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Radiolysis of Gaseous Hydrogen Halides

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RADIOLYSIS OF GASEOUS
HYDROGEN HALIDES

by

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ABSTRACT

Ion pair yields of 4.1 and 4.7 have been measured for the radiolysis of pure gaseous hydrogen chloride and hydrogen bromide respectively, using Co^{60} gammas. These yields, together with the W values for HCl (24.8 eV) and HBr (24.4 eV) obtained, lead to calculated G-values of 8.3 and 9.6 respectively, for the two gases.

The effect of the scavengers bromine and sulphur hexafluoride on the radiolysis of the two gases revealed that there are at least two hydrogen forming species present. One of these is a 'thermal' hydrogen atom which may or may not have the electron as its precursor, the other is a 'hot' hydrogen atom which cannot be scavenged. The results with chlorine as scavenger on the HCl radiolysis brought out the importance of back reactions taking place as the concentration of chlorine builds up during the irradiation of pure gaseous hydrogen chloride.

A study of the effect of an applied electric field during the radiolysis of the two gases showed that reactions involving the recombination of ions were unimportant as a means of producing hydrogen.

This study has shown that dissociative excitational processes are as important as ionization processes in the decomposition of these two hydrogen halides. The HBr molecules appear to undergo dissociative excitational processes more readily than the HCl molecules.

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SECTION I

INTRODUCTION

1.1 GENERAL

It will be worthwhile to review briefly the historical development of radiation chemistry as it reflects both the shifting interest and interpretations which have marked the steady growth of this subject. With the discovery of X-rays and radioactivity towards the end of the 19th century, chemists became aware of the chemical changes brought about by various types of radiations. At the turn of the century Sir William Ramsey(1), working in this field on the decomposition of simple gases in the presence of radon, wrote that, "Whenever radium emanation produces chemical action, then, other conditions being unaltered, each particle of emanation as it disintegrates produces the same amount of change." This statement made radiation chemists realize that there was some quantitative relation between energy absorption and chemical change.

At first most of the research in the field of radiation chemistry was carried out on gases as evidenced by the pioneer work of Lind(2) and Mund(3). Their study of gaseous reactions involved the use of radon (i.e.α-

particles) and it was therefore natural for them to relate the observed chemical changes to the amount of ionization produced in the system. Thus the term ion pair yield (M/N, i.e. the number of molecules destroyed or formed per ion pair produced) developed to illustrate the connection between the physical and the chemical actions of radiation. Since this ratio was only measurable in the case of gases, the term G-value, defined as the number of molecules changed per 100 electron volts of energy absorbed by the system, was introduced so that workers in the condensed phases could have a means of comparing yields. The G-value and ion pair yields are related by the equation

$$G = \frac{100}{W} \cdot \frac{M}{N}$$

where W is the mean energy required to form an ion pair in the irradiated gas. Values of W for gases were found to be approximately twice their ionization potential. This led Essex(4) to point out that part of the chemical action of high energy radiation may be due not only to ions but also to the reactions of electronicly excited species.

The classic paper of Eyring, Hirschfelder and Taylor(5), in which they discussed ortho-para hydrogen conversion and hydrogen-bromine combination, demonstrated firstly, the importance of molecular ions having the valency properties of free radicals and secondly, the importance of neutral free radicals and atoms as chain carriers. It further stated that it was unnecessary to put forward the existence of ion-molecule clusters to explain large ion pair yields. This led to the almost complete rejection of ionic processes in radiation chemistry until the recently proven occurrence of ion molecule reactions in the mass spectrometer(6).

Within the last two decades, due to the development of the nuclear reactor and various machines for producing high energy radiations, research in this field increased tremendously and has been centered mainly on aqueous solutions (thanks to Fricke for laying its foundation) and organic compounds.(7)

At present, studies in this field are carried out both for their intrinsic interest and their possible industrial use.

1.2 INTERACTION OF IONIZING RADIATION WITH MATTER

The chemical effects produced by high energy radiations in an attenuating medium result from the interactions of fast charged particles. These particles may constitute the incident radiation such as α- or β-rays, or be produced by the primary interaction of uncharged species such as γ-rays, X-rays or neutrons. It is imperative that the radiation chemist should have some knowledge of the physical processes involved in the above interactions. Only a brief description of the primary energy loss processes of electromagnetic radiation, and electrons will be considered.

1.2.1 Electromagnetic radiations

The effect of an absorbing medium on a beam of electromagnetic radiation is to reduce the number of photons passing through. This reduction in beam intensity (-dI) is given by the relationship

$$-dI = I_o \mu dx$$

where I_o is the intensity of the incident radiation, dI is the reduction in intensity of the beam after passing through a distance dx of the medium and μ is called the total linear absorption coefficient. This coefficient is the sum of a number of partial coefficients representing various processes of absorption. These processes are the photoelectric effect, Compton effect, pair production, coherent scattering and photonuclear reactions. Coherent scattering only occurs at low photon energies (<0.1 MeV) and in high atomic number (Z) materials and even so is negligible in comparison with the photoelectric effect at these low energies. Photonuclear reactions take place with photon energies above 10 MeV and therefore will be of no consequence in this study.

(a) Photoelectric effect

In this type of interaction, which occurs mainly with low energy photons, the entire energy of the photon (E_γ) is transferred to a single atomic electron. This electron is ejected from the atom with an energy (E_e) equal to the difference between the photon energy and the binding energy (E_s) of the electron in the atom.

$$E_e = E_\gamma - E_s$$

At low photon energies, the electrons are ejected mainly at right angles to the direction of the incoming photon, but as the energy of the photon increases the distribution shifts increasingly towards the forward direction. To conserve energy and momentum, the remainder of the atom is recoiled. This means that photoelectric interaction is not possible with free electrons. At sufficiently high energies, K-shell interactions account for 80% of these events, the rest being L-shell interactions. The vacancy created in the K-shell, or L-shell, is filled by an electron from an outer shell with the emission of characteristic X-radiation or Auger electrons. For low Z materials the binding energy of the inner electron shells is relatively small and therefore the secondary X-rays and Auger electrons will have low energies and will be absorbed in the immediate vicinity of the original interaction. The atomic absorption for this effect, varies approximately as $\lambda^3 Z^4$ and is therefore important only at low photon energies and materials with high Z.

(b) Compton effect

If the X- or γ-ray energy is sufficiently large, rather than interacting with the atom as a whole, the X- or γ-ray may interact with any of the orbital electrons as though they were essentially free electrons. Only a fraction of the photon energy will be transferred to the electron and a modified photon of longer wave length emerges from the collision in a direction differing by an angle θ from the original photon. These Compton electrons, produced from a radiation of given quantum energy, have a very broad spectrum of energies which can be calculated from the Klein and Nishina(8) formula. This spectrum is a continuous one, extending over a range given by

$$E = h\nu \left(\frac{\delta\lambda}{\lambda + \delta\lambda} \right)$$

where $h\nu$ and λ refer to the incident photon and $\delta\lambda$ is the change in wave length after collision. On applying the law of conservation of energy and momentum, it can be shown that

$$\delta\lambda = \frac{h}{m_o c} \left(1-\cos\theta \right)$$

where h and $m_o c$ have their usual significance. For a medium containing exclusively light elements, Compton absorption predominates for photon energies between 0.2 and 2 MeV and the total energy absorbed per gram of the medium is nearly proportional to its electron density.

(c) Pair production

For electromagnetic radiations of energies greater than $2m_o c^2$ (1.02 MeV), a fraction of the energy is absorbed in the production of an electron-positron pair. The available kinetic energy ($h\nu - 2m_o c^2$) is shared unequally by the two particles formed. Both of these particles are slowed down by interactions with the medium. Eventually the positron and an electron will combine, annihilating themselves, and producing two photons of 0.51 MeV energy each, in opposite directions. The atomic absorption coefficient for this process is approximately proportional to Z^2 and increases with increasing photon energy.

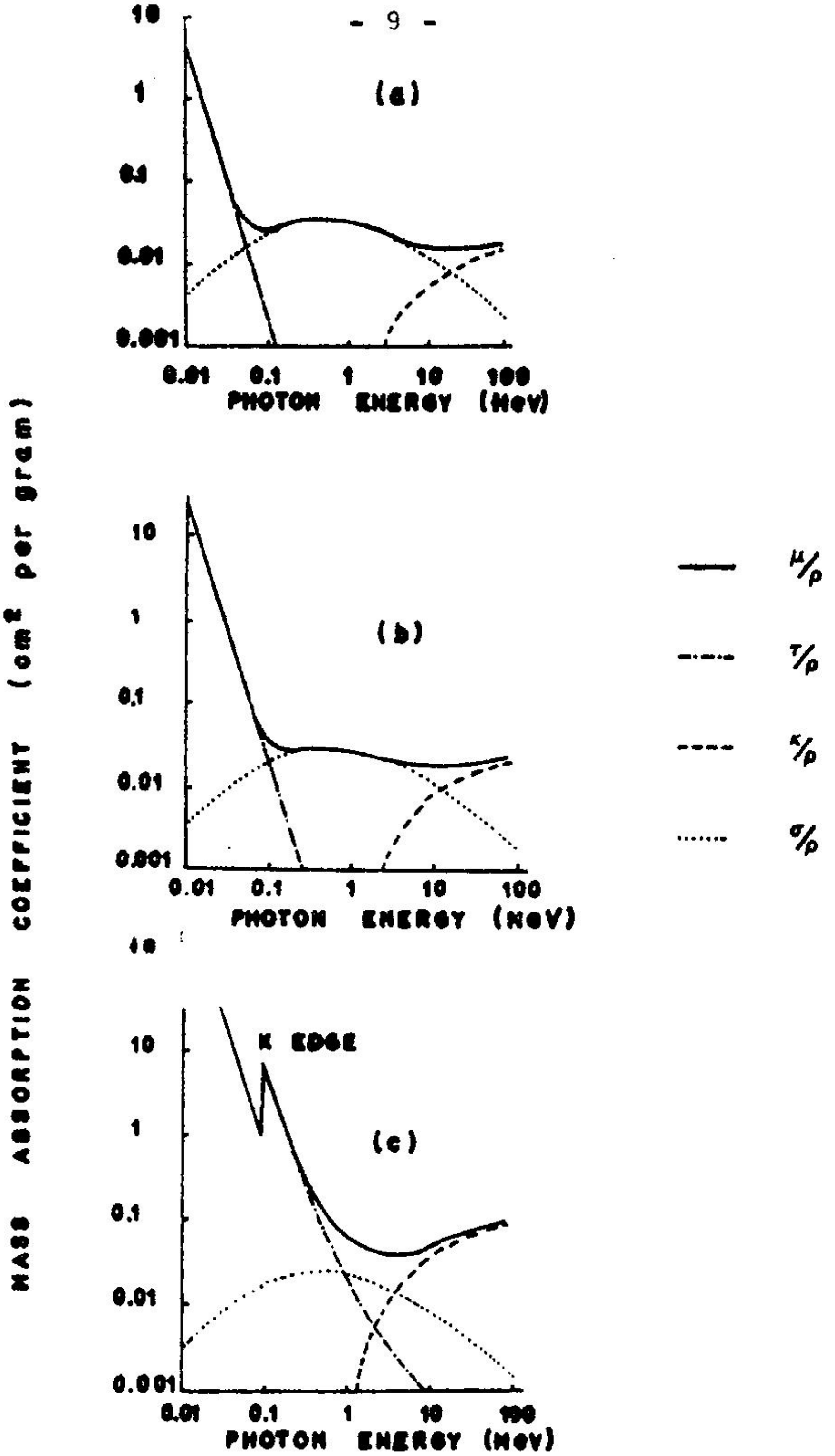
The relative importance of these three processes is shown in fig. 1 for the media water, aluminum and lead(9). It can be seen that for Co^{60} gammas of mean energy 1.25 MeV, Compton scattering is the predominant process.

1.2.2 Fast electrons

In the three processes described above, it is seen that electromagnetic radiation on interaction with matter produces high energy electrons. These fast electrons dissipate their energy by the following processes-emission of radiation (Bremsstrahlung), inelastic and elastic scattering, and polarization(10). The relative importance of these processes depends on the electron energy and to a lesser extent on the composition of the medium.

The rate at which electrons lose energy in a particular medium is referred to as the stopping power or linear energy transfer (LET) and is denoted by $-\frac{dE}{dx}$. For non-relativistic velocities the simple equation

FIG. 1



MASS ABSORPTION COEFFICIENTS FOR (a) WATER (b) ALUMINUM (c) LEAD AS FUNCTIONS OF THE QUANTUM ENERGY OF THE INCIDENT RADIATION

FIG. 1

$$-\frac{dE}{dx} = \frac{2\pi e^4 N}{m_o V^2} \cdot Z \ln \frac{m_o V^2}{4I}$$

can be developed where e, m_o and Z have their usual significance, N is the number of atoms per cubic centimetre, V is the electron velocity and I the mean excitation potential of the medium. Bethe(10) has modified the above equation for the case of electrons at relativistic velocities to the following

$$-\frac{dE}{dx} = \frac{2\pi e^4 N}{m_o V^2} \cdot Z\left[\Phi - 2 \ln I\right]$$

where Φ is a complex function of β (V/c) and the electron energy.

According to Bragg's law of additivity of stopping powers,(11) the stopping power of an element is independent of its state of chemical combination. Thus the stopping power of a hydrogen halide is equivalent to the sum of the stopping power of an equimolar mixture of hydrogen and halogen.

The Bethe equation above does not take into account contributions to LET from the emission of Bremsstrahlung or polarization effects.

For an electron of energy E MeV, the ratio of the energy loss by radiation to the loss by collision is given by

$$\frac{(dE/dx)_{rad}}{(dE/dx)_{col}} \simeq \frac{EZ}{1600\, m_o c^2}$$

Therefore, for electron energies below 1 MeV and low atomic number materials (<16), the contribution of Bremsstrahlung is less than 2%.

1.2.3 Secondary electrons

Charged particles, on travelling through a medium, leave ions and excited molecules along their tracks. Many of the electrons ejected by the incident fast particle will possess enough energy to cause additional ionizations and excitations. Since these electrons (referred to as secondary electrons) will have relatively low velocities, their rate of energy loss will be extremely high(12). For secondary electrons of energies less than 100 eV, the formation of a few ion pairs will be sufficient to reduce the electron to sub-excitation energies (5 eV). The mean energy involved in the formation of an ion pair is about 30 ± 10 eV. This means that a secondary electron of 100 eV energy on being moderated will produce clusters of about 3 to 4 ion pairs along with several excited molecules. For low LET primary particles, the clusters will appear as widely separated beads along the particle track, whereas for densely ionizing radiation (e.g. α-particle), these clusters will be produced so close together that they will form a columnar envelope of ion-pairs.

When the kinetic energy of the secondary electrons is in excess of 100 eV, they can produce their own tracks which diverge from the direction of the primary track. These secondary electrons are referred to as delta-rays.

1.3 FUNDAMENTAL PROCESSES IN RADIATION CHEMISTRY

Ionizing radiation, on passing through matter, transfers its energy to the molecules of the absorbing medium by the various physical mechanisms described briefly in section 1.2. The chemical aspects of the various processes immediately following the primary radiation act (i.e. dissipation of energy) must now be considered. This stage, often referred to as the physico-chemical stage, can be classified into (1) primary processes and (2) secondary processes.

1.3.1 Primary processes

(a) Ionization

When a fast electron or any charged particle passes close to a molecule of the absorbing medium, a coulombic field is set up. This field will strongly polarize the molecular electrons in their orbitals. If the energy released in this interaction is larger than the binding energy of an electron in its parent molecule, then the electron can be expelled leaving a positive ion;

$$XY \rightsquigarrow XY^+ + e \qquad (1)$$

($\rightsquigarrow$ designates a primary radiation chemical process). The observed induced conductivity of gases provides evidence for the presence of such ionizations.

The positive ion XY^+ produced above may or may not carry an excess of energy; moreover if XY is a large polyatomic molecule, then the XY^+ would be unstable and dissociate;

$$XY^+ \longrightarrow X^+ + Y \qquad (2)$$

This type of fragmentation process has been observed in the mass spectrometer(13). It occurs with a high probability e.g. the hexane ion dissociates (below)

$$n\ C_5H_{12}{}^+ \longrightarrow C_3H_7{}^+ + C_2H_5$$

$$\text{or} \qquad \longrightarrow C_3H_6{}^+ + C_2H_6$$

to give smaller ions and radicals, or even radical ions and neutral molecules. Alternatively, the interaction of a fast electron with a molecule may lead to a dissociative ionization process in which reactions (1) and (2) occur simultaneously

$$XY \longrightarrow X^+ + Y + e + \text{Energy} \qquad (3)$$

The minimum amount of energy for process (1) is known as the ionization potential of the molecule and this can be accurately measured by electron impact methods(14). Since the energy required to form an ion pair is usually about twice the ionization potential(15), this excess energy may be used up in forming excited species.

(b) Excitation

If the energy transferred to a molecular electron is less than the ionization potential, it may still be large enough to displace the electron from its ground state to an "excited state."

$$AB \longrightarrow AB^* \qquad (4)$$

[* designates excited species]

The excited state here is similar to that produced by the absorption of a quantum of light

$$AB + h\nu \longrightarrow AB^*$$

and therefore much information on the behaviour of AB^* can be obtained from photochemical studies.

1.3.2 Secondary processes

(a) Reactions of ions

Positive ions and their daughter ions are continuously produced in a system under irradiation. Along with these, there is an equivalent number of negative charges (i.e. free electrons or negative ions) and therefore two possible neutralization processes must be considered

(i) ion-electron recombination and

(ii) positive ion-negative ion recombination.

Besides these, the ions may interact chemically with neutral molecules or else undergo charge transfer with impurities.

(i) Positive ion-electron recombination

If an electron, ejected from a primary ionization, becomes "thermalized" in the vicinity of a positive ion, recombination occurs owing to the strong coulombic interaction and an excited molecule is produced;

$$XY^{+} + e \longrightarrow XY^{*}$$

The excited molecule here has gained energy equal to the ionization potential of the molecule XY (10 to 15 eV). Consequently the molecule will undergo dissociation and will lead to a permanent change. Samuel and Magee(16) have calculated that an electron of kinetic energy below 5 eV becomes thermalized and recombines with its parent ion in less than 10^{-13} sec. in the case of water (absorbing medium). Conflicting with the above view is the Lea(17), Gray(18) and Platzman(19) theory which says that the electron will escape from the coulombic field and will attach itself to a neutral water molecule becoming an aquated electron. In the case of gases, either an ion or electron may become separated and react individually with the neutral molecule XY.

(ii) Positive ion-negative ion recombination

If ions of opposite charge are to recombine, their total internal energy must decrease as a result of the reaction. The energy release may be achieved through an increase in the kinetic energy of the neutralized particles by transfer of energy to a third body, by emission of electromagnetic radiation, or by electronic excitation of the neutralized species. Hence recombination may proceed by any one of the following mechanisms(20)

$$X^+ + Y^- + Z \longrightarrow XY + Z \qquad (1)$$

$$X^+ + Y^- \longrightarrow XY + h\nu \qquad (2)$$

$$X^+ + Y^- \longrightarrow X^* + Y^* \qquad (3)$$

The three body recombination (1) is the most important mechanism at pressures greater than a few mm. Hg. Radiative recombination (2) and mutual neutralization through charge exchange (3) will predominate at very low pressures(21), since only two bodies are involved.

If one or both of the ions are molecular, then there is the possibility of dissociative mutual neutralization thus

$$XY^+ + Z^- \longrightarrow X + Y + Z \qquad (4)$$

(iii) Ion-molecule reactions

Mass spectroscopic studies have provided evidence beyond doubt for the occurrence of ion-molecule reactions. The theory of this type of reaction has been well developed by Schissler and Stevenson(22) so much so that for the ($D_2^+ + D_2$) reaction, k_{cal} is 8.7×10^{11} l. per mole per sec. compared with k_{exp} (8.6×10^{11} l. per mole per sec.). There is also excellent agreement for the ($Ar^+ + H_2$) reaction. The theory further predicts that rates of all ion-molecule reactions are so large that there is a high probability of reaction upon every encounter. These reactions are temperature independent and are mostly exothermic.

Ion-molecule reactions are of two kinds

(A) Hydrogen transfer reactions

$$RH^+ + M \longrightarrow MH^+ + R$$

where R is a free radical and M a stable molecule and

(B) Condensation reactions

$$A^+ + CD \longrightarrow AC^+ + D$$

where AC is a condensation product and D a stable molecule.

These reactions are becoming more and more important in the interpretation of many radiation chemical processes.

(iv) Charge transfer process

If an impurity or a substance in very small amount is present during the irradiation then the following process may occur

$$A^+ + B \longrightarrow B^+ + A$$

where A is the main component of the mixture. For this reaction to occur at ordinary temperatures the lowest ionization potential of A must be higher than that of B. This type of reaction was invoked to explain the increased ionic yield when acetylene was irradiated in the presence of Argon.

$$Ar^+ \text{ (I=15.7 eV)} + C_2H_2 \longrightarrow Ar + C_2H_2^+ \text{ (I=11.3 eV)}$$

(b) Electron capture by neutral species

All the electrons ejected in the primary ionization of a molecule of the absorbing medium lose their kinetic energy either by further ionizing or by exciting other molecules. These electrons then lose their freedom by two processes (1) combination with a positive ion (already discussed) and (2) electron capture by a neutral species.

There are at least five mechanisms by which electrons may react

(i) Radiative capture by a neutral atom

$$e + A \longrightarrow A^- + h\nu$$

(ii) Capture by an atom with a third body taking up the excess energy

$$e + A + B \longrightarrow A^- + B + \text{K.E.}$$

(iii) Capture by a molecule with the vibrational excitation of the molecule ion, and its subsequent stabilization in a collision with another molecule.

$$e + XY \longrightarrow (XY^-)^*$$

$$(XY^-)^* + A \longrightarrow XY^- + A + \text{K.E.} + \text{P.E.}$$

(iv) Dissociative attachment

$$e + XY \longrightarrow (XY^-)^* \longrightarrow X + Y^-$$

(v) Ion pair production: the non captive dissociation of a molecule into positive and negative ions by electron impact

$$e + XY \longrightarrow e + X^+ + Y^-$$

A simple calculation can show that mechanism (i) cannot compete with (ii), (iii) and (iv) at ordinary temperatures and pressures. For electrons of energies above 20 eV, mechanism (v) will become important and at low pressures (ii) and (iii) become unimportant compared with (iv). A more complete discussion of these processes is given by Massey(23).

Figs. (2) and (3) taken from the work of Frost and McDowell(24) display the possibility of dissociative attachment occurring with chlorine and bromine. The main difference in the two halogens is that the threshold energy for electron capture by chlorine is about 1.6 eV whereas bromine has a zero energy threshold. This means that bromine will be a much more efficient scavenger for thermal electrons than chlorine.

(c) Reactions of excited species

Excited species formed by the primary radiation process may undergo the following reactions

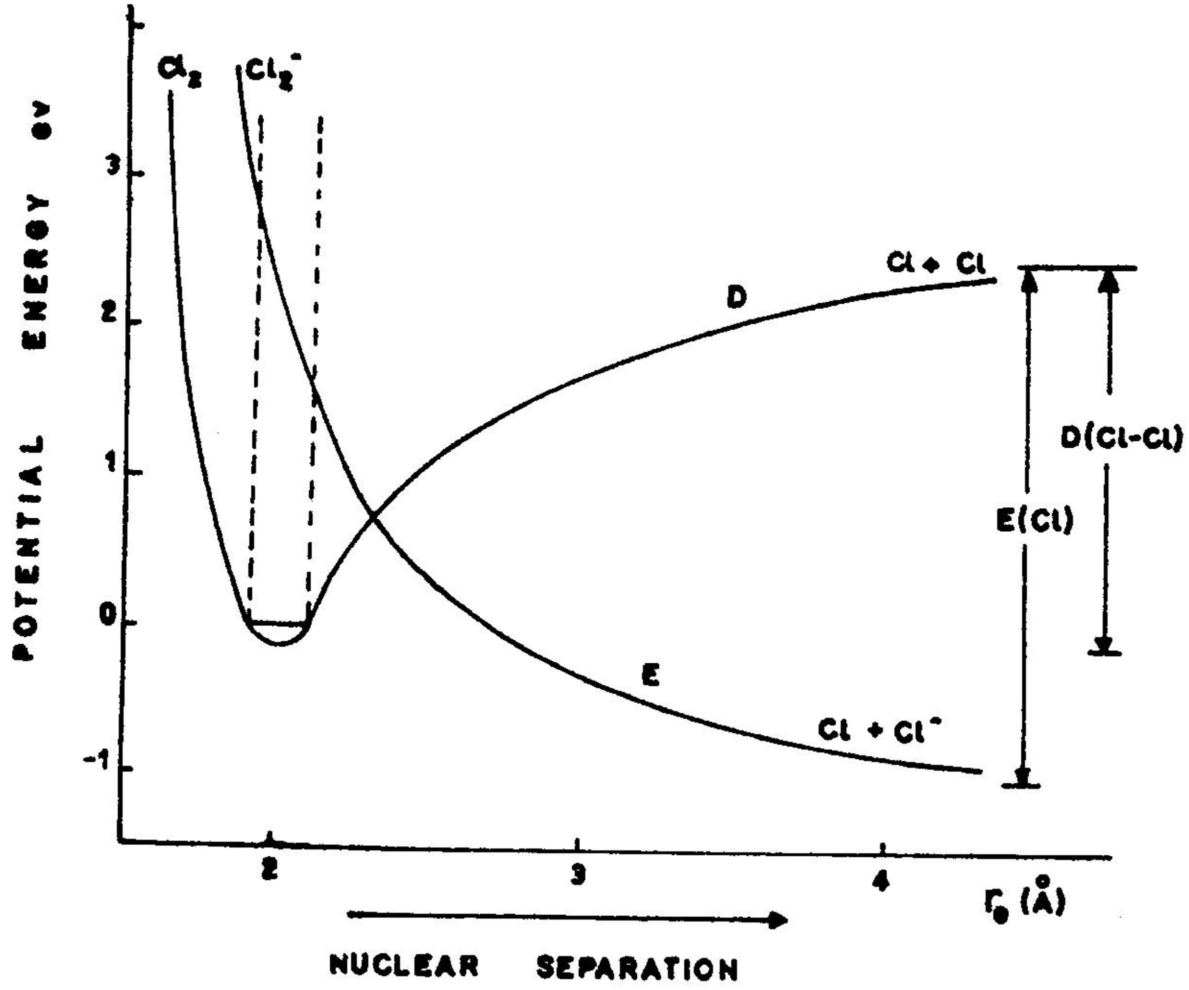

POTENTIAL ENERGY eV
3
2
1
0
-1
Cl2
Cl2-
D
Cl + Cl
E
Cl + Cl-
E(Cl)
D(Cl-Cl)
2
3
4
re (Å)
NUCLEAR SEPARATION

FIG. 2

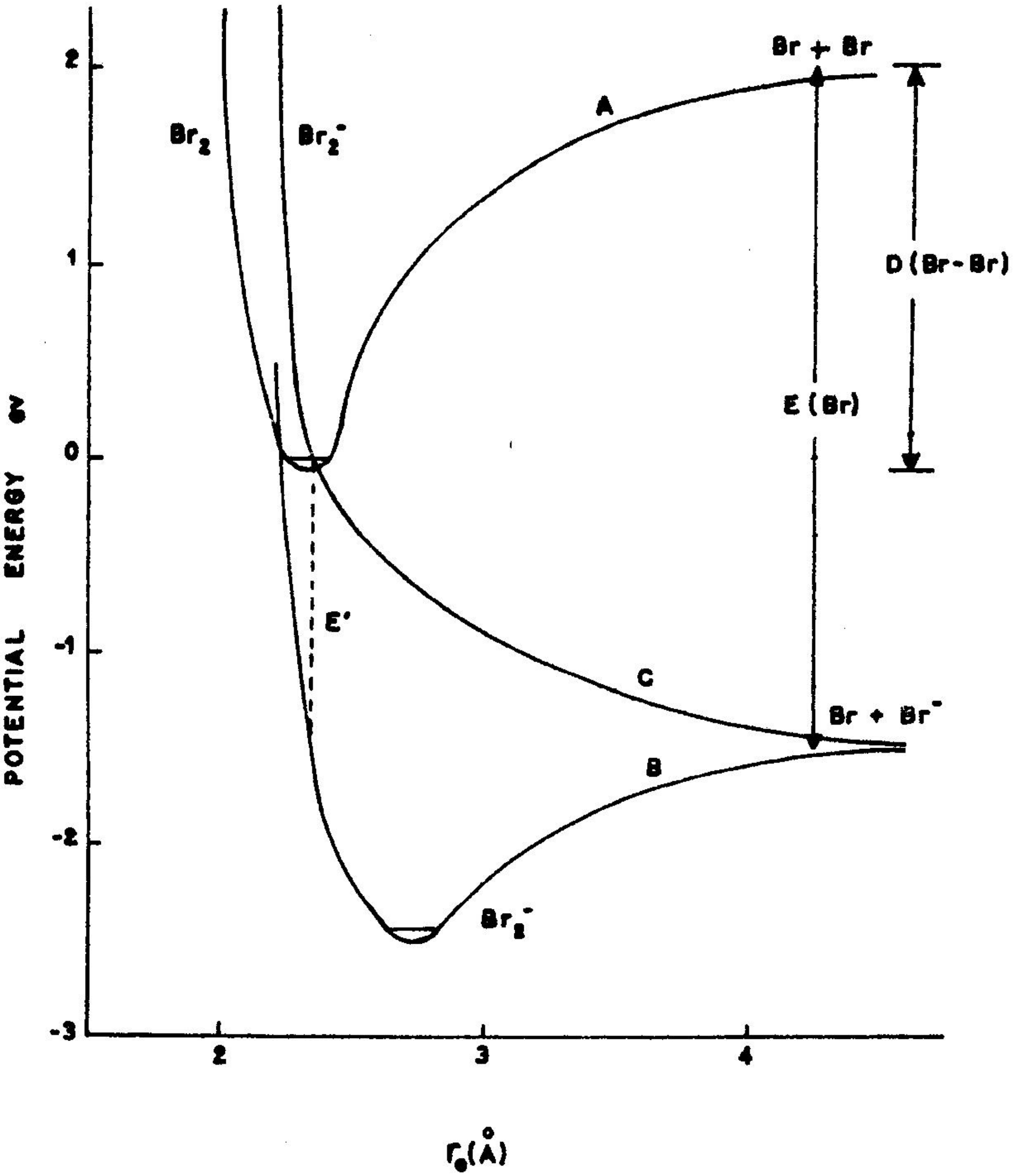

POTENTIAL ENERGY eV
2
1
0
-1
-2
-3
2
3
4
r_e(Å)
Br_2
Br_2^-
A
Br + Br
D (Br-Br)
E (Br)
E'
C
Br + Br^-
B
Br_2^-

FIG. 3

(i) Dissociation into free radicals

$$XY^{*} \longrightarrow X + Y$$

The free radicals X and Y formed from the dissociation of highly excited molecules may carry an excess of kinetic energy and are referred to as "hot" radicals. These radicals are highly reactive.

