine for 63 hours. Aliquot portions of the pyridine mixture were placed in a mixture of equal volumes of benzene and ether and extracted with 0.1 N sodium hydroxide. The alkaline extracts were analyzed for ionic chloride. Of the total chlorine content of the original fraction, 52.8 per cent was found in this aqueous layer. This fact indicates that the hexachloro addition product of toluene was probably present in the original

material and suffered elimination of three molecules of hydrogen chloride while being treated with pyridine. The proof of structure is being given further consideration.

In an effort to ascertain whether the addition reaction could be applied to other substituted aromatic systems, benzyl chloride, benzal chloride, and benzotrichloride were each treated with chlorine under gamma irradiation at 20°C for 30 minutes. In each case, practically no increase in chlorine content was found and the starting material remained virtually unchanged.

Because of the nearly complete nonreactivity of the side-chain-substituted chlorine compounds of toluene, it seemed valuable to ascertain the effect their presence would have on the rate of reaction of chlorine with benzene under gamma irradiation. A series of runs was made in which mixtures of benzene and benzyl chloride were treated with chlorine under gamma irradiation for a 15-minute interval, at the end of which time the solid benzene hexachloride was separated and weighed. Table VI gives the results of these runs.

TABLE VI

EFFECT OF THE PRESENCE OF BENZYL CHLORIDE ON THE REACTION  
BETWEEN BENZENE AND CHLORINE

Mole Per Cent of Benzyl Chloride	Per Cent Yield of Benzene Hexachloride in 15 Minutes	Temperature Rise over Control Point
5	0.72	None observed
4	0.01	None observed
2	3.6	None observed
1	5.7	10°F after 13 minutes
0.5	5.6	22°F after 9 minutes
0.5		20°F after 10 minutes

The above table shows that the presence of benzyl chloride has a pronounced effect on the rate of addition of chlorine to benzene. The exact mathematical character of the function is not satisfactorily indicated by the data because of the experimental difficulties which arose at the minimum and maximum concentrations. The time for running the experiments was set at 15-minutes because previous work in this laboratory has shown that solutions of benzene

TABLE VII

IRRADIATION OF OXYGEN-BENZENE  
MIXTURES IN 1-KC COBALT-60 GAMMA SOURCE AT 1 ATM ABS AND ROOM TEMPERATURE

Page	Starting Date	Time	Hours Irrad.	Dose Rate Rep/hr	Dose, Rep	Procedure	Observations
132121	17 Jan 53	1615	0	65,000±10%	0	100 ml Benzene into vault	
132121	17 Jan 53	1626	0.18		12,000.	Oxygen on	
132121	17 Jan 53	1705	0.83		54,000.	Oxygen off	
132121	17 Jan 53	1707	0.87		57,000.	Out of vault	No changes in temperature or tail gas rate.
132122	20 Jan 53	-	-	-	-	5 ml of 132121 Product with sat'd. Bromine water, Evaporate on watch glass	No visible Ppt. in liquid. Cloudiness in benzene layer.
132122	21 Jan 53	-	-	-	-		Small oily smear on water glass, smelled of halogenated hydro-carbons.

diluted with carbon tetrachloride reacted almost completely in this length of time. Although great care was taken to control the temperature of the reaction by adequate cooling, some of the reactions displayed a tendency to "run away" after an initial period of good temperature control; this effect was more marked at lower concentrations of benzyl chloride. In the last run reported in Table VI, the mixture heated up so rapidly that chlorine escaped and no quantitative yield could be ascertained.

### 3. Oxidations

Several attempts have been made to oxidize partially some aromatic compounds by procedures analagous to those used in chlorinations runs.

Pure oxygen was bubbled through benzene for 30 minutes while the mixture was being subjected to gamma irradiation at the rate of 50,000 rep/hr. The results are reported in Table VII. No changes in temperature or tail-gas flow rate were noted during irradiation, no changes were noted in the color or odor of the product, and no visible reaction occurred between a sample of the product and saturated bromine water.

An attempt to oxidize toluene as reported in Table VIII, was carried out in a manner similar to that just described for benzene. The same equipment and dose rate were used and oxygen was bubbled through the toluene at 68°F for 1/2 hour. No changes were noted in temperature, tail-gas flow rate, color, or odor of the reaction product.

TABLE VIII

IRRADIATION OF OXYGEN-TOLUENE  
MIXTURES IN 1-KC COBALT-60 GAMMA SOURCE AT 1 ATM ABS and 68°F

Page	Starting Date	Time	Hours Irrad.	Dose Rate Rep/hr	Dose, Rep	Procedure	Observations
132126	31 Jan 53	1708	0.	65,000 $\pm$ 10%	0.	100 ml Toluene into source.	
132126	31 Jan 53	1712	0.07	65,000 $\pm$ 10%	4,500.	Oxygen on	
132126	31 Jan 53	1732	0.40	65,000 $\pm$ 10%	25,000.	Oxygen off	
132126	31 Jan 53	1735	0.45	65,000 $\pm$ 10%	30,000.	Toluene out of vault	No noticeable change in toluene



TABLE IX

IRRADIATION OF POTASSIUM PERMANGANATE - TOLUENE  
MIXTURES IN 1-kc COBALT-60 GAMMA SOURCE AT 1 ATM ABS and ROOM TEMPERATURE

Page	Starting Date	Time	Hours Irrad.	Dose Rate, Rep/hr	Dose, Rep	Procedure	Observations
132125	29 Jan 53	1056	0	65,000 $\pm$ 10%	0.	0.5g permanganate 25 ml acetone, 25 ml toluene	
132125	29 Jan 53	1400	3.1	65,000 $\pm$ 10%	200,000.	inspect sample	Supernatant liquid clear pink when shaken.
132125	29 Jan 53	1409	3.1	65,000 $\pm$ 10%	-	resume irradiation	-
132125	29 Jan 53	1530	4.5	65,000 $\pm$ 10%	300,000.	inspect sample	still faint pink
132125	29 Jan 53	1531	4.5	65,000 $\pm$ 10%	-	resume irradiation	-
132125	29 Jan 53	1616	5.1	65,000 $\pm$ 10%	330,000.	inspect sample	Supernatant liquid clear. Faint pink when shaken. Pungent odor.
132125	29 Jan 53	1627	5.1	65,000 $\pm$ 10%	-	resume irradiation	-
132125	30 Jan 53	1519	28.0	65,000 $\pm$ 10%	1,800,000.	inspect sample	Supernatant liquid clear and remained clear on shaking; decolorized bromine water; slowly decolorized a solution of permanganate in acetone; did not react visibly with aqueous bromide- bromate. The central sample had also decolorized.

In a different type of oxidation a sample consisting of 25 ml of acetone, 0.5 gram of potassium permanganate, and 25 ml of toluene was irradiated 28 hours at a dose rate of about 50,000 rep/hr, as reported in Table IX. Observations were made at intervals, and it was noted that there was a gradual bleaching of the permanganate color. The unirradiated control sample also bleached, but not as rapidly as the irradiated sample.

A solution of 0.25 gram of iodine in 50 ml of toluene was irradiated 44.5 hours at a dose rate of about 50,000 rep/hr, as reported in Table X. No difference was discernible between the irradiated sample and the unirradiated control.

TABLE X

IRRADIATION OF IODINE-TOLUENE  
MIXTURE IN 1-KC COBALT-60 GAMMA SOURCE AT 1 ATM ABS AND ROOM TEMPERATURE

Page	Starting Date	Time	Hours Irrad.	Dose Rate, Rep/hr	Dose, Rep	Procedure	Observations
132130	4 Feb 53	2108	44.5	65,000±10%	2,900,000.	0.25 g. iodine dissolved in 50 ml toluene	No discernible difference between run and control kept in dark.

4. A Dosimetry Reaction

Preliminary tests were made of the use of starch-iodide solutions for dose measurements. A solution of 1 gram of potassium iodide and 1 drop of glacial acetic acid in 100 ml of water was prepared together with a 1-per cent water solution of soluble starch. Samples consisting of 1 part of the starch solution to 19 parts of the iodide solution were subjected to doses of 5,000 to 300,000 rep, and the results are reported in Table XI. Visual observations indicated correspondence between dose and depth of color.

Since the above results indicate that an iodide system might be used for dose measurements, application of the method is considered: The possibility of measuring the concentrations of iodine produced in the oxidation of an iodide by means of a concentration potential for the solution of the mixture was discussed in Progress Report 4. Consider the usual voltage equation for an electrode dipping into a solution of iodine and iodide:

$$E = E^\circ - \frac{2.303 RT}{N F} \log_{10} \frac{(\gamma_{B C_B})^b}{(\gamma_{A C_A})^a}$$

$$= E^\circ - \frac{0.05915}{N} \log_{10} \frac{(\gamma_{B C_B})^b}{(\gamma_{A C_A})^a}$$

TABLE XI

IRRADIATION OF SOLUTIONS OF POTASSIUM IODIDE IN I-KC COBALT-60 GAMMA SOURCE  
AT 1 ATM ABS AND ROOM TEMPERATURE: POSSIBLE DOSIMETRIC METHOD

Stock Solution was: 100 ml water, 1 g potassium iodine, 1 drop glacial acetic acid.  
Starch Solution was: 100 ml water, 1 g soluble starch.

Page	Starting Date	Time	Hours Irrad.	Dose Rate, Rep/hr	Dose, Rep	Observation
132127	3 Feb 53	1430	0	65,000±10%	0.	Add 1 ml starch soln. to 100 ml stock soln. 5 samples, 25 drops each, then put into vault Remove one at stated time.
132127	3 Feb 53	1435	0.083	65,000±10%	5,500.	Faint blue tint
132127	3 Feb 53	1500	0.50	65,000±10%	33,000.	Moderate blue
132127	3 Feb 53	1630	2.0	65,000±10%	130,000.	Purplish blue
132127	3 Feb 53	2030	6.0	65,000±10%	390,000.	2 out-both blue-black; put one sample into clean tube, added starch, color darkened.
132128	4 Feb 53	0930	0.	65,000±10%	0.	Add 75 drops starch soln. to 90 ml stock soln. and starch from 132127. Made 5 samples, 25 drops each, put all into vault. Remove one at stated time.
132128	4 Feb 53	0935	0.083	65,000±10%	5,500.	No change - clear.
132128	4 Feb 53	0940	0.17	65,000±10%	11,000.	No change - clear.
132128	4 Feb 53	1010	0.7	65,000±10%	45,000.	Moderate blue.
132128	4 Feb 53	1530	6.0	65,000±10%	390,000.	Deep purple; control clear.
132129	4 Feb 53	1030	0.	65,000±10%	0.	10 g potassium iodide, 100 ml water, 1 drop glacial acetic acid, 5 ml starch soln. Procedure as above.
132129	4 Feb 53	1035	0.083	65,000±10%	5,500.	Faint blue.
132129	4 Feb 53	1040	0.17	65,000±10%	11,000.	Light blue.
132129	4 Feb 53	1110	0.7	65,000±10%	45,000.	Deep blue; control clear.

where

$E$  = the single-electrode potential at 25°C of the electrode,

$E^\circ$  = the single-electrode potential of the electrode when the concentration of all reactants and products involved is one molar (unit activity),

$F$  = coulombs per Faraday of charge,

$N$  = number of electrons involved in the electrode reaction,

$C_A$  = concentration of the reactant, iodide, for which the activity coefficient is  $\gamma_A$ ,

$C_B$  = concentration of the product, iodine, for which the activity coefficient is  $\gamma_B$ , and

$a$  and  $b$  are the stoichiometric coefficients of the reactants and products respectively, in the electrode reaction.

Now let two identical aqueous solutions of acidic iodide be prepared, such that a reaction will occur in either of them when it is subjected to gamma irradiation. Then concentration of iodine in the irradiated solution will be increased by a small amount. A concentration cell employing platinum electrodes and these two solutions, one irradiated and one not, will then have a potential as follows:

$$\begin{aligned} E &= E_1 - E_2 \\ &= \left( E^\circ - \frac{2.303 RT}{NF} \log_{10} \frac{(C_B)^b \text{ control}}{(C_A)^a \text{ control}} \frac{\gamma_B^b}{\gamma_A^a} \right) \\ &\quad - \left( E^\circ - \frac{2.303 RT}{NF} \log_{10} \frac{(C_B)^b \text{ test}}{(C_A)^a \text{ test}} \frac{\gamma_B^b}{\gamma_A^a} \right) \end{aligned} ,$$

where

$C_A$  = iodide concentration, and

$C_B$  = iodine concentration.

Since the iodide concentration of the control solution is approximately equal to the iodide concentration of the test solution for small degrees

of reaction, the above equation simplifies to:

$$E = 0.05915 \frac{b}{N} \log_{10} \frac{C_B \text{ test}}{C_B \text{ control}} \quad (7)$$

Equation (7) shows that a small change in the amount of product may be detected by measuring accurately the oxidation potential corresponding to the ratio of the test value to the control value.

### C. THERMODYNAMICS AND KINETICS OF REACTIONS

In the study of chemical equilibria, the standard free energy of reaction is a criterion of the degree of reaction to be anticipated at equilibrium in a given system. As usually defined, a negative standard free energy for a given reaction indicates the possibility of obtaining a preponderance of the product of the reaction in the equilibrium mixture. In addition, a reaction with a negative standard free energy of reaction may proceed spontaneously, but a positive free-energy change precludes the possibility of a spontaneous reaction. Only reactions with negative standard free energies of reaction will be considered in the following discussion. It is often assumed that the standard free energy of reaction is merely the net change in the energy of the system, and that the rate of the reaction may be explained on the assumption that a certain energy of activation must be possessed by a molecule or group of molecules before a reaction can occur. (See Fig. 31).

In a given system the fraction of molecules possessing a given energy is a statistical function of the energy possessed. Energies greater than or equal to the energy of activation needed for chemical reaction will be possessed by a certain fraction of molecules at a temperature above absolute zero. The rate of a chemical reaction proceeding as a result of thermal activation will vary exponentially with temperature if other conditions are fixed, since the number of molecules possessing energies equal to or greater than the energy of activation will vary exponentially with temperature.

As an alternative to thermal activation, energy might be introduced into a system in the form of electromagnetic radiation. For photon energies from 500 kev to 5 mev the predominant process would be ionization as a result of Compton scatter. The resulting ions or excited molecules, radicals or other excited species would have large energies compared with those ordinarily derived from statistical distribution of thermal energy. Each excited species activated by the encounter with radiation would probably possess sufficient

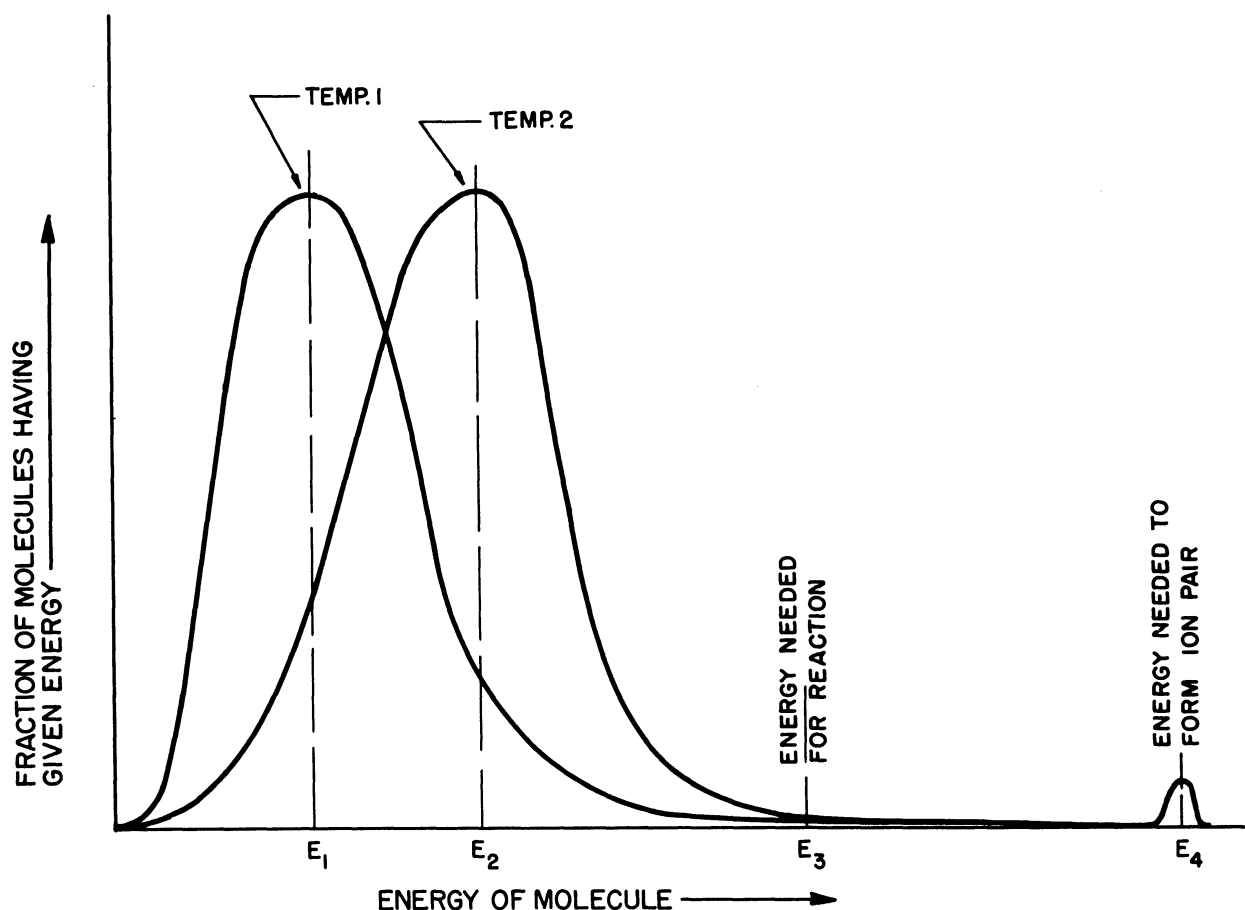


Fig. 31. Energy Distribution Among Molecules.

energy to react. Therefore, radiation might be used to induce chemical reactions in a system at a temperature too low for these reactions to occur measurably by thermal activation.

If the probability of attaining a sufficiently high energy to overcome the activation barrier were left to the Maxwell-Boltzmann distribution of energies among the molecules, the fraction reacting in unit time would be a function of the temperature only. In addition, for an exothermic reaction the net energy of the reaction is released and increases the random energy of the system as a whole. Thus in a sense the passage of each molecule over the barrier of activation helps to raise other molecules over this barrier.

However, if ions are produced by the absorption of highly energetic electromagnetic radiation and these ions react directly or indirectly to produce chemical products, then such an occurrence would not be a function of the temperature of the system. Rather the probability of such an occurrence would be governed by the intensity and energy of incident radiation. The energy of reaction and probably also the energy of ionization (barring fluorescence) would be released to the system and cause an increase in the random energy of the system as a whole, similar to that noted by thermal activation. However, there are cases in which the temperature is so low that this additional energy is not

sufficient to increase thermal activation by a measurable amount. Therefore, each molecule reacting as a result of radiation activation does not "lift" another molecule over the barrier of activation. Under these conditions, molecular interactions induced by radiation would be random events when considered as a function of the reacting system only, but the number of such interactions would be proportional to the dose rate of radiation. Furthermore, since the rate of reaction due only to thermal activation increases exponentially with the temperature, it should be possible to attain a temperature above which the contribution of radiation to the rate of reaction would become negligible compared with that of thermal activation.

In a chain reaction the energy of activation is transmitted directly from reacted molecules to unreacted molecules. It then becomes unnecessary for the energy of activation to be distributed at random among all molecules and then concentrated by random motion to activate the unreacted molecule. In effect the rate of a single-hit reaction is maintained in the chain reaction, but multiplied by the chain length.

The influences of radiation and temperature on the rate of a given reaction may be described quantitatively as follows:

The Arrhenius equation may be assumed to hold for the specific reaction velocity constant,  $k_t$ .

$$k_t = Ae^{-E_t/RT} \quad , \quad (8)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature,  $E_t$  is the energy of activation, and  $A$  is a frequency factor for the reaction. It can be shown<sup>5</sup> that the factor  $e^{-E_t/RT}$  represents the fraction of molecules having energies equal to or greater than  $E_t$ , the energy of activation. By postulate, these molecules are the only ones with sufficient energy to initiate reaction.

The specific reaction velocity constant,  $k_{tr}$ , of a reaction occurring in a field of radiation may be examined and equation (8) may be modified to:

$$k_{tr} = A(e^{-E_t/RT} + g) \quad , \quad (9)$$

where  $g$  is the fraction of molecules activated by irradiation.

Equations (8) and (9) may be rearranged and combined as follows:

$$\begin{aligned} \ln(k_{tr} - Ag) &= \ln Ae^{-E_t/RT} \\ &= \ln k_t \quad . \end{aligned} \quad (10)$$

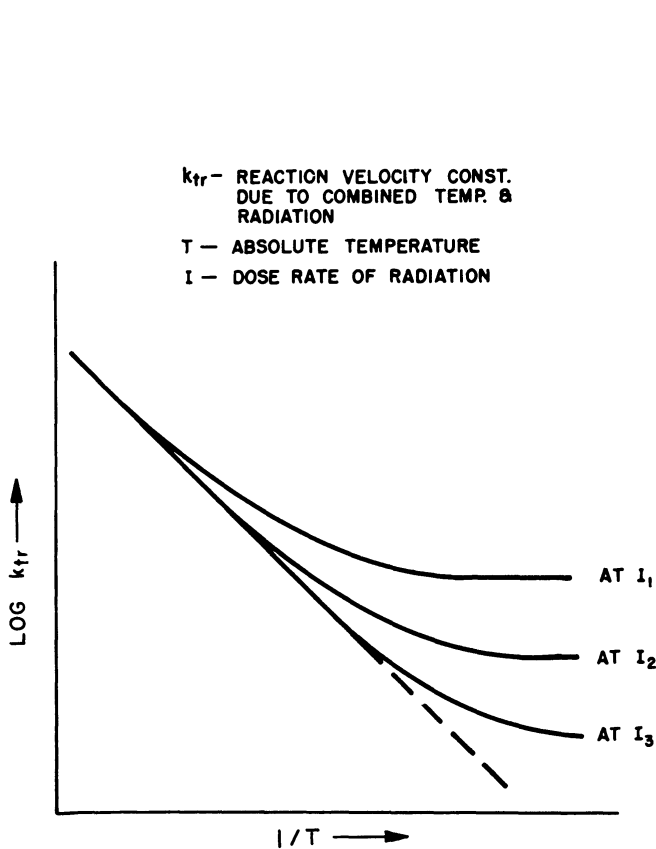


Fig. 32. Log  $K_{tr}$  Versus Reciprocal Temperature Plot.

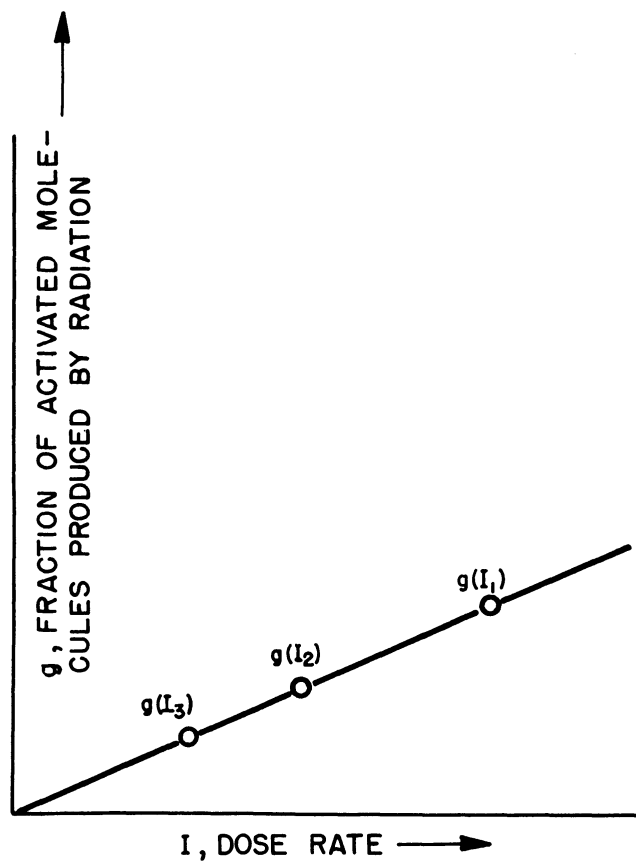


Fig. 33. Fraction of Activated Molecules as a Function of Dose Rate.

The validity of equation (10) may be tested as described below. Note that a plot of  $\ln(k_{tr} - Ag)$  versus  $1/T$  should be linear. Consequently a plot of  $\ln k_{tr}$  versus  $1/T$  would be expected to be curved (see Fig. 32). If such a plot were obtained experimentally (as by Bretton et al.<sup>2</sup>), it could be straightened by the subtraction of an empirically determined parameter from  $k_{tr}$ . The parameter determined by this method would equal  $Ag$ , the part of  $k_{tr}$  due to radiation alone.

The values of  $E_t$  and  $A$  could be closely approximated from equation (8) at temperatures sufficiently high that  $k_{tr}$  would be nearly indistinguishable from  $k_t$ . Then the value of  $g$  could be computed from equation (9). Then  $g$  could be plotted as a function of the dose rate, as shown in Fig. 33. Thus the separate effects of temperature and gamma radiation on the kinetics of a reaction with no temperature-dependent chain could be studied.

Figure 31 indicates that the fraction of molecules with energy sufficient to react is almost solely a function of radiation effects at temperature 1. However, at temperature 2 the area under the curve due to thermal excitation



in the region lying above  $E_3$  is a considerable proportion of the total area lying above  $E_3$ . These observations illustrate the conclusion drawn from equation (10) above. That is, the rate of a reaction induced by gamma radiation is dependent on the dose rate and may be nearly independent of temperature over a wide range of temperatures less than temperature 2. However, at temperatures above the neighborhood of temperature 2 the rate of reaction becomes a function of both the temperature and dose rate due to radiation. At still higher temperatures the reaction due to thermal activation is sufficiently great that the rate due to radiation becomes small by comparison.

#### D. DOSIMETRY PROBLEMS

For any quantitative study of the effect of radiation on chemical reactions, it is necessary to know the dose rate of the radiation. Considerable work has been done since the last progress report on measurement of dose rates. The following discussion is taken from an article on that subject which was written by four of the authors of this report (Harmer, Lewis, Martin and Nehemias) for the 1953 Gordon Research Conference on Radiation Chemistry.

##### 1. Experimental Procedure

Dose rates were measured chemically by the method employing the oxidation of ferrous sulfate solutions. Dilute solutions of ferrous sulfate ( $5 \times 10^{-4}$  M) in aerated 0.8 N sulfuric acid solution were exposed to gamma radiation for doses of between 5 and 20 kilorep. The ferric ion produced by the gamma radiation depends on the presence of a small amount of oxygen, which is readily furnished by first passing air through the solution. For quantitative determinations of the ferric ion produced by irradiation, the spectrophotometric method described by J. Weiss<sup>9</sup> of Brookhaven National Laboratory was employed. This method makes use of a spectral absorption peak of ferric ion at about 304 millimicrons in the ultraviolet region. Optical densities of the irradiated solutions are measured at 305 millimicrons and compared with those of known ferric solutions made up by dilution of standardized ferric stock solution.

In converting the chemical yield to radiation dosage, a value of 15.4 micromoles/liter-kilorep was used. This value is based on the absorption of 93 ergs/gm of water for each equivalent roentgen of radiation. The solutions were irradiated in glass bottles about 3 cm in inside diameter, which were filled to a depth of about 4 cm.

The bottles of solution were placed inside and outside the 10-kilocurie source, as shown in Figs. 34 and 35, and inside the 1-kilocurie source. (See

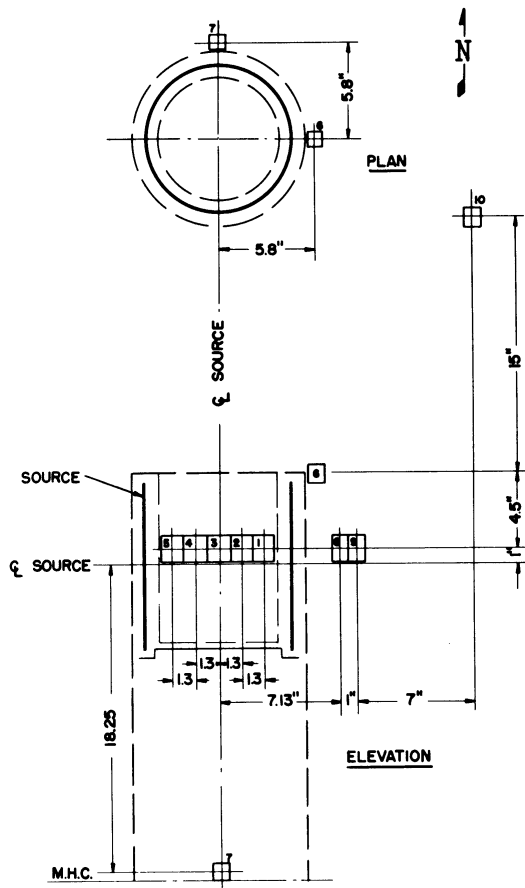


Fig. 34. Location of Samples--  
10-kc Source Dosimetry.

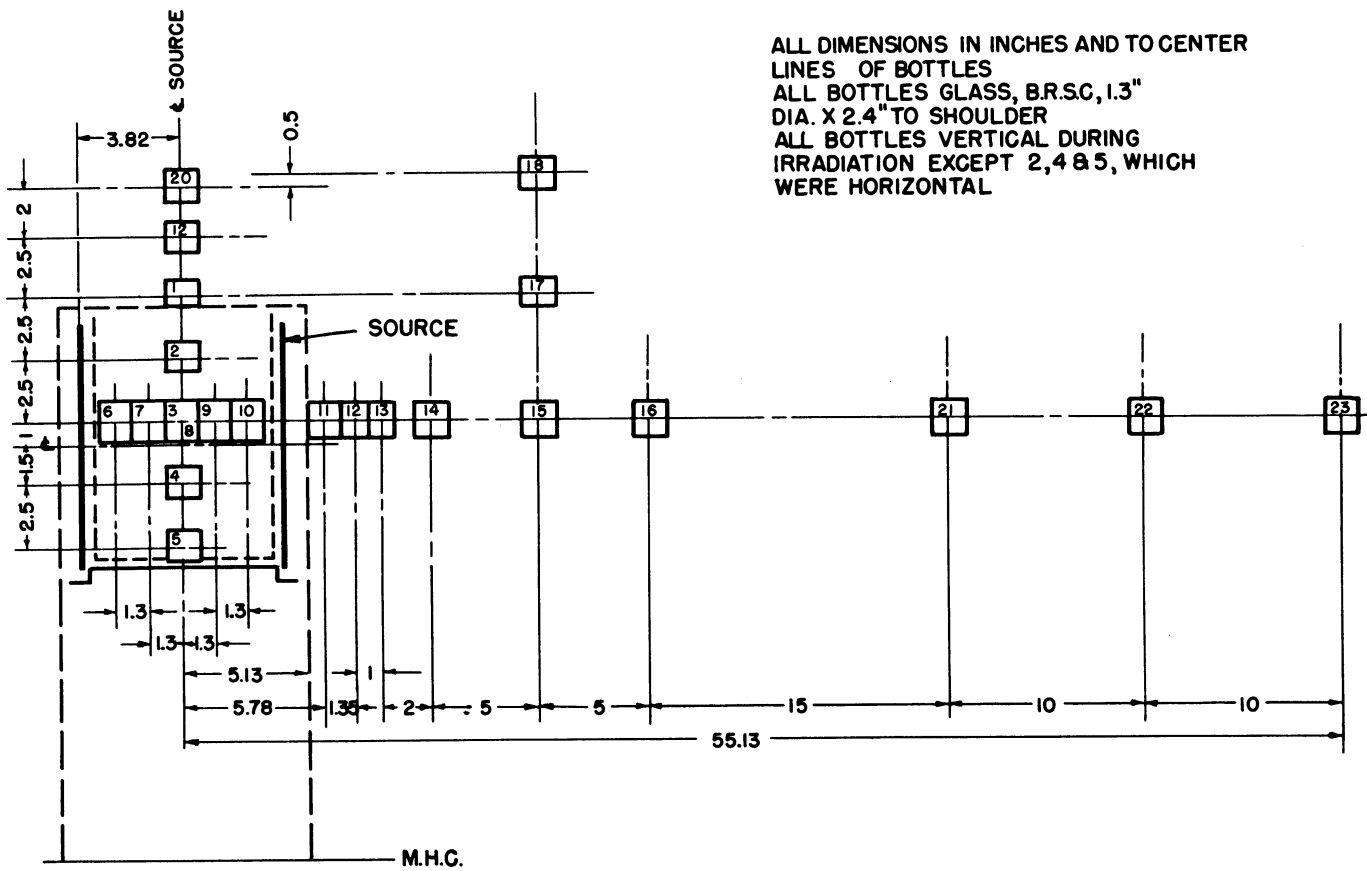


Fig. 35. Location of Samples--10-kc Source Dosimetry.

Table XII). Proper exposure times were calculated to fall within the range of the method of ferric ion determination. Measurement of dose rate in the 1-kilocurie source was carried out at times separated by an interval of 1 year, and values were found to be consistent after corrections for radioactive decay were applied. Measurements using a ceric sulfate system were also made and found to agree within experimental error with the ferrous sulfate results.

TABLE XII

IRRADIATION OF FERROUS SULFATE  
 SOLUTIONS IN COBALT-60 SOURCE - DOSIMETRY BY METHOD OF WEISS<sup>9</sup>  
 DATA FROM 10-KILOCURIE SOURCE UNLESS NOTED OTHERWISE

Page 132308		Page 132306	
Date 16 Mar 53		Date 13 Mar 53	
<u>See Fig. 34 For location of Samples</u>		<u>See Fig. 35 For Location of Samples</u>	
<u>Sample Number</u>	<u>Dose Rate, Kilo rep/Hr</u>	<u>Sample Number</u>	<u>Dose Rate, Kilo rep/Hr</u>
1	280	1	144
2	250	2	194
3	242	3	249
4	244	4	261
5	292	5	266
6	342	6	281
7	38	7	243
8	102	8	234
9	80	9	248
10	8	10	274
1 kilocurie	57	11	168
1 kilocurie	60	12	86
		13	115
		14	52
		15	24
		16	13
		17	22.
		18	17
		19	74.
		20	42.
		21	4.4
		22	2.6
		23	2.0
		1 kilocurie	55.

Physical determinations of dose rate have also been carried out on both sources. Two instruments have been employed in these determinations: a Victoreen roentgen rate meter, which measures the current flow between electrodes in an ionization chamber which is placed in the radiation field; and a Victoreen r-meter, which measures the drop in potential of a charged condenser due to ionization current caused by the radiation. The rate meter was calibrated against radium standards by the manufacturer, while the r-meter was calibrated against a cobalt standard at the University of Michigan.

Within 50 cm of the center of the 10-kilocurie source the rate-meter readings were 15 to 20 per cent lower than the ferrous sulfate determinations. The r-meter readings were 15 to 20 per cent higher than the ferrous sulfate measurements in the 10-kilocurie source, and were 25 to 30 per cent higher in the 1-kilocurie source. The detailed significance of these differences is not clear.

## 2. Calculation Procedure

Since gamma radiation from a point source may be assumed to follow the usual inverse-square relation, it is possible to calculate the dose rate

at any position in the neighborhood of a source of known shape and total activity by an integration technique similar to that employed in radiant heat transfer. If the geometry of the source shape is complicated, the resulting integration may be difficult. As a simple shape somewhat similar to the two cobalt-60 sources, consider first a hollow cylinder of negligible wall thickness and assign to it the power or curie rating of the actual source. The dimensions of the cylinder are taken to correspond as nearly as possible to those of the actual source, and the assigned curies are assumed to be distributed uniformly over the surface of the cylinder. Then the contribution to the radiation intensity at any given point due to an element of source area,  $dA$ , at a distance  $\rho$  is given by equation (11); see Fig. 36.

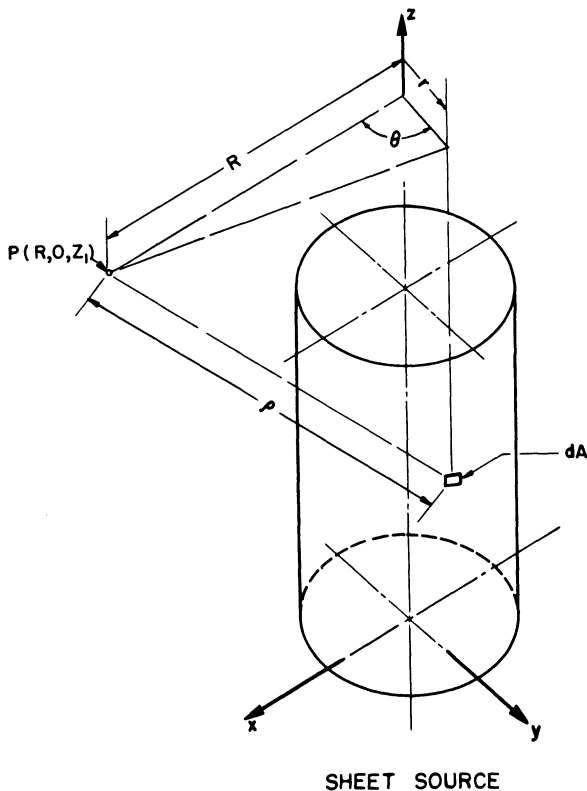


Fig. 36. Source With Negligible Wall Thickness.

$$dI = \alpha \frac{dA}{\rho^2} \quad (11)$$

The total intensity at the given point is obtained by summing the contributions from all elemental areas as

$$I = \int_{Z=0}^{Z=L} \int_{\theta=0}^{\theta=\pi} \frac{\alpha r d\theta dZ}{R^2 + r^2 - 2Rr \cos\theta + (Z_1 - Z)^2} \quad (12)$$

Integrating equation (12) gives

$$I = \frac{2\alpha\pi r}{R+r} \left[ F\left(\tan^{-1} \frac{R+r}{Z_1-L}, k\right) - F\left(\tan^{-1} \frac{R+r}{Z_1}, k\right) \right] \quad (13)$$

for

$$Z_1 > L > 0, R \geq 0, r > 0, 0 \leq \tan^{-1} \frac{R+r}{Z_1-L}, \tan^{-1} \frac{R+r}{Z_1} < \frac{\pi}{2}$$

and,

$$I = \frac{2\alpha\pi r}{R+r} \left\{ 2K(k) - \left[ F\left(\tan^{-1} \frac{R+r}{L-Z_1}, k\right) + F\left(\tan^{-1} \frac{R+r}{Z_1}, k\right) \right] \right\} \quad (14)$$

for

$$L \geq Z_1 > 0, R \geq 0, r > 0, R \neq r, 0 \leq \tan^{-1} \frac{R+r}{L-Z_1}, \tan^{-1} \frac{R+r}{Z_1} < \frac{\pi}{2} .$$

An alternative form may be obtained as shown by equation (15). Dewes and Goodale<sup>3</sup> have indicated the preliminary steps in this development.

$$I = \frac{2\alpha\pi r}{R+r} \left[ F\left(\tan^{-1} \frac{Z_1}{|r-R|}, k\right) - F\left(\tan^{-1} \frac{Z_1-L}{|r-R|}, k\right) \right] \quad (15)$$

for  $Z_1 \geq 0, R \geq 0, r > 0, R \neq r, -\frac{\pi}{2} < \tan^{-1} \frac{Z_1-L}{|r-R|} < \frac{\pi}{2}, 0 \leq \tan^{-1} \frac{Z_1}{|r-R|} < \frac{\pi}{2} .$

A relation given by Hancock<sup>4</sup> permits the transformation of equations (13) and (14) into equation (15), and vice versa. Equation (15) is considered more convenient in most computations, except for  $R=r, Z_1 > L$ , where equation (13) may be used to advantage.

