ENGINEERING RESEARCH INSTITUTE
UNIVERSITY OF MICHIGAN
ANN ARBOR

PROGRESS REPORT I

UTILIZATION OF THE GROSS FISSION PRODUCTS

By

L. E. BROWNELL
Supervisor

L. C. ANDERSON
H. J. GOMBERG
J. J. MARTIN
R. A. WOLFE
W. W. MEINKE
L. THOMASSEN
E. T. VINCENT

Assisted by

R. E. ANDERSON
H. S. DOMBROWSKI
M. E. GLUCKSTEIN
D. E. HARMER
W. KERR
P. K. LASHMET
J. G. LEWIS
D. OVERBECK
R. D. PIERCE
F. L. TOBEY

Project M943

U. S. ATOMIC ENERGY COMMISSION
CONTRACT NO. AT (11-1)-162
CHICAGO 80, ILLINOIS

August 31, 1951

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

PROGRESS REPORT I

UTILIZATION OF THE GROSS FISSION PRODUCTS

INTRODUCTORY ABSTRACT

This report describes the progress on this project since the preliminary report of April 15, 1951. Plans for the laboratories have been made, and construction has started. Some of the alterations called for in the plans have been completed. Various items of equipment have been ordered and received, including the cobalt-60 radiation vault and the 220 kvp Westinghouse X-ray machine. Some experimental work has been performed.

The project organization is discussed first, followed by a description of the laboratories and equipment. The research problems under investigation are described including a review of the pertinent literature.

PART I. PROJECT ORGANIZATION

At a conference held on April 26 at the Chicago Operations Office of AEC it was decided to initiate the research on utilization of the fission products by the investigation of the influence of radiation on (1) performance of combustion engines (both reciprocating and jet), (2) chemical reactions, and (3) food preservation. It was also agreed that limited exploratory research on other and new ideas should be undertaken. To improve the project organization it has been decided to set up these research investigations as subprojects with a separate budget for each. The hazardous equipment in the Fission Products Laboratories, such as the x-ray machines, gamma- and beta-radiation sources, are operated and handled by a small group of trained technicians. This insures maximum safety and minimum training of personnel. This group is a service group to the research investigators and will prepare and irradiate specimens at their request. As a matter of convenience, the Fission Products Laboratories will be operated as a subproject also. The subprojects with their supervisors and budgets are as follows:

Title		Supervisor	Budget, 1951-52
UTILIZATION OF FISSION PRODUCTS,	M943	L. E. Brownell	$116,000.00
Alterations and Special Equipment			31,000.00
			$ 85,000.00
1. EFFECT OF RADIATION ON COMBUSTION ENGINE PERFORMANCE			$ 24,000.00
RECIPROCATING ENGINES	M943A	R. A. Wolfe	$ 11,800.00
JET ENGINES	M943B	E. T. Vincent	$ 12,200.00
2. EFFECT OF RADIATION ON CHEMICAL REACTIONS	M943C	J. J. Martin L. C. Anderson	$ 18,000.00
3. EFFECT OF RADIATION ON FOODS	M943D	L. E. Brownell	$ 12,000.00
4. EXPLORATORY RESEARCH ON NEW IDEAS	M943E with	L. E. Brownell H. J. Gomberg W. W. Meinke L. Thomassen	$ 17,000.00
5. OPERATION OF FISSION PRODUCTS LABORATORIES	M943F advised by	L. E. Brownell H. J. Gomberg W. W. Meinke L. Thomassen	$ 14,000.00
			$ 85,000.00

The anticipated budgets for the subprojects, which include cost for personnel, materials, equipment, supervision, and overhead total $85,000.00. Of the $31,000.00 balance, $14,395.00 has been allocated and approved for construction and installation of the special facilities, such as radioactive-fume hoods, decontamination rooms, and counting rooms. The remaining $16,605.00 is allocated for additional sources and special equipment.

Each subproject will be handled according to the procedure established for the other projects in Engineering Research Institute. Monthly work reports will be prepared and monthly financial statements will be received by the respective supervisor for each subproject. At appropriate periods, presumably every three or four months, progress reports will be prepared. Additional reports will be prepared whenever advisable.

PART II. DESCRIPTION OF THE RADIATION LABORATORIES

A. X-RAY LABORATORIES

1. X-ray Machines: Three x-ray machines have been used in the preliminary investigation for this project. Two machines are located in the lead-shielded x-ray room, 4046 East Engineering Building. The larger machine in the room, a 220 kvp Westinghouse x-ray unit, is the property of the project. Fig. 1 is a photograph of this machine in the lead-shielded room. In Fig. 1 the equipment shown below the x-ray tube is that used in some of the studies of the effect of radiation on chemical reactions. The 150 kvp Westinghouse x-ray machine, located in the same room is the property of the Department of Chemical and Metallurgical Engineering. It is available for project use when not being used for instructional purposes. The third x-ray machine is located in Room 32a of the Radiation Laboratory (formerly the Palmer Ward Building) and is the property of the Department of Roentgenology. This machine is also available for project use when not in use by the Department of Roentgenology. This machine has a 200 kvp Westinghouse tube with Kelly-Koett Manufacturing Company controls.

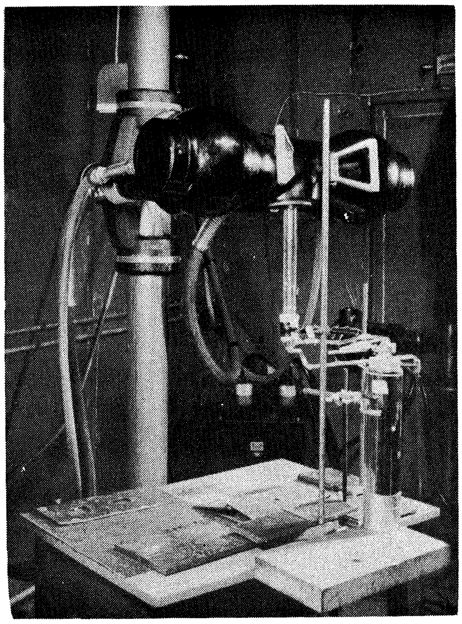


Fig. 1. 220 kvp Westinghouse X-Ray Machine

2. Calibration of X-ray Machines: The smaller x-ray machine (150 kvp) has been calibrated, and similar calibrations will be available for the other machines. Calibration was performed with a Victoreen Roentgen-Rate Meter Model 510 (FPL No. 37). This instrument reads directly in roentgens per minute as delivered to a small sensitive volume at the end of a probe. The x-ray tube was fixed in a horizontal position with the axis of radiation pointing vertically downward. The Victoreen probe was clamped to a ring-stand and placed under the x-ray tube. Readings of roentgen output vs tube voltage and current were taken at a distance of 12 in. from the x-ray tube window. Measurements were then taken at various distances from the tube window with the tube operating at its maximum allowable continuous-duty voltage and current. A final series of measurements were taken to plot the field distribution of the tube. These were recorded at a fixed distance of 18 in. from the window, at the maximum tube rating.

The results of this survey are plotted in Figs. 2, 3, 4, and 5. Fig. 2 indicates that the tube output in roentgens per minute is practically linear with current. Tube output in terms of kilovoltage is nonlinear, as may be seen from Fig. 3, but it varies approximately as the second power of voltage at low kvp settings and powers less than one as the maximum kvp rating are approached. Applying a correction for the target-to-window distance, the inverse square law is seen to hold quite well for this unit according to Fig. 4. Lead plates were used to minimize back scatter when taking these data. Fig. 5 shows that the field distribution is not symmetrical about an axis perpendicular to the window. Radiation intensity falls off quite sharply on the anode side of the tube and appears to be more uniform on the cathode side of the tube. The radiation intensity may be considered fairly uniform within a cone of about 40 degrees about the perpendicular to the tube window. The diameter of specimens to be irradiated, should be somewhat less than the distance from the window in order to receive uniform radiation.

The measurements made in this survey indicate that maximum dose rates of about 1300 roentgens per minute are possible with this machine. The larger machine, whose continuous rating is 20 ma at 220 kvp, should be capable of maximum dose rates in the neighborhood of 2000 roentgens per minute.

B. HIGH-LEVEL LABORATORY

The High-Level Laboratory of the Fission-Products Laboratories is located in Room 52 of the Radiation Laboratories (formerly the old bakery of the Palmer Ward Building), as shown in Fig. 6. The new plan for the radiation laboratory is shown in Fig. 7, with the cobalt-60 vault indicated in the southwest corner of Room 52.

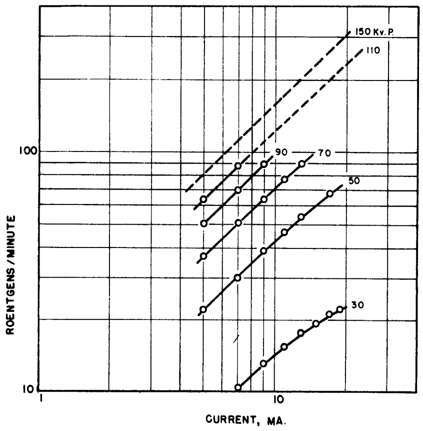


FIG. 2
OUTPUT, ROENTGENS / MINUTE
vs.
TUBE CURRENT, MILLIAMPERES

WESTINGHOUSE INDUSTRIAL X-RAY UNIT
STYLE 982036 SER. No. 87252
DISTANCE: 12 IN. FROM WINDOW
VICTOREEN R-METER MOD. 510 FPL No. 37

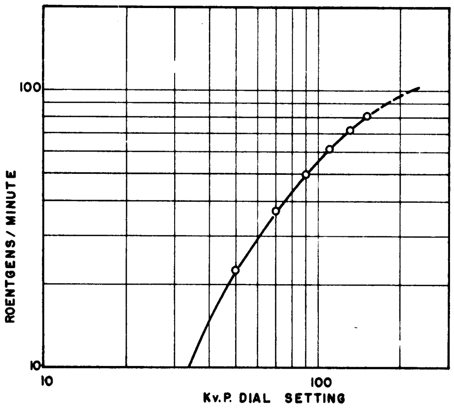


FIG. 3
OUTPUT, ROENTGENS / MINUTE
vs.
KILOVOLTS PEAK, DIAL SETTING

WESTINGHOUSE INDUSTRIAL X-RAY UNIT
STYLE 982036 SER. No. 87252
DISTANCE: 12 IN. FROM WINDOW
VICTOREEN R-METER MOD. 510 FPL No. 37

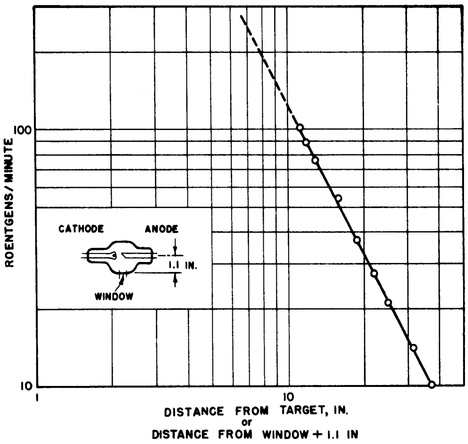
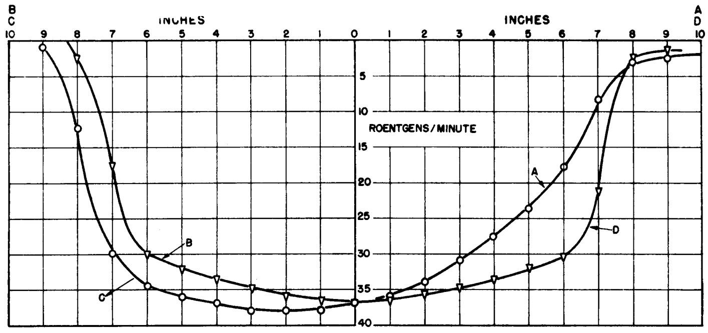


FIG. 4
OUTPUT, ROENTGENS / MINUTE
vs.
DISTANCE FROM X-RAY-TUBE TARGET, INCHES

WESTINGHOUSE INDUSTRIAL X-RAY UNIT
STYLE 982036 SER. No. 87252
150 Kv. P 5MA.
VICTOREEN R-METER MOD. 510 FPL No 37



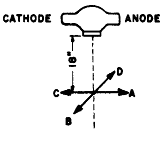


FIG. 5
FIELD DISTRIBUTION PLOT OUTPUT, ROENTGENS / MINUTE
vs.
POSITION RELATIVE TO TUBE WINDOW

WESTINGHOUSE INDUSTRIAL X-RAY UNIT
STYLE 982036 SER. No. 87252
150 Kv. P. 5MA.
VICTOREEN R-METER MODEL 510 FPL No. 37

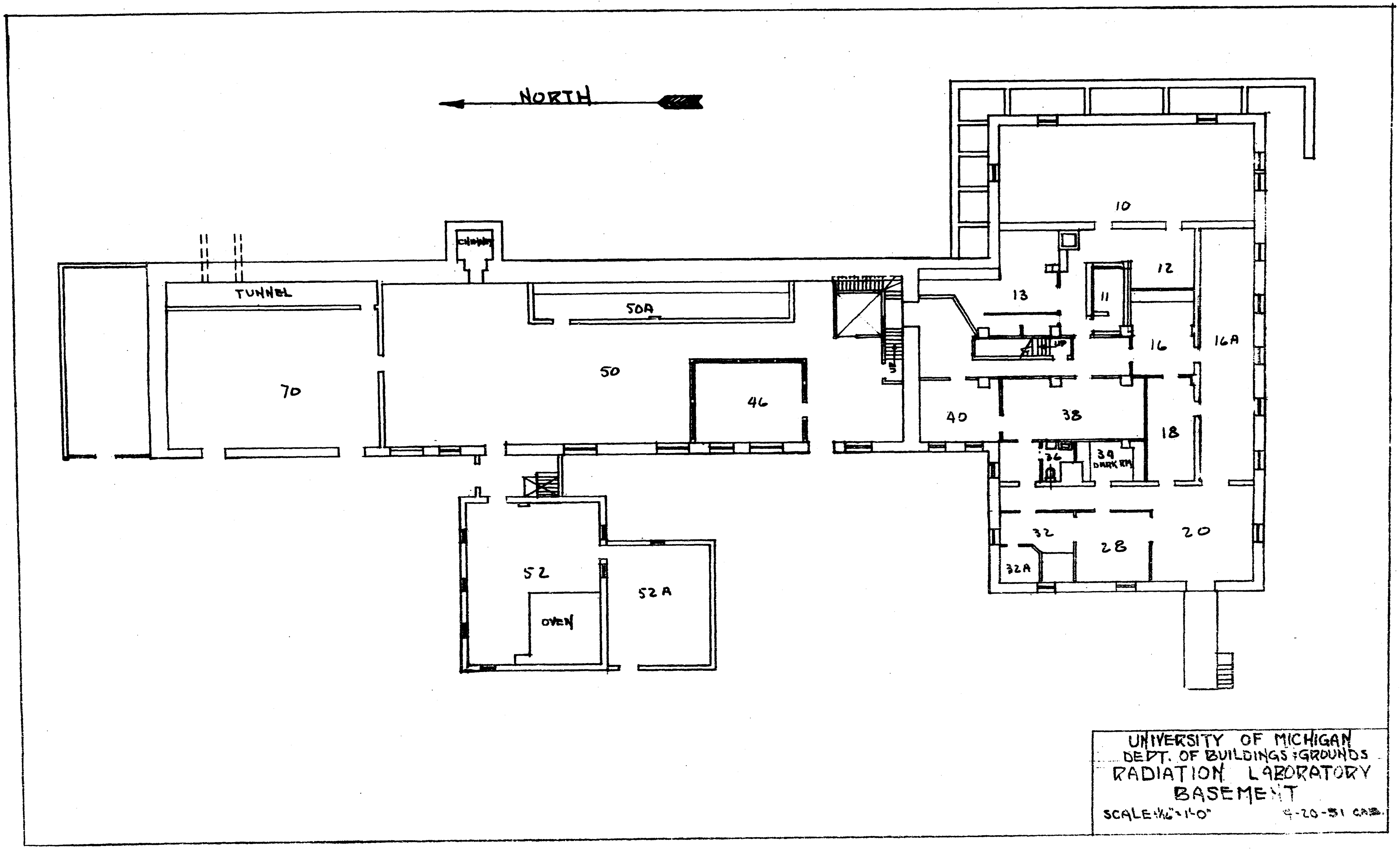


Fig. 6. Plan of Present Radiation Laboratory

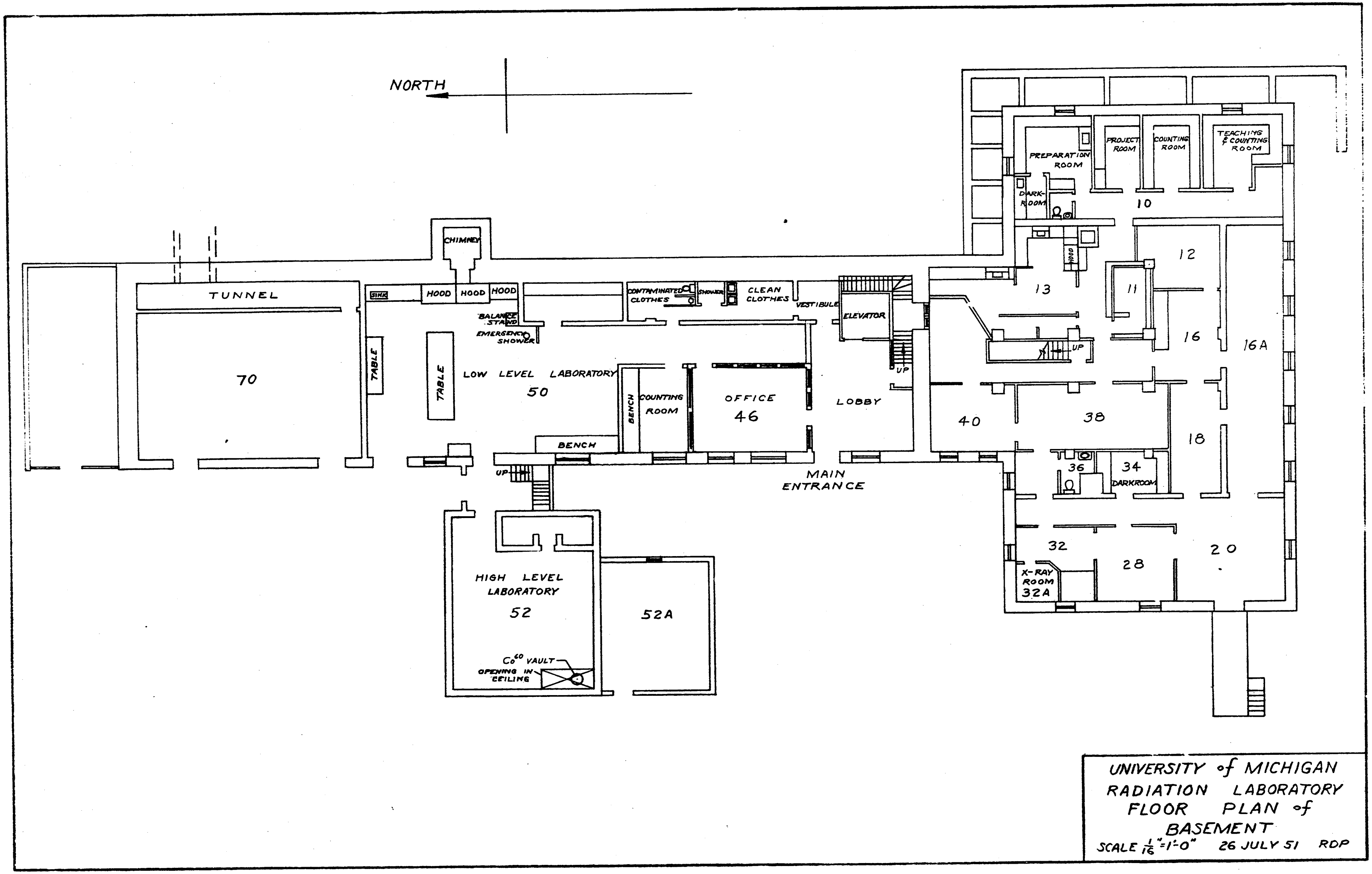


Fig. 7. New Plan for Radiation Laboratory

The High-Level Laboratory is to be used for studies of the effect of irradiation on various materials and processes. All the space in the High-Level Laboratory is allocated for use by the project, which makes this building space the most desirable from the standpoint of safety in working with radioactive materials of high activity.