(ii) Dissociation into "molecular products"

$$XY^{*} \longrightarrow A + B$$

where A and B are saturated or unsaturated molecules. This is possible for excited states formed from positive ion electron recombination.

(iii) Reaction with other molecules

$$XY^{*} + CD \longrightarrow \text{products}$$

Little is known about this type of reaction except for a suggestion by Burton et al(25) to explain condensation reactions involving hydrocarbons.

(iv) Transfer of excitation

The reaction may be written

$$X^{*} + Y \longrightarrow Y^{*} + X$$

Here molecule Y must possess at least one excited state below the energy level of X^*. In certain gas phase radiolyses where the increased ionic yield could not be explained by a charge transfer process, excitation transfer has been suggested. Burton(26) pointed out that if the electron is attracted back to its parent ion in less than 10^{-13} sec., then primary ions will have an extremely short lifetime and hence the observed energy transfer process should be mainly due to transfer of excitation rather than charge.

1.4 DOSIMETRY

The radiation chemist requires to know the effectiveness of a particular chemical action of ionizing radiation. This is usually measured by (a) the ion pair yield (M/N) in the case of gases and (b) the 100 eV yield (G) for condensed phases. Both of these terms have already been defined, where it was pointed out that they are related by the equation

$$G = \frac{100}{W} \cdot \frac{M}{N}$$

It is not very difficult to obtain ion pair yields in gaseous systems; however for a determination of G, an accurate value for W is required.

By an application of the Bragg-Gray cavity ionization chamber theory$^{(27)}$ the quantity of ionization observed in a small cavity can be related to the energy absorbed by the cavity walls during exposure to ionizing radiation. It is expressed simply by the equation

$$E_m = S^m g\ E_g = S^m g\ W_g\ J_g$$

where E_m and E_g are energies absorbed per unit mass in the wall and gas respectively, $S^m g$ is the ratio of the mass stopping powers of the wall to that of the gas and

J_g is the number of ions produced per unit mass of gas in the cavity.

Since the energy absorbed by the wall is independent of the characteristics of the gas, then by filling the chamber with various gases successively, the equation

$$W_1 \; J_1 \; S^m{}_1 = W_2 \; J_2 \; S^m{}_2$$

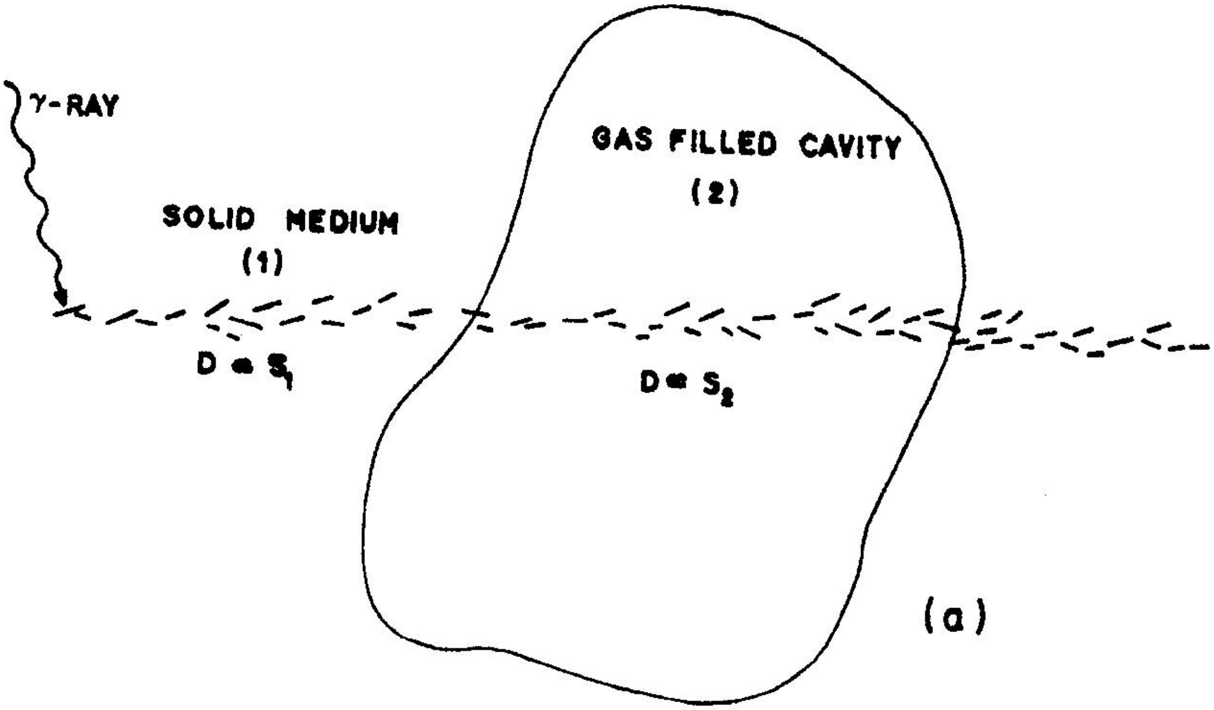
can be obtained, where the subscripts (1) and (2) apply to two different gases.

It follows that

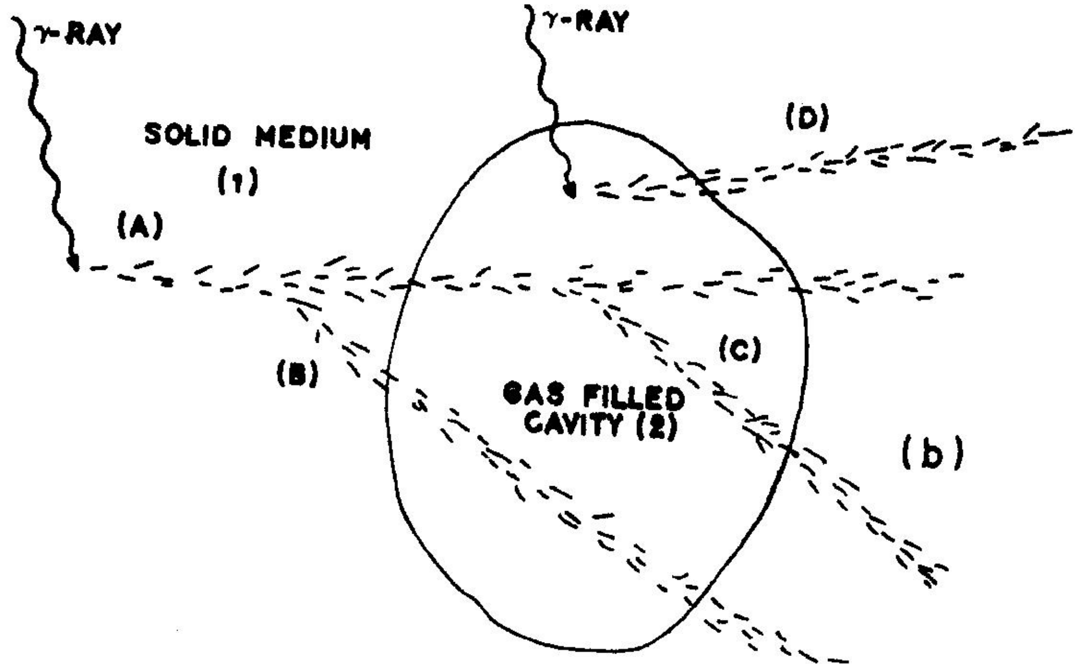
$$W_1 = W_2 \left(J_2 / J_1\right) S^1{}_2$$

Therefore if a standard gas of known W is used, then W for an unknown can be calculated from measurements of the saturation ion currents and the stopping power ratio ($S^1{}_2$), calculated from the Bethe equation(10).

The Bragg-Gray theory of cavity ionization is depicted in fig. 4 (a) where it can be seen that the radiation chemical reaction is carried out only by electrons emanating from the walls due to Compton interaction of the γ-rays. A more general picture appears in fig. 4 (b). Spencer and Attix(28) were able to modify



BRAGG-GRAY THEORY OF CAVITY IONIZATION



GENERAL CASE OF CAVITY-IONIZATION PROBLEM

FIG. 4

the Bragg-Gray picture to take into account the processes (B) and (C). In their calculation "Fast" secondaries of the type (B) are added to the primary electron spectrum and their effect subtracted from the stopping power of the medium, whereas the "Fast" secondaries of the type (C) are not added to the electron spectrum but their effect is subtracted from the stopping power of the gas.

The ratio of the energy dissipated per unit mass in a small gas filled cavity to that in the surrounding wall (due to Spencer and Attix modifications) is given by the equation(29)

$$f_g\ (T_o, \Delta\ ) = \frac{(Z/A)_m}{(Z/A)_g} \left[1 + C_g\ (T_o, \Delta\ ) \ln \frac{I_g}{I_m} + d_g\ (T_o) \right]$$

Here subscripts m and g refer to wall and gas respectively, Z and A to atomic numbers and weights, and I to the mean excitation potential. The term $d_g\ (T_o)$ is a polarization correction to energy losses in the wall and depends only on wall material and the initial electron energy T_o. $C_g(T_o,\Delta)$ is a function of the average wall separation and the pressure of the cavity gas. The pressure dependence results from its dependence on Δ , which is the energy of an electron of range in the cavity gas equal to the average wall separation. This expression predicts departure from the constancy of the ratio of saturation ionization currents to pressure at low pressures, and for materials with Z_{wall} differing from Z_{gas}. For $Z_{wall} < Z_{gas}$ the departure decreases and for $Z_{wall} > Z_{gas}$ it increases.

1.5 A SUMMARY OF THE PRESENT STATE OF THE RADIOLYSIS OF HYDROGEN HALIDES

The three hydrogen halides, hydrogen chloride, hydrogen bromide and hydrogen iodide have all been irradiated in the gas phase by various workers. The ionic yields obtained increase in order of increasing atomic number of the halogen ($-M_{HCl}/N \simeq 3.3$; $-M_{HBr}/N \simeq 5$; $-M_{HI}/N \simeq 6$). Hydrogen iodide has been irradiated both with α-particles and with X-rays independently by different workers(30) and in each case the ion pair yield was approximately 6 within experimental error. Following is the proposed mechanism

$$HI \longrightarrow HI^+ + e \qquad (1)$$

$$e + HI \longrightarrow H + I^- \qquad (2)$$

$$HI^+ + I^- \longrightarrow H + 2I \qquad (3)$$

$$H + HI \longrightarrow H_2 + I \qquad (4)$$

$$I + I + M \longrightarrow I_2 + M \qquad (5)$$

This mechanism gives an ion pair yield of 4. However, if instead of reaction (3) the ion molecule reaction

$$HI + HI^{+} \longrightarrow H_2I^{+} + I \tag{6}$$

is chosen, followed by

$$H_2I^{+} + I^{-} \longrightarrow 2H + 2I \tag{7}$$

an ion pair yield of 6 is obtained.

In the X-radiolysis of gaseous hydrogen bromide, ion pair yields varying from 4.6 to 5.2(31) were obtained. Hamill et al. put forward a similar mechanism to reactions (1) to (5) above and suggested that the yield above 4 may be due to contributions from the excitational processes which may be depicted as follows

$$HBr \longrightarrow HBr^{*} \tag{8}$$

$$e + HBr^{+} \longrightarrow HBr^{*} \tag{9}$$

$$HBr^{*} \longrightarrow H + Br \tag{10}$$

The only work published on gaseous hydrogen chloride before this investigation was undertaken, is that of Vandamme(32). An ion pair yield of about 3.3 was obtained for α-radiolysis. No attempt was made in this paper to put forward a mechanism.

In the case of radiolysis of hydrogen halides in the condensed phases, Armstrong and his group(33) have studied the effects of scavengers on product yields. They have proposed the following possibilities in accordance with the Samuel-Magee model(16)

(a) $$HCl \rightsquigarrow HCl^{+} + e$$

$$HCl^{+} + e \longrightarrow HCl^{*} \longrightarrow H(hot) + Cl$$

(b) $$HCl \rightsquigarrow HCl^{+} + e$$

$$HCl + HCl^{+} \longrightarrow H_2Cl^{+} + Cl$$

$$\begin{aligned} H_2Cl^{+} + e &\longrightarrow H(hot) + HCl \\ &\longrightarrow H(hot) + H + Cl \end{aligned}$$

Both of these mechanisms are likely to produce "hot" hydrogen atoms.

The effects of the scavenging of chlorine and bromine on both hydrogen chloride and hydrogen bromide suggest the following electron capture process

$$e + H\text{-}X.......H\text{-}X \longrightarrow H + X\text{-}H.........X^{-}$$

along with

$$H_2X^{+} + X\text{-}H......X^{-} \longrightarrow 3HX$$

These papers show clearly the presence of two hydrogen forming species. Table I summarizes the kinetics of the radiolysis of hydrogen chloride in the presence of chlorine and bromine on the assumption that the following competitions occur

$$H + HCl \longrightarrow H_2 + Cl$$

$$H + X_2 \longrightarrow HX + X$$

$$H(hot) + HCl \longrightarrow H_2 + Cl$$

$$H(hot) + X_2 \longrightarrow HX + X$$

The G values for liquid hydrogen chloride and hydrogen bromide were found to be 6.5 and 12.4, respectively.

TABLE I

Results (Ref. 33) of liquid phase radiolysis of hydrogen chloride

	Chlorine		Bromine	
	G	k_{HCl}/k_{Cl_2}	G	k_{HCl}/k_{Br_2}
First species	2.3	1.7×10^{-3}	2.4	7.9×10^{-4}
Second species	4.2	0.10	4.1	-

1.6 AIM AND SCOPE OF THE PRESENT INVESTIGATION

In the previous section it can be seen that the mechanism for the radiolytic decomposition of hydrogen halides in the condensed phase differs considerably from that proposed for the gas phase radiolysis.

From his study, Armstrong has obtained evidence for the presence of two hydrogen forming species. In the condensed phase radiolysis he has placed emphasis on the occurrence of excited species as a precursor to "hot" hydrogen atoms.

In view of the above differences it was considered desirable to reinvestigate the gas phase radiolysis. Also the irradiations in the previous gas phase studies had been carried out to high percentages of decomposition where the accumulated products would interfere with the initial yields and hence G values quoted in previous publications may have been too low.

Since the appearance of the first communication on this investigation(34), it has been pointed out by Dr. Henry J. Gomberg, Director of the Puerto Rico Nuclear Center, that due to the high G values obtained with hydrogen halides, these gases would be ideal for use in a regenerative type fuel cell. The hydrogen halide would be decomposed by ionizing radiation and the products hydrogen and halogen recombined in a closed system type fuel cell. The efficiency of the fuel cell could be over 90%(35). The theoretical E.M.F. produced with a hydrogen-chlorine type fuel cell is 1.36 volts. Assuming a G(H_2) value for hydrogen chloride to be 8.3, an energy conversion of 11.3% is obtained. This appears more attractive than the present SNAP systems. These Systems for Nuclear Auxiliary Power are of two types-reactor systems and radioisotope systems. In the radioisotope systems energy conversion is carried out mainly by a thermoelectric process. The overall RTG (radioisotope thermoelectric generator) efficiency is only about 5%.(36) A thorough investigation of the mechanism of the decomposition of these hydrogen halides would prove to be of immense value towards the adoption of this idea.

SECTION II

EXPERIMENTAL

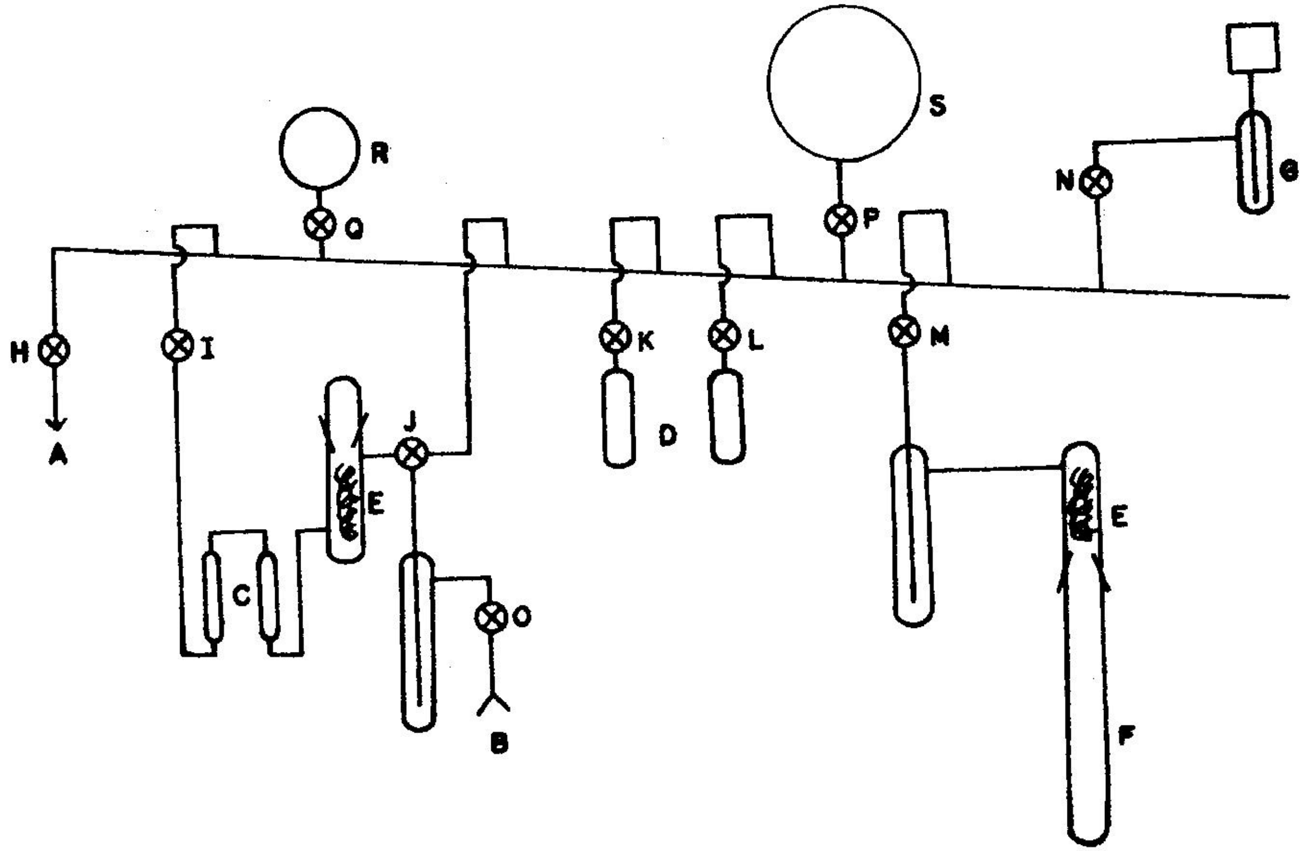
2.1. APPARATUS

The main pieces of equipment used in this investigation consisted of two high vacuum systems, a variety of irradiation cells, several radiation sources, a diaphragm gauge, and instruments both for applying an electrical potential and for measuring very small electrical currents. The following is a description of these and other relevant pieces of apparatus.

2.1.1 Vacuum system for purification of sample

A mercury-free vacuum line (figs. 5&6) was constructed for purifying and storing gaseous samples. A high vacuum of about 10^{-6}mm.Hg. was maintained by a Duo-Seal forepump and a water-cooled oil diffusion pump. The low pressures were monitored by an ionization gauge. The oil diffusion pump was arranged in such a way that hydrogen from the irradiated samples could be transferred from this vacuum system to a conventional hydrogen analysis line. In this way irradiated samples could be re-irradiated without coming into contact with mercury vapour from the analysis line. This was to prevent hydrogen halides or scavengers from forming undesirable products by reacting

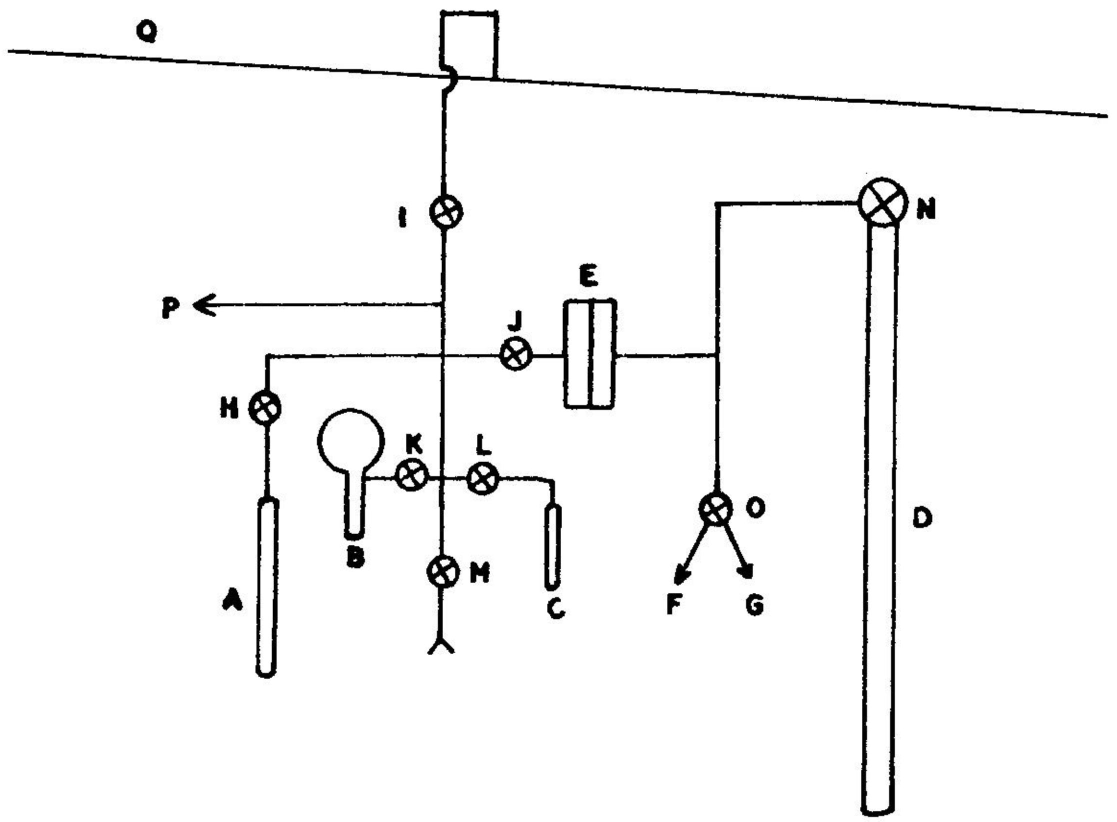
FIG. 5



VACUUM LINE FOR SAMPLE PURIFICATION

FIG. 5

FIG. 6



MEASURING SYSTEM

FIG. 6

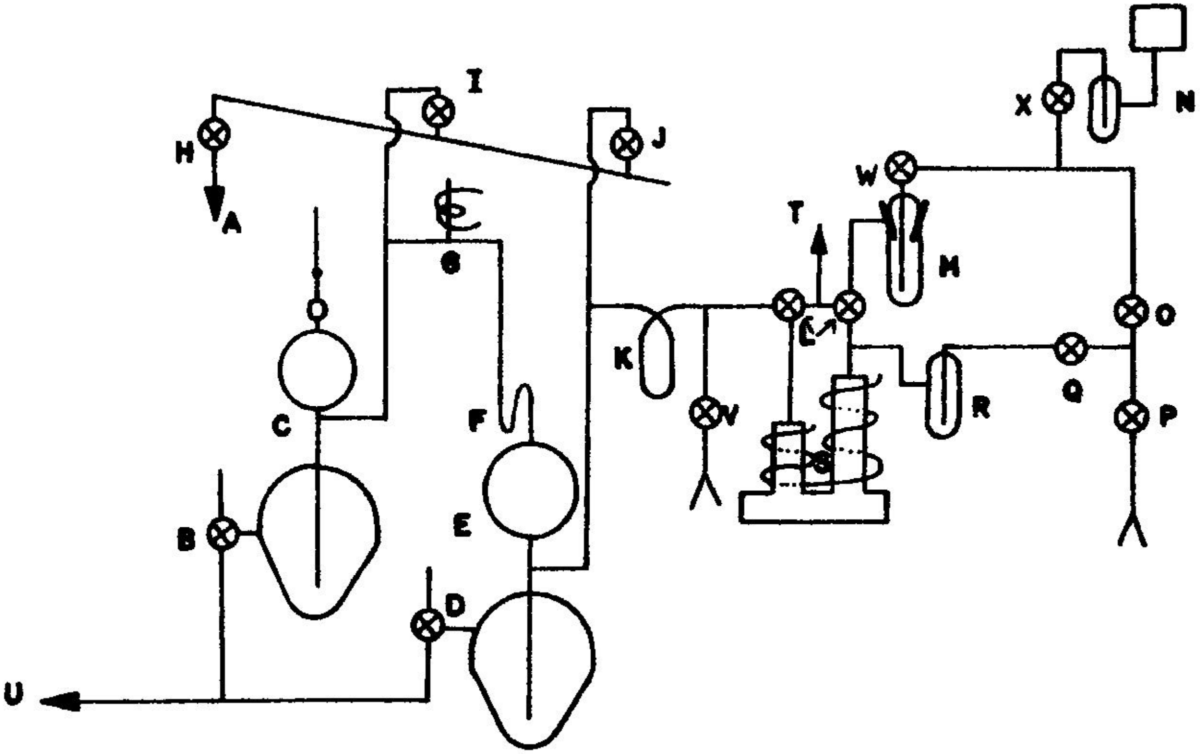
with mercury.

