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THESIS

presented for the degree of
Doctor of Philosophy

by

J.R.Richards, M.Sc., A.A.C.I.,

entitled

PHYSICAL PROPERTIES OF FREE RADICALS,

being an account of the work carried out at the
Londonderry Laboratory for Radiochemistry,
Durham Colleges in the University of Durham,
during the period 1948-1953, under the
direction of

Professor F.A. Paneth, Ph.D., F.R.S.

August,1953.

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PREFACE

For more than twenty years it has been recognised that the free aliphatic radicals play an important part in many reactions. A large amount of experimental work has been done, principally on vapour phase reactions, where their presence is much more easily detected. The major types of reaction in which they occur are now known, and there is general agreement on the mechanisms by which they are formed and react to yield the final products. A not inconsiderable amount of information has also been gained about the energetics of these processes.

At the same time, attempts have been made, on theoretical grounds, to calculate the properties of these radicals. Thus, for example, if such quantities as their entropy and heat of formation could be calculated, it would then be possible to predict the course of radical reactions which are not easily accessible by direct experimental methods. Attempts have been made in this direction (1,2). One piece of information required in these calculations, as well as being of interest for its own sake, is the spatial configuration of the radical.

It should, in principle, be possible to predict this by means of wave-mechanical calculations. In practice, however, the mathematical difficulties of a rigorous treatment are almost insuperable, except in the very simplest of cases, and some form of approximation is required. Conflicting conclusions have been drawn from these studies. Until quite recently, the general opinion has been that the free methyl radical is flat, with the carbon atom in the plane defined by the three hydrogen atoms, and the three C-H bonds at 120° to each other. There have, however, been contrary views expressed from time to time, and more recent theoretical treatments have suggested that, although the methyl radical is undoubtedly flatter than the CH_3- group in methane, it is not completely planar.

It is generally accepted that any "heteronuclear" bond must have a small electric dipole associated with it. If this is so, it might be expected that, if the radical were not planar, it would have a net dipole moment. On the other hand, the three C-H electric vectors would cancel out in the planar model. It has been suggested (3,4) that an experiment designed to test this point would be of considerable interest.

The work to be described in the following pages was carried out with this end in view. The project is one which contains many pitfalls, with the result that an answer has not yet been obtained. It is considered, however, that the possibilities of improvement in the technique described are by no means exhausted.

Chapter I is devoted to a general review of the developments in free radical studies, with the emphasis on methods of production and detection, followed by a short account of the

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CHAPTER I. INTRODUCTION

FREE RADICALS

An important consequence of the rise of chemistry to the status of an exact science, following upon the advent of quantitative methods of measurement, was the evolution of the concept of the radical - that is, any group of atoms which preserves its identity throughout a series of chemical reactions. Although this definition covers groups which contain no carbon atom, and are therefore to be classed as inorganic, by far the greatest number lies in the field of organic chemistry, as a result of the well known stability of the carbon to carbon bond. In this discussion we shall restrict ourselves to a very small corner of this latter field.

The many early attempts (see refs. 5,14,15) to isolate these radicals proved, without exception, to be abortive and, in the latter part of the last century, were abandoned as the increasing weight of available evidence pointed to the truth of the postulate that the carbon atom is invariably tetravalent. This postulate, together with the additional one that these form "valency bonds" were distributed tetrahedrally in space, succeeded so well in interpreting the known facts, and gave such a sound basis for the development of structural models, that it came to be accepted that it was a fundamental condition for stability in organic molecules. On this basis the independent existence of a free radical, such as methyl, CH_3, or ethyl, $CH_3.CH_2$, was manifestly impossible.

Thus it came as a great surprise when Gomberg (6), in 1900, published his results which indicated, from chemical evidence, that the triphenylmethyl radical was capable of independent and continued existence in solution. Several years later (7), he was able to show that it was present in amounts sufficiently great to have an appreciable effect on the apparent molecular weight of solutions of hexaphenylethane, from which it is derived by dissociation.

A great deal has been discovered about radicals of this type, which are aromatic in character, and it would appear that the principles underlying their stability are by now fairly well understood (8,9,10,11).

They are mentioned here, however, only because they provided the first clear evidence that molecules containing "tri-valent" carbon were capable of relatively stable existence.

Very soon afterwards suggestions began to appear that the corresponding free alkyl radicals might also be capable of a transitory existence, although it was recognised that they may well be very reactive.

Bone and Coward (12), for instance, in 1908, suggested that free radicals of this type, including free methyl, could help to explain the processes taking place in the vapour phase pyrolysis of hydrocarbons. They were, perhaps, the first to do so. Likewise, H.S.Taylor (13), at a meeting of the Faraday Society in 1925, suggested that these radicals might be taking part in the reactions induced in gases by light quanta.

Attempts to establish their existence by direct methods, however, proved fruitless until 1929, when the first of a series of papers was published by Paneth (14) and his co-workers, which proved beyond any doubt that free methyl and free ethyl (15) did exist, and provided a method of detecting and identifying them. In these experiments the radicals were produced by the pyrolysis, in a stream of carrier gas at relatively low pressures (1-3 mm.Hg.), of the corresponding lead tetra-alkyl compound, $Pb(CH_3)_4$ or $Pb(C_2H_5)_4$. Attempts to produce the higher aliphatic radicals by this method proved unsuccessful (20). Compounds attributable to methyl or ethyl radicals were isolated in all cases, with the single exception of benzyl, which was successfully prepared by several methods (20) and detected by the mirror method.

PRODUCTION

The publication of these results resulted almost immediately in an ever increasing flow of papers in which free radicals were postulated as intermediates in a variety of reactions taking place in the gas phase and in solution (8,21,22,23,27). At the same time the mirror method of detection was successfully applied in attempts to confirm that they were, in fact, present in the reactions as postulated. These reactions can be classified into three main types.

1. Pyrolytic Reactions.

Most organic compounds will decompose into simpler products if heated to a sufficiently high temperature. This had been known for quite some time. By 1933, not only were the major decomposition products and their relative proportions known for a considerable number of compounds, but sufficient kinetic evidence had been accumulated to make possible an estimation of the dissociation energies of a number of bonds (23).

As he and his colleagues had been able to demonstrate (22), by the use of Paneth's mirror technique, that methyl radicals were present in thermally decomposing vapours, F.O.Rice (24) was enabled to put forward a reaction scheme which was consistent, in large measure, with the proportions of product found by experiment. This involved, firstly, the formation of radicals by the rupture of a carbon to carbon bond, and their subsequent reaction with other molecules present, or with each other. If these subsequent reactions resulted in the formation of more radicals, then a "chain" would result. Although this scheme has had to be modified in the light of more recent knowledge, the basic ideas are still recognised as valid.

Among other compounds which were shown at this time to yield radicals on heating were azomethane (25) and methane (26).

2. Photolytic Reactions.

The study of these reactions had its origin in an attempt to explain the absorption spectra observed when electromagnetic radiations were passed through the vapours of many substances. It was known that, for wavelengths longer than a certain value which can now be associated with the "strength" of a particular bond (27), the spectrum often showed a series of bands which, in the simpler molecules at any rate, could be assigned to definite changes in the energy states of the molecule. In other cases, or at shorter wavelengths, a region of continuous absorption could be observed, which could now be associated (27) with the splitting of a covalent bond in the molecule. The resulting fragments could well be free radicals - that is, molecular fragments carrying no net charge, in which not all the carbon valencies were satisfied.

This postulate received direct experimental confirmation by Pearson (28), who used the mirror technique to show that free methyls were present when acetone was irradiated with ultraviolet light.

These two fields of study are now recognised to be closely related, in that they both involve the splitting of the molecule into two initial fragments. One of these fragments may be unstable and decompose further. Both may be, and often are, very reactive and disappear very quickly either by attacking neighbouring molecules, by combining together to form the final products, or, if unstable, partly by a process of internal re-arrangement. The decomposition of many substances has been investigated under both sets of conditions.

Careful quantitative study has shown, however, that radicals are not necessarily produced in all cases. Some decompositions, indeed, proceed at the same time by two parallel reactions, one involving radical formation, and the other, molecular re-arrangements (29).

3. "Sodium Flame" Reactions.

At about the same time that Paneth and his co-workers were making their first discoveries in this field, Polanyi had become interested in the study of the theory of chemical reactions (30). Since a "three body" interaction is much more amenable to exact calculation than the more usual "double decomposition" reaction, which involves at least four atoms, he sought a reaction which would typify the simpler case.

His choice fell upon the reaction between a halogen gas and sodium (or potassium) vapour, which is known to be predominantly monatomic at only moderately elevated temperatures (31,32). This was the first of the sodium flame reactions.

As a logical outcome of this work, the vapour phase reaction between sodium and organic halides was investigated (33,34). Direct experimental evidence of the presence of radicals in this type of reaction was furnished by Horn, Polanyi, and Style (35). They reacted methyl chloride with sodium vapour, and passed the products of this reaction immediately into an atmosphere containing iodine. Methyl iodide was isolated in the products.

This type of reaction has since been used successfully by a great many investigators (36), both as a convenient source of radicals, and for quantitative data on the effect of structure on the "strengths" - that is, dissociation energies - of bonds in a molecule.

By its use it has been found possible to produce higher aliphatic radicals, such as propyl (37,38), in sufficient concentration to make possible a study of their rate of decomposition at various temperatures.

4. Electron Impact Method.

Electron impact methods such as are used in mass spectrometry produce, as a rule, ionised fragments. These cannot be classified as free radicals since, by definition, a radical has no net charge.

However, an ingenious method for the production of an atomic beam has recently been published (39). It might prove possible to apply it to the production of a beam of radicals.

A beam of N^+ ions was produced, collimated, and accelerated by the usual method. This beam was then bombarded with a second electron beam of sufficient intensity to neutralise most of the positive ions by electron capture. This process did not seem to affect the collimation already achieved. The ions not so neutralised were deflected by suitable electric and magnetic fields. The resulting beam of neutral atoms was claimed to have a much higher intensity than that obtained by the normal effusion method (see Chapter II).

DETECTION

This review must of necessity be very brief, because of the large amount of work carried out in this field (40,41). For this reason, attention has been directed for the most part to the earlier publications which laid the foundations upon which most of the succeeding workers have built. It is proposed to conclude this experimental section with a summary of the methods available for the detection, or estimation, of free radicals.

CHEMICAL methods are the most popular, and can be classed, broadly speaking, into two main groups. We shall call these, for convenience, the direct or indirect methods.

Historically, the indirect method was the first, although its full significance was only realised when it had been established that free radicals did take part in vapour phase reactions.

This method is, in fact, an extension of the traditional methods of chemical kinetic studies, in which the course of the reaction is inferred from observations on the identity, and relative proportions, of the products of the reaction under different sets of experimental conditions.

Since radicals can react with almost every molecule with which they collide, the number of products resulting from even the simplest system is liable to reach bewildering proportions, if radicals are involved. This effect can be minimised if it is arranged that only a small proportion of the starting materials decompose. In this way the chance of interaction between radical and initial product, to form further products, is greatly reduced.

This can be achieved in one of two ways. If a static system is used, the heating, or the irradiation, is allowed to proceed for only a short time. The total pressure is observed at regular intervals during this period.

Alternatively, a continuous flow system is used. The reactants are made to pass quickly through the reaction zone, and the mixture of reactants and products is collected immediately afterwards in a cold trap.

In both methods, a complete analysis is subsequently carried out. From the information so obtained, it is possible to deduce which radicals must be involved, and also something about the kinetics of the process. Hence it is possible to obtain the activation energies of initial decomposition reactions and subsequent radical reactions in many cases (43).

Although accumulated experience makes it possible to reject some reactions as improbable when devising the reaction scheme, all possible reactions must be considered in the first instance. These would include reaction of the radicals with other radicals, with the starting materials, with product molecules, or with carrier gas if used. Very often some other substance is introduced into the system in order to study its reaction with the radicals. The possibility of decomposition or re-arrangement of the radicals, or of some re-arrangement reaction not involving radicals at all, must not be overlooked (8-11,29,40-42).

Thus it is obvious that great difficulties of interpretation can be associated with this method, and, although a lot of information about radicals may be obtained in this way, and even, by deduction, their concentrations may be estimated, objections may be raised about its reliability as an indication of their presence. It is possible, however, to devise variations of this method which will do this.

If the carrier gas is hydrogen, then it is possible, by the use of hydrogen enriched with deuterium, to isolate "heavy" methane in the reaction products. This could be taken as evidence for the formation of methyl radicals, and their subsequent reaction with the carrier (44).

In cases of chain reactions (24) involving radicals, the introduction of nitric oxide into the reacting mixture has been found to slow down the reaction rate to a considerable extent (45). At the same time the nitric oxide itself is slowly consumed, indicating that it reacts with the radicals, and thus "breaks" the chain.

The same effect can be obtained by the use of gaseous iodine (29,41) and the effect is used, in fact, as a test for the occurrence of a chain reaction involving radicals.

If radioactive iodine (37,38) is used, it is possible to detect very small quantities of combined iodine in the products and, by fractional distillation, to determine the identity of the product thus formed. This method gives, then, a direct indication of the presence and identity of the radicals and, at the same time, an estimate of the number formed. It is assumed, with some justification (29,35), that every collision of a molecule of iodine with a radical results in reaction.

This "inhibitor" method can thus be regarded also as an example of the direct method of detection. Direct methods of detection most commonly employed, however, are usually extensions of the original Paneth mirror technique.

In the original papers, mirrors of Bi, As, Sb, Zn, Cd, and S were used, as well as Pb (14-19). Subsequent workers have used these, and also a number of other substances, such as Te (20,28), Hg (22,23), Be (17), Se (20).

Rice and his co-workers used mercury (24) because the alkyl products, on reaction with mercuric halides, yielded compounds with well defined melting points. This was of considerable advantage for identification purposes.

Subsequent workers (37,46,47) have used radioactive mirrors, and followed their reaction with the radicals either by the detection of activity in the products (46), or by a direct observation of the decrease in mirror activity with time (37).

There is one further chemical method of detection which is worthy of mention. It has been known for many years that hydrogen atoms will reduce the white (or yellow) oxides of tungsten and molybdenum to a blue compound of indefinite composition. In 1949, Melville and Robb (48), in the course of an investigation of the reaction of hydrogen atoms with olefines, used tungsten, or more often molybdenum, oxide as a competitor with the olefine for the hydrogen atoms. In making their calculations they allowed for the possibility that free radicals, formed by the addition of one hydrogen atom to a double bond, could also turn the white oxide blue. A trial irradiation of mercuric dibutyl in the absence of hydrogen gas did, in fact, produce a blue coloration in the solid oxide.

From their calculations they were able to estimate, for a number of radicals, the ratio of their blueing effect to that of hydrogen atoms (k_R).

In no case reported by them was this ratio less than 0.3. In some cases it was much larger. It is of interest to note that complicated radicals seem to be more effective in this regard than simpler ones (49).

Of PHYSICAL properties of radicals used for their detection, two may be mentioned. The heat evolved (50) when radicals impinge on to a platinum surface has been used in an attempt to measure the intensity of free methyls in a beam. The sensitivity of this method increases with decreasing temperature, and it has been estimated to respond to about 10^{12} to 10^{13} radicals cm^{-2} sec^{-1} at liquid air temperature.