The symbols used above are defined as follows:

$I$  = dose rate, equivalent roentgens/hour;

$A$  = area of source;

- $\rho$  = distance from elemental area  $dA$  to the point at which  $I$  is taken;  
 $\alpha$  =  $\left( \frac{\text{total activity, curies}}{\text{area of source, cm}^2} \right) \left( \frac{1000 \text{ millicuries}}{\text{curie}} \right) \left( \frac{\text{equivalent roentgens at 1 cm}}{\text{hour x millicurie point source}} \right)$ ;  
 $r$  = radius of source  
or constant radius vector of cylinder;  
 $R$  = radial distance of point at which  $I$  is taken from axis of source;  
 $\theta$  = central angle from  $R$  to  $r$ ;  
 $Z$  = distance parallel to axis of source from base of source to element  $dA$ ;  
 $Z_1$  =  $Z$  coordinate of point at which  $I$  is taken;  
 $k$  =  $\frac{2\sqrt{Rr}}{R+r}$  ;  
 $F(\phi, k)$  = elliptic integral of first kind of modulus  $k$  and amplitude  $\phi$ ; and  
 $K(k)$  = complete elliptic integral of first kind of modulus  $k$ .

Self-absorption of a hollow cylindrical source of finite thickness may be approximated along the axis of the source by the following procedure (see Fig. 37). It will be assumed (1) that the source is of uniform unit-volume activity and density, (2) that absorption occurs only within the source, (3) that scattered radiation due to the absorber will not affect the dose rate, (4) that radiation intensity and dose rate vary inversely with the square of the distance from a point source and inversely with an exponential function of absorber thickness, and (5) that the part of the source lying outside the cone,  $\phi = \tan^{-1} [r_1 / (Z_1 - L)]$ , also fulfills the foregoing assumptions. The resulting differential equation and its approximate integration are as shown in Fig. 38, where

$P$  = distance between point and element of volume;

$\rho$  = density, grams/cm<sup>3</sup>

$\mu$  = mass absorption coefficient, cm<sup>2</sup>/gram;

$V$  =  $\left( \frac{\text{total activity, curies}}{\text{volume of source, cm}^3} \right) \left( \frac{1000 \text{ millicuries}}{\text{curie}} \right) \left( \frac{\text{equivalent roentgens at 1 cm}}{\text{hour x millicurie point source}} \right)$ ;

$dv$  = element of volume of source;

and all other terms are defined as above or in Fig. 37.

$$dI = V \frac{dy}{P^2} e^{-\mu P'} \quad \text{EQ. (16)}$$

$$I = \int_{r=r_1}^{r=r_2} \int_{z=0}^{z=L} V \frac{rd\theta dz dr}{r^2 + (z_1 - z)^2} e^{-\mu \rho(r-r_1) \csc \phi} \quad \text{EQ. (17)}$$

if a three-term approximation to the exponential is employed:

$$I = 2\pi V \left[ r_2 \left( \tan^{-1} \frac{z_1}{r_2} - \tan^{-1} \frac{z_1 - L}{r_2} \right) - r_1 \left( \tan^{-1} \frac{z_1}{r_1} - \tan^{-1} \frac{z_1 - L}{r_1} \right) \right. \\ \left. + \frac{z_1 - L}{2} \ln \frac{1 + \left( \frac{r_1}{z_1 - L} \right)^2 + \frac{z_1}{2} \ln \frac{1 + \left( \frac{r_2}{z_1} \right)^2}{1 + \left( \frac{r_1}{z_1} \right)^2} \right] \\ + 2\pi V \mu \rho \left[ \left( \frac{r_2^2}{2} - r_2 r_1 \right) \left( \sinh^{-1} \frac{z_1 - L}{r_2} - \sinh^{-1} \frac{z_1}{r_2} \right) \right. \\ \left. + \frac{r_1^2}{2} \left( \sinh^{-1} \frac{z_1 - L}{r_1} - \sinh^{-1} \frac{z_1}{r_1} \right) \right. \\ \left. + \left( \frac{z_1 - L}{2} \right) \left( r_2 \sqrt{\left( \frac{z_1 - L}{r_2} \right)^2 + 1} - r_1 \sqrt{\left( \frac{z_1 - L}{r_1} \right)^2 + 1} \right) \right. \\ \left. - \frac{z_1}{2} \left( r_2 \sqrt{\left( \frac{z_1}{r_2} \right)^2 + 1} - r_1 \sqrt{\left( \frac{z_1}{r_1} \right)^2 + 1} \right) \right. \\ \left. + (z_1 - L) r_1 \ln \frac{r_1}{r_2} \left( \frac{\sqrt{\left( \frac{z_1 - L}{r_1} \right)^2 + 1} + 1}{\sqrt{\left( \frac{z_1 - L}{r_2} \right)^2 + 1} + 1} \right) \right. \\ \left. - z_1 r_1 \ln \frac{r_1}{r_2} \left( \frac{\sqrt{\left( \frac{z_1}{r_1} \right)^2 + 1} + 1}{\sqrt{\left( \frac{z_1}{r_2} \right)^2 + 1} + 1} \right) \right]$$

$$+ \pi V \mu^2 \rho^2 L \left[ \frac{r_2^2 - r_1^2}{2} - 2r_1 (r_2 - r_1) + r_1^2 \ln \frac{r_2}{r_1} \right] \quad \text{EQ. (18)}$$

for  $z_1 \geq 0$ ,  $-\frac{\pi}{2} < \tan^{-1} \frac{z_1 - L}{r_1}$ ,  $\tan^{-1} \frac{z_1 - L}{r_2} < \frac{\pi}{2}$ ;

$0 \leq \tan^{-1} \frac{z_1}{r_1}$ ,  $\tan^{-1} \frac{z_1}{r_2} < \frac{\pi}{2}$ ;  $r_1 > 0$ ,  $r_2 > 0$ ,  $r_1 \neq r_2$ .

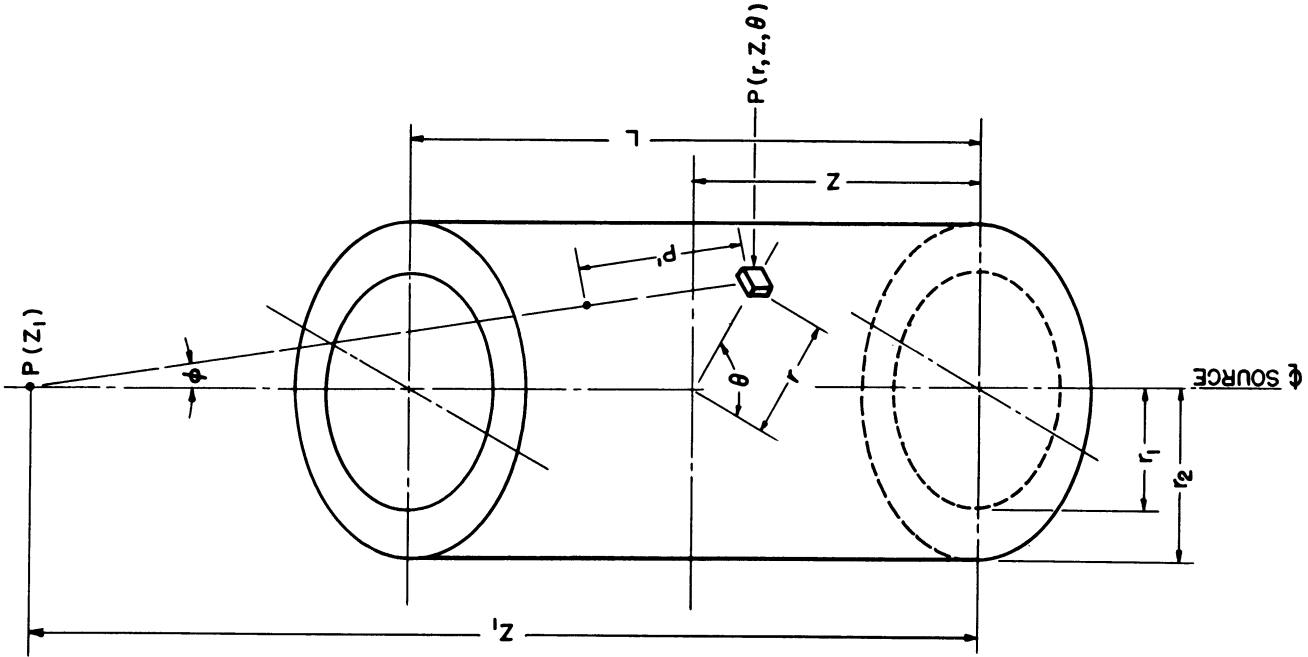


Fig. 37. Source with Finite Wall Thickness.

Fig. 38. Differential Equation and Its Integration for Source with Finite Wall Thickness. (Dosimetry Calculations)

Equations (15) and (18) were applied to both the 1000- and 10,000-curie sources. In the case of the 1000-curie source, it was simple to assume a cylinder with dimensions corresponding to the actual cobalt cylinder. In the case of the 10,000-curie source, the nest or bundle of 100 rods was assumed equivalent to a cylinder whose inside and outside diameters were the shortest and longest diametrical distances across the rod bundle. The 10,000 curies was assumed to be uniformly divided throughout this volume and the density of the assumed cylinder was taken so that its mass equalled that of the rods themselves.

Calculated and observed values of dose rate for the 10-kilocurie source of cobalt-60 are compared in Tables XIII and XIV and are plotted in Figs. 39 and 40. The calculated values were based on an assumed activity of 10,000 curies. The observed values are considerably less than the calculated values.

TABLE XIII

DOSE RATES ON AXIS OF 10-KC SOURCE

$$Z_1 - \frac{L}{2} = \text{Distance above midplane, cm; } R = 0$$

$Z_1 - \frac{L}{2}$	Calculated Rep/hr for 10,000 curies			$Z_1 - \frac{L}{2}$	Measured Rep/hr	
	Annular Source		Sheet Source		Ferrous Oxidation*	Victoreen Rate Meter
	No Absorption	With Absorption	No Absorption			
0	1,020,000	830,000	1,010,000	0	242,000 (16 Mar 53)	
6.35	910,000	747,000	928,000	2.5	249,000	
12.7	665,000	527,000	662,000	2.5	234,000	
25.4	222,000	154,000	218,000	8.9	194,000	
38.1	97,000	61,000	96,000	15.2	144,000	
63.5	-	-	32,000	20.3	-----	61,000
				21.6	74,000	-----
				22.8	-----	48,000
				25.4	-----	38,000
				26.7	42,000	-----
				38.1		16,000
				50.8		8,100
				60.8		5,000
				76.2		3,300

\* 13 Mar 53 unless noted.



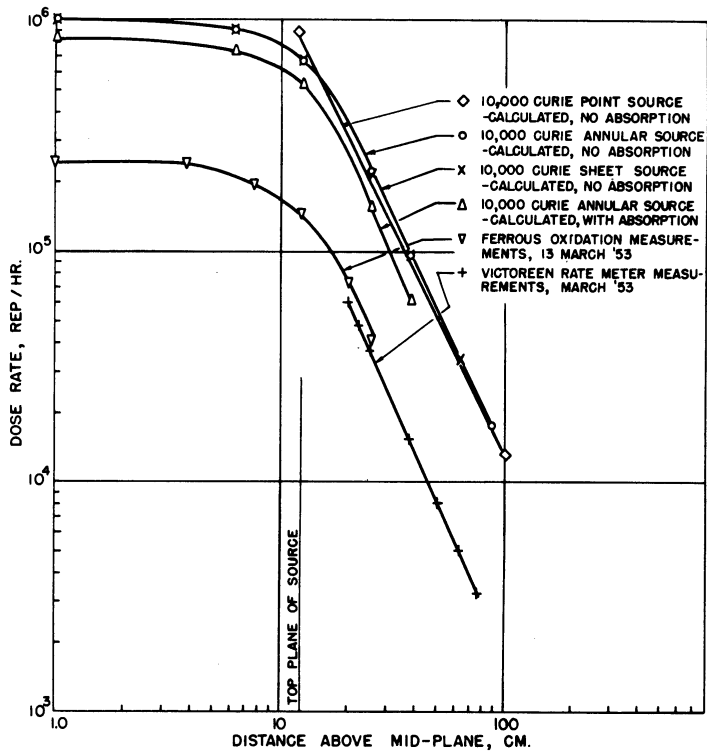


Fig. 39. Dose Rate on Axis of 10-kc

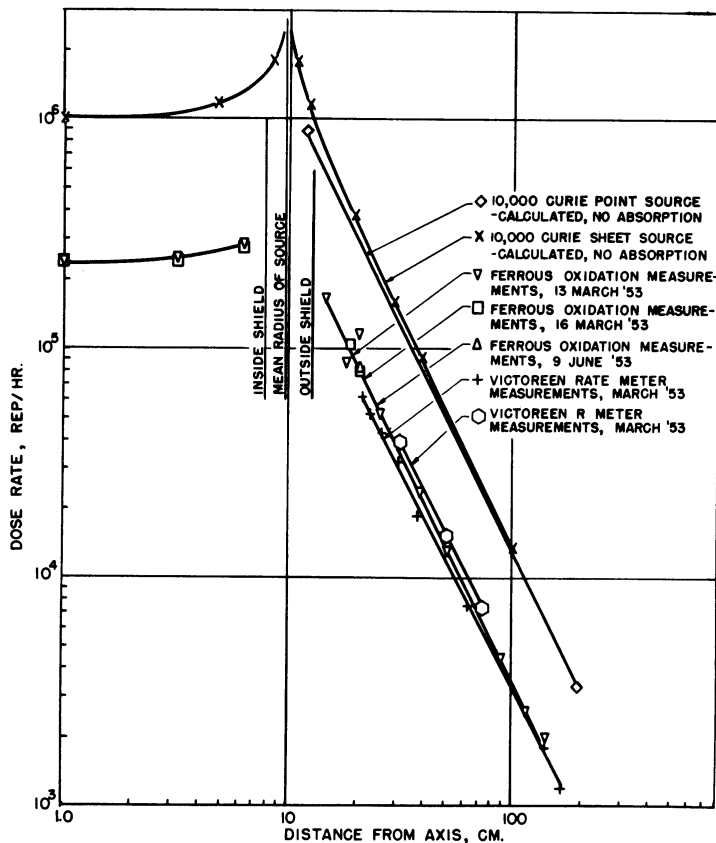


Fig. 40. Dose Rate on Mid-Plane of 10-kc Cobalt-60 Source.

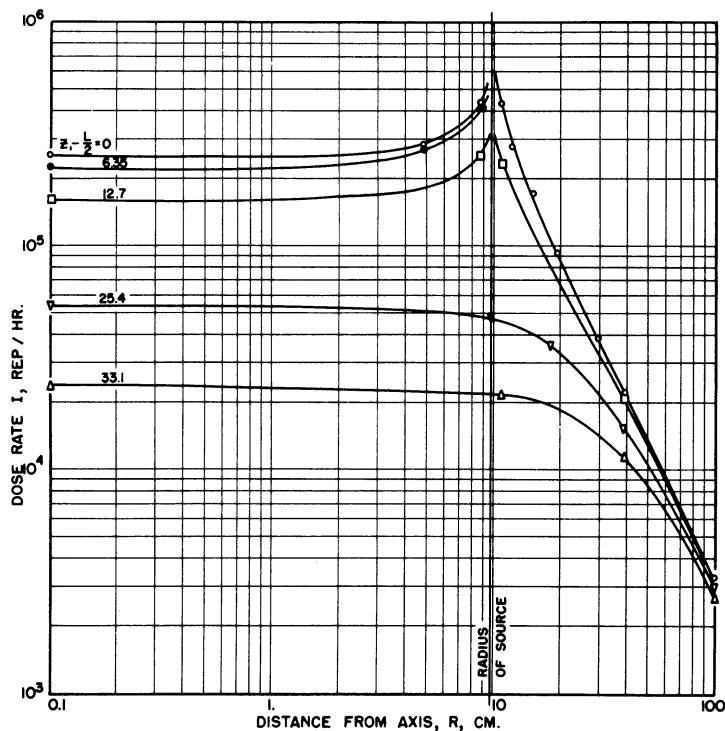


Fig. 41. Dose Rates Parallel to Mid-Plane Interpolated from Measurements-- 10-kc Source.

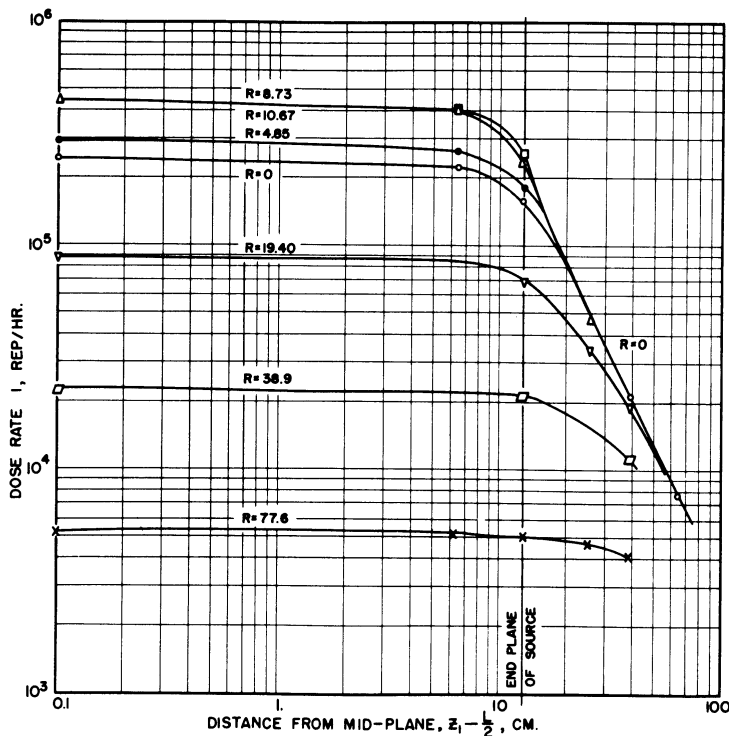


Fig. 42. Dose Rates Parallel to Axis Interpolated from Measurements-- 10-kc Source.

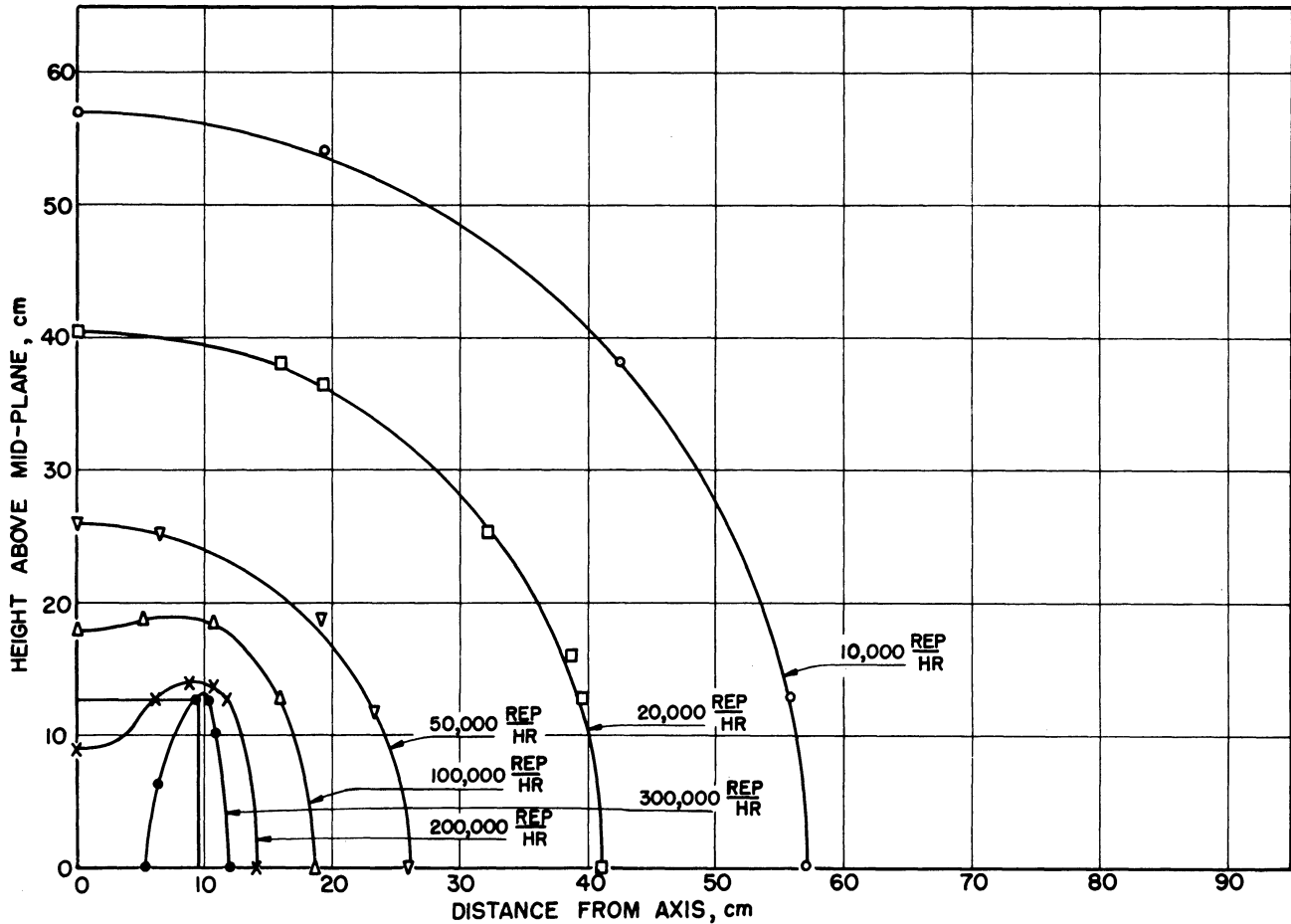


Fig. 43. Isodose Surfaces Interpolated From Measurement--10-KC Source.

For any given method of measurement the observed values are a nearly constant fraction of the calculated values. In Figs. 41, 42, and 43 appear cross plots of equation (15) when the latter is made to agree with data from the oxidation of ferrous ion. The data were taken on the midplane and on the axis in March, 1953. The source was irradiated at the Chalk River NRX reactor and was rated at 9250 curies on shipment from the Chalk River site in January, 1953. The activity computed from each means of measurement appears in Table XV. In the extreme right column of Table XV the ratio of the curies estimated from observed values of dose rate to the 9250-curie nominal value after correction of the latter value for decay appears. If self-absorption is not considered, the activity is estimated to be from 17 to 33 per cent of the nominal value. If self-absorption is considered, the activity is estimated to be from 28 to 33 per cent of the nominal value. These figures are computed from data taken both on the midplane and on the axis. No estimate of self-absorption was made on the midplane however.

Calculated and observed values of dose rate and curies for the 1-kilocurie source are compared in Table XVI and in Fig. 44. The 1-kilocurie source was irradiated at Brookhaven National Laboratory and was assumed to have a nominal activity of 1000 curies in July, 1951. The activity computed from each means of

TABLE XIV

## DOSE RATES ON MIDPLANE OF 10-KC SOURCE

$$Z_1 = \frac{L}{2} = 12.7 \text{ cm}; \quad R = \text{Distance from Axis, cm.}$$

R	Rep/hr for Sheet Source; No Absorption Calculation for 10,000 curies	R	Rep/hr for Ferrous Oxidation		R	Rep/hr for Victoreen Meters	
			13 Mar 53	16 Mar 53		Rate Meter	R- Meter
0	1,000,000.	0	249,000.	242,000.	21.3	61,000.	
		0	234,000.	-			
4.85	1,120,000.	3.30	243,000.	250,000.	23.1	52,000.	
8.70	1,800,000.	3.30	248,000.	244,000.	26.2	43,000.	
9.70	$\infty$	6.30	281,000.	280,000.	30.8	32,000.	
10.7	1,800,000.	6.30	274,000.	292,000.	31.8	-----	40,000.
12.0	1,150,000.	14.7	168,000.	-	38.4	18,500.	-----
19.4	379,000.	18.1	86,000.	102,000.	51.0	-----	15,500.
29.1	160,000.	20.6	115,000.	79,500.	64.0	7,500.	-----
38.8	92,000.	25.7	52,000.		73.9	-----	7,500.
100.	14,000.	38.4	24,000.		140.	1,800.	
		51.0	13,000.		165	1,200.	
		89.1	4,400.				
		114.8	2,600.				
		140.0	2,000.				
		20.6		82,000			

9 June 53

TABLE XV

ESTIMATES OF ACTIVITIES FROM MEASUREMENTS  
OF DOSE RATES

Source	Measurements		Date	Estimate of Activity, Curies*			Mean Value Divided By Decayed Nominal Value
	Where Taken	Method		Maximum	Minimum	Arithmetic Mean	
10-KC	Axis	Ferrous Oxidation	Mar 53	2500	2100	2300	0.26
				3100A	2800A	2950A	0.33A
		Victoreen Rate Meter	Mar 53	1700	1400	1550	0.17
	2600A			2500A	2550A	0.28A	
	Mid-plane	Ferrous Oxidation	Mar 53	2600	2200	2400	0.27
				2500	2000	2250	0.25
Victoreen R Meter		Mar 53	3000	2900	2950	0.33	
1-KC	Axis	Ferrous Oxidation	May 52			140	0.16
						180A	0.20A
			May 53			130	0.16
					170A	0.21A	
	Victoreen Rate Meter	Feb 53	150	110	130	0.16	
			190A	150A	170A	0.20A	
Victoreen R Meter	May 52			170	0.19		
				230A	0.26A		
		May 53			160	0.20	
				210A	0.26A		

\* A after value indicates self-absorption was considered.

TABLE XVI

DOSE RATES ON AXIS OF 1-KC SOURCE

$Z_1 - \frac{L}{2}$  = Distance above midplane, cm

R = 0

r = 2.493 cm

Calculated Rep/hr for 1,000 curies				Measured Rep/hr			
$Z_1 - \frac{L}{2}$	Annular Source		Sheet Source	$Z_1 - \frac{L}{2}$	Ferrous Oxidation	Victoreen Rate Meter	Victoreen R-Meter
	No Absorption	With Absorption	No Absorption		Feb 53		
0	442,000.	341,000.	460,000.	0	62,300. } May, 52		79,000. } May, 52
8.75	429,000.	336,000.	450,000.	0	57,200. } May, 53		72,000. } May, 53
17.5	232,000.	184,000.	240,000.	1.3		51,600.	
35.0	-----	-----	15,200.	3.8		52,800.	
87.5	-----	-----	1,900.	6.3		54,000.	
				8.9		55,800.	
				11.4		57,500.	
				14.0		46,800.	
				16.5		19,200.	
				19.0		9,300.	
				21.6		5,150.	
				24.2		3,240.	
				26.7		1,860.	
				29.2		1,320.	
				34.2		490.	

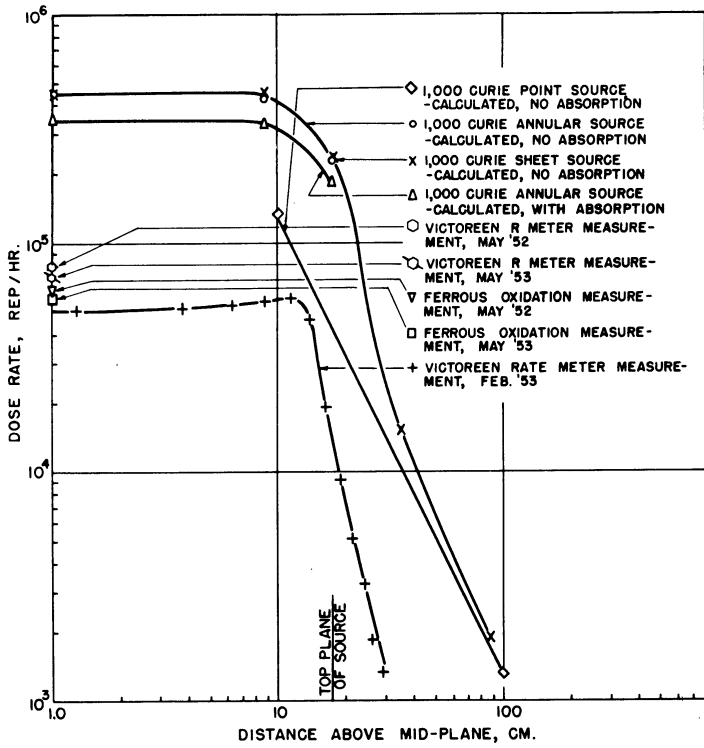


Fig. 44. Dose Rate on Axis of 1-kc Cobalt-60 Source.

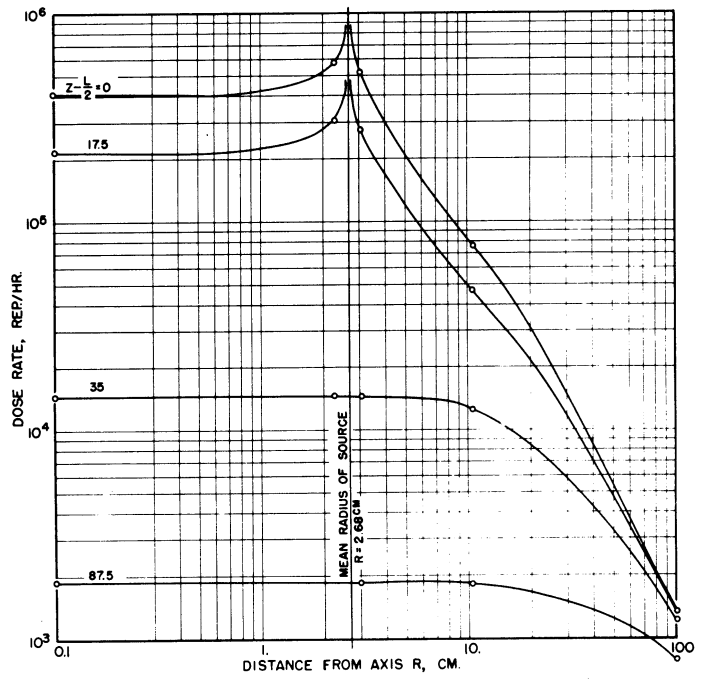


Fig. 45. Calculated Dose Rates Parallel to Mid-Plane--1-kc Source.

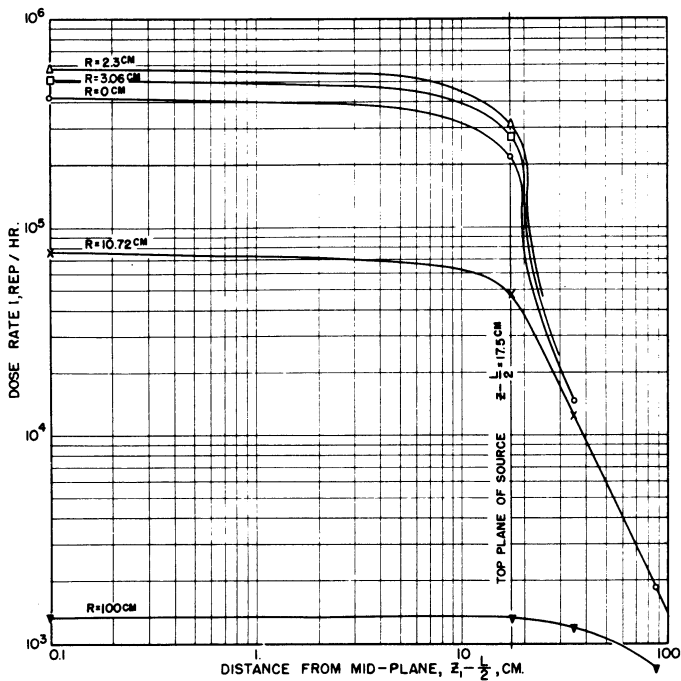


Fig. 46. Calculated Dose Rates Parallel to Axis--1-kc Source.

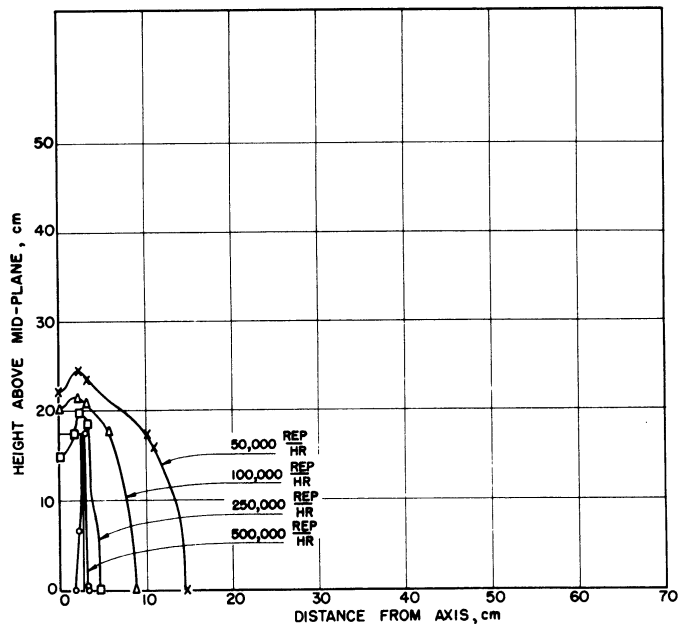


Fig. 47. Calculated Isodose Surfaces--1-kc Source.

measurement is given in Table XV. The ratios of observed to decayed nominal curies appear in the right column. If self-absorption is not considered, the activity is estimated to be from 16 to 20 per cent of the nominal value. If self-absorption is considered, the activity is estimated to be from 20 to 26 per cent of the nominal value. These figures are computed from data taken on the axis only, since it was not possible to make measurements external to the source. However, it was desired to compare the dose rates predicted by equation (15) for the 1-kilocurie source with those predicted for the 10-kilocurie source in order to observe differences caused by the different geometrical proportions of the two sources. Consequently Figs. 45, 46, and 47 are presented to portray the dependence of dose rate on position in the neighborhood of the 1-kilocurie source. The data for these figures were computed on the assumption that the source actually contained 1000 curies.

Judging from the above results, there appears to be about a threefold discrepancy between the curies in the 10-kilocurie source as estimated from ionization measurements and as calculated from neutron absorption. The comparisons for the 1-kilocurie source are not so meaningful, since no firm estimate of the activity of the source was supplied by Brookhaven National Laboratory.

The errors in the methods of calculation summarized in equations (13), (15), and (18) probably arise chiefly from the simplifying assumptions made. The assumption that the source has no thickness is evidently justified by the agreement of values calculated on this assumption with those in which the thickness of the source is considered (see Figs. 39 and 44). The results in Tables XII and XVI show that absorption is not negligible. However, in Figs. 39 and 40 it can be seen that the plots from data and from equations (13), (15), and (18) differ by an approximately constant factor between any pair of curves. This result is interpreted to mean that equations (13) and (15) may be used within limits to predict the distribution of dose rates without consideration of self-absorption, but that accurate prediction of dose rates requires consideration of self-absorption.

The 1-kilocurie source is evidently not of uniform activity throughout its whole volume. This conclusion was reached from a study of Fig. 44. Note that the measured dose rates in the 1-kilocurie source do not vary with distance along the axis in the manner predicted by the calculated curves. The depression near the midplane is probably caused by lower unit activity inside the source in this region, which in turn is probably caused by failure of neutrons to penetrate to the interior of the source near the midplane as abundantly as near the ends.<sup>8</sup> The other assumptions introduced are thought to be reasonably acceptable, although equation (18) converges much more slowly as  $Z_1$  is increased. The value of 13.5 equivalent roentgens/hour at 1 cm per millicurie point source of cobalt-60 was taken from the work of Marinelli, Quimby, and Hine<sup>7</sup>, and was assumed to be correct within our experimental error.

Although there were some differences between the chemical and physical dosimetry measurements, they were not sufficiently large to account for the factor of three or four between the nominal activities of the sources and those which result from the dosimetry measurements themselves. In an attempt to understand this discrepancy, attention was turned to the calculations of activity of a cobalt sample which is subjected to neutron radiation. Neutron absorption calculations are generally used to predict activities of irradiated samples.