The hydrogen halides were introduced into the line directly from Matheson tanks via stopcock O (fig. 5) and condensed after purification (to be described later) in the sample storage F. The bulbs B and C (fig. 6) were calibrated and used for measuring out quantities of scavengers. The pressures of the hydrogen halides and scavengers were measured using a metal diaphragm gauge E (fig. 6) connected to a mercury manometer. The diaphragm separated the measured gases from coming into contact with mercury vapour.

2.1.2 Analysis line

The analysis line is shown in fig. 7. It consists of a calibrated McLeod gauge, a Toepler pump, and a palladium thimble which could be heated. The irradiated sample was put either into the mercury free line and the hydrogen to be analyzed pumped via the diffusion pump into the analysis line, or else was just placed at the sample inlet V and the hydrogen toeplered into the McLeod gauge while liquid nitrogen was placed around the U trap K to condense any mercury vapour. The volume of the McLeod gauge and associated dead space were measured accurately. Pressures of hydrogen as low

FIG. 7



HYDROGEN ANALYSIS SYSTEM

FIG. 7

as 2×10^{-4} mm.Hg. could be measured.

2.1.3 Metal diaphragm gauge

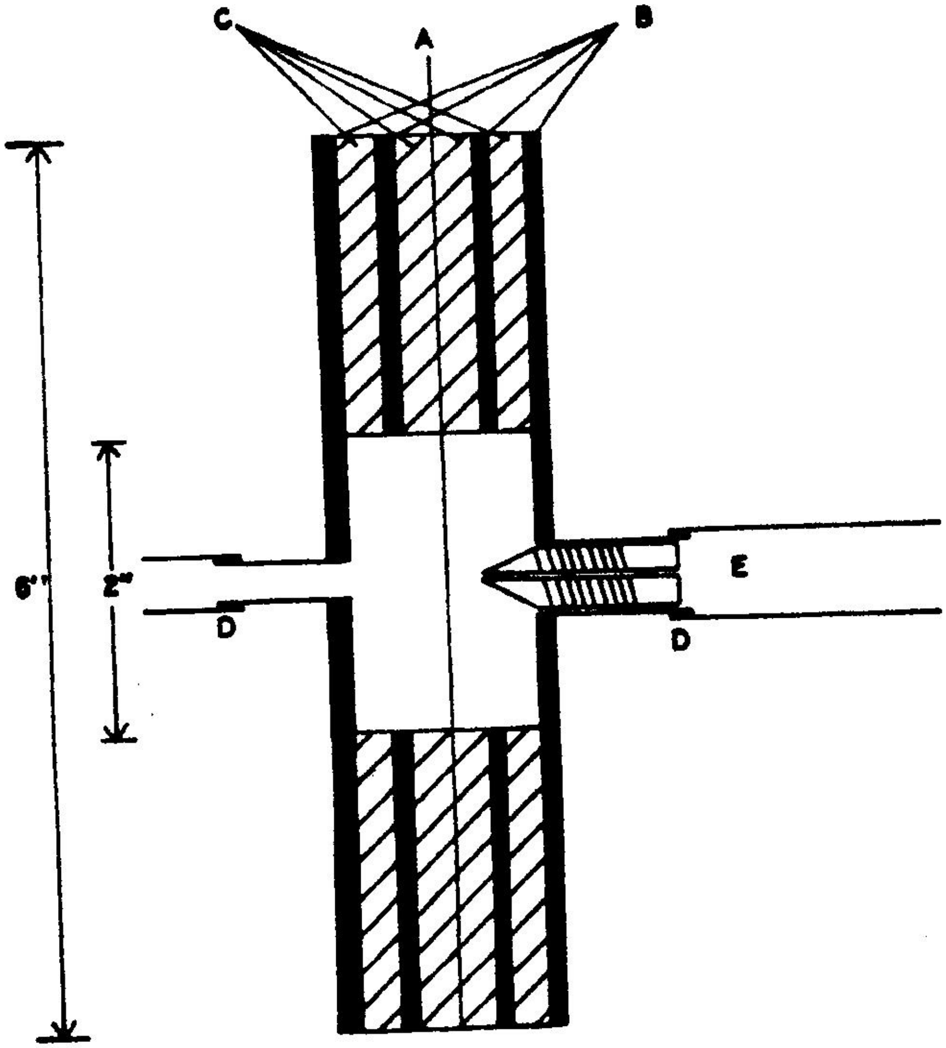
This gauge (fig. 8) had a diaphragm made from a 6" circular piece of 316 stainless steel of 0.002" thickness. The diaphragm was held between teflon and stainless steel (316) annulars alternately as shown in the figure. To each of the outside steel plates were soldered Kovar glass seals. Inside one of these Kovar seals was a screw with a minute hole through the center. This screw could be adjusted to increase the sensitivity of the gauge. The whole system was held together by six evenly spaced bolts (not shown in the diagram). The diaphragm A and the screw were connected to a milliammeter and a 6 volt dry cell. By means of equilibrating the pressure on both sides of the diaphragm with the aid of the milliammeter, pressures could be measured to an accuracy of 0.05 cm.Hg.

2.1.4 Radiation sources

(a) A 200 curie Co^{60} gamma source

This source was contained in a lead castle mounted into the side of a concrete cave. The leaden cave door was fixed on a movable trolley which could slide in such a way as to position samples on the trolley

FIG. 8



METAL DIAPHRAGM GAUGE

FIG. 8

opposite the source when the source was out of its lead castle. The source could be activated by lowering the isotope. Safety precautions were such that the door could neither be opened if the source had been lowered nor could the source be lowered if the door was open. Samples to be irradiated had to be placed in special containers and bolted on to the trolley. This was done to ensure reproducibility of dose rates.

(b) Gamma-cell

Samples were prepared and sent to Atomic Energy of Canada Limited, Chalk River, to be irradiated at high dose rates using their 12,000 curie Co^{60} gamma cell.

(c) X-ray machine

Samples were subjected to 87kV X-rays supplied by a conventional therapeutic machine at the Holy Cross Hospital, Calgary.

(d) A 1200 curie Co^{60} gamma source

This was the source used at the Puerto Rico Nuclear Center. The Co^{60} was contained in twelve pencil type capsules, each containing approximately 100 curies. These capsules were inserted into twelve hollow aluminum cylinders. The cylinders were positioned to form a Hollow Cylinder Variable Geometry Irradiator. The irradiator was remotely controlled and could be adjusted to form a hollow cylinder from 5 to 19 1/2 inches in diameter. The shielding was provided by water in the form of a pool 9' x 8' and 14 1/2' deep. The capsules were about 10' under water. Samples to be irradiated were placed in special containers and lowered into the pool.

2.1.5 Electronic equipment

Ionization currents were measured with a Keithley 410 C micro-microammeter which covered current ranges from 10^{-4} to 10^{-13} amp. The applied potential was supplied by a Hamner N413 high voltage supply capable of producing 5000 volts. Both of these instruments were connected to the irradiation cell via coaxial cables.

2.1.6 Ionization chambers and irradiation cells

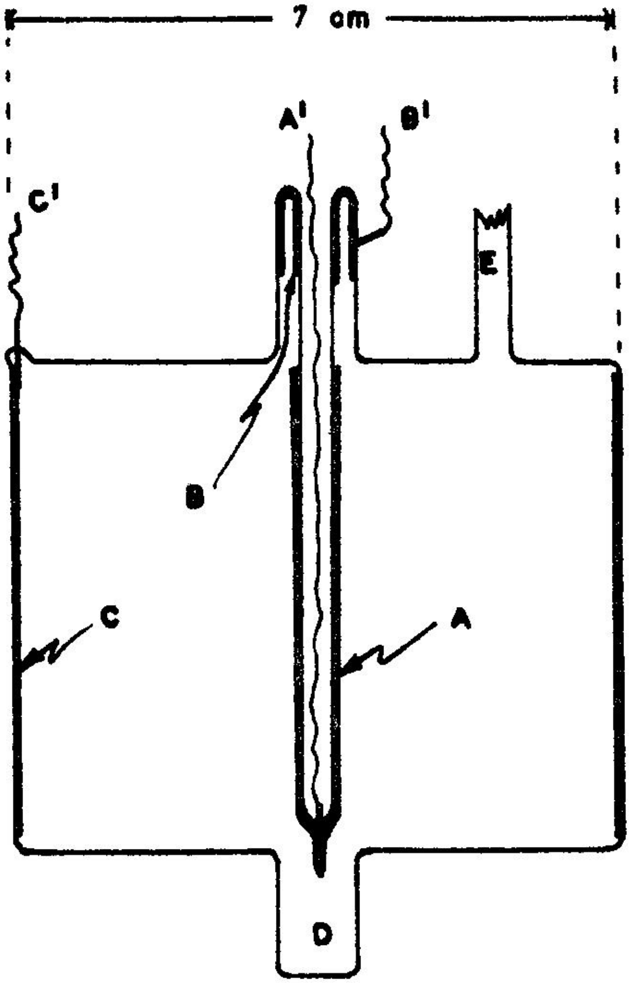
Two types of ionization chambers were used

(a) a concentric cylindrical chamber

(b) a parallel plate chamber

(a) The concentric cylindrical ionization chamber (similar in design to Back's(37)), used for measuring ionization currents, is shown in fig. 9. The 2.5 mm thick cylindrical wall C was coated internally with colloidal graphite to form the collecting electrode. The central high voltage electrode A, which consisted of a 7 mm outer diameter

FIG. 9



CYLINDRICAL IONIZATION CHAMBER

FIG. 9

pyrex tube, and a guard ring B, were coated in a similar manner. After the coatings had been applied through the tube D, this end was sealed to form a thimble trap for condensing the hydrogen halide using a liquid nitrogen bath. Tungsten wires passing through the glass walls provided contact between the graphite coatings and shielded electrical leads A', B', and C'. Gases were admitted to the irradiation cell via a stopcock attached to a 30 cm extension of tube E. This stopcock was shielded during irradiations.

(b) The parallel plate cell shown in fig. 10 was made by flattening the ends of a cylindrical tube. The distance between plates varied from 2 to 3 cm from cell to cell. These flat faces were coated with colloidal graphite through the end I which served the same purpose as the end D in the previous description. Platinum leads were soldered to tungsten, and the joint encased in glass for the metal glass seals. Within the cell a platinum rod came into contact with the graphite face. On the outside the tungsten leads were connected via coaxial cables to the electronic equipment.

The irradiation cells not used for the measurement of ion current are shown in fig. 11. These were

FIG. 10

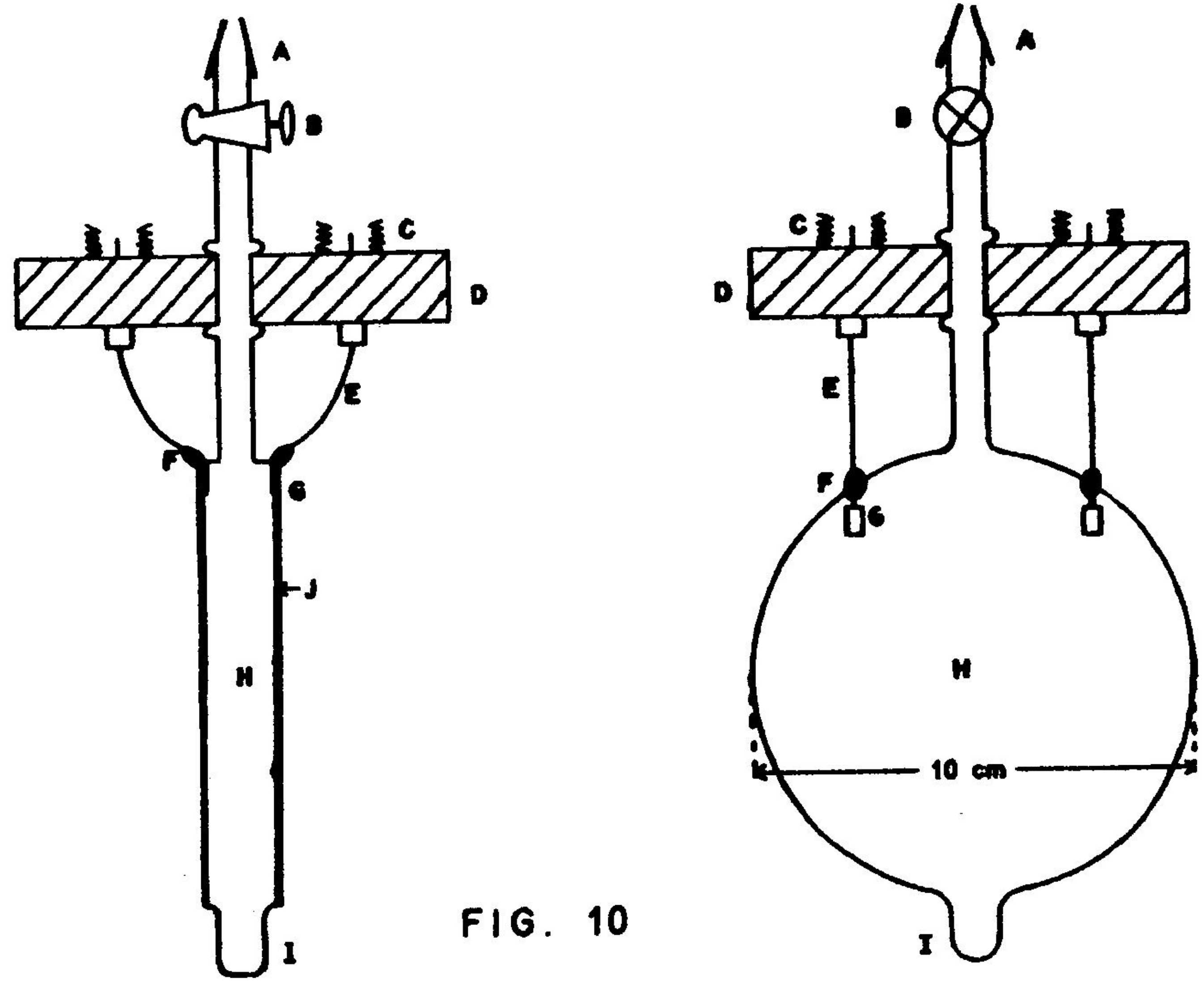
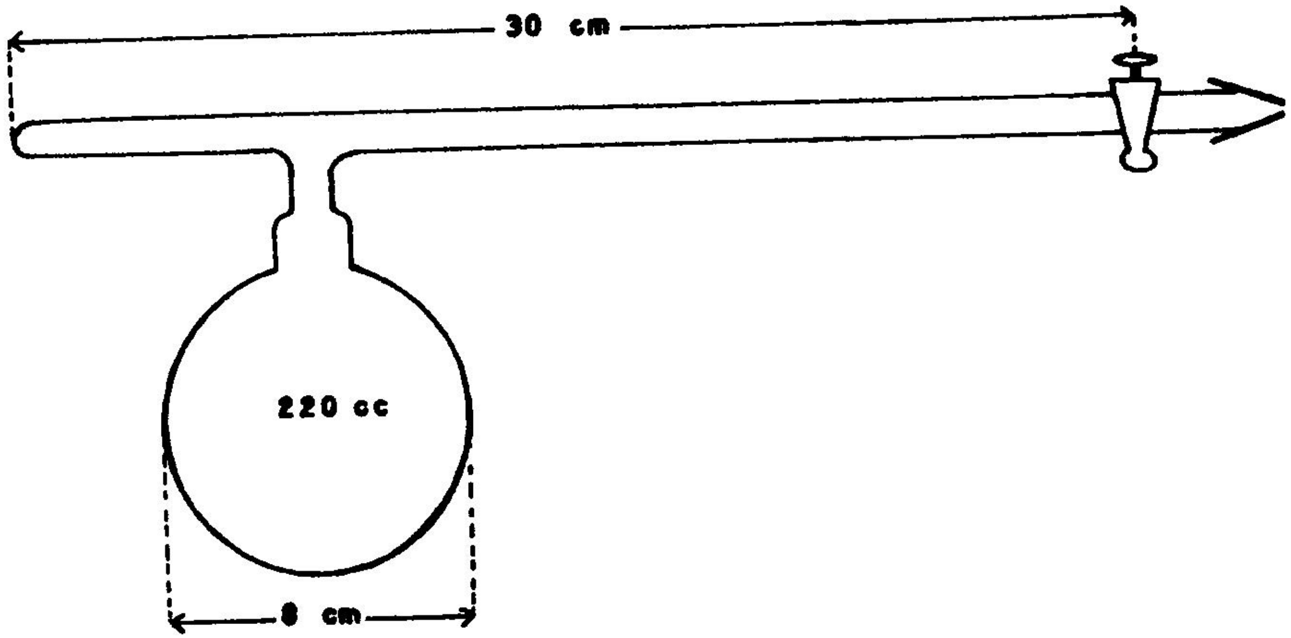


FIG. 10

PARALLEL PLATE IONIZATION CHAMBER



IRRADIATION CELL FIG. 11

made from pyrex round bottom flasks and had a side arm with a stopcock and a thimble for admitting gases and freezing hydrogen halides respectively. The cell volume varied around 230 cc and one large cell had a volume of 3690 cc. This type of cell was used both with the 200 curie Co^{60} gamma source and the X-ray machine.

For the Chalk River irradiations at high dose rates the cells were similar in shape to the cylindrical ionization chamber. They were uncoated and carried no electrode attachments. In these the stopcocks were replaced by break seals.

2.2 MATERIALS AND PURITY

2.2.1 Hydrogen chloride

Hydrogen chloride gas of 99.0% minimum purity obtained from Matheson & Co. was degassed several times after being introduced into the vacuum line through stopcock O (fig. 5) directly from the Matheson gas cylinders. It was then purified from hydrogen bromide by pre-irradiation in the solid phase for a day in the presence of about 1% chlorine. This procedure oxidized the hydrogen bromide to bromine which, together with excess chlorine, was removed by trap to trap distillation through copper mesh. The hydrogen chloride was finally distilled from an alcohol/liquid nitrogen bath to a liquid nitrogen bath, retaining only the middle fraction. It was then stored in the solid state whenever possible. Silicone grease was used in all stopcocks which were to be in contact with the hydrogen halides for long periods.

2.2.2 Hydrogen bromide

Hydrogen bromide gas of 99.8% minimum purity, also obtained from Matheson and Co. was pre-irradiated overnight and thereafter treated in exactly the same manner as hydrogen chloride.

2.2.3 Chlorine

Chlorine (99.5% minimum purity) obtained from a Matheson lecture bottle was degassed several times. It was then purified further by bulb to bulb distillations from a trap at -80°C to a liquid nitrogen trap. After each distillation the non-condensable gases were pumped away from the nitrogen cooled solid. The chlorine was then stored as a solid at liquid nitrogen temperature in storage A (fig. 6).

2.2.4 Bromine

Bromine (reagent grade) was obtained from the Baker and Adamson Co. It was further purified by distilling through phosphorus pentoxide and collected at dry ice temperature. After degassing several times it was stored in a storage trap similar to trap A (fig. 6) and cooled by a dry ice/alcohol mixture.

2.2.5 Sulphur hexafluoride

Sulphur hexafluoride obtained as a compressed gas from Matheson and Co. was subjected to several bulb to bulb distillations from -80°C to liquid nitrogen temperature. The sample was degassed after each distillation and finally stored in a one litre flask R (fig. 5) as a gas.

2.2.6 Ethylene

Research grade ethylene (Phillips Petroleum Co.) was further purified by distilling over phosphorus pentoxide and by bulb to bulb distillation. It was then stored as a gas in a large 4 litre flask S (fig. 5).

2.2.7 Argon

Research grade argon (obtained from Matheson and Co.) was used without further purification.

2.3. IRRADIATION TECHNIQUES

2.3.1 Cell treatment and sample preparation

The pyrex irradiation cells were left overnight in a glass blower's oven at 600°C before use. The cells were then attached to the mercury free vacuum line and evacuated for over an hour to a pressure of about 10^{-6} mm.Hg. During the evacuation the cells were flamed to release any moisture that may have been absorbed by the glass.

The appropriate hydrogen halide was distilled from the copper mesh storage reservoir into a tube adjacent to the cell. It was then allowed to vaporize slowly, filling the cell and dead space. The pressures were monitored by the diaphragm gauge. When the desired pressure had been reached the cell and dead space were isolated from the rest of the system. The differential pressure across the diaphragm gauge was now reduced to zero and the pressure read from the mercury manometer.

When a scavenger had to be introduced, it was measured in a small calibrated bulb at the pressure calculated to give the mole percent required. The scavenger was then condensed into the irradiation cell.

The procedure for filling an ionization chamber was similar to the above. In this case the chamber was heated overnight in an oven at 110°C instead of at 600°C.

2.3.2 Irradiation procedure

After the cells were filled, they were removed from the vacuum line and allowed to come to equilibrium at room temperature (23±2°C). They were then placed in cell holders and carefully positioned on the trolley of the concrete cave or attached to the X-ray machine.

When using the gamma pool source, the parallel plate type ionization chamber was always employed. This was placed in a stainless steel cylindrical can 5 inches in diameter. A rubber gasket was clamped on to the can by the cover with 6 evenly spaced bolts. The cover had a concentric hole through which passed the coaxial cables for electrical measurements. These cables were enclosed in a 1" internal diameter tygon tubing 15' long. This tubing was in turn clamped on to a tube in the cover of the steel can. The whole can was lowered into the pool between the 12 Co^{60} rods and these were immediately adjusted to grasp the steel can tightly. The open end of the tygon tubing was always kept out of the pool, enabling the system to be water tight.

2.4 MEASUREMENTS OF IONIZATION CURRENTS

The Hamner high voltage power supply and the Keithley micro-microammeter were connected to the cell before irradiation. As soon as the steel can was in position the voltage was applied and ionization currents read. In the cases where a clear saturation curve was not obtained the saturation ionization currents were calculated from a plot of 1/i versus i/v^2 in accordance with Greening and Scott(38).

2.5 MEASUREMENT OF HYDROGEN YIELDS

After the sample had been irradiated, it was attached to the mercury free line via a 10/30 joint, or else glass blown on in the cases of the 3690 cc cell and those that were irradiated at Chalk River. The whole system, including the hydrogen analysis line, was pumped down to a pressure of 10^{-6}mm.Hg. When this pressure had been maintained for some time, the thimble of the cell was frozen with liquid nitrogen. With the system isolated in such a way that any gas from the cell would go directly to the diffusion pump, the stopcock to the cell was opened (or the break seal broken for the Chalk River experiments by means of a steel bar and magnet).

After pumping for about 3 minutes, all the non-condensable gas (mainly hydrogen) would have been transferred from the cell to the analysis line. The gas was then toeplered a few times into the McLeod gauge. By opening tap B (fig. 7) to the atmosphere, the mercury was forced into the capillary section of the McLeod. The differences in the heights of the mercury columns in the McLeod were measured with a cathetometer and the pressure calculated. The gas was now allowed to expand by pulling the mercury down in the gauge and the palladium thimble was heated for a few minutes by means of nichrome wire or an infrared lamp. The measuring process was repeated until there was no further decrease in pressure. This decrease was due to the loss of hydrogen through the heated palladium thimble. The number of molecules of hydrogen was then calculated from the measured pressure and temperature of the gas and the volume of the McLeod assuming ideal behaviour for the gas.

SECTION III

RESULTS

The principal method of studying the radiation induced reactions has been by a determination of hydrogen yields as described earlier. All the results presented in this section are due solely to the interaction of radiation with the specified systems. Irradiation of an evacuated sample cell with and without a silicone greased stopcock did not produce any detectable hydrogen. Also, no hydrogen could be detected in unirradiated cells which had stood for several hours at room temperature.

3.1 DOSIMETRY

It has already been pointed out that the simplest and most direct method of dosimetry for gaseous systems is by the measurement of saturation ionization currents. These can then be converted to absorbed energy provided the value of W, the energy required to form an ion pair in the gas, is known. W values for hydrogen halides are unavailable; however there are reliable measurements of W for the inert gases. It follows from the equation

$$W_1 = W_2 \left(J_2/J_1 \right) S^1{}_2$$

(S^{1}_{2} - ratio of stopping powers; J_2/J_1 - ratio of saturation ionization currents) developed in section 1.4, that by comparing a hydrogen halide gas with the inert gas adjacent to the particular halogen in the periodic table, the W values for the hydrogen halides can be determined.

A definite advantage of choosing the inert gases for comparison lies in the fact that they would be isoelectronic with the corresponding hydrogen halide. This would mean that their electron stopping power will not differ appreciably and their Compton scattering cross-section will be the same.

The ratio of stopping powers for hydrogen chloride to argon, and hydrogen bromide to krypton have been calculated using the Bethe equation and the Bragg's law of additivity. Table 2 shows these ratios as a function of electron energy.