At present, 1000 curies of cobalt-60 are being used in the High-Level Laboratory for the irradiation of specimens. The 1000-curie cobalt source was obtained from Brookhaven National Laboratory, and the container was fabricated at the Universty. Fig. 8 shows a sectional view of the cobalt-60 container or vault. Fig. 9 shows the details of the plugs and loading tubes for closing and charging the cobalt-60 vault. The design is basically that used by the Brookhaven National Laboratory for the similar sources which they have prepared. It consists essentially of a stainless-steel cylinder filled with lead for shielding. Fig. 10 shows the mechanism for charging samples into the vault by remote control. Figs. 11 through 17 are photographs (by courtesy of Brookhaven National Laboratory) of the cobalt source and container. Fig. 11 shows the lower portion of the vault with a mock cobalt cylinder held above the opening. Fig. 12 shows the cobalt cylinder photographed with flood lights while under several feet of water. Fig. 13 shows the radioactive-cobalt cylinder photographed with its own glow, also under several feet of water, which acts as a shield. Fig. 14 shows the personnel at the Brookhaven National Laboratory moving the radioactive-cobalt source into position under water for charging into the lead container. Fig. 15 shows how the upper portion of the lead container is lowered to enclose the cobalt. Fig. 16 shows the small plug used to complete the closure of the vault. Fig. 17 shows the vault raised for inspection of the bottom. Fig. 18 shows the loaded vault being received at the University. L. E. Brownell and M. E. Gluckstein are holding the plug and the aluminum tube, which is used to hold samples charged into the vault. Fig. 19 is a photograph taken while the vault was being calibrated to determine safe operating distances. Mr. D. M. Gardiner, health physicist from the Chicago Operations Office of the AEC, is shown in the lower left; Dr. G. M. Ridenour, University of Michigan Radiation Safety Officer, is shown directly behind Mr. Gardiner; Dr. H. J. Gomberg, Director of the Phoenix Radiation Laboratory, is shown to the right beside the Victoreen Rate Meter used in the test; Mr. W. Kerr of the Electrical Engineering Department is shown in the far left.

1. Calibration of the Cobalt-60 Vault: Some preliminary values of the radiation emitted from the vault were obtained from the Brookhaven National Laboratory. Prior to use of the radiation vault in the University Radiation Laboratories it was necessary to determine safe working areas and to obtain the calibration of the radiation beam emerging from the open vault. These tests were made under the guidance of Mr. D. M. Gardiner of the Chicago

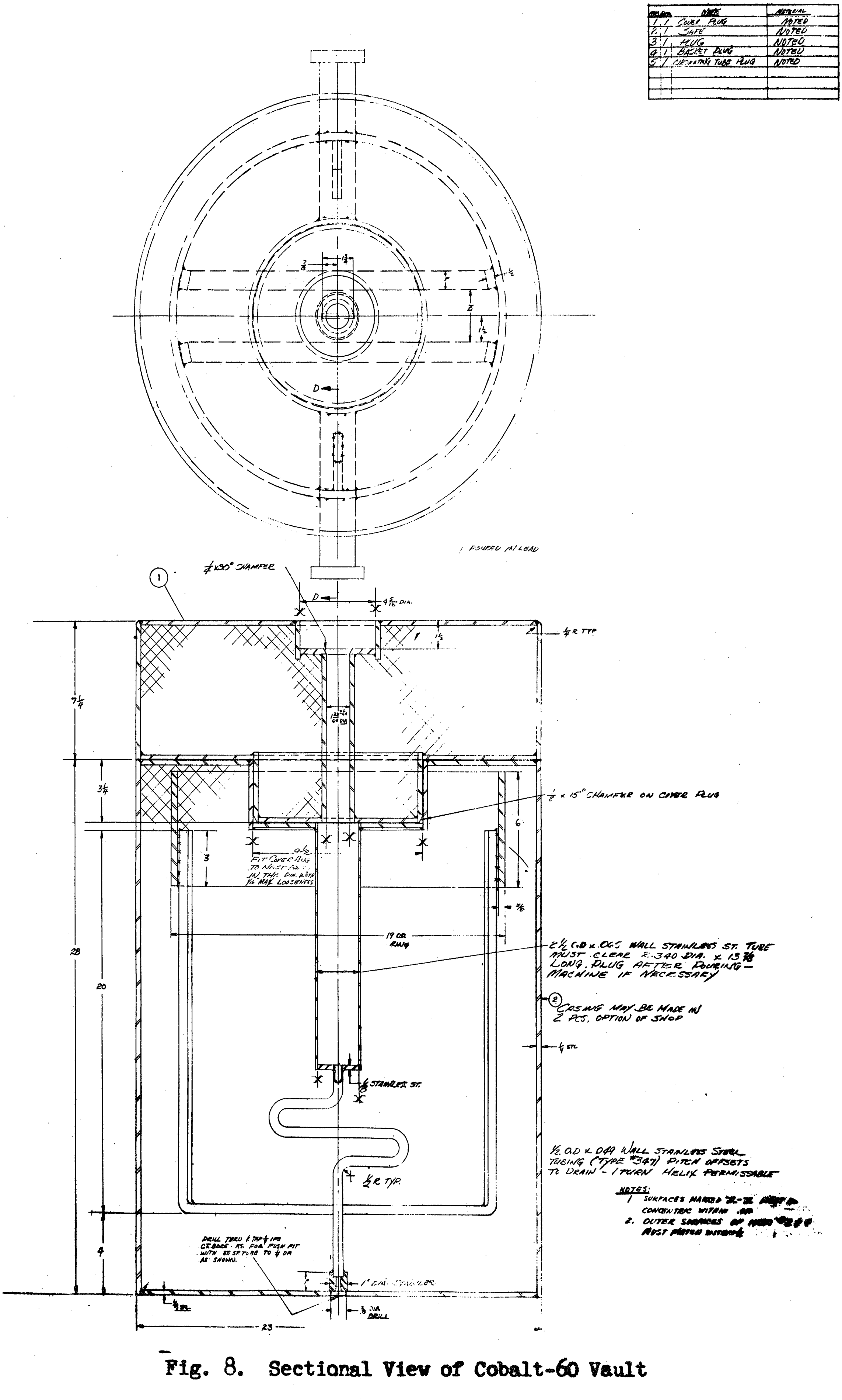


Fig. 8. Sectional View of Cobalt-60 Vault

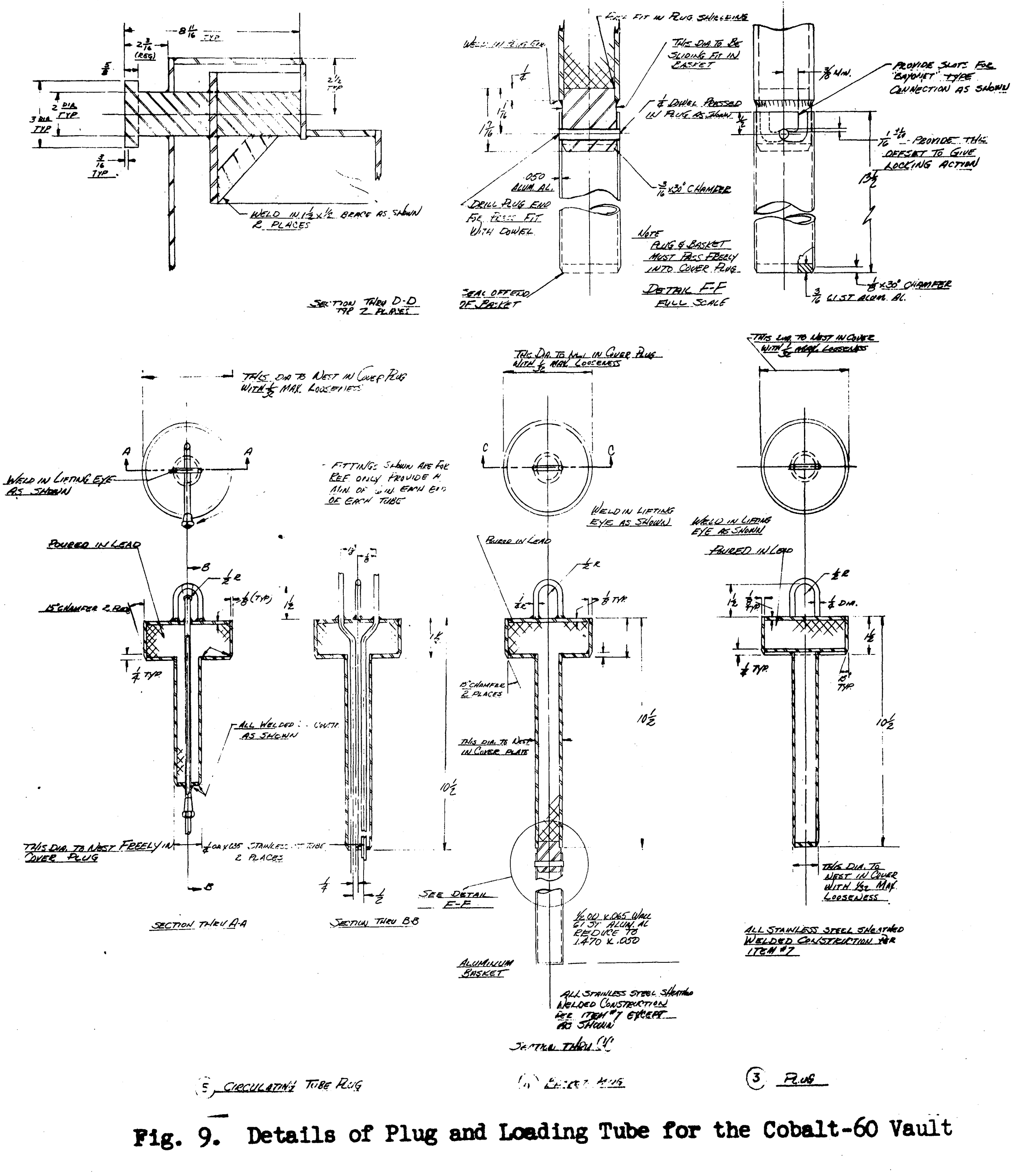
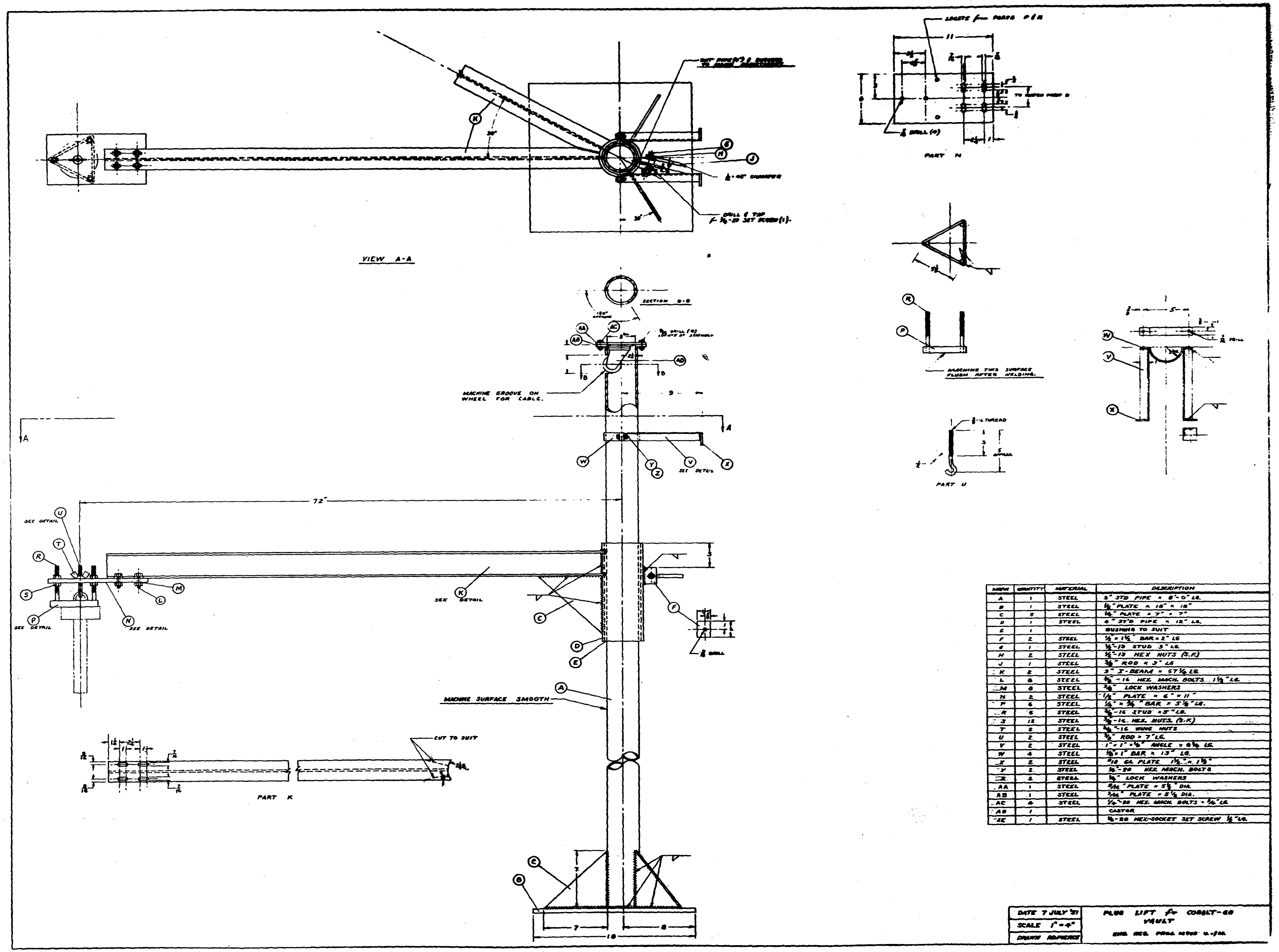


Fig. 9. Details of Plug and Loading Tube for the Cobalt-60 Vault



MARK	QUANTITY	MATERIAL	DESCRIPTION
A	1	STEEL	3" STD PIPE × 8'-0" LG.
B	1	STEEL	1/2" PLATE × 18" × 18"
C	5	STEEL	1/4" PLATE × 7" × 7"
D	1	STEEL	4" ST'D PIPE × 12" LG.
E	1		BUSHING TO SUIT
F	2	STEEL	1/2" × 1 1/2" BAR × 2" LG
G	1	STEEL	1/2"-13 STUD 3" LG.
H	2	STEEL	1/2"-13 HEX NUTS (S.F.)
J	1	STEEL	3/8" ROD × 3" LG
K	2	STEEL	3" I-BEAM × 57 1/4 LG.
L	8	STEEL	3/8"-16 HEX. MACH. BOLTS 1 1/2" LG.
M	8	STEEL	3/8" LOCK WASHERS
N	2	STEEL	1/2" PLATE × 6" × 11"
P	6	STEEL	1/4" × 3/4" BAR × 5 1/8" LG.
R	6	STEEL	3/8"-16 STUD × 5" LG.
S	12	STEEL	3/8"-16 HEX. NUTS (S.F.)
T	2	STEEL	3/8"-16 WING NUTS
U	2	STEEL	3/8" ROD × 7" LG.
V	2	STEEL	1" × 1" × 1/8" ANGLE × 8 3/4 LG.
W	4	STEEL	1/8" × 1" BAR × 13" LG.
X	2	STEEL	#18 GA. PLATE 1 1/2" × 1 1/2"
Y	2	STEEL	1/4"-20 HEX. MACH. BOLTS
Z	2	STEEL	1/4" LOCK WASHERS
AA	1	STEEL	9/16" PLATE × 5 1/2" DIA.
AB	1	STEEL	3/16" PLATE × 5 1/2 DIA.
AC	4	STEEL	1/4"-20 HEX. MACH. BOLTS × 3/4" LG.
AD	1		CASTOR
AE	1	STEEL	1/4-20 HEX-SOCKET SET SCREW 1/2" LG.