### 3. Consideration of Neutron Activation Equations

Exact computation of the absolute amount of an isotope produced during neutron bombardment is dependent on precise knowledge of several factors. The relationship commonly used for such computations is:

$$C = \frac{0.6\phi\sigma Mr}{3.7 \times 10^{10} A} \left(1 - e^{-0.693t/T}\right), \quad (19)$$

where

C = total activity of isotope produced, curies;

$\phi$  = thermal neutron flux, particles/cm<sup>2</sup>-sec;

$\sigma$  = activation cross section, barns;

A = atomic weight of irradiated isotope, grams;

t = length of irradiation, arbitrary time units;

T = half-life of isotope produced, same time units;

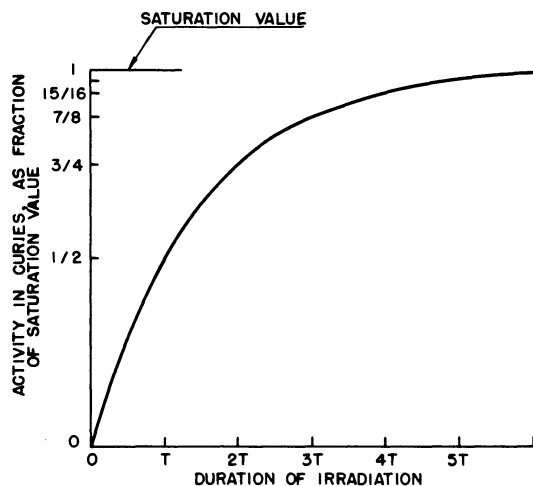
M = mass of element present, grams; and

r = fraction of irradiated isotope present.

The factors which might contribute to a serious error in the computed value of C will be considered. Of these factors, A is known accurately in most cases and t, the length of irradiation, may be measured as accurately as desired, the limiting consideration being the length of time required for insertion and removal of the samples.

Half-life may in general be measured as accurately as desired. Exceptions to this statement must be made for extremely long- and extremely short-lived isotopes. The buildup of activity under bombardment is exponential (Fig. 48). The plateau or saturation value of activity is simply the coefficient of the





T = HALF LIFE OF ISOTOPE RESULTING FROM IRRADIATION

Fig. 48. Increase in Activity During Neutron Irradiation.

bracketed term in equation (19). It can readily be seen that in the case of short-lived isotopes, i.e., for  $T \ll t$ , the exponential term is of negligible importance, and that errors in the determination of  $T$  have little effect on the computed value of  $C$  at the time of removal. For long-lived isotopes, however, the exponential term becomes:

$$1 - e^{-0.693t/T} \approx 1 - (1 - 0.693t/T) = 0.693t/T \quad (20)$$

and errors in the determination of  $T$  have a direct effect on the computed value of  $C$ .

The case of cobalt-60, with a half-life of the order of 5 years and irradiations of the order of months, is still on the nearly linear portion of the activation curve. However, recent determinations of the half-life of cobalt-60 are within 5 per cent of one another. Differences of this magnitude, although serious in many cases, cannot be considered as significant contributions to the discrepancy under discussion.

The accurate determination of the remaining factors (neutron flux density,  $\phi$ , and activation cross section,  $\sigma$ ) is not as straightforward as those previously discussed. There are several reasons for this difficulty.

First, the determinations as commonly made are interdependent. To measure  $\phi$  using an isotope of known  $\sigma$ , or to measure  $\sigma$  using a neutron source of known  $\phi$  is relatively simple. However, the calibration of the quantity to be used as a reference is more complex. A closer examination of these measurements might uncover a factor partially responsible for the observed discrepancy, but it seems unlikely that such a factor could explain a threefold error.

Second, in any practical case the observed neutron flux is not completely thermalized but contains a finite range of energies higher than thermal. The activation cross section is a function of energy. Therefore it is necessary in principle to know the neutron spectrum and the cross section as a function of energy. In general, however, the cross section at nonthermal energies is vanishingly small, with the exception of occasional resonance energies. Such activations could contribute a source of error to activity computations, but the computed value would then be too low rather than the observed high value.

Third, local neutron depression caused by the insertion of irradiation samples of high cross section must be considered. It is this consideration which seems the most probable source of the observed discrepancy. Recent work of Levin and Hughes<sup>6</sup> indicates that this correction is of the order of magnitude of the observed discrepancy. Therefore, at this writing it is believed that the activity of a source calculated from neutron absorption, such as the 9250 curies mentioned above for our source, may be several times too high because of the depression of the neutron flux in the vicinity of the cobalt.

#### E. DOSE RATE WITHIN A CYLINDRICAL PRESSURE REACTOR

All the foregoing calculations and dosimetry measurements are for points in air lying at different distances from the sources. In the experiments reported on the polymerization of ethylene, however, the reaction took place inside a stainless-steel pressure vessel. A series of calculations was therefore made on the intensity of radiation inside the pressure vessel, taking into account the absorption of gamma radiation by the walls of the vessel (see Fig. 49).

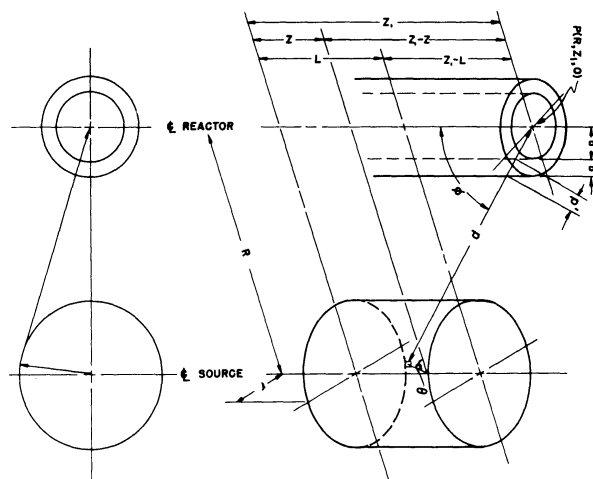


Fig. 49. Gamma Source and Pressure Reactor Shown Diagrammatically.

It is assumed (1) that the source of gamma radiation is a cylindrical sheet of no thickness and of uniform activity per unit area, (2) that the source is transparent to its own radiation, (3) that the dose rate varies inversely with the square of the distance and inversely with an exponential function of absorber thickness, and (4) that no absorption occurs inside the reactor.

Let the terminology be defined as in Fig. 49 and as follows:

$I$  = dose rate at  $P(R,Z)$ , rep/hr;

$\alpha$  =  $\left( \frac{\text{activity of source, curies}}{\text{area of source, cm}^2} \right) \left( 1000 \frac{\text{millicuries}}{\text{curie}} \right) \left( \frac{\text{equivalent roentgens at 1 cm}}{\text{hr x millicurie point source}} \right)$

$\mu$  = absorption coefficient,  $\text{cm}^2/\text{gram}$ ;

$A$  = area of source,  $\text{cm}^2$ ;

$P$  = distance from  $dA$  at  $P(r,Z,\theta)$  to  $P(R,Z)$ ;

$P'$  = distance through bomb wall,  $\text{cm}$ ;

$K(k)$  = complete elliptic integral of first kind of modulus  $k$ ;

$k_1$  =  $\frac{2\sqrt{Rr}}{R+r}$  ;

$\rho$  = density of bomb wall,  $\text{grams}/\text{cm}^3$ ; and

$X$  = distance in Fig. 50 from source to point at which  $I$  is measured.

See Fig. 50.

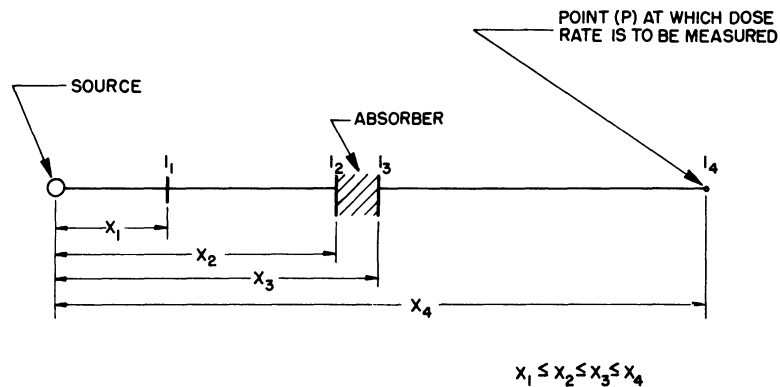


Fig. 50. Attenuation of Gamma Radiation by Absorption and Distance.

From assumption (3) above the following equation may be written:

$$dI = -\mu I dX - \frac{\partial}{\partial X} I dX \quad (21)$$

Integration and substitution of limits yields the expressions:

$$I_2 = \left( \frac{X_1}{X_2} \right)^2 I_1 \quad (22)$$

$$I_4 = \left( \frac{X_3}{X_4} \right)^2 I_3 \quad (23)$$

$$\frac{I_3}{I_2} = \left( \frac{X_2}{X_3} \right)^2 e^{-\mu(X_3 - X_2)} \quad (24)$$

Combining equations (22), (23), and (24) results in the expression:

$$I_4 = \left( \frac{X_1}{X_4} \right)^2 I_1 e^{-\mu(X_3 - X_2)} \quad (25)$$

From equation (25) we may deduce that the location of an absorber is immaterial as long as it is between the source and point P. Only the thickness of the absorber need be considered.

Now the equations may be written for dose rate on the axis of the bomb (see Fig. 49):

$$P' = b \csc \phi \quad , \quad (26)$$

$$\csc \phi = \sqrt{\frac{R^2 + r^2 - 2Rr \cos \theta + (Z_1 - Z)^2}{R^2 + r^2 - 2Rr \cos \theta}} \quad , \quad (27)$$

and

$$dI = \alpha_p \frac{dA}{2} e^{-\mu P'} \quad (28)$$

Equation (28) must be integrated over the entire source, as shown by equation (29). A three-term approximation to the exponential is employed.

$$\begin{aligned}
I = & \int_{Z=0}^{Z=L} \int_{\theta=0}^{\theta=\pi} \alpha r d\theta dZ \left\{ \frac{1}{R^2+r^2-2Rr \cos \theta + (Z_1-Z)^2} \right. \\
& - \frac{\mu b \rho}{\sqrt{R^2+r^2-2Rr \cos \theta + (Z_1-Z)^2} \sqrt{R^2+r^2-2Rr \cos \theta}} \\
& \left. + \frac{\mu^2 b^2 \rho^2}{2!} \frac{1}{(R^2+r^2-2Rr \cos \theta)} - \dots \right\} \quad (29)
\end{aligned}$$

The first term within braces has been integrated above, and presented as equation (15). Integration of equation (29) yields equation (30).

$$\begin{aligned}
I = & \frac{2\alpha\pi r}{R+r} \left[ F\left(\tan^{-1} \frac{Z_1}{|r-R|}, k_1\right) - F\left(\tan^{-1} \frac{Z_1-L}{|r-R|}, k_1\right) \right] \\
& - 2\alpha\mu b \rho \sqrt{\frac{r}{R}} \int_{Z_1-Z=Z_1-L}^{Z_1-Z=Z_1} \frac{K(k) dk}{1-(k/k_1)^2} + \frac{\alpha\pi r L \mu^2 b^2 \rho^2}{R^2-r^2}, \quad (30)
\end{aligned}$$

where

$$k = k_1 \frac{(Z_1-Z)}{\sqrt{(R-r)^2 + (Z_1-Z)^2}}$$

Equation (30) holds for

$$Z_1 \geq L > 0, \quad 0 < \tan^{-1} \frac{Z_1-L}{|r-R|}, \quad \tan^{-1} \frac{Z_1}{|r-R|} < \frac{\pi}{2}, \quad R \neq r \neq 0$$

If, however,

$$L \geq Z_1 > 0, \quad R \neq r \neq 0, \quad ,$$

then

$$\begin{aligned}
I = & 2 \frac{\alpha\pi r}{R+r} \left[ F\left(\tan^{-1} \frac{Z_1}{|r-R|}, k_1\right) - F\left(\tan^{-1} \frac{Z_1-L}{|r-R|}, k_1\right) \right] \\
& - 2\alpha\mu b \rho \sqrt{\frac{r}{R}} \left[ \int_{Z_1-Z=Z_1-L}^{Z_1-Z=0} \frac{K(k) dk}{1-(k/k_1)^2} + \int_{Z_1-Z=0}^{Z_1-Z=Z_1} \frac{K(k) dk}{1-(k/k_1)^2} \right] \quad (31) \\
& + \frac{\alpha\pi r L \mu^2 b^2 \rho^2}{R^2-r^2} - \dots
\end{aligned}$$

Since  $k$ , defined above, is the modulus of an elliptic integral of the first kind,

$$1 \geq k \geq 0 \quad .$$

Consequently, for equation (31) the following definitions are employed.

$$k = k_1 \frac{(Z_1 - Z)}{\sqrt{(R-r)^2 + (Z_1 - Z)^2}} \quad \text{for } Z_1 \geq Z$$

$$k = k_1 \frac{(Z - Z_1)}{\sqrt{(R-r)^2 + (Z_1 - Z)^2}} \quad \text{for } Z > Z_1$$

If

$$Z_1 \geq L \geq 0, R=0$$

then

$$I = 2\alpha\pi \left( \tan^{-1} \frac{Z_1}{r} - \tan^{-1} \frac{(Z_1 - L)}{r} \right) - 2\alpha\mu b\rho\pi \ln \left( \frac{Z_1 + \sqrt{r^2 + Z_1^2}}{(Z_1 - L) + \sqrt{r^2 + (Z_1 - L)^2}} \right) + \frac{\alpha\pi L\mu^2 b^2 \rho^2}{r} - \dots \quad , \quad (32)$$

where

$$0 \leq \tan^{-1} \left( \frac{Z_1}{r} \right), \tan^{-1} \left( \frac{Z_1 - L}{r} \right) < \pi/2$$

If, however,

$$L \geq Z_1 \geq 0, R=0,$$

then

$$I = 2\alpha\pi \left[ \tan^{-1} \left( \frac{Z_1}{r} \right) + \tan^{-1} \left( \frac{L - Z_1}{r} \right) \right] - 2\alpha\mu b\rho\pi \ln \left\{ \frac{\left[ (L - Z_1) + \sqrt{r^2 + (L - Z_1)^2} \right] \left[ Z_1 + \sqrt{r^2 + Z_1^2} \right]}{r^2} \right\} + \frac{\alpha\pi L\mu^2 b^2 \rho^2}{r} - \dots \quad , \quad (33)$$

where

$$0 < \tan^{-1}\left(\frac{Z_1}{r}\right), \tan^{-1}\left(\frac{L-Z_1}{r}\right) < \pi/2$$

In equations (30) and (31) terms of the form:

$$\int \frac{K(k)dk}{1-(k/k_1)^2}$$

may be integrated graphically.

#### F. EQUIPMENT CHANGES

A number of additions to and modifications of the equipment in the laboratory have been made during the past several months. These are as follows:

Some special heaters were designed and built to maintain the stainless-steel reactor at elevated temperatures. The heaters were designed to be added to or removed from the reactor readily and to absorb a minimum of gamma radiation. Chromel-A resistance wire previously wound around a 1/8-inch arbor was wound around porcelain tubes. The turns were insulated from each other by winding asbestos rope soaked in water glass between turns. An insulating jacket of asbestos paper and a protective jacket of steel shim stock were applied over each element. A photograph of the heaters appears in Fig. 51, and details of construction appear in Figs. 52 and 53.

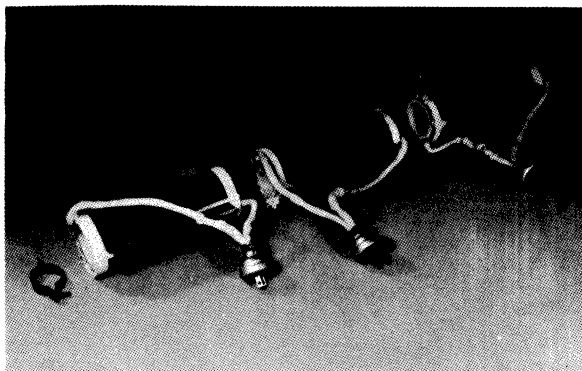


Fig. 51. Heaters for Pressure Reactor.

A steel rack was designed and built for the purpose of positioning the stainless-steel reactor approximately symmetrically with respect to the 10-kilo-curie source; see Figs. 54 and 55 for details. Extension legs (Fig. 56) permit use of the rack to hold the reactor on the axis of the source. The new steel

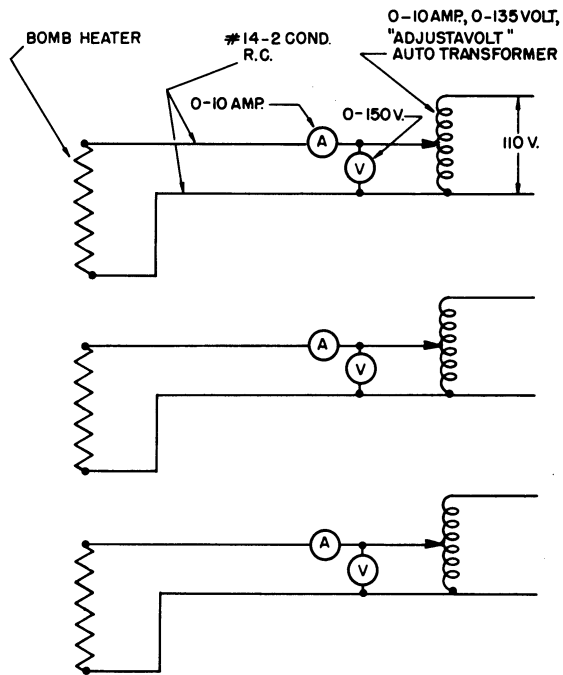


Fig. 52. Wiring Diagram for Heaters for Pressure Reactor.

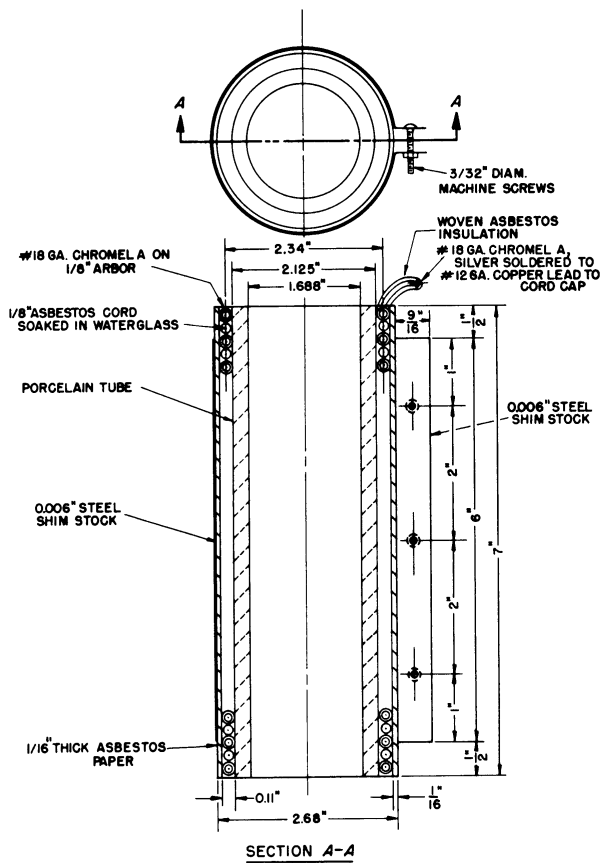


Fig. 53. Details of Heaters for Pressure Reactor.

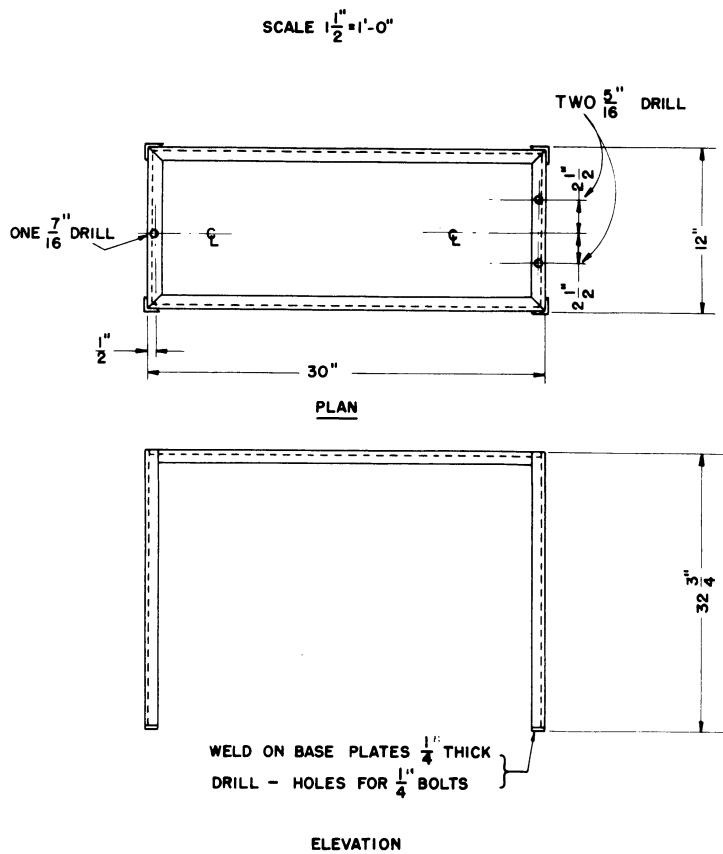


Fig. 54. Rack for Pressure Reactors.





Fig. 55. Pressure Reactor in Rack and Connected to High Pressure Gas Cylinder.



Fig. 56. Rack for Pressure Reactor.

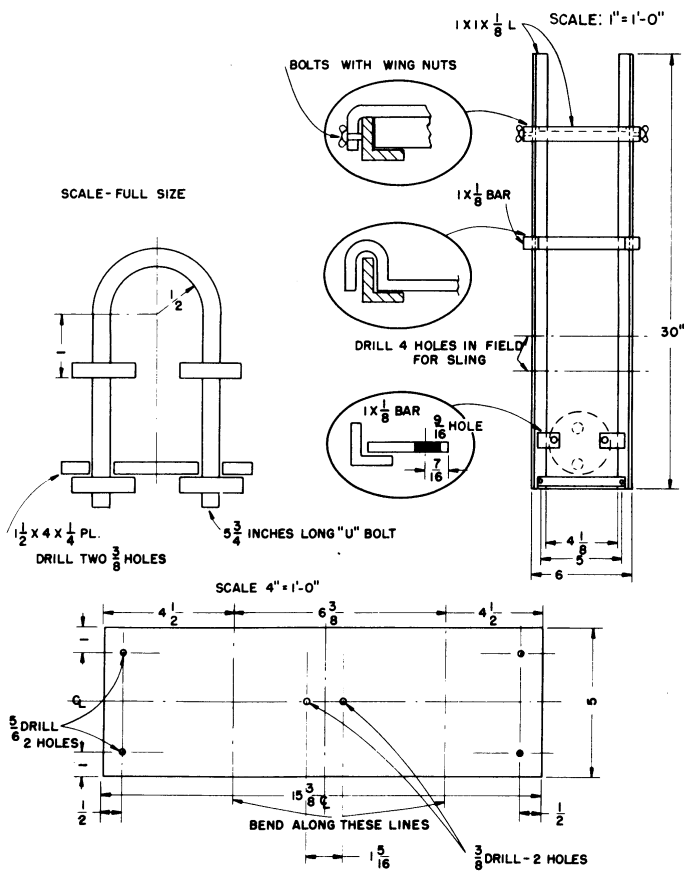


Fig. 57. Sling for Pressure Reactor.

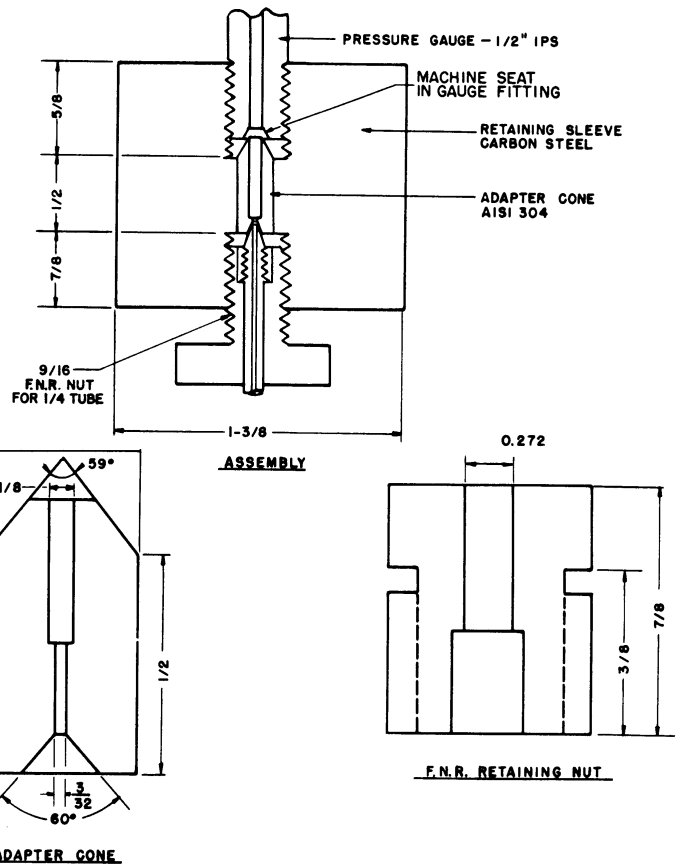


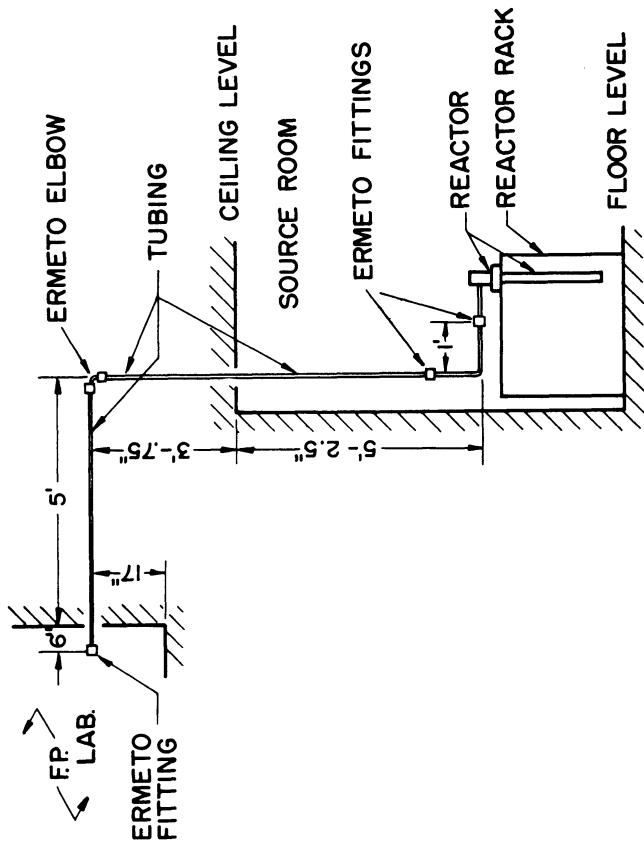
Fig. 58. Cone Joint to Iron Pipe Thread Adapter.

rack was designed to accommodate the sling (Figs. 56 and 57) previously constructed for the purpose of supporting the reactor with its attached tubing in the 1-kilocurie source.

A special connection was constructed to permit attaching a compression tubing fitting to a pressure gauge having an iron-pipe-size thread. The details are given in Fig. 58. The pressure gauge fitting was machined out to provide a cone seat to match the standard cone on the end of the tubing. This kind of joint was used to provide a better seal than was thought to be possible by the use of tapered pipe threads.

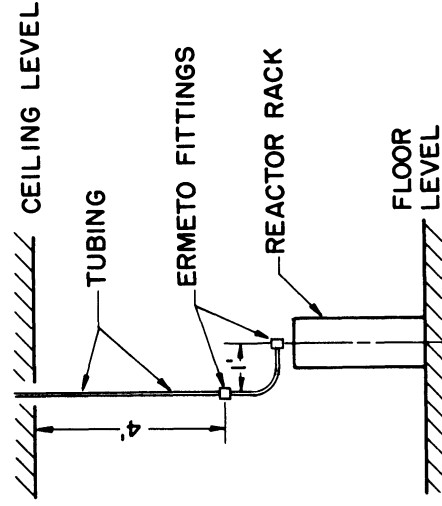
An access opening was provided during the construction of the shielding for the 10-kilocurie source; see Figs. 59 and 60. Electrical leads and aluminum tubing lines were placed in this opening to permit the operation of the pressure reactor remotely from the second floor of the laboratory. Two copper leads were also carried through this opening to connect a thermocouple cold junction in the vault with a potentiometer on the second floor. Assembly of the screwed compression joints for the aluminum tubing was accomplished by means of specially constructed socket wrenches (Fig. 61). Two wrenches were required, one to be inserted from each leg of the right-angled access opening and over the length of tubing extending out from the tubing ell. The wrenches were constructed by brazing spark-plug wrenches to the ends of pieces of electrical conduit of appropriate diameter. The socket was then turned by means of a pipe wrench. A special wooden holder was devised in order to protect and support glass tubing introduced into the same opening with the electrical leads and aluminum tubing.

A modified form of the original glass chlorination reactor has been designed and constructed for use with the 1-kilocurie cobalt-60 source. This equipment is illustrated in Figs. 62 and 63. The use of concentric tubes joined at the top by means of ground joints facilitates cleaning of the reactor and at the same time assures a tighter seal for the gaseous contents than the earlier design afforded. In runs where a large heat of reaction is not anticipated, cooling may be done with water. The water is in turn cooled by recycling through a chamber containing ice frozen around a can containing a mixture of chloroform, carbon tetrachloride, and dry ice. If a large heat of reaction is expected, the water may be replaced with methyl alcohol cooled well below the freezing point of water. A knife-type heater has also been installed, actuated by means of a double-throw switch on the temperature controller, in order to provide better temperature control.

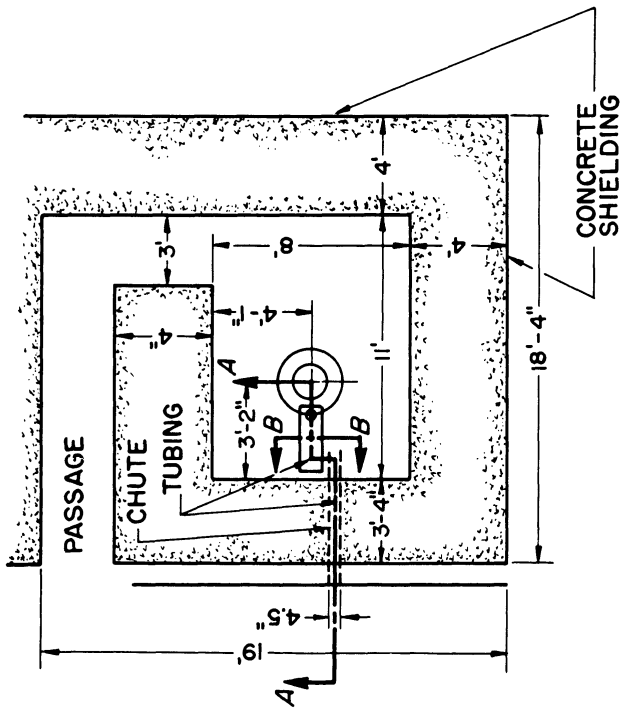


TUBING AS SEEN IN POSITION A-A

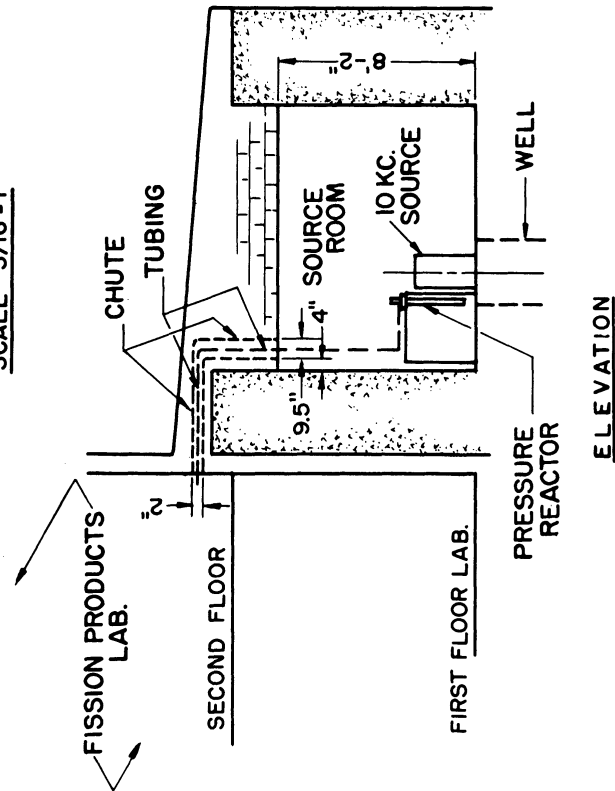
SCALE - 3/8"=1'



AS SEEN IN B-B



PLAN  
SCALE - 3/16"=1'



ELEVATION

Fig. 59. Location of Tubing Between Fission Products Laboratory and 10-ke Source.

Fig. 60. Details of Tubing Shown in Figure 59.

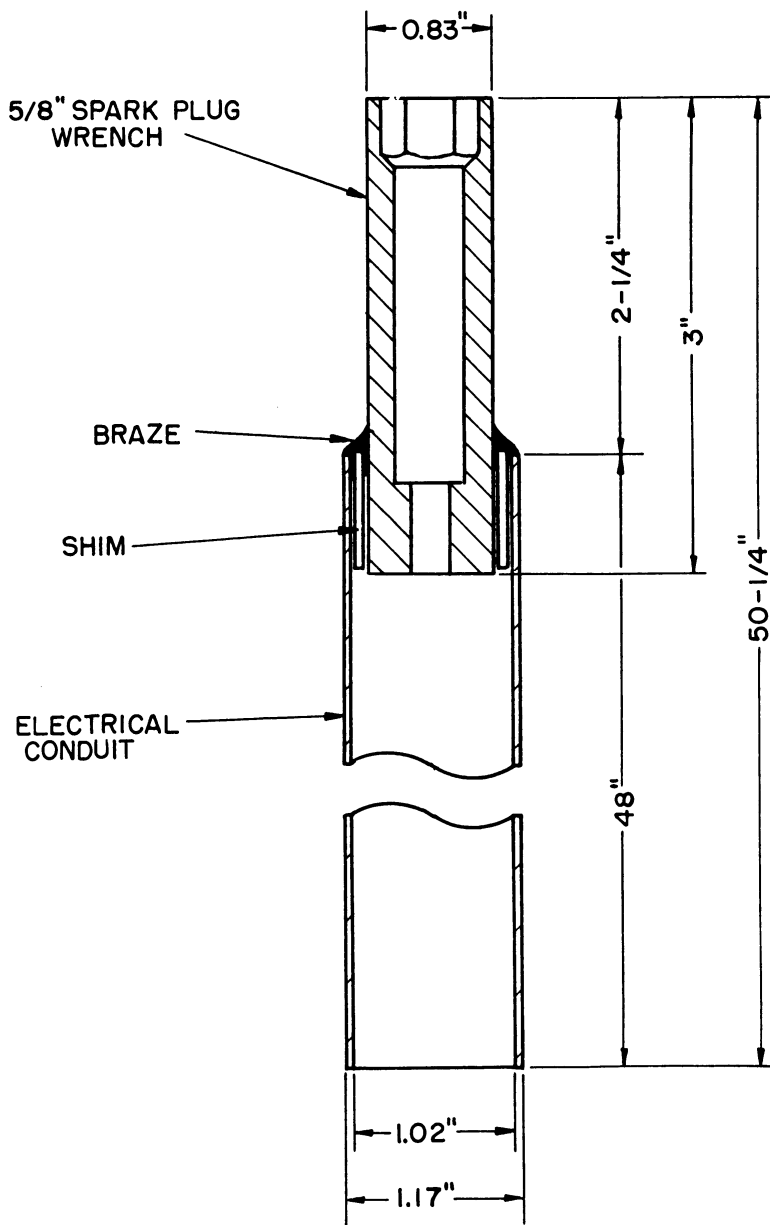


Fig. 61. Socket Wrench Brazed to End of Electrical Conduit Used for Installing Aluminum Tubing for 10-kc Source.



Fig. 62. Glass Apparatus Used in Chlorination Runs.

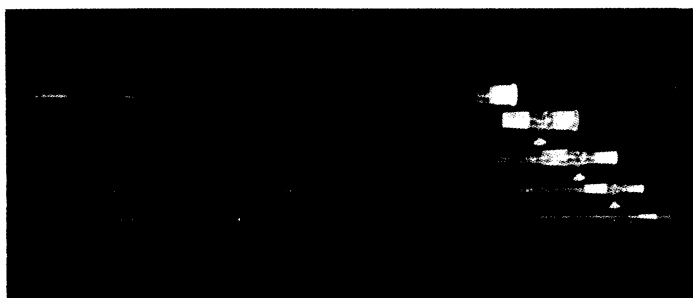


Fig. 63. Glass Apparatus Used in Chlorination Runs.

## G. FUTURE WORK

It is expected that the work in the near future will concentrate on the following objectives: (1) Determine the conditions that cause ethylene to polymerize (and also not to polymerize) under the influence of gamma radiation. (2) Analyze more completely the products produced by irradiating ethylene. (3) Continue studies on the analysis of products from the chlorination of toluene. (4) Chlorinate other hydrocarbons. (5) Study the kinetics in the chlorination of benzene under gamma radiation. (6) Perhaps try some partial oxidations of olefins and aromatics and also some nitrations.

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Progress Report No. 6

UTILIZATION OF THE GROSS FISSION PRODUCTS

The Effect of Gamma Radiation on Chemical Reactions

J. J. Martin  
L. C. Anderson  
D. E. Harmer  
J. G. Lewis  
F. Bashore

R. A. Carstens  
C. E. Eckfield  
J. P. Holmes  
R. L. Kinney  
R. L. Klemm



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PART II. SUBPROJECT M943-4, THE EFFECT OF  
RADIATION ON CHEMICAL REACTIONS

Personnel:

Subproject Supervisors: Joseph J. Martin, Associate Professor of Chemical and Metallurgical Engineering; and Leigh C. Anderson, Professor and Chairman of the Department of Chemistry.

Senior Research Assistants: David E. Harmer and John G. Lewis.

Assistants in Research: F. Bashore, R. Carstens, C. Eckfield, J. Holmes, R. Kinney, R. Klemm.

A. INTRODUCTION

Since the last report the efforts of this group have been concentrated on studying the effects of gamma radiation on two types of chemical reactions: (1) the polymerization of ethylene and other gases at high pressures; and (2) the chlorination of aromatic hydrocarbons. In the case of the ethylene polymerization, considerable amounts of ethylene polymer were produced as a powder and then formed, by heating under pressure, into sheets that could be subjected to physical testing. In the case of chlorination, major interest centered on producing and analyzing the addition product of chlorine and toluene. A large amount of this material was made and some of it was sent to the Department of Agriculture for testing as a possible insecticide. The following sections of the report discuss the details of these reactions, both of which are of sufficient importance to be considered seriously for patenting.

