Radiochemical studies on free radicals

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RADIOCHEMICAL STUDIES ON FREE RADICALS.

- THESIS -

presented in canditature for the degree of

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by

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The work described in this thesis was carried out in the Radiochemical Department of the Science Laboratories, Durham, between September 1947 and August 1949 under the supervision of Professor F. A. Paneth, F.R.S..

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I am happy to have this opportunity of expressing my gratitude and sincere thanks for the privilege of working under the direction of Professor Paneth and for his never-failing interest in this study.
I wish to thank also Mr. G. R. Martin for many valuable discussions and suggestions.

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SUMMARY.

This thesis is divided into two parts. Part One deals with the reactions of free radicals in the gas phase. After a brief historical introduction, some of the limitations of the classical mirror method and the advantages to be obtained by the use of radioactive mirrors are discussed. An examination of the extensive literature on free radicals has revealed that very little work has been published on the application of radiochemical methods to their study. Such work as has been published is noted.

Preliminary experiments with non-radioactive mirrors and with mirrors of thorium B are described. Details are given of a modification of the Geiger-Muller tube designed for special application to flow-tube methods. This counter was not developed when it became evident that it was not essential for the work in hand.

The theoretical work of Paneth and Hertzfeld on the length of mirror necessary to eliminate free radicals completely from a gas stream is reviewed. A so-called "slit" method based on the use of a radioactive mirror is described for the direct measurement

of this length. Unsatisfactory results were obtained with mirrors of radioactive antimony, but results in good agreement with the theoretical calculations were gained with mirrors of radium E.

Part Two deals with the reactions of free radicals in the liquid phase. Here the reactivity of the various radicals is of practical importance, particularly in connection with polymerisation studies. The mean life period of a radical is an inverse function of its reactivity, so that the determination of the lifetime of radicals in solution would be of value. Little work has yet been published on this aspect, and none where radiochemical methods have been used.

After a review of the reactions suitable for study, three radioactive indicator methods are described for the direct measurement of the lifetimes of free radicals. Negative results were obtained with two of these which were flow methods based on the mirror technique. A so-called "static" method is described by which the values of 5 and 8 sec. have been obtained for the approximate lifetime of the radicals formed in the decomposition of dibenzoyl peroxide in boiling benzene solution. In this method finely divided radioactive antimony is rapidly stirred in the decomposing peroxide solution. The quantity of antimony which reacts is much less when ethyl alcohol instead of benzene is used as a solvent. Possible explanations for this difference in reactivity are given.

Improvements of the technique will be required for definite results to be obtained by the use of radioactive indicator methods. To this end suggestions for further work are made.

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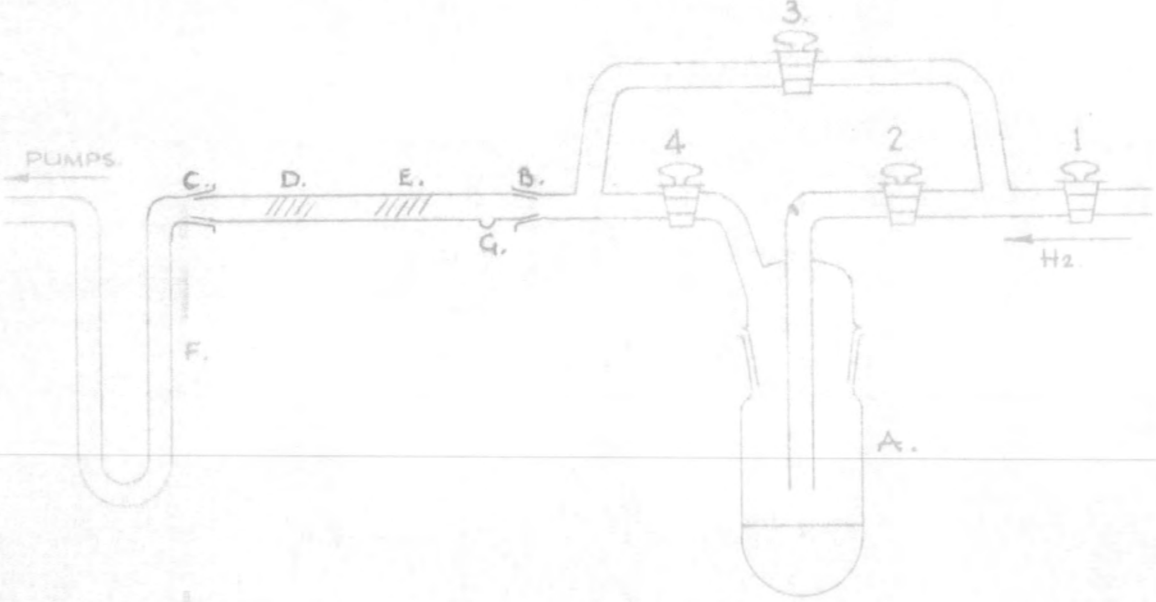
PART TWO.

REACTIONS IN THE LIQUID PHASE.

PART ONE.

REACTIONS IN THE GAS PHASE.

CHAPTER ONE.



—FIG. 1.—

CHAPTER ONE

THE RADIOACTIVE INDICATOR MODIFICATION OF THE MIRROR METHOD.

1. Historical Introduction.

Free radicals may be defined as molecular complexes of abnormal valency, which possess additive properties, but do not carry an electrical charge and are not free ions (83). The independent existence of an organic radical, triphenylmethyl $Ph_3C\cdot$, was first discovered by Gomberg in 1900 during his investigation of hexaphenylethane (33). Subsequently the existence of free alkyl radicals was often suggested (9), but it was not until 1929 that Paneth and Hofeditz first prepared free methyl by the thermal decomposition of lead tetramethyl. (55).

$$Pb.(CH_3)_4 \rightleftharpoons Pb + 4CH_3\cdot$$

The following method was used. Specially purified hydrogen was drawn over a small quantity of lead tetramethyl contained in the tube A (Fig. 1.) which was cooled to about -70°C. The taps 1, 2, 3 and 4 regulated the concentration of lead tetramethyl in the gas stream. A fast pumping system was used so that a streaming velocity of 10 to 20 metres per second at a pressure of 1 to 2 mm. was maintained in the long silica tube BC.

The silica tube was heated with a bunsen burner at D where a mirror of lead was deposited due to the decomposition of lead tetramethyl vapour. When the tube was cooled at D and then heated at E, a second mirror formed at E with the simultaneous disappearance of the first mirror at D. Therefore one of the products of pyrolysis of lead tetramethyl at E must be a gas which can react with cold metallic lead at D. The product of reaction at D was isolated by cooling trap F in liquid air and was found to be lead tetramethyl.

It was proved that neither hydrogen nor the possible gaseous decomposition products such as methane and ethylene would react with a lead mirror even when passed through a very hot tube, so the reactive gas must be the free methyl radical $\cdot CH_3$. When acetylene was passed through a hot tube the mirror was attacked. This was the first real evidence for the production of free radicals by pyrolysis of a hydrocarbon, though Bone (9) had previously suggested their existence in this type of decomposition.

Mirrors of other metals were obtained by heating a small fragment of metal held in a depression in the reaction tube as at G. It was found that -- in addition to lead -- antimony, bismuth, zinc, cadmium and tellurium were readily attacked by free methyl radicals. Except for tellurium, it was found that a trace of oxygen would prevent removal of the mirror. With tellurium it was thought possible that the volatile oxide TeO_2 was formed, which might then sublime leaving a clean metallic surface.

Pearson, Robinson and Stoddart used antimony and lead in their "guard mirror" technique for detecting either atomic hydrogen or aliphatic free radicals in a mixture of both. (61). Both free radicals and atomic hydrogen attack antimony and tellurium, but lead is attacked by free radicals only. Low concentrations of free radicals in a mixture can be detected by passing the gas over a thin lead mirror placed in advance of an antimony mirror. Only if free radicals are present will the first mirror be attacked. For detecting atomic hydrogen mixed with free radicals, the gas is passed first over a long heavy mirror of lead and then over a thin antimony mirror. The second mirror will only be attacked if atomic hydrogen is present.

In 1931 Paneth and Lautsch prepared the free ethyl radical $\cdot C_2H_5$ by the thermal decomposition of lead tetraethyl (56), and found that its properties were very similar to those of free methyl. The free methyl and ethyl groups were identified by combining them with zinc and showing that the properties of the resultant compounds were identical with those of zinc dimethyl and zinc diethyl. Later workers used the compounds formed with sodium and with carbon tetraiodide (72), mercury and tellurium (68,69), arsenic (63), and lead (38) for identification purposes.

Paneth and Lautsch obtained chiefly methyl radicals from the thermal decomposition of lead tetra-n-propyl and lead tetra-iso-butyl and concluded that the alkyl radicals higher than ethyl were unstable and rapidly broke down to methyl or ethyl radicals. However, Pearson and Purcell later showed that the n-propyl radical is the chief active product formed by the photolysis of di-n-propyl ketone. (64).

Paneth and Lautsch got free benzyl $C_6H_5-CH_2\cdot$ by decomposing tin tetrabenzyl (59), but were unable to obtain definite evidence for the production of the free phenyl radical $\cdot C_6H_5$ by the pyrolysis of lead tetraphenyl. Glazebrook and Pearson were successful in preparing the free phenyl radical by photolysis of acetophenone. (31). In 1933 Leermakers showed that the thermal decomposition of azomethane yielded free methyl radicals (47), and in 1934, F. O. Rice and his collaborators (70) produced free methyl and ethyl radicals by the high temperature pyrolysis of many different stable organic compounds including paraffin hydrocarbons, aldehydes and ketones, ethers, alcohols, amines, etc.. Pearson (62) had free methyl by the photolysis of acetone vapour in the same year and by the photolysis of acetaldehyde vapour in 1935 (63).

Polanyi and his collaborators (66) formed free radicals by the action of a metal on an organic halogen compound. They used sodium vapour which is monatomic to effect single electron transfers with aliphatic halides.

$$H_3CCl + Na\cdot \longrightarrow H_3C\cdot + NaCl$$

Using the same type of reaction, Bawn and his co-workers claimed the production of free phenyl radicals from chlorobenzene (2) and derived the diradical trimethylene $\cdot CH_2-CH_2-CH_2\cdot$ from trimethylene dibromide (6,7).

In his quantitative experiments, Paneth measured the time required to remove antimony mirrors placed at different distances from the source of radicals. A mirror of constant thickness was made by matching its opacity against that of a standard as in the Marsh technique for arsenic analysis. The rate of removal of the mirror was found to decrease exponentially with the distance between the mirror and the source of free radicals, and the concentration of radicals at the mirror could be expressed by the usual equation for first order processes :

$$C_t = C_o e^{-kt}.$$

Apart from the reaction between the radicals and the metallic mirror, there are also the possible reactions with the carrier gas and the walls of the tube to be considered.

$$CH_3\cdot + H_2 \longrightarrow CH_4 + H\cdot \quad \text{--------(A)}$$

$$2CH_3\cdot + M \longrightarrow C_2H_6 + M \quad \text{--------(B)}$$

(A) will appear to be first order with a large excess of hydrogen, and (B) will appear to be first order if the radical attaches itself to the wall, becoming deactivated and later reacting with another radical. Paneth and Hertzfeld (58) calculated that each collision of a radical with a metallic mirror of lead or antimony resulted in combination, so the overall reaction will appear first order. Later, in more accurate experiments, Paneth, Hofeditz and Wunsch (60) found that the reaction at room temperature was not strictly first order but that it became first order when the tube between the mirror and the source of free radicals was maintained at 350°C.

The half-life of methyl and ethyl radicals was found to be about 6×10^{-3} sec.. The mean free life was found to depend to some extent on the diameter and temperature of the reaction tube and the nature of the transport gas (28,58,60). The value of the half-life obtained when nitrogen, helium or helium-neon mixtures were used as carrier was approximately the same as when hydrogen was used. Changing the diameter of the reaction tube from 5-15 mm. altered the half-life of methyl radicals from $5\text{-}15 \times 10^{-3}$ sec.. It appeared, therefore, that the radicals disappeared primarily by recombination on the wall. In their later work Paneth, Hofeditz and Wunsch obtained evidence to show that the wall effect had previously been over-estimated, and that even at room temperature the homogeneous gas reaction

$$CH_3\cdot \quad + \quad H_2 \longrightarrow CH_4 \quad + \quad H\cdot$$

occurs to significant extent. It was estimated that only 1 in 1000 collisions of the radical with the wall produced recombination on cold glass or quartz, the ratio becomes 1 in 10,000 at 500°C when helium is the carrier.

2. Limitations of the classical mirror method.

One of the difficulties encountered in the classical experiments was that of obtaining a reproducible standard mirror, and the method of comparing the opacity with that of a standard/reference mirror was tedious and strictly limited the thickness which could be used. A further disadvantage was that the course of the reaction could not be followed continuously, although Prileshajeva and Terenin (65) accomplished this by placing the mirror between a light source and a photo-electric cell. Here again the initial thickness was limited to that which would just transmit light.

Recently, a new technique for obtaining reproducible mirrors of zinc by decomposition of zinc diethyl vapour by a uniform beam of ultra violet light has been described (49). A method has also been published which might be used for following the attack on a metallic mirror continuously. In this method the rate of change of electrical conductivity of the mirror is measured (86).

3. Advantages obtained by the use of radioactive mirrors.

The use of radioactive mirrors makes possible the direct and immediate observation of the rate of reaction at the mirror. Provided the mirrors used in each experiment are obtained from the same stock of radioactive metal, it is no longer necessary to use a standard mirror, and the thickness of the mirror is limited only by the specific activity of the radioactive metal used and the sensitivity of the counting equipment employed. Apart from the elegance of the method of radioactive indicators, the sensititity of the mirror technique for detecting free radicals is enormously increased, particularly when tracers such as RaE, or ThB, which can easily be obtained with a very high specific activity, are used.

4. Previous work.

The only instances quoted in the literature of the use of radioactive tracers in free radical studies are by Leighton and Mortensen in 1936 (48), Burton, Ricci and Davis in 1940 (12), Harris and Tickner in 1947 (35), and Durham, Martin and Sutton in 1949 (19).

Leighton and Mortensen used a mirror composed of RaD, E and F obtained from old emanation tubes to prove that photolysis, like pyrolysis, of lead tetramethyl produced free methyl radicals. Their results showed that the radicals attacked RaD in preference to RaE. No significance can be attached to this because of the qualitative nature of the experiments. Inactive lead and bismuth are attacked equally readily by free radicals and there is no reason to suppose that their radioactive isotopes would show a difference in reactivity. They suggested that ThB would have advantages over RaD as an indicator, "...since ThB and its immediate decomposition products have beta activities and half-lives which would make possible direct and immediate observations of the rate of disappearance of the metal on the tube."

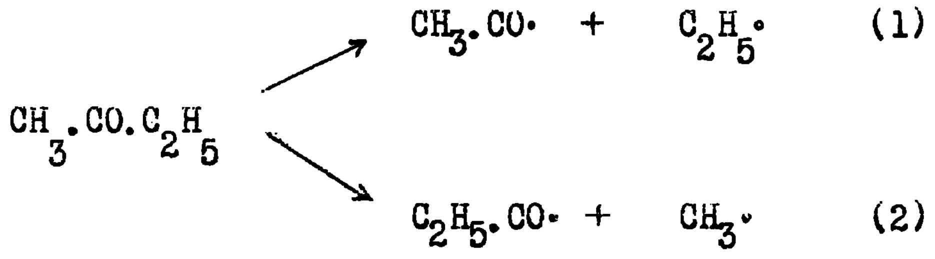
A paper published in February 1950 by Leighton and his collaborators (76) describes work on the photochemical decomposition of acetone and some other aliphatic compounds. It is of interest to note that the original mirror method was used to detect free radicals formed in the decompositions. The major portion of the experimental work was carried out in 1938. Then, it would appear that as a result of his earlier work with radioactive mirrors, Leighton considered no advantage was to be obtained by their use. It seems clear that he did not derive much benefit from the use of radioactive indicators because he measured their radioactivity not with a counter, but with an electroscope.

Burton, Ricci and Davis modified Leighton's method to detect the production of free radicals in the pyrolysis of acetaldehyde also using RaD as the indicator. Here again the experiments were qualitative.

Harris and Tickner employed the Paneth technique with bismuth mirrors containing RaE to study the reaction between atomic hydrogen and mercury dimethyl. A volatile radioactive bismuth compound was produced. They concluded that the reaction between atomic hydrogen and mercury dimethyl is a gas phase reaction and not a heterogeneous reaction on the bismuth surface, since neither mercury dimethyl nor atomic hydrogen alone reacted with the bismuth.

Durham, Martin and Sutton used radioactive iodine for the detection and estimation of free methyl, ethyl and propyl radicals. In their experiments the radioactive element was used in the vapour form, not as a mirror. The free radicals were allowed to react with iodine labelled with 8-day iodine-131, and the resulting alkyl iodides, likewise labelled, were frozen out in liquid air. At the conclusion of the experiment, excess iodine was removed and a small amount of carrier for each of the alkyl iodides involved was added. After separation by fractional distillation, and conversion of each fraction into silver iodide, simple beta particle counts gave directly the relative proportions of the various radicals initially present.

The method was also used to investigate the photochemical decomposition of methyl ethyl ketone. Their results indicated that reaction (1) is more probable than reaction (2).



$$CH_3.CO.C_2H_5 \rightarrow CH_3.CO\cdot + C_2H_5\cdot \quad (1)$$

$$CH_3.CO.C_2H_5 \rightarrow C_2H_5.CO\cdot + CH_3\cdot \quad (2)$$

5. Radioactive elements suitable for use in free radical studies.

A list of the radioactive isotopes of the elements suitable for use in free radical studies is given in Table 1. Whilst most of these have only become readily available since 1945 (by neutron reactions in the atomic pile), the naturally occurring members, RaE and ThB, each of convenient half-life, have long been known.

Some of these isotopes are more difficult to obtain and to use than others; the one to be employed must obviously be chosen to fit in best with the conditions of the particular experiment on hand. Generally, if a high specific activity is required, then an indicator must be chosen which can be produced by a non-isotopic reaction.

It is interesting to note the small use of radioactive tracer techniques in the period 1929-39. The reason may have been the unsuitability of the classical methods of estimating radioactivity when applied to continuous kinetic studies. Thermionic-valve counting and scaling circuits had been published, but the equipment was not being made commercially so that each investigator had to construct his own.

One result of the enormous development in the fields of nuclear physics and radiochemistry since 1940 has been the development and large-scale manufacture of refined electronic counting equipment. This equipment, in conjunction with the wide range of radioactive isotopes now generally available, has made possible a much greater and easier application of the method of radioactive indicators to general scientific problems, as evidenced by the multitude of papers now appearing on the subject.

TABLE 1.