The other method is based on the possibility that the ionisation potential of a free radical is lower than that of any other molecule which may be present. Fraser (51), in 1933 was the first to suggest this as a possible method of detecting radicals in a beam, following upon the work of Estermann (52) which had been just previously published. The essence of this idea was to allow the beam to impinge on to a slit in a metal "cage", along the axis of which lay an electrically heated wire. If the potential difference between the box and wire is greater than the ionisation potential of the molecules entering, these will be ionised, thus providing an increased current from box to wire.

Under Fraser's direction, Jewitt (53) carried out some trials. They found that better results were obtained with organic compounds if the simple "Kingdon Cage" were replaced by an ionisation gauge. But even so the results showed quite a large "scatter".

Recent work with mass spectrometers brings out very clearly the difficulties associated with this method. In these instruments the positive ions are also produced by electron bombardment. But, because of the more refined arrangement, the conditions are more easily controllable. It is found (54) that the efficiency of the ionisation process depends on the electron energy, which in its turn depends on the potential used for accelerating the electrons.

If the intensity (B) of the ion beam, for a given mass number, is plotted as a function of electron accelerating volts (V), a curve of the type (a) shown in figure 1 is obtained.

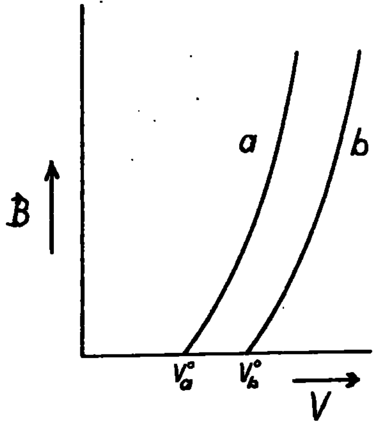


Fig. 1.

The voltage V_a^0, at which the curve is no longer distinguishable from the V-axis, is defined as the appearance potential, A_{R^+}, of the ion in question. This will be equal to the ionisation potential (I_{R^+}) if the ion is formed by the process

$$CH_3 \longrightarrow CH_3^+ + e^-.$$

If the process is $CH_4 \longrightarrow CH_3^+ + H + e^-$, more energy will be required, as a bond must then be broken, and

$$A_{CH_3^+} \geq I_{CH_3^+} + D(CH_3 - H).$$

One reason for the "tail" on the appearance potential curve is that the electrons are not mono-energetic. They are produced by emission from a hot filament and will, therefore, have a range of energies statistically distributed about a mean value. It is to be noted that these energies will be dependent on filament temperature.

At the lowest accelerating voltage, only the more energetic electrons will be able to cause ionisation. As these will be relatively few in number, the resulting ion current will be small. As the voltage is raised, the proportion of electrons with sufficient energy will increase more rapidly as the "hump" of the velocity distribution curve becomes involved.

Let us now consider the curve (b) where the appearance potential is only slightly greater than that of our first substance (a), and consider the implication of these two curves for Fraser's method of beam detection. Here we do not have any means of mass selection, and each substance in the beam will start making its contribution to the ion current as soon as the potential difference exceeds its appearance potential. It is clear that, if we wish to register (a) and not (b), the volts must be less than V_b^o. At this voltage the "sensitivity", that is, the amount of ion current per unit quantity of material, will be relatively small. The closer is V_b^o to V_a^o, the smaller will be the sensitivity attainable for (a).

To take an example, let us compare the ionisation potentials CH_3, 10.0_7 volt; C_2H_6, 11.7 volt; CH_4, 13.3 volt (55). All of these substances are likely to occur in a beam of methyl radicals. Thus, if we wish to detect only methyl, our collecting voltage must not be greater than 11.7 volt, or, to be on the safe side, rather less. It must, however, be as close to that value as possible, or else the sensitivity will not be very great. All variables, such as volts, heater current, and so on, will have to be closely controlled. It is desirable to keep the temperature of the wire as low as possible, in order to minimise thermal cracking of the molecules, which would tend to give a false impression of the radical concentration. On the other hand, a low filament temperature means low electron emission, and, as a consequence, a lower sensitivity to the radicals which are present. If Jewitt's figure (56) of 9.1 volt for the ionisation potential of methyl iodide is correct, then the presence of this substance in the beam would render the method useless for the detection of free methyl.

The first report on the application of the mass spectrometer to radical detection was published by Eltenton (57) in 1942. Subsequently (58), in a more detailed report on his exploratory experiments, he showed that it could be applied to the estimation of radical concentrations in a variety of reactions, including combustion. Although, at the present time, some caution is sometimes required in the interpretation of results obtained with this instrument (59), it is capable of giving results in agreement with those obtained by well tried methods (59a, 60).

It has the great advantages, moreover, of selectivity, given by the possibility of measuring the ion current due to only one species of ion, and of a great sensitivity which will be, no doubt, further increased within the near future. Even at the present time it is capable of yielding very useful information (61,62).

PHYSICAL PROPERTIES

Just as, in the experimental work, the study of radicals is but a specialised aspect of a much larger field of study, so the theoretical predictions of their properties arises almost as a by-product of the study of the whole field of molecular structure and properties.

The most fundamental of these studies is that of the distribution of the valency electrons in the molecule, an extension of the wave-mechanical theory of atomic structure. As is well known, this theory was developed in the early part of this century in order to explain the newly discovered phenomenon of radioactivity, and the results obtained from quantitative measurements on atomic spectra.

The mathematical complexities of the subject are so great that a rigorous treatment has been possible only in the very simplest of cases. Such a treatment has been carried out for hydrogen and helium atoms, the hydrogen molecule, and their ions. For atoms or molecules other than these, it has been found necessary to make some form of approximate treatment.

In the study of molecules two general methods of attack have been used (63). In the one, the valence bond method first developed by Heitler, London, Pauling, and Slater, the atoms constituting the molecule are first considered separately. Where necessary, appropriate combinations of atomic electronic orbitals, sometimes excited, are taken in such a way that each orbital which is to be involved in the formation of a bond contains only one electron. This process is known as hybridisation, and the resulting orbital is a "hybridised orbital". Any orbital, hybridised or not, is capable of containing two electrons with opposing spins. The next step is based on the postulate that the energy evolved in the process of bond formation is proportional to the degree of "overlap" of the atomic orbitals of the two electrons, one from each atom, forming the bond. Thus the most stable bond is that one in which the greatest degree of overlap is attained. The relative directions in space of the bond-forming orbitals and the degree of hybridisation are inter-related. Thus it is possible, by a long series of calculations, to calculate the most probable configuration of a given molecule, and at the same time the relative "energy" of a bond.

Qualitatively, the picture presented by this method of approach is one which is readily intelligible from the chemist's point of view, and its terminology has been absorbed, to a large extent, into chemical language.

The other method is an extension of the original theory of electron configurations in atoms. In this, the molecular orbital treatment first developed by Hund and Mulliken, the configuration of the nuclei is accepted from experimental data, and the electrons are "fed in" one by one. They are thus, in the first instance, not regarded as being restricted to the neighbourhood of any particular bond, but are treated as though capable, in principle, of being anywhere at all in the whole molecule. It is claimed (63) that this is the more appropriate approximation when it is intended to study such phenomena as ionisation potentials, or spectral terms.

Both methods, because of the very complexity of the systems under investigation, involve a considerable number of approximations and the answers obtained, in the earlier treatments in particular, tended to vary a great deal, according to the number and type of refinements applied. In principle, if the refinements are carried far enough, the same possible wave functions should eventually be derived from both methods. Both methods, however, still tend to rely rather heavily on experimental data, to which they are "fitted" in order to obtain the best possible answer (63,64,65).

Even so, the quantitative predictions in more recent treatments are usually of the right order of magnitude and, for a particular property in a series of related molecules, the trend predicted agrees with that observed experimentally. Properties which have been investigated by these methods include ionisation potentials and spectral terms (63,66,67), bond energies (64,65, 68), vibrational force constants (64), structure, and bond polarity (69).

We shall concern ourselves here only with the last two.

Dipole Moments. From a more empirical point of view the experimental measurement of molecular dipole moments has proved to be of great value, particularly in the elucidation of molecular structure (70,71).

It is assumed that each bond connecting unlike atoms in a molecule has associated with it a small electric vector, which might be regarded as arising from the unequal distribution of the electrons forming the bond, because of differences between the two atoms in their powers of attraction for the electrons (electronegativities). The resulting "charges" would, in general, amount to considerably less than unit electronic charge. The product of this "charge" times the distance between the nuclei is then termed the "bond moment".

In these empirical studies it is further assumed that the bond moment, for example, μ_{C-H} of the C-H bond, is a constant for that bond and independent of the nature of the adjoining bonds "attached" to the other three valencies of the carbon atom. From an analysis of measured dipole moments of a large number of compounds whose structures are known, it is then possible to assign a value for μ to every type of bond. It must be emphasised that this procedure can only at best be a first approximation, as it would appear from the theory that it is not correct to assume that a bond is un-influenced by its environment in the molecule (69,70,72,73). Nevertheless it has been found in a great many cases that molecular dipole moments, calculated for molecules of known structure by vectorial addition of these bond moments, agree quite well with the moment as actually measured.

On the basis of arguments such as these it is generally accepted that μ_{C-H} is small, and of the order of 0.4D. This figure is confirmed by independent estimates obtained, for instance, from infra red absorption measurements on the methyl halides (74).

If we consider the tetrahedral methane molecule, it can be shown by a very simple calculation that the vectorial sum of three of the C-H bond moments is equal in magnitude to, and is directly opposed to, the moment of the fourth bond. Thus methane has no net dipole moment, a result in agreement with experiment.

In free methyl, however, one would, on this basis, expect in general a net moment in the direction of the missing hydrogen. The magnitude of the moment would depend on the configuration. If the radical preserved the tetrahedral configuration of methane (bond angle $\widehat{HCH} = 109\frac{1}{2}^{\circ}$), its dipole moment would be 0.4D, if we accept this figure as the value for the C-H bond moment. It will be shown later that this is not considered a likely possibility. If, on the other hand, the radical is planar

($\widehat{HCH} = 120°$), the three C-H bond moments would "cancel out", and the total moment would be zero. For any intermediate configuration ($109\frac{1}{2}° < \widehat{HCH} < 120°$), a dipole moment $0 < \mu_{CH_3} < 0.4$ would be expected.

Although there were a few opinions to the contrary (see ref.69), the general consensus of the pre-war opinion was that the sign of the C-H moment was $C^- H^+$. That is, carbon was thought to be more electronegative than hydrogen.

In recent years, however, wave mechanical techniques have improved, and results obtained may be considered to be fairly reliable. Coulson (75), in 1942, published a fairly thorough calculation for the C-H bond in methane, and obtained the value $\mu_{C-H} = 0.4D$ in methane, in agreement with experimental values. His calculation indicated that the direction of the moment is $C^+ H^-$. Mueller and Eyring (76), in a more recent calculation, agree with this conclusion, although the magnitude of the moment obtained by them was smaller.

At the same time, Coulson thought his calculations indicated that the value of the C-H bond moment was a "constant for all normal chemical compounds, and independent of whether the carbon atom is aliphatic, ethylenic, or aromatic". In more recent calculations, however (98), he corrects this, and concludes that the value of μ_{C-H} will depend on the degree of hybridisation in the carbon orbital responsible for the C-H bond. Or, as Walsh put it in his most interesting paper, (72a), "The more s character in a carbon valency, the more electro-negative is the carbon atom in that valency".

More recent calculations (73,76) seem to bear this out.

It is of interest to notice in passing, that, although the process of hybridisation involves appreciable energy changes (65,98), and we speak of, for example, sp^2 and sp^3 types of hybridisation, which are of different energy content, it seems to be generally accepted that degrees of hybridisation between any two such definite states are equally possible.

The small amount of experimental evidence available since Gent wrote his review (69) would seem to offer some support to these general ideas. Thus Barrow and McKean, in a study of the infra-red absorption of methyl halides, deduced values of μ_{C-H} (74). These values tend to vary a little. This might perhaps be attributed to slight changes in hybridisation because of the varying electronegativities of the halogen atoms. They quote a mean value of 0.4D, and show that there is some slight evidence that the polarity is $C^+ H^-$. Kelly, Rollefson, and Schurin (77) determined μ_{C-H} in acetylene, and give its value as 1.05D. Cole and Thompson (78) have reported an extension of the work of Bell, Thompson, and Vago (81) on the analysis of the vibration bands in the spectra of halogen substituted benzenes. Their results indicate that, in benzene, the polarity is $C^- H^+$. The magnitude depends on the nature of the substituent, but, in as far as they can speak of an average, it seems to be in the neighbourhood of 0.6D. Barriol and Régnier (79) have calculated μ_{C-H} for the substances methane (0.35D), ethylene (0.60D for l_{C-H} = 1.06 Å, 0.62D for l_{C-H} = 1.09 Å), benzene (according to the value of the atomic polarisation accepted, between 0.67 and 0.36D), acetylene (0.9D). These results are tabulated for clarity.

TABLE I

Molecule	C valency towards H (72)	Walsh (72) postulates	Observed (D)		
CH	p	C^+ relatively large.			
CH_4	sp^3	C^+ small	C^+0.4(74)	.307(80)	.35(79)
C_2H_4	sp^2	C^- small			0.60 to 0.62(79)
C_6H_6	sp^2	C^- small	C^-0.4(81)	C^-0.6 (78)	0.36 to 0.67(79)
C_2H_2	sp	C^- larger		1.05(77)	0.9(79)

Gent (ref.69, p.388) records other values for ethylene which were obtained from spectroscopic evidence. They depend very markedly on the type of bending mode with which they are associated. On the same page he reports the results of calculations based on measurements of the dipole moments of polymethylene oxides. In such compounds one might expect essentially tetrahedral bonds and, in fact, he deduces a bond moment 0.4D ($C^+ H^-$). At the end of his review he records his expectation that the C-H moment in ethylene is likely to be close to zero. It is difficult to envisage how this can be reconciled with the results he quotes from spectroscopic data, and with the results of Barriol and Regnier.

Mulliken (65) claims that his calculations lead to the conclusion that the CH bond in the CH radical is not a pure p bond, but is hybridised to the extent that $\alpha^2 = 0.155$ (where α is defined by the equation $h_\beta = \alpha s + \beta p_\sigma$, h_β being the hybrid C orbital responsible for the bond in the radical). This leads him to the conclusion that H and C in this radical are almost equally electronegative. His treatment seems to be very approximate, and therefore, perhaps, is not to be relied on in this particular case. It seems to be at variance with most other contemporary ideas on bond polarities (c.f. ref.72).

To sum up, then, it would seem from the available evidence that the polarity is $C^+ H^-$ in methane and its simpler derivatives (predominantly sp^3 hybrids), and $C^- H^+$ in benzene and its derivatives (predominantly sp^2 hybrids). In acetylene it is larger numerically, and probably $C^- H^+$, if we accept Walsh's postulate, which does not appear to be altogether unacceptable (see, however, 73b).

