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A STUDY OF RECOIL PROCESSES IN NEUTRON IRRADIATED ORGANIC HALIDE SYSTEMS

by

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INTRODUCTION

Section 1. General considerations

A group of nuclear transformations which has been extensively studied are those which result in chemical effects in the medium in which they occur. The history of the subject dates back to 1934 when SZILARD and CHALMERS (1) irradiated ethyl iodide with neutrons and found that some of the iodine activity could be extracted into water, which showed that the iodine had freed itself from the chemical bond holding it in the organic molecule and had been stabilized in inorganic form. This effect was interpreted by AMALDI et al. (2) as being due to the recoil imparted to the nucleus during the gamma emission of the binding energy of the neutron following its incorporation into the nucleus.

With the rapid development of the subject, several types of nuclear reactions were used for activation, such as (γ,n), $(n,2n)$ or (d,p). But the (n,γ) reaction (usually referred to as radiative neutron capture) has been the most commonly used mode of activation. And the bulk of research work in the field, especially in the earlier stages, has been concerned with liquid and solid organic halides, because the halogens Cl, Br and I proved to be particularly useful for the study of the chemical effects of nuclear transformations. When an atom undergoes a nuclear transformation, it may acquire kinetic energy, energy of electronic excitation or positive charge.

Kinetic energy may be imparted to an atom during emission of particles or gamma quanta by the nucleus, as a consequence of momentum conservation. The acquisition of positive charge occurs through loss of electrons by internal conversion of gamma rays. In an isomeric transition, kinetic energy due to recoil from quantum emission is negligible. But the internal conversion of the gamma rays may lead, via a vacancy cascade, to the build-up of a charge of several units. The distribution of this charge over the entire molecule in which the atom is bonded may lead, through Coulombic repulsion, to fragments with a considerable amount of kinetic energy. In an (n, γ) reaction the atom will generally have high kinetic energy from recoil, but there is a significant probability that this atom may also acquire a charge through the internal conversion of some of the softer components in the gamma cascade.

Formulae have been developed for calculating the total recoil energy for both particle and quantum emission (3-7).

In the (n, γ) reaction with thermal neutrons, the momentum of the incoming neutron is negligible, so that the recoil of the target atom will be due only to gamma emission. The recoil energy is given by (3,5)

$$E_{rec} = \frac{536 E_{\gamma}^{2}}{M} \quad (e.v) \qquad (1)$$

where E_{γ} is the energy of the gamma ray and M the mass of the atom (in a.m.u.)

If it is assumed that the binding energy of the neutron is emitted in a single quantum, then in the case, for example, of the reaction Br^{81} (n,γ) Br^{82} in which the binding energy of the neutron is ~ 7.6 Mev, the recoil energy would be ~ 380 e.v. Generally, binding energies lie in the range 5-10 MeV, so that recoil energies should always be of the order of a few hundred electron volts, far in excess of chemical bond energies. It would then be expected that the chemical bond should be ruptured in 100 per cent of the events.

But the binding energy of the neutron is usually emitted in the form of a cascade of gammas (8) and there is a possibility of mutual cancellation of individual recoil momenta with the net result of a reduced total recoil momentum. So at one stage it was thought that whenever, after nuclear activation, the activated atom was found in the form of the target material, this might have been due to its failure to rupture the chemical bond because of momentum cancellation.

Many investigators tried to calculate the probability of failure of bond rupture because of cancellation effects. COBBLE and BOYD (9) calculated that the percentage of atoms which receive less than 10 ev recoil energy from the Br^{81} (n,γ) Br^{82} reaction will be, approximately, 5,3 and 1.5 if the total energy available for radiation is emitted in 6,4 and 3 equi-energetic gamma rays, respectively. Generally, the problem can be tackled by a random walk in momentum space (10,11) of either equal or unequal steps, on the assumptions that the recoil momenta can be vectorially combined and that the gamma quanta are emitted isotropically (12, 13). If the time between emission of consecutive quanta in a cascade is greater than the time required for the recoiling atom to move about one atomic diameter ($\sim 10^{-14}$ sec), the recoil momentum due to the individual quanta will be effective and bond rupture may occur even in cases where extensive or even complete cancellation of momenta would have occurred if the consecutive quanta had been emitted simultaneously. Thus, for the random walk treatment to be applied, some information is required about the lifetimes of excited nuclear states involved in (n, γ) cascades. It is known from nuclear theory that emissions of the first few quanta involve high energies, are usually electric dipole transitions and therefore involve lifetimes of the order of 10^{-15} or less (14,18) in which case the assumption that the recoil momenta can be vectorially combined will be valid (9).

Another point which should also be considered is what fraction of the recoil energy is available for bond rupture. This problem has been treated by SUESS (19). If the atom M in a molecule MA acquires recoil energy E_r and the molecule does not dissociate instantaneously, this energy will be divided between translational energy of the total mass, E_{tr}, and internal energy of the molecule E_{in}, leading to activation or dissociation. Thus

$$E_r = E_{tr} + E_{in} \qquad (2)$$

In such a case the energy available for bond strain, E_{in}, will be given by

$$E_{in} = E_r - E_{tr} = 536\, E_\gamma^2 \left\{ \frac{1}{M} - \frac{1}{M+A} \right\} = E_r \cdot \frac{A}{M+A} \qquad (3)$$

It is obvious that the fraction of the recoil energy available for bond rupture will become small only when a heavy recoiling atom is bonded to a very light partner, e.g. HBr.

The problem of evaluating the total internal energy increase following the acquisition of recoil momentum by an atom in a molecule and, hence, the net recoil energy which this atom must receive in order to break its chemical bond has been treated by HSIUNG and GORDUS (20) on a classical mechanical basis.

Calculations on the basis of all the above show that, in the (n,γ) activation of halogens, the probability of sufficient cancellation of momentum to result in failure of bond rupture is very low, so that bond rupture might be expected in practically all cases. This effect should be especially evident in gases, particularly under very much reduced pressures, where the chance of recombination due to caging effects is extremely low. WEXLER and DAVIES (21) showed that failure of bond rupture during the neutron activation of bromine in gaseous ethyl bromide (at a pressure of approximately 2×10^{-3} mm Hg) occurred in less than 1 per cent of the events for the reaction Br^{79} (n,γ) Br^{80m}. HORNIG, LEVEY and WILLARD (22) found that in the irradiation of gaseous ethyl iodide with neutrons (at a pressure of 80-mm Hg) about 2-6 per cent of the I^{128}, formed by the I^{127} (n,γ) I^{128} reaction, is found in organic combination. In the presence of iodine at a pressure of 0.2mm Hg, the amount of I^{128} in organic combination was about 1 per cent. LIBBY (23) found that only 4.5 per cent of radio-bromine from the reaction Br^{79} (n,γ) Br^{80m} in a mixture of gaseous ethyl bromine (390 mm Hg) and air (370 mm Hg) enters organic combination. GORDUS and HSIUNG (24) found that the failure of bond rupture in the Br^{79} (n,γ) Br^{80} reaction for various gaseous organic bromides was: CH_3Br - 0.25%, CH_2Br_2 - 0.12%, CF_3Br - 0.11%, CCl_3Br - 0.066%, $CHBr_3$ - 0.05%, C_2H_5Br - 0.33%. (The pressure of the bromides was 10-15 mm Hg and NO, at a pressure of 700 mm Hg had been added, to prevent recombination effects). In a number of other papers (25-27) it was reported that radiohalogens produced by radiative neutron capture in the gas phase are nearly always found in organic form.

In liquids the 'apparent' failure of bond rupture should be higher due to caging effects of neighbouring molecules. Thus, a way to test the true efficiency of bond rupture is to irradiate very dilute solutions of the parent molecule in a diluent which, on reaction with the recoil atom, will form a species that can be separated from the parent molecule before radioactivity measurements. LIBBY (23) irradiated CBr_4, diluted with ethanol, with neutrons and found that the percentage of Br^{80m} in organic combination drops from 28 ± 5% at 1.15 mole % CBr_4 to 0 ± 2% at 0.064 mole %. ADITYA and WILLARD (28) found that only 5% of Br^{80} in organic combination following isomeric transition of Br^{80m} in a solution of 10^{-5} mole fraction of ethyl bromide in pentane could be attributed to failure of bond rupture. These results support those from experiments in the gas phase as to the high efficiency of bond rupture.

But in solids and liquids the observed retentions are in the range of 20-90%. This must be due to re-entry processes by which the recoil atom, after it has broken free from its parent molecule, returns into organic combination.

Several models have been proposed in the attempt to account for the processes responsible for secondary retention.

Section 2. Early models and secondary retention

The first attempt to account for the secondary retention in liquid organic halides was made by LIBBY (3). He assumed that a recoil atom with energy very much in excess of chemical bond energies, after it has freed itself from the parent molecule, loses its energy predominantly by momentum transfer in elastic ('billiard-ball') collisions with atoms of its surroundings. These atoms in the molecules of the environment are regarded as a loosely coupled assembly of hard spheres.

The fractional energy transfer per collision, of the recoil atom resulting from the application of the laws of elastic collisions, is given by

$$E_{tr} = \frac{E_{loss}}{E_{initial}} = \frac{4\ Mm}{(M + m)^2} \cos^2\theta \qquad (4)$$

where M is the mass of the struck atom, m the mass of the recoiling atom and θ is the angle between the direction of the projectile and the line of the centres of the two atoms at the moment of impact. It is obvious that this energy transfer can range from 0 (for a 'glancing' collision) to a maximum of $4Mm/(M+m)$ for a 'head-on' collision.

In a collision, the struck atom can receive enough energy to break the bond holding it to the rest of the molecule. If the impinging recoil atom is left with kinetic energy less than a critical amount necessary to escape from the 'cage' of molecules (29) around the collision site, it has a high probability of combining with the radical left by the struck atom. Now, clearly, the only collisions which can reduce the energy of the recoil atom below the above mentioned critical value are head-on or nearly head-on collisions ($\theta \sim 0°$ or $180°$)with an atom of equal mass, e.g. the case of a recoil bromine atom colliding with another bromine atom in an ethyl bromide molecule. In this case the transfer of energy is nearly complete, the struck atom is projected into the medium and the recoil atom is trapped in the solvent cage with the ethyl radical, thus combining to form a labelled ethyl bromide molecule. For greater values of the collision angle Θ, the amount of energy transferred to the struck atom may be sufficient for bond rupture but, at the same time, the impinging atom would be left with sufficient energy to escape through the wall of surrounding molecules before it had a chance to combine with the organic radical.

A collision, even a head-on one, with a hydrogen atom or even a whole molecule fragment such as $CH_3^\bullet$ would again result in the recoil atom retaining a sufficient amount of energy to allow it to escape from the site of collision without undergoing combination reactions.

The 'billiard-ball' collision model was further extended by MILLER, GRYDER and DODSON (30) to relate the yields of various molecular species, into which the activated atom becomes incorporated, to the composition and properties of the liquids, and by CAPRON and OSHIMA (31) to obtain the total retention as a sum of partial retentions for an infinite number of collisions.

In the form described above, the billiard-ball model would predict that all the activity found in organic combination would be in the form of the parent molecule.

A strong point of criticism about the billiard-ball collision model has been concerned with the assumption that the collisions of the recoil atom with the atoms in the molecules of the environment in the liquid and solid phase may be regarded as elastic ones between hard spheres. There is some justification for this assumption. At kinetic energies of the recoil atom many times greater than the chemical bond energies in the molecules of the environment, the time scale of a collision between the recoil atom and a molecule is very much shorter than the time required for vibrational relaxation, which results in the energy transferred in the collision being inefficiently transmitted by the bonds. Thus the atoms in the molecule can be expected, to some extent, to behave like an assembly of loosely coupled hard spheres. But this is, of course, without taking into account the effect which the 'backing' of adjacent molecules may have on the behaviour of the struck molecule.

But it was observed that organic retention, defined as the fraction of halogen in organic combination, occurred during the neutron irradiation of solutions of iodine in pentane (32) and that dibromo-propanes were formed during the irradiation of propyl-bromide (33). These effects could not be explained by the billiard-ball collision hypothesis. An 'epithermal' reaction scheme was then proposed by FRIEDMAN and LIBBY (33). They suggested that when the energy of the recoil atom is reduced to a level where the time scale of the collision becomes comparable to that of vibrational relaxation, it may transfer energy by colliding *inelastically* with molecules as a whole, the impact is efficiently transmitted by the bonds and this energy is taken up in the intramolecular vibrations. Due to this vibrational excitation, bond rupture may occur and if a carbon-hydrogen bond is broken, the halogen atom would be left in the solvent cage with the radical and would have a definite probability of combining with it to give a stable product in which the halogen would have replaced the hydrogen.

An epithermal reaction mechanism has been suggested by MILLER and DODSON (34). According to them, when the energy of the recoil atom has been reduced to a few ev, it can form an excited complex with an organic molecule of the medium. This complex can then decompose by a number of paths to give a variety of labelled products.

The billiard-ball collision - epithermal collision model has been applied by FRIEDMAN and LIBBY (33) and ROX and LIBBY (35) to the (n,γ) reactions of Br in solid and liquid propyl bromides, in order to account for differences in the yields of the various organic products in the two phases and for the differences in the yields of the various bromine isotopes due to their recoil energies (35,36).

The epithermal collision models account for the fact that the radiobromine atom is found in organic combination other than that of the parent form and that organic retention can occur during the neutron irradiation of solutions of halogens in hydrocarbons.

Both the billiard-ball and epithermal collision mechanisms predict a phase effect.

The LIBBY model was successful in predicting that the yields of products formed by high-energy (hot and epithermal) reactions should be temperature-independent. But it could not correlate all the experimental results in a consistent way. For example, it was found by LEVEY and WILLARD (39) that the organic retention of some alkyl iodides is the same in the liquid phase at room temperature and in the solid phase at - 196°C. Again it was found (38,39) that the radioactive atoms enter inorganic as well as organic combination by high energy processes. Such a possibility is not provided for in the LIBBY model.

Above all, this model cannot explain the 'scavenger effect'. It had long been known that the addition in such systems, prior to irradiation, of small quantities of substances e.g. elemental halogens, which can react readily with thermalized halogen atoms, caused a sharp decrease in the organic retention of radiohalogen (41). The billiard-ball and epithermal collision mechanisms are based on high-energy localized reactions which should be insensitive to low concentrations of scavenger.

WILLARD and co-workers (37-40) studied this 'scavenger effect' in a systematic way and found that at small concentrations of scavenger there is a sharp drop in the retention but this drop becomes less pronounced at higher scavenger concentrations. To explain the scavenger effect, WILLARD (42) suggested another mechanism, the 'brush-heap' or 'random-fragmentation(model. According to this model, an activated halogen atom in a molecule of a liquid halide acquires a few hundred ev of recoil energy, breaks free and starts moving through the medium, until it encounters a solvent molecule.(This happens after it has moved a distance not greater than a molecular diameter). If this were an isolated molecule, the ensuing events would be the same as those described in the billiard-ball model. But in a liquid, the struck molecule is surrounded by a thick wall of other molecules backing it up, so that it can no longer be regarded as an isolated molecule. The result is that the recoil atom dissipates its energy by breaking bonds in a random manner. When its energy has been reduced below bond breaking energies, it will find itself in or very close to a spot of high concentration of radicals and inorganic atoms. Then it will either combine with one of these before it has a chance to diffuse in the environment as a thermal atom or will give a stable labblled species by a 'thermal process' after it has diffused in thermal equilibrium with the medium.

On the basis of this model, the initial sharp drop in retention is attributed to the quenching, by the scavenger, of thermalized recoil halogen atoms, thus inhibiting their recombination by thermal diffusive reactions, with the radicals they produced in their slowing-down process. The less sensitive part of the retention is attributed to high-energy reactions which should include those postulated by the billiard-ball and epithermal collision models. These reactions show an apparent insensitivity to low scavenger concentrations, in the sense that the retention due to them is not affected.

The 'random-fragmentation' model predicts that the relative probability of different types of bond rupture in inelastic collisions affecting the relative numbers and types of molecular fragments will depend on the chemical nature, density and liquid structure of the medium and on the mass (and, possibly, the energy) of the recoil atom. The phase conditions are expected to influence the relative chances of the diffusion of the various fragments away from the thermalized recoil atom.

When it was found that an appreciable organic yield existed in gases, the 'random fragmentation' model was extented to take into account direct displacement reactions (22,26,42-43).

The models described so far have been developed almost entirely in response to results from neutron-irradiated organic halides. They predict hot and thermal processes. But they cannot be applied quantitatively in, for example, predicting retentions in liquid systems.

The use of high-energy tritium atoms in recoil studies in the gas phase has added a great amount of information about the mechanisms of retention and has led to the development of a more sophisticated approach to hot reactions (The 'impact model' of ESTRUP and WOLFGANG and its application to liquid systems by MILMAN).

An account of hot reactions in the gas and liquid phases is given in the next section. Hot reactions have the following characteristics:

(1) They are temperature-independent.

(2) They are unaffected by low concentrations of scavengers.

(3) They are affected by inert additives that remove the kinetic, vibrational or electronic energy of the excited species before it undergoes reactive collisions.

Section 3. Gas and liquid phase Reactions

A. Gas-phase reactions

It has already been said that the neutron activation of halogens in the gas phase proved to be very useful in that it revealed in an unambiguous way the high probability of bond rupture.

Gas-phase studies were given greater attention after interesting results had been obtained by WILLARD and co-workers (22) during the study of the I^{127} (n,γ) I^{128} reaction in CH_4. It was found that about 50% of the I^{128} activity was in the form of CH_3I^{128}. Since 'billiard-ball' collisions cannot be responsible for the retention (the only collisions that can take place are I-C and I-H) and since the 'nest of radicals' hypothesis of the 'random-fragmentation' model cannot hold in this case, a direct displacement reaction of the type : I + $CH_4 \longrightarrow CH_3$ I + H was suggested. Two possible mechanisms for this reaction were proposed, one through a complex I^{128}- CH_4 activated by the recoil energy of the iodine atom and another through the neutralization of the change on I^{128}, acquired by internal conversion (WEXLER and DAVIES (21) have found that 50 per cent of the I^{128} from the reaction I^{127} (n, γ) I^{128} carried positive charge). An attempt to discriminate between the two by adding inert gas moderators to remove the kinetic energy of I^{128} and by adding gases with ionization potentials lower than atomic iodine to remove its charge, showed that both mechanisms are operative (43), that based on the charge being more important than the other.

RACK and GORDUS (44,45) extrapolated the curves of organic yields of the I^{127} (n,γ) I^{128} reaction in CH_4, with the various additives, to unit mole fraction of additive. They found three steps in the reduction of the organic retention, depending on the additive. They concluded that, of the 54% retention in the absence of any additive, 18% is formed by a kinetic-energy dependent mechanism, 25% by a mechanism involving electronically excited I^+ ($^1D_2$) ions and 11% by a mechanism involving I^+ in lower states than I^+ ($^1D_2$) ions.

In the Br^{79} (n, γ) Br^{80} reaction in methane, RACK and GORDUS (46) found that organically combined Br^{80} results mainly from the kinetic energy mechanism.

The study of the reactions of high kinetic energy tritium atoms with gaseous methane (51-54) and the establishment of the fact that these atoms undergo 'hot' reactions (identified by their characteristic features referred to in Section 2) led ESTRUP and WOLFGANG to develop a purely kinetic theory for hot-atom reactions in gaseous media (47, 48-50). An outline of this theory, is given below.

Hot atoms are generated with initial energy E_o in a thermal environment of one or more components. The hot atoms lose energy in collisions, but may react to enter combinations only in an energy range E_2 to E_1. Above E_2 the collisions are too energetic to allow stable combination; E_1 is the minimum amount of energy required for retention - causing hot reactions.

The reaction probability per collision between the hot atom and a molecule of component j is denoted by p_j (E). This quantity is finite in the interval $E_2 > E > E_1$ and zero elsewhere. Then the number of hot reaction products is given by

$$N_{hot} = N_s \sum_j \int_{E_2}^{E_1} f_j p_j(E) n(E) dE \qquad (5)$$

where N_s is the total number of hot atoms available for reaction

f_j is the relative probability of collision with compound j

and n(E)dE is the number of collisions undergone between E + dE and E.

The basic assumptions made, in order to obtain an expression for n(E), are the following:

1. The collisions of the recoil atom can be treated as elastic ones.
2. Eo is sufficiently high, so that the hot atom has made a number of collisions before reaching the upper limit of the retention zone E_2, thus ensuring a statistically well-defined distribution of energies for the hot atoms in the range E_2 to E_1.
3. E_1 is large compared to thermal energies.

Working on the above assumptions, ESTRUP and WOLFGANG found that the activity of a single hot reaction product, Ai, is related to the activity of all products, As, by the expression:

$$\frac{\alpha}{f} \quad \frac{A_i}{A_s} \quad \simeq \quad I_i - \frac{f}{\alpha} K_i \qquad (6)$$

In this expression, α is the average logarithmic energy loss per collision.

$$\alpha = \sum_j f_j \alpha_j \qquad (7)$$

and

$$\alpha_j = 1 - \frac{(M_j - m)^2}{2M_j m} \ln \left| \frac{M_j + m}{M_j - m} \right| \qquad (8)$$

where m is the mass of the hot atom and M_j that of the struck molecule. Eq.(8) is derived from the slowing-down process of neutrons (55,57).

f is a collision probability between the hot atom and molecules capable of giving the product for which A_i is measured. I_i has the form

$$I_i = \int_{E_1}^{E_2} \frac{P_i\,(E)}{E}\, dE \qquad (9)$$

K_i has the form

$$K_i = \int_{E_1}^{E_2} \frac{P_i\,(E)}{E} \left[\int_{E}^{E_2} \frac{P\,(E)}{E}\, dE \right] dE \qquad (10)$$

Eq. (6) can be used to test the theory. A plot of $\alpha A_i \,/\, fA_s$ versus f/α should approximate a straight line (at least for small values of f) and give I_i as intercept.

ESTRUP and WOLFGANG applied this treatment successfully to the reaction of hot tritium atoms in CH_4 with inert gas moderators (47), and to the reaction of hot tritium atoms in methyl fluoride (56). It was also applied successfully to hot bromine and iodine atom systems (44,46).

In recent years a great amount of work on hot tritium reactions has been done aiming at understanding their chemistry, obtaining information about collision efficiencies and investigating the modes in which energy is transferred and reactions are induced.

CROSS and WOLFGANG (58), for example, studied the nature of collisions of high-energy tritium atoms on the basis of LIBBY'S 'billiard-ball' model (which assumes both very weak coupling by valence bonds in the struck molecule and also that the reaction can be represented by an atom-atom collision) and 'epithermal' model (which assumes strong valence bond coupling). Calculations on the billiard-ball model for the reaction $T^{*} + CH_4 \rightarrow H + CH_3T^{*}$ leads to an estimate of its relative cross section as a function of energy. An isotope effect for reaction with CH_4 and with CD_4 was calculated and measured experimentally. It was found that the billiard-ball model is unimportant in the reactions of gas-phase recoil tritium and that reactions occur nearly exclusively at less than 10-20 ev of kinetic energy, by mechanisms involving strong bond coupling.

The failure of the elastic-collision model in the reactions of recoil tritium in CH_4 - D_2 mixtures was reported in a later paper by ROOT and ROWLAND. (59).

The calculation of the energy degradation of hot atoms through α, the average logarithmic energy loss per collision, on the assumption of rigid-sphere collisions on the one hand and the more realistic, 'softer' intermolecular potentials on the other, leads to large differences in the values of α (60). The kinetic theory of ESTRUP and WOLFGANG is not affected, but the interpretation of hot-atom data is shown to depend strongly on which interaction model is used.

ROWLAND and COULTER (94) have performed Monte Carlo calculations on a hypothetical hot tritium system to test the accuracy of the assumptions of the ESTRUP-WOLFGANG theory as they are involved in expressions like the one for the reactivity integral

$$I = \int_{E_1}^{E_2} \frac{P\ (E)}{E}\, dE$$

They consider all non-reacting collisions to be elastic between hard spheres. For a pure reactant system (f = 1), the above equation is exact when $\alpha = 1$, and a very good approximation for other values of α. In moderated systems, the above expression gave a good fit for $P \ll 1$, and for $P \sim 1$ when α_{mod} and α_{react} were similar.

In systems of high reactivity ($P \sim 1$) where α_{mod} and α_{react} were dissimilar, deviations appeared which were due to the fact that the equation used for computing α does not take into account that some of the collisions will lead to combination rather than moderation of the hot atom.

The whole subject of hot-atom chemistry in gas-phase systems, with special emphasis on hot tritium reactions, has been critically discussed by WOLFGANG in a recent review (62) (along with an extensive list of references), while in a shorter article (63) he has given a summary of the field of hot-atom chemistry. In another paper (61), the same author, gives a more complete formulation of the 'impact' model.

B. Liquid-phase reactions

Although the study of high-energy reactions following nuclear activation in the gas-phase, and particularly those in which recoil tritium atoms are involved, has contributed invaluable information towards a better understanding of the nature of high-energy processes, the greater part of the earlier work in the field was done in liquid (and solid) organic halides. The nuclear characteristics of halogens (relatively high neutron capture cross-sections, convenient half-lives) along with the chemical and physical properties of their compounds (easy to study in the gas, liquid and solid states - usually undergoing halogen-halide exchange reactions to a negligible extent) justified the preference.

But investigators in the field were faced with some difficulties in their work with liquid organic halide systems. For example, the interference of even minute amounts of impurities with the effects produced by nuclear activation, through their reaction with thermalized halogen atoms and radicals, created the problem of rigorous purification of the substances used. Again, the host of reactions involved and products formed during the neutron irradiation presented a serious problem in the elucidation of mechanisms, especially in earlier investigations. A very important development towards this end has been the use of gas-chromatography for the separation of products (64-67). This technique has also been used for the purification of target materials. Other problems have been the calculation of initial recoil energies, the dependence of hot-reaction retentions on the energy and any possible isotope effects. The lack of complete gamma cascade schemes for the (n,γ) reactions did not allow a calculation of the spectrum of recoil energies. An exception is the fairly well studied gamma cascade scheme from the reaction Cl^{35} (n,γ) cl,^{36} for which the recoil spectrum has been calculated by the random walk method (13). In a few cases it has been assumed that the average recoil energy of (n,γ) activated I and Br atoms may be taken, on a rough approximation, to be the same as that of Cl^{36}.

A number of studies of hot reactions in the liquid phase have been carried out with the aim of obtaining information about their dependence on the energy of the recoil atom. Two main routes have been followed. Firstly, the comparative study of the effects of the $Br^{80m} \xrightarrow{I.T.} Br^{80}$ reaction on the one hand, and the Br^{79}(n,γ) Br^{80}, Br^{79} (n,γ) Br^{80m} and Br^{81} (n,γ) Br^{82} reactions on the other. The latter give a radioactive atom with a considerable amount of kinetic energy of recoil, while in the former the kinetic energy is negligible but a highly changed species may result because of internal conversion of the soft radiation and consequent Auger cascades.

Neutralization of the charge may then impart a kinetic energy significantly greater than chemical bond energies (97). Alternatively, distribution of the charge over the entire molecule or parts thereof may cause disruption by Coulombic repulsion, resulting in fragments with some kinetic energy. For example, in the case of two atoms 10^{-8} cm apart, each carrying a single electronic charge, the repulsive energy is $e^2/10^{-8} = 2.3 \times 10^{-11}$ ergs (7) or, approximately, 330 Kcal $mole^{-1}$, which is greater than the energies of chemical bonds. Secondly, the comparative study of the reactions (n,γ), (d,p) and (n,2n). The first of these reactions gives an average recoil energy of the order of 100 ev for a case such as Cl^{35} (n,γ) Cl^{36}, while the recoil energy from the other two reactions is of the order of 10^5 ev.

Although the results are sometimes controversial (e.g. 40, 65, 68-80), there is evidence, particularly from the closely similar effects of the (n,γ) and I.T.processes, that generally the initial recoil energy plays a rather unimportant role in hot processes. Due to this evidence, work in the field has not been seriously affected by the lack of detailed information about recoil energy spectra.

Still another problem that should be referred to here is that connected with the relative importance of the charge and kinetic energy in determining the fate of the activated atom. An ion slowed down from high energies by a large number of collisions, in a non-ionic environment, becomes neutralized while still possessing high kinetic energy. This is the case with recoil tritium atoms (52) and would most probably be true for iodine undergoing (d,p) and (n,2n) reactions in liquid organic systems, because the recoil energy is very high. But the results of SCHULER (68-69) from the comparison of the (n,γ) (d,p) and (n,2n) reactions seem to suggest that iodine undergoing the (n,γ) reaction also reacts as an atom, because the same products and distributions are obtained from all three reactions. Generally, it may be expected that a closely packed medium, such as a liquid, will favour neutralization of the charge on the recoil atom.

It has already been said that the scavenger technique made it possible to distinguish at least two kinds of retention - causing mechanism in the liquid phase - thermal diffusive reactions away from the collision site which are sensitive to the radical - scavenging effect of additives and hot localized reactions near the site of collision, which are affected only by very high concentrations of scavenger and which should include LIBBY'S 'billiard-ball' and 'epithermal' reactions.

The scavenger technique has been used to obtain information on the chemistry of the scavenger-insensitive hot reactions, the influence of environmental conditions on their yields and their dependence on the kinetic energy of the recoil atom.

MILMAN and SHAW (79) studied the scavenger effect and their results gave support to the concept of two types of reactions - hot and diffusive. They also showed that the retention of several aliphatic bromides fell linearly when the mole fraction of bromine scavenger was greater than 0.2. This linear form of the scavenger vs. retention graph is consistent with the interpretation that in this region the retention is mainly due to high energy processes. This retention, R_E, should be proportional to $1-N_s$, where N_s is the mole fraction of bromine scavenger. Then, for a given product, the ratio of R_E at $N_s = 0$ (obtained by extrapolation) to that found at $N_s = 0.27$ is $1/(1 - 0.27) = 1.37$. A ratio greater than this would indicate that the formation of that particular product had been interfered with by diffusion-dependent reactions. The use of this relation in the distribution of products from neutron-irradiated C_2H_5Br revealed that the thermal diffusive reactions yielded mainly the parent molecule. On the other hand, it was found that products resulting from fragmented ethyl bromide molecules were formed by hot reactions.

If 'billiard-ball' collisions were the type prevailing at high-energy processes, then R_E would increase in the case of molecules with more bromine atoms. MILMAN and SHAW found that their results did not support the concept of a simple elastic-collision replacement process in irradiated C_2H_5Br, CH_2BrCH_2Br, CH_3CHBr_2, $CH_2BrCHBr_2$, and $CHBr_2CHBr_2$. The whole picture suggested a localized recoil atom - radical recombination before thermal diffusive recombination. Evidence for a 'billiard-ball' mechanism was found in the case of ethylene dibromide.

NESMEYANOV et al (82) found an increase in the retention, in the form of the parent compound, due to hot processes with an increase in the number of Br atoms in the molecule and concluded that at least part of the hot processes give retention in the form of the parent molecule by the 'billiard-ball' mechanism.

Some interesting results were reported by HARRIS (64) in the study of the bromine scavenger effect on the irradiation products of bromomethane. He again found two main types of reactions - hot and diffusive. The latter give retention mainly in the form of the parent molecule and can be eliminated by small amounts of elemental bromine scavenger. This is in agreement with the results of MILMAN and SHAW (79). The former reactions could be divided into two classes: (1) reactions completely insensitive to bromine concentration, no matter how high and (2) reactions slowly suppressed by very high bromine concentrations. This last group of reactions were termed 'hot-spot' diffusive' reactions. In order to distinguish between the products formed by the 'hot' and by the 'hot-spot diffusive' reactions, HARRIS normalized the observed per cent yields of the individual products by multiplying by 1/(1-C), where C is the mole fraction of bromine. (This normalization corrects for the dilution effect of increasing amounts of bromine). The normalized retentions were plotted against the mole percentage of bromine, and three sets of straight lines were obtained.

Set.1: Products with 1 carbon atom but more highly brominated than the parent. Their yields were independent of the bromine concentration. These products are attributed to hot processes (38) involving direct reaction of the recoil atom and a molecule or fragment in its environment.

Set.2: All non-parent products other than those in Set 1. For example, in the case of irradiated dibromomethane, these products consisted of monobromomethane and all of the bromoethanes. They fell on a straight line which extrapolated to zero at 100 mole % of bromine. These were attributed to 'hot-spot diffusive' reactions. They must occur in the hot spot, because they are only slightly suppressed by high concentrations of scavenger (under this condition there is a significant chance of a scavenger concentration, comparable to that of the reacting fragments, being present in the hot-spot zone).

Set.3: Parent products which fell on straight lines and extrapolated to a finite value at 100 mole % bromine. These were attributed as formed by both hot and hot-spot diffusive reactions.

The 'hot' and 'hot-spot diffusive' reactions may be considered as roughly corresponding to the 'primary' and 'secondary' recombination reactions, respectively, as they were discussed by NOYES (85).

Using gas-chromatographic techniques for the analysis of products, SHAW et.al. (67) investigated neutron-irradiated mixtures of ethyl bromide/bromine. Some of their results are summarized below:

(a) Tentative support of LIBBY'S 'billiard-ball' collision model for the retention in the form of the parent compound. If collisions between atoms of similar mass are the most important in the slowing down process of the recoil atom, as postulated by LIBBY, then, in bromoethane/bromine mixtures, if the chance of the recoil atom making 'head-on' collisions with bromine atoms in bromoethane molecules (at a concentration 1-C) and with bromine atoms in bromine molecules (at a concentration 2C) are equal, the retention due to collisions of this kind should be proportional to

$$\frac{(1 - C)}{(1-C)+2C} = \frac{1 - C}{1 + C}$$

which proved to be the case in those mixtures (for $c > 0.1$).

(b) the di- and tribromoethane yields show the expected (1-C) dependence (see also ref. 64). These products result from the reaction of a recoil bromine atom and a single ethyl bromide molecule, forming dibromoethanes or dibromoethyl radicals, which then react with the bromine present to give the tribromoethanes. This sort of reaction was considered by the authors as similar to the LIBBY 'epithermal' reactions.

(c) The tribromoethane retentions show a (1-C) dependence from C = 0.1 to C = 0.3, but at higher C the retentions increase. This was explained on the basis of the possibility of mamy bromine molecules being present in the cage, where the dibromo-radical could react with one of them to form tribromoethane.

(d) The difficulties encountered in a previous work (79) in explaining the scavenging effect of 1,2 - dibromoethylene in connection with a thermal recombination involving many radicals and atoms were eliminated and the quantitative treatment of diffusive processes by ROY et al (84) was given further support.

(e) The (1-C)/(1+C) dependence of the yield of parent bromoethane agrees with the results of HARRIS (83).

(f) There is a specific correlation between the inorganic and organic species from a given capture event, indicating the presence of few radicals and atoms. This is in conflict with the 'random-fragmentation' model.

In another work, MALLINSON, MILLER and SHAW (86) found further confirmation for a 'billiard-ball' mechanism operating in the formation of labelled parent compound, from bromoethane and 1,2-dibromoethane with bromine or hydrogen bromide as scavenger. They again used the normalization procedure. An interesting result in this work was the increase in the parent yield in bromoethane with decrease in temperature. In an attempt to account for this and other observations (28) on hot reaction products being affected by temperature, SHAW (87) calculated the yield of parent compound in neutron irradiated ethyl bromide on a mechanistic model, which regards the reactions following neutron capture in terms of 'thermal spikes' and which can explain retentions in solvent systems in terms of the physical properties of the components.

The experimental results from the (n,γ) reaction in ethyl bromide show clearly the restricted pattern of reactions following neutron capture. In view of this, MILMAN (88) made an attempt to apply the impact model to the reactions of activated halogens in liquid organic halides. By analogy to the reactions of hot hydrogen atoms in gases (48-49), she set up the following scheme (X = halogen, X^* = radiohalogen):

I. Abstraction of H or X atom to form inorganic activity.

$$RCH_2X + X^* \longrightarrow RCHX^\bullet + HX^*$$

$$\text{or } RCH_2^\bullet + XX^*$$

II. Halogen atom displacement to form parent compound

$$RCH_2X + X^* \longrightarrow RCH_2X^* + X$$

III. Displacement of one H atom

$$RCH_2X + X^* \longrightarrow RCHX_2^* + H$$

IV. Displacement of an alky group

$$RCH_2X + X^* \longrightarrow RX^* + CH_2X^\bullet$$

$$\text{or } CH_2XX^* + R^\bullet \quad \text{e.t.c.}$$

V. Radical formation by:

(a) Displacement of 2H atoms giving $RCXX^{*}\cdot$ + H + H or displacement of 2X atoms

(b) Displacement of one X and one H giving $RCHX^{*}\cdot$ + H + X

(c) Displacement of alkyl and H or X giving $CHXX^{*}\cdot$ + R + H or CH_2X^{*} + RX + H

(d) The radicals may suffer further decomposition to give a smaller radical and an alkene.

It can be seen that this scheme does not provide for thermal reactions of the recoil halogen atom with radicals formed in a random way (42) during its cooling-off process.

In the basis of the experimental results for liquid organic halides, MILMAN proceeds to test the consistency of this scheme with these results.

1. <u>Hot displacement reactions to yield molecular species (types II, III, IV)</u>.

The retention of these fractions will be sensitive only to high concentrations of scavenger; its dependence on scavenger concentration will be a function of the number of collisions the hot atom undergoes in a given energy range and on the amount of organic halide molecules available. That means that if the scavenger has the same moderating power and total reaction cross section as the organic halide, the yield of the resulting compound will be proportional to (1-C) (where C is the mole fraction of elemental halogen scavenger). This seems to be the case for the dibromoethane (formed by III) and dibromomethane (formed by IV) fractions found by SHAW et al., (67).

Direct displacement reactions leading to stable molecules should not be greatly influenced by a change of phase from liquid to solid. This was found to be the case in the (n,γ) irradiation of bromine in benzene (89), where only direct hot displacement reactions take place. HOFF and ROWLAND (90) found that the same thing happened during the change of phase in hot tritium reactions in acetone.

2. Hot Displacement reactions to yield radicals (type V)

The formation of radicals may be followed by their immediate or delayed recombination. The I.R.R. (Immediate Recombination Reactions) take place in the original solvent cage, between radicals and atoms produced by the hot reactions. These IRR are thus strictly correlated to the type of hot reaction that created the radicals. They are essentially thermal reactions, their only difference from thermal diffusive reactions lying in the fact that only very high concentrations of scavenger can interfere with them. Radicals escaping IRR will diffuse away from the hot reaction site and undergo 'diffusive' recombination reactions.

The dependence of IRR on scavenger concentration is twofold. Firstly, the probability of formation of an organic radical incorporating the radioactive atom will be proportional to (1-C). Secondly, the fate of this radical will be again a complicated function of C. The result of the two effects is a dependence of the yield of the resulting product on scavenger concentration which is steeper than that characteristic for stable molecules formed directly by mechanisms II, III and IV.

The I.R.R. cannot be significant in the gas phase due to lack of cage effects. They are favoured by the closer packing of the liquid cage. A change of state from liquid to solid should enhance them.

The results obtained by SHAW et al (67) can be rationalized on the basis of the above. E.g. the yield of parent compound and halomethane decrease more steeply than one would have expected if they had been formed only by mechanism I or IV, thus suggesting the contribution of I.R.R. The retention of dibromoethane and methane decreases as (1-C) which again is to be expected if the total contribution of I.R.R. was negligible and they were produced by mechanisms III and IV.