Fig. 10. Plan of Mechanism for Charging Sample into Vault by Remote Control

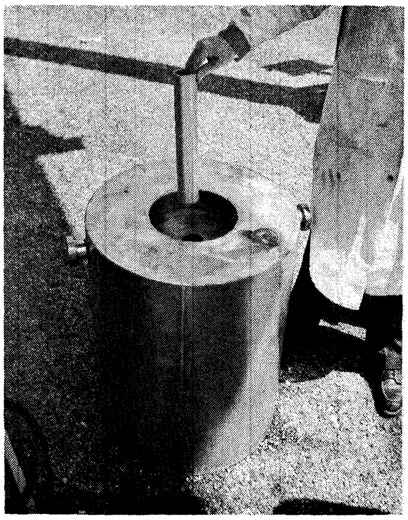


Fig. 11. **Mock Cobalt Cylinder**

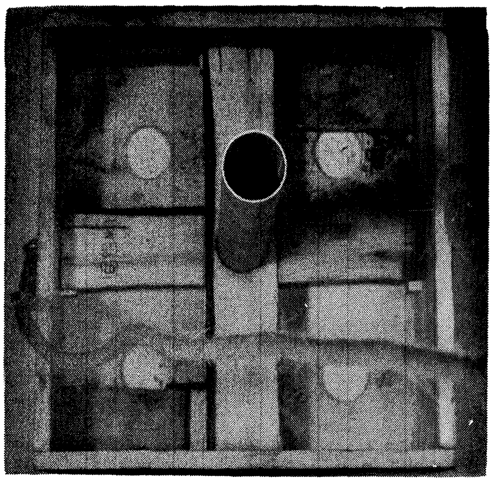


Fig. 12. Radioactive Cylinder Under Artificial Illumination

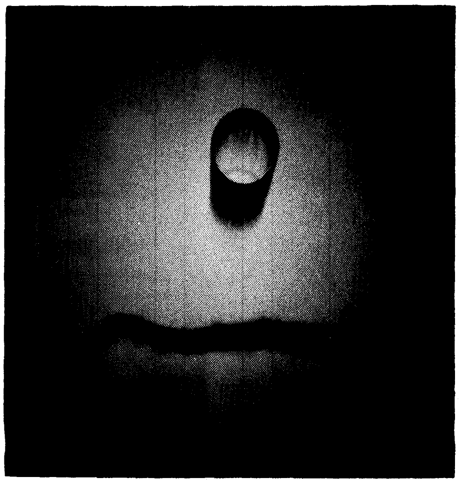


Fig. 13. Glowing Radioactive Cylinder

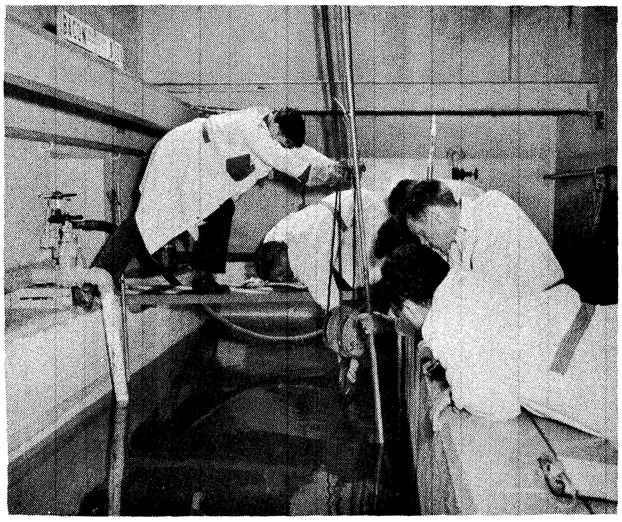


Fig. 14. Positioning Cobalt Source Under Water.

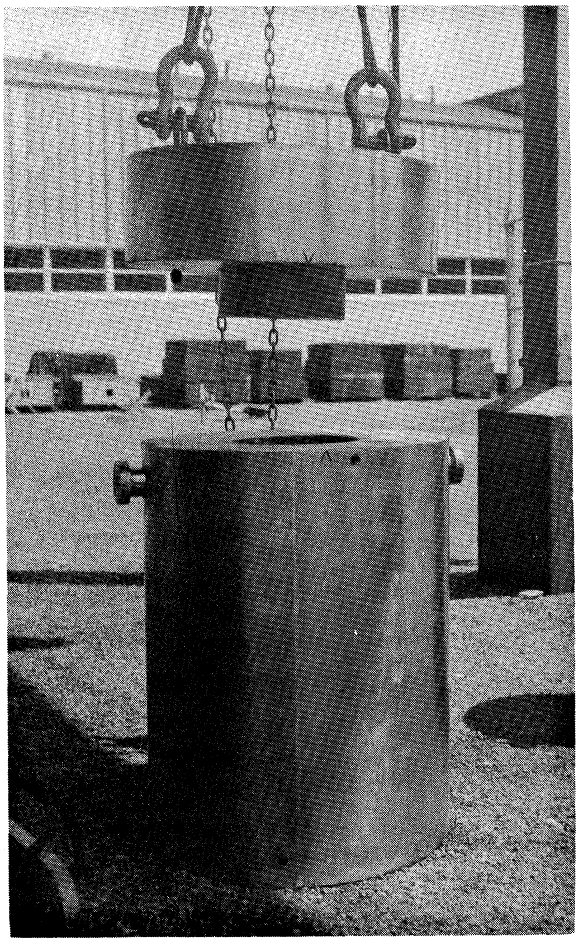


Fig. 15. Separation of Upper and Lower Sections of Lead Container

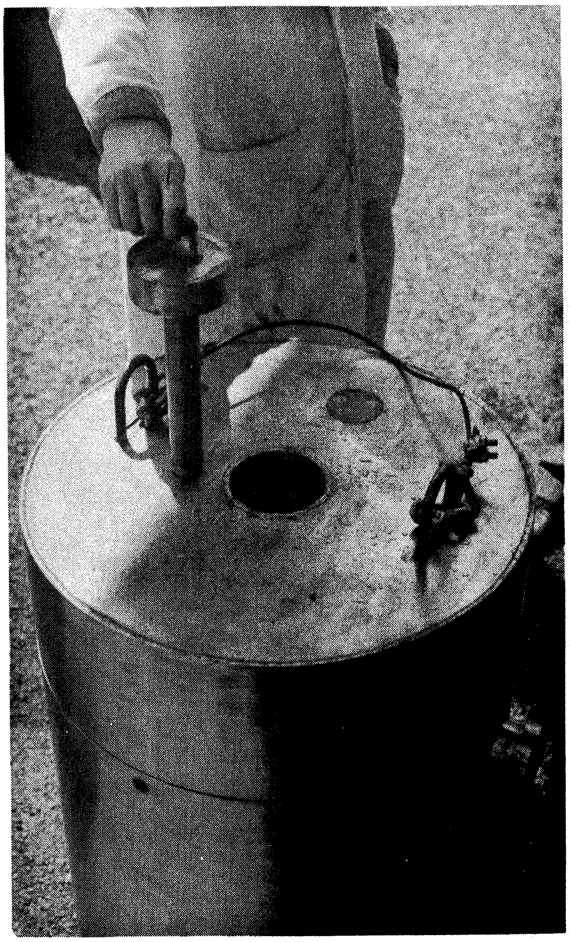


Fig. 16. Vault with Closure Plug

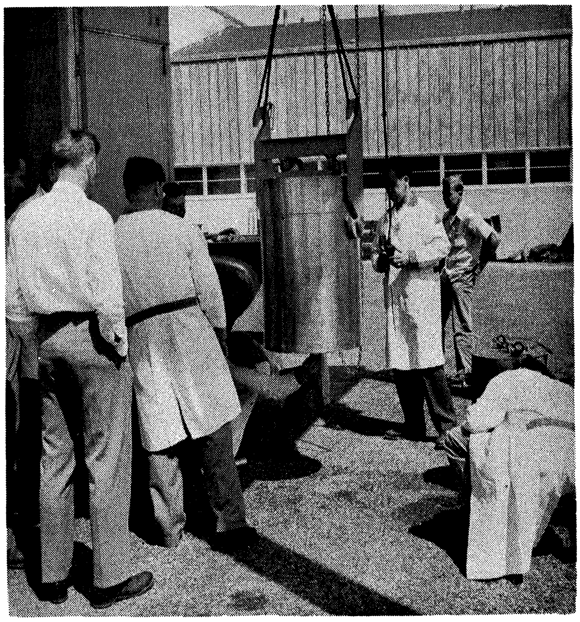


Fig. 17. Vault Raised for Bottom Inspection

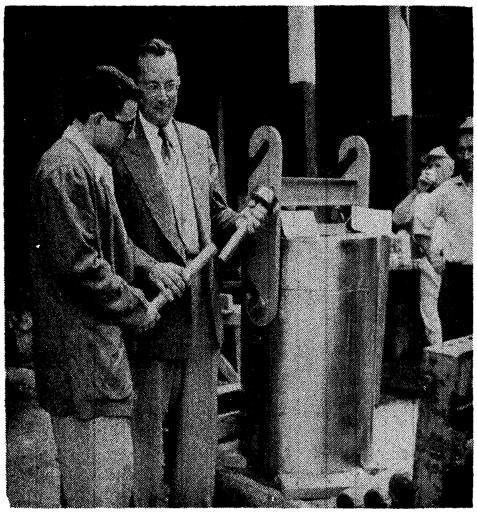


Fig. 18. Vault on Arrival at University Radiation Laboratory

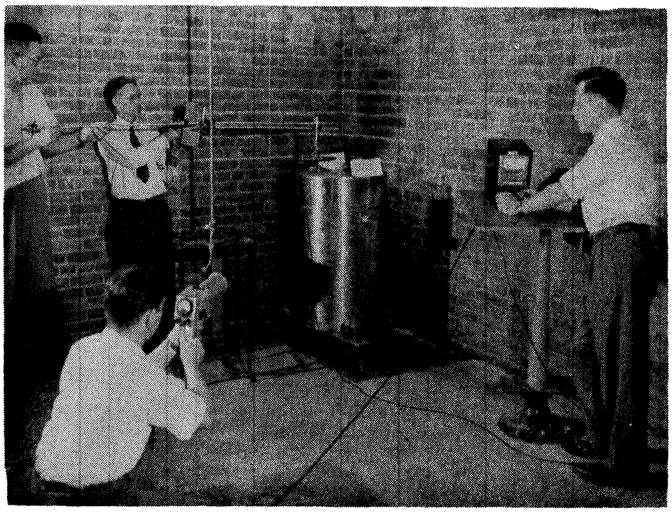


Fig. 19. Photograph During Calibration Tests on Cobalt-60 Vault

Operations Office of the AEC, and of representatives of the University of Michigan Radiation Safety Committee, Dr. G. M. Ridenour and Dr. H. J. Gomberg.

Radiation measurements were recorded using the following instruments: (1) Victoreen Roentgen-Rate Meter Model 510, (2) Nuclear Instrument Corporation Survey Meter Model 2610A, (3) Technical Associates Survey Meter Model SIC 117, and (4) a Radioactive Products Survey Meter. The Victoreen Meter was used to register the high-intensity dose rates near the open plug hole, and the Technical Associates and Nuclear Instrument Corporation meters were employed for low-level measurements.

With the plug in place in the vault, the radiation intensity at all points along the walls of the vault was found to be about 0.04 mr per hour, or approximately twice the normal background level for this area. The radiation intensity in the immediate vicinity of the plug, however, was recorded at about 6 mr per hour and at a point under the vault near the drain outlet, the reading was approximately 0.06 mr per hour.

A plot of the results of the survey with the plug removed from the vault is shown in Fig. 20. It should be noted that the section of the second floor of the building above the vault was removed to reduce radiation scatter. Field traverses were made in the horizontal as well as the vertical directions with reference to the top surface of the vault and the center of the plug hole. The radiation intensity 1/2 inch above this point reference was recorded as 40 roentgens per min. Maximum radiation intensity at the second-floor level directly over the plug hole was 2.3 r per hour and the corresponding value on

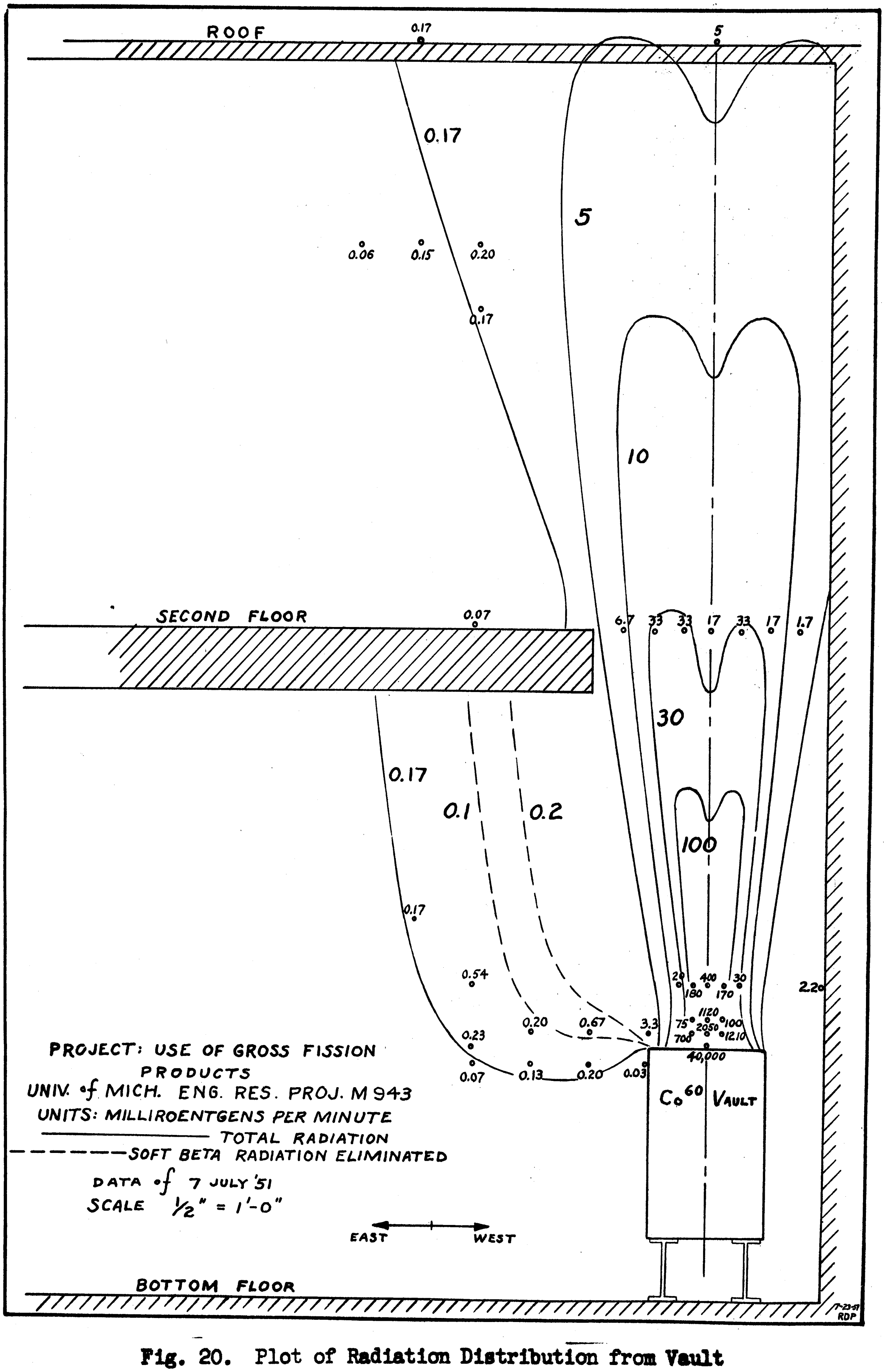


Fig. 20. Plot of Radiation Distribution from Vault

the roof of the laboratory building was 0.3 r per hour. (The building has only two floors.) Considerable data were taken in the vicinity of the plug hole in an effort to define the cone of radiation emanating from the open hole. Numerous readings were taken along the walls, on the second floor, and in the working spaces where personnel might conceivably stand while operating the vault. Dose rates of about 10 mr per hour, generally considered the maximum allowable for 8-hours-a-day exposure, were recorded at a distance of approximately 3 feet from the surface of the vault at shoulder level on the vault floor. On the second floor the edge of the hole above the vault may be approached to within three feet before this dose rate is exceeded. A survey of the radiation coming through the roof revealed an area approximately 7 feet square in which the radiation intensity is over 10 mr per hour. These safe working limits will be clearly marked and railed off when the plastering and refinishing of the vault room are completed. A warning system will be installed to indicate when the plug is out of the vault.

By utilizing various filters attached to the radiation-measuring instruments it was demonstrated that the radiation from the vault is predominately gamma in character. In the horizontal traverses above the open plug hole, two definite maxima in radiation intensity were noted and are shown in Fig. 20. Also, it is noted that the radiation field as a whole is not symmetrical about the center axis of the vault. This is believed to be caused by a slight misalignment of the cobalt-60 cylinder in the vault, but it may also result in part from scattering from the walls of the room near the vault.

Considering the time element involved in opening and closing the vault, it is safe for operating personnel to work to within two feet of the vault. No position directly above the vault can be considered a safe place to work unless the vault is closed with the plug.

C. LOW LEVEL LABORATORIES

Fig. 7 shows the plans for the Radiation Laboratories. The Low-Level Laboratories, designated as room Number 50 in the plan, will be used for handling fission products and radioisotopes in smaller quantities. Three fume hoods for radioactive materials are to be located along the east wall, and will discharge filtered air into the chimney shown on the plan. A stainless-steel sink is to be located directly north of the hoods and an emergency shower directly to the south of the hoods. An equipment storeroom is located in the southeast corner of the Low-Level Laboratory. Directly to the south of the storeroom is a decontamination room with a shower, wash bowl, toilet facilities, and separate areas for contaminated clothes and clean clothes, respectively. Laboratory personnel will enter the laboratory through the decontamination room and change clothes before entering the laboratory. Room 46 is an existing office which will be used for office space for project personnel. A counting room will be provided directly north of the office.

In addition to the space just described, the project will have the use of some space in the Phoenix laboratories at the southeast end of the building. The counting rooms shown in Fig. 7 in area No. 10 will be completely air-conditioned. Project M943 will be allowed to keep its most sensitive counting equipment in these rooms and to use the counting rooms and some space in the adjoining area when needed. In addition to the laboratories described above, a wide variety of other laboratories in various departments of the University will be available for project work of non-radioactive character.

PART III. REPORTS ON SUBPROJECTS

A. PROJECTS M943A AND M943B. — THE EFFECT OF RADIATION ON THE PERFORMANCE OF COMBUSTION ENGINES

The effect of radiation on the performance of combustion engines may be of importance both in the field of reciprocating (M943A) and jet engines (M943B), and it is intended to explore the possibilities in both fields. However, much of the theory is common to both types of engines and therefore, to avoid unnecessary duplication, the preliminary search of the literature has been limited to that for reciprocating engines (M943A). This will be followed by a supplementary search of the literature specific to jet engines (M943B).

No evidence has been found in the nonclassified literature of previous investigations on this subject; therefore, the literature search was concentrated on two related problems: (a) the fundamental nature of ignition, combustion, and detonation in inflammable gases and vapors, particularly the experimentally demonstrated facts (some consideration was also given to the more plausible theories that have been proposed and how well these agree with experiment); (b) the observed effects on vapors and gases of irradiation or corpuscular bombardment, including the effects of light in the visible and ultraviolet region, x-rays, cathode rays, and slow-speed electrons (100 volts or less), as well as of the radioactive sources which have been available in the past.

In the field of reciprocating combustion engines the possible results include (a) more efficient use of existing fuels in internal combustion engines, (b) development of formerly inferior fuels for internal combustion engines, (c) a possible increase in efficiency, and (d) a possible reduction in the weight of diesel engines as a result of reduced ignition pressures.