As we now proceed to consider the little that has been published on the problem of the configuration of the free methyl radical, it would seem that the important point to bear in mind is that all properties of a molecule, in as far as they are related to the arrangement of the electrons, will thus be related to the degree of hybridisation. This certainly seems to be the case for molecular configuration (83), as will be apparent from a study of Table I. For methane, we know, is tetrahedral; in ethylene the two adjacent C-H bonds are at an angle of approximately 120° to each other, and the four hydrogens are coplanar; and in acetylene the two hydrogens lie on the line through the two carbon atoms.

Thus we would expect that a planar methyl radical would have sp^2 hybrid bonds, with a pure singly occupied p orbital at right angles to the plane, whereas a non-planar radical would presumably involve C-H bonds somewhere intermediate between sp^2 and sp^3, with the "centre of gravity" of the remaining singly occupied orbital at the apex of the pyramid, and directed away from the hydrogens.

On this basis the value and sign of μ_{C-H} itself would depend on the configuration of the radical, and would almost certainly be not greater than 0.4D. Indeed, for a configuration somewhere intermediate between tetrahedral and trigonal, it would seem that μ_{C-H} is likely to be smaller than this value, with a sign depending on whether the radical is nearly planar, or nearly "tetrahedral", (c.f. ref.72a, p.22).

In the absence of a detailed calculation it is rather difficult to predict the effect this would have on the dipole moment of the radical as a whole, since the singly occupied orbital may well also have some contribution to make. At first sight, however, it would appear that even more than the usual amount of caution would be needed in drawing any conclusions about the configuration of the radical if a determination of its dipole moment yielded an answer indistinguishable from zero. On the other hand, it would seem that positive evidence that it has a moment, however small, could be taken as evidence that, whatever its configuration, the radical is not planar.

Configuration. Experimental evidence about the structure of free methyl is meagre, and at best very indirect. One thing that does seem quite certain, however, is that it differs from the configuration of the methyl group in methane (64,82).

Analysis of the energetics of the successive removal of hydrogen atoms from methane is hampered by the uncertainty about the latent heat of vaporisation of carbon. Despite this uncertainty it does seem to be fairly generally accepted that the energy of dissociation $D(CH_3-H)$ of methane, to give methyl plus hydrogen, is smaller than it might otherwise be because there is an evolution of energy associated with the "re-organisation" of the resulting methyl radical. Glockler (84), however, infers that there is little reorganisation energy involved in the formation of the free ethyl radical from ethane. It might be expected that these two radicals should be very similar in their behaviour; although Coulson (85) infers that a resonance effect is possible in free ethyl, but not in free methyl.

Further arguments about the expected configuration have been based on the results obtained with organic reactions in solution (see ref.40, p.175). The argument is as follows:

Suppose the reaction to be investigated is, for example, of the type

$$HCR_1R_2R_3 + Cl_2 \longrightarrow ClCR_1R_2R_3 + HCl$$

It is assumed that this takes place via the reaction of atomic chlorine with the substituted methane. The starting material is optically active.

Suppose, further, that the reaction takes place through the initial formation of the radical $\cdot CR_1R_2R_3$ and HCl. Then, if this radical is planar, it can react with molecular chlorine from either side of the plane, to yield racemic product and a further chlorine atom. If the radical, on the other hand, is not flat, or if the reaction goes directly without radical formation, an optically active product would be expected.

In the case quoted by Waters the product was racemic. This, then, would imply that complicated radicals such as these are planar. In other examples, however, the opposite result has been obtained (86).

In any case, it is not at all safe to assume that results obtained for these radicals have any bearing at all on the configuration of the free methyl radical itself.

At the Faraday Society Discussion on the Labile Molecule in 1947, Walsh (72a) argued that free methyl must be planar by the application of his ideas on electronegativity to some results obtained by Bak (87), who deduced that the CH_3 group in methyl chloride is flatter than the same group in methane. This result seems to be open to question, however (88).

Until quite recently no one seems to have treated the matter very thoroughly from the theoretical point of view, although quite a number of attempts have been made to obtain an answer by semi-qualitative arguments. Van Vleck (89), and Voge (90) came perhaps the closest to a thorough calculation, although they both were careful to point out that their treatments were only approximate. Both came to the similar conclusion that the $\widehat{HCH}$ angle in free methyl is greater than the $\widehat{HNH}$ in ammonia, and that the radical "may conceivably even be plane" (Van Vleck).

In even less rigorous arguments, however, Mulliken (67) guessed that methyl is probably pyramidal like ammonia, and Lennard-Jones and Pople (68) content themselves with the conclusion that it "may be planar or very nearly planar". Penney (64) also used a similar sort of argument in deciding on a planar configuration.

Despite this uncertainty, however, most authors seem to have based their arguments on the planar model (1,2,73b,85,91,92,93), although some have been rather more non-committal (94,95).

Bryant (2), however, although he used the planar model for the calculation of the molecular entropy of free radicals, pointed out that the adoption of a pyramidal model would not affect his answer materially. He quoted Kistiakowsky as having expressed the opinion that methyl might "be closer to tetrahedral".

Within the last two years, theoretical opinion seems to have been tending towards the idea that the radical is not planar.

Linnett and Poë (4) concluded, again on the basis of wave-mechanical argument, that they would expect the $\widehat{HCH}$ angle to be intermediate between 109½° and 116½°, and Walsh (96), in a preliminary report of some calculations which might appear to have been fairly rigorous, claims that "AH_3 molecules containing six valency electrons should be planar in their ground states, pyramidal in their first excited states. AH_3 containing more than six valency electrons should be pyramidal in their ground states".

Luft (97), in a discussion, quotes the $\widehat{HCH}$ angle to be 113 ± 4° in free methyl, but does not mention a source for this figure.

It would seem, then, that there is a fair chance that the free methyl radical may be pyramidal. Since this would lead us to expect it to have a dipole moment, it would appear that, as was suggested by Fraser (3) and Linnett and Poë (4), an experiment designed to test this point would be of value.

A development of the ideas summarised in this chapter, however, would lead us to expect that the looked for moment is probably very small, say of the order of 0.1D. Therefore the method used must be capable of detecting very small moments indeed.

CHAPTER II. INTRODUCTION (CONTINUED)

MOLECULAR BEAM METHOD

Two important points must be kept in mind when deciding on the method to be adopted in this investigation.

Firstly, there is the expectation that the moment will be small.

And secondly, the radical is very reactive. The result of this is that the concentration of radicals will be small, even under the most favourable conditions - relatively low total pressure in the gas phase, and complete decomposition of the parent substance. Thus Forsyth (99), in experiments on the pyrolysis of acetone (0.6 mm.Hg. pressure at the source), estimated that there were 1.94 10^{-8} g/lit of methyls at a distance of 12.35 cm. from the furnace. This would correspond to a pressure of some 2.10^{-5} mm.Hg. at that point. The pressure at points closer to the furnace would be somewhat higher than this. Gomer and Kistiakowsky (100) irradiated both acetone and mercury dimethyl with ultraviolet light. They estimated that, under the strongest attainable conditions of illumination, the methyl concentration was about 10^{-12} mole/cc in a total gas concentration of 10^{-7} mole/cc, that is, about 10^{-5} mm.Hg. in a total pressure of about a millimeter or so of carrier gas. Lossing and Tickner (60) attained partial pressures of methyl, resulting from the pyrolysis of mercury dimethyl at high flow rates, which they estimated to be of the order 10^{-3} to 10^{-2} mm.Hg. The conditions in their experiments seem to have been especially favourable, and this, then, would seem to be about the maximum concentration attainable, using methods at present available.

It would thus seem unlikely that the standard methods of dipole moment estimation - by means of dielectric constant or refractive index measurements (101) - would be of much avail for this class of molecule, since much higher pressures than these are required in these methods (cf. 77, 80).

Dipole moments are sometimes determined by analysis of infra-red absorption spectra (cf. 74, 78). The same objection applies to this method also. And here, in addition, the great multitude of spectral lines arising from the other much more abundant molecules present would make the sorting out process almost impossible. Similar objections may be applied also to the possible application of micro-wave techniques, and to other less used methods such as electrostriction (ref. 101, p.38).

It would seem, then, that there is only one method which could be of use in the present investigation. That is the electric deflection of a molecular beam, first used for the analogous magnetic case by Gerlach and Stern (102), and developed in a series of investigations by Stern and his co-workers in Hamburg during the succeeding years. The technique has been fully described in a mongraph by Fraser (103) (see also ref.104).

PRODUCTION OF BEAM

Although the underlying principles of molecular beam production are very simple, in practice it is found that considerable attention to fine details is necessary for success in the technique. These conditions were clearly set out by Stern (105) in 1926.

In bare outline, the apparatus consists of a vacuum system divided by two partitions into three separate compartments (fig.2), which we shall call the source, O, collination chamber, C, and target chamber, T. In each partition there is a narrow slit, or aperture, S_1 and S_2 respectively. These slits are carefully aligned and are the only means of interconnection between the three chambers. C and T are evacuated independently by means of fast diffusion pumps. For most purposes separate pumping of the source is not necessary, as its volume is usually small compared with that of the other two chambers.

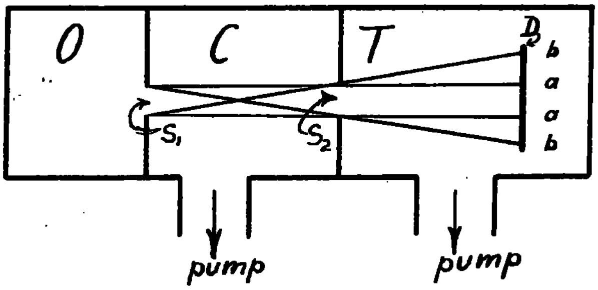


Fig. 2.

If the substance with which the beam is to be formed is not already in the vapour state, the source must be heated. Since this was necessary in all the original experiments, it was often referred to as the furnace ("Ofen") chamber (105).

Subject to the condition that the mean free path of the molecules in O is not less than the width of the source slit S_1 (condition for molecular effusion), molecules passing through the aperture into C will continue in a rectilinear path in this chamber until they are deflected from this path by collision with other ("stray") molecules, or with the walls of the chamber.

For an aperture of negligible "thickness" (i.e. slit defined by very sharp jaw edges), the angular distribution of molecules in the "pencil" issuing into C is governed by a cosine law, similar in form to the intensity distribution of light emitted from a point source. An increase in the thickness of the slit seems (ref.103, p.17) to have little or no effect on the intensity along a line from the centre of the slit, and normal to its face, but results in a marked diminution of the intensity at all other angles.

Thus, since the width of S_1 is usually of the order 0.01 to 0.1 mm. (the "length" of a rectangular slit, which may be at least 100 times greater, does not seem to be of importance in this regard), the pressure in O must not be greater than, say, 1 mm.Hg. to 0.1 mm.Hg. Scattering of the "pencil" of molecules in C is kept to a minimum by ensuring a good vacuum in this section. The limiting condition is obviously that the pressure must be so low that the mean free path, corresponding to the pressure of the stray molecule, is greater than the distance S_1 S_2.

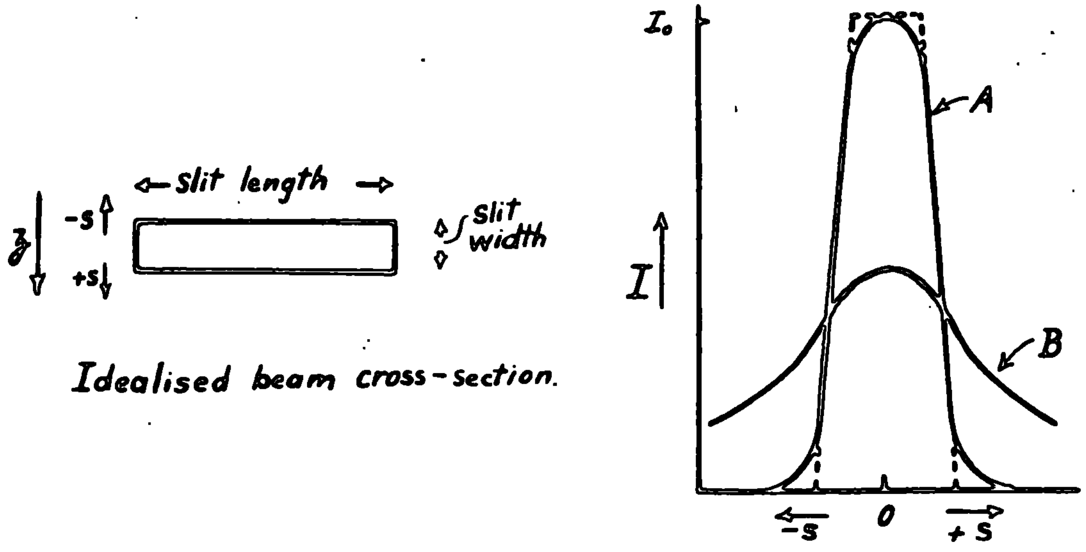
For a distance $S_1 S_2$ of 9 cm., the pressure in C must not be greater than about 10^{-4} mm.Hg. As was pointed out by Knauer and Stern (106), it is desirable to have the pressure considerably lower than this limit. They quote a maximum pressure of 5.10^{-6} mm.Hg. for a distance of 12 cm. This can be achieved a) by fast pumping, and b) if the molecules are easily condensible, by the introduction into the vacuum of a sufficient area of surface which is cooled to a temperature at which the vapour pressure of the substance is negligible.

Slit S_2, the <u>image</u> or <u>collimator slit</u>, permits the central portion of the "pencil" to pass into chamber T. Thus a beam is formed in T, and it finally impinges on D, the <u>detector</u>, or <u>target</u>. As the distance S_2 D is usually greater than $S_1 S_2$ by a factor of about two, the limiting pressure conditions apply in T even more stringently than in C.

The analogy between this system and a system of slits used for defining a beam of light is very marked. In both cases the beam is not of uniform intensity across its cross section, but is strongest at the centre, and falls off towards the edges. Thus, with molecular beams also, we speak of the portion aa (fig.2) at D as the "umbra", and the portions ab as the "penumbra".

The dimensions of the beam (umbra and penumbra) at D may be calculated simply from the known geometry of the arrangement.

<u>Intensity</u>. For a beam of rectangular cross section, as defined by slits of that shape, a plot of intensity (molecule



Idealised beam cross-section.

a

b

Fig. 3.

cm.$^{-2}$ sec.$^{-1}$, measured at the detector) as a function of distance across the width of the beam (z in Fig.3a) would thus be trapezoidal in the ideal case (dotted lines, fig.3b). In practice the intensity distribution is as depicted by the full line (curve A in fig.3b).