B. POLYMERIZATION OF ETHYLENE BY MEANS OF GAMMA RADIATION

The erratic nature of the results observed when attempting to polymerize ethylene by exposure to gamma radiation has been mentioned previously (see Progress Report 5.<sup>2</sup> In the earlier work some attempt was made to correlate the observed rates of polymerization with oxygen content in the monomeric ethylene

and with the order of the run made. Neither of these approaches yielded satisfactory results.

Other ideas were therefore advanced in order to account for the erratic polymerization rates observed. It was suggested that some polyethylene might have been present in the storage cylinders and might have been introduced during charging of the reactant to the pressure reactor; however, the conditions usually required for the polymerization of ethylene were unlikely to have prevailed in the storage cylinder.

Another possibility was that some unknown inhibitor or some unknown promotor was present sporadically. The substances most likely to fall into these categories are impurities in the ethylene, gases from the air, materials used in cleaning the reaction equipment, and the reaction equipment itself. The last possibility was tested tentatively by allowing polymer to accumulate on the walls of the reactor and then checking the rate of reaction in a subsequent run; no influence on the rate of reaction was noted. The influence of various solvents and other materials thought possibly to have been present accidentally in the successful runs was checked by adding the following materials successively to separate batches of the reactant ethylene: acetone, acetaldehyde, air and acetone, air and water, carbon dioxide, sulfur dioxide, and aluminum chloride. Sulfur dioxide and aluminum chloride were the only additives producing detectable effects, and the latter material produced a tar instead of the white powder sought. The addition of sulfur dioxide resulted in the production of a white powder at relatively high rates of reaction (see Fig. 4); however, this powder proved to have a sulfur content rather close to that of the equimolar addition product of sulfur dioxide and ethylene. Matthew and Elder<sup>10</sup> and Snow and Frey<sup>12</sup> have reported similar reactions between sulfur dioxide and olefins under ultraviolet light.

Next, the composition of the reactant gases was examined in some detail. The ethylene was analyzed (see Tables 4 and 5) immediately on removal from the storage cylinders, after charging to the reactor but before irradiation, and on removal from the reactor after irradiation. Components determined were "soluble in bromine," carbon dioxide, oxygen, carbon monoxide, paraffin hydrocarbons, and nitrogen. Higher olefins and acetylenic compounds were not detected separately by the methods used.

From the results of the above experiments it was concluded that an inhibitor could have been present and responsible for the erratic yields observed, but the inhibitor could not be identified. However, the answer was finally found when the reactor was then left in the radiation field for periods longer than those previously used. Larger yields of polyethylene were obtained as a result, and it was shown that after a certain minimum induction period the yield increased to a nearly constant and reproducible value.

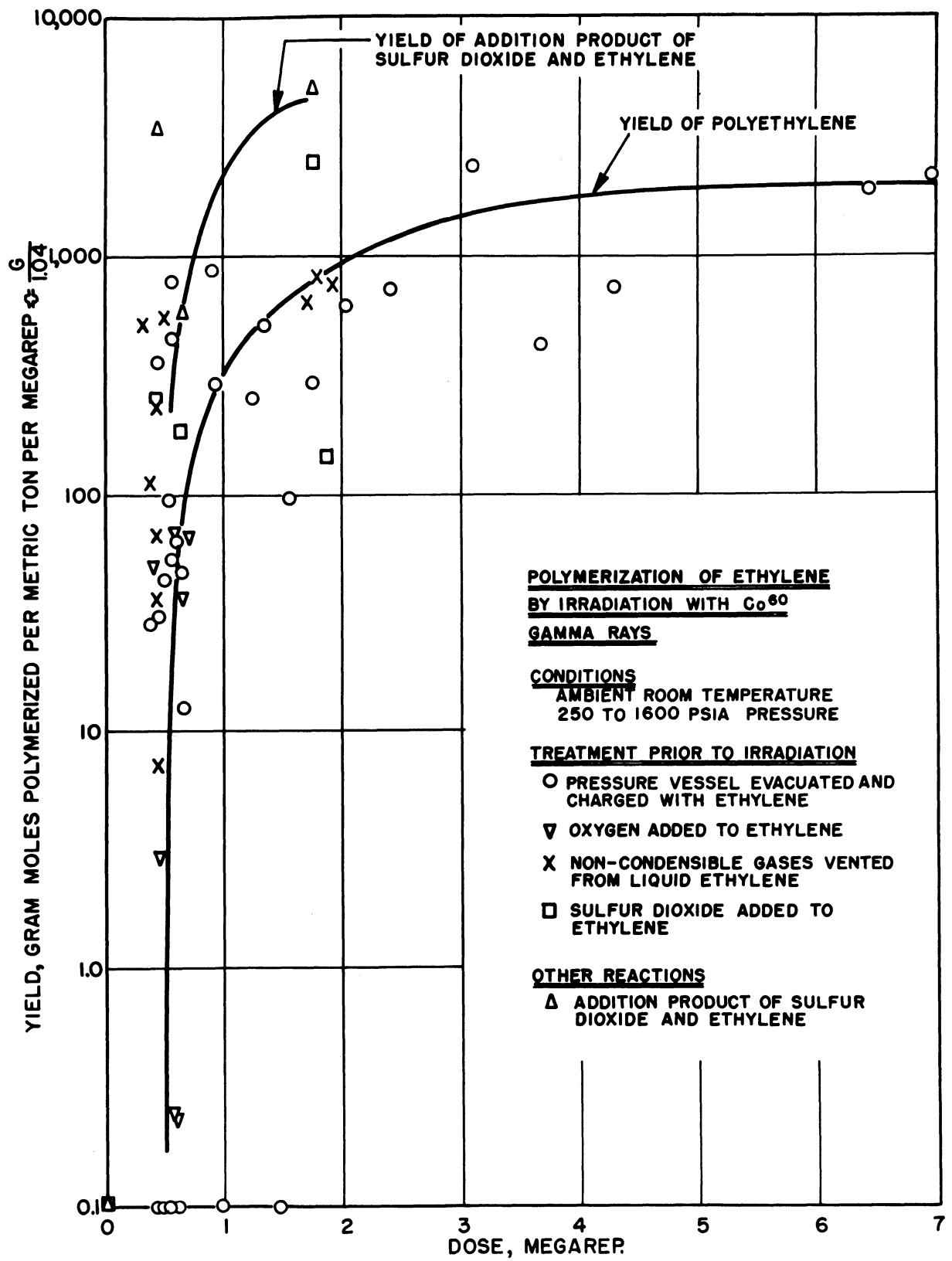


Fig. 4. Radiation Yield as Function of Dose of Radiation in Polymerization of Ethylene.

TABLE 4

## ANALYSES OF ETHYLENE FROM STORAGE CYLINDERS

Material No.	Mfg.	%CO <sub>2</sub>	%O <sub>2</sub>	%CO	%N <sub>2</sub>	% Combustible as marked	Number of Determinations
1	Math FF737	0.06	0.02	0.02	0.15	0.1 propane?	duplicate
2	Math 5772	0.06	0.02+	0.00	0.07	0.29 propane	duplicate
3 5	OC G28087	0.10±	0.02±	0.00+	0.47	total ethane?	single sample
4	C and C JK370331	0.37	0.02	0.05	1.7	0.8 pentane	triplicate
5	USI IC-1065	0.08	0.05	0.005(?)	0.21	0.45 methane	duplicate

TABLE 5

## ANALYSES OF ETHYLENE FROM REACTOR

Material No.	Dose G	Page No.	%CO <sub>2</sub> *	%O <sub>2</sub> *	%CO*	%N <sub>2</sub>	%Combustible as marked	Number of Determinations
4	3.09	132363	0.37 0.62	0.02 0.07+	0.05 0.07	0.00	3.8 ethane	duplicate; first sample of 1.1 or more
2	2.40	132366	0.06 0.05	0.02 0.008	0.00 0.002	0.12	0.14 ethane(?)	duplicate
2	0.45	132369	0.06 0.02	0.02 0.05	0.00 0.01	0.22	total -?-	duplicate
4	0.57	132370	0.37 0.34	0.02 0.01	0.05 0.01+	2.49	total -?-	duplicate
2	0.91	132372	0.06 0.05+	0.02 0.005	0.00 0.00	0.23	total -?-	duplicate; acetaldehyde added
2	6.97	132373	0.06 0.05	0.02 ≠0.01	0.00 0.00	0.09	0.18 methane	single
3	6.43	132375	0.10 0.11	0.02 0.02	0.00 0.009	0.16	0.32 ethane(?)	single
5	4.29	132376	0.08 0.07	0.05 0.009	0.005(?) 0.00	0.10	0.63 methane	single

B6

\* Top, before irradiation (no removal by distillation and no addition to ethylene unless noted)  
Bottom, after irradiation

1. Experimental Procedure. In all of this work ethylene was irradiated with cobalt-60 gamma radiation at room temperature and at pressures of 250 to 1600 psi. Some tests were made in which ethylene was reacted alone and some in which the ethylene was used with other reactants. A stainless-steel bomb (Figs. 5 and 6) was used as the reaction vessel. The bomb was evacuated to pressures of less than 1 mm of mercury absolute and ethylene added from a cylinder. Pressures of about 1100 psi and room temperature were employed in most of the tests. The bomb was then placed in either the 1-kilocurie source or the 10-kilocurie source until the proper dose had been accumulated. After irradiation, the bomb was removed from the source, the unreacted ethylene was vented and analyzed by an Orsat analyzer, and the accumulated polymer was removed mechanically.

In order to remove possible oxygen or other volatile gases from the ethylene, the bomb was evacuated, ethylene was charged under cylinder pressure, and then the ethylene was condensed by immersing the bomb in a flask containing dry ice. The bomb was then vented until the pressure had dropped to a pre-determined value or until a given volume of gas had been released. The ethylene was then vaporized and the bomb and contents irradiated as before.

2. Results of Polymerization of Ethylene. In order to conduct a quantitative study of the effect of gamma radiation on the polymerization of ethylene, it was necessary to adopt some criterion of gamma radiation effectiveness. For this purpose it seemed desirable to calculate the radiation yield in terms of the G value, i.e., the number of molecules of ethylene undergoing polymerization per 100 electron-volts of energy absorbed from the radiation. The roentgen equivalent physical, or rep, was adopted as the unit of measure of the absorption of gamma radiation by ethylene. The rep was assumed to correspond to the absorption of 93 ergs per gram of absorber. The dose rate in rep per hour in the absorber was determined by a combination of methods. Chemical dosimetry was conducted, using the method of Weiss<sup>14</sup> and the results were correlated and extended by the methods of Lewis, Nehemias, Harmer and Martin.<sup>8</sup> The dose rates determined in this way were applied to the calculation of the radiation yields.

The degree of polymerization of the ethylene was determined by terminating the reaction at a stage such that the conditions during reaction had been reasonably constant, venting the unreacted ethylene, and then removing the polymer mechanically and weighing it. The conditions prevailing during reaction were averaged and the average values were assumed to have prevailed throughout the course of the reaction. Instead of G, the quantity A was sometimes calculated in this work. A was defined as the gram moles reacted per metric ton subjected to one megarep. By a comparison of units the following relation can be established:



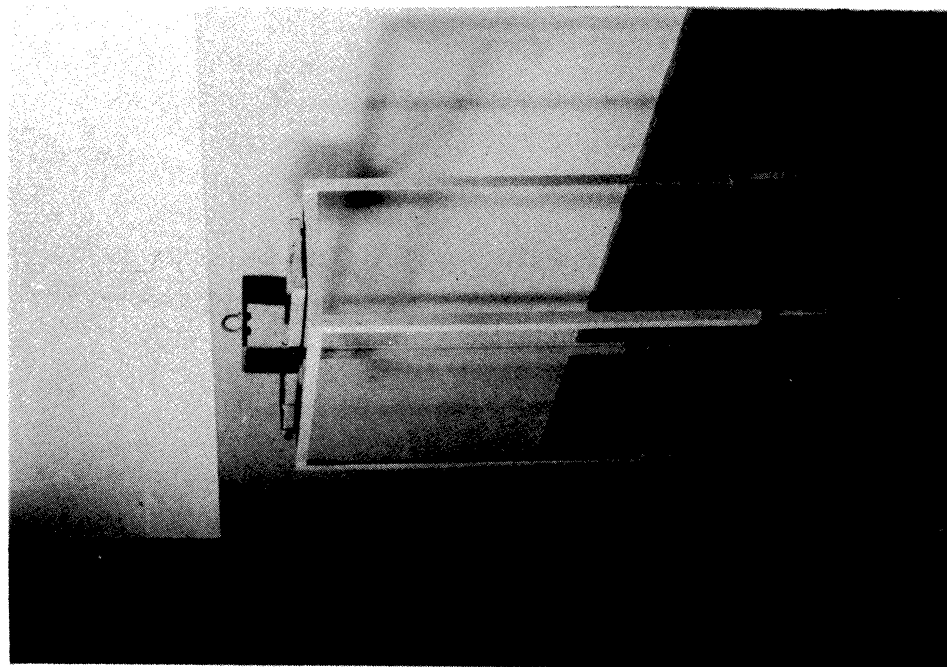


Fig. 5. Rack and Sling for Pressure Reactor.

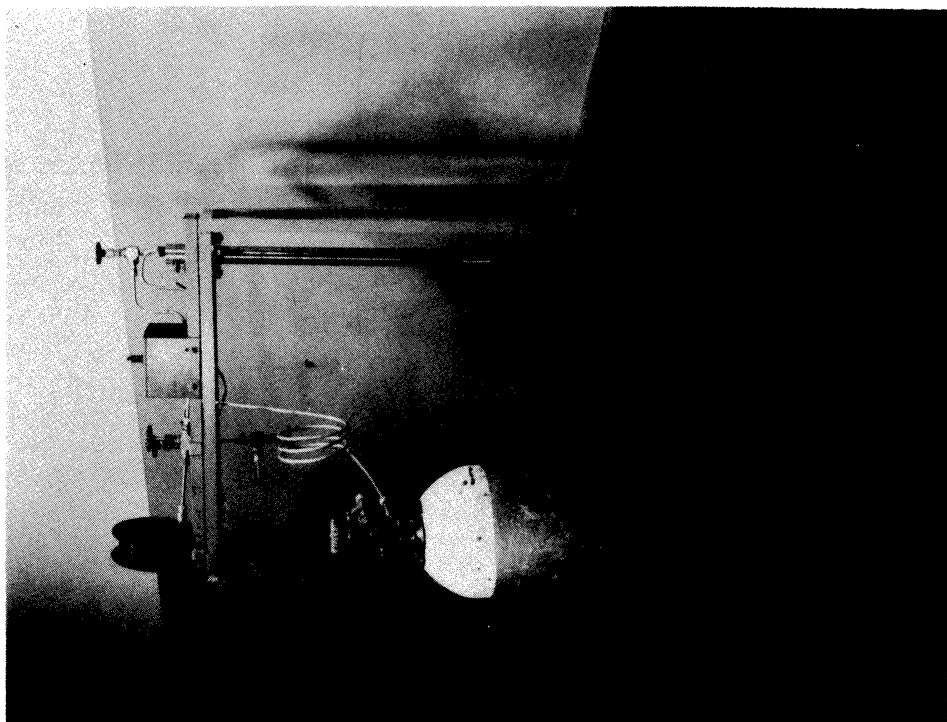


Fig. 6. Pressure Reactor: Tubing Assembly and Gas Cylinder.

$$A, \frac{\text{gram moles reacted}}{(\text{metric ton})(\text{megarep})} = \frac{G}{1.04}, \frac{\text{molecules reacted}}{100 \text{ electron volts}}$$

Consequently, A is almost equal numerically to G. With some simplification the following relation was developed:

$$A, \frac{\text{gram moles reacted}}{(\text{metric ton})(\text{megarep})} = \frac{\text{weight fraction ethylene reacted} \times 10^6}{(\text{molecular weight of ethylene})(\text{dose, megarep})}.$$

This simplified relation was used in calculating A values in the following work.

A white, solid polyethylene resulted from the irradiation of ethylene with cobalt-60 gamma rays. See Table 6 for the experimental results. The yield of polymer was found to be quite small until the system had received a dose of about 1/2 megarep. The yield increased rapidly to a value of about 2500 gram moles reacted/(metric ton)(megarep) at about 3 megarep, and remained nearly constant up to doses of 7 megarep, the highest dose studied (see Fig. 4). About one-third of the monomer was polymerized in three days in the center of the 10-kilocurie source. The amount of ethylene charged to the bomb was calculated from the observed temperature, pressure, and volume and the thermodynamic properties of ethylene taken from the work of York and White.<sup>15</sup>

3. Discussion of Polymerization of Ethylene. From Fig. 4 it can be seen that the yield of polymer per unit of energy absorbed from the radiation is a function of the total dose of radiation. This relation is evidently due to the presence of an induction period for the reaction. No correlation could be observed between contents of the following gases in the monomer and the yield as a function of dose: carbon dioxide, oxygen, carbon monoxide, hydrogen, paraffin hydrocarbons, nitrogen, and sulfur dioxide. It appeared, however, that the venting of noncondensable gases from the liquid ethylene did increase the initial rate of reaction a little. The data for the analyses of gases before and after irradiation are given in Tables 4 and 5.

In view of the evidence just mentioned, it cannot yet be stated what effect chemical additives have on the rate of polymerization of ethylene by gamma radiation. It is possible, however, that the induction period is caused by the presence of chemical compounds other than ethylene.

Average values of dose rates used in these studies varied from about 30 kilorep/hour to about 90 kilorep/hour. It should be noted, however, that errors exist in the method of calculating the dose rates used in estimating the G or A values. A Victoreen ratemeter was used to measure the dose rates on the axis of the bomb. This instrument would detect the secondary photons produced by scatter from the wall of the bomb, but probably would not detect



the scattered electrons. These scattered electrons would be quite effective in producing chemical reaction because nearly all their energy would be imparted to the chemical system. Consequently it can be seen that more ionization probably occurred than was taken into account by the calculations, in which the effect of the bomb wall was neglected. The effect of this error is that the G values given are too high.

On the other hand, as a calculation device the primary beam was assumed to undergo no appreciable absorption within the ethylene in the bomb. Rather the beam was assumed to maintain within the bomb a value which would be attained on the axis if the bomb were full of air. It was recognized, of course, that absorption within the ethylene was assumed to be causing the reaction. If account were taken of absorption of primaries within the ethylene, then somewhat greater credit for initiating reaction would have to be given to each primary photon, and this would increase the G values given.

Thus, neglect of nonequilibrium secondaries and neglect of the absorption gradient of primary gamma intensity within the ethylene compensate each other to some extent. The importance of accounting for the above errors in dosimetry is recognized. However, the complexity of the measurement problems would seem to indicate the desirability of pursuing this work further in future studies. Therefore, the values given for G in Fig. 4 should be regarded as relative rather than absolute, since all determinations were made in the same equipment and using similar procedures.

No consistent effect of pressure on the G value was noted.

Elevated temperatures were investigated only briefly, but preliminary results indicated that increased rates of polymerization would result in irradiated systems at temperatures of 200-400°F as compared with those obtained at room temperature.

4. Evaluation of the Polyethylene Product. a. General: The polyethylene obtained as a result of gamma irradiation of ethylene was subjected to a brief program of evaluation. The properties considered most basic to an understanding of the material were investigated. Most experimental work was concerned with determinations of solution viscosity, melt viscosity, density, and tensile strength. Melting points of some samples were also determined. Molecular weights were estimated from the determinations of viscosities of solutions and of melts. Crystallinity was estimated from determinations of density. The other measurements were made by conventional means.

These measurements and derived quantities probably need no further explanation with the exception of the concept of the crystallinity of a polymer. The degree of crystallinity of a polymer is measured by the degree to which the

molecules of polymer are arranged parallel to each other. An arrangement of parallel molecules results in a repetitive structural pattern such as that found among the molecules of a crystal. A random orientation of molecules similar to a pile of jackstraws might be expected to be less dense than a parallel arrangement such as that just described, and it has been found that percentage crystallinity may be correlated with the density of polyethylene (see Kirk-Othmer).<sup>7</sup>

From the data obtained in experiments on the polymer, molecular weight and crystallinity are presented as functions of dose and all the properties of the polyethylene are presented as functions of the radiation yield of the polymerization reaction because of the following considerations. The radiation yield of the polymerization of ethylene may be expressed as the G value. Lind<sup>9</sup> has shown that in many gaseous systems, approximately one molecule reacts per ion pair formed in the system. In the irradiation of ethylene a variable number of molecules, usually much greater than one, react for each ion pair formed. The polymerization of ethylene is therefore evidently a chain reaction. For this calculation it is assumed that one chain is initiated for every ion pair formed, that all chains are of equal length, and further that the formation of each ion pair requires 32.5 electron-volts of energy, a value approximately correct for gases at one atmosphere. The densities of ethylene under the conditions of reaction were greater than at one atmosphere, however, and therefore the energy required per ion pair may be quite different from the value given. The G value may therefore be divided by three to give the approximate number of molecules reacted for each ion pair formed, and this result may then be multiplied by the molecular weight of the monomer in order to arrive at the molecular weight of the polymer.

Consequently, the G value is directly proportional to the molecular weight which would be expected of the polymer if the above assumptions held. Furthermore, the properties of a polymer are frequently found to be functions of its molecular weight. It therefore seems advantageous to consider the properties of the polyethylene as functions of the G value.

The results of most determinations could be correlated against the G value, or radiation yield, somewhat better than they could against dose, although the G value has been shown to be a function of dose. In Fig. 4, for example, the G value was about 0.1 to 1.0 until about 0.5 megarep had been received. The G value then increased rapidly with increasing dose until it reached a nearly constant value of about 2000 molecules per 100 electron-volts for doses of about 3 to 7 megarep.

b. Experimental: All the samples of polyethylene were white. Some were fluffy powders and others were tough, coherent masses.

Portions of each of the samples of polyethylene which were obtained in yields of 4 grams or more were molded into sheets as an operation preliminary to further examinations. A two-compartment mold was used, one compartment at a time. Samples were placed between aluminum foil in the mold, preheated to 300°F, pressed at 1000 psi, and cooled to about 125°F under pressure. The resulting sheets were 2.5 by 4 by 0.025 inch. All such sheets proved to have the characteristic milky, translucent appearance of polyethylene. The sheets molded from the powders were brittle, while those from the tough reaction products were also tough.

Molecular weights were estimated from viscosities of solutions, measured as follows: Solutions of some samples were prepared in concentrations of 0.01 percent and of 0.125 percent by weight in tetralin. Viscosities of these solutions and of the tetralin were measured in modified Ostwald pipettes at 212°F. Specific viscosities were calculated and divided by the respective concentrations. The resulting ratios were plotted as a function of the concentration of polymer, and the plots were extrapolated to zero concentration to give intrinsic viscosity. Intrinsic viscosity was assumed to be directly proportional to molecular weight. The concentration was computed in units of gram moles of monomeric ethylene per liter of solution. The constant of proportionality was computed by the author to cause the observed value for the molecular weight of Bakelite DYNH to agree with the value of 20,000 for the weight-average molecular weight given by Dienes and Klemm.<sup>4</sup> The value of the constant was computed in this way to be  $0.42 \times 10^{-4}$  liter per gram. (See also the work of Tani<sup>13</sup> on intrinsic viscosities of polyethylene in tetralin.)

The method of Dienes and Klemm<sup>4</sup> was used to estimate molecular weights from melt viscosities. Viscosities were measured in a parallel-plate plastometer with an attached dial gauge reading to 0.01 millimeter. The entire assembly was placed in an oven. Temperatures of 248°F and 266°F were used. The samples were placed between sheets of aluminum foil about 1-1/2 mils thick. The thickness of the sheets of foil was measured in the plastometer before each determination.

Crystallinity was estimated by correlation with density (see Kirk-Othmer).<sup>7</sup> Densities were determined by the use of Archimedes' principle. Weighings were made directly in water, after the sample had first been degassed by use of reduced pressure while it was immersed in water.

Tensile properties of the polyethylenes were examined by the following procedure. Specimens for testing were cut from the molded sheets by means of a die. The resulting specimens were 0.079 by 0.025 inch in the smallest cross section. The narrowest section was 1-1/2 inches long. Tension was applied in a Gardner-Parks testing machine shown in Fig. 266 of Gardner.<sup>5</sup> This machine had a capacity of 2.5 kilograms.

Melting points were determined on a melting-point bar of the type used by Dennis<sup>3</sup> (see Fig. 8).

c. Results. Results of evaluation of the properties of the radiation-polymerized polyethylene are summarized in Table 7. The molecular weight is plotted as a function of radiation yield in Fig. 7, and the molecular weights and crystallinities are plotted as functions of dose in Fig. 9.

The significance of the determination of molecular weights by means of solution viscosity is not clear. The values obtained were assumed to be weight-average molecular weights, based on the weight-average molecular weight of Bakelite DYNH of 20,000 (see Table 7). However, differences in crystallinity and cross-linking, mentioned above, may invalidate the comparison of the thermally polymerized sample with the radiation-polymerized samples.

Determinations of molecular weight by melt viscosity may be subject to similar criticism. As shown in Figs. 7 and 9, the molecular weights determined by solution viscosity do not agree well with those determined by melt viscosity. Neither do the molecular weights from solution viscosity appear to display any regular variations with dose or with G value, in contrast to the regular behavior of molecular weights from melt viscosities. The reasons for these discrepancies are not clear.

Values of crystallinity are plotted as a function of radiation yield in Fig. 10. The crystallinities varied from about 77 percent for samples of low radiation yield to about 71 percent for samples of high radiation yield. All these samples were of considerably higher crystallinity than was the Bakelite DYNH, which had a crystallinity of about 61 percent. It is possible that the radiation-polymerized samples were of higher crystallinity than the thermally polymerized sample of DYNH because the temperature of polymerization was lower for the radiation-polymerized samples. The samples of low radiation yield would be expected to be more highly crystalline than those of high radiation yield. Since radiation yield has been shown to increase with dose (Fig. 4), cross-linking and branching would probably also increase with dose, and increases in either cross-linking or branching would cause decreased crystallinity.

Tensile properties are reported in terms of stress as a function of strain in Fig. 11. The irradiated samples all have properties similar to those of a brittle material, and the samples subjected to higher doses have higher tensile strengths and are more ductile than those subjected to lower doses of radiation. Such behavior would be likely if the irradiation increased cross-linking and branching. The Bakelite DYNH shows the characteristic elongation of several hundred percent before rupture (see Kirk-Othmer<sup>7</sup> page 942). Ultimate tensile stress as a function of radiation yield is plotted in Fig. 10. The ultimate tensile stress increased markedly with radiation yield and consequently

TABLE 7

## PROPERTIES OF POLYETHYLENE PRODUCED

Page Number	Dose, Megarep	Radiation Yield, A	Melting Point, °F Lower/Upper	Density g/cm <sup>3</sup>	Ultimate Tensile, psi	Elongation, Percent at rupture	Crystallinity Percent	Viscosity by Melt	Viscosity by Solution
132250	1.55	95	219/226						
132268	0.61	37	216/225						
132269	0.58	71	205/217						
132276	0.60	63	207/214						
132281	0.54	52	196/205						
132297	1.91	750	241/244	0.951	450	4	77	26,300	insol.
132362	0.37	28	234/235						
132363	3.09	2400	248/689	0.941	2200	42	71	34,400	insol.
132366	2.40	730	210/248	0.951	770	2	77	28,100	4200
132369	0.45	0.1							
132370	0.57	790	203/252						8800
132372	0.91	298	199/207						insol.
132373	6.97	2200	234/720	0.943	2100	29	72	40,500	insol.
132375	6.43	1900	241/610	0.941	2300	79	71	37,300	insol.
132376	4.29	745	241/244	0.951	630	3	77	11,900	3700
Bakelite DYNH				0.921	1500	550	61	21,800	20,000 assumed



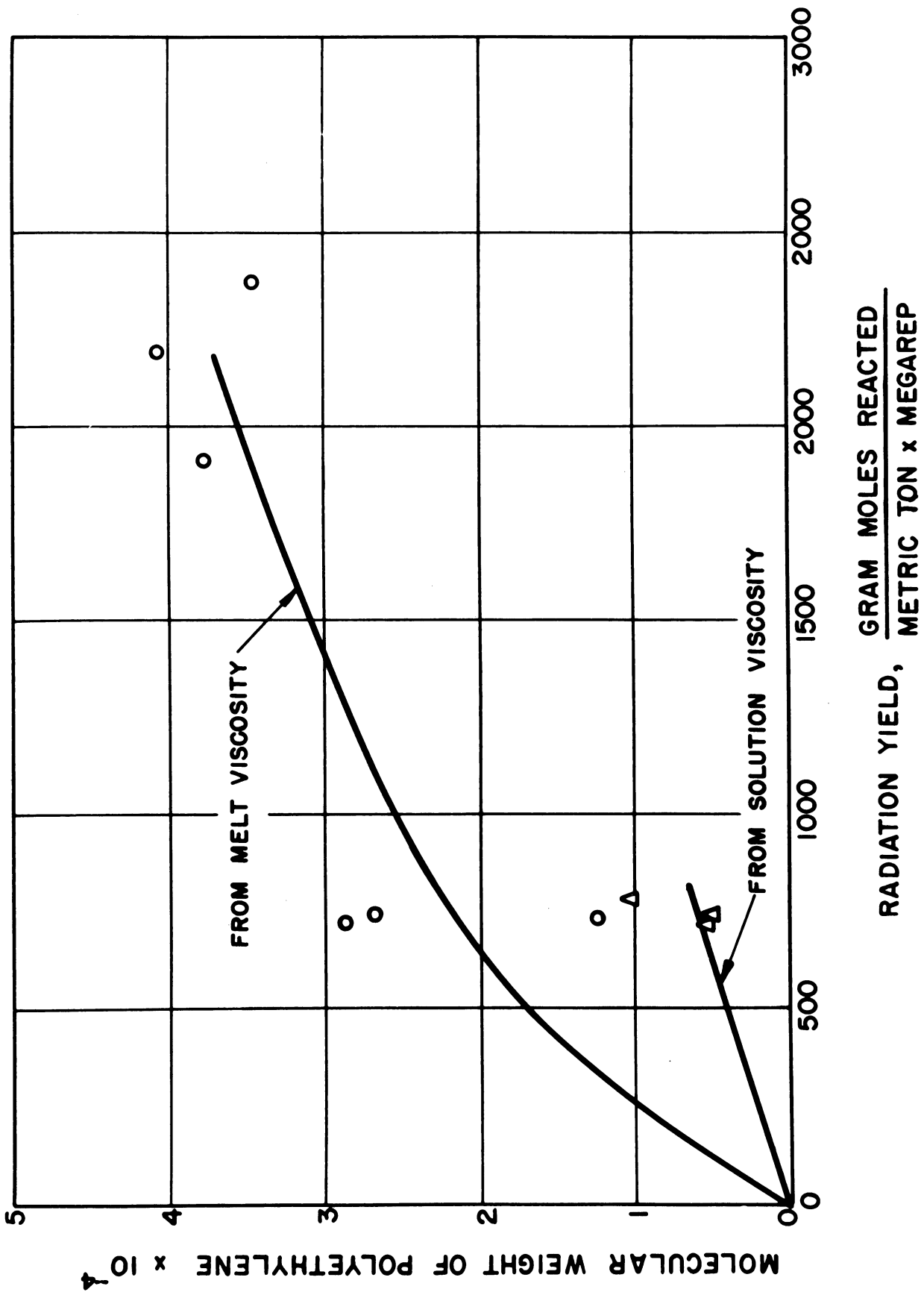


Fig. 7. Molecular Weight as Function of Radiation Yield of Polyethylene.

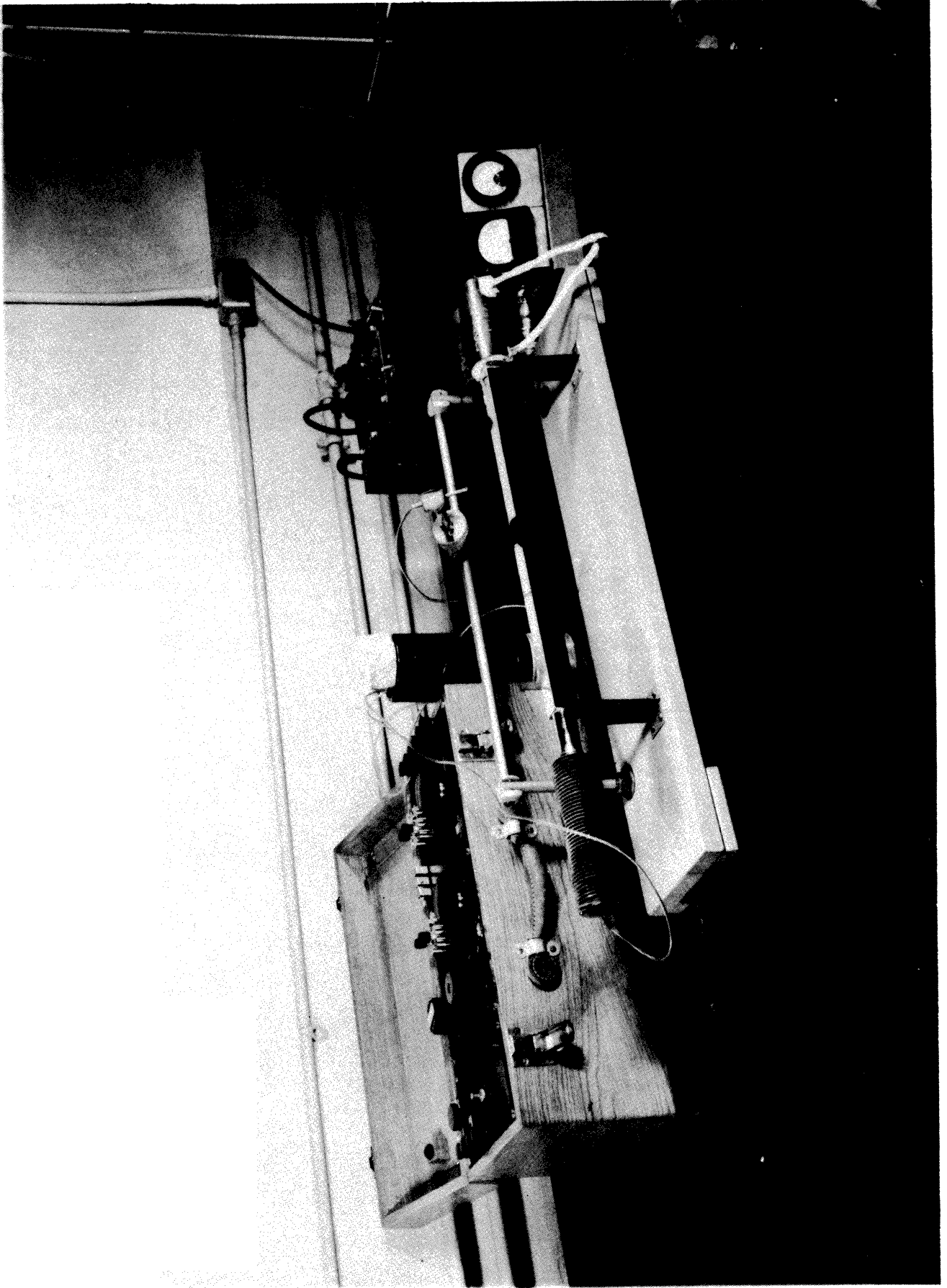


Fig. 8. Melting-Point Bar.

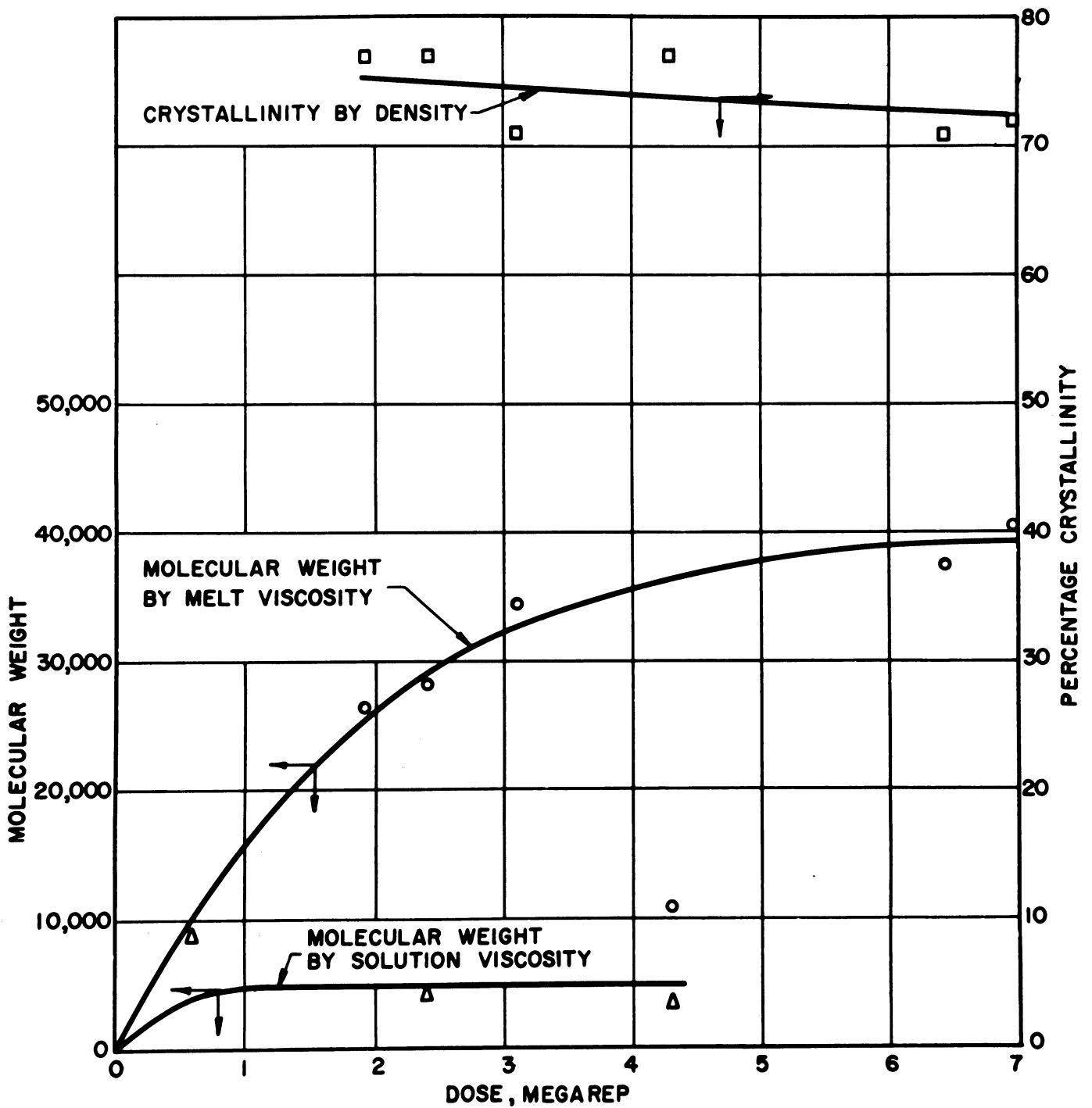


Fig. 9. Molecular Weight and Crystallinity as Functions of Radiation Dose for Polymerization.