Ionization current measurements were made with both the parallel plate and the concentric plate chambers. Tables 3 and 4 display typical measurements of ionization currents with applied electrical field at various pressures. Table 4 is depicted graphically in fig. 12. In the cases where saturation has not been reached, a Greening type plot of $1/i$ against i/V^2 has been made and

TABLE 2

Calculated stopping power ratios from the Bethe equation(39)

E(MeV)	β^2	Φ	S^{HCl}_{Ar}	S^{HBr}_{Kr}
0.02	0.0739	19.64	1.033	1.021
0.05	0.1704	21.83	1.028	1.017
0.10	0.3006	23.15	1.023	1.015
0.20	0.4836	24.48	1.021	1.013
0.30	0.6031	25.30	1.021	1.012
0.40	0.6854	25.90	1.019	1.012
0.50	0.7446	26.41	1.019	1.011
0.60	0.7885	26.83	1.018	1.011
0.70	0.8219	27.20	1.018	1.011
0.80	0.8481	27.53	1.016	1.010
0.90	0.8688	27.83	1.015	1.010
1.00	0.8857	28.09	1.016	1.008
1.10	0.8995	28.34	1.017	1.010
1.20	0.9109	28.59	1.016	1.010

Mean excitation potential used

I_{Ar} = 174 eV(40)

I_{Air} = 85 eV(41)

I_{Br} = 359 eV(41)

I_{Cl} = 169 eV(40)

I_H in HX = 17.9 eV(41)

I_{Kr} = 360 eV(41)

TABLE 3

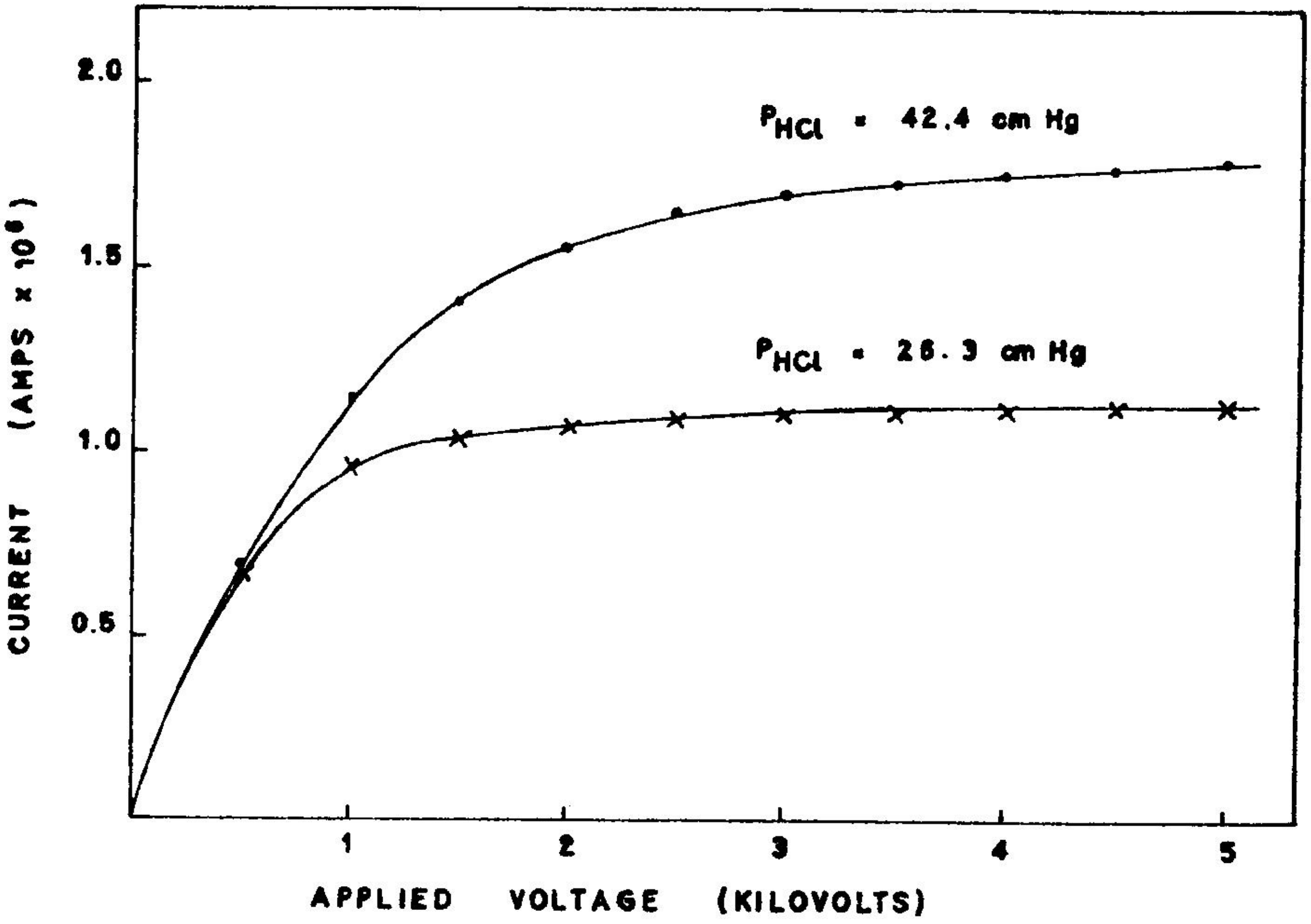
Typical ionization current measurements for hydrogen chloride (p=26.8 cm Hg) in parallel plate chamber

V (Volts)	I Amps x 10^6		Polarity Reversed
	Start	End	
300	0.42	-	-
500	0.58	0.57	0.58
800	0.75	-	-
1000	0.80	0.79	0.78
1300	0.84	-	-
1500	0.87	0.86	0.85
1800	0.88	-	-
2000	0.89	0.88	0.88
2300	0.90	-	-
2500	0.90	0.89	0.88
3000	0.90	0.90	0.89
3500	0.91	0.90	0.90
4000	0.91	0.90	0.90
4500	0.92	0.90	0.90
5000	0.92	0.91	0.91

TABLE 4

Typical current-voltage measurements

Applied Voltage (kilovolts)	Current (Amps x 10^6) P_{HCl} (cm Hg)	
	42.4	26.3
0.5	0.70	0.68
1.0	1.15	0.97
1.5	1.41	1.04
2.0	1.55	1.08
2.5	1.65	1.10
3.0	1.70	1.11
3.2	1.72	1.12
3.5	1.74	1.12
3.8	1.76	-
4.0	1.77	1.13
4.2	1.78	-
4.5	1.79	1.13
4.8	1.79	-
5.0	1.79	1.13



TYPICAL CURRENT - VOLTAGE PLOTS

FIG. 12

the saturation ionization current obtained by extrapolation to $i/V^2 = 0$. This type of analysis is only reliable for current measurements that are in excess of 0.7 of the true saturation current.

Table 5 displays typical results used in a Greening type plot. A plot of the current versus voltage for this table is shown in fig. 13. Fig. 14 is a typical Greening plot.

The results for figs. 15 and 16 were obtained using the concentric plate chamber. It should be noted that here the dose rate is much lower than the previous set of results obtained with the parallel plate chamber.

As a test to the equation

$$W_1 = W_2 \left(J_2/J_1\right) S^1{}_2$$

the W values for air (33.7 eV)(42) and argon (26.2 eV)(42) were inserted along with a calculated value of 1.13 for S^{Ar}_{Air}. This value corresponded to a weighted mean electron energy of 0.15 MeV(43). J_2/J_1 was calculated to be 1.46, in excellent agreement with the experimental value of 1.48 (fig. 16).

Carrying out the J measurements for hydrogen chloride, argon, hydrogen bromide and krypton (W_{Kr}=25.0)(42),

TABLE 5

Typical ionization current measurements for hydrogen chloride (p=73.0 cm Hg) in parallel plate chamber

V (Volts)	i(Amps) x 10^6	1/i (Amp^{-1}) x 10^{-6}	i/V^2 ($Amps/volts^2$) x 10^{13}
500	0.58	-	-
1000	1.08	-	-
1500	1.80	-	-
2000	1.83	-	-
2500	2.08	-	-
3000	2.28	0.438	2.53
3200	2.35	0.425	2.29
3500	2.42	0.413	1.98
3800	2.49	0.401	1.72
4000	2.53	0.395	1.58
4200	2.56	0.390	1.45
4500	2.60	0.384	1.28
4800	2.64	0.378	1.15
5000	2.66	0.374	1.07

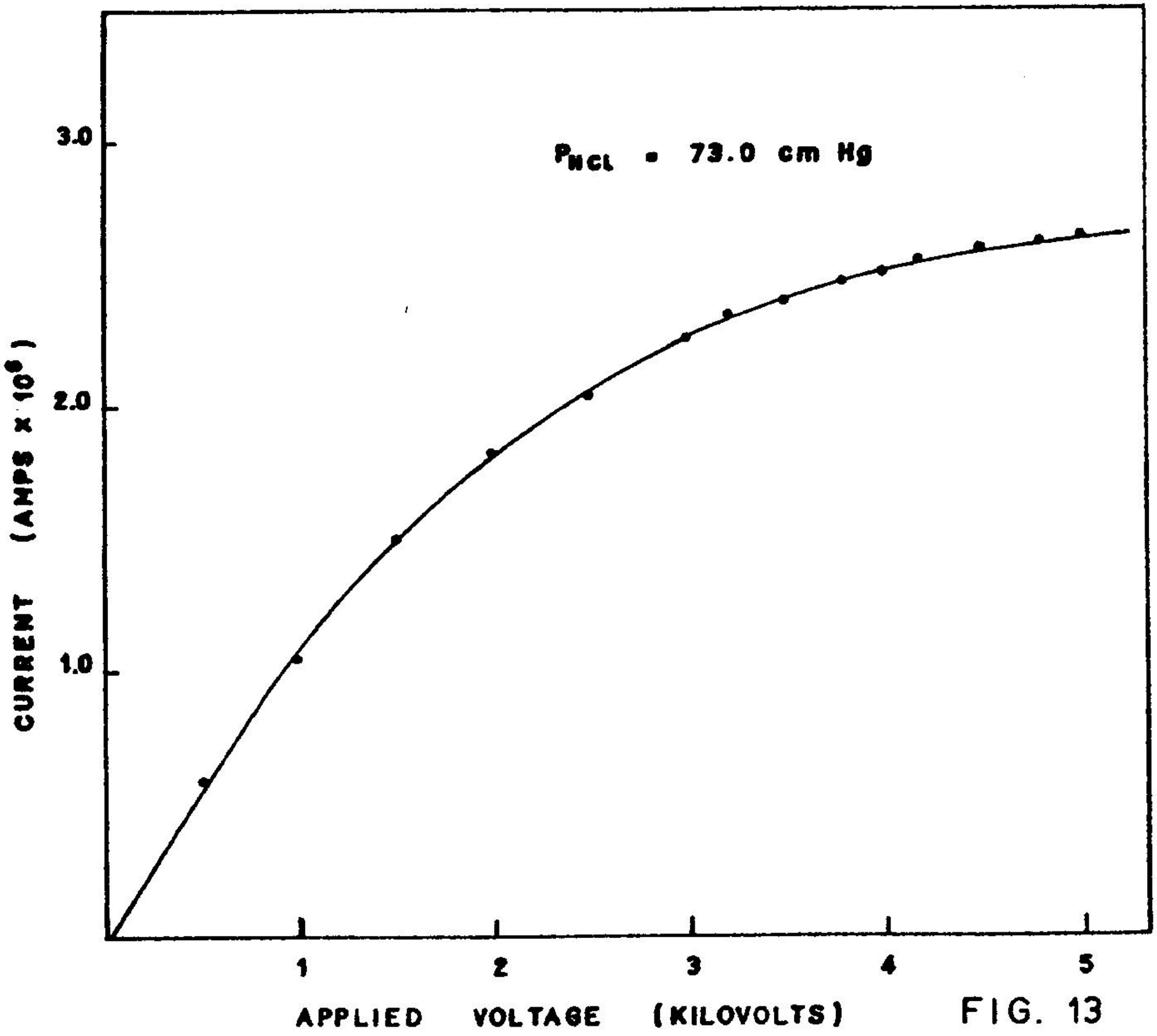
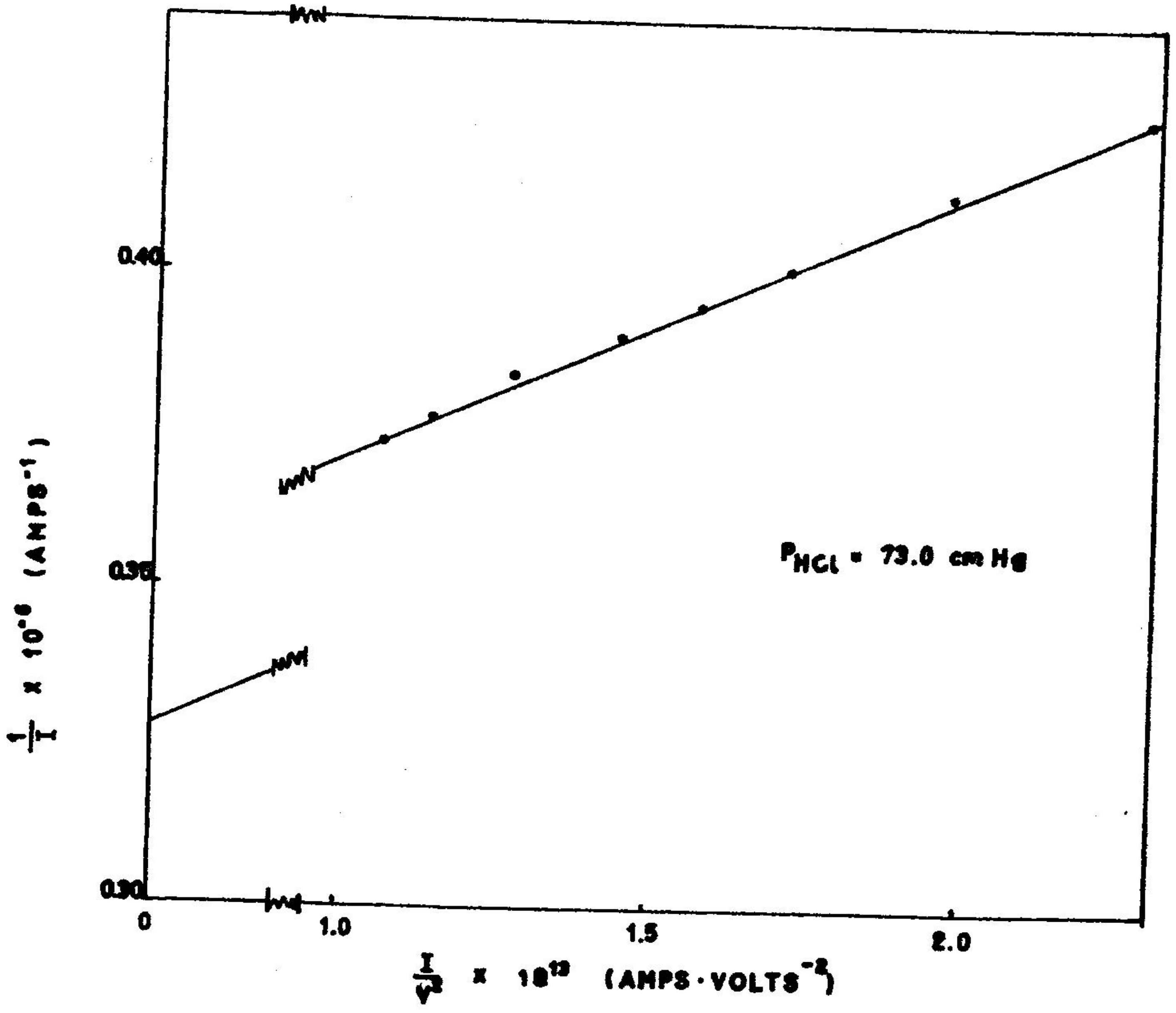

P_{HCL} = 73.0 cm Hg
CURRENT (AMPS x 10^8)
3.0
2.0
1.0
1
2
3
4
5
APPLIED VOLTAGE (KILOVOLTS)

FIG. 13



A TYPICAL GREENING PLOT FIG. 14

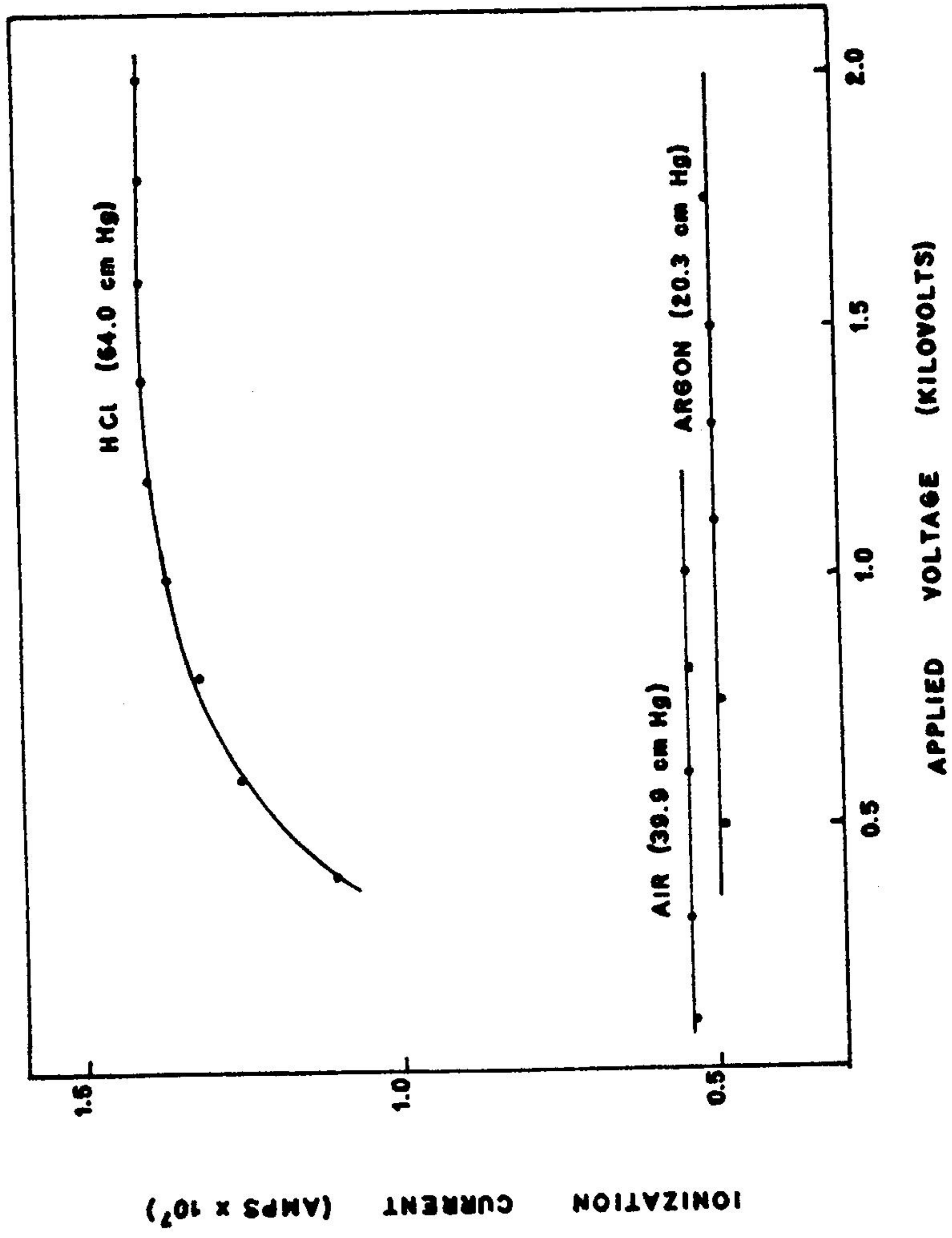

HCl (64.0 cm Hg)
ARGON (20.3 cm Hg)
AIR (39.9 cm Hg)
0.5
1.0
1.5
2.0
APPLIED VOLTAGE (KILOVOLTS)
1.5
1.0
0.5
IONIZATION CURRENT (AMPS x 10⁷)

FIG. 15

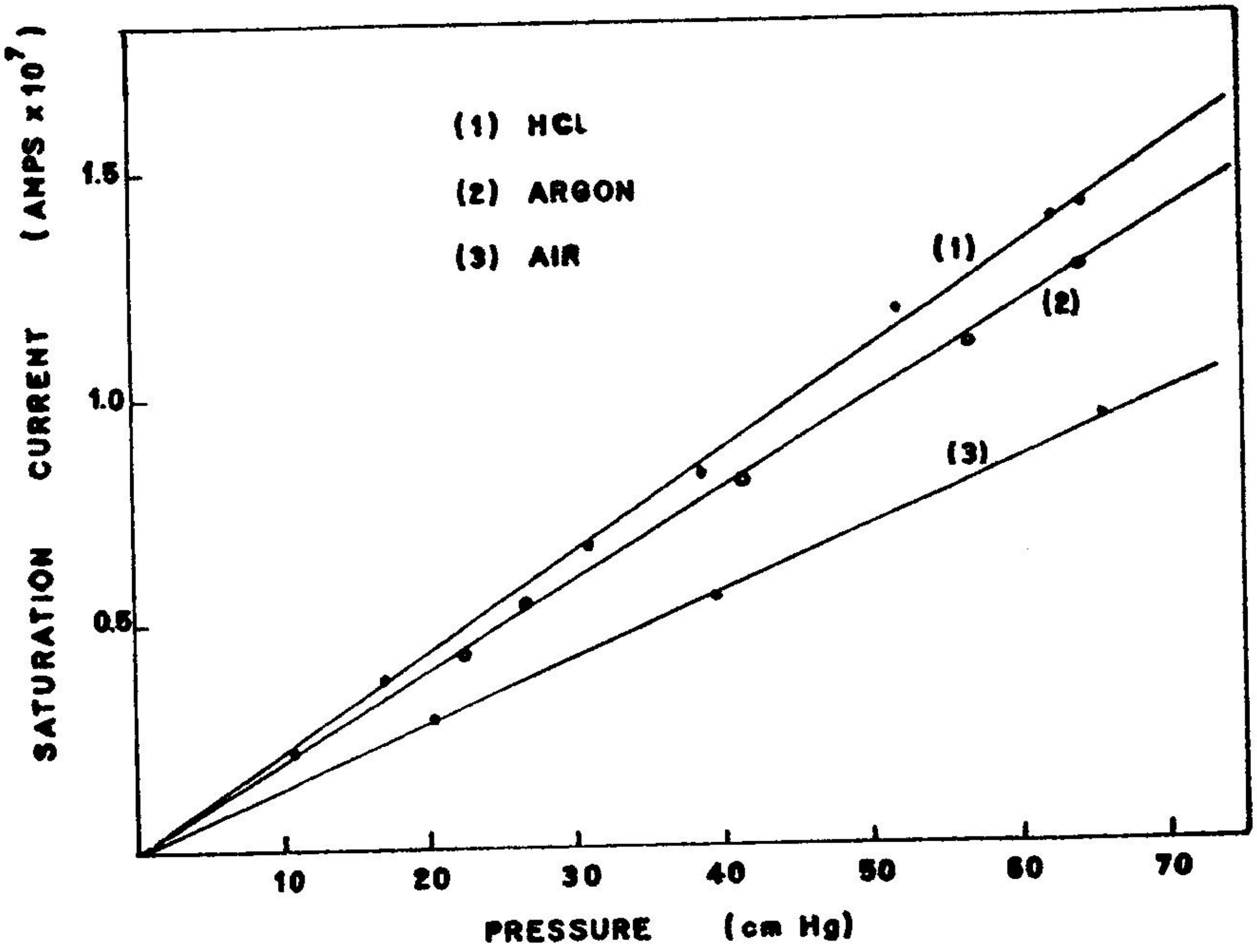

(1) HCL
(2) ARGON
(3) AIR
(1)
(2)
(3)
SATURATION CURRENT (AMPS x 10^7)
1.5
1.0
0.5
10
20
30
40
50
60
70
PRESSURE (cm Hg)

FIG. 16

W_{HCl} and W_{HBr} were then computed to be 24.8 eV and 24.4 eV respectively.

G values can now be computed from the ion pair yields. These are given in table 6 for hydrogen chloride and hydrogen bromide.

3.2 RADIOLYSES OF PURE HYDROGEN CHLORIDE AND HYDROGEN BROMIDE.

The radiolysis of each of the gases, hydrogen chloride and hydrogen bromide was carried out in a cell of volume 228.8 cc (fig. 11). These were all performed in exactly the same position on the trolley to ensure the same dose rates. Various pressures and doses were used. The formation of hydrogen from the two gases is shown in tables 7 and 8 to be linearly dependent on pressure and dose. These results are also illustrated in figs. 17 and 18. The hydrogen yields are expressed in moles of hydrogen formed per cm.Hg. pressure of gas used, per minute.