The intensity at the maximum, i.e. directly in line with the centres of the slits, may be calculated from the expression (104, 105, ref.103, p.14)

$$I_0 = \frac{N}{(2\pi RMT)^{1/2}} \cdot \frac{pa}{\pi r^2} \quad \text{molecule cm.}^{-2}\ \text{sec.}^{-1} \qquad (2.1)$$

where p is the source pressure, in dyne cm.$^{-2}$, a the source slit area in cm.^{2}, r the distance in cm. from the source slit and the other symbols have their usual significance. Or, if p is expressed in the more usual terms of mm.Hg., and constants are collected together, the expression may be written in the form

$$I_0 = \frac{pa}{(MT)^{1/2} r^2} \cdot 1{\cdot}12.10^{22} \quad \text{molecule cm.}^{-2}\ \text{sec.}^{-1} \qquad (2.2)$$

For a numerical example, consider a beam of air molecules (M approx. 29), at a source temperature of 550°K., source pressure 0.5 mm.Hg., slit dimensions 0.05 mm. x 3 mm. ($a = 1.5.10^{-3}$ cm.^{2}), and a distance $S_1D = r = 26.6$ cm.

We obtain $I_0 = 9.6.10^{13}$ molecule cm.$^{-2}$ sec.$^{-1}$

It is to be noticed that the intensity falls off with the square of the distance from the source slit, a further similarity with the optical case.

Detection. This intensity is quite small. This is made clear when it is expressed as the "pressure of beam" – that is, the change in momentum of the molecules striking unit area of detector surface in unit time. As many of the orthodox methods of intensity measurement in molecular beam work consist of some pressure measuring device, this method of expressing beam intensity is instructive in that it gives an idea of the sensitivity which must be attained in the design of these devices.

For an example, let us round off the figure we obtained above for I_0 and call it 10^{14} molecule cm.$^{-2}$ sec.$^{-1}$. This is a typical value.

The molecules, although unidirectional, are moving in the beam with thermal velocities corresponding to the temperature in the source chamber. Thus we can write down the root mean square velocity, $\bar{C} = (3RT/M)^{1/2}$, where $R, T, M,$ are the gas constant ($8.31.10^7$ erg deg^{-1} mole^{-1}), absolute temperature (°K.) and molecular weight, respectively.

The mass of an individual molecule is M/N, where N is the Avogadro number ($6.02.10^{23}$).

Since, to a close approximation, all molecules in the beam will impinge normally on to D, the change of momentum of a single molecule on impact (assuming a perfect gas, i.e., elastic collision) will be of the order of $2(3RTM)^{1/2}/N$.

The total change of momentum per square centimeter per second due to the impact of the beam will be 10^{14} times this, and if we take once more $T = 550°K.$, $M = 29$ (to a close approximation, air or ethyl), and convert from C.G.S. units to mm.Hg., we obtain that the "pressure of beam" is of the order of 5.10^{-7} mm.Hg.

This is the pressure at the axis of the beam. It is desirable that the detector should be capable of measuring pressures at least one hundred times smaller - i.e. of the order 10^{-9} to 10^{-10} mm.Hg.

Pressures as small as this are much smaller than the overall pressures usually attainable in practice. However, if the manometric device is placed behind a third slit (<u>target slit</u>) it has been shown (ref.3, p.9; ref.103, p.34) that the whole scale of pressures to be measured can be raised by a factor of 10 for an "ideal" slit (no thickness), and by a further factor of at least 10 if the target slit is given "canal" form. Thus, in this latter case, the pressure measured by the manometer may be of the order of 10^{-5} mm.Hg., and differences of 10^{-8} mm.Hg. must be detectable. This is then quite possible.

Among the manometric devices which have been used for this purpose are hot wire gauges of the Pirani type (107, 108, 109) and the ionisation gauge (53). The McLeod gauge may be used for the permanent gases, although it has the disadvantage that it does not give continuous readings.

Other quantitative devices have been described from time to time (see, for example, ref.104). Of these we recall one (50) which has been applied to a beam of radicals. This measures thermal effects resulting from the condensation, and sometimes recombination, of the atoms or molecules in the beam on the target. The method has been used successfully for hydrogen atoms (110, 111). The heat of dissociation of molecular hydrogen is 103.3 Kcal/mole. For comparison, the heat of the reaction $C_2H_6 \longrightarrow 2CH_3$ is $\sim$ 85 Kcal/mole. It ought, therefore, to be possible to apply this method to the detection of a beam of methyls, if the intensity is sufficiently great (cf. ref.50).

In the early experiments (102, 106, 112, for example), "condensation" targets were used. These consist merely of some suitable flat surface which is held at a temperature sufficiently low for the rate of condensation to be large compared with the rate of removal of molecules, either by re-evaporation or by surface migration. Under the right conditions an image, of calculable dimensions, appears as the molecules condense. The "time of appearance" is taken to be linearly dependent on the reciprocal of the intensity. The sensitivity of the method is high, with experienced operators, and can be even further increased by the use of radioactive methods (113). It is not very suitable, however, for quantitative measurements of the intensity distribution in the beam, partly because surface migration takes place even at relatively low temperatures (cf. ref.103, p.90), and also because the personal factor, which varies from time to time even with the same operator, is so important in "time of appearance" measurements. The condition of the surface, also, seems to be important, and to vary from time to time in a not very consistent manner which, very generally, seems to depend on its previous history. The method is, however, very useful as a preliminary, qualitative, check on the technique used.

One other early type of detector is worthy of mention. This is the "chemical" target, a flat surface coated with some substance which reacts in a visible way (e.g. change of colour) with the beam material. One example is a surface coated with white molybdenum (or tungsten) oxide, which turns blue when hydrogen atoms collide with it (114).

DIPOLE MOMENTS

If the individual, electrically neutral, atoms or molecules which constitute the beam have a permanent moment, either electric or magnetic, they will be deflected from their rectilinear course in T (fig.2) when an inhomogeneous field (electric or magnetic respectively) is placed between S_2 and D in such a way that the inhomogeneity is perpendicular to the direction of the beam.

A small energy change is associated with the entry of the particles into the field. Thus the number of directions in space which they can take up with respect to the field direction is limited by quantal considerations. This is true whether the field is homogeneous or not. In the presence of an inhomogeneity there is a net force on the particles, which will suffer either a positive or a negative deflection in the direction of the inhomogeneity according to the directions they take up with respect to the field. These statements, so far, apply equally well to either the magnetic or the electric case.

The simplest example, and the one which was first investigated (102), is that of an atom with one unpaired electron. Because there are two possible spin states for this electron, the resulting magnetic moment can have only one of two possible orientations in a magnetic field. Both of these orientations are almost equally probable. If, therefore, an inhomogeneous magnetic field is applied across a beam of these atoms, it is to be expected that they would be deflected in equal proportions to each side of the position of the undeflected beam. Such, indeed, was found to be the case. Silver (102) and hydrogen atoms (114) were among the many atoms studied (see 103, pp.134 ff.).

The atoms in the beam are not of uniform velocity, but have a range of velocities distributed about a mean value according to the usual Maxwellian distribution law. The deflection suffered by an individual atom will depend on the time it spends under the influence of the inhomogeneity - that is, on its velocity. As a result the two resulting beams are each more diffuse than the original, undeflected beam. This effect would apply with equal force to molecules.

The distinct splitting of the beam can only be observed, however, with atoms.

For molecules the number of possible quantum states is immediately increased because of the contributions to the total energy of the rotation states. The effect now obtained when an inhomogeneous field is applied is a general symmetrical broadening of the beam, with a consequent diminution of intensity at the maximum. This has been observed both for the magnetic case with molecular oxygen (115), and for the electric case with a large number of molecules (e.g. ref.103, chap.VI; ref.112). Because of the symmetry of their structure, atoms can not have an electric moment. It has, however, been possible to observe a small asymmetric deflection of atomic beams in an electric field. This has been ascribed to their "polarisation". (cf. ref.3, p.65).

This electric polarisation effect, which is very small for most atoms, will in general be larger for molecules, although smaller than the deflection caused by the interaction of the inhomogeneity with the resultant of the permanent moment in the field direction. The resulting deflection, where present, is always in the direction of increasing inhomogeneity. Its magnitude will be dependent on the field strength.

Fraser (ref.3, p.54) quotes a figure for this induced moment of 5.10^{-22} E.S.U. (i.e., 5.10^{-4} Debye units) for a molecule of average polarisability in a strong field of 500 E.S.U. (150 kV cm.$^{-1}$). In the following discussion it will be seen that a moment of this order is smaller than even the most unfavourable case of a rigid "dumb-bell" type molecule. For the "symmetrical top" molecule, to which class belongs the free methyl, the resultant of the permanent moment is much larger, and the polarisation effect may be neglected in most cases (111). This is very convenient, for it means that it is not necessary to plot the complete peak shape every time for both the deflected and undeflected beams. Expressions have been derived which makes it possible to determine the dipole moment simply from the ratio of peak heights with and without the deflecting field.

For this it is necessary to use a quantitative method of intensity measurement. It is, however, possible to make an estimate of the order of magnitude of the moment by using the original type of detector. This is done by estimating the width of the deflected image, which is compared with that of the image for no field.

The actual form of the expression to be used in deriving the value of the moment from the experimental data is determined by two sets of conditions. The first is the geometrical arrangement of the electrodes which produce the inhomogeneous field - in particular, the relationship between the field direction and the direction of the inhomogeneity. The second is the geometry of the molecule itself - that is, the relative orientations of the axes of symmetry, the axes of rotation, and the moment axis of the molecule.

In making these derivations, most authors have simplified matters in the first instance by considering the deflection suffered by a single molecule in its path through the field. The expression is then generalised to take account, firstly, of the distribution functions, at the temperature of the experiment, of the energies of translation, E_t, and rotation, E_r, and of the orientation of the molecules with the field, ϕ; and secondly, of the actual cross sectional shape of the beam, which is treated up to this point as though it were of infinitely small width. It is then found convenient to express the result in terms of a parameter s_0 (or sometimes $\sigma = s/s_0$), where s is the deflection suffered by any given molecule, taking the centre of the undeflected beam as the origin, and s_0, the "normal" deflection, is the deflection suffered by a molecule in a particular state, often taken to be $E_t = E_r = kT$, $\phi = 0$ (116, also 103, pp.161 ff.). The ratio of maximum intensities $I(0)/I_0$ for the deflected beam, $I(0)$, and field free beam, I_0, can then be expressed as a function of s_0 (or σ), and, after some very lengthy arithmetic, it is possible to calculate the required moment μ.

Field Geometry. The effect of field geometry will be considered first.

In general terms we may note that, if a molecule, from any cause whatsoever, has an effective moment $\bar{\mu}$ in the direction of the field X then the change in energy which results when it comes under the influence of the field is $\Delta W = \bar{\mu} X$ and the components of the force acting on the molecule in three directions mutually at right angles will be

$$F_x = \bar{\mu}\,\frac{\partial X_x}{\partial x}, \quad F_y = \bar{\mu}\,\frac{\partial X}{\partial y}{}_y, \quad F_z = \bar{\mu}\,\frac{\partial X}{\partial z}{}_z.$$

In a homogeneous field, therefore, where $\frac{\partial X}{\partial x} = \frac{\partial X}{\partial y} = \frac{\partial X}{\partial z} = 0$, there will be no deflection.

It is often found convenient to arrange the axes of reference so that one of them, say the x direction, lies along the axis of the beam, and the other two are parallel to the boundaries of the rectangular slit. We shall consider the y direction to be parallel to the length of the slit (fig.3a), and the z direction to be parallel to the width of the slit. The deflection, s, will thus be in the z direction for maximum sensitivity.

Two types of field arrangement are found to be convenient. In the first, which is the electrical analogue of the original Stern-Gerlach magnetic experiments, the directions of X and $\partial X/\partial s$ are the same.

This can be achieved if the two electrodes are arranged as two coaxial cylinders whose axis is parallel to, and lies close to, the axis of the beam. The central cylinder must be of small radius, so that the inhomogeneity in its neighbourhood may be as great as possible. A fine wire has often been used for this purpose. Since only one side of the cylinder is used, it is clear that neither electrode need be completely circular in cross section. Indeed Scheffers (117) has used electrodes of cross section shown in fig.4. These are conveniently held in place by hard rubber (117) or amber (109) spacers, which also serve as insulation.

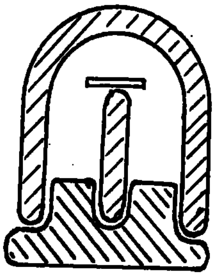


Fig. 4.

Arrangements of this type have the advantage that both X and $\partial X/\partial z$ are calculable from a knowledge of the voltage supplied, and the geometry.

The deflection S of a molecule, energy of translation E_t is given by the relationship

$$S = \frac{\bar{\mu}}{4E_t}\cdot\frac{\partial X}{\partial s}\cdot l^2$$

where l is the length of path in the field, or by

$$S = \frac{\bar{\mu}}{4E_t}\cdot\frac{\partial X}{\partial s}\cdot l_1^2\left(1 + 2\frac{l_2}{l_1}\right) \qquad (2.3)$$

where l_1 is the length of path in the field, and l_2 is the length of path between the point where the molecule leaves the field, and the detector.

The major disadvantage of this arrangment is that, in order to obtain a sufficiently high inhomogeneity the beam must be sent very close to the central electrode, which itself must, as has already been pointed out, have as small a radius as possible. This latter condition places a limit, because of "spark over", to the voltage which may be applied, and the former is objectionable because the inhomogeneity itself alters rapidly with the distance from the axis in this region. Thus, if a beam of long, narrow cross section is employed in an attempt to increase the intensity, the deflection is not uniform along the length of the "trace".

Scheffers, nevertheless, prefers this arrangement to that of the second type, which was first put forward by Rabi, for the magnetic case in the first instance (118). In this type, X and $\partial X/\partial s$ are at right angles to each other. This is achieved by the use of a parallel plate condenser, arranged in such a way that the beam passes symmetrically between the plates, which are rectangular in shape, and are arranged in such a way that the field between them is parallel to the length of the slits, and the axis of the beam makes a small angle θ with one edge (fig.5). In this particular case the axes of reference are often taken parallel to the condenser plate edges. Since θ is small, however, this is very nearly equivalent to the convention adopted above.

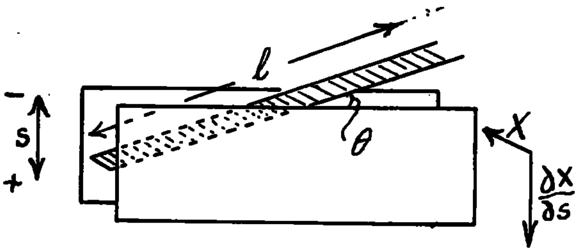


Fig. 5.

Subject to the condition that the beam traverses completely the region of inhomgeneity at the edge of the condenser, the deflection is given by

$$S = \frac{\bar{\mu}}{4E_t} \cdot \frac{\bar{X}\,l}{\tan\theta} \qquad (2.4)$$

where $\bar{X}$ is the "corrected", or averaged, value of the field over the path of the beam, and l is the length of the path in the field $\bar{X}$. It is assumed that the field continues right up to the detector. Provided that the gap is appreciably greater than the length of the beam cross section, the inhomogeneity is sensibly constant in the direction of the field. This confers the advantage that the deflection is uniform along the whole length of the resulting image. It has also been claimed for this arrangement that, since the distance between the electrodes, and the voltage, are relatively easy to measure accurately, it is much more reliable than the other for absolute measurements. However, the sensitivity of this arrangement is not so great as that of the other, for the smallness of θ which is possible is limited by the condition, mentioned above, that the beam must traverse the whole of the inhomogeneity. And the magnitude of the deflection depends quite markedly on the glancing angle when this is small. Moreover, small angles are not easy to measure accurately, and this then introduces a serious source of error.

