GAMMA INITIATED
IODINATION OF METHANE

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SCOPE AND CONTENTS: The use of gamma radiation to initiate the iodination of methane in liquid phase was studied using a semi-batch technique whereby the methane was bubbling through a column of iodine solution in a reactor. Yields of CH_3I and CH_2I_2 lower than 10% and $G < 500$ were obtained as contrasted with the 60% yield and $G=7x10^7$ reported in the gas-phase reaction.

In view of the propensity of the iodine as a radical scavenger and the endothermic nature of the reaction, various attempts to improve the low yields were carried out. Results are given that indicate the chances of achieving a large G value for liquid-phase reaction are very low even if the operating conditions are optimized.

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I INTRODUCTION

In view of the large amount of gamma energy currently being wasted as spent fuel elements, much effort has been expended to investigate the potential use of the gamma energy in chemical processing. However, in spite of the great effort, only two or three commercially feasible processes have emerged. The reasons associated with this are for example (1) insufficient return per unit energy cost to be competitive with alternative methods of processing (2) the radiation chemistry of the reactions is frequently extremely complex and (3) the non-specific character of radiolysis always results in many side reactions.

Not much improvement can be made on the latter two disadvantages so that much effort has been focussed on the cost factor. In order to achieve a reasonable cost in producing a low molecular weight chemical, a long chain reaction is necessary. It is well known that many halogenation reactions are chain reactions. In particular, a fair amount of work on chlorination reactions has been done.

Recently this halogenation work has been extended to gas-phase iodination of methane, even though the prospects of chain iodination are unpromising and despite the propensity of iodine as radical scavenger. Nevertheless, the yields of iodomethanes were reported to be very high (31). This led to the present study of liquid phase iodination of methane.

The original purpose of this project is to evalute the practicability of producing iodomethanes directly in a continuous flow liquid-phase process with the aid of gamma radiation as contrasted with the earlier work on the gas-phase iodination in a batch reactor. However, the first few preliminary experiments indicated that the liquid-phase reaction proceeded with very low conversions. A secondary objective thus arose, "How to make this reaction proceed in liquid phase?". The new objective forms the entire discussion in this thesis.

II LITERATURE SURVEY

II-1 RADIATION CHEMISTRY AND PHYSICS

Radiation chemistry deals with the chemical changes produced by a high-energy radiation. It is an essential branch of physical chemistry and may be regarded as an extension of photochemistry. Radiation physics deals with the action of a high-energy radiation on matter and the energy changes in the system. Therefore, the two subjects are closely related to each other and they will be briefly surveyed together in this section.

II-1.1 Definitions and Units

The definitions and units are presented here in order to clarify the later use of the terms in this thesis.

Absorbed dose (D) As defined by the International Commission on Radiological Units in 1962 (1) the absorbed dose is equal to $\Delta E/\Delta m$, where ΔE is the energy imparted by the radiation to the matter in a volume element and Δm is the mass of matter in that volume element. Absorbed dose thus depends upon the material being irradiated, the nature of the radiation and the geometric relationship between the source and material. The official unit of absorbed dose is rad which is defined as 100 ergs/gram and equivalent to 6.24×10^{13} electron volts/gram. Other units such as roentgen and rep are often used but they will not be used here.

Absorbed dose rate (DR) It is the ratio of ΔD to Δt, where ΔD is the increment in absorbed dose in time Δt.

Strength of source (S) The strength of a source is the intensity of radioactivity of the source and it is graded in curies, defined (2) as the quantity of any radioactive nuclide in which the number of disintegrations per sec. is 3.700×10^{10}. For example one gram of radium has an activity of one curie.

G value (G) This term is used to expressed the energy yield of a radiation-induced reaction and is defined as the number of molecules changed (produced or destroyed) per 100 eV of energy absorbed in the system. For example, in the present work in a semi-batch reactor the G value of a product, X can be expressed as :

$$G_X = \frac{6.023 \times 10^{25} \times [X]}{D \times [I_2] \times 253.809}$$

where $[X]$ is the concentration of X produced in the system in (mole/volume), $[I_2]$ is the initial iodine concentration in (mole/volume) and D is the total absorbed dose in eV/gm.

A typical G value for the simple dissociation of a molecule is 3 to 10. When a chemical chain reaction occurs, G can become very high depending on how many reaction steps occur before a termination reaction is experienced.

II-1.2 High Energy Radiation

High-energy radiations generally include all electromagnetic radiations of wavelengths less than 100 Å to 1000 Å, or of energies greater than 10 eV. Fig. 1 gives a spectrum of electromagnetic radiation, showing roughly the means by which various types of radiation are produced. Although these radiations are energetic enough to ionize simple molecules, the energies of most conventional radiations are much higher than 100 eV. For example most work on radiation-induced reactions is carried out with either X-rays, gamma rays or accelerated electrons of 0.5 to 3.0 MeV.

The common effect produced by these radiations as will be seen in more detail in Section II-1.3 is that they often result in the ejection of energetic electrons which lose their energies by causing ionization and excitation as they proceed in trajectories through the matter. However, it is found in practice that different types of radiation often produce different effects for a given amount of energy absorbed (Chap. I of 2).

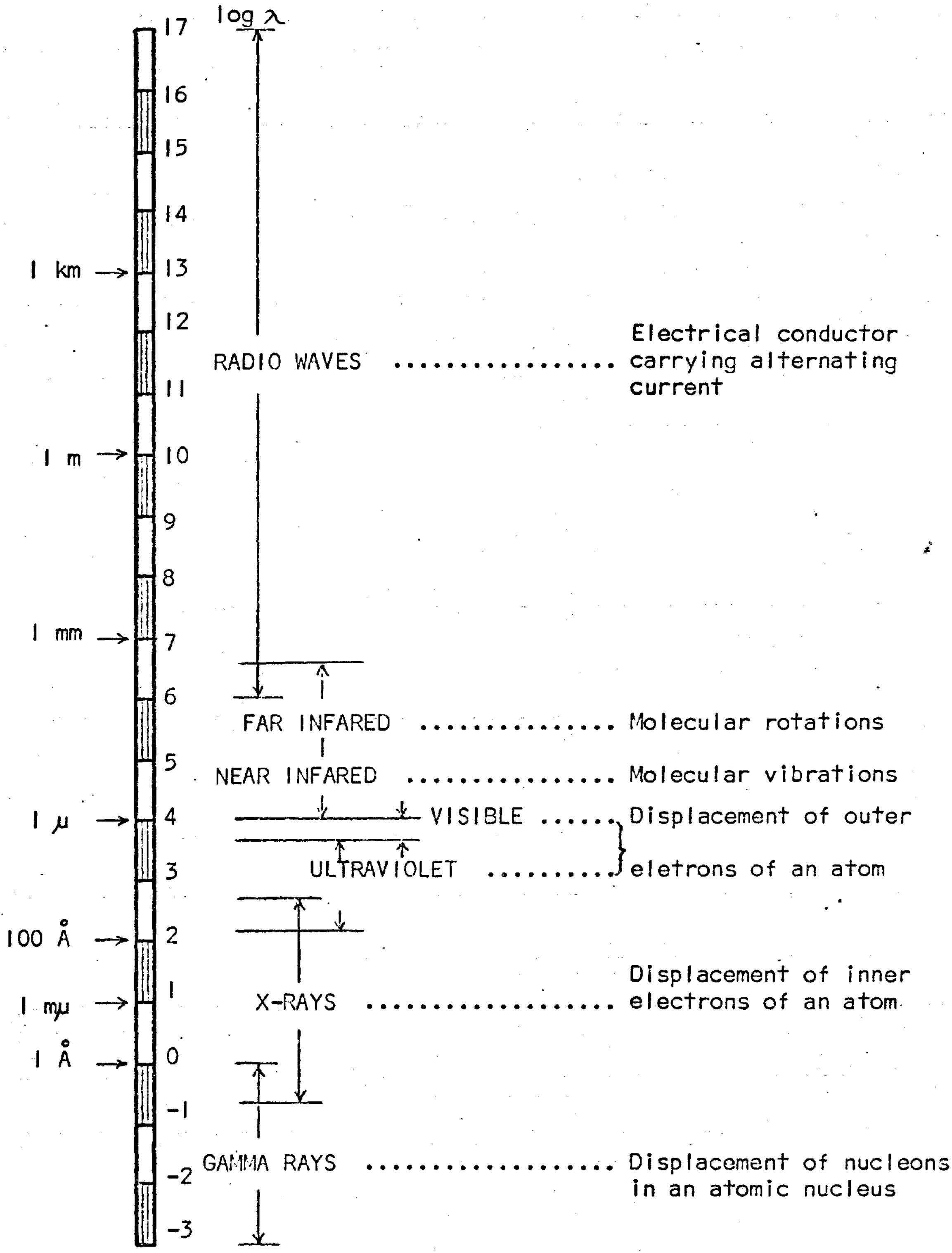


FIG. 1 THE SPECTRUM OF ELECTROMAGNETIC RADIATION (51)

Such differences are basically due to differences in the linear density of events along the track which is termed as "linear energy transfer" or LET, expressed in keV absorbed per micron of track in the medium. For example the LET of cobalt-60 gamma rays in water is 0.42 keV/μ compared with 150 keV/μ for polonium alpha particles.

In practice, high-energy radiations are limited to X-rays, gamma rays,accelerated electrons and reactor radiation. Since only gamma rays are involved in the present work, they will be discussed next in more detail.

II-1.2.1 Gamma radiation

Gamma rays are photons of high quantum energy. Generally the quantum energy of gamma rays is above 40,000 eV and they are considered to have higher energy than that of the X-rays. But as shown in Fig. 1, X-rays may have energies comparable to or even greater than the energies of the low energy gamma radiations.

Gamma rays can be obtained by impinging fast moving particles (electrons) on a metal target or from radioisotopes when they undergo nuclear transformation. A broad spectrum of quantum energies will be produced by the first method but radioisotopes emit gamma rays either monoenergetic or have a very small number of discrete energies. Thus gamma rays emitted from radioisotopes are mostly used in practice. One of the earliest gamma emitting radioisotopes is radium, but nowadays the most widely used gamma source is the artificial radioisotope cobalt-60 which is of interest here. Another useful artificial gamma source is cesium-137 which is becoming more attractive industrially because it has a long half-life of 30 years.

II-1.2.2 Cobalt-60 gamma radiation

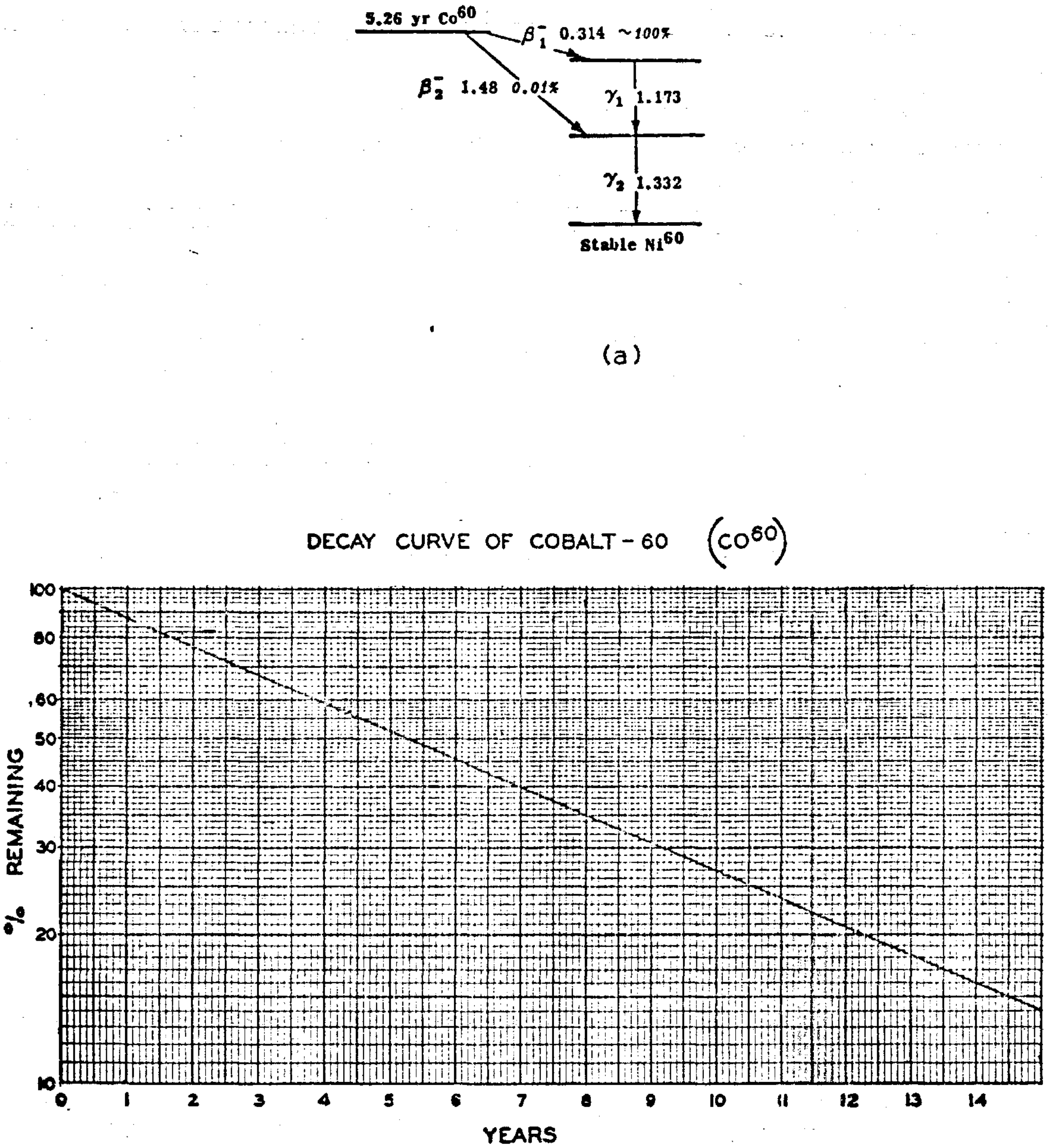
Radioisotope cobalt-60 is produced in nuclear reactors by the neutron bombardment of cobalt-59. It emits two gamma photons of 1.173 and 1.332 MeV respectively for every radioactive disintegration and it has a half-life of 5.26 ± 0.02 years.

The decay pattern of cobalt-60 is relatively complex, involving β, γ transition to the ground state as shown in Fig.2(a). The main transition is the negatron of energy 0.314 MeV decays to a first gamma photon of 1.173 MeV and then to a second gamma photon of 1.332 MeV. However, this complex decay pattern follows a first-order equation as shown by Eq.(1). Thus the radioactivity (A) of a source decreases exponentially with time (t) :

$$- dA/dt = \lambda A \qquad (1)$$

or

$$A = A_o e^{-\lambda t} \qquad (2)$$



(a)

DECAY CURVE OF COBALT-60 (CO^{60})

(b)

FIG. 2 DECAY SCHEME AND DECAY CURVE OF COBALT-60 (3) where A_o is the original activity and λ is the decay constant. Fig.2(b), which is a graphical presentation of Eq.(2), shows the decay curve of cobalt-60. λ is found to be 3.60×10^{-4} (days)$^{-1}$ from the slope of the curve.

Because of the high photon energy, gamma rays have very high penetrating power so that gamma source above a few millicuries in strength requires special shielding. Many methods of shielding are in use. For example, the source can be kept in a lead container, under water, below ground or in a room with thick concrete wall. The required thicknesses to reduce the gamma radiation are shown in Figs.3 and 4 for lead and concrete absorbers respectively. Notice that the gamma rays emitted from Ce-137 and Co-60 follow Beer's law in both lead and concrete absorbers but radium in a lead absorber departs from the law. This subject will be discussed further in Section II-1.4.

II-1.3 Interaction of Radiation with Matter

There are several ways by which gamma rays may lose energy by interacting with matter, depending upon the quantum energy of the photon and the nature of the matter. In the range of energies between 10 keV and 10 MeV, the three major interacting processes are

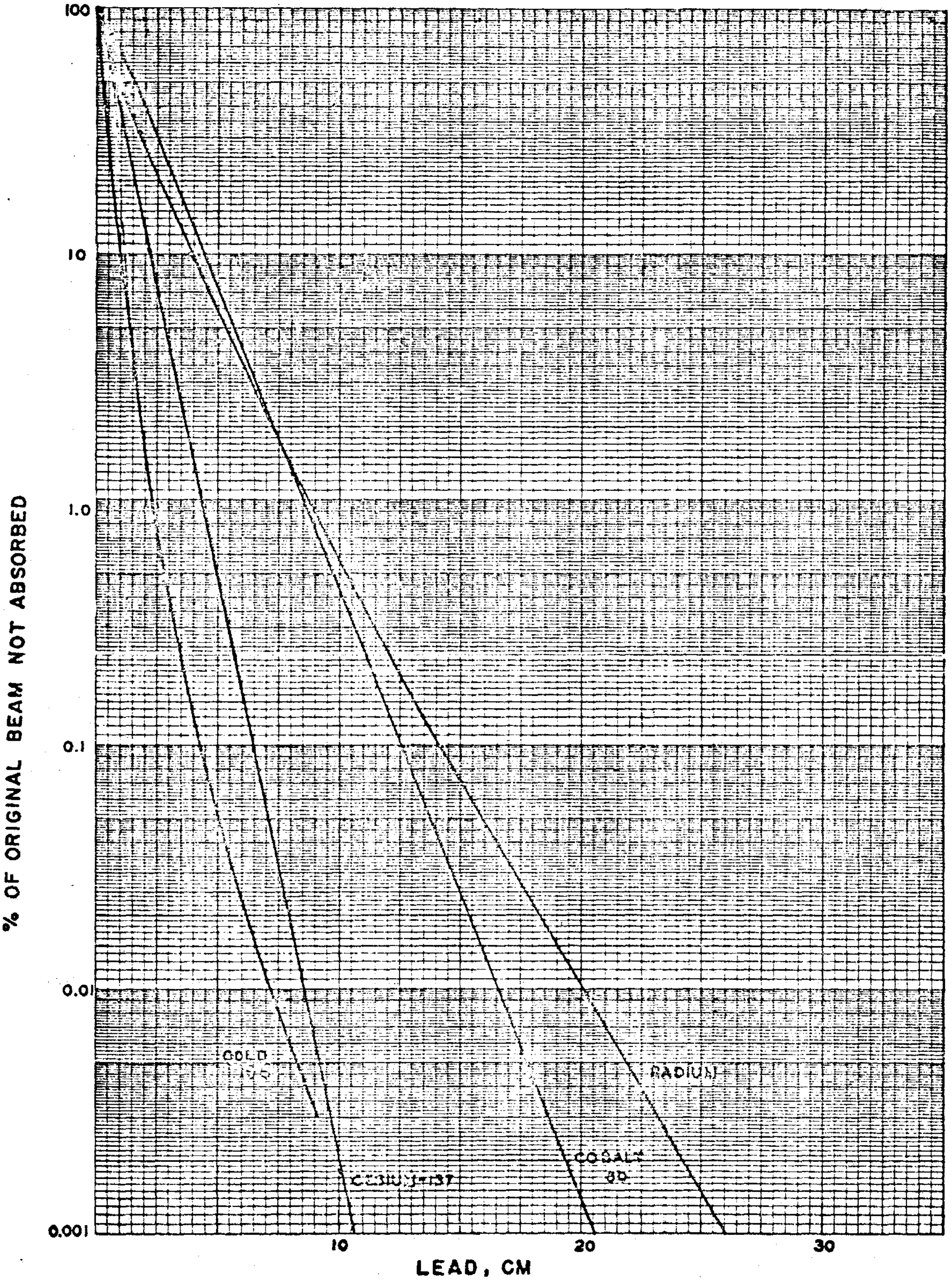


FIG. 3 GAMMA RAY ABSORPTION BY LEAD (3)

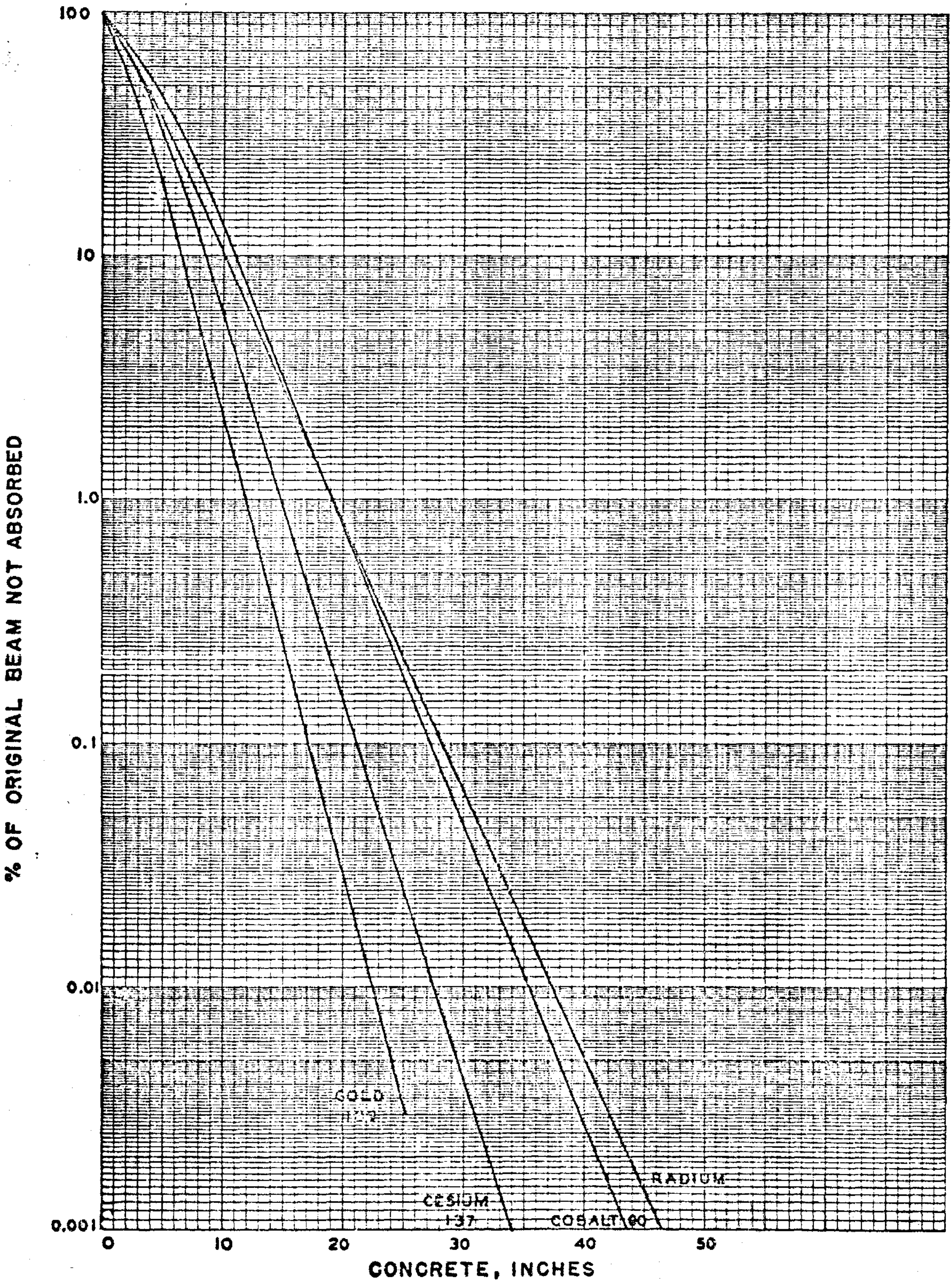


FIG. 4 GAMMA RAY ABSORPTION BY CONCRETE (3)

photoelectric effect, Compton scattering and pair production. Other minor processes are for example coherent electron scattering, annihilation radiation, bremsstrahlung and fluorescence radiation.

Photoelectric effect (Fig.5-a)

In the photoelectric effect, the incident photon is completely absorbed by an atom with the ejection of a fast orbital electron which bears all the energy of the incident photon minus the binding energy of the electron in the atom.

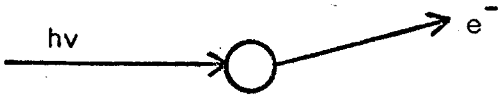
Compton scattering (Fig.5-b)

This interaction is an inelastic scattering. The photon imparts only part of its energy to an atom which then ejects an excited electron at some angle θ, relative to the direction of the incident photon. The remaining energy ($h\nu'$) is retained by the photon which scatters at another angle ϕ and interacts further, either by Compton scattering or some other processes.

Pair production (Fig.5-c)

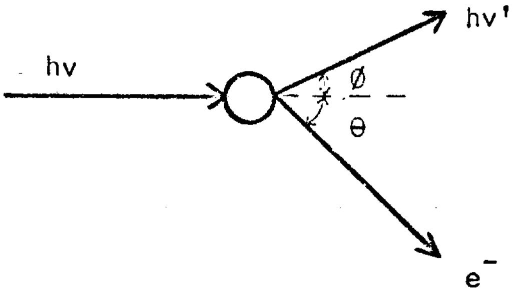
This process is an interaction of a photon within the electron cloud or in the nucleus of an atom resulting in the formation of a positron-electron pair, in which the photon energy is transferred to the pair. The minimum energy at which the process occurs is 1.022 MeV, which

(a) Photoelectric effect



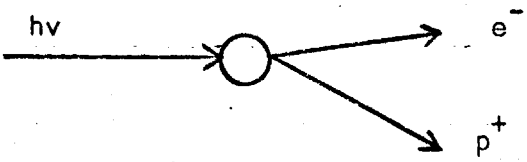
($E = hv - E_b$)
(E_b= binding energy)

(b) Compton scattering effect



($E = hv - hv'$)

(c) Pair production



(Rest energy = 1.022 MeV)

FIG. 5 RADIATION INTERACTING PROCESSES WITH MATTER is the total rest energy of a positron-electron pair. This process is always followed by the emission of two 0.511 MeV photons for each pair production, owing to the recombination of the positron with the electron.

Obviously, the consequence of the gamma rays interaction with matter is the subsequent disappearence of the photon and the production of energetic electrons. These electrons in turn will cause ionization and/or excitation in the matter. Fig.6 shows the relative contribution of each process to the total mass absorption coefficient (see Section II-1.4) of water. In the energy range below 100 keV, the photoelectric effect is predominant and no pair production appears because pair production can only occur when the photon energy is greater than 1.022 MeV. At the region of 1 MeV, Compton scattering is practically the only interaction. This is generally true not only for water but also for all other kinds of absorbers, because when gamma rays emitted from Co-60 (quantum energy = 1.25 MeV) interact with matter, Compton scattering is often the only important interaction observed. In fact, this single interaction characteristic of Co-60 gamma rays is the main reason why the absorption of the radiation so closely follows Beer's law as shown in Figs.3 and 4.

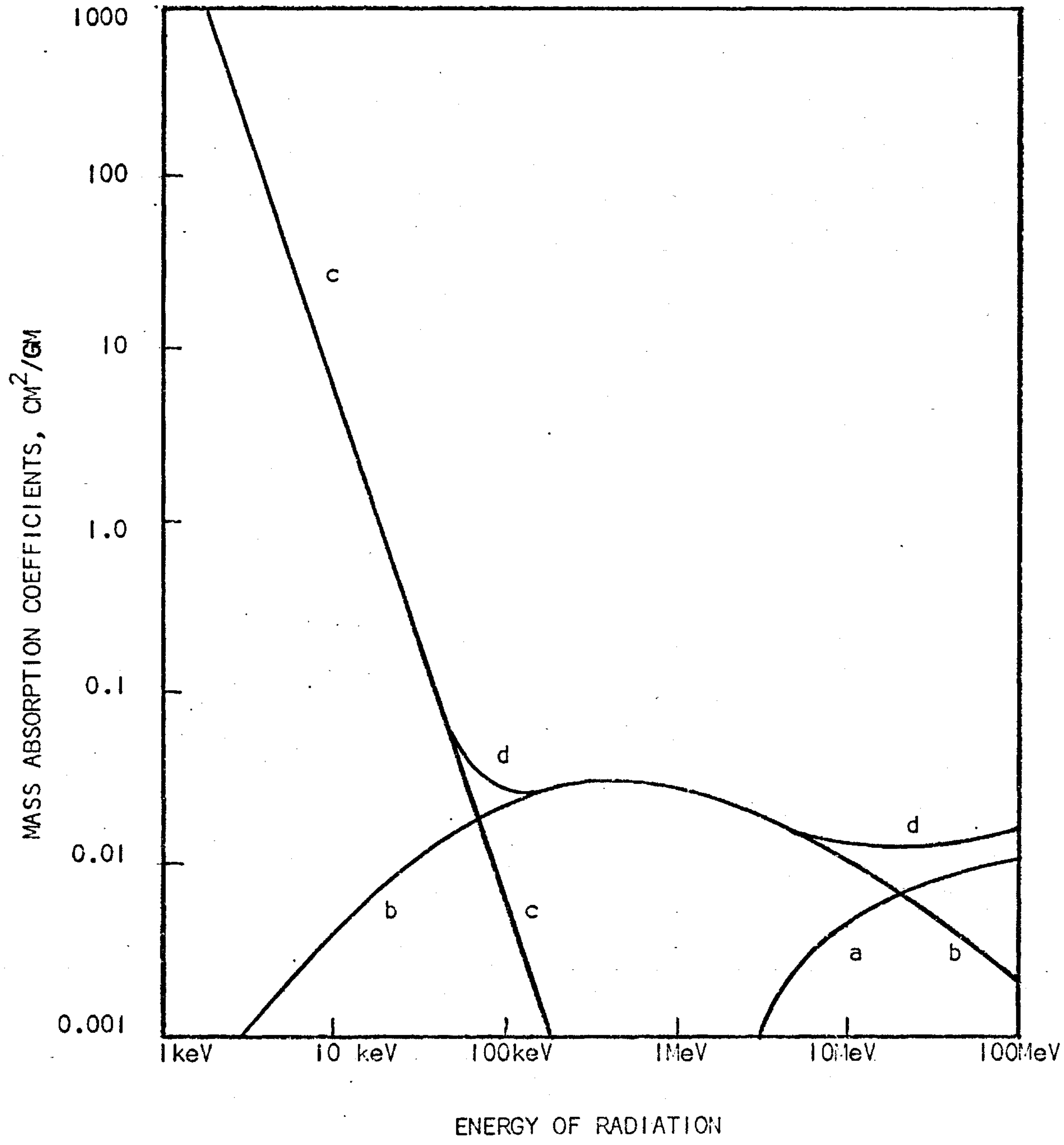


FIG. 6 VARIATION OF MASS ABSORPTION COEFFICIENTS OF WATER WITH ENERGY (2)

(a) PAIR PRODUCTION (b) COMPTON SCATTERING

(c) PHOTOELECTRIC (d) TOTAL REAL ABSORPTION COEFFICIENT

II-1.4 Attenuation of Radiation In Matter

In passing through a finite thickness of matter, some photons tend to lose much of their energies as a result of those interactions described in Section II-1.3. Those photons that do not interact will penetrate with their original energy and direction. The amount of energy being absorbed in a single interaction is found to follow the well known Lambert-Beer's law :

$$I = I_o e^{-\mu x} \qquad (3)$$

which states that the intensity of radiation (I) decreases exponentially with the thickness (x) of the matter. μ (unit: reciprocal length) is the linear absorption coefficient and the value depends upon the physical properties of the material and the photon energy. In cases where comparison of absorption energies by two systems of different phases, use of the mass absorption coefficient is preferable to the linear absorption coefficient. The mass absorption coefficient is simply the ratio of the linear absorption coefficient to the density of the material (μ/ϱ). The conventional unit is cm^2/gm and x of Eq.(3) is then expressed in units of mass per unit area (gm/cm^2).

