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THE IRRADIATION EFFECTS ON A MODEL TBP-DECAHYDRANAPHTHALENE SOLVENT EXTRACTION SYSTEM

by 1050 710

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TABLE OF CONTENTS

page

LIST OF TABLES i

LIST OF FIGURES. ii

NOMENCLATURE iv

INTRODUCTION 1

THEORY 13

EXPERIMENTAL PROCEDURE 18

RESULTS AND CONCLUSIONS. 25

BIBLIOGRAPHY 49

ACKNOWLEDGEMENTS 54

APPENDICES 55

APPENDIX A (physical properties of the TBP-decalin system). . .56

APPENDIX B (distillation of decalin). 57

APPENDIX C (calibration data) 66

APPENDIX D (error analysis) 78

APPENDIX E (calculator programs). 81

LIST OF TABLES

page

I. Radiolysis Product Yields of the TBP-Decalin System. 35

II. Mass Spectrometer Analysis of the Radiolysis Gas of Pure TBP 36

III. Radiolysis product concentrations produced from irradiations . 37

IV. Radiolysis yields of pure TBP. 38

V. Yields of Various Diluent Systems. 39

A-I. Physical properties of butyl phosphates. 56

A-II. Physical properties of decalin 56

A-III. Densities of TBP-decalin mixtures. 56

C-I, Chromatogram Calibration of $C_{10}H_{16}$ 66

C-II. Chromatogram Calibration of DBP. 67

C-III. Chromatogram Calibration of MBP. 68

C-IV. Initial Product Concentrations in Standard Solutions 69

C-V. Calibration of the Fricke dosimeter. 70

C-VI. Calculation of the absorbed dose at various gamma cell positions using the Fricke dosimeter. (January 21, 1974) . . . 71

C-VII. Electron Fraction of TBP in the solutions analyzed 72

D-I. Maximum Experimental Errors. 80

LIST OF FIGURES

page

1. Molecular Structure of TBP 11

2. Molecular Structure of "cis"-decalin 12

3. Molecular Structure of "trans"-decalin 12

4. Schematic view of the position of the sample cells in the sample holder 22

5. Sketch of the irradiation cell 23

6. Schematic view of Saunders-Taylor apparatus. 24

7. Variation of G(X) as a function of Dose. 40

8. Variation of G(X) with Electron Fraction of TBP, Decalin + TBP. Absorbed Dose, 2 watt-hr/liter 41

9. Variation of G(X) with Electron Fraction of TBP, Decalin + TBP. Absorbed Dose, 4 watt-hr/liter 42

10. Variation of G(X) with Electron Fraction of TBP, Decalin + TBP. Absorbed Dose, 6 watt-hr/liter 43

11. Variation of G(X) with Electron Fraction of TBP, Decalin + TBP. Absorbed Dose, 8 watt-hr/liter 44

12. Variation of G(MBP + DBP) with Electron Fraction of TBP, Decalin + TBP. Absorbed Dose, 2 watt-hr/liter. 45

13. Variation of G(MBP + DBP) with Electron Fraction of TBP, Decalin + TBP. Absorbed Dose, 4 watt-hr/liter. 46

14. Variation of G(MBP + DBP) with Electron Fraction of TBP, Decalin + TBP. Absorbed Dose, 6 watt-hr/liter. 47

15. Variation of G(MBP + DBP) with Electron Fraction of TBP, Decalin + TBP. Absorbed Dose, 8 watt-hr/liter. 48

B-1. Chromatogram of the unpurified decalin as obtained from a commercial distributor. 59

B-2. Chromatogram of the distillate from the first distillation of the decalin shown in figure B-1. 60

B-3. Chromatogram of the distillate after adding fresh decalin to a stillpot over half filled from the previous distillation. 61

B-4. Chromatogram of the decalin collected from the distillation of the waste decalin. 62

B-5. Chromatogram of the decalin collected from the first distillation of the bottoms. 63

B-6. Chromatogram of the decalin collected from the second distillation of the waste decalin. 64

B-7. Chromatogram of the decalin collected from the second distillation of the bottoms 65

C-1. The Absorbance of .8N H_2SO_4 and 10^{-3}M NaCl, of Standard Ferric Solutions. 73

C-2. Calibration Curve for Converting the Planimeter Reading to the Concentration of $C_{10}H_{16}$ in Solution. 74

C-3. Calibration Curve for Converting the Planimeter Reading to the Concentration of DBP in Solution. 75

C-4. Calibration Curve for Converting the Planimeter Reading to the Concentration of MBP in Solution. 76

C-5. Calibration Curve for Converting the Weights of the Chromatogram DBP Peak to the Concentration of DBP in Solution. 77

NOMENCLATURE

kg	kilogram, 10^3 gram
cal	calorie(s)
mole	molecular formula weight
MeV	mega-electron volts, 10^6 electron volts
Co-60	Cobalt isotope 60
Mwd	mega-watt days
eV	electron volt
G(X)	the yield of "X" component in molecules per one hundred electron volts
ml	milliliter, 10^{-3} liter
M	molecular formula weight per liter of solution
N	gram equivalent weight of solute per liter of solution
torr	millimeters of mercury
^oC	degrees centigrade
cm	centimeter, 10^{-2} meters
mm	millimeter, 10^{-3} meters
hr	hour(s)
^oK	degrees Kelvin
atm	atmosphere(s)
gm	gram(s)
mp	millipoise, 10^{-3} poise
x_f	fraction of the component "x" in the feed for the distillation column
x_w	fraction of the component "x" in the waste from the distillation column
x_D	fraction of the component "x" in the distillate

min	minute
nm	nanometer, 10^{-9} meters
mM	millimolar, 10^{-3} moles per liter
mg	milligrams, 10^{-3} grams
n	number of molecules produced by irradiation
E	energy absorbed in units of 100 eV
I	energy absorption rate in units of one hundred electron volts per unit time
t	time

1. INTRODUCTION

The complete fuel cycle for nuclear reactor operation consists of several steps: 1) fuel preparation and fabrication, 2) core loading, 3) reactor operation, 4) core unloading, 5) fuel element "cooling", 6) chemical processing of the spent fuel, and 7) refabrication of the processed fuel into new elements. Completion of the fuel cycle is a time related occurance involving each of these steps which, therefore, affects the total fuel inventory which must exist to keep the reactor operating at maximum performance. This inventory could be reduced through reduction of the time required for each of these fuel cycle steps. Currently, fuel element "cooling" requires the longest time and is thus of greatest interest when reductions are sought[1].

These "cooling times" are established in part by the ability of the organic solvents used in reprocessing to withstand degradation by "hot fuel" radiation, and in part by methods developed to remove the degradation products which interfere with extraction[2]. An important factor in processing nuclear reactor fuels is the radiation damage to process reagents[3]. The magnitude of the chemical changes that are produced by radiation is sufficient to affect the performance, and even the feasibility of some chemical processes used to recover elements such as uranium and other materials from burnt reactor fuels[4].

The main effort in this research is to gain understanding of the basic chemistry involved in the problem of solvent degradation by utilizing a system that shows promising application

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in solvent extraction[5].

Of the various processing methods[6,7,8,9,10,11,12], solvent extraction[10] has been developed on a production scale for: 1) separation of plutonium and uranium from fission products, 2) separation of enriched uranium from fission produsts, and 3) separation of uranium and thorium from fission products[4,10].

The limited irradiation stability of solvents used for the extraction and purification of fertile and fissionable materials has been indicated to be a factor of potential significance in defining the applicability of solvent extraction for the use in fuel reprocessing[4]. This is of particular concern in the planning for the processing of fast reactor fuels because burnups of the order of 100,000 Mwd/metric ton may be achieved in U-Pu ceramic fuels[13], and because of the economic considerations associated with large fuel inventory in a fast reactor may make it highly desirable to process fuels after as short a cooling period as one month. Estimates of the radiation density in the aqueous feed to such processes are as high as 100 watt/liter[14].

Extraction with organic solvents has proven to be a valuable tool in the separation and purification of certain inorganic materials. The formation of coordination compounds between the solute and the solvent requires that the solvent possess structural groups capable of coordination, such as oxygen containing groups. Some solvents that are known to possess this ability to coordinate are esters, ethers, alcohols, aldehydes, ketones, and those containing nitro groups. Additional requirements on chemical and physical properties such as volatility, inflammability,

viscosity, etc., may tend to limit the usefulness of many organic compounds that have the necessary structural characteristics as far as extraction alone is concerned[10,15,16].

Methods employed for the extraction of uranium from nitrate solutions require the use of "salting" agents to drive uranyl nitrate into the organic solvent phase. The use of nitric acid as a salting agent in such a process has advantage over metallic nitrates, but requires that the solvent be stable towards reaction with this acid. Tributyl phosphate (TBP) is an organic ester of phosphoric acid that possesses high stability toward the reaction with nitric acid[17] and has a high affinity for uranium and other fissionable materials. Developmental work has been done extensively with TBP because it is commercially available and it does have desirable properties[18,19,20,9].

The tertiary butyl ester of ortho phosphoric acid has been assigned the structure as shown in figure 1, and is known either as tributyl phosphate or more simply as butyl phosphate. The monobutyl ester of ortho phosphoric acid in which there are two acid hydrogens is known as either monobutyl phosphoric acid or monobutyl phosphate (MBP). Similarly the dibutyl ester is known as either dibutyl phosphoric acid or dibutyl phosphate (DBP)[15].

The high extraction power of TBP for uranyl ions has been investigated by Ferguson and Runion[17] and they have indicated the formation of a coordination compound between uranium and TBP. The ratio of uranium and nitric acid to Bu_3PO_4 (or TBP) in the saturated mixture was found to be approximately 0.5 moles of uranium and about 1.0 moles of nitric acid per mole of Bu_3PO_4, which indicates a complex

of the general formula

$$UO_2(NO_3)_2 \cdot 2Bu_3PO_4 \cdot 2HNO_3.$$

Pure TBP is water-white, somewhat viscous, and used industrially as a plasticizer and an anti-foaming agent[21]. Important physical properties with reference to solvent extraction are its very low solubility in aqueous solutions and its low vapor pressure. (Some physical properties for the butyl phosphates are listed in table A-I of Appendix A.)

Commercial TBP usually contains small amounts of butyl alcohol and dibutyl ether and may also contain dibutyl phosphate, monobutyl phosphate, and some condensed phosphates such as tetrabutyl pyrophosphate[22]. These products may result in the manufacture of TBP or by degradation reactions. TBP is very stable towards oxidation, and its resistance to nitric acid is excellent. TBP and other alkyl phosphates will undergo alkaline hydrolysis, proceeding through DBP and MBP to phosphoric acid[23]. This reaction occurs in the aqueous phase and was demonstrated to involve P-O bond rupture[22].

In general, the physical properties of TBP make it attractive for use in the solvent extraction process for nuclear fuels, but the properties of high viscosity and a density similar to that of water, necessitates the use of a hydrocarbon diluent. The diluents have been light saturated hydrocarbons, ethers, chlorinated hydrocarbons, and commercial kerosene-like solvents[22].

Hydrocarbon diluents are generally used in Purex type[10] extraction processes to dilute the phosphate complexing agent in order to reduce the viscosity and to obtain a density for the solvent mixture which will provide an adequate difference in density between

it and the aqueous phase, and to limit the concentration of heavy metals which can be complexed in the organic phase. Highly paraffinic kerosene-range hydrocarbon mixtures have been used the most[24, 25,21,26,27,28,29,30] because they combine stability with reasonably low viscosity and high flash point. Potential diluents for TBP in the Purex process can be classified into the following groups[24]:

1. Normal paraffins, such as synthetic dodecane, and fractions isolated by urea treatment.

2. Nonaromatic petroleum fractions: Shell E2342, Bayol-D, Supersol, Ultrasene, Shell 16550, and Shell 82000. The composition of these will vary from 60 to 70 percent naphthenes plus 5 to 10 percent normal paraffins in Shell E2342 to 20 to 30 percent naphthenes plus 50 to 60 percent normal paraffins in Shell 82000. Branched hydrocarbons most probably make up the balance.

3. Highly aromatic fractions: such as Penoa 100 and Amsco D95El.

4. Synthetic alkylates produced by hydrogenation and polymerization of short-chain olefins, copolymers, etc.; Soltrol 170, Amsco 125, and Amsco 450.

The chemical stability of paraffins is expected to decrease in the order: normal, branched, and cyclic. Compounds with tertiary hydrogen atoms are assumed to be particularly susceptable to degradation[24]. The radiolytic and chemical stability of the above compounds is discussed in reference [24].

The instability of commercial hydrocarbon mixtures to the effects of chemical (acid) attack and irradiation have prompted many studies on the performance of specially purified hydrocarbon mixtures and of pure hydrocarbons from various sources. A contribution from Savannah River on this subject is a report on the evaluation of a commercial dodecane that is designated "Adecane" and is prepared presumably from fatty acid glycerides. Analysis of this product indicated the materials were about 90% dodecane with a few percent

adjacent hydrocarbons and the properties of the mixture were essentially those of dodecane. Chemical and radiolytic stability were almost the equivalent of pure dodecane and were markedly superior to those of typical petroleum base diluents[27].

The results of Baroncelli, Brignocchi, and Gasparini[31] indicate a preference for a pure compound rather than a mixture. For this reason such paraffinic diluents such as n-dodecane, or hydrogenated tetrapropylene, can be used for the chemical processes with TBP or tertiary amines as an alternative to the conventional diluents such as Amsco or kerosene.

Since the problem of a good diluent is of general interest to nuclear fuel reprocessing and will be still more interesting with the reprocessing of fast reactor fuels where higher activities are expected, it is useful to discuss some criteria for the choice of the diluent.

Marston, West, and Wilhite[25] have conducted investigations which have led to the adoption of n-paraffins as a diluent for Purex solvent. One of the principle criterion for the stability of a diluent is the resistance of the diluent to form degradation products that may complex with zirconium[24]. Normal paraffins were the most stable of all hydrocarbons tested, and pure n-paraffins in the C_{10} to C_{16} range did not retain significant amounts of zirconium after degradation. The stability of isoparaffins was found to be a function of the volatility of the isoparaffin. The stabilities of all other hydrocarbons that were tested were generally less than that of refined kerosene; therefore, these compounds were undesirable either in the pure form or as impurities in candidate diluents.

Decahydranaphthalene (Decalin), a paraffinic hydrocarbon, shows

promise as a Purex diluent to take advantage of its 50% higher solubility for the thorium-TBP complex. Also use of decalin would eliminate the need of an aluminum nitrate salting agent for the Thorex process[10] because of its chemical stability in nitric acid solutions[24].

Decalin is composed of two cyclohexane rings fused together and sharing two carbon atoms in common (figure 2). It is predicted that this substance can exist in a "cis" and a "trans" form. Both of these forms are stable and the transformation of the "cis" into the "trans" form is accomplished only under drastic conditions.

It is suggested that "cis" and "trans" decalin are formed of two boats and two chairs, respectively, but all conformations containing even one unstable boat form are now disregarded. The forms are both chair-chair forms; that for "cis"-decalin can change freely into another equivalent one that likewise has one equatorial and one axial bridge head-hydrogen atom. In trans-decalin, both bridge bonds are axially positioned. The fact that the heat of combustion is lower than that of the cis-isomer by 2.1 kg-cal/mole indicates greater stability of the "trans" form[33].

Radiation damage to the solvent extraction systems used in reprocessing irradiated fuels is very important. Some of the radiation damage effects are[30,34] : 1) formation of gaseous products, such as hydrogen and methane, 2) formation of liquid products more volatile than the original material, 3) formation of products of greater molecular weight than the original material, and 4) formation of unsaturated products.

The radiolysis of pure TBP has been studied extensively[35,36,

29,37,24,38,39,40,38]. Chemical and irradiation effects on the TBP complexing agent are of major importance concerning the problem of solvent deterioration[24]. The liquid products from Co-60 gamma radiolysis of pure TBP have been found to include dibutyl phosphate, monobutyl phosphate, butyl alcohol, butyl ether, phosphoric acid, hydrocarbons, and polymers[35].

Burr[42] has found that the primary radiolysis products are hydrogen, DBP, and polymer. He suggests that the probable primary processes are:

1. $C_4H_9OPO_3Bu_2 \xrightarrow{\gamma} \cdot C_4H_8OPO_3Bu_2 + H\cdot$

2. $C_4H_9OPO_3Bu_2 \xrightarrow{\gamma} C_4H_9\cdot + \cdot OPO_3Bu_2.$

Since the amounts of DBP, polymer, and hydrogen formed were roughly equivalent in Burr's investigation, he assumed the two reactions occur with about the same probability.

Burr also suggests that the formation of hydrogen, DBP, and polymer are in accord with the following reactions:

3. $H\cdot + C_4H_9OPO_3Bu_2 \longrightarrow H_2 + \cdot C_4H_8OPO_3Bu_2$

4. $\cdot OPO_3Bu_2 + e \longrightarrow [OPO_3Bu_2]^-$

   or

   $\cdot OPO_3Bu_2 + RH \longrightarrow HOPO_3Bu_2 + R\cdot$

5. $2C_4H_8OPO_3Bu_2\cdot \longrightarrow$ Polymer

A typical hydrogen abstraction reaction is represented by reaction (3). Owing to the strong electron affinity of oxygen, the formation of DBP (reaction 4) seems to be more probable by reaction of the phosphate radical with thermal electrons than by hydrogen abstraction. Reaction (5) is a typical dimerization process and it is suggested that other products of the reaction result mostly from reactions of the butyl radicals.

Damage to solvents (such as TBP) may result in emulsifiers or species which form insoluble or non-extractable complexes with uranium and fission products; the first causes entrainment in column operation, the second causes poor uranium yields during stripping or erratic distribution of fission product contamination in both phases. Any degradation product may impair or prevent efficient head-end treatment of fuel elements cooled only a short time[36].

The reaction products found by Burger[22] to be of greatest importance are DBP, MBP, phosphoric acid, and butyl alcohol. Butyl alcohol may act as an unwanted reducing agent, however, butyl alcohol is preferentially distributed in the aqueous phase and therefore is removed in the aqueous waste streams. It is also volatile and is removed during the initial portion of the concentrating of an aqueous product stream.

Phosphoric acid will form complexes with uranium, plutonium, and many of the fission products. At the very low concentrations formed from normal hydrolysis, the effects are probably negligible. DBP and MBP cause more concern. Studies of the behavior of various cations towards a mixture of butyl acid phosphates and dibutyl ether reveal, in general, that the trivalent and tetravalent metals gave precipitates and the divalent metals extracted into the organic phase included uranyl, gold, molybdenum, and chromium. It also has been shown that the same system could be used to extract zirconium from other fission products. More detailed studies have shown that while both DBP and MBP form aqueous insoluble salts, DBP tends to form organic soluble compounds, especially with divalent and tetravalent cations. The solubility is dependent on the organic

solvent used, for example, uranyl dibutyl phosphate, $UO_2(DBP)_2$, is quite soluble in ethers or in a 30% TBP solvent, but only slightly soluble in paraffin hydrocarbons[22].

Since MBP is water soluble, it would be expected to be found primarily in aqueous plant streams and in organic streams in negligible proportions. On this basis most experimental efforts are directed towards DBP[23].

The purity of the diluent or carrier for the TBP solvent used in radiochemical processing is an important factor in the operation of a solvent extraction system. The presence of easily oxidizable substances and aromatics in the diluent tends to lead to the formation of coloured impurities, the formation of emulsions or interfacial "cruds" in the solvent extraction columns, and the retention of fission products in the organic solvent[3].

As with TBP reaction products, one of the more important aspects of diluent degradation is the question of whether the reaction products will form complexes with fission products, thus decreasing decontamination of uranium in the extraction cycle. Some tests by Burger [22] on diluents in the absence of TBP have shown that this may occur. There is however little information on these reactions.

Burger has found that it can generally be said that unless the diluent is chemically pretreated, the decomposition reactions of hydrocarbon diluents are more reactive than TBP, and its reactions may lead to low uranium decontamination and to poor physical behavior unless considerable control is maintained over its composition.