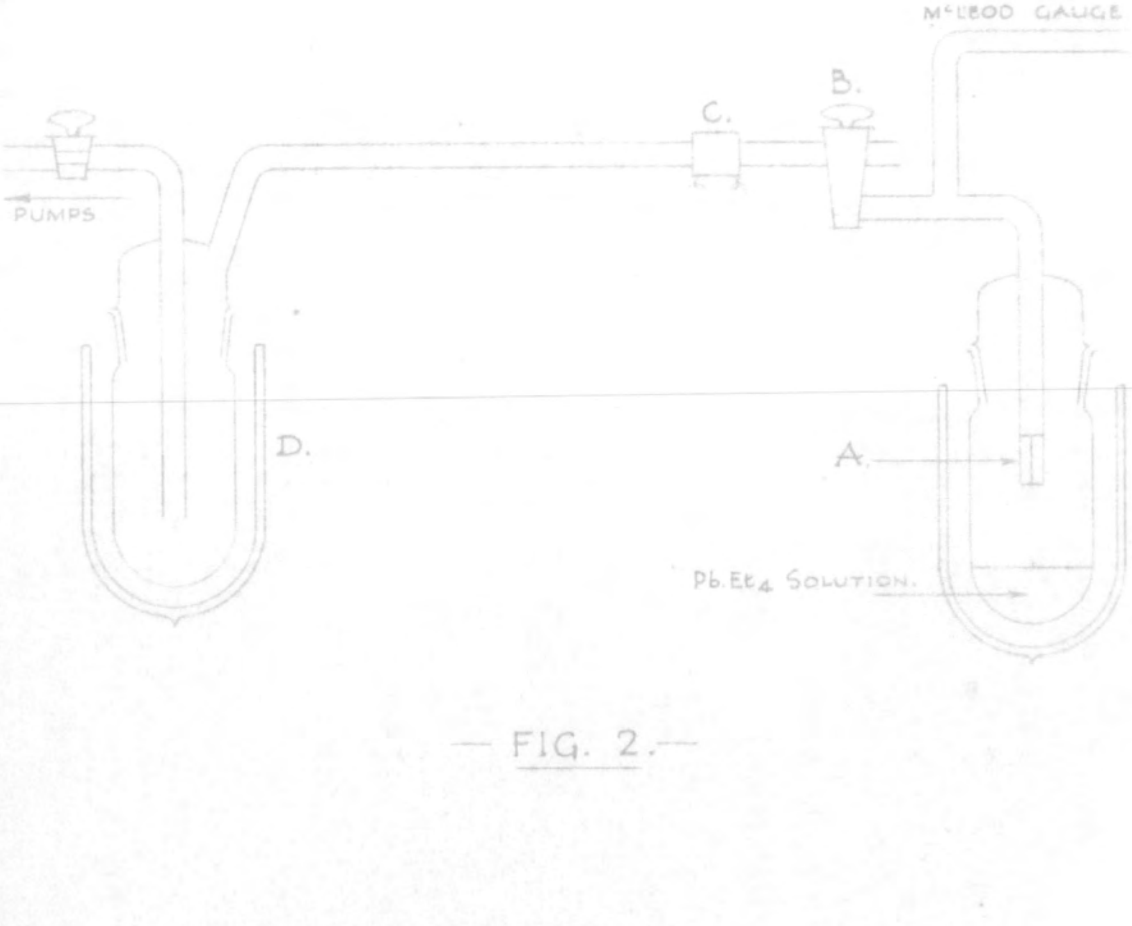
Radioactive isotopes suitable for use in free radical studies.

Isotope	Radiation	Half-life	Radiation Energy Mev		Produced by
			β rays	γ rays	
^{14}C	β^-.	10^3y.	0.145	no	C-d-p N-n-p
^{22}Na	β^+, γ.	3.0y.	0.58	1.3	Mg-d-α F-α-n Ne-d-n
^{24}Na	β^-, γ.	14.8h.	1.4	2.8	Na-d-p Na-n-γ Mg-n-p Al-n-α Mg-d-α
^{42}K	β^-.	12.4h.	3.5		K-d-p K-n-γ Ca-n-p Sc-n-α
^{65}Zn	γ.	250d.		1.14	Zn-d-p Cu-d-2n Cu-p-n
^{74}As	β^-, γ.	16d.	1.3	0.582	As-n-2n Ge-d-n Se-d-α Ge-p-n
^{82}Br	β^-, γ.	34h.	0.465	1.35	Br-n-γ Br-d-p Se-p-n Se-d-2n Rb-n-α
^{115}Cd	β^-, γ.	2.5d.	1.11	0.55	Zn-n-γ Cd-d-p Cd-n-γ Cd-n-2n U-n

Table 1. (cont'd)

Isotope	Radiation	Half-life	Radiation Energy Mev β rays	 γ rays	Produced by
^{124}Sb	β^-, γ.	60d.	1.53	1.82	Sb-d-p Sb-n-γ I-n-γ
^{131}I	β^-, γ.	8.0d.	0.687	0.4	^{131}Te β^- decay (from U-n)
^{210}RaE	β^-.	5.0d.	1.17		RaD β^- decay
^{212}ThC in equilib. with ^{212}ThB	β^-.	10.6h.	2.2		ThA α decay

CHAPTER TWO.



— FIG. 2. —

CHAPTER TWO

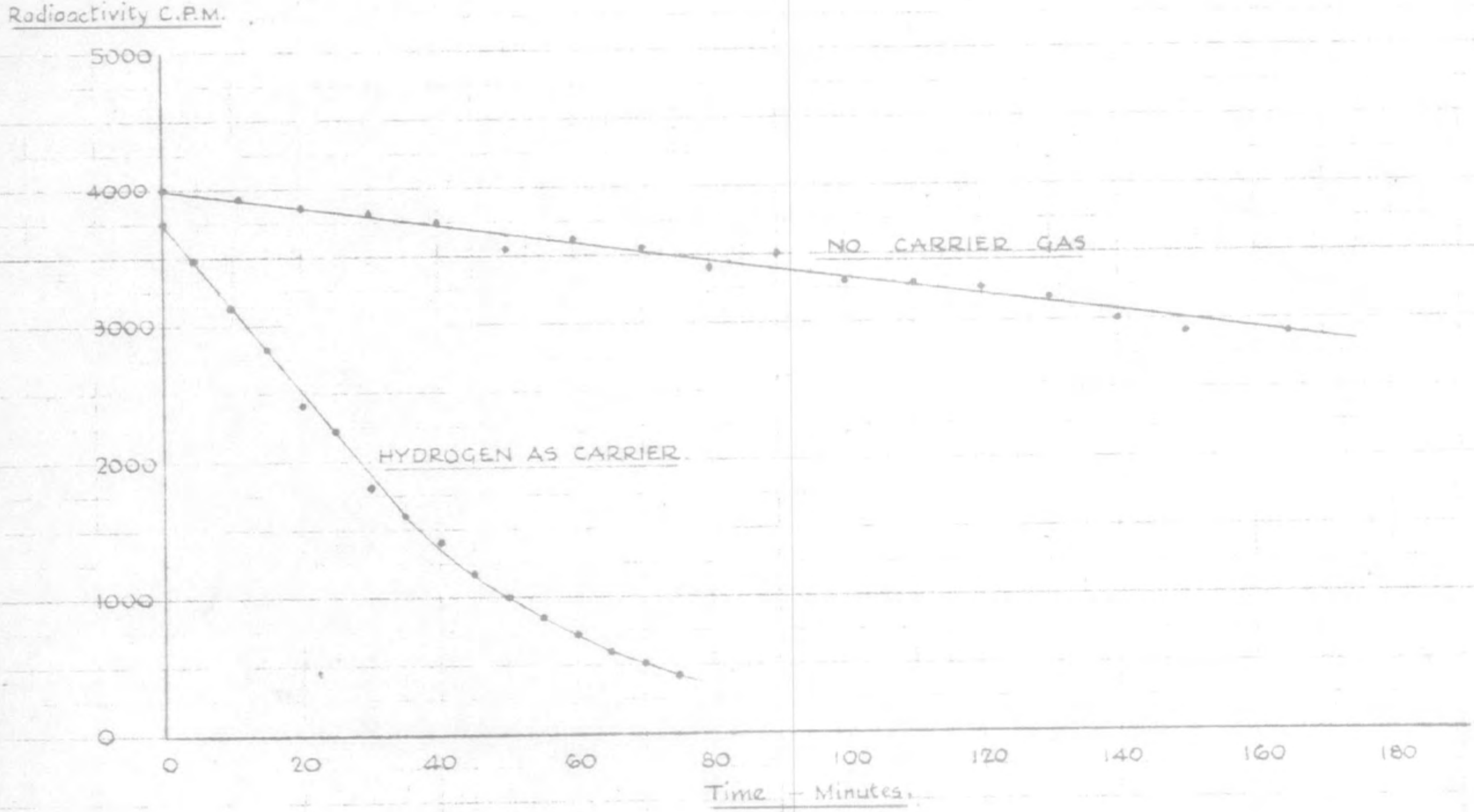
PRELIMINARY WORK.

1. Experiments with non-radioactive mirrors.

In order to achieve familiarity with the technique for dealing with free radicals some of the classical lead mirror experiments were repeated. It was decided to use acetone vapour as a carrier, as described by Rice (70), because the apparatus required is simpler than that used by Paneth. Also, since the acetone is frozen out by liquid air after traversing the reaction tube, it is not necessary to use such a high pumping speed as when a permanent gas like hydrogen is used.

The apparatus took the form shown in Fig. 2. The size of capillary tubing, A, required to obtain a suitable flow rate was determined by experiment. B is a two-way tap, one limb of which was open to the atmosphere, and provided a convenient means of letting air into the apparatus. C is an annular electric furnace which could be moved along the tube at will. A thermocouple was used to measure the temperature of the furnace. The reaction tube was made of 'Pyrex' glass since quartz tubing was unobtainable.

—FIG. 3.—


Radioactivity C.P.M.
5000
4000
3000
2000
1000
0
0
20
40
60
80
100
120
140
160
180
Time – Minutes.
NO CARRIER GAS
HYDROGEN AS CARRIER

A 1% solution of lead tetraethyl was made up with AR acetone and free radicals were obtained by thermal decomposition of the lead tetraethyl at about 500°C. Some considerable time was spent in becoming familiar with the technique required. It was clear that the very slightest leak in the apparatus would prevent the removal of a lead mirror by free ethyl radicals; but even when leaks were absent, erratic results were obtained.

Acetone as a carrier was finally abandoned, and the experiment was then tried without using a carrier gas -- simply by sucking over the vapour of lead tetraethyl at room temperature. Consistent results were obtained by this method, but the time required to remove thick mirrors was inconveniently long -- one experiment requiring more than a day for completion. Raising the temperature of the lead tetraethyl bath to as much as 50° and removing capillary restrictions did not increase the concentration of radicals appreciably. But the rate of mirror removal was increased nine or ten fold when hydrogen was used as a carrier, and this method was finally adopted. See Fig. 3 for comparative rates of removal, with and without carrier gas.

2. Experiments with ThB.

A. Method.

Antimony was chosen as the indicator to be used in experiments with radioactive mirrors because it is readily attacked by free radicals, and its isotope ^{124}Sb has a hard gamma activity with the convenient half-life of 60 days. Whilst some powdered metallic antimony was being irradiated in the uranium pile at the Atomic Energy Research Establishment, Harwell (irradiation period 3 months), some experiments were tried using ThB.

ThB has a half-life of 10.6 hours, and though its beta emmission is soft, its decay product ThC (an isotope of bismuth T = 60.5m.), emits beta particles which can be used for measurement if sufficient time is allowed for ThC and ThB to come to equilibrium. There was a solution of radiothorium available and it was decided to separate ThB by electrolysis, depositing it anodically as the dioxide. If a suitable electrode is employed, it can be detached from the electrolytic cell and introduced into the free radical apparatus where the oxide can be reduced to metal in a stream of hydrogen and subsequently deposited on the walls of the reaction tube in the form of a mirror. Inactive lead was added to the solution for electrolysis so that the final deposit in the reaction tube should be a visible mirror. This was to avoid possible complications due to the attachment of an invisible metallic film to the surface of the tube.

B. Apparatus.

Three drops of a solution of radiothorium and its decay products, to which approximately 4 mg. of inactive lead had been added, were acidified with 5 cc. 2N nitric acid and electrolysed at 0.5 amp. for 15 minutes in a special cell. This cell was made from a boiling tube to which had been fused a side-arm fitted with a B14 socket. A Pt wire to which was attached a sheet Pt cathode was fused through the side of the boiling tube. The anode consisted of a spiral of platinum wire the ends of which were sealed through the closed end of a B14 cone. The electrolyte was stirred rapidly. At the end of electrolysis, the anode was washed with distilled water, dried by alcohol and ether, and then transferred to the main apparatus, where it was plugged into a socket in the reaction tube after greasing. The apparatus used was similar to that shown in Fig. 2 with the addition of a side-arm on the reaction tube connected to a charcoal trap which could be cooled in liquid air. Tank hydrogen was passed through this trap (to remove oxygen) and into the apparatus.

The apparatus was evacuated, and a stream of hydrogen passed over the platinum spiral carrying the mixture of $ThBO_2$ and PbO_2 whilst a current was passed through it sufficient to heat it to a dull red colour. After about 15 minutes it was assumed that the reduction was complete. Then the current was increased until the spiral glowed brightly, and the mixture of ThB and Pb was deposited on the wall of the reaction tube which was cooled with wet cotton wool. The apparatus was then filled with hydrogen to atmospheric pressure, to minimise the risk of atmospheric oxidation, whilst the anode was withdrawn and substituted by a plain closed cone. The apparatus was then evacuated once more. It was found possible to move the mirror only a short distance along the tube in a stream of hydrogen because of the readiness with which it "burnt" into the glass. A Geiger-Muller tube was placed over the reaction tube opposite the mirror, and lead blocks were built up around it to screen it from external radiation as much as possible.

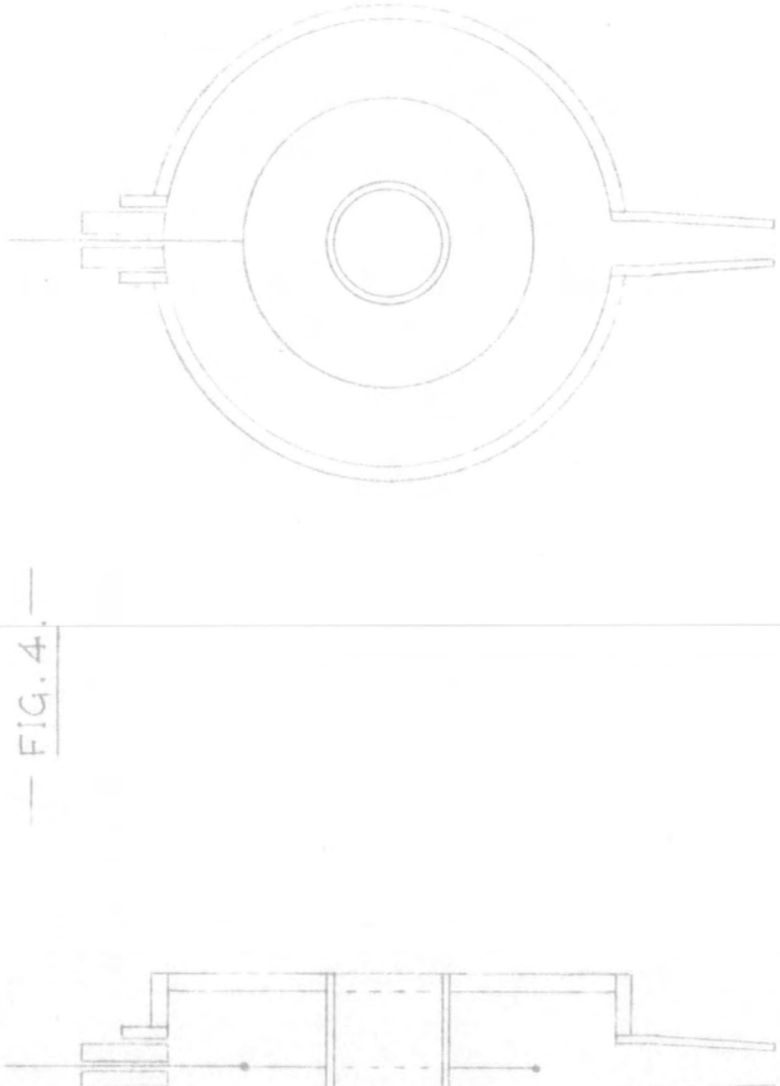


FIG. 4.

C. Results.

In one experiment the activity of the mirror was reduced from 1150 cpm. to 900 cpm. in 45 min. Without the action of free radicals, the activity would have decayed to 1095 cpm. in this period.

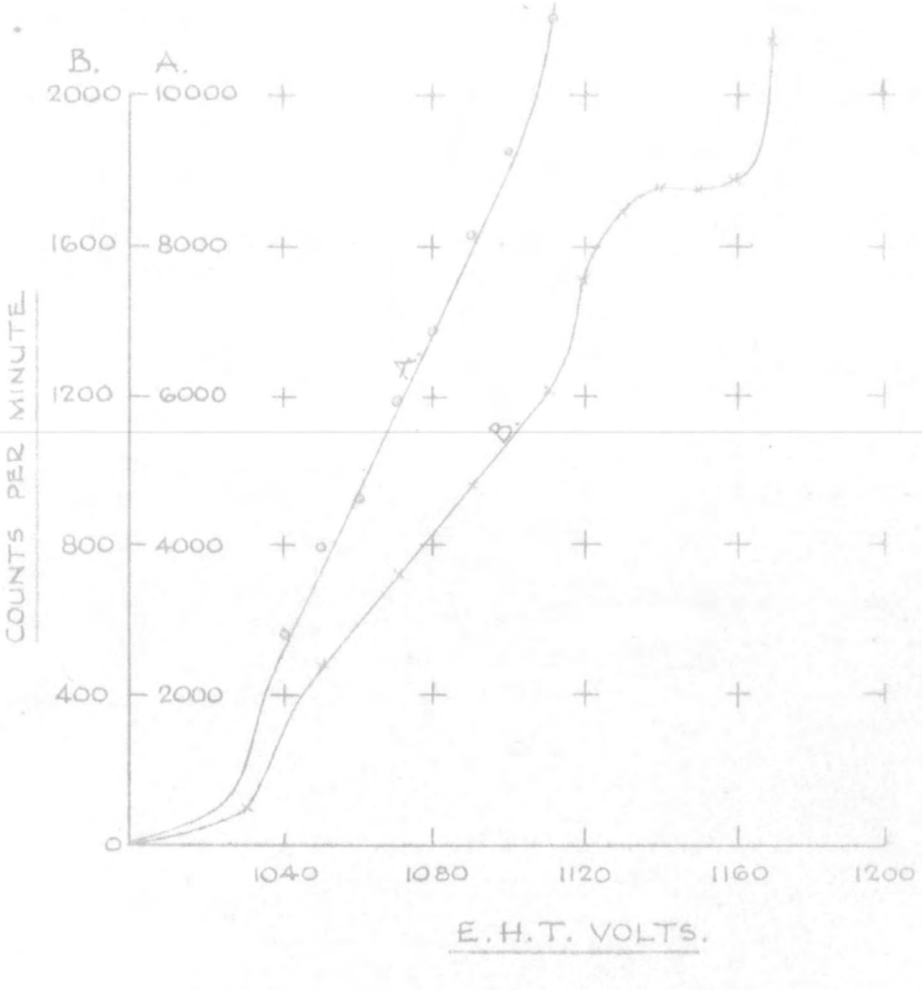
The experiments with ThB were not satisfactory and were not pursued when radioactive antimony became available. The poor results obtained were undoubtedly due in great measure to using acetone as a carrier.

3. Modification of the Geiger-Muller tube for use in the mirror method.

A special counter was designed for use with radioactive mirrors. Its form may be seen in Fig. 4. The body was made of polished brass and the annular window was of thin copper tubing. The central tungsten electrode was brought out through a piece of glass capillary tubing. Joints were made either with solder or wax.