Since three important interactions might possibly result from the radiation of matter, depending on the photon energy, it should be emphasized here that Eq.(3) is valid only for narrow or collimated beams of monoenergetic photons. In other words Eq.(3) is valid for cases where the photons are absorbed from the beam by the same interaction. For example, gamma ray emitted from cobalt-60 interacts with matter mainly by Compton scattering and other interactions are of negligible importance. However, in Compton scattering photons are removed from the beam both by absorption and by scattering (see Section II-1.3). Thus the absorption coefficient (μ) in Eq.(3) is actually the total absorption coefficient.

For a small sample where the scattered photons do not interact further, the actual amount of radiation absorbed by the matter should be measured by the energy absorption coefficient (μ_a) rather than the total absorption coefficient (μ). Consider a target irradiated by a gamma ray. The intensity at any depth in the target is :

$$I = I_o \, e^{-\mu x} \tag{3}$$

The rate of removal of energy by absorption alone will be :

$$dI_a/dx = I_o \, \mu_a \, e^{-\mu x} \tag{4}$$

Therefore the energy really absorbed by the entire target thickness is :

$$\int_o^{I_a} dI_a = I_o \, \mu_a \int_o^{x} e^{-\mu x} \, dx$$

or $$I_a = \frac{I_o \mu_a}{\mu} (1 - e^{-\mu x}) \tag{5}$$

Compare this with the value calculated by Eq.(3) using total absorption coefficient (μ) :

$$I_{a'} = I_o (1 - e^{-\mu x}) \tag{3-a}$$

Notice that if $\mu_a = \mu$, (i.e. only absorbing, and no scattering in the interaction process) then Eq.(5) can be reduced to Eq.(3-a).

Normally, for a large target interacting with radiation by Compton scattering, most but not all of the scattering photons will remain and interact further so that $\mu_a < \mu$. Therefore the energy absorbed by the target if calculated by Eq.(3-a) based on the total or narrow beam absorption coefficient (μ), will be larger than is actually the case. Or, in other words, the calculated dose required to do a job will be too small. Thus in order to bring up the calculated dose, a correction factor which is called the buildup factor is used. It is defined (4) as the ratio of the 'true' dose as exactly calculated or measured divided by the 'narrow beam' dose (i.e. calculated by Eq.(3)). The buildup factors are available from the literature (5,6) and most of them are for point sources in infinite homogeneous media. For more complex geometries, the buildup factor expressed in some form may be incorporated with the narrow beam expression and then the final expression is integrated. An expression for the dose buildup factor which is especially useful because of its simplicity is given by Taylor, (4,5):

$$B = A\, e^{-\alpha_1 \mu r} + (1-A)\, e^{-\alpha_2 \mu r} \qquad (6)$$

where B is the buildup factor; μ is the total absorption coefficient; and A, α_1, α_2 are constants,adjusted to fit the tabulated data for μr. All these constants are tabulated in the literature (4,5). However, even this method of handing buildup factor is not completely satisfactory and for some very complex geometrical arrangements, the calculations could be so laborious and approximate that a buildup factor of 1 is often used to replace the mathematical expression especially in the preliminary study of irradiator design. In experiments where the target is small, the energy absorption coefficient (μ_a) is used directly on Eq.(3) with μ replaced by μ_a and the buildup factor is disregarded.

II-1.5 Transient Entities Formed By Radiation

The two fundamental actions of radiation are to ionize and to excite. Therefore, immediately after the physical interactions of gamma rays with the matter, ions, excited molecules and free radicals are found in the material. These energetic species are referred to as transient entities. The formation and properties of these species are affected by the photon energy, phase and nature of the matter. Generally, if the energy imparted by the incident photon is large enough to overcome the binding energy of an orbital electron to a stable molecule then this electron may be expelled, leaving behind a positive charged ion :

$$AB \rightsquigarrow AB^{+} + e^{-} \qquad (7)$$

This ionization process should be considered as the removal of an electron from the molecule as a whole rather than just from one part. The ejected electron from Eq.(7) may cause further ionization and excitation if it is sufficiently energetic. The positive ion, however, will usually possess enough energy to undergo molecular fragmentation into a free radical and an ion as Eq.(8).

$$AB^{+} \longrightarrow A^{+} + B^{\cdot} \qquad (8)$$

In cases where the energy released to the orbital electron is less than the ionization energy, the electron may be raised from its ground state to an excited state as :

$$AB \rightsquigarrow AB^{*} \qquad (9)$$

This excited molecule may dissociate into free radicals as Eq.(10) or it may fall back to the ground state by

$$AB^* \longrightarrow A^\cdot + B^\cdot \qquad (10)$$

releasing the energy as heat or light as Eq.(11).

$$AB^* \longrightarrow AB + h\nu \text{ or heat} \qquad (11)$$

Obviously Eq.(7) to Eq.(11) are not the only ways by which the ions or excited molecules are created. For example molecules which have electronegative atoms or groups, e.g. OH, CN, Cl and Br may possibly give ions by direct splitting into a positive and a negative ion.

$$CCl_4 \rightsquigarrow CCl_3^+ + Cl^- \qquad (12)$$

The excited molecule of the major constitutent may transfer its energy to the minor constituent (e.g. impurity) and ionize it as in Eq.(13). Another common way in which a

$$He^* + A \longrightarrow He + A^+ + e \qquad (13)$$

highly excited molecule can be formed by radiation is from the neutralization of a positive ion by an electron or a negative ion.

Thus the primary interaction of radiation with matter gives rise to positive and negative ions, electrons and free radicals. The reactions which then follow may be the interaction of these active species with one another or with the molecules of the surrounding medium. This results in great reaction complexity which represents difficulty and challenge in the elucidation of radiation chemistry.

II-1.5.1 Free-radical reactions

Free-radical reactions are the most important reactions induced by radiation and many of them are quite well understood. However, as it was pointed out by Chapiro (7, Chap. III of 8) that in the radiolysis of the simple organic molecules, such as saturated hydrocarbons, only about half (not all) of the products were formed as the result of free radical reaction.

Free-radical reactions quite often result in chain reactions although many free-radical reactions proceed without involving chain reaction. For example the radiation-induced oxidation of hydrocarbons to form peroxides is not a chain reaction at room temperature (Chap. IV of 2). The reason for this is that probably at the high dose-rates used, the $RO_2\cdot$ radicals formed by addition of oxygen to organic radicals as Eq.(14) do not

$$R\cdot + O_2 \longrightarrow RO_2\cdot \tag{14}$$

abstract hydrogen from other molecules, so giving hydroperoxides and other chain propagating radicals, but rather react with each other. However, at temperature above 100°C, the reaction becomes a chain reaction.

Normally, most workers on radiation-induced reactions are interested in chain reactions in order to increase the efficiency of using the radiation source as will be discussed in Section II-1.7. The most common free-radical chain reactions are for example the chlorination of hydrocarbons and the polymerization reactions. The chain reaction scheme for chlorination of methane is presented in Section II-3. The chain reactions which occur in these reactions are mainly due to the very low activation energies required to bring about the reactions, or the radicals formed are so highly excited that they can react with other molecules and create other new radicals. For example, in chlorination of methane the activation energy for a chlorine atom to attack methane and methyl chloride are 3.85 and 3.36 kcal/mole respectively (Chap. 8 of 52). Thus the chlorination of methane is an extremely rapid process (see Section II-3). Similarly for polymerization reaction the activation energies in the propagation steps are very low. A value of about 5 kcal/mole is suggested for most common polymerizations (53). Thus as long as an adequate mode of initiation* is available, a polymerization reaction will proceed rapidly.

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*For most initiators, the activation energies are in the range of 30-40 kcal.mole (53).

The free radicals produced by radiation quite often behave slightly differently from those produced in other ways. Occasionally the radiation imparts excess energy to the radicals forming 'hot radicals' that may overcome the high activation energies of some reactions which would not normally take place with ordinary thermal radicals. Also the radicals formed by radiation are highly localized along the tracks of photons and therefore they tend to react with each other more than would be expected if the distribution were uniform. Finally, the free-radical reaction in solid state can only be performed by using radiation.

II-1.5.2 Ionic reaction

As far as reactions of ions are concerned, positive ions are more important than negative ions because many systems do not formed negative ion at all and positive ions generally appear to be more reactive than negative ions (Chap. I of 2). The most common reactions are the ion-molecular reactions which can be distinguished into proton transfer reactions and condensation reactions. In proton transfer reactions, the positive ions react with other molecules as :

$$RH^{+} + RH \longrightarrow RH_2^{+} + R\cdot \qquad (15)$$

An example of this is in the case of methane :

$$CH_4^{+\cdot} + CH_4 \longrightarrow CH_5^{+} + CH_3\cdot \qquad (16)$$

In condensation reactions, carbon-carbon bonds are formed such as :

$$R^{+} + RH \longrightarrow R - R^{+} + H_2 \qquad (17)$$

or

$$CH_3^{+} + CH_4 \longrightarrow C_2H_5^{+} + H_2 \qquad (18)$$

Ion-molecular reactions can be extremely fast, occuring at every collision. Many radiation-induced processes such as crosslinking have been interpreted in terms of such reactions although these have not been proved experimentally.

Another important type of ionic reaction is known as cationic-polymerization in which the free propagating ions are so active that they lead to extremely high rate of propagation. However, these cationic chains are only expected to propagate if the electrons produced in the primary interaction e.g. Eq.(7) are held back from the rapid recombination to the positive ions. (In non-polar media the life time of the ion is about 10^{-8} to 10^{-7} sec.)

II-1.5.3 Reactions of excited molecules

As mentioned before in Eq.(9) to Eq.(11), excited molecules, if they do not decompose to free radicals, will fall back to their ground unexcited state by releasing energy as heat or photons. But in addition to these, excited molecules can undergo energy transfer to other molecules. There are four suggested mechanisms of energy transfer: (1) The energy of an electronically excited molecule is transferred to a molecule in its ground state through simple collision. For example:

$$Xe^{*} + H_2 \longrightarrow Xe + H_2^{*} \qquad (19)$$

(2) The energy of an excited molecule is released by emission of a photon, which is then absorbed by another molecule. (3) The energy is transferred by quantum-mechanical resonance from for example a solvent molecule to a distant solute molecule without the aid of intermediate molecules. (4) The energy is transferred rapidly from molecule to molecule and the residence time of energy in any particular molecule is less than the period of one vibration. This process is known as exciton transfer.

However, by far the most common reaction of an excited molecule is the decomposition into free radicals as shown in Eq.(10). This reaction is believed to be one of the most important sources of free radicals in radiation-chemical processes (Chap. II of 8). But unless the decomposition is an energetic one there is, in condensed phases at any rate, the possibility that the radicals may recombine within the solvent 'cage' (Franck-Robinowitch effect) leading to no net reaction (2,8). This effect should be especially marked with large molecules. For the highly excited molecules such as those resulting from charge-neutralization processes, the dissociated radicals may be energetic enough to escape from the 'cage' and recombination is less likely to occur.

Other reactions of excited molecules include the dissociation into saturated or unsaturated molecule as:

$$AB^* \longrightarrow C + D \qquad (20)$$

and the reaction with other molecules as:

$$AB^* + CD \longrightarrow \text{Products} \qquad (21)$$

II-1.6 Dosimetry

In the study of radiation chemistry, it is necessary to know the energy absorbed by a system. This is usually carried out by measuring the dose rate of a source with a dosimeter and then the dose absorbed by the system can be calculated from the measured dose rate as will be described in the later part of this Section.

II-1.6.1 Method of dosimetry

Many methods of dosimetry have been developed, such as calorimetry, ionization methods, cobalt glass, and chemical method. The details of the methods can be obtained in many texts or original papers in radiation chemistry or physics (e.g. 2,8,9). Since chemical method is one of the most convenient methods of dosimetry and the one selected for the present work, it will be briefly presented here. Besides the above experimental methods, it is also possible to calculate the dose rate straight from the source strength as will be given here as well.

(a) Chemical method

This method involves the irradiation, in the place of interest, of a system with a known radiation yield (G value). Then from the measurement of the amount of chemical change in this system, the energy absorbed by the system can be calculated.

Many criterias have been suggested for a desirable dosimetry system. One of the most widely used system is the ferrous ammonium sulphate system or Fricke dosimeter which has been extensively studied. The detailed procedure is presented in Appendix A.

(b) Calculation from source strength

This method is rarely used in the laboratory work, but is becoming important in irradiator design. By knowing the strength of a source in curies (disintegration per sec.) and the photon energy (eV per disintegration), the energy (E) emitted by the source can be calculated as for example in the case of cobalt-60:

$$E \text{ (per curie)} = 3.700 \times 10^{10} \times (1.173+1.332) \times 10^{6}$$
$$= 9.283 \times 10^{16} \text{ eV/sec/curie}$$

The value of E is then divided by the total surface area of the source to obtain the intensity. The intensity at any point distant from the source surface can be calculated, but notice that it depends on the geometry and location of the point and the material interposed between the point and the source. The treatment of this radiation intensity is analogus to that of the heat transfer by radiation (4,6).

From the radiation intensity, the absorbed dose at that point can be computed by using the relationship (Page 80 of 9):

$$D_M = 0.01 \ (\mu_a/\rho)_M I \ t \quad \text{rads} \qquad (22)$$

where $(\mu_a/\rho)_M$ is the mass energy absorption coefficient in (cm^2/gm), I is the radiation intensity at the point in (ergs/cm^2-sec.), and t is the time of exposure in seconds.

II-1.6.2 Comparison of absorbed energies by two systems

The calculation from source strength is a direct method and will give the doses absorbed by systems of interest, whereas the chemical method is an indirect method and will give the doses absorbed by the chemical dosimeter (e.g. Fricke dosimeter), not the doses absorbed by the systems of interest (e.g. iodine solution in a reactor). To obtain the absorbed dose of a system, it is necessary to know the ratio of the mass absorption coefficient of the system to that of the dosimeter. i.e.

$$R_{\text{single effect}} = \frac{(\mu_a/\rho)\ \text{system}}{(\mu_a/\rho)\ \text{dosimeter}} \tag{23}$$

Where the energy absorption is not of a single effect, but other effects such as photoelectric effect, Compton scattering and pair production are occuring at the same time, Eq.(23) should be modified to Eq.(24).

$$R_{\text{multiple effects}} = \frac{[h(\mu_a/\rho)+c(\mu_a/\rho)+p(\mu_a/\rho)+\ldots]_S}{[h(\mu_a/\rho)+c(\mu_a/\rho)+p(\mu_a/\rho)+\ldots]_D} \tag{24}$$

where $h(\mu_a/\rho)$, $c(\mu_a/\rho)$ and $p(\mu_a/\rho)$ are the mass absorption coefficients contributed by photoelectric effect, Compton scattering and pair production respectively. The mass absorption coefficients are available for many elements and compounds as a function of photon energy in the literature (<u>10</u>,<u>11</u>,<u>56</u>,<u>57</u>,<u>58</u>). Some values related to the present work are given in Appendix B. For a compound $X_m Y_n$ at a given photon energy, the mass absorption coefficient can be estimated (<u>12</u>) by Eq.(25)

$$(\mu_a/\rho)_{X_mY_n} = mW_X(\mu_a/\rho)_X + nW_Y(\mu_a/\rho)_Y \qquad (25)$$

where W is the atomic weight of element (X or Y) divided by the total molecular weight of the compound and m, n are stochiometric numbers. Eq.(25) can be extended for a compound of more than two elements or for a mixture of two or more compounds. An illustration of this is given in Appendix B.

II-1.7 Economics of Radiation

The economic aspect of the use of radiation is often the main factor that determines the acceptance of a process under consideration in the industry. Although extensive efforts have been expended to apply high energy radiation to chemical industry, in general its use is not widely applicable because of the high cost per unit of energy. The energy cost for producing a chemical can be estimated by the following equation.

$$EC = SC/(0.373 \times G \times MW) \qquad (26)$$

where EC = cost of energy per gram of product (\$/gm)

G = G value of product

MW = molecular weight of product

SC = cost of source energy (\$/kw-hr.)

Thus, in order to cut down the energy cost of production, either the G value and/or the molecular weight has to be extremely large as it is demonstrated in Table 1.

TABLE 1

COST ESTIMATION OF COBALT-60 ENERGY FOR DIFFERENT PROCESSES

Process	G value	M.W.	Weight kg/kw-hr	Cost* $/kg.
Chemical reaction	5	100	186.5×10^{-3}	25.00
Chain reaction	5,000	100	186.5	0.025
Polymer reaction	5	100,000	186.5	0.025

* Cost of cobalt-60 energy: $5.00/kw-hr.

Normally a G value of at least 20,000 is required to justify a commercial application to the production of a simple chemical which has low molecular weight. Such a large G value can only be achieved in a chain reaction. This is the reason why chain reactions are necessary for the present work. The molecular weights of iodomethanes are in the range of 142 to 394. On the other hand, if the molecular weight is high (such as a polymer), the energy cost can be reduced, because the weight of material produced per photon is high.

For a chemical process where both the G value and the molecular weight are moderate, then other cost factors have to be considered, such as the capital cost, maintenance cost, cost of energy source. For example, if the processing plant is linked to an existing radiation plant, less capital cost and maintenance cost are required than for a new isolated radiation plant. Another way that could possibly reduce the cost is to make use of those cheap spent fuel elements, which at present, can be considered as a waste from the nuclear energy plants. In some special cases where radiation might be the only means to provide a satisfactory product, the process might worth consider, even though the G value and the molecular weight are not very large. Examples for this are : (1) the grafting of acrylic acid on to Telflon surface by gamma radiation. (2) reactions in solid state and (3) crosslinkage of polymer.

II-2 RADIOLYSIS OF PURE COMPOUND

Methane is the simplest organic compound and its radiation chemistry is reasonably well understood. Iodine, on the other hand is well known in the field of radiation chemistry as a free radical scavenger, or a free radical detector and identifying agent (13). In this section, some discussion will be presented on the radiolysis of methane and on the radical scavenging propensity of iodine. Since methyl iodide is expected to be one of the products in the present work, its radiolysis will also be discussed. The radiolyses of other expected organic products are not available in the literature.

II-2.1 Radiolysis of Methane

When a sample of pure methane is subjected to a high energy radiation, both ionization and excitation of methane happen simultaneously (14,15,16):

$$\text{ionization} \qquad h\nu + CH_4 \longrightarrow CH_4^{+} + h\nu'$$

$$\text{excitation} \qquad h\nu + CH_4 \longrightarrow CH_4^{*} + h\nu''$$

where $\nu > \nu'$ or ν''

In fact by doing an energy balance comparing the number of ions formed during radiation with total energy deposited, one can find that for every ion formed, 0.74 excited molecules are produced (see Section 3.2.1 of 12). Or if the calculation is based on 100 eV of absorbed energy (G value), then there will be 3.66* ionizations and 2.71 excitations.

The average energy (W) required to form an ion-pair for pure methane varies with the nature of the radiation but an average value of 26.8±0.4 eV was reported by Weiss et al. (17). The formation of ions from methane is found to be consecutive and hence the appearance potential for the CH_4^+ ion is less than that for CH_3^+ ion and so on. The values are given in Table 2, together with the relative amount of the ions as found in the mass spectrum of the products. However, according to the ionic decomposition pattern shown in Fig.7 the relative distribution of the ions will be CH_4^+ (65.5%),

TABLE 2

APPEARANCE POTENTIAL AND RELATIVE AMOUNT OF THE IONS FORMED FROM METHANE (18)

Ion	CH_4^+	CH_3^+	CH_2^+	CH^+	C^+
Potential (eV)	13.12	14.39	19.20	22.4	26.2
Amount (%)	50	38.2	7.9	3.0	1.05

---

[*] The value can be obtained if the average energy (W) required to form an ion-pair is known. G=100/W.

CH_3^+ (24.1%), CH_2^+ (9.9%), CH^+ (0.5%) and C^+ (neglected), (see ref. 29 of 12).

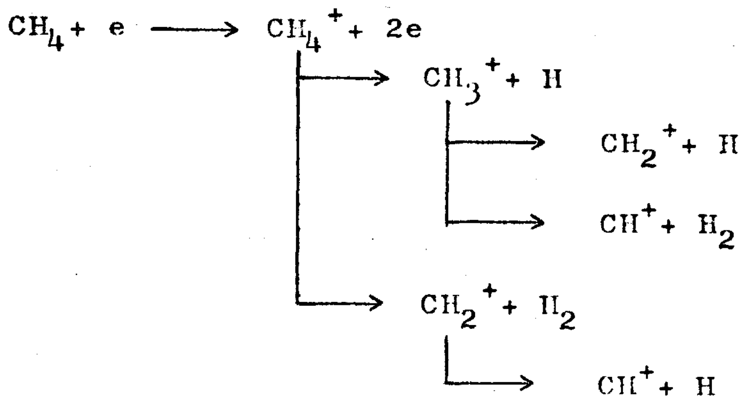


FIG.7 IONIC DECOMPOSITION PATTERN OF METHANE

Although the relative ionic distributions in both cases are different, they agree with each other in that the principal ions in this primary interaction process are CH_4^+ and CH_3^+. The reactions thus followed will mainly involve these two species. From mass spectroscopic experiments (14,20) two ion-molecular reactions (Section II-1.5.2) are known to occur:

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3^{\cdot} \qquad (27)$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \qquad (28)$$

The rate constants for these reaction are of the order of 10^{-9}cc/molecule/sec.(20). The secondary ions (CH_5^+, $C_2H_5^+$) are then normally neutralized by electrons to produce for example another methyl radical and a hydrogen molecule from CH_5^+ in reaction (27) and mainly C_2H_4 and a hydrogen atom from $C_2H_5^+$ in reaction (28). Iodine has been used to confirm the formation of the methyl radical (19). Traces of ethyl radicals have also been detected and they may arise from neutralization of a small fraction of the $C_2H_5^+$ ions. The fates of the other primary species e.g. CH_2^+, CH^+ are uncertain, but the iodine scavenger work (Section II-2.2) has suggested that the CH_2^+ may be neutralized by an electron to give a $CH_2^\cdot$ free radical.

The role of excited methane in the radiolysis is a subject of considerable doubt and controversy. Magee (16) proposed that both photolysis and radiolysis of methane proceed mainly by a free radical process and/or by reactions of excited molecules, than by reactions of ions. However, the proposed ionic mechanism (14) discussed above is able to account quantitatively for all the major products detected (20) and hence the excited methane plays no part in the radiolysis (14, Chap.4 of 2). Nevertheless, one thing in common here is that the free-radicals are formed both by dissociation of excited methane and neutralization of methane ions as summarized below:

$$\begin{tikzcd}
 & M \arrow[dl] \arrow[dr] & \\
M^* \arrow[d] & & M^+ + e \text{ (or } M) \arrow[ll] \arrow[d] \\
R_1^\cdot + R_2^\cdot & & R_3^\cdot + R_4^\cdot
\end{tikzcd}$$

Therefore free radicals undoubtedly occur as important intermediates in the methane radiolysis and hence they are responsible for the formation of different final products and quantities.

The final product distribution, however, is very difficult to predict from the distribution of the free radicals, because the molecules formed during the process may react with the free radicals or with one another resulting in the formation of polymeric products. For instance, ethylene is believed to be one of the main product but it reacts with hydrogen atom or other radicals as soon as it is formed and very little ethylene remains after irradiation. Hydrogen is formed partly from the reaction of hydrogen atoms and partly from Reaction (28). Ethane is formed mainly by dimerization of methyl radicals Table 3 shows the G values of the products of radiolysis

TABLE 3

RADIOLYSIS OF METHANE

Product	G value	
	Gamma radiation (21)	1.7 MeV electrons (20)
H_2	6.4	5.7
C_2H_6	2.1	2.1
C_3H_8	0.3	0.14
C_2H_4	0.1	0.05
C_4H_{10}	0.2	0.04
CH_4	-9.1	-7.6

of methane. These G values are not largely affected by some of the physical variables such as temperature, gas pressure and radiation intensity (14,19). Therefore, the effects of these variables on the radiolysis of methane were not intensively studied in the past.

II-2.2 Radiolysis of Iodine —— Radical Scavenger

The most direct way of studying free radicals is by electrons spin resonance but reliable results can also be obtained by determining the final products of irradiation, either with or without a radical scavenger. Using a scavenger as a solute in a mixture, the free radicals formed from the solvent have the choice of reacting with each other or with the solute (scavenger). At a sufficiently high solute concentration, but less than approximately 10^{-3}M, nearly all of the radicals disappear by reaction with solute to form some detecable final products. Thus by determining the amount of the products, one can obtain the corresponding radicals formed by irradiation. Iodine is demonstrated (13) to be a very efficient radical scavenger for reactions of the type:

$$R^{\cdot} + I_2 \longrightarrow RI + I^{\cdot} \qquad (29)$$

This method has been adopted by many workers in studying the radiolysis of hydrocarbon (19,22,23,24).

The method, however, has difficulties that need to be resolved in order to make the method more reliable. One of the difficulties is that the reaction mechanism is not always known, and this leads to some uncertainty. Another difficulty is that there is a possibility of charge or energy transfer from solvent to solute which may act as an energy sink. Extensive work has been done on the possibility of minimizing this complication. One possible solution is to lower the solute concentration. Fessenden (22) reported that the yield for the formation of alkyl iodide from cyclohexane in deaerated solution was independent of iodine concentration from 10^{-5}M to 5×10^{-3}M but was somewhat higher at higher concentrations. But solute concentration below 10^{-3}M was recommended (23).

Although the radiation-induced iodination of methane has a completely different objective from the objective of the radiolysis of methane using iodine as radical scavenger (see Section II-3.3) and hence the two reactions are expected and hoped to be different, yet it is interesting to study the scavenger work applied to the radiolysis of methane in somewhat more detail. Experimentally (19), the radiolysis of methane has been performed in a 500 cc. spherical flask having a small 'window' to reduce absorption of soft radiations of the X-rays. The gaseous methane plus approximately 10^{-3} M of iodine are introduced by vacuum distillation into the flask which is then closed by a glass seal and irradiated. Using the X-rays or electrons of 2 MeV, the sample is irradiated for a period of time that produces about 50% reaction with the iodine. The results are summarized in Table 4. Notice that the variations of the pressures of the components and the intensity of the radiation appear to have no significant effect on the relative amount of products.

TABLE 4

RADIOLYSIS OF METHANE USING IODINE AS RADICAL SCAVENGER (19)

Radiation Source	Pressure of CH_4 mm Hg	Pressure of I_2 mm Hg	Products (Relative Yield %)		
			MeI	EtI	CH_2I_2
X-rays	120	.14	74	5	21
X-rays	120	.14	74	5	21
e	120	.07	71	5	24
e	120	.14	77	5	18
e	120	.175	76	5	19
e	120	.14	74	4	22
e	22 (CH_4) 18 (H_2)	.14	77	6	17
e	20	.14	80	4	16
e	20	.14	77	4	19
e	334	.14	80	7	13
e	576	.14	77	5	18

II-2.3 Radiolysis of Methyl Iodide

In the radiolysis of methyl iodide, the fragmentation is most likely to happen at the C-I bond rather than the C-H bonds (19,25). The reasons for this are that the

C-I bond is by far the weakest in the molecule and the iodine atom has far more electrons than any other atom of the molecule and therefore, ionization or excitation at this point is most likely. Most work (25,26) on the radiolysis of liquid methyl iodide is using X-rays of 100 keV energy but it has been demonstrated (25) that the decomposition by gamma radiation produces the same relative yields of products as that produced by the X-rays.