1. Literature Review for M943A

a. Chemical Effects of Irradiation and Bombardment of Gases: When gases are irradiated with alpha particles the reactions which have been observed include oxidation, polymerization, and decomposition (1,2,3). If radon is used as the radiation source, the reaction velocity is proportional to the total quantity of radon, rather than proportional to the concentration, and to the gas pressure(1). In the case of the polymerization reactions it was found that, if nitrogen or one of the noble gases was added to the reactants, the ions of the former appeared as effective in producing reaction as did the ions of the reactants (3,6). For the carbon monoxide--oxygen reaction the ionization of the carbon dioxide proved only about 14.5 per cent as effective as the ionization of the reactants (4). Later experiments which employed strong electrostatic fields to sweep out ions as fast as they were formed, indicated that, at least for the decomposition of ammonia, ionized particles accounted for only about 30 per cent of the decomposition, the remainder being attributed to the formation of excited molecules and other mechanisms not involving ionization (5).

Lind and Vanpee (6) thought it possible that ionization might be transferred, since all the inert gases had higher ionization potentials than the reactants that had been investigated. Accoringly a mixture of xenon, hydrogen, and oxygen was irradiated. Xenon has a lower ionization potential than either of the other two and therefore could not transfer the ionization. Xenon ions were still found to be 50 per cent efficient in producing this reaction. It was found to have a slight accelerating effect on the reaction of a carbon monoxide plus oxygen mixture.

Other information on alpha-radiation includes the stopping power of various hydrocarbon vapors (7) and the observation that alpha-particles produce ultraviolet radiation in gases (8).

No extensive work on the chemical effects of beta rays was found. However, Otvos (9) has reported that the relative ionization probabilities of a number of gases appear to depend on the number of valence electrons and on some geometrical factors. Ionization probability appears unrelated to ionization potential or other chemical properties of the gas molecules for these high-energy particles.

One would expect high-energy cathode rays to give the same results as beta radiation. Early workers, using energies of the order of 150-200 kilovolts found that for those gases in which reactions occurred the yield depended on voltage, space current, and duration of irradiation (10). Calculations of ion yield gave values of the same order of magnitude as were obtained for alpha rays.

Numerous experiments have been carried out with controlled electrons of energies of from 30-200 volts. Various gases have been bombarded and the relative abundance of the fragments determined by mass-spectrograph methods.

In many respects the action of light on gases appears similar to that of other radiation. Polymerization and decomposition of the aliphatic aldehydes has been observed (17,18). It was found that the chemical action increased with decreasing wave length. In some cases the presence of small quantities of other gases such as Hg vapor is necessary to sensitize the reaction to light (22).

The work of Norrish and his coworkers is of particular interst (20,21). They maintained a slow reaction in formaldehyde and in ethylene in an electric furnace at about 400 mm pressure. When the reaction vessel was erradiated with a high-pressure Hg source, they found that the reaction rate, measured as the rate of pressure change (mm Hg per min), was definitely accellerated. Furthermore, the ignition lag was markedly reduced.

In a later experiment a high-intensity discharge tube filled with one of the rare gases was placed beside a quartz reaction tube. The intensity was such that the concentration of active carriers was of an order of magnitude comparable to the concentration of reactants. Many organic compounds were decomposed into carbon and hydrogen, the former appearing as "cobwebs" strung across the reaction chamber. Using a single 4000-joule flash lasting less than 2 milliseconds, nearly 100 per cent decomposition was achieved for NO_2 and 40 per cent and 50 per cent for CH_3 $COCOCH_3$ and formaldehyde, respectively.

It is interesting to note that as far back a 1913 J. R. Thompson (67) studied the ignition of hydrogen and oxygen by hot platinum wires and concluded that ignition always occurred at that temperature at which platinum starts to emit electrons. As a further check, when the platinum was irradiated by x-rays, ignition occurred at once.

For more extensive bibliographies see references (49) and (50).

Where spark ignition is to be used, consideration must also be given to the effect of the radiation on the spark itself. Considerable work has been done on this problem since the discovery of radioactivity. For recent investigations see references (53,55). The work of Bak and associates (55) is particularly interesting, involving as it does, electrons and gamma rays obtained from a tube operating at 3000 kilovolts. It was shown that the electrons had much more influence than the gamma rays. If the discharge started at the anode, irradiation furthered it; if it started at the cathode, irradiation quenched it. If the electron beam was parallel to the spark gap, there was an effect on the gap only if the negative electrode was turned toward the tube.

b. Ignition, Combustion, and Detonation of Gases: Experiments have shown that most mixtures of inflammable gases show a definite inflammability range of pressures above and below which ignition does not occur (23,24). These pressure limits, however, are very much dependent on the means of ignition (26,29). Finch and Thompson concluded that the frequency of a spark discharge was far more important than the energy expended.

Many observers have found that the addition of inert gases actually increases inflammability at the lower pressure limits (24,27,28,30,31,32).

Later work of Linnet and coworkers indicates that two opposing effects operate and that for sufficient diluent the lower ignition pressure is again raised (34,39).

There is some doubt as to the effects of size and shape of vessel, some workers reporting a dependence and others not (23,27,28,31,34-37). A number of workers report a dependence on the nature and previous history of the walls (27,31). Frost and Linnet (34) found no wall effect at half an atmosphere and suggested that the reason that other workers did find wall effects lay in the low pressures used. Thompson for example used pressures of about 40 mm (30), while the work on phosphorus vapors was carried on at pressures of the order of a millimeter of mercury (28,51).

The nature of the electrodes and electrode separation affect the ignition pressures. Electrodes coated with glass almost to the tips have been found more effective in producing ignition than bare electrodes (23,33). Lewis and Von Elbe reported that ignition energy remains constant over a considerable range of electrode separations but increases rapidly outside these ranges (35).

Many reaction mixtures are strongly sensitized or strongly inhibited by the presence of relatively small traces of other vapors (33,37-39). For instance, Frost and Linnet found that changing the pressure of water vapor in a $(2CO + O_2)$ mixture from 2 mm to 7 mm lowered the ignition pressure from 370 mm to 230 mm.

If the air used for tests is first passed through an arc discharge, the inflammability limits are increased. Lewis and Kreutz (63) attributed this to the introduction of ions into the gas, but Burgoyne and Thoms (46) consider the effect as a result of the production of small solid particles of about 300-500 Å diameter.

Hydrocarbon combustion generally is very complex and temperatures, pressures, and products of combustion vary considerably with conditions. A great deal of work has been done by groups working with burners and internal combustion engines.

Herman's group (65), investigating an acetylene-oxygen flame by spectroscopy, found the following: (a) with excess oxygen the OH and CH bands remained strong, C_2 bands were weakened, and the O_2 and hydrocarbon bands intensified; (b) with CO_2 the hydrocarbon bands intensified and CO bands appeared.

Gaydon and Wolfhard (66) were able to investigate hydrocarbon flames in more detail by using wide tubes and pressures of about .01 atm. These conditions yielded a thick reaction zone (inner cone). They found C_2, OH, and CHO bands emitted early in the reaction zone and CH emitted somewhat later. In flames supported by N_2O, C_2 and NH, bands occur before CN and NH_2.

Chemical analysis of products of hydrocarbon combustion have shown the presence of aldehydes in considerable quantity, particularly formaldehyde, and some ketones (20,41,43,46). Wheeler and coworkers (64) sampled the contents of a test-engine cylinder and measured concentrations of aldehydes and peroxides at various stages of the cycle and at varying compression ratios. Peroxide maxima were observed to occur at 7-1/2 to 8° beyond top dead center. For nonknocking operation a maximum of about 15 ppm was found. At 30 ppm knocking was severe.

The aldehyde maxima varied from 300 to 900 ppm and were attained at 8-1/2 to 11° beyond top dead center.

Addition of tetra-ethyl lead reduced the aldehyde maximum by about 25 per cent and the peroxide maximum by about 50 per cent.

At temperatures well below ignition, hydrocarbon-oxygen mixtures may show the phenomenon of stepped ignition; i.e., cool flames are observed followed by ignition after an induction period of from seconds to hours (45).

Two mechanisms have been suggested for ignition and explosion: the thermal theory and the chain reaction theory.

The thermal theory postulates that a sufficient volume of mixture must be heated to a sufficiently high temperature, i.e., the reaction energy transferred from the "minimum flame sphere" to surrounding masses of gas must be sufficient to heat a larger volume of the gas above the ignition temperature of the gas mixture. A mathematical treatment of several forms of heat sources was carried out by Taylor-Jones and coworkers (25). They showed that for a given total energy transfer an instantaneous heat source should be more effective than a continuous one and that a surface distribution should be superior to point or volume sources. If the rate of liberation of heat energy accelerates continuously a (thermal) explosion occurs.

The principal objection to the thermal theory of ignition is that it fails to explain the marked discontinuity in reaction rate observed on initiation of explosions; e.g., the phosphorus vapor-oxygen reaction may change from a negligibly small rate to an almost infinite rate with a slight change in pressure.

It also seems unable to explain such reactions as the ignition of H_2-Cl_2 mixtures by photons.

The chain theory postulates that the reaction depends on the presence of certain reaction "carriers", i.e., active molecules or ions or free radicals which react readily with one of the main constituents. During the course of the reaction cycle the active carriers are regenerated. More than one carrier may be involved in the cycle. If during each reaction cycle, more than one active carrier of a given type is reproduced, the possibility of explosion exists.

A simple example of a branching chain reaction is that proposed by Linnet and Frost (34) for the reaction of hydrogen and oxygen:

(1) $H + O_2 = OH + O$

(2) $O + H_2 = OH + H$

(3) $OH + H_2 = H_2O + H$

Note that if the active carriers (O, H, OH) always reacted as indicated, three hydrogen atoms would be produced for each one consumed.

Since carriers may be made unavailable by a number of processes, including spontaneous decay, recombination, collision with other molecules, and diffusion from the ignition volume, it can be shown that the criterion for ignition is that some minimum concentration of active carriers must be supplied artificially in the ignition region. When these are supplied the reaction rate will accelerate indefinitely and explosion results (51,52,27, 28,30,33).

Leah (68) has calculated the atomic oxygen concentration in the explosion wave of a $CO-O_2$ mixture by comparing the temperature-time curves of quartz-coated and uncoated platinum wires. The latter heats up more rapidly, an effect which Leah attributes to the catalytic reaction of atomic oxygen with CO at the surface. He finds a peak concentration of atomic oxygen of 1.3 per cent.

The chain reaction mechanism of ignition is fairly well accepted at present. However, this does not rule out the possibility of thermal mechanism of flame propagation in which the heat liberated by the reacting mass extends the reaction to the unreacted material ahead of the flame front.

Recent workers seem to regard both mechanisms as possible, and, in fact, Linnet and Frost (34) consider that either may predominate for the the same constituents, depending on the pressures involved.

For more extensive bibliographies see references 33, 47, and 48.

2. Method of Approach

On the basis of the previous discussion it seems reasonable to expect that radiation of sufficient intensity should exert some effects on gaseous expolsions. If the chain theory of ignition holds, then the concentration of the active carriers is critical. Such carriers might conceivably be ions, free radicals, or merely excited molecules. Radiation in gases is known to produce ions and molecule splitting (i.e., free radicals). At the energies involved it does not seem reasonable that chemical effects of the bombarding particles could be very specific. Hence, one would expect many types of molecular excitation to occur also.

As a first step, reaction rates of gaseous mixtures will be measured at pressures too low for explosion to take place. Mixtures used will probably include methane-oxygen, hydrogen-oxygen and carbon monoxide-oxygen at pressures below 4 cm Hg.

The apparatus to be used will consist of a spherical glass reaction chamber, approximately 6 inches in diameter, connected to a high-vacuum system. Pressures will be measured with a McLeod gauge. A means is provided for inserting discharge electrodes and a probe to which the radioactive sources may be attached.

The ignition source may be varied, but a glow discharge will be tried first. A full-wave rectified d-c power source has been constructed which will yield a continuously variable open circuit potential of up to 1500 volts.

It is contemplated that different types of radioactive sources will be used, including beta and gamma rays of varying intensity and energy. Low-energy beta rays will be used first.

The tentative work schedule is:

1) assembly and testing of apparatus
2) running of control experiments, i.e., without radioactive sources present
3) running of experiments with radioactive sources present

Once a knowledge of the effects under nonexplosive conditions is obtained, an investigation of explosions should be undertaken. This might include explosions in steel bombs or actual use of test engines.

Bibliography for Project M943A

1. Lind and Bardwell, "Chemical Effects of α-Particles in Gases," *J. Am. Chem. Soc.* *47* 2675 (1925).

2. Lind, Bardwell, and Perry, "Chemical Action of α-Particles on Unsaturated Hydrocarbons," *ibid.* *48* 1556 (1926).

3. Lind and Bardwell, "Chemical Actions of α-Particles in Presence of Inert Gases," *ibid.* *48* 1575.

4. Rosenblum, "Chemical Effects of α-Particles on Gas Reactions in Presence of CO_2," *J. Phys. Chem.* *37*, 53 (1933).

5. Smith and Essex, "Effect of Electric Fields on Decomposition of NH_3 by α-Rays," *J. Chem. Phys.* *6*, 188 (1938).

6. Lind and Vanpee, "Effect of Xe Ions on the Chemical Action of α-Particles," *J. Phys. and Colloid. Chem.* *53*, 898 (1949).

7. Gibbs and Lockenvitz, "Stopping-Power of Some Hydrocarbon Isomers for α-Particles," *Phys. Rev.* *73*, 652 (1948).

8. Audubert and Lormeau, "Production of Ultraviolet Radiation in Gases by α-Radiation," *Compt. Rend.* *228*, 318 (1949).

9. Otvos, "Ionization by C^{14} in the Ionization Chamber," *Phys. Rev.* *73*, 537 (1948).

10. Busse and Daniels, "The Chemical Effects of Cathode Rays on O_2, Air, NO and CO_2," *J. Am. Chem. Soc.* *50*, 3271 (1928).

11. Hustrulid, Kusch, and Tate, "Dissociation of Benzene, Pyridene and Cyclohexane by Electron Impact," *Phys. Rev.* *54*, 1037 (1938).

12. Delfosse and Bleakney, "Electron Bombardment of Propane, Propylene and Allene," *ibid*, *56*, 256 (1939).

13. Kambara, "Dissociation and Ionization of n-Hexane By Electron Impacts," *J. Phys. Soc. Japan* *2* *No.* *3*, *25* (1947); "Dissociation and Ionization of Cyclo-Hexane and Benzene by Electron Impacts," *ibid.* *No.* *4*, *57*.

14. Viallard and Magat, "Electron Impact Fragmentation of Linear Carbon Chains," *Compt. Rend.* *228*, 1118 (1949).

15. Mohler, "Tables of Mass Spectra of Hydrocarbons," *J. Research Nat. Bur. Stand.* *42*, 369 (1949).

16. Geerk and Neuert, "Ionization and Dissociation of CH_4, CH_3OH and Methylal by Electron Impact," *Z. Naturforsch.* *5a*, 502 (1950).

Bibliography (cont'd)

17. Leighton and Blacet, "Photolysis of Aliphatic Aldehydes: I: Propionaldehyde," *J. Am. Chem. Soc.* 54, 3165 (1932).

18. Leighton and Blacet, "Photolysis of Acetaldehyde," *ibid.* 55, 1766 (1933).

19. Vantiggelen, "Photosensitization and Inhibition of Methane Combustion," *Anales Mines Belg.* 46, 159 (1945-46).

20. Norrish and Patnaik, "Effect of Light on the Combustion of Hydrocarbons," *Nature* 163, 883 (1949).

21. Norrish and Porter, "Photochemical Reactions Due to Very High Light Intensities," *Nature* 164, 658 (1949).

22. Lee and LeRoy, "Mercury Photosensitized Reaction of Atomic H with CH_3Cl," *Canad. J. Research* B 28, 500 (1950).

23. Coward, Cooper, and Warburton, "Ignition of Electrolytic Gas by the Electric Discharge," *J. Chem. Soc.* 101, 2278 (1912).

24. Coward, Cooper, and Jacobs, "Ignition of Some Gaseous Mixtures by Electric Discharge," *ibid.* 105, 1069 (1914).

25. Taylor-Jones, Morgan, and Wheeler, "Ignition of Gases," *Phil. Mag.* 43, 359 (1922).

26. Coward and Meiter, "Chemical Action in the Electric Spark Discharge: Ignition of Methane," *J. Am. Chem. Soc.* 49, 396 (1927).

27. Dalton and Hinshelwood, "Oxidation of PH_3 at Low Pressures," *Proc. Roy. Soc.* A 125, 294 (1929).

28. Melville and Ludlam, "Effect of Diluent Gases on the Ignition of Phosphorus Vapor," *ibid.* A 132, 108 (1931).

29. Finch and Thompson, "Ignition of CO-Air Mixtures," *ibid.* A 134, 343 (1931).

30. Thompson, "The Explosive Combination of H_2 and O_2; Function of the Walls," *Trans. Faraday Soc.* 28, 299 (1932).

31. Hadman, Thompson, and Hinshelwood, "Explosive Oxidation of CO at Low Pressures," *Proc. Roy. Soc.* A 138, 297 (1932).

32. Hinshelwood and Moelwyn-Huges, "The Chain-Reaction between H_2 and O_2," *ibid.* A 138, 311 (1932).

33. Bradford and Finch, "The Mechanism of Ignition by Electric Discharges," *Chem. Rev.* 21, 221 (1937).

34. Linnet, Raynor, and Frost, "The Mechanism of Spark Ignition," *Trans. Faraday Soc.* 41, 487 (1945).

35. Von Elbe, et al., "Ignition of Gas Mixtures by Electric Sparks," *J. Chem. Phys.* 15, 798 (1947).

36. Kogarko and Zel'dovich, "Detonation of Gaseous Mixtures," *Doklady. Akad. Nauk. S. S. S. R.* *63*, 553 (1948).

37. Voevodskii and Tal'roze, "Ignition of Hydrogen-Oxygen Mixtures. Effect of Water Vapor and Vessel Dimensions," *Zhur. Fiz. Khim.* *22*, 1192 (1948).

38. Dubovitskii, "Conjugated Oxidation in Mixtures of $2CO + O_2 + H_2$ and $2CO + O_2 + PH_3$," *Doklady. Akad. Nauk. S. S. S. R.* *63*, 689 (1948).

39. Frost and Linnet, "The Mechanism of Spark Ignition," *Trans. Faraday Soc.* *44*, 416, 421 (1948).

40. Friedman and Burke, "Ignition of Gas Mixtures by Sparks," *J. Chem. Phys.* *17*, 667 (1949).

41. Norrish, "The Role of Aldehydes in the Oxidation of Hydrocarbons," *Rev. Inst. Franc. Petrole* *4*, 288 (1949).

42. Zel'dovich and Shlyapintokh, "Ignition of Explosive Gaseous Mixtures in Shock Waves," *Doklady. Akad. Nauk. S. S. S. R.* *65*, 871 (1949).

43. Norrish and Harding, "Role of Formaldehyde in the Oxidation of Ethylene," *Nature* *163*, 797 (1949).

44. Herman, Hopfield, and Hornbeck, "Infra-Red Emission Bands from Oxygen in the CO-O_2 Flame," *J. Chem. Phys.* *17*, 220 (1949).