In use, the counter would be mounted on the reaction tube which would pass through the annulus. The window would then cover the whole circumference of the mirror, and a larger count should be obtained with a given mirror than with the normal end-window

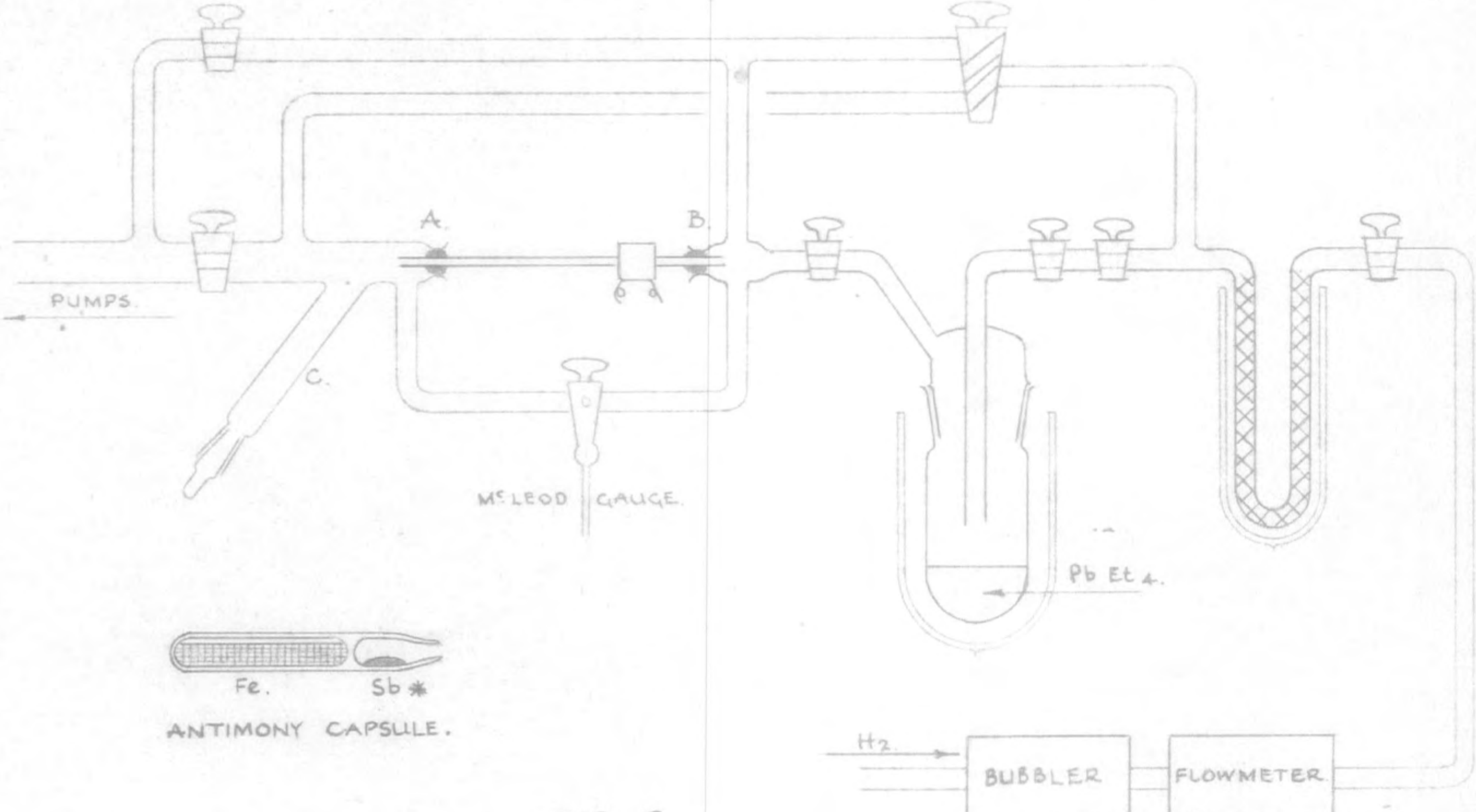
—FIG. 5.—


B.
A.
2000
10000
1600
8000
1200
6000
800
4000
400
2000
0
COUNTS PER MINUTE
1040
1080
1120
1160
1200
E.H.T. VOLTS.
A.
B.

type of counter. Fig. 5 shows the characteristics obtained with two sources of different strength and a filling of 9 cm. argon and 1 cm. alcohol. The background count was 170 per min. at 1150 volts.

This counter was not developed when it became apparent that an end-window counter was adequate for the experiments in hand.

CHAPTER THREE.


A.
B.
PUMPS.
C.
M^c LEOD GAUGE.
Pb Et 4.
Fe.
Sb *
ANTIMONY CAPSULE.
H2.
BUBBLER
FLOWMETER.

— FIG. 6. —

CHAPTER THREE

EXPERIMENTS WITH RADIOACTIVE ANTIMONY.

1. Apparatus.

The final form of apparatus used with radioactive mirrors is shown in Fig. 6. It was so arranged that hydrogen could be passed either way along the reaction tube thus facilitating the handling of mirrors. Tank hydrogen, the flow of which was regulated by a fine control needle-valve (as described by Alcock, Peiser and Pont (1)) passed through a sulphuric acid bubbler into a flowmeter which had been previously calibrated. The calibration was carried out by passing hydrogen through the flowmeter and then into a horizontal tube which had a side-arm so arranged that a small pellet of mercury, sufficient to block the tube, could be introduced into it and carried down by the hydrogen to sweep out a measured volume. The time intervals for this volume to be swept out at different pressures on the manometer were recorded. Butyl phthalate was used as the manometric fluid.

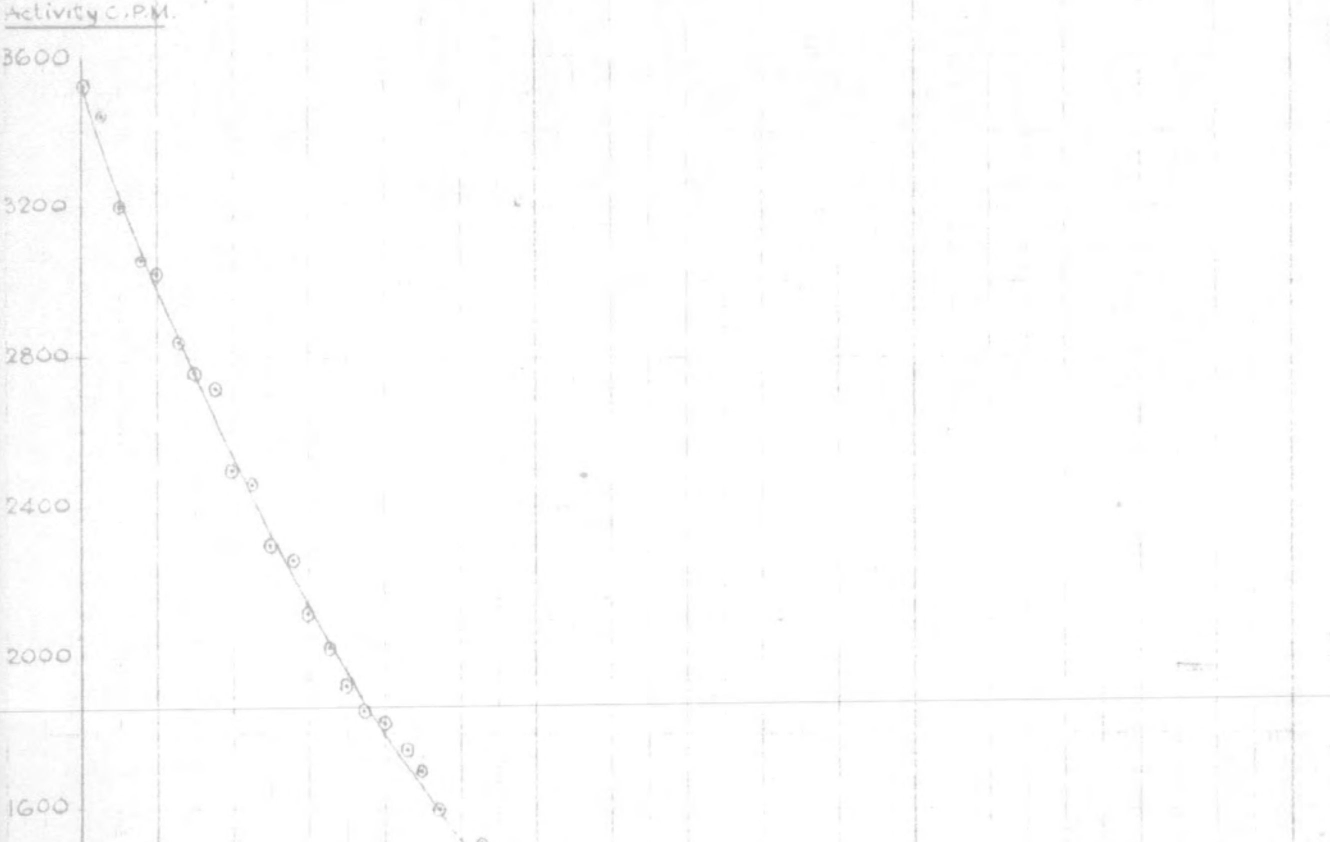
The hydrogen was purified by passing through a charcoal trap immersed in liquid oxygen or nitrogen. This trap was first baked out at about 300° under vacuum for an hour and then cooled and allowed to adsorb hydrogen to atmospheric pressure. At the conclusion of an experiment, this trap was evacuated and left under vacuum until the start of a new experiment. Baking out was only repeated when air had been admitted to the trap. The flowmeter was fitted with a by-pass tap to allow rapid filling of the charcoal trap. The gas was drawn off into the apparatus as required through a leak-tap (i.e. an ordinary vacuum tap having a shallow V filed round the central periphery of the key so that a fine flow-control could be obtained). A second tap used as an On-Off control was placed in series with the leak-tap so that the latter could be left set in the same position for a number of experiments.

A mixture of acetone and solid carbon dioxide was used to cool the lead tetraethyl resevoir. The silica reaction tube was joined to the rest of the apparatus by means of picein wax. A McLeod gauge could be connected through a two-way tap to either end of the reaction tube which enabled the pressure gradient across the tube to be measured. Radioactive material contained in a small 'Pyrex' capsule could be brought into the reaction tube from the horizontal side-tube C (shewn vertical in Fig. 6 for the sake of clarity) as required by means of a magnet. By cautious heating of the silica tube it was possible to distil some of the metal out of the capsule onto the wall of the reaction tube. The capsule was then withdrawn into the side-tube and the mirror manipulated in a stream of hydrogen in the usual way.

Long mirrors were obtained by heating a heavy deposit of metal in a very rapid stream of hydrogen. Very thick mirrors were liable to be stripped off as foil by the gas stream. Oxidation of the mirror became apparent as a white bloom over the bright metallic surface. A Geiger-Muller tube on a suitable platform was placed over the reaction tube opposite the mirror. Interlocking lead blocks were arranged on an iron platform to form a protective 'castle' round the mirror and counter to cut down the background count as much as possible.

The pumping system consisted of a two-stage mercury vapour diffusion pump (Edwards Type 7) backed by a rotary oil pump (Edwards Speedivac Type 1A) and was capable of producing streaming velocities up to 80 m./sec.

— FIG. 7. —


Activity C.P.M.
3600
3200
2800
2400
2000
1600
1200
800
400
0
0
40
80
120
160
200
240
280
320
Time – Minutes.

in tubing 5 mm. in diameter.

Standard counting equipment of the type made for the A.E.R.E. was used.

2. The effect of varying the length of the mirror - The Paneth - Hertzfeld calculations.

Experiments showed that the decrease in radioactivity of the mirror was a linear function of time only with long mirrors. With mirrors less than about 1 cm. in length the decrease in activity per unit time was not constant -- see Fig. 7. This was a direct qualitative demonstration of the effect treated mathematically by Paneth and Hertzfeld (58). These authors found that a lead guard mirror 10 mm. wide completely eliminated the radicals when the velocity of the gas stream was 25 m/sec., whilst on reducing the width of the mirror to about 5 mm., a second so-called "proof mirror" was quite distinctly attacked.

The following is extracted from their paper.

"The following questions arise from these facts:-

1). What must be the theoretically calculated width of a completely efficient guard mirror, assuming that every collision of the radical with the metallic mirror results in chemical combination ?

2). What fraction of the radicals disappears by collision with the glass wall of the tube ?

Without any calculation our experiments show that this last portion must be very small, for it follows from the efficiency of the guard mirror that every radical on moving through a distance of 1 cm. collides at least once with the wall and yet in the absence of metallic mirrors is present in appreciable concentration even at a distance of 40 cm. from the source. A more precise answer to these two questions can be given only when we obtain by theoretical physical calculations the fraction of radicals which collide with the walls of the tube, and when we know which explanation for the sticking of the radicals to the walls of the tube agrees with the experimental conditions."

The deduction of the requisite formulae is then described. "These formulae enable us to answer the two questions mentioned above. First we will discuss the efficiency of the guard mirror and calculate what fraction of the radicals is still present after having passed over a mirror 1 cm. wide.

N = Loschmidt Number

C = concentration.

D = diffusion coefficient in $cm^2 sec^{-1}$ of the radical in H_2
(for ethyl radicals, $D_{normal} = 0.5$)

Ro = radius of the tube.

x = length of tube along its axis.

Vo = velocity of the gas stream in the direction of the x axis.

$\beta = \frac{VoRo}{2D}$.

λ = the first root of the zero order Bessel function = 2.40 .

Z = number of particles colliding with 1 cm^2 of wall per sec.

α = fraction of the radicals colliding with the wall which disappear.

In the case of ethyl the calculation is made assuming $\alpha = 1$.

Neglecting the higher order terms,

$$Z = 2NCo \frac{D}{Ro} e^{(\beta - \sqrt{\beta^2 + \lambda^2}) \frac{x}{Ro}}$$

$2\pi RoZdx$ radicals collide with an element of wall of length dx.

We begin measuring from the point $x = 0$, and concentration $C = Co$.

The number of radicals colliding between $x = 0$, and $x = x_1$ is $Zox_1 = n - Zx_1\infty$, where n is the total number of radicals per unit time passing through the cross section at the point x = 0 and

$$Zx_1\infty = 2\pi Ro \int_{x_1}^{\infty} Z(x)dx$$

$$n = NCo\pi Ro^2 Vo$$

in our experiment at 2 mm. pressure, $D = 0.5 \times 380 = 190.$ $Ro = 0.25$, $Vo = 2500$, $\lambda = 2.40$, $\beta = 1.65$;

$$\therefore \frac{\beta - \sqrt{\beta^2+\lambda^2}}{Ro} = -\frac{1.27}{0.25} = -5.04$$

and $$Zx_1\infty = 4\pi DNCo \int_{x_1}^{\infty} e^{-5.04x}dx$$

$$= \frac{2400}{5.04} NCo.10^{-2.2x_1}$$

when $x = 1$

$$Z_{1\infty} \text{ becomes } \frac{2400 \times 6.4 \times 10^{-3}}{5.04} NCo = 3NCo$$

$$n = \pi \times 0.25^2 \times 2500NCo = 490NCo$$

490NCo radicals enter the volume of the tube covered by the mirror at the point $x = 0$ whilst only 3NCo radicals exist at the point $x = 1$. 99.4% of the radicals combine with the mirror when it is 1 cm. wide. When the width of the mirror is reduced to only 0.5 cm. we have

$$Z_{0.5\infty} = \frac{2400}{5.04} \text{NCo} \times 10^{-1.1}$$

$$= \frac{2400 \times 8 \times 10^{-2}}{5.04} \text{NCo} = 38\text{Nco}$$

Of the 490NCo radicals entering, now no more than 452NCo or 92% are combined and 8% pass the guard mirror. These theoretical results are in excellent agreement with the experimental data. As mentioned above, a guard mirror of 1 cm. width is so efficient that practically no free radicals can be detected behind it, whilst on reducing the mirror width by one half a remarkable proportion passes it. From this we may conclude that the assumption $\alpha = 1$ in the calculation is very near to the actual facts and that practically every radical colliding with the metal mirror combines at the first impact. As the formation of volatile lead tetraethyl requires four radicals, this reaction might probably first result in combination of the radical with the surface of the metal; and only when four ethyl groups meet at one and the same lead atom -- an event which is doubtless favoured by the migration of ethyl groups on the lead surface -- is the volatile lead tetraethyl formed. This leads to the disappearance of the mirror due to the action of free radicals which is one of the fundamental facts of our experiments.

The second question, what fraction of the radicals disappears by collision with the glass walls of the tube -- this fraction is called "Haftkoeffizient" (accommodation coefficient) -- may be answered by making the appropriate substitutions in the expression for α when we obtain

$$\alpha = \frac{D.k}{2V_1.Vo} \left(\frac{VoRo}{D} + \frac{kRo}{Vo}\right)$$

$$V_1 = \frac{\text{mean velocity of radicals}}{4} = \sqrt{\frac{RT.}{2\pi M}}$$

For small values of Ro the calculation shows that the second term in brackets may be neglected yielding the following simple formula for α

$$\alpha \doteq \frac{kRo}{2V_1}$$

which no longer contains the velocity of the gas or the diffusion constant. Therefore α ought to be nearly independent of the nature of the transport gas if this gas does not influence k -- for instance by adsorption on the glass wall. Calculation of α shows that its magnitude is always of the order of 10^{-3} so that only about 1% of the colliding radicals are not reflected."

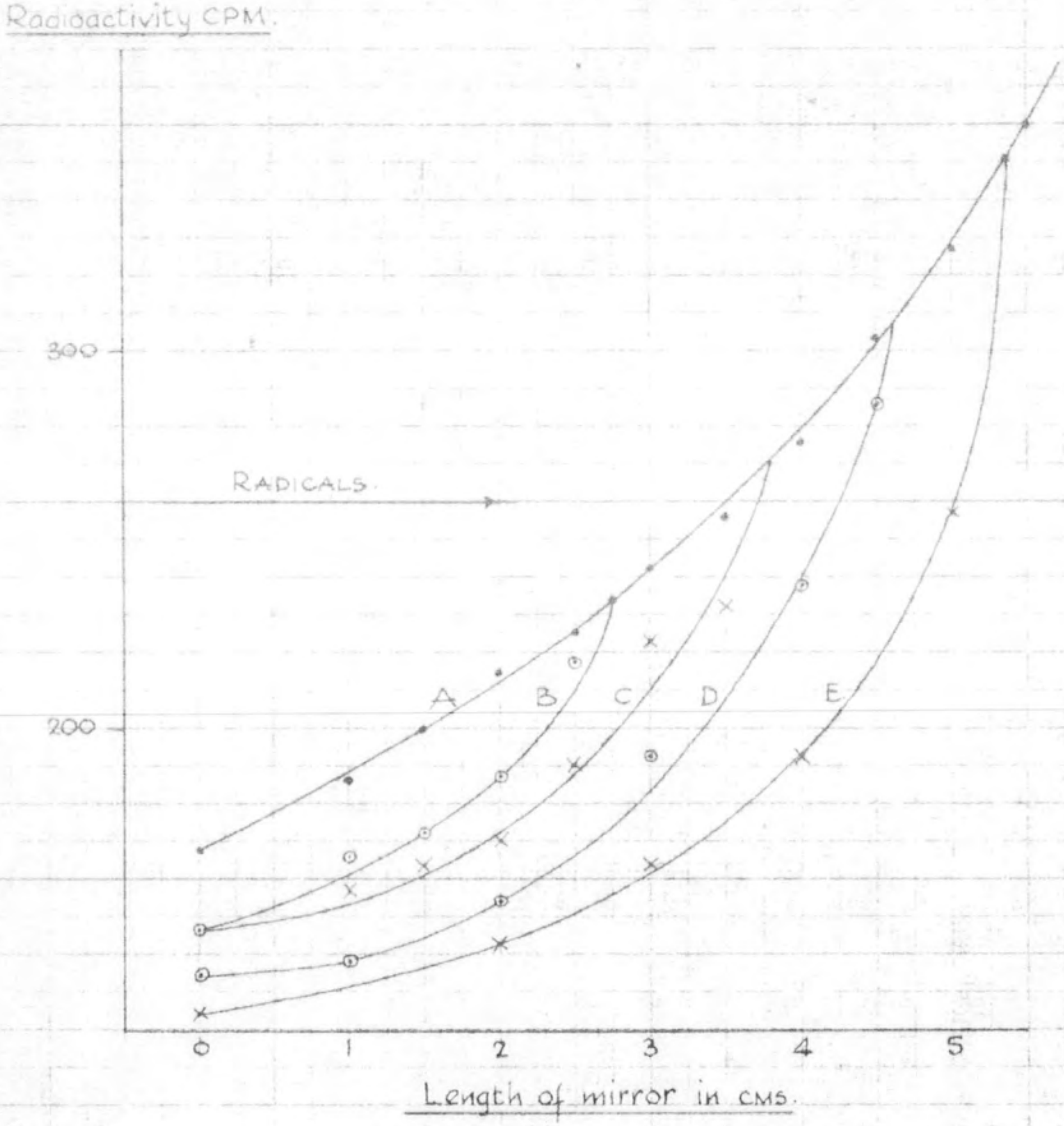
3. The "slit method" for direct experimental verification of the Paneth - Hertzfeld calculations.