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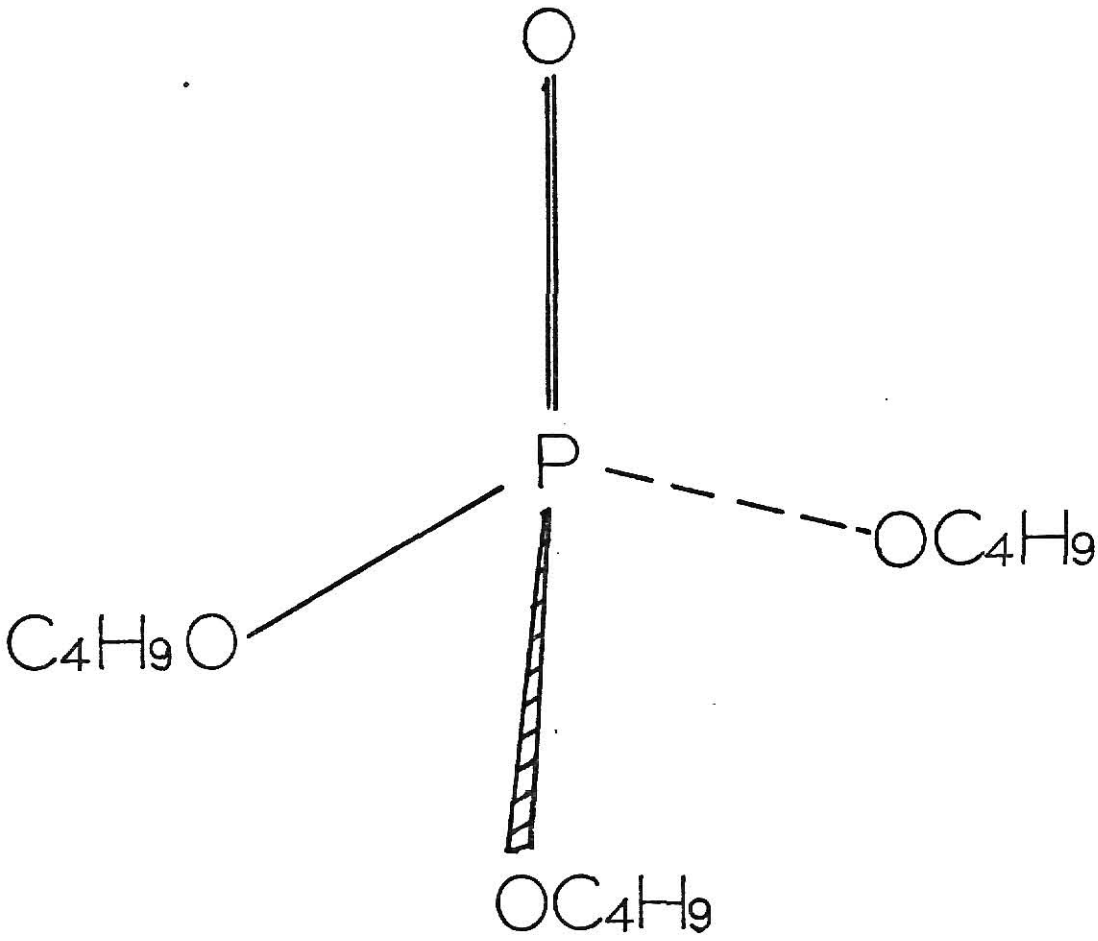

Fig. 1: Molecular Structure of TBP.

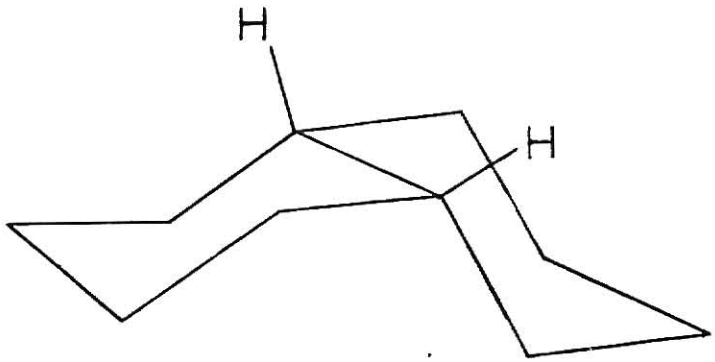

Fig. 2: Molecular Structure of "cis"-decalin.

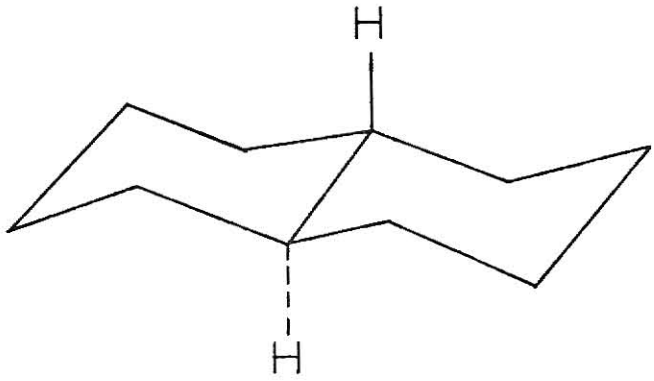

Fig. 3: Molecular Structure of "trans"-decalin.

2. THEORY

The magnitude of radiation damage in chemical processing depends on the concentration and nature of the radioactivity and the length of time the process reagents are exposed to radiation. In reprocessing of reactor fuel containing fission products, the beta-activity generally produces more chemical damage than the gamma since the beta-activity is almost totally absorbed in the process materials. The damage resulting from absorption of alpha-radiation is similar to that resulting from beta, in that absorption of alpha-radiation is complete in a few millimeters. In all three types of radiation, ionization and excitation produce the chemical damage[3].

The passage of radiation through matter initiates various collisional processes which lead to the formation of energetic and transient species. These transient species lose their energy and identity through physical and chemical transformation. The result in a chemically reactive system are stable chemical products formed by such transformations.

Gamma rays emanating from a Co-60 source have two discrete energies whose average is 1.25 MeV. The mechanism by which this radiation is attenuated in liquid organic systems containing mostly hydrogen and carbon atoms is known as the Compton effect. This is basically a photon-electron collision process in which the recoiling electrons acquires part of the energy of the incident photon. The energy spectrum of the recoil electrons can be calculated by the application of the Klein-Nishina formulas. In Co-60 irradiation,

the average energy of the recoil electrons is approximately 0.6 MeV. These electrons mainly interact with the electrons of the medium by coulombic type interactions and cause excitation and ionization of the molecules of the medium[43].

The specificity of ionizing radiation action is manifested in the formation in an irradiated system of a large number of free radicals each with an excess of kinetic energy and of molecules excited to various levels at all temperatures, down to the very lowest. Charged particles (ions) may also play a certain part in the reactions but are usually less important in non-polar organic media.

The chemical individuality of the end products of radiation chemical processes depends primarily on the nature of the active species formed under the action of the radiation. These primary uncharged particles may be divided into three groups[32,44,45] :

1. Free radicals resulting from the recombination of an ion pair showing no tendency for recombining into the initial molecule.

2. Free radicals that are formed as a result of the dissociation of an excited molecule and showing a marked tendency to recombine into the initial molecule, particularly in the liquid state.

3. Excited molecules, which decompose into molecular products or that react with other molecules without dissociation into radicals.

Free radicals may react with non-excited molecules of the substrate, initiating chains, or may enter into various non-chain reactions with each other. The non-chain mechanism is also characteristic of reactions between excited molecules which do not dissociate into radicals[32]. Experimental data by Bach[32] show that the domination of reactions of one type or another in chemical systems that

are subjected to the action of radiation depends on the structure and properties of the irradiated compounds. The general regularities governing this relationship are one of the most important problems of radiation chemistry[32].

In the radiolysis of binary mixtures of organic liquids, it is often found that there is either enhanced or reduced decomposition of one of the components due to the presence of the other. These observed increases or decreases are in excess of those expected from the mixture law and often can be interpreted as an indication that either charge or energy transfer occurs between solvent and solute.

It must be kept in mind that many interactions may occur in mixtures. In addition to charge exchange, energy transfer, and electron capture, radical and ion-molecule reactions can also occur. These effects should be taken into account in arriving at any conclusions about energy or charge transfer. The necessary condition for charge exchange to occur is that the ionization potential of the acceptor must be less than that of the donor. For energy transfer to occur, the acceptor molecule must have a low lying energy level. For electron capture to occur, the specific rate constant for the reaction of the electron with the solute must be large.

A great deal of evidence for charge and energy transfer is based on the mixture law. The mixture law states that energy is initially absorbed in a mixture in proportion to the electron fraction of the components in the mixture. Thus the predicted yield of a product or intermediate is given by the yield of that product or intermediate in the radiolysis of a pure component times the electron fraction

of that component in the mixture.

In the radiolysis of mixtures, it is very difficult to distinquish charge transfer from excitation transfer. Excited molecules can be formed upon ion neutralization and the interaction of the solute with ions can have the same effect as the interaction with excited molecules[46].

Summarizing, it can be concluded that the passage of Co-60 gamma rays in liquid organic systems creates excited molecules, ions and electrons. Several states are possible for the excited molecules and ions can also be formed in an excited state. The reactions of the intermediates which result in the formation of radiolysis products are of great interest in radiation research. The general practice in radiation chemistry is to relate the absorbed energy to the changes brought about on the absorption of energy. The energy that is imparted to matter by ionizing radiation per unit mass of matter is called the absorbed dose. In the case of energy absorption by the Compton effect, the absorbed dose is a function of the number of electrons per unit mass of the material. The chemical effects are denoted in units of "G" which can be defined as the number of changes of a specific type induced in the system for every 100 eV of energy absorbed by the system. The G-value can be mathematically represented as

$$G = \frac{dn}{dE} ,$$

where "n" is the number of molecules formed or destroyed and "E" is the energy absorbed in units of one hundred eV. If the dose rate is constant, the G-value can be represented by

$$G = \frac{1}{I} \frac{dn}{dt} ,$$

where "I" is the energy absorption rate in units of one hundred electron volts per unit time and "t" is the time. The G-value for the stable product, "X", is denoted as G(X) [43].

As such, a model extraction system can be evolved consisting of TBP diluted with a pure paraffinic hydrocarbon, decalin. By varying the TBP electron fraction in this system, the corresponding radiolysis product yields, upon Co-60 irradiation, can be determined and compared for compliance to the mixture law[46]. This comparison along with the relative amounts of radiolysis products produced can be used as an initial investigation as to the feasibility of such a system for the solvent extraction of irradiated nuclear reactor fuel.

3. EXPERIMENTAL PROCEDURE

The preparation of samples and the various analytical equipment used in this research will now be discussed. Appendix B gives a more detailed discussion of equipment operation and the operating procedures used.

Preparation of the System

The overall system to be analyzed consisted of various volume percentages of tributyl phosphate (Matheson, Coleman, and Bell) dissolved in the solvent, decahydranaphthalene (Aldrich Chemical Comp. Inc.; Milwaukee, Wis.). The preparation of the system consisted of purification of the solvent, preparation of the solutions, and degassing of the samples.

Purification of the solvent. By gas chromatograph analysis it was determined that the solvent, decalin, contained quantities of impurities that would cause interference upon analysis of the radiolysis products (see Appendix B). Precipitation of the unsaturated hydrocarbon impurities with a strong acid (H_2SO_4, Fuming-30% SO_3; Fisher Scientific Company) was tried but the chromatographic analysis of the sample showed negligible amounts of the impurities precipitated. It was determined that distillation of the decalin would be necessary to acceptably purify the sample.

The decalin was thus distilled in a packed bed fractionating column (Precise Fractionation Assembly Model A, Todd Scientific Co.). The various distillations performed on the decalin are described

in Appendix B.

Preparation of solutions. The TBP-decalin solutions were prepared in 25 ml. volumetric flasks. Solutions of 5%, 10%, 15%, 20%, and 30% TBP in decalin (by volume) were prepared and these were used for the irradiations.

Degassing of the solutions. Refer to reference [43] for the degassing procedure followed.

Irradiation of the System

The irradiations were done under degassed conditions. The cells used are shown in figure 5. There were four cells total, using two cells for each irradiation. The cells were put in positions "L" and "j" of the sample holder (figure 4). Each cell in these positions should receive the same dose but with the Frick dosimeter, the individual doses could be calculated (see Appendix C). The final radiolysis product concentrations that were determined are the arithmetic averages of the two cells. If one cell measurement was determined faulty due to an experimental mishap, then the irradiations were repeated.

The irradiations were done for time intervals of 10, 20, 30, and 40 hours at a dose rate of .2 watt/liter (Appendix C) on each of the various percentages of TBP solutions. Also a similar set of irradiations was done on pure decalin and pure TBP.

The absorbed dose to each cell was determined by using a Fricke dosimeter[43]. The solutions used for this dosimeter consisted of 10^{-3}M ferric ion, 10^{-3}M NaCl, in 0.8N H_2SO_4 and also 10^{-3}M ferrous ion, 10^{-3}M NaCl in 0.8N H_2SO_4. The ferric ion and the ferrous ion were obtained by using iron wire and ferrous ammonium sulphate,

respectively. (See Appendix C for the dose determination using this dosimeter for each position in the sample holder.)

Estimation of the Radiolytic Products

Certain physiochemical techniques, characterized by high sensitivities and resolutions were used for the analysis of the radiolytic mixtures. The techniques were mass spectrometry and gas chromatography[43].

Mass Spectrometry. This technique is based on the fact that singly charged positive ions trace, in a magnetic field, radial paths corresponding to their masses. A quadrupole type (EAI 250, Ultek) instrument was used for the analysis of the gaseous radiolysis products. By using this instrument, a component with a partial pressure of 10^{-11} torr could be detected at a total pressure of 4×10^{-8} torr. The radiolysis gases were separated from the irradiated solution, measured, and collected by means of a Saunders-Taylor apparatus[43]. All of the mass spectrometric analysis was done by the Chemistry Department.

The gas samples that were analyzed with this technique were those obtained from the various irradiations of pure decalin and pure TBP. The percentages resulting from the ratios of the peak heights from the mass spectrometer output was used to finally determine the amounts of different radiolysis gases that the sample contained.

Gas Chromatography. This is based on the equilibrium properties of a gaseous mixture and the liquid phase with which it is in contact. The differences in the gas-liquid distribution ratios of each of the components in the mixture results in a timewise separation of the components. A recording detector traces out areas

which are resolved in time and are proportional to the abundance of components in the mixture. The apparatus used was a F & M Model 700 (Hewlett Packard) fitted with dual columns and dual hydrogen flame ionization detectors. Zero helium was used as the carrier gas[43,49,50,51]. A 15% JE-30 on Chromosorb, six foot column was operated at temperatures of 150°C, 200°C, 225°C, and 250°C to scan the various components with adequate resolution.

Once the major liquid radiolysis products were determined, the resulting chromatograms with the best resolution were analyzed. This analysis consisted of measuring the peak areas with a polar planimeter[52,53].

Calibration of the gas chromatograph to these products was done by acquiring these products in pure form, preparing numerous solutions varying in concentration, and obtaining a chromatogram of each solution corresponding to a known concentration. (Note: very pure decalin was used as a solvent for all calibrations.)

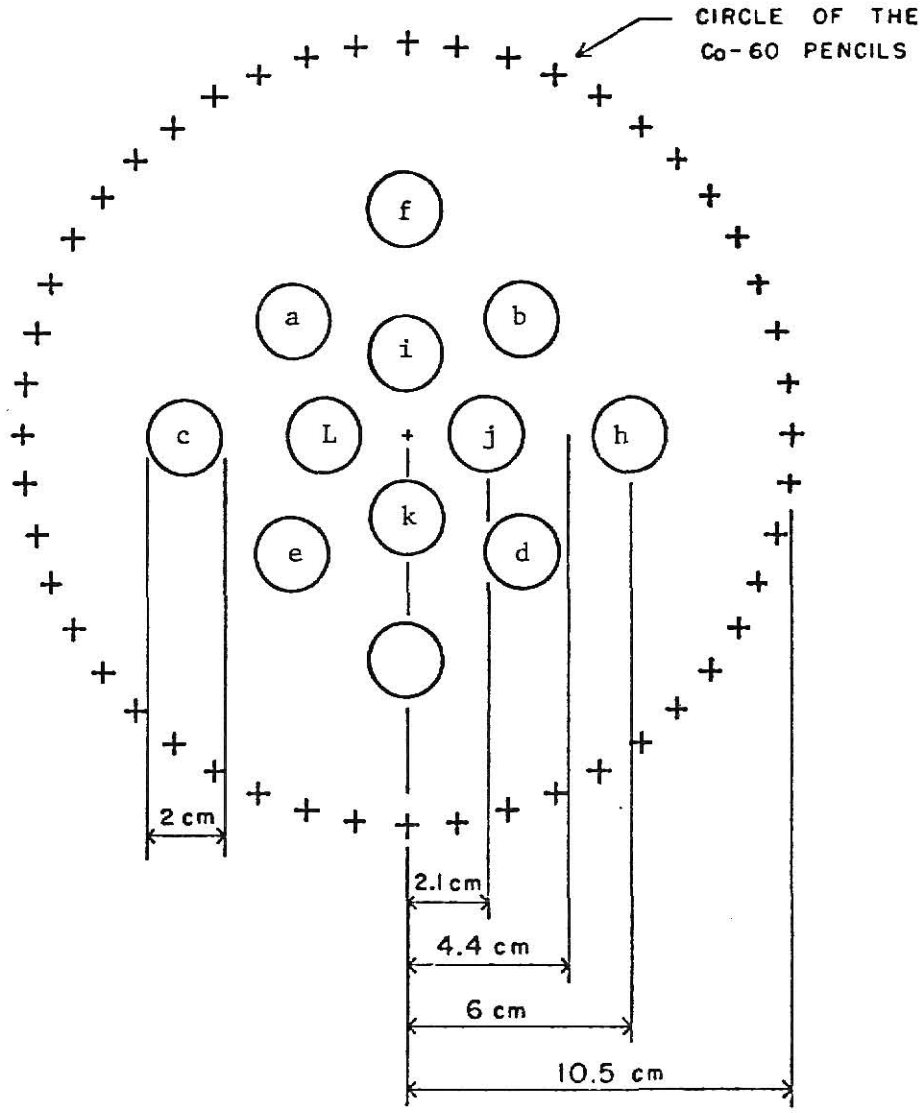

Fig. 4: Schematic view of the position of the sample cells in the sample holder[43].

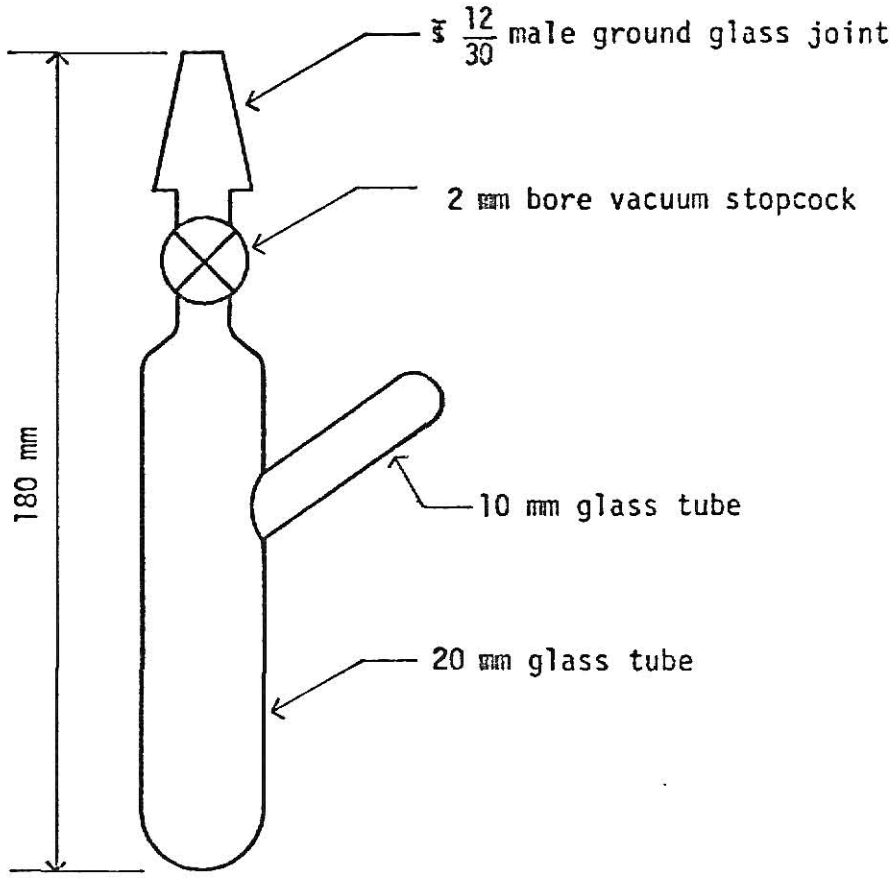

Fig. 5: Sketch of the irradiation cell[43].