45. Rögener, "Ignition of Hydrocarbon-Air Mixtures by Adiabatic Compression," *Z. Elektrochem.* *53*, 389 (1949).

46. Burgoyne and Thoms, "Effects of Fine Solid Particles on Flame Propagation," *Nature* *163*, 765 (1949).

47. Walsh, "Processes in the Oxidation of Hydrocarbon Fuels," *Trans. Faraday Soc.* *42*, 269 (1946); *43*, 297 (1947).

48. Lewis and Von Elbe, *Combustion, Flames and Explosions in Gases*, Cambridge, 1938.

49. Noyes and Leighton, *The Photochemistry of Gases*, ACS Monograph, Reinhold, New York, 1941.

50. "Symposium on Radiation Chemistry and Photochemistry," *J. Phys. Colloid. Chem.* *52*, 437-611 (1948).

51. Semenov, "The Kinetics of Chain Reactions," *Phys. Rev.* *6*, 347 (1929).

52. Mole, "The Ignition of Explosive Gases," *J. Phys. Soc.* (London) *48*, 857 (1936).

53. Khastgir and Rahman, "Dielectric Constant and Electrical Conductivity of Gases and Vapors Ionized by X-Rays of Ultra-High Radio Frequency," *Phil. Mag.* *29*, 353 (1940).

54. Knaffl, "Application of Laws of Similarity to Streaming of Electricity in Gases Ionized by X-Rays and γ-Rays," *Akad. Wiss Wien. Ber. 143 2a 1-2*, 45-70 (1934).

55. Bak, Zingerman, and Nikolaevskaya, "Effect on the Discharge Gap of Irradiation by Electrons," *Zhur. Tekh. Fiz. 17*, 589 (1947).

56. Willows and Peck, "Action of Radium on the Electric Spark," *Proc. Phys. Soc. 19*, 464 (1905); *Phil. Mag. 9*, 378 (1905); *Sci. Abst.*,1036 (1905).

57. Bert, "Radioactive Substances and Electric Discharge," *N. Cimento 10*, 39 (1905); *Sci. Abst.*,352 (1906).

58. Meyer and Hess, "Attainment of Saturation in Ionization by Alpha-Rays," *Akad. Wiss. Wien. Ber. 120 2a*, 1187 (1911); *Sci. Abst.*, 546 (1912).

59. Barkla and Simons, "Ionization in Gaseous Mixtures by Roentgen Radiation," *Phil. Mag. 23*, 317 (1922); *Sci. Abst.*, 900 (1912).

60. Hammershaimb, "Influence of X Rays on the Disruptive Discharge," *Arch. des. Sciences 5* 292 (1923); *Sci. Abst.*, 281 (1924).

61. Warburg (with Gorton), "Effect of Radiations on the Point Discharge," *Deutsch. Phys. Gesell. Verh. 7, 10*, 217 (1905); *Sci. Abst.*, 1618 (1905).

62. Gorton, "New Photoelectric Experiment," *Deutsch. Phys. Gesell. Verh. 7,2*, 42 (1905); *Sci. Abst.*,607 (1905).

63. Lewis and Kreutz, "Influence of Ionization on the Ignition of Combustible Gases," *J. Chem. Phys. 1*, 89 (1933).

64. Wheeler, Downs, and Walsh,"Knock in Internal Combustion Engines," *Nature 162*, 893 (1948).

65. Herman, Hornbeck, and Laidler, "Kinetic Mechanisms of Combustion and Hydrocarbon Flame Spectra," *Science 112*, 497 (1950).

66. Gaydon and Wolfhard, "Free Radicals in Low Pressure Flames," *Discussions Faraday Soc. 1947* No. 2, 161.

67. Thompson, "Ignition Due to Ion Emission by Platinum," *Phys. Zeitschr. 14*, 11 (1913); *Sci. Abst. 16* No. 631, 207 (1913).

68. Leah, Roundthwaite, and Bradley, "Atomic Oxygen in Carbon Monoxide Explosions," *Phil. Mag. 41*, 468, 478, 1289 (1950).

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 ($3H_2 + N_2$) 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 1.08 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.

Boullé 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.

---

* 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_2, the decomposition of CO and the decomposition of NH_3, 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 Å 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 $Ra(SO_4)$ in platinum needles; for gamma rays plus neutrons, 78 mg $Ra(SO_4)$ 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,α) 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 CH_3^+ and CH_2^+ does not increase with an increase in chain length. The ratios of CH_2^+/CH_3^+ and $C_2H_4^+/C_2H_5^+$ 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 $C^{14}O$ and $C^{14}O_2$. 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 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, A 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 catylyst 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 $(CNO)_x$, 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 $(C_2H_3)_x$ and carbon dioxide, a fact which contradicted the former statements that a $(CHO)_x$ 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_2, with traces of CO_2 and H_2O. The carbon-to-hydrogen ratio of the remaining solid was 11.65 and 12.08. The amount of O_2 which reacted was 5-1/2 times the CO formed. This ratio suggested an oxidation solid of $C_{39}H_{40}O_{10}$, or an original polymer of $(C_2H_2)_{20}$. The heat of polymerization was calculated as 47 kcal per gram-mole of C_2H_2 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 evolvement of gaseous hydrogen were observed. CO_2 was produced from certain acids, especially from those having an oxygen-containing group in the alpha position. No liberation of CO, hydrocarbons, or O_2 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 hydorcarbons 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 radiations, 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 Weiss (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 3.5×10^4 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-β-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 3α:12α-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 salicyic acid (59). Up to a dose of 5×10^4 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 5×10^4 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. <u>Literature Review - Theoretical</u>: 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)):

1. Ionization $A \genfrac{}{}{0pt}{}{\rightsquigarrow A^+ + e}{\rightsquigarrow B^+ + C + e}$

2. Discharge $A^+ + e \rightarrow A^*$ (excited)

3. Decomposition $A^* \genfrac{}{}{0pt}{}{\nearrow \text{stable molecules}}{\searrow \text{free radicals}}$

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,

$$AB^+ + e \rightarrow A + B, \text{ or,}$$

$$AB^+ + M^- \rightarrow A + B + M.$$

(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^2 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_2, O_2, and H_2O_2 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_2O 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 Americal 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 HNO_3 from H_2, N_2, and 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. <u>Proposed Research — Organic Reactions:</u> 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.

Bibliography for Project M943C

1. Allen, A. O., *Chemical Effects of Ionizing Radiation on Simple Inorganic Compounds and Aqueous Solutions.* U. S. Atomic Energy Commission, MDDC-363, 1946.

2. Allen, A. O., *Effects of Radiation on Materials.* U. S. Atomic Energy Commission, MDDC-962, 1947.

3. Allen, A. O., "Radiation Chemistry of Aqueous Solutions," *J. Phys. and Colloid. Chem. 52,* 479-90 (1948).

4. Alyea, Hubert N., "Chain Reactions Produced by Light and by Alpha Radiation," *J. Am. Chem. Soc. 52,* 2743 (1930).

5. Boullé, André, "Catalysis by Cathodic Projection," *Bull. Soc. chim. 10,* 361-71 (1943).

6. Breger, Irving A., and Burton, Virginia L., "The Effects of Radioactivity on a Naphthenic Acid," *J. Am. Chem. Soc. 68,* 1639-42 (1946).

7. Broda, E., "Mode of Chemical Action of X-rays on a Non-aqueous Solution," *Nature 151;* 448 (1943).

8. Burr, J. G., and Garrison, W. M., *The Effect of Radiation on the Physical Properties of Plastics.* U. S. Atomic Energy Commission, AECD-2078, 1948.

9. Burton, Milton, "Radiation Chemistry," *J. Phys. and Colloid. Chem. 51,* 611-625 (1947).

10. Burton, Milton, "Radiation Chemistry IV. An Interpretation of the Effect of State on the Behavior of Some Organic Compounds and Solutions," *J. Phys. and Colloid. Chem. 52,* 564-577 (1948).

11. Burton, Milton, "Effects of High-Energy Radiation on Organic Compounds," *J. Phys. and Colloid. Chem. 51,* 786-797 (1947).

12. Burton, Virginia L., "The Effects of Radioactivity on Oleic Acid," *J. Am. Chem. Soc. 71,* 4117 (1949).

13. Chapiro, Adolphe, "Polymerization by Gamma Rays," *Compt. rend. 228,* 1490-2 (1949).

14. Coolidge, W. O., "High Voltage Cathode Rays Outside the Generating Tube," *Science 62,* 441-2 (1925).

15. Dainton, F. S., "On the Existence of Free Atoms and Radicals in Water and Aqueous Solutions Subjected to Ionizing Radiation," *J. Phys. and Colloid. Chem. 52,* 490-517 (1948).

16. Dainton, F. S., "Effect of Gamma and X-rays on Dilute Aqueous Solutions of Acrylonitrile," *Nature 160,* 268 (1947).

Bibliography (cont'd)

17. Dainton, F. S., "Chemical Reactions Induced by Ionising Radiations," Annual Reports on the Progress of Chemistry, vol. 45, 1948. London, Chemical Society, Richard Clay and Co. Ltd., 1949 (149 references).

18. Dale, W. M., and Davies, J. V., "Deamination of Aqueous Solutions of L-Serine by X-Radiation," Nature 166, 1121 (1950).

19. Dale, W. M., Davies, J. V., and Gilbert, C. W., "The Deamination of Glycine by Alpha-Radiation from the Disintegration of Boron in a Nuclear Reactor," Biochemical J. 45, 543-6 (1949).

20. Dale, W. M., Davies, J. V., and Gilbert, C. W., "The Kinetics and Specificities of Deamination of Nitrogenous Compounds by X-Radiation," Biochemical J. 45, 93-99 (1949).

21. D'Alieslager and Jungers, Bull. Soc. chim. Belg. 40, 75 (1931).

22. Davidson, W. L., and Geib, G., "The Effects of Pile Bombardment on Uncured Elastomers," U. S. Atomic Energy Commission, MDDC-1449 (1947).

23. Eyring, H., Hirschfelder, J. O., and Taylor, H. S., "The Radiochemical Synthesis and Decomposition of Hydrogen Bromide," J. Chem. Phys. 4, 570-5 (1936).

24. Farmer, F. T., Stein, G., and Weiss, J., "Chemical Actions of Ionising Radiations on Aqueous Solutions. Part I. Introductory Remarks and Description of Irradiation Arrangements," J. Chem. Soc. 3241-5 (1949).

25. Fricke, Hugo, Hart, Edwin J., and Smith, Homer P., "Chemical Reactions of Organic Compounds with X-ray Activated Water," J. Chem. Phys. 6, 229-40 (1938).

26. Garrison, Warren M., "On the Polymerization of Unsaturated Hydrocarbons by Ionizing Radiations," J. Chem. Phys. 15, 78-9 (1947).

27. Gibbs, Thomas E., and Lockenvitz, Arthur E., "A Comparison of the Relative Molecular Stopping Power of Some Hydrocarbon Isomers for Alpha-Particles from Polonium," Phys. Rev. 73, 652 (1948).

28. Gmelins Handbuch der anorganischen Chemie, 8. Aufl. Syst. Nr. 4, Lief. 2, Berlin, 1936. Deut. Chem. Ges. (131 references on ammonia formation and decomposition by means of alpha rays, canal rays, cathode rays and ultraviolet light).

29. Goldstein, Richard Frank, The Petroleum Chemicals Industry, New York, Wiley, 1950.

30. Harker, George, "Influence of Sensitisers on Chemical Reactions Produced by Gamma Radiation," Nature 133, 378 (1934).

Bibliography (Cont'd)

31. Hart, E. J., "Mechanism of the Gamma-ray Induced Oxidation of Formic Acid in Aqueous Solution," J. Am. Chem. Soc. 73, 68-73.

32. Heisig, G. B., "The Action of Radon on Some Unsaturated Hydrocarbons," J. Am. Chem. Soc. 53, 3245 (1931).

33. Heisig, G. B., "Action of Radon on Some Unsaturated Hydrocarbons, II. Propylene and Cyclopropane," J. Am. Chem. Soc. 54, 2328-32 (1932).

34. Heisig, G. B., "Heats of Formation and -M/N ratios," J. Phys. Chem. 36, 1000-5 (1932).

35. Hirschfelder, J. O., "Chemical Reactions Produced by Ionizing Processes," J. Phys. and Colloid. Chem. 52, 447-50 (1948).

36. Honig, R. E., and Sheppard, C. W., "An Experimental Comparison of the Chemical Effects of Deuterons and of Alpha Particles on Methane and n-Butane," J. Phys. Chem. 50, 119-143 (1946).

37. Hopwood, F. L., and Phillips, J. T., "Polymerization of Liquids by Irradiation with Neutrons and Other Rays," Nature 143, 640 (1939).

38. Keller, M., and Weiss, J., "Chemical Actions of Ionising Radiations in Solution. Part VI. Radiation Chemistry of Sterols. The Action of X-rays on Cholesterol and 3-β-Hydroxypregn-5-en-20-one," J. Chem. Soc. 1950, 2709.

39. Keller, M., and Weiss, J., "Chemical Actions of Ionising Radiations in Solution. Part VII. Radiation Chemistry of Sterols. The Action of X-rays on Cholic Acid in Aqueous Solution," J. Chem. Soc. 1951, 25-6.

40. Keller, M., and Weiss, J., "Chemical Actions of Ionising Radiations in Solution. Part IX. Radiation Chemistry of Sterols. The Action of X-rays on (+) Œstrone-b in Aqueous Solution," J. Chem. Soc. 1951, 1247-9.

41. Lind, S. C., The Chemical Effects of Alpha Particles and Electrons, 2nd ed., ACS Monograph Series No. 2, New York, The Chemical Catalogue Company, 1928 (508 references).

42. Lind, S. C., "Chemical Action Produced by Radium Emanation, I. The Combination of Hydrogen and Oxygen," J. Am. Chem. Soc. 41, 531-51 (1919).

43. Lind, S. C., "Chemical Action Produced by Radium Emanation, II. The Chemical Effect of Recoil Atoms," J. Am. Chem. Soc. 41, 551-59 (1919).

44. Lind, S. C., "Radiochemical Equilibrium in Ammonia Synthesis," J. Am. Chem. Soc. 53, 2423-4 (1931).

45. Lind, S. C., and Bardwell, D. C., "The Chemical Effects in Ionized Organic Gases," Science 62, 422-24 (1925).

46. Lind, S. C., and Bardwell, D. C., "Chemical Action of Gaseous Ions Produced by Alpha Particles, VI. Reactions of the Oxides of Carbon," J. Am. Chem. Soc. 47, 2675 (1925).

47. Lind, S. C., and Bardwell, D. C., "The Chemical Action of Gaseous Ions Produced by Alpha Particles, VIII. The Catalytic Influence of Ions of Inert Gases," J. Am. Chem. Soc. 48, 1575-84 (1926).

48. Lind, S. C., and Bardwell, D. C., "Chemical Action of Gaseous Ions Produced by Alpha Particles, IX. Saturated Hydrocarbons," J. Am. Chem. Soc. 48, 2335 (1926).

49. Lind, S. C., and Bardwell, D. C., "The Synthesis of Ammonia by Alpha Rays," J. Am. Chem. Soc. 50, 745-8 (1928).

50. Lind, S. C., Bardwell, D. C., and Perry, J. H., "The Chemical Action of Gaseous Ions Produced by Alpha Particles, VII. Unsaturated Carbon Compounds," J. Am. Chem. Soc. 48, 1556-75 (1926).

51. Lind, S. C., and Glockler, George, "The Chemical Effect of Electrical Discharge in Ethane," Trans. Am. Elect. Soc. 52, 37 (1927).

52. Lind, S. C., and Glockler, George, "Control of the Molecular Weight of Liquid Hydrocarbons Produced by Electrical Discharge in Ethane," J. Am. Chem. Soc. 50, 1767-72 (1928).

53. Lind, S. C., and Glockler, George, "III. The Chemical Effects of Semi-Corona Discharge in Gaseous Hydrocarbons," J. Am. Chem. Soc. 51, 2811-21 (1929).

54. Lind, S. C., and Glockler, George, "IV. The Chemical Effects of Electrical Discharge in Butane. Fractionation of the Liquid Product," J. Am. Chem. Soc. 51, 3655-60 (1929).

55. Lind, S. C., and Glockler, George, "V. The Condensation of Hydrocarbons by Electrical Discharge. Comparison with Condensation by Alpha Rays," J. Am. Chem. Soc. 52, 4450-61 (1930).

56. Lind, S. C., and Schiflett, C. H., "Studies of the Oxidation of Alpha Ray Cuprene," J. Am. Chem. Soc. 59, 411-13 (1937).

57. Lind, S. C., and Vanpee, M., "The Effect of Xenon Ions in Chemical Action by Alpha Particles," J. Phys. and Colloid. Chem. 53, 898 (1949).

58. Laebl, H., Stein, G., and Weiss, J., "Chemical Actions of Ionising Radiations on Aqueous Solutions. Part V. Hydroxylation of Nitrobenzene by Free Radicals Produced by X-rays," J. Chem. Soc. 1950, 2704.

Bibliography (cont'd)

59. Laebl, H., Stein, G., and Weiss, J., "Chemical Actions of Ionising Radiation on Aqueous Solutions. Part VIII. Hydroxylation of Benzoic Acid by Free Radicals Produced by X-rays," J. Chem. Soc. 1951, 405-7.

60. Loiseleur, J., Latarjet, R., and Crovisier, C., "Formation of Peroxides in Aqueous Solutions of Organic Compounds Irradiated With X-rays," Compt. Rend. Soc. Biol. 136, 57-60 (1942).

61. Magee, J. L., "Theory of Radiation Chemistry. I. Some Effects of Variation in Ionization Density," J. Am. Chem. Soc. 73, 3270-5 (1951).

62. Magee, J. L., and Burton, M., "Elementary Processes in Radiation Chemistry I. Some Considerations of Mechanism of Electron Capture," J. Am. Chem. Soc. 72, 1965-74 (1950).

63. Magee, J. L., and Burton, M., "Elementary Processes in Radiation Chemistry II. Negative Ion Formation by Electron Capture in Neutral Molecules," J. Am. Chem. Soc. 73, 523-32 (1951).

64. Manion, J. P., and Burton, M., "Radiolysis of Hydrocarbon Mixtures," Abstracts of Papers, 119th Meeting Am. Chem. Soc. 41p, 1951.

65. Mund, W., "Ionization by Radon in Spherical Vessels," J. Phys. Chem. 30, 890-894 (1926).

66. Mund, W., and Koch, W., "The Chemical Action of Alpha-Particles on Acetylene," J. Phys. Chem. 30, 289-93 (1926).

67. Newton, A., "Radiation Chemistry of Alcohols," from Wakerling, R. K., Summary of the Research Progress Meeting, Dec. 21, 1950, University of California, Radiation Laboratory, UCRL-1175.

68. Otvos, John W., "Ionization by C^{14} Radiation in the Ionization Chamber," Phys. Rev. 73, 537 (1948).

69. Penneman, R. A., Effects of Radiation on Aqueous Solutions of Carboxylic Acids. U. S. Atomic Energy Commission, AECD-2136, 1948.