Using radioactive mirrors it should be possible to verify these theoretical deductions by more-direct experiments than those employed by Paneth and Hertzfeld. For if the distribution of the radioactivity of the mirror along its length can be measured, then the extent of change in this distribution due to the action of free radicals gives immediately the length of mirror necessary to reduce the concentration of free radicals to zero.

The measurement of the distribution of radioactivity of mirrors along their length was accomplished by mounting the Geiger-Muller tube on a block of lead 1 cm. thick which had a narrow slit cut through it opposite the window of the Geiger-Muller tube and which was also grooved to fit and slide along the reaction tube. With this arrangement the distribution of radioactivity could be quite easily measured by taking counts at intervals along the reaction tube. This procedure will be referred to as "taking a sectional count".

The method was to deposit a long mirror on the

— FIG. 8. —



A = Activity at start of experiment.

B = " after removal of 1 C.M. of mirror

C = " " " 2 " " "

D = " " " 3 " " "

E = " " " 3·75 " " "

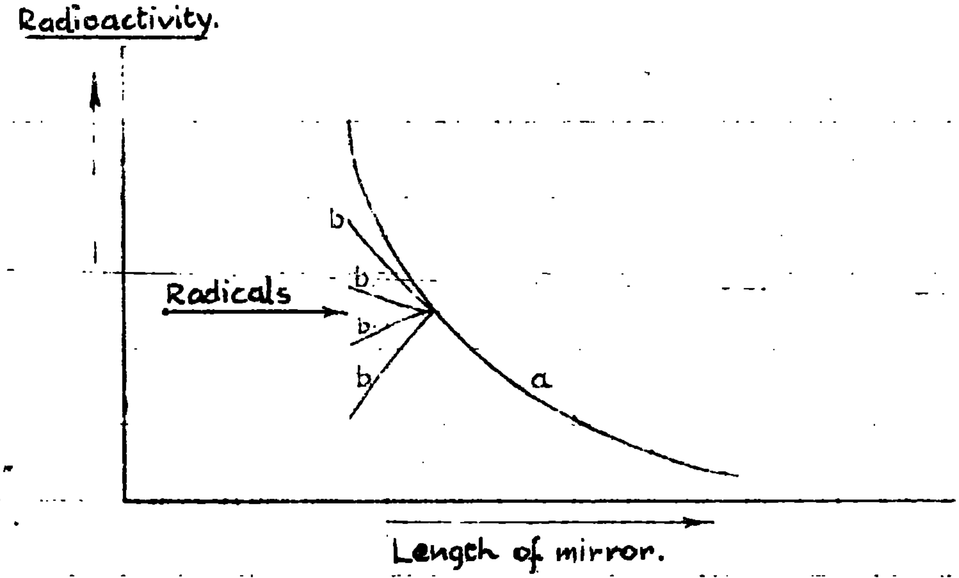
reaction tube and then to take sectional counts before and after free radicals had been passed over it. Then, by plotting the activities obtained from the sectional counts against the corresponding distances along the mirror, it was hoped that a sufficiently accurate estimate of the extent of the attack could be obtained.

4. Results.

The results of a typical experiment are shown in Fig. 8. The limit of attack by the radicals is easily seen. But the distance between source and mirror was not constant, since part of the mirror was removed with each run. It will be noticed that some radioactivity apparently remained at the original leading edge of the mirror even after the mirror had been removed from the immediate vicinity. This was due to gamma radiation from the more distant parts of the mirror penetrating the counter platform.

In the next series of experiments, the mirror was deposited with its thick end nearer the source of free radicals. In this case the thickness of the mirror would be reduced with succeeding periods of attack, but the mirror would not be completely removed for some distance as formerly. The results should then appear

— FIG. 9. —



"a" LINE DENOTES ORIGINAL ACTIVITY.

"b" LINES DENOTE ACTIVITY AFTER SUCCESSIVE ATTACKS BY FREE RADICALS.

as in Fig. 9, with the lines representing successive changes in radioactivity converging to one point, provided the conditions remain constant. These experiments were, however, inconclusive.

5. Discussion.

As a tracer, the antimony used suffers from two disadvantages as far as this slit method is concerned :-

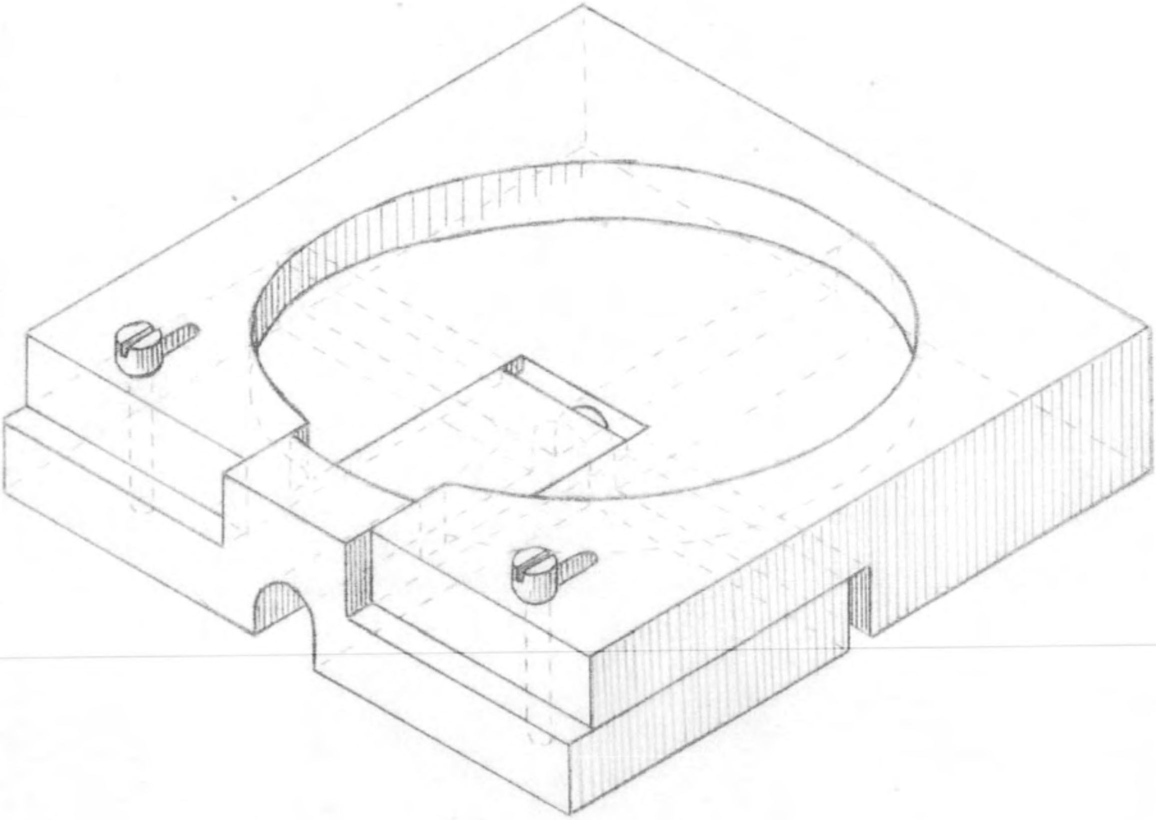
1. Low specific radioactivity.
2. It emits both beta particles and gamma rays.

Its low specific activity made sectional counting a slow procedure if the statistical error was to be kept sufficiently low. The emission of gamma rays in addition to beta particles meant that only a diffuse picture of the distribution of the activity was obtained, since the Geiger-Muller tube was exposed to gamma radiation passing through the body of the counter platform as well as that which passed through the slit.

In an attempt to overcome this second disadvantage two counts were recorded for each interval along the mirror. The first as formerly, the second with a thin sheet of lead interposed between the Geiger-Muller tube window and the slit of the counter platform. The difference between these two counts gave the count due to the beta particles which passed through the slit aperture. In practice however, it was found that this difference was too small -- 50 cpm. was the highest recorded.

It was clear that for the method to succeed, the tracer used must emit beta particles only. Radium E, an isotope of bismuth, fulfils this condition and some spent radon tubes were obtained so that this indicator might be used.

CHAPTER FOUR.



— FIG. 10. —

CHAPTER FOUR

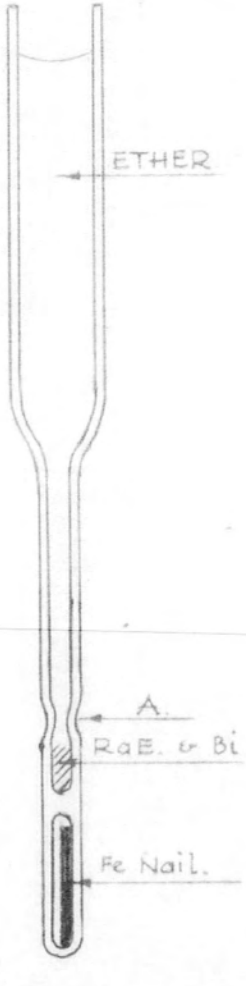
EXPERIMENTS WITH RADIUM E.

1. Final form of "slit".

In its final form, the slit used for taking sectional counts consisted of a block of lead 6x6x1 cm. made in two parts adapted to slide into each other, and held together by two fixing screws to make an adjustable slit at the centre of the block. The block was grooved on the under side to fit and slide along the reaction tube. The Geiger-Muller tube was seated in a well cut in the top surface of the block. The sliding surfaces and the faces constituting the adjustable aperture were milled flat (see Fig. 10).

2. Extraction of radium D. and E from spent radon tubes.

The crushed tubes were heated to 400° for a quarter of an hour to drive off mercury, and were then digested with aqua regia and the solution filtered off from glass and charcoal. 1 mg. each of lead and bismuth was added and precipitated as hydroxide with ammonia. After washing, the precipitate was taken up in dilute acetic acid. Precipitation with hydrogen sulphide followed.



— FIG. 11. —

After washing, the precipitate was taken up in 3N nitric acid and this stock solution of radium D with radium E was divided into equal volumes of convenient radioactive strength.

3. Mirror material obtained by chemical precipitation.
Radium E was separated from the radium D stock solution after the addition of about .1 mg of bismuth by treatment with sodium dihydrogen phosphate solution. This precipitated the radium E and bismuth phosphates but left lead and radium D in solution. The radium E-bismuth phosphate was then dissolved in normal hydrochloric acid and reduced with sodium hydrosulphite solution, when the metal in finely divided form was precipitated. This precipitate was washed and centrifuged, and finally dried with acetone and ether and then transferred by micro-pipette to specially made micro-centrifuge tubes. The radium E-bismuth was centrifuged to the bottom of the tube which was cut at A (Fig. 11) after the excess solvent had been removed by micro-pipette. The capsule was then transferred to the free radical apparatus for manipulation in the usual way.

It was found that

a) on evacuation of the apparatus, the precipitate of radium E-bismuth (being damp and so coherent) lost the attached solvent violently with the result that the mixture was shot out of the capsule into the apparatus and lost:

or

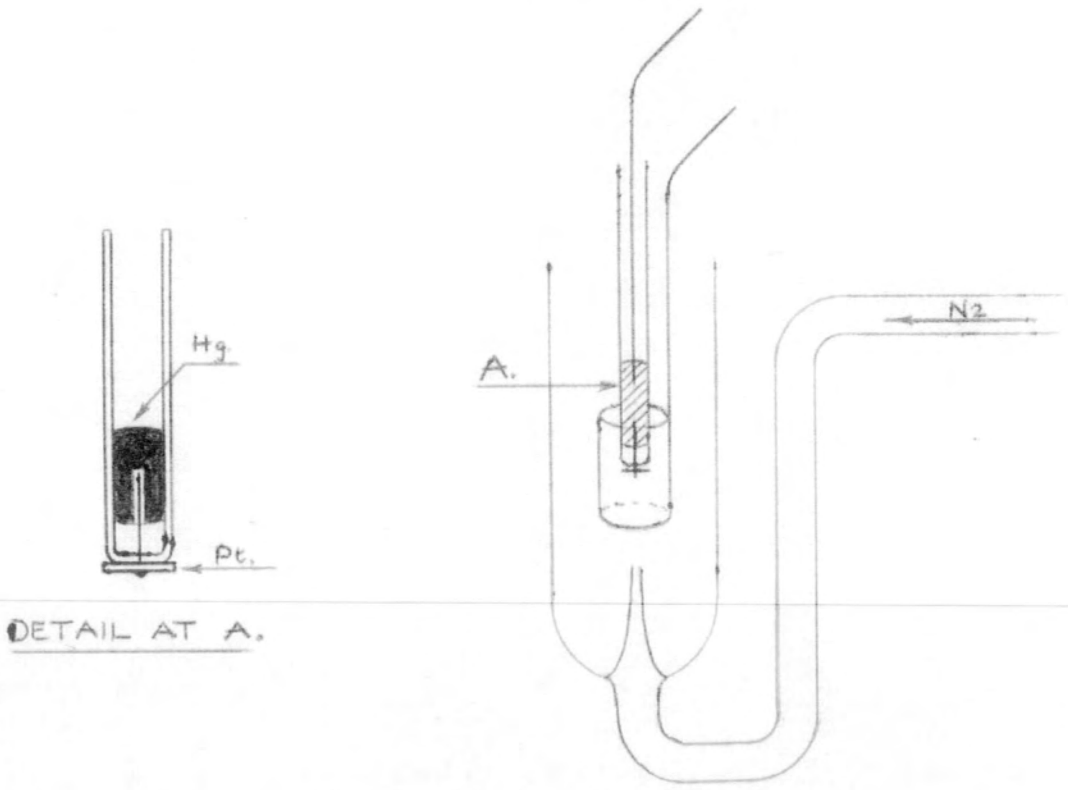
b) that should evacuation be accomplished without mishap, it was more than likely that the radium E-bismuth in dry powder form would be spilt and lost when the capsule was moved by the magnet into the reaction tube.

So the chance of obtaining a radioactive mirror by this method was small. Furthermore, the mirror obtained seemed to be heterogeneous, the thin part being brightly metallic whereas the thicker part was a greyish colour with a sharp line of demarcation between the two. It was not possible to improve this by prolonged distillation in hydrogen. There was some contamination of the radium E-bismuth precipitate by sulphur, but no improvement in the appearance of the mirror was obtained by extracting the sulphur with carbon disulphide, so another method of reduction was tried.

In this method the phosphate was dissolved in hydrochloric acid and then the hydroxide was precipitated with caustic soda and redissolved in excess caustic soda and glycerine. Solid dextrose was added to the solution which was then heated on the boiling water bath. Finely divided radioactive bismuth was precipitated and was washed, dried and transferred to the apparatus as previously described. But this metal did not give a homogeneous mirror either.

4. Mirror material obtained by electrolysis.

The problem was finally solved by electrolytic deposition of the metal onto a cathode of special design. This cathode was then transferred to the free radical apparatus where the metal was "flashed off" by induction heating. This method enabled a homogeneous mirror to be obtained without the risk of losing the radioactive material in the process. A platinum wire to which was welded a platinum disc, was sealed through the end of a 'Pyrex' tube 4 mm. in diameter. Mercury placed in the tube enabled an electrical connection to be made to the disc. To the solution of radium D (containing about 0.5 mg. lead as holdback carrier) was added about 1.5 mg. of bismuth in solution as nitrate, 0.5 cc. concentrated nitric acid, two drops of 50% hydrazine hydrate solution and distilled water to make



— FIG. 12. —

up to 10 cc.

The mixture was electrolysed between platinum electrodes at 0.8 volts potential difference, with nitrogen stirring between 60-70° in the apparatus shown in Fig. 12 until electrolysis was almost complete (45-60 min. depending on the average current). The current was found to drop from an initial value of about 1.2 ma. to about 0.3 ma. Two minutes before the end of electrolysis the potential difference between anode and cathode was raised to 0.9 volt. The cathode was then removed, washed well with water and dried with alcohol. After the mercury had been emptied and an iron nail sealed in its place the electrode was transferred to the free radical apparatus. The apparatus was evacuated and the radioactive metal was "flashed off" the platinum disc onto the reaction tube by electrical induction heating. The mirror thus formed lost its bright metallic appearance after being distilled in a current of hydrogen, but the greyish-pink mirror which resulted appeared to be homogeneous throughout its length and was very readily attacked by free radicals.

5. Experimental.

The volume of hydrogen passing over the lead tetraethyl was adjusted by means of the leak-tap before starting an experiment to give the desired rate of flow in the reaction tube. The setting of the tap was then left undisturbed until a different flowrate was required, the tap in series being using to admit or shut off the hydrogen supply.

After the metal had been "flashed" onto the reaction tube it was distilled along the tube in a current of hydrogen several times and left finally so that the thick end was nearer the source of radicals. Attempts to obtain a uniform distribution of radioactivity along the length of the mirror were not successful. A millimetre scale was placed under the reaction tube so that the distance moved along the mirror by the slit could be measured. The aperture of the slit was adjusted to 1 mm.

Whilst the electric furnace was attaining a steady temperature the initial sectional count was carried out. Then by turning on the hydrogen supply and opening the lead tetraethyl resevoir tap to the pumps, free radicals were produced in the reaction tube and allowed to attack the mirror for about ten minutes. During this period readings were taken on the flow meter and McLeod gauge. After the supply of radicals had been stopped by closing the taps on either side of the lead tetraethyl resevoir, a further sectional count was taken. The whole process could be repeated three or four times before it was necessary to deposit another mirror.

It was not always possible to reproduce exactly the same flow conditions in each series of experiments even though the setting of the hydrogen leak-tap was left undisturbed.

6. Results.

The lengths of mirror necessary to eliminate free radicals completely from the gas stream are obtained directly from the sectional counts as plotted in Figs. 13 to 18. These figures show sectional counts before and after attack on the mirror by free radicals in each experiment.

The results of calculations on the experimental data using Paneth and Hertzfeld's formulae are shown in Table 2. Included in the table for comparison are the results obtained by direct experiment.