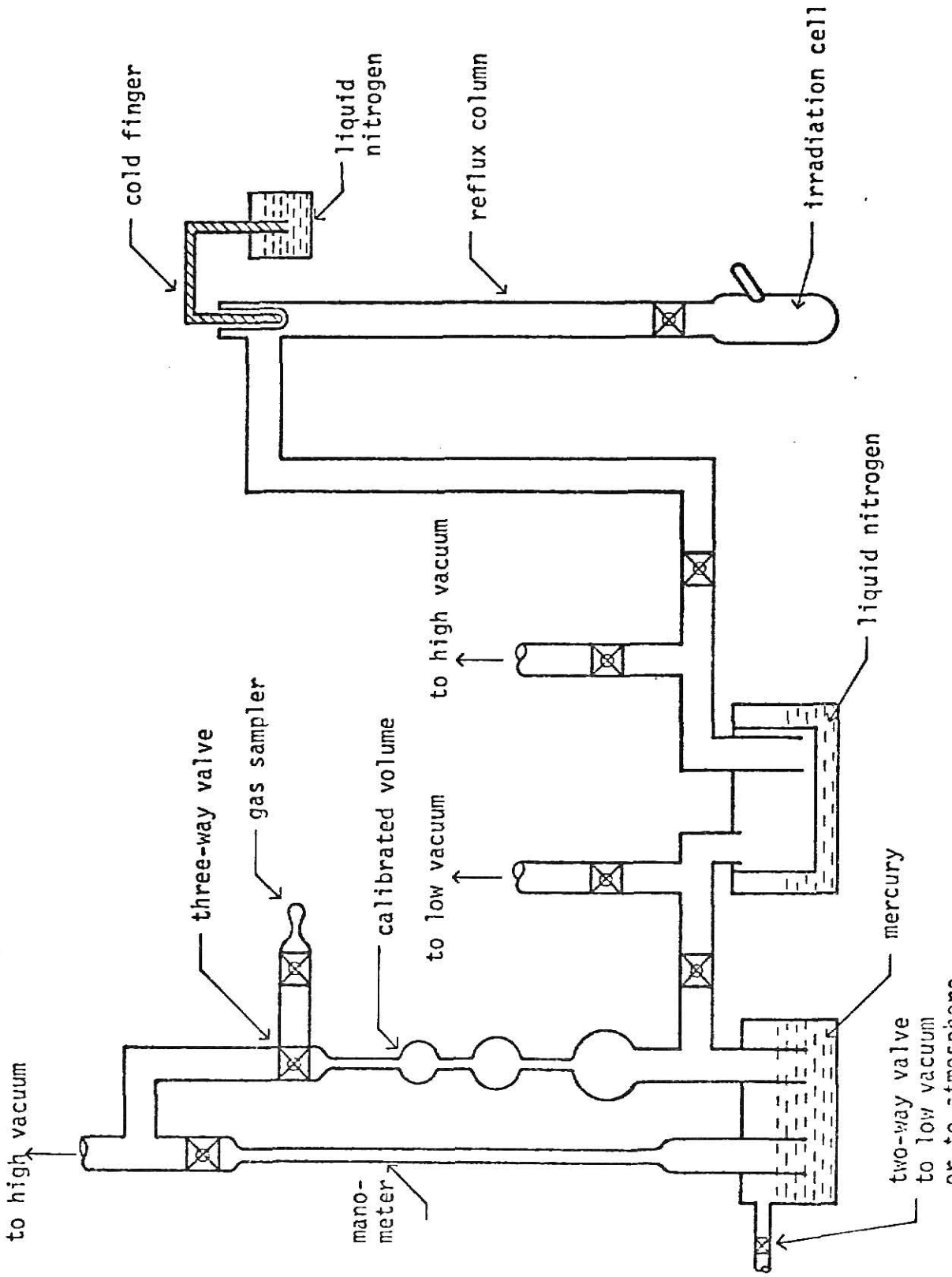

Fig. 6: Schematic view of Saunders-Taylor apparatus[43].

4. RESULTS AND CONCLUSIONS

American experience of large scale nuclear fuel extraction plants has revealed that the useful life of a hydrocarbon-TBP solvent system is limited by the formation of unidentified compounds by the interaction of the hydrocarbon with radiation. This may also by enhanced by the interaction of nitric or nitrous acids with the hydrocarbon under the influence of radiation. Unlike the decomposition products of TBP, these degradation products are not removed by aqueous alkalies in the solvent wash systems, but will slowly accumulate and reduce the performance of the solvent to a point where it has to be discarded and replaced by a fresh charge. These degraded solvents show poor phase separation, decreased mass transfer coefficients for uranium, retention of fission products in the solvent after aqueous alkaline washing and leakage of fission products into the uranium and plutonium streams[54].

The investigations done in this research were based only on the Co-60 gamma radiation effects on such a TBP-hydrocarbon system. The effects of oxygen, nitric acid, or nitrous acid were not considered. The radiation doses used varied between 2 to 8 watt-hr/liter. This is close to the expected radiation dose of 10 watt-hr/liter[55] for conventional short-cooled fuels.

The TBP-hydrocarbon system investigated consisted of various volume percentages of TBP diluted with a pure paraffinic hydrocarbon, decahydranaphthalene (decalin). This is a representative system since the composition of most conventional diluents used in fuel

reprocessing plants consist almost entirely of paraffinic compounds[27]. For example, the analysis of the composition of a popular diluent, Ultrasene, was found to contain; 40% normal paraffins, 57% branched and cyclic paraffins, 3% aromatics, and less than 0.1% olefins[56].

The liquid radiolysis products produced upon irradiating various fractions of TBP-diluent systems were determined by gas-liquid chromatography. DBP, MBP, and a $C_{10}H_{16}$ compound were the main constituents of the radiolysis products that could be observed. The resulting yields of these products were determined at various volume fractions of TBP in the mixture and are given in table I.

The gaseous products, non-condensible at $77^{o}K$, were determined from a mass spectrometer analysis of the gases produced upon irradiation of the pure samples. Analysis of decalin showed H_2 to be the only radiolysis product, whereas the radiolysis products from pure TBP were H_2 and methane. The yields of these gases for pure decalin and TBP as functions of dose are shown in figure 7. Table I also contains the total gas yields produced upon irradiation of various volume % fractions of TBP. (Note: The mixtures ranged only to 30% TBP because this is the volume percentage used in most Purex processes[10].)

These resulting yields for the radiolysis products were plotted as a function of the TBP electron fraction as shown in figures 8 through 15. The purpose of these plots was to determine if the mixture law dictated the behavior of the yields.

This law says that the yield of product P in a mixture of A and B should be given by the folowing equation

$$G(P) = G_A(P)\varepsilon_A + G_B(P)\varepsilon_B$$

where ε_A and ε_B are the respective electron fractions of A and B (this equation is represented by the solid line in figures 8 to 15). Deviations from this mixture law can indicate that transfer of either energy or charge has occurred[46]. By analysis of figures 8 to 11, it can be seen that a least squares fit of the yields of the $C_{10}H_{16}$ compound is in accord with the mixture law with a fairly small standard deviation for each plot. It can thus be inferred that the radiolytic production of this compound in the mixture is independent of the TBP fraction. On the other hand, the total gas yield deviates from the mixture law line, indicating that there is an interaction between decalin and TBP. This interaction may be energy transfer or electron or free radical scavenging by TBP.

Although there is an uncertainty in the total acid yields, it still is possible to say that there is a significant deviation from the mixture law. The measured yields of total acid are three to five times larger than the predicted yields (see figures 12 to 15). A G-value of 4.90 molecules/100 eV was assumed for TBP (ε_A=1) in the ten and twenty hour irradiations. Sensitized decomposition of TBP is the result of interaction between decalin and TBP.

It is convenient to describe the processes leading to the radiolytic products in terms of a kinetic sequence. The following assumptions are made:

a) the components in a mixture absorb energy proportional to their electron fraction;

b) the solute reduces the hydrogen yield by interferring with some intermediate;

c) the solute is itself activated as a result of this reaction and behaves as if it had been primarily activated.

On this basis, the following kinetic sequence is proposed for pure decalin, and then the effect of TBP will be considered,

$$C_{10}H_{18} \xrightarrow{\gamma} C_{10}H_{18}^{+} + e^{-} \quad (1)$$

$$\xrightarrow{\gamma} C_{10}H_{18}^{*} \quad (2)$$

$$C_{10}H_{18}^{+} + e^{-} \longrightarrow C_{10}H_{18}^{*} \quad (3)$$

$$C_{10}H_{18}^{*} \longrightarrow C_{10}H_{16} + H_2 \quad (4)$$

$$\longrightarrow C_{10}H_{17}\cdot + H\cdot \quad (5)$$

$$C_{10}H_{17}\cdot + H\cdot \longrightarrow C_{10}H_{18} \quad (6)$$

$$C_{10}H_{18} + H\cdot \longrightarrow C_{10}H_{17}\cdot + H_2 \quad (7)$$

$$C_{10}H_{17}\cdot + C_{10}H_{17}\cdot \longrightarrow C_{10}H_{17}\text{-}C_{10}H_{17} \quad (8)$$

$$\longrightarrow C_{10}H_{16} + C_{10}H_{18} \quad (9)$$

$$C_{10}H_{16} + H\cdot \longrightarrow C_{10}H_{17}\cdot \quad (10)$$

where $C_{10}H_{18}^{*}$ is some electronically excited state of decalin. Reaction (8) is included in the sequence even though the dimer was not observed in the gas chromatographic analysis. If the rate constant for reaction (8) is greater than the rate constant for reaction (9), this could explain the large difference between $G(H_2)$ and $G(C_{10}H_{16})$ observed in the radiolysis of decalin.

The addition of TBP would change the reaction sequence. The following reactions could explain the deviation from the mixture law observed with the total gas and total acid yields.

$$TBP + e^{-} \longrightarrow TBP^{-} \quad (11)$$

$$TBP^{-} + C_{10}H_{18}^{+} \longrightarrow TBP + C_{10}H_{18} \quad (12)$$

$$TBP^{-} \longrightarrow DBP^{-} + C_4H_9\cdot \quad (13)$$

$$C_4H_9\cdot + H\cdot \longrightarrow C_4H_{10} \quad (14)$$

$$DBP^{-} + C_{10}H_{18}^{+} \longrightarrow DBPH + C_{10}H_{17}\cdot \quad (15)$$

$$DBPH + e^- \longrightarrow DBPH^- \quad (16)$$

$$DBPH^- \longrightarrow MBP^- + C_4H_9\cdot \quad (17)$$

$$MBP^- + C_{10}H_{18}^+ \longrightarrow MBPH + C_{10}H_{17}\cdot \quad (18)$$

$$TBP + H\cdot \longrightarrow \cdot C_4H_8DBP + H_2 \quad (19)$$

$$H\cdot + \cdot C_4H_8DBP \longrightarrow TBP \quad (20)$$

Reaction (11) and eventually reaction (16) would compete with reaction (3). This would result in a decrease in the production of molecular hydrogen from reaction (4) and hydrogen atoms plus the $C_{10}H_{17}\cdot$ radical from reaction (5). Reaction (14) would compete with reactions (6), (7), and (10), decreasing the yield of molecular hydrogen and $C_{10}H_{17}\cdot$ free radicals. Reactions (15) and (18) could compensate for the decrease in $C_{10}H_{17}\cdot$ concentration, so that the yield of $C_{10}H_{16}$ would be unaffected or possibly increase at low concentration of TBP. Reactions (19) and (20) would also compete with reactions (6), (7), and (10) and may also have the effect of lowering the C_4H_{10} produced by reaction (14). It is plausible that TBP could act as an electron scavenger since it contains oxygen atoms which have a high affinity for electrons[57].

Various investigations have been done on the radiolysis of pure TBP and TBP-diluent systems. It may be advantages to consider some of these as a comparison to the results obtained in this investigation. Table IV lists the yields of the various radiolysis products of pure TBP irradiation. From these values, it can be seen that the resulting yields deviate a great deal. No actual error in these measurements could be found in the various references cited. In this work the error for these readings was found to be fairly large (Appendix D) with a value that will put the

calculated yields within the range of previous investigations.

It is also interesting to compare the yields of various TBP-diluent systems that certain investigators have studied. Table V lists some gas and DBP yields for various systems. It should be noted that a value of G(dodecane) = 3.8 molecules/100 eV is listed in this table. Dodecane is a normal paraffin and the value of 3.8 compares well with the value of 4.3 that was obtained in this work using a cyclic paraffin, decalin, at comparative dose levels. In summary, the values obtained in this work are in agreement with other work done under somewhat similar conditions.

In radiochemical processing, the interest is in the effects of radiation damage on the recovery of fissile or fertile material and on the decontamination of this material from fission products[4]. This decontamination is due mainly to the amounts of radiolysis products that may be chemically reactive to the preferentially extracted materials and also to fission products.

A study has been made at Savannah River of solvent-extraction decontamination performance in relation to other process variables. It was concluded that solvent quality, as indicated by activity level, is the principal variable affecting process performance, and with good solvent quality, decontamination approaches a limiting factor that can represent the ultimate efficiency that is attainable with the given process and equipment. With a given solvent treatment system, the quality of the treated solvent is simply the result of an equilibrium established between the rate of damage done to the input solvent and the rate of removal of degradation products in the solvent treatment operation[28].

The evaluation of the behavior of a diluent on a laboratory scale can be performed only by using a comparative criterion based on information that is obtained from rigorously controlled experiments[31]. Burger[22] has found that the chemical reactions of the diluents become, to a large extent, the reactions of the trace constituents. Double bonds are readily available sites for oxidation or for addition of radio-iodine. This latter reaction is very undesirable in that the product is very difficult to remove from the solvent. Since nitric acid is usually present in most processing systems, a low olefinic content is usually acceptable in order to avoid nitration reactions which occur with most hydrocarbon diluents and are responsible for the yellow color which develops on continued use of the solvent. Most products from these reactions are fairly successfully removed by the alkaline washing processes used to remove DBP and MBP from the solvent[22].

The solutions examined in this research indicate a small olefin production which varies little with dose or the electron fraction of TBP. The comparison to the radiolysis yield of unsaturated hydrocarbons in dodecane of 1.85 molecules/100 eV[71], shows a marked difference which may be highly advantages if the olefin produced in decalin irradiation can easily be removed in the solvent wash cycle of an extraction process.

Chemical and irradiation effects on the TBP complexing agent are of major importance concerning the problem of solvent deterioration. Decomposition of TBP to DBP and MBP can result in the production of a variety of salts whose solubilities in the aqueous phase may be limited, and which also may have other effects on extraction processes. Oak Ridge Laboratory has measured solubilities of the

dibutyl and monobutyl phosphates of uranium and ferric iron in typical extraction process solutions which have been equilibrated with the corresponding immiscible phases. These resulting solubility data confirm the tendency for TBP degradation products to retain uranium in the organic phase. These compounds appeared to be interface seekers when their solubilities are exceeded, since dense layers were formed in the solutions[24].

In the use of TBP-hydrocarbon diluent mixtures for the solvent extraction of solutions of irradiated fuel, it has been observed that the production of DBP is an undesirable process because DBP forms stable complexes with fission product zirconium which are soluble in the organic phase. If the concentration of DBP is sufficiently high, insoluble compounds, including compounds of uranium, may be formed in the process streams. The results of these effects are poor decontamination and product losses[39].

Retention of plutonium and uranium by degraded solvents is largely attributed to the presence of monobutyl and dibutyl phosphates[72]. These products are known to have a marked effect on the chemistry of plutonium. The DBP is known for its strong complexing action with Pu(IV), and MBP for its tendency to form a precipitate with Pu(IV) [73].

The sensitized production of DBP and MBP may have a deleterious effect on an extraction process. It has been shown that the TBP-decalin system does result in an increased total acid yield under the influence of gamma radiation. At long contact times in the extraction contactors, this added effect may decrease decontamination of the solvent in the wash cycle. Once these radiolysis products

reach the wash cycle, if they are uncomplexed, they are easily removed which may tend to indicate that the basic consideration for this sensitized production would be the contact time with the irradiated fuel.

Operative conditions which have been chosen for the degradation of a mixture of hydrocarbons have sometimes a great influence on the results. Therefore it is not always possible to judge their reliability for use in a solvent extraction system. For example, the irradiation performed in the presence or in the absence of the extractant, in open or closed vessels, with or without the presence of nitric acid, can lead to erroneous evaluations on the behavior of the studied diluents. Therefore it seems that the most reliable results can only be obtained in experimental conditions which are very close to the process ones, implying a recycling of the solvent and interposing alkaline washing stages in order to avoid accumulation of radiolysis products[31].

In summary, the gamma irradiation of the TBP-decalin system produced very little olefinic type compounds in comparison to the production of olefinic compounds that are produced in the irradiation of dodecane (a diluent used commercially for solvent extraction processing of irradiated fuel). In contrast, the production of the dibutyl and monobutyl phosphates were sensitized in the presence of the decalin diluent. This could result in DBP complexing with zirconium, plutonium, or uranium in a reprocessing process with the result being losses of desired products in the process streams and poor solvent decontamination in the wash cycles. In comparison to a TBP-dodecane system with yields listed in table V, this sensitized effect seems also to be present in this system since the DBP

yields are consistent with the fraction of TBP in solution. Due to the uncertainties in the total DBP and MBP yields in this work, the values determined cannot be directly compared to the values listed in table V. The gas yields in the two systems are similar such that the effects on the extraction system would not differ.

Table I.

Radiolysis Product Yields of the TBP-Decalin System

Dose {watt-hr/liter}	Volume %TBP	G{molecules/100 eV}		
		gas {total}	$C_{10}H_{16}$	Total acid {MBP + DBP}
2	0	4.26	0.11	0.00
	5	2.45	0.27	2.31
	10	3.78	0.22	5.08
	15	3.72	0.17	2.24
	20	3.08	0.26	2.84
	30	3.30	0.16	3.76
	100	2.42	0.00	----
4	0	4.27	0.16	0.00
	5	3.48	0.24	1.65
	10	3.41	0.21	1.67
	15	3.36	0.16	3.93
	20	3.15	0.21	3.19
	30	4.09	0.14	3.72
	100	2.26	0.00	----
6	0	3.69	0.21	0.00
	5	3.46	0.20	2.20
	10	3.53	0.20	3.03
	15	3.29	0.15	4.19
	20	3.07	0.15	2.62
	30	3.04	0.12	2.10
	100	2.23	0.00	4.79†
8	0	3.84	0.25	0.00
	5	3.48	0.16	2.96
	10	3.38	0.19	2.80
	15	3.23	0.14	4.08
	20	3.05	0.10	1.83
	30	3.12	0.10	3.91
	100	2.07	0.00	4.93†

† determined from weight calibration

Table II.

Mass spectrometer analysis of the radiolysis gas of pure TBP†

Dose {watt-hr/liter}	$\%H_2$	$\%CH_4$	St. dev. {%}	G{molecules/100 eV}	
				H_2	CH_4
2	0.920	0.080	0.017	2.23	0.19
4	0.913	0.087	0.002	2.06	0.20
6	0.928	0.062	0.006	2.09	0.14
8	0.924	0.076	0.001	1.91	0.16

† the analysis of pure decalin showed H_2 the only product

Table III.

Radiolysis product concentrations produced from irradiations
(Dose rate = 0.2 watt/liter)

Volume %TBP	Irradiation time{hours}	$C_{10}H_{16}$ $\{10^{-4}M\}$	DBP $\{10^{-3}M\}$	MBP $\{10^{-3}M\}$	Total gas $\{10^{-5}$ moles$\}$
0	10	0.64	0.00	0.00	0.55
	20	2.18	0.00	0.00	0.97
	30	4.70	0.00	0.00	1.45
	40	5.99	0.00	0.00	2.00
5	10	2.11	1.47	0.04	0.32
	20	2.95	1.38	0.77	0.91
	30	4.53	3.99	0.33	1.36
	40	4.34	5.59	2.13	1.83
10	10	2.16	1.75	1.58	0.50
	20	2.46	2.19	3.83	0.89
	30	3.86	5.76	0.22	1.39
	40	6.23	3.71	3.64	1.78
15	10	1.75	0.78	0.70	0.49
	20	2.97	2.58	2.61	0.89
	30	3.19	5.59	2.72	1.30
	40	4.39	5.24	5.56	1.71
20	10	2.77	0.78	1.10	0.41
	20	3.03	2.42	1.80	0.83
	30	3.63	3.69	1.51	1.22
	40	4.20	2.86	1.99	1.62
30	10	2.32	2.52	----	0.44
	20	3.05	3.87	1.10	1.09
	30	3.23	3.74	0.48	1.22
	40	4.12	7.92	2.54	1.67
100†	10	0.00	----	----	0.34
	20	0.00	----	----	0.64
	30	0.00	10.18	----	0.95
	40	0.00	13.95	----	1.17

† weight calibration used

Table IV.

Radiolysis yields of pure TBP

Type of Radiation	Dose {watt-hr/liter}	G{molecules/100eV} Gas	DBP	MBP	Reference
Co-60	6 to 60	2.7	2.1		[41]
Co-60	6 to 60	2.54	2.64		[41]
Co-60	6 to 60		2.35		[41]
Co-60	6 to 60		2.4		[41]
Co-60	6 to 60	1.5	1.86		[41]
Co-60	7	1.8			[35]
Co-60	400	2.2			[2]
Co-60	250		2.2		[18]
Co-60	520	1.34	2.52	0.30	[61]
Co-60	300	1.87		0.39	[62]
Co-60	8	2.07	4.93		[this work]
Co-60	6	2.23	4.79		[this work]
Electrons, 1MeV	6 to 60	1.1	1.67		[41]
Electrons, 1MeV	6 to 60	1.85	1.76		[41]
Electrons, 1MeV	1230	1.46	1.79		[63]
Electrons, 1MeV	467	1.28	0.18	2.09	[64]
Electrons, 1MeV	190	2.07	1.37	0.03	[65]
Electrons, 1MeV	1420	2.44	0.39	2.25	[66]
Electrons, 1MeV	1420	2.44		0.39	[67]
Electrons, 1.66MeV	6 to 60	3.1	2.58		[41]
Electrons, 1.66MeV	386	3.10	2.78	0.065	[42]
Electrons, 1.66MeV	1500	2.72	2.44	0.14	[42]
Uranium slugs(irrad.)			4.5		[68]

Table V.