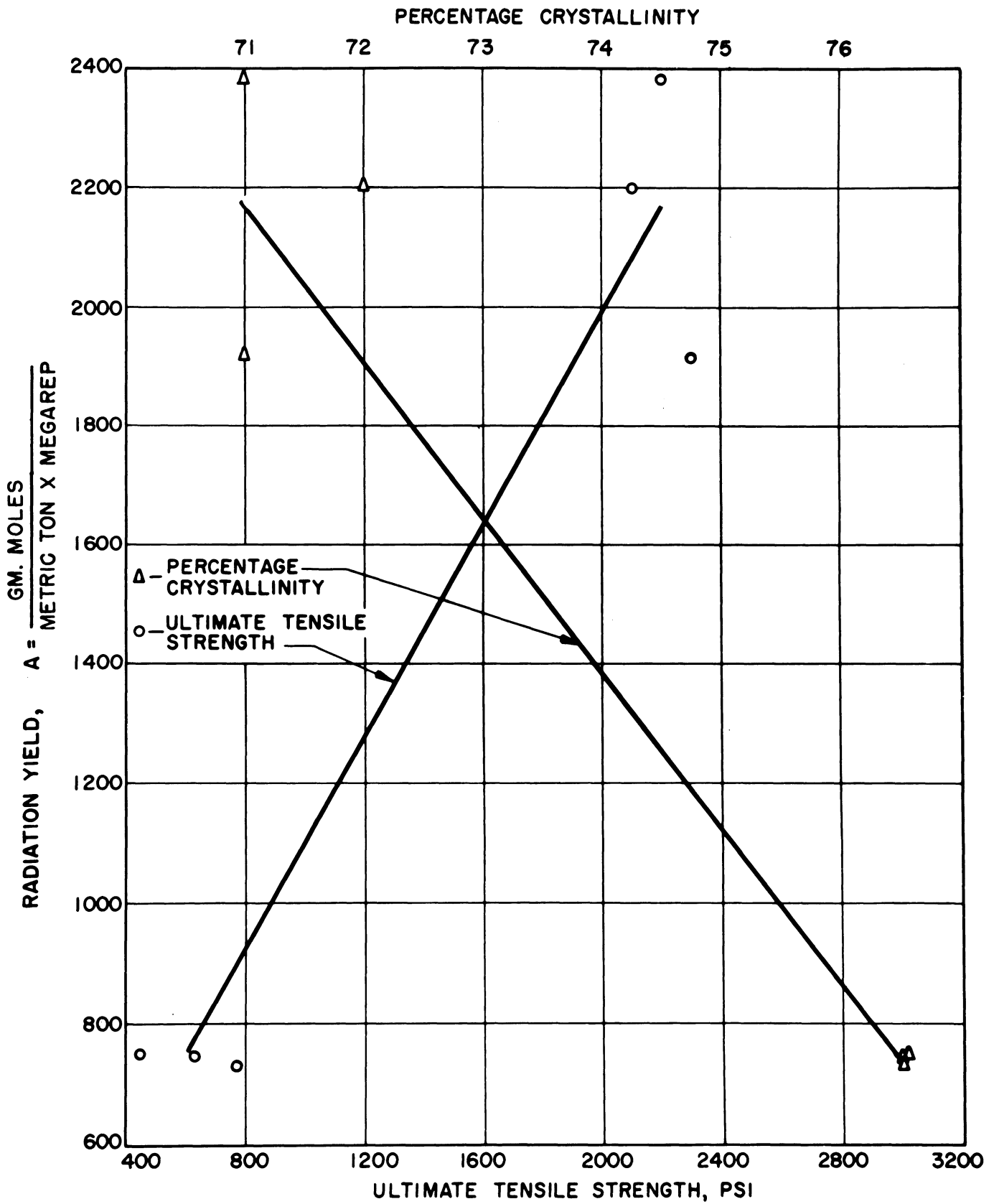


Fig. 10. Crystallinity and Tensile Strength as Functions of Radiation Yield for Polyethylene.

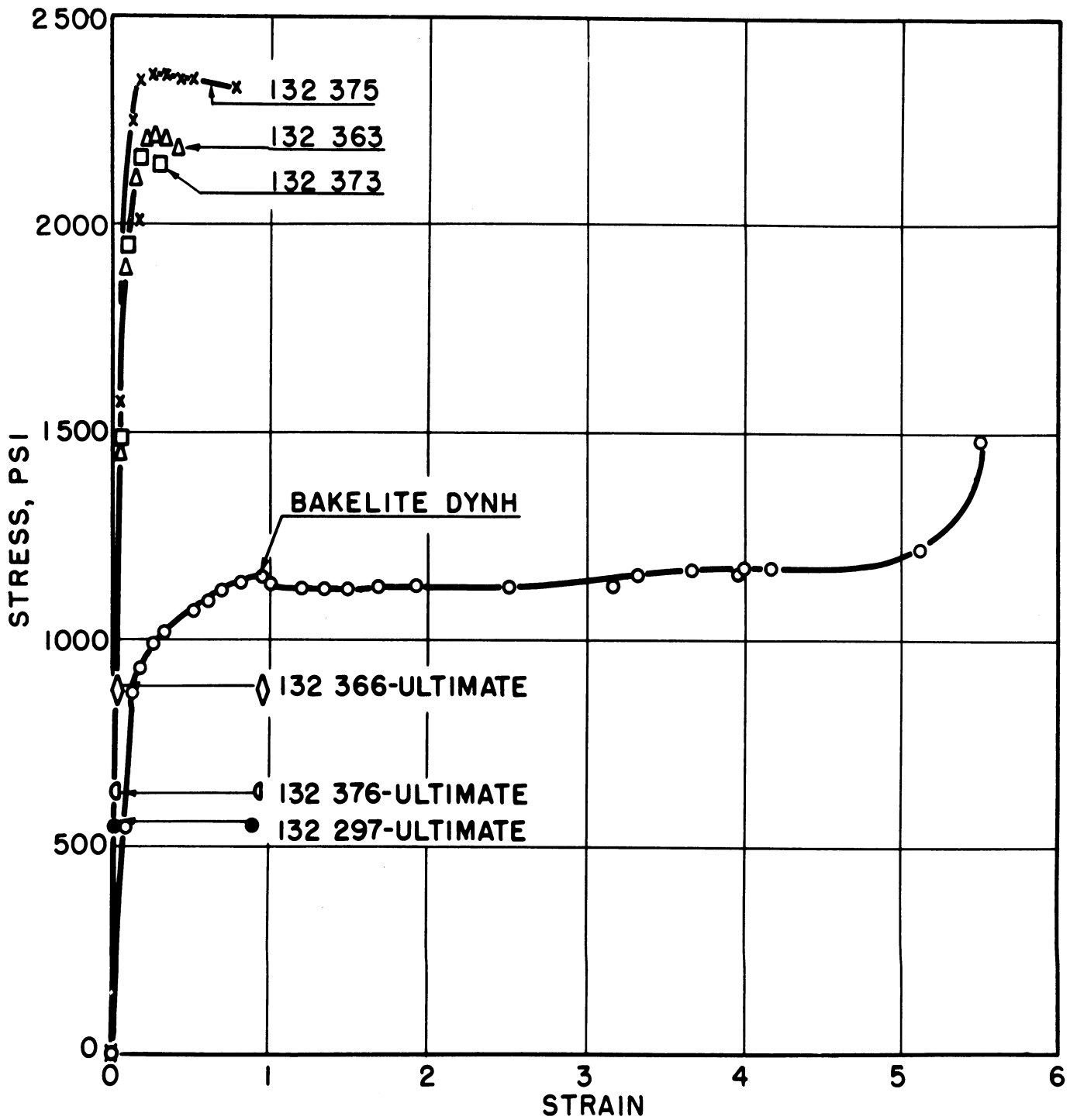


Fig. 11. Stress-Strain Plots for Test Specimens of Polyethylene.

with dose. A set of structural properties such as those just described for the radiation-polymerized polyethylene might be desirable for certain applications, but the properties differ from those of most polyethylene currently marketed.

Melting points are plotted as a function of radiation yield in Fig. 12. Curves are given for both the upper and the lower ends of the melting-point range. The results show that there is a small increase in the temperature of initial softening with increase in radiation yield, and that there is a large increase in the temperature of complete melting. The higher melting points indicate higher degrees of cross-linking as a result of the higher doses of radiation, and are thus in conformity with the results of the other determinations.

### C. CHLORINATION OF AROMATIC COMPOUNDS

The reactions of chlorine with various aromatic hydrocarbons have been reported by this laboratory previously.<sup>2</sup> During this period covered by this report, the study of toluene reactions has been continued and monochlorobenzene has also been reacted with chlorine.

1. Description of Apparatus. In order to utilize the 10-kc cobalt-60 gamma source for reactions employing large volumes of toluene, new equipment was designed and constructed. In this equipment, up to 1.5 liters of toluene may be reacted with chlorine gas. The chlorine was fed from a cylinder located in the second floor chemical laboratory of the Fission Products Laboratory. Gases returning from the reacting system passed through bubbler bottles or solutions for absorption and were vented to the outdoors. This part of the system was the same as that illustrated in Progress Report 4 (1, pages 26 and 29) in the system used with the 1-kc source.

The apparatus located in the source room consisted of a water-cooled reactor section, a storage section, and inlet and outlet tubes for gases leading to the chemistry laboratory. The apparatus is shown in Fig. 13, and details of individual parts of this apparatus appear in Fig. 14. Referring to Fig. 15, the gases entered the apparatus through tube (1), and passed through the jet injector assembly (2). The gas then bubbled through the outer jacket of the reactor section (3), passed through the connecting tube (4) and bulb (5), and emerged from tube (6). In passing through the jet injector (see Figs. 16 and 17 for detail), and in rising through the vertical reactor section, the gases caused the reacting liquids to circulate through the tubes of the system. After being carried across the upper connecting tube (4), the liquid returned to the storage bulb (7) until it was recirculated through the lower connecting tube (8). The upper storage bulb (5) provided space for increase in the volume of the

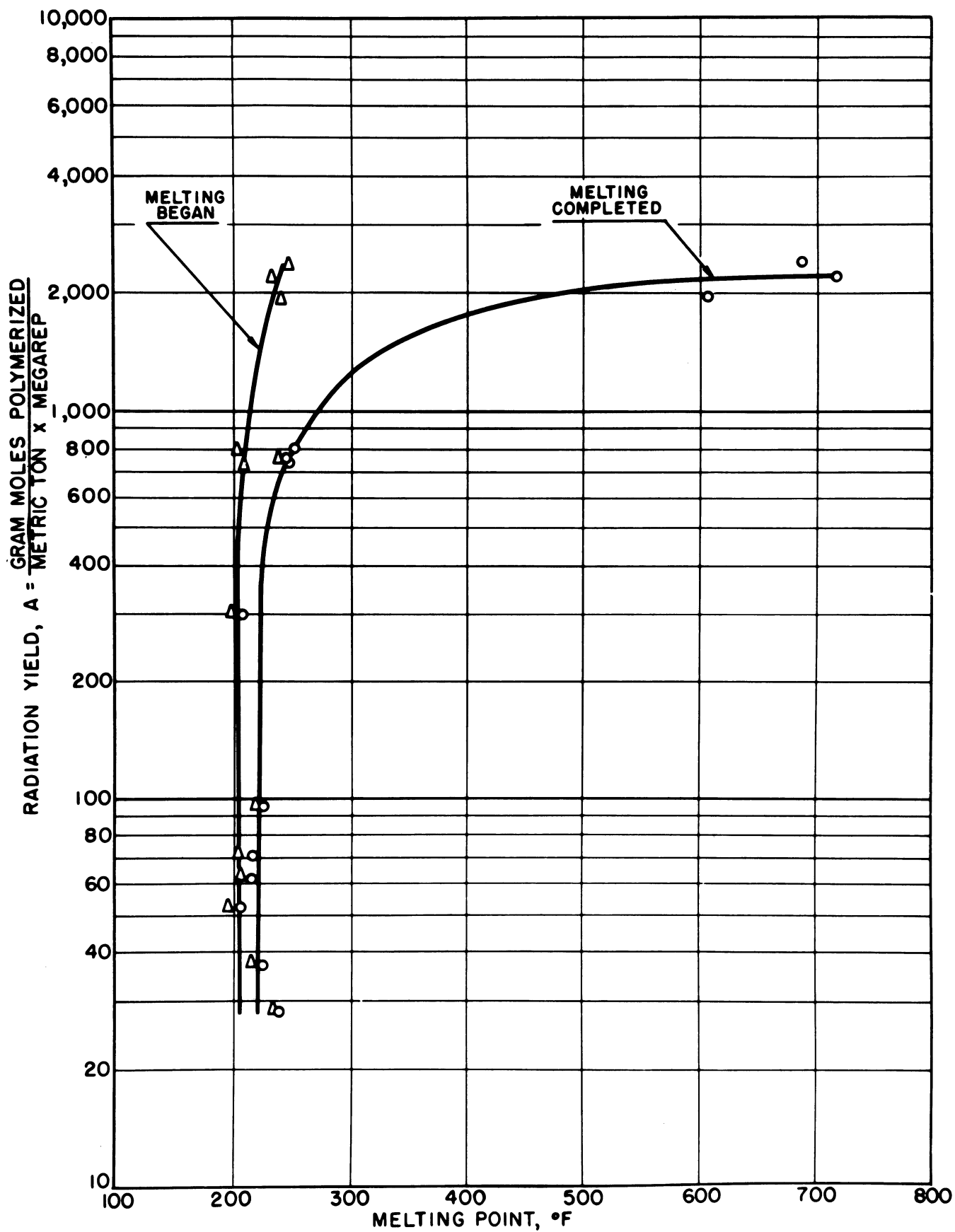


Fig. 12. Melting Points as Functions of Radiation Yield of Polyethylene.

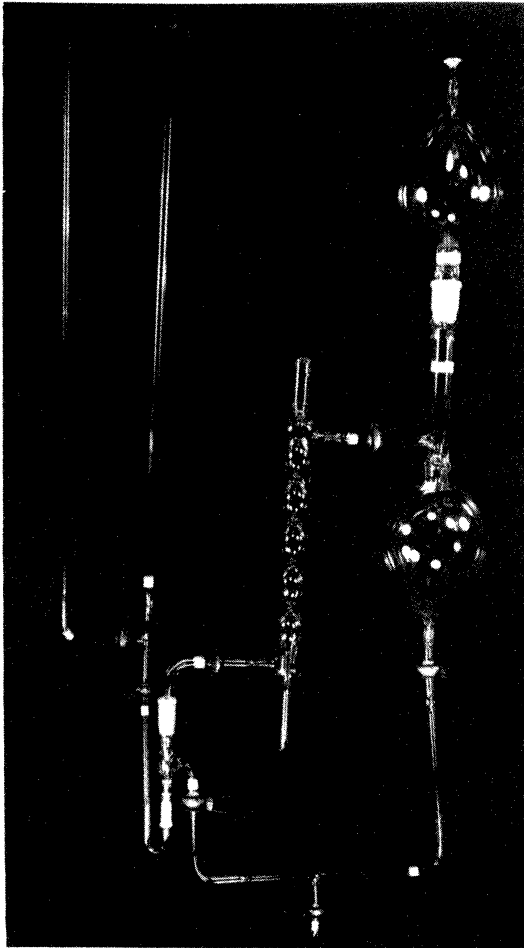


Fig. 13. Apparatus for Reaction of Liquids with Chlorine Gas in the 10 kc Cobalt-60 Gamma Source.

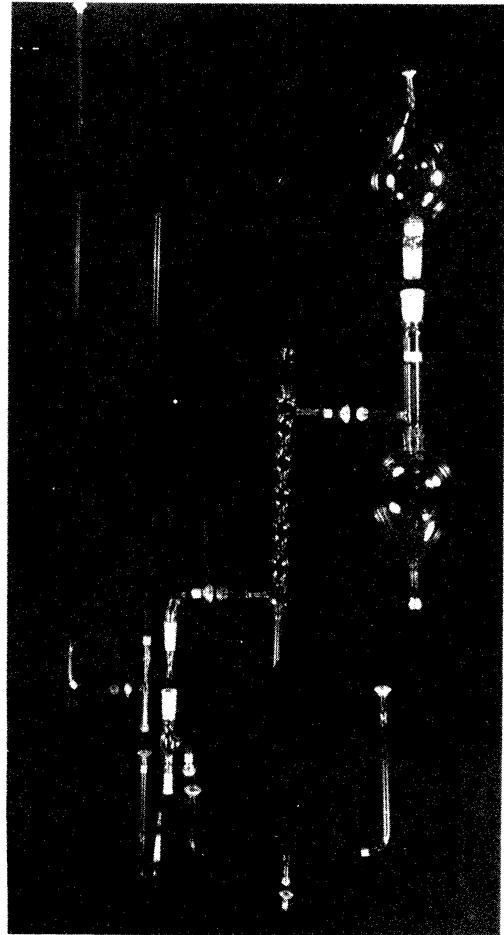


Fig. 14. Individual Parts of the Apparatus for Reaction of Liquids with Chlorine Gas.



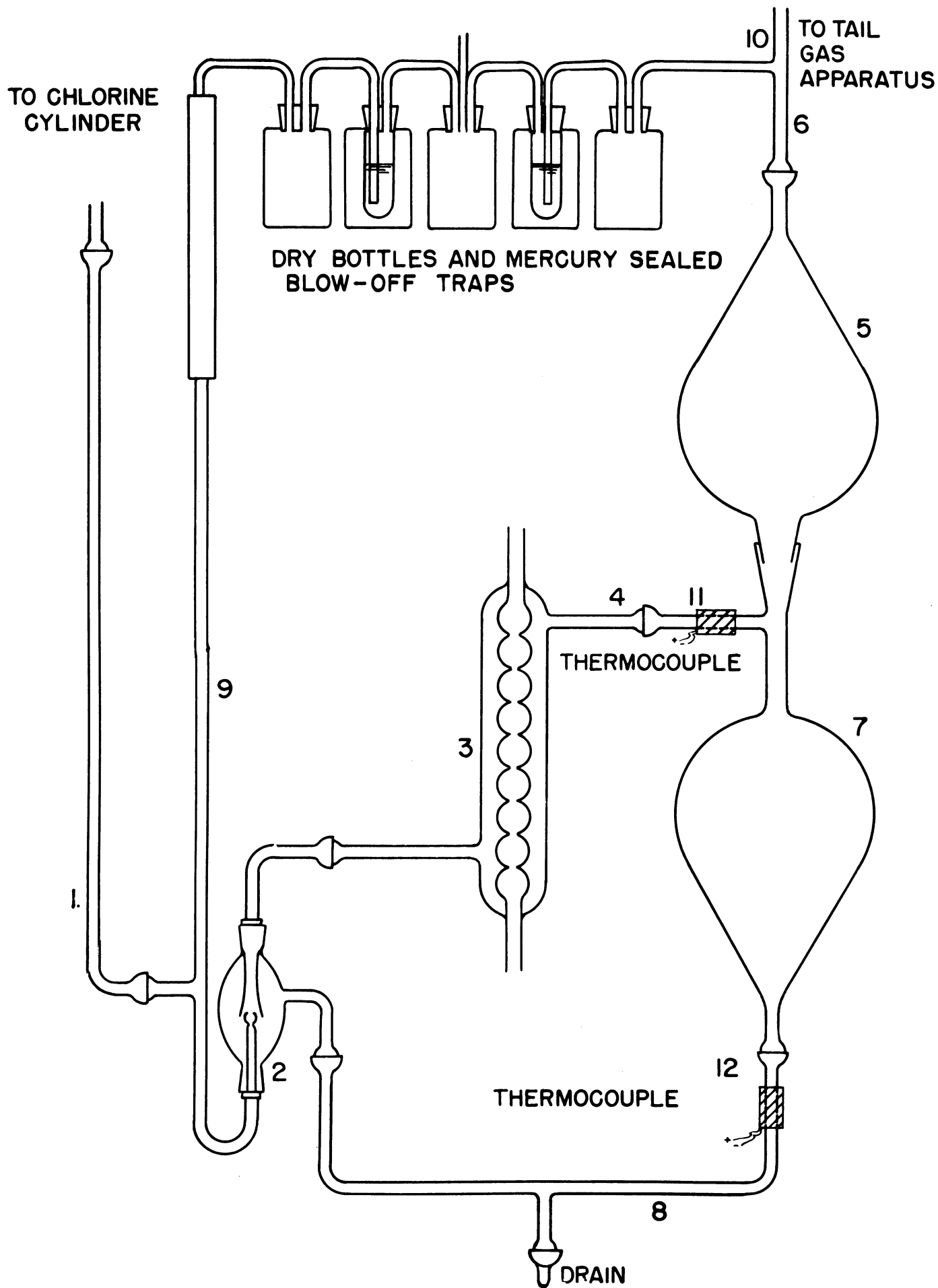


Fig. 15. Drawing of Apparatus for Reaction of Liquids with Chlorine Gas.

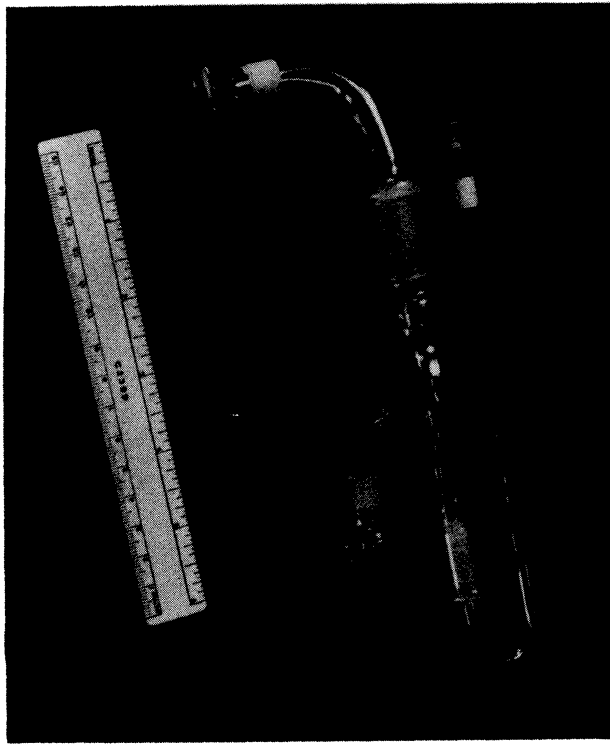


Fig. 16. Photograph Showing Detail of the Jet Injector for Gases used on the Apparatus for Liquid-Gas Injections in the 10 kc-Source.

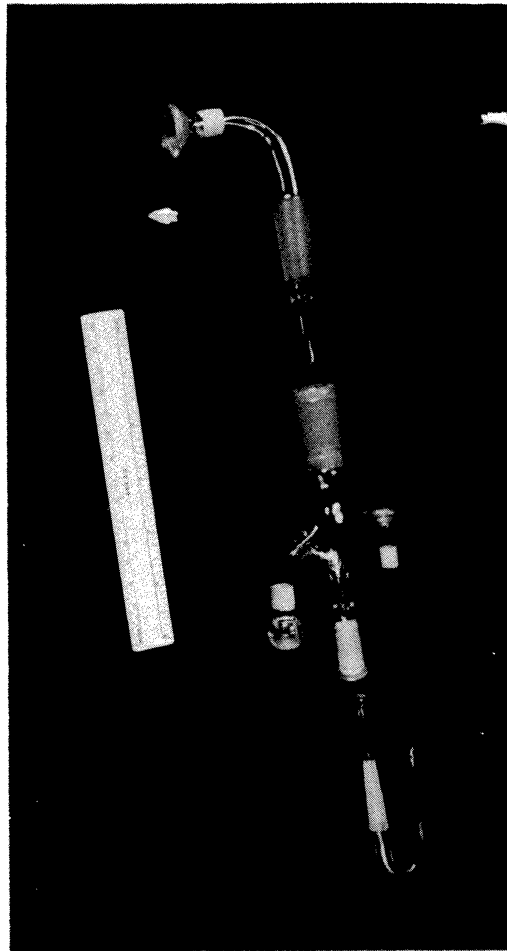


Fig. 17. Component Parts of the Glass Jet Injector, Disassembled.

reacting mixture, since the apparatus was initially filled to the level of the upper connecting tube (4). It also served to separate the exit gases from spray and foam at the surface of the liquid.

Vent lines were included at the inlet (9), and exit (10) of the apparatus. These lines were connected to dry bottles and thence to mercury-sealed traps so that safety was assured in case of rapid reaction or buildup of gas pressure due to plugged lines.

For the recording and controlling of temperature, thermocouples were fastened to the outside of the glass at points (11) and (12). The temperatures of the thermocouples were recorded on chart recorders located in the chemical laboratory. The thermocouple on the upper connecting tube (4) also activated a temperature controller, so that the temperature of the coolant circulating through the inner jacket of the reactor section (3) was controlled by the temperature of the liquid as it left the reacting section.

The coolant was recirculated through a modification of the cooling system described in Progress Report 4 (1, pages 28 and 30). Figure 18 is a schematic drawing of this apparatus. By means of a pump (1) the coolant was recirculated through the cooling jacket of the reaction apparatus, and returned to the mixing can (3). A knife heater (6) in this mixing can was activated by the recorder-controller to which the thermocouple was attached and was wired to a recirculating pump (2) through a double-throw switch. When this pump was activated by the controller, water was pumped into an upper cooling can (4), from which it overflowed into the mixing can (3) again. In the cooling can (4) was a smaller can (5) containing a mixture of dry ice, carbon tetrachloride, and chloroform which cooled the recirculation liquid as it was pumped around it. When only moderate cooling was required, water was used as the recirculating coolant, in which case a layer of ice was kept frozen around the inner part of the cooling can arrangement. For low-temperature runs, methanol can be used as the recirculating coolant.

When ready for use, the glass reactor equipment was assembled on a portable support frame, and placed in a portable exhaust hood adjacent to the 10-kc gamma source (Figs. 19 and 20). In use, the reaction section could be centered as close as 2 inches from the gamma source. A plastic shield was placed over the open side of the hood to prevent the corrosive liquids from splashing out into the source room in case the glass reaction equipment should break.

After the apparatus had been set in place in the source room, it was connected to the gas control rack in the chemical laboratory by means of glass lines connected by ball-and-socket ground joints. The installation of these feed lines required some special consideration. As shown in Progress Report 5

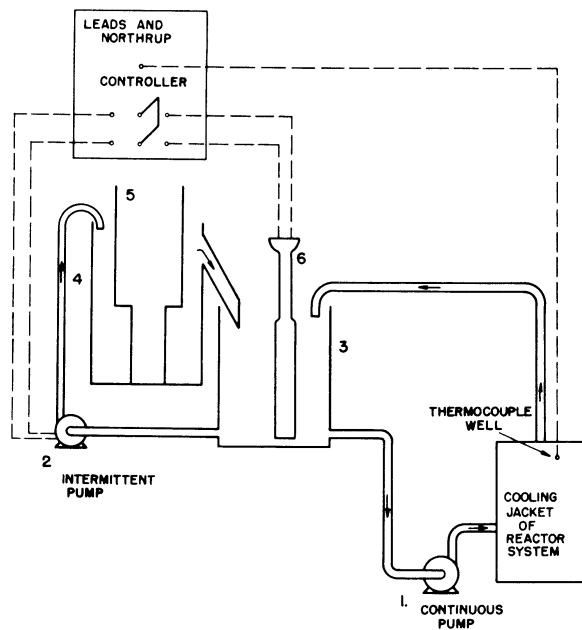


Fig. 18. Schematic Drawing of Apparatus for Temperature Control of Reactions in the 1 and 10 kc Cobalt-60 Gamma Source.

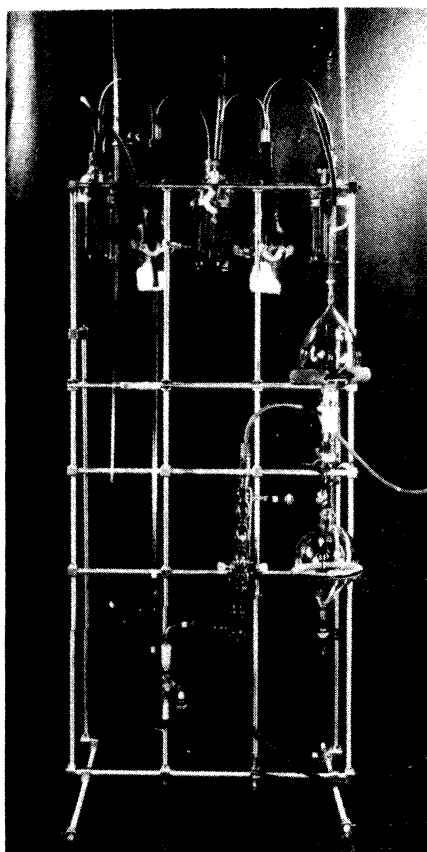


Fig. 19. Apparatus for Reaction of Liquids with Chlorine Gas, Assembled to go into the Portable Hood next to the 10 kc Gamma Source.

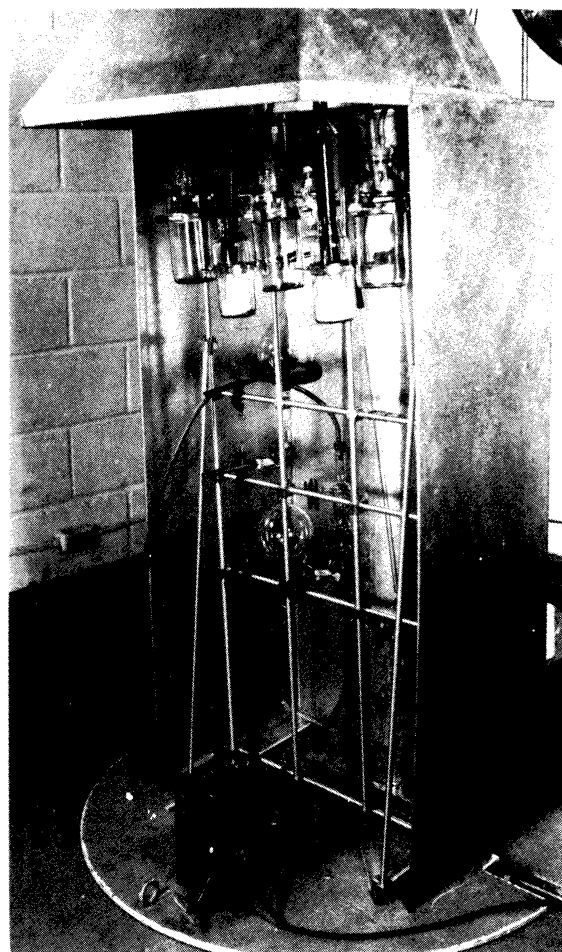


Fig. 20. Portable Hood and Glass Apparatus in use for Reactions in the 10 kc Source.

(page 66)<sup>2</sup> access to the source room from the chemical laboratory was gained through a small chute with a right angle through the shielding. In this chute were the leads for thermocouples and electrical cable. The problem of making a gas-tight connection of glass tubing at the right angle of the chute was solved in the following manner. A wooden support board was constructed which was of the same width and somewhat longer than the horizontal portion of the access chute (see Fig. 21). The glass tubes, which were fitted with ball-and-socket joints, were affixed to this board by means of small spring clamps made from spring clothespin clips. One end of each tube had a short right-angle bend in it. These were rotated to lie flat against the supporting board so that the entire assembly could be pushed into the access tube. Wooden strips along the sides and one one end of the board acted as runners and allowed the glass tubing to hang from the bottom of the board, while cables and aluminum tubing lay on top of the support board in the chute. Once in place, the glass tubing was rotated so that the right-angle bends lead downward placing the ground glass ball in position to receive the next (vertical) section of tubing with its ground-glass socket. Since clips are necessary to assure a gas-tight seal at the ball-and-socket ground joint, a special tool was devised to affix a clip to the joint located at the right angle of the chute. This tool (Fig. 22) was inserted through the vertical section of the chute from below in the source room, and could be manipulated to attach or remove the ball-joint clips. A diagram of the entire setup is shown in Fig. 23.

2. Experimental Procedure and Results. A number of runs using toluene and chlorine were made in the apparatus described above. For these runs, about 1.5 liters of toluene were placed in the reactor. Nitrogen was run through the system for 10 to 20 minutes before each run to displace all air and the solutions were saturated with chlorine before the source was raised at the start of the reaction. During the entire period of chlorination to minimize photochlorination, only red light was used whenever it was necessary to observe the equipment. It should be noted that when the source is raised in the dark, a faint blue glow can be seen in the toluene solution, probably caused by Cerenkov radiation. At periodic intervals, the source was lowered to allow personnel to add more dry ice to the temperature control system. When desirable, however, it is possible to place part of the cooling system at a remote position so that uninterrupted runs can be carried out.

In most runs, the storage-bulb section of the glass apparatus (7, Fig. 15) was shielded by lead bricks from the direct radiation of the source. In one run, however, no shielding was employed and the reaction became so violent after about 15 seconds of irradiation that the chlorine and hydrogen chloride escaping from the hot toluene solution blew open a glass joint. In another run, the shielding bricks were removed after the run had continued for some time, in order to attempt to compensate for an apparently decreasing reaction rate as the reaction proceeded; the rate of reaction increased, but the temperature could still be controlled.

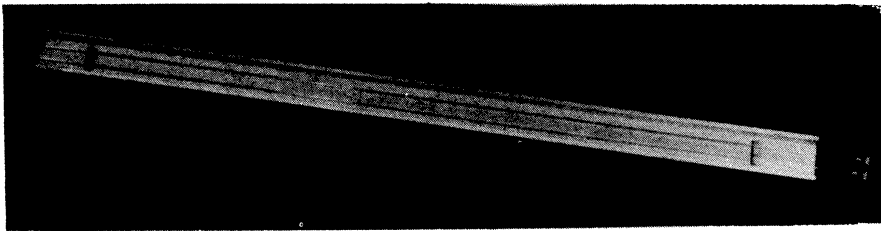


Fig. 21. Wooden Support Board for Glass Tubing to be put through the Chute Providing Access to the 10 kc Source Room. In Use, the Side Shown is Placed Down, when the Assembly is Put into the Chute.

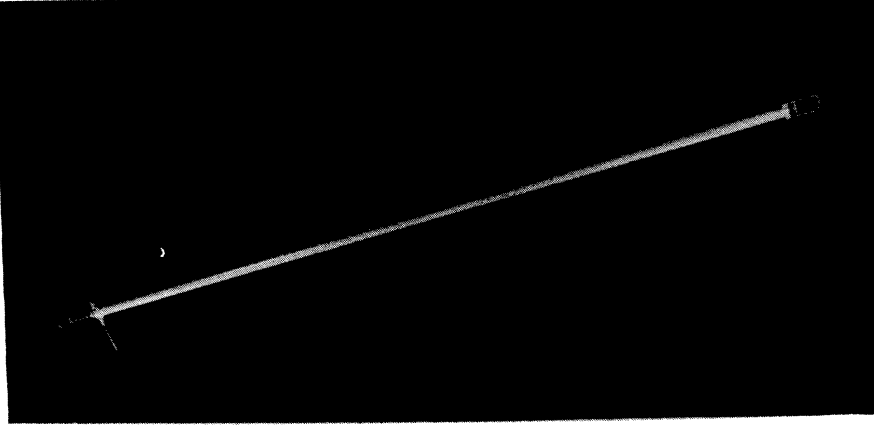


Fig. 22. Special Tool for Attaching and Removing Clips from Joints Located at Right Angle of the Access Chute to 10 kc Gamma Source.