The ionic processes in the over-all decomposition are believed to be the most important readiation processes. The methyl iodide, after absorption of the radiation energy, will become excited or decompose to various ions as Eq.(30) depending on the absorbed energy. Note that

$$h\nu + CH_3I \longrightarrow CH_3I^* \qquad h\nu < 9.5 \text{ eV} \qquad (30\text{-a})$$

$$\longrightarrow CH_3I^+ + e^- \qquad 9.5 < h\nu < 12.4 \text{ eV} \qquad (30\text{-b})$$

$$\longrightarrow CH_3^+ + I\cdot + e^- \qquad h\nu > 12.4 \text{ eV} \qquad (30\text{-c})$$

the appearance potential of CH_3^+ ion is 12.4 eV (27) and the ionizing potential of methyl iodide is 9.5 eV. The excited CH_3I^* of Eq.(30-a) may dissociate into high energy 'hot radicals' as:

$$CH_3I^* \longrightarrow CH_3\cdot + I\cdot \qquad (31\text{-a})$$

$$\longrightarrow CH_2\cdot + HI \qquad (31\text{-b})$$

Since many free electrons are produced in ionization, these electrons may attach themselves to the solvent methyl iodide as:

$$CH_3I + e^- \longrightarrow CH_3I^- + 3.6\ eV \qquad (32)$$

Thus the charge neutralization reactions followed will be numerous. Some of the postulated reactions are given below.

$$CH_3I^+ + e^- \longrightarrow CH_3I^* + q \leq 9.5\ eV \qquad (33)$$

$$CH_3I^+ + CH_3I^- \longrightarrow CH_3I + CH_3I \qquad (34\text{-a})$$

$$\longrightarrow CH_3CH_3 + I_2 \qquad (34\text{-b})$$

$$CH_3^+ + CH_3I^- \longrightarrow CH_3CH_3 + I\cdot \qquad (35\text{-a})$$

$$\longrightarrow CH_3\cdot + CH_3I \qquad (35\text{-b})$$

$$CH_3I^+ + I^- \longrightarrow CH_3\cdot + I_2 \qquad (36)$$

The neutralization processes are highly exothermic so that the products may or may not be stable depending upon the distribution of the energy in the system. The final product distribution, relative to the yield of iodine as unity, was found (<u>25</u>) to be hydrogen (0.067), methane (0.47), ethane (0.90), ethylene (0.067), acetylene (0.026) and a trace amounts of methylene iodide and ethyl iodide. The yields of these products are directly proportional to the total irradiation dose given to the sample with very little or no induction period being observed. The high yield of ethane suggests the importance of ionic processes such as Reactions (34-b) and (35-a). The hot methyl radicals, for example from Eqs(31-a), (35-b) and (36) are believed to be responsible for the large fraction of methane and methylene iodide production. Hydrogen presumably is formed directly by the dissociation of the highly excited molecules and ionic species. The association of hydrogen atoms is not likely because the lack of strong effect of iodine (radical scavenger) on the hydrogen yield (Fig.8) indicates the hydrogen atoms are not produced as intermediates.

The presence of small amounts of iodine produced as a result of the decomposition does not apparently inhibit the formation of products to any appreciable extent but if free iodine is added to the sample before the irradiation, the yields are found to decrease as shown in Fig.8. Thus the iodine only affects the production to an appreciable extent when it presents at a relatively high concentration (0.1-4 M in iodine). Notice that the effect of iodine on the production of ethane is much larger than that of hydrogen.

Recently, Vilenchich and Hodgins (31) reported that at dosages between 7.7 x 10^{16} and 7.5 x 10^{19} eV/(gm)(min.), the decomposition of methyl iodide in a 2 ml. glass ampoules was negligible at room temperature.

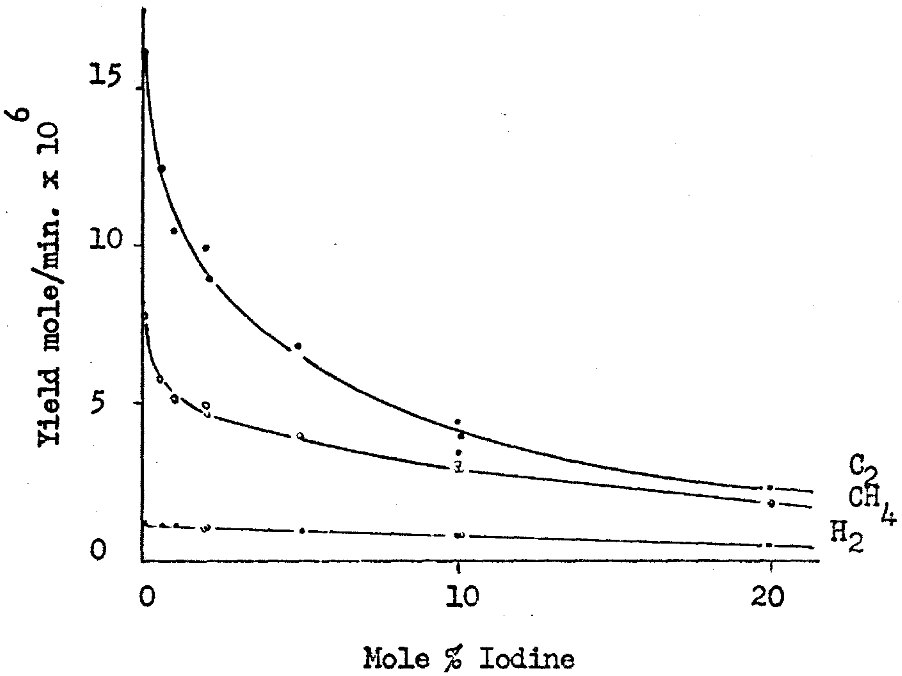
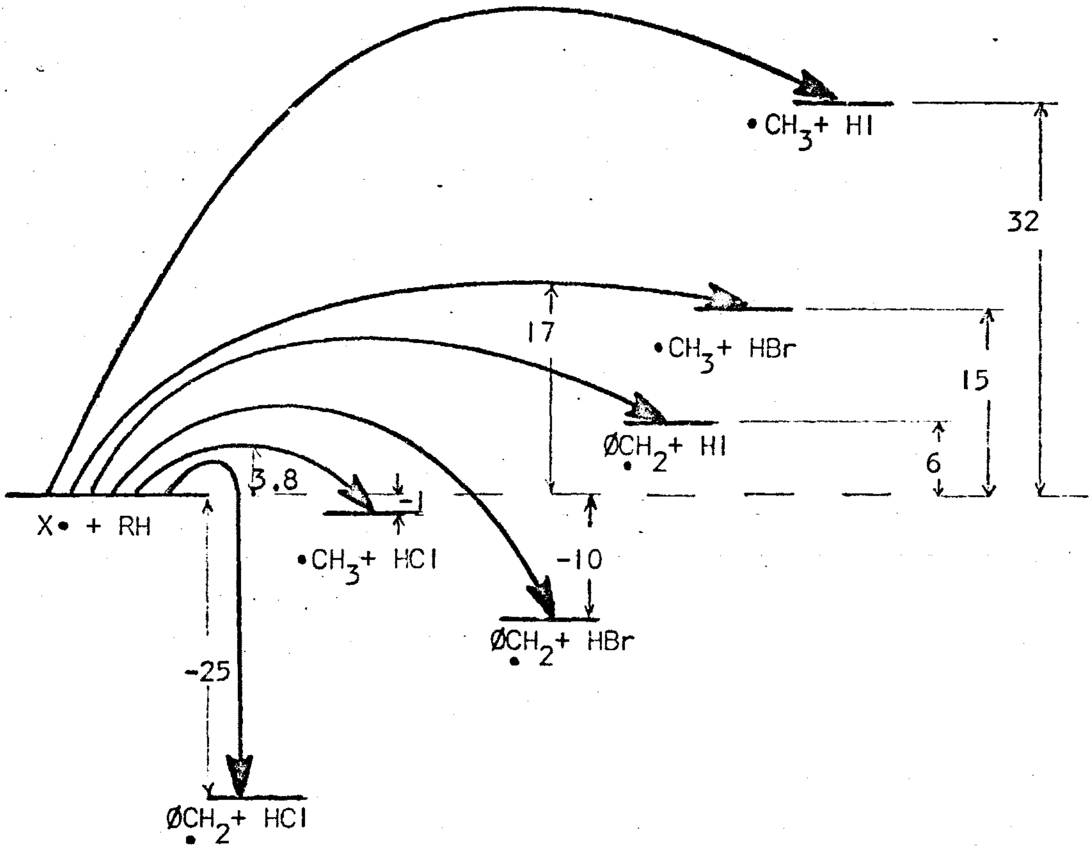


FIG. 8 EFFECT OF ADDED FREE IODINE ON THE YIELDS OF RADIOLYSIS OF CH_3I (25)

II-3 GAMMA - INITIATED HALOGENATION REACTIONS

Gamma-initiated chlorination of aromatic compounds (28,29) and methane (12,30) have been studied with an ultimate aim of producing these chlorinated compounds using high-energy radiation as an initiating agent. Although the commercial use of radiation to produce these chemicals has not yet become a reality, this kind of halogenation work has been extended to other halogen such as iodine (31) in order to achieve a better understanding on this almost unexplored area. Obviously the feasibility of producing these halogenated compounds relies on the possibility of having chain reactions since low molecular weight compounds are contemplated (see Section II-1.7).

It is well known in the elementary chemistry that the tendency to undergo radical chain halogenation decreases in the order $F > Cl > Br > I$, because the heat of reaction increases from F to I. Fig.9 compares the heats of reaction and activation energies of chlorine, bromine and iodine radicals. The attack of chlorine atom on the C-H bonds is an exothermic, low activation energy process, whereas the attack of bromine atom is endothermic except for the very weak C-H bonds. The heat of formation for the displacement step with the iodine atom is high; 32.6 kcal for methane and 6.0 kcal for toluene. Thus the



$$X\bullet + CH_4 \longrightarrow \bullet CH_3 + HX$$

$$X\bullet + \text{Ø}CH_3 \longrightarrow \text{Ø}\underset{\bullet}{C}H_2 + HX$$

FIG. 9 HEATS OF REACTION AND ACTIVATION ENERGIES OF •Cl ,•Br AND I• RADICAL REACTIONS (52) prospects of chain iodination by iodine atoms are unpromising (52).

II-3.1 Chlorination of Aromatic Compounds

The chlorination reactions induced by gamma radiation are generally considered as extremely fast and G values are as high as 10^4 to 10^6 (2,29). In fact for chlorination of benzene, the reaction proceeds so rapidly that the reactants have to be diluted with some solvent such as carbon tetrachloride in order to slow down the reaction for better control. The other aromatic compounds which have been studied are for example toluene and chlorobenzene with the use of gamma radiation from 1-kilocurie and 10-kilocurie cobalt-60 sources. The G values reported are about 85,000 for chlorination of benzene and 14,000 to 18,000 for chlorination of toluene (28,29).

The chlorination of toluene occurs both by addition to the ring and substitution in the side chain. It was found (29) that the initial rate of the reaction was proportional to the radiation intensity and the chlorine concentration as follows:

$$R_o \propto (I^{0.5}[Cl_2]^2)_{subs.} + (I^{0.5}[Cl_2]^{0.5})_{add.}$$

Impurities such as oxygen and benzyl chloride are added to the system for investigating the effect of impurity. For the case of oxygen, when about 1.7% oxygen is added to the chlorine, the rates of addition and substitution are decreased to about one fifth and one twelfth respectively of the value obtained without the oxygen. This strong oxygen inhibition is presumably caused by the following reaction:

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (14)$$

which is reported in many radiation-induced reactions (2). For the case of benzyl chloride, its present in benzene or toluene to the extent of more than 1 mole % virtually stopped the usually rapid addition reaction of chlorine to the aromatic ring (28).

II-3.2 Chlorination of methane

The radio-chlorination of methane was investigated recently (30). The results showed that radio-chlorination process followed different mechanisms and/or has different rate constants from the photo-chlorination process, even though both processes produced the same products. A reaction scheme for the radio-chlorination has been proposed (32,33) as follows:

Chain steps:

$$Cl_2 \rightsquigarrow 2Cl\cdot \qquad (37)$$

$$Cl\cdot + RH \rightleftarrows R\cdot + HCl \qquad (38)$$

$$R\cdot + Cl_2 \rightleftarrows RCl + Cl\cdot \qquad (39)$$

Overall:

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl \qquad (40)$$

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl \qquad (41)$$

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl \qquad (42)$$

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl \qquad (43)$$

Above 500°C:

$$CH_4 + 2Cl \longrightarrow C + 4HCl + \text{heat} \qquad (44)$$

Thus the four chlorinated methanes are expected in yields depending upon the experimental conditions. The experimental parameters studied together with the parameter ranges are given below (30).

Initial gas pressure (mm Hg)	100-10,000
Initial gas conc. (mole % Cl_2)	10-95
Initial gas temperature (°C)	30-120
Absorbed dose (eV/gm)	5.0×10^{17}-2.0×10^{19}

The reaction was carried out in gas-phase in a batch reactor of approximately 50 ml. capacity. With gamma radiation from a 5300-curie cobalt-60 source, the G values were reported to be as high as 7.2×10^5. The product formation, as shown in the overall reaction scheme above, is of the consecutive nature with methyl chloride concentration initially the highest (Fig.10). As the conversion proceeds the methyl chloride concentration decreases while the concentrations of the other products

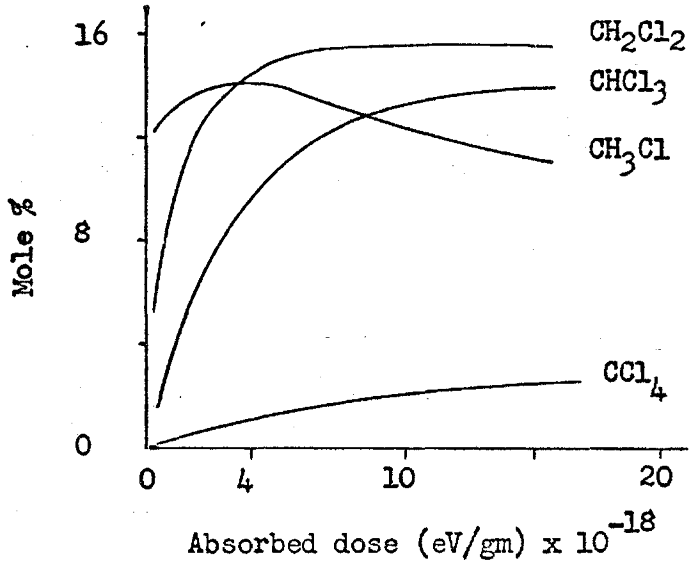


FIG.10 CHLORO-METHANES PRODUCT DISTRIBUTION (INITIAL GAS COMPOSITION: 50 MOLE % Cl_2) (30)

are building up. In general, at a given temperature and dose rate, the lower the initial chlorine concentration, the more favoured is the production of lower chloromethane. For instance, maximum production of methyl chloride occurs at about 30 mole % Cl_2, at about 60% for methylene chloride, at about 70% for chloroform and at about 90% for carbon tetrachloride. Also the chlorine utilization was found to be complete for gas bends of less than 30 mole % Cl_2. Above 30 mole % Cl_2, the average chlorine conversion was 98.6%.

The throughput, at 1000 mm.Hg pressure is too low and the energy utilization is too high for this process to be commercially attractive and so high pressure and high temperature work has been investigated. Results had shown that the increase in temperature and pressure did not decrease the conversion. In fact, slightly higher conversions were obtained and the optimal G values were in the order of 10^6. However, at high temperature, with this highly exothermic reaction as discussed before, large excess of heat will be generated in the system. The side reaction, Eq.(44) might proceed under such circumstances. In fact reaction (44) was reported (30). Thus proper heat exchangers have to be included to the reactor to remove the excess heat.

II-3.3 Iodination Reactions

As shown in Eq.(37) to Eq.(39), the chlorine atom formed by dissociation abstracts hydrogen atom from hydrocarbon molecule, giving hydrogen chloride. However, in the case of iodine as mentioned before and shown in Fig.9, the iodine atom cannot do this because the reaction would be highly endothermic. Instead the iodine atom will react with other radicals or with each other. If the iodine atom is attacking other free radicals and forming 'dead' species, the iodine will act as a radical scavenger and this is in fact precisely the function of iodine in much radiation chemistry work - the detection and determination of free radicals formed in the systems (see Section II-2.2). It should be noted, however, that in the radical scavenger work the iodine is present in a very low concentration (less than 10^{-3} M) and this presence of iodine, at a first approximation, is neglected in the primary processes and no iodine radical is formed (19). Radicals of the hydrocarbon are assumed to form through reactions in the primary processes such as the one shown in Section II-2.1, page 38, or summarized as:

$$M \rightsquigarrow R_1\cdot + R_2\cdot \tag{45}$$

These free radicals might then attack the iodine as Eq.(46) in the secondary reaction processes. Other possible secondary reactions of the radicals are suggested as shown in Eqs.(47) and (48).

$$R_1\cdot + I_2 \longrightarrow R_1I + I\cdot \tag{46}$$

$$R_1\cdot + R_2\cdot \longrightarrow R_1R_2 \tag{47}$$

$$R_1\cdot + R_3H \longrightarrow R_1H + R_3\cdot \tag{48}$$

Reaction (47) is very small in comparison to (46) or (48) when the radical concentration is small at moderate reaction rates. Reaction (48) has an higher activation energy (10-15 kcal.) than that of Reaction (46), probably about 1 kcal. Thus Eq.(46) seems to be the predominating reaction at temperature about 25°C and at low iodine concentration.

All the work, in the past, on the radiation-induced reactions between iodine and various hydrocarbons were concentrated in the low iodine concentration region with the purpose of using iodine for quantitative determination of radical production in the radiolyses of these hydrocarbons. Weber et al. (34) gave a brief review on the subject and the results expressed in term of G value of iodine consumed were presented. Generally, with the iodine concentrations in paraffins and their derivatives at about 10^{-3} to 10^{-4}M, the G values for the iodine consumed fell in the range of 2.6 to 4.5. For aromatic hydrocarbons at the similar iodine concentration range, the $G(-I_2)$ varied from 0.3 to 1.49. In Weber's work, X-radiation was used and sample of liquid hydrocarbon (10ml.) containing the desirable concentration of iodine was sealed in an irradiation cell after degassing by repeated freezing and pumping.

Thus, at this stage of the discussion, it seems hopeless to expect that the radio-iodination of methane is of any commercial value because the G value is going to be very low. However, recently Vilenchich and Hodgins (31) reported that the gas-phase gamma initiated iodination of methane yielded G values as high as $7x10^7$. Such surprisingly high yield was believed to be the result of autocatalytic effect of iodine which had also been reported in the iodine exchange reactions between

4-iodoantipyrene and iodine in carbon disulphide, benzene and aliphatic alcohols (36). This gas-phase reaction was carried out in a stainless steel reactor of 300 ml. capacity. In preparing an experimental sample, the reactor was first evacuated to 10^{-6} mm. of mercury. Iodine in ether solution was then introduced into the evacuated reactor by a syringe. Methane was then added to an appropriate pressure.

The experimental parameters studied and their values are as follows (31):

Initial pressure (atm.)	1-2
Initial vapor conc.(mole % I_2)	10-90
Temperature (°C)	80-230
Dose rate (eV/gm-min.)	$7.7\text{x}10^{16}$-$7.5\text{x}10^{19}$
Absorbed dose (eV/gm)	$4.6\text{x}10^{17}$-$5.7\text{x}10^{21}$
Irradiation time (min.)	2-76

The identified products in the reaction were methyl iodide, methylene iodide, iodoform, ethyl iodide and hydrogen iodide. No carbon tetraiodide had been detected. The extremely high G values obtained indicate that a long chain reaction must have taken place. Reaction scheme such as Eq.(45) followed by Eq.(46) will not be possible to provide those large G values because these two reactions are of radical scavenging nature and G values will never be larger than 10. Thus, instead the reaction scheme could follow that proposed for the chlorination reaction, Eq.(37) to Eq.(43). Accordingly the following iodination reactions were proposed (31):

Chain steps:

$$I_2 \rightsquigarrow 2I^{\cdot} \qquad (49)$$

$$I^{\cdot} + RH \rightleftharpoons R^{\cdot} + HI \qquad (50)$$

$$R^{\cdot} + I_2 \rightleftharpoons RI + I^{\cdot} \qquad (51)$$

where RH can be CH_4, CH_3I, CH_2I_2 or CHI_3

Overall:

$$CH_4 + I_2 \longrightarrow CH_3I + HI \qquad (52)$$

$$CH_3I + I_2 \longrightarrow CH_2I_2 + HI \qquad (53)$$

$$CH_2I_2 + I_2 \longrightarrow CHI_3 + HI \qquad (54)$$

$$CH_3I + CH_2I_2 \longrightarrow CH_3CH_2I + I_2 \qquad (55)$$

However, it should be noted that Eq.(50) is thermodynamically not favourable because it is an endothermic reaction. Reaction (55) was believed to be catalysed by the ferric iodide which was formed on the inner wall of the reactor over a long period of use.

The thermal reaction between equimolar quantities of methane and iodine at 126°C for 8 hours and at 160°C for 48 hours was not observed. Therefore no reaction would be possible unless gamma radiation was used. Also it was reported that within the experimental range, the reactant concentration had relatively little effect on the yields of methyl iodide (except for 130°C runs), methylene iodide and iodoform. The temperature, dose rate and total absorbed dose were found to be the most important interacting variables. Experimentally, the optimal conditions for the formations of methyl iodide and methylene iodide were at 130°C, an initial iodine concentration of 7 mole %, a dose rate of 7.7×10^{16} eV/gm min. and a total dose of 1233 rads. Yields of CH_3I and CH_2I_2 at these conditions were 60 weight %, $G = 7 \times 10^7$ and 17 weitht %, $G = 1.47 \times 10^8$ respectively.

An interesting experimental phenomenon observed during the experiment is that the reactor pressures in some cases build up suddenly and then drop back to normal pressure. Since there is no change in the total number of molecule according to Eq.(52) to Eq.(55), one possible explaination to this phenomenon is the sudden increase of temperature inside the system. This will imply that the overall reaction is exothermic. But the values of the heat of reaction for Eqs.(52) and (53) at 25°C are estimated from the standard heats of formation (37) to be 14.109 kcal/g-mole and 2.32 kcal/g-mole respectively.

The positive values of heat of reaction indicate that both reactions (52) and (53) are endothermic reactions. The heat of reaction for Eq.(52) at 130° has also been estimated using the standard equation (38) such as:

$$\Delta H^{o}_{130} = \Delta H^{o}_{25} + \left[\Sigma_{\text{prod.}} (nc_p) - \Sigma_{\text{rect.}} (nc_p) \right] (130-25)$$

The molal heat capacities of HI, I_2 and CH_4 are available in the literature (39). For CH_3I, the molal heat capacity is roughly estimated by Kopp's rule (page 130 of 38). The value of ΔH^{o}_{130} is estimated to be 14.562 kcal/g-mole, which again shows that reaction (52) is endothermic. Thus the suggestion of sudden increase of temperature in the reactor in order to account for the sudden increase of reactor pressure is not satisfactory unless the reactions do not follow the proposed reaction scheme, Eq.(49) to Eq.(55).

This phenomenon has not yet been explained successfully by the authors (31). Although it is only a small experimental observation, it could be a clue to the unexpectedly high G values obtained in the experiments. Obviously, what the gamma radiation has done on the intermediate state of the iodination process has to be further elucidated.

III EXPERIMENTAL

III-1 INTRODUCTION

With the ultimate (original) objective (see Section I) in mind, a flow system was designed for carring out the gamma-initiated iodination in liquid phase. The reasons for this decision are: (1) a flow system is more practical for any commercial scale reaction and (2) the gas phase iodination requires larger reactor and hence larger and more expensive gamma radiation source.

Appendix D gives a detailed discussion of the design of a flow system. For the present work, the design is basically similar to the one used by Harmer et al. (40,41) in the Dow Chemical's ethyl bromide process and by Harmer et al. (28,29) in their chlorination work. It involves a continuous bubbling of methane through a column of iodine solution. The iodine solution can either be fed into the reactor continuously or only at the beginning of the experiment in a semi-batch process. Almost all the present experimental work was performed in a semi-batch process because of its simplicity and other reasons which will be presented later.

Although there is an ultimate (original) objective to be studied, an immediate objective arose during the course of the study has to be first solved. This immediate objective is to get the reaction to proceed at a reasonable rate in the liquid phase (see Section III-5). In fact, this thesis is focussing on this immediate objective. Thus the areas of experimentation, as presented in Section III-5, were designed to handle this immediate objective.

The chemicals used in this study were of reasonably pure grade and no further purification was done on them. The specifications for these chemicals are given in Section III-2.

Because of the very corrosive nature of iodine and the degrading nature of gamma radiation, all parts of apparatus in contact with iodine and radiation were made of glass (Pyrex). The details will be given in Section III-3 and Appendix D.

Product analysis was carried out with a gas chromatograph. Liquid samples from cold trap, reactor and gas-liquid separator were injected into the column of the chromatograph via a micro syringe. In this preliminary exploratory work, only the liquid sample which contained practically all the carbon containing products was of interest and thus the gaseous product stream mainly consisting of unreacted methane, hydrogen iodide was not analysed.

III-2 CHEMICALS

A large number of chemicals was involved in this work. Some of their important physical constants that will be referred to are tabulated in Appendix F. These chemicals can generally be classified into five groups for purposes as follows:

(A) Reactants

The two reactants used in this work were methane and iodine. Both reactants were purchased in 1968 and used by Vilenchich (31) for gas-phase iodination reaction.

Methane — Certified grade (C.P. grade) methane supplied by the Matheson Company, Whitby, Ontario was used. The minimum purity is 99 mole %. A typical analysis of C.P. grade methane is as follows:

Component	Mole %
Methane	99.1
Ethane	0.12
Carbon dioxide	0.2
Nitrogen	0.6
Propane	0.03
Oxygen	0.005

This C.P. grade methane behaved identically to the research grade methane (minimum 99.99 mole %) as far as the chlorination reaction of methane was concerned (12). Its use was therefore continued in this work.

Iodine — Reagent grade, resublimed iodine, supplied by Shawinigan, the McArthur Chemical Co. Ltd., Montreal. The maximum impurities are:

Non-volatile	0.010%
Chlorine & Bromine (as Cl)	0.005%

(B) Solvents

A total of eleven solvents were used including the products methyl iodide and methylene iodide. The specifications of methyl and methylene iodides will be given next under the headline of products and the remaining nine solvents are summarized as follows:

Solvent	Grade	Supplier
Benzene (Thiophene free)	Certified (spectranalyzed)	Fisher Sc. Co. N.J.
Carbon tetrachloride (low sulfur)	Analytical Reagent	Mallinckrodt Chem. Works Ltd.Montreal
Ethyl iodide	Reagent	The British Drug House Ltd.
n-Hexane	Reagent	Fisher Sc. Co. N.J.
Methanol (Methyl hydrate)	Reagent	The McArthur Chem. Co. Ltd.,Montreal
Tetrachloroethylene (stablized with Thymol)	Spectro	Eastman Organic Chemicals, N.Y.
Toluene	Analytical Reagent	Mallinckrodt Chem. Works Ltd.,Montreal
1,2,4-Trichlorobenzene	Reagent	Eastern Chem.Corp. N.J.
Trichloroethylene	Reagent	Allied Chem. N.J.

(C) Products

Three carbon containing products were purchased for the purpose of analysis references and gas chromatograph calibration. They are:

Chemical	Grade	Supplier
Methyl iodide (stabilized with metal copper)	Fisher Certified (not less than 99.5%)	Fisher Sc. Co.
Methylene iodide (stabilized with metal copper)	Purified	Fisher Sc. Co.
Iodoform	Reagent	The British Drug House Ltd.

(D) Fricke dosimetry

Chemicals involved here were all analytical reagent grade. They can be subdivided into four groups for four purposes as follows:

(1) Dose rate vs. absorbance calibration curve.
Chemicals: Ferric sulphate (crystal), sulphuric acid.

(2) Determination of Ferric concentration by titration.
Chemical : Potasium permanganate.

(3) Standardization of potasium permanganate solution.
Chemicals: Iron wire, hydrochloric acid, Stannous chloride, mercuric chloride manganese sulphate, sulphuric acid, phosphoric acid.

(4) Dosimetric solution
Chemicals: Ferrous ammonium sulphate, sodium chloride, sulphuric acid, oxygen, triply distilled water.

(E) Chromatographic columns

The coated column packing that was used successfully in the present work was chromosorb W, AW-DMCS treated with 10% silicone gum rubber SE 30, 60/80 mesh size, supplied by the Chromatographic Specialties, Brockville, Ontario.