3.3 THE EFFECT OF CHLORINE ON THE RADIOLYSIS OF HYDROGEN CHLORIDE.

Hydrogen chloride was next irradiated with various concentrations of chlorine present, in cells of volume 228.8 cc and 3690 cc respectively, using Co^{60} γ

TABLE 6

p_{HX} (cm Hg)	ion pairs (10^{-17})	H_2 molecules (10^{-17})	$(M/N)_{-HX}$	$G(H_2)$
(I) HCl results				
26.80	3.42	7.15	4.18	8.4
40.45	3.25	6.58	4.08	8.2
77.20	2.67	5.47	4.10	8.3
		mean	4.12 ± 0.1	8.3 ± 0.1
(II) HBr results				
22.25	1.94	4.51	4.65	9.5
22.25	1.86	4.29	4.62	9.4
22.25	2.27	5.44	4.80	9.8
24.50	2.26	5.34	4.74	9.7
40.60	2.74	3.54	4.76	9.7
		mean	4.71 ± 0.1	9.6 ± 0.1

TABLE 7

Hydrogen formation from γ-radiolysis of pure hydrogen chloride and hydrogen bromide gases (228.8 cc cell)

HX Pressure (cm Hg)	Irradiation time (mins)	R(rate of H_2 formation) $x10^{12}$(moles/cmHg/min)
Hydrogen chloride		
46.85	995	2.78
50.90	934	2.97
51.42	668	2.93
59.95	1072	2.66
95.90	1038	2.61
119.90	450	2.79
120.20	480	2.79
		mean 2.79 ± 0.13
Hydrogen bromide		
18.70	1321	7.66
18.70	1243	7.73
36.00	480	7.39
36.00	751	7.40
60.30	1095	7.41
60.30	831	7.60
60.30	457	7.69
60.30	469	7.80
		mean 7.59 ± 0.14

TABLE 8

Hydrogen formation from γ-radiolysis of pure gaseous hydrogen chloride and hydrogen bromide (3690 cc cell)

HX pressure (cm Hg)	Irradiation time (mins)	R x 10^{12} (moles/cmHg/min)
Hydrogen chloride		
91.30	1170	23.85
91.30	1124	24.46
91.30	366	24.94
49.95	1160	23.80
19.90	1165	23.45
19.90	1133	23.90
		mean 24.1 ± 0.5
Hydrogen bromide		
41.65	718	66.59
53.15	439	67.76
50.55	194	66.79
49.45	978	66.12
49.45	1020	67.05
		mean 66.8 ± 0.5

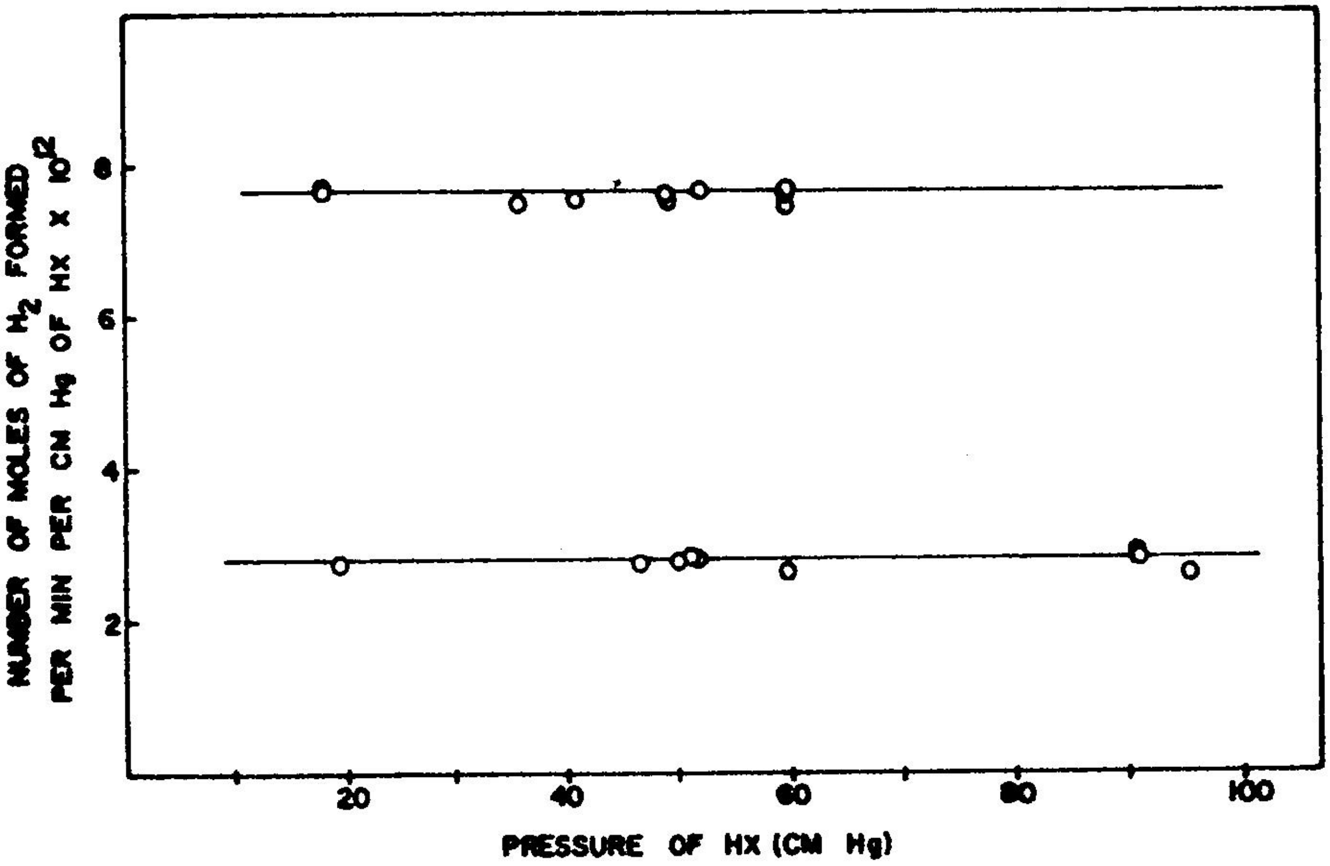

NUMBER OF MOLES OF H_2 FORMED PER MIN PER CM Hg OF HX X 10^{12}
8
6
4
2
20
40
60
80
100
PRESSURE OF HX (CM Hg)

FIG 17

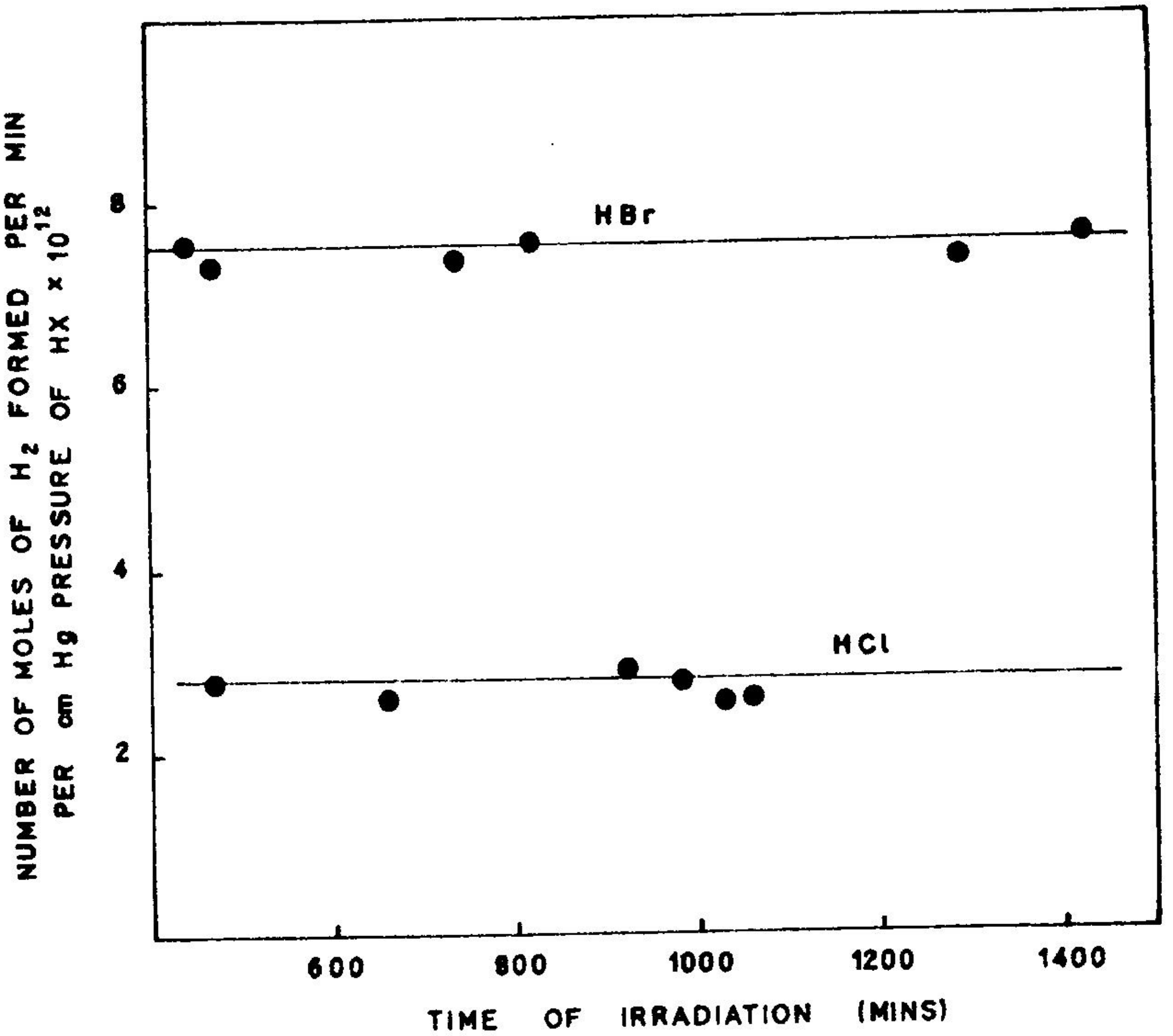

NUMBER OF MOLES OF H_2 FORMED PER MIN
PER cm Hg PRESSURE OF HX × 10^{12}
8
6
4
2
HBr
HCl
600
800
1000
1200
1400
TIME OF IRRADIATION (MINS)

FIG. 18

rays.

Chlorine has the effect of lowering the yield of hydrogen and this scavenging effect may be attributed to competition between the two following reactions.

$$H + HCl \xrightarrow{k_1} H_2 + Cl$$
$$H + Cl_2 \xrightarrow{k_2} HCl + Cl$$

A kinetic treatment of the above would produce the relationship (see appendix I)

$$\frac{1}{\Delta G(H_2)} = \left[1 + \frac{k_1 P_{HCl}}{k_2 P_{Cl_2}}\right] \Big/ G_H$$

where $\Delta G(H_2) = G(H_2)_{Max} - G(H_2)_S$

G_H is the yield of H; $G(H_2)_{Max}$ and $G(H_2)_S$ are the yields of hydrogen in the absence and presence of the scavenger respectively. P_{HCl} and P_{Cl_2} are the partial pressures of hydrogen chloride and chlorine.

Table 9 gives the results of the scavenging effect of chlorine on hydrogen chloride using two cells of different sizes. Fig 19 is drawn from the results in table 9. The results obtained with the large cell have been normalized to those of the small cell, and a plot of the above equation is shown in fig. 20. From the

TABLE 9

γ-Radiolysis of gaseous hydrogen chloride with chlorine as scavenger

Mole % Cl_2	$R \times 10^{12}$ (moles/cmHg/min) 228.8 cc cell	3690 cc cell	$\frac{P_{HCl}}{P_{Cl_2}}$	$\frac{1}{\Delta R}$
0.00	2.79	23.80	-	-
0.102	2.27	19.35	980	1.92
0.151	2.14	-	662	1.55
0.306	1.74	-	327	0.980
0.327	1.72	14.75	306	0.934
0.550	1.43	-	182	0.735
0.700	1.25	10.69	143	0.649
0.986	1.09	-	101	0.588
1.97	0.854	-	51	0.517
2.50	0.735	5.75	40	0.498
4.49	0.704	-	22	0.429

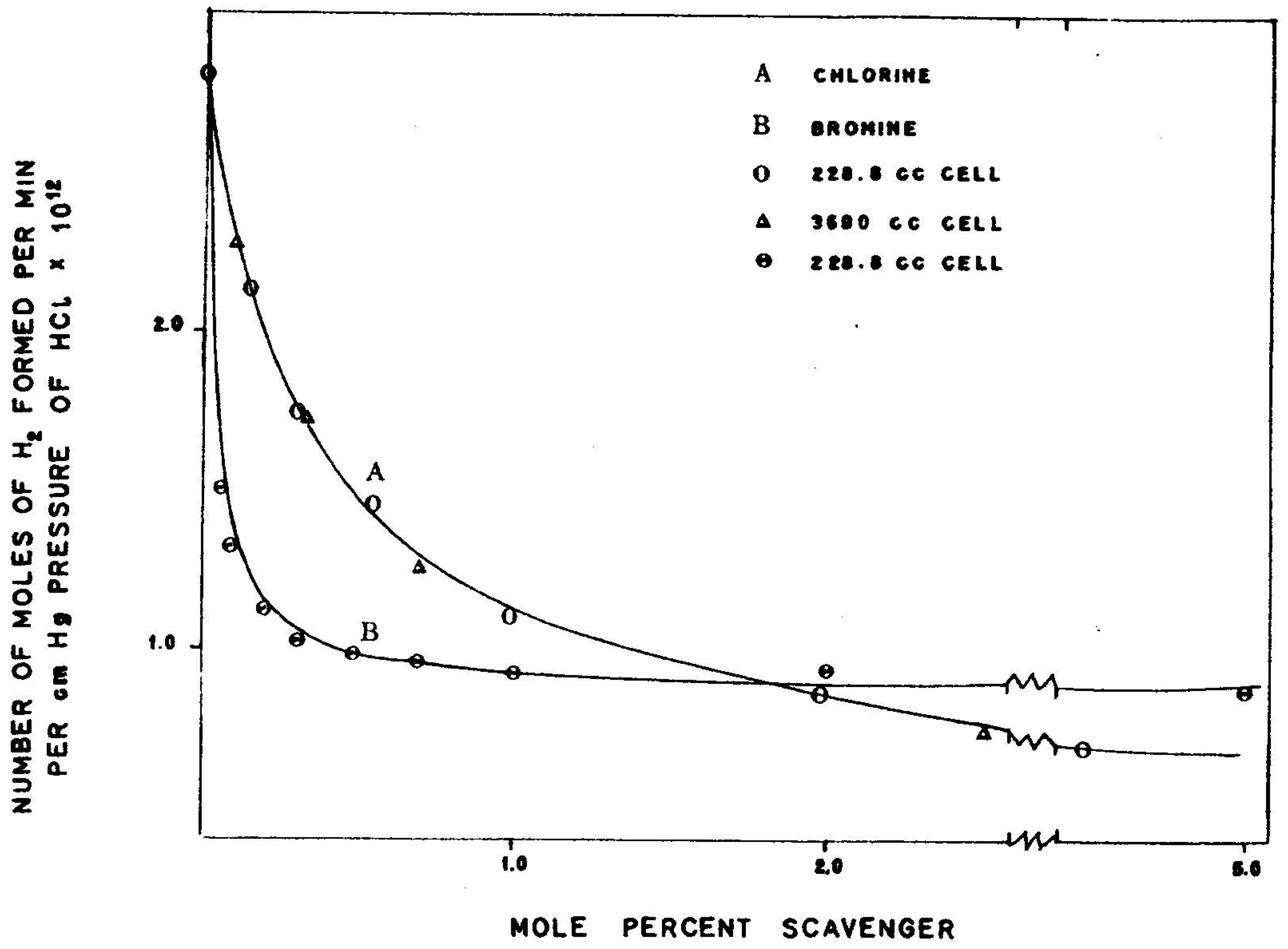

A CHLORINE
B BROMINE
O 228.8 CC CELL
Δ 3680 CC CELL
⊖ 228.8 CC CELL
A
B
NUMBER OF MOLES OF H_2 FORMED PER MIN PER cm Hg PRESSURE OF HCL x 10^{12}
2.0
1.0
1.0
2.0
5.0
MOLE PERCENT SCAVENGER

FIG. 19

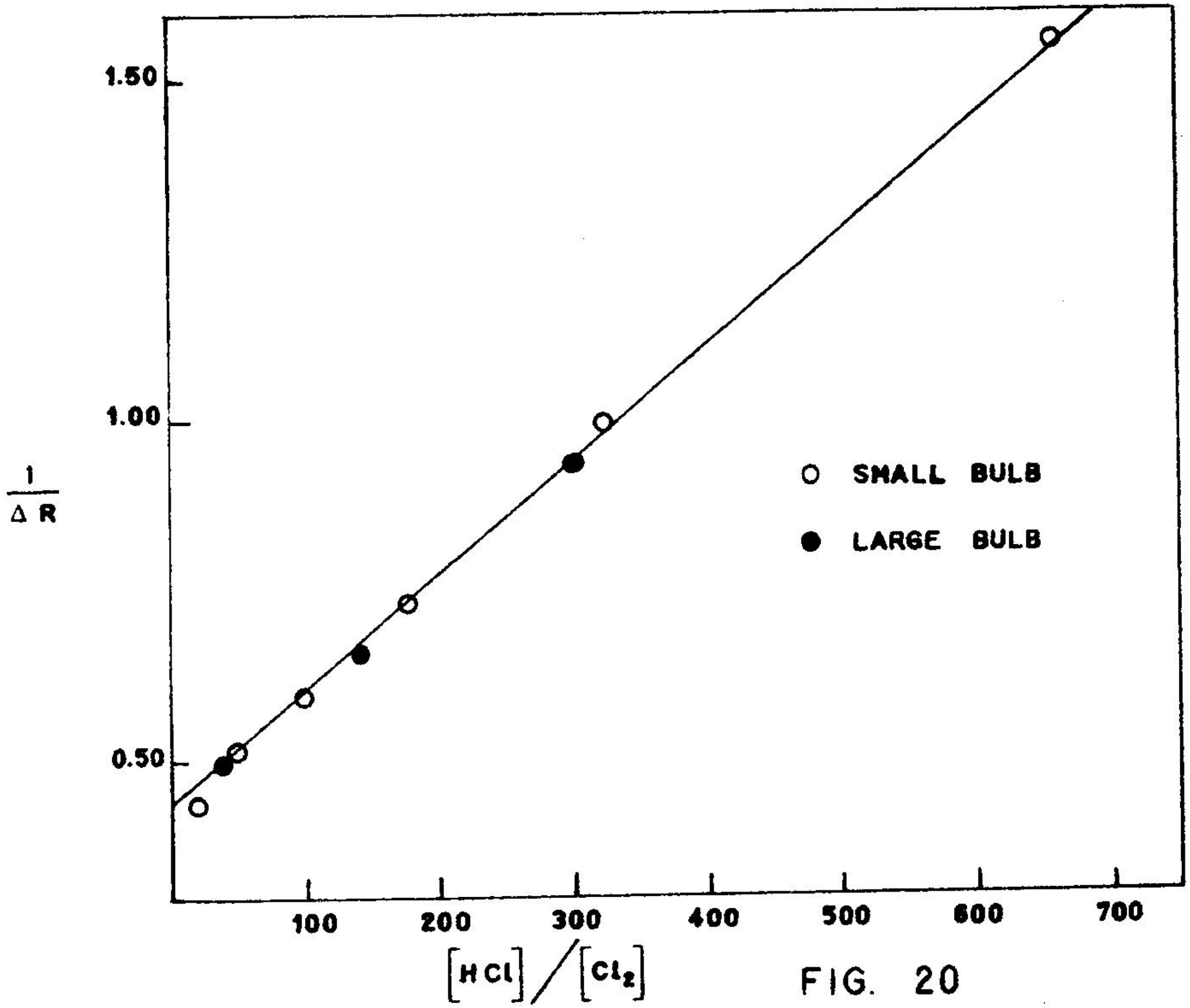

$\frac{1}{\Delta R}$
1.50
1.00
0.50
100
200
300
400
500
600
700
[HCl]/[Cl$_2$]
○ SMALL BULB
● LARGE BULB

FIG. 20

slope of the line in fig. 20, a value of (3.80 ± 0.15) x 10^{-3} can be calculated for k_1/k_2 and a value of 6.75 for G_H. The value for k_1/k_2 is not in agreement with 1.07 x 10^{-2} calculated from the equation

k_1/k_2 = (0.147 ± 0.033) exp-(1540/RT) at 23°C put forward by Klein and Wolfsberg(44) for competition reactions of hydrogen chloride and chlorine for thermal hydrogen atoms.

It can be concluded that the H represented above is not a thermal hydrogen atom, but some other species which will be referred to as H^*.

3.4 RADIOLYSIS OF HYDROGEN CHLORIDE WITH BROMINE AS SCAVENGER

The radiolysis of hydrogen chloride in the presence of bromine was carried out in cells of different sizes at different pressures. These results are given in tables 10,11 and 12. The results of table 10 are plotted in fig. 19 to show the comparative effect of bromine and chlorine as scavengers. It is clear from this figure that bromine is a much more efficient scavenger at low mole percentage concentrations; however, at high concentrations it does not reduce the hydrogen yield as

TABLE 10

γ-Radiolysis of gaseous hydrogen chloride with bromine as scavenger in 228.8 cc cell

HCl pressure (cm Hg)	Irradiation time (mins)	Mole % Br_2	$R \times 10^{12}$ (moles/cmHg/min)
119.90	450	-	2.79
119.90	939	0.10	1.32
119.90	1103	0.20	1.11
119.90	1500	0.30	1.05
119.90	1190	0.50	0.98
119.90	1067	0.70	0.95
111.55	1123	0.05	1.54
111.55	1135	0.05	1.48
111.55	1060	1.0	0.92
111.55	980	2.0	0.90
111.55	1172	5.0	0.88

TABLE 11

γ-Radiolysis of gaseous hydrogen chloride with bromine as scavenger in 3690 cc cell

HCl pressure (cm Hg)	Irradiation time (mins)	Mole % Br_2	R x 10^{12} (moles/cmHg/min)
91.30	1124	-	24.46
91.30	366	-	24.94
91.30	1208	0.05	13.05
91.30	1228	0.05	12.77
91.30	1080	0.10	11.00
91.30	1126	0.10	10.88
91.30	1090	0.20	9.64
91.30	1087	0.40	9.14
91.30	1105	0.60	8.79
91.30	1170	1.0	8.38
91.30	1191	2.0	8.07
91.30	1103	4.0	7.86
91.30	1116	6.0	7.73

TABLE 12

γ-Radiolysis of gaseous hydrogen chloride with bromine as scavenger in 3690 cc cell

HCl pressure (cm Hg)	Irradiation time (mins)	Mole % Br_2	R x 10^{12} (mole/cmHg/min)
19.90	11.65	-	23.45
19.90	1133	-	23.90
19.90	1000	0.05	12.02
19.90	1045	0.05	12.12
19.90	985	0.10	10.35
19.90	1096	0.15	9.56
19.90	1256	0.20	9.10
19.90	1213	0.40	8.60
19.90	1143	0.60	7.98
19.90	1105	0.60	8.08
20.10	1117	1.0	7.80
20.10	1020	2.0	7.42
20.10	1293	4.0	6.97
20.10	977	4.0	7.26

much as chlorine.

Fig. 21 is a similar plot to fig. 20 using the results of tables 10 and 11 normalizing the pure hydrogen chloride yield to unity. Values of 1.96×10^{-4} and 5.65 are obtained for $\frac{k_{(H^{\prime} + HCl)}}{k_{(H^{\prime} + Br_2)}}$ and $G_{H^{\prime}}$ respectively, assuming a competition for H′ by hydrogen chloride and bromine. The comparison of these results with those of Armstrong and Rumfeldt(45), provides further evidence for the assumption that H′ is not a thermal hydrogen atom. An immediate possibility appears to be that the scavengers may be scavenging electrons which could be the precursor for H atoms.

3.5 RADIOLYSIS OF HYDROGEN CHLORIDE WITH SULPHUR HEXAFLUORIDE AS SCAVENGER.

The foregoing results have indicated that the species H′ was not a thermal hydrogen atom, but could be a mixture of thermal hydrogen atoms and thermalized electrons, in which case the rate constant ratios obtained would be complex rate constant ratios. Sulphur hexafluoride, a good electron scavenger(46), was therefore chosen. The activation energies for the two competing reactions

(a) $H + SF_6 \longrightarrow SF_5 + HF$

and (b) $H + HCl \longrightarrow H_2 + Cl$

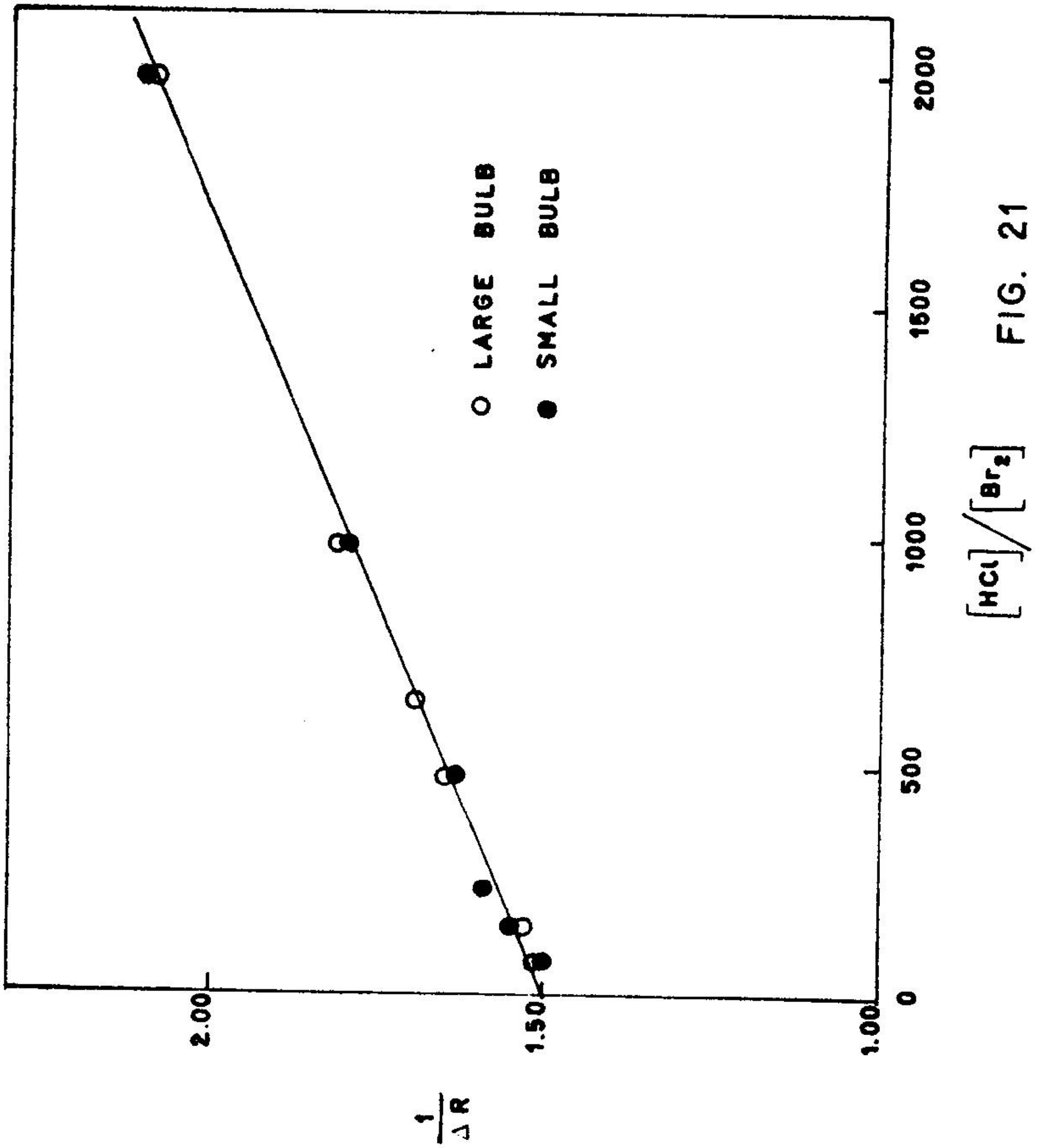

$\frac{1}{\Delta R}$
2.00
1.50
1.00
0
500
1000
1500
2000
$[HCl]/[Br_2]$
○ LARGE BULB
● SMALL BULB

FIG. 21

are about 10 K cals/mole(47) and 3 K cals/mole(48) respectively. Sulphur hexafluoride would therefore be unable to compete with hydrogen chloride for thermal hydrogen atoms at room temperature and at the sulphur hexafluoride concentrations used.

The same technique was used as in the cases of chlorine and bromine. The results are presented in table 13 and plotted in fig. 22. On comparing figs. 19 and 22 it can be seen that the sulphur hexafluoride has reduced the hydrogen yield more rapidly than either bromine or chlorine at low concentrations; however, the plateau obtained with sulphur hexafluoride is somewhat higher than with either chlorine or bromine. Both bromine and sulphur hexafluoride at low concentrations must be scavenging mainly electrons, since they both have maximum electron capture cross section for electrons at zero energy. If it is now assumed that the sulphur hexafluoride will only scavenge electrons, then from fig. 22 about 46% of the total hydrogen formed will have thermalized electrons as its precursor.