70. Ponsaert, Bull. Soc. Chim. Belg. 38, 110 (1929).

71. Rexer, Ernst, "Accelerated Polymerization by Radiation with Gamma and Röntgen Quanta," Reichsber. Physik (Beihefte, Physik. Z.) 1, 111-19 (1944).

72. Rosenblum, Charles, "Benzene Formation in the Radiochemical Polymerization of Acetylene," J. Phys. and Colloid. Chem. 52, 474-8 (1948).

73. Schoepfle, C. S., and Fellows, C. H., "Gaseous Products from Action of Cathode Rays on Hydrocarbons," Ind. Eng. Chem. 23, 1396 (1931).

Bibliography (cont'd)

74. Stein, Gabriel, and Weiss, J., "Chemical Effects of Ionizing Radiations," *Nature 161,* 650 (1948).

75. Sheppard, Charles W., and Burton, Virginia L., "The Effects of Radioactivity on Fatty Acids," *J. Am. Chem. Soc. 68,* 1636-39 (1946).

76. Sheppard, C. W., and Honig, R. E., "A Theoretical Analysis of the Relative Chemical Effects of Alpha Particles and Deuterons," *J. Phys. Chem. 50,* 144-51 (1946).

77. Snyder, W. S., and Powell, J. L., *Absorption of Gamma Rays,* U. S. Atomic Energy Commission, AECD-2739, 1949.

78. Steacie, E. W. R., "The Relation of Radiation Chemistry to Photochemistry," *J. Phys. and Colloid. Chem. 52,* 441-6 (1948).

79. Stein, G., and Weiss, J., "Chemical Actions of Ionising Radiations on Aqueous Solutions. Part II. The Formation of Free Radicals. The Action of X-rays on Benzene and Benzoic Acid," *J. Chem. Soc. 1949,* 3245-54.

80. Stein, G., and Weiss, J., "Chemical Actions of Ionising Radiations on Aqueous Solutions. Part III. The Actions of Neutrons and of Alpha Particles on Benzene, *J. Chem. Soc. 1949,* 3254-6.

81. Stein, G., and Weiss, J., "Chemical Actions of Ionising Radiations on Aqueous Solutions. Part IV. The Action of X-rays on Some Amino-acids," *J. Chem. Soc. 1949,* 3256-63.

82. "Symposium on Radiation Chemistry and Photochemistry." *J. Phys. and Colloid. Chem. 52,* 437-611 (1948) (339 references).

83. Toulis, William J., "The Decomposition of Water by Radiation," U.S. Atomic Energy Commission, UCRL-583 (1950).

84. Treiman, L. H., "Effect of Electron Beams on Aqueous Dichromate Solutions," U. S. Atomic Energy Commission, MDDC-1732, 1948.

85. Viallard, R., and Maget, M., "The Fragmentation of Linear C Chains by Electron Impact," *Compt. rend. 228,* 1118-20 (1949).

86. Watson, John H. L., Vanpee, Marcel, Lind, S. C., "The Solids Condensed from Carbon Monoxide by Alpha Particles," *J. Phys. and Colloid. Chem. 54,* 391-400 (1950).

87. Weiss, J., "Radiochemistry of Aqueous Solutions," *Nature 153,* 748-50 (1944).

88. Weiss, J., "Some Aspects of the Chemical and Biological Action of Radiations," *Trans. Faraday Soc. 43,* 314-24 (1947).

Bibliography (cont'd)

89. Wildschut, A. J., "Stralingschemie en Polymerisatie," Chemisch Weekblad 45, 2-8 (1949).

90. Williams, Nelson T., and Essex, Harry, "Effect of Electric Fields on the Decomposition of Nitrous Oxide by Alpha-rays," J. Chem. Phys. 16, 12, 1153 (1948).

91. Zimmer, K. G., Naturwissenchaften 32, 375-6 (1944).

C. PROJECT M943D — THE EFFECT OF RADIATION ON FOOD

1. Introduction

Food spoilage is a complex phenomenon. The most obvious form of spoiling is caused by the action of microorganisms, such as the souring of milk by lactic acid bacilli, fermentation of fruit juices by yeast, putrefaction of meat by a variety of bacteria, molding of bread, etc. Such spoilage is generally characterized by changes in odor, flavor, texture, and appearance.

Fresh fruits and vegetables may spoil as a result of microorganisms, but more often they become overripe as a result of enzyme action. The process of growth and ripening is controlled by enzymes present in all cells produced in the life process. Enzymatic degradation is part of the natural life cycle of all living organisms. The overripening of melons, bananas, and other fruits, and the loss in flavor in fresh vegetables after picking are examples of spoilage from enzyme action.

Food also spoils as a result of oxidation and dehydration. The rancidity of old butter and vegetable oils is a typical example of spoilage by oxidation. The shrivelling of fresh fruit prior to spoilage from enzymes or bacteria is spoilage by dehydration.

Numerous methods have been devised to prevent or delay food spoilage. These include canning, freezing and refrigeration, drying and dehydration, smoking, salting, and the use of chemical preservatives. In general, these methods involve a form of sterilization and enzyme inactivation. Sterilization kills the microorganisms present in or on the food as received but does not necessarily prevent recontamination later. Enzymes are inactivated by heat or some other means. Freezing and refrigeration, for example, limit the rate at which enzymatic degradation proceeds. Salting, smoking, and preservation in the form of jams, etc., present conditions that prevent the growth or entry of bacteria in or on the food material and diminish enzyme activity. All these food preservation processes tend to modify in one manner or another the flavor, appearance, texture, or food value of the food treated. In some cases the natural vitamin content of the foods is seriously decreased.

There is considerable evidence that ionizing radiations can be used for sterilization and enzyme inactivation. Since the nature of food decay is closely related to the action of bacteria, molds and enzymes, there is reason to believe that foods may be preserved for long periods of time through exposure to ionizing radiation.

2. Literature Review

a. Effect of Radiation on Microorganisms

Microorganisms can be readily destroyed by various types of ionizing radiation, with the vegetative bacteria being the most sensitive to radiation and the smaller viruses being the most resistant.

1. Bacteria

Table I, from the data of Brasch, Huber, Friedemann, and Traub (5), lists 100 per cent sterilization doses for many bacteria irradiated with high-intensity electron bursts from a Capacitron. Table II lists some data of Dunn, Campbell, Fram, and Hutchins (12). These data were obtained by irradiating bacteria with x-rays and include results on sporeforming and nonsporeforming bacteria. These tables show that the nonsporeformers, the vegetative bacteria, are the more sensitive to these radiations. None of the nonspore samples which were bombarded by electrons required dosages larger than 200,000 rep (roentgen-equivalent-physical) for 100 per cent sterilization. The bacteria which form an inactive, resistant spore, the "sporeformers", however, required doses up to 550,000 rep from the Capacitron to achieve 100 per cent sterilization. The same relative resistance is illustrated by the bacteria which were irradiated with x-rays.

Although these data were obtained with x-ray and electron radiation, similar results are obtained with the other forms of radiation. The lethal dosage is defined by Lea (27) as the dosage required to kill 63 per cent of the original bacteria. Lea found that for the vegetative bacteria the dosages required increased in the following order: beta rays, gamma rays, hard x-rays, soft x-rays, neutrons, and alpha rays. His results for the vegetative bacteria, B. coli, and the spore B. mensenterious are shown in Table III. It is noted that with the spore the alpha rays are the most effective. Lea explains that for spores the effectiveness of the radiation increases when the specific ionization is increased, that is, when the ion pairs produced per centimeter path of the rays are increased. This means that in the radiation of spores, the lethal action either requires more than one ionization or at least is more effective if there are several ion clusters. Alpha rays produce high specific ionization. It has been

TABLE I

100 PER CENT STERILIZATION DOSES FOR NONSPOREFORMERS AND SPORES WITH HIGH-INTENSITY ELECTRON BURSTS FROM THE CAPACITRON

(After Brasch, Huber, Friedemann, and Traub (5))

Species	100 Per Cent Sterilization Dose "rep"
A. Nonsporeformers:*	
Strep. hemolyticus	200,000
Brucella abortus	200,000
B. tularense	150,000
B. prodigiosus	100,000
B. coli	100,000
Pneumococcus	200,000
Staph. aureus	200,000
B. Pyocyaneus	100,000
B. Dysenteriae	200,000
Salmonella Newport	200,000
B. Friedlander.	100,000
Pasteurella avacida	100,000
B. Proteus	200,000
Aerobacter Aerogens	150,000
L. casei	150,000
H. pertussis	100,000

* Bacteria: 24-hour cultures at 37.5°C in brain-heart broth of bacto-agar. 10^5-10^{10} organisms per ml.

B. Spores:*	
Aspergillus clavatus	550,000
B. subtilis	250,000
Cl. Tetani	400,000
Cl. Sporogenes	400,000
B. anthracis	500,000
Cl. Botulinus	400,000
Cl. Welchii	250,000
Cl. Novyi	350,000
Airborne	200,000

* Spores: 8-day cultures at room temperature in Savita or Thioglycolate broth. After harvest 30 minutes heating to 80°. 10^4-10^9 organisms per ml.

TABLE II

DATA ON LETHAL EFFECTS OF X-RAYS ON SELECTED BACTERIA
(After Dunn, Campbell, Fram, and Hutchins (12))

Organism	Morphology	Gram Reaction	No. of Organisms per ml. x 10^{-6}	No. of Roentgens Necessary for Destruction x 10^{-6}	Special Comments
Nonsporeformers					
Aerobacter aerobenes	rods	neg.	238	less than 0.25 more than 0.10	
Escherichia coli	rods	neg.	700	less than 0.15 more than 0.09	Of sanitary significance
Pseudomonas fluorescens	rods	neg.	760	less than 0.14 more than 0.14	Produces fluorescence
Serratia marcescens	rods	neg.	380	less than 0.50 more than 0.25	Produces red pigment
Sarcina flava	cocci	pos.	2.4	less than 0.35 more than 0.14	Produces yellow pigment
Staphylococcus aureus	cocci	pos.	1000	less than 0.25 more than 0.10	Produces orange pigment
Spores					
Bacillus mesentericus	rods	pos.	6.2	less than 1.5 more than 1.0	Strain especially resistant to heat
Bacillus sterothermophilus	rods	neg.	75	less than 1.5 more than 1.0	
Bacillus subtilis	rods	pos.	4.8	less than 1.0	
Bacillus thermoacidurans	rods	pos.	240	less than 1.0 more than 0.5	Produces flat-sour spoilage of tomato juice
Canco No. 6B	rods	pos.	420	less than 1.0	Causes spoilage of canned foods
Flat sour (No. 1518)	rods	pos.	1.1	less than 1.0 more than 0.5	Causes flat-sour spoilage
Spore former from catgut suture	rods	pos.	13	less than 2.0 more than 1.5	Resistant organism

TABLE III

LETHAL DOSAGE FOR B. COLI AND SPORES OF B. MENSENTERICUS
(After Lea (26,28))

Type of Radiation	B. coli Dosages in Roentgens	Spores of B. Mensentericus Dosages in Roentgens
beta rays	$4x10^3$	$1.1x10^5$
gamma rays	$5.2x10^3$	$1.3x10^5$
hard x-rays	$6.0x10^3$	
soft x-rays		
1.5Å	$6.5x10^3$	$1.3x10^5$
4.1Å		$1.1x10^5$
8.3Å	$7.5x10^3$	$1.5x10^5$
neutrons	$7.1x10^3$	
alpha rays	$24x10^3$	$0.26x10^5$

suggested that spores are a dual complement of genes, both of which must be inactivated in order to inhibit multiplication (26). This perhaps explains why 100 per cent sterilization of spores takes about twice the dose required for 100 per cent sterilization of vegetative cells.

Many investigators have confirmed the fact that for any one radiation the dose required to kill a microorganism is independent of the time or continuity of the radiation. This phenomenon helps to substantiate the target or direct-hit theory. This theory proposes that although many ionizing particles pass through the bacterium before it is killed, its death, when it does occur, is caused by one of these particles alone. This fatal particle happens to pass through a specially sensitive region or target in the organism (27). Such one-shot killing would be independent of the time during which the shots were made. Further, if the effect were the cumulative effect of many ionizations, one could expect some recovery to be exhibited by the bacterium in time, necessitating higher dosages for the lower intensities: this is contrary to experimental observations.

This target theory is further supported by experimental observations of the exponential characteristic of the survival curve for microorganisms exposed to radiation. Many observers have noted that the percentage of the microorganisms killed by any dose is independent of the initial concentration of organisms. If the chance of being hit in the target were 1 in 1000 for a given dose then 1/1000 of the total bacteria exposed would be destroyed by that dose independently of the number of bacteria exposed.

2. Molds and Yeasts

Dunn, Campbell, Fram, and Hutchins report some results obtained in irradiating mold growths with high-voltage x-rays (12). (Although the term "mold" has no exact definition, it is generally taken to include all of the woolly, cobweb-like, or powdery growths which develop on food, etc.) One hundred per cent of the Aspergillus niger molds were killed by a dosage of 250,000 to 500,000 roentgens, while a dosage of only 50,000 roentgens destroyed 99 per cent of the molds. However, when they irradiated a species of the genus Mucor, using essentially the same procedure, a dose of 1,000,000 roentgens killed all the molds while a dose of 500,000 destroyed 99 per cent of them. Thus the species of Mucor was considerably more resistant to the x-rays. Although only these limited data are available, it is indicated that considerable variation in sensitivity to radiation can be expected among the different mold species.

Yeasts examined by Dunn, Campbell, Fram, and Hutchins (12) appeared to be only slightly more resistant to x-radiation than the nonsporeforming bacteria. A summary of the data on yeasts radiated with x-rays is given in Table IV.

3. Viruses and Bacteriophages

Many diseases are carried by foods contaminated with viruses; therefore, the sensitivity of viruses to radiation is important. Table V shows some of the results of Brasch, Huber, Friedemann, and Traub (5) for the 100 per cent sterilization of a few viruses and bacteriophages which were exposed to high-intensity electron bursts from a capacitron. The dosages required to kill viruses are noted to be higher than those required to destroy bacteria. This could be explained by the target theory because the viruses are of much smaller size. The influence of size is seen in Table V, for example, Murine Encephalomyelitis, which has a diameter of 8 to 12 millimicrons, required 1,700,000 rep for 100 per cent sterilization, while vaccinia, which has a diameter of 250 millimicrons, required but 600,000 rep for 100 per cent sterilization.

The bacteriophages, which are parasites of bacteria, resemble the viruses in their resistance and several of the other properties, although they are different in their action. These phages, although about the same size as the viruses, require slightly lower dosages for sterilization. The phages investigated by Brasch, Huber, Friedemann, and Traub (5) required doses of 600,000 and 650,000 rep for 100 per cent sterilization.

TABLE IV

DATA CONCERNING THE LETHAL EFFECTS OF X-RAYS ON YEASTS

(After Dunn, Campbell, Fram, and Hutchins (12))

Designation of Yeast	Number of Roentgens Required for Destruction	
	Less than	More than
Saccharomyces cerevisiae strain 1	500,000	250,000
S. Cerevisiae (strain 2)	500,000	250,000
S. cerevisiae (strain 3)	500,000	250,000
S. cerevisiae (strain 4)	500,000	250,000
S. cerevisiae (strain 5)	1,000,000	500,000
S. cerevisiae (strain 4) (dry state)	1,500,000	1,000,000
Torulopsis pulcherrima	500,000	250,000
Torulopsis rosea	1,000,000	500,000

TABLE V

100 PER CENT STERILIZATION DOSES FOR VIRUSES AND BACTERIOPHAGES WITH HIGH-INTENSITY ELECTRON BURSTS FROM A CAPACITRON

(After Brasch, Huber, Friedemann, and Traub (5))

Strain	Diameter mμ	100 Per Cent Sterilization Dose
A. Viruses		
Murine Encephalomyelitis SK strain	8 - 12	1,700,000
Poliomyelitis		
a. Aycock		1,550,000
b. Lansing	15	1,600,000
Equine Encephalitis western, eastern	35	1,300,000
Fowl Plague, Newcastle	75	1,000,000
Mumps		800,000
Influenza		
Human	100	800,000
Swine		800,000
Rabies	125	850,000
Vaccinia	250	600,000
B. Phages		
Coli Templeton		650,000
Flexner I, type V		650,000
Staph. V.	50	600,000

b. Effect of Radiation on Enzymes

Since enzymes are responsible in part for the spoilage and degradation of foods, a review of the literature pertaining to the effect of various radiations on these enzymes is in order.

Considerable work has been done by Huber and coworkers (4,22,23) on the inactivation of bacteria and enzymes by high-energy bursts of electrons. While this type of radiation is not identical with that emanating from fission products, both are ionizing radiation. Huber's results may therefore give some information as to what might be expected with other types of ionizing radiation.

Some of the results of Huber's work on enzymes is shown on Table VI. His work was carried out on the powder form of the enzyme in order to eliminate the effect of activated solvent molecules. The radiation sensitivity was found to vary a good deal with the individual enzyme, hydrolyses being more sensitive than oxidases or proteolytic enzymes. Hyaluronidase was found to be 13 per cent inactivated with a dose of 500,000 rep. This was the only enzyme found to be significantly inactivated with dosages which are necessary for 100 per cent sterilization of bacteria. Apparently biological units which are capable of reproduction are particularly sensitive to radiation. Huber (22) reports full activity of oxidases and proteolytic enzymes in foods that were fully sterilized by radiation. However, these foods remained in their natural state and showed no noticeable change in taste, odor or appearance after long periods of storage. From this observation it appears that, while the enzymes show a positive test for activity, they do not perform their usual role in promoting food spoilage in the irradiated samples. Huber offers two possible explanations for this unexpected effect: (1) inactivation may have occurred at a point of the enzymatic chain which is not reflected in the testing technique, and (2) the extent as well as the speed of enzymatic breakdown of the food without the assistance of microorganisms has been considerably overestimated. The first explanation is dismissed somewhat by Huber on the basis of the variety of tests used to determine enzyme activity.

Dale (10,6) gives evidence of decreasing the activity of some enzymes by x-rays. His dosages were low, being of the order of tens of thousands of roentgens. Some enzymes (carboxopepidases) were found to resist inactivation in the presence of their substrates (materials whose reactions the enzymes catalyze). He also reports a significant protective effect attributed to the presence of carbohydrates and fats (8). Dale also shows that dilute solutions of enzymes are more easily inactivated than concentrated solutions. This author proposes various theories to explain these effects (7,9).