The yield of tribromoethane and methane increases at $C > 0.3$ mole fraction. This can be explained as follows:

Mechanism Va: $CH_3CH_2X + X^* \longrightarrow CH_3CX_2^*\cdot + 2H$

Mechanism Vc: I.R.R. in absence of scavenger: $CH_3CX_2^*\cdot + H \longrightarrow CH_3CHX_2^*$

I.R.R. in presence of scavenger: $CH_3CX_2^*\cdot + X_2 \longrightarrow CH_3CX_3^*$

The decrease in retention as the parent molecule (ethyl bromide) with increasing scavenger concentration is explained on the argument that the hot reaction producing this species (mechanism II) should show a (1-C) dependence, but the interference of I.R.R. producing the same species (mechanism Vb) will cause a steeper independence than (1-C). This is because the production of parent molecule is reduced not only by the larger moderating affect of the increased bromine concentration but also by the chemical effect of bromine on reaction Vb producing dibromoethane instead of the parent monobromoalkane.

$$\mathrm{RCHBr}^{*}\cdot + \mathrm{Br}_2 \longrightarrow \mathrm{RCHBr}_2^{*}$$

(This explanation should be compared with that of ref (67) where the decrease in retention as the parent compound was explained on the basis of LIBBY's model - retentions proportional to (1-C)/(1+C)).

There are a few more interesting points about MILMAN'S postulation of I.R.R. For example, it explains the fact that the yield for n-propyl iodide and sec-propyl iodide is the same. Again, it rationalizes the observation that in reactions in halides, the result is normal bromide from both primary and secondary bromides and secondary iodide from both primary and secondary iodides.

There is also a discussion of thermal diffusive reactions, products falling outside the scope of the impact model and the effect of moderators.

On the basis of present evidence, however, it would be unjustified to come to the definite conclusion that direct hot-atom reactions are the dominant processes in all liquid alkyl halide systems. GEISSLER and WILLARD (102) analysed by gas-chromatography the products of the I^{127} (n,γ) I^{128} and Cl^{37} (N,γ) Cl^{38} reactions in solutions of CH_3I, C_2H_5I, $CH_3(CH_2)CH_2I$ and $CH_3CH_2CH_2Cl$ in pentane and found that the largest fraction of the I^{128} activity was found in the parent form even in the presence of I_2 scavenger. They suggested that the recoil I^{128} atoms react with parent-type R radicals which are formed at high localized concentration in their immediate vicinity by reactions such as $RI + e^- \longrightarrow R + I^-$ and $RI + H \longrightarrow R + HI$ made possible by the internal conversion and Auger cascade occurring at the end of the recoil track. This might be true for the fate of other recoil species.

In another paper (91) MILMAN gave a tentative formulation of the kinetics of hot reactions in liquid media by extending the ESTRUP-WOLFGANG theory. She notes that, in using a simple kinetic treatment of hot reactions in liquids, two serious difficulties arise, namely - (a) the fact that it is impossible to separate the yields resulting from true hot reactions and those resulting from I.R.R. when they give the same product. The effect of I.R.R. should be negligible in the gas-phase where, due to the absence of cage effects, the fragments can diffuse away before they have a chance of reacting.

(b) the fact that the way in which the recoil atom gives up its energy in a condensed environment is not known, i.e., whether the collisions are with isolated molecules or molecules backed up by a wall of neighbouring ones. There is some evidence in work by ROWLAND et. al (92) in support of the isolated nature of collisions.

MILMAN noted that a few more assumptions, in addition to those made by ESTRUP and WOLFGANG, are necessary for the application of their model to hot reactions of bromine in liquids. These assumptions are:

(a) <u>The neutral state of the atom</u>

There is enough evidence to allow the tentative conclusion that (n,γ) activated atoms react in liquids as neutral species. MILMAN (88,91) gives an account of that evidence. She also quotes the evidence of RACK and GORDUS (46). In a study of the differences and similarities of the (n,γ) and isomeric transition processes in n-propyl bromide, KAZANJIAN and LIBBY (93) concluded that recoil bromine in reactions leading to combinations in liquids reacts as atoms.

(b) <u>The energy distribution function</u>

The initial kinetic energy of the hot atoms is assumed to be high enough, so that they undergo a number of collisions such as to have a statistically defined distribution of energies when they reach the upper limit of energies over which they react to enter combination.

This assumption is justified in the case of recoil tritium atoms generated by the reaction He^3 (n,p) H^3. It is assumed that it is justified in the case of recoil bromine atoms. Then the number of moderating non-reactive collisions of the atom between the energies E and E + dE (i.e. the distribution function) will be given by

$$dn = - \frac{dE}{\alpha E} \qquad (11)$$

where α is the average logarithmic energy loss per collision,

$$\alpha = \ln \frac{E \text{ (before coll.)}}{E \text{ (after coll).}} \qquad (12)$$

Since the spectrum of the γ- cascades following neutron capture is not completely known, this can only be an assumption which is taken as justified in the case of bromine.

(c) The energy transfer in non-reactive collisions of the hot atom with molecules of the environment.

In the case of hot atom reactions in gases, α was assumed to be of the form (47b):

$$\alpha_{(M)} = 1 - \frac{(M_1 - M_2)^2}{2M_1M_2} \ln \left| \frac{M_1 + M_2}{M_1 - M_2} \right| \qquad (13)$$

where M_1 the mass of the struck molecule

M_2 the mass of the recoil atom

This form of α ($\alpha_{(M)} = \alpha$ molecular) implies that the hot atom collides with molecules as a whole (cf. Libby's epithermal reactions)

It was found (56) that $\alpha_{(M)}$ was not valid for collisions of tritium atoms with molecules other than noble gases. Another extreme way of evaluating α in gaseous systems would be to consider collisions with individual atoms, weakly coupled to the rest of the molecule (cf. Libby's 'billiard-ball' collisions).

In a case like this, the energy loss per collisions can be calculated using α's for each of the various atoms of the struck molecule (calculated by Eq. (13) where M_1 would be the mass of the struck atom) weighed by a probability factor 'g' for striking that particular atom. This factor 'g' should take into account the relative size of the atoms and the steric configuration of the molecule and is chosen so that:

$$\sum_{\text{all atoms}} g_{\text{atom}} = 1 \qquad (14)$$

Then the fractional energy loss per collision becomes:

$$\alpha_{(A)} = \sum_{\text{all atoms}} g_{\text{atom}} \cdot \alpha_{\text{atom}} \qquad (15)$$

where $\alpha_{(A)} = \alpha$ atomic = fractional energy loss per collision with the weakly coupled atoms of a molecule.

In the case of a condensed medium there is no 'a priori' criterion as to the manner of energy degradation of the recoil atom. What one can do is estimate an order of magnitude for this parameter, using experimental data.

(d) The relative probability of collision with compound j is defined as:

$$f_j = \frac{Mfrj \cdot Sj}{\sum_j Mfrj. \; Sj} \qquad (16)$$

where Mfrj = Mole fraction of compound j

and Sj = Collision cross-section of the hot atom with compound j.

fj is assumed to be independent of energy and temperature.

(e) I.R.R. are taken as negligible.

Using the above assumptions, MILMAN obtained, for the retention due to hot reactions, the equation

$$R_{hot} = I_1 \cdot f_1/\alpha \qquad (17)$$

I_1 was calculated by using the retention corresponding to $f_1 = 1$, that is the retention for zero bromine concentration, which can obtained by the back-extrapolitan of the scavenger curve (79,89).

A very interesting result in this work is that retention curves calculated by using $\alpha_{(M)}$ in the case of hydrocarbons gave a very good fit with the experimentally found points for the retention, suggesting that the moderating collisions of a hot bromine atom in a hydrocarbon are with whole molecules.

In the case of bromoform, the experimental points appear to lie between the two theoretically calculated curves corresponding to $\alpha_{(M)}$ and $\alpha_{(A)}$.

Finally, FILATON, NESMEYANOV and CHEPYZHEV (103) have developed a kinetic treatment for the reactions of hot bromine atoms in liquid binary systems based on some drastic mechanistic assumptions. They found evidence for elastic collisions being responsible for the formation of labelled parent compound. They also found that the yield of products of hydrogen replacement may be explained on the basis of inelastic energy transfer.

The kinetic treatment of recoil bromine atom reactions in ternary systems described in this thesis is an attempt to develop a method for calculating retentions to be expected in the neutron activation of two organic halide/halogen or organic halide/hydrocarbon /halogen mixtures, on the basis of two types of parameters which can be a) determined experimentally from studies in binary mixtures of the halide/halogen or hydrocarbon/halogen type and b) deduced from nuclear and chemical data. It is based on the concept of 'billiard-ball' collisions, as postulated by LIBBY, for the energy degradation of the recoil atoms but makes no other assumption as to the particular mechanisms by which retention occurs. It provides, however, for a discrimination of the type of collisions - atomic or molecular.
The connection of this treatment with that of ESTRUP-WOLFGANG-MILMAN (EWM) (91) is discussed. A less complete formulation of the treatment has appeared in another paper (100).

CHAPTER 1

Section 1. Theoretical Treatment of Recoil Effects in Ternary Liquid Systems

For convenience, we shall describe this treatment in terms of the ternary system $C_2H_5Br/Br_2/C_6H_5Br$. All the systems investigated in the present work were either of the two organic halide/bromine or the halide/hydrocarbon/halogen type. The applicability of the treatment to all these systems will become obvious. Explicit or implicit assumptions are discussed in the notes.

Let us consider the events following the generation of a hot recoil bromine atom in an environment consisting of ethyl bromide, bromine and phenyl bromide, with mole fractions x,y,z, respectively. Since x + y + z = 1, these quantities are set, respectively, equal to the fractional chance that the recoiling bromine atom will collide with a molecule of one of these three substances. (See note (1)). The parameters α , β and γ are defined as being, respectively, the fractional chance that the recoiling bromine atom shall, in a single collision, become organically retained if the collision is with an ethyl bromide molecule, inorganically retained if the collision is with a bromine molecule or organically retained if it is with a phenyl bromide molecule. Thus in the first collision of several recoil bromine atoms we have

1st Collision

Fraction of these atoms becoming organically

retained .... $= \alpha x + \gamma z$

Fraction of these atoms becoming inorganically

retained .... $= \beta y$

Thus, the total fraction, p, of atoms that are elastically scattered is given by

$$p = (1 - \alpha)x + (1 - \beta)y + (1 - \gamma) z$$

$$= (1 - \alpha x - \beta y - \gamma z) \qquad (1)$$

(See note II)

These elastically scattered recoil atoms, having suffered only a fractional reduction of their energy, will undergo subsequent collisions, to each of which the same argument will apply. For instance, in the second collision, the situation will be as follows

2nd Collision

Fraction of atoms becoming organically

retained.................. $= p\,(\alpha x + \gamma z)$

Fractions of atoms becoming inorganically

retained .... $= p.\beta y$

Thus, the total fraction, p', of atoms that are elastically scattered is given by

$$p' = p\left[(1 - \alpha)x + (1 - \beta)y + (1 - \gamma)z\right] = p^2 \qquad (2)$$

and it is seen that the fraction of recoil bromine atoms entering subsequent collisions will be p^2, p^3, p^4, ...p^i,......etc. (see note III)

Now let E_o be the initial energy of the recoil bromine atom, E_1 the energy below which a collision between the recoil atom and a phenyl bromide molecule cannot lead to organic retention, and E_2 the corresponding energy for a collision with an ethyl bromide molecule. Also let m be the average number of collisions required to reduce E_o to E_1 and n the average number of collisions required to reduce E_o to E_2. As it is commonly assumed that recoil atoms, which have escaped capture until they have become thermalised, are eventually scavenged by the reaction

$$^{*}Br + Br_2 \longrightarrow {}^{*}Br \cdot Br + Br^{\bullet}$$

there is no reason for imposing a lower energy limit for the process leading to inorganic retention when the recoil atom collides with a bromine molecule (note IV).

The pattern of events is shown schematically in Fig.1, the symbols being defined in Table I. (note V)

The organic retention between the energy limits E_o and E_1 is the sum of the partial retentions occurring in each one of the m collisions

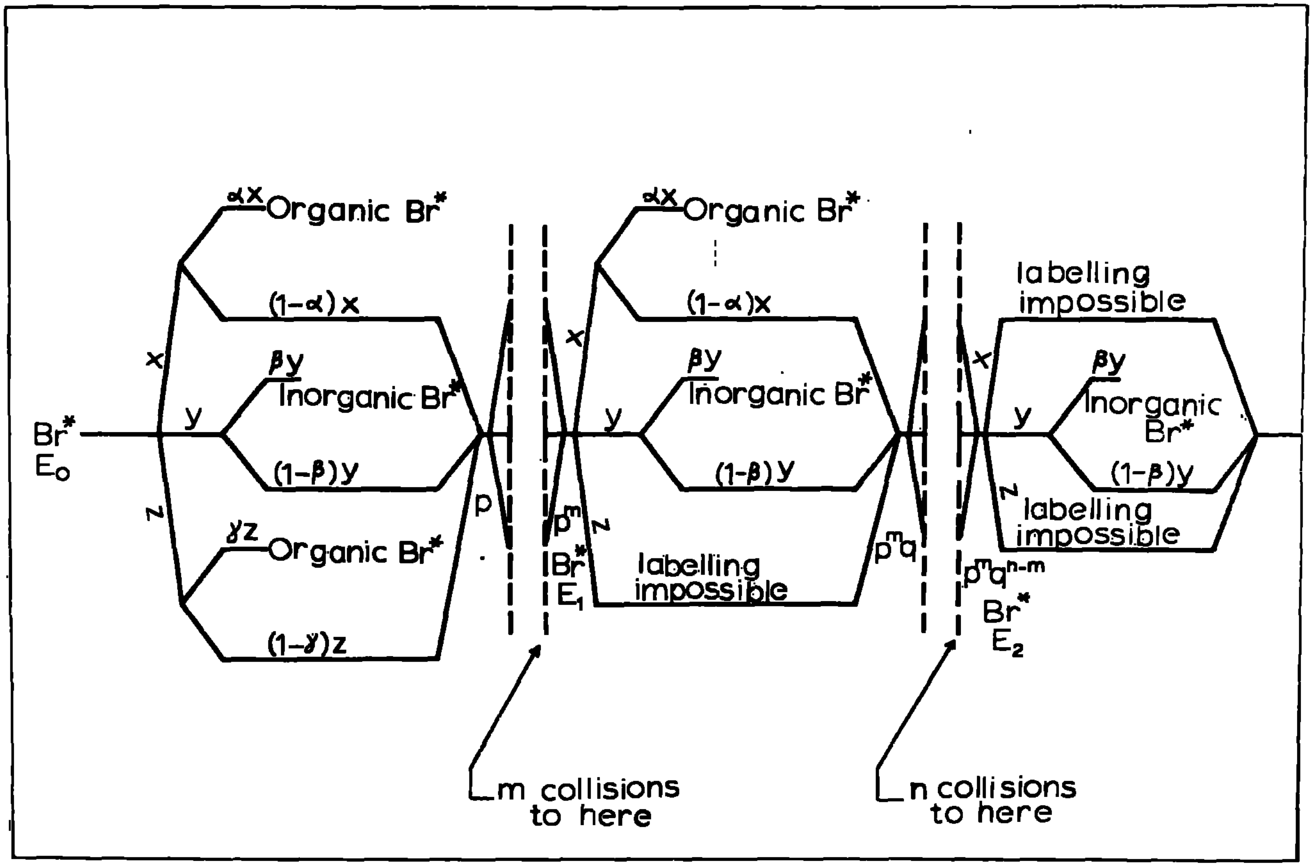


Fig.1

Schematic Representation of Retention Mechanism

TABLE 1

x : mole fraction of C_2H_5Br in the mixture

y : mole fraction of Br_2 in the mixture

z : mole fraction of C_6H_5Br in the mixture

α : fractional chance that a collision between a recoil Br^* atom and a C_2H_5Br molecule will result in producing organically bound Br^*, either in the form of the parent compound or some other organic molecule.

β : fractional chance that a collision between a recoil Br^* atom and a Br_2 molecule will result in producing $Br.Br^*$ (or some other inorganic species)

γ : fractional chance that a collision between a recoil Br^* atom and a C_6H_5Br molecule will result in producing organically bound Br^*, either in the form of the parent compound or some other organic molecule.

E_o: Initial energy of the recoil atom

E_1: Energy of the recoil atom below which it cannot be organically retained on colliding with a molecule of C_6H_5Br

E_2: Energy of the recoil atom below which it cannot be organically retained on colliding with a molecule of C_2H_5Br

p : fraction of recoil atoms which escape being retained in the first collision either organically or inorganically (and are elastically scattered).

q : the equivalent, between the energy limits E_1 and E_2, of p.

m : average number of collisions between the energy limits E_o and E_1.

n : average number of collisions between the energy limits E_o and E_2.

m_1: average number of collisions between E_o and E_1 in the binary system C_6H_5Br/Br_2

m_2: average number of collisions between E_o and E_2 in the binary system C_2H_5Br/Br_2

m_a: mean effective collisional mass of a particular mixture

m_b: mass of the bromine atom

R : fractional retention of radioactive Br atoms in organic form

1st Collision . . . . $R_1 = \alpha x + \gamma z$

2nd Collision . . . . $R_2 = p\,(\alpha x + \gamma z)$

3rd Collision . . . . $R_3 = p^2\,(\alpha x + \gamma z)$

. . . .

. . . .

m th Collision . . . . $R_m = p^{m-1}(\alpha x + \gamma z)$

and consequently,

$$R_{(E_o \text{ to } E_1)} = R_1 + R_2 + R_3 + \ldots\ldots\ldots + R_m$$

$$= (\alpha x + \gamma z) + p\,(\alpha x + \gamma z) + p^2\,(\alpha x + \gamma z) + \ldots + p^{m-1}(\alpha x + \gamma z)$$

and since $1 > p > 0$, this geometric series is convergent and, on summation, it gives

$$R_{(E_o \text{ to } E_1)} = (\alpha x + \gamma z)\,.\,\frac{1 - p^m}{1 - p} \qquad (3)$$

After the m th collision, the fraction of recoil bromine atoms entering the (m + 1)th collision is p^m. On the other hand, after the m th collision the chance of the recoil atom becoming organically retained on colliding with a phenyl bromide molecule is zero. Thus, in the (m + 1)th collision, which is the first between the energy limits E_1 and E_2, the situation is as follows (only ethyl bromide molecules now being involved)

Fraction of recoil atoms becoming organically

retained . . . . $= p^m.\alpha x$

Fraction of recoil atoms becoming inorganically

retained . . . . $= p^m.\beta y$

Thus, the total fraction of atoms that are elastically scattered after the (m + 1)th collision is given by

$$p'' = p^m \left[(1 - \alpha)\, x + (1 - \beta)\, y + z \right]$$

$$= p^m \cdot q$$

where $q = (1 - \alpha x - \beta y)$ (4)

(q is the equivalent of p between the energy limits E_1 and E_2.)

Again the elastically scattered atoms will suffer further collisions and the fraction of them entering subsequent collisions will be $p^m.q$, $p^m.\ q^2$, ..., $p^m.q^{j-m-1}$,.....e.t.c.

The organic retention between the energy limits E_1 and E_2 is again the sum of the partial retentions occurring in each one of (n - m) collisions

(m + 1)th Collision . . . . . $R_1' = p^m.\alpha x$

(m + 2)th Collision . . . . . $R_2' = p^m.q.\alpha x$

(m + 3)th Collision . . . . . $R_3' = p^m.q^2.\alpha x$

. . . .

. . . .

(n - m)th Collision . . . . . $R_{n-m}' = p^m.\ q^{n-m-1}.\alpha x$

and, consequently,

$$R_{(E_1 \text{ to } E_2)} = R_1' + R_2' + R_3' + \ldots\ldots + R_{n-m}'$$

$$= p^m.\alpha x + p^m.\ q.\alpha x + p^m.\ q^2.\alpha x + \ldots + p^m.q^{n-m-1}.\ \alpha x$$

and, since $1 > q > 0$, this geometric series is again convergent, and, on summation, it yields

$$R_{(E_1 \text{ to } E_2)} = \alpha x \cdot p^m \frac{1 - q^{n-m}}{1 - q} \qquad (5)$$

The total organic retention between the energy limits E_o and E_2 is

$$R = R_{(E_o \text{ to } E_1)} + R_{(E_1 \text{ to } E_2)}$$

$$= (\alpha x + \gamma z) \frac{1 - p^m}{1 - q} + \alpha x \cdot p^m \cdot \frac{1 - q^{n-m}}{1 - q}$$

Substituting for p and q from Eqs. (1) and (4) in the denominators of the above equation we get

$$\boxed{R = \frac{\alpha x + \gamma z}{\alpha x + \beta y + \gamma z} \cdot (1 - p^m) + \frac{\alpha x}{\alpha x + \beta y} \cdot p^m \cdot (1 - q^{n-m})} \quad (6)$$

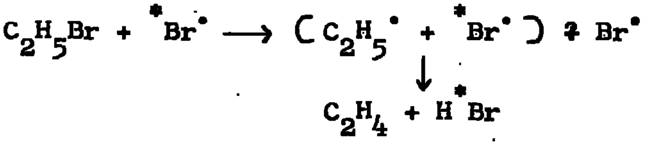
Notes

Note (i)

Setting x,y,z equal to the fractional chance that a recoil bromine atom will collide with an ethyl bromide, bromine and phenyl bromide molecule, respectively, implies the assumption that these three molecules have equal collision cross-sections. Generally, this is not true and is in conflict with MILMAN's definition of the corresponding quantity, fj, in her application of the ESTRUP-WOLFGANG treatment in liquid systems (91). But it can be seen that x, y and z are always accompanied by α, β and γ, respectively, in the mathematical formulation of the theory. So, it has been considered that the corrections for differences in the collision cross-sections are comprised within α, β and γ and hence taken into account where these three parameters are determined experimentally. Should this prove to be incorrect and should the need arise for making corrections, the way to do this is described in APPENDIX A.

Note (ii)

The use of $(1-\alpha)$, $(1-\beta)$ and $(1-\gamma)$ as the fractional chance that the colliding recoil bromine atoms will be elastically scattered is tantamount to making the assumption that a collision with an organic molecule cannot lead to inorganic retention by a mechanism such as



$$\begin{array}{l} C_2H_5Br + \overset{*}{Br}^{\bullet} \longrightarrow [\,C_2H_5^{\bullet} + \overset{*}{Br}^{\bullet}\,] + Br^{\bullet} \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad C_2H_4 + H\overset{*}{Br} \end{array}$$

where the square brackets denote fragments held in a 'solvent cage'. Apart from that, the way α, β and γ are defined and used makes no assumption as to the exact mechanism by which retention occurs.

Note (iii)

The use of the same values of α, β and γ for successive collisions makes the implicit assumption that these parameters are not functions of the energy of the recoil atom. Apart from the fact that they contain a cross-sectional area term, α, β and γ are, by definition, equivalent to the $p_i(E)$ of the E-W treatment. But the use of the same α, β and γ throughout the whole range of energies with the implied assumption that they are independent of the energy of the recoil atom (which is the same assumption made by ROWLAND and COULTER (94)) makes α, β and γ equivalent to integrals of the type

$$\frac{1}{E_o - E_1} \int_{E_1}^{E_o} P_i \, (E)dE$$

Note (iv)

E_1 and E_2, respectively, have been identified with the activation energies of the reactions

$$C_6H_5Br + \overset{*}{Br}^{\bullet} \longrightarrow C_6H_5\overset{*}{Br} + Br^{\bullet}$$

$$C_2H_5Br + \overset{*}{Br}^{\bullet} \longrightarrow C_2H_5\overset{*}{Br} + Br^{\bullet}$$

and E_o with the average recoil energy of bromine atoms, calculated by taking the γ- decay scheme of the (n, γ) reaction into account as far as this is known.

Although the use of constant values of α, β, γ through the range E_o to E_1/E_2 implies the non-existence of distinctive epithermal mechanisms, it is interesting that the lower limits for all the systems in this work(E_1/E_2 range = 5 - 50 Kcal.mole^{-1}, see RESULTS) are very much the same as those derived by LIBBY for the escape of the recoil atom from the solvent cage.

Note (v)

The mechanism of Fig.1 implies that retention can occur even when the energy of the recoil atom is as high as E_o and in this respect it differs from the treatment of E-W and E-W-M. The assumption of a retention-free zone below E_o is necessary in the E-W treatment in order to integrate equation (6) of Ref (47b) and, anyway, it is inherently likely for recoil atoms starting off with an energy of 0.2 MeV. This sort of assumption is not necessary in the treatment developed in this work. On the other hand, bearing in mind that some retention by LIBBY 'billiard-ball' labelling is a possibility, and that recoil bromine atoms probably have an average initial energy of about 100 ev, there seems to be no good reason for supposing that the E-W assumption of a retention-free energy zone is necessary or likely for the systems of this work. After all, E_o is only an average initial energy and, due to the γ cascade processes following (n,γ) activation, recoil bromine atoms with various energies above and below this value will be produced.

Equation (6) is the basic expression, resulting from the mechanism of Fig.1, which will be used in calculating retentions in ternary systems. It is obvious that, in order to use this equation, one has to determine the parameters m and n and the parameters α, β and γ (whereupon p and q become determinate.)

Section 2. Determination of m and n

It is now necessary to define the mass of the 'collision partner' of the recoil bromine atom. Since the behaviour during collisions of liquid systems is not known, the mean effective collisional mass of a ternary mixture, m_a, is defined in three different ways, in view of the possibility of different 'types' of collisions, by one of the equations

$$m_a = \frac{x^{\bullet} M_1 + y^{\bullet} M_2 + z^{\bullet} M_3}{x^{\bullet} n_1 + y^{\bullet} n_2 + z^{\bullet} n_3} \qquad (7a)$$

$$m_a = x^{\bullet} M_1 + y^{\bullet} M_2 + z^{\bullet} M_3 \qquad (7b)$$

$$m_a = \frac{x^{\bullet} M_1 + y^{\bullet} M_2 + z^{\bullet} M_3}{x^{\bullet} 1 + y^{\bullet} n_2 + z^{\bullet} n_3} \qquad (7c)$$

where M_i are the molecular weights of the components and n_i are the numbers of atoms in the molecules of the components. In Eq.(7a) it is assumed that collisions are of an 'atomic' nature for all the organic components. In Eq.(7b) that the collisions are of a 'molecular' nature, again for all the components and Eq.(7c) is a combination of the other two for the case where the collisions are 'atomic' for one of the organic components and 'molecular' for the other.

The way of defining the mean effective atomic collisional mass of a ternary mixture by Eq.(7a) implies the two assumptions, namely -

Assumption 1: All constituent atoms in the molecules of the components are loosely coupled.

Assumption 2: All constituent atoms in the molecules of the components are equally accessible to the recoil atom.

This is definitely an extreme model, which has been tested by others (57,91).

The way of defining the mean effective molecular collisional mass of a ternary mixture by Eq.(7b) implies the assumption that the molecules of all the components have equal collision cross-sections. Should the need for correction arise in this case, the only way of doing it would be by inserting the actual cross-sectional areas of the molecules in the above equation.

All three ways of defining m_a, as well as the correctness of the assumptions underlying them will, at least in part, be tested in the present work by the fit obtained between the theoretically calculated and the experimentally found retention values.

The fractional energy retention per collision by the projectile sphere in an elastic collision between two hard spheres of masses m_1

and m_2 (averaged over all possible angles of collision) is given by (see APPENDIX B)

$$E_{ret}\,(\,av) = \frac{m_1^2 + m_2^2}{(m_1 + m_2)^2} \quad (8)$$

Using m_b (the mass of a recoil bromine atom) and m_a as the collision partners in place of m_1 and m_2 in Eq(8) between, the energy limits E_o and E_1 (that is, for m collisions) we can calculate the parameter m from the equation

$$\left[\frac{m_a^2 + m_b^2}{(m_a + m_b)^2}\right]^m = \frac{E_1}{E_o} \quad (9)$$

and, between, the energy limits E_o and E_2, the parameter n from the equation

$$\left[\frac{m_a^2 + m_b^2}{(m_a + m_b)^2}\right]^n = \frac{E_2}{E_o} \quad (10)$$

provided, of course, we know the values of E_1/E_o and E_2/E_o.

It should be noted here that the values of m and n are not very critically dependent on the value chosen for E_1/E_o (or E_2/E_o) because Eqs.(9) and (10) take the form

$$m\ (\text{or } n) = \frac{\log_{10}\,(E_{1\text{ or }2}/E_o)}{\log_{10}\,(E_{ret}\,(av))} \quad (11)$$

For example, in the case of the $C_2H_5Br/Br_2/C_6H_5Br$ systems, for a value of E_1/E_o of 10^{-2}, m would be 11.8, while for a value of 2×10^{-2} m would be 10, that is a 15 per cent variation for a twofold variation in E_1/E_o.

Another way of calculating m or n, again based on elastic collisions, is by using the <u>average logarithmic energy loss per collision,</u> which is given by

$$\left\{ \ln \frac{E \text{ before}}{E \text{ after}} \right\}_{av} = \xi = 1 - \frac{(m_a - m_b)^2}{2m_a m_b} \ln \left| \frac{m_a + m_b}{m_a - m_b} \right| \quad (12)$$

and is derived from the slowing down of neutrons. Then m and n can be obtained from the equations

$$m = \frac{\ln \left\{ \frac{Eo}{E1} \right\}}{\xi} \qquad n = \frac{\ln \left\{ \frac{Eo}{E2} \right\}}{\xi} \qquad (13)$$

Both ways of calculating m and n, that is by Eqs.(11) and (13) will be tried and the fit between experimental retention values and calculated ones will be tested in both cases.

Since it is a generally accepted fact that inelastic collisions must play some role in the cooling-off process of hot recoil atoms, especially in liquid systems, it would be interesting to calculate the energy degradation of hot recoil atoms by inelastic collisions.

Unfortunately, a mathematical formulation for doing this does not exist. At this stage in the development of the theory, it is expected that the agreement or otherwise between theory and experiment will be a criterion as to whether the assumption of elastic collisions can describe the behaviour of the ternary mixtures. For example, the logic of the formulation of the theory requires that the parameter β, being a property of the bromine molecule, should be the same in all systems. However, the calculation of β from results for any binary mixture (organic component/bromine) depends upon a computation of the number of collisions needed to reduce the energy of the recoil atom from E_o to E_1 or E_2. But the number of collisions so required will depend upon the degree of inelasticity in such collisions: if the probability of transfer of recoil atom kinetic energy to molecular excitation is small (i.e. collisions essentially purely elastic)then the use of one of formulae (7) will give a result of the correct magnitude, whereas, if the same probability is high, the number of collisions calculated by one of formulae (7) will be mugh higher than actually occur. Thus, if discrepant values of β should be found (as they are - see RESULTS) then this might be because

(a) this theoretical treatment is totally inappropriate to liquid systems.

(b) the degree of inelasticity in collisions varies from one organic reagent to another, so that apparent variations in β simply reflect varying degrees of error introduced by the use of equations (7).

(c) differences in the rigidity of the liquid structures from one organic reagent to another render equations (7) similarly of varying accuracy.

(d) the assumption that β is a function solely of a bromine molecule may be erroneous. Three examples of effects which might modify β according to the environment of the bromine molecule are:

(1) The formation of a loose complex between bromine and one of the organic components but not the other.

(2) The possibility of one organic component of a pair being much more or much less prone to produce inorganic retention by reactions similar to the one referred to in Note (ii)

(3) The presence in one of the organic components of a pair of an impurity capable of both trapping radiobromine atoms much more effectively than molecular bromine and regeneration in, for example, reactions as

$$^{*}Br^{\bullet} + A \longrightarrow D$$

$$D + Br_2 \longrightarrow A + (\text{inorganic } \overset{*}{Br})$$

This possibility can, of course, be eliminated by purifying the materials.

Thus it is obvious that at this stage one has to proceed on the assumption of elastic collisions and on the assumption that all the other situations referred to either do not exist or do not occur to any significant extent. It may then be possible to show that failure to fit the theory to experimental results can be correlated with one or another of these effects which would give some information about the behaviour of these systems and indicate the sense in which the equations used in this treatment must be corrected.

Section 3. Analysis of the Properties of Equation (6)

Before proceeding to describe the method for the determination of the parameters α, β and γ, it would now be instructive to examine some of the features of Eq.(6).

Suppose first that one fails to impose a lower energy limit, below which organic retention can no longer occur. Then the retention mechanism of the recoil atom could be represented by the first part of Fig.1, the parameter m would tend to infinity and the second term in Eq(6) would vanish and, since $p < 1$, p^m would tend to zero. Then Eq.(6) takes the form

$$R = \frac{(\alpha x + \gamma z)}{(\alpha x + \beta y + \gamma z)} \qquad (6a)$$

If additionally, one sets $y = o$ in Eq(6a), this condition being equivalent to a scavenger-free system, then $R = 1$. That is, with no lower-energy limit and no scavenger, this equation leads to fractional retentions of unity by hot-atom mechanisms alone, whereas, even with the additional thermal diffusive reaction retentions known to occur as the scavenger concentration is reduced, no organic halide system has ever been observed in which the retention ever approaches unity. It is thus vital to retain the $(1-p^m)$ term, that is, to impose a lower energy limit.

Now, suppose one has the general case where both lower energy limits exist. By setting again $y = o$, Eq.(6) takes the form

$$R = (1 - p^m) + p^m (1 - q^{n-m}) \quad (6b)$$

It can be seen from this equation that the retention observed in the absence of halogen scavenger is closely related to the quantities p^m and q^{n-m}. The second term in Eq.(6b) gives the additional retention occurring in ethyl bromide between the energy limits E_1 and E_2. It should be noted here that, since $E_1-E_2 \ll E_o-E_1$, the contribution to the retention of the second term in Eq.(6b) would generally be expected to be very small compared to that of the first term (Situations can be envisaged, however, in which the second term contribution could become significant, for example, when $\gamma \gg \alpha$).

Ignoring the second term for the present, we see that the factor $(1-p^m)$ sets the upper limit to the retention due to hot reactions in a given ethyl bromide/phenyl bromide mixture in the absence of elemental bromine scavenger.

From Eq.(1) it is quite clear that p is explicitly a function of the mixture composition. The same is true for m, because it depends on m_a. Thus, any change in the mixture composition will affect $(1-p^m)$ both through changes in p and changes in m. But it is to be expected that there will be some mutual compensation in these two effects. This is shown clearly in Table II, where m and $(1-p^m)$ have been calculated for some mixtures (N represents mole fraction)

TABLE II

	Medium	$\mathfrak{m}_a{}^1$	$E_{ret}(av)^2$	m	$(1 - p^m)$ $p = 0.98^3$	 $p = 0.95^3$
1.	Pure C_6H_5Br	13.08	0.758	17.15	0.293	0.585
2.	$N_{C_6H_5Br} = 0.3$ $N_{C_2H_5Br} = 0.7$	13.41	0.754	16.81	0.288	0.578
3.	Pure C_2H_5Br	13.62	0.751	16.58	0.285	0.573
4.	Equimolar $C_2H_5Br/Br_2/$ C_6H_5Br	19.35	0.686	12.59	0.224	0.476
5.	$N_{C_2H_5Br} = 0.57$ $N_{Br_2} = 0.33$ $N_{C_6H_5Br} = 0.10$	20.33	0.676	12.12	0.217	0.463
6.	Equimolar C_6H_5Br/Br_2	22.63	0.656	11.26	0.203	0.439
7.	Equimolar C_2H_5Br/Br_2	26.88	0.623	10.03	0.183	0.402
8.	Pure Br_2	79.92	0.500			

1. m_a's were calculated from Eq. (7a).

2. The energy values used for calculating m's were:

   $E_o = 100$ ev, $E_1 = E_2 = 20$ Kcal. mole^{-1} = 0.8676 ev

3. The values of p are arbitrary (not calculated by means of Eq.(1)) but fairly reasonable, on the basis of the LIBBY mechanism.

Inspection of Table II reveals that as the proportion of the molecule with a greater individual m_a in a mixture increases, the m_a of the mixture will increase, m will decrease and, consequently, $(1 - p^m)$ will decrease (values down each of the two subcolumns of the last column). But a molecule with a greater individual m_a, as defined by Eq.(7a), would generally be expected to have a larger value of α or γ than a molecule with a lower individual m_a. This expectation stems from the fact that a significantly greater individual m_a would result from the presence of more heavier atoms (for example, m_a for C_2H_5Br = 108.97/8 = 13.62 while m_a for $C_2H_3Br_3$ = 266.79/8 = 33.35) which would increase the chance of the recoil atom being retained in elastic collisions.

It is obvious that the retention due to hot reactions for an organic halide when its mole fraction is unity or the retentions in binary mixtures of that halide and elemental halogen should be governed by α, β and γ, since these parameters are, by definition, properties of the molecule, independent of the composition of any mixture in which that molecule might find itself. $(1 - p^m)$ would set the upper limit of the retention due to hot reactions also in a binary mixture, if p were set equal to $(1-\alpha x)$ or $(1 - \gamma z)$ and m calculated for that particular system.

Equation (6) for the binary systems would take the form

For C_2H_5Br/Br_2 $(z = o)$ $$R = \frac{\alpha x}{\alpha x + \beta y} \left(1 - p_1^{m_1} \right) \quad (14)$$

For C_6H_5Br/Br_2 $(x = o)$ $$R = \frac{\gamma z}{\gamma z + \beta y} \left(1 - p_2^{m_2} \right) \quad (15)$$

where p_i, m_i have been used to emphasize the fact that the values of these parameters to be used in binary mixtures will be different from the corresponding values of p and m that would be used in ternary mixtures of these components. Equations (14) and (15) are quite important because they form the basis of a method by which the parameters α, β and γ can be determined experimentally from studies of the retention in binary systems.

Section 4. Method of Determining α, β and γ

On reciprocating Eq.(14) one gets

$$\frac{1}{R} = \frac{1}{1 - p_1^{m_1}} \left(1 + \frac{\beta}{\alpha} \frac{y}{x} \right) \qquad (16)$$

Assuming that $(1-p_1^{m_1})$ is constant, it is seen that a plot of $1/_R$ vs. $y/_x$ would be a straight line with an intercept of

$1/\{1 - p_1^{m_1}\}$ (at $y/_x = 0$) and the slope of which would be given by the relation : slope/intercept = β/α. But, since both p_1 and m_1 vary with the mixture composition, it is clear that $(1 - p_1^{m_1})$ is not constant. Now, let us see what the behaviour of Eq.(16) is when $y \rightarrow 0$. For this system $p_1 = (1 - \alpha x - \beta y)$ and $x + y = 1$. It can be seen that as $y \rightarrow o$, $x \rightarrow 1$ and $p_1 \rightarrow (1 - \alpha)$. If, therefore, only dilute bromine solutions are considered, p_1 will be reasonably constant, since in such solutions x is very much greater than y, so that relatively large variations in y will result in small variations in x.

Thus substituting $(1 - \alpha)$ for p_1, one gets

$$\text{Intercept} = \frac{1}{\left[1 - (1-\alpha)^{m_1}\right]}$$

from which α can be determined and then β can be calculated from the relation

$$\beta = \alpha \times \frac{\text{limiting slope}}{\text{intercept}}$$

A similar treatment for the other binary system (by setting x=o instead of z=o) will give a value of γ and a duplicate value for β.

But there is one point which should be stressed in connection with dilute bromine solutions. At bromine concentrations so low that the scavenging of the mixtures is incomplete, additional retention would be produced due to thermal diffusive reactions. Such additional retention must be discounted in drawing the limiting slope on graphs of $1/_R$ vs. $y/_x$ or $y/_z$.

It is also to be expected that the retentions observed in ternary mixtures at very low bromine concentrations will be higher than the calculated ones due to this same cause.

$\mathfrak{m}_1$ and $\mathfrak{m}_2$ can be calculated by means of Eq.(9), provided that we have values for E_1/E_o and E_2/E_o. The fact that the same ratios will also be used for calculating the values of m in three-component mixtures, thus resulting in a compensation of errors, is an additional reason for which an error in these values is not very important.