Yields of Various Diluent Systems

Material Irradiated	Dose {watt-hr/liter}	G(X) Gas	G(X) DBP	Reference
Amsco 125-82	467	1.45		[64]
Solvesso-100	467	0.22		[64]
Dodecane	6 to 60	3.8		[40]
25%TBP-dodecane	6 to 60	2.7	1.2	[40]
46%TBP-dodecane	6 to 60	2.8	1.6	[40]
50%TBP-dodecane	6 to 60	2.8	1.3	[40]
50%TBP-toluene	6 to 60	0.34	0.44	[40]
50%TBP-benzene	6 to 60	0.26	0.31	[40]
50%TBP-cumene	6 to 60	0.44	0.65	[40]
50%TBP-mesitylene	6 to 60	0.52	0.46	[40]
50%TBP-cymene	6 to 60	0.53	0.50	[40]
50%TBP-isopropyldiphenyl	6 to 60	0.19	0.22	[40]

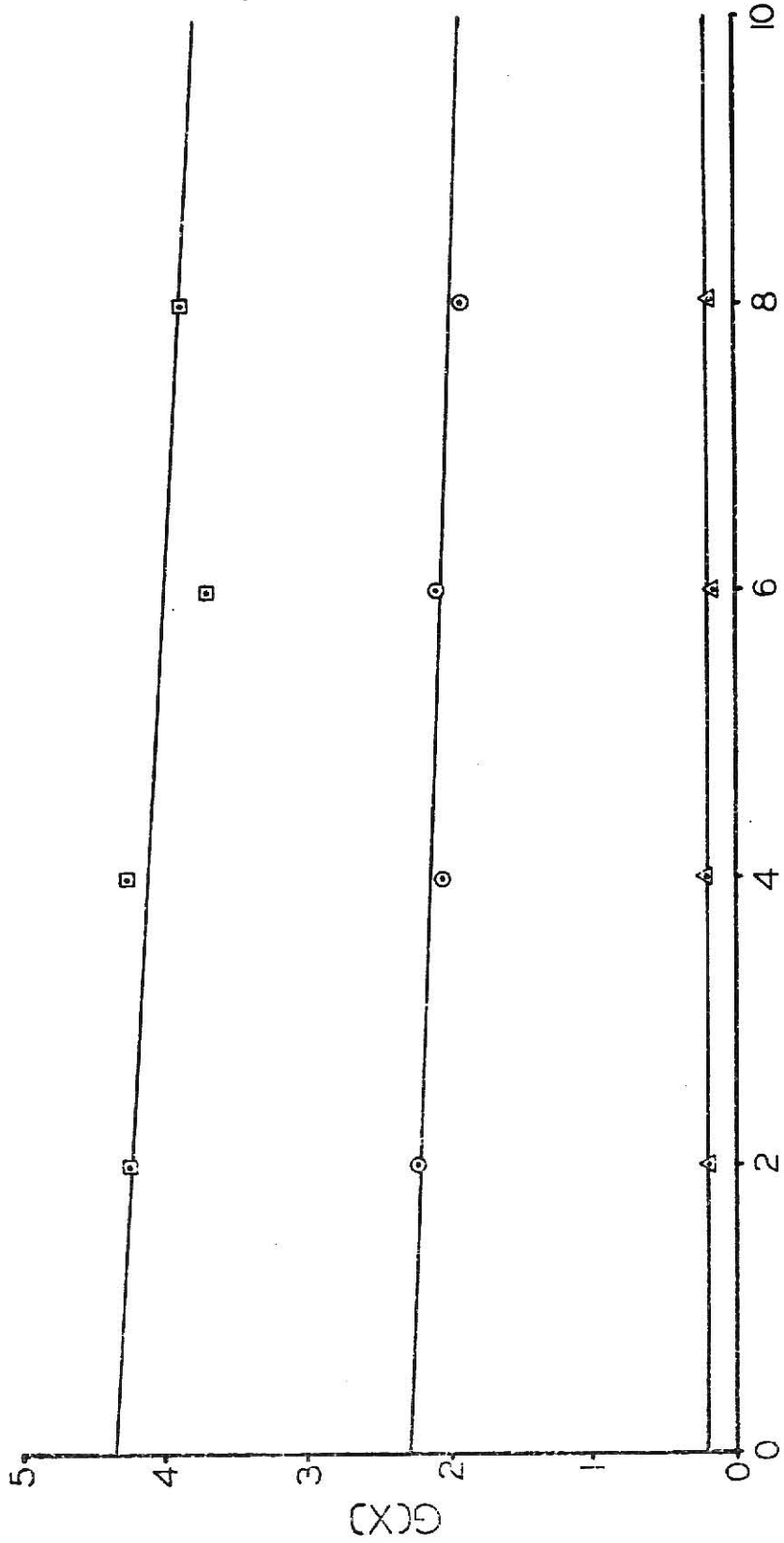

Fig. 7: Variation of G(X) as a Function of Dose
□, $G(H_2)$ -decalin; ○, $G(H_2)$ -TBP; △, $G(CH_4)$ -TBP

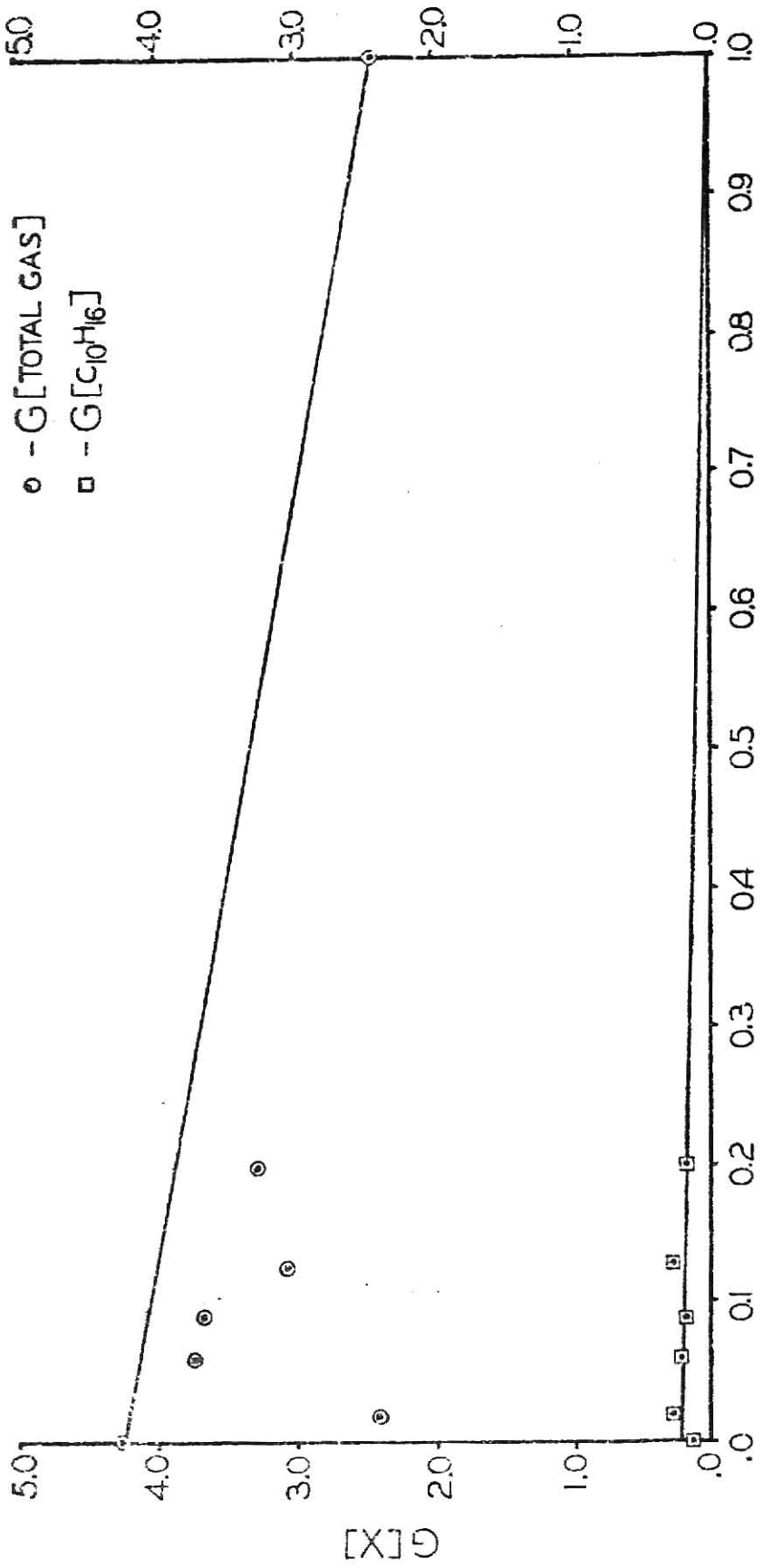

Fig. 8: Variation of G(X) with Electron Fraction of TBP
Decalin + TBP. Absorbed Dose, 2 watt-hr/liter.

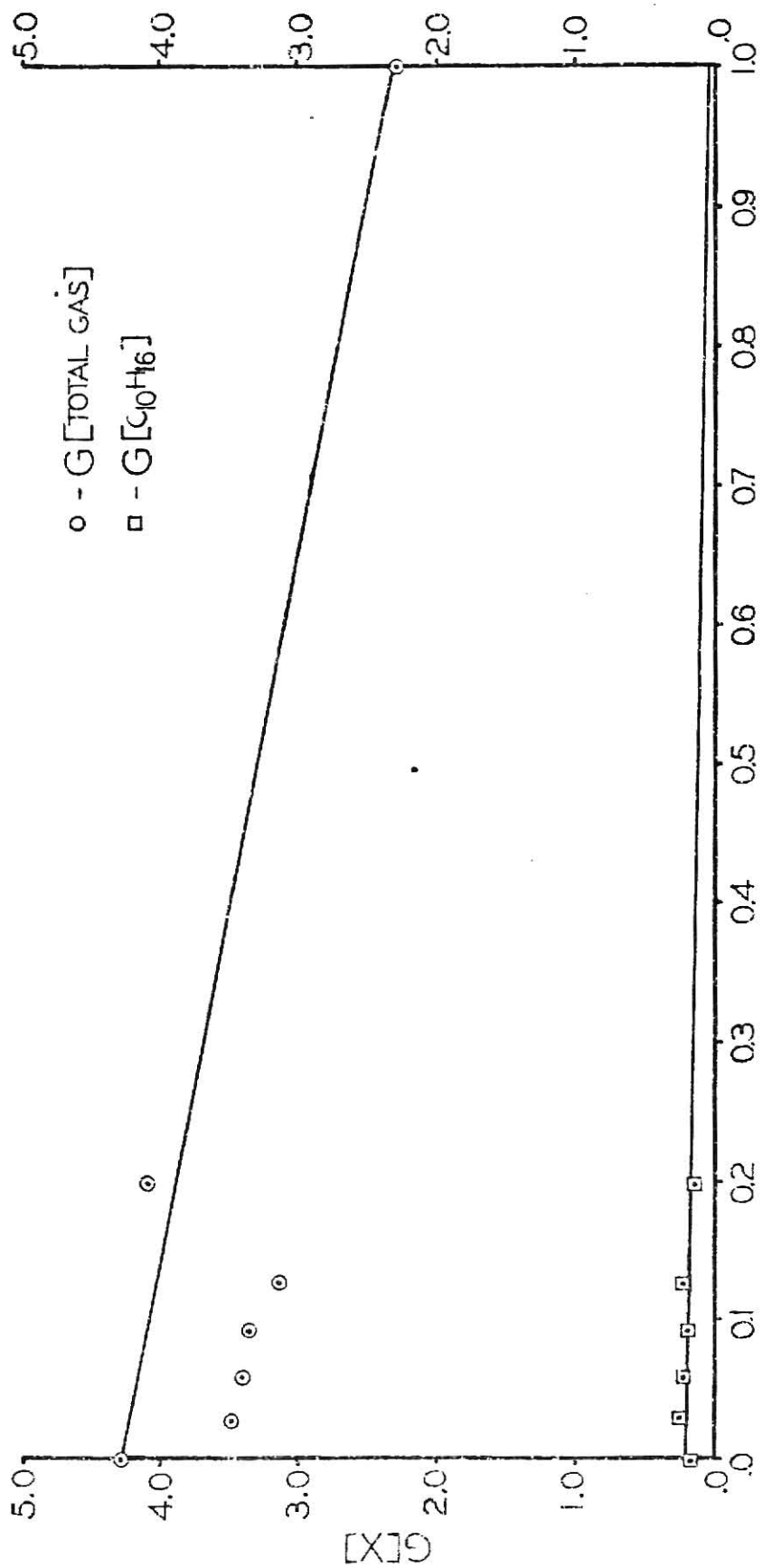

Fig. 9: Variation of G(X) with Electron Fraction of TBP
Decalin + TBP. Absorbed Dose, 4 watt-hr/liter.

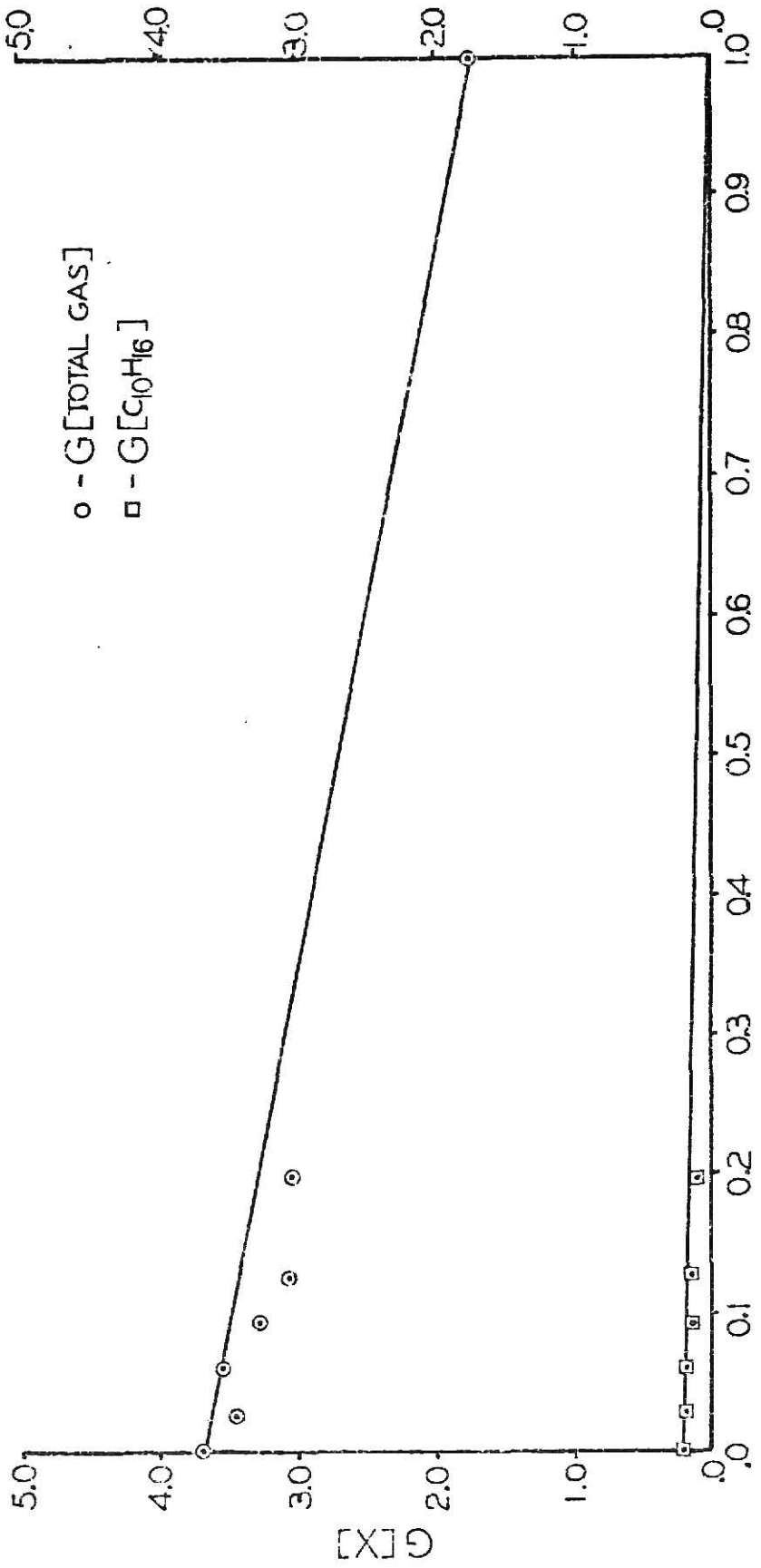

Fig. 10: Variation of G(X) with Electron Fraction of TBP
Decalin + TBP. Absorbed Dose, 6 watt-hr/liter.

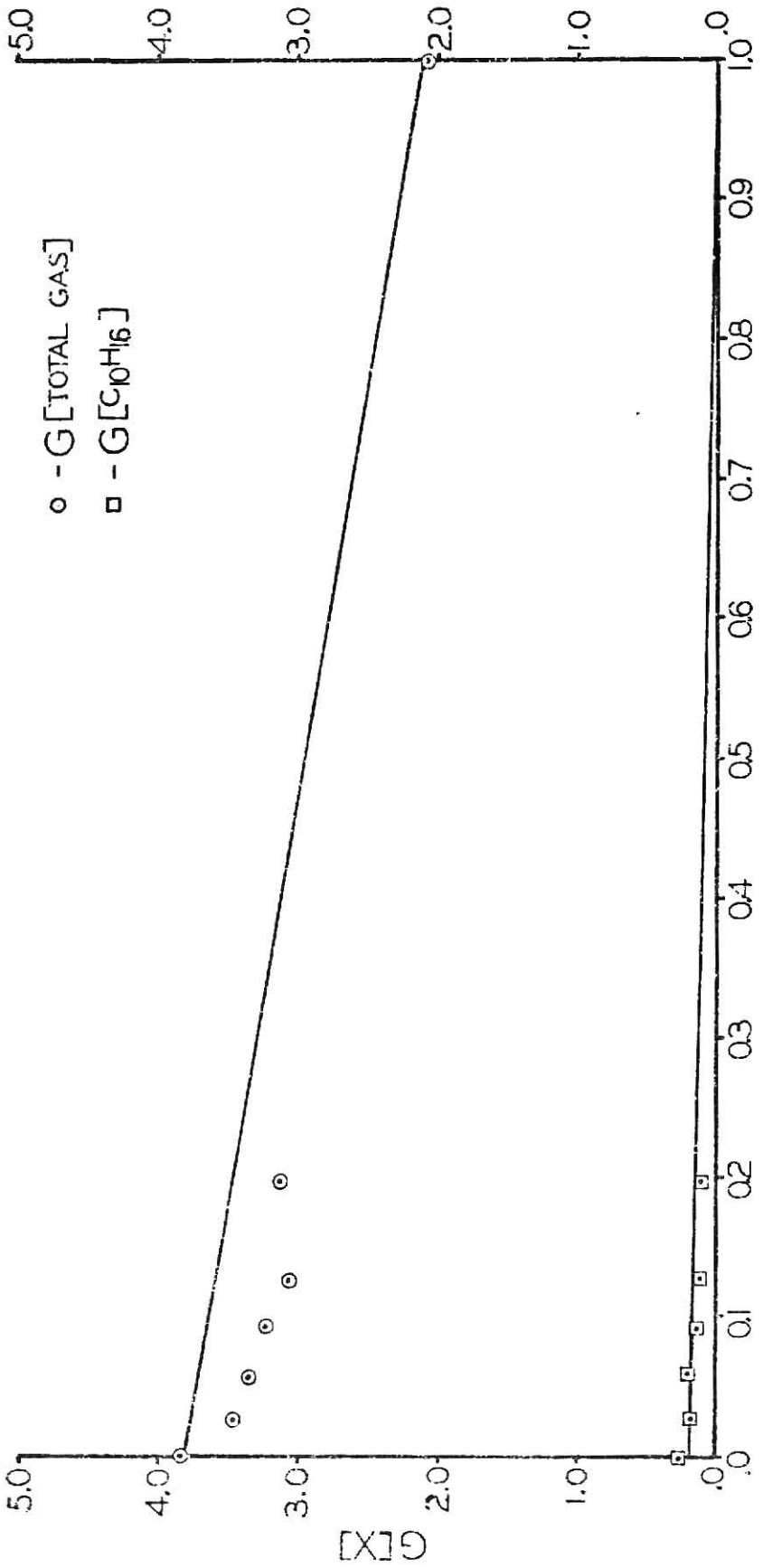

Fig. 11: Variation of G(X) with Electron Fraction of TBP Decalin + TBP. Absorbed Dose, 8 watt-hr/liter.