A slightly more complicated system of three electrodes was proposed by McMillan (119) in 1931. It was claimed for this that the deflecting force would be independent of the position of the molecule in the field. It does not, however, seem to have received any further attention, possibly because of the technical difficulties involved in the construction of such a system.

It is therefore to be concluded that the first arrangement is to be preferred, particularly as only a small moment is to be expected.

Molecular Type. Next to be considered is the actual value of $\bar{\mu}$, which depends on the geometry of the molecule.

In the general case, for a polyatomic molecule, there are three moments of inertia, J_A, J_B, J_C, about three mutually perpendicular directions, and a dipole moment, μ. The quantum number for the total angular momentum is denoted by n. This has a component (quantum number q) in the direction of the moment μ. n has a component p in the direction of the applied field. The quantum restrictions are $-n \leqslant p \leqslant +n$, $-n \leqslant q \leqslant +n$.

The mathematical difficulties of a general solution to cover all possible cases are much too great. Attention will be confined to cases where μ lies along one of the figure axes. There are two special cases of this for which treatments have been published. They are :- 1. the linear rotator, or dumb-bell, type molecule (ref.3, chap.IV, ref.103, chap.VI, 107), and 2. the symmetrical top type molecule (ref.3, chap.IV).

The treatment published by Scheffers (116) for both these cases is, perhaps, the most rigorous to appear so far. The following summary is based in the main, on this paper.

Case 1. (e.g. HCl) $J_A = J_B = J$, $J_C = 0$. No rotation about the figure (dipole) axis. Thus the total angular momentum has no component in this direction, and $q = 0$.

When a molecule of this type passes through the field, the molecular dipole will, to a first approximation, have an orientation opposed to the field direction for the same length of time as it is oriented in the field direction, provided that the time of flight through the field is long compared with the period of the rotation. Thus, to a first approximation, the molecule suffers no deflection as it passes through the field.

To a second approximation, however, it is found that the field has the effect of perturbing the rotational motion. There is a slight acceleration as the dipole comes into alignment with the field, and a corresponding deceleration as it swings into opposition to the field. Thus there results a "time averaged" moment which is proportional to the field strength. This moment is not to be confused with the small induced moment resulting from polarisation of the electronic structure. They will, in fact, be of opposite sign.

Mathematical analysis yields the result that

$$\bar{\mu} = \frac{8\pi^2 J}{h} \cdot \mu^2 \cdot \frac{X}{(2n-1)(2n+3)} \cdot \left[\frac{3p^2}{n(n+1)} - 1\right]$$

where h is Planck's constant.

Provided that the temperature is high enough, so that $\frac{h^2}{8\pi^2 J} \cdot \frac{1}{kT} \ll 1$, and provided also that $\frac{\mu X}{E_n} \ll 1$, (Boltzmann's constant, $k = \frac{R}{N}$), this expression reduces to

$$\bar{\mu} = \frac{\mu^2 X}{4E_r}\left(3\cos^2\phi - 1\right) \qquad (2.5)$$

where $\cos\phi = P/n$, ϕ being the angle which the rotation axis makes with the field direction.

Combining 2.3 and 2.5, we obtain

$$s = \frac{\mu^2}{16} \cdot \frac{X}{E_t \cdot E_r} \cdot \frac{\partial X}{\partial s} \cdot \ell_1^2\left(1 + 2\frac{\ell_2}{\ell_1}\right)\left(3\cos^2\phi - 1\right) \qquad (2.6)$$

Or, for the "normal" deflection (p.45)

$$s_0 = \frac{\mu^2}{8} \cdot \frac{X}{k^2 T^2} \cdot \frac{\partial X}{\partial s} \cdot \ell_1^2\left(1 + 2\frac{\ell_2}{\ell_1}\right) \qquad (2.7)$$

This is the class of molecule which has most often been investigated in the past (107, 110, 117; see also ref.3, 103). It is to be noticed that the deflection depends on both X and $\partial X/\partial s$ (or, for the parallel plate arrangement, upon X^2). Scheffers calls this the quadratic effect. As it is only a second order effect, the time averaged moment is small.

Thus, for the "normal" molecule, $E_r = kT$, $\phi = 0$. If we take T = 300°K., μ = 1 D = 10^{-18} E.S.U., X = 500 E.S.U., we obtain $\bar{\mu}$ = 6.10^{-3} D. This is still larger, by an order of magnitude, than the induced moment resulting from electronic polarisation, which we saw was of the order of 5.10^{-4} D.

The resulting deflection is also small. Thus again, for T = 300°K, $\partial X/\partial s = 10^4$ E.S.U. cm.$^{-1}$, ℓ_1 = 10 cm., ℓ_2 = 0, we obtain $s_0 \approx 4.10^{-2}$ cm.

Estermann and Fraser (107), using the Rabi field, obtained normal deflections which were somewhat lower, of the order of 10^{-3} cm.

<u>Case 2</u>. (e.g. CH_3Cl, NH_3) $J_A = J_B \neq J_C$, $J_C \neq 0$. It is this type with which we are concerned in this investigation.

It can be shown that

$$\bar{\mu} = \frac{qp}{n(n+1)}\mu - \left(\psi_{n,q,p} - \psi_{(n+1),q,p}\right)\mu^2 X . \frac{8\pi^2 J_A}{h^2}. \qquad (2.8)$$

When $J_C = 0$, $q = 0$, the first term vanishes, and only the second term remains. This is then the dumb-bell case once more. In most cases where $J_C \neq 0$, the second term is small compared with the first, and can therefore be neglected.

Whence
$$\bar{\mu} \approx \frac{qp}{n(n+1)}\mu \quad , \qquad (2.9)$$

or, if the temperature is high enough $\left(\frac{h^2}{8\pi^2 J_A} \cdot \frac{1}{kT} \ll 1\right)$ to use the classical expression for the distribution of rotational energies, we may put $\cos\psi = q/n$, $\cos\phi = p/n$ where ψ is the angle between figure axis (μ direction) and the axis of total angular momentum, and ϕ the angle between the total angular momentum axis and the field direction.

Whence
$$\bar{\mu} \approx \mu\cos\phi\cos\psi \qquad (2.10)$$

Since, to a first approximation, the "effective" moment is independent of the field strength for this type of molecule, the deflection suffered will be directly proportional to the field strength. Scheffers calls this the <u>linear</u> effect.

Since q and p (or γ and ϕ) are equally capable of positive or negative values, these equations once more imply that deflections to either side of the undeflected beam are equally probable. That is, application of an inhomogeneity will once more result in a "flattened" peak, symmetrically placed about the point of maximum intensity in the undeflected beam. The broadening, for a given value of applied field, will be considerably greater than that obtained for the dumb-bell type molecule, for the effect we are now considering is a first order one. For a molecule with the properties $E_t = kT$, $\phi = \psi = 0$, $\bar{\mu}_0 = \mu =$, say, 1.0 D (10^{-18} E.S.U.), and other values as before, we obtain deflections of the order of 1.0 cm.

The intensity diminution at the maximum will be correspondingly greater. Thus it should be possible to detect small moments in molecules of this type with relative ease.

For the ammonia molecule, which exhibits, according to Scheffers (109), a moment of about 0.5 D under these conditions, a 30% reduction in peak height was obtained with a field of only 79 E.S.U. With 158 E.S.U. the reduction was nearer to 65%. These figures are to be compared with the results obtained for dumb-bell type molecules. Thus Scheffers (117), using KI, which has a moment $\mu = 6.8$ D, obtained a 53% reduction in peak height with the use of a field of 179 E.S.U. The difference between the two classes of molecule is even more apparent when it is noticed that in these earlier experiments the condenser was almost twice the half width of the undeflected beam. For a symmetrical top molecule the effective moment is, as we have seen, independent of field strength, and so the "normal" deflection depends only on C the apparatus constant (eqn. 2.11).

Hence $I(0)/I_0$ depends on the ratio C/b, which we might call the "resolving power" of the apparatus, and which must be as large as possible.

APPARATUS SPECIFICATIONS

We have now sufficient information to enable us to specify the conditions for obtaining maximum sensitivity in our search for a possible dipole moment in a molecule, at least in so far as instrument design is concerned.

Firstly, b must be as small as possible. We have seen, however, that one of the difficulties in the molecular beam technique lies in obtaining intensities of sufficient magnitude, even for the undeflected beam. I_0 depends on the product pa (eqn. 2.1). The maximum possible source pressure is limited by the mean free path condition for molecular effusion (see p.35), i.e. $\lambda \nless 2b$ where, in the system to be investigated here, λ and p must refer to the total pressure of gas in the source, and not merely to the partial pressure of the radicals in which we are interested. Thus we must combine the condition of minimum possible width of source slit with maximum possible area.

Throughout this discussion the beam-forming apertures have been referred to as slits. A long narrow slit is, in fact, the best solution to this problem. It has the further advantage that the beam intensity is independent of slit width. For, as the width is reduced, the pressure may be increased by an amount just sufficient to compensate for this reduction, so that I_0 remains unaltered (cf. ref.103, p.15).

The length of the slit, however, and hence the number of molecules arriving at the detector in unit time, is limited by a further consideration - that the beam must traverse a region of the field which is as nearly uniform as possible, both in X and $\partial X/\partial s$, along the length of the slit. For a long narrow beam travelling parallel to, and just above, a charged wire, this condition is even approximately satisfied only in the central portion of the beam. Hence the amount of deflection obtained will vary along the length of the trace. This is not particularly of importance when only a qualitative answer is required from the inspection of a visible trace. It is, however, extremely important if more quantitative methods of plotting peak shapes are envisaged.

Furthermore, exact alignment of the slits becomes more critical, and more difficult, as the length of the slits is increased. The use of optical methods, such as a microscope with cross-wires, is permissible with relatively short slits (ref.103, p.52), but this is not sufficiently reliable for longer, narrower slits.

The second condition for maximum sensitivity is that the apparatus constant C (eqn. 2.11) should be as large as possible.

The condition that $\partial X/\partial s$ be large is quite evident, and has already been discussed. It is preferable to arrange that this condition be satisfied for the minimum possible X, in order to keep polarisation effects as small as possible. ℓ_1, the length of path through the field, should be as large as can be conveniently arranged. If, however, the wire is too long, it may happen that, for large deflections, it will encroach on the line of flight of the molecules. In this case it might be preferably to place a limit on ℓ_1, and set the detector back a distance ℓ_2 from the end of the wire. The effective deflection at the detector will be correspondingly increased. There is, however, a limit to this as well, for the intensity falls off with the square of the distance from the source. The sensitivity of the detector thus places a limit on the total length of beam which is practicable. Finally, the temperature of the source must be as low as possible.

SUMMARY

Thus we require

1. A method of radical production, at as low a temperature as possible, which gives the highest possible yield of radicals.
2. A sensitive detector which responds only to radicals in the beam.
3. For the formation of the beam, narrow slits of medium length.

4. An efficient pumping system.
5. For the deflection of the beam, a high inhomogeneity combined with not too high a field strength, and of reasonable length.

CHAPTER III. EXPERIMENTAL

RADICAL PRODUCTION

The two major factors which must be considered in the choice of production method were indicated at the end of the last chapter. Of these, the most critical one is undoubtedly the requirement of the maximum possible radical concentration, combined with the lowest possible concentration of other types of molecule in the resulting beam. Only when this has been satisfied can the preference for a relatively low temperature be exercised. If a choice still remains after this, availability of starting materials and ease of operation are worth considering.

Furthermore, it is desirable to choose a method which can be easily modified to produce radicals other than methyl. For it may turn out that the methyl moment is too small to be detected. This answer would be of more significance if it could be shown that the apparatus is capable of detecting the moment of, say, the ethyl radical. Because of its asymmetry, this radical should have a small moment, quite independent of the configuration of the $\cdot CH_2 \cdot$ group.

Thus, of the production methods reviewed in Chapter I, that of photolysis can be ruled out, for the maximum concentration obtained in this way seems to be much less than the concentrations obtained by other methods.

Pyrolytic methods have the advantage of simplicity of operation, and of the possible starting materials, four seem to be worthy of further consideration:-

1. Lead tetramethyl was, as we have seen, the original source of radicals used in the experiments which demonstrated their existence. Unfortunately this material does not appear to be manufactured in this country. Since its high volatility makes particularly serious the well-known toxic hazards associated with these metal alkyls, and also because the standard method of preparation seems to involve a definite risk of explosion, it was felt that the preparation and use of this material was to be avoided if possible. Furthermore, the temperature required for complete decomposition seems to be relatively high. The results obtained by Eltenton (57) indicate that this takes place only at about 730°C. The results of Hipple and Stevenson (61) would seem at first sight not to agree with this figure. In their apparatus they had no means of measuring the pyrolysis temperature, and therefore the temperatures they quote are only rough estimates. They obtained a maximum ion current for $m/e = 15$ at around 300-350°C. It is not at all certain, however, that the change in ion current with pyrolysis furnace current which they obtained bears any real relationship to the degree of pyrolysis at these

temperatures, for they obtained a very sharp maximum at the temperature quoted. Their results, however, are of interest in that they show very clearly that insufficient heating gives rise to a wide variety of fragments, and also that the desired radical is not necessarily the major component in the beam.

Nevertheless, since a sample of lead tetraethyl was available in the laboratory, this material was sometimes used in the preliminary experiments when a source of radicals was required quickly, for the extra apparatus required was very simple. Some of these experiments and the equipment used will be described in the next chapter, in connection with the account of the investigations into methods of detection.

2. Mercury dimethyl has been used successfully by Lossing and Tickner (60) for the production of relatively high radical concentrations. However, it also is toxic and does not decompose until relatively high temperatures are attained. Ingold and Lossing (59b) estimate that it does not decompose at temperatures lower than about 600°C., and that complete decomposition occurs only at about 800°C.

Moreover, the molecular beam apparatus to be described in Chapter V contains a considerable area of brass exposed to the vacuum. Consequently any compound capable of yielding mercury vapour is to be avoided wherever possible.

3. Di-tert-butyl peroxide ($Bu_2^tO_2$). Since the discovery (120,121) that this material decomposes to yield

almost exclusively two methyls and two acetone molecules per molecule, it has come into increasing use as a convenient source of these radicals. The corresponding di-amyl compound yields ethyls in the same way. It is, moreover, claimed for this material that decomposition takes place at relatively low temperatures. Durham and Steacie (47) used temperatures around 325°C., whereas Milas and Surgenor (120) and Raley, Rust, and Vaughan (121) used even lower temperatures (250 to 300°C., and 225°C. respectively). However, it would seem that, under conditions of very high flow rate, much higher temperatures than this are needed. Thus Lossing and Tickner (60) found that the maximum concentration of methyls from this material, in their arrangement, was obtained at about 850°C. Some preliminary trials carried out in the present investigation would seem to support this (cf. p.159). Results quoted by Lossing and Tickner also indicate that the concentration of radicals obtained from this substance was not as high as that obtained by the use of mercury dimethyl. This result is not altogether surprising since, with $Bu_2{}^tO_2$, the initial decomposition step is the rupture of the O-O bond, and the methyls are formed later by decomposition of the fragments. If these have an appreciable half life, methyl formation will only take place after the fragments have been swept away from the reaction zone and from the neighbourhood of the aperture leading to the ionisation chamber of their mass spectrometer.