Of course, it should always be kept in mind that m_1 and m_2 depend on the mixture composition. But to ensure a fairly constant value of $(1 - p_1^{m_1})$ and $(1 - p_2^{m_2})$, attentions has been confined to dilute bromine solutions. This same limitation will be responsible for a fairly constant value of m_1 and m_2. But m_1 = constant would also mean m_a = constant. Thus, it is evident that the range of bromine concentrations over which the graph of $1/_R$ vs. $y/_x$ or $y/_z$ can be expected to exhibit straight line behaviour will depend very much on how closely the m_a of the mixture in this range agrees with the mass of the recoil bromine atom.

It has been the general practice to obtain a value for the retention due to hot reactions in binary systems by extrapolating the almost linear part of the retention vs. mole fraction of scavenger graph back to zero scavenger concentration. It is quite clear that the value obtained in this way and the $(1-p^m)$ value of this work are not the same.

Section 5. Choice of systems investigated in this work

Let us now summarize the various points, as they were discussed in the previous sections, that influenced the choice of the systems investigated in this work.

(a) The m_a's

It can be seen from Table II that an increase in m_a results in a decrease in E_{ret} (av). This decrease is sharp when m_a is very much smaller than m_b, becomes smoother as m_a approaches m_b, and reaches a minimum for $m_a = m_b$. After that, a further increase in m_a results in a slow increase in E_{ret}(av). This effect is shown in Fig.2. In the region of the sharp decrease in E_{ret}(av), m decreases rapidly and so does $(1 - p^m)$, - see the two subcolumns of the last column in Table II - for constant values of p. But insofar as increases in m_a are caused by increasing numbers of heavy atoms in the molecule, on simple qualitative ides, this increasing m_a would be accompanied by an increase in α (or γ), consequent decrease in p, and consequent increase in $(1-p^m)$. Thus the expected large changes in $(1-p^m)$ may be largely internally compensated.

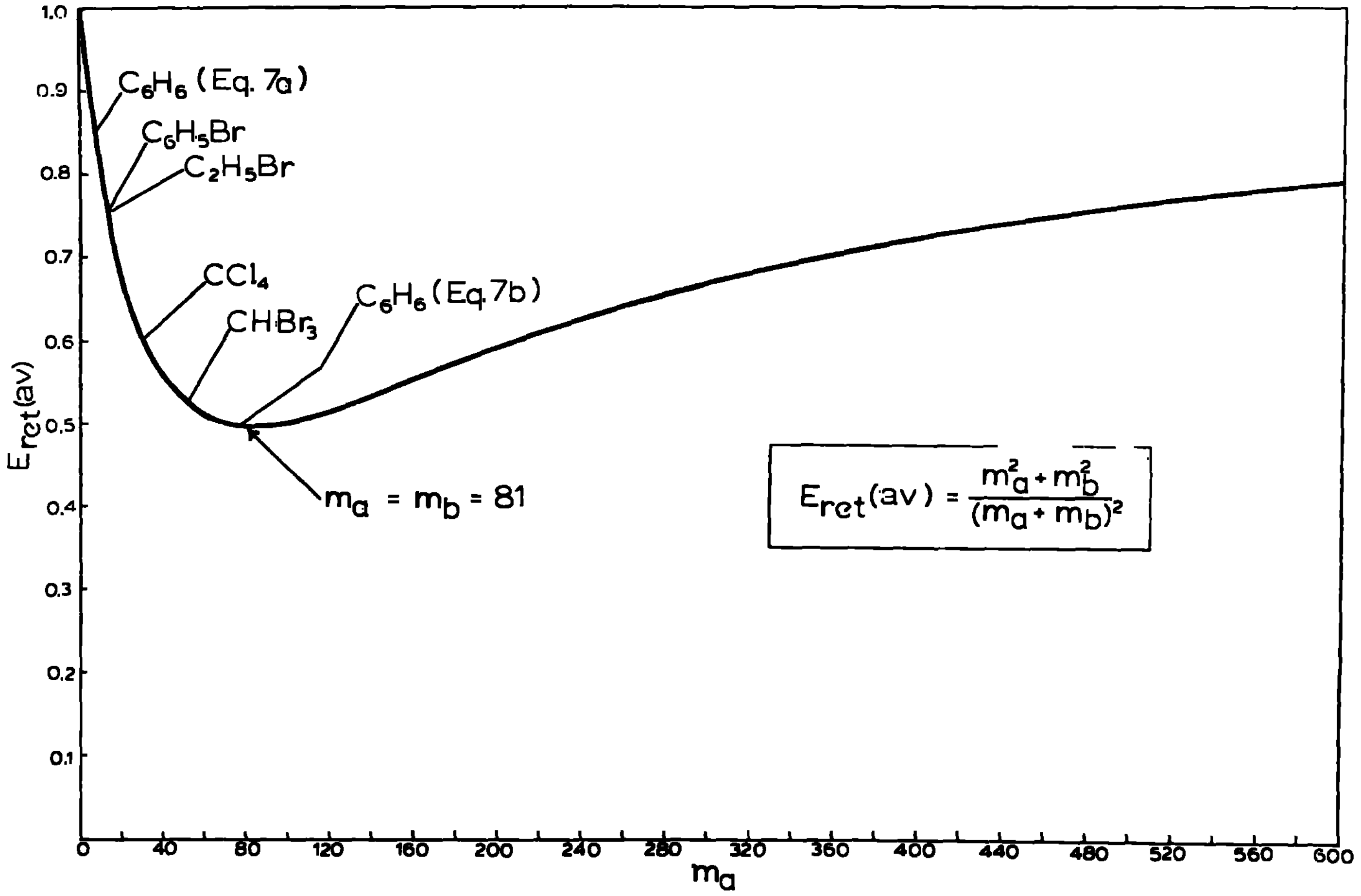

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
$E_{ret}(av)$
0
40
80
120
160
200
240
280
320
360
400
440
480
520
560
600
m_a
C_6H_6 (Eq. 7a)
C_6H_5Br
C_2H_5Br
CCl_4
$CHBr_3$
C_6H_6 (Eq. 7b)
$m_a = m_b = 81$
$E_{ret}(av) = \frac{m_a^2 + m_b^2}{(m_a + m_b)^2}$

Fig.2

Again, in the $1/_R$ vs. $y/_x$ or $y/_z$ graphs, the range of bromine concentrations over which these graphs can be expected to show straight line behaviour depends on how closely the m_a of the particular mixture in this range agrees with the mass of the recoil bromine atom. All the above suggested the investigation of systems in which the individual m_a's would cover the whole range from very small values to values quite close to m_b (m_a's as defined by Eq.(7a)).

(b) The nature of collisions

It had already been reported by others (91) that collisions in halides seem to be more of an 'atomic' nature, while those in hydrocarbons more of a 'molecular' nature. With a view to testing this, the systems investigated in this work included hydrocarbons as well as halides. The definition of m_a by Eqs. (7a,b,c) was also introduced for the same purpose.

Another point that was taken into account was the possibility of differences in the behaviour of the organic compounds in collisions due to their aliphatic or aromatic character.

(c). Retentions in the binary systems

A practical aspect in the choice of systems was the necessity to have as large differences as possible between the retentions of the two organic components used in ternary mixtures, so that their relative influence upon each other would show clearly.

The systems investigated, along with their features in connection with all the above, are listed below:

(1) $C_2H_5Br/Br_2/C_6H_5Br$

(i) Both its organic components are monobromides, with m_a's which are very much the same (defined by Eq.(7a)) and largely different from m_b.

(ii) The retentions in phenyl bromide/bromine solutions are sufficiently higher than in ethyl bromide/bromine ones.

(2) $C_2H_5Br/Br_2/CCl_4$

This treatment was originally developed in response to the results from the above system.

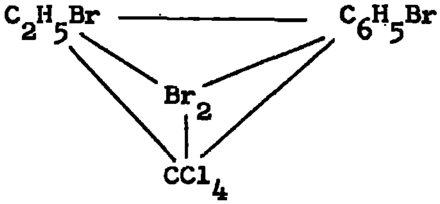
(i) Both its components are halides

(ii) Their m_a's (defined by Eq.(7a) are significantly different. CCl_4 contains four atoms capable of lowering the $E_{ret}(av)$ of the recoil bromine atoms significantly in elastic collisions. Its m_a is about half-way between 0 and m_b.

(iii) The retentions in carbon tetrachloride/bromine mixtures are sufficiently higher than in ethyl bromide/bromine ones.

(3) $C_6H_5Br/Br_2/CCl_4$

This system was investigated because it was the only other possible combination of the substances used in systems (1) and (2). It was thought interesting to test the fit of the treatment by a 'triangle' of systems, as shown below



After that it was decided to investigate 'extreme' cases of m_a's as well as cases where the nature of collisions should be expected to be different. These led to the choice of the next system.

(4) $C_6H_6 - Br_2 - CHBr_3$

(i) The m_a's of the two organic components are vastly different (as defined by Eq.(7a)) and they lie farthest (C_6H_6) and closest ($CHBr_3$) to m_b in Fig.2, thus representing a very unfavourable and a very favourable case, respectively, for energy loss by elastic collisions on the one hand and for straight line behaviour in the $1/_R$ vs. $y/_x$ or $y/_z$ graph on the other. In connection to the above one should add that C_6H_6 contains no heavy atoms whatever, while $CHBr_3$ is rich in heavy atoms which are the same as the recoil atom.

But there is another important feature about C_6H_6. If the collisions of the recoil atom in this substance are 'molecular' rather than 'atomic' in nature, its m_a which should then be defined by Eq. (7b) is 78.11, that is quite close to m_b, this being an extremely favourable situation for both energy degradation of the recoil atom and straight line behaviour in its $1/_R$ vs. $y/_x$ graph.

In addition to that, when m_a for C_6H_6 is taken as 78.11, the m_a's for both the organic components of the above ternary system lie in that region of the graph of Fig.2 where changes in E_{ret} (av) and, consequently, in m are very small. Thus, one would expect $(1-p^m)$ to be mainly influenced by changes in p only, which actually proves to be the case (see Table III).

(ii) One more feature about this system is that E_1 (for C_6H_6) and E_2 for ($CHBr_3$), taken as 50 Kcal. $mole^{-1}$ and 5 Kcal. $mole^{-1}$ (see RESULTS) again represent extreme cases for all the E_1's and E_2's in this work.

(iii) The retentions in benzene/bromine mixtures are sufficiently lower than those in bromoform/bromine ones.

TABLE III

Medium	m_a	$E_{ret}(av)$	m	$(1-p^m)$	
				p = 0.96	p = 0.93
1. Pure $CHBr_3$	50.55	0.525	9.52	0.322	0.499
2. $N_{C_6H_6} = 0.1$ $N_{CHBr_3} = 0.9$	51.15	0.524	5.93	0.215	0.349
3. $N_{C_6H_6} = 0.5$ $N_{CHBr_3} = 0.3$	55.14	0.517	5.81	0.211	0.344
4. $N_{C_6H_6} = 0.1$ $N_{Br_2} = 0.4$ $N_{CHBr_3} = 0.5$	58.27	0.512	5.72	0.208	0.339
5. Equimolar $C_6H_6-Br_2-CHBr_3$	61.34	0.508	5.65	0.206	0.336
6. $N_{C_6H_6} = 0.9$ $N_{CHBr_3} = 0.1$	68.27	0.503	5.57	0.203	0.332
7. $N_{C_6H_6} = 0.5$ $N_{Br_2} = 0.4$ $N_{CHBr_3} = 0.1$	71.26	0.502	5.56	0.203	0.332
8. Pure C_6H_6	78.11	0.500	5.53	0.202	0.330

CHAPTER 2.

Experimental Procedure

Section 1. Materials

Bromine (B.D.H. 'Analar' grade) was used throughout this work without further purification.

Ethyl Bromide (B.D.H. laboratory grade), after one initial distillation, was shaken with concentrated sulphuric acid until no coloration developed in the acid, washed several times with dilute sodium carbonate solution, washed several times with distilled water, dried over anhydrous magnesium sulphate and fractionally distilled four times (in a 37 cm x 2 cm column packed with glass helices), with intermediate dryings over anhydrous magnesium sulphate. In the last distillation the middle 70%, boiling within a 0.2°C range, was retained for use.

Phenyl Bromide (B.D.H. laboratory grade), after one initial distillation, was dried over fused calcium chloride and fractionally distilled four times (in a 30 cm x 2.5 cm column packed with glass helices) with intermediate dryings over fused calcium chloride. In the last distillation the middle 70%, boiling within a 0.5° C range, was retained for use.

Carbon tetrachloride (B.D.H. 'Analar' grade) was treated in exactly the same way as phenyl bromide. In the last distillation, the middle 60%, boiling within a 0.7° C range, was retained for use.

<u>Benzene</u> (B.D.H. 'Analar' grade) was allowed to stand in daylight with elemental bromine for 35-40'. Then the bromine was extracted with aqueous sulphite solution and the benzene was washed several times with distilled water and dried over anhydrous magnesium sulphate. Then it was shaken with successive portions of concentrated sulphuric acid until no coloration developed in the acid, washed several times with dilute aqueous bicarbonate solution, washed several times with distilled water, dried over anhydrous magnesium sulphate and distilled over phosphorous pentoxide (in a 37 cm x 2 cm column packed with glass helices) and the middle 65-70% was retained. This was passed through a column packed with silica gel (chromatographic grade), fractionally distilled in the same column as above (the middle 80% being retained), again passed through the silica gel column and, finally, fractionally distilled as before. The middle 80% (boiling within a 0.5°C range) was retained for use.

<u>Bromoform</u> (Eastman Chemicals'SPECTRO' grade or Hopkin & Williams 'SPECTROSOL') was used without any further purification.

In all cases, great care was taken to exclude the possibility of the substances taking up even traces of water during purification, storage and use.

Special purity tests for these materials were not carried out. The fact that the fractions retained for use distilled within a very small temperature range, the agreement of the retention values for the binary systems with those of other investigators (wherever comparison was possible), the very good reproducibility of results at low bromine concentrations and the very good reproducibility of retention values in the purified substances (in the case of bromides) in the absence of scavenger, were considered as satisfactory criteria for the purity of the materials. Also, the fact that the same substances were used in both the binary and the ternary systems and the fact that the theory is tested in the range of bromine concentrations where any effect of trace impurities is expected to be completely outweighed by the presence of the scavenger (that is, at $N_{Br_2} > 0.1$) were considered as safeguards against the presence of minute amounts of impurities. Table IV shows the reproducibility of retention values for C_2H_5Br, C_6H_5Br and $CHBr_3$, in the absence of bromine scavenger, for sets of runs from the same batch of purified material and for sets of runs from different batches.

TABLE IV

Retentions for C_2H_5Br, C_6H_5Br and $CHBr_3$ in the absence of scavenger [ab]

Substance	1st Batch	2nd Batch	3rd Batch
C_2H_5Br	32.0 ± 1.0 32.4 ± 1.0 32.2 ± 1.0	32.5 ± 1.0 32.5 ± 0.8 32.6 ± 0.8	
C_6H_5Br	68.5 ± 1.5 68.3 ± 1.5 68.6 ± 1.4	69.6 ± 0.9 68.9 ± 1.3 68.5 ± 1.3	69.0 ± 1.1 68.8 ± 1.0 68.3 ± 1.3
$CHBr_3$	70.5 ± 0.5 70.5 ± 0.5 70.4 ± 0.5		

a. Irradiation time was 17 hrs in the case of C_2H_5Br and C_6H_5Br and 18 hrs in the case of $CHBr_3$, with a nominal 3c Sb - Be neutron source. Counting was always about 4 hrs after the end of irradiation.

b. The error in these figures is that due to the statistics of counting only.

Section 2. Preparation of solutions

A volume of one of the two organic components was run into a volumetric flask (to act as solvent for the bromine and minimize losses of bromine vapour) and weighed. A quantity of bromine was then added and weighed again. The exact quantities of the two organic components required to make up a solution of the desired mole fraction were then calculated and added to the solution, great care being taken to reduce bromine losses to a minimum. Aliquots were taken by pipette and the bromine concentration was determined by titration with sodium thiosulphate solutions that had been standardized against potassium iodate, to confirm that no significant loss of bromine had occurred.

Section 3. Neutron Irradiations

A nominal 3c Sb/Be neutron source was used throughout this work. The irradiation assembly consisted of a central glass tube, in which the source was fixed, surrounded by eight other glass thimbles equally spaced in a circle in the horizontal plane of the source. The whole assembly was kept in a large, concrete-shielded tank of water.

10 ml aliquots of each solution were pipetted into glass-stoppered tubes and lowered into the glass thimbles for irradiation. All glassware was of soda glass, to minimise neutron losses.

Irradiations were carried out at room temperature and in the dark (to preclude any photochemical reactions). Irradiation times, in all but the C_6H_6-Br_2-$CHBr_3$ system, were always 17 hrs. to ensure the same relative activities of the various bromine isotopes. In the case of the C_6H_6 - Br_2 - $CHBr_3$ system, irradiation times were 18 hours.

Preliminary experiments were always carried out to find whether any exchange reactions between radioactive bromine and the substances used occurred. This was done as follows:-

(i) Mixtures of each one of the organic substances, with Br^{82} - labelled bromine of high specific activity over a wide range of bromine concentrations were allowed to stand in the dark for approximately 20 hours and then extracted and counted.

(ii) Samples of the same composition as in (i) were put in Cd shields (to preclude neutron activation) and subjected to the γ- radiation of the neutron sources for a length of time equal to that of the actual neutron irradiation.

In both cases, bromination effects, exchange or γ- induced exchange reactions we found to occur to a negligible extent, if at all, under our experimental conditions.

Section 4. Extraction procedure

The irradiated solutions were extracted with a (2M sodium sulphite + 0.5M sodium hydroxide + 0.05M potassium bromide) solution. To minimize the loss of bromine, the first extraction was carried out in the irradiation tubes. The mixture was transferred to a separating funnel and the two layers were separated. The portions of extractant for subsequent extractions were used to rinse out the irradiation tubes. The organic layer was then re-extracted. All portions of aqueous solution were withdrawn from a burette, so that the total volume of extractant (which varied with the bromine concentration of the irradiated sample) was known when these portions were finally combined and mixed. In order to minimize losses through evaporation during transfers, it was necessary to cool to prevent heating during extraction of solutions with high bromine concentrations.

Strictly speaking, the addition of carrier is unnecessary with solutions containing bromine. But although the observed retentions for the pure substances were the same for extraction with and without carrier, nevertheless carrier was always used since the amount of activity on the walls of the irradiation tubes was found to be greater in the absence of carrier. The use of sodium hydroxide in the extractant proved to have an effect similar to that of the carrier in the removal of that residual activity. After repeated rinsing of the tubes, this activity was always found to be negligible.

Section 5. Counting

5 ml aliquots of each of the aqueous and organic layers were taken by pipette into polythene snap-closure tubes and counted in a well-type NaI (Tl) crystal of a γ- scintillation counter.

All samples were counted 3 to 4 hours after the end of the irradiation, when equilibrium had been established between the Br^{80m} (4-5 hrs.) and its daughter Br^{80} (18 min.) activities. From the complex decay curve it was shown that, under these conditions, decay corrections were unnecessary over the time interval needed for counting the samples (5 to 10 minutes according to the counting rates) and provided the two layers from the same sample were counted in succession.

In the cases of binary and ternary mixtures containing carbon tetrachloride (where Cl^{38} (37.3 min) activity was initially present), the samples were counted 6 hours after the end of the irradiation, when virtually all the Cl^{38} activity had decayed. The pulse height analyzer used in conjunction with the scintillation counter was set in such a way as to minimize the effect due to the presence of chlorine activity, that is to maximize the (Bromine count)/(Chlorine count) ratio. Then a 10 ml sample of pure carbon tetrachloride was irradiated and counted under standard conditions and it was found that the count rate was indistinguishable from background.

All counts were corrected for background. Dead time corrections and absorption corrections were negligible.

It is obvious from the above that the count rates were mainly due to the Br^{82} activity, along with some participation from the Br^{80} activity resulting from the isomeric transition of Br^{80m}. It had been reported by others (40, 65, 79-80) that there is no difference in the retention of the various bromine isotopes, so the retentions in this work have been calculated on the basis of the total count of the 4 hour-after-the-end-of-irradition counting. Counting the samples after 24 hours, when only the Br^{82} activity was present, gave results which were, within experimental error, the same as those obtained after 4 hours.

When this work was started, it had not yet been reported that the Br^{82} comes mostly from Br^{82m} ($t^{1/2} \sim 6$ min) through an isomeric transition. No attempt was made to check upon any possible isotope effect in the retentions due to this. (See the [illegible]

Section 6. Calculation of experimental retention values

Although 10 ml aliquots of each mixture were taken (by pipette) for irradiation, the total volume of the organic layer remaining after the extraction of bromine is less than 10 ml by the volume of the bromine extracted. This volume was calculated from the known bromine concentration and hence the reduced volume of the organic layer. From this volume and the count rate of a 5 ml portion of this layer, the count rate of the total organic layer was obtained.

The volume of extracting solution used was known (from the burette reading), and the total volume of the aqueous layer was taken as the sum of the volume of extractant and that of the bromine extracted from the organic layer. This correetion is no doubt approximate, since it is not certain that the increase in volume of the aqueous layer will be exactly equal to the volume of the bromine dissolved. But, on the other hand, this correction is negligible for low bromine concentrations and never more than 2-3% for higher bromine concentrations. So, even if it is approximate, it could not produce a significant overall error. It was thought that this error would be greater if this correction was not introduced at all. The count rate of the total aqueous layer was then readily calculated from the observed count rate of the 5 ml portion of this layer. The fractional organic retention was obtained as the ratio of the count rate of the total organic layer to the sum of the count rates of the total organic and aqueous layers.

To ascertain that decay corrections were negligible, another way of calculating retentions was the following:-

The two layers were counted alternately, that is, in the order: organic (1) - aqueous (1) - organic (2) - acqueous (2) and the retention was calculated by the combinations

$$\text{a. Retention} = \frac{1/2 \left\{ \text{organic (1)} + \text{organic (2)} \right\}}{\text{aqueous (1)} + 1/2 \left\{ \text{organic (1)} + \text{organic (2)} \right\}}$$

b. $$\text{Retention} = \frac{\text{organic (2)}}{\text{organic (2)} + {}^{1}/2 \left\{ \text{aqueous (1)} + \text{aqueous (2)} \right\}}$$

It was found that the differences between the two retention values from the above combinations and the retention value calculated on single counts were negligible and, in any case, within the limits of the error due to the statistics of counting.

The errors given for the organic retentions (see RESULTS) are those resulting from the statistics of counting. No other possible sources of experimental error have been included.

All the retention values throughout this work represent the mean from two experiments. In more than 90 per cent of the cases, the results of such pairs do not differ by more than 1 per cent and in no case by more than 1.5 per cent.

CHAPTER 3

RESULTS

The calculations of retentions reported in this work have been based on the assumption that E_o should be identified with the average initial recoil energy of the bromine atoms. The complete neutron capture gamma-ray cascade spectrum for the reactions Br^{79} (n,γ) Br^{80}, Br^{79} (n,γ) Br^{80m} and $Br^{81}(n,\gamma)$ Br^{82} is not known and, consequently, the spectrum of recoil energies cannot be determined. Therefore, following RACK and GORDUS (46), E_o has been taken as 100 e.v., this figure being based on the average recoil energy of the reaction Cl^{35} (n,γ) Cl^{36}, calculated by HSIUNG, HSIUNG and GORDUS (13), and assumed to be a fairly good approximation for the case of bromine.

E_1 and E_2 have been identified with the activation energies of the exchange reactions of the types

$$RX + Br^{*} \longrightarrow RBr^{*} + X$$

$$RH + Br^{*} \longrightarrow RBr^{*} + H$$

and, since they do not appear to have been measured, they have been estimated (see APPENDIX C for supporting arguments). Their values are given below

System : C_2H_5Br/Br_2 $E = 20$ Kcal $mole^{-1}$ (i.e. 0.8676 e.v.)

" : C_6H_5Br/Br_2 $E = 20$ Kcal $mole^{-1}$

" : CCl_4/Br_2 $E = 50$ Kcal $mole^{-1}$

System : C_6H_6/Br_2 $E = 50$ Kcal mole^{-1}
" : $CHBr_3/Br_2$ $E = 5$ Kcal mole^{-1}

For each ternary system, series of mixtures were investigated at two constant mole fractions of one of the organic components.

1. Ternary system $C_2H_5Br/Br_2/C_6H_5Br$

Setting $E_1 = E_2$ for this system has the effect of making the second term in Eq.(6) of the theory (see Chapter 1) redundant. Since E_1 and E_2 are only estimated values, it may prove that they are slightly different. But, anyway, as long as E_o is taken as 100 e.v., $E_1 \sim E_2 \sim 20$ Kcal mole^{-1} and as long as $|E_1 - E_2|$ does not exceed 10 Kcal mole^{-1}, the contribution of the second term to the retention will be negligible (0.5 - 1% of the first term).

The results for the binary mixtures C_2H_5Br/Br_2 and C_6H_5Br/Br_2 are shown in Tables V and VI. The retention versus mole fraction of bromine graphs are shown in Fig.3., while the corresponding $1/_R$ versus $y/_x$ or $y/_z$ graphs are shown in Fig.4.

It will be recalled that, in drawing the limiting slope on graphs of $1/_R$ vs. $y/_z$ or $y/_x$, two points should be kept in mind. Firstly, that it is necessary to discount the additional retention due to thermal diffusive reactions at low bromine concentrations. Secondly, that for the approximation $p \longrightarrow (1 - \alpha)$ (or $p \longrightarrow (1 - \gamma)$) to be reasonably good, the limiting slope should be drawn at low bromine

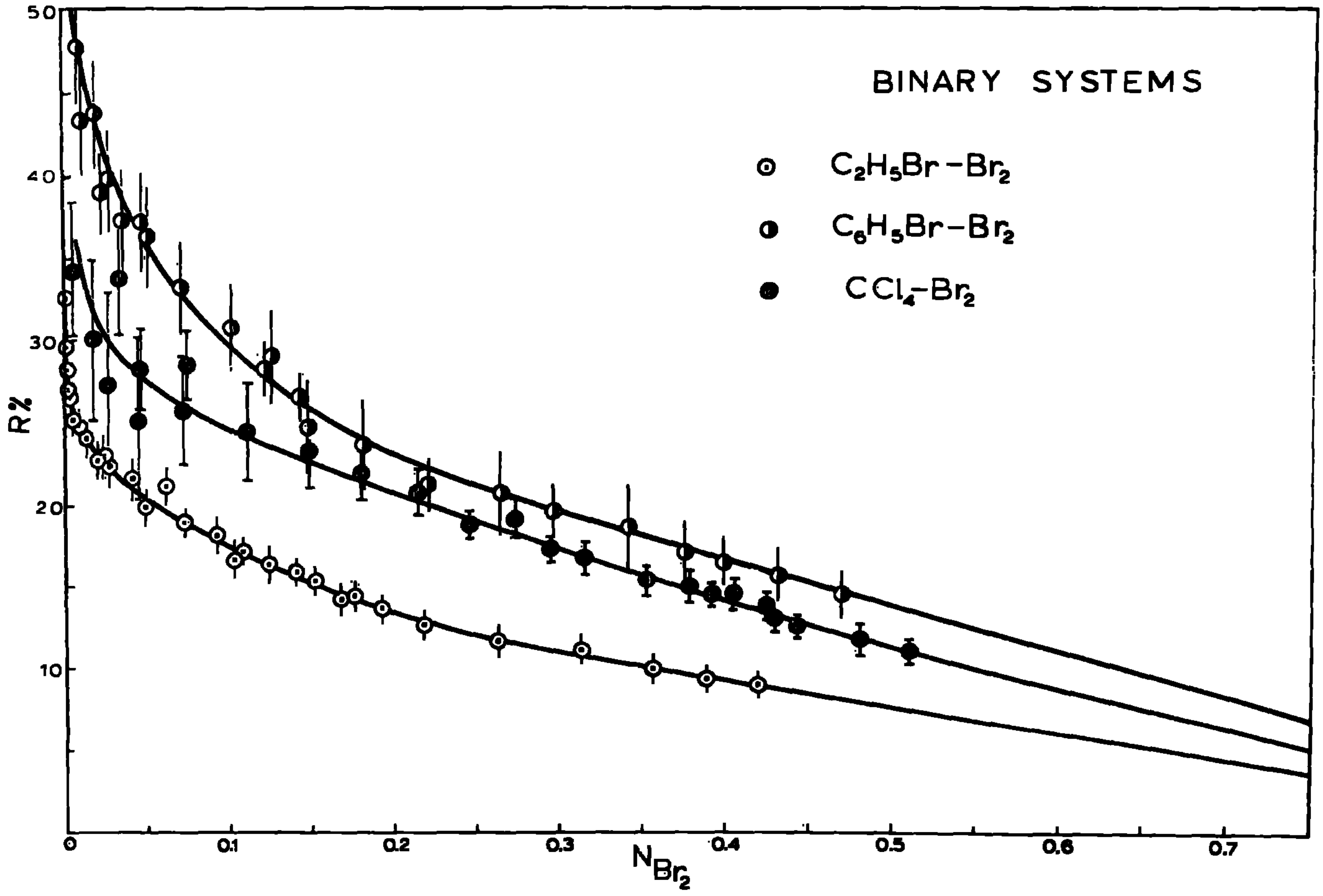

BINARY SYSTEMS
○ $C_2H_5Br-Br_2$
◐ $C_6H_5Br-Br_2$
● CCl_4-Br_2
R%
50
40
30
20
10
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
N_{Br_2}

Fig.3

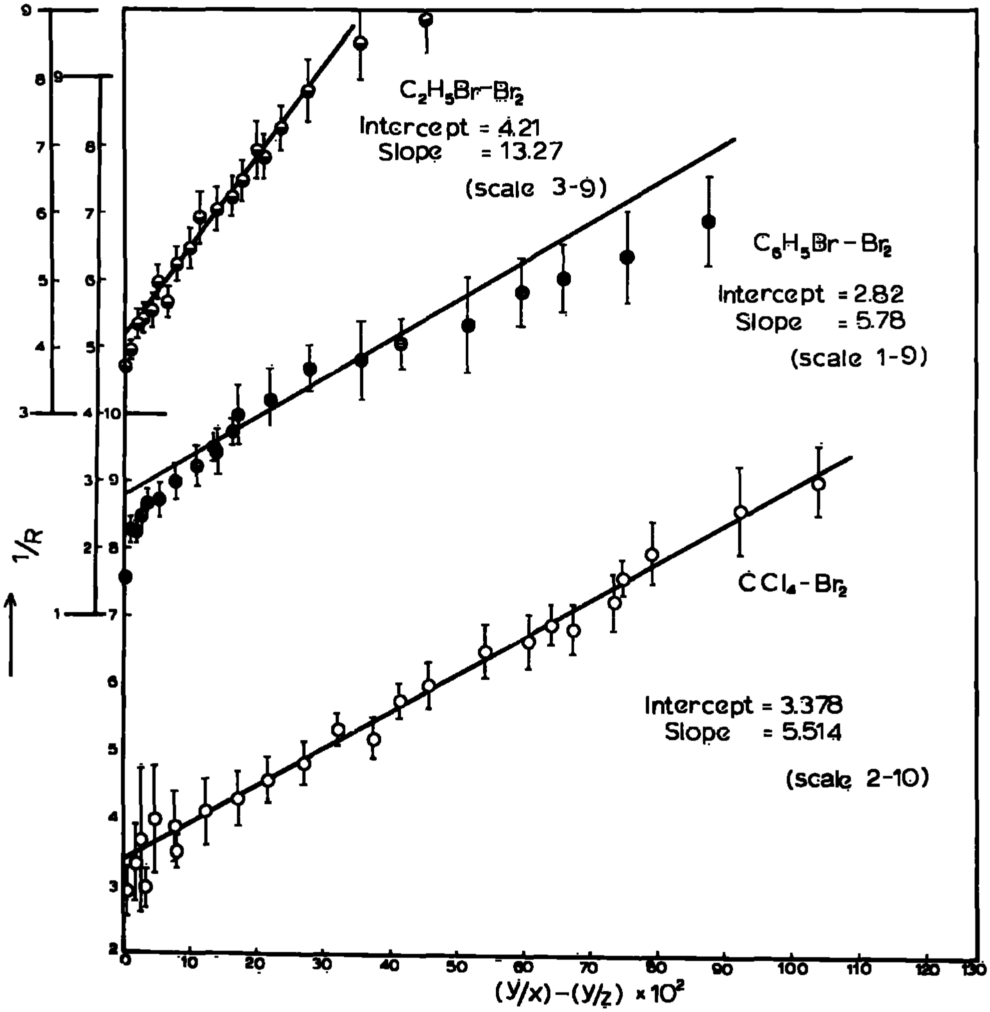


Fig.4

Plot of $^1/R$ versus $y/_x$ or $y/_z$ for binary systems

y: mole fraction of Br_2

x or z: mole fraction of organic component

TABLE V

THE BINARY SYSTEM : C_2H_5Br / Br_2

MOLE FRACTION Br_2 (Y)	FRACTIONAL RETENTION	$^{1}/_{R}$ ± $^{6}1/_{R}$	$Y/_{X}$ x 10^2
0.0002	0.296 ± 0.010	3.373 ± 0.110	0.020
0.0005	0.283 ± 0.010	3.526 ± 0.119	0.050
0.0012	0.271 ± 0.009	3.691 ± 0.122	0.120
0.0025	0.267 ± 0.009	3.750 ± 0.129	0.250
0.0043	0.252 ± 0.009	3.966 ± 0.149	0.432
0.0083	0.249 ± 0.009	4.018 ± 0.147	0.837
0.0123	0.242 ± 0.010	4.137 ± 0.180	1.245
0.0193	0.228 ± 0.011	4.381 ± 0.209	1.968
0.0230	0.231 ± 0.012	4.332 ± 0.223	2.385
0.0269	0.224 ± 0.011	4.455 ± 0.222	2.764
0.0407	0.217 ± 0.010	4.603 ± 0.220	4.242
0.0489	0.199 ± 0.010	5.010 ± 0.251	5.141
0.0612	0.212 ± 0.010	4.715 ± 0.231	6.519
0.0726	0.189 ± 0.009	5.274 ± 0.247	7.828
0.0910	0.181 ± 0.009	5.509 ± 0.288	10.011
0.1022	0.168 ± 0.011	5.959 ± 0.383	11.383
0.1071	0.171 ± 0.008	5.834 ± 0.282	11.994
0.1221	0.165 ± 0.008	6.071 ± 0.306	13.908
0.1406	0.160 ± 0.007	6.262 ± 0.294	16.360
0.1512	0.154 ± 0.007	6.493 ± 0.295	17.813
0.1672	0.144 ± 0.009	6.955 ± 0.416	20.077
0.1746	0.146 ± 0.007	6.854 ± 0.319	21.153
0.1914	0.137 ± 0.006	7.273 ± 0.328	23.670
0.2170	0.127 ± 0.007	7.837 ± 0.467	27.714
0.2625	0.117 ± 0.007	8.547 ± 0.482	35.593
0.3127	0.112 ± 0.006	8.905 ± 0.507	45.497
0.3553	0.101 ± 0.006	9.881 ± 0.586	55.111
0.3877	0.095 ± 0.005	10.515 ± 0.608	63.318
0.4187	0.091 ± 0.006	10.977 ± 0.687	72.028

TABLE VI

THE BINARY SYSTEM : C_6H_5Br /Br_2

MOLE FRACTION Br_2(Y)	FRACTIONAL RETENTION R	$^1/_R \pm 6^1/_R$	$^y/_x \times 10^2$
0.0027	0.621±0.036	1.609 ± 0.093	0.271
0.0079	0.477 ± 0.033	2.095 ± 0.147	0.796
0.0099	0.432 ± 0.032	2.313 ± 0.174	0.999
0.0187	0.437 ± 0.032	2.286 ± 0.170	1.905
0.0218	0.390 ± 0.024	2.566 ± 0.161	2.228
0.0267	0.397 ± 0.031	2.515 ± 0.196	2.743
0.0340	0.373 ± 0.030	2.682 ± 0.219	3.573
0.0467	0.372 ± 0.029	2.689 ± 0.213	4.899
0.0501	0.363 ± 0.030	2.752 ± 0.231	5.274
0.0722	0.331 ± 0.028	3.015 ± 0.259	7.782
0.0988	0.307 ± 0.027	3.251 ± 0.286	11.086
0.1198	0.283 ± 0.016	3.537 ± 0.203	13.610
0.1240	0.289 ± 0.028	3.452 ± 0.335	14.155
0.1409	0.265 ± 0.015	3.775 ± 0.213	16.401
0.1466	0.248 ± 0.027	4.023 ± 0.443	17.178
0.1801	0.237 ± 0.027	4.223 ± 0.478	21.966
0.2191	0.212 ± 0.015	4.717 ± 0.335	28.057
0.2629	0.207 ± 0.025	4.831 ± 0.588	35.667
0.2942	0.197 ± 0.014	5.084 ± 0.369	41.683
0.3406	0.186 ± 0.024	5.365 ± 0.705	51.653
0.3741	0.171 ± 0.019	5.851 ± 0.667	59.770
0.3976	0.165 ± 0.013	6.049 ± 0.494	66.002
0.4300	0.157 ± 0.016	6.396 ± 0.677	75.469
0.4671	0.145 ± 0.014	6.906 ± 0.672	87.793

concentrations. It can be seen that the way the limiting slopes have been drawn represents a compromise between the above two requirements, the criterion being a fairly sharp change of slope in both the curves at about $y/_x = 0.08$ for C_2H_5Br/Br_2 and $y/_z = 0.12$ for C_6H_5Br/Br_2, this change having been regarded as internal evidence of the onset of thermal diffusive reactions. It is obvious that, in the case of the C_6H_5Br/Br_2 mixtures, the scattering of points makes it more difficult to decide on the position of the limiting slope, while in the case of C_2H_5Br/Br_2 the freedom of movement is much more limited. In a previous paper (100) the limiting slopes had been drawn at somewhat different positions on the curves with the purpose of producing concordant values of β. The later addition of more experimental points, especially for C_2H_5Br/Br_2 mixtures, made a readjustment necessary. The values of the parameters (calculated with m_a as defined by Eq. (7a) of the theory) resulting from the lines of Fig.4 are as follows:

For the C_2H_5Br/Br_2 system: $\alpha = 0.01605$

$\beta = 0.05058$

For the C_6H_5Br/Br_2 system: $\gamma = 0.02495$

$\beta = 0.05114$

The experimental results for the $C_2H_5Br/Br_2/C_6H_5Br$ mixtures are shown in Table VII and in Fig.5, where the lines (1a) and (2a) have been calculated with m_a as defined by Eq. (7a) (see also Table VIII). It can be seen that the calculated line is in excellent agreement with the experimental results for the series of solutions at 0.3198 mole fraction of phenyl bromide and in fairly good agreement for the series of solutions at 0.5496 mole fraction of phenyl bromide. It can also be seen that, as expected, the observed retentions become progressively higher than the calculated ones at very low bromine concentrations, which is to be attributed to the incomplete quenching of thermal diffusive reactions. Included in Fig.5 are the lines (1b) and (2b) which have been calculated with m_a as defined by Eq. (7b). In this case, there is no agreement between theory and experiment (see also DISCUSSION).

The value of the parameter β used for the calculations in the ternary mixtures was the average of the two individual values from the binary systems, since they are very much the same.

2. Ternary systems $C_2H_5Br/Br_2/CCl_4$ and $C_6H_5Br/Br_2/CCl_4$

The results for the binary mixtures CCl_4/Br_2 are shown in Table IX. The retention *versus* mole fraction of bromine graph is shown in Fig.3, while the corresponding $1/R$ *versus* y/z graph in Fig.4.