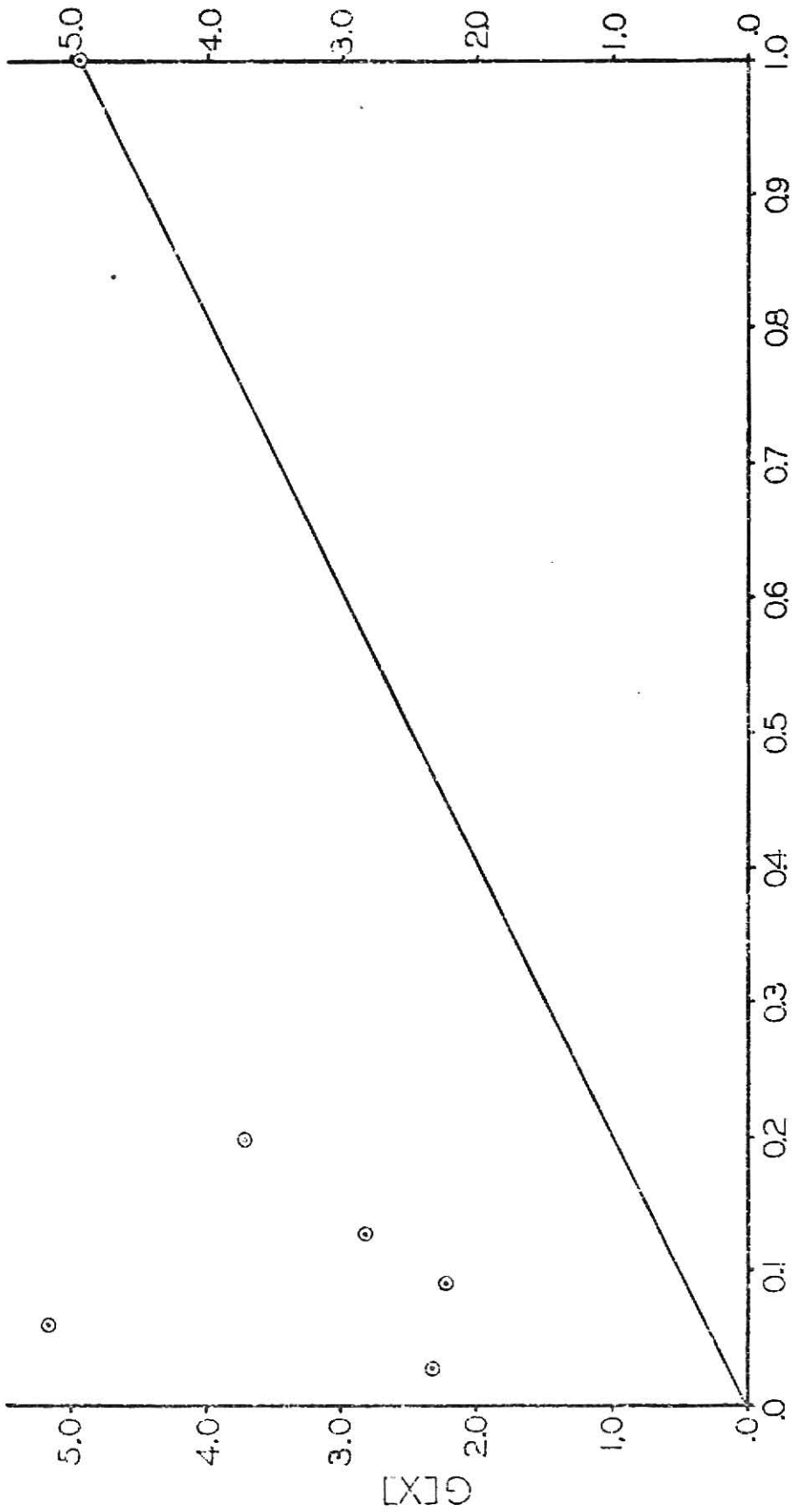

Fig. 12: Variation of G(X) with Electron Fraction of TBP
Decalin + TBP. Absorbed Dose, 2 watt-hr/liter
G(X) = G(MBP + DBP).

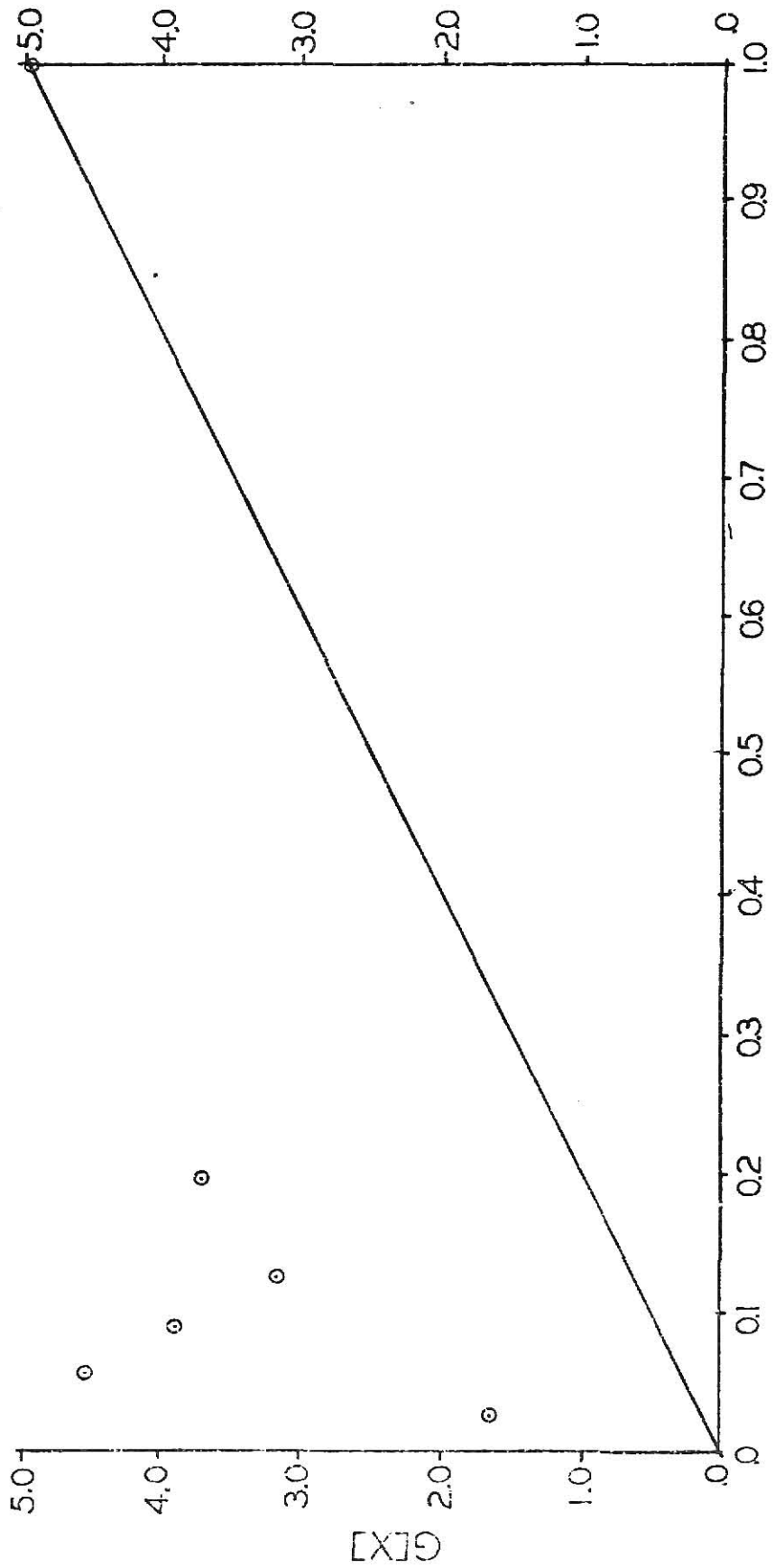

Fig. 13: Variation of G(X) with Electron Fraction of TBP
Decalin + TBP. Absorbed Dose, 4 watt-hr/liter.
G(X) = G(MBP + DBP).

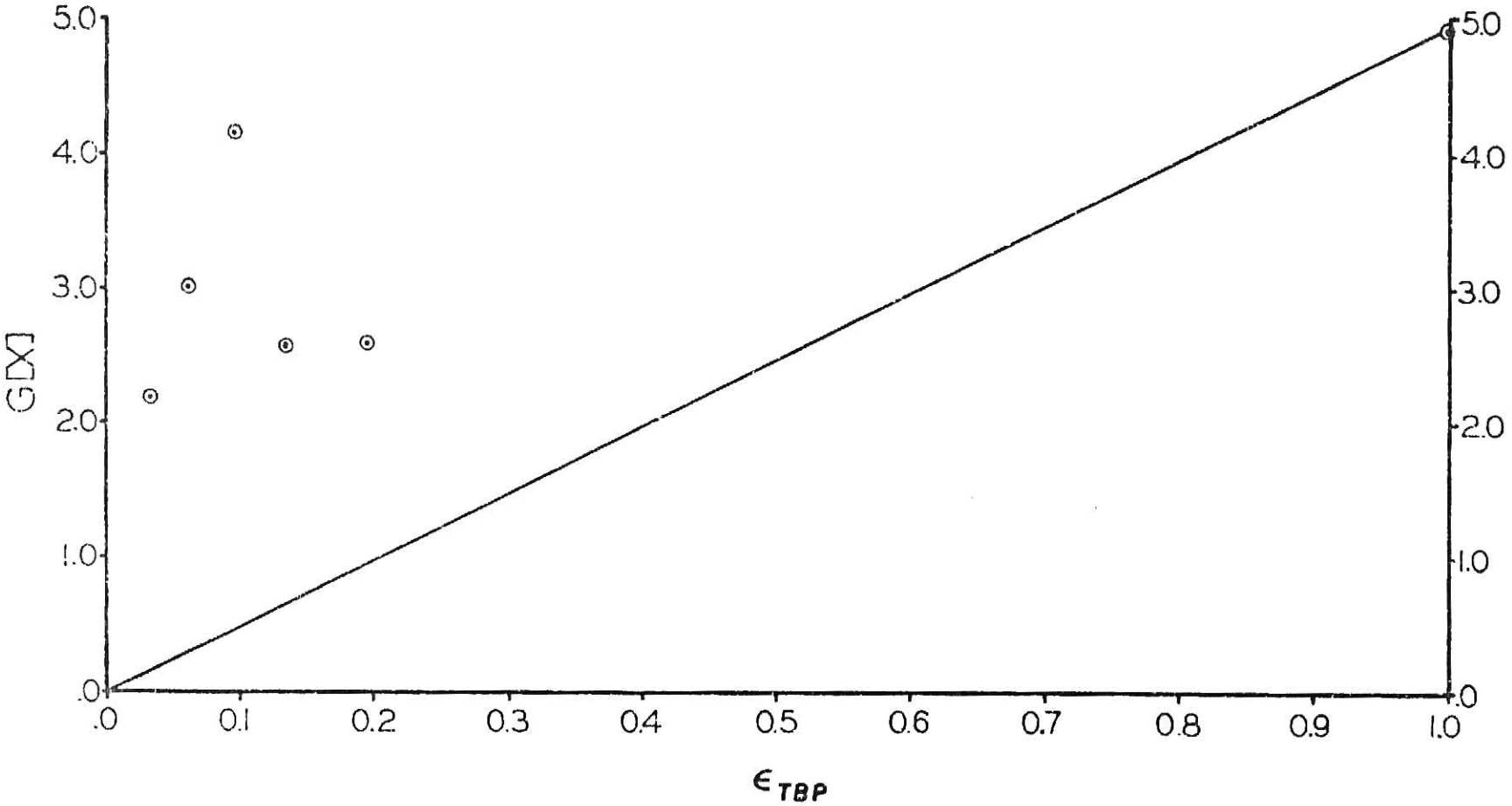

Fig. 14: Variation of G(X) with Electron Fraction of TBP Decalin + TBP. Absorbed Dose, 6 watt-hr/liter. G(X) = G(MBP + DBP).

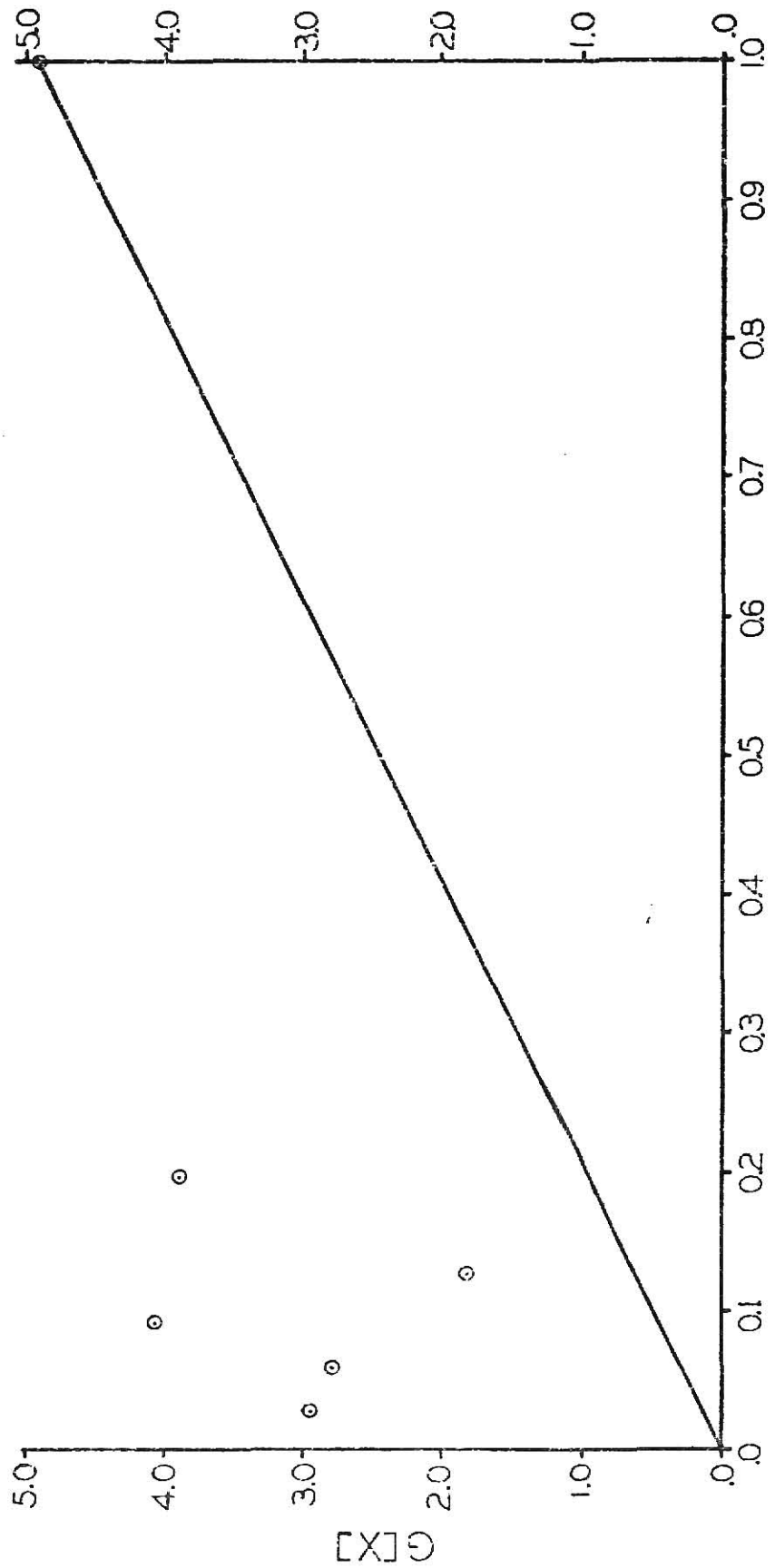

Fig. 15: Variation of G(X) with Electron Fraction of TBP
Decalin + TBP. Absorbed Dose, 8 watt-hr/liter.
G(X) = G(MBP + DBP).

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7. APPENDICES

APPENDIX A.

Some Physical Properties of the TBP-Decalin System.

Table A-I.

Physical properties of butyl phosphates

Property	TBP	DBP	MBP
†molecular weight	263.3	210.2	154.1
†density (25°C)	0.976	1.065	1.220
†viscosity (mp, 25°C)	33	520	4300
††boiling pt. (1 atm.)	289°C		
††solubility in water (gm/liter)	0.2		

† reference [23]
†† reference [32]

Table A-II.

Physical properties of decalin†

Property	"cis-"	"trans-"
melting point	-43.3°C	-31.5°C
boiling point	194 °C	185 °C
specific gravity D_4^{20}	0.895	0.870
molecular heat of combustion (kg-cal)	1502.4	1500.3

† reference [33]

Table A-III.

Densities of TBP-decalin mixtures

Composition {volume %}	density {gm/ml}
5	0.9003
10	0.9042
15	0.9079
20	0.9118
30	0.9195

APPENDIX B.

Distillation of Decahydranaphthalene (Decalin).

A batch distillation column with reflux acts as an enriching column[69]. Initially, at the beginning of the distillation, the composition of the liquid in the reboiler (still pot) is the original feed composition "x_f". At time "t", the still pot composition is "x_w" and the distillate is "x_D". (See reference [69] for a more detailed theory of operation.) Generally speaking, the composition of the component "x_w" varies with time in the still pot. Initially, it is a large percentage and as the distillation proceeds, the value of "x_w" is decreased, while the percentage of the higher boiling components increase. A point in the distillation will be reached where the percent of higher boiling components will be comparable to the value of "x_w" and larger amounts (although still rather small amounts) of the higher boiling will come out into the distillate if a column with a small number of equilibrium contacts (or stages) is used. Such is the case for this research. Knowledge of this can lead to proper manipulation of waste and distillate to obtain a desired sample.

The gas chromatographic analysis of the original decalin resulted in the chromatogram shown in figure B-1. After batch distillation with a reflux ratio of 50:1, the resulting chromatogram is shown in figure B-2. It should be mentioned that the reflux ratio for the distillation column means that for a total of 51 units of time, during one of these units distillate is collected, and during the remaining 50 units, the distillate "refluxes" in the distillation

column in order to increase vapor-liquid equilibrium.

Upon refilling the still pot with fresh feed and continuing the distillation, the effect of the increased percentage of the higher boiling components in the still pot is shown in figure B-3. This is seen in the increased third decalin peak.

The procedure used in the distillation is as follows. First, the still pot was filled with decalin feed. The first distillate was collected (at 25:1 reflux ratio) until gas chromatographic analysis showed the distillate to be of desired purity. Then the decalin was collected at a reflux of 50:1. Each time a distillation was done, the bottoms in the stillpot were saved along with the distillate waste.

By distilling the distillate waste and bottoms numerous times, various samples of decalin with varying isomer concentrations were obtained (figures B-4 through B-7). Figure B-5 shows the decalin sample used as the diluent for gas chromatograph calibration of the radiolysis products. This sample shows no impurities in the range where the radiolysis products were detected upon gas chromatograph analysis of the irradiated samples.

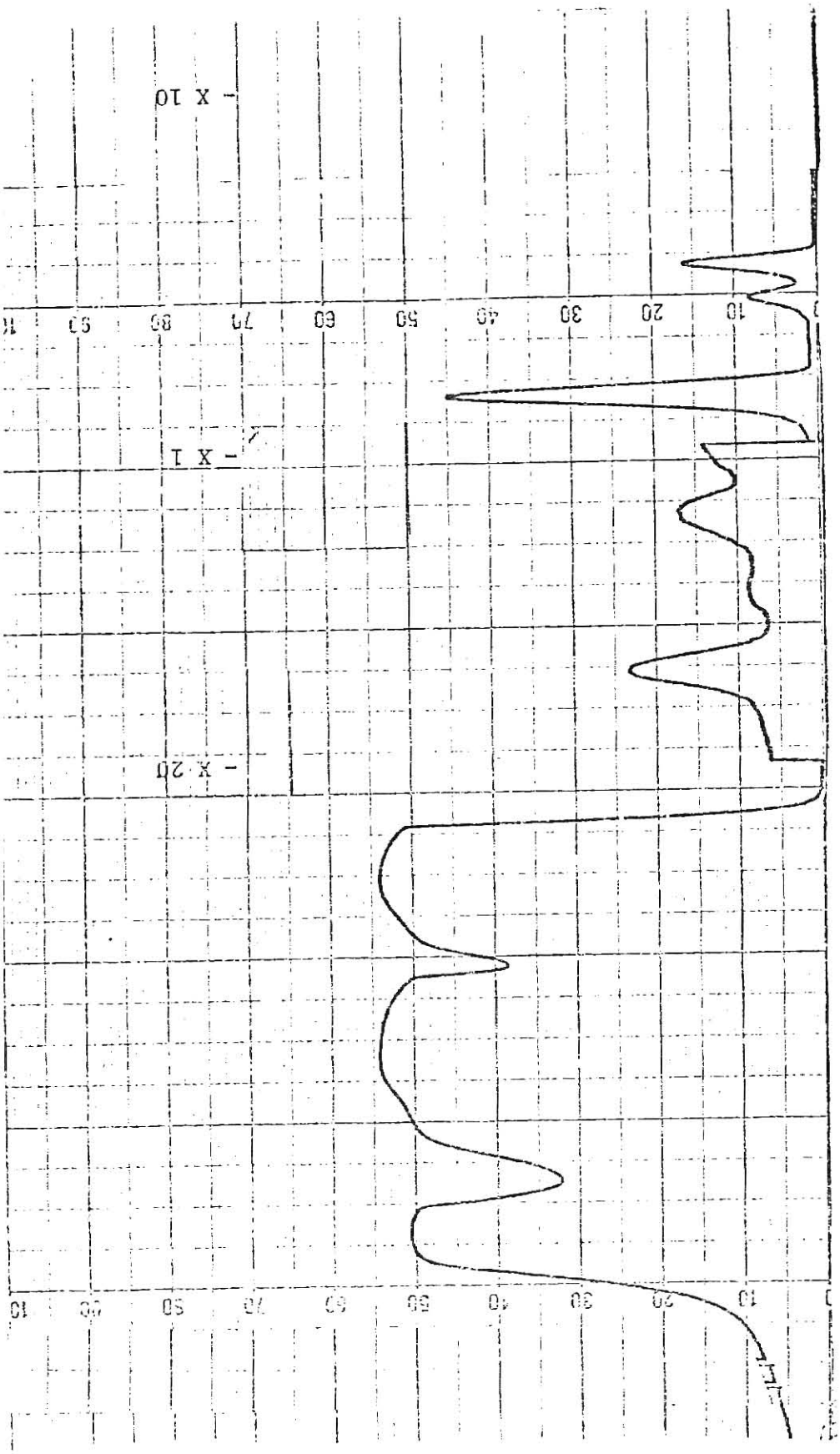

Figure B-1: Chromatogram of the unpurified decahydranaphthalene as obtained from a commercial distributer. Column temperature is 150°C with injection port and detector at 250°C.