3.6 RADIOLYSIS OF HYDROGEN CHLORIDE WITH ETHYLENE

Ethylene is known to react with thermal H atoms to form an ethyl radical. It was therefore thought

TABLE 13

γ-Radiolysis of gaseous hydrogen chloride with sulphur hexafluoride as scavenger in 3690 cc cell

HCl pressure (cm Hg)	Irradiation time (mins)	Mole % SF_6	$R \times 10^{12}$ (moles/cmHg/min)
39.05	1171	-	22.62
39.75	1183	-	22.69
39.75	1098	0.034	12.96
39.75	1180	0.069	12.68
39.75	1072	0.102	12.60
39.75	1022	0.305	12.29
39.05	1172	0.480	12.53
39.05	1080	1.28	11.86
39.05	1140	2.56	11.12
39.05	1068	3.10	10.88
39.05	1200	5.01	10.63
39.05	1147	6.86	10.65

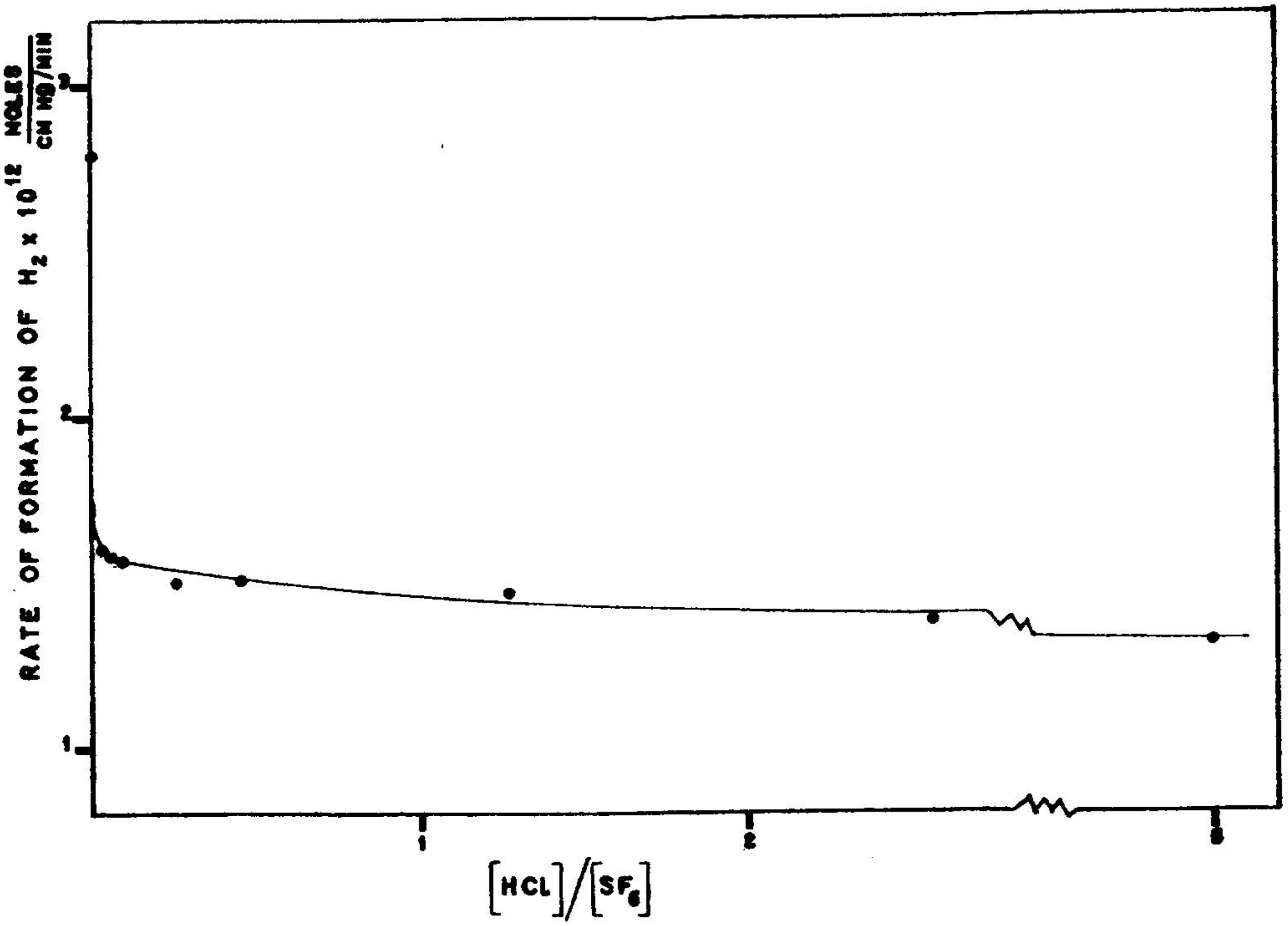

RATE OF FORMATION OF $H_2 \times 10^{12}$ $\frac{\text{MOLES}}{\text{CM HG/MIN}}$
3
2
1
1
2
8
$[\text{HCL}]/[\text{SF}_6]$

FIG. 22

necessary to see what scavenging effect this gas would have on the radiolysis of hydrogen chloride. Little was done on this reaction and before it could be discussed a more systematic and thorough investigation would have to be carried out. The results obtained are given in table 14, from which it can be seen that the higher the mole percent ethylene used the lower the hydrogen yield, and also that this yield increases with time of irradiation since the concentration of ethylene would have decreased with time. These preliminary experiments indicated (a) a scavenging effect of ethylene on the hydrogen yield and (b) consumption of the ethylene in a chain reaction (i.e. $G_{-C_2H_4}$ is of the order of several thousand). This suggested that the mechanism was quite complex and would need a detailed study. Before this study could be pursued further a publication appeared(49) on this reaction putting forward a chain mechanism.

3.7 DOSE RATE EFFECT

Three similar cells (fig. 9) without electrical connections, all containing break off seals, were sent to Chalk River (A.E.C.L.) to be irradiated with a Gammacell. These cells were filled with pure hydrogen chloride

TABLE 14

γ-Radiolysis of gaseous hydrogen chloride with ethylene as scavenger in 228.8 cc cell

HCl pressure (cm Hg)	Irradiation time (mins)	Initial mole % C_2H_4	Mole % C_2H_4 used up	$R \times 10^{12}$ (moles/cmHg/min)
46.85	995	-	-	2.79
52.30	420	5.3	3.3	1.82
54.85	726	4.9	3.6	2.21
54.85	960	5.1	3.9	2.12
48.40	480	9.8	4.2	1.59
56.70	736	9.7	5.7	1.80
46.40	995	10.7	7.1	1.99

at first and then various mole percentages of bromine were introduced. The reduced hydrogen yields are shown in table 15 together with a comparison of the results obtained with a 200 Curie Co^{60} source.

The nature of the experiment made it difficult to carry out too many runs. The samples had to be carefully packed and shipped each time for their journey to and from Chalk River. The few runs, however, indicate that there was very little difference in the scavenging at the higher dose rate.

3.8 EFFECT OF COATING THE CELL

The cell used here was coated with colloidal carbon in a manner similar to that described by Back et al(37). These results compared with those from uncoated cells are given in table 16. It was found that the coating had a tendency to absorb bromine and therefore the cells had to be baked out under vacuum to remove absorbed bromine if a second series of runs were to be carried out. These results demonstrate that coating had little or no effect (within experimental error) on the relative reduced hydrogen yields.

3.9 RADIOLYSIS OF A MIXTURE OF HYDROGEN CHLORIDE AND HYDROGEN BROMIDE CONTAINING BROMINE AS A SCAVENGER.

Measured amounts of a mixture of hydrogen chloride

TABLE 15

Radiolysis of hydrogen chloride with bromine at very high dose rate

	HCl pressure (cm Hg)	Irrad. Time	Mole % Br_2	R x 10^{12} (moles/cmHg/min)	% H_2 yield reduced	
Cell I	49.75	89.19	-	22.62		-
Cell II	51.30	89.57	-	22.83		-
Cell III	50.05	89.60	-	24.41		-
					γ-cell	200 Ci ^{60}Co
Cell I	49.25	90.0	2.97	8.03	64.7	67.8
Cell II	50.25	90.0	0.51	9.57	58.1	64.0
Cell III	50.05	90.0	0.11	10.87	55.5	55.7

TABLE 16

Effect of cell coating

HCl pressure (cm Hg)	Irradiation time (mins)	Mole % Br_2	R x 10^{12} (moles/cmHg/min)	% H_2 yield reduced	
61.45	993	-	7.56	-	
61.45	1000	-	7.44	-	
				coated	uncoated
61.45	1077	1.0	2.60	65.4	66.0
61.45	1115	1.99	2.48	66.8	67.3
61.45	1113	4.0	2.30	69.3	68.2

and hydrogen bromide were first irradiated in a manner similar to those already described. Small amounts of bromine were then added to observe its effect on the above mixture.

On the assumption of the following competing reactions

$$H^{\cdot} + HCl \xrightarrow{k_1} H_2 + Cl$$

$$H^{\cdot} + HBr \xrightarrow{k_2} H_2 + Br$$

$$H^{\cdot} + Br_2 \xrightarrow{k_3} HBr + Br$$

a similar calculation to that given in appendix I can be carried out and the following equation obtained.

$$\frac{1}{G_{H_2}} = \frac{1}{G_{H^{\cdot}}} \left[1 + \frac{k_1 \ (HCl)}{k_3 \ (Br_2)} + \frac{k_2 \ (HBr)}{k_3 \ (Br_2)} \right]$$

The results are presented in table 17. Fig. 23 depicts the scavenging effect and fig. 24 is the reciprocal plot of fig. 23. The rate of production of hydrogen in the absence of bromine was normalized to 100. From fig. 24, k_2/k_3 can be evaluated using the previously obtained value for k_1/k_3, to be $1.96 \pm 0.15 \times 10^{-4}$. The calculation gives the value $k_2/k_3 = 6.1 \pm 0.3 \times 10^{-3}$ which is not in agreement with the ratio 0.12 for thermal H atoms obtained by conventional gas kinetic techniques (50). This provides further evidence for

TABLE 17

γ-Radiolysis of a mixture of hydrogen chloride and hydrogen bromide containing bromine in 3690 cc cell

HCl pressure (cm Hg)	Mole % HBr	Irrad. time (mins)	Mole % Br_2	$R \times 10^{12}$ (moles/cmHg/min)
16.40	5.31	1187	-	27.12
16.40	5.31	1066	0.050	19.50
16.40	5.31	1182	0.099	16.97
16.40	5.31	1126	0.198	14.98
16.40	5.31	1131	0.287	14.45
39.95	5.33	1052	-	26.88
39.95	5.33	1203	0.53	13.54
39.95	5.33	1158	1.02	11.96
39.95	5.33	1106	1.56	11.28

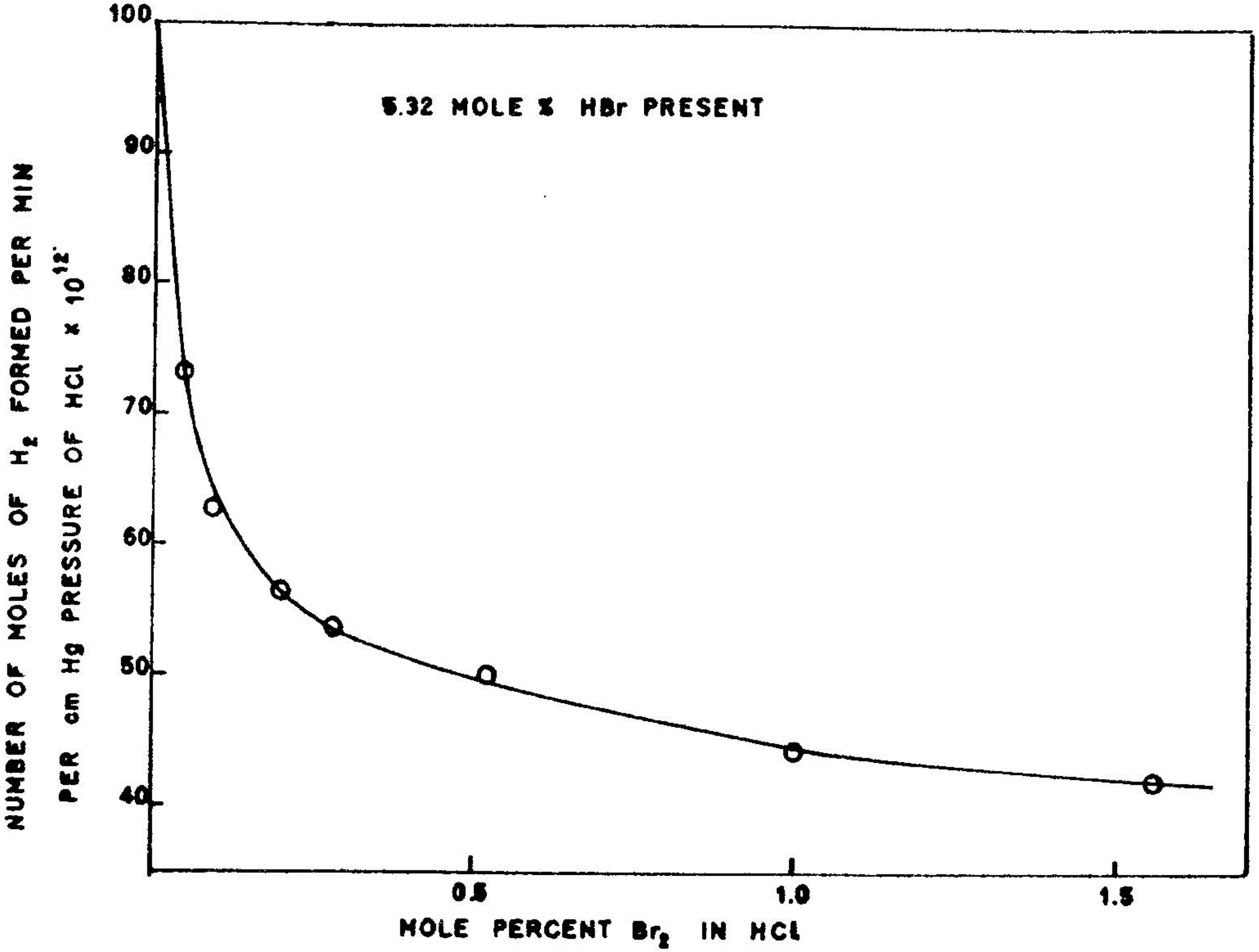

5.32 MOLE % HBr PRESENT
NUMBER OF MOLES OF H_2 FORMED PER MIN
PER cm Hg PRESSURE OF HCl x 10^{12}
100
90
80
70
60
50
40
0.5
1.0
1.5
MOLE PERCENT Br_2 IN HCl

FIG. 23

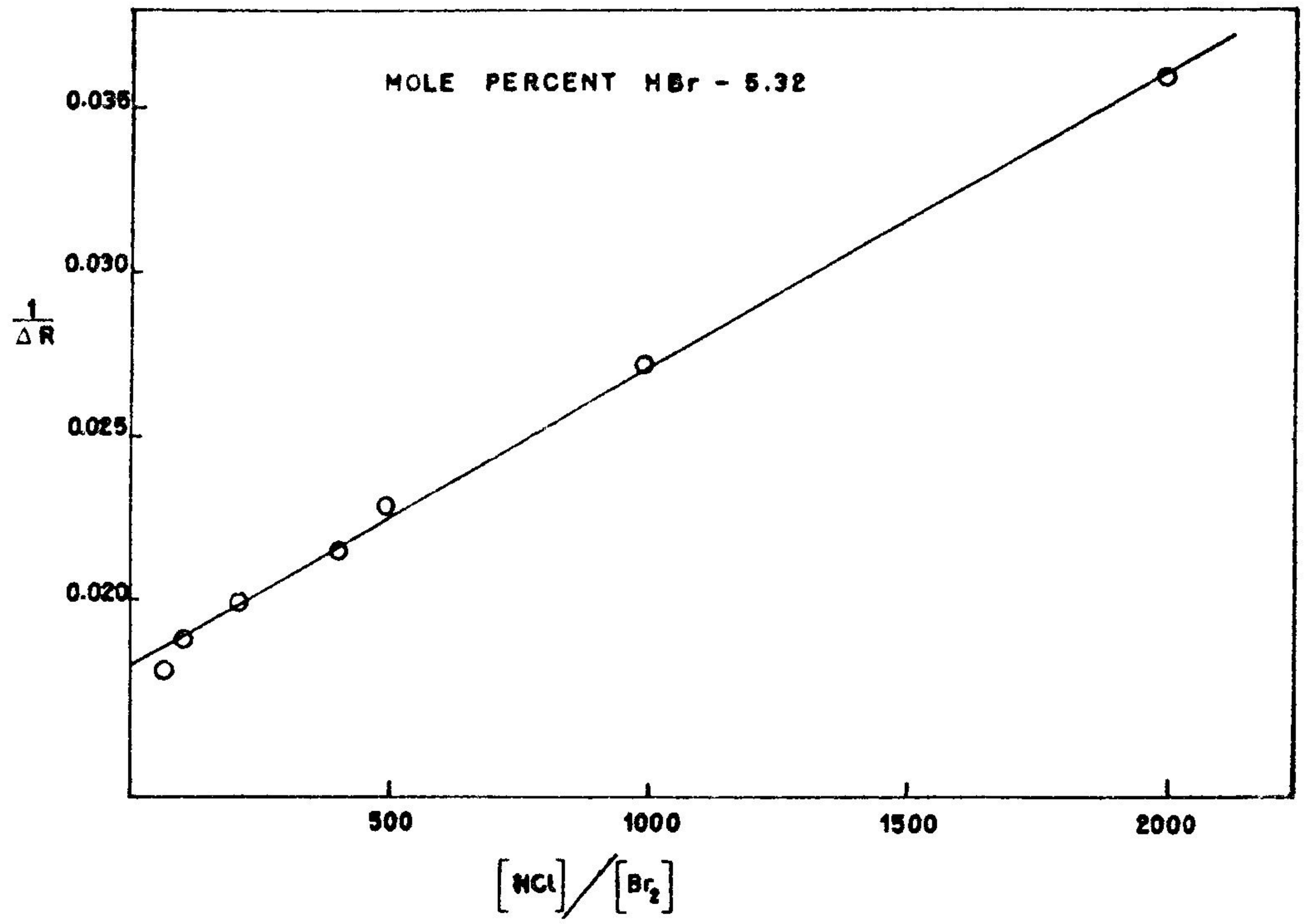

MOLE PERCENT HBr - 5.32
$\frac{1}{\Delta R}$
0.035
0.030
0.025
0.020
500
1000
1500
2000
[HCl]/[Br$_2$]

FIG. 24

referring to the species H above as H'.

3.10 HYDROGEN BROMIDE IRRADIATED WITH X-RAYS IN THE PRESENCE OF BROMINE

Three similar cells A,B and C (fig. 11) were used. These cells were each filled with hydrogen bromide and irradiated with X-rays from a standard X-ray therapeutic machine using 87Kv. These irradiations were all carried out at the Holy Cross Hospital, Calgary. The volumes of the cells were all about 230 cc differing by only about 3 cc. Next, small amounts of bromine were added and the cells re-irradiated.

A treatment of the results (table 18) similar to those of hydrogen chloride with bromine gives the equation

$$\frac{1}{G_{(H_2)}} = \frac{1}{G_{H'}}\left[1 + \frac{k_2\,(HBr)}{k_3\,(Br_2)}\right]$$

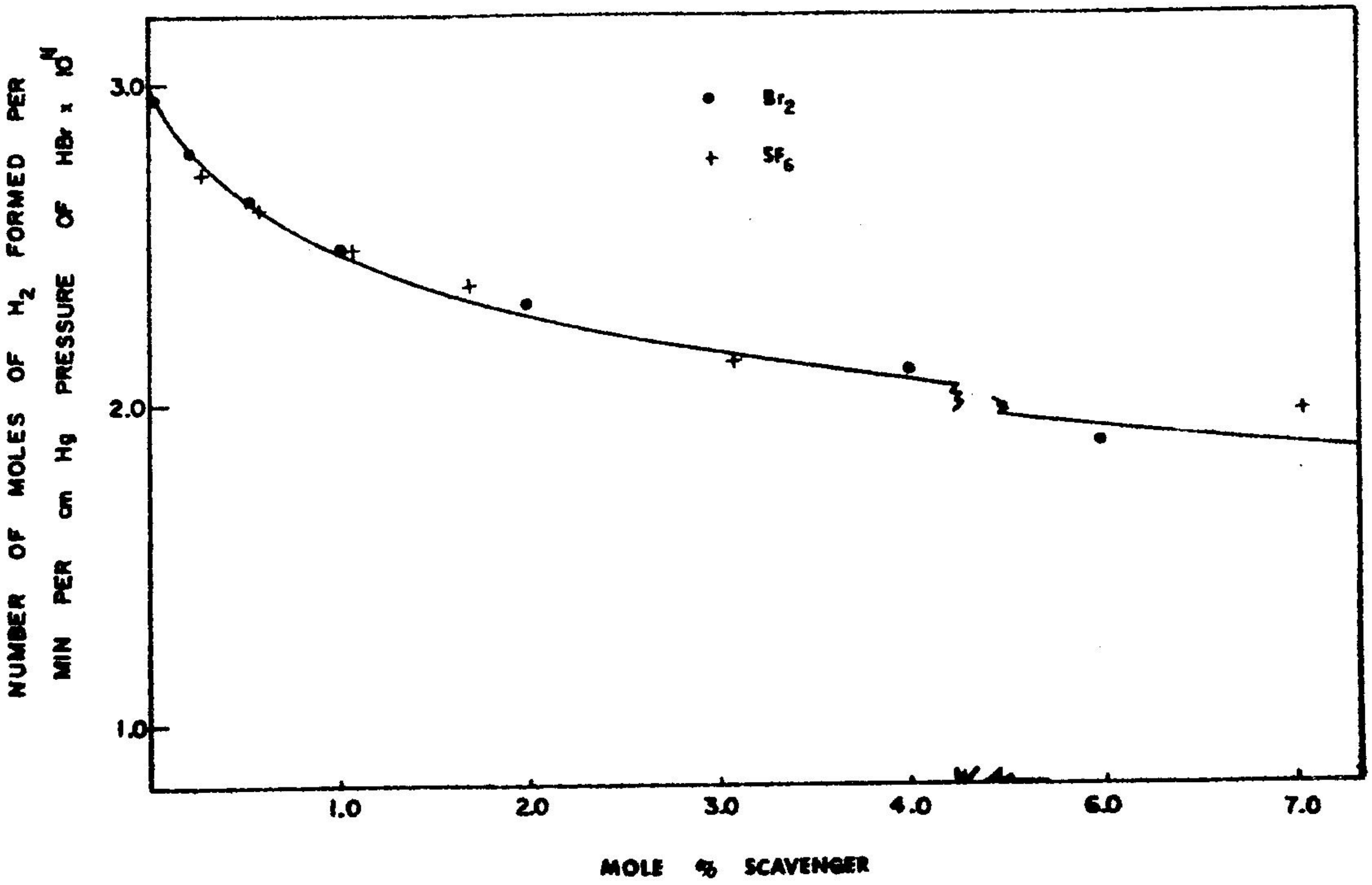
Figs. 25 and 26 show the scavenging effect and the reciprocal plot.

From the reciprocal plot a value of (5.9 ± 0.3) x 10^{-3} for $\dfrac{k_{(H' + HBr)}}{k_{(H' + Br_2)}}$ is obtained. This provides further justification for referring to the scavenged species as H' rather than H.

TABLE 18

Radiolysis of hydrogen bromide containing bromine using X-rays in cell of approximately 230 cc

HBr pressure (cm Hg)	Irrad. time (mins)	Mole % Br_2	Cell	$R \times 10^{11}$ (moles/cmHg/min)
55.88	15	-	B	2.97
55.88	15	-	B	2.97
55.68	10	-	A	2.98
55.68	5	-	A	2.95
56.26	15	-	C	3.01
56.14	15	0.20	A	2.77
55.88	15	0.50	B	2.60
55.88	15	1.01	B	2.47
55.41	15	1.02	B	2.47
56.26	15	1.01	C	2.51
55.50	15	2.03	C	2.39
55.50	15	2.03	C	2.31
55.50	15	4.01	C	2.10
55.41	15	6.03	B	1.84
55.41	15	6.03	B	1.87



NUMBER OF MOLES OF H_2 FORMED PER MIN PER cm Hg PRESSURE OF HBr x 10^{N}
3.0
2.0
1.0
1.0
2.0
3.0
4.0
6.0
7.0
MOLE % SCAVENGER
● Br_2
+ SF_6

FIG. 25

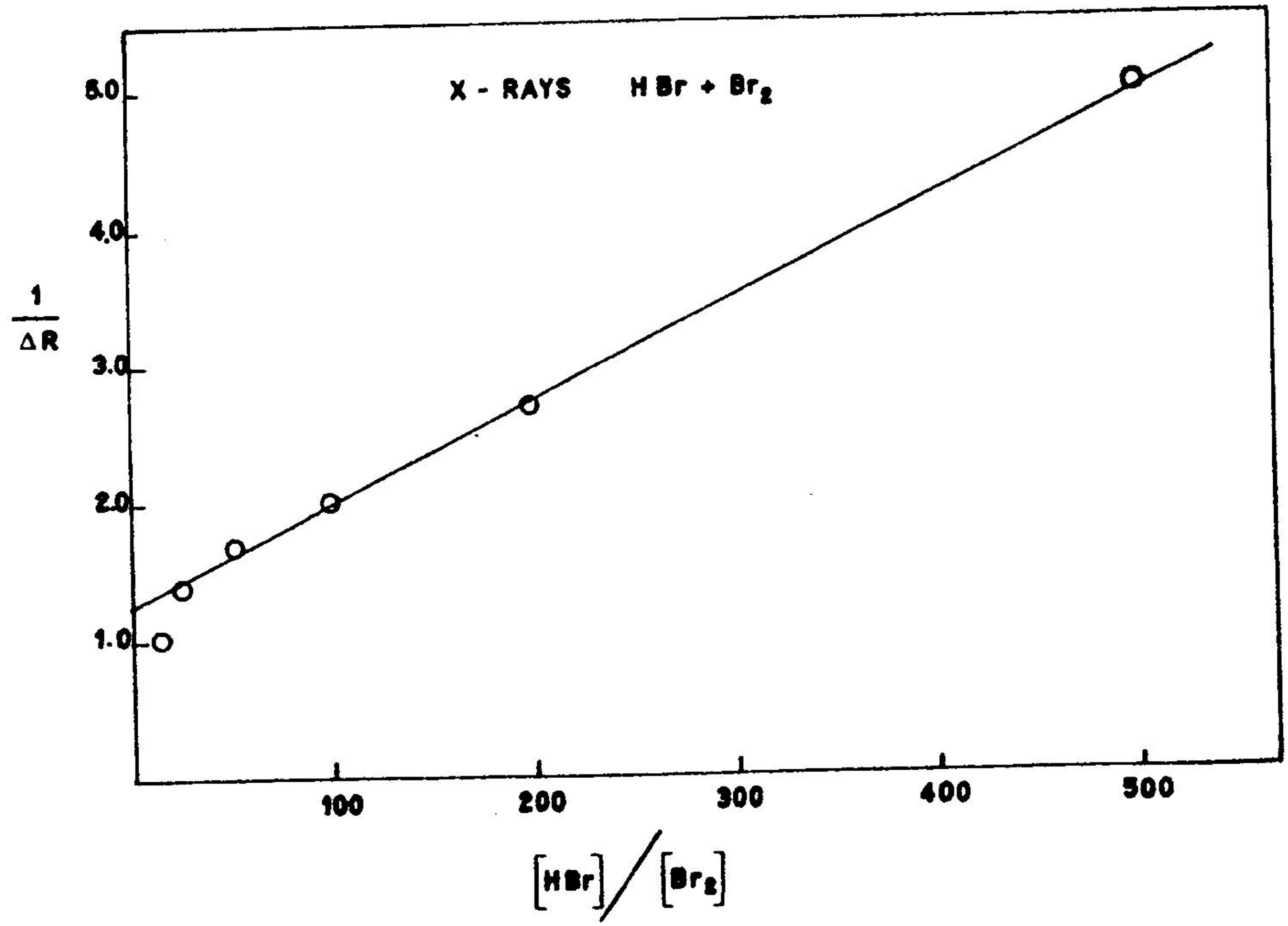

X - RAYS HBr + Br_2
$\frac{1}{\Delta R}$
5.0
4.0
3.0
2.0
1.0
100
200
300
400
500
[HBr]/[Br_2]

FIG. 26

3.11 RADIOLYSIS OF HYDROGEN BROMIDE WITH SULPHUR HEXAFLUORIDE USING X-RAYS.

This was carried out in exactly the same manner as the previous irradiations using sulphur hexafluoride instead of bromine.