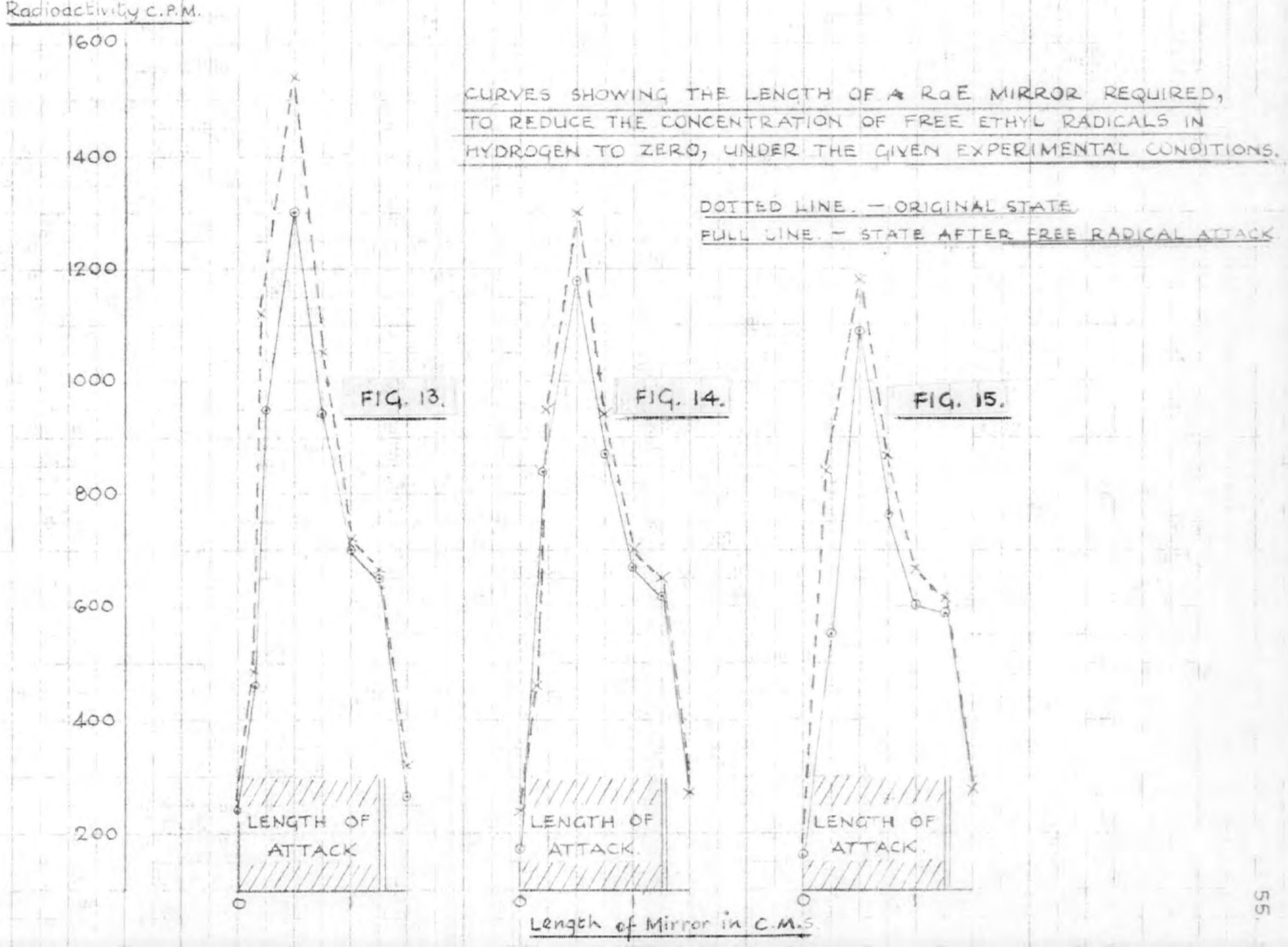


FIG. 13.

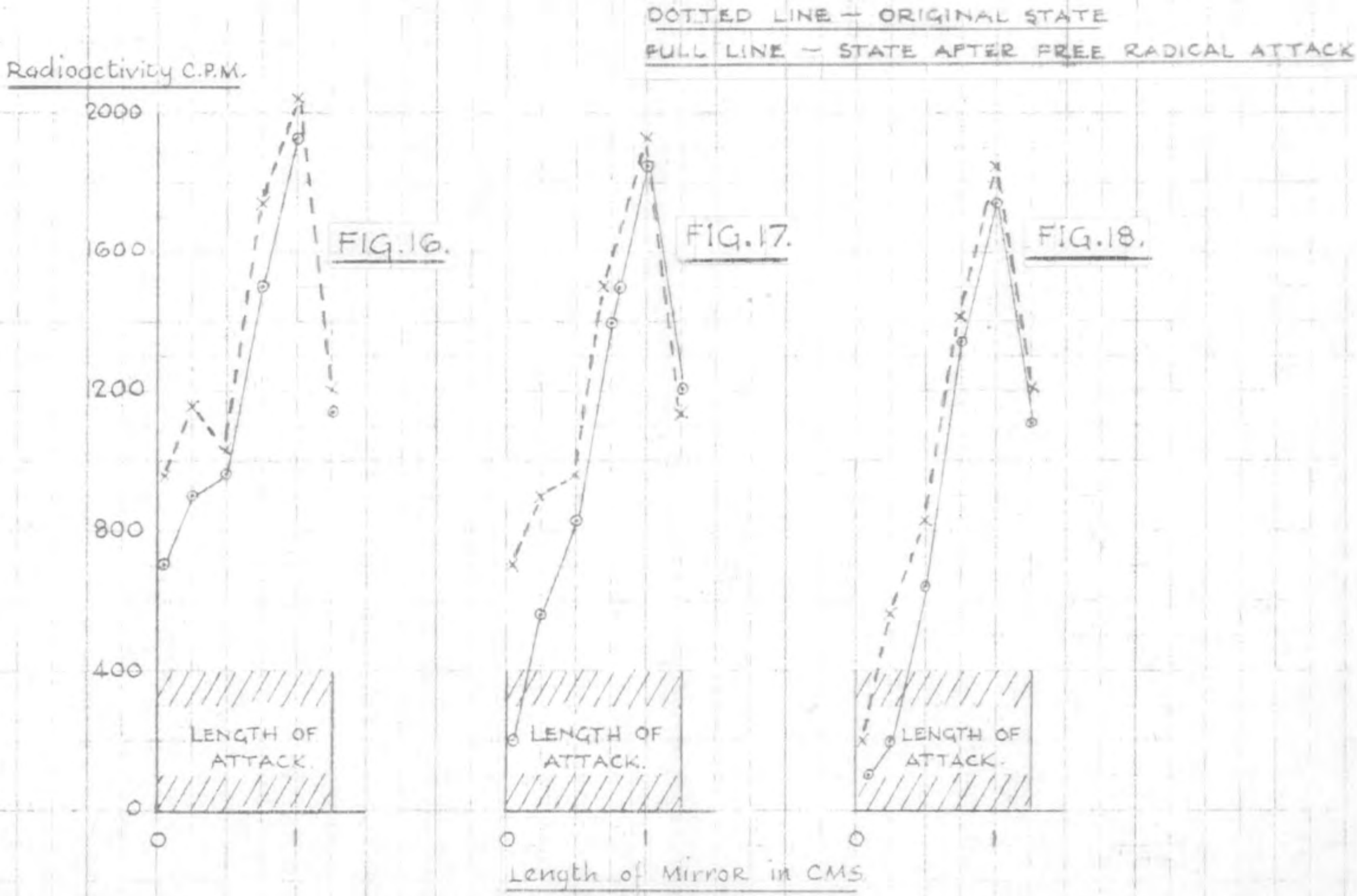
FIG. 14.

FIG. 15.

CURVES SHOWING THE LENGTH OF A RaE MIRROR REQUIRED, TO REDUCE THE CONCENTRATION OF FREE ETHYL RADICALS IN HYDROGEN TO ZERO, UNDER THE GIVEN EXPERIMENTAL CONDITIONS.

DOTTED LINE. — ORIGINAL STATE.
FULL LINE. — STATE AFTER FREE RADICAL ATTACK

CURVES SHOWING THE LENGTH OF A RaE MIRROR REQUIRED, TO REDUCE THE CONCENTRATION OF FREE ETHYL RADICALS IN HYDROGEN TO ZERO, UNDER THE GIVEN EXPERIMENTAL CONDITIONS.



— TABLE. 2. —

Exp.	Pb Et4 °C.	Furnace °C.	Ro c.m.	Vo c.m./sec.	β	$\frac{\beta-\sqrt{\beta^2+\lambda^2}}{R_0}$	$Z_{x,\infty}$	n	A.	B	C
1.	−25	530	0·26	3870	1·09	−5·92	$984\,NC_0\,10^{-2\cdot57x}$	$822\,NC_0$	1·2	0·8	1·0
2	"	"	"	3330	"	"	"	702 "	"	"	1·25
3	"	"	"	3450	"	"	"	733 "	"	"	"
4	"	"	"	"	"	"	"	" "	"	"	"
5	"	420	"	2640	1·36	−5·38	$588\,NC_0\,10^{-2\cdot34x}$	560 "	1·3	0·9	1·3
6	"	490	"	3240	1·22	−5·65	$769\,NC_0\,10^{-2\cdot46x}$	688 "	1·2	0·8	"
7	"	"	"	3960	1·36	−5·38	$792\,NC_0\,10^{-2\cdot34x}$	841 "	1·3	0·9	"
8	−30	530	0·25	3190	1·39	−5·56	$646\,NC_0\,10^{-2\cdot40x}$	626 "	"	"	1·25
9	−31	"	"	"	1·24	−5·84	$693\,NC_0\,10^{-2\cdot54x}$	627 "	1·2	0·8	"
10	−30	"	"	3280	"	"	"	" "	"	"	"
11	"	"	"	6500	1·45	−5·40	$1300\,NC_0\,10^{-2\cdot35x}$	1276 "	1·3	0·9	1·4
12	"	"	"	5700	1·46	−5·44	$1125\,NC_0\,10^{-2\cdot36x}$	1120 "	"	"	"
13.	"	"	"	5100	"	"	$1009\,NC_0\,10^{-2\cdot36x}$	1001 "	"	"	1·3

A. = X in cms. when 0·1% of the radicals pass the mirror.

B. = X " " " 1·0% " " " " " "

C. = Length of the mirror in cms. to stop radicals completely as determined by experiment.

A specimen calculation is given below.

In experiment 1.

At 0.82 mm., $D = \frac{0.5 \times 760}{0.82} = 463.$

$Ro = 0.26$, $Vo = 3870$, $\lambda = 2.40$, $\beta = \frac{Vo.Ro}{2D} = 1.09.$

(Vo is the gas velocity at the centre of the mirror.)

$$\therefore \quad \frac{\beta - \sqrt{\beta^2 + \lambda^2}}{Ro} = -5.92$$

and

$$Zx_1\infty = 4\pi DNCo \int_{x_1}^{\infty} e^{-5.92x}\, dx$$

$$= 984\ NCo \times 10^{-2.57x_1}$$

$$n = \pi Ro^2 VoNCo = 822\ NCo.$$

n is the total number of radicals per second passing through the cross section of the tube at the point $x = 0$, where x is the distance along the mirror.

$Zx_1\infty$ is the number of radicals per second colliding with the wall from the point $x = x_1$ to ∞.

Then for 0.1% of the radicals to pass the mirror

$$Zx_1\infty = 0.001n$$

$$\text{i.e.} \quad 984\ N_{Co} \times 10^{-2.57x_1} = 0.822\ N_{Co}$$

$$x_1 = 1.20.$$

which is the length of the mirror in cm. necessary to reduce the concentration of free radicals by 99.9%.

The agreement between the theoretically calculated lengths of mirror necessary to stop the radicals and those obtained by direct experiment confirms the assumption which Paneth and Hertzfeld made in these calculations, that every collision of a free radical with a metallic mirror results in combination.

In order to obtain values of α for the silica tubing used in these experiments it was necessary to obtain values of the reaction constant. As mentioned earlier (p.10), it is not necessary to use standard mirrors for this purpose when radioactive metals are employed. The rate of removal of the mirror at any point is proportional to the concentration of free radicals at that point provided the proportion of radioactive to inactive material in each mirror remains unaltered. All that is necessary is to record the decrease in radioactivity of the mirror over a suitable period of time at different distances from the source.

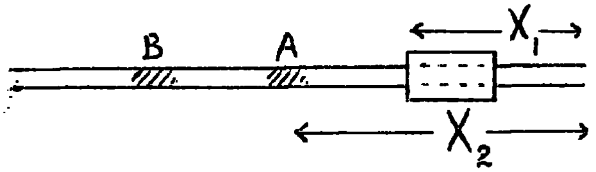
TABLE 3.

Exp.	Ro	$PbEt_4$ temp.	Vo cm/sec	k	Half-life x 10^3sec.	α x 10^3
1.	0.26 cm	-25°	2120	233	3.0	2.6
2.	0.25 "	-30°	2430	211	3.3	2.3
3.	0.26 "	-25°	3525	94	7.4	1.0

It was found difficult to maintain the same gas velocity in several successive runs so that the values of k given in Table 3 are obtained from the rates of attack at two points only along the reaction tube. It should be possible to obtain satisfactory control of the gas velocity by changing the McLeod gauge for a continuous-reading instrument such as a Bourdon gauge (22).

Specimen calculation.

In experiment 3.



The time z taken by the radicals in travelling the distance between source and mirror is given by

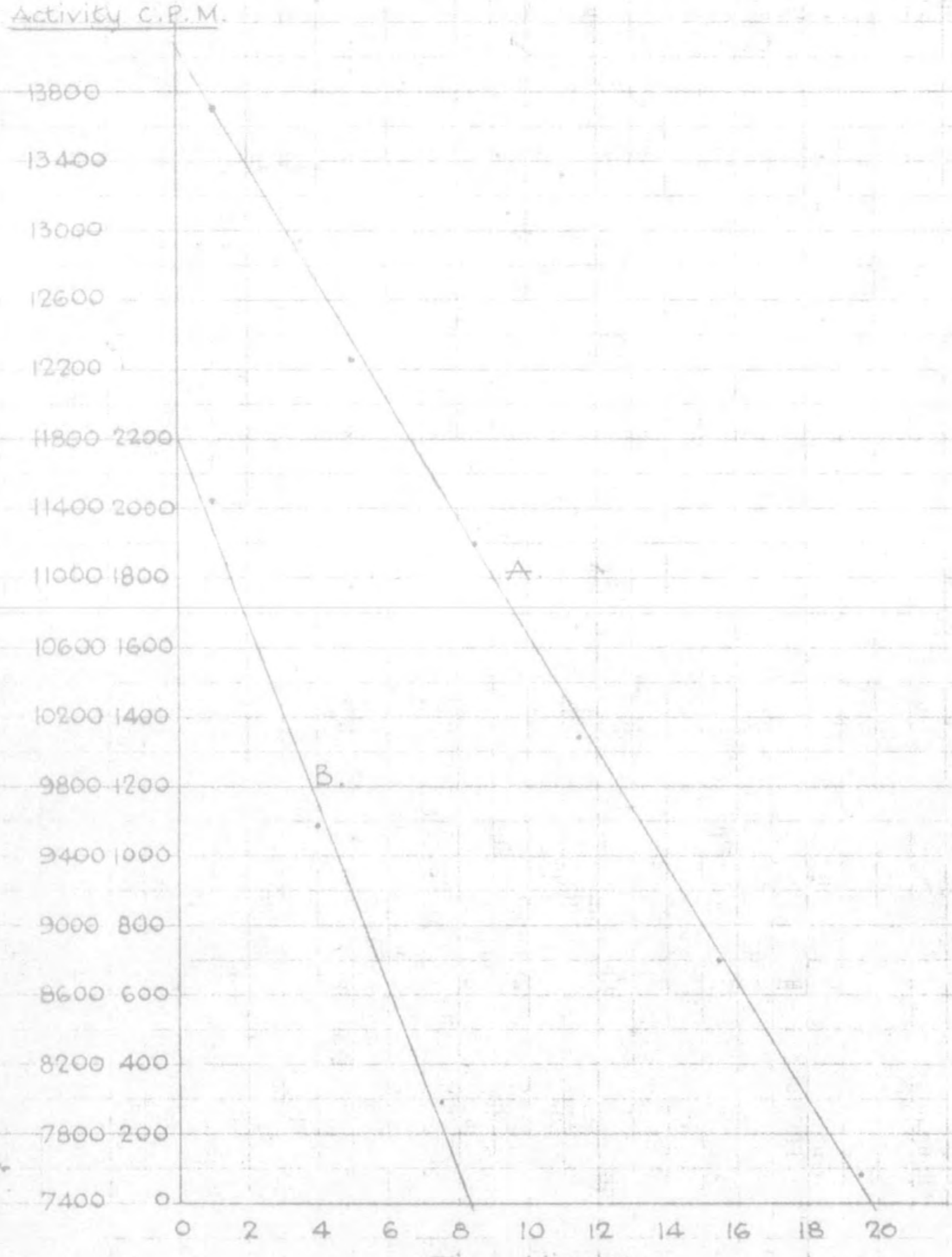
$$z = \frac{X_2 - X_1}{Vo} - \frac{G(X_2^2 - X_1^2)}{2Vo.Po} \qquad (56)$$

where

X_2 is the distance from the centre of the mirror to the begining of the reaction tube,

X_1 is the distance from the begining of the reaction tube to the end of the furnace nearer the mirror,

— FIG. 19. —


Activity C.P.M.
13800
13400
13000
12600
12200
11800 2200
11400 2000
11000 1800
10600 1600
10200 1400
9800 1200
9400 1000
9000 800
8600 600
8200 400
7800 200
7400 0
0
2
4
6
8
10
12
14
16
18
20
A.
B.
Time Minutes.

Po and Vo are the pressure and streaming velocity respectively at the begining of the tube,

G is the average pressure gradient across the tube.

$X_1^A = 5.5$ cm. $= X_1^B$; $X_2^A = 10$ cm. ; $X_2^B = 22.25$ cm. ;

$V_o = 3525$ cm. sec^{-1} ; $G = 0.02$ mm. cm^{-1} ; $P_o = 1.00$ mm. ;

$Z_A = 1.0 \times 10^{-3}$sec ; $Z_B = 3.3 \times 10^{-3}$sec .

The rate of attack on the mirror in the positions A and B obtained from the results plotted in Fig. 19

is 333 cpm./min. at A,

and 268 cpm./min. at B,

$$k = \frac{2.30}{Z_B - Z_A} \cdot \log \frac{\text{rate A}}{\text{rate B}} = 94.$$

$$t_{\frac{1}{2}} = \frac{0.69}{k} = 7.4 \times 10^{-3}\text{sec.}$$

For ethyl $V_1 = 1.15 \times 10^4$ cm. sec^{-1}.

$$\alpha = \frac{k.R_o}{2 V_1} = 1.0 \times 10^{-3}.$$

7. Conclusion.

The use of radioactive mirrors for studying free radicals facilitates the direct and immediate observation of the rate of reaction at opaque mirrors and makes it possible to dispense with the use of standard mirrors in quantitative studies.

The use of a suitable radioactive indicator with a special counting technique enables the distribution of radioactivity along the length of a mirror to be measured. By this method it is possible to determine directly the length of mirror necessary for complete elimination of free radicals in a gas stream. The theoretical calculations of Paneth and Hertzfeld in this respect have thus been confirmed experimentally by a more direct method than that of the guard mirror technique.

An assumption made by Paneth and Hertzfeld was that reaction occurred on the first collision of the radical with the mirror. The confirmation of this assumption (for bismuth and ethyl) means that by using a long heavy mirror of known specific radioactivity free radicals may be counted much more easily than by the microchemical methods hitherto employed -- for example compare Feldman, Ricci and Burton (23) and Leighton and Mortensen (48).

PART TWO.