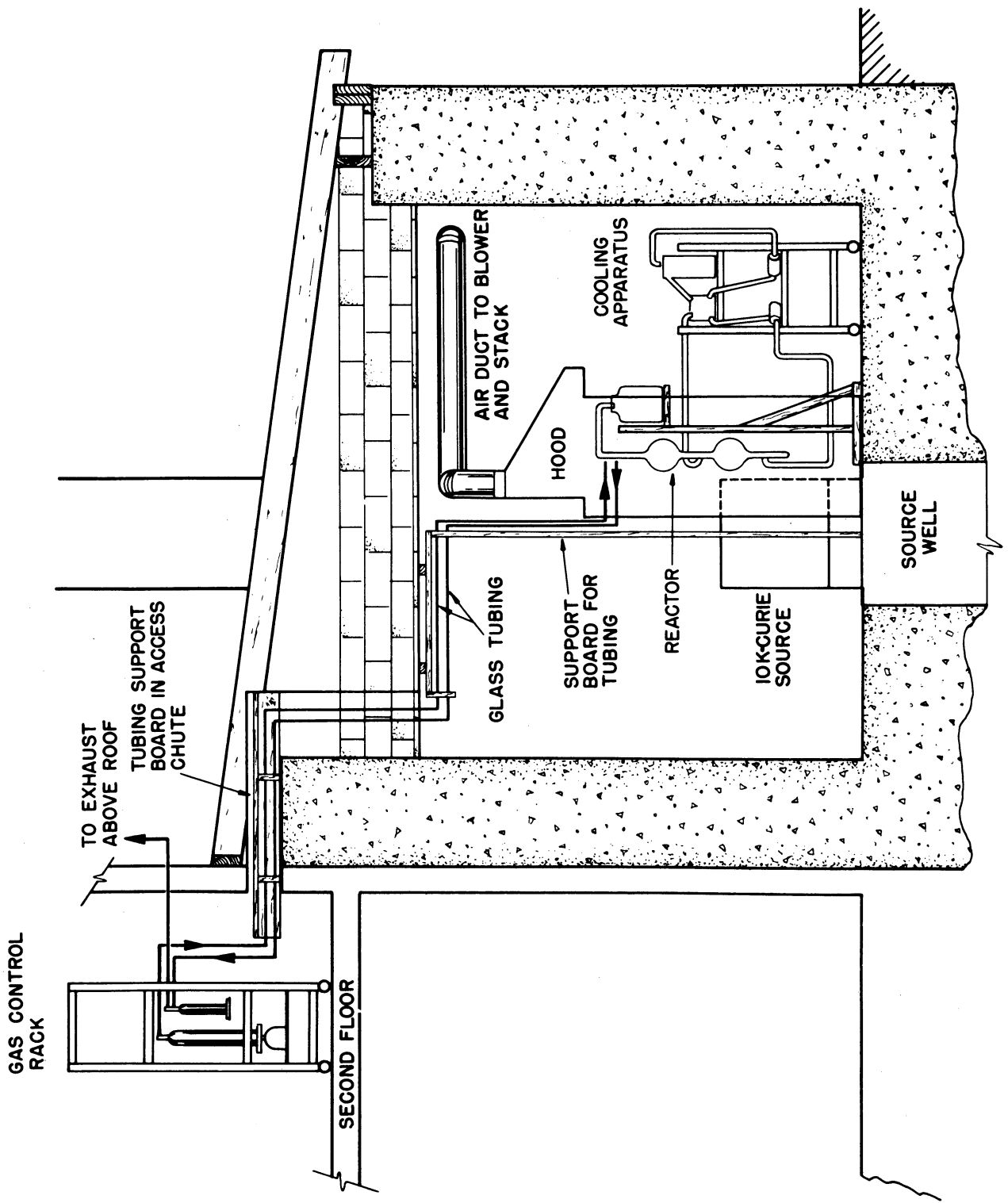


Fig. 23. Diagram of Complete Set-up for Reactions of Liquids with Chlorine Gas in the 10 kc Source.

The reaction mixture from one of these runs was distilled under vacuum, and high-boiling fractions were vacuum-distilled again. Table 8 summarizes the information on these fractions. Overlapping of temperature ranges was probably due to variations in pressure as receivers were changed. The theoretical chlorine content for a hexachloro addition product of toluene is 69.78% Cl.

TABLE 8

HIGH BOILING FRACTIONS OBTAINED FROM REDISTILLATION  
OF PRODUCTS OF REACTION BETWEEN TOLUENE AND CHLORINE

Fraction Number	Volume, ml	Temperature Range, °C	Pressure, Microns Hg	% Cl
VII-A	6.6	85-102	100-200	
VII-B	29.4	98-111	100-200	68.6
VII-VIII	4.0	110-115	100-200	
VIII-A	18.4	111-115	100-200	69.6
VIII-B	18.0	112-120	100-200	70.5
VIII-IX	3.1	120-125	100-200	
IX-A	10.0	125-135	100-200	70.7

The individual fractions were syrupy, crystal-clear liquids. After several weeks of standing, part of which was under refrigeration, some of the liquids became cloudy and crystals appeared to be precipitating out slowly. This production of liquids is perhaps not unusual, for if the product is 1,2,3,4,5,6-hexachloro-1-methylcyclohexane, a great number of stereoisomers may be expected from total addition of chlorine to toluene. It is possible to write twenty such different stereoisomers, and it seems probable that at least half of these should be important constituents of the mixture of reaction products. Thus it is not surprising that the combined effects of many mixed isomers and high viscosity prevented appreciable crystallization of the products.

In an effort to study the behavior of the reaction during its course, a run was made in which the chlorine-gas cylinder was weighed continually, and in which samples of the exit gas were taken for analysis. Figure 24 summarizes the resulting data. The analytical methods were not precise in this run, so data on the material balance of the chlorine can be regarded as only roughly indicative of the true reaction rates.



REACTION OF TOLUENE AND CHLORINE — 10 KC SOURCE 141540

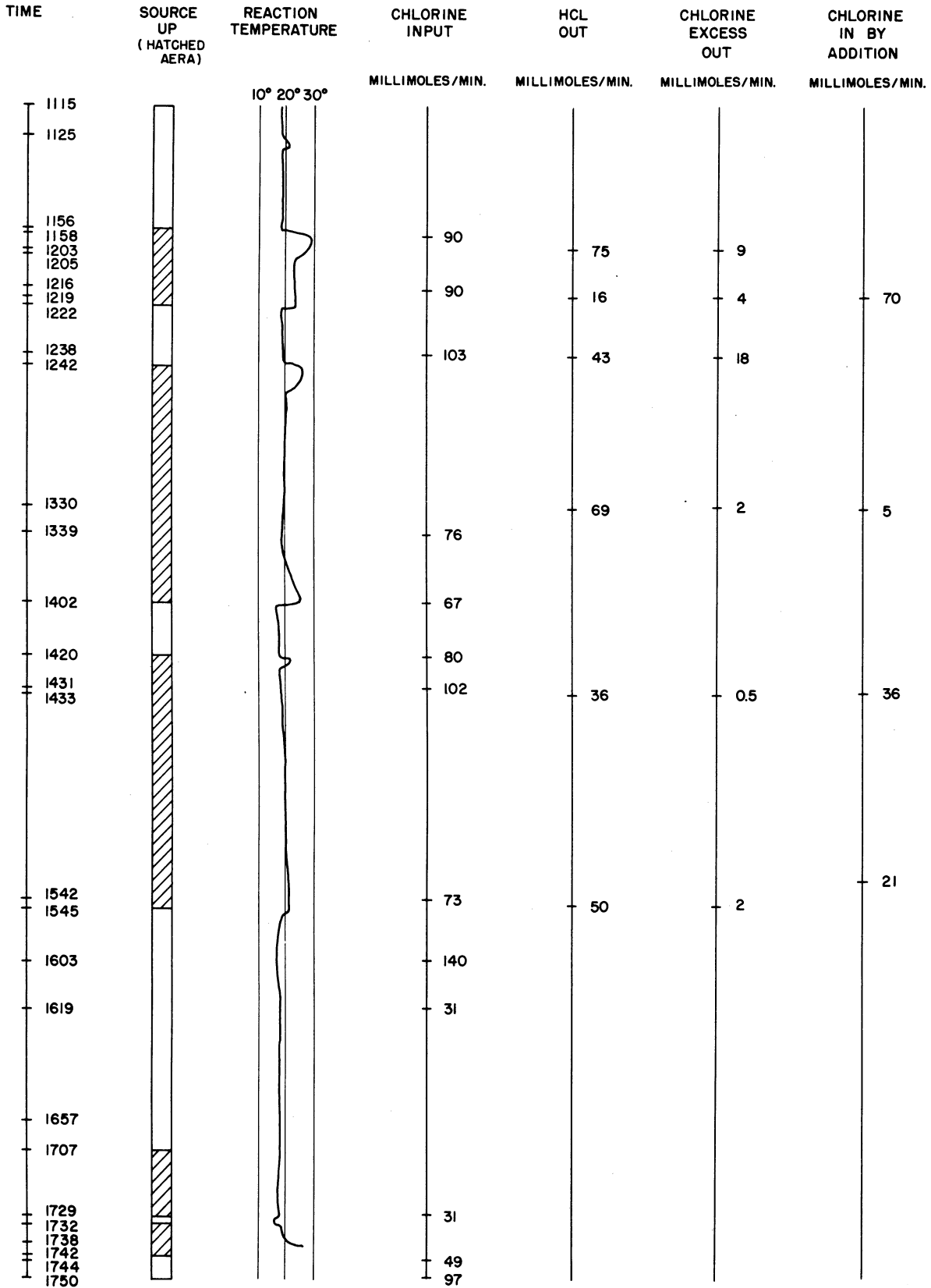


Fig. 24. Chart and Graph Showing Radiation, Temperature, and Material Balance at Various Times during a Reaction of Chlorine and Toluene in an Average Radiation Flux of 22 k Rep/Hour.

The behavior of the temperature curve is a striking example of the dependence of the reaction on the radiation field. Because of the nature of the temperature control system, a short time for readjustment was always required after a sudden change in heat production of the system. Thus, it can be seen that each time the source was raised into position for irradiation the temperature displayed a sharp increase, while each time the source was lowered the temperature dropped off. Furthermore, this effect is more pronounced at the start of the reaction than at a later time, when the rate had apparently decreased.

A summary of information on the runs made with toluene in the 10-kc source is presented in Table 9. The estimated average gamma flux rate was based on flux measurements in air at the centers of each of the two components (reaction and storage) of the glass apparatus. The overall yield was based on moles of supposed hexachloro addition products (high-boiling fractions with chlorine content in the 69-71% range) obtained from a given number of moles of toluene originally placed in the apparatus. Calculation of radiation yields in moles per liter per kilorep and in terms of "G" (molecules reacted per 100 electron-volts of gamma energy) was made using the density which was determined from a reactor solution used in one of the runs saturated with chlorine gas.

Inspection of the G values (Table 9) for the addition reaction in these compounds reveals that they are all in the neighborhood of 17,000.

The high values for G found in all these cases are somewhat unusual in radiation chemistry at the present time, and indicate a long reaction chain. Assuming about three primary ionization events per 100 electron-volts,<sup>11</sup> the chain lengths must be of the order of  $5 \times 10^3$  or greater. This figure also assumes that each primary ionization event produces a chain of molecules which react completely and solely to give the hexachloro addition product. The fact that appreciable substitution takes place indicates that the chain length for the addition process itself might be much larger. It is very interesting that the products obtained by gamma activation differ markedly from those usually obtained through actinic radiation activation (mostly sidechain substitution in this case). In view of the long reaction chain lengths the product isolated contained negligible amounts of those molecules originally activated in the primary process. Thus the reaction chains in the gamma-activated process would seem to be propagated by a different mechanism than those of the ultraviolet-activated process. This difference is being investigated further.

From one of the reaction runs of toluene and chlorine, 120 grams of those fractions which distilled over at 90-156°C (90-240 microns Hg pressure) were sent to be tested for entymological poison activity, since the supposed compound is the methyl-substituted derivative of commercial benzene hexachloride, which is currently used extensively as a pesticide.

TABLE 9  
SUMMARY OF THREE REACTION RUNS OF TOLUENE AND CHLORINE  
IN THE 10 KC 60 GAMMA SOURCE

Run Number	Volume of Sample ml	Control Temp., °C	Total up Time, min	Estimated Average Gamma Flux Rate, kilorep/hr	Total Dose Received, kilorep in air	Weight of Hexachloro Product Produced, grams	Moles of Product Produced	Overall Yield, %	Average Moles per (liter) (kilorep)	Average Value of G for Addition
141500	1440	20	71	24	28	185	0.61	4.5	0.014	14,000
141534	1450	20	121	22	44	371	1.2	8.8	0.017	18,000
141540	1500	20	226	22	82	778	2.5	18	0.018	19,000

F

After consideration of the rapid addition of chlorine to benzene and to toluene, and the nonreactivity of benyl, benzal, and benzo trichlorides under the same conditions<sup>2</sup> (page 29), a run was carried out in which chlorobenzene was treated with chlorine gas in the 1-ke cobalt-60 gamma source. In this case, the reaction proceeded at a more rapid rate than that for toluene. Table 10 summarizes the information obtained in this run.

The yield in Table 10 is based on the weight of crude product obtained by steam-distilling off the unreacted chlorobenzene and drying the solid residue; this procedure may yield values that are high. A sample of recrystallized material gave a chloride analysis of 76.0%, as compared to the calculated value of 76.3% for heptachlorocyclohexane, which would result from addition of six chlorine atoms to chlorobenzene. A run has been made in darkness with other conditions the same as those used during the gamma-induced reaction. Analysis of reaction products gave a value for chlorine content which was so close to the calculated value for unreacted chlorobenzene that virtually no reaction was indicated.

#### D. SUGGESTIONS FOR FUTURE WORK

It would be of interest to investigate further the polymerization of ethylene under gamma radiation with the objective of determining the cause for the induction period observed for the polymerization. It seems possible that small concentrations of impurities are responsible for the induction period. However, it is also possible that such an induction period might be characteristic of the gamma-induced polymerization and independent of chemical parameters.

If the ethylene could be removed shortly after polymerizing, then a continuous process for the polymerization might be developed. Such a procedure would permit closer control of those properties of the polymer which are dependent on total dose of radiation.

As mentioned earlier, under "Discussion of the Polymerization of Ethylene," elevated temperatures in conjunction with irradiation caused greater rates of polymerization of ethylene than did irradiation alone. Investigation of the influence of both elevated temperatures and irradiation of the polymerization of ethylene is certainly in order. Some suggestions for such a program were advanced in Progress Report 5,<sup>2</sup> based on some of the foregoing studies of radiation chemistry and on the work of Kennard.<sup>6</sup>

The electrical properties of the polyethylene made by gamma irradiation might well be studied.

The reaction between ethylene and sulfur dioxide proceeds rapidly enough under gamma radiation that it should be possible to secure much

TABLE 10

## REACTION OF CHLOROBENZENE WITH CHLORINE UNDER GAMMA IRRADIATION

Sample Volume, ml	Control Temp., °C	Total Reaction Time, min	Gamma Flux Rate in air, kilorep/hr	Total dose, kilorep in air	Weight of Hexachloro Addition Product, Grams	Moles of Product Produced	Overall Yield, %	Moles per (liter) (kilorep)	G for Addition
100	20	30	52	26	38	0.12	12	0.042	43,000

information concerning the behavior of this reaction., The physical properties of this polymer molded into massive form should be investigated.

The work on chlorination of aromatic compounds should be pursued with the object of attempting to find and correlate those reactions which differ from reactions promoted by chemical catalysis or ultra-violet radiation. This work would involve further study of reaction rates for those reactions already partially investigated, and the study of the reaction of other aromatic compounds with chlorine. Such studies might provide insight into the manner in which gamma irradiation promotes reactions which have large G values, and establish unique uses for the gamma radiation of fission products.

#### E. SUMMARY

1. Polymerization of Ethylene. (a) Ethylene has been polymerized by exposure to gamma irradiation from cobalt-60. The rates of reaction were sufficiently large that further work on this reaction appears to be promising.

(b) Polyethylene formed by gamma irradiation has been subjected to a preliminary evaluation. The polymer was found to be denser, less ductile, and of a higher ultimate strength than Bakelite DYNH polyethylene. Molecular weights of the radiation-polymerized materials increased with radiation dose to a value of about 40,000 when estimated from melt viscosities. Most samples were insoluble in tetralin, but estimates of molecular weights from solution viscosities were not conclusive. Crystallinities estimated from densities varied from 71 to 77 percent.

2. Chlorination of Aromatic Compounds. (a) Toluene and chlorine were reacted in the presence of gamma irradiation using up to 1.5 l. of toluene in one run. Fractional vacuum distillation of the reaction products yielded high boiling materials whose chlorine content is close to that for a hexachloro addition product of toluene and chlorine in addition to products of substitution reactions. For some runs of varying total gamma dosage, the G value for addition was in the neighborhood of 17,000. Preliminary rate data for one run have been taken.

(b) Chlorobenzene and chlorine were reacted under gamma irradiation. It was found that the addition reaction proceeded with a G value of about 43,000.

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Progress Report No. 7

UTILIZATION OF THE GROSS FISSION PRODUCTS

The Effect of Gamma Radiation on Chemical Reactions

J. J. Martin

L. C. Anderson

B. G. Bray

D. E. Harmer

R. A. Carstens

C. E. Eckfield

J. P. Holmes

R. R. Nissle

W. M. Sergy

H. H. Yang



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PART II. SUBPROJECT M943-4, THE EFFECT OF  
RADIATION ON CHEMICAL REACTIONS

Personnel:

Subproject Supervisors: Joseph J. Martin, Associate Professor of Chemical and Metallurgical Engineering; and Leigh C. Anderson, Professor and Chairman of the Department of Chemistry

Senior Research Assistants: B. G. Bray, David E. Harmer

Assistants in Research: R. A. Carstens, C. E. Eckfield, J. P. Holmes, R. R. Nissle, W. M. Sergy, H. H. Yang

A. INTRODUCTION

Since the preparation of Progress Report 6, work has been carried out on three major fronts: (1) The polymerization of ethylene under gamma radiation has been studied over a wide range of temperature. At the same time the copolymerization of ethylene and sulfur dioxide has received a small amount of additional attention. (2) The rate of reaction of chlorine with toluene under gamma radiation has been studied in more detail than reported by this laboratory earlier, and fractions of the product have been subjected to further tests to prove the presence of large amounts of the addition product of chlorine and toluene. (3) On the basis of reaction-rate data for the chlorination of benzene under gamma radiation, a preliminary design has been made of a plant to produce benzene hexachloride. A comparison is given between the estimated cost of the product from this gamma-activated process and product from the conventional ultraviolet process which is employed commercially.

The following sections of this report describe these studies in greater detail.

## B. POLYMERIZATION OF ETHYLENE

The study of the effect of gamma radiation on the polymerization of ethylene as inaugurated by Lewis<sup>2,3,4,21</sup> has been considerably extended. Lewis carried out all polymerization runs at room temperature and at varying pressures and radiation dosages. In the work reported here, primary interest has been in varying the temperature of the polymerization reaction to determine its effect on the rate of the reaction and the nature of the products.

### 1. Equipment Used

The high-pressure stainless-steel bomb built by Lewis<sup>21</sup> was used for all polymerization runs. A set of heaters built by Lewis was placed around the bomb in all runs, regardless of whether heating was required, so that the radiation flux within the bomb would be the same in all cases. The bomb was loaded and emptied in the same manner described by Lewis.<sup>21</sup> The temperature was raised from 13 to 220°C, while the reacting pressure of pure ethylene was varied from 1075 to 1950 lb/sq in.

### 2. Visual Inspection of the Products

In the case of the three runs at the lowest temperatures (runs 145800, 145801, and 145807 described in Table 2) three distinct layers of solid polyethylene product were found in the bomb at the conclusion of the runs. The top layer was a spongy, white mass that adhered to the sides of the bomb with a physical consistency much like that of a fine porous sponge. The middle layer was a white curdy material, much resembling the curds in cottage cheese, and was directly opposite the center of the gamma radiation source; therefore, receiving the highest dose rate. The bottom layer was a hard solid layer that rested on the bottom of the bomb. This layer was from three quarters to two inches thick and had to be cut out of the bomb with a chisel.

Runs 145808 and 145812 yielded a finely divided white powder which adhered to the sides of the bomb. There was no particular variation in the physical appearance of this powder within the bomb. The powder did not always fall to the bottom of the bomb, but usually remained attached on the sides of the stainless-steel vessel.

The runs conducted at the highest temperatures (runs 145813 and 145814) were made at approximately 220°C and yielded a creamy white opaque

liquid of high viscosity with an odor similar to that of used motor oil. After standing several days, a finely divided white powder precipitated out from the product and left a clear cream-colored liquid layer.

TABLE 2  
IRRADIATION OF ETHYLENE

Run Number	Initial Pressure, psig	Reaction Temp, °C	Hours Irradiated	Averaged over Reactor		Polymer, gm	Radiation Yield A, gm-moles reacted	
				Dose Rate, kilorep/hr	Total Dose, megarep		(metric) (ton)	(mega-) (rep)
145800	1450	13	65.1	54.2	3.53	21.8	2370	
145801	1260	13	91.75	53.8	4.94	39.7	3570	
145807	1950	39	70.9	53.5	3.79	45.6	5860	
145808	1500	88	71.33	26.6	1.90	1.4	438	
145812	1400	90	91.93	47.0	4.32	3.8	542	
145813	1425	220	77.8	53.0	4.12	6.3	1695	
145814	1075	217	114.5	35.4	4.06	17.9	3860	
145817*	940	25	98.25	37.8	3.72	15.1	2130	
145824**	410	25	64.0	62.5	4.00	33.9	7030	

\*42 psig gaseous SO<sub>2</sub> added to reaction.

\*\*20 gm liquid SO<sub>2</sub> added to reaction; vapor pressure was 42 psig.

### 3. Physical Properties of the Solid Polyethylene Product

The radiation yields (A values) given in Table 2 are in general higher than those reported by Lewis<sup>21</sup> but the dose rate to the reactor also was usually higher. The melting points and tensile strengths of the polyethylene prepared by polymerizing ethylene in a field of gamma radiation are listed in Table 3. The tensile strengths are somewhat higher than those reported by Lewis. These tensile strengths were made on an Instron tensile tester with a head and/or jaw speed of ten inches per minute. This speed was selected to eliminate the cold flow phenomenon observed in plastics in general and polyethylene in particular. The tensile strengths determined by Lewis were made on a Gardiner-Parks tensile testing machine where the cold-flow phenomenon was present.

The film for the tensile specimen was molded in a two compartment mold at 300°F at 1500 psi for 5 minutes. The sample was then punched from

TABLE 3

## PROPERTIES OF IRRADIATED ETHYLENE

Run Number	Sample Section	Melting Point, °F		Tensile Strength, psi	Elongation at Rupture, in./in.
		Lower	Upper		
145800	Middle	258.4	>700	3354	.24
145801	Middle	263.0	>700	3211	.23
145801	Top	259.0	>700	2947	.30
145807	Top	257.2	>700	2455	.24
145807	Bottom	260.4	>700	2600	.25
145808	Total	222.0	230.4	{ Too small }	
145812	Total	217.2	221.7		
145813	Total	Liquid		Liquid	
145814	Total	Liquid		Liquid	
145817	*Total	>465			
145824	*Total	>450			

\* Decomposes before melting at the temperature indicated.

the film with a standard sample die. The sample was somewhat larger than those used by Lewis.

Melting points of the polyethylene solids were determined on the laboratory melting-point bar<sup>3</sup> and in general are higher than those obtained by Lewis. They are, however, consistent with those of Lewis when account is taken of the difference in dose rates.

#### 4. Other Work on Polymerization of Ethylene

Hayward and Bretton<sup>17</sup> at Yale University, working with a 400-curie gamma ray cobalt-60 source, have investigated the polymerization of ethylene under conditions ranging from 80 to 460°F and from 0.5 to 21 atmospheres. Both liquid and solid products were obtained.

Lewis<sup>21</sup> observed the effect of pressure on the polymerization of ethylene in both 1-kilocurie and 10-kilocurie sources at this laboratory. He observed little effect of pressure at constant temperature on the rate of polymerization.

A comparison of the ranges of temperature and pressure covered by Hayward and Bretton and by Lewis is shown in Fig. 8 of this report.

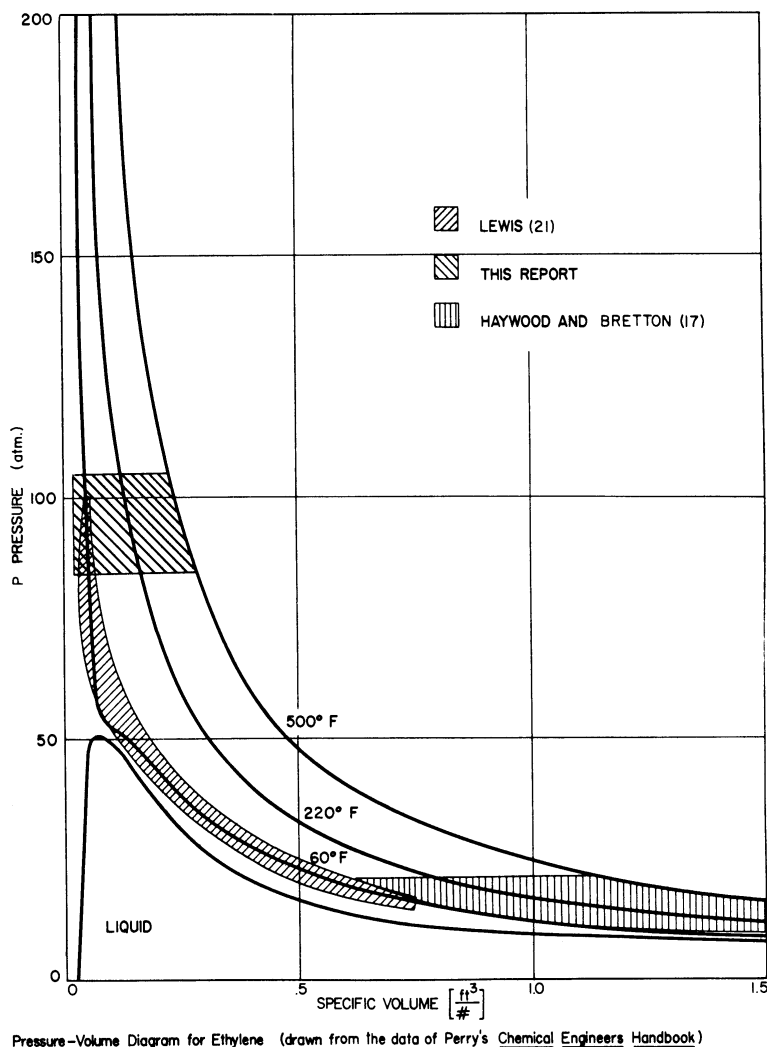


Fig. 8. Regions of Investigation of Polymerization of Ethylene under the Influence of Gamma Radiation.

### C. POLYMERIZATION OF ETHYLENE AND SULFUR DIOXIDE

As reported by Lewis, the addition of sulfur dioxide to ethylene in the reaction bomb under gamma radiation produces a copolymer of the two compounds. The results of the two runs conducted in this study are reported in Tables 2 and 3. A fluffy white granular product was obtained which decomposed before melting at greater than 450°F; leaving a brown and black residue. All attempts to press this polymer into a film in order to obtain tensile test specimens resulted in decomposition of the product. The film produced contained black and brown decomposition specks and was very brittle.

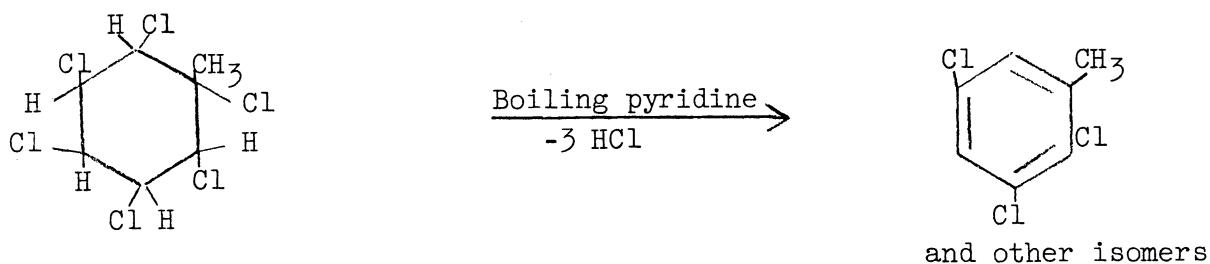


These two runs are reported here in the interest of coupling with the results of prior work. The physical properties of these products are being investigated more fully and future work is planned in the copolymerization of the two compounds.

#### D. CHLORINATION OF AROMATIC COMPOUNDS

##### 1. Investigation of the Structure of the Primary Product Obtained from the Gamma Ray Activated Reaction of Toluene with Chlorine

(a) Dehydrohalogenation. The supposed hexachloro addition product which has been obtained by reaction of toluene with chlorine under gamma radiation<sup>4</sup> has been investigated more closely in order to establish whether it is indeed the postulated product. The first step in the investigation was the degradation to a supposed trichloro toluene by means of dehydrohalogenation in boiling pyridine.



Previously it was demonstrated that nearly one-half of the total chlorine content was eliminated during this reaction.<sup>3</sup> As starting materials for the reaction, mixtures of high-boiling products obtained from the chlorination runs in the 10-kilocurie-source equipment<sup>4</sup> were used and several dehydrohalogenations were carried out.

The initial materials used for one dehydrohalogenation were 176 gm of a material boiling at 123 to 154°C (50 to 60 microns of Hg) mixed with 89 gm of a material boiling at 125 to 158°C (65 to 75 microns Hg). The theoretical chlorine content for a hexachloro addition product of toluene and chlorine is 69.8 percent; the materials used contained 69.8 to 70.1 percent chlorine, respectively, indicating the presence of some higher chlorinated material in the latter of the two. This mixture of materials was added to about 1.5 l of redistilled pyridine and refluxed for 47 hours. On cooling, crystals, presumably pyridine hydrochloride, formed in the dark green liquid. The material in the flask was added to a large excess of dilute cold hydrochloric acid, and after standing, the upper aqueous layer was decanted off. The organic residue was heated to about 70°C and filtered; some gummy residue which seemed to contain most of the dark green coloration

remained on the filter paper. The filtrate was a dark brown oil, density 1.4 gm/cc, weight 87.7 gm. Assuming the starting materials to be  $C_7H_8Cl_6$  and the oil to be  $C_7H_5Cl_3$ , a yield of 53.3 percent is indicated for the dehydrohalogenation reaction.

The oily product from the dehydrohalogenation was fractionally distilled in a Podbielniak column at atmospheric pressure; a summary of these data is presented in Table 4. Each of the first nine fractions obtained by distillation was recrystallized from methanol, while the remainder, being nearly insoluble in methanol, was recrystallized from ethanol. Fractions three through eight gave two phase mixtures when the methanol was partially evaporated and the resulting residues cooled, so these phases were separated and crystals taken from each. Melting points were taken on a melting-point bar. Some fractions were analyzed for chlorine content by the use of sodium diphenyl reagent followed by a Volhard titration, but the values thus obtained are only approximate because of small sample size. Carbon-hydrogen analyses were also taken on certain samples.

It is apparent from the chemical analyses of these materials that both tri- and tetrachloro compounds are present, although the majority of material appears to be the expected trichloro compound. The presence of the tetrachloro material may arise from either or both of two causes; the dehydrohalogenation may have been incomplete, or the higher chlorine content of part of the starting material may have been carried through as an extra chlorine atom in some of the molecules.

The melting-point ranges found in many of these compounds indicate that separation was not complete. However, they indicate that one of the products is undoubtedly the known compound, 2,4,5-trichlorotoluene, whose melting point is given in the literature as 80 to 82°C<sup>11,24,28</sup> and whose boiling point has been given as 229 to 230°C.<sup>30</sup>

(b) Oxidation of the Dehydrohalogenated Material. A quantity of supposed hexachloro addition product of toluene and chlorine was dehydrohalogenated as before and then oxidized to obtain an acid. For this treatment, 60 gm of material boiling at 90 to 156°C (90 to 240 microns of Hg) were placed in 100 ml of pyridine and heated at just below the reflux temperature for 48 hours. Water was added to extract the pyridine hydrochloride and excess pyridine. The organic layer was neutralized with nitric acid, then 750 ml of 20% nitric acid were added. About one-half of this two-phase mixture was sealed into glass tubes and heated for 66 hours at 135 to 153°C. On cooling, large flocculant crystals and a solid phase separated out from the solution.

TABLE 4

FRACTIONS OBTAINED BY THE DISTILLATION AND RECRYSTALLIZATION  
OF THE DEHYDROHALOGENATED PRODUCT FROM REACTIONS OF CHLORINE  
WITH TOLUENE UNDER GAMMA IRRADIATION

Fraction Number	Weight, gm	Boiling Range, Upper or Lower °C		Layer from Methanol Mixture	Melting Point, °C	% by Analysis		
		(atm pressure)				Cl	C	H
1	0.9	210.5-231.0						
2	1.3	228.0-238.5						
3	8.0	238.5-241.5	Lower	77.5	54.0	43.0	2.68	
4	1.5	242.0-242.5	Lower	77.3-78.6				
			Upper	79.8				
5	9.3	241.5-242.0	Lower	77.5-78.0	54.2			
			Upper	77.8-78.6				
6	4.4	242.0-243.0	Lower	78.0-78.6	56.8	43.0	2.50	
			Upper	76.4-77.8				
7	2.7	243.0-245.5	Lower	76.4-78.0				
			Upper	77.0				
8	3.0	245.5-257.0						
9	0.6	258.0-272.0		66.7-70.2				
10	1.3	273.0-277.0		80.2-88.8				
11	3.3	277.0-279.5		88.2-89.8	61.4	36.7	1.86	
12	1.1	279.5		80.2-86.6				
13	1.1	277.0-278.5		87.6-88.8	61.1			
14	1.6	278.5		87.5-90.0	61.1			
15	3.1	Hold-up drained from column	Not recrystallized	94.0-96.8	61.4			

Theoretical values for percent of C, H, and Cl:

Trichlorotoluene: C = 43.00 %, H = 2.58 %, Cl = 54.4 %

Tetrachlorotoluene: C = 36.6 %, H = 1.75 %, Cl = 61.7 %

Tetrachloromethyl cyclohexadiene (incomplete dehydrohalogenation product): C = 36.2 %, H = 2.61 %, Cl = 61.2 %

The solids were filtered off from the nitric acid solution and dissolved in ammonium hydroxide solution. This solution was extracted with toluene to remove nonionic materials. The organic acid was then precipitated by addition of nitric acid, filtered, washed, and dried. The yield was 9.5 gm, or 42 percent overall, based on the original starting materials and assuming trichlorobenzoic acid as the product.

Identification of the final product required separation of the crude product into its various isomers. Since each isomer should differ in its acid strength, the first attempted separation was based on this property. A series of extractions was carried out on 4 gm of acid so that during each step one-half of the acid would dissolve in an aqueous ammonium hydroxide layer, while the other half would be retained in the organic phase. These extractions were carried out until 32 divisions were obtained. However, when the melting points of these 32 fractions were taken, long ranges indicated that practically no separation had been effected.

Since the differences in acid strength of these materials thus appeared to be quite small, it seemed advisable to turn to a chromatographic type of separation. Still making use of the acid strength characteristics of the material, ion-exchange chromatography was employed. A highly basic anionic resin, Dowex-1, 8 percent cross linked, 200 to 400 mesh, was used. Two columns were used in series, the first 400 x 10 mm ID and the second 20 x 6 mm ID, each being packed two thirds full of resin. The first column was jacketed and water at 55°C was circulated around it. Before use, the resin was backwashed and put through a chloride-hydroxide cycle twice.

After several experiments, it was found that the following conditions were satisfactory for operation of the column. The resin was prepared for use in the chloride form. The mixed isomers of the acid (about 1 gm) were introduced at the top of the column as the ammonium salt solution in 75% ethanol (10 ml volume). The column was washed with distilled water and elution was carried out with 0.01N and 0.1N hydrochloric acid in 75% ethanol (25% water). Twenty 5-ml samples were collected at a slow rate, 1 to 16 with 0.01N acid and 17 to 20 with 0.1N acid. Initially, dark bands were observed to move down the column, but these became indistinguishable as they approached the base of the upper section

It was found on evaporation of the solvent from the fractions that the first two contained nearly no solids, while numbers 3 through 9 contained about equal amounts of solids. Numbers 10 through 12 contained small amounts of impure solids, and the remaining fractions contained only traces of solids. The solid materials were recrystallized from hot water.

The degree of separation of isomers obtained is illustrated in Fig. 9, which is a graph showing melting ranges of the series of samples.

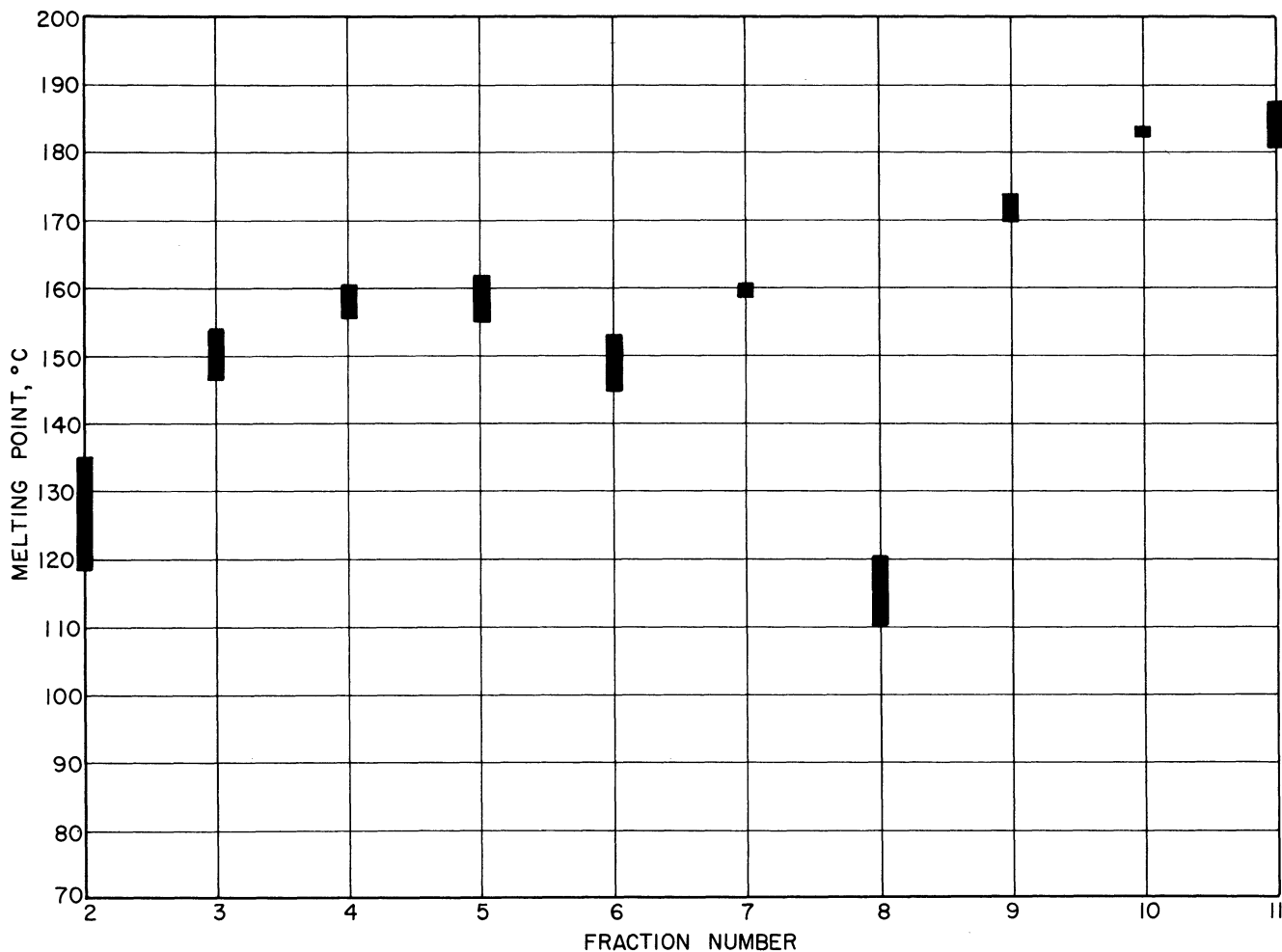


Fig. 9. Melting-point Ranges for Fractions of Isomeric Trichlorobenzoic Acids Separated by Ion-exchange Chromatography.