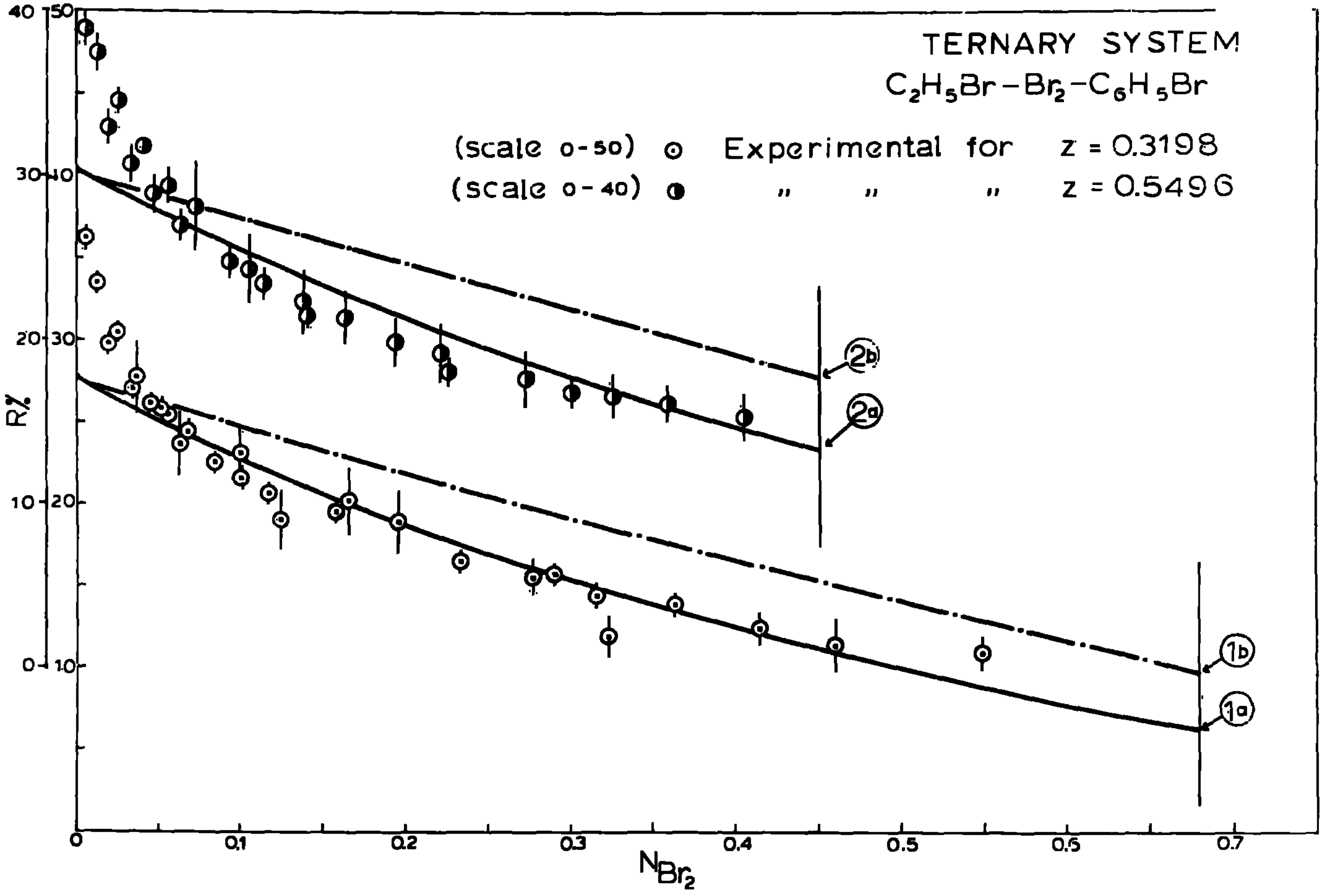


Fig.5

Lines (1a) - 2(a) calculated on atomic collisions
Lines (1b) - 2(b) calculated on molecular collisions
z: mole fraction of C_6H_5 Br

TABLE VII

THE TERNARY SYSTEM : C_2H_5Br / Br_2 / C_6H_5Br

Experimental Retention Values

z = 0.3198			z = 0.5496		
MOLE FRACTION		FRACTIONAL RETENTION	MOLE FRACTION		FRACTIONAL RETENTION
Br_2 (Y)	C_2H_5Br (X)		Br_2 (Y)	C_2H_5Br (X)	
0.0044	0.6758	0.362 ± 0.007	0.0043	0.4461	0.389 ± 0.009
0.0115	0.6687	0.335 ± 0.005	0.0119	0.4385	0.375 ± 0.009
0.0182	0.6620	0.298 ± 0.006	0.0186	0.4318	0.330 ± 0.009
0.0207	0.6595	0.297 ± 0.007	0.0247	0.4257	0.346 ± 0.008
0.0243	0.6559	0.305 ± 0.006	0.0324	0.4180	0.308 ± 0.010
0.0335	0.6467	0.271 ± 0.006	0.0398	0.4106	0.318 ± 0.010
0.0353	0.6447	0.281 ± 0.007	0.0469	0.4035	0.289 ± 0.011
0.0364	0.6438	0.277 ± 0.019	0.0549	0.3955	0.294 ± 0.010
0.0438	0.6364	0.262 ± 0.005	0.0662	0.3842	0.270 ± 0.008
0.0511	0.6291	0.259 ± 0.006	0.0712	0.3792	0.283 ± 0.026
0.0559	0.6243	0.254 ± 0.006	0.0927	0.3577	0.248 ± 0.009
0.0619	0.6183	0.237 ± 0.019	0.1033	0.3471	0.242 ± 0.022
0.0670	0.6132	0.245 ± 0.006	0.1130	0.3374	0.234 ± 0.008
0.0837	0.5965	0.226 ± 0.005	0.1378	0.3126	0.224 ± 0.018
0.0989	0.5813	0.231 ± 0.017	0.1381	0.3123	0.216 ± 0.008
0.0997	0.5805	0.216 ± 0.005	0.1626	0.2878	0.214 ± 0.013
0.1167	0.5635	0.207 ± 0.005	0.1922	0.2582	0.199 ± 0.014
0.1234	0.5568	0.191 ± 0.017	0.2192	0.2312	0.193 ± 0.017
0.1574	0.5228	0.196 ± 0.006	0.2240	0.2264	0.181 ± 0.008
0.1622	0.5180	0.203 ± 0.020	0.2711	0.1793	0.178 ± 0.014
0.1950	0.4852	0.189 ± 0.018	0.2988	0.1516	0.169 ± 0.007
0.2330	0.4472	0.166 ± 0.006	0.3255	0.1249	0.167 ± 0.012
0.2766	0.4036	0.156 ± 0.012	0.3575	0.0929	0.162 ± 0.009
0.2900	0.3902	0.157 ± 0.006	0.4305	0.0469	0.155 ± 0.012
0.3151	0.3651	0.145 ± 0.007			
0.3222	0.3580	0.119 ± 0.012			
0.3624	0.3178	0.139 ± 0.005			
0.4137	0.2665	0.124 ± 0.010			
0.4597	0.2205	0.114 ± 0.015			
0.5483	0.1319	0.109 ± 0.010			

TABLE VIII

THE TERNARY SYSTEM $C_2H_5Br/Br_2/C_6H_5Br$

Retentions Calculated from Theory on $E_{ret}(av) = \frac{m_a^2 + m_b^2}{(m_a + m_b)^2}$

MOLE FRACTION Br_2(y)	FRACTIONAL RETENTION			
	z = 0.3198		z = 0.5496	
	m_a		m_a	
	From Eq. (7a)	From Eq. (7b)	From Eq. (7a)	From Eq. (7b)
0.01	0.2718	0.2704	0.2989	0.2971
0.05	0.2522	0.2594	0.2792	0.2858
0.09	0.2339	0.2485	0.2607	0.2746
0.13	0.2168	0.2377	0.2432	0.2636
0.17	0.2006	0.2270	0.2267	0.2526
0.21	0.1855	0.2164	0.2112	0.2417
0.25	0.1713	0.2059	0.1966	0.2309
0.29	0.1580	0.1965	0.1828	0.2202
0.33	0.1454	0.1852	0.1697	0.2096
0.37	0.1336	0.1750	0.1574	0.1991
0.41	0.1225	0.1648	0.1457	0.1887
0.45	0.1120	0.1548	0.1347	0.1784
0.49	0.1021	0.1449		
0.53	0.0929	0.1351		
0.57	0.0841	0.1254		
0.61	0.0759	0.1159		
0.65	0.0682	0.1063		

It can be seen that, although the experimental uncertainties on the points are rather large, especially for very low bromine concentrations, the $1/_R$ vs. $y/_z$ line exhibits a more pronounced straight line behaviour than in the case of the C_2H_5Br/Br_2 and C_6H_5Br/Br_2 systems. This might be attributed, at least partly, to the fact that the value of m_a for CCl_4 (as defined by Eq.(7a)) has shifted significantly towards the mass of the recoil bromine atom, a situation which, according to the theory, would favour straight line behaviour. In drawing the limiting slope, the experimental points below $y/_z \sim 0.1$ have not been taken into account.

The values of the parameters (calculated with m_a as defined by Eq.(7a)) are:

For the CCl_4/Br_2 system $\gamma = 0.04561$

$\beta = 0.07447$

In a previous paper (100) the results for CCl_4/Br_2 mixtures were very few and the CCl_4 used in these experiments had not been purified. Thus, the limiting slope had been drawn in such a way as to give values for the parameters that led to a good fit between experimental and calculated retention values in the ternary mixtures. The discrepancy in the value of the parameter β in comparison to those from the C_2H_5Br/Br_2 and C_6H_5Br/Br_2 systems had been thought of as being due to experimental inaccuracies or to some special feature of that system (e.g. the influence of the recoil effects of Cl) although the possibility of discrepant values of β because of other reasons was briefly discussed.

It can be seen that, with more extensive experimental results with purified CCl_4, the value of β is still different (in fact, the discrepancy has become larger) from those obtained from the other two binary systems.

The experimental results for the $C_2H_5Br/Br_2/CCl_4$ mixtures are shown in Table X and in Fig.6 where the lines (1a) and (2a) have been calculated with m_a as defined by Eq.(7a). In this system, E_1 = 50 Kcal $mole^{-1}$ and E_2 = 20 Kcal $mole^{-1}$, consequently both terms of Eq.(6) have been calculated. The contribution from each term is shown in Table XI. The value of the parameter β used for the calculations of theoretical retentions was a weighed mean of the values of this parameter from the two binary systems, that is

$$\beta = \frac{x \cdot \beta_1 + z \cdot \beta_2}{x + z}$$

where β_1 is the value from the C_2H_5Br/Br_2 system

and β_2 is the value from the CCl_4/Br_2 system

It can be seen that the calculated lines are in excellent agreement with the experimental results for both the series of solutions

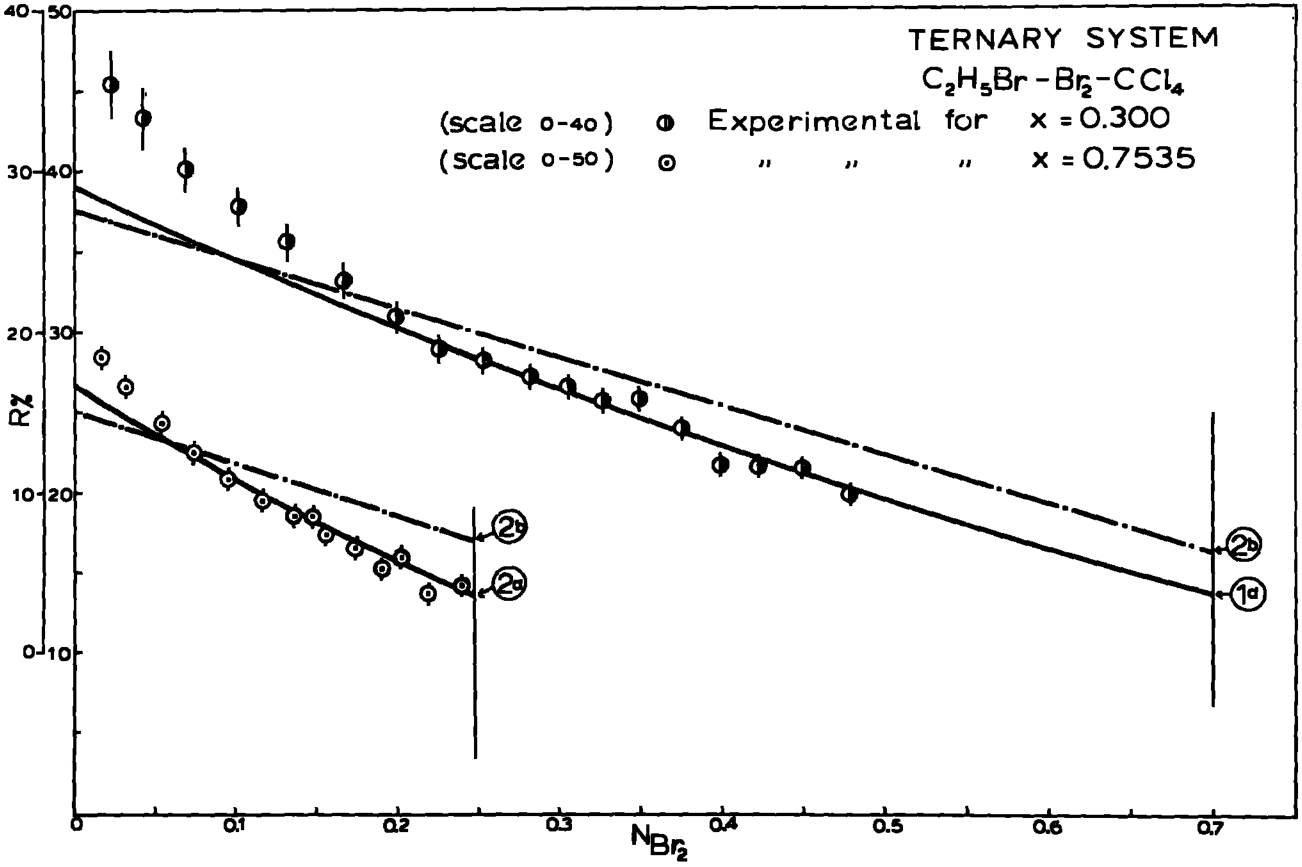


Fig.6

Lines (1a) - (2a) calculated on atomic collisions
Lines (1b) - (2b) calculated on molecular collisions
x : mole fraction of C_2H_5Br

TABLE IX

THE BINARY SYSTEM : CCl_4 / Br_2

MOLE FRACTION Br_2(Y)	FRACTIONAL RETENTION R	$^1/_R \pm {}^{\delta 1}/_R$	$^Y/_Z \times 10^2$
0.0051	0.342 ± 0.042	2.919 ± 0.362	0.512
0.0168	0.300 ± 0.050	3.330 ± 0.553	1.709
0.0255	0.272 ± 0.058	3.672 ± 1.057	2.617
0.0323	0.338 ± 0.034	2.961 ± 0.297	3.338
0.0446	0.251 ± 0.050	3.976 ± 0.793	4.668
0.0450	0.283 ± 0.023	3.538 ± 0.292	4.701
0.0712	0.257 ± 0.032	3.889 ± 0.486	7.666
0.0734	0.285 ± 0.020	3.501 ± 0.246	7.921
0.1101	0.244 ± 0.029	4.093 ± 0.494	12.372
0.1472	0.233 ± 0.022	4.291 ± 0.400	17.261
0.1785	0.219 ± 0.016	4.570 ± 0.340	21.728
0.2138	0.207 ± 0.013	4.819 ± 0.315	27.194
0.2440	0.187 ± 0.008	5.333 ± 0.228	32.275
0.2729	0.192 ± 0.011	5.210 ± 0.305	37.532
0.2935	0.173 ± 0.007	5.780 ± 0.248	41.543
0.3142	0.167 ± 0.009	5.983 ± 0.338	45.815
0.3516	0.154 ± 0.009	6.507 ± 0.377	54.226
0.3779	0.150 ± 0.009	6.660 ± 0.394	60.746
0.3908	0.145 ± 0.006	6.889 ± 0.287	64.150
0.4033	0.146 ± 0.008	6.831 ± 0.373	67.588
0.4236	0.138 ± 0.008	7.234 ± 0.415	73.490
0.4284	0.131 ± 0.005	7.608 ± 0.277	74.947
0.4422	0.125 ± 0.007	7.975 ± 0.448	79.276
0.4804	0.116 ± 0.009	8.597 ± 0.643	92.456
0.5100	0.111 ± 0.006	9.037 ± 0.495	104.081

TABLE X[illegible]

THE TERNARY SYSTEM C_2H_5Br / Br_2 / CCl_4

Experimental Retention Values

x = 0.3000			x = 0.7535		
MOLE FRACTION		FRACTIONAL RETENTION	MOLE FRACTION		FRACTIONAL RETENTION
Br_2 (Y)	CCl_4 (Z)		Br_2 (Y)	CCl_4 (Z)	
0.0228	0.6772	0.355 ± 0.020	0.0162	0.2303	0.285 ± 0.009
0.0423	0.6577	0.334 ± 0.018	0.0315	0.2150	0.267 ± 0.008
0.0685	0.6315	0.301 ± 0.013	0.0535	0.1930	0.244 ± 0.006
0.1018	0.5982	0.279 ± 0.012	0.0738	0.1727	0.225 ± 0.005
0.1312	0.5688	0.256 ± 0.011	0.0953	0.1512	0.209 ± 0.005
0.1669	0.5331	0.233 ± 0.009	0.1163	0.1302	0.195 ± 0.005
0.1989	0.5011	0.210 ± 0.008	0.1365	0.1100	0.185 ± 0.005
0.2248	0.4752	0.190 ± 0.007	0.1476	0.0989	0.185 ± 0.005
0.2529	0.4471	0.183 ± 0.007	0.1560	0.0905	0.174 ± 0.004
0.2818	0.4182	0.172 ± 0.006	0.1742	0.0723	0.165 ± 0.004
0.3059	0.3941	0.166 ± 0.006	0.1900	0.0565	0.153 ± 0.004
0.3260	0.3740	0.157 ± 0.006	0.2025	0.0440	0.160 ± 0.004
0.3486	0.3514	0.158 ± 0.006	0.2193	0.0272	0.137 ± 0.004
0.3751	0.3249	0.140 ± 0.005	0.2398	0.0067	0.143 ± 0.004
0.3988	0.3012	0.117 ± 0.004			
0.4223	0.2777	0.117 ± 0.004			
0.4491	0.2509	0.115 ± 0.004			
0.4787	0.2213	0.098 ± 0.004			

TABLE XI

THE TERNARY SYSTEM: $C_2H_5Br/Br_2/CCl_4$

Retentions calculated from theory m_a from Eq. (7a) and

$$E_{ret}(av) = \frac{m_a^2 + m_b^2}{(m_a + m_b)^2}$$

	FRACTIONAL RETENTION					
	x = 0.3000			x = 0.7535		
MOLE FRACTION Br_2 (y)	$R_{(E_o, E_1)}$	$R_{(E_1, E_2)}$	R	$R_{(E_o, E_1)}$	$R_{(E_1, E_2)}$	R
0.01	0.2775	0.0073	0.2848	0.2336	0.0251	0.2587
0.05	0.2594	0.0071	0.2665	0.2119	0.0247	0.2366
0.09	0.2418	0.0070	0.2488	0.1907	0,0243	0.2150
0.13	0.2247	0.0069	0.2316	0,1702	0.0239	0.1941
0.17	0.2081	0.0067	0.2149	0.1503	0.0236	0.1739
0.21	0.1920	0.0066	0.1986	0.1309	0.0233	0.1542
0.25	0.1763	0.0065	0.1828			
0.29	0.1612	0.0064	0.1676			
0.33	0.1464	0.0063	0.1527			
0.37	0.1321	0.0062	0.1383			
0.41	0.1182	0.0061	0.1243			
0.45	0.1047	0.0061	0.1108			
0.49	0.0917	0.0060	0.0976			
0.53	0.0790	0.0059	0.0849			
0.61	0.0546	0.0058	0.0604			
0.65	0.0430	0.0058	0.0488			
0.69	0.0316	0.0058	0.0374			

TABLE XII

THE TERNARY SYSTEM : $C_2H_5Br/Br_2/CCl_4$

Retentions calculated from theory on m_a from Eq. (7b) and

$$E_{ret}\ (av) = \frac{m_a^{\ 2} + m_b^{\ 2}}{(m_a + m_b)^2}$$

	FRACTIONAL RETENTION					
	x = 0.3000			x = 0.7535		
MOLE FRACTION $Br_2(y)$	$R_{(E_o, E_1)}$	$R_{(E_1, E_2)}$	R	$R_{(E_o, E_1)}$	$R_{(E_1, E_2)}$	R
0.01	0.2615	0.0121	0.2736	0.2165	0.0306	0.2471
0.05	0.2489	0.0120	0.2609	0.2041	0.0302	0.2343
0.09	0.2364	0.0118	0.2482	0.1918	0.0297	0.2215
0.13	0.2240	0.0117	0.2357	0.1796	0.0292	0.2088
0.17	0.2116	0.0116	0.2232	0.1675	0.0287	0.1962
0.21	0.1993	0.0114	0.2107	0.1555	0.0282	0.1837
0.25	0.1871	0.0112	0.1983			
0.29	0.1749	0.0111	0.1860			
0.33	0.1628	0.0109	0.1737			
0.37	0.1508	0.0108	0.1616			
0.41	0.1389	0.0106	0.1495			
0.45	0.1271	0.0104	0.1375			
0.49	0.1153	0.0102	0.1255			
0.53	0.1036	0.0100	0.1136			
0.57	0.0920	0.0098	0.1018			
0.61	0.0805	0.0095	0.0900			
0.65	0.0691	0.0093	0.0784			
0.69	0.0578	0.0089	0.0667			

at 0.7535 and 0.300 mole fraction of ethyl bromide. The effect of incomplete scavenging at low bromine concentrations again appears as expected, but it should perhaps be noted that, for the series of solutions at 0.300 mole fraction of ethyl bromide, this effect appears at the rather high ($\sim$0.2) mole fraction of bromine. This could possibly be due to error in the experimental points in the region of $N_{Br_2} \sim 0.1 - 0.2$.

Included in Fig.6 are the lines (1b) and (2b) which have been calculated with m_a as defined by Eq.(7b) (see also Table XII). In this case, there is no agreement between theory and experiment (see also DISCUSSION).

The experimental results for the $C_6H_5Br/Br_2/CCl_4$ mixtures are shown in Table XIII and in Fig.(7). Again, the lines (1a) and (2a) have been calculated with m_a as defined by Eq.(7a). In this system, E_1 = 50 Kcal mole^{-1} and E_2 = 20 Kcal mole^{-1}, so both terms of Eq.(6) have been calculated and their contribution to the retention is shown in Table XIV. The value of the parameter β used for the calculations was again a weighed mean. In this system one series of solutions was with constant mole fraction of C_6H_5Br (= 0.3184) and the other with constant mole fraction of CCl_4 (=0.546). This had the result of giving two calculated lines which are practically

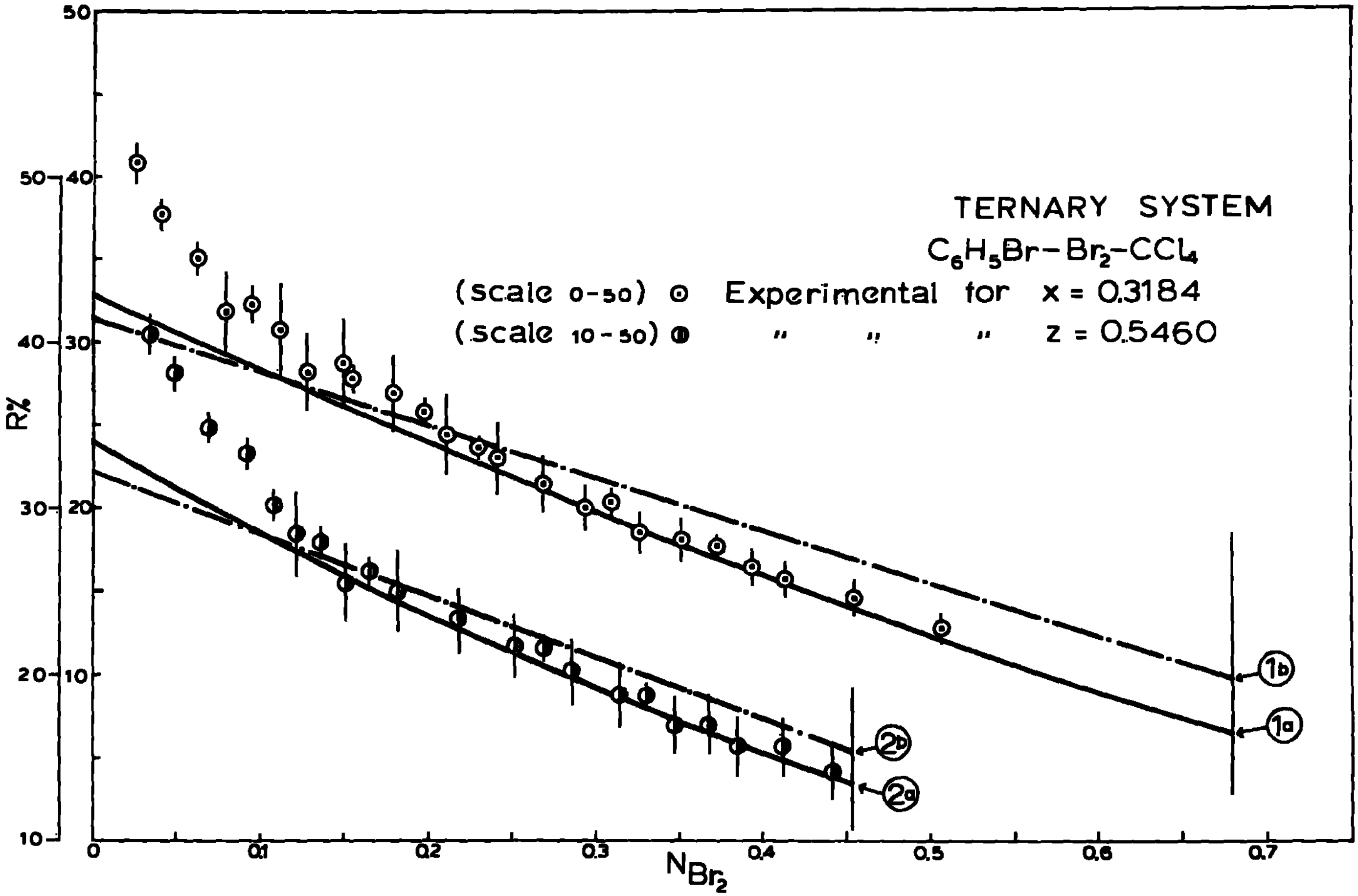


Fig.7

Lines (1a) - (2a) calculated on atomic collisions
Lines (1b) - (2b) calculated on molecular collisions
x: mole fraction of C_6H_5Br
z: mole fraction of CCl_4

TABLE XIII

THE TERNARY SYSTEM : C_6H_5Br /Br_2 /CCl_4

Experimental Retention Values

X = 0.3184

MOLE FRACTION		FRACTIONAL RETENTION
Br_2 (Y)	CCl_4 (Z)	
0.0095	0.6721	0.517 ± 0.014
0.0251	0.6565	0.408 ± 0.012
0.0404	0.6412	0.377 ± 0.009
0.0620	0.6196	0.351 ± 0.010
0.0783	0.6033	0.319 ± 0.023
0.0938	0.5878	0.325 ± 0.010
0.1117	0.5699	0.308 ± 0.028
0.1277	0.5539	0.283 ± 0.023
0.1493	0.5323	0.288 ± 0.027
0.1551	0.5265	0.279 ± 0.008
0.1785	0.5031	0.270 ± 0.023
0.1977	0.4839	0.259 ± 0.007
0.2107	0.4709	0.245 ± 0.024
0.2305	0.4511	0.237 ± 0.006
0.2410	0.4406	0.231 ± 0.022
0.2683	0.4133	0.215 ± 0.016
0.2932	0.3884	0.201 ± 0.013
0.3091	0.3725	0.205 ± 0.007
0.3258	0.3558	0.186 ± 0.012
0.3508	0.3308	0.182 ± 0.013
0.3726	0.3090	0.177 ± 0.006
0.3931	0.2885	0.165 ± 0.011
0.4129	0.2687	0.157 ± 0.010
0.4542	0.2274	0.147 ± 0.010
0.5059	0.1757	0.128 ± 0.009

Z = 0.5460

MOLE FRACTION		FRACTIONAL RETENTION
Br_2 (Y)	C_6H_5Br (X)	
0.0331	0.4209	0.405 ± 0.010
0.0484	0.4056	0.381 ± 0.010
0.0687	0.3853	0.349 ± 0.009
0.0919	0.3621	0.334 ± 0.009
0.1070	0.3470	0.302 ± 0.008
0.1208	0.3332	0.285 ± 0.025
0.1357	0.3183	0.280 ± 0.008
0.1508	0.3032	0.256 ± 0.023
0.1649	0.2891	0.263 ± 0.007
0.1811	0.2729	0.251 ± 0.024
0.2173	0.2367	0.233 ± 0.019
0.2513	0.2027	0.218 ± 0.018
0.2686	0.1854	0.216 ± 0.006
0.2855	0.1685	0.203 ± 0.018
0.3140	0.1400	0.188 ± 0.019
0.3306	0.1234	0.188 ± 0.006
0.3471	0.1069	0.170 ± 0.016
0.3671	0.0869	0.171 ± 0.017
0.3845	0.0695	0.157 ± 0.018
0.4118	0.0422	0.157 ± 0.016
0.4417	0.0123	0.143 ± 0.015

TABLE XIV

THE TERNARY SYSTEM : $C_6H_5Br/Br_2/CCl_4$

Retentions Calculated from theory on m_a from Eq. (7a)

and $$E_{ret}(av) = \frac{m_a^2 + m_b^2}{(m_a + m_b)^2}$$

	FRACTIONAL RETENTION					
	x = 0.3184			z = 0.5460		
MOLE FRACTION $Br_2(y)$	$R_{(E_o, E_1)}$	$R_{(E_1, E_2)}$	R	$R_{(E_o, E_1)}$	$R_{(E_1, E_2)}$	R
0.01	0.3110	0.0123	0.3233	0.3139	0.0184	0.3323
0.05	0.2921	0.0120	0.3041	0.2937	0.0161	0.3098
0.09	0.2737	0.0118	0.2855	0.2744	0.0139	0.2883
0.13	0.2558	0.0116	0.2674	0.2559	0.0119	0.2678
0.17	0.2384	0.0114	0.2498	0.2382	0.0100	0.2482
0.21	0.2215	0.0113	0.2328	0.2213	0.0082	0.2295
0.25	0.2050	0.0111	0.2161	0.2052	0.0066	0.2118
0.29	0.1889	0.0109	0.1998	0.1898	0.0051	0.1949
0.33	0.1732	0.0108	0.1840	0.1752	0.0037	0.1789
0.37	0.1580	0.0106	0.1686	0.1614	0.0024	0.1638
0.41	0.1432	0.0105	0.1537	0.1485	0.0012	0.1497
0.45	0.1287	0.0104	0.1391	0.1364	0.0001	0.1365
0.49	0.1147	0.0103	0.1250			
0.53	0.1010	0.0102	0.1112			
0.57	0.0877	0.0101	0.0978			
0.61	0.0747	0.0101	0.0848			
0.65	0.0620	0.0101	0.0721			

TABLE XV

THE TERNARY SYSTEM : $C_6H_5Br/Br_2/CCl_4$

Retentions calculated from theory on m_a from Eq.(7b) and

$$E_{ret}(av) = \frac{m_a^2 + m_b^2}{(m_a + m_b)^2}$$

	FRACTIONAL RETENTION					
	x = 0.3184			z = 0.5460		
MOLE FRACTION $Br_2(y)$	$R_{(E_o, E_1)}$	$R_{(E_1, E_2)}$	R	$R_{(E_o, E_1)}$	$R_{(E_1, E_2)}$	R
0.01	0.2933	0.0182	0.3115	0.2935	0.0253	0.3188
0.05	0.2804	0.0179	0.2983	0.2804	0.0228	0.3032
0.09	0.2675	0.0177	0.2852	0.2675	0.0203	0.2878
0.13	0.2547	0.0175	0.2722	0.2547	0.0178	0.2725
0.17	0.2420	0.0173	0.2593	0.2421	0.0155	0.2576
0.21	0.2294	0.0171	0.2465	0.2296	0.0131	0.2427
0.25	0.2168	0.0168	0.2336	0.2172	0.0109	0.2281
0.29	0.2043	0.0166	0.2209	0.2049	0.0087	0.2136
0.33	0.1919	0.0164	0.2083	0.1928	0.0065	0.1993
0.37	0.1796	0.0161	0.1957	0.1809	0.0044	0.1853
0.41	0.1673	0.0159	0.1832	0.1690	0.0023	0.1713
0.45	0.1551	0.0156	0.1707	0.1573	0.0002	0.1575
0.49	0.1430	0.0154	0.1584			
0.53	0.1309	0.0151	0.1460			
0.57	0.1190	0.0148	0.1338			
0.61	0.1071	0.0144	0.1215			
0.65	0.0952	0.0141	0.1093			

the same. It is evident that the agreement between theory and experiment is very good in both cases and the trend at low bromine concentrations the same as before.

Included in Fig.(7) are the lines (1b) and (2b), calculated with m_a from Eq. (7b) (see Table XV). It can be seen that there is no agreement between theory and experiment (see also DISCUSSION).

3. Ternary System $C_6H_6/Br_2/CHBr_3$

The results for the binary mixtures C_6H_6/Br_2 and $CHBr_3/Br_2$ are shown in Tables XVI and XVII. The retention *versus* mole fraction of bromine graphs are shown in Fig.8, while the corresponding $1/R$ *versus* y/x or y/z graphs are shown in Fig.9. The trend of the retention *versus* mole fraction of bromine graph for the $CHBr_3/Br_2$ mixtures is the familiar one with a pronounced scavenger effect at low bromine concentrations and a much less pronounced dependence of retention on scavenger concentration for higher mole fraction of bromine. The results for the binary mixtures C_6H_6/Br_2 are very much the same as those obtained by MILMAN (89) for Br^{80} reactions in benzene. The scarcity of thermal diffusive reactions is obvious, although it was impossible to establish the form of the graph at very low bromine concentrations due to extremely low counting rates and hence very large experimental error.

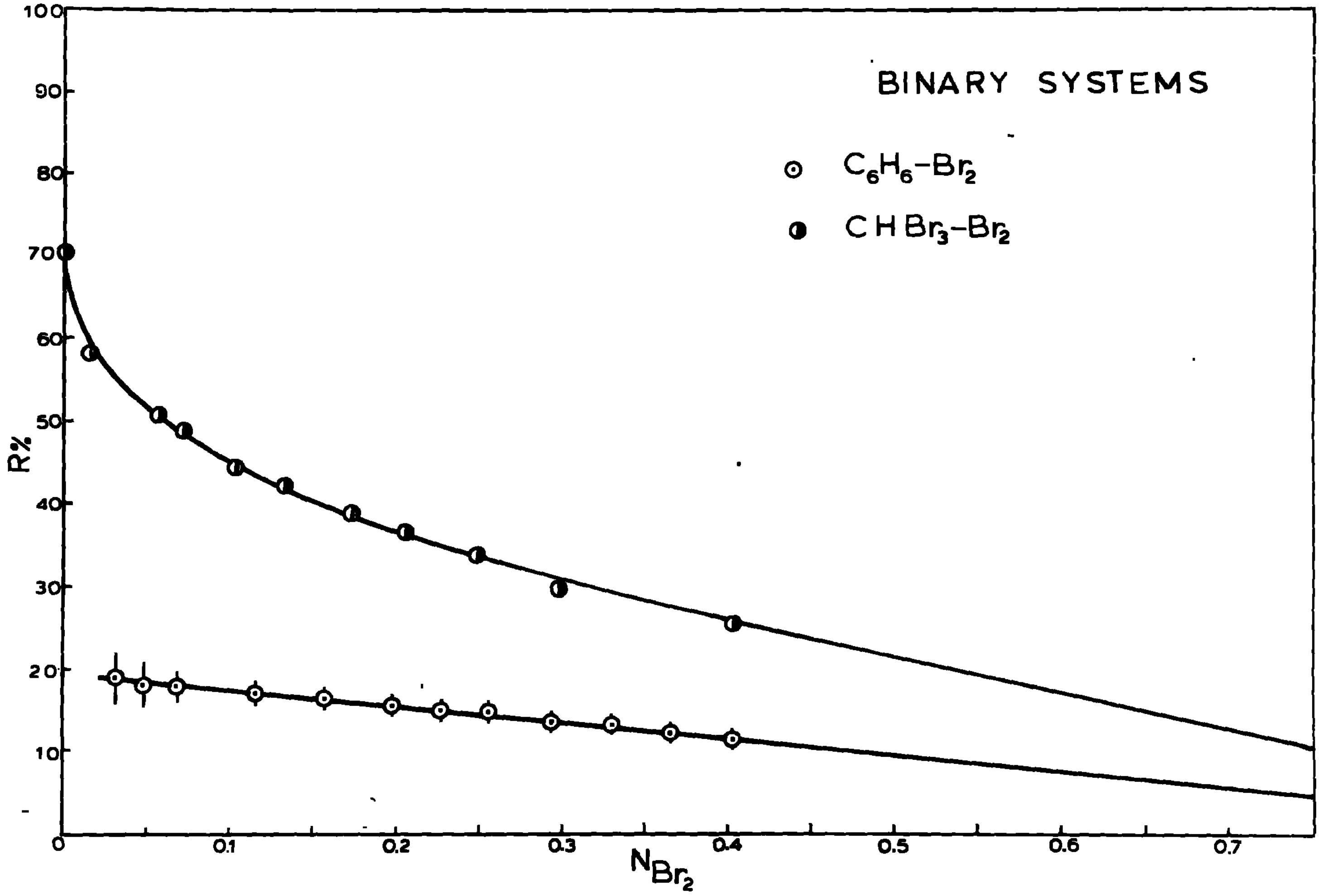

BINARY SYSTEMS
○ $C_6H_6-Br_2$
● $CHBr_3-Br_2$
R%
100
90
80
70
60
50
40
30
20
10
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
N_{Br_2}

Fig.8

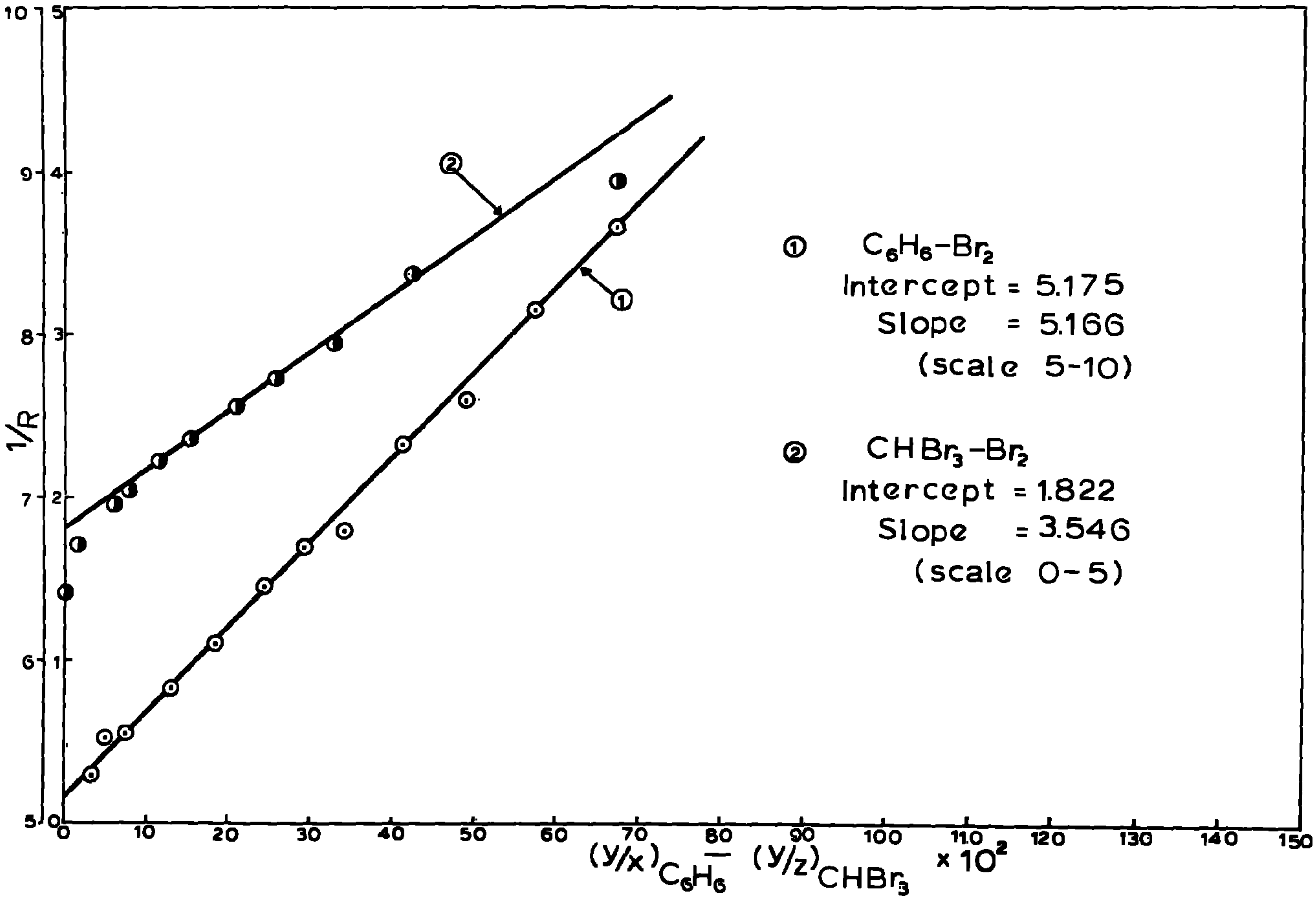


Fig.9

Plot of $^1/R$ versus $y/_x$ or $y/_z$ for binary systems

y: mole fraction of Br_2

x or z: mole fraction of organic component

TABLE XVI

THE BINARY SYSTEM : C_6H_6 / Br_2

MOLE FRACTION Br_2(Y)	FRACTIONAL RETENTION R	$1/_R \pm 6 1/_R$	$Y/_X$ x 10^2
0.031	0.189 ± 0.014	5.291 ± 0.392	3.199
0.047	0.181 ± 0.013	5.525 ± 0.397	4.932
0.068	0.180 ± 0.011	5.549 ± 0.343	7.331
0.115	0.171 ± 0.010	5.831 ± 0.342	13.071
0.156	0.164 ± 0.010	6.108 ± 0.372	18.568
0.197	0.155 ± 0.010	6.453 ± 0.416	24.548
0.226	0.149 ± 0.009	6.707 ± 0.405	29.299
0.255	0.147 ± 0.008	6.796 ± 0.370	34.228
0.292	0.136 ± 0.008	7.331 ± 0.432	41.223
0.329	0.132 ± 0.007	7.593 ± 0.401	49.009
0.365	0.122 ± 0.007	8.156 ± 0.470	57.579
0.402	0.115 ± 0.006	8.686 ± 0.453	67.364

TABLE XVII

THE BINARY SYSTEM : $CHBr_3$ / Br_2

MOLE FRACTION $Br_2(Y)$	FRACTIONAL RETENTION R	$1/R \pm \delta_{1/R}$	$Y/Z \times 10^2$
0.000	0.705 ± 0.005	1.419 ± 0.010	0.000
0.015	0.582 ± 0.004	1.716 ± 0.012	1.554
0.056	0.508 ± 0.005	1.967 ± 0.019	5.898
0.071	0.488 ± 0.005	2.049 ± 0.021	7.677
0.103	0.445 ± 0.004	2.247 ± 0.020	11.495
0.132	0.423 ± 0.005	2.364 ± 0.028	15.287
0.173	0.391 ± 0.004	2.559 ± 0.026	20.977
0.205	0.366 ± 0.004	2.732 ± 0.030	25.770
0.248	0.339 ± 0.004	2.948 ± 0.035	33.032
0.298	0.296 ± 0.004	3.375 ± 0.045	42.511
0.402	0.253 ± 0.004	3.953 ± 0.062	67.336

A striking feature about the $1/_R$ vs $y/_x$ or $y/_z$ graphs is that they both exhibit straight line behaviour. In the case of $CHBr_3$/Br_2, there is a sharp change in slope at about $y/_x \sim 0.1$ and the points, for higher $y/_z$ values, fall on a straight line. This might be due, as predicted by the theory, to the fact that the m_a of $CHBr_3$, as defined by Eq.(7a), has shifted very much towards m_b, the shift having been achieved by the insertion of heavy atoms practically the same as the recoil atom. In the case of C_6H_6/Br_2, where the m_a (by Eq.(7a)) lies the farthest away from m_b, the straight line seems to be merely a consequence of the form of the retention vs mole fraction of bromine graph. Of course, the m_a of C_6H_6, as defined by Eq.(7b), is very much the same with m_b, which should be an extremely favourable situation for straight line behaviour in the $1/_R$ vs $y/_x$ graph, provided that the collisions are elastic in character and with whole molecules.