III-3 APPARATUS

The flow sheets of both flow and semi-batch processes are shown in Fig.11 and Fig.12 respectively. The dimensions and discussion of the design of the equipments are detailed in Appendix D. In the flow process both methane and iodine solution are continuously fed into an overflow reactor. However, if the iodine solution feed line is removed from Fig.11, the continuous flow process becomes a semi-batch process. For convenience, this semi-batch process is referred to as an overflow semi-batch process. In this process, the methane vaporized and carried away part of the iodine solution from the reactor so that the solution level in the reactor could not be maintained unless the iodine solution was feeding in continuously as the flow process. Hence the contact time between a methane bubble and the surrounding medium would be reduced as the level was dropping. Thus the overflow process was modified as shown in Fig.12. A Pyrex condenser with coiled condensing tube cooled by ice water and located on top of reactor was acting as a reflux condenser. Under this condition, only the unreacted methane, and the uncondensible vapors at about 4°C, such as iodine, solvent and products could escape from the reactor. This small quantity of escaped vapors, did not

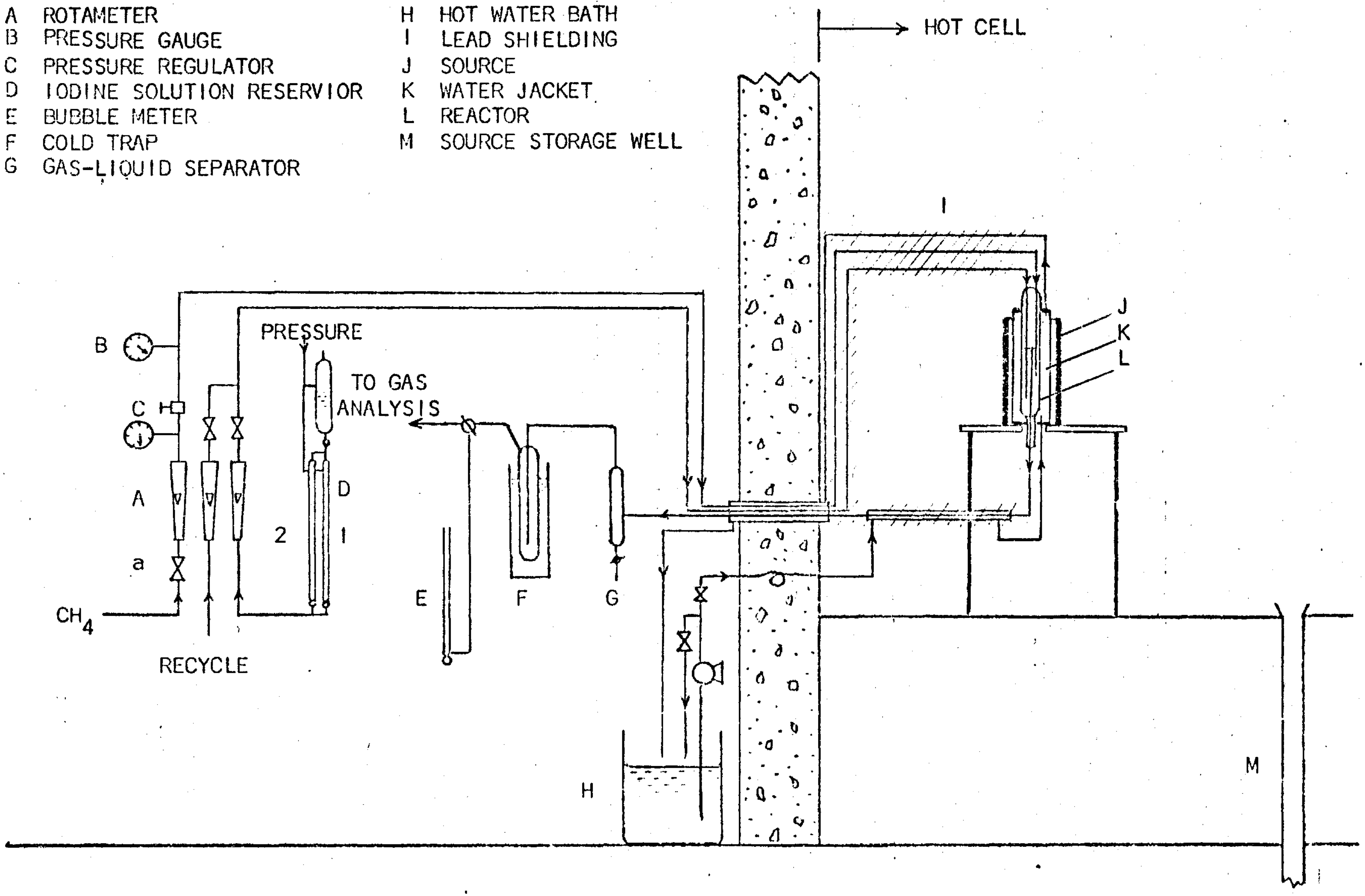
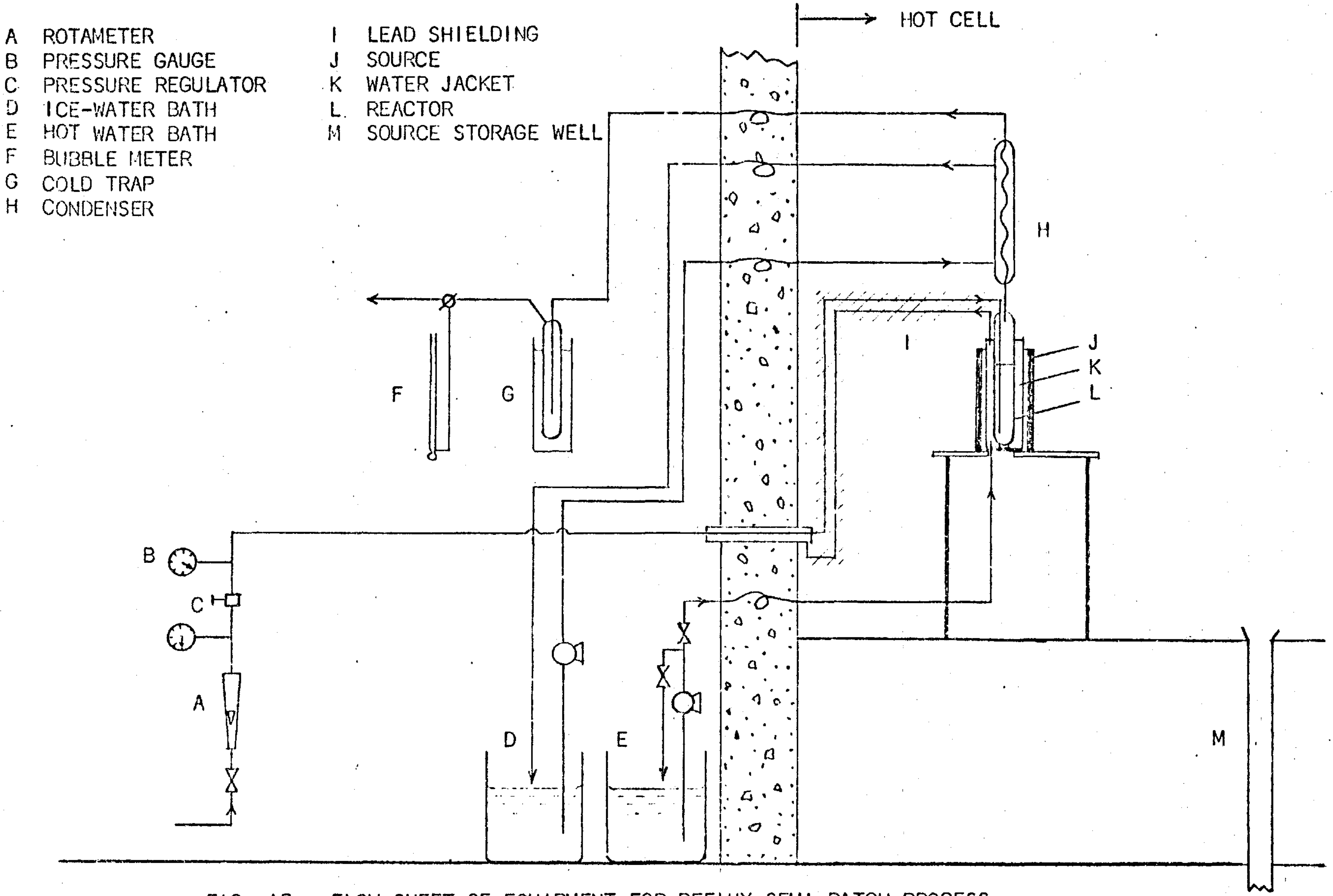


FIG. 11 FLOW SHEET OF EQUIPMENTS FOR CONTINUOUS FLOW PROCESS

NOTE : BY REMOVING THE LIQUID FEED, THE SYSTEM BECOMES AN OVERFLOW SEMI-BATCH PROCESS.



A	ROTAMETER
B	PRESSURE GAUGE
C	PRESSURE REGULATOR
D	ICE-WATER BATH
E	HOT WATER BATH
F	BUBBLE METER
G	COLD TRAP
H	CONDENSER
I	LEAD SHIELDING
J	SOURCE
K	WATER JACKET
L	REACTOR
M	SOURCE STORAGE WELL

FIG. 12 FLOW SHEET OF EQUIPMENT FOR REFLUX SEMI-BATCH PROCESS

change the solution level appreciably. This process is called as a reflux semi-batch process to distinguish it from the overflow semi-batch process.

Generally, the apparatus can be divided into three sections, namely the feed rate controlling system, the reactor and the products collecting system.

III-3.1 Feed Rate Controlling System

This part of the apparatus was built outside of the hot cell so that it enabled the operator to control the system without being exposed to the radiation inside the hot cell. As shown in Fig.11 the methane from a gas cylinder was controlled and metered by a needle valve (a) and a calibrated rotameter (A). Since the methane had to force its way through about 4 inches of solution in the reactor (see Fig.D-4 in Appendix D), a pressure of 3 psig (see Appendix E) was maintained by a pressure regulator (C) down stream of the rotameter in order to avoid fluctuation of the rotameter floats. The reactor pressure was indicated by a pressure gauge (B) which normally should read zero psig.

The iodine solution from a reservoir (D) was drained through a three-way valve into burets 1 and 2 alternatively. A nitrogen pressure of 10-15 psig was used to force the solution into the rotameter and the flowrate was then controlled by a Nupro bellows type 4BG morel valve. The rotameter for iodine solution was not calibrated because different solvents and different iodine concentrations were expected to be used in this work. Thus the exact quantity of solution fed into the reactor was read from the two burets with the deduction of the solution hold up in the line (62.0 ml.). The rotameter was therefore merely acting as an indicator for constant feed rate.

A third rotameter had also been set up to meter and control the flow rate of the recycle stream, but was not used in this preliminary work.

All rotameters were purchased from the Brooks Instrument Co., Ontario. The specifications are given in Appendix E together with the methane flow rate calibration curve.

The transporting tubings as shown in Fig.11 were unavoidably long and therefore the only way to decrease the liquid hold up in the tubings was to reduce the tube diameter. Thus a 2 mm. ID capillary had been used for a fast transportation of the products and the unreacted reactants from the reactor to the separator in order to avoid any further reaction inside the tubing.

III-3.2 Reactor

Two kinds of reactor were used for the experiment, referred to as overflow reactor and reflux reactor as shown in Fig.D-4 in Appendix D. Both reactors could be classified as conventional backmix reactors. The mixing in the reactors was carried out by the bubbling methane and with a small volume (28 ml.) of solution inside the reactor, a normal methane flow rate of 20 ml./min. provided vigorous mixing.

The reactor consisted of a 10 in.x $\frac{3}{4}$ in. ID Pyrex tube surrounded by a 10$\frac{1}{2}$ in.x 1$\frac{3}{4}$ in. OD Pyrex water jacket. The reaction zone is only 4.5 in. deep located at the lower part of the inner tube. The maximum solution capacity of the overflow reactor was 28 ml. so that normally it was charged with 25 ml. of iodine solution. For the reflux reactor a volume of 35 ml. was normally used. The solution in this region was levelled in such a position that longitudinal uniformity of dose rate could be obtained (see Appendix C). Although water in the jacket fell between the reactor and the cobalt-60 source, it was found that the reduction of radiation by the water layer was neglectable. Nevertheless, dosimetry was performed with the water running through the jacket.

Two copper-constantan thermocouples were used to measure the temperatures inside the reactor and the water jacket. The temperatures were recorded continuously on a calibrated Honeywell temperature recorder. The temperature in the water bath was controlled by a Haake temperature regulator and the reactor and water jacket temperatures were maintained within ± 1°C. When the reactor temperature was below the boiling point of the solution, the reactor and jacket temperatures coincided. When the reaction was carried out at boiling temperature, the water jacket temperature was kept at about 4°C higher than the temperature inside the reactor. The condenser on top of the reflux reactor was maintained at constant temperature by circulating ice water through the condenser. Those sections of transporting tubings, inside the hot cell were shielded from gamma radiation by $\frac{1}{4}$ inch lead sheet.

In order to begin irradiation, the source was opened on a longitudinal hinge by a pair of slave manipulators, and positioned coaxially about the reactor. The positioning stand for the reactor and source is illustrated in Fig.C-4 (Appendix C). Its function was to ensure that the reactor and the source were always in the same geometric relationship.

III-3.3 Products Collecting System

As the methane was bubbling through the solution, it removed the solution (both iodine and solvent) from the reactor through vaporization. Thus a collecting system for this solution was needed.

The original design of the products collecting system as shown in Fig.D-5(b), Appendix D was a gas-liquid separator with an ice water condenser on top of it. Such arrangement would collect all liquid from the reactor. Since the three expected organic products are either liquid or solid at room temperature, by the time the products arrived at the separator, they would condense as liquid. In passing through the condenser, very little product would be left in the gaseous stream which would be mainly the unreacted methane and hydrogen iodide. The liquid products collected in the separator were then withdrawn from the bottom. Part of it was used in the gas chromatograph analysis and most of it recycled back to the reactor either untreated, or through a product separator step. (crystallization or distillation).

For the present work, in the continuous flow process, the original system was used except that the product stream was not recycled to the reactor. In addition to this, the condenser on top of the separator was replaced by a dry ice-acetone cold trap as shown in Fig.11. This system was used for the overflow semi-batch process, but for the reflux semi-batch process, only the cold trap was used as shown in Fig.12. The methane together with the uncondensed vapors (if any) escaping the cold trap passed through either a soap bubble meter or a Pyrex gas sampling bottle and a gas sampling bomb. The soap bubble meter indicated the flowrate and the Pyrex sampling bottle was used to collect samples for vapor density measurements. The gas sampling bomb was used to collect gas sample for gas chromatograph analysis. However, in this preliminary work, emphasis was placed on the carbon-containing products which should be of a neglectable quantity in the gaseous stream after the cold trap. Therefore no gas sample was taken and for the same reason this section of the apparatus did not appear in Fig.11 and Fig.12.

III-4 EXPERIMENTAL PROCEDURE

The experimental work was mainly carried out in the semi-batch process, with only a few continuous flow experiments performed. The three main steps involved in the procedure were (1) the reactant preparation, (2) the irradiation and (3) the product analysis.

III-4.1 Reactant Preparation

The iodine solution was prepared by dissolving a known quantity of iodine in a solvent in a volumetric flask. Because any impurity might act as a reaction inhibitor,all the glassware used in the experiment was thoroughly cleaned with chromic acid, distilled water and oven dried. A high vacuum silicon grease produced by Dow Corning, U.S.A. was used for all ground joints. All tubings leading the reactants to the reactor were kept away from dust and purged with nitrogen or methane before attachment to the reactor. The tubes were cleaned and dried between runs.

III-4.2 Irradiation

A measured quantity of iodine solution was introduced into the reactor. The heating water was then circulated through the system with the temperature indicated on the recorder. When a constant reactor temperature was achieved, the methane was switched to the reactor for 5 to 15 minutes in order to displace any dissolved gases (mainly oxygen). The cobalt-60 source was then positioned as described in Section III-3.2 and the timer was started. The irradiation normally lasted from one to four hours.

When the irradiation was completed, the source was lowered into the well. The total time taken in bringing up the source in position and then lowering it back to the well was 1.5 to 2 minutes. The small dosage error introduced in this manipulation period is discussed in Appendix B.

The dose rate of the source was calibrated using a Fricke dosimeter as detailed in Appendix A. The absorbed dose by the system was calculated as described in Section II-1.6 and illustrated in Appendix B. No correction being made for the decay of the source strength as explained in Appendix B.

III-4.3 Product Analysis

In the work of gas phase iodination of methane, the product analysis was carried out by ultraviolet spectrophotometry on a Beckman Model DK-1 Spectrophotometer, calibrated against prepared pure and mixed standards (31). But the optical absorbances of the iodo-methanes were very high and the absorption spectra overlapped. Therefore the analytical problem required special techniques for resolution (42). The complexity of the resolution technique suggested that other analytical methods should be considered.

The method of product analysis chosen for this work was gas chromatography. The instruments used for this purpose were a Varian Aerograph Series 1520B gas chromatograph with a thermal conductivity detector, a single pen one millivolt Westronics strip chart recorder, and a Hamilton micro syringe of 10 μl capacity.

III-4.3.1 Sample for gas chromatographic analysis

Only the liquid product stream which contained practically all the iodomethanes was analysed in this primary investigation.

For the continuous flow process, liquid from the reactor was collected in the gas-liquid separator and a sample was withdrawn and analysed every half hour. The vapor condensate from the cold trap was analysed at the end of each experimental run. A sample was also taken from the reactor when the solution had been cooled down to room temperature.

In the semi-batch process, samplings were performed only at the end of the experimental run. For the overflow semi-batch process, samples were taken from three places —— separator, cold trap and reactor. For the reflux semi-batch process, samples were taken only from cold trap and reactor.

The quantity of liquid collected in trap or separator depended upon the operating temperature, time, gas bubbling rate and the volatility of the solvent used. Generally very little liquid (0 to 2 grams) was collected in the cold trap especially in the reflux semi-batch process where the condenser would bring most of the vapor back to the reactor. The amount of liquid collected in the separator varied quite largely, from few grams to nearly the total weight of solution introduced into the reactor. This extreme of complete vaporization of the solution from the reactor happened when the operating temperature was close to the boiling point of the solvent. However, if the temperature was kept 20 to 30°C lower than the solvent boiling point temperature for a reasonable length of time (2 hours), less than 10%* of the liquid

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* From vapor pressure data of pure CCl_4 at about 56°C (b.p.=76.5°C) and assuming the 20 ml/min. flowrate of CH_4 is saturated with the vapor, about 7 gm. of CCl_4 will be vaporized in 2 hours. This constitutes about 17% the original reactor solution.

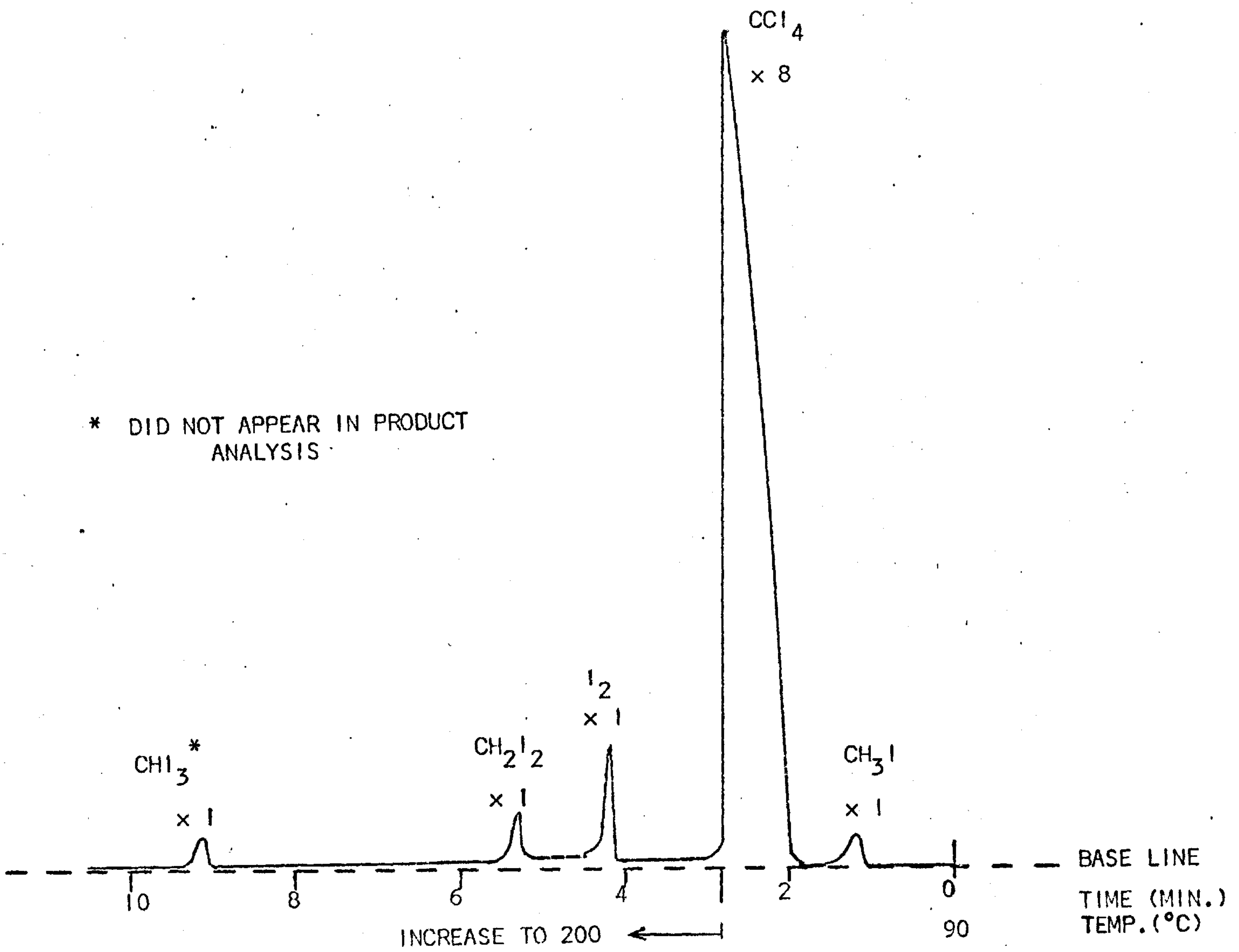
in the reactor would be vaporized and about 3 to 7 gm. of liquid was collected in the separator.

Quantitative studies (see Section III-5) were made on a few experimental runs where carbon tetrachloride was used as solvent because they were considered to be the 'best' results obtained in the present work. Thus in those cases, all the liquid samples were weighed. These weights coupled with the gas chromatographic analysis would provide the data for computing the conversion and yields of the reaction, the radiation yields (G values) and for making a material balance of the system. A sample calculation is given in Appendix H.

III-4.3.2 Column and chromatographic operating conditions

The liquid product stream was expected to consist of methyl iodide, methylene iodide, iodoform, iodine and solvent. A study of the literature did not reveal any column which had been successfully used to separate all these compounds except in one case (43) where a column was suggested generally for many iodide compounds. It was a 9 meter column packed with 30% TCEP (1,2,3, tris-(cyanoethoxy)-propane) absorbed on some kind of supporter which was not given. A supporter called chromosorb W, AW-DMCS, 80/100 mesh was used with the TCEP and the column was tested with the three iodomethanes. No separation was observed although by changing the chromatograph operating conditions, separation might be possible. However, this was not carried out because a new column was found which was generally good for compounds of large difference in boiling point. Since the three expected iodomethanes have large boiling point differences, they were tested on the new column and the separation was good. The new column packing was 60/80 mesh chromosorb W, treated with 10% silicone gum rubber, SE30. When iodine and solvent (such as carbon tetrachloride) was injected together with the three iodomethanes, the separation was not as good, but with a longer column (15 ft.x 1/8 in. OD stainless steel tube) and a new set of chromatographic operating conditions, the separation was clean as shown in Fig.13. Notice that iodoform which was not detected in the present work was 'added' to Fig.13 in order to show the complete spectrum of the chromatograph. The final operating conditions are summarized as follows:

Column	10% silicone gum rubber on chromosorb W (15 ft.x 1/8 in. OD stainless steel tube)
Carrier gas flowrate	Helium at 40 ml/min.
Detector temperature	280°C
Detector current	150 ma.
Inject port temp.	275°C



* DID NOT APPEAR IN PRODUCT ANALYSIS

FIG. 13 TYPICAL CHROMATOGRAM

Sample size	4-8 µl
Column temperature	90°C* then 200°C
Normal analysis time	6 to 10 minutes per injection

When the solvent involved had characteristics that made it difficult to separate from the other components at the usual operating conditions, other operating conditions had to be employed, such as changing the initial column temperature, and manual programming of the temperature.

III-4.3.3 <u>Instrument calibration</u>

The thermal conductivity detector response to each component was determined by calibration (44,45). A mixture of all the components expected in the concentration regions found in the experiments was injected. The chromatograph peak area of each component was estimated by multiplying the peak height by the peak width at half height. Then by assigning a response factor of 1 to the solvent, the relative response factors of methyl iodide, methylene iodide and iodine could be calculated. The method of calibration is detailed in Appendix G. Since carbon tetrachloride was the most interesting solvent

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* For a different solvent, the initial temperature varied from 70 to 130°C. But normally the initial temperature was 90°C and remained constant until the solvent completely eluted, at which time the temperature was increased manually to 200°C.

in the present work, the relative response of the instrument was calibrated with CCl_4 as solvent. For other solvents no calibration was carried out.

III-4.3.4 Chemical analysis of iodine

Chemical titration methods of determining the iodine concentration had been investigated at the early state of the experiment because iodine was not recommended for gas chromatographic analysis (46). The reasons for this are: (1) Iodine has a high boiling point and therefore it tends to condense for example in the detector cell if the detector temperature is not high enough. But the higher the detector temperature, the lower will be the detector current (i.e. lower sensitivity). (2) At high column temperature, iodine being chemically active might undergo decomposition or react with the column packing. (3) The very corrosive nature of the iodine suggests that any part of the instrument in contact with iodine should be at least made of stainless steel or even better with glass.

Thus the iodine had to be removed from the sample before it was injected into the gas chromatograph. At the same time the concentration of the unreacted iodine had to be determined in order to make the material balance of the system possible. Both colorimetry and chemical titration were considered but the latter was studied more carefully and adopted.

The chemical titration method involved the titration by a standard solution of sodium thiosulphate (Chap.15 of 47). However, both aqueous and organic phases existed in a same system and mixing of the two layers was found to be very important. The so called back titration method had also been tried. In this back titration method, an excess of sodium thiosulphate was added to the sample and the excess was then determined by titrating with potasium dichromate. Although the back titration method seemed to provide a better result, it involved too much tedious titration work. Moreover it was later discovered that the iodine could be analyzed by gas chromatography with the same column packing without trouble.

III-5 AREAS OF EXPERIMENTATION

The experimentation in this study was originally designed to evaluate the iodination reaction in a continuous flow, liquid phase process, as contrasted with the earlier work on the gas phase iodination in a batch reactor (31). However, the first few preliminary runs indicated that the liquid phase reaction proceeded with very low conversions. This was surprising in view of the very high G values obtained in the gas phase reaction. The problem then became, "Under what conditions can this reaction be made to go ?", rather than "What are the optimal conditions for this process?" In the light of this new question, it is preferable to use the semi-batch technique for the feasibility studies. When a reasonably high conversion has been achieved in this semi-batch process, the knowledge gained would then be applied to the attempted conversion in the continuous flow process.

Thus the experiments here are in the nature of exploratory work, with the aim of finding a good solvent medium and a set of operating parameters such as temperature, irradiation time, iodine concentration in solution and methane flow rate. Since most of the experimental runs yielded more or less similar low conversion results, it was decided to study most of the work semi-quantitatively, so that a large variety of experimental runs could be made. The semi-quantitative study here meant to determine whether any iodomethanes were produced and their relative concentrations were approximately expressed as the percentage of total gas chromatograph peak area. The semi-quantitative data were good enough to provide a basis of choice of solvent and operating conditions. Nevertheless, quantitative studies, i.e. the conversion, the yield, G value, material balance of the system were made on a few experimental runs where carbon tatrachloride was used as solvent.

III-5.1 Factors Governing The Choice of A Solvent

The fact that gaseous methane was going to react with iodine dissolved in a solvent medium and that the reaction is endothermic suggested that a good solvent should have a high boiling point and high solubilities for both methane and iodine. A high boiling point is desirable to permit higher operating temperature. Vilenchich and Hodgins (31) used temperature above 80°C (see Section II-3.3). Furthermore the solvent should be able to transfer energy quickly from solvent to the solute. These three factors form three main areas of experimentation as will be discussed in the following sections. The other three areas of experimentation are focussing on some possible factors that could favourably affect the reaction.

III-5.2 Solubilities of Reactants In Solvent

This kind of problem always arises when a two-phase reaction is concerned and the problem is so large that it constitutes a separate subject in the field of Chemical Engineering — mass transfer with chemical reactions.

In some reacting systems, where two-phases are involved, both kinetics and diffusion control may be important depending upon the operating conditions e.g. temperature. For simple reactions, there are methods available for determining the relative importance of these two possible controls under a given set of operating conditions (see e.g.(64)). However, these methods required the knowledges of the kinetic rate expression and the rate of diffusion of the system, which are not available for the present reaction. Thus there is no other simple way to test whether the present reaction is chemically controlled by the kinetics (activation energy etc.) or physically by the diffusion process.

The methods of experimentation carried out in this work were to try some solvents which have high solubilities for methane and/or iodine and also to study briefly the agitation effect and the effect of the interfacial area between the methane bubbles and the solvent medium. The solubility data for iodine and methane in various solvents are available in the literature (48) and some data related to this work are given in Appendix F.

For a given solvent, the increase of agitation or the interfacial area would increase the rate of absorption of methane in the solvent. In the experiment, attempts were made to increase the agitation in the reactor by changing the methane flowrate and to increase the interfacial area by breaking up the methane bubbles into numerous tiny bubbles with a piece of sintered glass.