The melting-point maxima are accompanied by a decrease in temperature range showing an increase in purity of the material in that particular fraction. The much lowered melting points and long ranges of fractions 2 and 8 indicate possibly that these were collected at a point of transition from one chromatographic band to another. Fractions 7 and 10 exhibit the sharpest melting points and lie in a range close to that reported for isomers of trichlorobenzoic acid. The increased range but higher first melting point of fraction 10 could perhaps be attributed to the presence of amounts of a much higher melting isomer in this fraction. All melting points of this series of fractions are recorded in Table 5, together with chloride analyses and data for comparison with reported values for trichlorobenzoic acids.

Fractions 4 and 5 merit special attention. During the determination of melting points on a melting-point bar, these two fractions had the melting point listed when freshly contacted to the hot surface. However, when they were held below the melting temperature, part of the material

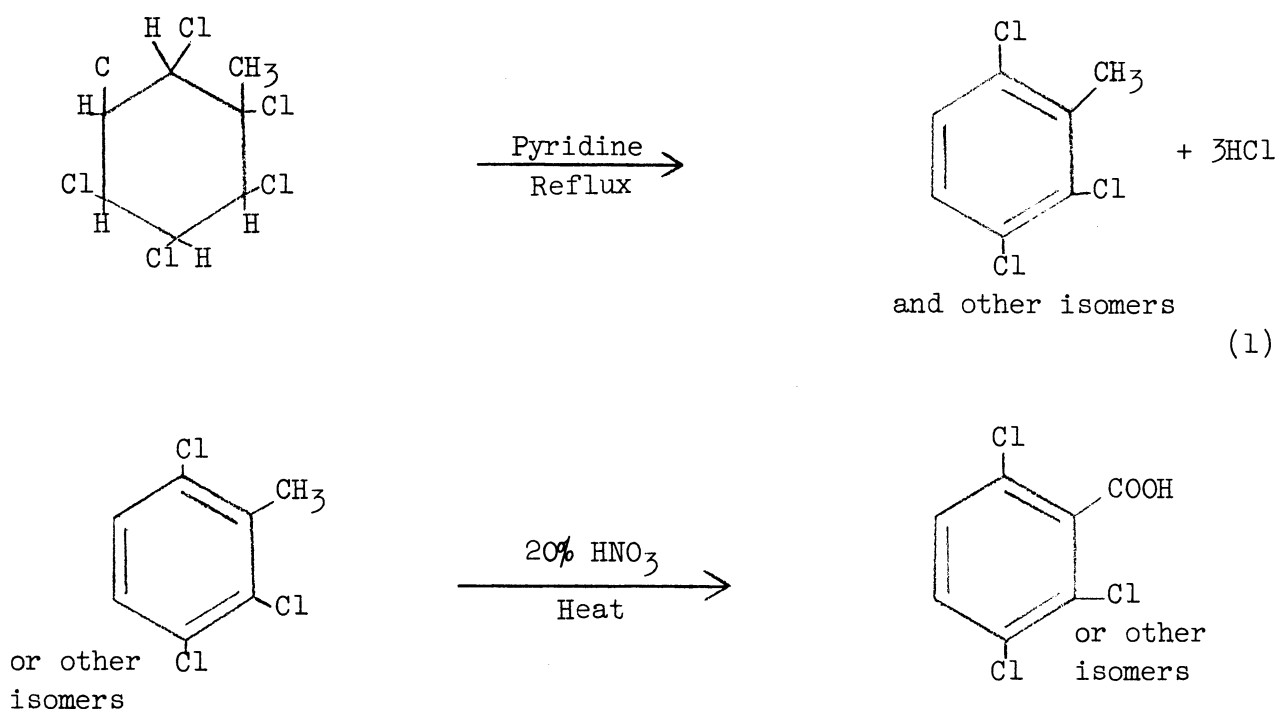
TABLE 5

FRACTIONS OBTAINED BY CHROMATOGRAPHIC SEPARATION OF ACIDS FROM THE  
DEHYDROHALOGENATED PRODUCT FROM REACTION OF TOLUENE AND CHLORINE

Fraction Number	Melting Point, °C	% by Analysis			Comparison Compound	Melting Point of Comparison Compound	% Calculated from Comparison Compound		
		Cl	C	H			Cl	C	H
2	118.7-135.0								
3	147.0-154.4								
4	156.0-160.6								
5	155.6-162.0								
6	145.6-153.2								
7	159.4-160.8	49	37.4	1.69	2,4,5 trichlorobenzoic acid	163	47.2	37.3	1.34
					2,3,6 trichlorobenzoic acid	163-4			
					2,4,6 trichlorobenzoic acid	164			
8	110.5-120.7								
9	170.2-173.8								
10	182.6-183.6	46			2,3,4 trichlorobenzoic acid	186-7	47.2		
11	180.8-187.2								

was found to sublime, leaving a material of a higher and sharper melting point. In a further investigation, quantities of fractions 4 and 5 were placed in a sealed melting-point tube. This tube was partially immersed in an oil bath at 180°C until a film of material had condensed on the cooler walls of the upper end of the tube. The tube was then sealed off at the center and melting points of the more volatile materials were taken. Table 6 is a summary of information on the products of this separation procedure and data for comparison with values reported for isomers of trichlorobenzoic acid.

Work on degradation of the product of the reaction of toluene with chlorine under gamma irradiation can be summarized by the following equations:



The products obtained by dehydrohalogenation and subsequent oxidation confirm the hypothesis that chlorine adds to the ring of toluene and further indicate that substitution of more halogen atoms for hydrogen atoms occurs in some of the molecules of the hexachloro addition compound.

## 2. Separation of Products of Chlorination of Toluene

(a) Attempted Crystallizations. Several unsuccessful attempts were made to obtain a crystalline solid from the syrupy form in which the hexachloro products were obtained. Carbon disulfide, methanol, petroleum ether, glacial acetic acid, and isopropyl alcohol were miscible with the chlorinated material; a mixture of 75% methanol in water formed a two-phase system when

TABLE 6

## MELTING POINTS OF SEPARATED COMPONENTS OF FRACTIONS 4 AND 5 OF TABLE 5

Fraction	Melting Point, °C	Comparison Compound	Melting Point of Comparison Compound	% Calculated		% by Analysis	
				Compound	C	H	C
4-sublimate	166.0-166.5	2,3,6 trichlorobenzoic acid	163-164	37.3	1.34	37.4	1.22
		2,4,6 trichlorobenzoic acid	164			in mixture before sublimation	in mixture before sublimation
4-residue	163.2	2,4,5 trichlorobenzoic acid	163	37.3	1.34		
5-sublimate	166.0-166.5	2,3,6 trichlorobenzoic acid	163-164	37.3	1.34	37.4	1.69
		2,4,6 trichlorobenzoic acid	164			in mixture before sublimation	in mixture before sublimation
5-residue	162.0	2,4,5 trichlorobenzoic acid	163	37.3	1.34		



mixed with the syrup, but repeated extraction procedures gave no evidence of separation of components of the chlorinated material or of production of crystalline solids.

(b) Analysis of Solids from the Reaction Mixtures. The liquid mixtures consist chiefly of unreacted toluene, benzyl chloride, and the chlorine addition products of toluene. The liquid product from several runs became cloudy after a period of standing and a small amount of very fine crystals slowly separated. The solids which formed were investigated further to determine whether they were crystalline 1,2,3,4,5,6-hexachloro-methylcyclohexane. They were separated from the mother liquors by centrifugation, placed on porous plate for oil removal, and recrystallized from methanol. Analysis for chlorine content showed variable composition (ranging from 72.1 to 72.8% chlorine) for materials from various runs and can probably be regarded as impure heptachloro products (theoretically 73.1% chlorine) arising from substitution of additional chlorine in the hexachloro product.

### 3. Investigation of Reaction Rates between Toluene and Chlorine

(a) Apparatus. A series of reactions between toluene and chlorine was carried out to obtain data from which the kinetics of this reaction could be determined in order to gain better insight into the nature of the activation produced by the gamma irradiation. The equipment used was a combination of certain parts described in previous reports. Gas handling and control equipment were similar to that outlined in Fig. 23 of Progress Report 6.<sup>4</sup> The glass reaction vessel shown in Figs. 62 and 63 of Progress Report 5<sup>3</sup> was used at various distances from the source and was connected to the glass lines leading to the gas-control apparatus located on the second floor.

In early experimental runs the amount of chlorine was ascertained by weighing the gas cylinder during the run, but it soon became apparent that this procedure was not accurate enough because of the inherent insensitivity of the type of balance usable under the large weight of the steel cylinder. An orifice-type meter was next used in which the pressure drop of the gas was measured as it passed through a calibrated glass orifice; results in this case also lacked reproducibility. Satisfactory measurements of the inlet gas flow were finally obtained with the use of a pair of "Rotometer" type flowmeters. These instruments were made of Pyrex with sapphire floats and were connected in series so that the two different ranges might be used without the need of stopcocks. They were calibrated against nitrogen, ethylene, butane, carbon dioxide, and ethane, according to the correlation of Martin.<sup>23</sup>

A four-way stopcock was used for taking samples of exit gas from the reaction; this made it possible to purge a gas absorption bottle with nitrogen, pass all the exit gas through it for a specified time, then purge out the connecting tubes with nitrogen again. The absorption bottles were provided with fritted-glass dispersion tubes to facilitate efficient absorption in the solution. The fritted tubes were calibrated frequently to assure that the pressure drop of the gas through each was not significantly different from the rest. During experimental runs, except for the periods during which samples were taken, the exit gas was vented to the atmosphere or passed through large absorption bottles containing 50% sodium hydroxide solution. Figures 10 and 11 illustrate the gas-handling equipment.

(b) Analytical Methods and Preliminary Results. The method used for analysis of exit gases, and hence, the choice of absorption solution, received considerable attention and several difficulties were encountered. Methods making use of liberated oxygen from hydrogen peroxide or of oxidation of iodine compounds were found to lack precision under the experimental conditions of this work. Since it can be shown theoretically that ferrous ion should be oxidized quantitatively to ferric ion by chlorine, an analytical procedure was devised making use of this reaction. In order to gain efficient solution of the gas, two liquids were used in each absorption bottle. A lower layer of reagent-grade carbon tetrachloride provided rapid absorption of excess chlorine in the exit gas, while an upper layer of aqueous acidic ferrous sulfate dissolved all hydrogen chloride in the gas stream. Examination of two absorption bottles in series showed that gas absorption was complete at the flow rates ordinarily used.

After absorption of the gas sample, the absorption bottle was shaken vigorously. This caused the dissolved chlorine in the lower layer to react completely with the ferrous sulfate of the upper layer. An aliquot portion of this layer was then titrated with ceric sulfate for ferrous ion content, which when subtracted from the original content gave the amount of chlorine absorbed. A second aliquot was oxidized with hydrogen peroxide to convert all ferrous ion to ferric ion and analyzed for chlorides by the Volhard method. Thus, free chlorine and total chloride could be determined from a single absorbed gas sample. Preliminary investigations indicated the method should be capable of giving precise results on free chlorine determinations. A series of experiments using the equipment previously described and using the ferrous absorption method were made. When the gas flowmeter had been properly calibrated and the reaction rates calculated, it was found that results were very scattered. Therefore, a very thorough investigation of analytical methods was imperative. Using samples of 99.5 to 99.8% pure chlorine gas, runs were carried out in which the gas passed through dry glass tubes only, and samples were taken in the usual manner. Several runs showed differences as great as 10 percent in the amounts of chlorine measured at the flowmeters, analyzed as free chlorine, and analyzed as chloride. When

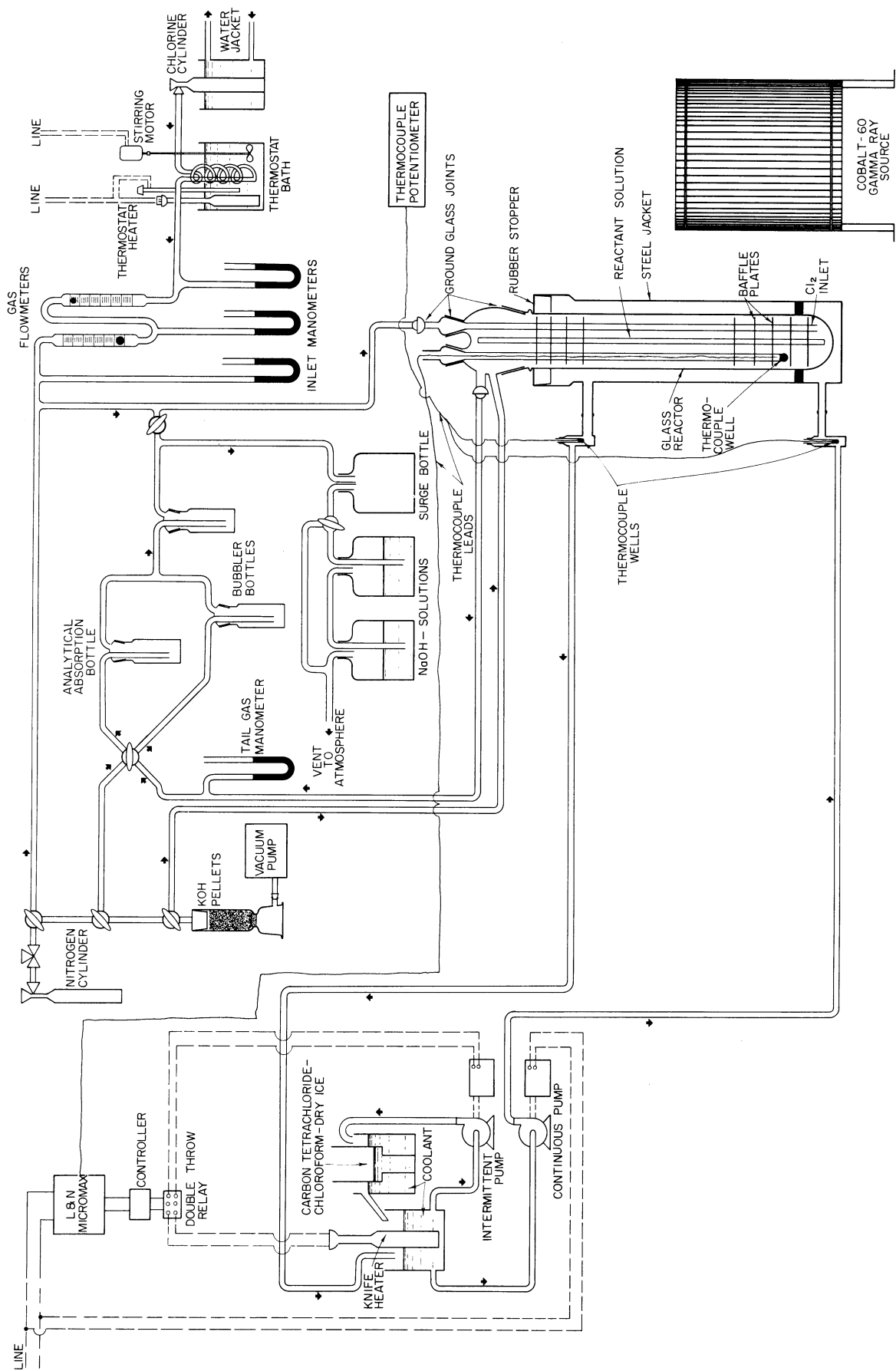


Fig. 10. Flowsheet for Equipment Used to Determine Reaction Rates between Toluene and Chlorine.

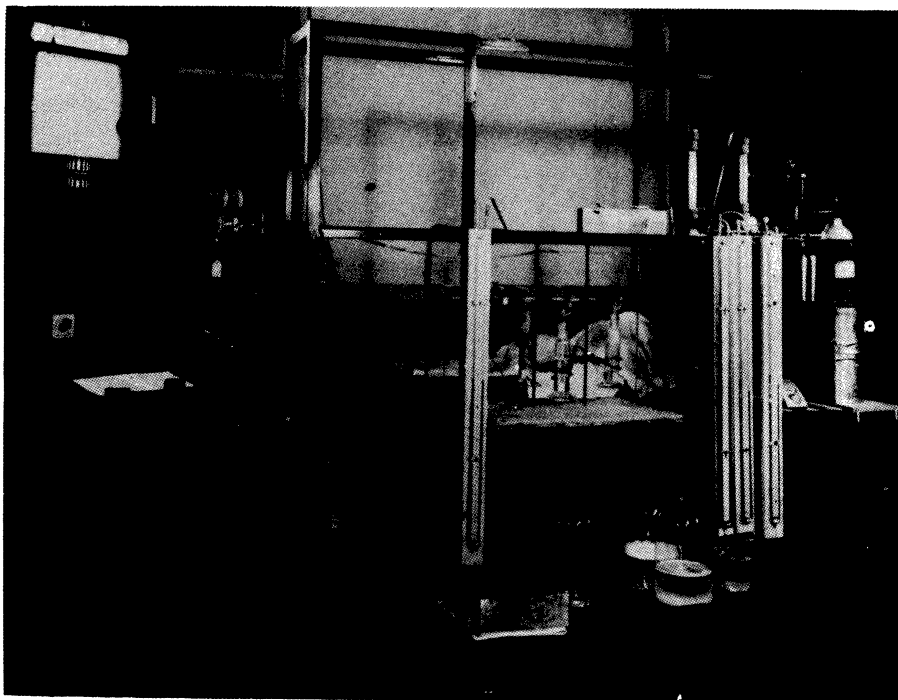


Fig. 11. Gas-Control Equipment Rack Used for Reactions between Toluene and Chlorine.

samples were absorbed in potassium iodide and titrated with sodium thiosulfate, a significantly different deviation from the flowmeter values was obtained. When potassium hydroxide was employed as absorbent, followed by hydrogen peroxide reduction of the hypochlorite formed, the chloride ion titrated in this solution showed still a different deviation from the flowmeter value. A satisfactory explanation for the failure of the ferrous sulfate method of analysis has not been found, but it was abandoned in favor of a more precise method.

Absorption of chlorine in alkaline sodium arsenite has been published as an analytical method.<sup>12,34,37</sup> By use of 0.2N sodium arsenite in 3N potassium hydroxide, it was found that absorption of the exit gas stream was rapid and complete. For analysis, an acidified aliquot portion was titrated with ceric sulfate, giving free chlorine by difference. A second aliquot was acidified and analyzed for chloride ion by the Volhard titration method. Thus, free chlorine and total chloride can be determined from a single absorption sample. The arsenite solution is sufficiently stable to eliminate the need for an inert atmosphere and the use of carbon tetrachloride as an absorbent is avoided. Agreement between free chlorine and chloride values is good, with deviations of 1 percent or less. A somewhat larger discrepancy is noted between the flowmeter values and the results of these analytical methods. A small correction on calculated flowmeter values may be necessary.

(c) Equipment Changes. Further refinements of technique for kinetic runs have involved certain modifications in equipment. A new all glass reactor, illustrated in Figs. 12, 13, and 14, has been constructed. The stream of chlorine gas is caused to bubble back and forth across a series of five baffle plates. Above this is a space for foam separation. Further up the tube is a series of baffles, placed so that the exiting gases follow a spiral path throwing entrained spray against the outer walls of the tube. The chief advantages of this design are larger contact time between the gas and liquid phases, more efficient separation of entrained liquid, less open space for gas above the liquid with resulting decreased lag in the time required for gases to return for analysis, complete separation of parts for cleaning, and location of the thermocouple well in a position for most accurate indication of temperature.

A steel jacket has been constructed to fit the new glass reactor in order to provide for a very rapid linear flow of coolant along the walls of the reactor tube. New larger diameter tubes have been installed in the 10-kilocurie-source room to permit the coolant circulation equipment to be placed outside the source room without causing undue pressure drops in the lead lines. This combination of improved cooling equipment should make temperature control more precise and flexible.

In order to insure that the glass reaction vessel is always free from contaminants which might catalyze or inhibit the reaction, special cleaning procedures have been adopted and equipment constructed to facilitate these procedures. After cleaning with solvents and drying, the reactor is placed in a mixture of concentrated sulfuric acid and chromic acid for a few hours. It is then rinsed in distilled water and placed in a steam cleaning tower. About one and one-fourth liters of water is vaporized and passed through this tower so that all surfaces of the disassembled reactor are thoroughly steamed. The parts of the reactor are then dried at 150°C in a special oven wherein the glass parts rest on a plate glass shelf and do not come in contact with any metal. When blown out with filtered air and cooled, the reactor is then assembled for use and filled with reactant liquid. This new equipment is now being used to study the kinetics of the chlorination reactions.

#### E. DESIGN OF A PLANT FOR THE CHLORINATION OF BENZENE UNDER GAMMA RADIATION

Benzene and chlorine react under a variety of conditions to produce either addition or substitution of chlorine to the benzene ring. In 1903, Slator<sup>32</sup> first showed that ultraviolet light selectively promotes the hexachloro addition product of chlorine and benzene, 1,2,3,4,5,6-hexachlorocyclohexane. Since 1903 the reaction has been studied under the influence of

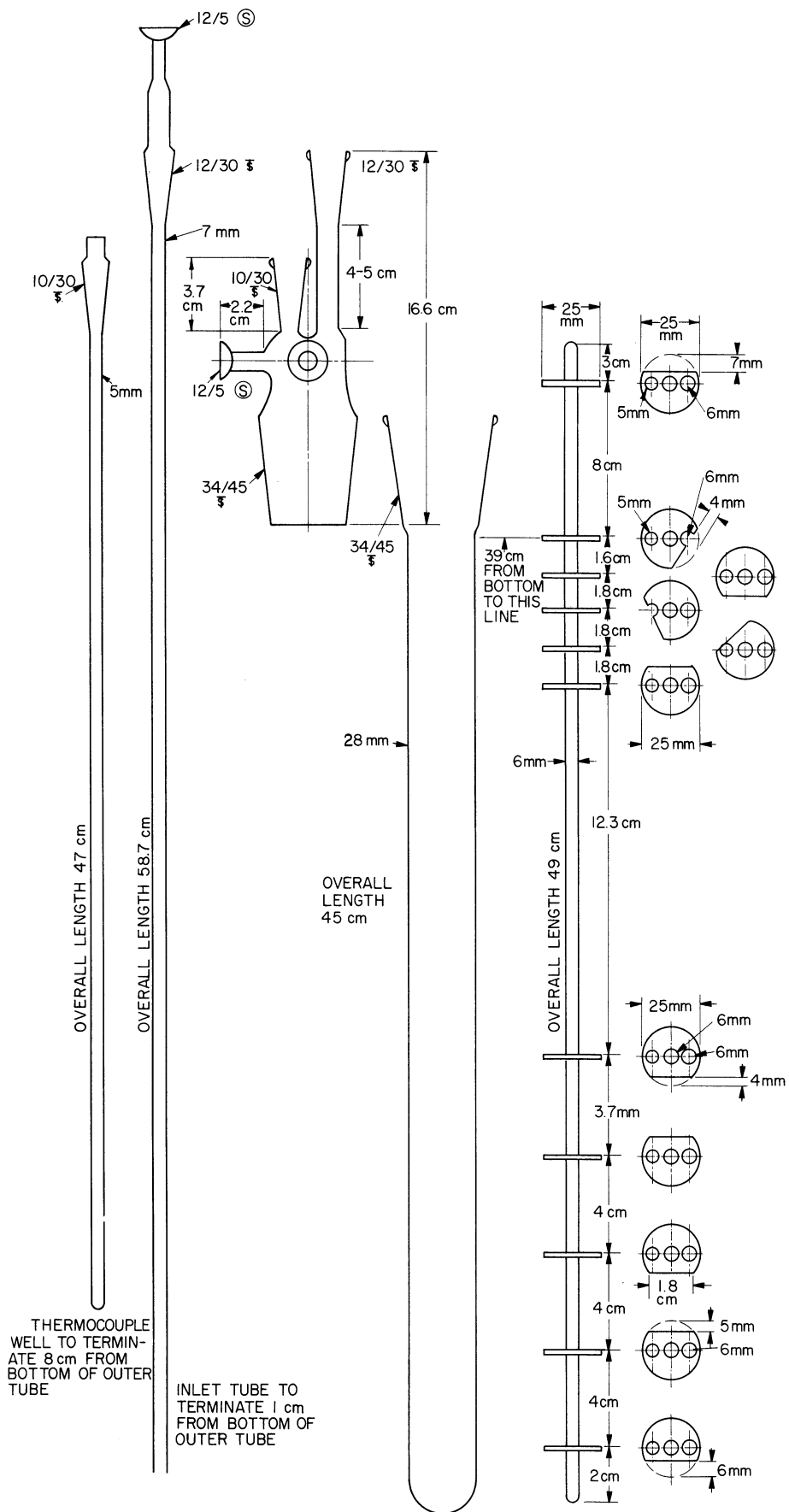


Fig. 12. Drawing of Glass Reactor Used in Determining Reaction Rates between Toluene and Chlorine.

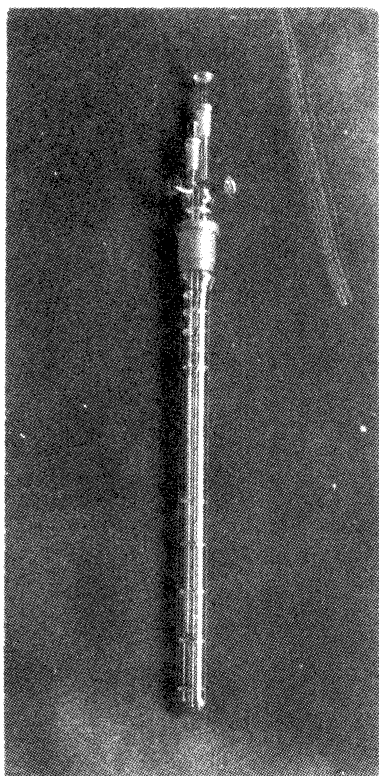


Fig. 13. Glass Reactor Used for Determining Reaction Rates between Toluene and Chlorine.

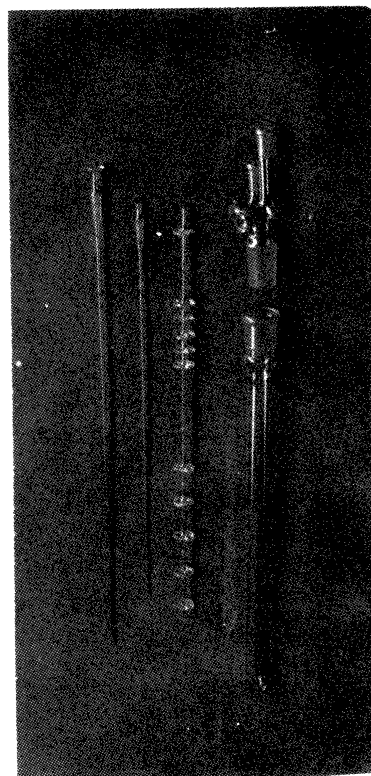


Fig. 14. Glass Reactor, Dissassembled.

ultraviolet light,<sup>10,14,22,25</sup> alpha radiation,<sup>1</sup> and gamma radiation.<sup>2,16,21</sup> Studies using gamma radiation were made in this laboratory with cobalt-60.

The commercial importance of this addition product lies in the insecticidal properties of the gamma isomer. These properties have been described by Slade<sup>31</sup> and others.<sup>9,10,18</sup>

#### 1. Laboratory Chlorination of Benzene in the Presence of Gamma Radiation

The procedure for chlorinating benzene under the influence of gamma radiation has been described previously.<sup>2,16,21</sup> In brief this procedure is as follows:

A glass reactor containing benzene and carbon tetrachloride was lowered into the cobalt-60 gamma source and purged of air with nitrogen. A cooling medium was passed through an outer jacket of the reactor. Chlorine was bubbled into the reaction mixture until the first traces of HCl or Cl<sub>2</sub> appeared in the off gas from the reactor and then was regulated at a rate so that there was no HCl or Cl<sub>2</sub> in the off gas. The reaction was usually conducted until all the benzene was consumed.

It was reported<sup>2</sup> that the temperature could not be controlled during the reaction if pure benzene was used; therefore, carbon tetrachloride, an inert in the reaction, was added to give greater reaction volume for closer temperature control and also to act as a solvent for the solid reaction product.

Part of the data taken has been reported<sup>2,16,21</sup> and this is further supplemented by Table 7 and Fig. 15. Due to equipment breakage and recovery problems, the solid product in some cases was not obtained. Rather than discard these runs as useless, a weight percent completion of reaction has been assumed. In those runs where an obvious excess of chlorine was added, the average completion obtained was assumed; this was 95-percent completion based on the benzene. In those runs where the reaction was stopped before completion, the amount of chlorine added was recorded and 95 percent of the benzene that would react with the chlorine stoichiometrically was calculated. This amounted to 90 percent completion based on the total benzene concentration. The reaction velocity constant for the complete reaction was calculated. This constant  $k_{tr}$  is due to the combined temperature and radiation effects. A discussion of this combined constant is to be found in the theoretical work by this laboratory in Progress Report 5<sup>3</sup>, pages 36-40. Figure 15 is a plot of this constant versus the reciprocal of the absolute temperature at a constant dose rate of 105 kilorep per hour.  $[G]$  values have also been calculated and are to be found in Table 7.

## 2. Rate of Reaction for the Addition Product of Chlorine and Benzene

The original investigation of this laboratory was concerned with the effect of gamma radiation on the yield of gamma isomer in the mixed isomer reaction products and it was determined that there was no apparent affect of gamma radiation on yield of gamma isomer. The rate of addition of chlorine to the reaction mixture was not constant nor uniform, and no data on the kinetics of the reaction based on chlorine concentration are available. This type of data is necessary to design a flow reactor for the system.

In the literature, Noyes and Leighton in Photochemistry of Gases<sup>25</sup> report the rate as approximately

$$r = \frac{dP}{dt} = kI^{1/2} [Cl_2] [C_6H_6]$$

In Chemical Action of Ultraviolet Rays,<sup>10</sup> the rate is given as

$$r \propto (PCl_2)^2$$



TABLE 7

 IRRADIATION OF BENZENE AND CHLORINE BY COBALT-60 GAMMA  
 RADIATION AT A DOSE RATE OF 105 KILOREP PER HOUR

Run Number	Volume C <sub>6</sub> H <sub>6</sub> , %	Yield C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub> , gm	Average Reaction Temp, °R	Reaction Time, min	Weight Percent Completion on C <sub>6</sub> H <sub>6</sub>	Reaction Velocity Constant, k <sub>tr</sub> $\frac{\text{gm-moles}}{(\text{hr})(\text{ft}^3)}$	G
129762	100						
129765	100	49.6	498	35	15.2	82.6	47,100
129766	30	*93	520	40	**95	136.0	51,600
129767	30	*93	525	35	**95	155.5	59,000
129768	30	102.8	526	25	105	241.0	91,400
129774	30	40.0	474	33	40.8	70.4	26,800
129861	25	*52.6	528	15	***90	205.0	76,000
129855	20	*62	528	14	**95	258.5	91,500
129769	20	*48	520	24	***90	116.5	42,500
129770	20	63.6	528	20	97.3	186.0	68,000
129771	10	32.0	528	25	98.0	74.7	26,100
129772	10	31.7	483	53	97.2	34.8	12,200
129773	10	40.8	477	46	125	51.8	18,100

\*Calculated values using assumed percent completion.

\*\* Weight percent completion on C<sub>6</sub>H<sub>6</sub> assumed by average of other runs where excess chlorine was introduced.

\*\*\* Weight percent completion on C<sub>6</sub>H<sub>6</sub> assumed on runs where stoichiometric amounts of chlorine were added.

$$r \propto I^{1/2} P_{Cl_2} P_{C_6H_6}$$

$$r \propto I^{(1.6)} .$$

Luther and Guldberg report<sup>22</sup>

$$r \propto [Cl_2] ,$$

while Slator reports<sup>32</sup>

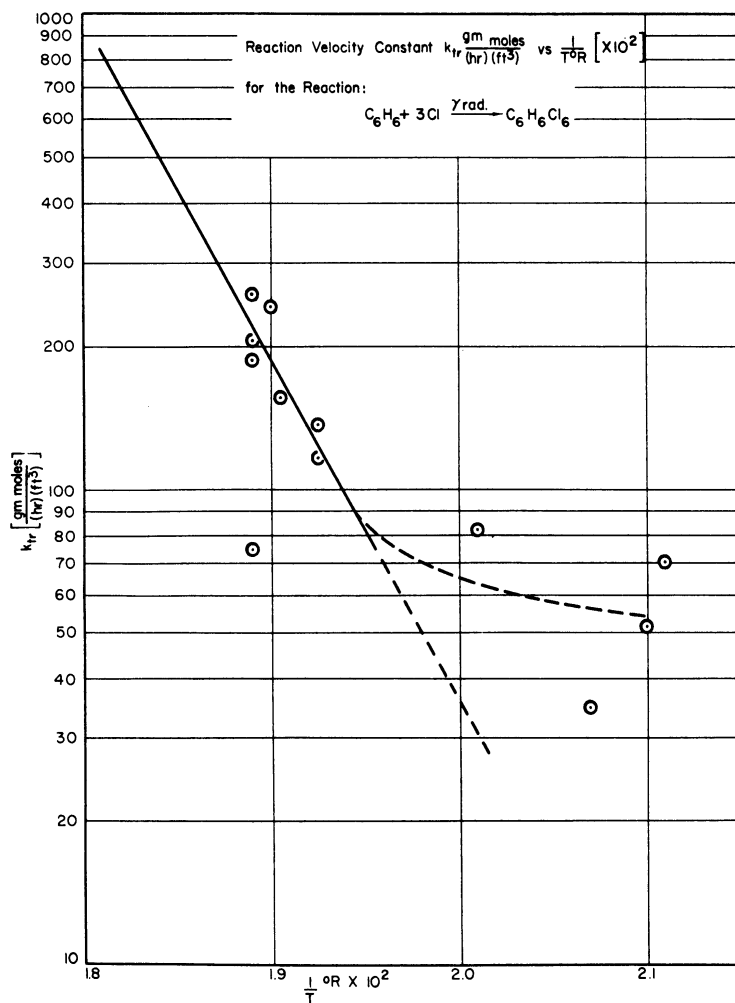


Fig. 15. Reaction Velocity Constant vs Reciprocal Temperature for the Chlorination of Benzene.

$$r \propto T^{1.5}$$

and  $10^6$  molecules of reaction product per quantum of light, where

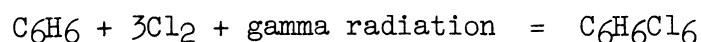
- P = total pressure
- p = partial pressure
- I = ultraviolet intensity
- T = temperature
- r = rate
- t = time
- k = reaction velocity constant
- [ ] = concentration.

### 3. Process Design Calculations for a Continuous Flow Reactor

For the purpose of this design calculation, it is necessary to make several assumptions regarding the data available. Enumerated with reasons for their selection, these assumptions are:

- (1) The reaction is first order with respect to the chlorine concentration. An excess of benzene is to be used and recycled through the reactor. This excess will reduce the effect of small benzene concentration on the reaction rate and also provide a medium to slurry out the solid product. This also assumes a similar mechanism of reaction under gamma radiation as under ultraviolet rays. Luther and Goldberg, quoted above, give reaction as first order with respect to chlorine.
- (2) The data obtained in this laboratory for different reaction temperatures give the reaction velocity constant. The plant is designed using the same radiation rate as was present in the laboratory. Only temperature is to be extrapolated.
- (3) Gunther<sup>14</sup> and others<sup>9</sup> report a yield of 42% gamma isomer in the reaction of chlorine and benzene under ultraviolet light rays on the addition of NaOH to the reaction mixture. An addition of 2% NaOH in the mixture is assumed to give 32% gamma isomer by weight.
- (4) The same reaction mechanism holds for the case of a mixture of liquid chlorine in benzene as for the case of bubbling gaseous chlorine through benzene. This permits the use of the reaction velocity constant of Table 7 and Fig. 15. The same percentage completion on the chlorine will be held. This allows use of these overall constants.

With these assumptions, the equation and material balance for the reaction capable of producing 1000 lb of gamma isomer per day on 95 percent completion of the chlorine are as follows:



Basis: 1000 lb gamma isomer per day

$$\text{Wt mixed isomers per day} = \frac{1000}{.32} = 3120 \text{ lb}$$

$$\text{Wt benzene per day} = \frac{(3120)(78)}{(.95)(291)} = 882 \text{ lb}$$

$$\text{Wt chlorine per day} = \frac{(3120)}{(.95)} \frac{(71)(3)}{(291)} = 2410 \text{ lb}$$

$$\text{Wt NaOH per day} = (3290) (.02) = 65 \text{ lb.}$$

If 100 percent excess benzene is used for the reasons in assumption 1, then the weight entering the reactor is

$$(882)(2) + (2410) + (65) = 4239 \text{ lb day or } 177 \text{ lb/hr .}$$

This corresponds to a feed rate of  $2.38 \text{ ft}^3/\text{hr}$  at  $85^\circ\text{F}$ . The equations for the rate of the reaction in the flow reactor (with the assumptions noted) of volume  $V_R$  are

$$\begin{aligned} r &= k_{tr} [Cl_2] \\ \int dV_R &= - \int \frac{dN_{Cl_2}}{r} = - \int \frac{dN_{Cl_2}}{k Cl_2} \\ &= -F \int \frac{dN_{Cl_2}}{k N_{Cl_2}} , \end{aligned}$$

where

$$F = \text{ft}^3/\text{hr Feed Rate}$$

$$(N_{Cl_2}) = \frac{(\text{lb-moles } Cl_2)}{(\text{hr})} \text{ Chlorine Rate}$$

$$k = \frac{1}{\text{hr}}$$

$$V_R = \text{ft}^3 .$$

By selecting  $85^\circ\text{F}$  as the operating temperature, a liquid phase reaction may be obtained at not too high a pressure. With the range of data available, long range extrapolation of the data is not advisable due to the possibility of error. Assuming that 95 percent of the chlorine is reacted in a single pass through the reactor, the limits of integration are

$$\text{Inlet } Cl_2 (N_{Cl_2}) = \frac{2410}{(71)(24)} = 1.41 \frac{(\text{lb-moles } Cl_2)}{(\text{hr})}$$

$$\text{Outlet Cl}_2 (N_{\text{Cl}_2}) = (1.41)(.05) = .07 \frac{(\text{lb-moles Cl}_2)}{(\text{hr})} .$$

The reaction velocity constant from Fig. 15 at 85°F is

$$445 \frac{(\text{gm-moles})}{(\text{hr})(\text{ft}^3)} .$$

Converted to units of 1/(hr) this is

$$k_{\text{tr}} = \frac{445 (\text{gm-moles}) (\text{ft}^3) (\text{lb-mole}) 78 \text{ lb}}{(\text{hr})(\text{ft}^3) (.88)(62.4)\text{lb} (454)(\text{gm-moles}) (\text{lb-mole}) (\text{hr})} = \frac{1.4}{(\text{hr})} .$$

The volume of the reactor under these conditions is then by integration of the above expression

$$V_R = \frac{(2.38)}{(1.4)} \text{Log}_e \frac{1.41}{.07} = 5.1 \text{ cu ft.}$$

Using a nominal three-inch OD high alloy stainless-steel or nickel pipe for a reactor, approximately one hundred feet are necessary. This would correspond to ten passes ten feet long in the field of gamma radiation.