TABLE VI

EFFECT OF HIGH-INTENSITY ELECTRON BURSTS ON ENZYMES
(After Huber (23))

Irradiation Temperature 18°C

Compound	Dose(rep)	Medium	Activity		Less %
			Control	Irradiated	
Amylase	$1x10^6$	Comm. Clarase Comp.	100%	94.5	5.5
Diastase	$3x10^6$	Malt Powder	183°L	149°L	18.5
Diastase	$6x10^6$	Malt Powder	183°L	126°L	31.0
Hyaluronidase	$C.5x10^6$	Powder	.250 TRU/mg	.219 TRU/mg	13.4
Hyaluronidase	$4x10^6$	Powder	.250 TRU/mg	.061 TRU/mg	75.8
Lipase	$1.5x10^6$	Flour	100%	86%	14.0
Urease	$2x10^6$	Soy Flour	25.4 cc N/10 HCl	23.0 cc N/10 HCl	9.4
Cytochrome oxidase	$1x10^6$	Ground Meat	Hydroquinone Q_{C_2}: .20	Hydroquinone Q_{O_2}: .30	
Papain	$3x10^6$	Ground Meat	96.5%	96.2%	
Trypsin	$3x10^6$	Ground Meat	No Loss in Tryptic and		
Pepsin	$3x10^6$	Ground Meat	Peptic Activity		

Forssberg (13,14,15) gives information on the inactivation of catalase by x-rays and the effects of environmental conditions upon this process. This enzyme catalyzes the decomposition of peroxides yielding atomic oxygen. His results on the dilution effect and substrate protection are in accord with that of Dale. Environmental conditions are to be regarded as a critical factor in enzyme inactivation, slight changes reportedly yielding dosage differences for equivalent inactivation of as much as 1000 per cent. Several mathematical expressions of inactivation as a function of dosage and dilution are presented (13).

Tytell and Kersten (37) investigated the effect of x-ray wave length, initial enzyme activity, and radiation temperature on enzyme inactivation. Long-wave x-rays were reported to give better results. Higher absorbtion of x-rays was found at low temperatures (6-8°C). The authors found that the per cent of inactivation was a function of the initial enzyme activity and that the higher the initial activity the higher the per cent of inactivation. Radiation was by means of a copper target, gas-filled tube operating at a maximum of 10 ma at 80 kvp. No dosage data are given. Purified enzyme preparations were used in these studies. Kempton and Maxwell report the range of inactivation of enzymes to be between zero and room temperature. They utilized 30,000-45,000 r of x-radiation at temperatures between 66-186°F (25).

In general, the investigators concerned with the effect of radiation on enzymes agree that inactivation is an exponential function of dosage (6-10,38,33,14). Forssberg, however, although he corroborates this expression for "high" concentrations of enzymes, offers a linear relationship for "low" concentrations (22). However, Forssberg fails to offer a clear definition of high and low concentrations of enzymes.

Pollard (33) has reported the inactivation of dry enzymes by deuteron bombardment. Pepsin, trypsin, and chymogen were employed. An exponential relationship for survival is given with dosages reported in terms of deuterons per square cm. Penicillin was little affected by the radiation.

The mechanism of enzyme inactivation in aqueous media is generally thought to be that of the formation of activated water molecules with subsequent reaction with the enzyme. This infers that the enzyme is inactivated by a secondary effect of the radiation (38,36,12,13). An extensive review of the radiochemistry of aqueous solutions is given by Weiss (38). Zimmer (39) disagrees with the activated-water hypothesis and believes that the direct-hit theory applies to inactivation.

The phenomenon of protection, i.e., the greatly increased dosage required to inactivate an enzyme in the presence of its substrate, can be explained. Dale, explains this action in terms of activated complex formation by using a treatment of enzyme kinetics given by Haldane (19), Szent-Gyorgyi (35), and others (18,29). The enzyme and its substrate form a complex which decomposes to form the products and at the same time liberates the enzyme. An intermediate activated complex is formed. This mechanism is exactly analagous to the Eyring theory as applied to other catalytic processes (21). Thus, if E represents the enzyme, S the substrate, the reaction may be represented as

$$E + S \overset{(1)}{\rightleftharpoons} ES \overset{(2)}{\rightleftharpoons} ES^* \overset{(3)}{\rightleftharpoons} E + \text{Products},$$

where the asterisk indicates the activated complex. Therefore, during the irradiation, the only enzyme available for inactivation is the unreacted enzyme.

Barron (3), working with the sulphydryl enzymes, states that the enzyme itself is not destroyed by irradiation but that the active groups in the same enzyme molecule are modified. He gives as examples the oxidation of the OH and SH groups. Barron, James (24), and others (Dale and Hevesy)(20, 5-10) suggest that some of the changes that accompany the irradiation of enzymes may be caused by changes in the colloidal properties of these compounds. In "solution", most enzymes are dispersed colloidally (29).

c. The Preservation of Foods by Radiation

The literature relating to the effect of radiation on the preservation of food from enzymes and microorganisms is limited. Nilova and coworkers (31) irradiated barley seed with x-rays and ultraviolet rays and produced a diminished catalase activity and some changes in the amylase. The peroxidases were not affected. A diminished rate of malting was also reported. Other investigators (32) irradiated butter and reported improved storage properties after irradiation and storage under atomspheres of carbon dioxide or nitrogen.

Huber (22) utilized electron bursts of approximately 1 microsecond duration and 3,000,000 volts to irradiate various foods and biological materials. The results of his numerous tests are shown in Tables VII-IX. Their results indicate that materials may be sterilized with dosages up to 1,000,000 rep without impairing enzyme activity. A more extensive treatment of sterilization is discussed later in this report. The same author reports that the off flavor and color developed in some of their electronically irradiated foods may be caused by the formation of oxides of nitrogen (4).

Nickerson, Goldblith, and Proctor, (30) treated mackerel tissue with 3,000,000-volt cathode rays. Their experiments show that sterilization may be attained but that protolysis, the enzymatic protein degradation, was not affected.

Studies on the effect of irradiation of vitamins and drugs have been carried out by a number of investigators (2,11,16,17). Proctor and O'Meara (34) treated ascorbic acid (vitamin C) with 3,000,000-volt cathode rays. The results show that the more concentrated solutions are more resistant than the dilute ones. Pure ascorbic acid solutions were more sensitive than solutions containing such added materials as glucose, proteins, etc. With dosages up to 500,000 rep on orange juice, the retention of ascorbic acid was 87 per cent. For the same dosage and a solution of pure ascorbic acid in the same concentration as in the orange juice, the retention was 60 per cent. One million rep gave 36.4 per cent retention. Freezing of the sample in each case gave better than 90 per cent retention of ascorbic acid content. Goldblith, Proctor, Hogness and Langham (17) irradiated niacin tagged with C^{14} in the carboxcylic group with 3,000,000-volt cathode rays and report that retention is a function of dosage. The retention varied from 94 per cent for 660,000 rep to 45 per cent for 2,640,000 rep. X-rays appear to have little effect on niacin with dosages up to 1,000,000 roentgens.

TABLE VII

COMPARISON OF CONTINUOUS AND ULTRA-SHORT-TIME RADIATION
(From Huber's "Electronic Preservation of Food" (22))

Substance	Continuous Radiation	Effect	Capacitron Impulses of 10^{-6} sec.
Ergosterol	u-v, alpha, beta	vitamin-D formation	no change
Casein, Egg Albumen	beta, gamma	decomposition, oxidation	no change
Butane, Heptane	alpha, beta	H_2, CH_4 evolution, polymerization	no change
Styrene	u-v, alpha, beta	polymerization	no change
Castor, linseed, tung oil	u-v, beta	polymerization, change of ref. index, iodine No. and color	development of slight flowery odor
Acetone	beta	condensation, gas formation	no change
Hemoglobin	u-v, alpha	inhomogenization, low molecular breakdown products	small per cent of methemoglobin
Rubber plant	beta	discoloration, drying latex formation	no change

TABLE VIII

EFFECTS OF CAPACITRON RADIATION ON FOODS
(From Huber's "Electronic Preservation of Food" (22))

Meats, Fish, Eggs

Food	Impulses (10^{-6} sec)	Storage Conditions (in air and light)		Appearance, Taste, Odor	Untreated Sample Decay (days)	Container
		Temp. °C	Time (days)			
Beef	4	room	264	unchanged, raw, and fried	2	glass
Veal	4	room	238	unchanged, raw, and fried	3	glass
Pork, fat	4	room	207	unchanged, no rancidity	2	glass
Flounder, filet	4	room	127	unchanged, no rancidity	1	glass
Roast beef, red	4	room	94	unchanged except for darkening of color	2	plastic

TABLE VIII (cont'd)

Food	Impulses (10^{-6} sec)	Storage Conditions (in air and light)		Appearance, Taste, Odor	Untreated Sample Decay (days)	Container
		Temp. °C	Time (days)			
Meat, Fish, Eggs						
Ham, boiled	4	room	63	fair, slight decomposition	2	plastic
Bacon, smoked	6	room	156	unchanged, no rancidity	6	aluminum
Chicken a la King	6	4	74	unchanged	4	plastic
Hamburger	4	4	83	unchanged	5	plastic
Eggs, pigeon	4	room	194	unchanged	18	cardboard
Fats and Oils						
Butter	5	room	97	preserved, but off taste, no rancidity	3	glass
Margarine	4	room	79	ditto	3	glass
Lard	4	room	182	unchanged, no rancidity	8	glass
Olive Oil	6	room	204	unchanged	10	glass
Cream Cheese	2	room	66	unchanged, off taste after irradiation disappeared in storage	4	tinfoil
Camembert	4	room	82	preserved, ripening process arrested; taste more like Cheddar	2	tinfoil
Vegetables						
Peas	6	room	184	unchanged, except for slight bleaching	5	glass
Beans, cut	6	room	184	unchanged, except for some bleaching	6	glass
Carrots, diced	6	room	147	considerable bleaching, some loss of texture	5	glass

TABLE VIII (cont'd)

Food	Impulses (10^{-6} sec)	Storage Conditions (in air and light) Temp. °C	Time (days)	Appearance, Taste, Odor	Untreated Sample Decay (days)	Container
Vegetables						
Potatoes, diced	4	room	64	unchanged, except for some browning	4	plastic
Lima beans	6	room	227	unchanged	5	glass
Cabbage, diced	4	room	234	unchanged	9	glass
Broccoli, diced	4	room	42	unchanged, except for some bleaching	2	plastic
Spinach, chopped	4	room	83	unchanged except for some bleaching	3	plastic
Mushrooms	4	room	33	unchanged, except browning of stem and slight loss of texture	1	plastic
Lettuce	3	room	2	soggy, flat tasting and considerable bleaching	1	plastic
Cauliflower, diced	4	room	234	unchanged, slight yellow discoloration	6	glass
Fruits						
Pineapple, sliced	4	room	94	unchanged	4	plastic
Coconut, sliced	4	room	86	unchanged	3	plastic
Peaches, sliced	4	room	83	well preserved, but slight loss in texture and some browning	1	glass
Apples, sliced	4	room	101	unchanged, except for some browning	2	glass
Blueberries	4	room	65	unchanged, except for slight loss in texture	2	plastic

TABLE VIII (cont'd)

Food	Impulses (10^{-6} sec)	Storage Conditions (in air and light) Temp. °C	Time (days)	Appearance, Taste, Odor	Untreated Sample Decay (days)	Container
Fruits						
Raspberries	4	room	69	unchanged, except for slight loss in texture	2	plastic
Strawberries	4	room	41	preserved, but marked loss in texture and color	2	plastic
Cherries, sweet	4	room	64	unchanged	2	plastic
Orange Juice	4	room	128	preserved, but some loss of aroma and sweetness	1	glass
Orange-Grapefruit Juice	4	room	134	unchanged	2	glass
Grapefruit Juice	4	room	134	unchanged	2	glass

TABLE IX

CAPACITRON STERILIZATION OF DRUGS

(From Huber's "Electronic Preservation of Food" (22))

Drug	Impulses (10^{-6} sec)	Contamination	Potency Untreated	Potency Treated	Container
Thiamine HCl	2-4	unknown	4.6 mg/cc	4.4 mg/cc	glass
Protein Hydrolysate	2	GNB, GPC	....	....	aluminum
Penicillin-NA	3	B. subtilis fungi spores	220,000U	220,000U	glass
Streptomycin-H_2SO_4	4	B. subtilis	100,000U	100,000U	glass
Testosteron	4	B. subtilis	100%	100%	glass
Prolactane	4	....	100%	110%	glass
Pituitary Hormone	2	unknown	3800 I.U.	4000 I.U.	plastic
Hyaluronidase	2	unknown	100%	97%	plastic
Clarase	2	unknown	100%	87%	aluminum
Trypsin	2	unknown	100%	100%	aluminum
Yeast	2-4	B. subtilis	....	....	plastic
Riboflavin	....	....	0.07 mg/gm	0.07 mg/gm	....
Pyridoxine	....	....	0.04 mg/gm	0.04 mg/gm	....
Pantothenic Acid	....	....	0.10 mg/gm	0.10 mg/gm	....
Niacin	....	....	0.35 mg/gm	0.35 mg/gm	....

Proctor and Goldblith, working with mixtures of niacin and ascorbic acid, have shown that vitamins may exhibit mutual protection (16). Anderson and Harrison (2) report the reduction of ascorbic acid concentration by a factor of one-half by treatment with x-ray doses of 5,000 roentgens. The solution used, however, was quite concentrated (0.5 mg per 100 ml.). Dunlap and Robbins (11) report no definite effect with 200 kvp x-rays on thiamine chloride. The dosages were low, being of the order of 10,000 roentgens. With beta radiation from radioactive phosphorus and radon, however, a definite inactivation was obtained.

In general, the inactivation of vitamins and other drug preparations appears to parallel the inactivation of enzymes quite closely. The same order of magnitude of dosages for any significant inactivation, and identical protective effects, dilution effects, etc., have been observed for both classes of compounds. It would appear, therefore, that both enzymes and vitamins would remain relatively unaffected by radiation dosages required for 100 per cent sterilization.

Dosages appreciably higher than one million roentgens are probably necessary to attain any significant degree of inactivation of enzymes.

3. Experimental Results on Food Preservation at the University of Michigan

The initial experimentation on food preservation by means of irradiation has been a preliminary survey of the effects of x-ray and gamma irradiation of a variety of foods. Some additional work has been performed by Dr. C. A. Lawrence of the Department of Bacteriology on the irradiation of pure cultures of bacteria and bacteria counts on specimens of irradiated food.

Food preservation from the effect of microorganisms has been quite successful in that perishable foods such as milk and meat have been preserved for some time. The tests on fresh fruits and produce in which irradiation was used in attempt to inactivate the enzymes have not been as successful. This confirms the results reported in the literature reviewed, namely, that enzymes are apparently more resistant to irradiation than are microorganisms.

In the work done on foods thus far the radiation technique has been essentially the same. The samples of fruit, meat, or liquid were exposed to x-rays or gamma rays either sealed in polyethylene bags or exposed to air. Some vegetables were blanched by immersion in boiling water for short times before packaging in the bags. The polyethylene (Visqueen) bags were obtained from the Visking Corporation and were heat-sealed with an open flame. In this manner it was possible to obtain a vapor-tight seal. The properties of polyethylene film are such that oxygen, hydrogen, and nitrogen may diffuse through, permitting the food materials to "respire" while moisture and odors are retained within the bag. The samples were placed under the x-ray beam or in the cobalt-60 vault for the required number of hours to give the preselected dosage. The x-ray generator was operated at constant kilovoltage and current ratings, usually at the maximum allowable for the equipment in order to reduce the exposure time.

Controls for the radiated samples were placed in a room held at a constant temperature of 77°F and 50 per cent humidity, or placed in an ice box at 32°F. In the case of milk, small samples of approximately 10 cc were prepared in plastic bags and subjected to the same treatment as the larger samples. These small samples were then submitted to the University of Michigan Bacteriology Laboratory for bacteria counts. After irradiation the samples were placed in the constant temperature room and held for observation. Photographs were taken at intervals to record the appearance of the irradiated samples and the corresponding controls. Whenever possible black and white film was used; however, in the majority of the tests it was necessary to use color film to obtain an accurate record of the changes in appearance. Observation as to the odor and firmness were recorded. The results of these tests are described in the following portion of the report.

a. Milk

Exploratory irradiation was performed on samples of raw milk and homogenized pasteurized milk sealed in polyethylene bags. Dosages up to 4,000,000* roentgens were used with subsequent storage at 77°F. Control samples of raw and homogenized milk soured within 24 hours. After 48 hours, curds of cheese formed and separated from a clear, greenish-yellow tinted whey. Samples of homogenized pasteurized milk irradiated for 24 and 40 hours were preserved for more than two weeks (at 77°F) at the writing of this report. As time passes the milk appears to become more creamy in color but otherwise appears unchanged. There is no noticeable change in odor. All samples of this milk subjected to gamma radiation for periods of 1, 4, 8, and 16 hours soured within 36 hours. Samples of homogenized milk exposed to 200 kvp x-rays for dosages of 100,000 and 400,000 roentgens also soured within 36 hours. However, a sample exposed to approximately 800,000 roentgens of x-radiation has shown no signs of souring after 10 days. The samples exposed to the x-ray machine were quite warm (approximately 150°F) after exposure. This heating may have effected a further pasteurization, thus accounting for the seemingly low dosage required to preserve this sample. Photographs of the gamma-radiated milk samples and control are shown in Fig. 21. A sample of raw milk obtained from a local farm was irradiated for 24 hours in the cobalt source. The irradiated raw milk appeared to be preserved for about 7 days after which a pink coloration developed in the cream layer. This color was also observed in the control which had soured. Samples of irradiated milk were prepared for plate counts in the bacteriology laboratory. These results are given in Table X, page 85. The conclusion from these tests is that although 500,000 r may be sufficient to destroy most bacteria, about 2,400,000 r are required to preserve pasteurized homogenized milk. Greater dosages may be required for raw milk. Additional tests will be required to establish these limits.

b. Meat

Several samples of raw beef have been irradiated with gamma radiation to dosages up to 2.4 million roentgens. Prior to the radiation, the meat had been stored under refrigeration. The meat was bought on the market, and the exact age of the carcass is not known. The samples sealed in

---

* Based on preliminary calibration of 100,000 r/hr in vault.

Fig. 21. Photograph of Irradiated Milk

Fig. 22. Photograph of Irradiated Beef Steak

Fig. 23. Photograph of Irradiated Bananas

Fig. 24. Photograph of Irradiated Bananas

Fig. 25. Photograph of Irradiated Grapes

Fig. 26. Photograph of Irradiated Apple Juice

polyethylene bags, were irradiated and then stored at 77°F. Control samples from the same section of meat were treated in exactly the same manner, except that they were not irradiated.

In one case, the beef was given a dose of 2,400,000 r of gamma radiation. It developed a surface darkening during the irradiation period. After irradiation and 24 hours of storage, the color began to lighten, returning to a crimson color characteristic of fresh meat after about 4 days. It is believed that the darkening is caused by the formation of oxidized material on the surface, which disappeared when all the oxygen was utilized. The color never returned to the bright red of fresh-cut meat. The control sample underwent little change during the first 48 hours in storage but underwent rapid change thereafter. Its color darkened to a muddy red-brown, the structure softened, and the characteristic odor of decaying flesh developed. No such changes have developed in the irradiated sample. A color photograph of these specimens is shown in Fig. 22.