Anyway, there is a very useful consequence of this form of the graphs, that is, the freedom of movement in drawing the limiting slopes is extremely restricted.

The values of the parameters (calculated with m_a as defined by Eq. (7a) resulting from the lines of Fig.9 are the following:

For the C_6H_6/Br_2 system $\alpha = 0.00827$

$\beta = 0.00826$

For the $CHBr_3/Br_2$ system $\gamma = 0.07984$

$\beta = 0.15538$

The experimental results for the $C_6H_6/Br_2/CHBr_3$ mixtures are shown in Table XVIII and in Fig.10, where the lines (1a) and (2a) have been calculated with m_a as defined by Eq.(7a), while the lines (1b) and (2b) with m_a as defined by Eq.(7b). In this system E_1 (C_6H_6) = 50 Kcal $mole^{-1}$ and E_2 $(CHBr_3)$ = 5 Kcal $mole^{-1}$, consequently both term of Eq.(6) have been calculated. The fact that $E_1 - E_2$ = 45 Kcal $mole^{-1}$ and that fact that $\gamma \gg \alpha$ make the contribution from the second term quite significant, as shown in Tables XIX and XX. The value of the parameter β used for the calculations of theoretical retentions was again a weighed mean of the β's from the two binary systems.

It can be seen that the theoretical lines calculated with m_a from Eq.(7a) are in discrepancy with the experimental results for both series of ternary solutions at 0.200 and 0.500 mole fraction of C_6H_6, while the fit between theoretical lines and experimental results is satisfactory with m_a from Eq.(7b). Another set of calculations is shown in Fig.11. These calculations were based on 'mixed' collisions, that is, the value of m_a was obtained from Eq.(7c). It is obvious that the theoretical lines calculated in this way give a perfect fit at mole fraction of C_6H_6 equal to 0.500, but a poor fit at 0.200 mole fraction of this component. Thus, it appears that in this system, the best fit between theory and experiment can be

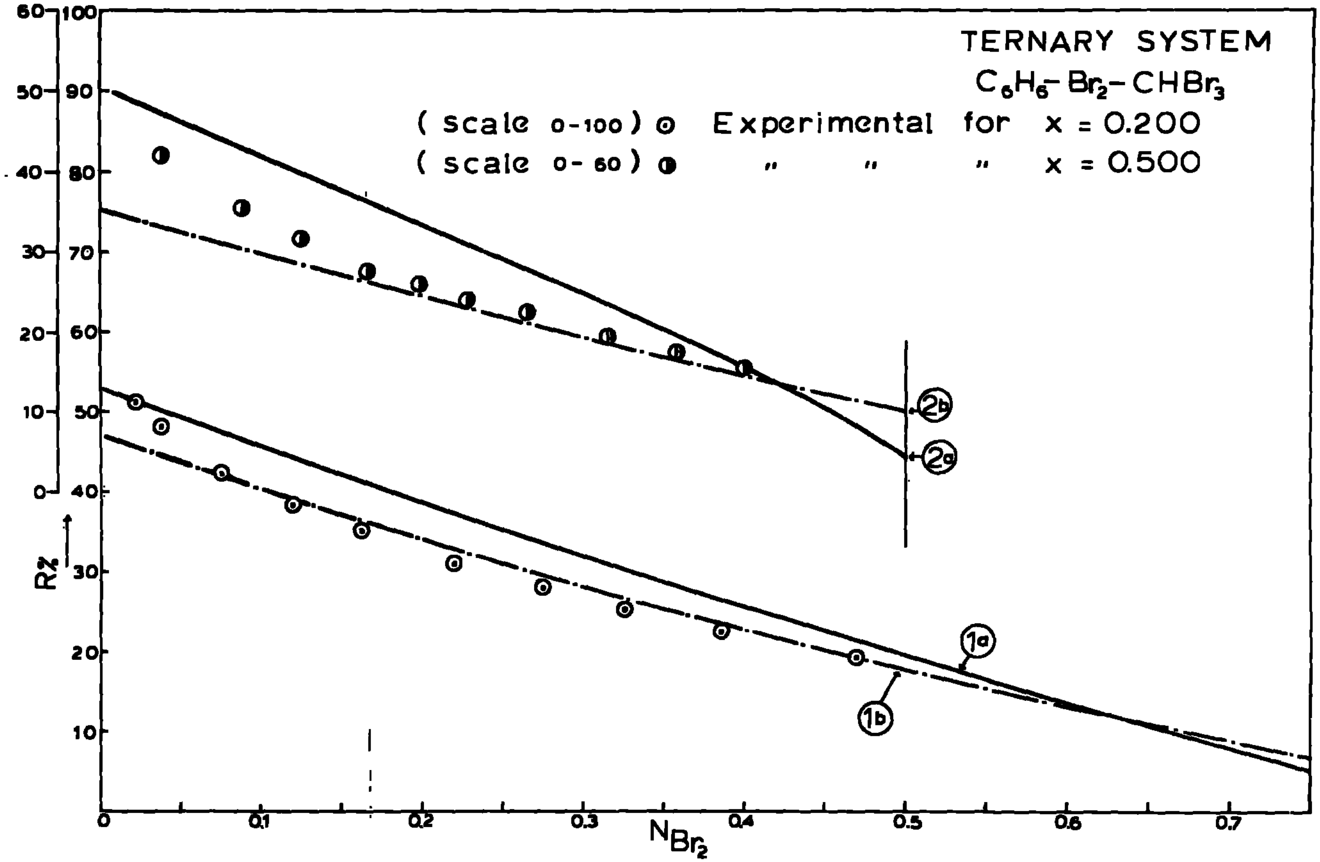


Fig.10

Lines (1a) - (2a) calculated on atomic collisions
Lines (1b) - (2b) calculated on molecular collisions
x: mole fraction of C_6H_6

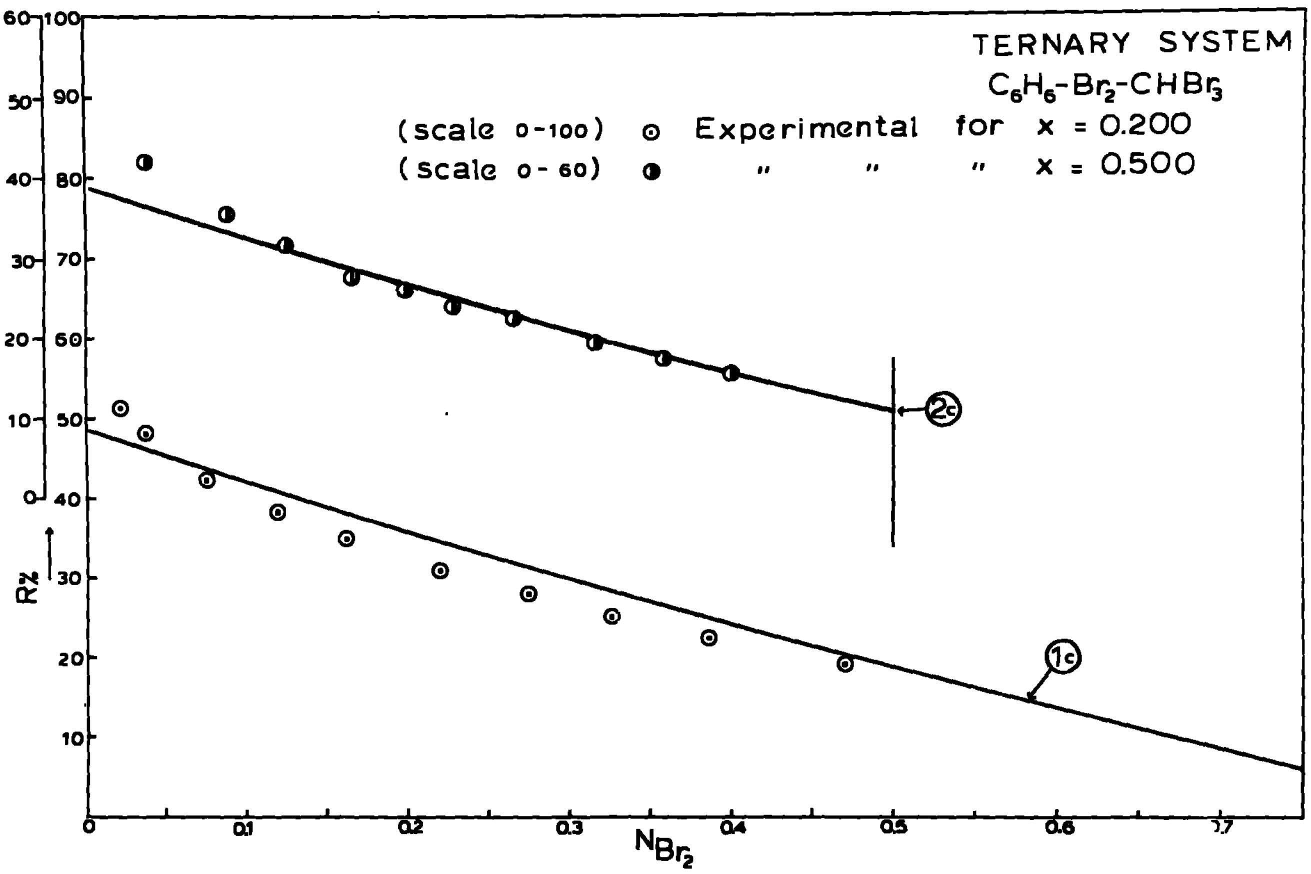


Fig.11

Lines (1c) - (2c) calculated on mixed collisions

x: mole fraction of C_6H_6

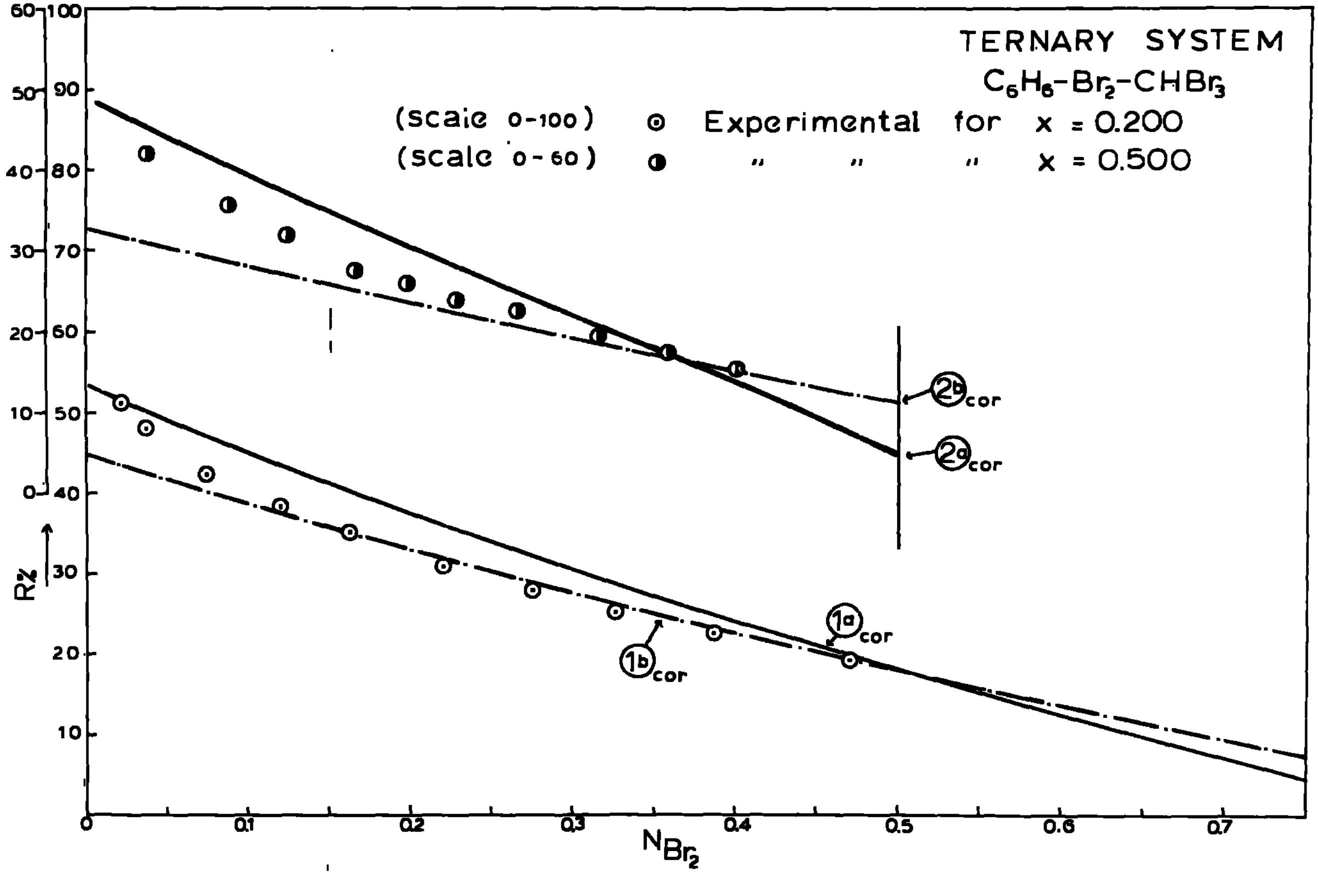


Fig.12

Lines (1a) - (2a) calculated on atomic collisions

Lines (1b) - (2b) calculated on molecular collisions

x: mole fraction of C_6H_6

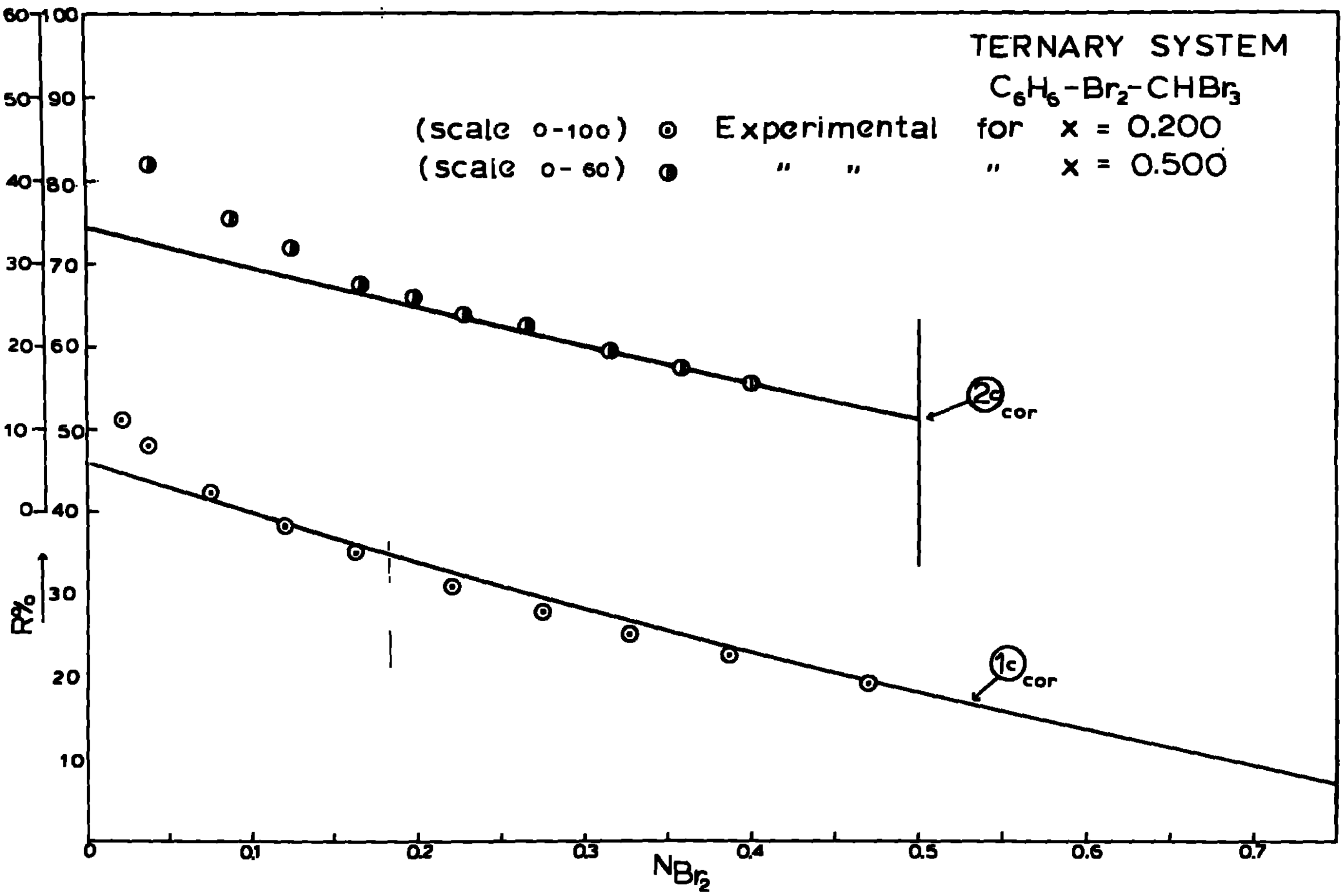


Fig.13

Lines (1c) - (2c) calculated on mixed collisions
x: mole fraction of C_6H_6

TABLE XVIII

THE TERNARY SYSTEM : $C_6H_6 - Br_2 - CHBr_3$

Experimental Retention Values

x = 0.200			x = 0.500		
MOLE FRACTION		FRACTIONAL RETENTION	MOLE FRACTION		FRACTIONAL RETENTION
Br_2 Y	$CHBr_3$ Z		Br_2 Y	$CHBr_3$ Z	
0.021	0.779	0.512 ± 0.008	0.038	0.462	0.421 ± 0.011
0.037	0.763	0.481 ± 0.009	0.087	0.413	0.356 ± 0.011
0.075	0.725	0.422 ± 0.008	0.124	0.376	0.317 ± 0.009
0.119	0.681	0.382 ± 0.008	0.164	0.336	0.275 ± 0.010
0.162	0.638	0.351 ± 0.009	0.197	0.303	0.260 ± 0.011
0.219	0.581	0.310 ± 0.008	0.227	0.273	0.240 ± 0.010
0.275	0.525	0.280 ± 0.008	0.264	0.236	0.226 ± 0.010
0.326	0.474	0.252 ± 0.007	0.315	0.185	0.195 ± 0.010
0.386	0.414	0.226 ± 0.007	0.357	0.143	0.175 ± 0.009
0.470	0.330	0.192 ± 0.005	0.400	0.100	0.156 ± 0.007

TABLE XIX

THE TERNARY SYSTEM : $C_6H_6/Br_2/CHBr_3$

Retentions calculated from theory on m_a from Eq.(7a) and

$$E_{ret}(av) = \frac{m_a^2 + m_b^2}{(m_a + m_b)^2}$$

	FRACTIONAL RETENTION					
	x = 0.200			x = 0.500		
MOLE FRACTION Br_2 (y)	$R_{(E_o,E_1)}$	$R_{(E_1,E_2)}$	R	$R_{(E_o,E_1)}$	$R_{(E_1,E_2)}$	R
0.01	0.3769	0.1492	0.5261	0.3628	0.1370	0.4998
0.05	0.3561	0.1393	0.4954	0.3379	0.1263	0.4642
0.09	0.3358	0.1298	0.4656	0.3131	0.1160	0.4291
0.13	0.3157	0.1207	0.4364	0.2884	0.1060	0.3944
0.17	0.2960	0.1120	0.4080	0.2638	0.0962	0.3600
0.21	0.2765	0.1037	0.3802	0.2392	0.0865	0.3257
0.25	0.2574	0.0957	0.3531	0.2145	0.0769	0.2914
0.29	0.2386	0.0881	0.3267	0.1895	0.0671	0.2566
0.33	0.2201	0.0807	0.3008	0.1642	0.0570	0.2212
0.37	0.2018	0.0737	0.2755	0.1382	0.0463	0.1845
0.41	0.1838	0.0669	0.2507	0.1113	0.0346	0.1459
0.45	0.1660	0.0603	0.2263	0.0831	0.0211	0.1042
0.49	0.1485	0.0540	0.2025	0.0529	0.0047	0.0576
0.53	0.1311	0.0478	0.1789			
0.57	0.1138	0.0418	0.1556			
0.61	0.0967	0.0358	0.1325			
0.65	0.0795	0.0297	0.1092			
0.69	0.0622	0.0233	0.0855			
0.73	0.0455	0.0164	0.0609			
0.77	0.0260	0.0080	0.0340			

TABLE XX

THE TERNARY SYSTEM $C_6H_6/Br_2/CHBr_3$

Retentions calculated from theory on m_a from Eq. (7b)

and $E_{ret}(av) = \dfrac{m_a^2 + m_b^2}{(m_a + m_b)^2}$

MOLE FRACTION Br_2 (y)	FRACTIONAL RETENTION					
	x = 0.200			x = 0.500		
	$R(E_o, E_1)$	$R(E_1, E_2)$	$\bar{R}$	$R(E_o, E_1)$	$R(E_1, E_2)$	$\bar{R}$
0.01	0.3390	0.1255	0.4645	0.2720	0.0774	0.3494
0.05	0.3201	0.1168	0.4369	0.2561	0.0702	0.3263
0.09	0.3017	0.1085	0.4102	0.2405	0.0633	0.3038
0.13	0.2837	0.1005	0.3842	0.2253	0.0566	0.2819
0.17	0.2662	0.0929	0.3591	0.2106	0.0502	0.2608
0.21	0.2492	0.0855	0.3347	0.1962	0.0438	0.2400
0.25	0.2327	0.0785	0.3112	0.1821	0.0376	0.2197
0.29	0.2166	0.0718	0.2884	0.1684	0.0316	0.2000
0.33	0.2008	0.0653	0.2661	0.1550	0.0256	0.1806
0.37	0.1855	0.0591	0.2446	0.1419	0.0196	0.1615
0.41	0.1706	0.0531	0.2237	0.1291	0.0137	0.1428
0.45	0.1561	0.0473	0.2034	0.1166	0.0077	0.1243
0.49	0.1420	0.0417	0.1837	0.1043	0.0016	0.1059
0.53	0.1282	0.0362	0.1644			
0.57	0.1147	0.0309	0.1456			
0.61	0.1015	0.0257	0.1272			
0.65	0.0887	0.0206	0.1093			
0.69	0.0762	0.0154	0.0916			
0.73	0.0638	0.0102	0.0740			
0.77	0.0518	0.0046	0.0564			

obtained by considering 'mixed' collisions in the series of mixtures at 0.500 mole fraction of C_6H_6 and 'molecular' collisions in the series of mixtures at 0.200 mole fraction of C_6H_6. (But we shall come back to that in the DISCUSSION).

The values of m_a calculated from both Eq.(7a) and (7b) the values of E_{ret}(av) calculated from Eq.(8) and the values of m (or n), calculated from Eq.(9) (or Eq.(10)), for all binary systems (at $y = o$) are given in Table XXI.

A complete list of the parameters α , β , γ calculated with m_a from both Eqs.(7a) and (7b) is given in Table XXII.

TABLE XXI

Values of m_a, E_{ret}(av) and m for

all the Binary systems

System	On Eq. (7a)			On Eq. (7b)		
	m_a	E_{ret}(av)	m	m_a	E_{ret}(av)	m
C_6H_6-Br_2	6.51	0.8607	25.54	78.11	0.5001	5.53
C_2H_5Br-Br_2	13.62	0.7511	16.59	108.97	0.5118	7.09
C_6H_5Br-Br_2	13.08	0.7582	17.15	157.02	0.5529	8.01
CCl_4-Br_2	30.77	0.5986	7.46	153.84	0.5500	6.41
$CHBr_3$-Br_2	50.55	0.5253	9.53	252.766	0.6350	13.50

TABLE XXII

Values of Parameters α, β, γ

Calculated on $E_{ret}(av) = \dfrac{m_a^2 + m_b^2}{(m_a + m_b)^2}$

System	m_a from Eq.(7a)	m_a from Eq. (7b)
$C_6H_6 - Br_2$	$\alpha = 0.00827$ $\beta = 0.00826$	$\alpha = 0.03809$ $\beta = 0.03802$
$C_2H_5Br - Br_2$	$\alpha = 0.01605$ $\beta = 0.05058$	$\alpha = 0.03764$ $\beta = 0.11863$
$C_6H_5Br - Br_2$	$\gamma = 0.02495$ $\beta = 0.05114$	$\gamma = 0.05347$ $\beta = 0.10960$
$CCl_4 - Br_2$	$\gamma = 0.04561$ $\beta = 0.07447$	$\gamma = 0.05359$ $\beta = 0.08749$
$CHBr_3 - Br_2$	$\gamma = 0.07984$ $\beta = 0.15538$	$\gamma = 0.05769$ $\beta = 0.11228$

CHAPTER 4

Discussion of Results

Section 1. Limiting Slopes in Binary Systems

From the way this treatment has been developed, the parameters α, β and γ must be determined from the experimentally derived $^1/R$ vs. $^y/x$ or $^y/z$ curves for binary mixtures (CHAPTER 1, Section 4). Theoretically the limiting slope as $^y/x$ or $^y/z \rightarrow 0$ is required, but this requirement is stated on the assumption that thermal diffusive reactions, which are not included in the theory, are absent. In practice the onset of thermal diffusive reactions as the bromine concentration, y, decreases cannot be clearly recognised on these graphs, although all except that for C_6H_6/Br_2 show the expected rapid fall in $^1/R$ at low values of $^y/x$ or $^y/z$. Consequently, drawing the required limiting slope so as to discount the thermal diffusive contribution to $^1/R$ is a subjective process. Nevertheless, if this graph for a particular binary system appears linear or nearly so (no matter for what reason) at values of $^y/x$ high enough to exclude thermal diffusive reactions, the limiting slopes that can plausibly be drawn are fairly severely restricted. It will be observed (Fig.9) that the graph for the binary system $CHBr_3/Br_2$ is very nearly linear at higher $^y/z$ values and the graph for the binary system CCl_4/Br_2 (Fig.4) is fairly nearly linear, so that for these systems the values of α, β and γ derived are probably free from subjective error.

It is interesting to recall that the theory suggests (see p.65) that the more closely the effective collisional mass, $\mathfrak{m}_a$, of the system approaches the mass of a recoil bromine atom, the more likely it is that $^1/R$ shall be a linear function of $^y/x$ or $^y/z$, thermal diffusive contributions to $^1/R$ being ignored. If $\mathfrak{m}_a$ is to be defined by Eq.(7a) (that is, assuming collisions are atomic in nature), then $\mathfrak{m}_a$ for the binary systems under discussion approaches the mass of the recoil bromine atom in the sequence

$$C_6H_6 \longrightarrow C_6H_5Br, C_2H_5Br_2 \longrightarrow CCl_4 \longrightarrow CHBr_3$$

and it can be seen that, excepting the C_6H_6/Br_2 system, the binary systems of these components with Br_2 exhibit improving linear behaviour in this same order (Fig.4 and 9). The appearance of these binary system graphs is thus consistent with, if not indeed confirmation of, the conclusions later reached from the results in ternary systems that collisions in these substances are atomic in character.

On this basis it appears odd that the graph for C_6H_6/Br_2 (Fig.9) should be so nearly linear, but when it is realized that the molecular weight of benzene is almost exactly equal to the mass of the recoil bromine atom it is seen that the graph is again confirmation of the subsequent conclusion that collisions in this compound are of a molecular nature.

The criterion of drawing the limiting slopes in such a way as to obtain values for the parameters α, β and γ giving good agreement between theory and experiment seems, at present, to be the way round the difficulty of recognizing the onset of thermal diffusive reactions, provided that the limiting slopes are drawn at reasonably low bromine concentrations. This criterion has been made use of in this work, especially for the binary systems C_2H_5Br/Br_2, C_6H_5Br/Br_2 and CCl_4/Br_2. In the case of the binary systems C_6H_6/Br_2 and $CHBr_3/Br_2$, the very nearly linear form of the $^1/R$ vs. $^y/x$ or $^y/z$ curves left very little space for manoeuvring.

With all the above in mind it is, however, important to realize that the freedom of movement in drawing the limiting slopes is much more limited than might appear. This can be seen as follows. In Table XXIII are shown (in an analytical way) some of the results obtained in the calculation of retentions in the $C_2H_5Br/Br_2/C_6H_5Br$ system for 0.32 mole fraction of C_6H_5Br (Fig.5, line (1a)).

From this table, it is obvious that the decrease in retention with increasing y depends entirely on the S factor. Thus, the calculated line will show acceptable behaviour only if the ratio of β

TABLE XXIII

Values of various factors in the calculation of Theoretical Retention Values

MOLE FRACTION Br_2 (y)	FRACTIONAL RETENTION R	$S = \dfrac{\alpha x + \gamma z}{\alpha x + \beta y + \gamma z}$	$(1 - p^m)$
0.01	0.2718	0.9736	0.2792
0.09	0.2339	0.7922	0.2953
0.15	0.2086	0.6837	0.3051
0.25	0.1713	0.5393	0.3177
0.45	0.1120	0.3378	0.3316

to the sum of α and γ is approximately correct. But this change in R operates at a level which is determined almost entirely by the factor $(1-p^m)$. Remembering that $p = (1 - \alpha x - \beta y - \gamma z)$, it can easily be realized that the correct magnitude for p^m can only be obtained if the sum of the values of α, β and γ is approximately correct. Again, the correct rise in the calculated retention values from one series of mixtures to another at a fixed mole fraction of one of the organic components will only be obtained if the parameter α or γ associated with this component is of the correct magnitude relative to the other two parameters. Finally, since α (or γ) and β are connected by the equation

$$\text{Limiting slope} = \text{Intercept} \times \frac{\beta}{\alpha\ (\text{or}\ \gamma)}$$

and since α (or γ) is an inverse function of the intercept, the values of α (or γ) and β cannot be independently adjusted.

All these conditions put together, and in combination with the general criterion of drawing the limiting slopes at low bromine concentrations, result in further restricting the freedom of manoeuvre in the $^1/R$ vs. $^y/x$ or $^y/z$ graphs.

A further restriction results from investigating all the possible ternary combinations of a number of binary systems, because then the values of the parameters α, β, γ derived from each one of the binaries are tested in more than one ternary. This was done in this work with the systems C_2H_5Br/Br_2, C_6H_5Br/Br_2 and CCl_4/Br_2 and their combinations $C_2H_5Br/Br_2/C_6H_5Br$, $C_2H_5Br/Br_2/CCl_4$ and $C_6H_5/Br_2/CCl_4$ (hereafter to be referred to as 'systems of the triangle',(see also pp 68-69).

It should be noted here that the values of the parameter β are different in the various systems (See Table XXII) while, according to the theory, they should be the same, since β is a property of the bromine molecule. In the RESULTS section of this work, it was said that the value of the parameter β used in the calculation of retentions in ternary mixtures was a weighed mean of the two values obtained from the corresponding binaries. The only exception was the ternary system $C_2H_5Br/Br_2/C_6H_5Br$, where the value of the parameter β used in the calculations was the average of those determined from the two binaries, since they were very much the same.

In the discussion of the results that follows this discrepancy in the values of β 's will be ignored and will be discussed separately later. All conclusions drawn are subject to a justification or explanation of these discrepancies.

Before proceeding to discuss the agreement between theory and experiment in each one of the systems and various other features of the results, it seems useful to discuss two general aspects of the treatment applying to all the systems investigated. These two aspects are (a) the effect on the retention values of the way of calculating the number of collisions required to reduce E_o to E_1 or E_2 and (b) the effect of changes in the value of E_o, again on the theoretical retention values.

Section 2. Calculation of the number of collisions

All the calculations in the RESULTS section of this work have been carried out by using the equation

$$E_{ret}(av) = \frac{m_a^2 + m_b^2}{(m_a + m_b)^2}$$

to calculate the energy degradation of the hot bromine atoms. Then the number of collisions is obtained from the equation

$$m = \frac{\log (E_1/E_o)}{\log (E_{ret}(av))}$$

But in both the ESTRUP-WOLFGANG treatment and in MILMAN'S application of it to liquid systems, the average logarithmic energy loss per collision has been used, given by the formula

$$\xi = 1 - \frac{(M - m)^2}{2Mm} \ln \left| \frac{M + m}{M - m} \right|$$

where M is the mass of the struck atom or molecule, and m is the mass of the hot atom.

In this case the number of collisions is given by

$$m = \frac{\ln (E_o/E_1)}{\xi}$$

All the calculations in this work were repeated by using the logarithmic energy decrement. In all cases, the results obtained were very much the same with those obtained by using E_{ret}(av) of the theory. Whenever differences appeared, they were never greater than 0.005 - 0.006 of the actual fractional retention values or, approximately, 2.5 per cent from one way of calculation to the other. These were well below the experimental uncertainties on the points. Some individual values for the systems of the triangle are given in Tables XXIV-XXVI, based on m_a as defined by Eq.(7a), to illustrate that in all three systems the differences are negligible.

The only case where the differences in the theoretical retention values, calculated on E_{ret}(av) and on Logarithmic Energy Decrement, are fairly larger than those given in the previous paragraph is the case of atomic collisions in the ternary mixtures $C_6H_6/Br_2/CHBr_3$.

TABLE XXIV

THE TERNARY SYSTEM $C_2H_5Br/Br_2/C_6H_5Br$

Comparison of retention values calculated in E_{ret}(av) and on Logarithmic Energy Decrement.