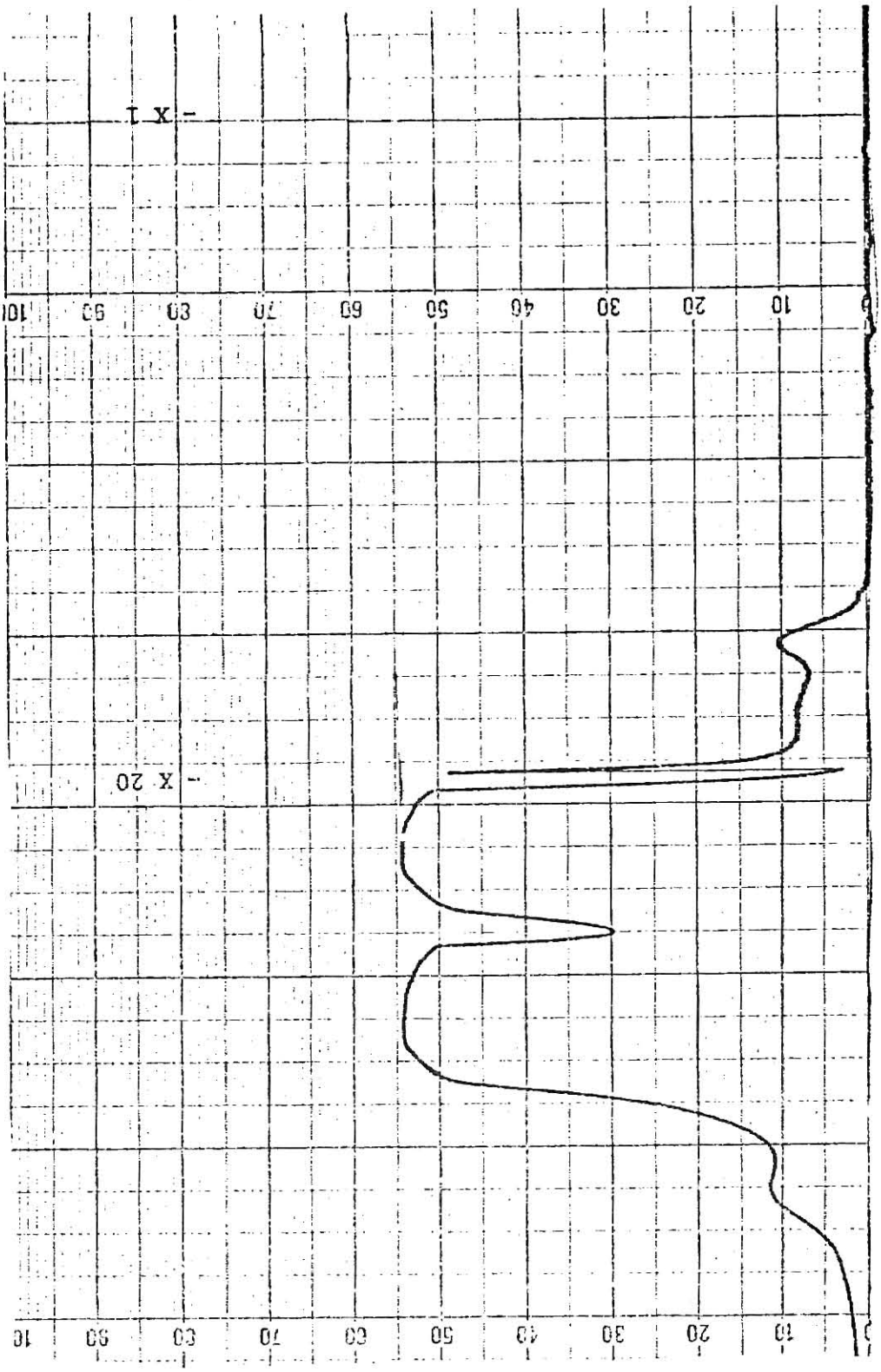

Figure B-2: Chromatogram of the distillate from the first distillation of the decalin shown in figure B-1. Column, inj. port, and detector temperatures are the same.

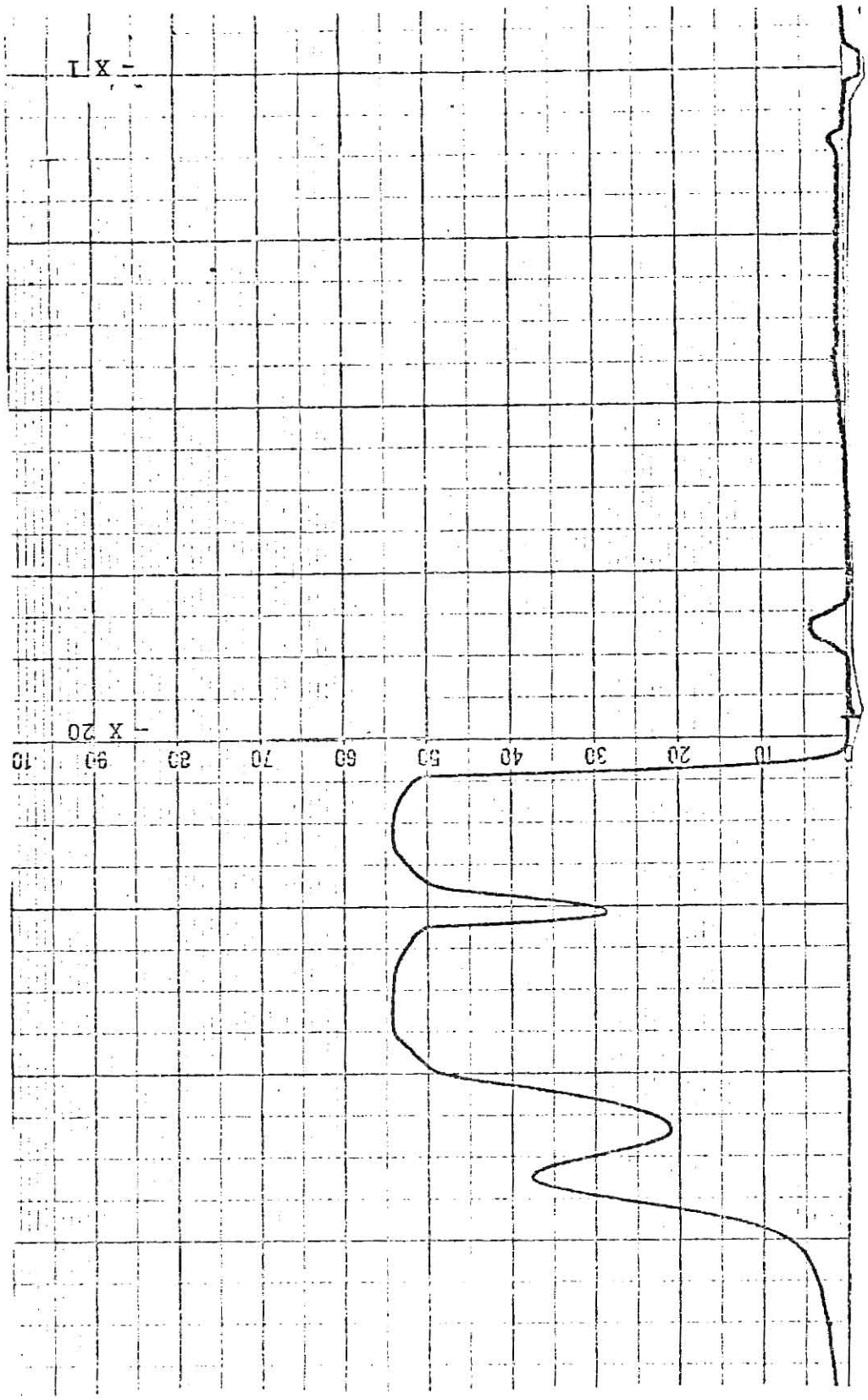

Figure B-3: Chromatogram of the distillate collected after adding fresh decalin (fig. B-1) to a stillpot over half filled from the previous distillation. (Column temp.,150°C; inj. port temp., 250°C; detector temp., 250°C)

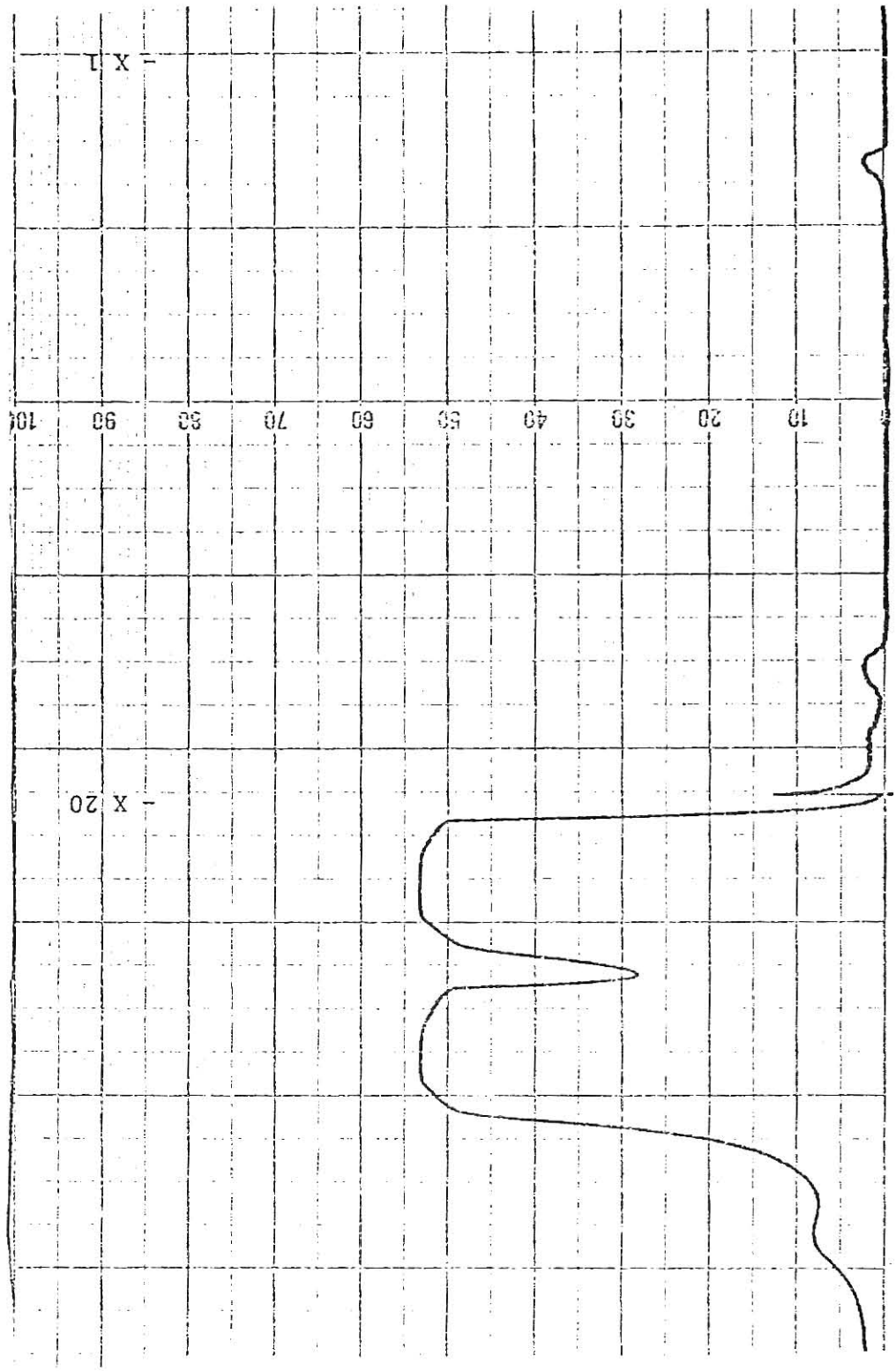

Figure B-4: Chromatogram of the decalin collected from the first distillation of the waste decalin. (Column temp., 150°C; inj. port temp., 250°C; detector temp., 250°C)

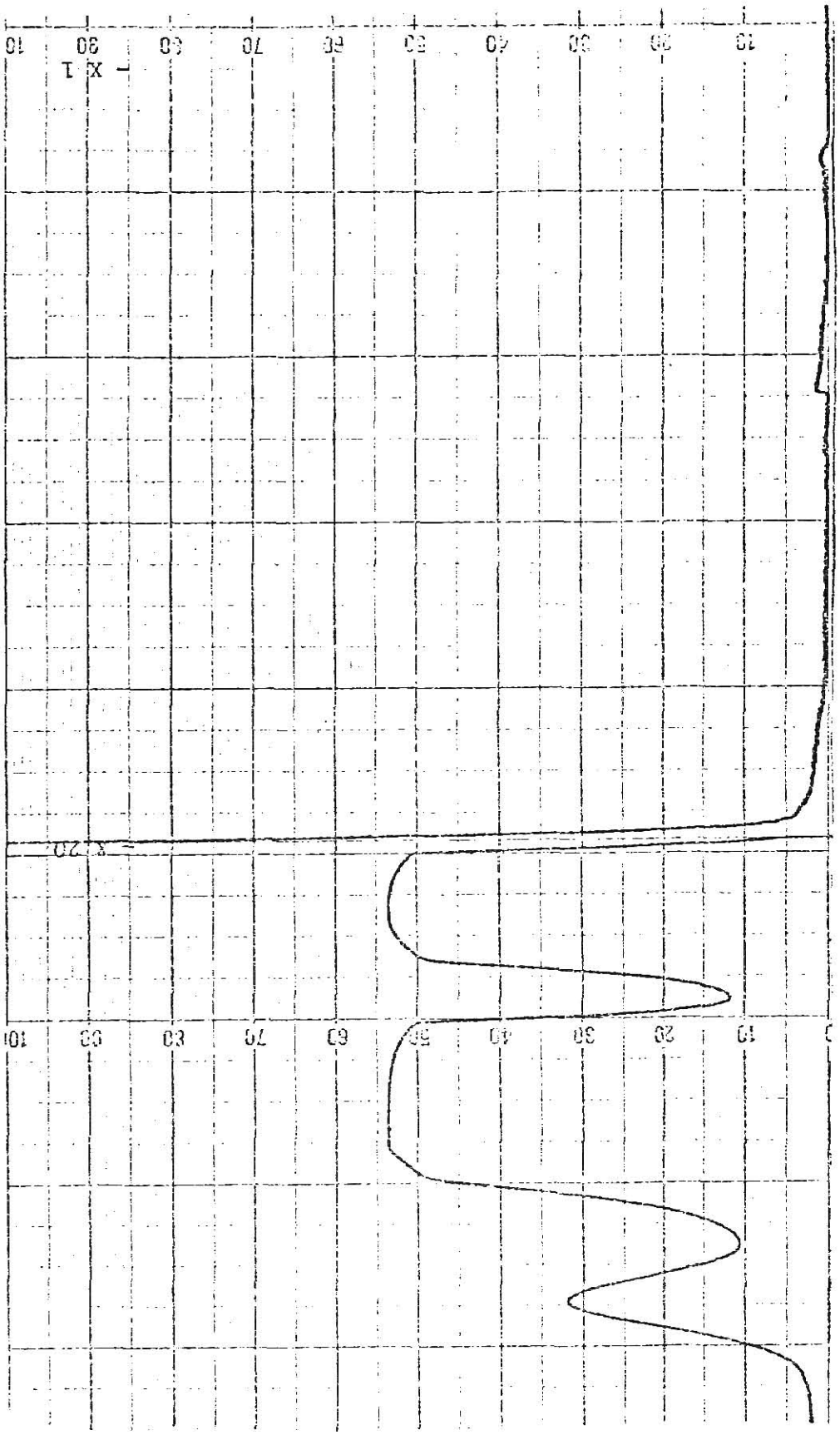

Figure B-5: Chromatogram of the decalin collected from the first distillation of the bottoms. (Column temp., 150°C; inj. port temp., 250°C; detector temp., 250°C)

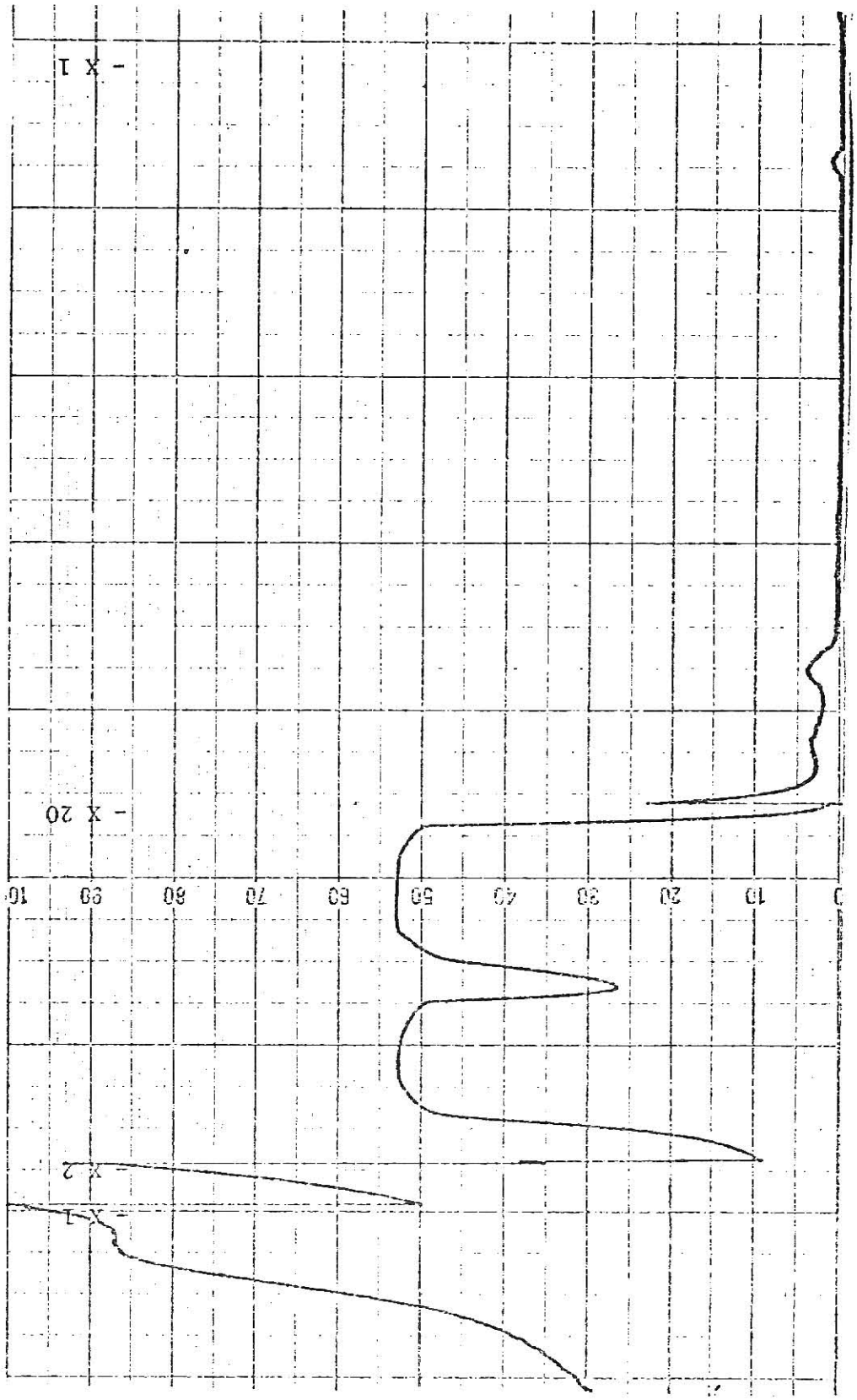

Figure B-6: Chromatogram of the decalin collected from the second distillation of the waste decalin. (Column temp., 150°C; inj. port temp., 250°C; detector temp., 250°C)

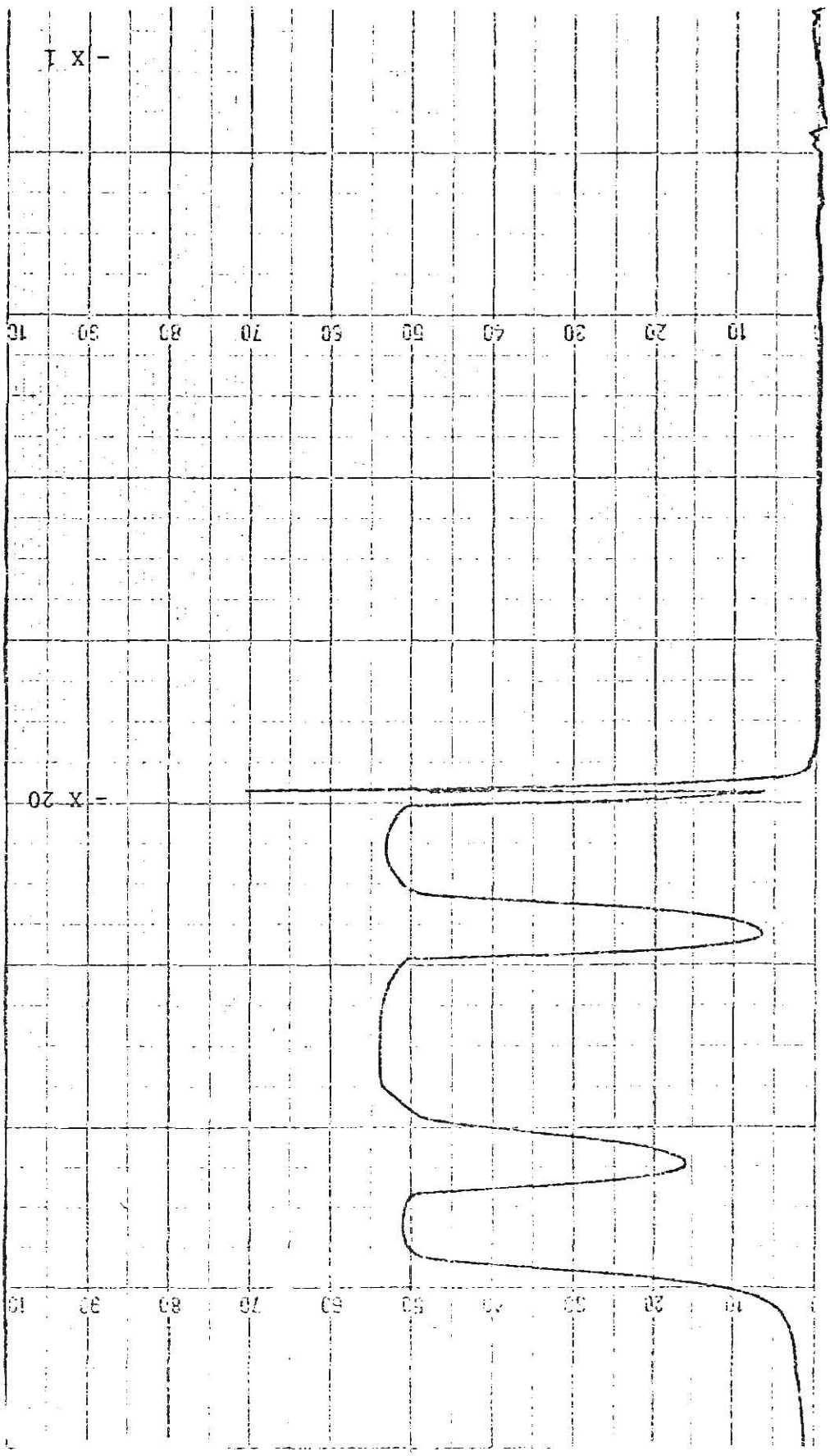

Figure B-7: Chromatogram of the decalin collected from the second distillation of the bottoms. (Column temp., 150°C; inj. port temp., 250°C; detector temp., 250°C)

APPENDIX C.