If the following competitions are assumed

$$e + HBr \longrightarrow H + Br^-$$

$$e + SF_6 \longrightarrow SF_6^-$$

then by treating the results similarly to the previous section a value for

$$\frac{k_{(e\ +\ HBr)}}{k_{(e\ +\ SF_6)}} \quad \text{can be calculated.}$$

The results are given in table 19 and plots are shown in figs. 25 and 27.

From fig. 27 the value of the above ratio is $(6.4 + 0.3) \times 10^{-3}$. This is within experimental error of the value for $\dfrac{k_{(H' \ +\ HBr)}}{k_{(H' \ +\ Br_2)}}$ and therefore it is not unreasonable to conclude that the H' represented above is not a thermal H atom but may be the thermalized electron.

The scavengers have a lesser effect in reducing

TABLE 19

Radiolysis of hydrogen bromide containing sulphur hexafluoride using X-rays in cell of approximately 230 cc

HBr pressure (cm Hg)	Irrad. time (mins)	Mole % SF_6	Cell	$R \times 10^{11}$ (moles/cmHg/min)
55.77	20	-	A	2.97
55.77	15	0.27	A	2.70
55.77	15	0.27	A	2.74
55.83	15	0.56	C	2.59
55.83	15	1.08	C	2.47
55.83	15	1.68	C	2.37
55.72	15	3.08	B	2.14
55.72	15	7.03	B	1.96
55.72	7	7.03	B	1.97

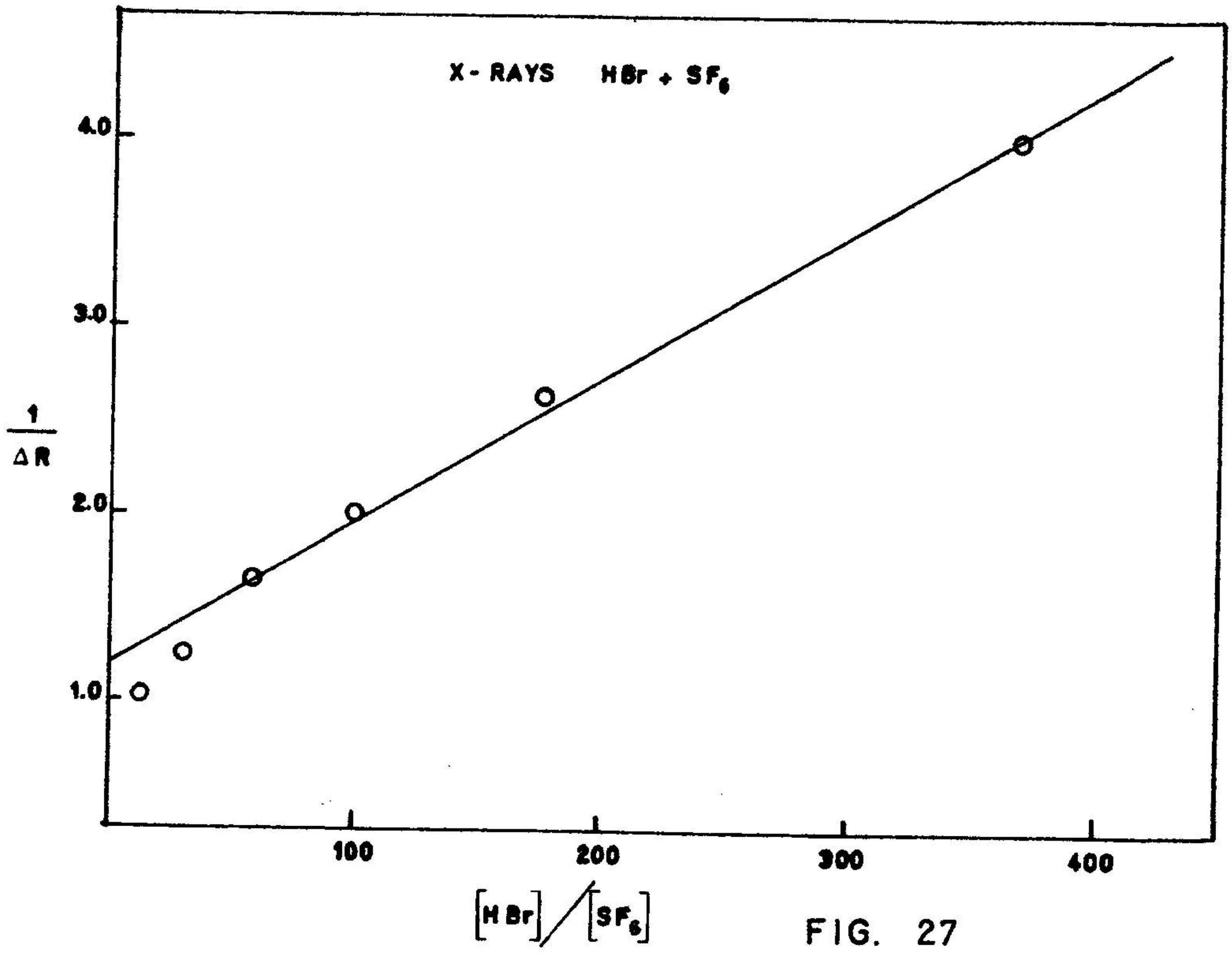


FIG. 27

the hydrogen yield in the case of hydrogen bromide than in hydrogen chloride.

3.12 THE EFFECT OF AN APPLIED ELECTRICAL FIELD ON THE γ-RADIOLYSIS OF HYDROGEN CHLORIDE AND HYDROGEN BROMIDE.

The cells used in this investigation are shown in fig. 10. They were filled with the desired amount of hydrogen chloride or hydrogen bromide separately, and as soon as they were placed in the irradiator, the saturation ionization currents were obtained. This was achieved by measuring ionization current with applied voltages in intervals of 500 volts at first and smaller intervals after 3000 volts. This took about 2 minutes. The applied voltage required was then set and the radiolysis carried out for 4 to 8 hours. At the end the ionization currents against voltage were rechecked. After this the cells were analyzed for hydrogen to obtain ion-pair yields.

The results are shown in tables 20 and 21. Plots of (a) ion pair yield of hydrogen against applied voltages and (b) ionization currents against applied voltages are demonstrated for hydrogen chloride and hydrogen bromide in figs. 28 and 29 respectively.

TABLE 20

P_{HCl} cm Hg	Applied Field V/cm/torr	Ion Pairs 10^{-17}	H_2 yield molecules x 10^{-17}	$(M/N)_{-HCl}$	$G_{(H_2)}$
26.80	0	3.42	7.45	4.18	8.4
77.20	0	2.67	5.47	4.10	8.3
77.20	0.87	2.79	5.98	4.29	8.7
77.20	1.30	3.18	7.08	4.46	9.1
77.20	1.73	2.49	5.12	4.10	8.3
77.20	1.73	2.47	5.21	4.22	8.5
77.20	2.16	2.52	5.60	4.46	9.1
77.20	2.16	2.40	5.04	4.20	8.4
26.80	2.50	2.90	6.27	4.32	8.7
26.80	3.74	3.51	7.74	4.40	8.9
26.80	4.97	2.54	5.32	4.19	8.4
26.80	4.97	2.56	5.47	4.27	8.6

TABLE 21

P_{HBr} cm Hg.	Applied Field V/cm/torr	Ion Pairs 10^{-17}	H_2 yield molecules x 10^{-17}	$(M/N)_{-HBr}$
22.3	-	1.94	4.51	4.65
22.3	-	1.86	4.29	4.62
24.5	-	2.26	5.34	4.74
15.3	0.70	2.08	4.84	4.65
15.3	1.60	2.16	4.97	4.60
22.3	2.01	1.96	4.60	4.64
22.3	4.02	2.31	5.15	4.73
24.5	5.36	2.32	6.13	5.28
24.5	5.36	2.33	6.10	5.26
22.3	5.58	1.50	4.06	5.42
22.2	6.43	1.50	4.65	6.20

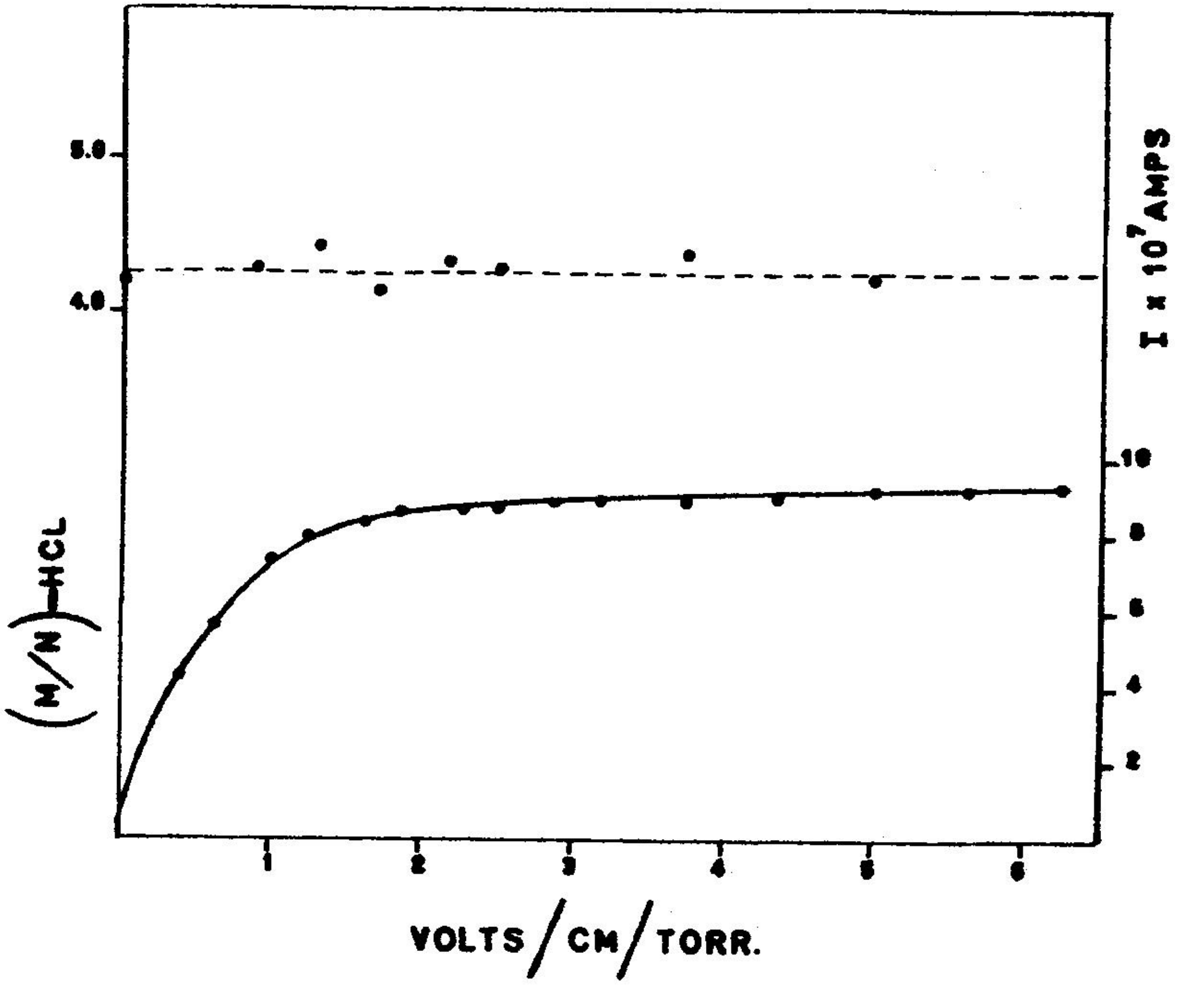
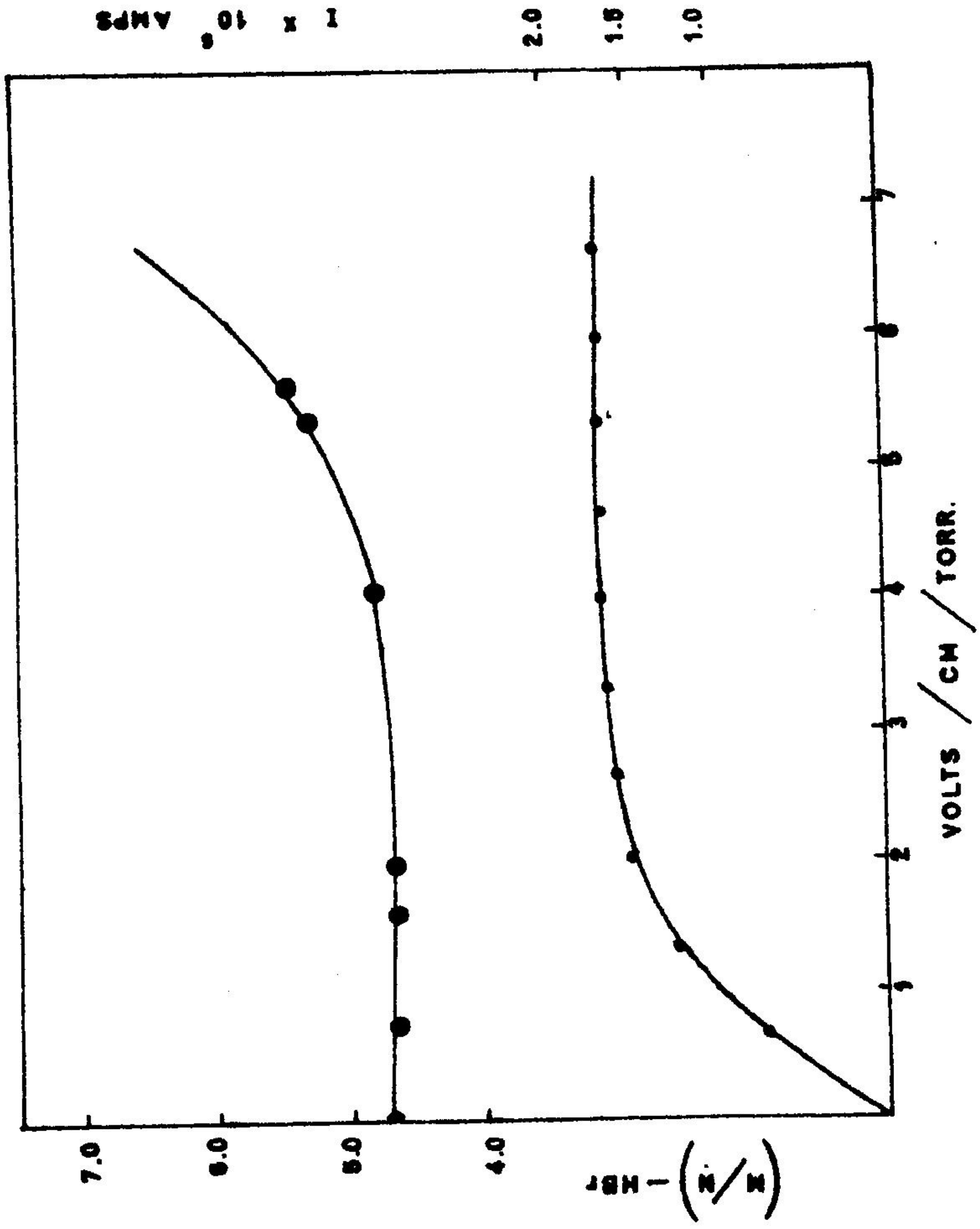

5.0
4.0
$\left(M/N\right)$—HCL
I x 10^{7} AMPS
10
8
6
4
2
1
2
3
4
5
6
VOLTS/CM/TORR.

FIG. 28


I x 10^{6} AMPS
2.0
1.5
1.0
7.0
6.0
5.0
4.0
(M/Ṁ) – HBr
1
2
3
4
5
6
7
VOLTS /CM /TORR.

SECTION IV

DISCUSSION OF THE HYDROGEN CHLORIDE RESULTS

4.1 RADIOLYSIS OF PURE HYDROGEN CHLORIDE GAS

In the introductory section the similarity of mass spectrometric studies to radiation chemistry was pointed out. Therefore, in considering the possible ionic reactions which are likely to occur in irradiated hydrogen chloride, it would be worthwhile to review briefly the mass spectral data on hydrogen chloride.

When hydrogen chloride is subjected to electrons of 150 eV impact energy the principal ions observed are HCl^+, HCl^{++}, Cl^+, Cl^{++} and H^+(51). The approximate relative abundance of the first four ions are estimated to be 100:11:10:3. The parent ion (HCl^+) is predominant in the mass spectrum and should also be the predominant primary ionic species formed in the radiolysis of gaseous hydrogen chloride:

$$HCl \rightsquigarrow HCl^+ + e \qquad (1)$$

Since the ionization potentials of Cl and H (12.96 and 13.60 eV respectively)(52) are slightly higher than that of the HCl molecule (12.74 eV)(53), the ions Cl^+ and H^+ should rapidly undergo the following charge transfer processes at high hydrogen chloride pressures.

$$Cl^+ + HCl \longrightarrow Cl + HCl^+ \quad \Delta H = -0.22\ eV \qquad (2)$$

$$H^+ + HCl \longrightarrow H + HCl^+ \quad \Delta H = -0.86\ eV \qquad (3)$$

The doubly charged HCl^{++} and Cl^{++} ions, because of the much larger values of second ionization potentials (e.g. second I.P. of Cl=23.8 eV(52)), would be capable of far more highly exothermic charge transfer processes with hydrogen chloride molecules. These processes (given below) may lead to excitation and dissociation of the product ion(54).

$$Cl^{++} + HCl \longrightarrow Cl^+ + Cl + H^+ \quad \Delta H = -5.7\ eV \qquad (4)$$

$$Cl^{++} + HCl \longrightarrow Cl^+ + Cl + H \quad \Delta H = -6.3\ eV \qquad (5)$$

$$HCl^{++} + HCl \longrightarrow H^+ + Cl + HCl^+ \qquad (6)$$

These reactions would obviously be followed by reactions (2) and (3). The overall stoichiometry for the primary ionization processes can therefore be represented as follows

$$(1 + x)HCl \longrightarrow HCl^+ + e + xH + xCl \qquad (7)$$

The value of x would obviously depend on the ion distribution in the radiolysis and on the fraction of energetic charge transfers leading to dissociation. If it is assumed that every charge transfer of HCl^{++} and Cl^{++} leads to dissociation, a value for x (0.26) can be estimated using the ion distribution obtained in the mass spectral data.

Before considering the possible reactions which the species HCl^+, e, H and Cl can undergo, the results of the experiments with scavengers will be discussed.

4.2 THE SCAVENGING EFFECTS OF CHLORINE, BROMINE AND SULPHUR HEXAFLUORIDE ON THE RADIOLYSIS OF GASEOUS HYDROGEN CHLORIDE.

It is quite clear from the results, that the three scavengers used, decrease appreciably the hydrogen yield in the radiolysis of gaseous hydrogen chloride. However, it is obvious (from the plateaux in figs. 19 and 22) that not all the hydrogen yield is being scavenged. This means that the scavengers must be competing with the hydrogen chloride for some species H' which can eventually lead to hydrogen formation. There must also be another species H^* which accounts for the unscavengeable yield, and for which the scavengers cannot compete. On this basis the following competitions can be envisaged

$$H' + HCl \longrightarrow H_2 + Cl \qquad (8)$$

$$H' + S \longrightarrow \text{products other than } H_2 \qquad (9)$$

$$H^* + HCl \longrightarrow H_2 + Cl \qquad (10)$$

$$H^{*} + S \longrightarrow \text{products other than } H_2 \qquad (11)$$

(S denotes scavenger)

Now if the species H^{*} is a 'hot' hydrogen atom reaction (11) will be unable to compete with reaction (10) at the scavenger concentrations used in these experiments. Reaction (9) must then be responsible for the reduction of hydrogen yields.

A summary of the results is shown in table 22 assuming the competitions depicted above. It can be seen that both k_8/k_9 and $G_{H\cdot}$ vary from one scavenger to the next.

Table 22

Scavenger	$G_{H\cdot}$	G_{H^*}	k_8/k_9	
			Radiolysis	H-atom
Cl_2	6.75	1.55	3.80×10^{-3}	10.7×10^{-3}(55)
Br_2	5.65	2.65	1.96×10^{-4}	6.5×10^{-3}(56)
SF_6	3.80	4.50	$<2 \times 10^{-4}$	>1

The last two columns in table 22 permit a comparison of the values of k_8/k_9 obtained from radiolysis and from conventional studies in which $H\cdot$ is a thermal hydrogen atom. The disagreement in the two sets of ratios indicates that the species H^* is not a thermal hydrogen atom.

Since it is known that sulphur hexafluoride is an extremely good scavenger for thermal electrons(57) and that it will not react with thermal H atoms at the sulphur hexafluoride concentrations used(58), it can be concluded that the G_{H^*} value obtained with sulphur hexafluoride should be identified with G_e. A value of 3.8 (estimated from the plateau in fig. 22) is in good agreement with 4.0 calculated from the W value for hydrogen chloride (24.8 eV).

Bromine reacts rapidly with thermal electrons as well as thermal hydrogen atoms and therefore the G_{H^*} (2.65) value obtained with bromine can be considered as being due entirely to processes not involving either thermal electrons or thermal hydrogen atoms as precursors. The difference between G_{H^*} for bromine and G_e implies that there is a source of thermal hydrogen atoms whose precursor is not the electron. A yield G_H of 1.85 thermal hydrogen atoms per 100 eV can be calculated from the difference in the G_{H^*} value obtained in the bromine and sulphur hexafluoride results. The k_8/k_9 ratios obtained with chlorine and bromine as scavengers are really functions of $k_{(H+HCl)}/k_{(H+S)}$ and $k_{(e+HCl)}/k_{(e+S)}$, and are best treated as "complex" rate ratios.

It has been suggested(59) that at high doses and high chlorine concentrations, the back reaction

$$H_2 + Cl \longrightarrow HCl + H \tag{12}$$

with an activation energy of 5.48 kcals/mole(60), may cause a slight reduction in the observed hydrogen yield. With bromine, the analogous reaction

$$H_2 + Br \longrightarrow HBr + H \tag{13}$$

is less likely to occur since its activation energy is 19.7 kcals/mole(60). Consequently, the differences in G_H* for these two scavengers may be ascribed to the effects of reaction (12).

The scavengers chlorine, bromine and sulphur hexafluoride, and the hydrogen chloride molecules can all react with electrons thus

$$e + HCl \longrightarrow H + Cl^- \tag{14a}$$

$$e + Cl_2 \longrightarrow Cl + Cl^- \tag{15}$$

$$e + Br_2 \longrightarrow Br + Br^- \tag{16}$$

$$e + SF_6 \longrightarrow SF_6^- \tag{17}$$

The energy thresholds for the above electron capture reactions are 0.65, 1.60, 0.00 and 0.00 eV(61) respectively.

Since the electrons would be expected to thermalize quite rapidly, reaction (15) could hardly compete effectively with reactions (14a&b) unless chlorine molecules were present in very high concentrations. The chlorine must therefore be competing with the HCl molecules for hydrogen atoms which are formed in reactions (14a) or (14b).

$$\begin{tikzcd} e + 2\mathrm{HCl} \arrow[r] & \text{electron-HCl complex} \arrow[d] \\ & \mathrm{H} + \mathrm{Cl}^- \end{tikzcd} \qquad (14b)$$

A study of the effect of chlorine on the radiolysis of a mixture of HCl and SF_6(70) has shown that chlorine reacts with the electron-HCl complex and with thermal hydrogen atoms, but not with thermal electrons. The other two scavengers bromine and sulphur hexafluoride would undoubtedly react with all the thermalized electrons.

It is obvious from the curve in fig. 19 that the accumulation of chlorine during the radiolysis of pure hydrogen chloride would cause a depletion in the radiolytic yield. The results obtained here can therefore be used in an empirical manner to correct those of Vandamme(32), whose radiolyses were all carried out to a high percentage decomposition (>0.3%) relative to this work (<0.04%). If R is the dose rate in eV per unit volume per unit time, then the equation for the rate of formation of hydrogen

TABLE 23

P_{HCl} (cm Hg)	Dose eV (10^{-18})	Dose ion pairs (10^{-17})	H_2 or Cl_2 yield molecules (10^{-17})	H_2 or Cl_2 yield Mole %	$(M/N)_{-HCl}$ Apparent	$(M/N)_{-HCl}$ corrected	$G_{(H_2)}$
Data of this study							
26.80		3.42	7.15	0.035		4.18	8.4
40.45		3.25	6.58	0.022		4.08	8.2
64.05	1.46		1.22	0.002		4.06	8.2
64.05	1.66		1.40	0.002		4.09	8.3
77.20		2.67	5.47	0.009		4.10	8.3
					mean values	4.1 ± 0.1	8.3 ± 0.1
Vandamme's data Ref (32)							
32.48	79.2	31.2	52.0	0.30	3.3	4.3	8.7
32.48	121.0	48.1	77.5	0.44	3.2	4.6	9.2
70.50	214.0	84.9	133.0	0.36	3.1	4.3	8.7
70.50	385.0	152.1	189.0	0.51	2.5	3.7	7.5
70.50	463.0	183.8	227.0	0.60	2.4	3.9	7.9
					mean values	4.1 ± 0.3	8.4 ± 0.6

at any time t, and any given chlorine concentration, is

$$\frac{d(H_2)}{dt} = R \times G(H_2) \left[A \times \left\{ 1 + \frac{k_{H^{\cdot} + Cl_2}(Cl_2)}{k_{H^{\cdot} + HCl}(HCl)} \right\}^{-1} + (1-A) \right]$$

where $G(H_2)$ is the 'true' initial total hydrogen yield and A the proportion of hydrogen formed by $H^{\cdot}$ (6.75/8.3 =0.815). Assuming that the values of $k_{(H^{\cdot}+ HCl)}/k_{(H^{\cdot}+ Cl_2)}$ (3.8×10^{-3}) and of A for the α-particle radiolysis and γ-radiolysis are the same, the above equation can be integrated (appendix II) to give the relationship

$$G(H_2) = \frac{1}{D} \left[\frac{(Cl_2)}{0.185} - 0.208\ (HCl)\ \log_{10} \left\{ 1 + 48.7\ \frac{(Cl_2)}{(HCl)} \right\} \right]$$

where D is the dose. Vandamme's results were corrected using the above equation. Table 23 shows these corrections and displays the close agreement in hydrogen yields between the α-particle and γ-radiolysis of pure hydrogen chloride.