(A) $\mathfrak{m}_a$ from Eq.(7a)

	FRACTIONAL RETENTION			
	z = 0.3198		z = 0.5496	
MOLE FRACTION Br_2 (y)	E_{ret}(av)	LOGARITHMIC ENERGY DECREMENT	E_{ret}(av)	LOGARITHMIC ENERGY DECREMENT
0.01	0.2718	0.2716	0.2989	0.2987
0.09	0.2339	0.2326	0.2607	0.2593
0.17	0.2006	0.1983	0.2267	0.2244
0.25	0.1713	0.1682	0.1966	0.1935
0.33	0.1454	0.1417	0.1697	0.1660
0.41	0.1225	0.1183	0.1457	0.1415
0.49	0.1021	0.0977		
0.57	0.0841	0.0795		
0.65	0.0682	0.0635		
(B) $\mathfrak{m}_a$ from Eq.(7b)				
0.01	0.2704	0.2703	0.2971	0.2970
0.09	0.2485	0.2497	0.2746	0.2753
0.17	0.2270	0.2291	0.2526	0.2535
0.25	0.2059	0.2084	0.2309	0.2317
0.33	0.1852	0.1877	0.2096	0.2100
0.41	0.1648	0.1671	0.1887	0.1884
0.49	0.1449	0.1466		
0.58	0.1254	0.1262		
0.65	0.1063	0.1060		

TABLE XXV

THE TERNARY SYSTEM: $C_2H_5Br/Br_2/CCl_4$

Comparison of retention values calculated on E_{ret}(av) and on Logarithmic Energy Decrement

(A) m_a from Eq.(7a)

	FRACTIONAL RETENTION			
	x = 0.3000		x = 0.7535	
MOLE FRACTION Br_2 (y)	E_{ret}(av)	LOGARITHMIC ENERGY DECREMENT	E_{ret}(av)	LOGARITHMIC ENERGY DECREMENT
0.01	0.2848	0.2904	0.2587	0.2641
0.09	0.2488	0.2522	0.2150	0.2173
0.17	0.2149	0.2163	0.1739	0.1733
0.23	0.1907	0.1908	0.1446	0.1421
0.33	0.1527	0.1512		
0.41	0.1243	0.1218		
0.49	0.0976	0.0943		
0.57	0.0725	0.0688		
0.65	0.0488	0.0450		
(B) m_a from Eq.(7b)				
0.01	0.2736	0.2743	0.2471	0.2477
0.09	0.2482	0.2495	0.2215	0.2236
0.17	0.2232	0.2249	0.1962	0.1996
0.23	0.2045	0.2067	0.1775	0.1817
0.33	0.1737	0.1764		
0.41	0.1495	0.1525		
0.49	0.1255	0.1288		
0.57	0.1018	0.1053		
0.65	0.0784	0.0820		

TABLE XXVI

THE TERNARY SYSTEM: $C_6H_5Br/Br_2/CCl_4$

Comparison of retention values calculated on E_{ret}(av) and on Logarithmic Energy Decrement

(A) m_a from Eq.(7a)

	FRACTIONAL RETENTION			
	x = 0.3184		x = 0.5460	
MOLE FRACTION Br_2 (y)	E_{ret}(av)	LOGARITHMIC ENERGY DECREMENT	E_{ret}(av)	LOGARITHMIC ENERGY DECREMENT
0.01	0.3233	0.3308	0.3323	0.3405
0.09	0.2855	0.2907	0.2883	0.2938
0.17	0.2498	0.2529	0.2482	0.2509
0.25	0.2161	0.2172	0.2118	0.2118
0.33	0.1840	0.1835	0.1789	0.1762
0.41	0.1537	0.1519	0.1497	0.1441
0.49	0.1250	0.1220		
0.57	0.0978	0.0940		
0.65	0.0721	0.0676		
	(B) m_a from Eq.(7b)			
0.01	0.3115	0.3114	0.3188	0.3187
0.09	0.2852	0.2854	0.2878	0.2879
0.17	0.2593	0.2597	0.2576	0.2579
0.25	0.2336	0.2342	0.2281	0.2286
0.33	0.2083	0.2089	0.1993	0.2000
0.41	0.1832	0.1838	0.1713	0.1720
0.49	0.1584	0.1590		
0.57	0.1338	0.1344		
0.65	0.1093	0.1099		

This is shown in Table XXVII. As will be seen when the results in these mixtures are discussed, atomic collisions with E_{ret}(av) give lines which are higher than the experimental points, and the use of the Logarithmic Energy Decrement simply increases the discrepancy. Consequently, it does not have any impact on the conclusions discussed there.

But the fact that these differences in the theoretical retention values obtained with the two formulae for the energy degradation appeared only in one system and for just one type of collision is interesting. It raises the question as to whether these differences could be forecast on the basis of the values of various parameters in the binary systems, in combination with the form of Eq.(6) of the theory. And it also raises another question, that is whether these differences, in other systems, might appear for a different type of collision e.g. molecular.

To answer these questions, Table XXIX has been constructed, in which the parameters m and α, β, γ, obtained with the two formulae for the energy degradation of the recoil atom, are tabulated for atomic and molecular collisions in the binary systems C_6H_6/Br_2 and $CHBr_3/Br_2$.

TABLE XXVII

THE TERNARY SYSTEM $C_6H_6/Br_2/CHBr_3$

Comparison of retention values calculated on $E_{ret}(av)$ and on Logarithmic Energy Decrement.

m_a from Eq.(7a)

	FRACTIONAL RETENTION			
	x = 0.200		x = 0.500	
MOLE FRACTION Br_2 (y)	$E_{ret}(av)$	LOGARITHMIC ENERGY DECREMENT	$E_{ret}(av)$	LOGARITHMIC ENERGY DECREMENT
0.01	0.5261	0.5555	0.4998	0.5527
0.09	0.4656	0.4908	0.4291	0.4742
0.15	0.4221	0.4444	0.3771	0.4168
0.21	0.3802	0.3999	0.3257	0.3600
0.25	0.3531	0.3711	0.2914	0.3221
0.29	0.3267	0.3431	0.2567	0.2837
0.35	0.2880	0.3022	0.2031	0.2242
0.41	0.2507	0.2627	0.1459	0.1600
0.45	0.2263	0.2370	0.1042	0.1122
0.49	0.2024	0.2119	0.0576	0.0578
0.55	0.1672	0.1747		
0.61	0.1324	0.1382		
0.65	0.1092	0.1137		

TABLE XXIX

	m_a from Eq.(7a)	
System	E_{ret}(av)	LOGARITHMIC ENERGY DECREMENT
C_6H_6/Br_2	$m_a = 6.51$ $m = 25.84$ $\alpha = 0.00827$ $\beta_1 = 0.00826$	$m_a = 6.51$ $m = 25.17$ $\alpha = 0.00851$ $\beta_1 = 0.00850$
$CHBr_3/Br_2$	$m_a = 50.55$ $m = 9.55$ $\gamma = 0.07984$ $\beta_2 = 0.15538$	$m_a = 50.55$ $m = 7.35$ $\gamma = 0.10267$ $\beta_2 = 0.19982$
	m_a from Eq.(7b)	
C_6H_6/Br_2	$m_a = 78.11$ $m = 5.53$ $\alpha = 0.03809$ $\beta_1 = 0.03802$	$m_a = 78,11$ $m = 3.84$ $\alpha = 0.05437$ $\beta_1 = 0.05428$
$CHBr_3/Br_2$	$m_a = 252.766$ $m = 13.39$ $\gamma = 0.05769$ ~~$\beta_2 = 0.11228$~~	$m_a = 252.766$ $m = 11.78$ $\gamma = 0.6537$ ~~$\beta_2 = 0.12723$~~

It can be seen that, for atomic collisions, there is practically no change in the parameters α and β_1 for C_6H_6 (because there is practically no change in the number of collisions, m), while the parameters γ and β_2 in $CHBr_3$ change significantly.

In the calculation of retention, in the ternary mixtures $C_6H_6/Br_2/CHBr_3$ by means of Eq.(6), the parameters α, β, γ combine with the mole fractions x, y and z. For constant mole fraction of C_6H_6 (which was the case in this work), the quantities αx and $\beta_1 x/x+z$ (β_1 the value of β from C_6H_6, $\beta_1 x/x+z$ the contribution to the weighed mean of β's) remain the same, since α and β_1 do not change. But for $CHBr_3$, the corresponding quantities γz and $\beta_2 z/x+z$ both change, because γ and β_2 change. Thus, the changes due to one component are not compensated by changes in the other and this accounts for the differences in the theoretical retention values in changing from E_{ret}(av) to Logarithmic Energy Decrement. And, since x = constant, z decreases with increasing y (because $x + y + z = 1$), and the differences in the retentions decrease with decreasing z and become negligible as $z \longrightarrow 0$. This can be seen in Table XXVII (compare adjacent values in 2nd and 3rd columns or in 4th and 5th ones).

The fundamental question which arises from this analysis is: when does E_{ret}(av) give values of m significantly different than those obtained with the Logarithmic Energy Decrement? or, to put it another way, can one predict, on the basis of m_a, whether the differences in the values of m calculated with the two formulae will be significant?

In Fig.17 the curves for E_{tr}(av) per collision (=1-E_{ret}(av)) and Logarithmic Energy Loss per collision (ξ) have been plotted against m_a. From these curves it becomes obvious that the differences in the number of collisions calculated by these two formulae will be very small for small m_a, will increase with increasing m_a until they reach a maximum at $m_a = 81 = m_b$ and then will start decreasing slowly as m_a increases further.

In the case of molecular collisions in the ternary mixtures $C_6H_6/Br_2/CHBr_3$, changes in the values of the parameters α, β and γ occur in both C_6H_6 and $CHBr_3$, in changing from E_{ret}(av) to Logarithmic Energy Decrement. Thus, the effects are compensated in the various factors of Eq.(6) and the theoretically calculated retentions are the same in the two cases.

Also, by applying the same consideration, it can easily be seen why in the case of mixed collisions the two formulae for the energy degradation of the recoil atom give theoretical retentions values that are practically the same.

In the systems of the triangle, there are no differences in the retentions calculated from E_{ret}(av) and Logarithmic Energy Decrement in both atomic and molecular collisions, because the effects are always compensated. This can be seen from Fig. 17 and by inspection of Table XXX which gives a full list of the parameters α, β and γ for all the binary systems. (The system C_5H_{12}/Br_2 is discussed later).

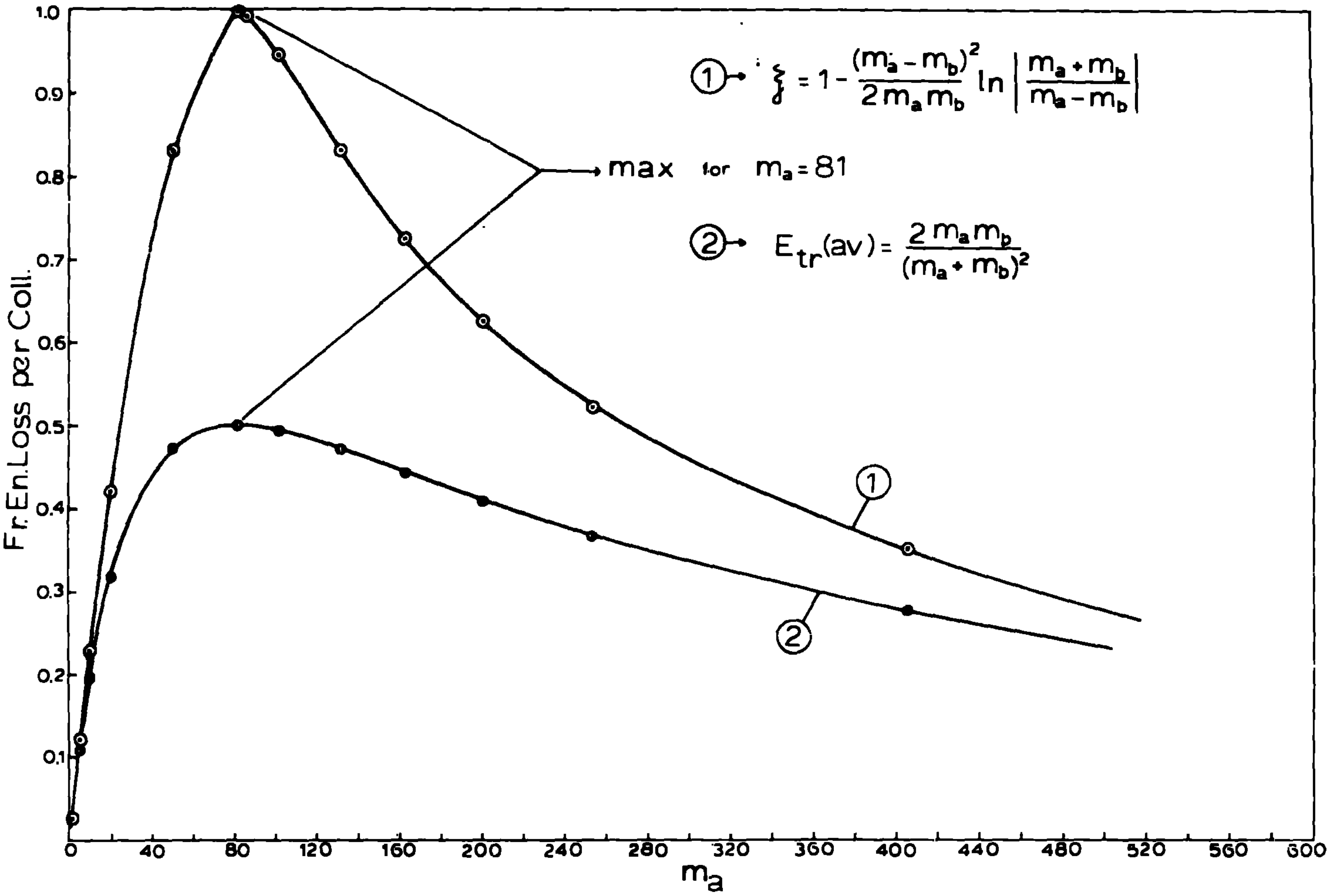


Fig.17

m_b: Mass of the recoil bromine atom

m_a: Mass of the collision partner

TABLE XXX

Values of parameters α, β, γ calculated on E_{ret}(av) of the theory and on Logarithmic Energy Decrement

	E_{ret}(av)		LOGARITHMIC ENERGY DECREMENT	
	m_a from:		m_a from:	
SYSTEM	Eq.(7a)	Eq.(7b)	Eq.(7a)	Eq.(7b)
C_6H_6/Br_2	α = 0.00827 β = 0.00826	α = 0.03809 β = 0.03802	α = 0.00851 β = 0.00850	α = 0.05437 β = 0.05428
C_2H_5Br/Br_2	α = 0.01605 β = 0.05058	α = 0.03764 β = 0.11863	α = 0.01708 β = 0.05385	α = 0.05091 β = 0.16047
C_6H_5Br/Br_2	γ = 0.02495 β = 0.05114	γ = 0.05346 β = 0.10960	γ = 0.02648 β = 0.05428	γ = 0.06600 β = 0.13529
CCl_4/Br_2	γ = 0.04561 β = 0.07447	γ = 0.05359 β = 0.08749	γ = 0.05311 β = 0.08671	γ = 0.06645 β = 0.10848
$CHBr_3/Br_2$	γ = 0.07983 β = 0.15538	γ = 0.05769 β = 0.11228	γ = 0.10267 β = 0.19982	γ = 0.06537 β = 0.12723
C_5H_{12}/Br_2	α = 0.00556 β = 0.00555	α = 0.03793 β = 0.03786	α = 0.00566 β = 0.00565	α = 0.05351 β = 0.05341

It can be seen from this Table that the values of the parameters α, β, γ obtained with the two formulae for the energy degradation of the recoil atom are somewhat different but of about the same order of magnitude. Again the fit between theoretical and experimental retention values obtained with either of them is the same. The only difference is that the use of the Logarithmic Energy Decrement partly eliminates the discrepancies in the values of the parameter β. But this will be discussed later.

Section 3. The effect of the value of E_o

It has already been said (see CHAPTER 1 Section 2) that the values of m and n (which eventually determine the values of the parameters α, β, γ) are not very critically dependent on the values of E_{1/E_o} and E_{2/E_o}. Also since m and n must be calculated for the determination of the parameters α, β, γ in the binary systems and recalculated when using these parameters to obtain the retention values in ternary mixtures, any errors in the values of E_{1/E_o} and E_{2/E_o} used in Eq. (9) and (10) of the theory would be expected to be largely self cancelling. In order to get a more precise idea of the effect of the energy values and, particularly, the effect of E_o on the fit of theoretical calculations to the experimental results, calculations were done by changing the value of E_o by a factor of 10. In Table XXVIII are shown the partial results of two sets of calculations, one for E_o = 100 e.v. and another for E_o = 10 e.v.,

TABLE XXVIII

	$\alpha = 0.01605$ $\beta = 0.05085$ $\gamma = 0.02495$					$\alpha = 0.03093$ $\beta = 0.09781$ $\gamma = 0.04788$				
	E_o = 100 ev					E_o = 10 ev				
MOLE FRACTION Br_2 (y)	R	$\frac{\alpha x + \gamma z}{\alpha x + \beta y + \gamma z}$	$1-p^m$	p	m	R	$\frac{\alpha x + \gamma z}{\alpha x + \beta y + \gamma z}$	$1-p^m$	p	m
0.01	0.2718	0.9736	0.2792	0.9808	16.8439	0.2717	0.9736	0.2791	0.9630	8.6739
0.03	0.2618	0.9235	0.2835	0.9801	16.5528	0.2618	0.9235	0.2835	0.9616	8.5240
0.05	0.2522	0.8768	0.2877	0.9794	16.2665	0.2523	0.8768	0.2878	0.9603	8.3766
0.07	0.2429	0.8331	0.2916	0.9787	15.9852	0.2431	0.8331	0.2917	0.9590	8.2317
0.09	0.2339	0.7922	0.2953	0.9780	15.7086	0.2341	0.7922	0.2955	0.9576	8.0893
0.11	0.2252	0.7538	0.2987	0.9773	15.4367	0.2254	0.7538	0.2990	0.9563	7.9492
0.13	0.2168	0.7177	0.3020	0.9766	15.1693	0.2170	0.7177	0.3024	0.9549	7.8116
0.15	0.2086	0.6837	0.3051	0.9759	14.9064	0.2089	0.6837	0.3055	0.9536	7.6762
0.17	0.2006	0.6516	0.3079	0.9752	14.6479	0.2010	0.6516	0.3085	0.9523	7.5431
0.19	0.1930	0.6212	0.3106	0.9745	14.3938	0.1934	0.6212	0.3113	0.9509	7.4122
0.21	0.1855	0.5924	0.3132	0.9738	14.1438	0.1859	0.5924	0.3139	0.9496	7.2835
0.23	0.1783	0.5652	0.3155	0.9731	13.8980	0.1788	0.5652	0.3163	0.9483	7.1569
0.25	0.1713	0.5393	0.3177	0.9724	13.6563	0.1718	0.5393	0.3186	0.9469	7.0324
0.27	0.1645	0.5147	0.3197	0.9717	13.4186	0.1650	0.5146	0.3207	0.9456	6.9100
0.29	0.1580	0.4913	0.3215	0.9710	13.1849	0.1585	0.4912	0.3226	0.9442	6.7897
0.31	0.1516	0.4689	0.3233	0.9703	12.9551	0.1521	0.4689	0.3244	0.9429	6.6713
0.33	0.1454	0.4476	0.3248	0.9696	12.7291	0.1459	0.4475	0.3261	0.9416	6.5549
0.35	0.1394	0.4273	0.3263	0.9689	12.5068	0.1399	0.4272	0.3276	0.9402	6.4405
0.37	0.1336	0.4078	0.3276	0.9682	12.2883	0.1341	0.4077	0.3290	0.9389	6.3280
0.39	0.1279	0.3892	0.3287	0.9675	12.0735	0.1285	0.3890	0.3303	0.9376	6.2174
0.41	0.1225	0.3713	0.3298	0.9668	11.8624	0.1230	0.3712	0.3314	0.9362	6.1086
0.43	0.1172	0.3542	0.3307	0.9661	11.6548	0.1177	0.3541	0.3324	0.9349	6.0017
0.45	0.1120	0.3378	0.3316	0.9654	11.4508	0.1125	0.3376	0.3334	0.9335	5.8967
0.47	0.1070	0.3220	0.3323	0.9647	11.2503	0.1075	0.3218	0.3342	0.9322	5.7935
0.49	0.1021	0.3069	0.3329	0.9640	11.0534	0.1027	0.3067	0.3349	0.9309	5.6920
0.51	0.0974	0.2923	0.3334	0.9633	10.8599	0.0980	0.2921	0.3355	0.9295	5.5924
0.53	0.0929	0.2782	0.3338	0.9626	10.6699	0.0934	0.2780	0.3360	0.9282	5.4946
0.55	0.0884	0.2647	0.3341	0.9620	10.4833	0.0890	0.2645	0.3364	0.9269	5.3985
0.57	0.0841	0.2517	0.3344	0.9613	10.3002	0.0847	0.2514	0.3367	0.9255	5.3042
0.59	0.0800	0.2391	0.3345	0.9606	10.1206	0.0805	0.2388	0.3370	0.9242	5.2117
0.61	0.0759	0.2269	0.3346	0.9599	9.9443	0.0764	0.2267	0.3371	0.9228	5.1209
0.63	0.0720	0.2152	0.3346	0.9592	9.7716	0.0725	0.2149	0.3372	0.9215	5.0320
0.65	0.0682	0.2039	0.3345	0.9585	9.6023	0.0687	0.2036	0.3373	0.9202	4.9448

for the ternary mixtures $C_2H_5Br/Br_2/C_6H_5Br$ at 0.3198 constant mole fraction of C_6H_5Br and assuming atomic collisions (line (1a) in Fig.5).

It can be seen that the values of the retention are very much the same (compare R columns). Thus, the fit or otherwise between theory and experiment is not affected by a change in E_o, in this case from 100 e.v. to 10 e.v. The values of the parameters α, β and γ in the two cases are considerably different. In fact it can be seen, that (the value of β being the average of the β's from the two binaries, which are very much the same),

$$\alpha_{10\ e.v.} = K_1 \times \alpha_{100\ e.v.}$$

$$\beta_{10\ e.v.} = K_2 \times \beta_{100\ e.v.}$$

$$\gamma_{10\ e.v.} = K_3 \times \gamma_{100\ e.v.}$$

and it turns out that

$$K_1 \simeq K_2 \simeq K_3 \simeq K \simeq 1.92$$

From these relations another one can be derived, that is

$$\left\langle \frac{\beta}{\alpha + \gamma} \right\rangle_{100\ e.v.} = \left\langle \frac{\beta}{\alpha + \gamma} \right\rangle_{10\ e.v.}$$

and this relation suggests the same behaviour of the calculated lines in both cases (see Section 2 of this chapter).

But it should be pointed out that in the above ternary mixtures, the m_a's for both the corresponding binaries are very much the same and also the β's are very much the same. Consequently, it is not surprising that K_1, K_2, K_3 have practically the same value.

The actual relations, connecting the parameters for two different values of E_o in ternary mixtures in which the m_a's of the corresponding binaries are different, are the following:

$$\frac{\log\,(1-\alpha)_{100\text{ e.v.}}}{\log\,(1-\alpha)_{10\text{ e.v.}}} = \frac{m_{10\text{ e.v.}}}{m_{100\text{ e.v.}}}$$

where m: number of collisions

and

$$\frac{\beta_{10\text{ e.v.}}}{\beta_{100\text{ e.v.}}} = \frac{\alpha_{10\text{ e.v.}}}{\alpha_{100\text{ e.v.}}}$$

and, in an analogous way, for the other binary, where the parameters are γ and β.

The other columns (except R) in Table XXVIII show clearly why the change in the values of the parameters α, β, γ does not affect the retention values. The factor $(\alpha x + \gamma z) / (\alpha x + \beta y + \gamma z)$ is the same. The number of collisions decreases markedly, as expected, with a large decrease in E_o. But this decrease in the number of collisions in the binary systems is responsible for the increase in the values of α, β, γ which, in turn, results in a decrease in p (through the relation $p = (1 - \alpha x - \beta y - \gamma z)$) and the overall effect is the adjustment of the factor $(1 - p^{m})$ at the right level.

The same insensitivity of the retention values to changes in the value of E_o is found in the case of molecular collisions ($\mathcal{m}_a$ from Eq.(7b)).

But the system $C_2H_5Br/Br_2/C_6H_5Br$ is the only one of the systems investigated in this work for which $E_1 = E_2$. The retentions, however, in systems where $E_1 \neq E_2$ should be expected to exhibit the same insensitivity to changes in the values of E_o, since the factors $\alpha x/(\alpha x + \beta y)$ or $\gamma z/(\gamma z + \beta y)$ and $(1 - q^{n-m})$ must vary in a way analogous to that of the factors $(\alpha x + \gamma z)/\alpha x + \beta y + \gamma z)$ and $(1-p^{m})$. The only effect (for obvious reasons), in changing from one value of E_o to another, will be a change in the relative contribution of the two terms of Eq.(6) to the total retention. This effect is illustrated in Table XXXI with some results for the ternary mixtures $C_6H_6/Br_2/CHBr_3$.

Thus, it is concluded that, for given slopes and intercepts in the binary systems, the theoretical retention values are 'buffered' to changes in the value of E_o, although all the parameters, with the exception of $\mathcal{m}_a$, change. This buffering effect is an intrinsic property of the theoretical treatment.

TABLE XXXI

THE TERNARY SYSTEM $C_6H_6/Br_2/CHBr_3$

Comparison of retehtions for (a) E_o = 100 e.v.

(b) E_o = 10 e.v. m_a defined by Eq.(7b)

	E_o = 100 e.v.			E_o = 10 e.v.		
	MOLE FRACTION C_6H_6 = 0.200					
MOLE FRACTION Br_2(y)	$R_{(E_o,E_1)}$	$R_{(E_1,E_2)}$	R	$R_{(E_o,E_1)}$	$R_{(E_1,E_2)}$	R
0.01	0.3390	0.1255	0.4645	0.2490	0.2146	0.4636
0.05	0.3201	0.1168	0.4369	0.2362	0.1998	0.4360
0.09	0.3017	0.1085	0.4102	0.2238	0.1856	0.4094
0.13	0.2837	0.1005	0.3842	0.2115	0.1720	0.3835
0.17	0.2662	0.0929	0.3591	0.1996	0.1589	0.3585
0.21	0.2492	0.0855	0.3347	0.1879	0.1463	0.3342
0.25	0.2327	0.0785	0.3112	0.1765	0.1341	0.3106
0.29	0.2166	0.0718	0.2884	0.1653	0.1225	0.2878
0.33	0.2008	0.0653	0.2661	0.1544	0.1112	0.2656
0.37	0.1855	0.0591	0.2446	0.1437	0.1004	0.2441
0.41	0.1706	0.0531	0.2237	0.1333	0.0899	0.2232
0.45	0.1561	0.0473	0.2034	0.1230	0.0798	0.2028
0.49	0.1420	0.0417	0.1837	0.1131	0.0700	0.1831
0.53	0.1282	0.0362	0.1644	0.1033	0.0605	0.1638
0.57	0.1147	0.0309	0.1456	0.0937	0.0512	0.1449
0.61	0.1015	0.0257	0.1272	0.0844	0.0422	0.1266
0.65	0.0887	0.0206	0.1093	0.0753	0.0334	0.1087

Consequently, the fit (or otherwise) between theoretical and experimental results cannot give any information about the value of E_o, even if E_1 and E_2 are known with accuracy. It might appear, then, that the value of E_o is a completely conventional figure. That this is not so can be realized by considering the change in the values of the parameters α, β and γ occurring when E_o changes from 100 e.v. to 10 e.v. In Table XXXII are tabulated the values of these parameters for all the binary systems. Interpreting the LIBBY mechanism in the loosest possible sence, that is, assuming that hot-atom retention occurs only when the energy of the hot atom is removed and that the removal of energy is a collisional process, one would expect that the retention-causing collision events could not be more than a few per cent of the total. The values of α, β, γ obtained when E_o = 100 e.v. are consistent with these considerations in C_6H_6, C_6H_5Br and C_2H_5Br, but they are rather high in CCl_4 and $CHBr_3$, even if the presence of more heavy atoms is taken into account. A decrease in E_o results in a considerable increase in the values of α, β, γ which, as it was said, are already high.

It is expected that, as more interlinked ternary systems are investigated, the agreement (or otherwise) between theoretical and experimental retention values will decrease the acceptable range of values for α, β, γ. This restriction, in

TABLE XXXII

Values of Parameters calculated for $E_o = 100$ e.v. and 10 e.v.

m_a as defined by Eq.(7a)

	E_{ret}(av)		LOGARITHMIC ENERGY DECREMENT	
System	$E_o = 100$ e.v.	$E_o = 10$ e.v.	$E_o = 100$ e.v.	$E_o = 10$ e.v.
C_6H_6/Br_2	$\alpha = 0.00827$ $\beta = 0.00826$	$\alpha = 0.02061$ $\beta = 0.02058$	$\alpha = 0.00851$ $\beta = 0.00850$	$\alpha = 0.02121$ $\beta = 0.02117$
C_2H_5Br/Br_2	$\alpha = 0.01605$ $\beta = 0.05058$	$\alpha = 0.03093$ $\beta = 0.09749$	$\alpha = 0.01708$ $\beta = 0.05385$	$\alpha = 0.03291$ $\beta = 0.10374$
C_6H_5Br/Br_2	$\gamma = 0.02495$ $\beta = 0.05114$	$\gamma = 0.04788$ $\beta = 0.09815$	$\gamma = 0.02648$ $\beta = 0.05429$	$\gamma = 0.05079$ $\beta = 0.10411$
CCl_4/Br_2	$\gamma = 0.04561$ $\beta = 0.07447$	$\gamma = 0.11043$ $\beta = 0.18030$	$\gamma = 0.05311$ $\beta = 0.08671$	$\gamma = 0.12785$ $\beta = 0.20874$
$CHBr_3/Br_2$	$\gamma = 0.07984$ $\beta = 0.15538$	$\gamma = 0.12472$ $\beta = 0.24273$	$\gamma = 0.10267$ $\beta = 0.19982$	$\gamma = 0.15923$ $\beta = 0.30991$

combination with some knowledge about the retention mechanism in these systems, will result in a restriction in the acceptable range of E_o values.

Finally a set of calculations was also run in the ternary system $C_6H_6/Br_2/CHBr_3$, by taking E_2 ($CHBr_3$) equal to 10 k.cal $mole^{-1}$ instead of 5 k.cal $mole^{-1}$. This made practically no difference to the total retention values, it only changed the relative contribution of the two terms in Eq.(6) of the theory and the values of the parameters γ and β for the binary system to which E_2 is connected. This is understandable because

$$\left|E_1 - E_2\right|_{E_2 = 5\ \mathrm{kcal}} \sim \left|E_1 - E_2\right|_{E_2 = 10\ \mathrm{kcal}} \quad \text{and } E_o = 100 \text{ e.v.}$$

In this section, the effect of the use of the two formulae for the energy degradation of the recoil atom and the effect of changing value of E_o on the theoretical retention values were discussed in connection with all the systems. In the next section, some other aspects of the results in the individual systems are discussed.

Section 4. Results in the Systems of the Two Halide/Halogen type (Systems of the Triangle)

The results for these systems are shown in Figs.5,6 and 7, and they have been calculated with E_{ret}(av).

When atomic collisions are considered for all the components (that is, m_a from Eq.(7a) of the theory is used) the resulting theoretical lines (1a) and (2a) are in very good agreement with the experimental retention values, except perhaps in the ternary mixtures $C_2H_5Br/Br_2/C_6H_5Br$ for the series of solutions at 0.5496 constant mole fraction of C_6H_5Br (line (2a) in Fig.5), where the fit is not quite as good as in all the other cases. It should be stressed once more that this agreement has been obtained by using the same values of the parameters α, β, γ (as determined from the binary systems C_2H_5Br/Br_2, C_6H_5Br/Br_2 and CCl_4/Br_2) in all the ternaries. The latter are linked, as shown by the triangle (see p.68-69), though the interchange of the components, one at a time.

When molecular collisions are considered for all the components (that is, m_a from Eq.(7b) of the theory is used), the theoretical lines obtained, (1b) and (2b), show a large discrepancy from the experimental points in all cases. Attempts to force a fit, by drawing the limiting slopes in the $^1/_R$ vs. $^y/_x$ or $^y/_z$ graphs even at positions hardly acceptable on the basis of the requirement of low bromine concentrations, failed.

These results suggest that in C_2H_5Br, C_6H_5Br and CCl_4, the collisions of the recoil bromine atom with these three substances are 'atomic' in character.

Section 5. Results in the Systems of the Hydrocarbon/Halide/Halogen Type

Before proceeding to discuss the results in the $C_6H_6/Br_2/CHBr_3$ mixtures investigated in this work, we shall give an account of the results of other work carried out in this laboratory (101) on the ternary system $C_5H_{12}/Br_2/C_2H_5Br$. This system is connected with the systems of the triangle through one of its components (C_2H_5Br)

(i) Ternary system $C_5H_{12}/Br_2/C_2H_5Br$

The application of the treatment developed in this work in the above mixtures gave results that can be summarized as follows:-

Atomic Collisions for both the organic components gave a good agreement between theoretical and experimental retention values for a series of solutions at 0.700 mole fraction of C_2H_5Br, but no agreement whatever for another series of solutions at 0.100 mole fraction of C_2H_5Br.

Molecular collisions for both the organic components led to converse results. That is, good agreement at 0.100 mole fraction of C_2H_5Br and no agreement at 0.700 mole fraction of this component.

Mixed collisions (m_a from Eq.(7c) of the theory) - molecular for C_5H_{12}, atomic for C_2H_5Br - gave a fairly good fit of theoretical lines to experimental results for both series of solutions.

The slopes and intercepts and the values of the parameters α , β , γ in that work were as follows:-

From Ref.(101)

Binary system C_2H_5Br/Br_2 (m_a from Eq.(7a))

Intercept = 4.65 α = 0.0143

Slope = 12.50 β = 0.0386

Binary system C_5H_{12}/Br_2 (m_a from Eq.(7b))

Intercept = 4.80 γ = 0.0412

Slope = 6.70 β = 0.0575

The results summarized above suggest that the collisions are atomic in C_2H_5Br, which is in agreement with the results in this work, and molecular in C_5H_{12}. They also show that the use of Eq.(7c) which takes into account both types of collisions, can describe the behaviour of the ternary mixtures.

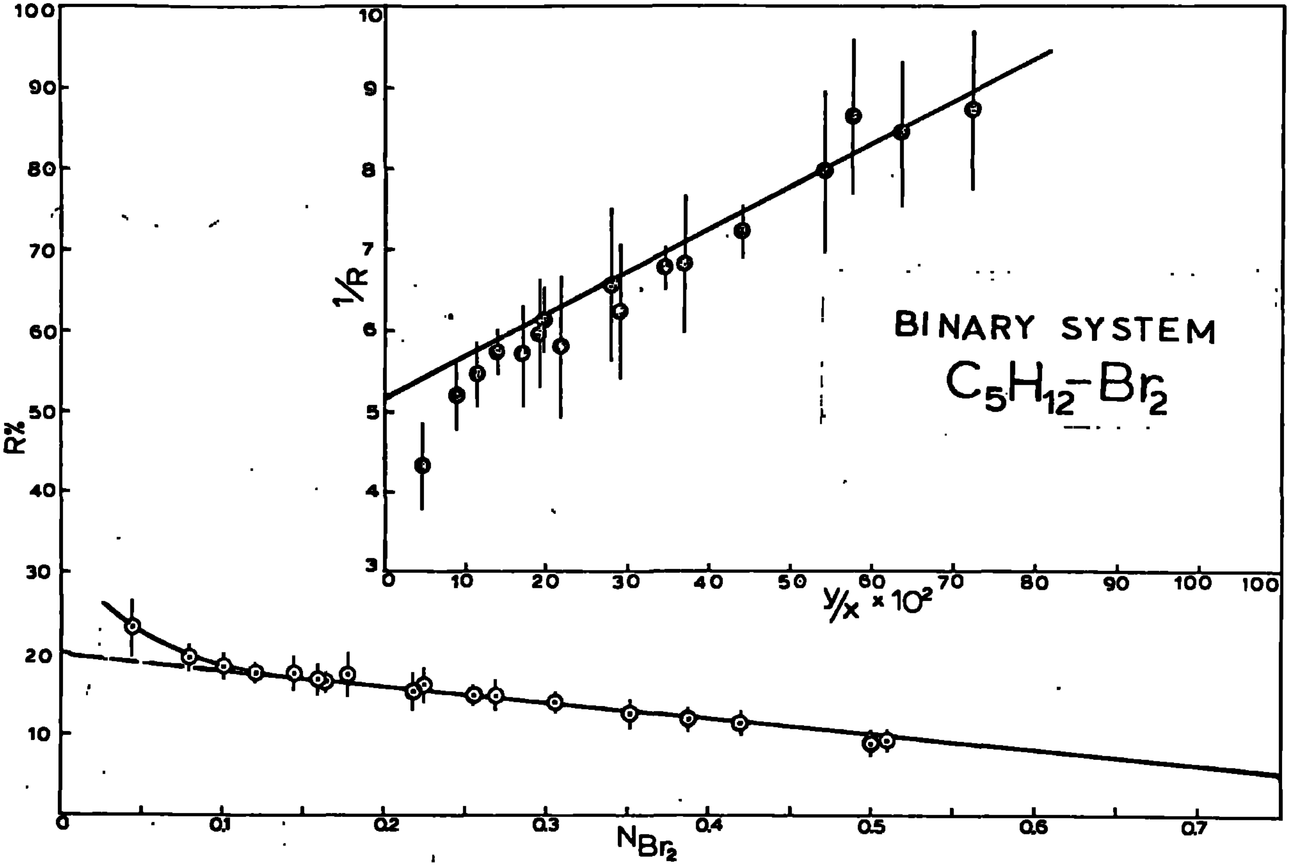
These results are in analogy with the later LIBBY ideas. Atomic collisions in C_2H_5Br - in LIBBY'S terminology, the 'billiard-ball' collisions - and molecular collisions in C_5H_{12} - collisions of this type were postulated by LIBBY in his epithermical-reaction scheme.

In an attempt to correlate these results with those obtained in this work, retentions were recalculated in the $C_5H_{12}/Br_2/C_2H_5Br$ mixtures by using, for the sake of consistency, the values for the slope and intercept in the binary system C_2H_5Br/Br_2 that were used in the systems of the triangle. (The C_2H_5Br in Ref.(101) has been purified in the same way as in this work, the results for the retention versus mole fraction of scavenger were in fairly good agreement with the results in this work but not so extensive and somewhat scattered). The results of these calculations are shown in Figs.15 and 16. Again, lines (1a - 2a), (1b - 2b) and (1c - 2c) have been calculated with m_a from Eqs. (7a), (7b) and (7c), respectively.

It can be seen that atomic collisions give no agreement whatsoever at 0.100 mole fraction of C_2H_5Br and a rather good agreement at 0.700 mole fraction of this component. The fit with molecular collisions is in the reverse order. All these are the same as in ref.(101). The only difference is that, in our set of calculations, mixed collisions (lines (1c) and (2c)) give a very good fit in one series of solutions but fail to do so in the other.