Calibration Data

Table C-I.

Chromatogram Calibration of $C_{10}H_{16}$

Concentration {M}	Planimeter reading†	Peak weight {grams}†
1×10^{-5}	0.383 (0.011)	0.00015 (0.00006)
2×10^{-5}	0.610 (0.023)	0.0004 (0.0001)
5×10^{-5}	0.705 (0.036)	0.0006 (0.00036)
8×10^{-5}	0.802 (0.030)	0.0008 (0.00036)
1×10^{-4}	0.824 (0.061)	0.00064 (0.0003)
2×10^{-4}	1.154 (0.023)	0.0024 (0.00036)
5×10^{-4}	1.545 (0.032)	0.00625 (0.00012)
8×10^{-4}	2.015 (0.138)	0.01205 (0.00042)
1×10^{-3}	2.330 (0.061)	0.0175 (-------)

† the number in the parenthesis is the probable error in the mean.

Table C-II

Chromatogram Calibration of DBP

Concentration {M}	Planimeter reading†	Peak weight {grams}
8.38×10^{-5}	0.2266 (0.016)	
1.67×10^{-4}	0.291 (0.022)	0.00045
4.19×10^{-4}	0.386 (0.019)	0.00085
6.70×10^{-4}	0.463 (0.019)	0.00095
8.38×10^{-4}	0.563 (0.019)	0.0016
1.67×10^{-3}	0.610 (0.019)	0.0019
4.19×10^{-3}	0.688 (0.025)	0.00285
6.70×10^{-3}	0.786 (0.017)	0.00395

† the number in the parenthesis is the probable error in the mean.

Table C-III.

Chromatogram Calibration of MBP

Concentration {M}	Planimeter reading†	Peak weight {grams}
1.07×10^{-4}	0.366 (0.024)	
2.14×10^{-4}	0.352 (0.025)	0.001
5.36×10^{-4}	0.344 (0.019)	0.00095
8.57×10^{-4}	0.464 (0.010)	0.0012
1.07×10^{-3}	0.494 (0.019)	0.0014
2.14×10^{-3}	0.518 (0.019)	0.00165
5.36×10^{-3}	0.564 (0.016)	0.00215
8.57×10^{-3}	0.534 (0.022)	0.00205

† the number in the parenthesis is the probable error in the mean.

Table C-IV.

Initial Product Concentrations in Standard Solutions
(planimeter calibration)

Volume %TBP	$C_{10}H_{16}$ $\{10^{-4}M\}$[a]	DBP $\{10^{-3}M\}$[b]	MBP $\{10^{-3}M\}$[c]
0	0.00	0.00	0.00
5	0.07	2.76	2.05
10	0.18	4.05	0.87
15	0.89	4.99	1.31
20	1.31	6.59	1.24
30	9.04	5.15	2.09
100[d]	0.00	35.46	81.82
100[e]	0.00	26.79	

a. standard deviation is $0.64 \times 10^{-4}M$
b. standard deviation is $1.34 \times 10^{-3}M$
c. standard deviation is $1.97 \times 10^{-3}M$
d. standard deviation is $0.96 \times 10^{-3}M$
e. obtained from weight calibration and the standard deviation is $0.88 \times 10^{-3}M$

Table C-V.

Calibration of the Fricke Dosimeter

Ferric ion concentration {M}	Absorbance		
	solution 1†	solution 2††	average
1.0×10^{-4}	0.218	0.206	0.212
1.5×10^{-4}	0.317	0.320	0.318
2.0×10^{-4}	0.441	0.426	0.434
2.5×10^{-4}	0.547	0.536	0.542
3.0×10^{-4}	0.640	0.665	0.653
3.5×10^{-4}	0.751	0.750	0.751
4.0×10^{-4}	0.875	0.860	0.868
4.5×10^{-4}	0.948	0.972	0.960

† solution 1 contains ferric ions from ferric sulphate
†† solution 2 contains ferric ions from iron wire

Table C-VI.

Calculation of the absorbed dose at various gamma cell positions using the Fricke dosimeter.† (January 21, 1974)

	absorption			
	Sample cell #2 {position L}	Sample cell #4 {position j}	Sample cell #7 {position j}	Sample cell #8 {position L}
	0.658	0.653	0.625	0.618
	0.659	0.641	0.613	0.614
	0.649	0.641	0.609	0.610
	0.648	0.624	0.600	0.605
	0.650	0.622	0.598	0.610
	0.651	0.628	0.597	0.618
	0.650	0.631	0.608	0.611
	0.649	0.631	0.606	0.610
	0.640	0.626	0.600	0.610
	0.658	0.623	0.605	0.619
Mean	0.651	0.632	0.606	0.613
Σd	0.042	0.078	0.061	0.039
Dose††	0.076	0.074	0.072	0.071

† irradiation time was 15 minutes

†† The units are 10^{18} eV/gm-min, and the error was determined to be ±0.003 X 10^{18} eV/gm-min for each position. The following physical constants were used in this calculation:

$G(Fe^{+2})$ is 15.6 molecules/100 eV
density of solution is 1.024 gm/ml
temperature was 20°C

Table C-VII.

Electron Fraction of TBP in the solutions analyzed

Volume %TBP	Electron fraction
0	0.000
5	0.029
10	0.060
15	0.093
20	0.126
30	0.199
100	1.000

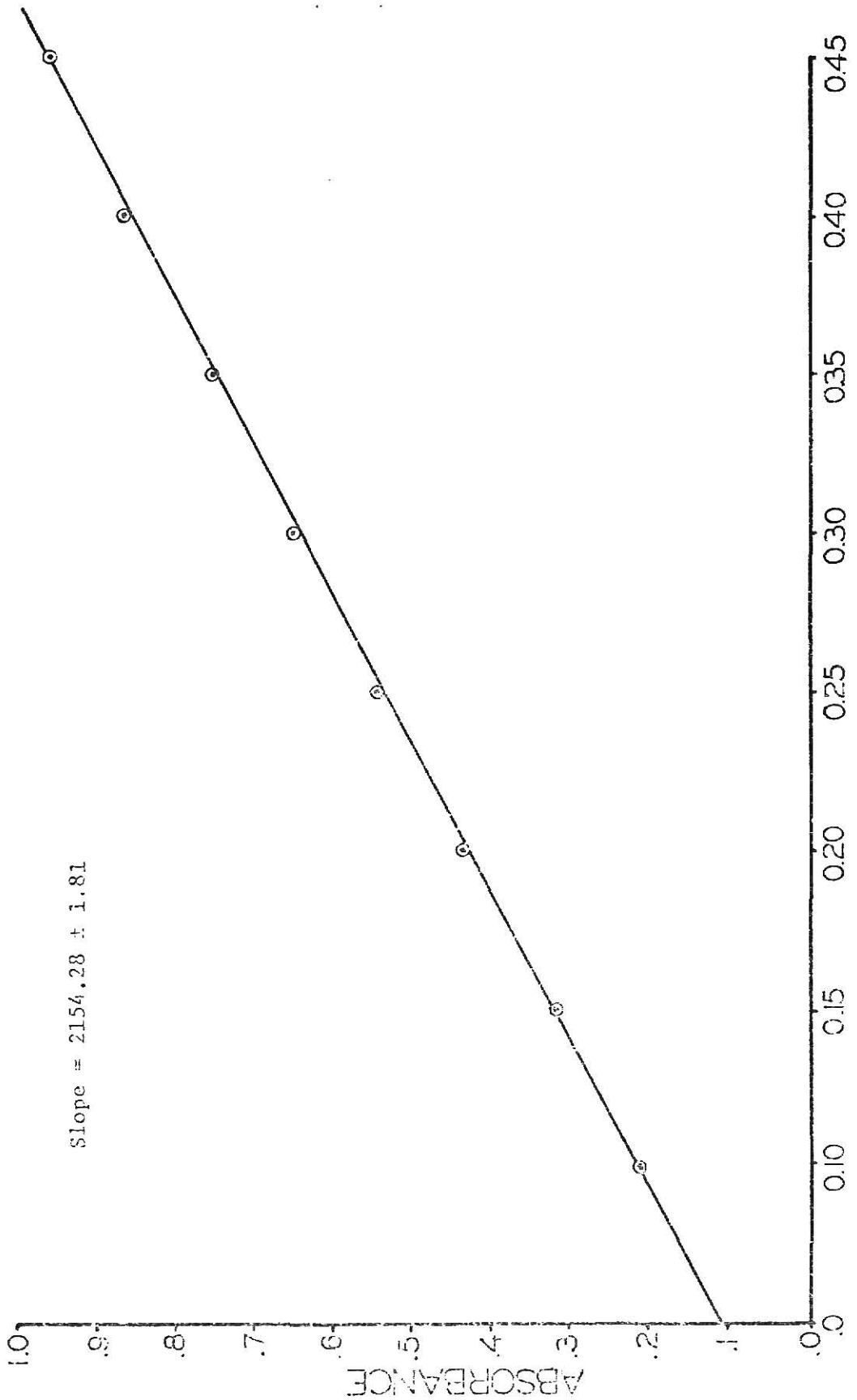

Fig. C-1: The Absorbance of .8 N H_2SO_4 and 10^{-3} M NaCl, of Standard Ferric Solutions. (wavelength = 304nm, slit width = 0.131mm, temp. = 20°C)

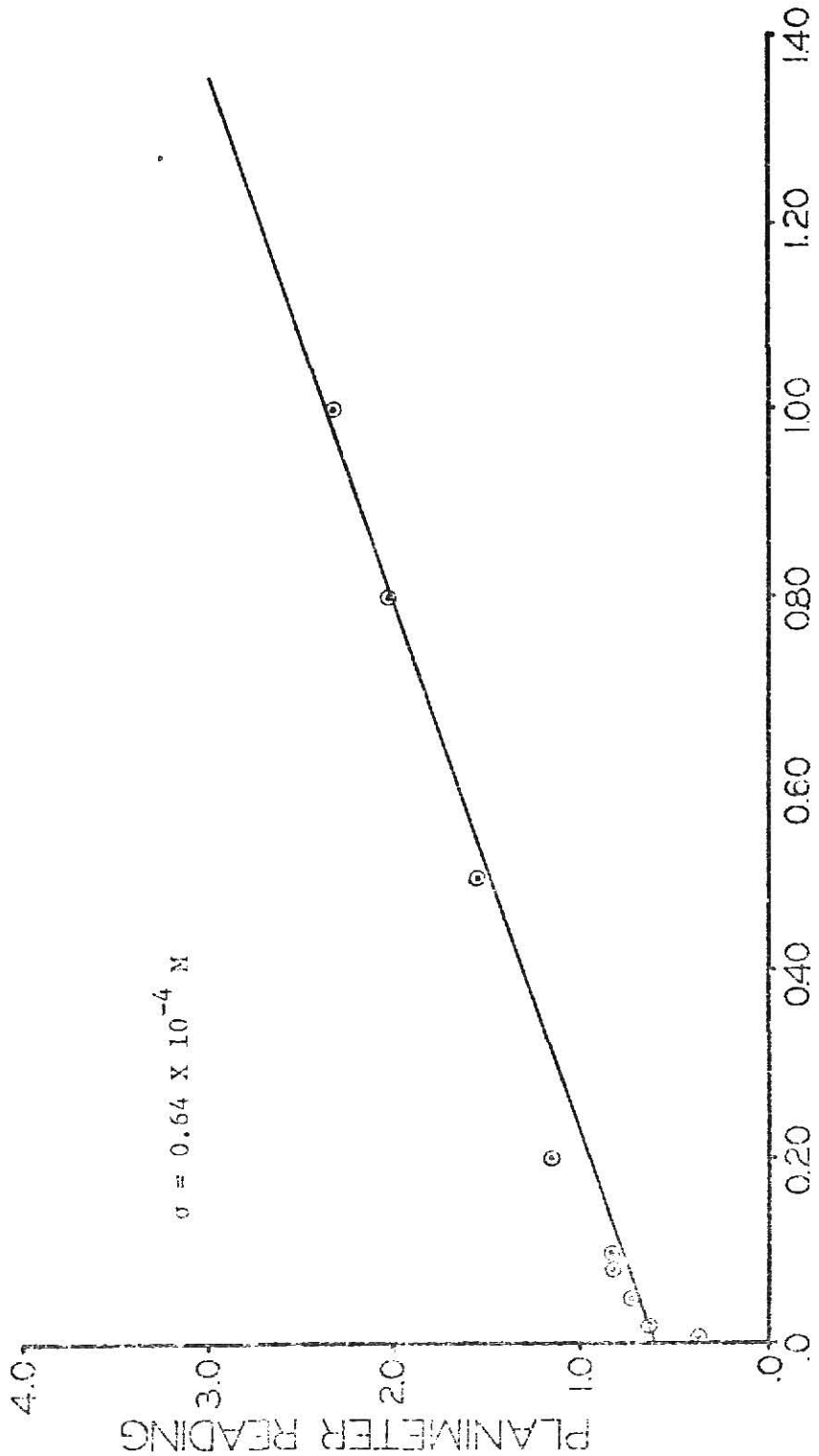

Fig. C-2: Calibration Curve for Converting the Planimeter Reading to the Concentration of $C_{10}H_{16}$ in Solution.

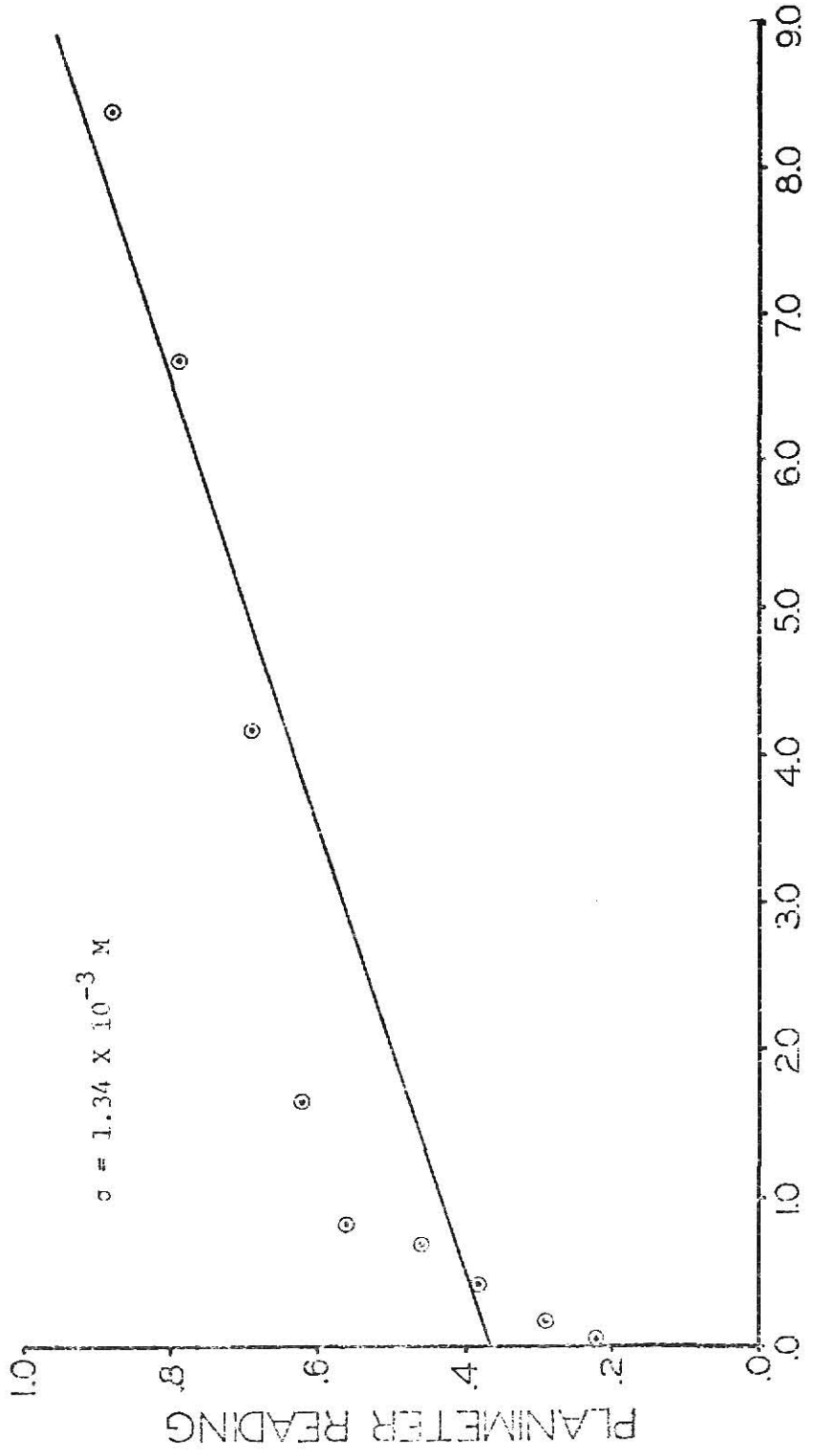

Fig. C-3: Calibration Curve for Converting the Planimeter Reading to the Concentration of DBP in Solution.