The results with Br_2 and SF_6 reveal that

$$\begin{array}{ccccccc} G_{total} & = & G_e & + & G_H & + & G_H^{*} \\ 8.3 & & 3.8 & & 1.85 & & 2.65 \end{array}$$

and therefore the mechanism for the radiolytic decomposition of hydrogen chloride must include reactions which provide that (1) about 46% of the total yield of hydrogen molecules have thermal electrons as their precursors (2) about 22.3% are formed from "thermal" hydrogen atoms (not originating from electrons) and (3) the remaining 31.7% originate from 'hot' hydrogen atoms.

4.3 THE EFFECT OF BROMINE ON A MIXTURE OF HYDROGEN CHLORIDE AND HYDROGEN BROMIDE.

In pure HCl, $G_{H^{\cdot}}=5.65$ and $G_{H^*}=2.65$ have been obtained using bromine as a scavenger. The value of $k_{H^{\cdot}+HCl}/k_{H^{\cdot}+Br_2}$ $\left(1.96 \times 10^{-4}\right)$ obtained is not in agreement with the value of 8×10^{-4} obtained in the liquid phase radiolysis of hydrogen chloride at -79°C, where the competition has been attributed to a competition for thermal hydrogen atoms. In view of the higher temperature and the fact that the activation energy E_{H+HCl} (3 kcals/mole(62)) is greater than E_{H+Br_2} (0.9 kcals/mole(63)), the gas phase ratio would be expected to be larger if the same species were involved. It is therefore apparent that the bromine is not scavenging the same species in the liquid and gas phase radiolysis. The rate constant ratio for k_{H+HBr}/k_{H+Br_2} at 25°C is known from conventional studies to be 0.12 ± 0.02(64). This value has been made use of, by comparing it with that obtained in the radiolysis of a mixture of hydrogen chloride and hydrogen bromide containing varying percentages of bromine. A value of 6.1×10^{-3} has been obtained for $k_{H'+HBr}/k_{H'+Br_2}$ using the method outlined in section 3.9. This adds to the evidence already accumulated in establishing that the species H' is not a thermal hydrogen atom.

4.4 THE EFFECT OF OTHER PARAMETERS

The effect of scavengers on the radiolysis of hydrogen chloride has been studied under a variety of different conditions. The "plateau yield" obtained with over one percent of added bromine was independent of hydrogen chloride pressure, radiation cell volume, dose and dose rate. It was also unaffected by coating the irradiation cells with colloidal graphite. These studies were useful in establishing that the plateau was not due to contributions from heterogeneous processes. The rate at which reactive intermediates diffuse to the walls should be inversely proportional to the pressure of hydrogen chloride (P) and the square of the radius of the irradiation cell (r^2); however the rate of homogeneous combination of the same species should be proportional to the dose rate (I). The value of IPr^2 (which should be a measure of the heterogeneous process) varied in these experiments from 1.3×10^{15} to 1.7×10^{17} during which the plateau remained the same within experimental error. The hydrogen produced in the bromine concentration range corresponding to the plateau may therefore be attributed to a homogeneous process involving the species H^* for which the bromine does not compete effectively.

4.5 APPLIED ELECTRIC FIELD RESULTS

This study was carried out in the hope of obtaining information on the fate of the ions produced during radiolysis. Since ions would be collected on application of an applied electric field, the use of this technique should interfere with the ion-recombination reactions.

In the absence of an electric field it would be expected that the HCl^+ ion would either undergo ion recombination with the electron or some other negative ion thus

$$HCl^+ + e \rightarrow HCl^* \rightarrow H^* + Cl \qquad (18)$$

$$HCl^+ + Cl^- \rightarrow H + 2Cl \qquad (19)$$

or else react with the neutral hydrogen chloride molecule as follows

$$HCl^+ + HCl \rightarrow H_2Cl^+ + Cl \qquad (20)$$

Assuming an ion recombination coefficient of 10^{-6} cc/ion sec(68) and the rate of ion formation to be 10^{11} ions/cc /sec in these experiments, the steady state approximation would give a concentration of 10^9 ions/cc and hence the calculated lifetime of the HCl^+ ion would be about 10^{-3} sec. For the ion molecule reaction (20) Schissler and Stevenson(65) have found the specific rate constant to be 4×10^{-10} cc/molecule sec. At a hydrogen chloride concentration of about 10^{19} molecules/cc (in this study) the lifetime of the HCl^+ ion is about 10^{-10} sec. Hence the ion molecule reaction will undoubtedly be responsible for the removal of HCl^+ ions. The H_2Cl^+ ion would be the principal positive ion collected at the cathode on application of an electric field.

The scavenger studies have demonstrated the importance of electrons as a precursor to hydrogen formation in the radiolysis of hydrogen chloride. These electrons produced from the initial ionization process (1) should rapidly become thermalized and eventually disappear by any of the three following processes: ambipolar diffusion to the walls of the vessel, ion-electron recombination ($H_2Cl^+ + e$) and attachment to a neutral hydrogen chloride molecule to form a negative ion.

The first order decay constant for electron-ion loss by ambipolar diffusion is given by D/Λ^2 where D is the ambipolar diffusion coefficient and Λ is a length characteristic of the vessel geometry. A typical value of D (0.09 cm^2/sec at 1 atm.)(66) and Λ (>1cm) for the system used, lead to $D/\Lambda^2 = 70/P$ mm per sec. This gives a diffusional loss time of at least 1 sec in this study.

The ion electron recombination has already been discussed where the estimated lifetime of the electron for this process is about 10^{-3} sec.

The electrons will lose their energy initially in reactions (21) and (22) viz:

$$e + HCl \longrightarrow H^+ + Cl^- + e \qquad (21)$$

$$e + HCl \longrightarrow HCl^* + e \longrightarrow H^* + Cl + e \qquad (22)$$

and finally to rotational and vibrational excitation of HCl molecules. They may also be captured in one of the following processes

$$e + HCl \longrightarrow H + Cl^- \qquad (23)$$

$$\begin{tikzcd} e + HCl + HCl \arrow[r] & \text{electron-HCl complex} \arrow[d] \\ & H + Cl^-_{(HCl)} \end{tikzcd} \qquad (24)$$

Both reactions (21) and (23) have been observed in the low pressure mass spectrum of hydrogen chloride. The energy thresholds for the dissociative capture process (23) and the ion pair formation reaction (21) are 0.6

and 14.5 eV respectively(67). The ionization current of Cl^- coming from the low energy resonance capture process at its peak was at least one order of magnitude greater than that for the ion pair formation reaction. The collection efficiencies for the Cl^- ion coming from the two reactions (21) and (23) should be the same, and therefore the cross section for the reaction (23) should be much greater than that for reaction (21).

Now the absolute cross section for reaction (23) has been measured by Buchnel'Nikova(46a) to be 3.9×10^{-18} cm^2 at the maximum. Using this and the data for energy loss per collision with hydrogen chloride as summarized by Healey and Read(68), it can be shown by the method of Magee and Burton(69), that only a small fraction (5%) of the subexcitation electrons which have energies in excess of 1.5 eV will be captured prior to thermalization. The excitation process (22) should occur at an energy of at least 4.5 eV. There is no information on the efficiency of this type of process.

Davidow(70) has obtained evidence that the electrons disappear in a termolecular reaction represented above as reaction (24). He estimates that the rate constant of this reaction is approximately 2.1×10^{-32}

cm^6/molecule^{2}sec, from which a mean lifetime for the electron would be of the order of 10^{-8} sec, assuming a concentration of hydrogen chloride molecules of about 10^{19} molecules/cc.

From the foregoing it can be concluded that the ions H_2Cl^+ and Cl^-, and maybe electrons would be collected at the electrodes on application of an electric field.

At a field strength of 10 V/cm/torr, the effective electron energy in HCl is estimated at 0.14 eV (71). This energy is much lower than the threshold energy of reaction (22).

$$e + HCl \longrightarrow HCl^* + e \longrightarrow H^* + Cl + e \qquad (25)$$

which requires an energy of at least 4.5 eV. This means that a reduction of hydrogen yield caused by neutralization of ions at the electrodes should not be compensated for by the above process.

The recent work of Kebarle(73) on ammonia and water in the gas phase near atmospheric pressure has shown that both the NH_4^+ and H_3O^+ ions are heavily clustered. In view of this, it would be expected that the H_2Cl^+ and Cl^- ions would also be heavily clustered. Consequently, in the absence of an electrical field, the occurrence of a non-dissociative combination, viz:

$$H_2Cl^+_{(nHCl)} + Cl^-_{(mHCl)} \longrightarrow (n+m+2)HCl \qquad (26)$$

is not unreasonable. This proposed reaction, whereby no hydrogen is formed, is in agreement with previous evidence obtained from a study of the scavenging effect of chlorine on a mixture of hydrogen chloride and sulphur hexafluoride.(59)

The application of an electrical field during the radiolysis shows no effect on the hydrogen yield in the ion-recombination region. One explanation is that the ions do not react to produce hydrogen, thus justifying the proposed reaction (26). The other explanation is that the clustered H_2Cl^+ ion on being neutralized at the cathode forms hydrogen. Very little is known about reactions taking place at electrodes in gaseous systems and until more is known, the first explanation appears quite reasonable and is in agreement with the experimental results.

4.6 FREE RADICAL REACTIONS

The free radicals produced in the ionic reactions and in the excitation process are mainly the H and Cl radicals. These radicals would be expected to react as follows

$$H + HCl \longrightarrow H_2 + Cl \qquad (27)$$

$$H + Cl \longrightarrow HCl \qquad (28)$$

$$H + H + M \longrightarrow H_2 + M \qquad (29)$$

$$Cl + Cl + M \longrightarrow Cl_2 + M \tag{30}$$

Reaction (27) has an activation energy of about 3 kcals/mole whereas the others (28), (29) and (30) would be expected to have zero activation energy; however, since the radicals H and Cl would be present in very low concentrations the reactions (28) and (29) would be unable to compete with reaction (27). As the products hydrogen and chlorine build up during the radiolysis (e.g. at high doses) the back reactions

$$H + Cl_2 \longrightarrow HCl + Cl \tag{31}$$

$$H_2 + Cl \longrightarrow HCl + H \tag{32}$$

can be expected to interfere with the hydrogen yield. Their activation energies are 3.0 kcals/mole and 5.48 kcals/mole, respectively.

In the stoichiometric equation

$$(1+x)HCl \longrightarrow HCl^+ + e + xH + xCl \tag{7}$$

an estimated maximum value of x was 0.26. Since W for hydrogen chloride is 24.8 eV, a contribution of up to 1.04 G units of H and Cl atoms can be expected from the ionization processes. The yields of H and H^* from reaction (7) may vary between 0 and 1.04, depending on the value of x.

With respect to the unscavengeable hydrogen yield, this must be coming from processes such as

$$e + HCl \longrightarrow HCl^* + e \longrightarrow H^* + Cl + e \tag{33}$$

$$H^* + HCl \longrightarrow H_2 + Cl \tag{34}$$

It can be postulated that some of the hot hydrogen atoms may be thermalizing before reaction. Very little is known about this type of phenomenon.

4.7 PROPOSED MECHANISM FOR THE RADIOLYTIC DECOMPOSITION OF HYDROGEN CHLORIDE.

Ionization

$$(1+x)HCl \longrightarrow HCl^+ + e + xH + xCl \tag{1}$$

$$HCl^+ + HCl \longrightarrow H_2Cl^+ + Cl \tag{2}$$

$$H_2Cl^+ + nHCl \longrightarrow H_2Cl^+_{(nHCl)} \tag{3}$$

$$\begin{array}{l} e + HCl + HCl \longrightarrow \text{electron-HCl complex} \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\quad H + Cl^-_{(HCl)} \end{array} \tag{4}$$

$$Cl^- + mHCl \longrightarrow Cl^-_{(mHCl)} \tag{5}$$

$$H_2Cl^+_{(nHCl)} + Cl^-_{(mHCl)} \longrightarrow (n+m+2)HCl \tag{6}$$

Excitation

$$e + HCl \longrightarrow HCl^* + e \longrightarrow H^* + Cl + e \tag{7}$$

$$H^* \xrightarrow[\text{deactivation}]{\text{collisional}} H \tag{7a}$$

Radical

$$H + HCl \longrightarrow H_2 + Cl \tag{8}$$

$$H^* + HCl \longrightarrow H_2 + Cl \tag{8a}$$

$$Cl + Cl + M \longrightarrow Cl_2 + M \qquad (9)$$

$G_{HCl^+} = G_{H_2Cl^+} = G_e = 100/24.8 = 4.0$ is in fair agreement with 3.8 obtained from the scavenger studies. Assuming an x value of 0.26, reactions (1) and (4) can account for up to a $G_H = 4.0 + 1.04 = 5.04$, the remainder to make G_H (5.65) may be coming from reaction (7a). The scavengers must be competing with reactions (4) and (8). At high doses the back reactions (10) and (11) become important

$$H + Cl_2 \longrightarrow HCl + Cl \qquad (10)$$

$$H_2 + Cl \longrightarrow HCl + H \qquad (11)$$

SECTION V

DISCUSSION OF HYDROGEN BROMIDE RESULTS

5.1 RADIOLYSIS OF PURE GASEOUS HYDROGEN BROMIDE

When pure gaseous hydrogen bromide is irradiated with Co^{60} gammas, an ion pair yield of 4.7 ± 0.1 (Table 6) for the decomposition is obtained. This is in very good agreement with the work of Hamill *et al.*(31a) on the radiolysis of this gas using X-rays. It appears from the above result that X- and γ-rays produce the same effect on HBr gas. This is to be expected since both of these rays are penetrating electromagnetic radiation only differing in their energies.

Before a mechanism for the decomposition of the gas is attempted, all the pertinent data will be reviewed. The mass spectral data on HBr using electrons of 150 eV impact energy show the occurrence of the ions HBr^+, HBr^{++}, Br^+, and Br^{++} in the relative abundances of 100:7:46:10 (51b). Charge transfer processes (shown below) similar to those postulated for HCl would be expected

$$Br^+ + HBr \longrightarrow HBr^+ + Br \quad \Delta H=-0.11 \text{ eV} \qquad (1)$$

(I.P. of Br=11.8 eV(52) and I.P. of HBr=11.69 eV)

$$H^+ + HBr \longrightarrow HBr^+ + H \quad \Delta H=-1.9 \text{ eV} \qquad (2)$$

$$HBr^{++} + HBr \longrightarrow HBr^+ + H^+ + Br \qquad (3)$$

$$Br^{++} + HBr \longrightarrow Br^{+} + H^{+} + Br \quad \Delta H=-1.8 \text{ eV} \qquad (4)$$

(2nd I.P. of Br=19.2 eV(52))

These equations would lead to an overall stoichiometric equation

$$(1+x)\ HBr \longrightarrow HBr^{+} + e + xH + xBr \qquad (5)$$

where x can be calculated from the distribution of ions given above to be 0.4

5.2 THE SCAVENGING EFFECT OF BROMINE AND SULPHUR HEXAFLUORIDE ON THE RADIOLYSIS OF GASEOUS HYDROGEN BROMIDE

In the radiolysis of gaseous hydrogen bromide, the scavengers bromine and sulphur hexafluoride reduce the hydrogen yield to about the same extent (fig. 25) and also at low scavenger concentrations their effects are almost identical. On comparing the effects of the scavengers on the HBr radiolysis with that on the HCl radiolysis (Tables 22 and 24), it can be seen that the scavengers are much less effective in the case of HBr than in HCl, in both reducing the hydrogen yield and in competing for the reactive species $H^{\cdot}$.

A kinetic analysis similar to that used for the HCl scavenging results, assuming that the scavenger and HBr compete for the reactive species $H^{\cdot}$, gives the results shown in Table 24. From the last two columns of this table it can be observed that the rate constant ratios $k_{H^{\cdot}+HBr}/k_{H^{\cdot}+Br_2}$ and $k_{H^{\cdot}+HBr}/k_{H^{\cdot}+SF_6}$ are not in agreement with the ratios obtained from conventional studies with 'thermal' hydrogen atoms. The scavengers must therefore be scavenging electrons since both bromine and sulphur hexafluoride are good electron scavengers having maximum capture cross sections at zero energy.

Table 24

Scavenger	$G_{H^{\cdot}}$	G_{H^*}	k_{HBr}/k_S	
			radiolysis	H atom
Bromine	2.6	7.0	5.9×10^{-3}	0.12
Sulphur Hexafluoride	2.7	6.9	6.1×10^{-3}	>1

$H^{\cdot}$ and H^* represent the scavengeable and unscavengeable species, respectively.

The scavenging results give a $G_{H^{\cdot}}$ value of 2.7 which should be equal to G_e. However, from the W value for HBr a $G_{ion}=G_e=4.1$ should have been obtained. This means that not all of the electrons are being scavenged as in the case of HCl.

During thermalization the electrons may interact with the HBr molecule as follows

$$e + HBr \longrightarrow H^{+} + Br^{-} + e \tag{6}$$

$$e + HBr \longrightarrow HBr^{*} + e \longrightarrow H^{*} + Br + e \tag{7}$$

$$e + HBr \longrightarrow H + Br^{-} \tag{8}$$

Finally, as in HCl, the three body process

$$\begin{array}{c} e + 2HBr \longrightarrow \text{Electron-HBr complex} \\ \downarrow \\ H + Br^{-}_{(HBr)} \end{array} \tag{9}$$

may occur. The energies required for reactions (6) and (7) are 13.8 eV and at least 3.75 eV, respectively. Reaction (8) has a threshold energy of 0.1 eV with a maximum capture cross section occurring at 0.21 eV, and reaction (9) should take place with thermalized electrons. The cross section for electron capture by an HBr molecule in reaction (8) is 15 times larger than that for the corresponding reaction with HCl and also, capture occurs at a much lower energy. It must therefore play a much greater part in the HBr radiolysis than in the HCl radiolysis. Reaction (6) gives ions which would be measured in the W value, but not be scavengeable by SF_6. Hence it may contribute to the difference between G_e from the scavenger data and $G_{ionization}$ (calculated from W value for HBr).

The rate constant ratio k_{H+HBr}/k_{H+Br_2} is $0.12^{(64)}$ and therefore at 6 mole % bromine concentration only one third of all the thermal hydrogen atoms formed in the system would be scavenged by bromine, in addition to the competition for electrons. Therefore, depending on the yield of thermal H atoms, a difference would be expected in the scavenging effects of the two scavengers. Clearly, from an inspection of fig. 25, this is not the case. Hence the 'thermal' hydrogen atom yield cannot be large and most of the hot hydrogen atoms must be reacting before becoming thermalized.

The H atoms resulting from the stoichiometric equation (7) of the previous section can contribute up to 1.6 G units to the G_H yield.

5.3 APPLIED ELECTRICAL FIELD EFFECT

The effect of an applied elctric field on the radiolysis of gaseous hydrogen bromide is illustrated in fig. 29. Here it can be seen that there is no change in the ion pair yield in the ion recombination region; however, as the field strength increases and before secondary ionization sets in, the ion pair yield increases.

It has already been pointed out that the electrons on slowing down can undergo the following reactions.

$$e + HBr \longrightarrow HBr^{*} + e \longrightarrow H^{*} + Br + e \qquad (7)$$

$$e + HBr \longrightarrow H + Br^{-} \qquad (8)$$

The stoichiometry of reaction (8) is the same as reaction (9), i.e. one H_2 molecule per electron. Reaction (7) can cause the observed effect since a constant applied electric field would be expected to increase the average energy of the electrons in the gas. A fraction of them may attain the threshold energy of reaction (7).

5.4 PROPOSED MECHANISM

The following mechanism has been put forward by Hamill et al. for the radiolytic decomposition of HBr using X-rays.

$$HBr \longrightarrow HBr^{+} + e \qquad (10)$$

$$e + HBr \longrightarrow H + Br^{-} \qquad (8)$$

$$HBr^{+} + Br^{-} \longrightarrow H + 2Br \qquad (11)$$

$$H + HBr \longrightarrow H_2 + Br \qquad (12)$$

$$Br + Br + M \longrightarrow Br_2 + M \qquad (13)$$

This scheme gives an ion pair yield of 4.0. These authors have attributed the yield in excess of 4.0 to a dissociative excitational process which may be depicted as

$$e + HBr \longrightarrow HBr^{*} + e \longrightarrow H^{*} + Br + e \qquad (14)$$

Since their investigation the rate constant for the ion molecule reaction

$$HBr + HBr^{+} \longrightarrow H_2Br^{+} + Br \qquad (15)$$

has been measured by Schissler and Stevenson(65) to be 4.7×10^{-10} cc/molecule sec. On carrying out similar calculations to those for the HCl case, it is seen that reaction (15) is a preferred reaction to reaction (11). Since the applied electric field results show that there is no change in the ion pair yield for either the production of hydrogen or the destruction of HBr molecules in the ion recombination region, reaction (16) below must be proposed as the ion recombination reaction.

$$H_2Br^{+} + Br^{-} \longrightarrow 2HBr \qquad (16)$$

For similar reasons to the HCl case, instead of reaction (16), reaction (17) would be expected.

$$H_2Br^{+}{}_{(nHBr)} + Br^{-}{}_{(mHBr)} \longrightarrow (n+m+2)HBr \qquad (17)$$

With the above modifications to Hamill's mechanism, the proposed mechanism for the radiolytic decomposition of gaseous hydrogen bromide should then be as follows.

Ionic reactions

$$HBr \longrightarrow HBr^{+} + e \qquad (a)$$

$$\begin{array}{l} e + 2HBr \longrightarrow \text{electron-HBr complex} \\ \qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\quad H + Br^{-}{}_{(HBr)} \end{array} \qquad (b)$$

$$e + HBr \longrightarrow H + Br^- \qquad (c)$$

$$HBr + HBr^+ \longrightarrow H_2Br^+ + Br \qquad (d)$$

$$H_2Br^+ + nHBr \longrightarrow H_2Br^+_{(nHBr)} \qquad (e)$$

$$Br^- + mHBr \longrightarrow Br^-_{(mHBr)} \qquad (f)$$

$$H_2Br^+_{(nHBr)} + Br^-_{(mHBr)} \longrightarrow (n+m+2)HBr \qquad (g)$$

Excitation

$$e + HBr \longrightarrow HBr^* + e \longrightarrow H^* + Br + e \qquad (h)$$

Radical reactions

$$H + HBr \longrightarrow H_2 + Br \qquad (i)$$

$$H^* + HBr \longrightarrow H_2 + Br \qquad (j)$$

$$Br + Br + M \longrightarrow Br_2 + M \qquad (k)$$

The scavengers would be competing with reactions (b) and (c) for electrons. Reaction (h) followed by (j) is responsible for the unscavenged hydrogen yield. The energy to form an ion pair in HBr is 24.4 eV. The I.P. of HBr is only 11.67 eV and therefore 12.7 eV is available for excitation, hence there is no reason why the ratio of excitational processes to ionization processes cannot be 3:2, thus accounting for the high unscavengeable yield of hydrogen.

APPENDIX I

Consider the two competitions below

$$H^{\cdot} + HCl \xrightarrow{k_1} H_2 + Cl$$

$$H^{\cdot} + Cl_2 \xrightarrow{k_2} HCl + Cl$$

Let $G_{H^{\cdot}}$ be the yield of $H^{\cdot}$

then in the presence of the scavenger Cl_2

$$G(H_2)_s = \left(\frac{k_1(H^{\cdot})(HCl)}{k_1(H^{\cdot})(HCl)+k_2(H^{\cdot})(Cl_2)} \right) G_{H^{\cdot}}$$

$\therefore$ The reduction in $G_{(H_2)}$ represented as $\Delta G_{(H_2)}$ is given by

$$\Delta G(H_2) = G_{H^{\cdot}} \left(1 - \frac{k_1(H^{\cdot})(HCl)}{k_1(H^{\cdot})(HCl)+k_2(H^{\cdot})(Cl_2)} \right)$$

$$= G_{H^{\cdot}} \left(\frac{k_2(Cl_2)}{k_1(HCl)+k_2(Cl_2)} \right)$$

$$\therefore \quad \frac{1}{\Delta G_{(H_2)}} = \left(1 + \frac{k_1(HCl)}{k_2(Cl_2)} \right) \Big/ G_{H^{\cdot}}$$

APPENDIX II

At any given chlorine concentration the rate of hydrogen formation will be given by the equation

$$\frac{d(H_2)}{dt} = R \times G\ (H_2) \left[A \times \left\{ 1 + \frac{k_{H^{\cdot} + Cl_2}(Cl_2)}{k_{H^{\cdot} + HCl}(HCl)} \right\}^{-1} + B \right]$$

where $G(H_2)$ is the "true" initial total hydrogen yield, A represents the proportion of hydrogen formed by the scavenged species $H^{\cdot}$ ($A = \frac{6.75}{8.3} = 0.815$; $B = 1-A$) and R is the dose rate in eV per unit volume per unit time.

Putting $$\frac{k_{H^{\cdot} + Cl_2}}{k_{H^{\cdot} + HCl}(HCl)} = C = \frac{1000}{3.8\ (HCl)},$$

$(Cl_2) = (H_2) = x$ and assuming that (HCl) is constant, the equation becomes

$$\frac{dx}{dt} = R\ G\ (H_2') \left\{ A(1 + cx)^{-1} + B \right\}$$

$$\therefore \int_0^x \frac{dx}{A(1 + cx)^{-1} + B} = \int_0^t R\ G(H_2)\ dt$$

$$\therefore \int_{o}^{x} \frac{1 + cx}{A + B(1 + cx)} \quad dx = R \; G(H_2) \; t$$

$$\therefore \int_{o}^{x} \frac{1}{(1 + Bcx)} \quad dx + \int_{o}^{x} \frac{cx}{(1 + Bcx)} \quad dx = R \; G(H_2) \; t$$

$$\therefore \left[\frac{1}{Bc} \ln \, (1 + Bcx) + \frac{x}{B} - \frac{1}{B^2c} \ln(1 + Bcx) \right]_{o}^{x} = R \; G(H_2) \; t$$

$$G(H_2)Rt = \frac{x}{B} - \left(\frac{1}{B^2c} - \frac{1}{Bc} \right) \ln \, (1 + Bcx)$$

$$G(H_2) = \frac{1}{D} \left[\frac{(Cl_2 \;)}{0.185} - 0.208 \; (HCl) \; \log_{10} \left\{ 1 + 48.7 \; \frac{(Cl_2)}{(HCl)} \right\} \right]$$

where D is dose.

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