III-5.3 Boiling Temperature of Solvent

The endothermic nature of this reaction suggested that operating temperatures higher than room temperature were necessary to bring about the reaction. Since many organic solvents boil at rather low temperatures, this somewhat restricts the use of higher operating temperatures unless the system is under pressure. The boiling points of various solvents used in this work are given in Appendix F.

Experimentally, solvents with high boiling points were studied. In order to prevent the loss of solution from the reactor due to vaporization at higher temperatures, an attempt had been made to presaturate the methane with the iodine solution at the reactor temperature before it entered the reactor. Strictly speaking, this process then became a continuous flow process rather than a semi-batch process because iodine solution was fed in with the methane continuously. Although the reflux reactor would maintain the solution level fairly well, the highest operating temperature was limited to boiling point of the solution. It has to be emphasized, however, that generally the higher the operating temperature, the lower will be the solubility of methane in the solvent.

III-5.4 Energy Transfer And Indirect Action

In mixture where one component is present in large excess, direct radiation action on the minor constituent is unimportant (Chap.IV of 2). Instead, the reaction of the minor constituent results from the attacking by active species (radicals, ion, etc.) formed in the first instance from the major constituent or the energy is transferred to it from the major constituent. For example, in the presence of an excess of inert gas such as argon, methane becomes attacked by ions formed from argon (14) as:

$$A^{+} + CH_4 \longrightarrow A + CH_3^{+} + H\cdot \qquad (56)$$

This phenomenon which is known as 'indirect action' (Chap. I of 2) is quite common when solvent medium is involved in a reaction. The transfer of energy via excited molecules has been presented in Section II-1.5.3.

In the present case, the iodine concentrations in the solution were quite low, typically about 2 gm. in 100 ml. or 0.079 mole/l. Thus a relatively large amount of radiation energy would be absorbed by the abundant solvent molecules than by the iodine molecules. Hence the iodine was more likely to be affected indirectly by the attack of the radicals from the solvent than directly by radiation. In order to accomplish this the solvent should be able to transfer energy promptly. Furthermore it should be stable in a sense that no net formation of products would take place on the solvent as the result of irradiation, otherwise the solvent would become one of the reactants and by-products would be produced that might require expensive separation processes in the industry.

Two solvents are of special interest here — carbon tetrachloride and ethyl iodide. These compounds can undergo exchange reaction (Chap.IV of 2) according to the sequence:

Carbon tetrachloride

$$CCl_4 \rightsquigarrow CCl_3{}^{\cdot} + Cl^{\cdot} \qquad (57)$$

$$CCl_3\cdot + Cl_2 \longrightarrow CCl_4 + Cl\cdot \qquad (58)$$

$$2Cl\cdot \longrightarrow Cl_2 + \text{energy} \qquad (59)$$

Ethyl iodide

$$C_2H_5I \rightsquigarrow C_2H_5\cdot + I\cdot \qquad (60)$$

$$C_2H_5\cdot + I_2 \longrightarrow C_2H_5I + I\cdot \qquad (61)$$

$$2I\cdot \longrightarrow I_2 + \text{energy} \qquad (62)$$

An isotopic technique has demonstrated (2) that the yield of $CCl_3\cdot$ radicals is less than G=3.5 and the G value for the exchange reaction of ethyl iodide is between 4 to 6. Thus both solvents are fairly stable and according to the sequence Eq.(57) to Eq.(62), there is very little or no net formation of products from them. The indirect action of the radicals and/or the excited molecules on the iodine molecules can thus follow as shown in Eq.(56) and described in Section II-1.5.3.

Although the reaction sequence, Eq.(57) to Eq.(62) would not result in new products, it has to be realized that each of these exchange reactions takes place at a pure state and therefore in the presence of other components (e.g. I_2 and CH_4 in the present work), the sequence will not necessary be followed.

III-5.5 Recombination of Iodine Radicals

As discussed in Section II-3.3, the gas phase iodination of methane is more likely to follow reaction sequence shown in Eq.(49) to Eq.(51) than Eq.(45) and Eq.(46). Thus in order that the former sequence may proceed as long as the reactants are available, the iodine radicals once formed, either via Eq.(49) or Eq.(51), should be prevented from recombination. The recombination of iodine atoms is very likely especially when the iodine radicals are present in a large concentration. In a gas phase iodination, the system is much more dilute than in a liquid phase system where the movement of the large iodine atoms will be restricted to some extent. Thus the recombination of iodine atoms is more likely in the liquid phase. Hence unless the iodine radicals formed are energetic e.g. by decomposition of very excited iodine molecules, Eq.(10), there is a possibility in condensed phase that the radicals may recombine within the solvent cage (see Sections II-1.5.3 and III-5.7). Experimentally, this recombination was minimized by reducing the usual iodine concentration in the solution to about 0.008 mole per litre.

III-5.6 Impurity In System

Many workers (12,22,28,41), have reported that small quantities of impurities in the system, can have dramatic effects. In fact, much early work had been discredited on this account. One important impurity is oxygen which affects nearly every radiation-induced reaction. One common remedy for this is to de-aerate the liquid sample by successively freezing , evacuating and sealing. Liquid impurities present in the solution can be removed by distillation or extraction.

With large doses, small quantities of impurity can be used up at the beginning of the reaction, which then proceeds normally. For example, as reported by Harmer (41) an induction period lasting three hours or more was observed when the solvent, ethyl bromide used was not produced by the radiation process, because even in high-grade commercial ethyl bromide made by the alcohol process, there are minor amounts of unreacted ethyl alcohol and other by-products of the reaction.

In the present work, all the glassware was cleaned by conventional methods as described in Section III-4.1 and all chemicals used were of the highest grade (see Section III-2) available in the market. It was the solvent, being present in greatest amount, which needed most care. Since the chemicals were not further purified, irradiation time of a few experimental runs had been extended to take into account of the possibility of induction period. Also in one case the iodine solution was exposed to the radiation for about two hours before the methane was fed in, hoping that the impurities, if any, would be used up. The oxygen, initially present in the system, was removed in this work by bubbling methane through the solution for 5 to 15 minutes before the irradiation of the solution was begun.

III-5.7 Effect of Reaction Phase

One distinct difference between the work of Vilenchich and Hodgins (31) and the present work is the reaction phase. Therefore the two processes could be expected to have some differences either in the kinetics or mechanism although this kind of extension from gas phase to liquid phase had been demonstrated successfully in other systems. For instance, the gas phase addition reaction between HBr and C_2H_4 carried out by Armstrong et al. (49) had resulted to the liquid phase Dow's ethyl bromide process (41).

The effects of phase on radiation-induced reactions have been reviewed by Jones et al. (50) and many related references are given in the paper. One of the obvious effects on the liquid phase reactions as discussed in Sections II-1.5.3 and III-5.5 is the so called 'caging' effect. In the gas phase the mean free path and average time between collisions are relatively large and there are no caging effects. Therefore two radicals formed by the dissociation of a molecule have a small chance of recombining. In liquid phase the cage effect could be very serious if the dissociation of molecules is not energetic and involves large molecules. For instance, it has been found by the flash photolysis technique (50) that only about 13% of the iodine atoms escape recombination with the parent partner when iodine solutions in carbon tetrachloride are activated by visible light. It has also been shown that the caging effect decreases with increasing temperature.

Another effect which becomes very important if the reaction proceeds by an ion-molecular reaction (Section II-1.5.2) is the recombination of ejected electrons to the parent ions in a condensed phase. This kind of neutralization seldom happens in the gas phase. Consequently, ion-molecular reactions that occur in the gas phase may be impossible or of little importance in liquid phase.

In the present work, solvent was present in large quantity surrounding the iodine atoms and molecules. Therefore it can be seen that cage effect is unavoidable in the present case. One of the attempts, as described in Section III-5.5, was to minimize the recombination of iodine radicals by reducing the iodine concentration. A second attempt to lower the cage effect was to increase the operating temperature. The last attempt, which was carried out after the installation of the new cobalt-60 source, was to minimize the effect by increasing the intensity (or dose rate) hoping that more free radicals and other active species would be formed. With the interaction of these active species it would therefore increase the possibility of forming for example hot radicals which could be energetic enough to escape the solvent cages.

The main effects of reaction phase here were the solvent cage effect and the recombination of ejected electrons to the parent ions. In addition to these, the coexisting of gas and liquid phases in the system presented another problem. This subject has been covered in Section III-5.2, but besides those attempts discussed in that section, it had also been suggested to replace the methane with methanol and other liquid paraffines such as n-hexane in order to obtain a homogeneous reaction phase. Although the reactions involved would then no longer be iodination reaction of methane, yet some similarities did exist between the iodination of methane and the iodination of n-hexane or methanol. Thus the experiments might provide some guides to this exploration.

IV RESULTS AND DISCUSSION

The results of each area of experimentation discussed in Section III-5 will be presented in this section together with some discussion. Since the experiments were in the nature of an exploratory work, a large variety of experiments was performed. Thus the results and discussion will be presented in subdivisions according to the areas of experimentation given in Section III-5. In addition, the results for the continuous flow process and the quantitative results with CCl_4 as solvent are given.

IV-1 QUANTITATIVE RESULTS WITH CCl_4 AS SOLVENT

As discussed before (III-5), most of the work here was studied semi-quantitatively and quantitative study was only made on a few runs where CCl_4 was used as solvent. The results are shown in Table 5. The conversion of iodine and the yields of methyl iodide and methylene iodide were generally low. No iodoform was detected in this work. Notice that the G values fell somewhat between the G values for simple chemical reactions ($G < 10$) and chain reactions ($G > 3,000$).

TABLE 5

QUANTITATIVE RESULTS WITH CCl_4 AS SOLVENT

Irradiation time: 2 hours
Methane: 20 ml/min. or 8.9×10^{-4} mole/min.

Run No.	Type of reactor	Conc. mole/l	Temp. °C	% I_2 conv.	Yield %		G		% peak area	
					CH_3I	CH_2I_2	CH_3I	CH_2I_2	CH_3I	CH_2I_2
33	overflow	0.08	49	5.2	9.0	2.8	500	154	0.08	0.05
43	reflux	0.08	60	3.3	2.8	3.1	147	164	0.01	0.03
44	reflux	sat'ed	77.5	2.0	0	2.7	0	173	0	0.04

TABLE 6

RESULTS OF THE CONTINUOUS FLOW PROCESS

Methane: 20 ml/min. Mole ratio: $CH_4 : I_2 = 22.5^* : 1$

I_2 solution: 0.5 ml/min. I_2 conc.: 0.08 mole/l

Run No.	Solvent	Temp. °C	Product (% peak area)	
			CH_3I	CH_2I_2
1	CH_3I	25	-	0
			-	0
			-	0
			-	0
			-	0
23	CCl_4	60.5	0	0
			0.01	0
			0.02	0
			0.02	0
			0.04	0
			0.05	0
21	Benzene	57.5	0.06	0

---

* Representing the total methane passed through the system, not the amount dissolved.

Therefore the present reaction in liquid phase was neither a chain reaction as reported for gas phase by Vilenchich and Hodgins (31) nor a reaction due to simple dissociation of methane i.e. a radiolysis reaction of methane with iodine as radical scavenger.

IV-2 CONTINUOUS FLOW PROCESS

Two experimental runs (Runs 1 and 23) were carried out in a flow process and the results are shown in Table 6. Run 21 was grouped under here because iodine solution was fed into the overflow semi-batch reactor continuously by way of saturating the methane with the solution (see Section III-5.3).

For Runs 1 and 23, a sample was taken from the separator every half hour and each experimental run lasted 3 hours. The %'s peak area for product CH_3I, in Run 1 were not certain because the product itself was the solvent so that a little formation (if any) of CH_3I would hardly change the large peak area of the solvent. However, two things were clear here: (1) The peak areas of the unreacted iodine in the product stream were not smaller than that of the feed stream. This suggested that either no significant amount of CH_3I was formed or part of the CH_3I solvent had been decomposed. (2) No CH_2I_2 was detected.

When CCl_4 was used in Run 23 at a higher temperature, a little CH_3I, but no CH_2I_2 was observed. For Run 21, the experiment lasted two hours (as compared to half hour per sample in Runs 1 and 23) and a sample at the separator was analyzed. More CH_3I was obtained but this may be arisen from longer reaction time as will be discussed later.

IV-3 SOLUBILITIES OF REACTANTS IN SOLVENT

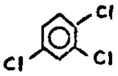
Table 7 presents the results of various runs using different solvents. From Runs 13 to 28 the overflow semi-batch reactor was used and below Run 35, the reflux semi-batch reactor was used. There was a slight (but no strong) evidence that the solubilities would increase the conversion of iodine but these experiments did show clearly that different solvents would produce different results and CCl_4 seemed to be the best solvent among all the solvents used. Another obvious difference was that none of the solvents yielded CH_2I_2 except CCl_4. However, if the irradiation time was increased, CH_2I_2 would show up as will be discussed in Section IV-7. A large % peak area for CH_3I was normally observed for the sample taken from the cold trap, but this sample was very small — one drop to less than 0.5 ml., so that its contribution to the final yield of CH_3I was not very significant.

An attempt to increase the rate of absorbing of CH_4 through some physical means was made. The results

TABLE 7

EFFECT OF SOLUBILITIES OF REACTANTS IN SOLVENT

I_2 concentration : 0.08 mole/l
Irradiation time : 2 hours
Methane : 20 ml/min.

Run No.	Solvent	Temp. °C	Solub. 25°C		Product (% peak area)		Place of sampling
			CH_4 cc/cc	I_2 g/l	CH_3I	CH_2I_2	
13	CCl_4	60	0.68	29	0.08	0.05	reactor
					0.10	0.04	separator
					7.7	0	trap
16	CH_2I_2	60	-	very	≃ 0	≃ 100	reactor
					52.4	61.7	trap
17	Toluene	72.5	0.45	3.6	0.07	0	reactor
					0.04	0	separator
					1.55	0	trap
20	Benzene	53	0.57	119	0.08	0	reactor
					0.04	0	separator
					0.03	0	trap
28	$ClCH=CCl_2$	55	-	39.6	0.07	0	reactor
					0.09	0	separator
35	$CCl_2=CCl_2$	71.5		30.6	0.02	0	reactor
37a	Methanol	40	0.45	21.3	+	0	reactor
39		90	0.48=	-	0	0	reactor
42	n-Hexane	66.5	0.60	8.8	0.04	0	reactor
					0	0	trap
43	CCl_4	60	0.68	29	0.01	0.03	reactor
45	C_2H_5I	69	-	-	*	0	reactor

\+ The separation between CH_3I and CH_3OH could not be achieved
* See Section IV-5
= For chlorobenzene

are presented in Table 8 for the effect of agitation and Table 9 for the effect of interfacial area between the methane bubbles and the surrounding solvent. By decreasing the flowrate of methane but keeping the total amount of methane flowing through the system constant, Table 8 shows that the production of CH_3I was decreased but CH_2I_2 was increased. This change of product distribution, however, was more likely due to the change in the irradiation time as will be discussed in Section IV-7. Therefore, it was acceptable to say that in such a small reactor (28 ml.) a normal methane flow rate of 20 ml/min. provided enough mixing.

In Table 9, again the results could be caused by the irradiation time, but obviously the conversion of Run 32 was higher than that of Run 10. It was rather weak to say that as the interfacial area was increased the conversion was increased. However, by combining the results of Tables 8 and 9 (also see Table 15) it was clear that for a given solvent, CCl_4 if the absorption of CH_4 was increased by way of increasing the agitation, interfacial area or bubbling time, the conversion seemed to be increased slightly. This is quite reasonable if one considers the rate of diffusion of methane in CCl_4. The diffusion coefficients for CH_4 in the solution (assuming pure CCl_4) were estimated (see Eq. 16.5-9 of <u>51</u>), using

TABLE 8

EFFECT OF AGITATION

Solvent : CCl_4 Temperature : 40°C

I_2 concentration : 0.08 mole/l Reactor : overflow

Run No.	Irrad. Time (hr)	Flow rate ml/min.	Product (% peak area)		Place of sampling
			CH_3I	CH_2I_2	
26	2	20	0.07	0.01	reactor
			0.04	0	separator
			0.04	0	trap
27	4	10	0.02	0.08	reactor
			0.01	0	separator
			0.05	0	trap

TABLE 9

EFFECT OF INTERFACIAL AREA

Solvent : CCl_4

I_2 concentration : 0.08 mole/l

Methane : 20 ml/min.

Reactor : overflow

Run No.	Irrad. time (hr)	Temp. °C	Opening for gas	Product (% peak area)	
				CH_3I	CH_2I_2
32	7	30	sintered glass	0.04	0.05
10	3	33.7	2 mm ID	0.02	0

Eq.(63) to be 1.15×10^{-5} and 2.02×10^{-5} $cm^2/sec.$ at $25^\circ C$

$$\mathcal{D}_{AB} = 7.4 \times 10^{-8} \frac{(\phi_B M_B)^{\frac{1}{2}} T}{\eta \tilde{V}_A^{0.6}} \qquad (63)$$

where $\tilde{V}_A$ = molar volume of solute A in cm^3/g-mole as liquid at its normal boiling point.

η = viscosity of solution in centipoises

ϕ_B = association parameter for solvent B=1

T = absolute temperature in $^\circ K$

and $60^\circ C$ respectively. The values are roughly in the same order as those for oxygen-water system (2.5×10^{-5} cm^2/sec), carbon dioxide-water system (1.96×10^{-5} cm^2/sec) and chlorine-water system (1.44×10^{-5} cm^2/sec). Thus the rate of absorption of methane by CCl_4 is not very fast so that any physical means to increase the rate of absorption would at least maintain if not increase the overall reaction rate.

The conversion however, as shown in Tables 8 and 9, was not improved markedly. Therefore, within the experimental range, diffusion might not be the most important factor that controlled the overall reaction rate although it could play a very important role in controlling the reaction rate. It was believed that both diffusion (physical) and thermodynamic equilibrium (chemical) were controlling the reaction and the latter factor was more important than the former one especially if the solvent with high CH_4 solubility was chosen.

IV-4 BOILING TEMPERATURE OF SOLVENT

The purpose of using a high boiling temperature solvent is to permit higher operating temperature. Tables 10, 11 and 12 show the effect of temperature on the reaction with respectively carbon tetrachloride, toluene and tetrachloroethylene as solvent. Generally, for a given solvent the product concentrations were increased as the temperature was raised, but for solvent, 1,2,4-trichlorobenzene at 90°C (Run 39 in Table 7) which was the highest operating temperature studied in this work, no CH_3I or CH_2I_2 was detected. Thus temperature might be the most important factor, but other factor, such as solvent, could not be ignored. Besides as shown in Table 12, a relatively good yield of CH_3I was obtained at very low temperature 6°C (but longer time). Note that tetrachloroethylene had also been used as solvent in the Dow Chemical's ethyl bromide process and was found to have a better yield at lower temperature, -4°C than room temperature (41).

In the gas phase iodination work (31), the lowest operating temperature was 80°C at which the yields were

TABLE 10

EFFECT OF TEMPERATURE

Solvent : CCl_4 Reactor : overflow
Methane : 20 ml/min. Time : 2 hours
Concentration : 0.08 mole/l.

Run No.	Temp. °C	Product (% peak area)	
		CH_3I	CH_2I_2
9	33.7	0.01	0
26	40	0.07	0.01
11	41	0.06	0.05
33	49	0.08	0.05
13	60	0.08	0.05

TABLE 11

EFFECT OF TEMPERATURE

Solvent : Toluene Reactor : overflow
Methane : 20 ml/min. Time : 2 hours
Concentration : 0.08 mole/l.

Run No.	Temp. °C	Product (% peak area)		Place of sampling
		CH_3I	CH_2I_2	
14	60	0.01	0	reactor
		-	0	trap
17	72.5	0.07	0	reactor
		0.04	0	separator
		1.55	0	trap
18	80	0.08	0	reactor
		0.07	0	separator
		1.0	0	trap
19*	81.5	0.09	0	reactor
		0.1	0	separator
		0.75	0	trap

* preirradiated for 100 mins., see Section IV-7.

TABLE 12

EFFECT OF TEMPERATURE

Solvent : $Cl_2C = CCl_2$ Reactor : reflux
Methane : 20 ml/min. Time : 2 hours
Concentration : 0.08 mole/l.

Run No.	Temp. °C	Time (hrs)	Product (% peak area)	
			CH_3I	CH_2I_2
36	6	3½	0.07	0
34	53.5	3	0.04	0
35	71.5	2	0.02	0

low and the optimal temperature was at 130°C. Although the effect of temperature as shown in Table 10 and 11 as well as the results of Run 39 (see above) and Run 36 of Table 12 were not very impressive, it was suspected that all the experiments were performed at temperatures well below the region where the temperature effect could have clearly shown up. Thus, it was felt that the temperature was still the key factor that controlled the reaction especially if one considered the endothermic nature of the reaction.

IV-5 ENERGY TRANSFER

Two solvents - carbon tetrachloride and ethyl iodide were used and the results are compared with that of n-hexane in Table 13. The advantage of using the high energy transfer agent as solvent did not really appear in these results. For example, the conversion of iodine for Run 43 was slightly higher than that of Run 42, but this did not prove that the slightly higher conversion was due to the energy transfer because it was simply not enough evidence to confirm this. Besides the study of energy transfer could be very sophisticated. The relative high yield of CH_3I for Run 42 could be slightly contributed from the radiolysis of hexane, because in

TABLE 13

EXPERIMENTAL RUNS WITH CCl_4 AND C_2H_5I AS SOLVENT

I_2 conc. : 0.08 mole/l. Reactor : reflux
Methane : 20 ml/min. Time : 2 hours

Run No.	Solvent	Temp. °C	Product (% peak area)	
			CH_3I	CH_2I_2
42	n-Hexane	66.5	0.04	0
43	CCl_4	60	0.01	0.03
45	C_2H_5I	69	*	0

* See discussion

the radiolysis of n-hexane with iodine as radical scavenger, a small but significant amount of CH_3I was detected (54) (also see Table 16).

The solvent, C_2H_5I for Run 45 contained some CH_3I as impurity. The analysis of the iodine feed solution consisted of 2.58% of G-C peak area for CH_3I, but the analysis of the product from reactor (with the same components) gave only 0.22% of peak area for CH_3I. Obviously most of the CH_3I had been decomposed. In fact, various low boiling, yet unidentified compounds were collected in the cold trap. Thus the methyl iodide was not stable at 69°C (boiling temperature) in a reflux reactor under the influence of gamma radiation. It should be noted that the reflux reactor was found to give a lower yield in CH_3I than the overflow reactor, e.g. by comparing Run 13 and Run 43 in Table 7. Petry (25) had found that the decomposition of CH_3I was proportional to the total irradiation dose given to the sample, but Vilenchich (31) reported that the decomposition was negligible at room temperature (see Section II-2.3). Thus the matter of stability of CH_3I further complicated the problem because it was then rather difficult to tell whether the system did (but decomposed immediately) or did not yield methyl iodide.

IV-6 RECOMBINATION OF IODINE RADICALS

As suggested (Section III-5.5) one method of reducing the recombination of iodine radicals was to lower the iodine concentration. Table 14 shows the effects of iodine concentration and radiation intensity. Since the initial iodine concentration for Run 38 was 10 times lower than that of Run 43, the conversion of iodine for Run 38 might be (no quantitative study for Run 38) larger than that of Run 43 even though the concentrations of CH_3I and CH_2I_2 in the product stream were equal or larger in Run 43. This uncertainty in the conversion was not further elucidated mainly because of the fact that such a low iodine concentration would not be commercially attractive unless the conversion was very high. The reasons for this are that a larger reactor would be required to produced a reasonable amount of iodomethanes in a reasonable time and a huge quantity of solvent would have to be separated from the products and recycled.

One thing that was clear in Table 14 was the effect of iodine concentration on the product distribution. At higher iodine concentration, more CH_2I_2 was detected. This observation was in accord with that of the chlorination of methane (30) (see Fig.10).

TABLE 14

EFFECTS OF IODINE CONCENTRATION AND RADIATION INTENSITY

Solvent : CCl_4 Reactor : reflux

Methane : 20 ml/min. Time : 2 hours

Run No.	Cobalt Source	Conc. mole/l	Temp. °C	Product (% peak area)	
				CH_3I	CH_2I_2
38	old	0.008	74.5*	0.01	0
43	old	0.08	60	0.01	0.03
44	old	sat'ed	77.5*	≃0	0.04
46	new	0.008	75*	0.01	0
47	new	sat'ed	76.5*	≃0	0.02

---

* Boiling temperature

IV-7 IMPURITY IN SYSTEM

The possibility of having an induction period owing to the impurity in the system was studied by increasing the reaction time or preirradiating the system (see Section III-5.6). The effect of reaction time is given in Table 15 for two solvents. The increase of time seemed to increase the production but there was no indication of induction period at all. Also as the reaction time was extended, more CH_2I_2 was formed, revealing the consecutive nature of forming the iodomethanes in the iodination of methane (see Eq.(52) to Eq.(54)). The pre-irradiation of the system, as shown by comparing Run 18 with Run 19 in Table 11, did not really improve the production significantly so that all the other experiments were not pre-irradiated.

IV-8 EFFECT OF REACTION PHASE

The caging effect of the solvent was the most important factor for the effect of reaction phase. The various attempts to minimize the caging effect as discussed in Section III-5.7 were (1) to lower the iodine concentration (2) to increase the temperature and (3) to increase the radiation intensity. The corresponding results are shown in Table 14 for the iodine concentration, Tables 10-12 for temperature and Table 14 for the radiation

TABLE 15

EFFECT OF REACTION TIME

Methane : 20 ml/min. Reactor : overflow
Concentration : 0.08 mole/l.

Run No.	Solvent	Temp. °C	Time (hr.)	Product (% peak area)	
				CH_3I	CH_2I_2
9	CCl_4	33.7	2	0.01	0
10	CCl_4	33.7	3	0.02	0
32*	CCl_4	30	7	0.04	0.05
29	$ClCH{=}CCl_2$	38	2	0.07	0
30	$ClCH{=}CCl_2$	38	4	0.08	0
31	$ClCH{=}CCl_2$	30	11	0.11	0.14

* Sintered glass was used, see Table 8.

TABLE 16

IODINATION OF METHANOL AND n-HEXANE

Methane : 0 ml/min. Time : 2 hours
Conc.: 0.08 mole/l. Reactor : reflux

Run No.	Solvent	Temp. °C	Product (% peak area)	
			CH_3I	CH_2I
37	CH_3OH	40	0*	0
41	n-hexane	68.5+	≃0	0

* CH_3I could not be separated from CH_3OH, but I_2 conc. remained constant.

\+ Boiling temperature

intensity. These results have been discussed in the previous sections and generally these three methods of minimizing the caging effect were not very sound. Therefore no statement could be made regarding the caging effect. But if one considers the results reported by Jones (50) (see Section III-5.7) there is no doubt that caging effect could exists to some extent in the present system.

By replacing the methane with methanol or n-hexane and as shown in Table 16, very little to no CH_3I or CH_2I_2 was detected except for Run 41, where a very small trace of CH_3I was observed. This small trace was obviously due to the result of radiolysis of n-hexane (54). By comparing Run 41 in Table 16 with Run 42 in Table 13, it was obvious that practically no CH_3I was observed unless methane was passing through the system.

IV-9 SUMMARY OF THE RESULTS

Although the results did not reveal strong evidence from which one could draw conclusions, yet the experiments did provide some fairly useful observations. They are summarized as follows:

(1) The liquid-phase iodination of methane was neither a chain reaction nor an iodine radical scavenging reaction.

(2) Different solvent media gave different conversions of iodine; varying from zero to less than 6%, and CCl_4 is considered to be the best solvent.

(3) At an irradiation time not more than two hours, only the reaction using CCl_4 as solvent could yield CH_2I_2 in addition to CH_3I.

(4) For a given solvent, an increase of temperature would increase the conversion slightly.

(5) The formation of CH_2I_2 would be increased if
  (a) the iodine concentration was increased.
  (b) the temperature was raised, and
  (c) the reaction time was extended.

(6) The reflux semi-batch process gave lower yield of CH_3I than the overflow semi-batch process.

(7) CH_3I was not very stable at high temperature in a reflux reactor under the influence of gamma radiation.

It has to be emphasized here that in the gas-phase iodination work (31) some experimental phenomena have not yet been explained successfully. For example, as reported (31)Eq.(55) could be catalysed by the ferric iodide which was formed on the inner wall of the corroded metal reactor over a long period of use and also there was a strange observation of sudden increase of pressure in the system (see Section II-3.3). These experimental phenomena could easily lead one to suspect that the high formation of iodomethanes reported could also be catalysed by the corroded reactor or other mechanisms could have occured instead of the one proposed (Eq.(49) to Eq.(55)). Ion-molecular reaction can proceed extremely fast (Section II-1.5.2). And if this ion-molecular reaction happened to be the main mechanism in the gas-phase (see Eq.(27)) then as discussed in Section III-5.7, the ion-molecular reaction would be impossible or of little importance in the liquid phase.

V CONCLUSION

At this stage, no strong conclusion can be drawn upon the nature of the liquid-phase iodination of methane because most of the results are not very much different from one another as discussed in Section IV. However, the experiments do show that, the chances of commercial success for the liquid-phase reaction are very slight. In addition, it is felt that the gas-phase iodination could be catalysed somehow by the metal reactor or could follow some mechanism which would not proceed under the present experimental range. Since such a large variety of experimentation has been studied, with the unfavourable results, the project should be terminated as far as the liquid-phase reaction is concerned.

VI RECOMMENDATION

The two extreme results of gas-phase and liquid-phase iodination reaction require further work to elucidate the subject. A more detailed study of the gas-phase reaction is recommendated.