This difference led to a readjustment of the limiting slope in the C_5H_{12}/Br_2 system (see Fig.14). Another set of calculations was run, using the following data:

Binary System C_2H_5Br/Br_2 (m_a from Eq.(7a))			
Intercept	=	4.21	From this work
Slope	=	13.27	


R%
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0.6
0.7
N_{Br_2}
1/R
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9
8
7
6
5
4
3
0
10
20
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100
$y/x \times 10^2$
BINARY SYSTEM
$C_5H_{12}-Br_2$

Fig.14

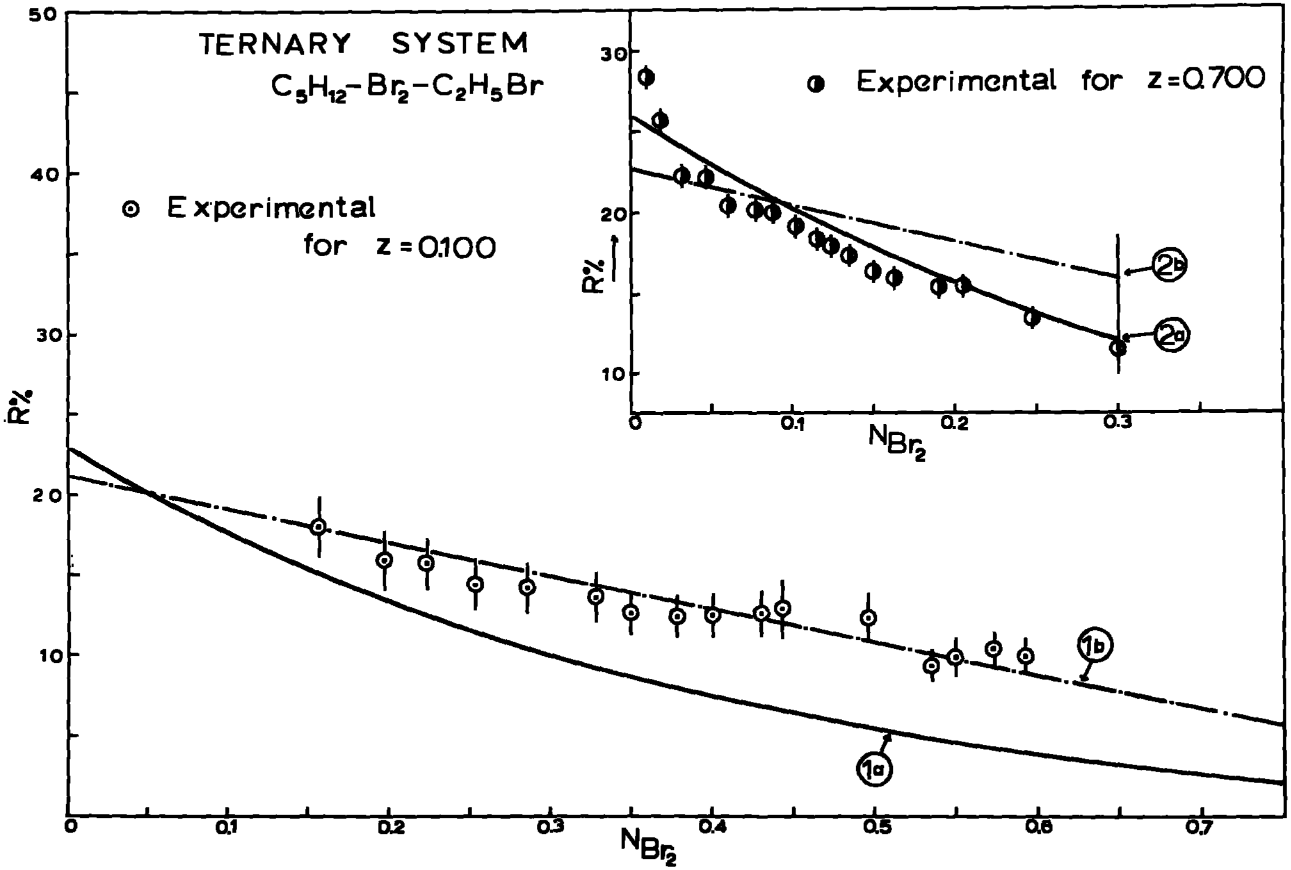

Fig. 15

Lines (1a) -(2a) calculated on atomic collisions
Lines (1b) - (2b) calculated on molecular collisions
z : mole fraction of C_2H_5Br

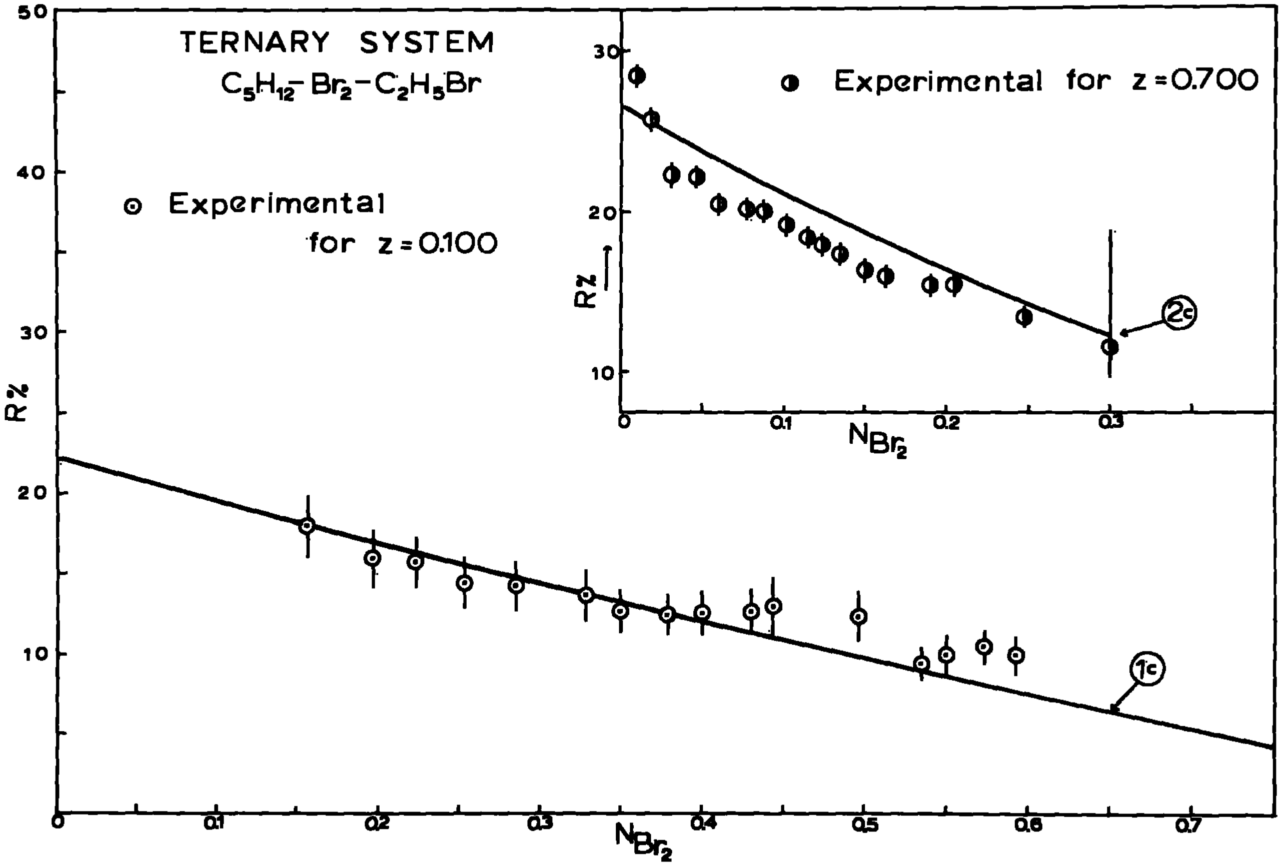

Fig.16

Lines (1c) - (2c) calculated on mixed collisions
z : mole fraction of C_2H_5Br

Binary System C_5H_{12}/Br_2 (m_a from Eq.(7b))

Intercept = 5.170 From Ref(101) but after readjustment

Slope = 5.160 of the limiting slope

The results are somewhat different (lower) than the ones obtained before (see Tables XXXIII and XXXIV). This is an improvement especially in the case of line (2c), which now lies closer to the experimental points.

Summarizing, atomic collisions for both the components describe the behaviour of the ternary mixtures $C_5H_{12}/Br_2/C_2H_5Br$ best at 0.700 mole fraction of C_2H_5Br while the best fit at 0.100 mole fraction of this component is obtained with molecular collisions for both C_5H_{12} and C_2H_5Br. Mixed collisions give a very good fit at 0.100 mole fraction of C_2H_5Br and a fairly good fit at 0.700 mole fraction of C_2H_5Br.

The conclusions from the above are the same as those in ref (101), which have already been referred to. But now they are given additional support by the fact that the calculations were done with values for the slope and intercept in the binary system C_2H_5Br/Br_2, which have already been used successfully in the systems of the triangle.

It is to be expected that the combination of C_2H_5Br and C_5H_{12} with a third substance, so as to form another triangle of interlinked systems, will help towards establishing the slope and intercept in the binary system C_5H_{12}/Br_2 in a more definite way.

TABLE XXXIII

Comparison of results for $C_5H_{12}/Br_2/C_2H_5Br$ mixtures from two sets of calculations

		MOLE FRACTION C_2H_5Br = 0.100	
	MOLE FRACTION Br_2	R as in Figs. 12, 13	R after adjustment in C_5H_{12}
Line (1a)	0.01	0.2255	0.2116
	0.09	0.1820	0.1714
	0.17	0.1464	0.1382
	0.25	0.1170	0.1108
	0.37	0.0822	0.0782
	0.45	0.0640	0.0611
	0.65	0.0315	0.0304
Line (1b)	0.01	0.2105	0.1945
	0.09	0.1926	0.1787
	0.17	0.1756	0.1636
	0.29	0.1509	0.1416
	0.41	0.1265	0.1197
	0.65	0.0765	0.0738
Line (1c)	0.01	0.2206	0.2029
	0.09	0.1982	0.1829
	0.17	0.1769	0.1639
	0.29	0.1467	0.1367
	0.37	0.1275	0.1192
	0.49	0.0995	0.0936
	0.65	0.0636	0.0603

TABLE XXXIV

Comparison of results for $C_5H_{12}/Br_2/C_2H_5Br$ mixtures from two sets of calculations

		MOLE FRACTION C_2H_5Br = 0.700	
	MOLE FRACTION Br_2	R as in Figs.12,13	R after readjustment in C_5H_{12}
Line (2a)	0.01	0.2540	0.2516
	0.05	0.2299	0.2281
	0.09	0.2080	0.2066
	0.13	0.1879	0.1869
	0.17	0.1696	0.1689
	0.21	0.1528	0.1524
	0.25	0.1375	0.1373
Line (2b)	0.01	0.2251	0.2200
	0.05	0.2160	0.2118
	0.13	0.1980	0.1952
	0.17	0.1889	0.1869
	0.21	0.1797	0.1784
	0.29	0.1611	0.1610
Line (2c)	0.01	0.2602	0.2504
	0.05	0.2381	0.2300
	0.09	0.2170	0.2105
	0.13	0.1969	0.1918
	0.17	0.1776	0.1739
	0.21	0.1591	0.1567
	0.25	0.1414	0.1401

(ii) Ternary system $C_6H_6/Br_2/CHBr_3$

The results for these mixtures are shown in Figs.10 and 11. They can be summarized as follows:-

Atomic collisions (lines (1a) and (2a)) give no agreement at all between theoretical and experimental retention values for both series of solutions at 0.200 and 0.500 mole fraction of C_6H_6.

Molecular collisions (lines (1b) and (2b)) give a very good agreement in both cases.

These results suggest that the collisions of the recoil bromine atom are of a molecular character in both C_6H_6 and $CHBr_3$.

It is interesting to see that the best fit in the ternary system $C_5H_{12}/Br_2/C_2H_5Br$, which was discussed before, was obtained with atomic collisions for C_2H_5Br, although the above ternary system, like the $C_6H_6/Br_2/CHBr_3$, consists of a hydrocarbon and a halide.

MILMAN (91) found that, in C_6H_6-Br_2 mixtures, she could obtain the best fit between experimental retentions due to hot reactions and those calculated from her application of the ESTRUP-WOLFGANG treatment in liquids by considering collisions of the recoil bromine atom with whole C_6H_6 molecules. In the case of $CHBr_3/Br_2$, her experimental points fell between the two lines calculated on the basis of collisions with individual atoms in the $CHBr_3$ molecule on the one hand and whole $CHBr_3$ molecules on the other.

In view of MILMAN'S results and the different behaviour of the ternary systems $C_5H_{12}/Br_2/C_2H_5Br$ and $C_6H_6/Br_2/CHBr_3$ observed in our results, retentions in the ternary mixtures $C_6H_6/Br_2/CHBr_3$ were recalculated with m_a as defined by Eq.(7c) of the theory, assuming molecular collisions for C_6H_6 and atomic collisions for $CHBr_3$.

The results of these calculations are shown in Fig.11. It can be seen that in the series of solutions at 0.500 mole fraction of C_6H_6 the agreement is very good, while for the other series of solutions it is poor, and anyway, worse than that obtained with molecular collisions (compare lines 1b-1c).

Thus, at this point, the best fit between theory and experiment is obtained by taking molecular collisions for both C_6H_6 and $CHBr_3$.

But something that one observes in Figs.10 and 11 is that, while in going from molecular collisions for both the components to mixed ones (that is molecular for C_6H_6, atomic for $CHBr_3$) the two lines obtained are only slightly different (compare lines (1b) and (1c) or lines (2b) and (2c)), in going from molecular collisions for both the components to atomic ones, again for both the components the two lines show a large discrepancy (compare either lines (1a)-(1b) or 2(a) - (2b)).

The explanation for this is to be found in Table XXI. It can be seen there that for the binary system C_6H_6/Br_2, a change from atomic to molecular collisions results in a large decrease in E_{ret}(av), while for the binary system $CHBr_3/Br_2$ the same change results in an small increase in E_{ret}(av). This is a consequence of the form of the curve in Fig.2. Thus the difference in the number of collisions calculated for atomic and molecular collisions will be much greater in C_6H_6 than in $CHBr_3$ and this will have the effect of the relative changes in the parameters α, β for C_6H_6 being much greater than those in $CHBr_3$. But even so, the question arises why these two effects, appearing in the binary systems do not compensate in their ternary mixtures. The answer is similar to that in the case of differences observed in the theoretical retentions for atomic collisions in changing from E_{ret}(av) to Logarithmic Energy Decrement. The mole fractions interfere with the ternaries only. It can be seen from Table XXI that the changes in E_{ret}(av) for the binary systems C_2H_5Br/Br_2, C_6H_5Br/Br_2 and CCl_4/Br_2, in going from Eq.(7a) to Eq.(7b), are all in the same direction, that is, decreasing. Consequently, the interference of the mole fractions would not affect a trend that is in the same direction for any combination of two of the above binaries in the ternary mixtures of the triangle. In the case of C_6H_6 and $CHBr_3$, the changes in E_{ret}(av), in going from Eq.(7a) to (7b) are in opposite direction and their relative magnitudes very much different. Consequently, the mole fractions now enhance or reduce either of the two changes, with the overall effect observed in the lines of Figs. 10 and 11.

This has an important implication. The best fit in the ternary mixtures $C_6H_6/Br_3/CHBR_3$ has been obtained with Eq.(7b) for both C_6H_6 and $CHBr_3$, this leading to the conclusion of the collisions being molecular in both cases. But the fact that line (2c) is as good a fit as line (2b) and the fact that line (1c) is a slightly worse fit than line (1b) suggest, considering the above analysis, that this might only be a consequence of the values of E_{ret}(av) from Eqs.(7a) and (7b) and that the collisions could as well be atomic.

In pursuing further the possibility of a more definite conclusion, the calculations in these ternary mixtures were repeated by including corrections for molecular collision cross sections and corrections for the probabilities of the different atoms in a molecule being hit. The way these corrections were made is outlined in APPENDIX A. The data used were obtained from MILMAN (91). They were:

Molecular diameters

C_6H_6 = 7.0 Å

Br_2 = 6.1 Å

$CHBr_3$ = 6.1 Å

Probability factors 'g'

	C_6H_6	Br_2	$CHBr_3$
g_H	6 x 1/12		1/8
g_C	6 x 1/12		1/8
g_{Br}		1	6 x 1/8

That is, the probabilities of H and C atoms being hit are taken as equal in both C_6H_6 and $CHBr_3$. That for Br in $CHBr_3$ is taken twice as large. E_{ret}(av) was used.

The results of the corrected set of calculations are shown in Figs. 12 and 13 and in Tables XXXV and XXXVI, along with the corresponding values that have been plotted in Figs. 10 and 11 (no corrections) for comparison. They are as follows:-

Atomic collisions cannot describe the behaviour of ternary mixtures, as it is obvious from the discrepancy between lines $(1a)_{cor}$ - $(2a)_{cor}$ and the experimental points.

Molecular collisions give, as before, a good fit between theory and experiment for the series of solutions at 0.200 mole fraction of C_6H_6, but a less good fit than before at 0.500 mole fraction of this component.

Mixed collisions give a very good agreement at 0.500 mole fraction of C_6H_6 as before, and a good agreement at 0.200 mole fraction of this component.

TABLE XXXV

THE TERNARY SYSTEM $C_6H_6/Br_2/CHBr_3$

		MOLE FRACTION C_6H_6 = 0.200	
	MOLE FRACTION Br_2	R No corrections	R corrected
Line (1a)	0.01	0.5261	0.5293
	0.09	0.4656	0.4615
	0.15	0.4221	0.4140
	0.25	0.3531	0.3407
	0.35	0.2881	0.2737
	0.45	0.2263	0.2119
	0.55	0.1672	0.1544
	0.65	0.1092	0.0996
Line (1b)	0.01	0.4645	0.4464
	0.09	0.4101	0.3961
	0.15	0.3716	0.3603
	0.25	0.3112	0.3041
	0.35	0.2553	0.2518
	0.45	0.2034	0.2031
	0.55	0.1549	0.1576
	0.65	0.1093	0.1146
Line (1c)	0.01	0.4838	0.4550
	0.09	0.4298	0.4024
	0.15	0.3911	0.3651
	0.25	0.3296	0.3069
	0.35	0.2717	0.2530
	0.45	0.2170	0.2029
	0.55	0.1651	0.1561
	0.65	0.1152	0.1120

TABLE XXXVI

THE TERNARY SYSTEM $C_6H_6/Br_2/CHBr_3$

		MOLE FRACTION C_6H_6 = 0.500	
	MOLE FRACTION Br_2	R no corrections	R corrected
Line (2a)	0.01	0.4998	0.4834
	0.09	0.4291	0.4046
	0.15	0.3772	0.3490
	0.21	0.3257	0.2957
	0.29	0.2567	0.2272
	0.35	0.2031	0.1769
	0.45	0.1042	0.0916
Line (2b)	0.01	0.3494	0.3248
	0.09	0.3038	0.2865
	0.15	0.2713	0.2589
	0.21	0.2400	0.2324
	0.29	0.1999	0.1982
	0.35	0.1710	0.1735
	0.45	0.1243	0.1335
Line (2c)	0.01	0.3848	0.3414
	0.09	0.3342	0.2993
	0.15	0.2976	0.2691
	0.21	0.2619	0.2399
	0.29	0.2156	0.2025
	0.35	0.1816	0.1754
	0.45	0.1252	0.1315

To summarize: Without corrections, the best fit is obtained with molecular collisions for both C_6H_6 and $CHBr_3$. The fit with mixed collisions is slightly less good. With corrections, the best fit is obtained with mixed collisions, the fit with molecular ones being slightly less good. The differences in the actual retention values are small in both cases.

Consequently, no definite conclusion can be drawn from these results as to whether the collisions in $CHBr_3$ are atomic or molecular. They might be either or the true situation might be somewhere in between the two extremes. To try and decide on one of the two alternatives from the actual differences between experimental points and theoretical lines would not be justified because, as it can be seen from Figs. 10, 11, 12, and 13, these differences are very small and certainly of the order of the experimental uncertainties on the points (these being represented by the diameters of the circles). And, of course, since these uncertainties are those due only to the statistics of counting including other possible errors (e.g. errors in the mole fractions) would increase there uncertainties.

Note: No collision probability corrections were made in the calculations for the systems of the triangle. The picture in these systems was quite clear-cut. Atomic collisions gave a very good fit, molecular collisions gave calculated lines which were in large discrepancy with the experimental points. After the study of the results in the $C_6H_6/Br_2/CHBr_3$, a set of calculations was run in the ternary mixtures $C_6H_5Br/Br_2/CCl_4$ with mixed collisions (atomic for C_6H_5Br, molecular for CCl_4) to test the possibility of describing these mixtures by Eq.(7c) of the theory. No fit was obtained. Consequently, it was thought that the corrections would not affect the actual picture of the behaviour of these systems.

Section 6. Comments on Eqs (7)

From the discussion of the results so far it has become obvious that the only indication as to the type of collisions in the various organic components has been which of Eqs.(7) gave the best fit between experimental retention values and theoretically calculated ones. The question now arises whether the ways m_a has been defined in these equations are the only possible ones and, if not, whether Eqs.(7) are the best for the purpose.

It is certain that Eqs.(7a) and (7b) represent the extreme cases of atomic and molecular collisions for all three components of a mixture. Eq.(7c) assumes molecular collisions for one of the organic components and atomic collisions for both the other organic component and bromine. This is because it has always been thought that the component most likely to undergo atomic collisions is bromine.

Two other, intermediate, ways of defining m_a can be thought of offhand, namely:

$$m_a = \frac{x \cdot M_1 + y \cdot M_2 + z \cdot M_3}{x \cdot 1 + y \cdot n_2 + z \cdot 1} \quad (7d)$$

(where $n_2 = 2$) and

$$m_a = \frac{x \cdot M_1 + y \cdot M_2 + z \cdot M_3}{x \cdot 1 + y \cdot 1 + z \cdot n_3} \quad (7e)$$

Eq.(7d) assumes molecular collisions for both the organic components and atomic collisions for bromine, while Eq.(7c) assumes atomic collisions for one of the organic components and molecular collisions for both the other organic component and bromine. But it has already become obvious, from the various sets of calculations, that the discriminatory power of the treatment is not high. Consequently, these intermediate m_a's would lead to more sets of theoretical retention values only slightly different from those already obtained. And certainly, the differences would be of the same order or in some cases lower than the experimental uncertainties. Thus the whole picture would become more confused instead of clearer. And, anyway, it has become clear from the ternary mixtures $C_6H_6/Br_2/CHBr_3$ that even the use of extreme cases like (Eq.7a) and (7b) cannot lead to a distinction between the type of collisions for reasons which were discussed there and will again be discussed later.

It should be stressed that Eq.(7c) simply combines the effects of different types of collisions in the organic components of a ternary mixture. It cannot give any information about the existence of an intermediate type of collisions in one and the same organic component. It can give such information only in connection with Eqs. (7a) and (7b).

Section 7. Comparison of Results in the Binary Systems C_6H_6/Br_2 and C_5H_{12}/Br_2

In correlating the results of Ref.(101) with the results in this work, it was realized that the retention vs. mole fraction of bromine scavenger curve for the binary system C_5H_{12}/Br_2 was almost the same as that for the binary system C_6H_6/Br_2. In fact, the two curves could practically be superimposed, for mole fraction of Br_2 greater than about 0.1. But while the form of this curve for the system C_5H_{12}/Br_2 is the familiar one with an initial sharp drop in retention and a much less sensitive part for $N_{Br_2} > \sim 0.1$, in the case of the system C_6H_6/Br_2, there is an absence of a marked scavenger effect (although it was not possible to establish the form of the graph at very low scavenger concentrations due to very large experimental uncertainties). The form of the curve in C_5H_{12}/Br_2 is similar to that of the corresponding curves in C_6H_{14}/Br_2 and C_6H_{12}/Br_2 mixtures found by MILMAN (91). Also, the absence of a marked scavenger effect in C_6H_6/Br_2 mixtures has been reported by MILMAN (89) and in C_6H_6/I_2 mixtures by MACRAE and SHAW (106). It has been attributed to a scarcity of radicals for thermal diffusive reactions with thermalized halogen recoil atoms.

These results for hot reactions in C_5H_{12} and C_6H_6 are interesting, because these two compounds have very different structure and chemical reactivity. But they are both hydrocarbons and have similar molecular weights and molecular sizes. Also, the best fit between theoretical calculations and experimental results in the ternary systems $C_5H_{12}/Br_2/C_2H_5Br$ and $C_6H_6/Br_2/CHBr_3$ of this work was obtained with molecular collisions for C_5H_{12} and C_6H_6. Thus, it appears that hot reactions in these two substances depend mainly on the weight and size of the molecules and not on their configuration or chemical reactivity. This is in agreement with results in Ref.(91).

In Table XXX the values of the parameters α and β are shown for C_5H_{12} and C_6H_6. It can be seen that the values of these parameters for molecular collisions in these two substances are very much the same. This is, of course, a consequence of the fact that the m_a's (from Eq.(7b)) of C_5H_{12} and C_6H_6 are similar and of the fact that the slopes and intercepts on the $^1/_R$ vs $^y/_x$ graphs for these two substances are very much the same.

Section 8. Upper Limit of R_{hot}

In this treatment, the upper limit of the total retention due to hot reactions, that is R_{hot} for $N_{Br_2} \longrightarrow 0$, is given by $(1-p^m)$ for binary systems and either by $(1-p^m)$ for ternary systems in which $E_1 = E_2$ or by $((1-p^m) + p^m (1-q^{n-m}))$ for ternary systems in which $E_1 \neq E_2$. In the case of binary mixtures, and for $N_{Br_2} \longrightarrow 0$, the quantity $(1-p^m)$ takes the form $(1-(1-\alpha)^m)$ or $(1-(1-\gamma)^m)$ and it is through these latter quantities and the limiting slopes and intercepts in the $^1/R$ vs. $^y/x$ or $^y/z$ graphs that the parameters α, β, γ are determined. Obviously, R_{hot} for $N_{Br_2} \longrightarrow 0$ can readily be read off the ordinate of these graphs, its reciprocal being equal to the intercept.

On the other hand, it has been the general practice of other workers to obtain the retention due to hot reactions at $N_{Br_2} = 0$ by extrapolating the less sensitive (almost linear) part of the retention vs. mole fraction of scavenger graph back to zero scavenger concentration (see, for examples, ref. 79,89).

The two extrapolated values for hot reactions, $(1-p^m)$ of this work and $R_{extrap.}$ of other workers will not generally, be the same. This is shown in Table XXXVII.

An interesting thing about these values is that, if the various systems are arranged in order of increasing $(1-p^m)$, then,

TABLE XXXVII

SYSTEM	$(1-p^m)\%$	$R_{extrap.}$ %
C_6H_6/Br_2	19.3	19.3
C_5H_{12}/Br_2	19.3	19.3
C_2H_5Br/Br_2	23.7	17.0
CCl_4/Br_2	29.5	25.5
C_6H_5Br/Br_2	35.5	28.0
$CHBr_3/Br_2$	55.0	45.0

with the exception of C_2H_5Br/Br_2, the $R_{extrap.}$ values increase in the same order. These latter values are the ones obtained in this work, but generally agree quite well with those of other investigators, for example $R_{extrap} = 17\%$ for C_2H_5Br/Br_2 agrees with that found by SHAW et.al., (67), $R_{extrap} = 19.3\%$ for C_6H_6/Br_2 with that found by MILMAN (89,91) and $R_{extrap} = 45\%$ for $CHBr_3$ with that found by MILMAN (91) and NESMEYANOV et.al.,(107).

No uncertainties have been given for the values in Table XXXVII. These uncertainties result from:

(1) $(1 - p^m)$

Uncertainties due to the way of drawing the limiting slopes.

(2) R_{extrap}.

Uncertainties because of the fact that the part of the retention vs. mole fraction of scavenger curves used for the back extrapolation is not always quite linear but exhibits a curvature e.g. in C_6H_5Br/Br_2, $CHBr_3/Br_2$.

And, of course, uncertainties for both $(1-p^m)$ and R_{extrap} resulting from large uncertainties on the experimental points in some cases e.g. in C_6H_5Br/Br_2 or CCl_4/Br_2.

An estimate for these uncertainties is that in the case of $(1-p^m)$ they are ($\pm$ 2%) while in the case of R_{extrap} they are ($\pm$ 1.0 — 1.5%).

Thus the situation is as follows:

$(1-p^m)$ and R_{extrap} represent two values for the retention due to hot reactions, at $N_{Br_2} \longrightarrow 0$. The fact that they both refer to hot reactions implies that thermal diffusive reactions are somehow discounted in obtaining these values. And, as it can be seen from Table XXXVII, they are different.

The question that automatically arises at this point is: what are the differences due to?

The answer is that the differences are due to two reasons:

First, the retention due to hot reactions in binary systems, on the basis of the treatment developed in this work, is given by the equation:

$$R_{hot} = \text{const.} \times \left(\frac{\alpha x}{\alpha x + \beta y} \right)$$

$$\text{where constant} = (1-p^m)$$

$$\text{and } y = N_{Br_2}$$

while in the other case

$$R_{hot} = \text{const.} \times (1 - y)$$

or, for generality,

$$R_{hot} = \text{cpnst.} \times (1-\mu y)$$

$$\text{where constant} = R_{extrap}$$

Thus, it is obvious that the two methods of extrapolation implicitly assume that R_{hot} is a different function of y in the two cases.

Second, the part of the retention vs. mole fraction of scavenger curve used for the extrapolation is different in the two cases. While, as it has already been said, to obtain R_{extrap} the almost linear part of the curve at higher bromine concentrations is used, in the case of $(1-p^m)$ the discounting of thermal diffusive reactions must be combined with the requirement of the treatment that $y \rightarrow 0$, in order to make p reasonably constant. Before proceeding to compare the two methods further, it is useful to see how the parameters α, β, (or γ, β) in this treatment, which are determined at low bromine concentrations, describe the binary systems over the entire range of bromine concentrations up to $N_{Br_2} = 1$? Or, in other words, to see if the extrapolation method of this work gives parameters which, when inserted in the equation $R = \text{const.} \times \left(\frac{\alpha x}{\alpha x + \beta y} \right)$, can describe the binary systems.

A few points for each binary system were calculated and plotted in Fig.18 along with the experimental results for the binary systems (the curves are the smooth lines through the experimental points shown in Figs.4 and 9).

It can be seen that the calculated points are in agreement with the experimental lines to within ± 2% and, often, better. It is interesting to observe that (in connection with Table XXXVII) the smaller the differences between $(1-p^m)$ and $R_{\text{extrap.}}$ the better the calculated points agree with the experimental lines.

The points have been calculated as follows:

In the binary systems C_2H_5Br/Br_2, C_6H_5Br/Br_2 and CCl_4/Br_2, the m_a's used have been obtained from Eq.(7a) (setting one of x or z equal to zero), that is by assuming atomic collisions for both the organic components and Br_2. This is in agreement with the way the calculations that gave the best fit in the ternary systems of the triangle were carried out.

With the calculations in the binary mixtures $CHBr_3/Br_2$ an interesting thing can be observed. It is helpful to recall here that from the results in the ternary mixtures $C_6H_6/Br_2/CHBr_3$ it

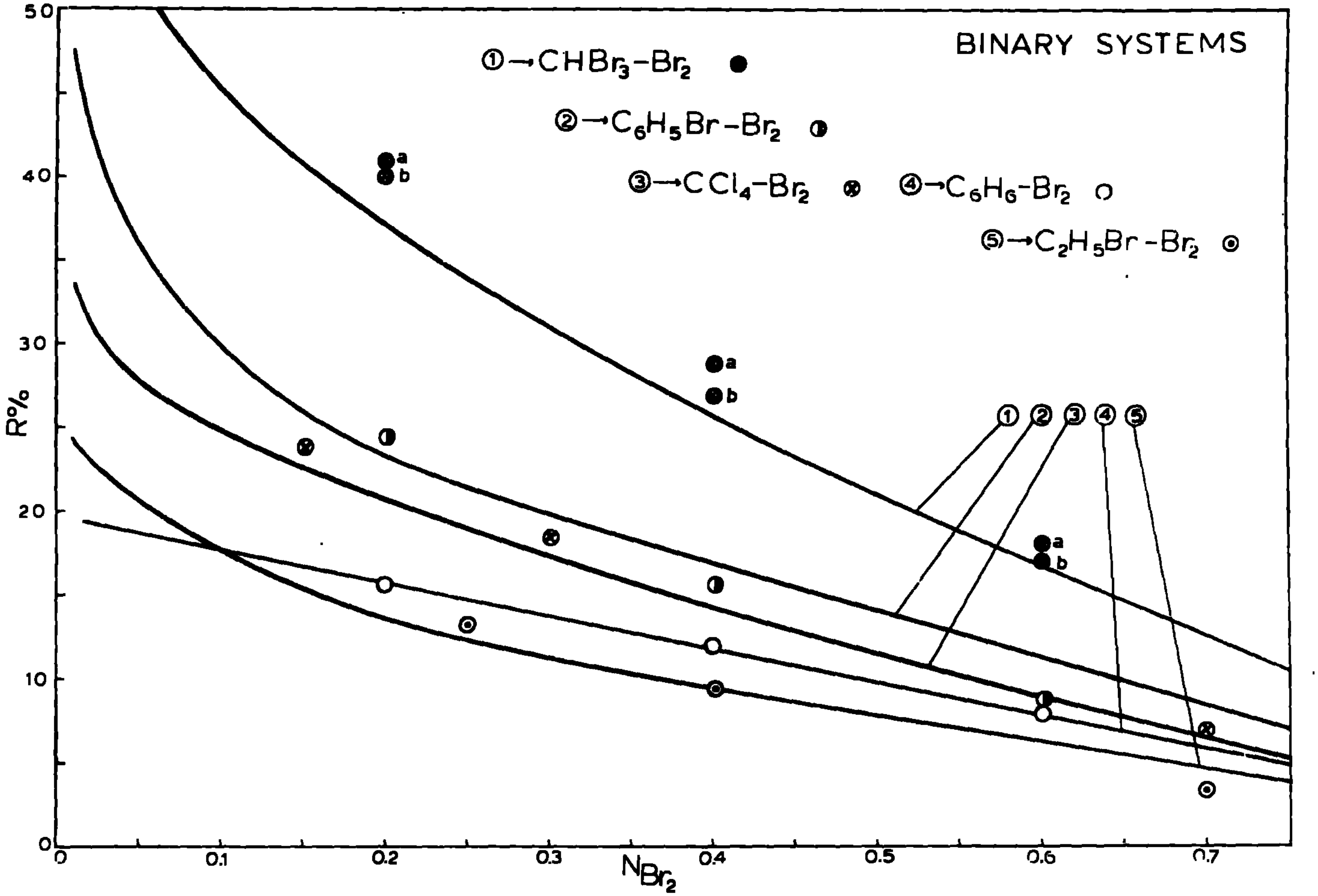

Fig. 18

Solid Lines: Experimental.

All points shown: Calculated from $R = (1-p^m)\left(\frac{\alpha x}{\alpha x+\beta y}\right)$ of the theory.

was not possible to conclude in a definite way whether the collisions in $CHBr_3$ were atomic or molecular in character (see p.149). It can now be seen in Fig.18 that calculations on atomic collisions give points (points marked (a)) which show a larger discrepancy with the experimental curve than points calculated on molecular collisions (points marked (b)). Thus, from the best fit between calculations and experimental results in the binary mixtures (provided the way of obtaining it does not disturb the best fit in the ternaries), it seems that the collisions in $CHBr_3$ are molecular rather than atomic in character.

In the case of the binary systems C_6H_6/Br_2, calculations on molecular collisions give points which fall <u>on</u> the experimental curve.

Now in order to compare the two methods of extrapolation, let us see the form of the lines calculated by them relatively to the experimental retention *vs.* mole fraction of scavenger curve. This is shown in Fig.19.

In order to see which of (a) or (b) is the more accurate, let us consider the region of $N_{Br_2} \gtrsim 0.2$, where thermal diffusive reactions are sufficiently quenched.

One clear advantage of (a) is that it gives at least a calculated line which is a curve (though not always the right

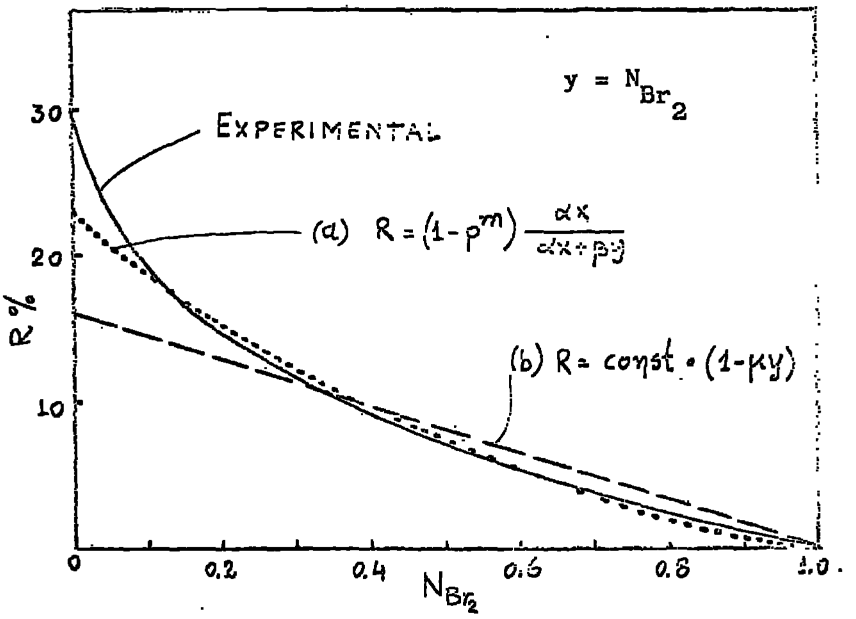

Fig. 19

Graphical Comparison of Extrapolation Methods for R_{hot}

curve). But it should be stressed here that it can give a straight line as well, as in the case of the C_6H_6/Br_2 system. The extent of linearily is determined by two parameters α and β which can be adjusted in each case in such a way as to give a line showing the same behaviour as the experimental one. The line obtained by a calculation based on (b) is necessarily a straight line.

As it can be seen from Fig.18 (a) gives points which sometimes are all above the experimental lines and sometimes some of them above and some below the experimental lines. (b) gives points some of which lie above and some below the experimental curve.

Consequently, both methods give errors. It is interesting to try and see which gives the least error. But, of course, one cannot consider errors unless all other sources of error are eliminated. And a serious source of error is the contribution of thermal diffusive reactions.

Assuming, as everybody does, that the role of Br_2 is to quench thermal diffusive reactions, method (b), which uses the part of the retention vs mole fraction of scavenger curve at high N_{Br_2} for the extrapolation, is likely to introduce less error resulting from failure to discount thermal diffusive reactions than method (a), which must attempt extrapolation in a region where these reactions make a bigger contribution.

Hence, although errors on Fig.18 are larger by method (a) than errors by method (b), we cannot exclude (a) since the larger errors probably stem from incomplete elimination of the thermal diffusive reaction contribution.

It is obvious that, on the above picture, it is not quite possible to rate the significance of errors.

A way of doing that is by examining the 'predictions' of the two methods for ternary mixtures. It has been seen in the results section of this work and in the discussion of the agreement between theoretical calculations and experimental results that the 'predictions' of method (a) are quite credible.

To test method (b) retentions were calculated for all the ternary systems of this work by means of the formula

$$R_{tern} = \frac{x \cdot R_1 + z \cdot R_2}{x + z}$$

where $R_1 = c_1 (1-\mu y)$ $R_2 = c_2 (1-ky)$

This way of calculation worked in a few cases but gave results worse than (a) in all the rest.

Thus, it seems that the balance of evidence is slightly in favour of method (a) especially because of its predictions in the ternary mixtures. But it is now easy to realize that the figures in Table XXXVII are simply differing estimates of an experimentally inacessible quantity. The differences simply represent the differing behaviour, at low bromine concentrations, of the equations giving R_{hot} by methods (a) and (b). As it has been said above, there is some slight evidence that (a) is more reliable than (b).

Section 9. The Parameters α, β, γ

A. The Parameters α, γ

The treatment developed in this work is founded on the basic idea that the hot recoil atom is slowed down by collisions with molecules and that there is a chance of retention at each collision. The smaller the number of collisions required to reduce the energy of the recoil atom, the greater the chance of the recoil atom being retained.

Consequently we have

(i) The more heavy atoms in the hit molecule, the greater the chance of retention per collision.

It can be seen from Table XXX (p.126) that α (or γ) increase from molcules with no bromine atoms to molecules with 3 Br atoms.

Cl atoms are not so effective as Br atoms, but, of course, they are more effective than either C or H atoms. If it is supposed, for the sake of argument, that the effectiveness of Cl atoms is about half that of Br atoms, then one should except $\alpha(\mathrm{RCl}) \sim {}^1/2\ \alpha(\mathrm{RBr})$. Since CCl_4 has four chlorine atoms, it should be expected that $\alpha(\mathrm{CCl}_4) \sim 4 \times \frac{1}{2}\,\alpha(\mathrm{RBr})$. It can be seen from Table XXX that the values of the parameter γ for CCl_4 is in fairly good agreement with this expectation (one should always keep in mind that there are uncertainties on the values of the parameters. One should also take into account the effect of varying contribution from varying numbers of H and C atoms).