The heat of reaction for this system calculated by an approximate method<sup>15,19</sup> is 271,000 Btu/(lb mole) of benzene hexachloride. Thus,  $(271,000) ((3120)/(24)(291)) = 121,000$  Btu/hr must be removed from the reaction mixture.

A five-inch OD steel pipe located concentric to the three-inch reactor pipe would make an effective heat-transfer jacket. The cooling medium would pass through the annuli between these pipes.

#### 4. Description of the Proposed Plant Process

The flowsheet of the proposed process is to be found in Fig. 16. The liquid benzene and chlorine pass from the storage to a mixer, and then in the liquid phase at 15 atmospheres pressure through the nickel reactor in the radiation chamber. A plan view of this chamber is to be found in Fig. 17. Ten passes are necessary at the dose rate of 105 kilorep per hour.

From the reactor in the radiation cave the slurry of benzene hexachloride in benzene passes through a chamber where the pressure is

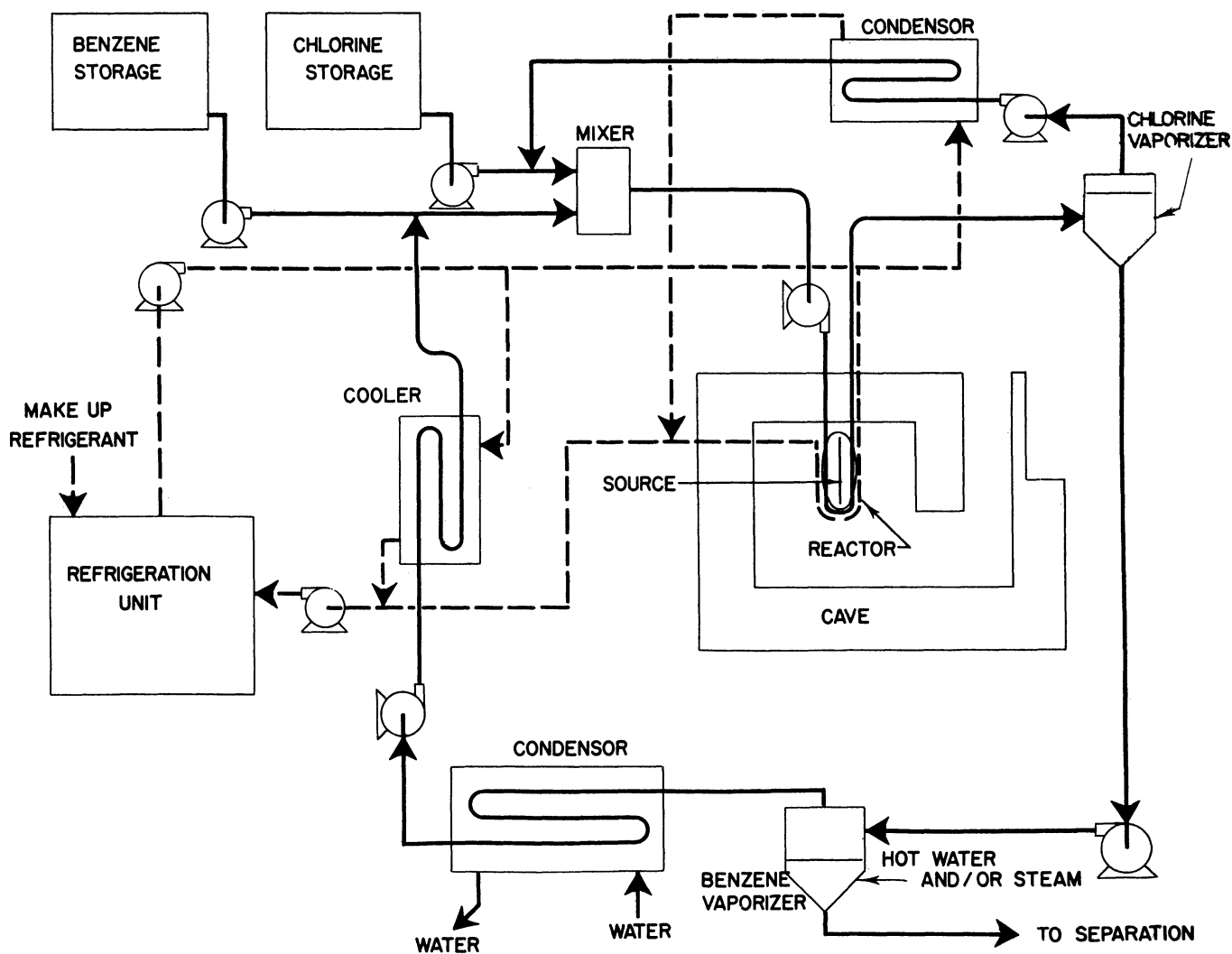


Fig. 16. Flowsheet of Proposed Plant Process for the Addition of Chlorine to Benzene under the Influence of Gamma Radiation.

reduced to 5 atmospheres. This will vaporize any remaining chlorine which may then be compressed and recycled back into the system. The benzene hexachloride stream from this chlorine vaporizer is pumped through a benzene vaporizer where it is sprayed on hot water or into steam. The pressure is reduced from 5 to 1 atmosphere. The excess benzene is vaporized and passed through a condenser and then recycled at 15 atmospheres into the reactor.

The vaporizing benzene leaves behind the benzene hexachloride in water which can be either dried or purified. The gamma isomer may be separated from the mixed isomers and sold as pure Lindane or as dusting powder in the unpurified form. This separation into the pure isomers is not of interest in this plant design. Methods of analysis and separation are reported in the literature.<sup>5,20</sup>

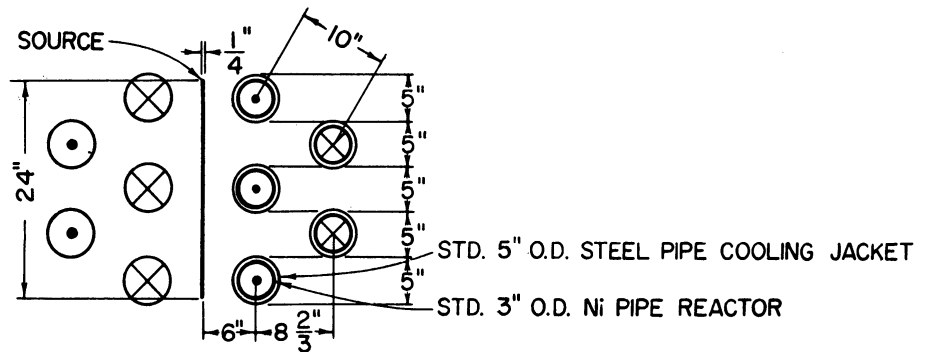
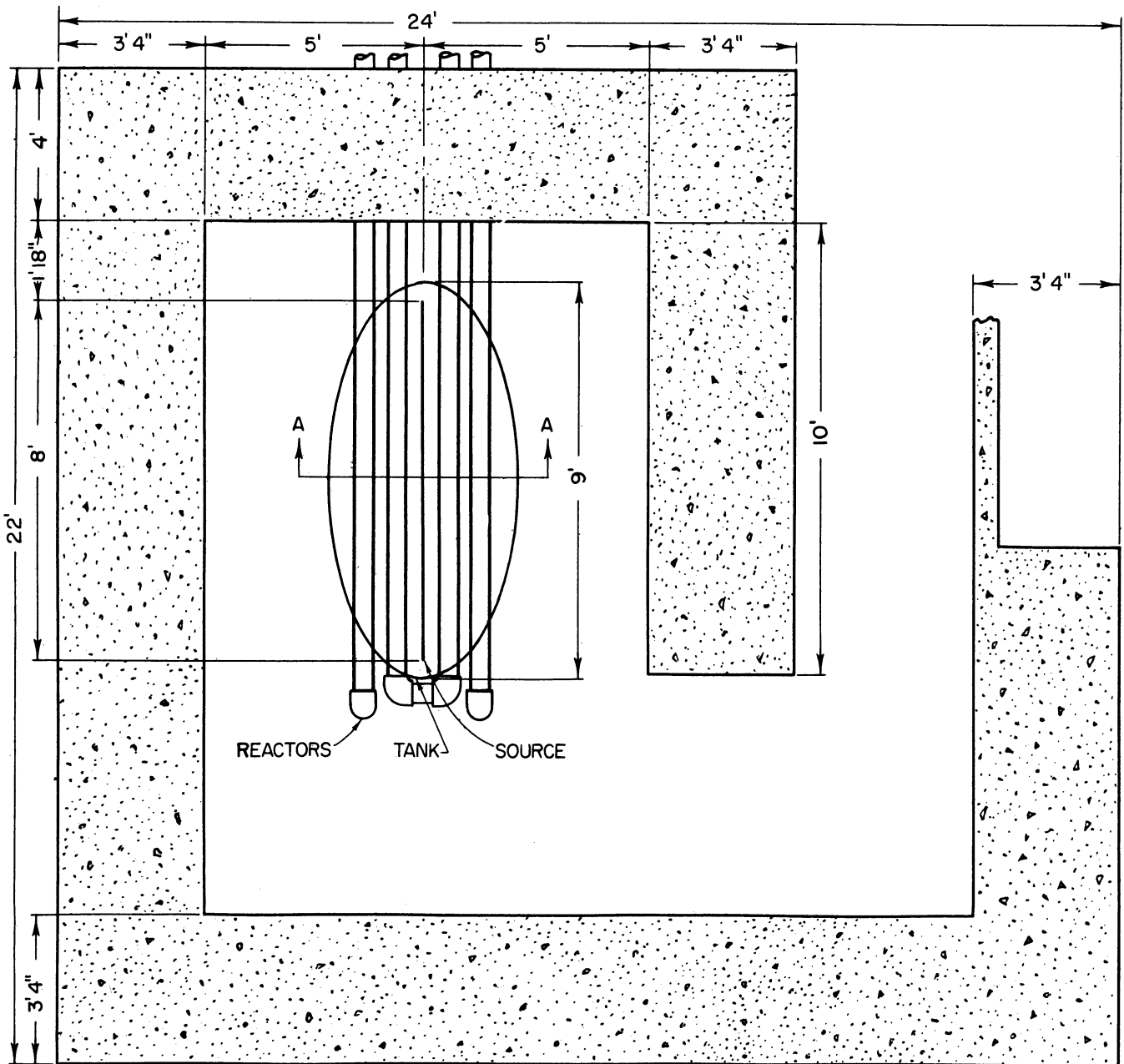


Fig. 17. Plan View of Proposed Reaction Cave Showing Reactors in Position.

Since the operating temperature was selected as 85°F for several reasons listed above, it is necessary to use a system of refrigeration to effect heat removal from the process. The cooling in the reactor, chlorine condenser, and benzene cooler must be accomplished by this refrigeration. This amounts to a removal of

Reactor		121,000 Btu/hr
Chlorine condensor	$\frac{(.07)(\text{lb moles})}{\text{hr}} (8800) \frac{\text{Btu}}{\text{lb mole}}$	= 620 Btu/hr
Benzene cooler	$(1.05) \frac{(882)}{24} \frac{\text{lb}}{\text{hr}} (.46) \frac{\text{Btu}}{\text{lb } ^\circ\text{F}} (70) ^\circ\text{F}$	= 1,250 Btu/hr
		<u>122,870 Btu/hr</u>

or approximately 123,000 Btu/hr from the three sources. The benzene condenser may have water as the cooling medium as it involves heat transfer at higher temperatures. At a higher operating temperature this refrigeration unit could be replaced by water as the cooling medium.

## 5. Calculation of Gamma Radiation Source Strength and Shielding

Two possible arrangements of the reactor tubes in relation to the source are considered. The gamma radiation source may be located inside the reactor or concentric to an annular flow reactor, or the source may be a finite rectangular plaque with the reactor located on either side.

This latter arrangement has been assumed for these calculations. The reactor size has been calculated to be ten passes each ten feet long. In order to utilize a rectangular radiation source most efficiently, the arrangement of reactor tubes is as pictured in cutaway AA of the plan view of Fig. 17. Five reactor tubes are placed on either side of the source with the first row six inches from the source. The second row is placed on an equilateral triangle pitch behind this first row.

Assuming a dose rate in the first row of tubes equal to that used in the laboratory work and correcting for any absorbing media between the source and this point the rate of gamma emission on the surface of the source may be calculated. Gomberg, et al.<sup>3,13</sup> and Brownell, et al.<sup>4</sup> have done this. Using the equation developed by Lewis<sup>21</sup> for the intensity of radiation through an absorption medium which in turn utilizes the adsorption coefficients ( $\mu$ ) of Snyder and Powell,<sup>33</sup> the strength of the source is then calculated to be



$$I = I_0 e^{-\sum \mu \rho x}$$

$$105 = I_0 e^{-2.54 \frac{\text{cm}}{\text{in.}} \left[ (.08) \frac{\text{cm}^2}{\text{gm}} (1.0) \frac{\text{gm}}{\text{cm}^3} (2.25) \text{in.} + (.075) \frac{\text{cm}^2}{\text{gm}} (8.38) \frac{\text{gm}}{\text{cm}^3} (.474) \text{in.} \right]}$$

where

$$\mu_{\text{H}_2\text{O and C}_6\text{H}_6} = .08 \frac{\text{cm}^2}{\text{gm}} ; \quad \mu_{\text{Fe and Ni}} = .075 \frac{\text{cm}^2}{\text{gm}}$$

$$105 = I_0 e^{-1.215}$$

$$I_0 = (3.37)(105) \frac{\text{krep}}{\text{hr}} = 354 \frac{\text{krep}}{\text{hr}}$$

- $I$  = radiation intensity, krep/hr  
 $\mu$  = absorption coefficients, ( $\text{cm}^2/\text{gm}$ )  
 $x$  = thickness absorber, (cm)  
 $\rho$  = density of absorber, ( $\text{gm}/\text{cm}^3$ ).

The specific activity of the gamma radiation source is assumed to be  $3.8 \times 10^3$  (rep)/(hr)(curie).<sup>3,13</sup> A rectangular source plaque two feet by eight feet is assumed for the commercial design as compared to  $16 \text{ cm}^2$  used in the laboratory experiment. Then the approximate total activity of the source plaque is

$$\frac{354 \frac{(\text{krep})}{(\text{hr})} \times 1000 \frac{(\text{rep})}{(\text{krep})} 2(\text{ft}) 8(\text{ft}) 144 \frac{(\text{in.}^2)}{(\text{ft}^2)} 6.45 \frac{(\text{cm}^2)}{(\text{in.}^2)}}{3.8 \times 1000 \frac{(\text{krep})}{(\text{hr})(\text{curie})} (16)(\text{cm}^2)} = 86,500 \text{ curies.}$$

The source-room size is selected and the concrete shielding necessary to protect the human operators can be calculated. Assuming that the dose rate in air varies immensely with the square of the distance from the source, the dose rate at a distance of five feet from the source would be

$$I = \left( \frac{x_0}{x} \right)^2 I_0$$

$$I = \left( \frac{1}{60} \right)^2 354,000 \frac{\text{rep}}{\text{hr}}$$

$$I = 985 \frac{\text{rep}}{\text{hr}} .$$

Assuming a .05 mr/hr to be a safe dose rate for the human operators,

$$I = I_0 e^{-\mu x}$$

$$(.05) \frac{\text{mr}}{\text{hr}} = 985 \frac{\text{rep}}{\text{hr}} \times 1000 \frac{\text{mr}}{\text{rep}} e^{-.2x}$$

where

$$\mu = 0.2 \text{ cm}^{-1} \text{ for concrete}$$

$$x = \text{thickness of concrete in cm}$$

$$e^{.2x} = \frac{985,000}{.05} = 1.97 \times 10^7$$

$$.2x = \ln 1.97 \times 10^7$$

$$x = \frac{(7.294)(2.303)}{(.2)} = 84 \text{ cm}$$

$$x = 33 \text{ in.}$$

Assuming .05 mr/hr to be a safe dosage for these calculations, based on narrow-beam coefficients, a wall thickness of forty inches or three feet four inches is selected. (Based on broad-beam coefficients and forty inches of concrete, the radiation level is computed to be increased to about one mr/hr.) A well of twelve feet of water will permit lowering the source to a sufficient depth to provide adequate shielding. A plan view of the radiation chamber is shown in Fig. 17. A cutaway perspective view of this chamber showing the reactor in place is shown in Fig. 18. The reactor-end supports and the source elevator have been omitted from the figure to clarify the picture.

## 6. Estimation of Cost for the Proposed Equipment and Radiation Chamber

An itemized cost summary of the proposed radiation chamber is given in Table 8. The cost estimation for all equipment used in the process of manufacturing benzene hexachloride by the proposed method utilizing gamma radiation is to be found in Table 9. These estimates exclude the cost of the radiation source itself or of the separation unit needed to purify and/or separate the isomers.

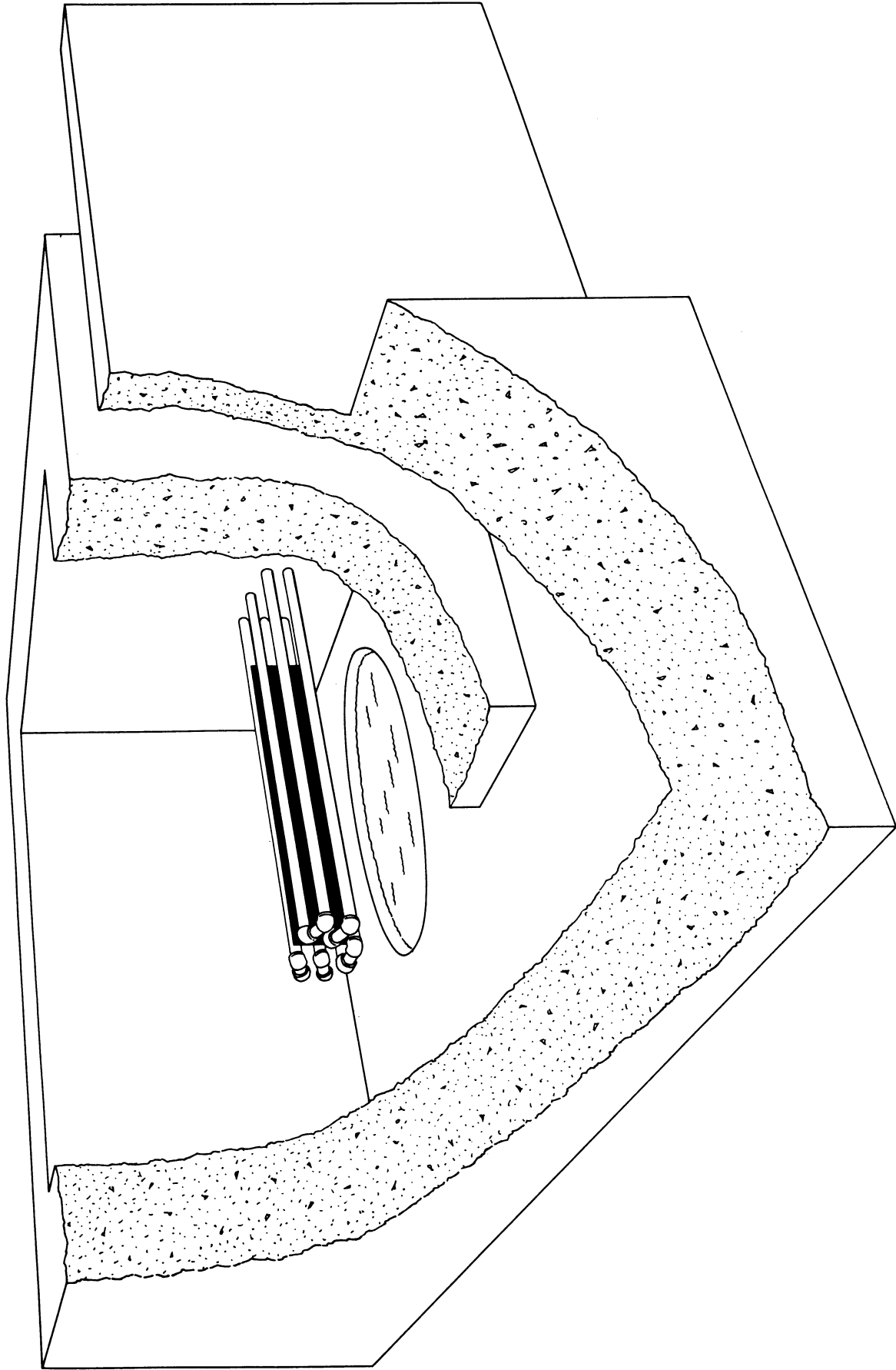


Fig. 18. Cutaway Drawing of Reactor Cave Showing Gamma Radiation Source and Reactor Placement.

TABLE 8

## COST ESTIMATES FOR RADIATION CHAMBER

Concrete for walls, roof, floor, and well 130 yd at \$20.00/yd	\$ 2600
Reinforcing	400
Excavation for footings and well	800
Forms for concrete	800
Labor	1800
Stainless-steel well	1500
Elevator for source	1500
Ion-exchange equipment	2000
Monitoring equipment	1800
Painting, wiring, plumbing, and ventilation for cave including labor	<u>3200</u>
	\$16,400
Miscellaneous contingencies (20%)	3300
Engineering (5%)	800
Contractors fee (10%)	<u>1600</u>
Total	\$22,100

TABLE 9

## COST ESTIMATES FOR EQUIPMENT EXCLUDING ISOMER SEPARATION

Nickel or stainless-steel reactor pipe and fittings into cave	\$ 900
Heat-exchange jacket	400
Pumps and pipe from pumps	1900
Two-flash vaporizers	3000
Chlorine compressor and connections	8000
Heat exchanger for benzene	3000
Refrigeration unit	18000
Benzene and chlorine storage	<u>4000</u>
Total	\$39,200
Installation (30% of cost)	11800
Building for housing pumps, control equipment, etc.	<u>9000</u>
Total	\$60,000

## 7. Comparison of Gamma Radiation Sources to Give Constant Source Strength

The source plaque as described in calculating the total gamma-radiation strength could be one solid sheet of radioactive material or it could be composed of a number of individual sections. This would be essentially a rack which held the source made of several sections. These sections could be in the form of strips or cannisters and could be removed and/or replaced as it became necessary. This replacement time would depend on the permissible flux variation of the source and the half life of the material used for the source. For the following calculations, it is assumed that a flux variation of 20 percent will not affect the rate of reaction of benzene and chlorine appreciably. The time (t) necessary for a radioactive material of original intensity ( $I_0$ ) to decay to an intensity (I) is

$$I = I_0 e^{-kt}$$

$$t = \frac{1}{k} \ln \frac{I_0}{I} ,$$

where k is a constant of the material. Letting the material decay to half its original value, then

$$I = \frac{I_0}{2}$$

$$t_{.5} = \frac{1}{k} \ln 2 = \frac{.693}{k}$$

or

$$k = \frac{.693}{t_{.5}} ,$$

where  $t_{.5}$  is the defined half life of the material. Then for any other time of decay

$$I = I_0 e^{-\left(\frac{.693}{t_{.5}}\right) t} .$$

Letting  $I = .80 I_0$ , then

$$.80 = e^{-\left(\frac{.693}{t_{.5}}\right) t_{.80}} ,$$

or

$$\frac{(.693)t_{.80}}{t_{.5}} = \ln \frac{1}{.80} = \ln 1.25 = .223$$

$$t_{.80} = \frac{.223}{.693} t_{.5} = .322 t_{.5} .$$

This equation is the relation of the time for any material of half-life  $t_{.5}$  to decay to 80 percent of its original value of intensity. Both  $t_{.80}$  and  $t_{.5}$  must be in the same units.

Assuming a finite number of sections of the source, then at the end of one .80-life, a quantity of gamma radiation equal to 20 percent of the rated source strength must be added to the source. If this means replacement of any section of the source, then the strength of the replaced section must also be present in the replacement section to keep the rated radiation value constant.

For example, assume that the rectangular plaque consists of twenty individual sections. At the beginning of any .80-life period, the plaque will be at the necessary rated strength calculated previously. The ratio of the section strength to the rated section strength will be  $(.8)^n$ , where  $n$  is the number of .8-lives since the section was replaced. Assuming one replacement per .8-life, the source will consist of twenty sections with strengths

Section	1	2	3	4	. . . .	19	20
	1	$(.8)^1$	$(.8)^2$	$(.8)^3$	. . . .	$(.8)^{18}$	$(.8)^{19}$ .

At the end of any .8-life each section will have decayed by a .8 amount and the source will consist of twenty sections of strengths

Section	1	2	3	4	. . . .	19	20
	$(.8)^1$	$(.8)^2$	$(.8)^3$	$(.8)^4$	. . . .	$(.8)^{19}$	$(.8)^{20}$ .

This shows that the addition of one section of rated section strength must replace a section of  $(.8)^{20}$  of rated section strength. The replacement section strength  $S$  must then be equal to

$$[1.000 - (.8)^{20}] S = (86,500)(.20) \text{ curies,}$$

where 86,500 curies is the total rated source strength; then

$$[1.000 - .0115] S = 17,300 \text{ curies}$$

$$S = \frac{17,300}{.988} = 17,500 \frac{\text{curies}}{\text{gamma section}} .$$

Table 10 is a comparison of four different gamma radiation sources of known half life. Three gross fission products, six-months old, one-year old, and two-years old, are compared with cesium-137. The approximate half lives of the fission products were taken from the literature.<sup>38</sup>

TABLE 10

COMPARISON OF FOUR GAMMA RADIATION SOURCES  
TO GIVE CONSTANT SOURCE STRENGTH FOR FIVE YEARS

Fission- Product Material	Half life $t_{.5}$ yr	$t_{.8}$ yr	Sections to Start in 5 yr	% Section Replacements	Total % Sections in 5 yr	Total Radiation Necessary for 5 yr, curies
Gross 6-mo old	.20*	.064	5	78.1	83.1	1,455,000
Gross 1-yr old	.30*	.097	5	51.5	56.5	990,000
Gross 2-yr old	1.10*	.354	5	14.1	19.1	334,000
Pure Cs-137	33.	10.6	5	0	5	86,500

\* Approximate half life for mixtures of elements of varying half life.

The calculations for the six-month-old fission-product material are illustrated here. The others follow similarly.

$$t_{.8} = .322 t_{.5} = (.322)(.20) \text{ year}$$

$$t_{.8} = .064 \text{ year} .$$

The number of gamma radiation sections to start is five. The number of gamma replacements in five years is

$$\begin{aligned} \text{Replacements} &= \frac{5.00}{t.80} = \frac{5.00}{.06} \\ &= 78.1 \end{aligned}$$

Then the total gamma sections necessary for five-years operation are

$$\text{Starting sections} + \text{Replacement sections} = \text{Total sections}$$

$$\text{Total sections} = 5 + 78.1 = 83.1 .$$

Then the total rated radiation in curies necessary for five years operation is

$$(\text{Total sections}) \left( \frac{\text{curies}}{\text{gamma section}} \right) = \text{Total radiation}$$

$$\text{Total radiation} = (83.1)(17,500) = 1,455,000 \text{ curies} .$$

In the case of cesium-137 it is seen that the half life is long enough that no replacement sections are needed. The original five sections have not decayed to the permissible .80 level of radiation.

#### 8. Cost Comparison of Benzene Hexachloride from Four Gamma Radiation Sources and from Present-Day Process

Little is known about the cost of either gross or concentrated fission products. There are some figures available for pure radioactive isotopes for specific purposes. A range of values expressed in dollars per curie is assumed in Table 11 for the four gamma radiation sources considered. The range is wide enough to take into consideration use of the fission product at the nuclear reactor site where no shipping is necessary and large quantities of hot fission products are presently in storage. These costs have been assumed on the basis of approximate equal cost per unit of energy of radiation delivered. Since the energy, E, delivered by a source is



TABLE 11

COMPARISON OF TOTAL PLANT COST FOR FOUR  
GAMMA RADIATION SOURCES

Fission- Product Material	Range of Estimated Cost for Radiation, Dollars per Curie		Total Radiation Cost, Dollars		Total Plant Cost, Dollars	
	Low	High	Low	High	Low	High
Gross 6-mo old	.0005	.05	728	72,800	82,900	154,900
Gross 1-yr old	.001	.05	990	49,500	83,100	131,600
Gross 2-yr old	.02	.25	6,680	83,500	88,800	165,600
Pure Cs-137	.50	5.00	43,250	432,500	125,400	514,600

$$E = \int_0^t I_0 e^{-\lambda t} dt = I_0 (1 - e^{-\lambda t}) / \lambda ,$$

it follows that the energy varies inversely as  $\lambda$  for large values of  $t$ . Since  $\lambda$  is the reciprocal of the half life, it follows that the energy delivered varies directly as the half life. Thus, a source with three times the half life of another can deliver three times as much radiation energy and is assumed to cost about three times as much.

The cost of long half-life sources is estimated to include packaging, shipping, and installation in a plant at some distance from where the source is prepared. The cost of very short half-life sources would be excessively high because of the large shipping cost. Therefore, it is assumed that the short half-life sources are to be used in the vicinity where they are produced. In this way it is believed that the cost per curie of the short half-life material (which might even be spent fuel elements) although low, is not unrealistic.

Table 11 is a comparison of the total plant cost including the radiation source for the radiation sources considered. The values and the method of calculation are presented for six-month-old fission-product material for the low cost estimated for the radiation.

$$(\text{No. curies})(\text{cost/curie}) = \text{Total cost for radiation}$$

$$(1,455,000 \text{ curies})(.0005 \text{ \$/curie}) = \$728$$

The total radiation cost plus the cost for equipment and for the radiation cave found in Tables 8 and 9 is the total plant cost.

Total cost for radiation	=	\$ 728	
Cost for radiation chamber	=	22,100	
Cost for equipment	=	<u>60,000</u>	
		\$82,828	or \$82,900

Table 12 is self explanatory. Carrying through the calculations for the low range value of six-month-old fission products and the annual cost of the proposed plant, amortizing the plant investment over a period of five years, and assuming 10 percent interest on the total plant, the investment amounts to

Annual plant cost, $82,900/5$	\$16,560
Interest, $(.10)(82,900)$	8,290
Working Capital	20,000
Operation and maintenance	<u>30,000</u>
Total Annual cost of plant operation	= \$74,850 per year

Assuming operation and production during 290 days of the year, the daily cost of the operating plant would be

$$\frac{\$74,850}{290} = \$258 \text{ per day.}$$

The cost of raw material is  $7,8,26$

Benzene at \$.42 per gal	=	\$50.50
Chlorine at \$3.50 per 100 lb	=	84.50

or a total operating cost of \$393 per day.

The cost of producing 3120 lb of mixed isomer is then

$$\frac{\$393 \text{ per day}}{3120 \text{ lb per day}} = \$.126 \text{ per lb mixed isomers.}$$

TABLE 12

COMPARISON OF TOTAL PRODUCTION PRICE OF THE GAMMA ISOMER OF  
BENZENE HEXACHLORIDE PRODUCED FROM FOUR GAMMA RADIATION SOURCES

Fission-Product Material, Dollars	Gross 6-mo old		Gross 1-yr old		Gross 2-yr old		Pure Cs-137	
	Low	High	Low	High	Low	High	Low	High
	Annual plant cost on 5-yr amortization	16,560	31,000	16,610	26,300	17,720	33,100	25,100
Annual interest to stockholders, 10% on total plant cost	8,290	15,490	8,310	13,600	8,880	16,560	12,500	51,460
Working capital	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000
Operation and maintenance of plant	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000
Total annual cost, excluding raw materials	74,850	96,490	74,920	89,900	76,600	99,660	87,600	204,460
Daily cost assuming 290 operating days per year	258	333	258	310	264	344	302	705
Total daily operat- ing cost, including raw materials	393	468	393	445	399	479	437	840
\$/( $\gamma$ unit)(lb isomers) on 32% $\gamma$ isomer yield	.00393	.00468	.00393	.00445	.00399	.00479	.00437	.00840
\$/( $\gamma$ unit)(lb isomers), assuming 20% $\gamma$ isomer yield	.0063	.0075	.0063	.00714	.0064	.00768	.0070	.01345

Defining the gamma unit as percent of gamma isomer per pound of mixed isomers, the cost per gamma unit assuming 32% gamma isomer produced is

$$\frac{.126}{32} = \$.00393 \text{ per gamma unit per pound.}$$

If the recovery was only 20 percent gamma isomer in the reaction of mixed isomers, as is true in many commercial ultraviolet units today, the production price for the same production of mixed isomers would be

$$\frac{.126}{20} = \$.0063 \text{ per gamma unit per pound .}$$

Benzene hexachloride is being sold at present market conditions<sup>8,26</sup> at \$.009 to \$.015 per gamma unit per pound in concentrations of 12 to 14% gamma isomer per pound. Using this lower figure for comparison, a savings of 50 to 225 percent can be realized by producing benzene hexachloride by gamma radiation activation as against conventional ultraviolet light activation. This is true for the whole range of costs of all the gross mixed fission products. Only the highest value estimated for cesium-137 falls above \$.009 per gamma unit per pound. This is, however, in the range of the price being asked today.

The separation cost of the isomers would be comparable to that method used today and has not been calculated. These calculations, however, reveal a more efficient means of obtaining the crude isomer mixture.

## 9. Conclusions and Summary

Several important improvements in existing plant operations have been overlooked in presenting this economic study. Some of the more important improvements present in this proposed plant design are

- (1) Elimination of necessarily small costly equipment due to the necessity for ultraviolet radiation penetration. Gamma radiation will penetrate to the very center of the reaction mixture due to its very nature and wavelength.
- (2) Elimination of glass or quartz equipment necessary to transmit ultraviolet radiation. Steel equipment may be used with gamma radiation.
- (3) Availability of higher temperatures and pressures in carrying out the reaction for the reason listed in (2).

- (4) The full capabilities in the use of gamma radiation have not been fully realized in this study due to the nature of the data used. There are several important regions where the use of gamma radiation could be investigated more fully. Enumerated they are:
- (a) Higher rates of radiation should be investigated. The data presented are for a constant rate of radiation. The possibility of utilizing larger radiation sources to give larger radiation fluxes and increased rate of reaction should be studied.
  - (b) Running a larger chlorine recycle stream and/or running to a less complete reaction based on the chlorine would undoubtedly increase the overall rate of reaction. The rate of reaction is faster at higher concentrations of chlorine and running to 95 percent completion on the chlorine decreases the overall rate of reaction.
  - (c) Running at even higher pressure than presented here would allow running a higher temperature with the chlorine still in the liquid phase. The data available, although dependable and consistent, cover too small a temperature range to allow long extrapolation. At a higher temperature the reaction rate would be greater.
  - (d) For simplicity of design only one effective absorbing bank of tubes has been used (see Fig. 3, Sec. AA). Other rows of tubes could be placed behind the tubes shown to absorb radiation not used in this design. Brownell, et al.<sup>3,4</sup> show an increase in efficiency of 500 percent in using a multipass package plant as against a single pass dead carcass plant for irradiation of meat. By increasing the capacity of the plant and putting more reactor bundles in the radiation chamber, the cost of crude benzene hexachloride would be reduced. Only equipment costs would increase in the cost estimate. The major expense of the radiation source would be the same.
  - (e) An annular reactor could be used with the source of gamma radiation in the center. This would presumably utilize a higher percentage of the radiation emitted and decrease the rated strength necessary in the source.
  - (f) The plant cost was written off in five years, but it must be realized that in all cases there is gamma activity left at the end of five years. Less than 10 percent of the radiation of Cs-137 has been used at the end of this five-year write-off period.

For these reasons it is thought that the value of gamma radiation on the reaction has been underestimated. A more complete investigation would

undoubtedly show a greater difference in the cost of benzene hexachloride as it is produced today by ultraviolet radiation and benzene hexachloride produced utilizing gamma radiation as presented here.

#### F. WORK CONTEMPLATED FOR THE NEAR FUTURE

Present plans are to make a few more runs on the polymerization of ethylene with gamma radiation to supplement the data already taken. Following that it is probable that no more experimental work will be undertaken on this reaction. However, a preliminary plant design, such as has been given for the chlorination of benzene, will probably be made to obtain an estimate of the cost of polyethylene produced by gamma radiation for purposes of comparison with the cost of polyethylene produced by the conventional high pressure process employed industrially today.

A few additional runs will be made on the rate of reaction of chlorine with toluene under gamma radiation utilizing the best technique for analysis of the off-gases of chlorine and hydrogen chloride. The proof that the addition compound is the principal product is now complete.

Chlorination of other compounds mentioned in previous reports will probably receive very high priority in the experimental work. The aromatics closely related to benzene and toluene, such as ethyl benzene, the xylenes, and naphthalene, will be chlorinated to determine whether gamma radiation favors the addition of chlorine to the double bonds. It is also expected to chlorinate some simple aliphatic alcohols, aldehydes, and acids. Some preliminary work along this line has shown that under gamma radiation chlorine probably converts a hydrated aldehydic group to an acidic group, a reaction which apparently does not occur when ultraviolet light is employed.

Some other high pressure polymerizations are scheduled to be tried soon. Also it is hoped to carry out a copolymerization under gamma radiation, with the combination of butadiene and styrene at low temperatures; this reaction will probably be tried first.

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