In regarding the study of the practicability of producing iodomethanes, a continuous flow, gas-phase process such as those given in Appendix D might be worth considering.

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APPENDIX A

FRICKE DOSIMETRY

This is one of the most convenient methods of dosimetry. It satisfies most of the criteria listed below for a good dosimetric system. These are:

(1) The energy yield (G value) should be independent of dose rate, of total dose and of radiation type or the linear energy transfer,(LET), over a wide range. Fricke dosimetry is found to be independent of energy in the range 0.1 to 2 MeV.

(2) The response of the system should be reproducible and temperature independent. No change will occur between 0 - 50°C in using Fricke dosimetry.

(3) The mean atomic number should be close to that of the system of interest.

(4) The dosimeter should be easy to prepare and analysis should be easy.

The theoretical aspects and the reaction mechanism of this system are discussed in Chap. III of (2). Briefly the reaction involved is the oxidation of an acid solution of ferrous sulphate to the ferric salt in the presence of oxygen and ionizing radiation. This standard method of dosimetry is available for example in the ASTM Standards (55) as method D 1671-63 which was adopted in this work.

As in most of the work in radiation chemistry, the method is extremely sensitive to impurities so that any impurity must be rigorously excluded. All containers or apparatus in contact with the solution were cleaned with chromic-sulphuric acid cleaning solution and then rinsed with distilled water. All reagents were at least of reagent grade (see Section III-2) and the distilled water had been redistilled from chromic acid and also alkaline permanganate solution to remove any trace of organic impurities.

Calibration Curve

An approximately 0.1 M ferric sulphate solution in 0.4 M sulphuric acid was prepared and the exact ferric concentration was determined by standard potassium permanganate solution as outlined in Chap. 14 of (47). The ferric solution was then diluted into seven portions with 0.4 M sulphuric acid and the absorbances of each of the seven portions were read from a Beckman Model Dk-1 UV Spectrophotometer at 305 mμ, using 0.4 sulphuric acid solution as the blank in the spectrophotometer. Using Equation (A-1), which had been derived in the original paper (55) with a G value for the production of ferric ions equal to 15.5, the ferric concentrations could be

$$\text{Rads} = \text{micromoles of } Fe^{+++} \text{ per liter} \times 60.9 \quad \text{(A-1)}$$

converted to the radiation unit rads. Thus a calibration curve of radiation dose (in rads) against the corresponding absorbances could be plotted as shown in Fig.A-1. This is a straight line passing through the origin with a slope of 2.63×10^4 rads/O.D. Mathematically Fig.A-1 could be expressed as:

$$\text{Rad} = 2.63 \times 10^4 \times \text{O.D.} \qquad \text{(A-2)}$$

where O.D. was the optical density (absorbance) measured at 30°C instrument temperature. A slope of 2.94×10^4 measured at 20°C was reported by Swallow (Chap.II of 2).

Dosimetry Procedure

The dosimetry container, as suggested, should be of approximately the same dimensions and geometry as those employed to hold specimens for irradiation and no container should be less than 8 mm in internal diameter. Therefore the best container for dosimetry in the present work was the reactor itself.

A dosimetric solution of 0.001 M ferrous ammonium sulphate, 0.001 M in sodium chloride and 0.4 M in sulphuric acid was prepared from a stock solution of 0.5 M Fe^{++} and 0.5 M NaCl. The 0.4 M sulphuric acid was saturated with oxygen during the same day before it was used to dilute the stock solution to give the dosimetric solution. A specimen of dosimetric solution (about same volume as the

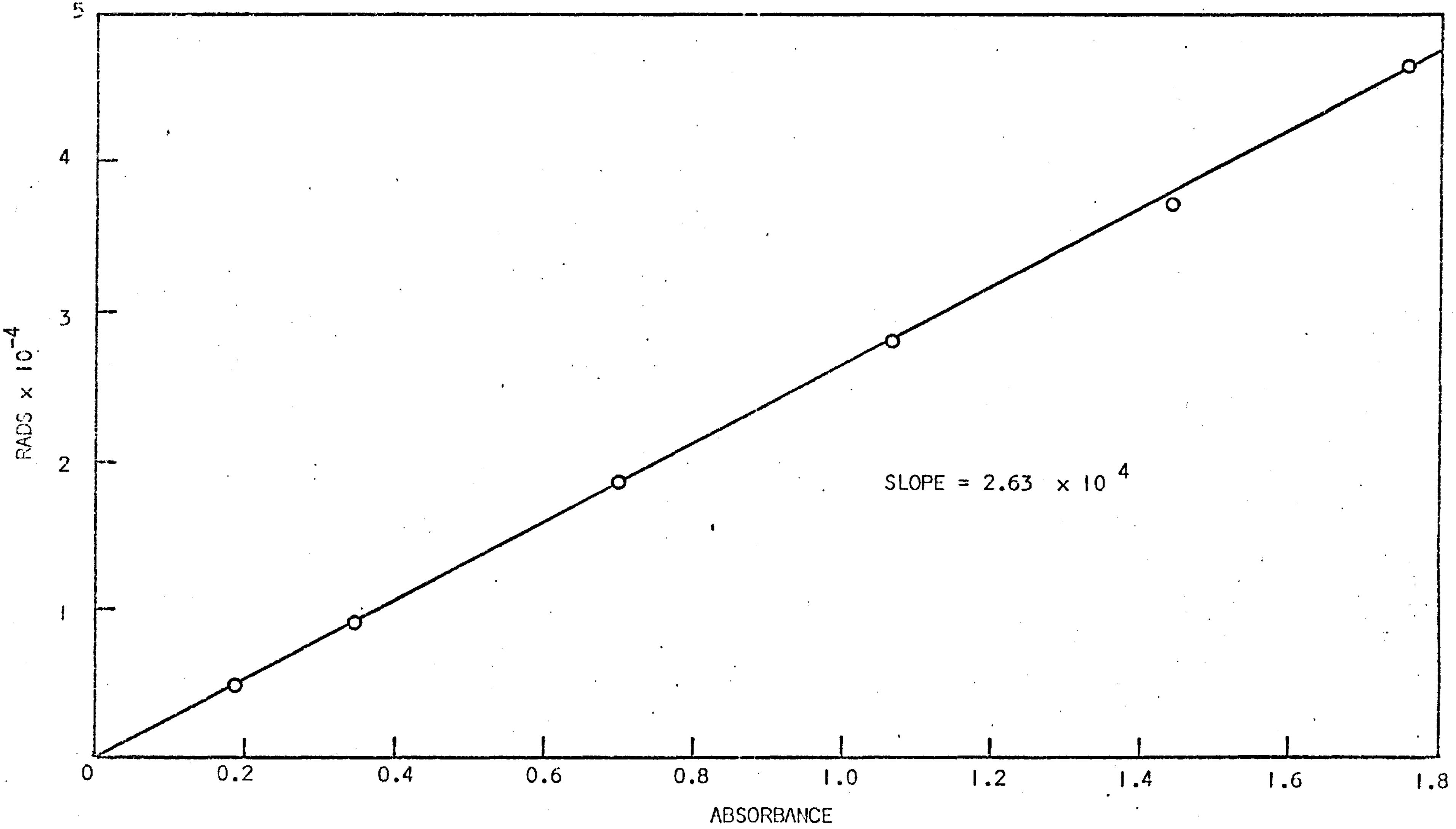


FIG. A-1 CALIBRATION CURVE FOR FRICKE DOSIMETRY MEASURED AT INSTRUMENT TEMPERATURE = 30°C reaction volume) was placed in the reactor and irradiated for a measured length of time (3 to 5 minutes). The recommended dose range is 0.2×10^4 to 4×10^4 rads. The absorbance of the irradiated solution was read from the spectrophotometer using the unirradiated solution as a blank. From the absorbance the absorbed dose was calculated from Eq.(A-2) or read from Fig.A-1. Since the measurements of absorbance were carried out at nearly constant temperature and were similar to the temperatures at which the calibration curve, Fig.A-1 was prepared, no temperature correction on the absorbance or the dose rate was necessary. However, if the temperatures are different in a temperature range of 20° to 30°C, a correction temperature coefficient of +0.7 % per degree C has to be used. For example, in Swallow's formula Eq.(A-3), a temperature correction term has been included in the equation.

$$\text{rad} = 2.94 \times 10^4 (1-0.007t) \times \text{OD} \qquad \text{(A-3)}$$

where t = measured temperature minus 20°C

Dosimetry Result

The measured dose rates for the cobalt 60 source used in this work are summarized in Table A-1.

TABLE A-1

RESULTS OF FRICKE DOSIMETRY MEASUREMENT

Date	Irradiation time (mins.)	Absorbance	Dose rad x 10^{-4}	Average dose rate rad/sec.
8/13/70	15	2	-	-
8/13/70	5	1.480-1.490	3.87-3.90	129
8/13/70	5	1.465-1.485	3.85-3.90	129
8/14/70	5	1.486-1.490	3.90	130
8/14/70	5	1.480-1.490	3.85-3.90	129
8/14/70	3	0.99 -1.00	2.60-2.63	139.5
8/14/70	3*	1.006-1.007	2.65	147

* No water in water jacket.

The discrepancy between the 5 minutes and the 3 minutes samples were mainly due to the inaccuracy in timing. As mention before, the time required to position the source and to remove the source varied from 1.5 to 2 minutes which were rather large compared with the total irradiation time of only 3 to 5 miuntes. Obviously, the error introduced in the 3 minutes samples would be larger than the 5 minutes samples. A correction factor for this pre-irradiation of the sample should be made, for example, by measuring the dose absorbed in the period of transporting the source. However, this was not carried out and instead a theoretical approach to correct the final dose rate was attempted as follows:

Assume that the same amount of extra dose have been absorbed by the 3 and 5 minute samples during the transportation of the source. i.e.

$$TD_3 = D_3 + E \qquad (A\text{-}4)$$

$$TD_5 = D_5 + E \qquad (A\text{-}5)$$

where TD_3 and TD_5 are total absorbed doses in 3 and 5 minute samples respectively; D_3 and D_5 are the doses that should be absorbed in 3 and 5 minutes and E is the extra dose absorbed by the system during the source transportation.

By combining Eq.(A-4) and Eq.(A-5), the extra dose E can be eliminated so that in 2 minutes time, the exact absorbed dose is

$$\begin{aligned} D_2 &= TD_5 - TD_3 \\ &= D_5 - D_3 \qquad (A\text{-}6) \end{aligned}$$

and the error due to source transportation is excluded. Hence the exact dose rate measured by the dosimetry can be calculated by dividing D_2 with 2 minutes.

Using this approach, the exact dose rate was equal to 109 rad/sec. which was used for the calculation of the absorbed dose of the iodine solution system as described in Appendix B.

For the interest of comparision, the dose rate had also been computed using Swallow's formula Eq.(A-3).

As expected, a slightly larger value, 134.8 rad/sec. (vs. 129.0 rad/sec.) or after the correction, a value of 111.8 rad/sec. (vs. 109.0 rad/sec.) was obtained.

APPENDIX B

CALCULATION OF THE MASS ABSORPTION COEFFICIENTS

The Fricke dosimetry only provides the energy absorbed by the ferrous sulphate solution, but this value can be related to the energy absorbed by a system of interest if the mass absorption coefficients of both the dosimeter and the system of interest are known. The relationship between them can be expressed as:

$$D_s = D_d \times (\mu a/\rho)_s \; / \; (\mu a/\rho)_d \qquad \text{(B-1)}$$

where s and d refer to the system of interest and the dosimeter respectively. Notice that the mass energy absorption coefficients (μ_a/ρ) were used in this work (see Section II-1.4) and no buildup factor was considered.

The mass energy absorption coefficients for various elements are available in the literature as a function of the photon energy (2,10,11,56,57,58). Some values related to this work were abstracted from those literature. By graphical interpolation of the data at 1.25 MeV (average of 1.173 and 1.332 MeV), the mass energy absorption coefficients are given in Table B-1, together with the mass total absorption coefficients. The mass absorption coefficient for a compound X_mY_n can

TABLE B-1

MASS ABSORPTION COEFFICIENTS FOR ELEMENTS AND COMPOUNDS AT 1.25MeV

Element or Compound	Energy μ_a/ρ $(cm^2/gm) \times 10^2$	Total μ/ρ $(cm^2/gm) \times 10^2$
Hydrogen	5.31	11.4
Carbon	2.68	5.68
Iodine	2.51	5.08
Chlorine	2.55	5.40
Oxygen	2.68	5.68
Methane*	3.34	7.12
Water*	2.97	6.32
CCl_4*	2.56	5.42

* calculated by Eq.(25)

be calculated by Eq.(25). For example, when the equation is applied to methane, it becomes

$$\left(\frac{\mu_a}{\rho}\right)_{CH_4} = \left(\frac{\mu_a}{\rho}\right)_c \times \frac{A.W.\ C}{M.W.\ CH_4} + 4\left(\frac{\mu_a}{\rho}\right)_H \times \frac{A.W.\ H}{M.W.\ CH_4}$$

Note that $\left(\frac{\mu_a}{\rho}\right)_{I_2} = \left(\frac{\mu_a}{\rho}\right)_I$

The values given in Table B-1 include the three main interacting effects, namely Compton scattering, photoelectric effect and pair production (see Section II-1.3)

In the present work, the system of interest is a mixture of iodine, solvent (CCl_4) and dissolved methane.

By extending Eq.(25) the mass absorption coefficient for the system can be calculated as:

$$\left(\frac{\mu a}{\rho}\right)_s = F_{I_2}\left(\frac{\mu a}{\rho}\right)_{I_2} \times F_{CH_4}\left(\frac{\mu a}{\rho}\right)_{CH_4} + F_{CCl_4}\left(\frac{\mu a}{\rho}\right)_{CCl_4} /Z \qquad \text{(B-2)}$$

where $F = N \times M.W.$

$Z = F_{I_2} + F_{CH_4} + F_{CCl_4}$

N = mole fraction

However, as demonstrated below, $\left(\frac{\mu a}{\rho}\right)_{CCl_4}$ can be used to substitute for $\left(\frac{\mu a}{\rho}\right)_s$, because the mole fractions of iodine and methane are so small compared with that of the carbon tetrachloride that they can be ignored. Thus the variation of iodine concentration in the solution will not affect the mass absorption coefficient at all. For example, in Runs 33 and 44, where the iodine concentrations varied from dilute to the saturation concentration, the mass energy absorption coefficients were computed as follows:

<u>Run 33</u>

At 49°C, the CH_4 solubility is 0.691 cc/cc of CCl_4

25 ml of solution (assume equal to 25 ml CCl_4) in reactor

0.5795 gm of I_2 dissolved in 39.1670 gm CCl_4

Compound	CH_4	I_2	CCl_4
No. of mole	0.00065	0.00228	0.25463
Mole fraction	0.0025	0.0089	0.9886

Using Eq.(B-2), it can be computed that

$$\left(\frac{\mu a}{\rho}\right)_s = 2.55 \times 10^{-2}$$

compare with

$$\left(\frac{\mu a}{\rho}\right)_{CCl_4} = 2.56 \times 10^{-2}$$

The difference between the two values is less than 0.4%. For Run 44 where the mole fractions were CH_4(0.0023), I_2 (0.0106) and CCl_4(0.9871), the $\left(\frac{\mu a}{\rho}\right)_s = 2.56 \times 10^{-2}$ which is exactly equal to the mass energy absorption coefficient for pure CCl_4.

After computing the mass energy absorption coefficient, the absorbed dose by the system of interest can be calculated by Eq.(B-1) as follows:

$(D.R.)_d = 109$ rad/sec. (From Appendix A)

The mass energy absorption coefficient of the Fricke dosimetric solution can be approximated by that of the pure water because the solution is very dilute (0.001 M), i.e.

$$\left(\frac{\mu a}{\rho}\right)_d = \left(\frac{\mu a}{\rho}\right)_{H_2O} = 2.97 \times 10^{-2}$$

$$\left(\frac{\mu a}{\rho}\right)_s = \left(\frac{\mu a}{\rho}\right)_{CCl_4} = 2.56 \times 10^{-2}$$

Therefore

$$(D.R.)_s = 109 \times 2.56/2.97$$

$$= 94.0 \text{ rad/sec.}$$

or $$= 5.86 \times 10^{15} \text{ eV/gm/sec.}$$

As mentioned before, no correction was being made for the decay of the cobalt source. For a period of four months the dose rate was not changing too much as demonstrated below:

The decay rate constant for cobalt-60 is

$$\lambda = 3.602 \times 10^{-4} \text{ day}^{-1}$$

$$D = D_o e^{-\lambda t}$$

$$= 94.0 \times e^{-3.602 \times 10^{-4} \times 120}$$

$$= 90.0 \text{ rad/sec.}$$

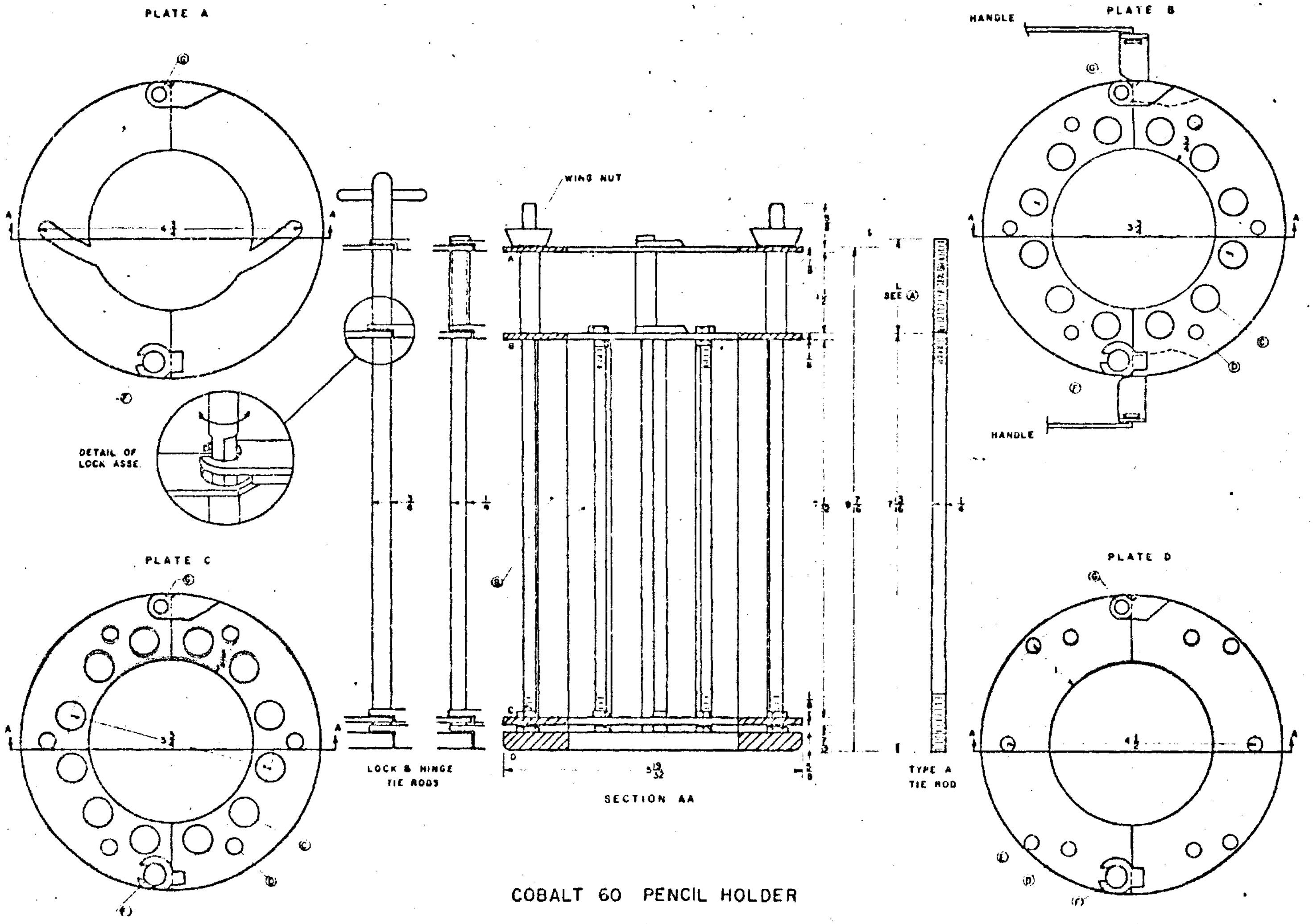
The difference between the two values is about 4% which is smaller than the other sources of errors from dosimetry (timing) and the method of estimating the absorbed dose using mass absorption coefficients.

APPENDIX C

THE COBALT-60 SOURCE

The gamma source used in this study was a cobalt 60 source purchased from the Atomic Energy of Canada,Ltd. in 1962 with a source strength, measured on October 9, 1962, of 5330 curies. A description of the source and its dose rate characteristics are available in the literature (59). A detailed design of the source container is reproduced in Fig.C-1. because the designs of apparatus, source positioning stand for the present work were based on the dimensions given in this figure.

The source is housed in the Hot Cell located in the McMaster University Nuclear Reactor. The hot cell has a rated capacity of 10,000 curies of cobalt-60. Its heavy concrete wall (4 foot thick) is equipped with removable concrete plugs of different diameter sizes. They can be removed if necessary for introducing tubings, electrical wires etc. into the hot cell. For a flexible tube or wire, a special concrete plug with coiled "tunnel" is used to replace the solid plug, but for non-flexible tube such as glass, such a special concrete plug is useless and proper shielding using lead blocks has to be built at one of the open ends. The hot cell



COBALT 60 PENCIL HOLDER

CONSTRUCTION NOTES

1. ALL MATERIAL WAS TYPE 302 STAINLESS STEEL
2. DIMENSIONS OF PLATES A–D ARE:
   I.D. = 3.00
   O.D. = $5\frac{19}{32}$
3. THE COMPLETE ASSEMBLY WAS PASSIVATED AGAINST STRAIN CORROSION

PC NO	DESCRIPTION
(A)	6 TIE RODS L = 2 FOR 2, L = $\frac{5}{8}$ FOR 4
(B)	12 SS TUBES (304) O.D. = $\frac{5}{8}$, I.D. = $\frac{1}{2}$
(C)	12 - $\frac{19}{32}$ DIA HOLES IN PLATES B&C FOR (B)
(D)	6 - $\frac{1}{4}$ DIA HOLES IN PLATES B–D FOR (A)
(E)	4 - $\frac{1}{4}$ DIA HOLES IN PLATE D
(F)	$\frac{3}{8}$ DIA. POSITIONING HOLE FOR LOCK TIE ROD
(G)	$\frac{1}{4}$ DIA. POSITIONING HOLE FOR HINGE TIE ROD

SCALE 1 = 1 INCH

Figure C-1

is also equipped with a viewing window (4 feet of 'leaded' glass), two master slave manipulators, a 20 foot storage water well and an electrically operated crane.

The cobalt source consists of 12 line sources called pencils. The are arranged symmetrically in a cyclindrical form so that the radiation fluxes from each of the 12 pencils are overlapping with one another. Hence a longitudinal dose uniformity can be achieved as shown in Fig.C-2, but the radial dose intensity is dropping drastically with increasing in radial distance as shown in Fig.C-3. In the present work, the reactor was placed in the centre of the source at a level where the longitudinal dose uniformity could be expected. Since the reactor had a small diameter, the variation of radial dose intensity in the reactor would not be very large. Moreover, the mixing in the reactor would eliminate the problem of non-uniformity of radial dose intensity. Thus it could be said that the reactor received uniform dose both longitudinally and radially.

A positioning stand for the source and the reactor as shown in Fig.C-4, was built in order to have the positions of the source and reactor fixed, and also to have an easy manipulating of the source with the pair of slave manipulators. It consisted of 3 pieces of ½ x 24 x 24 in. plywood held together with four ½ in. diameter

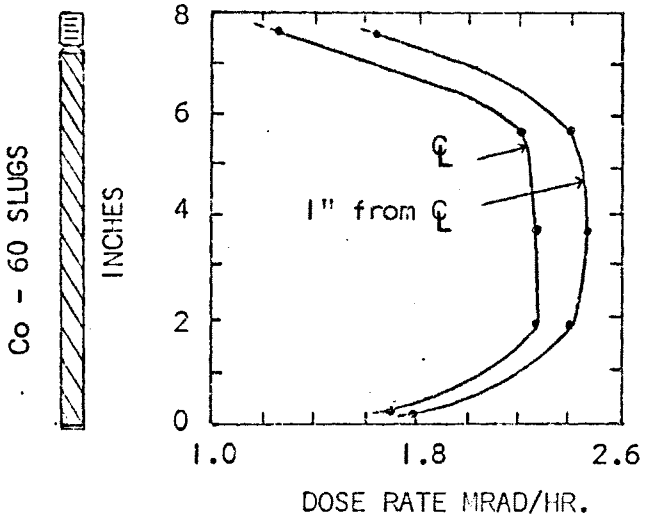


FIG. C-2 LONGITUDINAL FLUX PROFILE OF SOURCE (59)

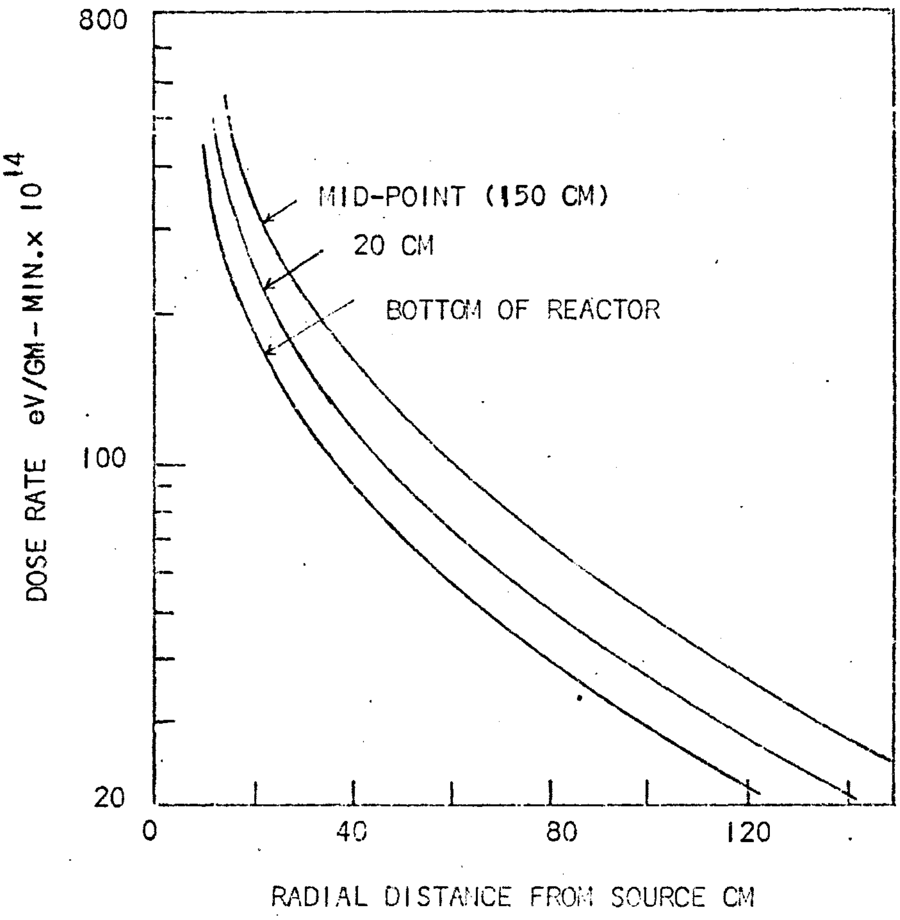
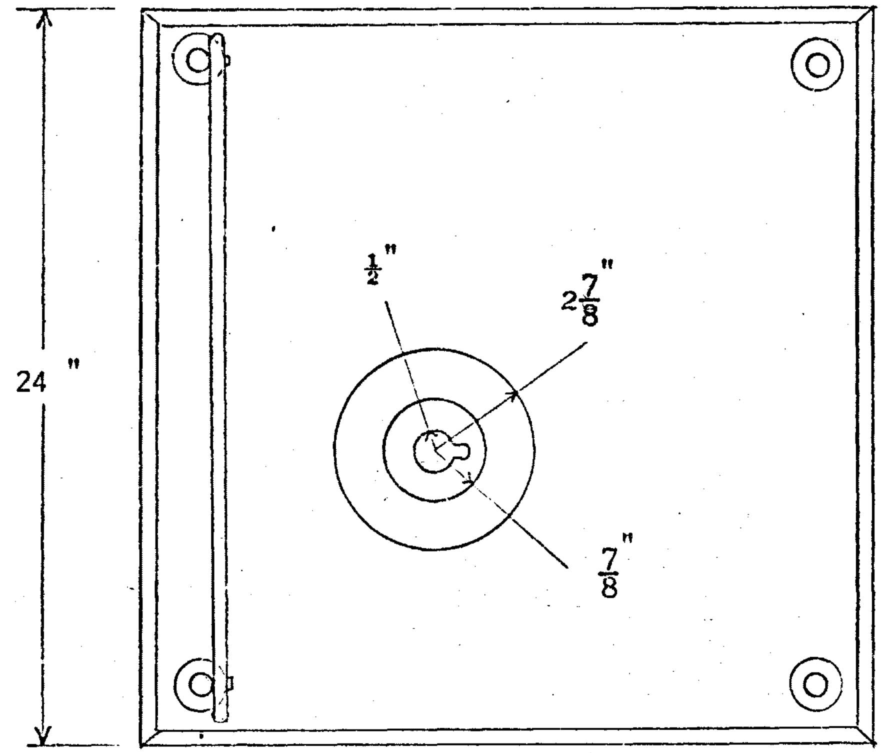


FIG. C-3 RADIAL FLUX PROFILE OF SOURCE (12)



TOP VIEW

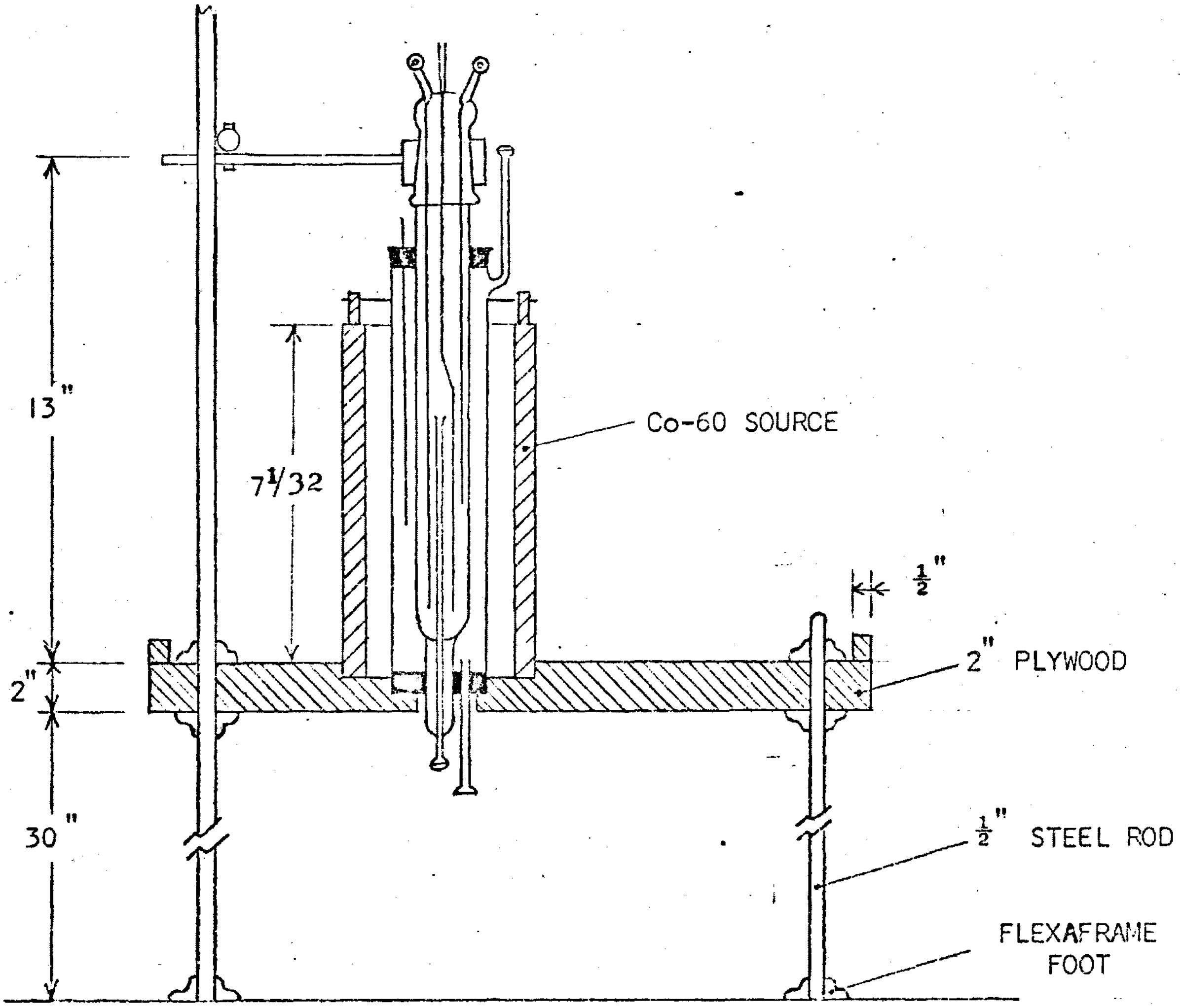


FIG. C-4 REACTOR AND SOURCE ON POSITIONING STAND steel rods by the flexaframe feet. Three concentric holes in different diameters were made on the three pieces of plywood, with the top piece having the largest hole and bottom piece the smallest. These three holes enabled the reactor and the source to sit at their fixed positions.