In the case of mercury dimethyl, however, free methyl is an immediate product of the decomposition step.

4. Azomethane has also been used as a source of methyls, and would seem (25) to decompose at the relatively low temperature of 400°C. This material, however, was not immediately available and has not been considered any further up to the present.

The other possibility to be considered was some modification of the sodium flame technique, which should, conceivably, be capable of high initial yields of radicals provided that the collision efficiency of the reaction is sufficiently great. This condition is satisfied in the case of the iodides (30). Results have been obtained (cf. ref. 123) which indicate that in the vapour state reaction of sodium and methyl iodide, one in every 1.5 collisions results in reaction (34) and, in the case of the sodium - ethyl iodide reaction (122), one in every 2.5 collisions is effective. Efficiencies of this order were ample for the arrangement envisaged for, at a pressure as low as 10^{-2} mm.Hg., the mean free path is still only about 1 mm. As the reaction zone is several centimeters in extent, every iodide molecule will almost certainly have a chance to react. Thus, in conditions of sodium excess, none of the iodide should reach the neighbourhood of the slit, and the beam should consist only of the radical and the products of its reaction with itself.

The sodium iodide is relatively involatile at the temperatures used, and deposits on the walls almost immediately adjacent to the zone of reaction. If the slit housing and the walls of the reaction vessel close to it are not heated, most of the excess sodium deposits there. It was found that, with the arrangement used, little if any sodium deposited on the slit itself.

A sodium vapour lamp placed near the reaction vessel provides visible proof that the sodium excess is being maintained, for the whole reaction space is filled with a yellowish-white glow under these conditions. If the vapour pressure of the iodide is increased sufficiently the glow is immediately extinguished. This is a very sensitive test, for this glow is visible in a darkened room for sodium pressures as low as 10^{-5} mm.Hg. or less (35). As the reaction proceeds, visibility becomes less because the heavy layer of sodium iodide tends to obscure the view. It was, however, found possible to use this check even after 15 to 20 hours running time, once experience had been gained.

The temperature of the reaction is determined by the vapour pressure of sodium required. At 400°C. this is about 0.35 mm.Hg.; at 440°C., about 1.0 mm.Hg. Pressures of this order should be more than sufficient and thus, in this respect, the method has a distinct advantage over the pyrolysis methods, while being, in principle, at least their equivalent in potential yield of radicals.

Since this method seemed to satisfy most of the requirements quite well, and the materials were readily available, it was decided to use it as the major source of radicals. It had the added advantage that it had been used successfully for other purposes by people at work in this laboratory. In one respect only is it inferior to pyrolysis methods. It is not so simple to operate, for it is necessary to introduce fresh sodium into the apparatus by distillation at regular intervals. This is a tedious procedure.

It has already been mentioned that the final aim was to obtain a beam containing the fewest possible number of molecular species. For this reason it was resolved to vary the usual procedure and to work, if possible without the use of carrier gas. Trial experiments in a simple apparatus, containing no slits, seemed to indicate that this was possible (cf. p.123). As long ago as 1933, Horn, Polanyi, and Style (35) had observed that appreciable back diffusion of the reactants is obtained under these conditions. This has been amply confirmed in the present investigations, but was not considered to be serious so long as the build-up of sodium iodide did not impede the flow. It would now seem, however, that a carrier gas is necessary. The conditions at the inlet of a mass spectrometer, such as that used by Lossing and Tickner (60), bear a very close resemblance to those obtaining in a molecular beam source. This work, published in 1952, indicates that the concentration of methyl radicals resulting from the pyrolysis of mercury dimethyl drops away very rapidly as the flow rate on the "high" pressure side of the source slit is diminished. In the absence of carrier gas, very low methyl concentrations were obtained even when separate pumping was maintained on the source side of the slit.

These results must be taken into account when future development of the molecular beam apparatus is being considered.

APPARATUS AND MATERIALS

In all descriptions of glass apparatus in this and succeeding chapters it may be assumed that pyrex glass was used, unless otherwise specified.

Source Pressure Control.

Whichever of these production methods is used, the first requirement is some means of regulating the pressure, and of measuring it.

With the exception of the sodium, all the starting materials discussed are relatively volatile liquids under normal conditions. It is possible to control the pressure in the reaction chamber by maintaining the liquid reservoir at some temperature at which the vapour pressure is much higher than required (say at room temperature or just below it), and to rely on the "resistance" of a capillary connection to reduce the pressure to the desired value. Used by itself this method is relatively inflexible, and controlled variation of the pressure is not easily carried out.

If the liquid is maintained at constant temperature, use of a valve or tap is the only means of pressure variation which presents itself. The simplest method is to modify an ordinary glass tap by scoring two grooves on the ground surface of the key. Each groove is at the level of the side arms on the barrel, and runs, in the same direction, from one end of the central hole about half way round towards the other end. The length of the capillary leak thus formed can be altered by a slight turn of the tap key. The length of the grooves is limited so that there is one setting of the tap where it cuts off completely. One disadvantage of this control method is that the groove tends to get clogged up with grease. The other is that all of the vapours whose use is proposed dissolve very readily in hydrocarbon tap greases (e.g. Apiezon products). These cannot, therefore, be used, for the stage is very quickly reached where the vapour pressure of the substance in the reaction zone is appreciable even when the tap is shut. Within a few days the grease becomes so mobile that it runs out of the tap, with deleterious effects on the vacuum. Lead tetraethyl was found to be particularly bad in this respect.

Other tap greases were tried. First, a sample of the old-fashioned "sugar" grease was obtained from Dr.L.Farkas. This grease had the composition mannitol (1.7), dextrol (3.5), glycerol (12.0), where the figures in brackets represent parts by weight. This mixture is quite resistant to the alkyl halides, but it has two disadvantages. Firstly, it rapidly becomes stiff, and needs replacement at frequent intervals. Secondly, it is extremely hygroscopic. During its preparation, therefore, care must be taken both with starting materials and with experimental conditions. And in subsequent storage it must be protected as far as possible from the atmosphere. Even so, it seems to absorb water vapour after a time. When this has happened a good vacuum is almost impossible of achievement. If this grease is used it must be protected from the atmosphere by a liberal coating of petroleum jelly placed on the outside of the tap at points where the grease would otherwise be exposed. The use of this grease was also discontinued after a time.

Dow-Corning silicone grease (high vacuum quality) was also used. This grease has the general disadvantage that it tends to "run", but it seems to be fairly resistant to organic vapours (see, however, p. 151). This grease was used on the main apparatus on the tap isolating the iodide reservoir from the rest of the apparatus during "shut down" periods. At these times the storage vessel was kept immersed in a Dewar flask which was replenished, at least once or twice a day, with liquid nitrogen.

A variety of designs for "greaseless" valves has been published. These often seem to be rather complicated in design, or fragile, and the simpler ones often involve the use of mercury, which was to be avoided in these experiments as far as possible. A new greaseless "cut-off" valve, employing a plastic diaphragm in an otherwise all metal construction, has recently come on to the market. It can be sealed to a glass apparatus by means of "Housekeeper" copper to glass seals. If the plastic diaphragm proved insufficiently resistant to these vapours, a metal one could be used. This, however, is not quite so vacuum tight. This tap would, however, prove very useful on the high pressure storage side of a system such as the one under consideration, as it would obviate the necessity for the daily visits to refill the Dewar flask.

For actual pressure control, however, attention was directed to the possibility of regulating the temperature of the liquid. If this is satisfactory, relatively wide connections between storage vessel and source are sufficient. The effect on pressure of minor temperature fluctuations can be reduced by the introduction of a "ballast" vessel into the line (c.f. fig. 26).

Lead tetraethyl, methyl iodide, ethyl iodide, have a vapour pressure of 0.1 mm.Hg. at temperatures approximately -8, -98, -79°C., respectively. The figures for the iodides were obtained by graphical extrapolation on semi-log. paper of data taken from a paper by Stull (124), and checked with figures given in Sanderson's book (125). Neither of these figures are absolutely certain, although of the two, more reliance can be placed in the one for ethyl iodide. The melting point of this substance is -105°C., and thus the only uncertainty is involved in the rather long extrapolation to temperatures well below those for which experimental data are available. At -98°C., methyl iodide is solid (M.P. -64°C.). Since no figures are available for vapour pressures in this state, estimates are correspondingly less reliable. Three figures for the boiling point of lead tetraethyl were found, one from each of three different standard reference books (Landolt-Börnstein, Lange's handbook, and I.C.T.). Vapour pressure estimates for this compound were made by extrapolation of these three figures in the same way as for the iodides. In this case there seems to be no recorded melting point, presumably because the substance must always freeze to a vitreous condition.

"Slush" baths may be devised (125) which will provide a steady temperature for periods of about half an hour. They are not suitable for longer periods, however, as violent temperature fluctuations are caused during the process of re-freezing. Moreoever, at temperatures below about -60°C., there are few organic liquids which are suitable for the maintenance of a steady pre-determined temperature, and the intervals between available temperatures are rather large, and do not constitute regular steps.

A moderately satisfactory control was achieved in the following manner. The storage vessel, which was constructed of glass tubing about 2 cm. diameter, was surrounded by a piece of copper tubing, closed at one end and rather larger in diameter. The intervening space was filled with finely granulated copper in order to provide some sort of thermal contact. This assembly was cooled down with either liquid nitrogen or an acetone-solid carbon dioxide bath. The Dewar vessel which contained this could be raised or lowered as the need arose. The tube was first cooled rapidly by raising the Dewar as far as it would go. When the temperature had fallen almost to the required value, the flask was lowered by stages until the heat loss from the tube to the coolant was just balanced by the heat gained by the exposed part of the copper tube from the surroundings. Alternatively, the coolant could be maintained at a constant height, and the heat input varied by passing current through a few turns of nichrome wire wrapped round the top of the tube. The heater was insulated from the copper with a few layers of asbestos paper. Control was not very close, however, as the arrangement has an appreciable time lag because of its relatively high thermal capacity. The best control attained was about ± 3° at -55°C. over a period of about an hour. To attain even this the arrangement required constant attention, particularly when liquid nitrogen was used, since an appreciable drop in the coolant level had the same effect as was obtained by lowering the flask. The rate of consumption of liquid nitrogen was high.

The device installed on the main apparatus was, however, much more satisfactory. Two of these were constructed. The first, which was used in the molecular beam experiments, was a fairly close copy of the design published by Comstock and Rollefson (126). The second, which was used only on the auxiliary apparatus, incorporated some slight modifications in an attempt to improve its operation even further. A similar piece of equipment has been used by Miller and Steacie (127), who call it "a trap similar to the Ward still" (128). In the present investigations it has been named a <u>low temperature thermostat</u>.

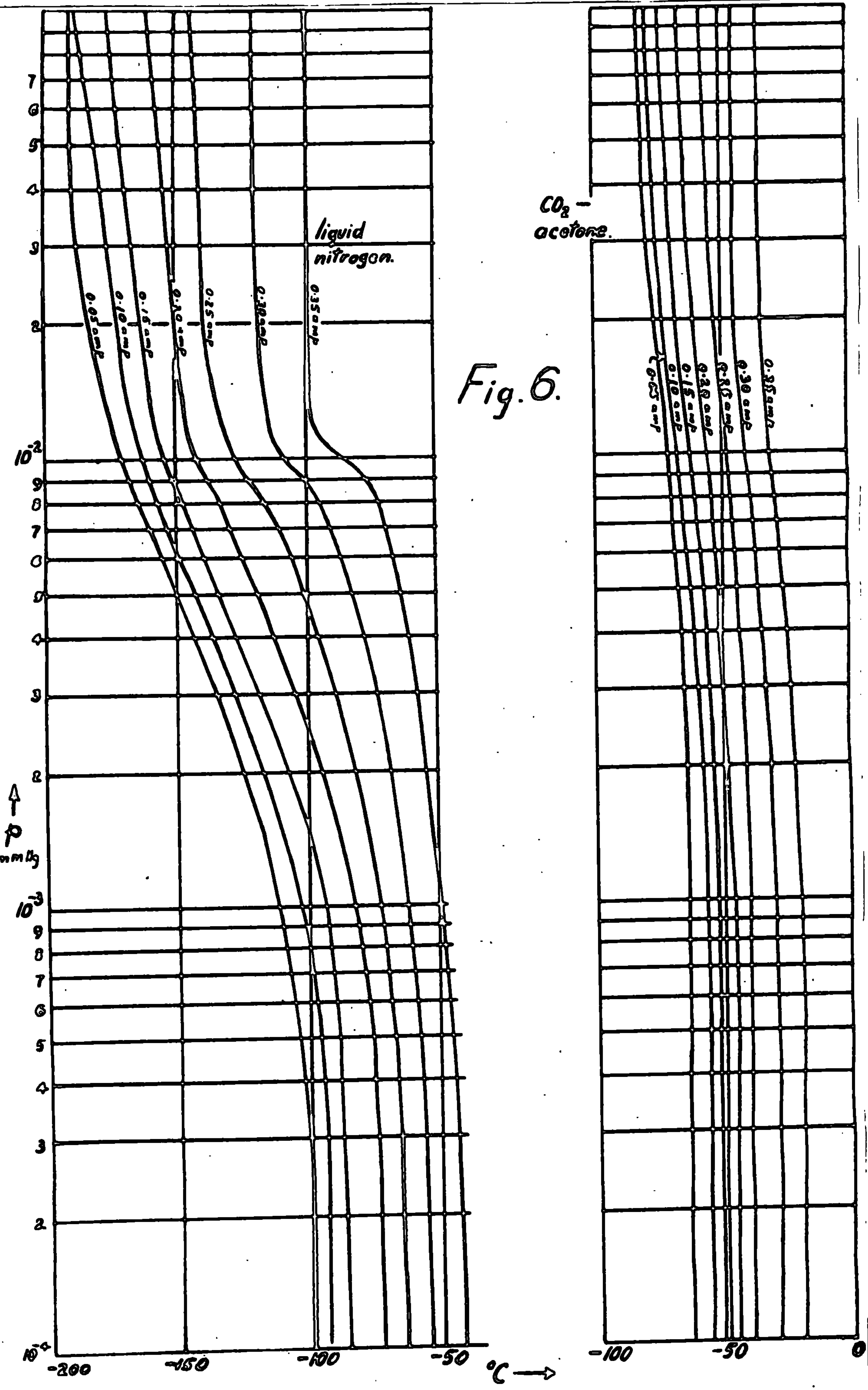
In broad principle its mode of operation bears some similarity to the device already outlined. That is, the temperature is maintained by balancing the heat input against the heat loss to the coolant. Both of these variables are, however, much more finely controlled, over a much greater range of temperatures.