REACTIONS IN THE LIQUID PHASE.

CHAPTER ONE.

CHAPTER ONE

THE MEASUREMENT OF THE LIFETIMES OF FREE RADICALS IN SOLUTION.

1. Introduction.

There is now much coherent evidence for the existence of free radicals in the liquid phase (21,39,80). They vary in type from the comparatively stable triphenylmethyl to the extremely reactive short-lived phenyl. The presence of free radicals in liquid phase reactions is usually deduced from the reaction kinetics and the nature of the products, particularly when it is difficult or impossible to account satisfactorily for them by an ionic or molecular mechanism. For example, the reaction between benzene diazo-acetate and pyridine produces phenyl pyridines in a total yield of about 60% (37). The three possible isomers, α , β and γ are present. This can only be explained as a reaction of phenyl radicals since phenyl cations would give a phenylpyridinium salt. Subsequent molecular rearrangement of this salt would yield α and γ phenyl pyridines and no β phenyl-pyridine.

Free radicals of short life possess sufficient energy to react with most normal molecules upon collision, as a result the odd electron of the radical R° becomes part of a stable electron pair and a new radical is produced since normal molecules contain an even number of electrons.

$$R\cdot + A{:}B \longrightarrow R{:}A + B\cdot$$

This new radical may then react in its turn, and so on.

$$B\cdot + C{:}D \longrightarrow B{:}C + D\cdot$$
$$D\cdot + A{:}B \longrightarrow A{:}D + B\cdot$$

The net result being the conversion

$$A{:}B + C{:}D \longrightarrow B{:}C + A{:}D$$

and this chain reaction continues until the active radicals are destroyed by mutual combination or by adsorption on the walls of the reaction vessel.

$$B\cdot + D\cdot \longrightarrow B{:}D + \text{energy.}$$

The chain reaction may be retarded or inhibited by the addition of a substance with which the active radicals will react to form another kind of radical which is so unreactive as to be unable to take any further significant part in the reaction.

The kinetic characteristics are :-

a) initiation by the formation of free radicals,

b) the reaction rate increases with time until the rate of production of free radicals equals the rate of their removal,

c) the reaction velocity remains constant and independent of the concentrations of the main reactants until one or both of these become exhausted.

The reaction velocity of most reactions in solution depends on the concentration of the main reactants according to the first or second order equations so that the occurrence of a chain reaction may be taken to indicate the presence of active free neutral radicals.

Ethylenic polymerisation in the liquid phase has received much attention. The polymerisation may be brought about photochemically, thermally or by organic catalysts such as benzoyl peroxide which are capable of generating free neutral radicals in solution. Polymerisation may also be effected by inorganic catalysts such as boron fluoride, aluminium chloride or stannic chloride which are electrophilic reagents and bring about polymerisation by a polar mechanism.

Hey and Waters suggested that in the benzoyl peroxide-catalysed polymerisation the active catalyst was the phenyl radical which could add on to the olefinic link (41).

$$Ph\cdot \quad + \quad CH_2{=}CH\text{-}Ph \longrightarrow PhCH_2\text{-}\dot{C}H\text{-}Ph$$

This view is supported by the kinetics of the reaction. The polymerisation is of zero order after an induction period, although the concentration of the benzoyl peroxide decreases unimolecularly. Also the average molecular weight of the resultant polymer is the greater the less the concentration of catalyst used. The ability of free radicals to initiate ethylenic polymerisation is so well substantiated that it is now used as a diagnostic test for them. (8).

In contrast with our knowledge of free radicals in the gas phase little is yet known of the lifetime of short-lived free radicals in solution. Hey and Waters considered 10^{-10}sec. a maximum value for the mean life in solution of free neutral radicals of high energy (40). The average life of the growing polymer molecule in the photo-polymerisation reaction of vinyl acetate has been given as 2.3×10^{-2}sec. at 16° by Burnett and Melville (11), and 1.3 sec. at 25° by Bartlett and Swain (4) who have given a possible

TABLE 4.

	Styrene			Methyl methacrylate
	0°	25°	100°	0°
Life of one radical	1.6×10^{-2}sec.	6.2×10^{-3}sec.	7.5×10^{-4}sec.	2.5×10^{-3}sec.
Life of growing polymer molecule	25 min.	2.8 min.	1.24 sec.	148 sec.
Life of kinetic chain	11 hr.	33 min.	3 sec.	816 sec.

explanation for the difference (74). Recently the absolute velocity constants have been determined for the initiation, propagation, transfer and termination reactions of free radicals in the photo-polymerisation of styrene and methyl methacrylate (3). Bamford and Dewar's values for the lifetime of the active particles calculated from these velocity constants are given in Table 4. This precise information does not exist at present for other radicals because of the difficulty in finding suitable simple reactions to which a detailed kinetic treatment may be applied.

Very recently Melville and Majury have published a method for obtaining the lifetime of radicals involved in the photo-polymerisation of liquid vinyl compounds by measuring the change in dielectric constant which accompanies the reaction (62). The instrument used has a sensitivity of 1 part in 10^8 of dielectric constant and a response time of 10^{-4}sec., the sensitivity to polymer formation is of the order of 1 part in 10^7. An average value of about 0.5 sec. is reported for the lifetime of the radicals concerned in the polymerisation of pure vinyl acetate photosensitized by α-azo-bis-iso-butyronitrile ($NC.(CH_3)_2C.N=N.C(CH_3)_2CN$).

The quantitative study of radical reactivities is of great theoretical interest. In this connection any method for determining directly the lifetime of a free radical in systems not permitting complete kinetic treatment is of value since the lifetime of a radical is an inverse function of its reactivity. The experiments described hereafter were made in an attempt to measure the lifetime of free radicals in solution.

2. Previous Work.

In 1926 Briers, Chapman and Walters investigated the reaction between aqueous solutions of potassium oxalate and iodine under the influence of light by a rotating sector method (10). They confirmed earlier observations that the rate of reaction is proportional to the square root of the intensity of the light and that the quantum yield is high indicating a chain reaction. Without making any assumptions as to the nature of the "unstable catalyst or chain of catalysts" involved they obtained the values of 3×10^{-2}sec. and 6.3 sec. for the mean life of the catalyst or chain in the light and in the dark respectively.

The reactions involved may be :-

$$I_2 + h\nu \longrightarrow 2I\cdot$$

$$C_2O_4^{=} + I\cdot \longrightarrow C_2O_4^{-} + I^{-}$$

$$C_2O_4^- + I_2 \longrightarrow 2CO_2 + I^- + I\cdot$$
$$C_2O_4^- + I\cdot \longrightarrow 2CO_2 + I^-$$
$$I\cdot + I\cdot \longrightarrow I_2$$

compare Cartledge (13) and Weiss (82)

in which two types of short-lived intermediates -- iodine atoms and the semi-oxidised oxalate ions -- are involved. No indication of their individual lifetimes is given by the results of Briers, Chapman and Walters.

The rotating sector method was also used by Burnett and Melville, and Bartlett and Swain in the experiments referred to in the previous section. Bamford and Dewar employed viscosity measurements to follow the course of polymerisation. No other methods for the determination of the life of free radicals in solution appear to have been published.

3. Choice of Experiment.

The reaction of free radicals in solution with elements has been observed; Dull and Simons refluxed lead tetraphenyl with mercury and obtained some mercury diphenyl (18), whilst Razuviev and Koton found that diphenyl disulphide was produced when lead tetra-phenyl, tin tetra-phenyl or mercury di-phenyl was heated in paraffin oil containing sulphur (67). Waters derived phenyl mercuric chloride when mercury was added to benzene diazo-acetate decomposing in carbon tetrachloride, and phenyl derivatives of mercury, tin, arsenic, antimony, sulphur, selenium and tellurium by the addition of the elements to benzene diazonium chloride decomposing under acetone.(79).

It may then be possible to measure the lifetime of the radicals by Paneth's method, using one of these elements as a mirror. The practical application of the method is difficult. Hartridge and Roughton have described a method for measuring the velocity of very rapid chemical reactions (36). In their method the reaction starts when two reactants under pressure are rapidly mixed and then passed through an observation tube. The rate of change is obtained by making observations at intervals along the tube. This method cannot be applied directly to the problem in hand since free radicals would continue to be produced all down the length of the tube and only the overall rate of production of the radicals could be obtained from the experiment. In order to measure their lifetime the radicals must be produced by primary reaction at one point only in the tube. The "capacity flow" technique described by Stead, Page and Denbigh (73) is inapplicable for the same reason though valuable as a method of maintaining a steady concentration of short-lived reaction intermediates.

The application of the mirror technique to radicals in solution requires -

a) a compound which though stable in solution can easily be decomposed with the formation of free radicals.

b) a detector which is insoluble in the solvent used but which reacts readily with free radicals to form a stable soluble product.

Since the concentration of free radicals is likely to be very small the detector should be one which is available in a radioactive form of convenient half-life to enable maximum sensitivity to be attained.

Production of free radicals by photochemical decomposition is the most convenient method practically. The photolytic decomposition of liquid lead alkyls or aryls is too slow (48) though the decomposition of lead tetra-ethyl in benzene solution would otherwise appear to be a very favourable reaction to investigate since Cramer has obtained evidence that the ethyl radicals produced by thermal decomposition do not attack benzene or naphthalene at temperatures below 300° but form ethylene by a disproportionation reaction (17). In these circumstances the radicals would be expected to have a comparatively long life and the measurements would not be complicated by the presence of radicals characteristic of the solvent in addition to those originating from the solute.

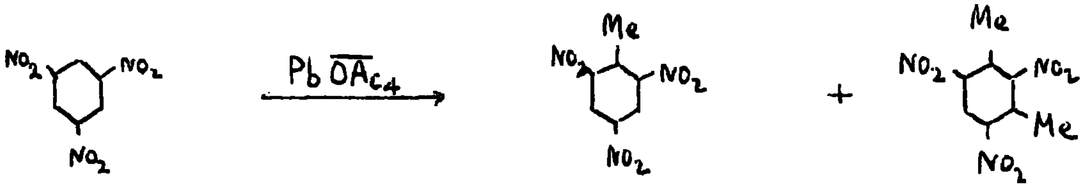
Radioactive antimony was available so that at first sight benzene diazonium chloride might appear to be well adapted for use in the method since it reacts readily under acetone or ethyl acetate with antimony to form soluble aryl stibines (78). The system must be rejected however because it seems doubtful whether any phenyl radicals produced in the decomposition can be considered to have an independent existence, for benzene diazonium chloride is stable under acetone below 50° but vigorous decomposition sets in immediately at 0° on addition of antimony powder. In any case, practical difficulty would be caused by the very slight solubility of the diazo compound.

Solutions of benzene diazo-acetate decompose spontaneously with the formation of free phenyl and acetate radicals (34) and the radicals produced are capable of reacting with metals (77). Experiments were therefore carried out to ascertain whether the rate of decomposition could be accelerated sufficiently by ultraviolet light for the reaction to be used in the flow system. The effect of the U.V. lamp available at that time on the rate of decomposition was too small to be of any practical value. A further disadvantage is that the compound cannot be kept more than a day or two without decomposing. Organic iodides decompose photochemically with the production of free radicals and iodine atoms. The low quantum yields observed are accounted for by the recombination of the radical with the iodine resulting from the primary process (54).

$$RCH_2I + h\nu \longrightarrow RCH_2\cdot + I\cdot$$

$$RCH_2\cdot + I\cdot \longrightarrow RCH_2I$$

Fieser and his collaborators have shown that some aromatic nitro compounds and naphthaquinones may be alkylated by heating with the quadrivalent lead salt of the corresponding carboxylic acid (25,26,27). For example, trinitro-toluene and trinitro-xylene were obtained from the action of lead tetra-acetate on trinitro-benzene in glacial acetic acid solution.



To explain the reaction Fieser suggested that the lead tetra-acetate decomposes thermally to give free acetate radicals possibly via diacetyl peroxide -

$$Pb\overline{OAc}_4 \longrightarrow Pb\overline{OAc}_2 + 2CH_3COO\cdot$$

$$CH_3COO\cdot \longrightarrow CH_3\cdot + CO_2$$

To confirm this hypothesis he showed that diacetyl peroxide would also methylate. By using the appropriate diacyl peroxide a wide range of saturated and unsaturated alkyl groups could be substituted in the quinonoid ring of quinones. The decomposition of lead tetra-acetate in glacial acetic acid was found to be promoted by the addition of methyl alcohol, iso-propyl ether, cyclo-hexane, benzene etc. with the evolution of varying quantities of neutral gas assumed to be ethane.

By analogy with the experiments of Waters (77) the addition of antimony to a decomposing solution of lead tetra-acetate might be expected to lead to the formation of an organo-metallic compound of antimony. When the experiment was carried out in the presence of chalk to keep the mixture neutral the antimony was indeed attacked. No volatile organic compounds of antimony were isolated but a considerable quantity of a yellow powder taken to be the acetate was obtained.

The photochemical or thermal decomposition of dibenzoyl peroxide takes place with the formation of carbon dioxide and diphenyl chiefly, together with some phenyl benzoate and benzene (20,24). In boiling benzene the products are carbon dioxide, diphenyl and benzoic acid accompanied by smaller amounts of phenyl benzoate, terphenyl and quaterphenyl (29). These products are easily accounted for by the formation of free radicals by the primary decomposition process. The evidence for this view has been summarised by Hey and Waters (39) and Waters (81).

$$\mathrm{PhCOO.OOCPh} \longrightarrow \mathrm{PhCOO}\cdot + \mathrm{CO_2} + \mathrm{Ph}\cdot$$

$$\mathrm{PhCOO}\cdot \longrightarrow \mathrm{Ph}\cdot + \mathrm{CO_2}$$

In benzene solution the chief reactions of the radicals with the solvent are -

$$\mathrm{Ph}\cdot + \mathrm{Ph.H} \longrightarrow \mathrm{Ph.Ph} + \mathrm{H}\cdot$$

$$\mathrm{PhCOO}\cdot + \mathrm{Ph.H} \longrightarrow \mathrm{PhCOOH} + \mathrm{Ph}\cdot$$

If the radicals produced have an appreciable lifetime they should react with antimony.

Powdered antimony (21 g.) was stirred with a boiling solution of benzoyl peroxide (5 g.) in ethyl alcohol (80 cc.) for three hours and then filtered off. The aqueous extract of the residue contained some antimony ions and antimony ions were obtained in quantity on extracting the residue with warm sodium tartrate solution. Radioactive antimony was stirred in a boiling benzene solution of benzoyl peroxide. After separation from solid particles the benzene solution was found to be strongly radioactive indicating the formation of a soluble antimony compound . The decomposition of dibenzoyl peroxide in benzene was chosen then as a suitable reaction in which to investigate the lifetime of the radicals taking part.

Reaction of antimony and lead tetra-acetate in solution.

30 g. of finely powdered antimony was heated on a waterbath under reflux with mechanical stirring together with 10 g. calcium carbonate, 18 g. lead tetra-acetate, 100 cc. chloroform and 20 cc. methyl alcohol. No antimony ions could be found in the aqueous extract of the residue. The organic solution was dried over anhydrous sodium sulphate for two days and then distilled. After most of the chloroform and methanol had been removed an almost colourless gel was left. A portion of this gel when distilled gave off a sweetish smelling vapour which did not condense and left a yellowish orange residue. On strong heating this residue underwent further decomposition and metallic

globules were formed. The residue was then taken up in hot concentrated hydrochloric acid and gave a solution with which positive Marsh and Gutzeit tests for antimony were obtained.

To the remainder of the gel was added ether. The gel immediately broke up precipitating a yellow powder. Water was added and the whole shaken. The powder did not dissolve. The ether layer was dried over sodium sulphate and distilled. After the ether had been distilled about one cc. of colourless liquid boiling at 115° was obtained -- acetic acid b.p. 118°. The powder was insoluble in water, acetone, ether and alcohol, hot dilute hydrochloric acid and hot concentrated nitric acid. It dissolved in cold concentrated hydrochloric acid and was not thrown out on dilution. This solution with hydrogen sulphide gave an orange precipitate soluble in ammonium sulphide and reprecipitating on acidification of the alkaline solution.

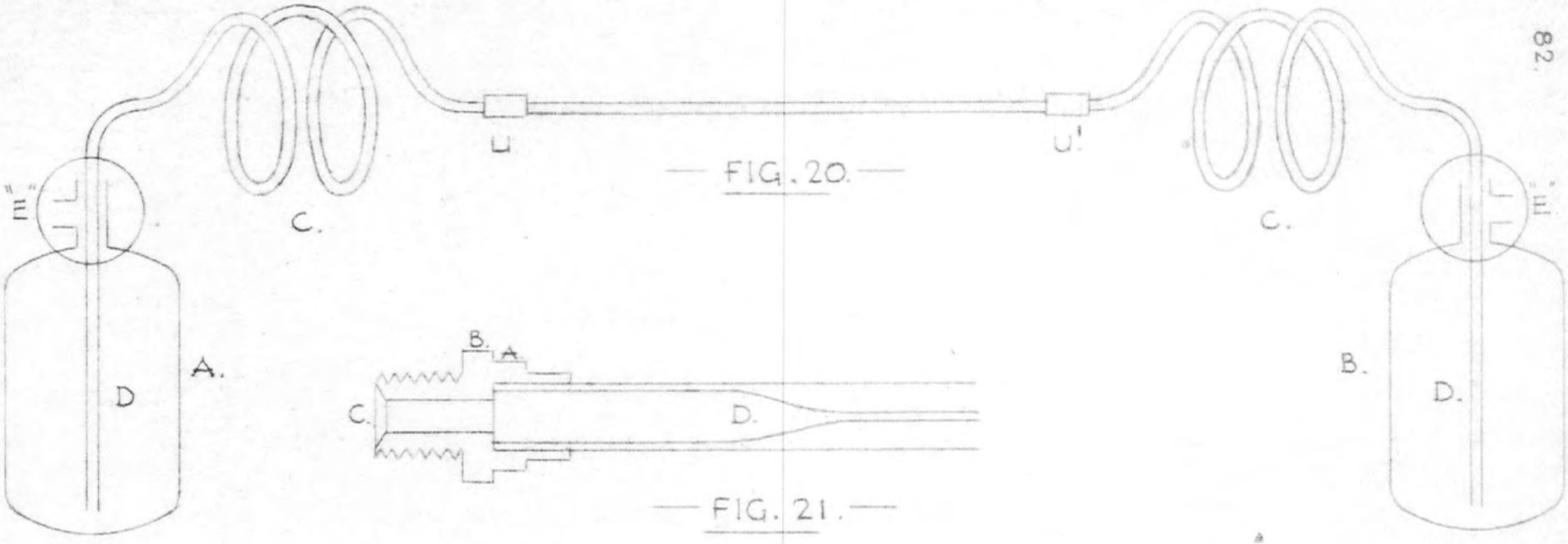
CHAPTER TWO.

CHAPTER TWO

THE FAST-FLOW METHOD.

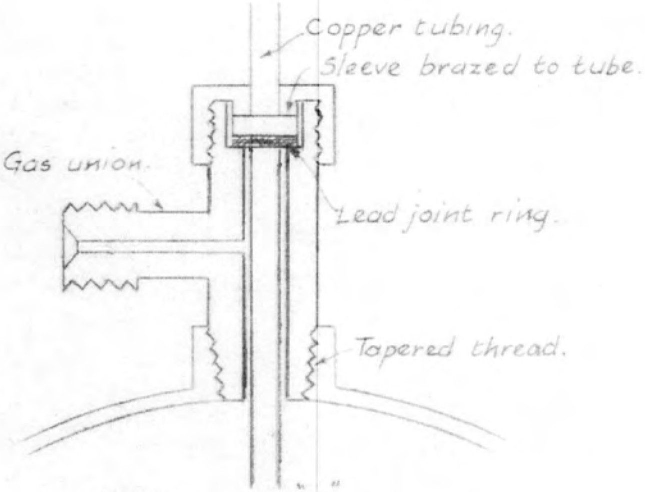
1. Introduction.