APPENDIX D

DESIGN OF APPARATUS

A continuous flow system was originally adopted for this work and there are several ways that a continuous flow system can be achieved. It is the purpose of this appendix to discuss these different ways briefly and the one chosen for the present experiment in more detail together with the other auxiliary parts required in the experiment.

D-1 Continuous Flow System

There are various ways to achieve a continuous flow system, but only four methods will be presented here. Two of them are using a plug flow reactor and the other two are using a backmix reactor. Notice that the two methods using plug flow reactor are carried out in the gas phase. Although the gas phase reaction is not of interest here, they are presented here as a comparison with the other methods.

(1) Plug flow with iodine feed as vapor

In this method, the methane and iodine vapor are fed into a plug flow reactor at a temperature high enough to prevent any iodine condensation. The reactor is placed in a field of gamma radiation. The products and unreacted reactants are condensed and collected in a condenser system.

Iodine is in solid form at room temperature and pressure. Thus in order to introduce the iodine into the reactor as a vapor, high temperature (at normal pressure) is necessary. In a laboratory, a continuous feed of iodine vapor can be achieved by using a carburettor containing some iodine over which an inert gas or methane will flow. The carburettor can be maintained at a constant temperature in a furnace or an oven. A fairly high temperature, probably near or above the melting point of iodine (note that iodine sublimes) has to be used in order to obtain a reasonable iodine feed concentration. For example, using the vapor pressure chart of iodine (Fig. D-1), at 105°C and at one atmospheric reaction pressure, the mole % of iodine in a methane iodine mixture is 7% and at 158°C is 50%. However, as the temperature is increased, the vapor pressure is more responsive to the temperature change. For instance at 150°C, the slope of the curve is about 8.3 mm Hg/°C which means that about 2.8% of error in vapor pressure at 150°C will be introduced per degree temperature change. Thus the temperature control of the carburettor becomes very critical.

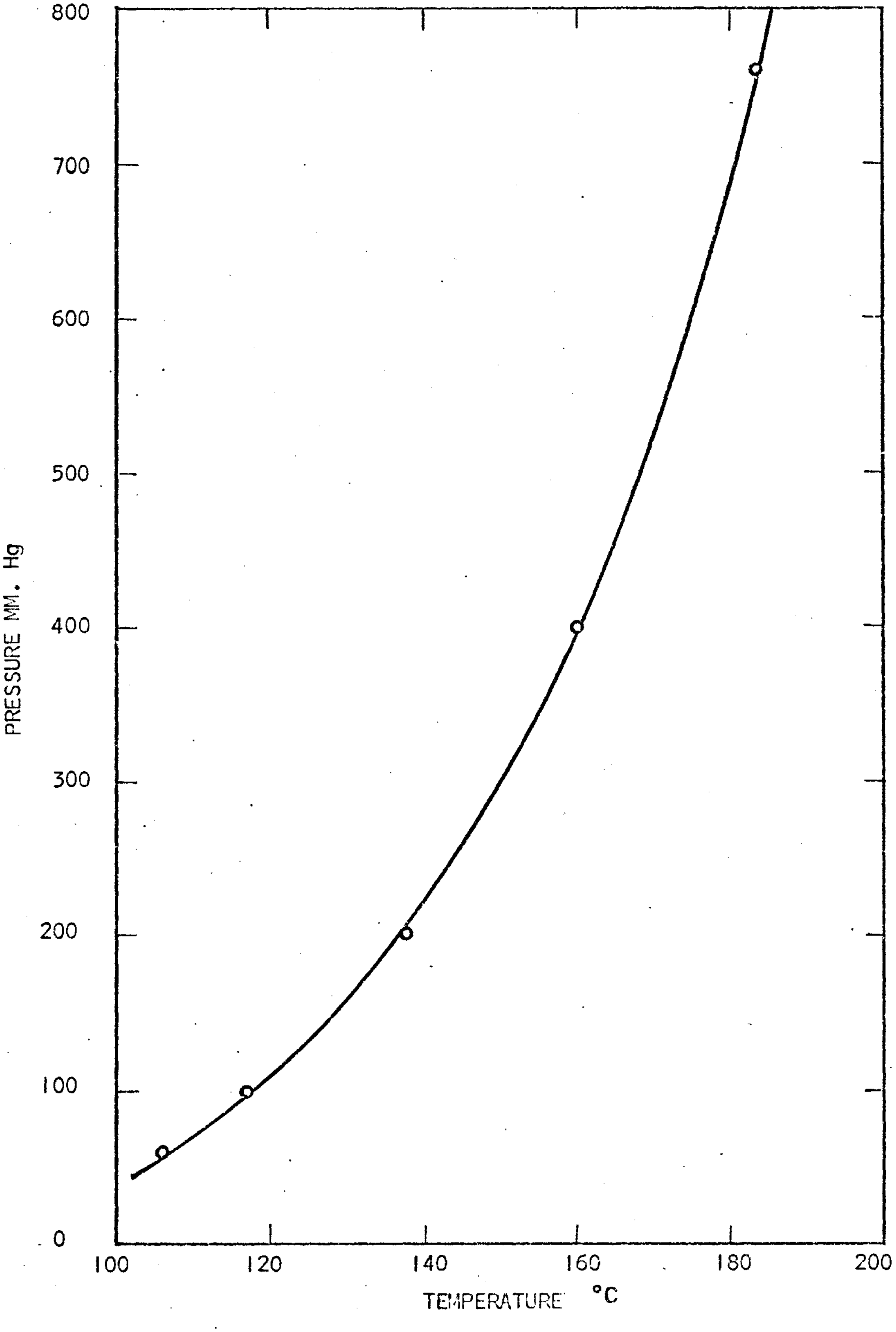


FIG. D-1 VAPOR PRESSURE VS. TEMPERATURE FOR IODINE

A method has been proposed (60) to replace the carburettor by a syringe pump used for introducing benzoic acid vapor into a reactor. Note that benzoic acid is solid and sublimes near its melting point. Using this method, the iodine at liquid state, in a syringe placed in some kind of heating medium is forced out of the syringe by a calibrated syringe pump into a vaporizer which will vaporize the liquid iodine into vapor iodine. The vaporizer used was designed for use in a gas chromatograph liquid inject port. In this case, the temperature control is less critical and the inlet iodine concentration has less constraint. However, some difficulties in using this method have been reported and needed to be improved (60).

(2) Plug flow with iodine feed as solution

The main difficulty encountered in the above method is that iodine will condense and plug up the system if there are cool spots in the system. One way of avoiding this is to introduce the iodine into the reactor by using iodine solution, provided that the solvent is not going to affect the reaction. The solution, when it enters the plug flow reactor, is immediately vaporized by the high temperature at the entrance of the reactor. The vaporized solution together with the incoming methane then move farther down the reactor and react with each other under the influence of gamma radiation.

(3) Backmix with iodine feed as vapor

The iodine vapor and the methane either premixed or not are bubbling through a column of solvent in a backmix reactor placed in a gamma radiation field. The iodine vapor can be obtained as described in method (1) above. However, the solvent has to be maintained at a fairly high temperature in order to prevent the iodine from condensing. At such a high temperature, heavy oils or some molten organics have to be used as solvent because ordinary liquid solvents will not stand these high temperatures.

(4) Backmix with iodine feed as solution

The method seems to be the easiest method to bring about a liquid phase reaction between iodine and methane. The G value obtained for the gas phase iodination was so high that it was assumed that the use of a solvent in this reaction would at most lower the rate of reaction or lower the G value but was still high enough for one to assess its commercial value. Therefore it was adopted for this study. In this process, both iodine solution and methane are fed into a backmix reactor which initially is filled with the iodine solution.

D-2 Design of Backmix Reactor

The kinetics equations and the natures of this gamma induced iodination reaction are not available in the literature. However, it was believed (31) that the reaction occurs by successive iodine substitution to the methane as shown from Eq.(49) to Eq.(54). This kind of reaction is referred to as a consecutive-competing (or series-parallel) reaction (61) and its general representation is

$$\begin{aligned} A + B &\longrightarrow R \\ R + B &\longrightarrow S \\ S + B &\longrightarrow T \end{aligned} \qquad \text{(D-1)}$$

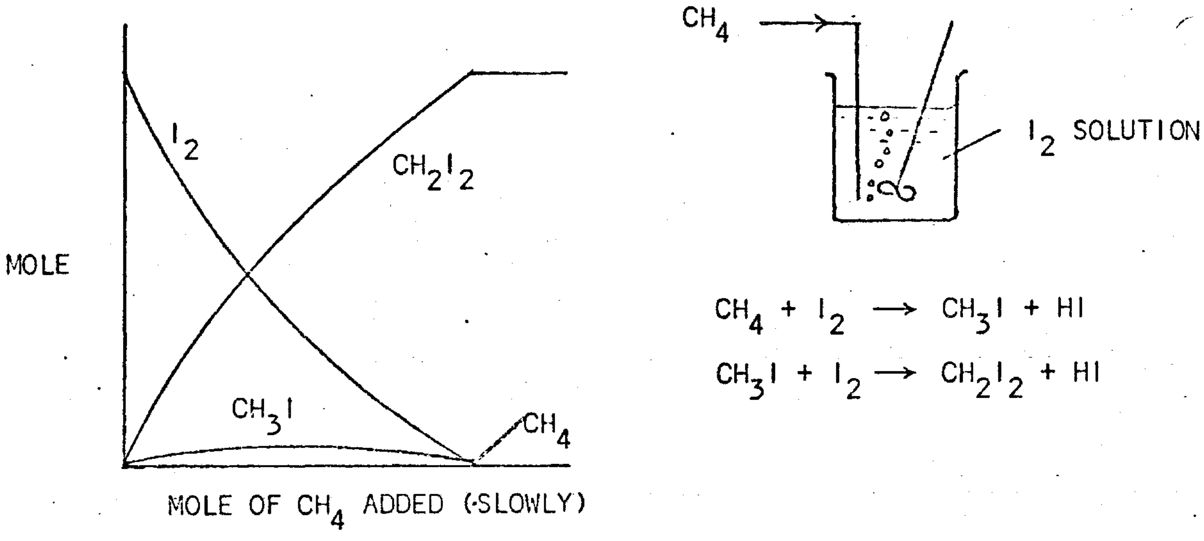
or

$$A \xrightarrow{+B} R \xrightarrow{+B} S \xrightarrow{+B} T$$

where B is the iodine, A is the methane and R, S and T are products. Thus qualitatively, it is possible to predict the product distribution according to the mode of bringing the two reactants together. For example, if methane is added (or dissolved) slowly into a backmix reactor full of iodine solution, the dissolved methane will react with the iodine to form methyl iodide. But the reaction will not stop there because in the presence of large amount of iodine, the methyl iodine will react further with the iodine to form methylene iodide. Thus the product distribution will behave as shown in Fig. D-2, and very little intermediate product will be produced.

On the other hand, if very little iodine is added slowly into a backmix reactor full of solvent which has been presaturated with methane, the intermediate product, methyl iodide will be produced. The concentration of CH_3I will buildup slowly until its concentration is high enough to compete with dissolved methane for the added iodine, so that its concentration begins to drop off as shown in Fig.D-3. In short, as summarized by Levenspiel (<u>61</u>) "For a given conversion of reactant A a maximum amount of intermediate is formed when we do not mix materials at different stages of conversion".

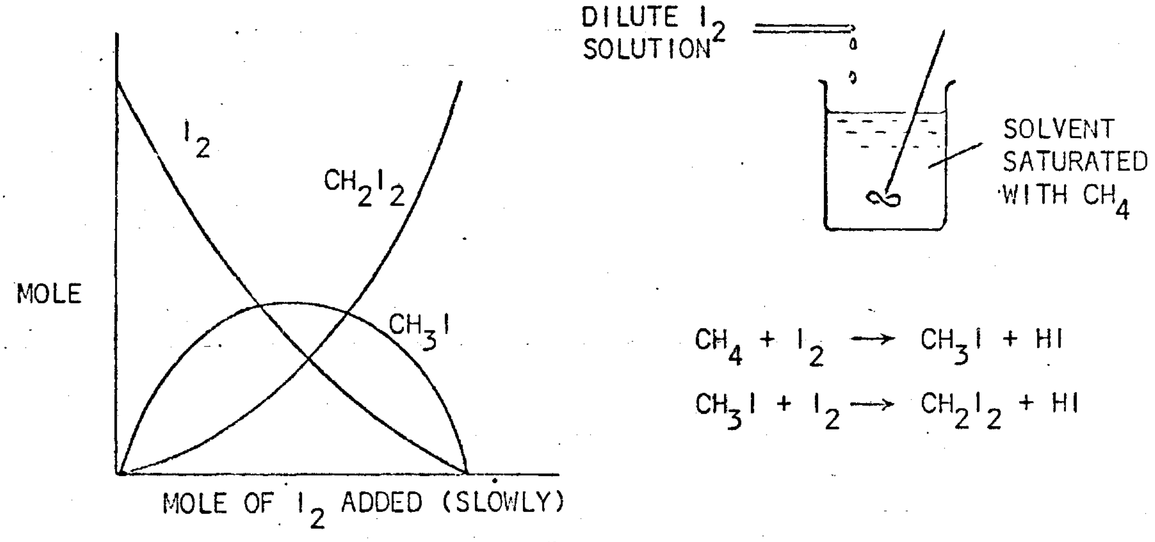
Thus in the present work, with the set up as described in Section D-1 (4) above, the product distribution shown in Fig.D-2 is more likely than that in Fig.D-3. (Provided the rate constants for each successive step are not too much different in magnitude). The product distribution shown in Fig.D-3 could be achieved if the content in the reactor is always saturated with methane and very dilute iodine is either fed into the reactor very slowly or by using a pulsation technique of feeding the iodine. However, the ultimate objective of this work is to produce the iodomethanes which can mean any of the three expected organic products. If the reaction



$CH_4 + I_2 \longrightarrow CH_3I + HI$

$CH_3I + I_2 \longrightarrow CH_2I_2 + HI$

FIG. D-2 PRODUCT DISTRIBUTION FOR SLOW ADDING OF CH_4



$CH_4 + I_2 \longrightarrow CH_3I + HI$

$CH_3I + I_2 \longrightarrow CH_2I_2 + HI$

FIG. D-3 PRODUCT DISTRIBUTION FOR SLOW ADDING OF I_2

turns out to favour the production of certain product, then the optimization of the process will be concentrated on that product.

Thus the reactor design will then only depend upon the size or dimensions and the dose characteristic of the cobalt 60 source. As discussed in Appendix C, the cobalt source provides a longitudinal uniform dose of about 4 inches and therefore a reaction zone of about 4 inch long was designed. The source was at its exhausted stage, and in order to get a maximum possible intensity out of that source, the reactor should be placed at the centre of the source where maximum dose rate could be obtained. Therefore the diameter of the water jacket cannot be larger than 3 inches which is the inside diameter of the source. The water jacket was kept as slim as possible to avoid any significant reduction of radiation due to the water. The final design of the two reactors are shown in Fig.D-4. The inner diameter of the reactor was rather small so that there was not much room for a piece of sintered glass to be joined to the tip of the methane inlet. Instead the methane inlet was sealed with five pin hole openings.

Other auxiliary glassware for this work is shown in Fig.D-5. There are (a) the reflux condenser for the reflux reactor in Fig.D-4(b), (b) the gas-liquid separator and (c) the iodine solution reservoir. The

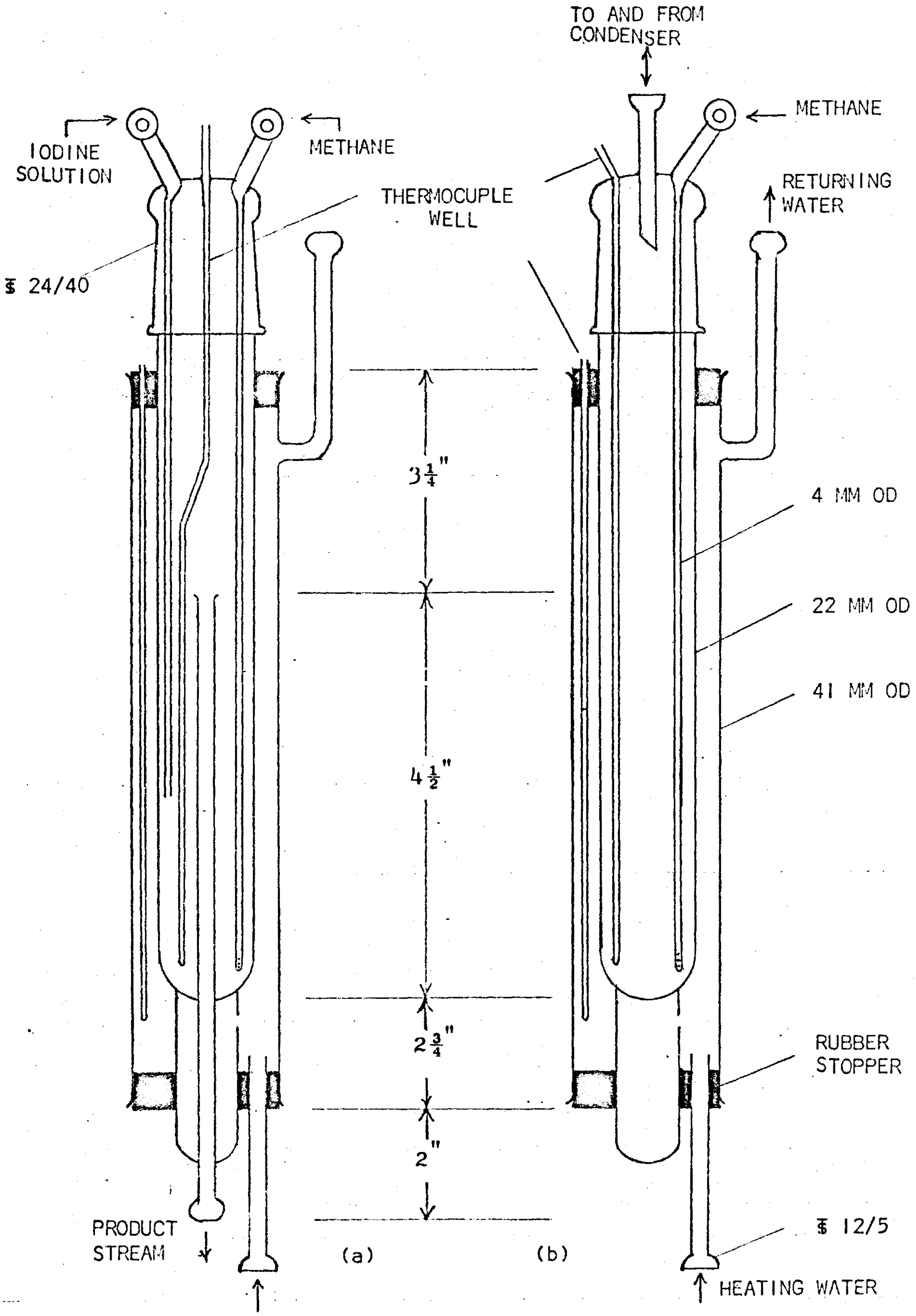


FIG. D-4 REACTORS USED (a) OVERFLOW (b) REFLUX

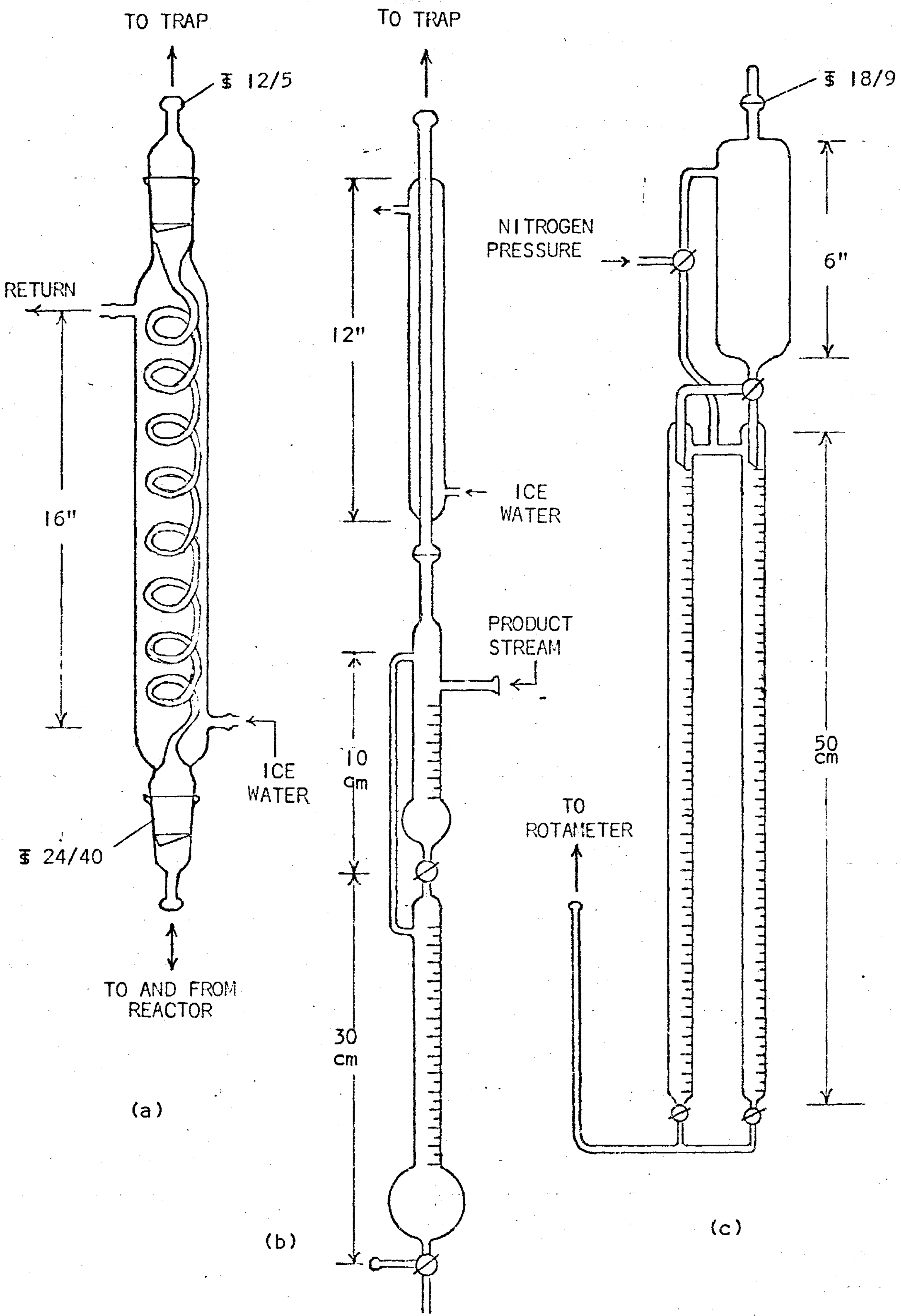


FIG. D-5 AUXILIARY GLASSWARE (a) REFLUX CONDENSER FOR REACTOR (b) GAS-LIQUID SEPARATOR AND (c) IODINE SOLUTION RESEVIR reflux condenser was an ordinary 400 mm long condenser with coiled tube and ground joint ($ 24/40) at both ends. The gas liquid separator consisted of three sections. The top section was a condenser for condensing the vapor of the product stream. The middle section was for taking small liquid sample with the smaller bulb calibrated to be 8.5 ml and total capacity of this section was 14.0 ml. This section also served as a temporary container while the liquid sample was being withdrawn from the bottom section. The bottom section was actually for collecting all liquid from reactor. The big bulb at the bottom was calibrated to be 30.5 ml.and the total capacity in this section was 50ml. As mentioned before the original plan of this work was to have most of the collected liquid recycled via the side tube of the three way value at the bottom of the gas-liquid separator. Thus the amount of sample withdrawn from the separator for gas chromatograph analysis had to be consistent or the fraction of the liquid withdrawn for this purpose had to be known. This was why the separator was scaled. The reservoir for the iodine solution consisted of two 50 ml. burets which permitted the feeding of iodine solution to the reactor as well as the refilling of solution from top vessel to the buret at the same time. A nitrogen pressure of

10 - 15 psig was used to provide a constant upstream pressure head for the rotameter. The three way valve for the nitrogen could cut off the pressure in the top vessel for refilling the top vessel if necessary.