(ii) The greater the effective collisional mass of the collision partner of the recoil atom, the fewer the collisions necessary to slow it down, hence the greater the chance of retention per collision. Since it was found that collisions in C_6H_6 and C_5H_{12} were molecular in character, their α's are higher than e.g. C_2H_5Br or C_6H_5Br.

(iii) In view of the fact that collisions in C_6H_6 are molecular C_6H_5Br could probably be regarded as a pair of masses 77/80 and this would explain why $\gamma(\mathrm{C_6H_5Br}) > \alpha(\mathrm{C_2H_5Br})$.

Thus, one concludes that there is nothing in the $\alpha(\gamma)$'s themselves inconsistent with the basic concept of the theory.

B. The Parameter β

The logic of the formulation of the theoretical treatment developed in this work requires that the paramter β should be the same in all the binary systems, since it is a property of the bromine molecule.

The values of the parameter β obtained in this work present two pictures, depending on whether E_{ret}(av) or the Logarithmic Energy Decrement is used in the calculations.

(i) Logarithmic Energy Decrement

It can be seen from Table XXX that, for molecular collisions in C_5H_{12}/Br_2 and C_6H_6/Br and atomic collisions in C_2H_5Br/Br_2 and C_6H_5Br/Br_2 (since these were the types of collisions that gave the best fit between theory and experiment in the ternary systems), the values of the parameter β are in very good agreement in these four binary systems.

The values of the parameter β in CCl_4/Br_2 (atomic collisions) and $CHBr_3/Br_2$ (atomic or molecular) are in discrepancy with the other four values referred to before. But considering the large uncertainties on the experimental points in the binary system CCl_4/Br_2 (see Figs.3-4), and the fact that results obtained by WILLARD (40) in this system (with more rigorously purified CCl_4) would give a lower value of β, one is not unjustified in assuming that the discrepancy in the value of β could be due to experimental reasons only. Thus, one ends up with concordant values of β for five binary systems out of six, and it is only the discrepancy in the value of β for the binary system $CHBr_3/Br_2$ that must be accounted for. It should be noted here that, since by the fit of the theoretical retention values to the experimental ones in the ternary mixtures $C_6H_6/Br_2/CHBr_3$ it is not possible to decide in a definite way whether the collisions in $CHBr_3$ are atomic or molecular, the discrepancy in the value of β will accordingly be of varying magnitude (Table XXX). But, clearly, this discrepancy, no matter which type of collision is taken into account, cannot be attributed to subjective error in drawing the limiting slope or to experimental uncertainties on the points (see Fig.9). The $CHBr_3$ used in this work contained Ph_2NH. It is possible that the presence of this preservative had an effect on the value of β. One cannot say in a positive way, because it depends on whether Ph_2NH is much more effective than Br_2 in catching Br^* (Ph_2NH is a noted radical trap).

Anyway, one cannot reject the theory on the basis of the results in one binary system (out of six) with a dubious reagent.

Consequently, it is concluded that, on this view, the theory is working with no internal inconsistencies, provided the Logarithmic Energy Decrement is used for calculating the number of collisions.

Note: It should be stressed here that there is no previous reason for preferring the Logarithmic Energy Decrement to $E_{ret}(av)$. (see also p.127).

(ii) $E_{ret}(av)$

Since there is no previous reason for preferring the Logarithmic Energy Decrement to $E_{ret}(av)$ (p.127) of this treatment and since the fit between theoretical calculations and experimental results is the same with these two formulae, the values of the parameter β calculated with $E_{ret}(av)$ should be examined. It can be seen from Table XXX that they are not concordant. With the type of collision for each binary system that gave the best fit in the ternaries, the picture of the β values is as follows:

TABLE XXXVIII

SYSTEM	Type of collision	β
C_6H_6/Br_2	Molecular	0.03802
C_5H_{12}/Br_2	Molecular	0.03786
C_2H_5Br/Br_2	Atomic	0.05058
C_6H_5Br/Br_2	Atomic	0.05114
CCl_4/Br_2	Atomic	0.07447
$CHBr_3/Br_2$	Atomic	0.15538
	Molecular	0.11228

In this sort of situation, one is faced with two interlinked questions:

(1) Is one correct in saying that the theory requires the β values to be concordant?

(2) If not, what are the causes and magnitudes of the 'expected' discrepancies?

In the theoretical section of this work (CHAPTER 1, Section 2), a number of reasons has been suggested why the values of the parameter β may not be concordant, namely:-

(a) The degree of inelasticity in collisions varies from one organic component to another, so that apparent variations in β simply reflect varying degrees of errors introduced by the use of Eqs.(7).

(b) Differences in the rigidity of the liquid structure from one system to another render Eqs.(7) similarly of varying accuracy.

(c) The possibility of formation of a loose complex between bromine and one of the organic components but not the other might again result in discrepant β values.

(d) The possibility of one organic component of a pair being much less or much more prone to produce inorganic retention by reactions similar to the one referred to in Note (ii) (p.50).

To the above, another two possibilities should be added:

(e) The theory is totally wrong

(f) α, β, γ are significant parameters, but their meaning is not fractional chance of retention per collision. But in this case, if the meaning of the parameters is not known, one cannot say whether β should be the same in all systems.

These possibilities are discussed below.

(c) Complex formation

The formation of a complex between the organic component and bromine in a binary system could affect the value of the parameter β for that particular system. But it is expected that the effect will not be significant, since the weak bonding in a complex cannot alter the collisional situation to any great extent. On the other hand, some of the compounds used in this work (C_2H_5Br, C_6H_5Br, $CHBr_3$) are not known to form complexes with Br_2. Consequently, the observed discrepancies in the values of β cannot be attributed to complex formation.

(d) Inorganic retention from hot atom collisions with organic molecules.

The possibility of inorganic retention resulting from reactions similar to the one referred to in Note (ii) (p.50) occurring to a significant extent would invalidate the whole treatment, because in such a case the definition and use of the quantities $(1-\alpha)$, $(1-\beta)$ and $(1-\gamma)$ in setting up the formulation of the treatment should be wrong. In such a case a greater number of parameters α_1, α_2, ---- β_1, β_2, ---- γ_1, γ_2, ---

for each binary system would be required, the determination of which cannot be done by the treatment. Consequently, for the time being, it has to be assumed that the above possibility is not strong enough to affect the retentions significantly.

(e) Theory totally inappropriate to liquid systems

If the results obtained up to now suggest that this is the case then, of course, it is meaningless discussing the individual points of the treatment any further. But it has become obvious that this treatment can give a satisfactory fit between theoretically calculated and experimentally found retention values in ternary mixtures. It is true, of course, that the number of systems investigated up to now is small, but, on the other hand, these systems comprise significantly different organic components, this fact lending support to the validity of the treatment. Consequently, the observed discrepancies in the values of the parameter β when E_{ret}(av) is used, must be attributed to the approximations involved in the treatment and not to the idea of the theory being totally inappropriate to liquid systems.

(a) and (b) Inelasticity in Collisions

There is no doubt that, as soon as one thinks in detail about collision mechanics, particularly in liquid systems, one realizes that there must be more to it than simple elastic billiard-ball collisions. There is however, strong body of opinion and experimental evidence (62, 79, 91, 108) that, despite the significance and extent of the inelastic element, elastic collision formulae can 'go a long way', that is they yield results of the correct order of magnitude. The errors will, of course, vary from case to case, depending on the varying importance of the inelasticity element. In the case of this work, introduction of additional energy loss to inelastic sinks means that the true number of collisions is smaller than that calculated, and the parameters α, β, γ would increase if the corrections for inelasticity could be made.

There are two aspects of the inelasticity involved in the collisions of the recoil atom with molecules of the environment.

(i) Inelasticity within the struck molecule

(ii) Inelasticity due to the 'backing' of the struck molecule by neighbouring ones, an effect which must be taken into account in closely packed systems.

Although it is not possible to get a quantitative idea of the relative importance of these two sources of inelasticity, it is intuitively felt that (i) must be more important than (ii).

Now, it is interesting to see what predictions can be made on the basis of this model.

<u>Part (i)</u>: Suppose for the purpose of argument that the extent of inelasticity in collisions is proportional to the number of vibrations

in the struck molecule, that is inelasticity $\propto (3n - 6)$, where n number of atoms in the molecule.

Hence, since the low β's in this work are connected with molecules with large numbers of atoms (e.g. C_6H_6, C_6H_5Br, C_2H_5Br), correction for a large inelastic element would result in a large increase in the values of β. On the other hand, high values of β are connected with molecules with small numbers of atoms (e.g. CCl_4, $CHBr_3$), hence correction for a small or negligible inelastic element would result in a small raising of β values. The overall affect could, therefore, be to bring the β values together.

But, of course, this simple argument treats all vibrations as equivalent and ignores differing frequencies etc. A more refined argument, allowing for these aspects, might explain why, for example $\beta(C_6H_5Br) > \beta(C_2H_5Br)$ or whether a readjustment should be made in the slopes (if possible) to reverse the order.

On the basis of the above, the observed discrepancies in the values of β could be explained quite well.

Part (ii): It is useful to examine the environmental aspect of inelasticity in order to ensure that it is not in conflict with the satisfactory argument discussed before.

One should expect that the inelastic element in the 'backing' of the struck molecule by neighbouring ones would increase with the density. Another aspect of the same effect is that the inelastic element would increase with increasing mass of the molecules, because of greater inertia. It can be seen from Fig.20(and Table XXXIX) that the parameter β increases with density.

TABLE XXXIX

SYSTEM	Density	Parameter β
C_5H_{12}/Br_2	0.626	0.03786
C_6H_6/Br_2	0.879	0.03802
C_2H_5Br/Br_2	1.455	0.05058
C_6H_5Br/Br_2	1.499	0.05114
CCl_4/Br_2	1.595	0.07447
$CHBr_3/Br_2$	2.890	0.11228

But this argument, then, goes the wrong way, because any correction for inelasticity would take the β values further apart instead of bringing them together.

Thus, one has to conclude that the contribution of (ii) must be smaller than the contribution of (i).

But all the previous arguments have been about collisional processes only and quite independent of the mechanism by which labelling occurs. But this mechanism, which has not so far been considered, does exist. If we look at the results from this point of view, it is realized that effects such as that of the inelasticity

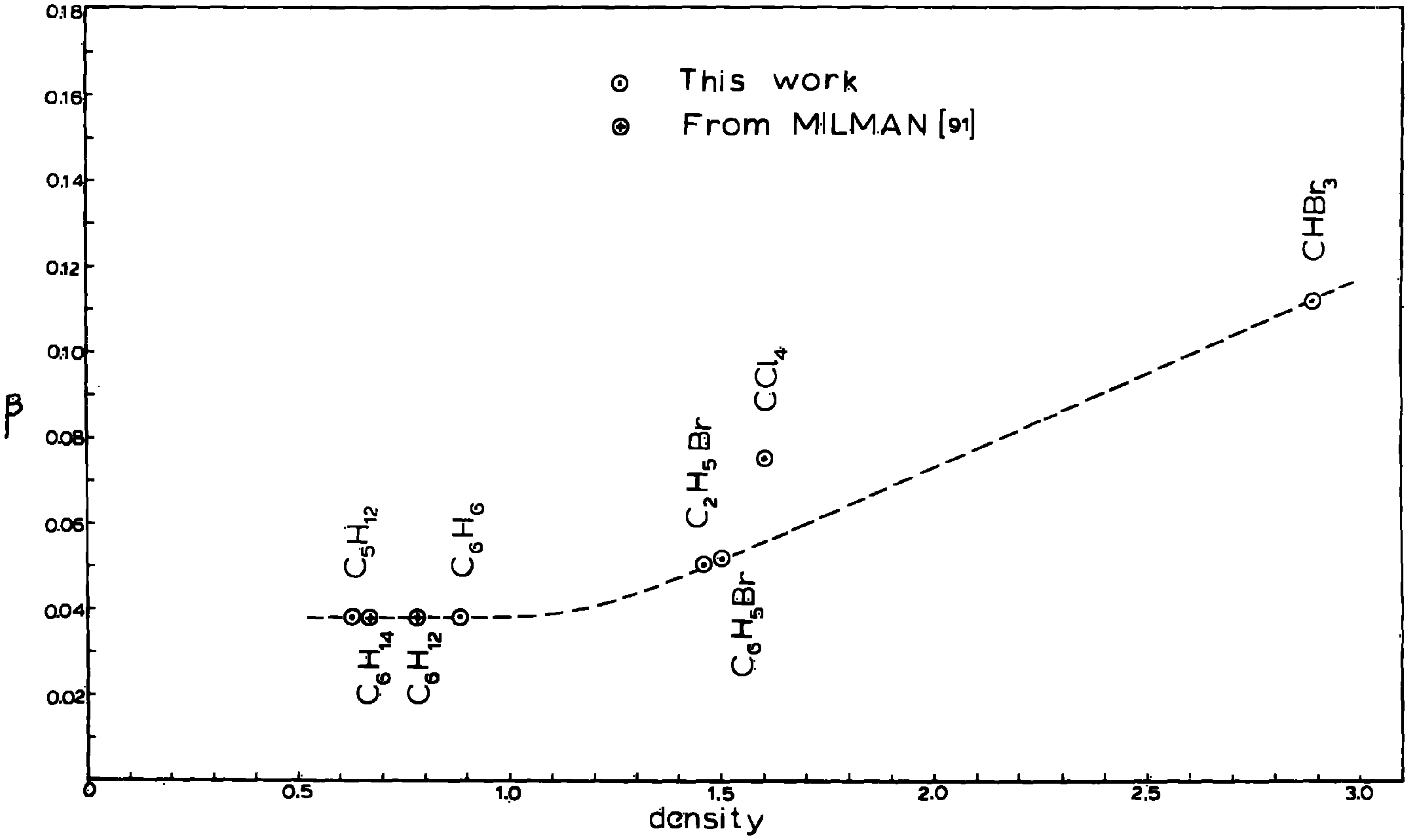

Fig.20

Plot of β values versus density

due to density may not be in conflict with the explanation of the discrepancies in the values of β on the basis of inelasticity within the molecule, but that the results can be accounted for on the basis of the mechanistic picture.

For example, an increase in density or in the molecular weight of the system would mean that the rigidity of the walls surrounding the hit molecule would increase, more energy would be dissipated in a smaller volume resulting at a greater damage at the collision site, that is, a higher concentration of fragments and a higher probability of the recoil atom combining with one of them. Alternatively, in a denser medium, the recoil atom would experience greater difficulty in escaping from the collision site.

The above show that the increase in the parameter β (and α, γ) is to be expected from the mechanism of retention.

Another source of error is calculating the number of collisions could be the accuracy in the values of E_1 or E_2 for the various binary systems. If the values of these parameters were all changed by the same factor, then this would result in different values for all the parameters α , β , γ but it would not eliminate the discrepancies. If small changes were brought about in some of these values but not in others, this would, of course, result in small changes in some of the parameters only but again would not eliminate discrepancies between values such as 0.038 and 0.0745 or 0.050 and 0.112. And it might well create discrepancies in cases where there is now agreement.

Summarizing all the above, it can be said that the theory works without internal inconsistency when the Logarithmic Energy Decrement is used. The observed discrepancies in the value of the parameter β, when $E_{ret}(av)$ is used, can be explained on the basis of varying element of inelasticity in the collisions, which makes the equations of the theory of varying degree of accuracy. And, although this kinetic treatment makes no assumption, apart from a collisional event, as to the particular mechanism by which retention occurs, the details of this mechanism may account for the observed results.

Section 10. Comparison of magnitudes of parameters α, β, γ with related quantities in the EW treatment.

The range of the values of the parameters α, β, γ as obtained in this work can be seen in Table XXX. It is interesting to compare these values with related quantities in the EW treatment. It has been noted (47b) that the mean values of the probability function $p_i(E)$ are given by

$$\overline{p_i(E)} = \frac{I_i}{\ln\ (E_1/E_2)}$$

where I_i is the reactivity integral for species i. CROSS and WOLFGANG (98) have given values for these integrals. For substitution reactions of halogen atoms with a hydrogen or halogen atom in halomethanes, the range of values of these integrals is 0.04 - 0.06.

If we take E_1 and E_2 of the EW treatment to be equal to E_o and E_2 of this work (in the EW treatment there is no need to assign values to these limits the only requirement being that these limits should exist), then α, β, γ, assumed to be mean values over the range $E_o - E_2$, are equivalent to $p_i(E)$ over this range. The values of $\overline{p_i(E)}$ derived from the values of I_i fall in the range 0.008 - 0.012 ($\ln (100/0.8676) = 4.749 \sim 5$). But these values of $p_i(E)$ refer to retention in an individual species in the gas phase whereas α, β and γ in this work refer to retention in all species in the liquid phase. It is thus seen that α, β and γ are comparable with results obtained by the E-W treatment.

APPENDIX A

CORRECTIONS FOR COLLISION CROSS-SECTIONS

Following MILMAN (91), we set f_x, f_y and f_z equal to the relative probabilities that the recoil bromine atom will strike an ethyl bromide molecule, a bromine molecule or a phenyl bromide molecule, respectively. These parameters are defined by equations such as

$$f_x = \frac{x \cdot S_x}{x \cdot S_x + y \cdot S_y + z \cdot S_z} \qquad \text{(A1)}$$

where x,y and z are the mole fractions of ethyl bromide, bromine and phenyl bromide, respectively, and S_x, S_y, S_z the collision cross sections of the hot bromine atom with these three materials. (MILMAN assumed that f_x, f_y and f_z are not functions of energy and to make this assertion as realistic as possible, she calculated the S's from viscosity data of the corresponding vapour at an arbitrary temperature - the same for all the components of a given system).

Now the procedure of calculating retentions from the theory by taking into consideration these relative probabilities is as follows:

I. M_a as defined by Eq.(7b)

Determination of parameters α, β, γ

For the binary system C_2H_5Br/Br_2 we have

$$M_a = x \cdot M_x + y \cdot M_y \quad \text{(From Eq.(7b))}$$

where M_x and M_y the molecular weights of C_2H_5Br and Br_2, respectively.

By correcting for the relative probabilities, we get

$$M_a = f_x \cdot M_x + f_y \cdot M_y \qquad \text{(A2)}$$

For $y \longrightarrow o$, $f_y \longrightarrow o$ and $f_x \longrightarrow 1$. Consequently

$$M_a = M_x$$

Thus, the correction makes no difference in the value of M_a. The parameters α and β will be determined by the same equations as in the theory.

The same is true for the other binary systems, C_6H_5Br/Br_2, from which γ and β will be obtained.

When it comes to the ternary system, M_a will be given by

$$M_a = x \cdot M_x + y \cdot M_y + z \cdot M_z \qquad \text{(From Eq.(7b))}$$

or, corrected,

$$M_a = f_x \cdot M_x + f_y \cdot M_y + f_z \cdot M_z \qquad \text{(A3)}$$

This value of M_a is used in calculating $E_{ret}(av)$ and, eventually, m and n-m. Eq.(6) takes the form

$$R = \frac{\alpha f_x + \gamma f_z}{\alpha f_x + \beta f_y + \gamma f_z} (1 - p^m) + \frac{\alpha f_x}{\alpha f_x + \beta f_y} p^m (1-q^{n-m}) \qquad \text{(A4)}$$

where $p = 1 - \alpha f_x - \beta f_y - \gamma f_z$

$q = 1 - \alpha f_x - \beta f_y$

II. M_a as defined by Eq.(7a)

In this case, there are two types of corrections that can be made:

(a) Correction for f_x, f_y and f_z only.

(b) Additionally corrections for the relative probability of the recoil atom hitting a particular atom in the struck molecule.

We shall treat each case separately.

Case (a): Molecules have different collision cross sections - there is an equal probability of any one atom being hit.

Determination of parameters α, β, γ

For the binary system C_2H_5Br/Br_2 we have

$$M_a = \frac{x \cdot M_x + y \cdot M_y}{x \cdot n_x + y \cdot n_y} \quad \text{(From Eq.(7a))}$$

where n_x and n_y the number of atoms in an ethyl bromide and a bromine molecule, respectively.

Correcting for f_x and f_y we get

$$M_a = \frac{f_x \cdot M_x + f_y \cdot M_y}{f_x \cdot n_x + f_y \cdot n_y} \qquad \text{(A5)}$$

and, again, for $y \longrightarrow 0$, $f_y \longrightarrow o$ and $f_x \longrightarrow 1$. Consequently

$$M_a = \frac{M_x}{n_x}$$

Thus, the correction makes no difference in the value of m_a. The parameters α and β will be determined as in the theory. The same is true for the other binary system, from which γ and β will be obtained.

In the ternary system, the equation for M_a is

$$M_a = \frac{f_x \cdot M_x + f_y \cdot M_y + f_z \cdot M_z}{f_x \cdot n_x + f_y \cdot n_y + f_z \cdot n_z} \qquad \text{(A6)}$$

This M_a is used in calculating $E_{ret}(av)$ and, eventually, m and n-m. Eq.(6) of the theory again takes the form (A4).

Case (b): Molecules have different collision cross sections - the various atoms in a particular molecule have different probabilities of being hit.

Determination of parameters α, β, γ

Again, in this case, the correction for f_x, f_y and f_z in the binary systems makes no difference since, at $y \longrightarrow o$, both f_x and $f_z \longrightarrow 1$.

But here, instead of calculating $E_{ret}(av)$ through the M_a of the molecule (that is $M_a = \frac{M_x}{n_x}$) the calculation is done as follows:

The atomic weight of a particular atom, M_{a_1}, is inserted in the equation for $E_{ret}(av)$ instead of M_a and a <u>partial</u> $E_{ret}(av)$ calculated. This then is multiplied by a probability factor 'g' of that particular atom being hit (see ref.(91)) and $E_{ret}(av)$ for the binary system is obtained by summing up the products of $E_{ret}(av)_{atom}$ x (probab. factor)$_{atom}$ for the different atoms in the molecule. In the case of C_2H_5Br/Br_2 the situation is as follows:

$$\begin{aligned} E_{ret}(av)_{Br-H} &= \frac{M_H^2 + M_b^2}{(M_H + M_b)^2} \\ E_{ret}(av)_{Br-C} &= \frac{M_c^2 + M_b^2}{(M_c + M_b)^2} \\ E_{ret}(av)_{Br-Br} &= \frac{(M_{Br} + M_b)^2}{(M_{Br} + M_b)^2} \end{aligned} \qquad (A7)$$

where M_H, M_C and M_{Br} the mass of a hydrogen, carbon and bromine atom, respedtively.

Then

$$\left[E_{ret}(av)\right]_{C_2H_5Br} = \left[E_{ret}(av)_{Br-H} \cdot g_H + E_{ret}(av)_{Br-C} \cdot g_C + E_{ret}(av)_{Br-Br} \cdot g_{Br}\right] \qquad (A8)$$

where g_H, g_C and g_{Br} the probability of a hydrogen, carbon or bromine atom being hit, respectively.

This $\left[E_{ret}(av)\right]_{C_2H_5Br}$ is used in calculating m for this binary system and an $\left[E_{ret}(av)\right]_{C_6H_5Br}$ in calculating n in the other binary system. The parameters α, β, γ are then determined as in the theory.

In calculating retentions in the ternary systems, and in order to take both corrections into account, we calculate $\left[E_{ret}(av)\right]_{ternary}$ as follows:

$$\left[E_{ret}(av)\right]_{ternary} = \left[\left[E_{ret}(av)\right]_{C_2H_5Br} \cdot f_x + \left[E_{ret}(av)\right]_{Br_2} \cdot f_y + \left[E_{ret}(av)\right]_{C_6H_5Br} \cdot f_z\right] \qquad (A9)$$

This corrects for f_x, f_y and f_z while the correction for atoms having different probabilities of being hit has already been taken up by the three partial $E_{ret}(av)$. This implies, of course, that these probabilities do not change when the molecules comprising these atoms become components of a ternary system.

APPENDIX B

DYNAMICS OF ELASTIC COLLISIONS

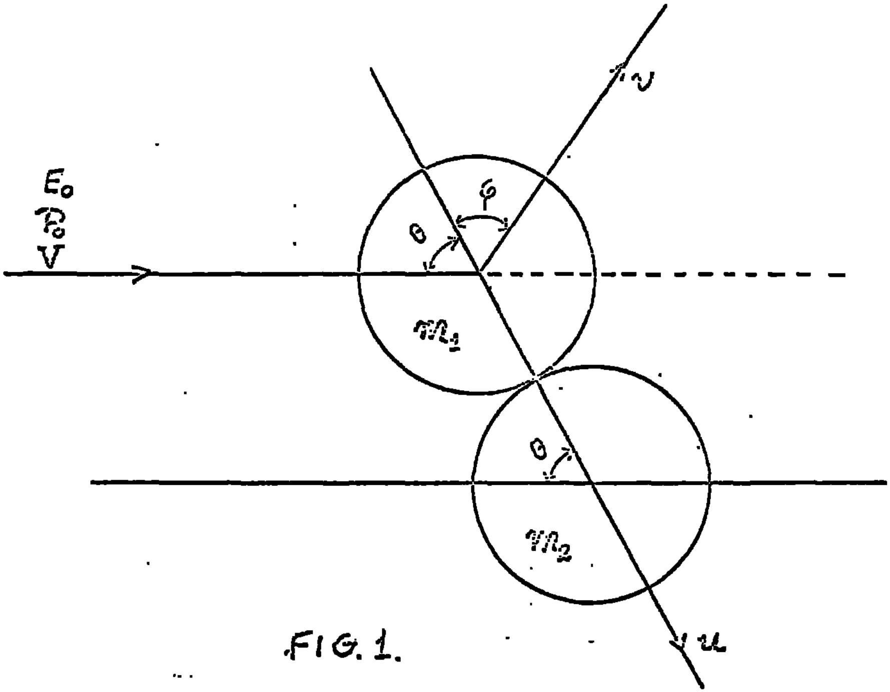

FIG. 1.

A sphere of mass m_1, with initial velocity V collides with a free sphere of mass m_2, which is initially at rest (FIG. 1). As a result of the collision, the incident sphere is deflected through an angle $[\pi-(\theta+\varphi)]$ while the struck sphere is projected at an angle θ with the original direction of m_1. The struck sphere acquires a velocity u; the velocity of the projectile sphere is reduced to v. The linear momentum of the system is unchanged by the collision. Kinetic energy is conserved in elastic collisions, hence we have

Conservation of Energy

$$\frac{1}{2} m_1 V^2 = \frac{1}{2} m_1 v^2 + \frac{1}{2} m_2 u^2 \qquad (B1)$$

Conservation of Momentum

(a) $\parallel^{el}$ direction : $m_1 V = m_1 v \cos[\pi - (\theta + \varphi)] + m_2 u \cos\theta$ (B2)

(b) $\perp^{ar}$ direction : $0 = m_1 v \sin[\pi - (\theta + \varphi)] - m_2 u \sin\theta$ (B3)

Note:

$$\cos[\pi - (\theta + \varphi)] = -\cos(\theta + \varphi) \qquad (B4)$$

$$\sin[\pi - (\theta + \varphi)] = \sin(\theta + \varphi) \qquad (B5)$$

From Eq. (B3)

$$\sin\theta = \frac{m_1 v}{m_2 u} \sin(\theta + \varphi)$$

or, (since $\sin^2\theta + \cos^2\theta = 1$),

$$\cos^2\theta = 1 - \left(\frac{m_1 v}{m_2 u}\right)^2 \sin^2(\theta + \varphi) \qquad (B6)$$

From Eq. (B2) (and taking into account (B4))

$$m_1\left[V + v\cos(\theta+\varphi)\right] = m_2 u\cos\theta$$

and using Eq.(B6)

$$m_1^2\left[V + v\cos(\theta+\varphi)\right]^2 = m_2^2 u^2 - m_1^2 v^2 \sin^2(\theta+\varphi)$$

or

$$m_1\left[m_1 V^2 + m_1 v^2\left[\cos^2(\theta+\varphi) + \sin^2(\theta+\varphi)\right] + 2m_1 v V\cos(\theta+\varphi)\right] = m_2^2 u^2 \quad (B7)$$

From Eq.(B1)

$$m_1 v^2 = m_1 V^2 - m_2 u^2$$

and from Eq.(B2) (in connection with (B4))

$$m_1 v\cos(\theta+\varphi) = m_2 u\cos\theta - m_1 V$$

Using these in Eq.(B7) we get

$$m_1\left[m_1 V^2 + m_1 V^2 - m_2 u^2 + 2V(m_2 u\cos\theta - m_1 V)\right] = m_2^2 u^2$$

or

$$m_1\left[2m_1 V^2 + 2V m_2 u\cos\theta - 2m_1 V^2 - m_2 u^2\right] = m_2^2 u^2$$

or

$$2V m_1 m_2 u\cos\theta = u^2 m_2(m_1 + m_2)$$

and, provided that $u \neq 0$

$$\boxed{u = 2V\frac{m_1}{m_1+m_2}\cos\theta} \qquad (B8)$$

Substituting in (B3)

$$m_1 v \sin(\theta+\varphi) = m_2 \sin\theta \, 2V \frac{m_1}{m_1+m_2} \cos\theta$$

or

$$\boxed{v = V \frac{m_2}{m_1+m_2} \frac{\sin 2\theta}{\sin(\theta+\varphi)}} \qquad (B9)$$

Substituting in (B1)

$$m_1 V^2 = m_1 V^2 \left(\frac{m_2}{m_1+m_2}\right)^2 \frac{\sin^2 2\theta}{\sin^2(\theta+\varphi)} + m_2 4V^2 \left(\frac{m_1}{m_1+m_2}\right)^2 \cos^2\theta$$

or

$$(m_1+m_2)^2 - 4m_1 m_2 \cos^2\theta = m_2^2 \frac{\sin^2 2\theta}{\sin^2(\theta+\varphi)}$$

or

$$m_1^2 + m_2^2 + 2m_1 m_2 \left(1 - 2\cos^2\theta\right) = m_2^2 \frac{\sin^2 2\theta}{\sin^2(\theta+\varphi)}$$

or

$$\boxed{\sin^2(\theta+\varphi) = \frac{m_2^2 \sin^2 2\theta}{m_1^2 + m_2^2 - 2m_1 m_2 \cos 2\theta}} \qquad (B10)$$

Consider the special case where $m_1 = m_2$

Then Eq. (B10) takes the form

$$\sin^2(\theta+\varphi) = \frac{\sin^2 2\theta}{2(1-\cos 2\theta)} = \frac{4\sin^2\theta\cos^2\theta}{2\cdot 2\sin^2\theta}$$

Finally,

$$\boxed{\sin(\theta+\varphi) = \pm\cos\theta} \qquad (B11)$$

(i) (+) sign

$$\sin(\theta+\varphi) = \sin\left(\tfrac{\pi}{2}+\theta\right) = \sin\left(\tfrac{\pi}{2}-\theta\right)$$

then

(a) $\theta+\varphi = \frac{\pi}{2}+\theta \longrightarrow \varphi = \frac{\pi}{2}$

(b) $\theta+\varphi = \frac{\pi}{2}-\theta \longrightarrow 2\theta+\varphi = \frac{\pi}{2}$

(ii) (−) sign

$$\sin(\theta+\varphi) = -\sin\left(\tfrac{\pi}{2}+\theta\right) = -\sin\left(\tfrac{\pi}{2}-\theta\right)$$
$$= \sin\left(-\tfrac{\pi}{2}-\theta\right) = \sin\left(\theta-\tfrac{\pi}{2}\right)$$

then

(a) $\theta+\varphi = -\frac{\pi}{2}-\theta \longrightarrow 2\theta+\varphi = -\frac{\pi}{2}$

(b) $\theta+\varphi = \theta-\frac{\pi}{2} \longrightarrow \varphi = -\frac{\pi}{2}$

These latter two solutions may be rejected as being negative.

Probability of Occurence of Various Values of θ

All lines of motion of the projectile sphere parallel to given direction of motion are equally probable. Therefore the probability of occurence of collisions at an angle θ will be proportional to the area of the spherical annulus at θ projected into a plane perpendicular to the direction of motion.

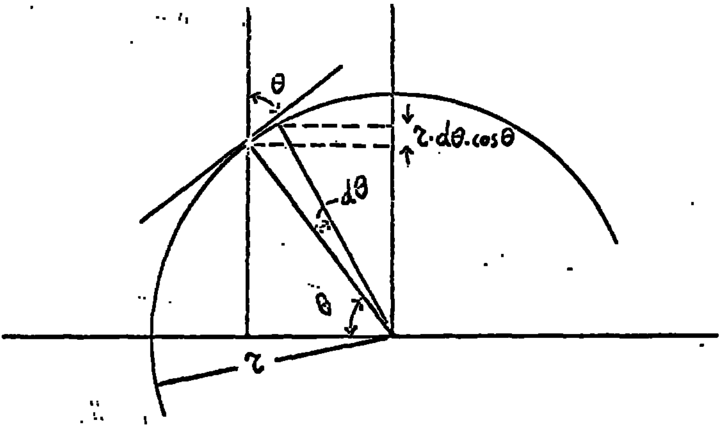

FIG. 2

Projected area of annulus $= 2\pi r \sin\theta \, r \, d\theta \cos\theta$

$= \pi r^2 \sin 2\theta \cdot d\theta$

Probability of collision occurring in this area = probability of collision occurring at angle θ =

$$= p(\theta) \cdot d\theta = \frac{\text{Area of Annulus}}{\text{total projected area}} = \frac{\pi r^2 \sin 2\theta \cdot d\theta}{\pi r^2}$$

or $$\boxed{p(\theta)\cdot d\theta = \sin 2\theta \cdot d\theta} \qquad (B\,12)$$

Energy Transfer in Collisions

In general, fractional energy transfer per collision =

$$= \frac{(E_{target})_{after\ collision}}{(E_{projectile})_{before\ collision}} = \frac{1/2\, m_2 u^2}{1/2\, m_1 V^2} =$$

$$= \frac{m_2}{m_1 V^2}\, \frac{m_1^2 V^2}{(m_1+m_2)^2} \cdot 4\cos^2\theta$$

or $$\boxed{E_{trans}(\theta) = \frac{4 m_1 m_2}{(m_1+m_2)^2} \cos^2\theta} \qquad (B\,13)$$

Maximum Energy Transfer per Collision

This occurs when $\cos\theta = 1$, i.e. $\theta = 0°$

$$\boxed{E_{trans}(max) = \frac{4 m_1 m_2}{(m_1+m_2)^2}} \qquad (B\,14)$$

Average Energy Transfer per Collision

$$E_{trans}\,(av) = \frac{\int_0^{\pi/2} E_{trans}(\theta)\cdot p(\theta)\cdot d\theta}{\int_0^{\pi/2} p(\theta)\cdot d\theta}$$

$$= \frac{\int_0^{\pi/2} \frac{4m_1 m_2}{(m_1+m_2)^2}\cdot\cos^2\theta\cdot\sin 2\theta . d\theta}{\int_0^{\pi/2}\sin 2\theta\cdot d\theta}$$

$$= \frac{4m_1 m_2}{(m_1+m_2)^2}\;\frac{\int_0^{\pi/2} 2\cos^3\theta . -d(\cos\theta)}{\int_0^{\pi/2} 2\cos\theta . -d(\cos\theta)}$$

$$= \frac{4m_1 m_2}{(m_1+m_2)^2}\;\frac{\left[\frac{\cos^4\theta}{4}\right]_0^{\pi/2}}{\left[\frac{\cos^2\theta}{2}\right]_0^{\pi/2}}$$

$$= \frac{4m_1 m_2}{(m_1+m_2)^2}\;\frac{\left[0/4 - \frac{1}{4}\right]}{\left[0/2 - \frac{1}{2}\right]}$$

$$\boxed{E_{trans}\,(av) = \frac{2m_1 m_2}{(m_1+m_2)^2}} \qquad (B15)$$

APPENDIX C

ACTIVATION ENERGIES

We require the activation energies of the following reactions

$C_2H_5Br + Br^* \longrightarrow C_2H_5Br^* + Br$ (B1)

$C_6H_5Br + Br^* \longrightarrow C_6H_5Br^* + Br$ (B2)

$CCl_4 + Br^* \longrightarrow CCl_3Br^* + Cl$ (B3)

$C_6H_6 + Br^* \longrightarrow C_6H_5Br^* + H$ (B4)

$CHBr_3 + Br^* \longrightarrow CHBr_2Br^* + Br$ (B5)

LIBERATURE and WIIG (95) studied the exchange between radioactive bromine and gaseous ethyl bromide and from a negative result concluded that the exchange had a relatively high activation energy. Calculation by the semi-empirical method yielded 25 Kcal. mole^{-1} for the activation energy of reaction (B1). The other four reactions do not appear to have been studied for the purpose of determining their activation energies, but an estimate can be made as follows.

Many ionic exchange reactions similar to (B1) (B2) and (B5) have been studied (105) and, for several aliphatic bromides, it was found that the activation energies were about 20 Kcal.mole^{-1}. The charge distribution occurring in the transition complex, $^{\delta-}Br\cdots CR_3\cdots\cdot Br^{\delta-}$ will help to stabilize the complex, but the easier attraction of electrons to an entering bromine atom in the absence of a negative charge might produce a compensatory lowering of energy for the corresponding radical complex. This argument suggests activation energies of about 20 Kcal.mole^{-1} for reactions (B1) and (B2).

A probable lower limit may be set as follows:

The activation energy of the reaction

$$CCl_3Br + Br^{\bullet} \longrightarrow CCl_3^{\bullet} + Br_2 \qquad (B6)$$

has been established (96) as 10.2 Kcal.mole^{-1}. As $D_{CCl_3 - Br} = 49$ Kcal and $D_{Br - Br} = 45.5$ Kcal, this reaction is 3.5 Kcal. mole^{-1} endothermic leaving 6.7 Kcal. mole^{-1} as the 'activation increment'. The transition complex for this reaction is R_3C ... Br ... Br, and as electrons are not so freely available on a carbon atom as on a bromine atom, it is likely that the transition complex for reactions (B1) - (B3), Br ... R_3C ... Br, is of higher energy. Allowing for this suggests that the 'activation increment' of reaction (B6) should be increased to perhaps 10-20 Kcal and as reactions (B1) and (B2) are thermoneutral, this would be the activation energy. The absence of any suggestion of exchange reactions in the extensive literature of bromination reactions may be taken as suggesting that the activation energies of the exchange reactions are higher than those typical of hydrogen abstractions that occur freely with activation energies in the range 10-20 Kcal mole^{-1} (99).

Reaction (B3) is ~ 30 Kcal mole^{-1} endothermic (D$_{CCl_3-Cl}$ = 80 Kcal, D$_{CCl_3-Br}$ = 49 Kcal) and its activation energy must be at least 30 Kcal. If the 'activation increment' is 10-20 Kcal as suggested above, this leads to an activation energy of 40-50 Kcal.mole^{-1} for reaction (B3).

The bond dissociation energies for the C_6H_5 - Br and C_6H_5-H bonds are 71 Kcal and 102 Kcal, respectively (99). Thus the activation energy of reaction (B4) must be at least 31 Kcal.mole^{-1}. It was said before that hydrogen abstraction reactions have activation energies in the range 10-20 Kcal.mole^{-1}. Since D$_{H-Br}$ is 87.5 Kcal.mole, the reaction

$$C_6H_6 + Br \longrightarrow C_6H_5\cdot + HBr \qquad (B7)$$

should be 14.5 Kcal.mole^{-1} endothermic leaving approximately 5 Kcal.mole^{-1} as the 'activation increment'. A replacement reaction such as (B4) should be expected to have a larger 'activation increment' of, perhaps, 10-15 Kcal mole^{-1}. Consequently, an approximate value of 40-50 Kcal.mole^{-1} can be set for the activation energy of reaction (B4).

HODGES and MICELI (104) studied the isotopic exchange between carbon tetra-bromide and bromine and found an activation energy of approximately 3 Kcal.mole^{-1}. On the basis of this, the activation energy for reaction (B5) was taken as 5 Kcal.mole^{-1}.

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