Another sample of beef steak, treated in a similar manner but with 1,700,000 r of gamma radiation developed a surface darkening 48 hours after irradiation. The control did not appreciably change, although it did darken somewhat. A slight putrid odor developed in the control after about 48 hours of storage. No such odor has developed in the irradiated sample. After storage for about 10 days a mold growth appeared on one sample. The results support those obtained with milk, indicating that a dose of about 2,400,000 r of gamma irradiation is required for preservation.

c. Fruits

Bananas were one of the first samples to undergo extensive radiation tests by x-rays and by gamma rays from the cobalt-60 source. Dosages in the range 10,000 to 6,750,000 roentgens were utilized. Softening of the interior of the banana was inhibited for periods up to 3 weeks. Samples cut open after this time revealed a yellow interior more firm than the interior of the samples of the control. A dosage of 1,000,000 roentgens or more turned the skin uniformly black. This effect was not limited to the yellow, ripe fruit (Fig. 23), since tests on fully green bananas reacted similarly (Fig. 24). The skin of samples exposed to less than 1,000,000 roentgens darkened and turned black in a manner and period similar to the unirradiated controls. In the thought that, in the case of x-rays, infrared radiation might be responsible for this blackening, a sheet of mica glass was placed between the sample and the x-ray tube window to minimize the effect of infra-red rays. However, the results were the same, indicating the blackening effect was caused by the x-radiation. The temperature of the sample was only slightly above room temperature. It appears that x-rays and gamma rays, while inhibiting enzymatic softening of the banana interior, may catalyze the surface oxidation reactions which turn the skins dark. It may be that, while destroying the enzymes that catalyze the darkening reaction in the skin, the radiation itself assumes the role of the enzymes in this reaction and thus permits the darkening to proceed. At the moment, bananas in their natural, whole state do not offer much promise from preservation by radiation. It may still be possible to preserve sliced bananas packed in various liquids or syrups. It is noted at this point that, for reasons of size limitations, bananas for irradiation in the cobalt source had to be sectioned and sealed in polyethylene bags. This permitted visual observation of both the flesh and skin of the fruit. Samples thus sealed were apparently rendered sterile as supported by the observation that they did not mold in periods up to three weeks. Unirradiated control samples, on the other hand, started to mold several days after being sealed, whereupon they softened and yielded to degradation. The bags soon inflated markedly from the evolution of gases from the fruit.

Fresh red plums were irradiated with both 150 and 200 kvp x-rays. In one case two plums were sealed in a bag and exposed to the 150 kvp x-rays for a total dosage of 100,000 roentgens. The sample exposed to the 200 kvp x-rays for 650,000 roentgens was not packaged, but was left exposed in air. For both tests, the controls darkened appreciably with some softening. The irradiated samples, however, retained their color and "blush" and remained firm for periods of over two weeks. Some evidences of local dehydration were visible on the unpackaged irradiated sample. It was noted in the case of the irradiated packaged sample that all the air present in the bag when sealed had been absorbed by the plums. This effect was not noted on the packaged control. These results need further investigation, but they are more promising than the tests on bananas.

A ripe peach was irradiated to 650,000 roentgens with the 200 kvp machine in an unpackaged state. Some browning was effected, but dehydration was inhibited for a period of about 7 days. After this period the irradiated sample proceeded to dehydrate at an accelerated rate and dried to a smaller size than the unirradiated control after 14 days. Future experiments with bagged and sealed peaches are planned.

Ripe Bing cherries were irradiated in the gamma source for a period of 24 hours and a total dosage of 2,400,000 roentgens. Upon removal from the vault a slight darkening as compared to the unirradiated control was observed. A sample of green, seedless grapes was exposed to the same radiation dosage with similar results. The grapes, however, darkened quite considerably to a brown color within a few hours of removal from the vault (see Fig. 25). There appeared to be little preservation of the fruit by visual observations made for two weeks after the test. Both samples and controls of the grapes and cherries proceeded to dehydrate and shrivel at roughly identical rates. The irradiated cherries appeared to retain their bright red color for a longer period than the control. The unirradiated control grapes retained the original green color practically through the dehydration stage while the irradiated sample continued to darken, shrivel, and assume the general appearance of swelled raisins. It is possible that the radiation dosage was too high in this case, and further experiments are contemplated in this direction.

Samples of firm, full-ripe red raspberries were sealed in polyethylene bags and subjected to dosages of 300,000 and 1,600,000 roentgens in the cobalt vault. The 300,000-roentgen sample was brighter and slightly softer than the control after removal from the vault. The 1,600,000 roentgen sample was also more brightly colored than the control and was softened considerably. This sample was partially liquified and had the appearance of being "cooked". The two samples and the control remained unchanged for several days after packaging treatment, but after about four days, mold growths were observed on the unirradiated control. The irradiated samples softened somewhat during a period of ten days but remained mold-free.

Blueberries treated in a manner similar to the raspberries yielded similar but less pronounced results. All the samples and control presented the same color and texture after irradiation and 10 days storage at room temperature. Extensive mold growth developed on the unirradiated berries but none on the irradiated berries.

d. Fruit Juices

A sample of orange juice sealed in a 1 in. by 8 in. test tube was irradiated for approximately 24 hours in the cobalt source. Darkening of the test tube by the radiation prevented observation of color changes on this particular sample. The control, however, blew its cork stopper after approximately 10 days, whereupon a mold growth developed on the surface of the juice. The stopper was replaced but blew again several days later. No mold growth has been noted in the irradiated sample to date after approximately 30 days. Another sample of orange juice was prepared, sealed in a polyethylene bag, and subjected to the same gamma radiation dosage. This sample permitted color observations in comparison with a control similarly packaged in polyethylene. Immediately after irradiation no color change was noted, and there was no difference in the appearance of the pulp sediment in the juice. The control turned sour in approximately 3 days. After 7 days, there has been no visible change in the irradiated sample, however, since then the irradiated juice has slowly darkened in color.

Apple juice, prepared from whole ripe storage apples, was sealed in polyethylene bags and exposed to the gamma radiation from the cobalt source for 24 hours. During the first 24 hours' storage (i.e., the irradiation period for the sample), the control turned a dark brown coffee color. Upon removal from the vault, the irradiated sample had retained its original, light brown, translucent color (see Fig. 26). After about 5 days' storage, the color of the control lightened and that of the sample darkened. A muddy brown precipitate developed in both. However, a strong alcoholic odor characteristic of fermentation developed in the control. There was no extensive evolution of gas from either sample. After approximately 8 days, a black mold began to develop and spread on the inside of the bag of the irradiated sample just above the liquid level. No particular alcoholic odor was detected for the irradiated sample at that time.

e. Bacteria

Samples of pure cultures of a variety of bacteria were irradiated in the cobalt-60 vault. This work was performed by Dr. C. A. Lawrence of the Department of Bacteriology under sponsorship of the Phoenix Project. The results are given in Table XI, which shows that 100,000 roentgens reduced E. coli to about 2.7 per cent of the original count and B. proteus to 25.2 per cent of the original count. Five hours of irradiation (500,000 roentgens) gave complete sterilization.

Dr. Lawrence also made some bacteria counts on samples of irradiated pasteurized milk, irradiated raw milk, and the controls. The results are given in Table X. Irradiation for 24 hours (2,400,000 roentgens) was sufficient to sterilize the sample of raw milk. The control, kept in the refrigerator for 24 hours, had a count of 20,000/ml, and the control kept at 77°F for 24 hours, a count of 143,750,000/ml, whereas the control, kept at the same temperature as that of the vault (about 80°F), gave a count of 4,500,000/ml.

TABLE X

EFFECT OF GAMMA RADIATION FROM COBALT-60 ON MILK FLORA

Sample Number		Dosage	Number of Colonies
M-10	(pasteurized milk)	Sample from original container 0-r.	805/ml
M-11	"	2 hours on top of vault 0-r.	250,000/ml
M-12	"	1 hour 32 min. in x-ray beam 200,000-r.	165/ml
M-14	"	2 hours in vault 200,000*-r.	155/ml
M-25	(raw milk)	24 hours at 77°F 0-r.	143,750,000/ml
M-26	"	24 hours on vault 80°F+ 0-r.	4,500,000/ml
M-27	"	24 hours in vault 80°F 2,400,000*-r.	0/ml
M-28	"	24 hours in icebox 32°F 0-r.	20,000/ml

TABLE XI

EFFECT OF GAMMA RADIATION FROM COBALT-60 ON E. COLI, B. PROTEUS, L. ARABINOSE

Organisms	Number of Colonies	
	Irradiated	Non-irradiated
<u>Experiment No. 1</u>	<u>Irradiation 24 hours or 2,400,000* Roentgen Total</u>	
E. Coli	0	815,000,000/ml
B. Proteus	0	1,593,750/ml
L. Arabinose	0	65,000/ml
<u>Experiment No. 2</u>	<u>5 hours — 500,000* Roentgens</u>	
E. Coli	0	1,138,000,000/ml
B. Proteus	0	1,898,750,000/ml
L. Arabinose	0	25,000/ml
<u>Experiment No. 3</u>	<u>1 hour — 100,000* total Roentgens</u>	
E. Coli	1,417,500/ml	52,500,000/ml
B. Proteus	35,000/ml	141,250,000/ml

---

* Based on a preliminary calibration of 100,000 r in the vault.

Bibliography for Project M943D

1. Alsopp, C. B., "Radiochemistry, A Review of Recent Progress," *Trans. Faraday Soc.* *40*, 79 (1944).

2. Anderson, R. S., and Harrison, B., "The Quantitative Effect of X-Rays on Ascorbic Acid in Simple Solution and in Naturally Occurring Substances," *J. Gen. Physicl.* *27*, 69 (1943).

3. Banon, E. S. G., *Some Aspects of the Biological Effects of Radiation*, U.S.A.E.C. Publication MDDC484, 1946.

4. Brasch, A., and Huber, W., "Reduction of Undesirable By Effects in Products Treated with Radiation," *Science* *108*, 536 (1948).

5. Brasch, A., Huber, W., Friedemann, U., and Traub, F. B., "Action of High Intensity Electrons on Biological Objects," *Proc. R. Virchow Med. Soc. N. Y.* *VIII* (1949).

6. Dale, W. M., "Action of X-Rays on Enzymes," *Bioch. J.* *34*, 1367 (1940).

7. Dale, W. M., "Effect of X-Rays on the Conjugated Protein d-Amino Acid Oxidase," *Bioch. J.* *36*, 80 (1942).

8. Dale, W. M., "Effect of X-Rays on Acetylcholine Solutions Showing Dilution and Protection Effect Shown for Enzymes," *J. Physiol.* 102, 50 (1943).

9. Dale, W. M., "Effect of X-Rays on Solutions of Biologically Active Compounds," *Brit. J. Radiol.* *16*, 338 (1939).

10. Dale, W. M., Meredith, W. J., and Tweedie, M. C. K., "Mode of Action of Ionizing Radiation on Aqueous Solutions," *Nature* *151*, 281 (1943).

11. Dunlap, C. E., and Robbins, F. C., "Effect of Roentgen Rays, Radon and Radioactive Phosphorous on Thiamin Chloride," *Am. J. Roentgenol. Radium Ther.* *50*, 641 (1943).

12. Dunn, C., Campbell, W., Fram, H., and Hutchins, A., "Biological and Photochemical Effects of High Energy, Electrostatically Produced Roentgen Rays and Cathode Rays," *J. Appl. Phys.* *19*, 605 (1948).

13. Forssberg, A., "Action of Enzymes on Catalase and Its Biological Significance," *Arki. Kemi. Minerol. Geol.* *27A*, 1 (1945).

14. Forssberg, A., "The Action of Roentgen Rays on the Enzyme Catalase," *Acta Radiol.* *27*, 281 (1946).

15. Forssberg, A., "Mechanism of the Action of X-Rays on Enzymes in Water Solution," *Nature* *159*, 308 (1949).

Bibliography (cont'd)

16. Goldblith, S., and Proctor, B. E., "Effect of High-Voltage X-Rays and Cathode Rays on Vitamins (Niacin)," Nucleonics 3, 32 (1948).

17. Goldblith, S., Proctor, B. E., Hogness, J. R., and Langham, W. H., "The Effects of Cathode Rays Produced at 3000 Kilovolts on Niacin Tagged with Carbon-14," J. Biol. Chem. 179, 1163 (1949)

18. Gottschalk, A., in Chapter 15 of The Enzymes Vol I, Part 1, K. Myrbäck and B. Sumner, Editors, New York, Academic Press, 1950.

19. Haldane, J. B. S., Enzymes, New York, Longmans Green and Co., 1930.

20. Hevesy, G., "Effect of Röntgen Rays on Cellular Division," Rev. Mod. Phys. 17, 101 (1945).

21. Hougen, C., and Watson, K., Chemical Process Principles, Part 3, Kinetics and Catalysis, New York, J. Wiley and Sons, 1947.

22. Huber, W., "Electronic Preservation of Foods," Electronics 21, 74-79 (March, 1948).

23. Huber, W., "Results and Analysis of Differential Radiation Mechanisms in Some Biological Systems," Naturwissenschaften 38, 21 (1951). (Preprint in English from Author.)

24. James, H. B., Status Report No. 3 June-Dec. 1947, ONR Project TIPU547, University of California, Berkley; Nuclear Sci. Abst. 1, 30.

25. Kempton, J. H., and Maxwell, L. R., "Effect of Temperature During Irradiation on the X-Ray Sensitivity of Maize Seed," J. Agric. Res. 62, 603 (1941).

26. Lea, D. E., Haines, R. B., and Bretscher, E., "The Bactericidal Action of X-Ray Neutron, and Radioactive Radiation," J. Hyg. 41, 1 (1941).

27. Lea, D. E., Haines, R. B., and Coulson, C. A., "The Mechanism of the Bactericidal Action of Radioactive Radiations," Proc. R. Soc. London B 120, 47-76 (1936).

28. Lea, D. E., Haines, R. B., and Coulson, C. A., "The Action of Radiations on Bacteria," Proc. R. Soc. London B 123, 1-21 (1937).

29. Molwyn-Hughes, A., in Chapter 2 of The Enzymes Vol I, Part 2. K. Myrbäck and B. Sumner, Editor, New York. Academic Press, 1950.

30. Nickerson, J. T. R., Goldblith, S., and Proctor, B., "A Comparison of the Chemical Changes in Mackeral Tissue Treated with Ionizing Radiation," Food Tech. 4, 84 (1950).

Bibliography (cont'd)

31. Nilova, V. P., "The Influence of X-Ray on the Enzymes of Seeds and Seedlings of Barley," Bulletin of Applied Botany of Genetics and Plant Breeding (U.S.S.R.) Ser. III, No. 14, 109 (1936); C. Abst. 31, 5840^9

32. Pimenov, M., "Factors which Affect the Preservation of Butter," Sbornik Rabot Leningradskogo Zootekh Instituta No. 3, 219 (1940); Khim. Referativnyi Zhurnal 4, 144 (1941); C. Abst. 37, 2088^8 (1943).

33. Polland,E., "Ionizing Radiation as a Test of Molecular Organization," Am. Sci. 39, 99 (1951).

34. Proctor, B. E., and O'Meara, J. P., "Effect of High Voltage Cathode Rays on Ascorbic Acid," Ind. Eng. Chem. 43, 74 (1948).

35. Szent-Oyorgyi, A., Oxidation, Fermentation, Vitamins, Health and Disease, Baltimore, The Williams and Wilkins Co., 1939.

36. Trump, J. G., and VandeGraaff, R. J., "Irradiation of Biological Materials with High Energy Roentgen Rays," J. Appl. Phys. 19, 599 (1948).

37. Tytell, A. A., and Kersten, H., "Effects of Soft X-Rays on Urease and Catalase," Proc. Soc. Exp. Med. Biol. 48, 521 (1941).

38. Weiss, J., "Radiochemistry of Aqueous Solutions," Nature 153, 748 (1944).

39. Zimmer, K. G., "An Eventual Participation of Radiochemical Reactions in Aqueous Solutions in Biological Effects of Radiation," Fund. Radio. 5, 168 (1940); C. Abst. 36, 6554^8 (1942).

D. PROJECT M943E — EXPLORATORY RESEARCH ON NEW IDEAS

This subproject has been established to permit exploratory research on new ideas without interrruption of the organized research programs. It is believed that new and better ideas will develop as the research progresses and that they will warrant some preliminary study prior to an organized research program. One such idea suggested is by H. J. Gomberg that of the direct conversion of radiation to electrical energy.

It is believed that it may be possible to develop a special type of vacuum tube in which intense beta radiation would be converted directly to electrical energy by decelerating the electrons with an opposing field. It is believed that some preliminary experiments might provide some information on the feasibility of this idea.

Another idea is the use of packaged concentrated fission products for pilot-plant experiments. If results from the research on the other subprojects are promising, it is anticipated that radiation sources considerably greater than 1000 curies will be required for pilot-plant studies. Methods of packaging the concentrated fission products probably should be investigated.

SUMMARY

The investigation of uses of the gross fission products has progressed sufficiently to warrant a progress report.

To improve the organization and to facilitate accounting procedures, the investigation has been divided into subprojects as follows:

Title		Supervisor	Budget, 1951-1952
UTILIZATION OF FISSION PRODUCTS, M943		L. E. BROWNELL	$116,000.00
Alterations and Special Equipment			31,000.00
			$ 85,000.00
1. EFFECT OF RADIATION ON COMBUSTION ENGINE PERFORMANCE			$ 24,000.00
RECIPROCATING ENGINES	M943A	R. A. Wolfe	$ 11,800.00
JET ENGINES	M943B	E. T. Vincent	$ 12,200.00
2. EFFECT OF RADIATION ON CHEMICAL REACTIONS	M943C	J. J. Martin L. C. Anderson	$ 18,000.00
3. EFFECT OF RADIATION ON FOODS	M943D	L. E. Brownell	$ 12,000.00
4. EXPLORATORY RESEARCH ON NEW IDEAS	M943E with	L. E. Brownell H. J. Gomberg W. W. Meinke L. Thomassen	$ 17,000.00
5. OPERATION OF FISSION PRODUCTS LABORATORIES	M943F advised by	L. E. Brownell H. J. Gomberg W. W. Meinke L. Thomassen	$ 14,000.00
			$ 85,000.00

Literature reviews have been conducted for subprojects M943A, M943C, and M943D and are described in the report.

Preliminary experimental results are reported for subproject M943D. The most promising results have been obtained with irradiated milk and meat. It was found possible to preserve these perishable foods for more than three weeks (to date) at 77°F after a gamma irradiation of 2,400,000 roentgens. Molds appear to be the most difficult microorganism to destroy. Enzymes have greater resistance to irradiation than microorganisms.

The laboratories are being made ready. A 1000-curie cobalt-60 source has been received from Brookhaven National Laboratory and other miscellaneous pieces of laboratory equipment are being received.

Subsequent progress reports will follow as the investigation progresses.