The use of liquids in fast flow experiments introduces some restrictions on the type of apparatus employed. The time occupied by each run must be small unless unwieldy reservoirs and large quantities of solvent are to be used. Fast flow rates require high pressures and, for safety, a metal apparatus to contain them. If photochemical decomposition is to be used, or the course of the reaction is to be observed, a quartz or glass inset is required with the attendant jointing difficulties. Experience with the mirror technique in the gas phase shows that a chemically pure mirror is necessary so provision must be made for vacuum deposition. The apparatus must then be capable of being subjected to a high vacuum and a pressure of several atmospheres alternately. It will consist essentially of a silica or glass tube which can be inserted in the glass gas apparatus (between A and B Fig. 6, p.28) for the deposition and cleaning of the radioactive mirror and then



— FIG. 20. —

— FIG. 21. —



DETAIL AT "E".

connected as the reaction tube between two metal reactant reservoirs. Photochemical decomposition will be effected by a lamp giving all-round illumination of the reaction tube. The lamp will be a modified version of the cooled mercury arc described by Bates and Taylor (5).

2. Apparatus.

See Fig. 20.

A and B are small metal gas cylinders of a type used for oxygen supply in Service aircraft having a volume of about 6.5 l. These were used as reactant reservoirs. Pressure was applied to A from a cylinder of compressed nitrogen and forced the peroxide solution into B through the reaction tube UU'. The nitrogen cylinder was fitted with a coarse needle valve and a pressure gauge reading up to 450 p.s.i.. The connection between the nitrogen cylinder and reservoirs was by copper tubing fitted with standard high pressure gas unions. The reaction tube of glass/silica was sealed into brass unions which could be screwed into standard high pressure gas nipples on the ends of the reservoir transfer tubes. These transfer tubes were made of 3/16" seamless copper tubing coiled as shown to give greater freedom of movement and so reduce the risk of breaking the reaction tube. Lead washers were used for the joints between transfer tube and reservoir neck and fibre washers for the union joints between transfer and reaction tubes.

It was found that with a pressure of 75 p.s.i. gauge on benzene a linear flow of about 17 m./sec. was obtained in a 1 mm. diameter reaction tube giving a total running time of about 6 min. for 5 l. solvent.

Details of the reaction tube are shown in Fig. 21. The brass unions sealed on to the ends of the silica capillary tube were threaded and cupped to take standard gas nipples. Flats were machined on the collars A to facilitate tightening of the unions. Collar B served as a jointing surface when the reaction tube was inserted in the gas apparatus. The annulus C was wide enough for the radioactive antimony carrier (Fig. 6, p.28) to be drawn through to D where it could be heated without spoiling the brass to silica seal.

Difficulty was experienced in obtaining a brass to silica/glass seal which besides being insoluble in benzene was leakproof with the system alternately under high vacuum and high pressure. Silver chloride seals were tried but silica tubing showed a strong tendency to crack near the seal. In addition the silver chloride deliquesced on the brass union and softened even when this had been silver plated. Jointing compounds made of phosphoric acid and copper oxide, sodium silicate and calcium carbonate, and bakelite cement were also tried. These joints withstood pressure very well but a high vacuum could not be obtained with them. Synthetic rubber rings under compression (Edwards & Co's "O" rings) would withstand a pressure of 15 atmospheres but again a good vacuum could not be obtained. Finally a species of De Khotinsky cement insoluble in benzene was used. With this it was possible to make a brass to glass/silica seal which was leakproof under both vacuum and pressure. The joint between the collar B and the glass gas apparatus was a source of trouble since it was difficult to make a leakproof union - gas apparatus seal without upsetting the union - reaction tube seal. This difficulty did not occur with glass reaction tubes since they could be joined directly to the gas apparatus and only fitted with unions after the mirror had been deposited. The same method could have been used with silica tubes if silica - glass graded seals had been available.

It was soon found necessary to place the reaction tube in a clamp since it was all too easily broken when connecting to or disconnecting from the reactant reservoirs. The copper tubing employed was too stiff for the system to have sufficient flexibility. The clamp was made of brass. During the assembly of the reaction tube this brass plate was heated to the melting point of the cement, the tube was then laid on the brass plate and the clamps secured whilst the cement was plastic. When the plate had cooled the reaction tube could be removed for insertion into the vacuum apparatus. After deposition of a radioactive mirror in the tube it was replaced on the hot plate, reclamped and allowed to cool. A piece of asbestos paper was placed round the tube opposite the mirror to keep it cool and minimise atmospheric oxidation. The use of the clamp precluded the use of the cooled mercury arc constructed specially for these experiments since the clamp was too wide to go through the inner tube of the lamp.

3. Experimental.

Experiments were conducted to ascertain the effect on the mirror of running benzene through at high velocity. Thin foil mirrors were easily stripped under a pressure of three or four atmospheres but very thin mirrors could usually be relied upon to withstand pressures of more than ten atmospheres without mechanical stripping. A 1% solution of benzoyl peroxide in benzene was then made up and a series of experiments commenced using light from low and high pressure mercury arcs to bring about photo-chemical decomposition of the peroxide. After proving the mechanical stability of a mirror by passing the peroxide solution through the reaction tube several times at high velocity its radioactivity was measured by a Geiger-Muller tube placed on a suitable platform over the reaction tube opposite the mirror. Interlocking lead blocks were arranged on an iron platform to form a protective 'castle' round the mirror and G-M tube to cut down the background count as much as possible.

The G-M tube and superstructure of lead bricks was then removed and replaced by the mercury vapour lamp. The lamp, fitted with an aluminium reflector, was fixed as near to the reaction tube as possible. The low pressure lamp (principle emission at 2537 Å) worked at only a few degrees above room temperature and could be used almost touching the reaction tube (51), whilst the high pressure lamp (125 w. G.E.C. with protective glass envelope removed) worked at a high temperature and had to be placed 2-3 cm. from the reaction tube in order that the latter should not heat up appreciably during a run. The length of reaction tube illuminated was arranged to end 3 or 4 mm. upstream of the mirror. With the lamp switched on the solution of benzoyl peroxide was then run through the reaction tube. When all the peroxide solution had been transferred from A to B the lamp was removed and replaced by the G-M tube and shield of lead bricks and the radioactivity of the mirror measured again. By applying pressure to B the peroxide solution could be returned to A ready for another run.

4. Results and Discussion.

No evidence was found of any attack on the mirror even when the mirror was situated in the middle of the illuminated section of the reaction tube. The majority of these experiments were carried out at a pressure of ten atmospheres gauge giving a linear flow of about 35 m./sec. in the 1 mm. bore reaction tubing used. Reducing the flow-rate progressively to 1 m./sec. made no difference.

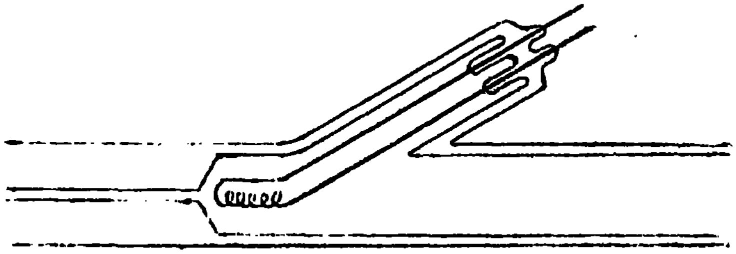
Only occasionally was it possible to obtain a good vacuum (of the order of 10^{-6}mm.Hg) in the system used for depositing the mirror in the reaction tube. That surface oxidation of the mirror accounts for the nil results is unlikely however in view of Water's successful experiments where no special measures were taken to obtain an oxide-free metallic surface (79). More likely explanations are that either

a) the lifetime of the radicals is considerably less than a millisecond or

b) the quantity of light usefully employed is so small and the exposure time so short that the initial concentration of free radicals produced is insufficient for detection by a mirror of low specific activity.

If a) is the case, then the method cannot be used for measuring the life-time of the radicals produced in this particular reaction.

If b) holds then progress might be made by increasing the initial concentration of radicals and by using a mirror of higher specific activity. There was no stronger lamp system available so recourse was made to thermal decomposition as a means of increasing the concentration of radicals. This introduces a complication in that the position of the source of radicals is no longer sharply defined but depends on the



— FIG. 22. —

temperature gradient along the reaction tube. Experiments showed that radioactivity was transferred to the solution when powdered radioactive antimony was rapidly stirred in a solution of benzoyl peroxide in benzene in which a small electrically heated wire spiral was immersed. The spiral was made hot enough to bring the neighbouring solution near to boiling point with the flask cooled externally by a freezing mixture.

Pyrex reaction tubes were made with heating elements sealed in through the glass. In some a small coil was located just outside the capillary bore. In others a loop projected into the capillary bore. (Fig.22). Heavy currents were passed but though decomposition undoubtedly occurred as evidenced by the accumulation of a brown resinous substance on the wire no diminution in the radioactivity of the mirror was observed. With a sufficiently large current the wire could be made red-hot under the full flow of liquid.

The failure of these experiments suggested that the lifetime of free phenyl and benzoate radicals is so brief that their concentration was too low for detection by the radioactive antimony available. From the current theory of free radical stability the benzyl radical would be expected to be more stable than the phenyl radical. It was thought that the decomposition of phenyl benzyl ether (44) might provide a sufficient concentration of benzyl radicals for detection by the mirror technique. To test this a mixture of radioactive antimony and benzyl phenyl ether (2.5 g.) dissolved in quinoline (25 cc.) was stirred rapidly under reflux at 250° for an hour. After cooling the solution was centrifuged for an hour to eliminate suspended antimony particles and a measurement of its radioactivity showed that about 2 mg. only of antimony was present in solution. This amount of reaction is too low to be of any use in the fast-flow method.

CHAPTER THREE.

CHAPTER THREE.

THE STATIC METHOD.

1. Introduction.

The observation that very nearly all of 35 mg. of powdered radioactive antimony had dissolved after being stirred in a boiling solution (approx. 1%) of benzoyl peroxide in benzene (100 cc.) for 2½ hours suggested that an approximate estimate of the life of the free radicals might be obtained from a static experiment.

If it is assumed that a radical approaching within a distance L of the antimony surface reacts, then there exists a reaction volume -- L x surface area of antimony -- which is related to the total volume of reactants in the same way as the quantity of radicals reacting with antimony is related to the total quantity of radicals produced. The average life of the radicals is the time taken for them to diffuse through the reaction distance L and is related to the diffusion coefficient in the following manner

$$D = \frac{L^2}{2t} \qquad (30)$$

where D is the diffusion coefficient of the radicals and t is the average life.

The surface area of the antimony in suspension can be obtained from a size-frequency analysis and the number of radicals reacting with antimony by measuring the radioactivity of the solution. A value for D must be assumed, probably that for C_6H_6 in C_6D_6, D_{50° 1.7 x $10^{-5}cm^2$/sec. (46) is not too far wrong. An estimate of t can then by made which should be of value in designing other experiments.

2. Experimental.

When experiments on these lines were carried out it was found that a white amorphous compound precipitated out more or less completely on diluting, centrifuging or filtering the reaction solution. The radioactivity of the solution was almost entirely associated with this compound and its peculiar instability in solution thus complicated the estimation of the antimony which had reacted.

The compound dissolved easily in cold dilute hydrochloric acid but not in glacial acetic acid, acetone, ether, alcohol or petroleum ether. When a stream of dry air was passed through some of the clear solution decanted off the reaction mixture, turbidity appeared after 25 minutes but a corked control sample also went turbid at the same time. The solution of this antimony compound appeared to be quite stable when left standing undisturbed over unreacted Sb. Tests showed that if the reaction mixture was rapidly filtered under suction through a No.4 sintered glass funnel no 'dissolved radioactivity' was lost in passing through the filter. Turbidity only appeared in the filtrate about 2 mins afterwards.

The specific radioactivity of the antimony in solution under given geometrical conditions was determined by dissolving a known weight in nitric acid and diluting until a count of about 2000 p.m. was obtained with 20 cc. contained in a glass tube clamped in a fixed position under the Geiger-Muller tube.

Antimony, finely powdered in an agate mortar, was roughly graded by flotation. After the heavier particles had been allowed to separate for one minute from a suspension obtained by vigorous shaking with benzene the particles remaining in suspension were decanted off with the benzene. The process was repeated on the antimony residue and the decanted suspensions were combined and centrifuged. The benzene was poured off and the antimony dried in an air oven at 85°. About 100 mg. of this antimony was weighed into a 150 cc.

round-bottomed flask and brought into suspension with 100 cc. benzene by vigorous stirring. After withdrawal of a 5 cc. sample for size-frequency analysis, about a gramme of benzoyl peroxide was weighed into the flask and 5 cc. of benzene added to bring the volume up to 100 cc. A reflux condenser was fitted to the flask. A stirrer shaft ran through the condenser tube and was driven by a high speed electric motor. The flask was heated on a boiling waterbath for about an hour. The reaction was stopped by running cold water over the flask. After the reaction mixture had settled for two hours, the radioactivity was determined of 5 cc. of the clear supernatent liquor diluted to 20 cc. in the glass tube previously used for measuring the specific activity of the antimony. 5 cc. aliquots of the reaction mixture were analysed for benzoyl peroxide. With some modifications, Vanino's method for the estimation of benzoyl peroxide in alcohol solution (75) can be used for solutions in benzene. The solution, containing not more than 0.1 g. peroxide, was heated on a waterbath to boiling point when 5 cc. saturated alcoholic potassium iodide solution was added followed by 1 cc. glacial acetic acid. The mixture was heated for a further 5 mins. then cooled and allowed to stand for half an hour before titrating the liberated iodine with 0.1N sodium thiosulphate solution. A method using glacial acetic acid as a solvent is given by Cass (14) and one using acetic anhydride by Nozaki and Bartlett (53). The sample of suspension taken for size-frequency analysis was diluted to 25 cc. and after vigorous shaking a drop on a haemocytometer was examined through a microscope. The mean radius of each antimony particle counted was measured. In calculating the surface area of the antimony it was assumed that the particles were spherical.

3. Results.

1. In boiling benzene solution.

Weight of Sb: 0.0797 g.

100 cc. benzene added, 5 cc. suspension removed for S.F.A.

0.9628 g. benzoyl peroxide and 5 cc. benzene added to remainder.

Reaction time 60 mins.

Radioactivity of 5 cc. solution 1470 c.p.m.

1 mg. Sb $\equiv$ 604 c.p.m.

Sb in solution $= \frac{1470 \times 100}{604 \times 5}$ mg. $=$ 48.6 mg.

5 cc. aliquots liberated iodine $\equiv$ 2.03 cc. 0.100N hypo.

1 cc. hypo $\equiv$ 0.0121 g. benzoyl peroxide.

Example of the Estimation of Antimony Surface Area by size-frequency Analysis.

Particle diam. M units.	No. of particles in 150 cells each of vol. 25×10^{-8} cc.	No. of particles in 95 cc. reaction mixt. $\times 10^{-8}$	Total area of particles in 95 cc. mixt.
0.1	13	1.65	0.1 cm^2
.2	201	2.66	9.2
.3	12	1.52	1.2
.4	6	0.76	1.1
.5	128	16.2	35.0
.6	23	2.92	9.2
.7	37	4.69	19.9
.8	68	8.62	47.8
.9	23	2.92	20.5
1.0	242	30.7	266.0
1.1	11	1.39	14.6
1.2	21	2.66	33.2
1.3	27	3.42	50.0
1.4	9	1.14	19.4
1.5	55	6.97	135.5
1.6	7	0.89	19.7
1.7	17	2.16	54.0
1.8	23	2.92	82.0
1.9	4	0.51	15.8
2.0	72	9.13	316.0
2.1	4	0.51	19.4
2.2	3	0.38	16.0
2.3	6	0.76	34.6
2.5	11	1.39	75.0
2.6	4	0.51	29.7
2.8	2	0.25	17.2
2.9	2	0.25	18.4
3.0	10	1.27	99.0
3.5	3	0.38	40.2
3.7	1	0.13	15.0
3.8	1	0.13	15.9
4.0	2	0.25	35.0
	1048		1865.6

$M \simeq 1.66 \times 10^{-4}$ cm.

$$\text{Peroxide remaining} = \frac{100}{5} \times 2.03 \times 0.0121 \text{ g.} = 0.4913 \text{ g.}$$

Peroxide consumed = 0.4715g.

$$\text{Fraction of radicals used} = \frac{3}{2} \cdot \frac{0.0486 \times 242.2}{0.4715 \times 121.8}$$

$$= 0.3075.$$

Surface area of Sb from SFA = 1865 cm^2.

$$\frac{1865\ L}{100} = 0.3075$$

$$L = 0.0165 \text{ cm.}$$

$$D = \frac{L^2}{2t}$$

$$t = \frac{0.0165^2}{2 \times 1.7 \times 10^{-5}} \text{ sec.}$$

$$= \underline{\underline{8.0 \text{ sec.}}}$$

2. In boiling benzene solution.

Weight of Sb 0.1041 g.

Weight of peroxide 1.1205 g.

Reaction time 77 mins.

Reaction volume 95 cc.

Radioactivity of 5 cc. of solution = 3000 c.p.m.

Sb dissolved 0.0944 g.

Peroxide remaining 0.4460 g.

Peroxide consumed 0.6745 g.

Fraction of radicals used	0.418.
Surface area of Sb	3027 cm^2.

$L = 0.0131$ cm.

$t = 5.0$ sec.

The reaction was also carried out in alcohol solution.

3. In boiling ethyl alcohol solution.

The small of acetaldehyde was evident as soon as the reaction commenced. When estimating the residual peroxide the colour of the solution due to liberated iodine was observed to fade. For the purpose of obtaining a rough estimate of the average life of the radicals the production of 1 mol. acetaldehyde per mol. of peroxide decomposed and the reaction of 1 mol. acetaldehyde with 3 atoms iodine was assumed. At the end of the experiment the antimony appeared to be unchanged.

Weight of Sb	0.0646 g.
Weight of peroxide	0.8735 g.

Reaction time 65 min.

Total radioactivity in solution 170 cpm. = 0.0003 g. Sb

10 cc. aliquots liberated iodine = 0.30 cc. 0.100N hypo.

Peroxide consumed 0.35 g.

Fraction of radicals used	0.0026.
Surface area of Sb	1812 cm^2.

$$t = 6 \times 10^{-4} \text{ sec.}$$

4. Photolytic decomposition in ethyl alcohol solution.

75 cc. of solution contained in a water-cooled quartz flask was illuminated by light of 2537Å for 35 mins. No smell of acetaldehyde was noticed during the reaction and the colour due to the iodine liberated when estimating the residual peroxide did not fade.

Weight of Sb	0.0578 g.
Weight of peroxide	0.5257 g.

Total radioactivity in solution 20 c.p.m. $\equiv$ 0.00004 g.

Peroxide consumed	0.110 g.
Fraction of radicals used	0.0011
Surface area of Sb	1620 cm^2

$$t = 8 \times 10^{-5} \text{ sec.}$$

4. Discussion.

The quantitative difference between the reaction of antimony with benzoyl peroxide decomposing in benzene solution and in alcohol solution is shown in Table 5.

TABLE 5.