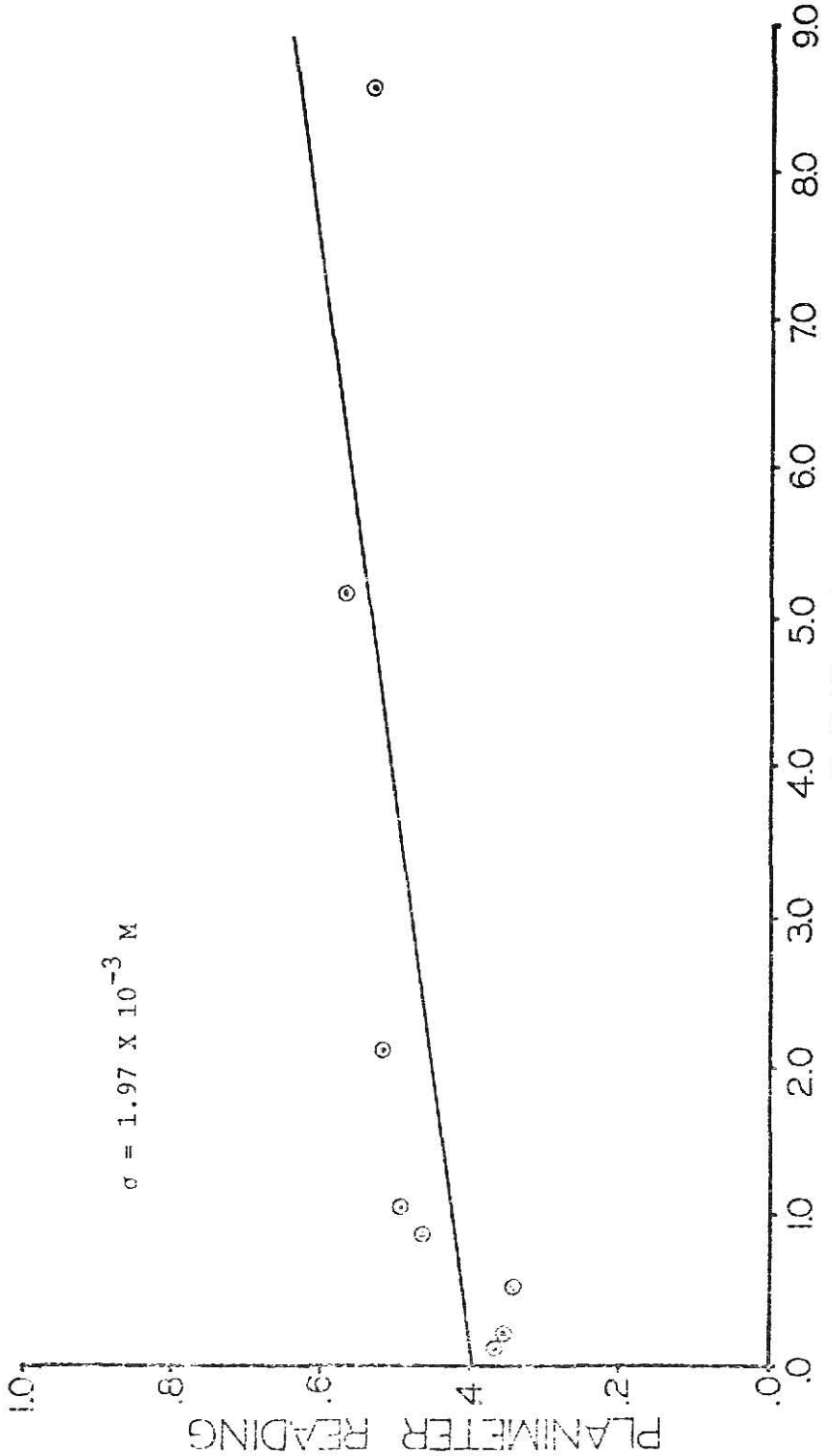

Fig. C-4: Calibration Curve for Converting the Planimeter Reading to the Concentration of MBP in Solution.

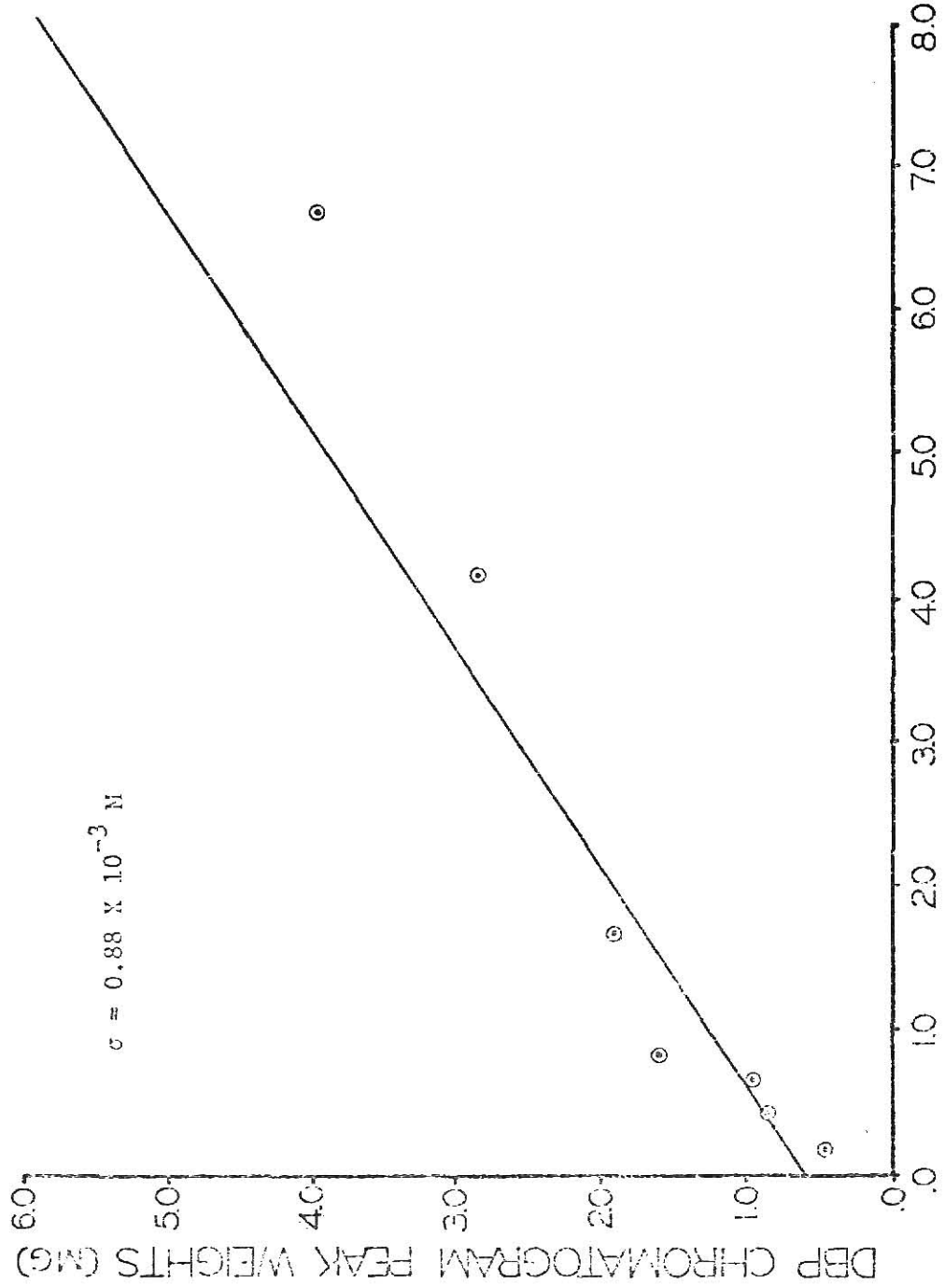

Fig. C-5; Calibration Curve for Converting the Weights of the Chromatogram DBP peak to the Concentration of DBP in Solution.

APPENDIX D.

Error Analysis

The error analysis in this research incorporated the following logic. Table 1 in Appendix C contains the chromatogram calibration data, that is, the readings from the planimeter and the weights of the chromatogram peaks that relate the respective measurements to standard molar solutions.

In the parenthesis is a value denoted as the probable error in the mean (P.E.). This means that the "true value" (the mean of a number of observations) has the same probability of falling in the interval, defined by this error, as it has of falling outside this interval. For example, a total of ten measurements (for the planimeter only) were taken, five from one chromatogram and five from another. The error in the parenthesis defines the interval of the measurement for that point whereby each additional reading made in determination of that point has a 50-50 chance of falling inside this defined error interval. (The Gaussian distribution curve is used as a basis for this analysis.)

The planimeter readings were used because ten separate measurements could be obtained as opposed to only two for the weight measurements. By studying these errors, it can easily be seen that they do not vary a great deal from one another as is expected since the same procedure and equipment were used in the measurements. In this light, assuming concentration acts linearly in a gas chromatograph (see reference [51]), a non-weighted least squares analysis can be performed on the data.

From this fit, the standard deviation for the fitted data can be obtained. A discussion of the calculator program used for these calculations along with the equations is given in Appendix E. From application of this program a standard deviation was obtained for each calibration curve.

These standard deviations were used when determining the individual product concentrations in the mixtures. A set of standard solutions (i. e., 5%-, 10%TBP, etc.,) were analyzed to determine the initial product concentrations in the mixtures (table C-IV). These values were then subtracted from the values of the concentrations measured after irradiation to obtain the desired concentrations (table III).

At this point a standard deviation for the concentrations has been obtained, but there is an error in the determination of the dose rate and it was found by fitting the calibration data of table C-V by a non-weighted least squares (calculator program). From the standard deviation calculated from fitting this data to least squares, and the errors determined from the measurements given in table C-VI, a deviation in the dose rate could be determined and is given in table C-VI. These dose rates were determined for each position in the gamma cell and since each one lies within the error (table C-VI), the average value of these dose rates was used for the determination of the radiolysis product yields.

From here on, the concern was now to find a maximum error for the final calculated data. That is, all determined errors were adjusted in the calculations in order to give the maximum value that could be obtained for a given set of yields. Or more simply,

a yield corresponding to a concentration and a yield for that same concentration with the experimental errors at their endpoints, was determined for each concentration measurement. The difference between these yields were then compared, with the resulting largest value taken to be an estimate of the maximum error that could be obtained. The results of this determination are given in the following table.

Table D-I.

Maximum Experimental Errors

Radiolysis product	Error {molecules/100 eV}
$C_{10}H_{16}$	± 0.145
DBP	± 3.009
MBP	± 4.427
Gas†	± 0.39

† the error analysis for the gas was done similarly

APPENDIX E.

Calculator Programs

Linear Least Squares

Analysis of the results in this research led to numerous fitting of data by linear least squares. The availability of the Tektronik Model 31 calculator initiated the development of a program to fit the data more quickly and accurately.

The use of a linear functional dependence of points leads to an equation of the form

$$y = a + bx. \tag{1}$$

If it is assumed that every measurement "y_i" has the same standard deviation (statistical weight), the estimators a* and b* can be obtained by[67]

$$a^* = \frac{\Sigma x_i^2 \Sigma y_i - \Sigma x_i \Sigma (x_i y_i)}{n\Sigma x_i^2 - \Sigma x_i \Sigma x_i} \tag{2}$$

$$b^* = \frac{n\Sigma (x_i y_i) - \Sigma y_i \Sigma x_i}{n\Sigma x_i^2 - \Sigma x_i \Sigma x_i} \tag{3}$$

with the standard deviations

$$\sigma_{a^*} = \sigma \frac{\sqrt{\Sigma x_i^2}}{\sqrt{n\Sigma x_i^2 - \Sigma x_i \Sigma x_i}} \tag{4}$$

$$\sigma_{b^*} = \sigma \frac{\sqrt{n}}{\sqrt{n\Sigma x_i^2 - \Sigma x_i \Sigma x_i}} \tag{5}$$

where (x_i, y_i) is each data point, "n" is the number of data points, and "σ" is the standard deviation (the same for each point). This "σ" can be determined by the following equation[68]:

$$\sigma^2 = \frac{1}{N-1} \sum (\bar{y}_i - y_i)^2 \qquad (6)$$

where "$\bar{y}_i$" is the experimentally measured value and "y_i" is the value determined by least squares fitting.

The program listed on the following pages uses the following logic:

1. The number of points to be fitted is entered when called for by the program.

2. Each successive point is entered and printed out, and at the same time the quantities for equations (2), (3), (4), and (5) are determined.

3. These quantities are applied to equation (2) and (3) and the resulting slope and y-intercept values are determined for equation (1).

4. Equation (1) is then utilized and the least squares y-values are determined and printed out for each x-value that was fed in--at the same time, the y-values that were fed in are recalled and used in equation (6) to determine the variance.

5. When equation (6) has been used for every point of the data, the value of the previously determined slope is printed out, equation (5) is utilized and the value of the standard deviation in the slope is printed.

6. Then the previously determined y-intercept is printed, equation (4) is used and this resulting standard deviation in the y-intercept is printed.

7. The square root of the value determined by equation (6) is then printed.

[It should be noted that if the "Flag" is set on the calculator, the printing of each y-value of the fitted data will be ommitted.]

```
CLR
    T
    H
    I
    S
    I
    S
    A
    L
    I
    N
    E
    A
    R
    N
    O
    N
    _
    W
    E
    I
    G
    H
    T
    E
    D
    L
    E
    A
    S
    T
    S
    Q
    U
    A
    R
    E
    S
    F
    O
    R
    A
    M
    A
    I
    M
    _
    M
    O
    F
    9
    9
    P
    O
    I
    N
    T
    S
PAPR
0
=
R___
0
0
0
=
R___
1
0
0
=
K_
0
=
K_
1
=
K_
9
=
K_
5
=
K_
4
CLR
1
0
0
=
R___
1
0
0
CLR
    T
    H
    E
    K
    U
    M
    B
    E
    R
    O
    F
    P
    T
    S
    A
    R
    E
STOP
PRNT
=
K_
6
R___
1
0
0
+
1
=
R___
1
0
0
R___
0
0
0
+
1
=
R___
0
0
0
CLR
    X
```

```
0163      =
0164  STOP
0165  PRNT
0166  =
0167  K_
0168
0169  EXC_
0170      A
0171  CLR
0172  EXC_
0173      B
0174  CLR
0175      Y
0176      =
0177  STOP
0178  PRNT
0179  =
0180  K_
0181  7
0182  EXC_
0183      C
0184  CLR
0185  EXC_
0186      D
0187  CLR
0188  R___
0189  0
0190  0
0191  0
0192  -
0193  K_
0194  6
0195  =
0196  IF=0
0197  GOTO
0198  0
0199  2
0200  0
0201  9
0202  CONT
0203  CLR
0204  GOTO
0205  0
0206  1
0207  3
0208  9
0209  CLR
0210  K_
0211  6
0212  *
0213  K_
0214  5
0215  -
0216  K_
0217  0
0218  *
0219  K_
0220  0
0221  =
0222  K_
0223  3
0224  CLR
0225  K_
0226  5
0227  *
0228  K_
0229  1
0230  -
0231  K_
0232  0
0233  *
0234  K_
0235  4
0236  )
0237  /
0238  K_
0239  3
0240  =
0241  K_
0242  2
0243  CLR
0244  K_
0245  6
0246  *
0247  K_
0248  4
0249  -
0250  K_
0251  1
0252  *
0253  K_
0254  0
0255  )
0256  /
0257  K_
0258  3
0259  =
0260  K_
0261  0
0262  CLR
0263  0
0264  =
0265  R___
0266  0
0267  0
0268  0
0269  =
0270  K_
0271  1
0272  IF=
0273  GOTO
0274  0
0275  3
0276  2
0277  4
0278  CONT
0279      T
0280      H
0281      E
0282
0283      R
0284      E
0285      S
0286      P
0287      E
0288      C
0289      T
0290      I
0291      V
0292      E
0293
0294
0295      O
0296      R
0297      D
0298      I
0299      N
0300      A
0301      T
0302      E
0303
0304      V
0305      A
0306      L
0307      U
0308      E
0309      S
0310
0311      B
0312      Y
0313
0314      L
0315      S
0316      T
0317
0318      S
0319      Q
0320
0321      A
0322      R
0323      E
0324  0
```

```
0325  =
0326  R___
0327  0
0328  0
0329  0
0330  1
0331  0
0332  0
0333  =
0334  R___
0335  1
0336  0
0337  0
0338  R___
0339  1
0340  0
0341  0
0342  +
0343  1
0344  =
0345  R___
0346  1
0347  0
0348  0
0349  R___
0350  0
0351  0
0352  0
0353  +
0354  1
0355  =
0356  R___
0357  0
0358  0
0359  0
0360  EXC_
0361      E
0362  CLR
0363  EXC_
0364      F
0365  CLR
0366  R___
0367  0
0368  0
0369  0
0370  -
0371  K_
0372  6
0373  )
0374  IF=0
0375  GOTO
0376  0
0377  3
0378  8
```

```
0379  6
0380  CONT
0381  GOTO
0382  0
0383  3
0384  3
0385  8
0386  CLP
0387  1
0388  /
0389  (
0390  K_
0391  6
0392  -
0393  1
0394  )
0395  )
0396  *
0397  K_
0398  1
0399  =
0400  SQRT
0401  =
0402  K_
0403  9
0404  CLR
0405       T
0406       H
0407       E
0408
0409       S
0410       L
0411       O
0412       P
0413       E
0414
0415       I
0416       S
0417  K_
0418  0
0419  PRNT
0420  PAPR
0421  CLR
0422  K_
0423  6
0424  /
0425  K_
0426  3
0427  =
0428  SQRT
0429  *
0430  K_
0431  9
0432  =
```

```
0433       W
0434       I
0435       T
0436       H
0437
0438       A
0439
0440       S
0441       T
0442
0443       D
0444       E
0445       V
0446
0447       O
0448       F
0449  PRNT
0450  PAPR
0451  CLR
0452       T
0453       H
0454       E
0455
0456       I
0457       N
0458       T
0459       E
0460       R
0461       C
0462       E
0463       P
0464       T
0465
0466       I
0467       S
0468  K_
0469  2
0470  PRNT
0471  PAPR
0472  CLR
0473  K_
0474  5
0475  /
0476  K_
0477  3
0478  =
0479  SQRT
0480  *
0481  K_
0482  9
0483  =
0484       W
0485       I
0486       T
```

```
0487      H
0488
0489      A
0490
0491      S
0492      T
0493
0494      D
0495      E
0496      V
0497
0498      O
0499      F
0500  PRNT
0501  PAPR
0502  CLR
0503      T
0504      H
0505      E
0506
0507      S
0508      T
0509
0510      D
0511      E
0512      V
0513
0514      F
0515      O
0516      R
0517
0518
0519      E
0520      A
0521      C
0522      H
0523
0524      P
0525      T
0526
0527      O
0528      F
0529
0530      T
0531      H
0532      E
0533
0534
0535      F
0536      I
0537      T
0538      T
0539      E
0540      D
0541
0542        L
0543        A
0544        T
0545        A
0546
0547        I
0548        S
0549  K_
0550  9
0551  PRNT
0552  PAPR
0553  CLR
0554  RSET
0555
0556        X
0557        3
0558        =
0559  PRNT
0560  CLDP
0600  NULL
0601  NULL
0602  NULL
0603  NULL
0604  NULL
0605  NULL
0606  LBL_
0607        A
0608  =
0609  R___
0610  R___
0611  1
0612  0
0613  0
0614  SUM0
0615  R AD
0616  GODP
0617  NULL
0618  NULL
0619  NULL
0620  NULL
0621  LBL_
0622        B
0623  K_
0624  8
0625  X↑2
0626  +
0627  K_
0628  5
0629  =
0630  K_
0631  5
0632  R AD
0633  GODP
0634  NULL
0635  NULL
0636  LBL_
0637        C
0638  =
0639  R___
0640  R___
0641  0
0642  0
0643  0
0644  SUM1
0645  R AD
0646  GODP
0647  NULL
0648  NULL
0649  NULL
0650  NULL
0651  LBL_
0652        D
0653  CLR
0654  K_
0655  8
0656  *
0657  K_
0658  7
0659  +
0660  K_
0661  4
0662  =
0663  K_
0664  4
0665  R AD
0666  GODP
0667  NULL
0668  NULL
0669  NULL
0670  NULL
0671  LBL_
0672        E
0673  CLR
0674  K_
0675  0
0676  *
0677  R___
0678  R___
0679  1
0680  0
0681  0
0682  +
0683  K_
0684  2
0685  =
0686  K_
0687  8
0688  IFPC
0689  R AD
0690  GODP
0691  CONT
0692  PAPR
0693  PRNT
0694  R AD
0695  GODP
0696  LBL_
0697        F
0698  CLR
0699  K_
0700  8
0701  -
0702  R___
0703  R___
0704  0
0705  0
0706  0
0707  =
0708  X↑2
0709  SUM1
0710  R AD
0711  GODP
```

THE IRRADIATION EFFECTS ON A MODEL TBP-DECAHYDRANAPHTHALENE SOLVENT EXTRACTION SYSTEM

by

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B. S., Kansas State University, 1972

AN ABSTRACT OF A MASTER'S THESIS

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MASTER OF SCIENCE

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ABSTRACT

A study of the radiolytic degradation of the solvent extraction system used for the Purex process was modeled by using a tributyl phosphate(TBP)-decahydranaphthalene solution.

Co-60 gamma irradiation were done on the system at a dose rate of .2 watt/liter with the doses varying from 2, 4, 6, and 8 watt-hr/liter. The electron fraction of the TBP was varied to investigate the effects of the TBP on the decahydranaphthalene in the organic mixture.

The primary liquid radiolytic products from the solutions were $C_{10}H_{16}$, dibutyl phosphate (DBP), and monobutyl phosphate (MBP). Hydrogen was the only gaseous product, non-condensable at $77^{o}K$, of the decahydranaphthalene. Hydrogen and methane were the only gaseous products, non-condensable at $77^{o}K$, of the TBP irradiation. The yields of $C_{10}H_{16}$, total DBP and MBP, and the total gas, were determined as a function of dose and certain electron fractions of TBP.

The mixture law was used as a comparative criteria to determine if any form of interaction between components of the mixture occurred upon irradiation. It was found that the TBP in the mixture lowered the total gas yield, but had no effect on the yield of the $C_{10}H_{16}$ compound. On the other hand, there was an indication that the production of the DBP and MBP radiolytic products was sensitized.