The liquid storage vessel was sealed into a glass outer jacket to which was attached a two-way glass tap (fig. 26).

One lead of this tap was connected to the auxiliary high vacuum system at A (fig.13, p.112), the other was drawn down to a capillary opening which made it possible to let any desired quantity of air slowly into the jacket space. The whole assembly was immersed in a coolant, usually liquid nitrogen.

Since the conductivity of the air space depends on the pressure, at low pressures, the rate of heat loss from the reservoir to the coolant could thus be controlled. Heat input was provided by a short length of nichrome tape (resistance about 12 Ω) wrapped around the reservoir, and silver soldered to two copper leads which were waxed into capillary side arms. With liquid nitrogen as coolant, a temperature of -50°C. was easily maintained with a heater current of about 0.2 amp and a good vacuum in the jacket ($< 10^{-4}$ mm.Hg.). The heat input was therefore of the order of 1/2 watt, and the consumption of coolant was quite low. The reservoir temperature, as measured by a copper-constantan thermocouple inserted down the thin re-entrant tube lying between reservoir and heater, seemed to be relatively insensitive, between quite wide limits, to the coolant level.

The method of operation was as follows: Sufficient air was let in through the two-way tap to give a pressure of a few millimeter of mercury, as measured by a mercury manometer attached to the side-arm (fig. 26). The arrangement was then



7
6
5
4
3
2
10^{-2}
9
8
7
6
5
4
3
2
↑ p mm Hg
10^{-3}
9
8
7
6
5
4
3
2
10^{-4}
-200
-150
-100
-50
°C →
liquid nitrogen.
0.05 amp
0.10 amp
0.15 amp
0.20 amp
0.25 amp
0.30 amp
0.35 amp
CO_2 - acetone.
0.05 amp
0.10 amp
0.15 amp
0.20 amp
0.25 amp
0.30 amp
0.35 amp
-100
-50
0

Fig. 6.

immersed in the coolant until the temperature was as low as possible. It was necessary to wait about 15 to 20 minutes after this had been attained before proceeding to the next step, to be sure that the interior of the device had become properly cool. Then the heater current was adjusted to the required value and the jacket pumped out to the required pressure. Once equilibrium was attained, the temperature remained sensibly constant for as long as the supply of coolant was maintained. The temperature did tend to drop slightly when vapour was being withdrawn, but this could easily be compensated by a slight adjustment of the heater current.

Before the device was finally installed, a complete calibration was carried out. The results are illustrated in figure 6, which shows the jacket pressure as a function of thermocouple temperature for a series of heater currents up to 0.35 amp. The thermocouple had been roughly calibrated against a pentane thermometer. The thermostat calibration was carried out using both liquid nitrogen and acetone - "drikold" as coolants. It will be seen that a much greater temperature range is available when liquid nitrogen is used. Currents greater than 0.3 amp. are not desirable as they cause the coolant to boil away rather too rapidly. When relatively high temperatures are required, therefore, it is better to change over to the "drikold" mixture. Liquid nitrogen is more convenient to use, however. The 0.05 amp. curve lies very close to the curve for no current at all.

This chart was found very useful for deciding on the operating conditions. The temperature necessary for the required vapour pressure was determined by consulting the semi-log extrapolations referred to on p. 71. Economy of coolant was achieved by choosing the jacket pressure which would give this temperature for minimum heater current.

The device responded fairly quickly to changes in heater current, and therefore it was found necessary to use a stable voltage supply. This was, for a time, achieved by means of a "Variac" connected to the stabilised 240 V. supply. The only available Variac did not, however, allow for very fine control. It was therefore changed for a fixed transformer, connected still to the stabilised 240 V., whose 6.3 V. and 4 V. windings were connected so as to give approximately 10 V. output. The current was controlled by means of a rheostat of about 100 Ω total resistance.

The only objection to this device was that the source pressure, as measured by the thermocouple gauge described in the next section, seemed to depend to a certain extent on the quantity of liquid in the reservoir. This could be ascribed to uneven heating by the nichrome wire because of the poor thermal conductivity of the pyrex glass.

In the second model an attempt was made to overcome this defect. The heater wire was replaced by a glass tube which slipped over the storage vessel, and extended from some distance below it (but well clear of the bottom of the jacket) almost to the top seal. This tube was coated, for most of its length, with a thin layer of metallic platinum obtained by "burning in" a thin coating of "liquid bright platinum" solution obtained commercially (c.f. method for making "ofen" heaters, ref.108, p.767). By a process of trial and error it was found possible to produce a coating, about 13 cm. long, which was reasonably uniform and had a resistance of 10 Ω. If the resistance was too low, it could be raised slightly by heating with a flame, but care was needed because the platinum coated glass rapidly became hot enough to bend. Once this happened, a fresh start had to be made. Adequate contact with this deposit was obtained by first burning in several thick coatings of platinising solution at each end, then twisting a platinum lead round the thickened portion, and finally burning in another few coatings at these two places. The platinum leads were then sealed into capillary side arms on the vacuum jacket with black wax as before. These leads served also as supports for the heater tube.

At the same time the construction of the inner reservoir was simplified. The "trap" form of the first model was not really necessary. Instead, the thermocouple well was placed down the centre of the tube, so that its end rested in the liquid. This had the advantage that, not only was the thermocouple now well away from the heater, thus measuring the actual temperature of the liquid and not something approximating to it, but the arrangement was now completely symmetrical about a vertical axis, with a corresponding improvement in the temperature gradients.

This model also worked well but, because of the greater thickness of glass, its response to changing conditions was slower. In some respects this is an advantage - e.g. when a steady temperature is to be maintained - but it greatly increased the starting up time. Provided that a more suitable method of making firm contact with the coating can be devised, a further improvement would be to deposit this coating directly on to the outside of the reservoir before construction is completed.

Source Pressure Measurement

Since the source pressure is such a critical factor in molecular beam work, it was deemed necessary to provide some means of measuring it directly, and not simply to rely on the indirect method of measuring the temperature of the liquid. In any system where a gas is being pumped along a tube there is a steady fall of pressure. It is therefore desirable to place the manometer as close to the slit as possible. With the apparatus as constructed (Chapter V) the closest possible position was some considerable distance further away than it should be for preference. Since the geometry of the arrangement is rather complicated, no attempt has been made to estimate the expected pressure drop between the manometer and the reaction chamber. But, as the slit is without doubt the narrowest part of the system, it was considered possible that it is not great.

Because of the importance of high source concentrations, however, this is a matter which should receive further attention when an apparatus of new design is being considered.

The pressure range to be measured is an awkward one from an instrumental point of view. What is really required is a device which is most sensitive in the range 1.0 to 10^{-2} mm.Hg.

The McLeod gauge cannot be used, for it is desired to measure the pressure of condensible vapours and, in any case, mercury cannot be allowed in the main vacuum system.

It is possible, with the aid of suitable electronic devices, to extend the range of the Bodenstein quartz spiral gauge. This is best used, however, as a null instrument, and would lead to undesirable complications in an apparatus which is already sufficiently elaborate.

The best solution was thought to be a hot wire manometer of the Pirani type. In the interests of simplicity it was decided to sacrifice a certain amount of sensitivity and try the thermocouple gauge.

This is a modification of the Pirani gauge in which the temperature of the heated wire is measured by means of a thermocouple attached to its centre. If no great sensitivity is required it is sufficient to connect the thermocouple leads directly to a microammeter (or millivoltmeter). The only other equipment required is an accumulator (2 V. output), a meter to measure the heater current, and a rheostat to control it. The external circuit is shown in fig. 26, attached to a drawing of the most recent model constructed.

It was found that the most sensitive range of this gauge is from 10^{-1} to 10^{-2} mm.Hg. It will, however, indicate pressures from about 4.10^{-1} to 2.10^{-3} mm.Hg. with reasonable certainty. The sensitivity in the high pressure range can be increased by the use of a suitable elaboration of the associated circuit (see 129,130,131).

In designing such a gauge, the conditions for maximum sensitivity will be very similar to those set out by Fraser (ref.103, pp.37-40) for the Pirani gauge.

"End effects" are minimised by making the wires, both heater and thermocouple, as long and as fine as possible. This ensures that heat losses by gaseous conduction predominate over metallic conduction. Thin ribbon like wires, by increased surface area, would increase this tendency even more (c.f., however, 131). Fine nickel ribbon which could be used for the heater was available, but there was little point in using such a thin heater when equally thin material for the thermocouple was not available. The heater was therefore constructed from the finest available constantan wire (approximate diameter 0.08 mm.), and the thermocouple of one length of this wire and a length of copper wire of comparable diameter. Both types of wire were coated, the one with cotton, the other with lacquer. This insulation was carefully scraped off before assembly.

Heat loss by radiation must also be kept to a minimum. This is achieved, firstly, by using wires which are as highly polished as possible, and secondly, by operating at the lowest convenient temperature. The ease with which the vapours are pyrolysed also places an upper limit on the amount of heater current. As against this, if the wire temperature, for the lowest pressures, is not very great, the maximum reading on the thermocouple meter will not be sufficient to allow of adequate sensitivity in the pressure readings. In practice, since the wires were fixed together with soft solder (MP ~ 200°C.), the heater current was run at a value which experience showed was just insufficient to melt the solder at pressures less than 10^{-4} mm.Hg. When appreciable pressures of iodide were present, the temperature was correspondingly less. After one year's operation there was no visible evidence of iodine liberation under these conditions. The only meter available had an internal resistance of 186 Ω (-50 to 0 to + 50 μA.). A meter with lower resistance would give a slight increase of sensitivity.

The temperature of the walls must be as low as possible. That immersion in liquid nitrogen has an appreciable effect was demonstrated with some of the earlier trial models during calibration runs with air. However, this is not possible when condensible gases are being used. It was found also that variations in room temperature had an appreciable effect on the reading. This is due, no doubt, partly to the effect on the temperature gradient from wire to wall mentioned by Fraser, and also to the effect on the virtual cold junction of the thermocouple, which would be either at the meter terminals or at the tungsten seals leading into the vacuum. This effect was kept to a minimum in the final model by surrounding it with a water jacket which was in series with the diffusion pump water supply. The tungsten seals for the thermocouple leads were mounted in a re-entrant seal in order that they should be well within the body of the gauge.

There is one final point not mentioned by Fraser (c.f.131). Since the sensitive range of the gauge seems to be in that pressure region where the mean free path of the gas molecules is roughly of the order of the wire to wall distance, an attempt was made to construct a gauge where this distance was as small as possible. This should shift the sensitive

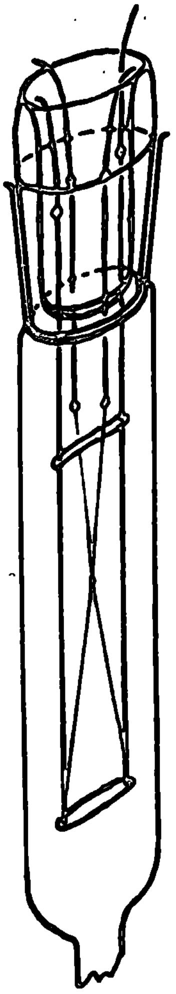


Fig. 7.

range to slightly higher pressures. Within the limits expected from the relatively minor differences in diameter of the two designs, the variation was in the expected direction.

Of the designs tried, only two were at all successful. The major feature of the first was that it was mounted with all four tungsten seals at the one end. These four wires were arranged at the corners of a square in the well of a re-entrant seal affixed to a B.29 glass cone. The seal protruded slightly below the end of the cone. The well was filled with Everett's wax, which served to protect the seals from breakage by holding the copper leads firmly, and at the same time was an "insurance" against the development of cracks in the glass. The tungsten wires were in pairs, at opposite corners of the square. The two long ones, of 1 mm. diameter for rigidity, were held apart at the free end with a glass spacer. Immediately below this the heater was soldered. The two thermocouple wires were soldered to the short tungsten wires. The application of soft solder to tungsten is facilitated by prior application of a layer of silver solder. Connection to the vacuum was made through the free end of the corresponding socket, which served as the outer wall of the gauge. This model had the advantage that, should the wires burn out or become unsoldered, it was a simple matter to replace them. It had the disadvantage that the wire to wall distance was relatively large, and that the presence of the

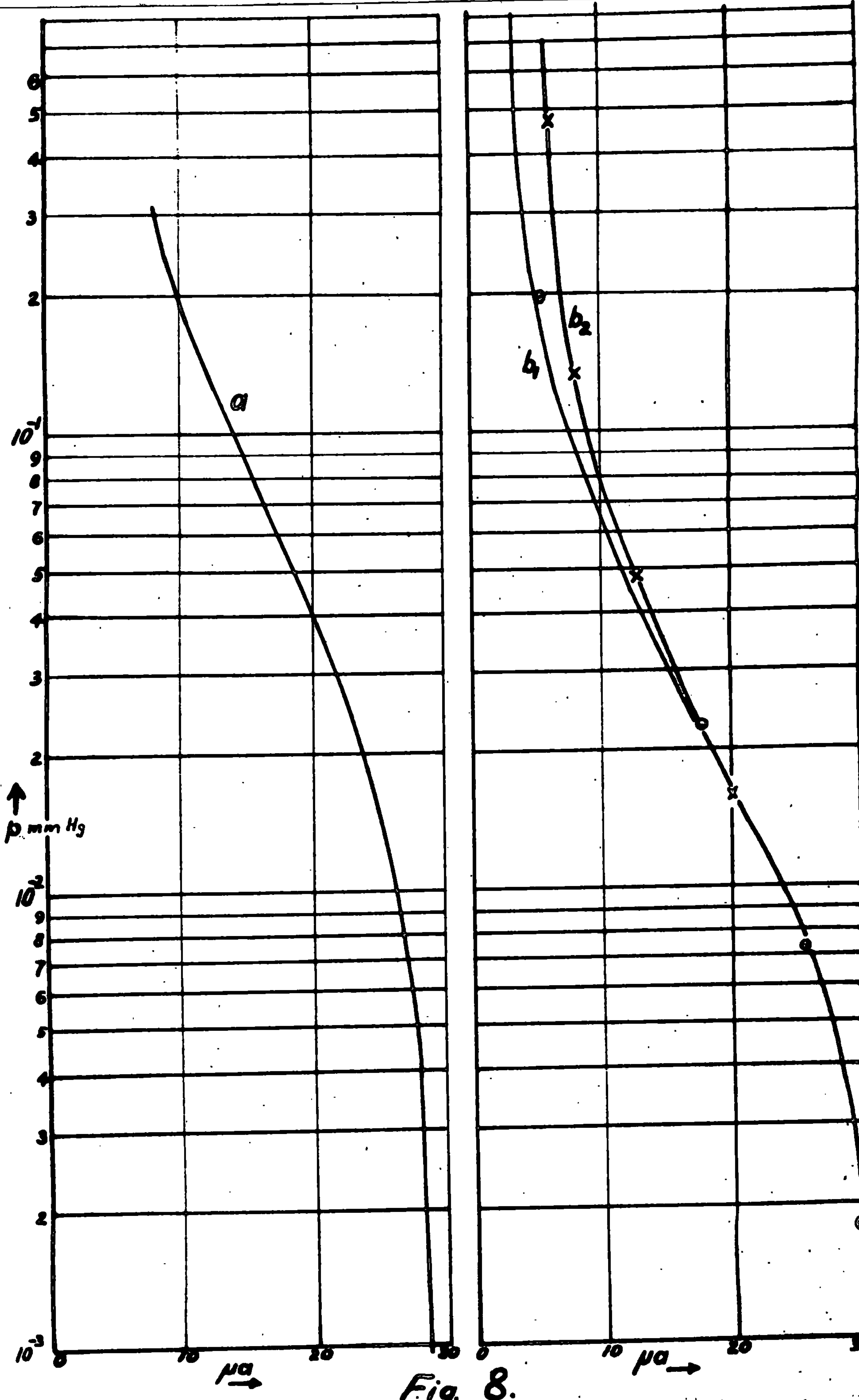

6
5
4
3
2
10^{-1}
9
8
7
6
5
4
3
2
p mm Hg
10^{-2}
9
8
7
6
5
4
3
2
10^{-3}
0
10
20
30
μa
a
b_2
b_1
0
10
20
μa

Fig. 8.

joint necessitated the use of some sealing compound. It was found that black wax was the least objectionable provided that it was not permitted to extend right up to the vacuum side of the joint. Even this, however, was capable of absorbing quantities of the vapour if the pressure were allowed to rise too far.