Type of Decomposition	Solvent	Sb % Reacted	$(BzO)_2$ % Reacted	Time	$\frac{\text{mol. peroxide decomp'd.}}{\text{mol. antimony reacted}}$
1. Thermal	Benzene	58.2	49.0	60 min.	5.1
2. "	"	90.8	60.2	77 min.	3.6
3. "	Ethyl Alcohol	0.005	40.7	65 min.	583
4. Photolytic	" "	-	20.9	35 min.	1375

The solubility of antimony in benzene is negligible. When radioactive antimony was heated under reflux with about 1 g. benzoic acid in 100 cc. benzene for an hour the amount of radioactivity transferred to the solution corresponded to about 0.25 mg. antimony and no white precipitate was obtained. Reaction with benzoic acid produced in the decomposition of benzoyl peroxide could account for antimony found in solution in experiments 3 and 4 but not in experiments 1 and 2. The effect of the solvent suggests that the phenyl radical is responsible for the attack on antimony since, in benzene solution, the apparent lifetime of this radical may be increased by the solvent regeneration process -

$$Ph\cdot \quad + \quad C_6H_6 \quad \longrightarrow \quad Ph.H \quad + \quad C_6H_5\cdot$$

and the benzoate radicals produced by primary decomposition may exist effectively as phenyl radicals by reaction with the solvent.

$$C_6H_5COO\cdot \quad + \quad C_6H_6 \quad \longrightarrow \quad C_6H_5COOH \quad + \quad C_6H_5\cdot$$

This latter reaction has been shown to occur by Wieland and his collaborators (84,85). They obtained some tetraphenyl methane from the reaction between benzoyl peroxide and triphenyl methyl in benzene solution. This is not due simply to reaction with phenyl radicals produced in the primary decomposition

$$\mathrm{PhCOO{-}OOCPh} \longrightarrow \mathrm{Ph}\cdot + \mathrm{CO_2} + \mathrm{PhCOO}\cdot$$

$$\mathrm{Ph}\cdot + \cdot\mathrm{CPh_3} \longrightarrow \mathrm{CPh_4}$$

but also involves the secondary process

$$\mathrm{PhCOO}\cdot + \mathrm{C_6H_6} \longrightarrow \mathrm{PhCOOH} + \mathrm{C_6H_5}\cdot$$

because tetraphenyl methane was also obtained when di-p-phenyl-benzoyl peroxide $(\mathrm{Ph{-}C_6H_4{-}COO}\cdot)_2$ replaced dibenzoyl peroxide.

From its instability in solution the antimony compound is not simply triphenyl stibine or triphenyl stibine dibenzoate (15). It may possibly be triphenyl stibonium oxide for triaryl stibonium oxides have been described as white amorphous solids, generally soluble in benzene and reacting with acids to form salts. (32).

On the other hand, the properties of the antimony compound are what could be expected of antimony benzoate in the colloidal state and may be compared with the gel formation encountered when eliminating solvent from the reaction mixture obtained with finely divided antimony and lead tetra-acetate, The ready formation of antimony benzoate would indicate the primary decomposition process in benzene solution as

$$\mathrm{PhCOO{-}OOCPh} \longrightarrow 2\mathrm{PhCOO}\cdot \qquad \text{(A)}$$

This mechanism is favoured by McClure, Robertson and Cuthbertson (50), by Cass (14) and by Nozaki and Bartlett (53).

The alternative mechanism

$$\mathrm{PhCOO{-}OOCPh} \longrightarrow \mathrm{Ph}\cdot + \mathrm{CO_2} + \mathrm{PhCOO}\cdot \qquad \mathrm{(B)}$$

is favoured by Hey and Waters (39,42,43,81). The uncertainty of the primary decomposition process has been noted by Cooper (16). If antimony reacts exclusively with benzoate radicals it may be possible to decide between the two mechanisms by obtaining the ratio of molecules peroxide reacted to molecules antimony reacted for different areas of antimony surface exposed to attack by the radicals. The ratio should decrease as the surface area of the antimony increases, approaching the limit 1.5 for mechanism (A) and 3 for mechanism (B).

The radicals produced by thermal decomposition in alcohol appear to react with the solution rather than with antimony.

The reactions may be -

$$\mathrm{PhCOO}\cdot + \mathrm{CH_3CH_2OH} \longrightarrow \mathrm{PhCOOH} + \mathrm{CH_3\dot{C}HOH}$$

$$\mathrm{PhCOO.OOCPh} + \mathrm{CH_3\dot{C}HOH} \longrightarrow \mathrm{PhCOOH} + \mathrm{CH_3CHO} + \mathrm{PhCOO}\cdot$$

$$\mathrm{PhCOO}\cdot + \mathrm{CH_3\dot{C}HOH} \longrightarrow \mathrm{PHCOOH} + \mathrm{CH_3CHO}$$

There was no apparent decrease in the quantity of elemental

antimony at the end of the experiment or change in its appearance.
However, these conjectures depend on the nature of the antimony compound and time available did not permit positive identification of this product.

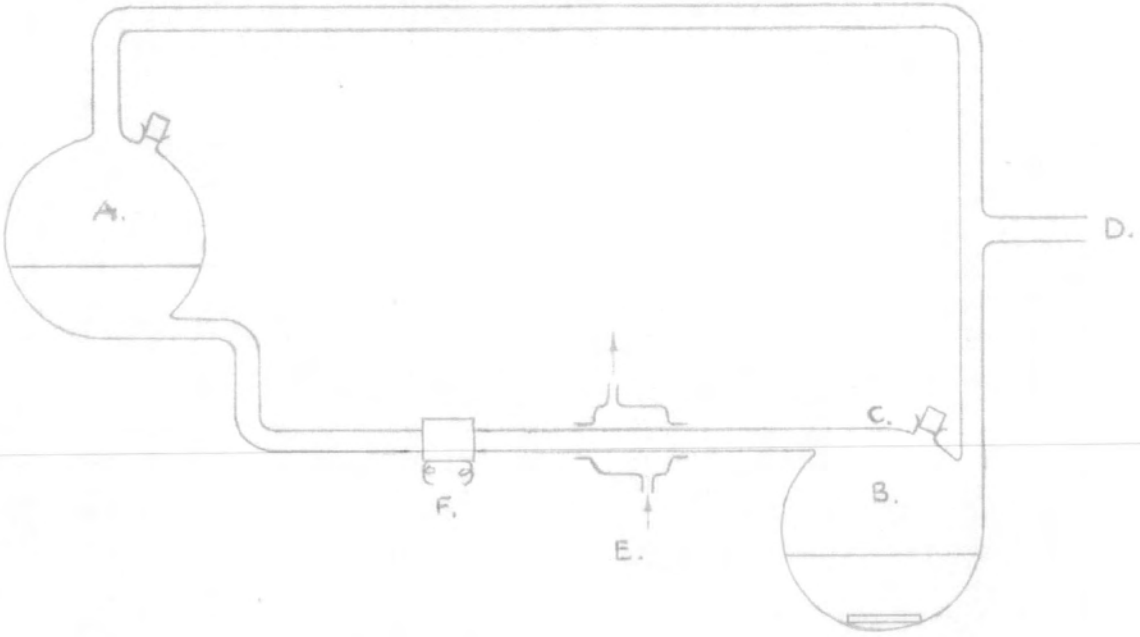
The estimate for the initial surface area of the antimony is made on the assumption that the particles are spherical. This value is likely to be low since the sphere is the body of least surface area for a given volume. Consequently the estimate for the mean life of the radicals will be too high. On the other hand, a large proportion of antimony had reacted when benzene was the reaction medium and the final surface area would thus be much different from the initial value, the average value being lower than the one used in the calculation. This effect will make the estimate for the life time too low. The values obtained are of the same order for the two experiments where the initial surface area and the percentage of the antimony reacted differ by a factor of two. See Table 6.

TABLE 6.

Initial surface area.	% Sb reacted	Duration of experiment.	Mean life of radicals.
1865 cm^2	58.2	60 mins.	8 sec.
3027 cm^2	90.8	77 mins.	5 sec.

If the reaction between antimony and benzoyl peroxide decomposing in benzene solution actually occurs through the intervention of free radicals having a meanlife of the order of a second, the measurement of their half-life by a flow method should be possible.

CHAPTER FOUR.



— FIG. 23. —

CHAPTER FOUR

THE SLOW FLOW METHOD.

1. Apparatus.

The method of using a suspension of finely divided radioactive antimony was adapted to suit the flow technique. An apparatus of the form shown in Fig. 23 was constructed in Pyrex. A solution of benzoyl peroxide in benzene in A is allowed to run through the reaction tube AC into a rapidly stirred suspension of finely divided radioactive antimony in benzene in B. Furnace F heats the solution sufficiently to bring about decomposition of the dissolved peroxide. The cooling jacket E stops further decomposition so that a point midway between the centres of the furnace and cooler may be taken as the source of free radicals. A proportion of the free radicals entering B will react with the suspended antimony. The quantity reacting may be obtained by filtering and measuring the radioactivity of the filtrate. Then in successive experiments the position of the source is moved, other conditions being kept constant. If the average flowrate is known a value for the half-life of the radicals may be obtained from the relation between the radioactivity transferred to the solution in B for different distances of the source from B.

2. Consideration of operating conditions.

Approximate values for the furnace temperature necessary to heat the solution to boiling point and the quantity of antimony which may be expected to react can easily be obtained.

Consider a linear flow of solution of 10 cm./sec. in a reaction tube 4 mm. inside diameter with wall thickness of 1 mm.. Then the volume flow is approximately 1.25 cc./sec. and the heat required to raise this quantity of benzene from 20° to 80° is approximately 31 cal./sec.

Substituting this quantity in the equation for heat transfer through the walls of a tube -

$$T - t = \frac{H}{2\pi Lk} . \ln . \frac{R}{r}$$

when H = heat transferred / sec.

k = thermal conductivity of glass (1.5×10^{-3} cal/cm^2/sec/$^{\circ}$/cm)

L = length of tube heated by furnace (say 6 cm.)

R = radius of outside surface.

r = radius of inside surface.

T = temperature outside tube.

t = temperature inside tube.

and assuming that the heat absorbed/unit time by the solution depends mainly on the thermal resistance of the reaction tube

$T - t \neq 225^{\circ}$ is obtained, i.e. the temperature of the furnace must be approximately 300°.

Previous experiments show about 50% decomposition of a 1% solution when heated in bulk for 60 mins. So, since the contact time of the solution in the heater is 0.6 sec., approximately 8×10^{-5} g. peroxide will be decomposed per 100 cc. Then assuming that each molecule of peroxide yields two radicals on decomposition and three radicals react with one atom of antimony, the maximum quantity of antimony reacting is approximately 3×10^{-5} g. per 100 cc.. The antimony has a specific activity of about 600 cpm./mg. therefore the maximum radioactivity 'in solution' will be approximately 20 c.p.m./100 cc.. It may be concluded that the rate of decomposition of benzoyl peroxide at 80° is too low for this method to give results. The temperature of the solution may be taken above 80° by working under increased pressure. Experiments were carried out at a pressure of about 3 atmospheres absolute when the boiling point of benzene is raised to 120°. The heater temperature required is within the range of a small electric furnace.

3. Experimental.

Pressure from a nitrogen tank was applied at D (Fig.23) through a reducing valve. The inlets to bulbs A and B were closed by rubber bungs which acted as safety valves, blowing out at 40 p.s.i. gauge. A magnetic stirring device was used to keep the radioactive antimony in suspension. In the first experiments radioactive antimony was added to the peroxide solution in A to test for the production of radicals on running through the furnace. The conditions are then similar to those in the static experiments except that the period of heating is much less. If decomposition occurs reaction with antimony will take place irrespective of the correctness of the assumption regarding the life period of the radicals.

In the apparatus used the capacity of the bulbs A and B was 250 cc. The diameter of the reaction tube was 3.75 mm., the size of the constriction in this tube near B was adjusted to give an average flow rate of about 1 cc. per second with the tube horizontal and 200 cc. solution in A. To the 1% solution of benzoyl peroxide in A was added a quantity of finely divided antimony such that it was all held in suspension on rapidly stirring the mixture. After the air in the apparatus had been displaced by nitrogen, bulbs A and B were corked, and with B tilted above A, the antimony was brought into suspension whilst the furnace was warming up. B was then quickly lowered to bring the reaction tube horizontal whereupon the antimony suspension ran through from A to B. When most of the antimony had settled a sample of the solution was withdrawn from B and filtered by suction through a No. 4 sintered glass funnel. The radioactivity of 20 cc. of the filtrate was determined as in the static experiments . The filtrate was returned to the apparatus, any loss of solvent being made up, and the reactants were run into A in preparation for the next experiments.

4. Results.

Table 7 (overleaf) shows the results obtained when the potential across the furnace was varied to alter its temperature.

TABLE 7.

Run.	Volts.	Radioactivity in 200 cc. solution	Increase
1	14	450 c.p.m.	450 c.p.m.
2	17	930 "	480 "
3	20	1330 "	400 "
4	38	110 "	-1220 "
5	40	60 "	-50 "
6	23	70 "	

This appeared to indicate that there is an optimum temperature above which decomposition of the antimony compound occurs together with de-activation of the antimony surface -- possibly by oxidation. A test with alcoholic potassium iodide solution showed that the peroxide content of the solution had not been exhausted. The antimony was separated and used with a fresh volume of peroxide solution. The experiment was repeated but no appreciable attack on the antimony occurred. When the antimony was replaced by a fresh sample the effect was repeated -- Table 8. (overleaf).

TABLE 8.

Run.	Volts.	Radioactivity in 100 cc. solution	Increase
1.	20	200 c.p.m.	200 c.p.m.
2	25	535 "	335 "
3	30	70 "	-465 "
4	25	65 "	
	Antimony replaced.		
5	20	450 "	385 "
6	22.5	700 "	250 "
7	25	1150 "	450 "
8	27.5	500 "	-650 "
9	30	515 "	
10	30	565 "	

Results were not invariably of this form. Data obtained for a different furnace is given in Table 9. (overleaf).

TABLE 9.

Run.	Volts.	Radioactivity in 100 cc. solution	Increase
1	28	90 c.p.m.	90 c.p.m.
2	29	255 "	165 "
3	29	450 "	195 "
4	29	255 "	-195 "
5	30	800 "	545 "
6	30	1370 "	570 "
7	31	1650 "	280 "
1	30	80 "	80 "
2	30	320 "	240 "
3	32	210 "	-110 "
4	35	515 "	305 "

These results, though very rough and erratic, showed that under these conditions a measureable radioactivity could be obtained in the peroxide solution. The next step was to discover if any radioactivity appeared in solution when a peroxide solution (free of antimony) was run through the reaction tube into a suspension of antimony in benzene in bulb B. To make the conditions as favourable as possible the solution in A was preheated to about 75°. No cooling jacket was used so that the furnace could be moved right up to the inlet to B. The flow rate was increased to 7 cc./sec. (60 cm./sec.) and the temperature of the furnace was increased so that the solution was just below boiling point on leaving it.

It was not possible to obtain any positive results in the time available.

CHAPTER FIVE.

CHAPTER FIVE

CONCLUSION.

1. Summary of results obtained.

Three radioactive indicator methods are described for measuring directly the lifetime of free radicals in solution. By a so-called "static method" the values of 5 and 8 sec. have been obtained for the approximate lifetime of the radicals formed in the decomposition of dibenzoyl peroxide in boiling benzene solution.

Negative results were obtained with two different flow methods based on the mirror technique.

A major reaction has been shown to occur between antimony and lead tetra-acetate decomposing in chloroform solution and with benzoyl peroxide decomposing in benzene solution. There is very little reaction between antimony and benzoyl peroxide decomposing in ethyl alcohol solution, and the reaction may be ascribed to the action of benzoic acid produced by decomposition of the peroxide and not to a free radical.

The use of radioactive antimony has indicated the formation in small yield of a soluble antimony compound by reaction with phenylbenzyl ether decomposing in quinoline solution. Here the intermediate responsible may be the benzyl radical.

For definite results to be obtained by the use of the radioactive indicator method in the liquid phase, further improvements of the technique will be required.

2. Suggestions for further work.

The failure of the flow experiments is considered to be due to the use of an inadequate experimental technique. The inhibitory effect of dissolved oxygen (14,53) has been neglected and it is believed that better results would be obtained with a more efficient detector of the radicals produced from a solution free of inhibitors.

In order to detect the very small concentration of free radicals obtained in the fast-flow experiments an indicator is required having a much higher specific radioactivity than the antimony used. Radium E is likely to be of use in this respect.

In the slow-flow experiments the use of an antimony suspension as a detector is rather clumsy and, had time permitted, antimony would have been replaced by radioactive iodine (^{131}I). The iodine can be obtained with high specific radioactivity from uranium fission products and since it will dissolve in benzene its efficiency and sensitivity as a detector should be much superior to antimony. The quantity of radicals reacting with iodine would then be obtained by the isotopic dilution method of Rittenberg and Foster (71). After a run, excess iodine would be removed by silver powder or sulphur dioxide water, and phenyl iodide added to act as carrier for the radioactive compound formed by reaction of the radicals with radioactive iodine. The mixture would be fractionally distilled and the radioactivity of the pure phenyl iodide fraction determined.

It is suggested that the decomposition in benzene solution of lead tetraethyl and phenyl acetyl peroxide should provide reaction systems in which radicals of comparatively long life take part, with good prospects of the successful application of the modified mirror method. Attention has already been drawn to the lead tetraethyl system (p.74). The thermal decomposition occurs at an inconveniently high temperature but the photochemical decomposition should present no great difficulty given a light source of sufficiently high intensity. Hey and Walker have shown that only dibenzyl is obtained from the decomposition of phenyl acetyl peroxide ($PhCH_2COO.OOCCH_2Ph$) in benzene solution (43). This is in accord with earlier observations of Kharasch, Kane and Brown (45). The benzyl radicals produced by the decomposition of the peroxide at 30^o are incapable of reacting with the solvent and disappear by dimerisation and will therefore have a comparatively long life.

The elucidation of the nature of the white antimony compound formed by reaction with benzoyl peroxide is necessary before the value for the average life obtained in Chapter 3 can be assigned to either the phenyl or the benzoate radical.

It is considered that the measurement of the lifetime of some free radicals in solution will be possible if the methods described in this thesis are developed.

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Abstract of the thesis entitled "Radiochemical Studies on Free Radicals".

In 1936 Leighton and Mortensen first used radioactive indicators to increase the sensitivity of the mirror method of Paneth and Hertzfeld for detecting free radicals in a gas stream. In the present work, ethyl radicals in the gas phase were allowed to react with a mirror of bismuth containing radium E. The use of a special counting technique enabled the distribution of radioactivity along the length of the mirror to be measured. By this method the length necessary for complete elimination of free radicals in the gas stream was determined directly. Theoretical calculations of Paneth and Hertzfeld have thus been confirmed experimentally by a more direct method than that of the guard mirror technique used by them in 1931.

Various methods were tried to obtain an estimate of the life-time of free radicals in solution. Finely divided radioactive antimony was found to react readily with benzoyl peroxide decomposing in boiling benzene solution with the production of a soluble antimony compound.

If it is assumed that a radical approaching within a distance L of the antimony surface reacts, there exists a reaction volume -- L x surface area of antimony -- which is related to the total volume of reactants in the same way as the quantity of radicals reacting with antimony is related to the total quantity of radicals produced. The average life t of the radicals is the time taken for them to diffuse through the distance L, and is related to the diffusion coefficient D as follows:

$$D = \frac{L^2}{2t}$$

The surface area of the antimony in suspension can be obtained from a size-frequency analysis, and the number of radicals reacting with antimony by measuring the radioactivity of the solution. Under the assumption of a plausible figure for D, a value of about 5 sec. was obtained for t by this method.