APPENDIX E

ROTAMETERS AND FLOWRATE CALIBRATION

Two sizes of rotameters were used in this work. They were purchased from the Brooks Instrument, Ontario, with the following specifications:

Meter size	Cat. No.		Max. flow (min. flow ≃ 1/10 max.flow)	
			Water	Air
2	R-2-15-AA	Glass	1.02	90.9
		Sapphire	1.98	138.8
		S. Steel	4.96	268.0
2	R-2-15-D	Glass	5.8	378
		Sapphire	10.5	518
		S. Steel	20.8	832

Rotameter No. R-2-15-AA with both glass and stainless steel floats was used to meter the methane flowrate. The calibration curve is shown in Fig. E-1. As mentioned in Section III-3.1, a pressure of 3 psig was maintained at the down stream of the rotamer by a pressure regulator (see Fig.11) in order to prevent the rotameter float been fluctuating. Hence the rotameter was calibrated at this condition. The choice of 3 psig was quite arbitrary,

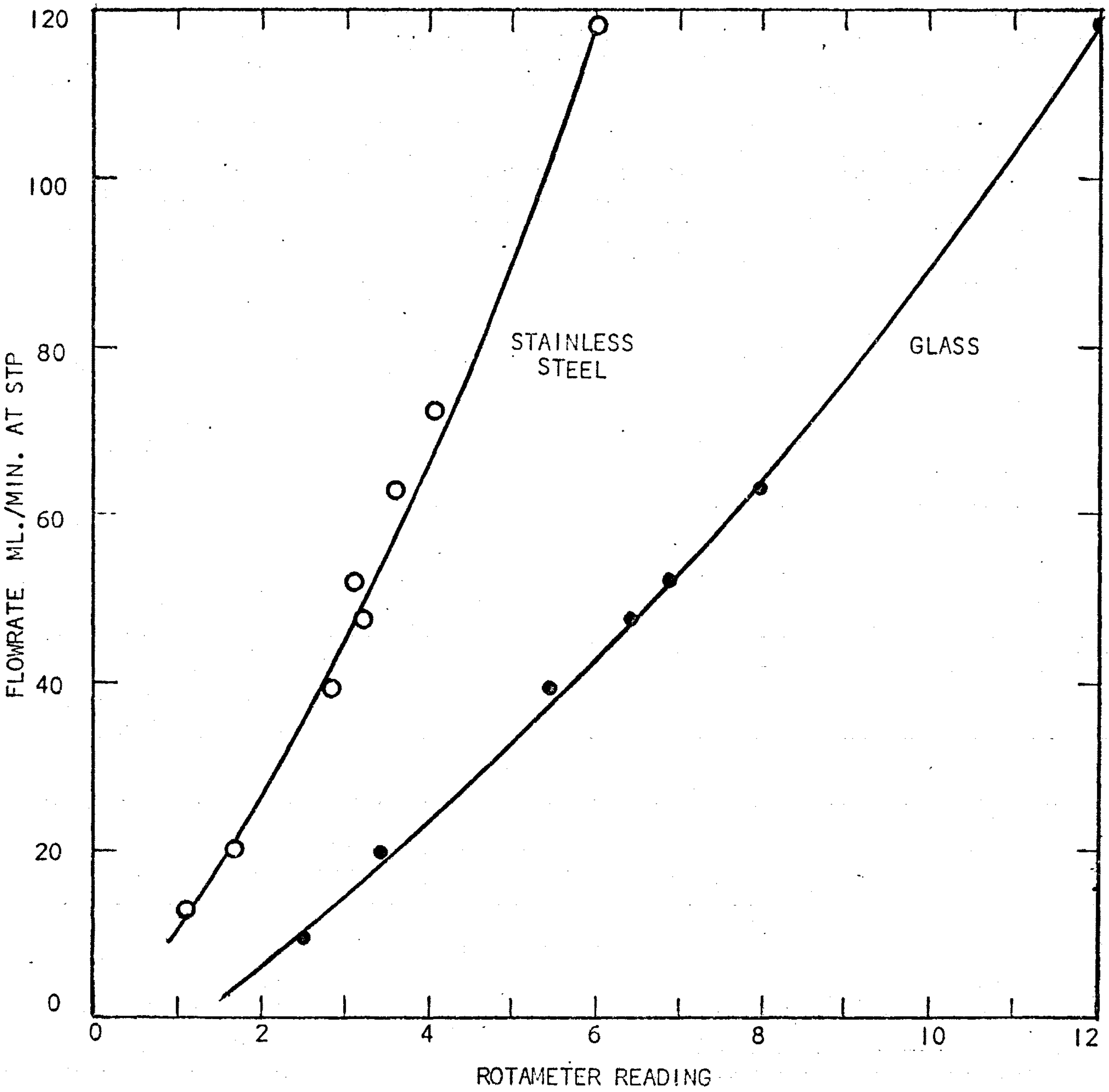


FIG. E-I ROTAMETER CALIBRATION FOR METHANE but it was chosen mainly because it is large compared with the 4 inches solution of hydraulic pressure in the reactor. The usual laboratory mercury manometer, which give a more sensitive and accurate reading, was substituted by a pressure gauge because no mercury was permitted to use in the nuclear reactor building. Another feature of the McMaster nuclear reactor is that the pressure of the building is always adjusting itself slightly (0.13 in. of water) below ambient pressure. However, this slight difference in pressure was ignored in converting the measured methane flowrate to standard temperature and pressure conditions. The methane flow-rates were calibrated using the conventional soap bubble meter method.

For metering liquid flowrate, both liquid feed and recycle, two rotameters (R-2-15-D) with glass and sapphire floats were used. Both ends of the rotameter were joined to two pieces of ball and socket joints so that the rotameter could be changed easily and only glass was in contect with the corrosive iodine solution. These rotameters were not calibrated mainly because different solvents and different iodine concentrations were expected to be used in this work. However, they acted as indicators for constant feeding rate and the total solution fed into the reactor could be obtained from the buret readings. Perhaps, as a recommendation, for handling such variety of solvents and concentrations in small flowrates, a syringe pump would probably be the best. Other kinds of pumps are not very satisfactory because either they are normally designed for a larger flowrate or they cannot resist the very corrosive nature of iodine solution and iodides. (Stainless steel is not suitable for long period of use).

APPENDIX F

PHYSICAL CONSTANTS OF CHEMICALS

Some physical constants such as molecular weight, boiling point, melting point, G value and solubility will be given in this appendix for reference because they play a very important role in this work. The values are presented in two tables; Table F-1 gives the molecular weight, boiling point, melting point and G value of all chemicals of interest and Table F-2 gives the detailed solubility data for iodine and methane in various solvents.

TABLE F-1

PHYSICAL CONSTANTS OF CHEMICALS

Chemical	Molecular Weight	Melting Point($^{\circ}$C)	Boiling Point($^{\circ}$C)	G value
Benzene	78.12	5.5	80.1	0.59-1.4
Carbon tetrachloride	153.82	-22.99	76.54	7.0 -25
Ethyl iodide	155.97	-108	72.3	2.7
Hexane	86.18	-95	68.95	7.6
Hydroiodic acid	127.91	-50.8	-35.38	-
Iodine	253.809	113.5	184.35	-
Iodoform	393.73	123	Ca 218	-
Methane	16.04	-184	-161.15	8.5
Methanol	32.04	-93.9	64.96	6.1 -15
Methyl iodide	141.94	-66.45	42.4	2.4
Methylene iodide	267.84	6.1	182.0	-
Tetrachloroethene	165.83	-19	121	-
Toluene	92.15	-95	110.6	0.40-2.4
1,2,4 Trichlorobenzene	181.45	16.95	213.5	-
Trichloroethene	131.39	-73	87	-

TABLE F-2

SOLUBILITIES OF IODINE AND METHANE

Solvent	Iodine Solubility	Temp. °C	Methene Solubility (cc/cc of s)	Temp. °C
Carbon tetrachloride	17.7 g/l	11	0.8109	-19.8
	20 5	15	0.7621	0
	22.5	18	0.7271	20
	25.1	21	0.7031	40
	29.1	25	0.6878	60
Methanol	(Ethanol)		0.5644	0
	16.72 Wt.%	0	0.4564	20
	21.33	25	0.3904	30
	24.60	35	0.3164	40
			0.1444	60
			0.0464	70
Benzene	11.23 Wt.%	16.3	0.5687	13.1
	14.09	25	0.5680	20
	16.10	30	0.5698	40
	20.05	40	0.5787	60
	25.51	50		
	119.34 g/l	20		
Toluene	3.56 g/l	25	0.454	50
Hexane	0.456mol.%	25	0.6035	22
Chlorobenzene			0.4802	20
			0.4748	99.6
Tetrachloroethene	23.2 g/l	18	-	-
	25.9	21		
	30.6	25		
Trichloroethene	30.5	18	-	-
	34.1	21		
	39.6	25		

APPENDIX G

CALIBRATION OF GAS CHROMATOGRAPH

It is generally accepted that the area under a chromatographic peak (A_i) is proportional to the amount or concentration (C_i) of that component in the mixture.

$$A_i = f_i(C_i) \tag{G-1}$$

Thus if the proportionality factor is known, the measured peak area can be converted to the concentration.

Many techniques are available for determining the peak area and the technique used in this work is to compute the area by multiplying the peak height at maximum by the peak width at half height. This method was fairly accurate for the present work because the shapes of the peaks were close to a triangular shape (see Fig.13).

The proportionality factor can be determined through calibration and there are various methods available for this kind of quantitative interpretation of the chromatogram as outlined in (44). The method used for calibration in this work is the so-called internal standard method. This is the most generally used method because the exact knowledge or the reproducibility of sample volumes is unimportant. This method can be explained as follows:

Using Eq.(G-1)

$$A_s = f_s C_s$$

$$A_i = f_i C_i$$

where the subscripts s and i refer to the internal standard and a particular component in the sample. Combining the above two equations, yields

$$A_s/A_i = (f_s/f_i)(C_s/C_i) \qquad (G\text{-}2)$$

If a detector response factor of one (or 100) is assigned to the internal standard, i.e. f_s=1.0, then the response factor of component i can be expressed relatively to that of the internal standard. Normally the concentration of the internal standard is fixed so that Eq.(G-2) can be simplified to

$$C_i = (C_s/f_i)(A_i/A_s)$$

or

$$C_i = \text{const.}(A_i/A_s)$$

because the fraction (C_s/f_i) is constant for a component. Hence a linear calibration curve plotting (A_i/A_s) against C_i can be established without actually determining the relative response factor. However, this method of fixing the internal standard concentration was not carried out because in that case an extra component had to be purposely added to the sample. This added component might disturbed the original chromatogram. Therefore, in the present work, the relative response factor of each component was determined by rearranging Eq.(G-2) into Eq.(G-3) with $f_s = 1$.

$$f_i = (A_i/C_i)/(A_s/C_s) \qquad (G\text{-}3)$$

Or if the amount of component (such as number of mole) is used, Eq.(G-3) can be written as

$$f_i = (A_i/M_i)/(A_s/M_s) \qquad (G\text{-}4)$$

The internal standard in the present work was the solvent (carbon tetrachloride). Actually it was not a very good choice because various solvents were expected to be used. Nevertheless, it was chosen because other candidates CH_3I, CH_2I_2 and CHI_3 did not always appear in a chromatogram and iodine peak sometimes would give tailing and made its area measurement inaccurate. Furthermore, if other solvent is going to be used besides CCl_4, it is not difficult to find the relative response factor of this solvent compared with that of CCl_4 and then the response factors of other components can be corrected accordingly.

Although the exact knowledge or the reproducibility of sample volumes is unimportant for this method, there is a limited range for the sample volume beyond which the response factor may no longer be constant. Also theoretically the response factor is independent on the type of column used, temperature, attenuation, concentration of the mixture etc., but in practice, it is recommended to keep the calibration conditions as close to the actual product analysis conditions as possible. Thus, in this work, the effect of sample size on the response factors was checked in order to determine the range of sample size in which the response factors were practically constant. Then using this range the calibration of the detector response factors for CH_3I, CH_2I_2, I_2 were determined at operating conditions similar to those of the actual product analysis (see Section III-4.3.2).

G-1 Effect of Sample Size

A 10 microlitre micro-syringe was used in this work. Three sample sizes, 4, 5 and 8 μl were used to study this effect. A solution with known amount of each component was prepared. Samples of 4, 5 and 8 μl were taken and injected into the gas chromatograph. The peak area of each component was measured and by using Eq.(G-4) the relative response factor of each component was computed. The same procedure was repeated so that altogether 6 samples were injected, 2 samples for each sample size. The results are given in Table G-1. Since the values were somewhat scattered, especially for the methylene iodide, it was rather difficult, by looking at those values to decide whether or not the response factors were affected by the injected sample size. Thus a

TABLE G-1

EFFECT OF SAMPLE SIZE ON THE RESPONSE FACTORS

Component	Sample Size	Relative Response Factor	Average f
CH_3I	4	0.812 0.733	0.772
	5	0.755 0.838	0.796
	8	0.852 0.761	0.806
CH_2I_2	4	1.287 1.314	1.300
	5	1.287 1.462	1.374
	8	1.505 1.319	1.412
I_2	4	0.670 0.668	0.669
	5	0.690 0.644	0.667
	8	0.683 0.641	0.662

satistical method of testing the results was used to decide this.

For each component, there were three means which were obtained from three groups (or three injected sample sizes). Each group consisted of two samples (which theoretically should be the same). The t-test for studing the difference between two means (62,63) could not be applied here because there were more than two means to be compared. If the comparisons are made two at a time, there are (n/2)(n-1) comparisons for n means and it is sometimes possible to obtain a least significant difference between two means simply because of the large number of comparisons even when no difference exists (62). Thus the method of analysis of variance was used, but a t-test was also used for comparing two means from the four μl and 8 μl samples.

G-1.1 Analysis of variance

The method of analysis of variance for comparison of several means is explained in many satistical texts such as reference (62). It will be presented here briefly in symbolic form and illustrated by applying to the present work. For a series of replicate data (e.g. number of injected samples) taken at different conditions of some factor G (e.g. different injected sample sizes), the values can be presented as:

TABLE G-2

SYMBOLIC DATA FOR VARIANCE ANALYSIS

Group	G_1	G_2	. . .	G_n
Item in group				
Run 1	X_{11}	X_{12}	. . .	X_{1n}
Run 2	X_{21}	X_{22}	. . .	X_{2n}
	.	.		.
	.	.		.
	.	.		.
No. of run	k_1	k_2	. . .	k_n
Total (T)	T_1	T_2	. . .	T_n

A table for the analysis of variance can then be set up as has been prepared by Volk (62) as shown in Table G-3. Following Table G-2, the present data can be tabulated as shown in Table G-4 for methyl iodide. The data in the bottom part of Table G-4 are coded by multiplying each value by 1000 to remove the decimal. Note that the coding by adding or subtracting a constant has no effect on the calculation of the sum of squares or the variance. The coding by multiplying by a constant will change the

TABLE G-3

ANALYSIS OF VARIANCE

Source	Sum of squares	Degree of freedom	Mean square or variance estimate
Total	$\sum x^2 - \frac{(\sum x)^2}{N}$	N - 1	
Among group	$\sum \frac{T_i^2}{k_i} - \frac{(\sum x)^2}{N}$	n - 1	$\frac{\text{Group sum of Sq.}}{n - 1}$
Within group	Difference	Difference	$\frac{\text{Difference sum of sq.}}{\text{Difference DF} = N - n}$

where N is the total number of runs = $\sum_{i=1}^{n} k_i$

TABLE G-4

DATA FOR VARIANCE ANALYSIS (CH_3I)

Group or sample volume (μl)	4	5	8
Run 1	0.812	0.755	0.852
Run 2	0.733	0.838	0.761

Coded data (multiplying each value by 1000)

Group or sample volume (μl)	4	5	8
Run 1	812	755	852
Run 2	733	838	761
Total (T)	1545	1593	1613
Mean	772.5	796.5	806.5

resulting variance by the square of this constant. But since the F-test is a ratio of two mean squares, the coding factor will cancel. If decoding is necessary, the coded value can be divided by the square of the constant.

The analysis of variance for CH_3I is shown in Table G-5 with the calculations given below the table. Since the calculated F was much smaller than the tabulated F value, at 0.05 level, there was no evidence of a factor among groups which caused a variation in the results greater than that could be accounted for by the variation within groups. In other words, there ~~was~~ no evidence of injected sample size effect which caused an error in the final result. The variation of the response factors could be considered to be the variation within the group (or within a injected sample size).

Similarly for methylene iodide and iodine, the calculated F's were much smaller than the tabulated F at 0.05 level. The calculated F's for methylene iodine and iodine were 0.586 and 0.0402 respectively. Therefore, the same statement as CH_3I could be made for CH_2I_2 and I_2.

By proceeding further, and using the concept of "wholly significant difference" (WSD), it is possible to test whether or not the multiple means are different

TABLE G-5

VARIANCE ANALYSIS FOR CH_3I

Source	Sum of square	D.F.	Mean sq.
Total	3,773,927-3,762,000=11,927	5	
Among group	3,763,221.5-3,762,000=1,221.5	2	610.7
Within group	11,927-1,221.5=10,705.5	3	3568.5

$$N = 6$$

$$\sum X = 812+733+ \; . \; . \; . \; +761=4,751$$

$$\sum X^2 = (812)^2+ \; . \; . \; . \; +(761)^2 = 3,773,927$$

$$(\sum X)^2 = (4,751)^2 = 22,572,001$$

$$\frac{(\sum X)^2}{N} = 22,572,001/6 = 3,762,000$$

$$\sum T^2 = (1545)^2 + (1593)^2 + (1613)^2 = 7,526,443$$

$$\frac{\sum T^2}{k} = 7,526,443/2 = 3,763,221.5$$

(Note: $k_1 = k_2 = k_3 = 2$)

$$F = \frac{\text{Mean sq. (Among G)}}{\text{Mean sq. (within G)}}$$

$$= \frac{610.7}{3568.5} = 0.171$$

From F- table at 0.05 level, at degree of freedoms of 2 and 3, the value of F is

$$F_{0.05,2,3} = 9.55$$

from one another (62). The method is illustrated by applying it to one of the present case, methyl iodide.

From Table G-5

mean square within group, $\bar{S}^2(X) = 3568.5$

$\therefore$ the pooled estimate of standard deviation,

$$\bar{S}\ (X) = \sqrt{3568.5} = 59.75$$

$$k = 2$$

$\therefore$ the estimate of variance of the means,

$$\bar{S}(\bar{X}) = \bar{S}(X)/\sqrt{k} = 59.75/\sqrt{2} = 42.2$$

$n = 3$

$v = N - n = 3$

From Table of $WSD/\bar{S}(\bar{X})$, at $n = 3$, $v = 3$

$$WSD/\bar{S}(\bar{X}) = 6.0$$

$$\therefore \quad WSD = (6.0)(42.2) = 253.2$$

By arranging the means (see Table G-4) in rank order (i.e. from small to large) the difference between the succeeding pairs is compared with the WSD as shown in Table G-6

TABLE G-6

WSD METHOD OF TESTING THE MULTIPLE DIFFERENCES AMONG A NUMBER OF MEANS (CH_3I)

Rank	Group No.	Mean	Difference
1	1 (4 μl)	772.5	24.0
2	2 (5 μl)	796.5	10.0
3	3 (8 μl)	806.5	

The differences between all the three groups were less than the WSD. Therefore it could be concluded that the difference in injected sample size did not give results significantly different from one another.

Similarly, using the same method, it was found that for methylene iodide and iodide, the differences between the three groups were less than the corresponding WSD's. Thus the same conclusion could be drawn for CH_2I_2 and I_2. In short, the sample size had no effect on the response factors for the range of 4 μl to 8 μl.

G-1.2 The t - test

The t expression to test the difference between two means is as follows:

$$t = \frac{|\bar{X}_1 - \bar{X}_2|}{\bar{S}(X)\sqrt{1/n_1 + 1/n_2}} \qquad \text{(G-5)}$$

where $\bar{X}_1$ and $\bar{X}_2$ = two separate means

n_1 and n_2 = number of samples

$\bar{S}(X)$ = pooled estimate of standard deviation

or $$\bar{S}^2(X) = \frac{\sum(X_i - \bar{X}_1)^2 - \sum(X_j - \bar{X}_2)^2}{n_1 + n_2 - 2}$$

Thus by applying this expression to the 4 μl and 8 μl sample sizes, the results are summarized in Table G-7. All the calculated t values were less than the tabulated t value at 0.05 level and two degrees of freedom. Thus

TABLE G-7

THE t-TEST FOR TWO MEANS

Component	CH_3I		CH_2I_2		I_2	
Sample size (μl)	4	8	4	8	4	8
Mean	.7725	.8065	1.3005	1.412	.669	.662
$\bar{s}^2(x)$	.00363		.00883		.00044	
t	1.13		2.38		0.667	
$t_{0.05,2}$			4.303			

the null hypothesis that the two means are equal or H_o; $\mu_1 = \mu_2$ was accepted. In other words, the mean obtained from the 4 μl samples could not be distinguished from the mean obtained from the 8 μl samples.

G-2 Response factors of components

The response of the detector was calibrated with a mixture of all the components. The concentration of each component was kept in a range that the actual concentration in the product stream would fall. The injected sample size was within the range of 4 to 8 μl, which had been proved (above) to have no effect on the

TABLE G-8

RESULTS OF RESPONSE FACTORS CALIBRATION

Sample No.	Component i	Approx Sample Size	Mole	Mole %	Average f_i
1	CH_3I	5	0.2114×10^{-3}	0.082	0.858
	CCl_4		0.2555	99.521	1.0
	I_2		0.7447×10^{-3}	0.290	0.628
	CH_2I_2		0.2744×10^{-3}	0.107	1.401
2	CH_3I	8	0.9229×10^{-4}	0.036	0.823
	CCl_4		0.2568	99.822	1.0
	I_2		2.864×10^{-4}	0.111	0.616
	CH_2I_2		0.7990×10^{-4}	0.031	1.825*
3	CH_3I	5	1.1413×10^{-3}	1.096	0.721
	CCl_4		0.1011	97.046	1.0
	I_2		0.7525×10^{-3}	0.722	0.713
	CH_2I_2		1.1835×10^{-3}	1.136	1.305
4	CH_3I	5	0.3896×10^{-3}	0.382	0.793
	CCl_4		1.006	98.742	1.0
	I_2		0.442×10^{-3}	0.434	0.699
	CH_2I_2		0.4500×10^{-3}	0.442	1.329
5	CH_3I	8	0.5636×10^{-4}	0.054	1.289*
	CCl_4		0.1045	99.795	1.0
	I_2		0.9456×10^{-4}	0.090	0.825*
	CH_2I_2		0.6422×10^{-4}	0.061	1.334

* The values were slightly higher because the concentration was so small that the peak area was very small. Therefore the peak area measurement would introduce some error.

responses. The mixture for gas chromatograph calibration was prepared as described in Section III-4.1. The results of the calibration are shown in Table G-8. Notice that at very low concentration, the peak area was so small that it bounded to have some error introduced in the measurement of the peak area.

Table G-9 shows the response factors of the three components related to that of CCl_4 which was assigned as 1.0

TABLE G-9

RESPONSE FACTORS OF COMPONENTS

Component	Response factor	Range+
CH_3I	0.797	0.723-0.858 (1.289)
CCl_4	1.0	
I_2	0.671	0.616-0.750 (0.825)
CH_2I_2	1.337	1.287-1.401 (1.825)

\+ Value in parentheses showed the extreme limits when those values with an asterisk in Table G-8 were included.

The values in Table G-9 were used for all the quantative analysis of the chromatograph of the product stream.

APPENDIX H

SAMPLE CALCULATIONS FOR QUANTITATIVE ANALYSIS OF PRODUCT

The original design of the experiment was a continuous flow process with liquid samples withdrawn solely from the gas-liquid separator. In this case the analysis of the conversion, selectivities and yields would be very simple with the response factors of each component given. For example, by rearranging Eq.(G-4) to Eq.(H-1), it can be seen that the conversion of iodine, selectivities of

$$M_i/M_s = (A_i/A_s)/f_i \tag{H-1}$$

methyl iodide and methylene iodine can be expressed as follows:

Conversion of I_2

$$X_3 = \frac{\frac{1}{2} M_1 + M_2}{\frac{1}{2}M_1 + M_2 + M_3(\text{remainding})} \tag{H-2}$$

where M_i = mole of component i.

Subscripts 1, 2 and 3 represent CH_3I, CH_2I_2 and I_2 respectively.

$$X_3 = \frac{\frac{1}{2} M_1/M_s + M_2/M_s}{\frac{1}{2}M_1/M_s + M_2/M_s + M_3/M_s} \tag{H-3}$$

Selectivity of CH_3I or CH_2I_2

$$S_1 = \frac{M_1}{\frac{1}{2} M_1 + M_2}$$

$$= \frac{M_1/M_s}{\frac{1}{2} M_1/M_s + M_2/M_s} \qquad (H-4)$$

$$S_2 = \frac{M_2/M_s}{\frac{1}{2} M_1/M_s + M_2/M_s} \qquad (H-5)$$

Yield of CH_3I or CH_2I_2

$$Y_1 = X_3 \times S_1 \qquad (H-6)$$

$$Y_2 = X_3 \times S_2 \qquad (H-7)$$

Unfortunately this simple method was not applicable for the semi-batch process because for example in the overflow semi-batch process, there were three samples taken from three places - separator, trap and reactor. Certainly the three samples, can be lumped together before a sample is taken for gas chromatograph analysis. However, this method has a disadvantage that it will not reveal which sampling place gives the most required product. Thus an alternative and longer method had to be used in the present work. This method involved the computation of the actual amount (in mole) of each product and unreacted iodine present in the sample. The method is illustrated as follows :

The mole ratio of component i to solvent is shown in Eq.(H-1). If all the mole ratios are summed up and each mole ratio is then divided by the summation, the quotient will be the mole fraction of that component in the sample.

$$\text{Mole fraction of i} = \frac{M_i}{\sum M_i} = \frac{M_i/M_s}{\sum(M_i/M_s)} \qquad \text{(H-8)}$$

Since the amount of sample in the present work was given as weight, the mole ratio (M_i/M_s) has to be converted to weight ratio by multiplying with a molecular weight ratio i.e.

$$\frac{W_i}{W_s} = \frac{M_i}{M_s} \times \frac{MW_i}{MW_s}$$

Similar to the computation of mole fraction it can be shown that :

$$\text{Wt. fraction of i} = \frac{(M_i)(MW_i)}{\sum\left[(M_i)(MW_i)\right]}$$

$$= \frac{(M_i)(MW_i)/(M_s)(MW_s)}{\sum\left[(M_i)(MW_i)/(M_s)(MW_s)\right]} \qquad \text{(H-9)}$$

Using this technique, the calculations, based on Run 33, are summarized in Table H-1.

TABLE H-1

QUANTITATIVE ANALYSIS OF PRODUCT STREAM

Item	Feed	Reactor			Separator		Trap
	I_2	I_2	CH_3I	CH_2I_2	I_2	CH_3I	CH_3I
A_i/A_s	0.00602	.00859	.000753	.000518	.001617	.000898	.001003
M_i/M_s	0.00897	.01279	.000945	.000387	.002409	.001127	.001258
W_i/W_s	0.01480	.02110	.000872	.000674	.003975	.001040	.001161
$\sum W_i/W_s$	1.01480		1.022646		1.005015		1.001161
W.F.	0.01458	.0206	.000853	.003955	.003955	.001035	.001160
Total W.	39.7465		25.6191		5.4380		1.5075
W.	0.5795	.5277	.0218	.0169	.0215	.0056	.0017

Note :

$f_{I_2} = 0.671$ $MW_{I_2}/MW_{CCl_4} = 1.650$

$f_{CH_3I} = 0.797$ $MN_{CH_3I}/MW_{CCl_4} = 0.923$

$f_{CH_2I_2} = 1.337$ $MW_{CH_2I_2}/MW_{CCl_4} = 1.741$

A_i/A_s	from peak area measurement
M_i/M_s	from Eq.(H-1)
W_i/W_s	$(M_i/M_s)(MW_i/MW_s)$
W. F.	from Eq.(H-9)
Total W	Weight of sample

From these values the conversion of iodine, yields of products, radiation yields and a iodine balance could be computed as follows :

(1) Conversion of I_2

Amount of unreacted I_2 = 0.5492 gm

or = 0.002164 gm-mole

Amount of I_2 in feed = 0.5795 gm

or = 0.002283 gm-mole

$$X_{I_2} = \frac{0.002283 - 0.002164}{0.002283} = 0.0521$$

(2) Yield

Amount of CH_3I produced = 0.0291 gm

or = 0.0002050 gm-mole

Amount of CH_2I_2 produced = 0.0169 gm

or = 0.000063 gm-mole

$$Y_{CH_3I} = \frac{0.0002050}{0.002283} = 0.0897$$

$$Y_{CH_2I_2} = \frac{0.000063}{0.002283} = 0.0276$$

(3) G values

$$G = \frac{6.023 \times 10^{23} \times 100 \, [i]}{D \times [I_2] \times 253{,}809}$$ (see section II-1.1)

$DR = 5.86 \times 10^{15}$ eV/gm/sec. (Appendix B)

$$D = 5.86 \times 10^{15} \times 2 \times 3.6 \times 10^{3} = 4.22 \times 10^{19} \text{eV/g}$$

Since this was a semi-batch process, the volume involved was the same for i and I_2 , assuming no lost of solution. Thus concentrations could be replaced by the gm-moles.

$$G_{CH_3I} = \frac{6.023 \times 10^{23} \times 100 \times 2.050 \times 10^{-4}}{4.22 \times 10^{19} \times 2.283 \times 10^{-3} \times 253.809}$$

$$= 5\,00.0$$

Similarly

$$G_{CH_2I_2} = \frac{6.023 \times 10^{25} \times 6.30 \times 10^{-5}}{4.22 \times 10^{19} \times 2.283 \times 10^{-3} \times 253.809}$$

$$= 154.0$$

(4) Iodine balance

Iodine used = 0.000119 mole

CH_3I formed = 0.0002050 mole

∴ Amount of I_2 in CH_3I = 0.0001025 mole

CH_2I_2 formed = 0.0000630 mole

∴ Amount of I_2 in CH_2I_2 = 0.0000630 mole

Total I_2 in iodomethanes = 0.0001655 mole

$$\% \text{ error} = \frac{0.0001655 - 0.000119}{0.000119} \times 100$$

$$= 38.1\ \%$$