When experience had been acquired in the operation of the gauge it was no longer necessary to provide for the re-mounting of the wires. In the later model, therefore, the two pairs of leads were sealed in at opposite ends. The length of the wires was at the same time increased, and the other improvements already mentioned were incorporated (see fig. 26).

The gauges were calibrated with air against a McLeod gauge on the test apparatus (fig.13). The trap was kept cold to prevent mercury from reaching the test section. Typical curves are shown in figure 8. Curve a is that for the first type, curve b_I for the later one.

As Fraser points out, however, the response of the gauge should depend to a certain extent on the molecular weight and specific heat of the gas. The expression involves only the square root of the molecular weight, and it might therefore be expected that the effect would not be large. Nevertheless it was decided to test this point by a further calibration of the second model, using ethyl iodide. The

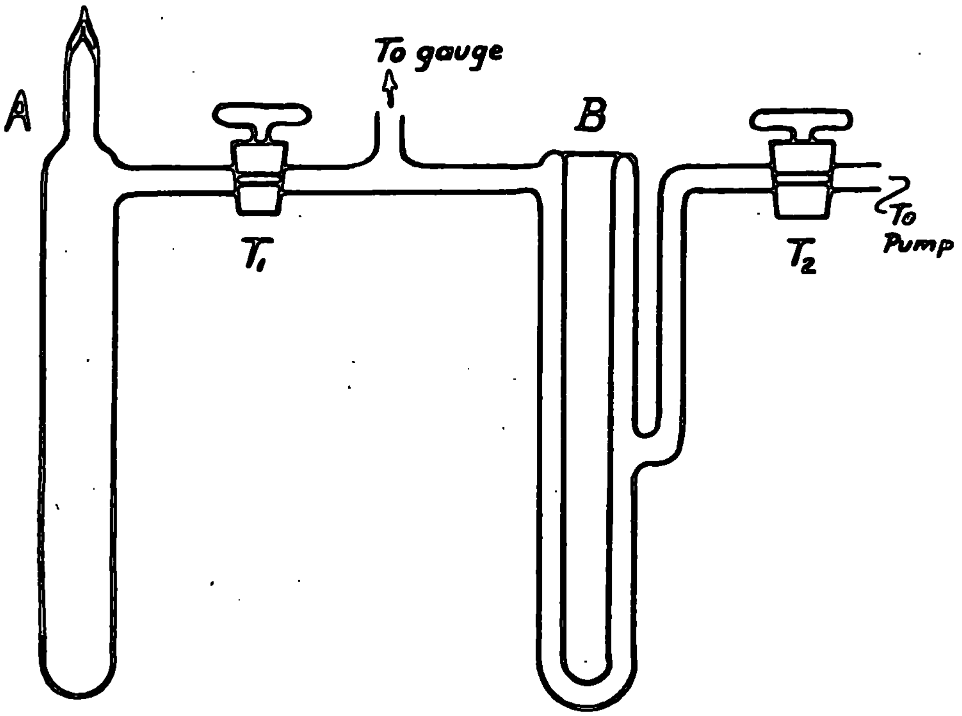


Fig. 9.

vapour pressure curve previously referred to was taken as sufficiently accurate for this purpose. The following melting points were also assumed to be correct: Toluene (Analar grade), -95°C.; trichlorethylene, -86°C.; n-butyl acetate, -76.8°C.; chloroform, -63.5°C. (Lange's Handbook).

The arrangement illustrated in figure 9 was sealed to the "test" vacuum line (see figures 13,22). The taps were lubricated with silicone grease.

The ethyl iodide was stored over anhydrous magnesium sulphate, together with a little silver powder, in vessel A. It was frozen with liquid nitrogen and the space above it was pumped until the gauge showed maximum reading. Then, with tap T_1 closed, it was allowed to melt. This procedure was repeated until no more gas bubbles formed on melting. It was then assumed to have been out-gassed.

A semi-frozen slush of toluene was then prepared at the temperature thus defined (-95°C.), ethyl iodide has a pressure of about $1.6 \cdot 10^{-2}$ mg and is in the liquid state. It is therefore safe to pump it continuously without risk of any great loss of material. This was done for several hours until the gauge reached a constant reading. It was then assumed that the ethyl iodide was sensibly pure. With tap T_2 closed the ethyl iodide was then transferred to vessel B. This was constructed with a re-entrant well just wide enough to accommodate comfortably a pentane thermometer. This vessel was then surrounded with a toluene slush bath, the taps were shut, and the pentane thermometer was placed in the well together with a little ethanol to provide thermal contact. A second pentane thermometer was placed in the toluene bath close to the outside of the vessel, and its height was adjusted so that the two thermometer bulbs were approximately at the same level. The bath was stirred. As the toluene bath warmed up, the gauge and the two thermometers were read at frequent intervals.

It is well known that pentane thermometers are not to be relied on for any great accuracy, neither over an appreciable temperature range nor for the same temperature on different days. To guard against this the toluene melting curve was not followed for more than about ten degrees above its melting point. The temperature at which each thermometer remained steady for several readings was assumed to be the true melting point. (It was necessary that at least part of the two "flats" should overlap in time) The other readings were then corrected on this assumption.

The same procedure was carried out using cooling baths made with the other three compounds whose melting points were listed above.

As was to be expected, the two thermometer readings did not always tally, even when corrected for the appropriate steady temperatures. For, even though the temperature changed only slowly, it was quite likely that the interior of the well should lag behind the bath. It was assumed, however, that the "effective" temperature of the ethyl iodide would lie somewhere between the two measured limits. The gauge readings at the actual steady temperatures for the four cooling baths were taken, however, to be definite fixed points.

The pressures corresponding to all the recorded temperatures were read off from the vapour pressure curve, and were plotted against the appropriate gauge reading. Where the two pressures for the one observation set differed, the two points were joined by a vertical line. The calibration curve was then drawn as the line of best fit which, at the same time, passed through the four fixed points. The resulting curve, without all the separate points, is shown in figure 8 (b_{II}). The crosses represent the four fixed points. The circles illustrate the effect of a slight increase of a few degrees in the water jacket temperature (<u>curve</u> b_I, air 16°C., water 15.2°C.; circles, air 19°C., water 20.5°C.).

Reaction Unit

A number of points had to be considered in the design of the source unit for the beam apparatus. The sodium, which should be in excess over the whole reaction zone, should not condense on the slit itself, but on the walls immediately preceding it. The reaction chamber should have the largest

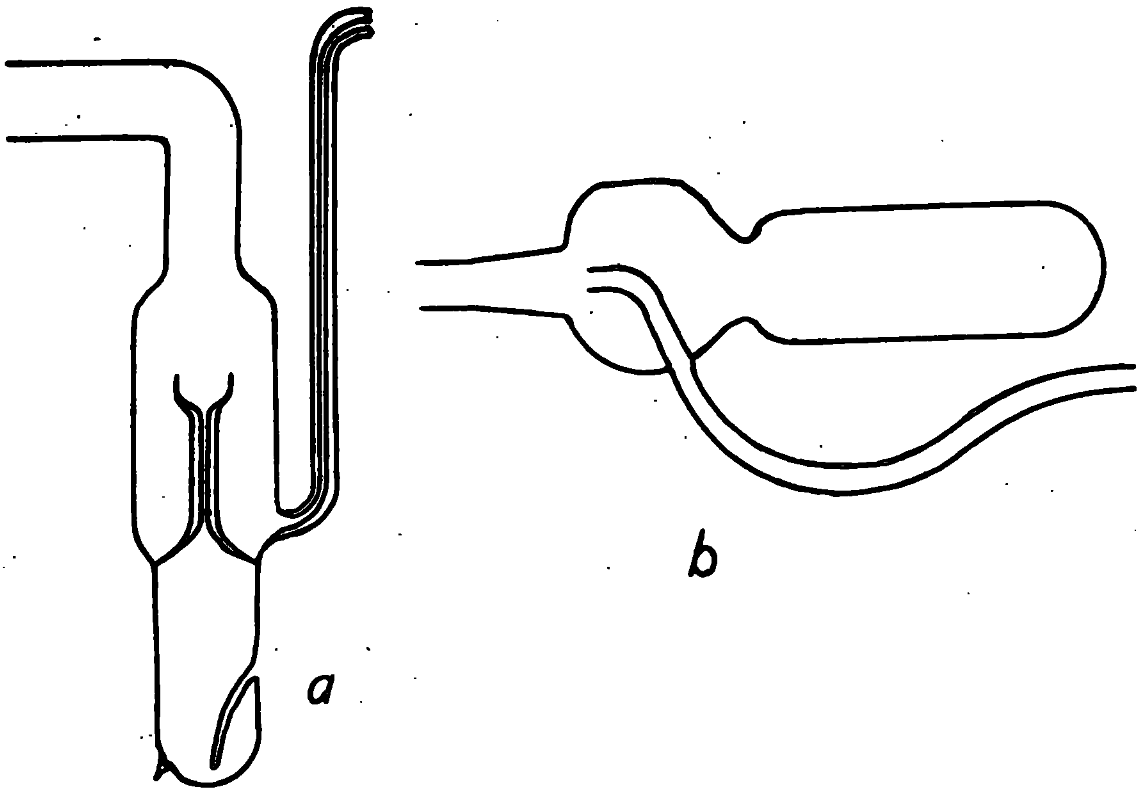


Fig. 10.

possible surface area in order to minimise the density of the sodium iodide deposit. The alkyl iodide should be introduced at a point immediately opposite the slit, and as near to it as is consistent with other constructional requirements. Provision must be made for heating it, and for measuring its temperature. Since the whole unit was inside the collimator chamber, it had to be designed so that it could be removed, cleaned, and replaced with the minimum of disturbance to the rest of the apparatus. Since the vacuum had to be let down to atmospheric pressure each time this cleaning process was necessary, some means had to be devised for distilling, and storing in vacuo, the sodium metal, and for opening this sodium to the reaction chamber by remote control once the vacuum had been restored.

The early sodium flame experiments on the test vacuum line (pp. 115, 123) were carried out with a reaction unit of the design shown in figure 10a. The capillary was provided between the sodium chamber (lower) and the reaction chamber in order to inhibit back diffusion of the alkyl iodide into the sodium chamber during operation. For it was thought that, if a crust of sodium iodide were formed on the surface of the sodium, the rate of evaporation would be so much diminished that insufficient sodium would reach the reaction zone at the normal operating temperatures (c.f., however, p. 149).

When a carrier gas is passed over the sodium, this capillary serves its purpose very well, However, in these experiments it was found that, in the absence of a carrier gas, the greatest amount of deposition took place on the end of the capillary with the result that it soon became blocked. In later (horizontal) models this capillary was omitted altogether.

The small well was placed in the sodium chamber so that a thermocouple (chromel-alumel) could be placed close to the sodium.

The reaction unit used in the later trial experiments (p.139), and in the molecular beam apparatus, was of the form illustrated in figure 10b. The reaction chamber was blown out to a roughly spherical shape, slightly flattened on top. The alkyl iodide entered via the small bent tube whose orifice was placed directly opposite the slit. The distance from this point to the slit was about 6 cm.

The extreme left hand end was left open until the sodium capsule had been introduced. It was then sealed, taking care to avoid heating the capsule as far as possible. The unit was not, therefore, annealed after this process. This omission did not subsequently prove to be deleterious. Connection to the slit system was made by means of an "extended" B.14 cone which fitted into a brass socket, attached to the slit backing by means of a metal bellows. The joint was lightly greased with silicone. The glass elongation served, to a certain extent, to prevent the radicals from coming into contact with the metal of the bellows. At the same time it protected the bellows from the condensing sodium.

Since the heating element was inside the vacuum chamber, none of the usual types of insulation could be used. A coil of stout "Kanthal" wire was finally employed. This wire, approximately 1 mm. diameter, was sufficiently rigid to support its own weight when hot. The coils were arranged so that they were closest together at the sodium chamber end, and opened out slightly towards the slit. This ensured that the temperature was greatest at the sodium capsule, where it was needed to produce a good supply of vapour, and at the same time it prevented the slit from becoming too hot. The reaction zone temperature was high enough to prevent the deposition of sodium in that region. Most of the sodium deposited on the cone and its extension. The heater resistance was 5.9 Ω (cold). Current was drawn from the 50 V. A.C. supply, and controlled with a high watt "step" variable resistance. Maximum current used was just under 4 amp.

At the temperatures thus attained the walls of the sodium chamber quite rapidly became brown, probably by reaction with the hot sodium vapour. This phenomenon was observed in all sodium flame experiments whenever the temperature approached 400°C. for any length of time. When the coloration was removed by prolonged soaking in water or ethanol, visible signs of attack on the glass could be observed.

The constriction between the reaction and sodium chambers served as an anchorage site for the thermocouple, which was strapped into place with a length of fine borated copper wire. The thermocouple, the wire strap, and the heater leads, were all threaded through glass sleeving to ensure that no accidental contacts took place. The junction of the thermocouple was not at the hottest part of the furnace (see above). The sodium pressures estimated from the recorded temperatures are therefore likely to be low. This would only prove important, however, if quantitative measurements were to be undertaken. For qualitative experiments, such as those undertaken in this work up to the present, it is probably sufficient to adjust the alkyl halide pressure to the desired amount, and then to adjust the sodium furnace current until the resonance glow persists. The thermocouple is then needed only as a guide to the temperature attained.

The whole unit was, in the beam apparatus, surrounded with a glass shield. This was constructed from tubing of sufficient diameter to encompass the heater wire. A slot was "pulled" along the underside so that it could be slid well forward over the iodide lead. Shield and reaction unit were adjusted to be roughly co-axial by means of three supporting "feet". Two were poked into the top of the slit end of the

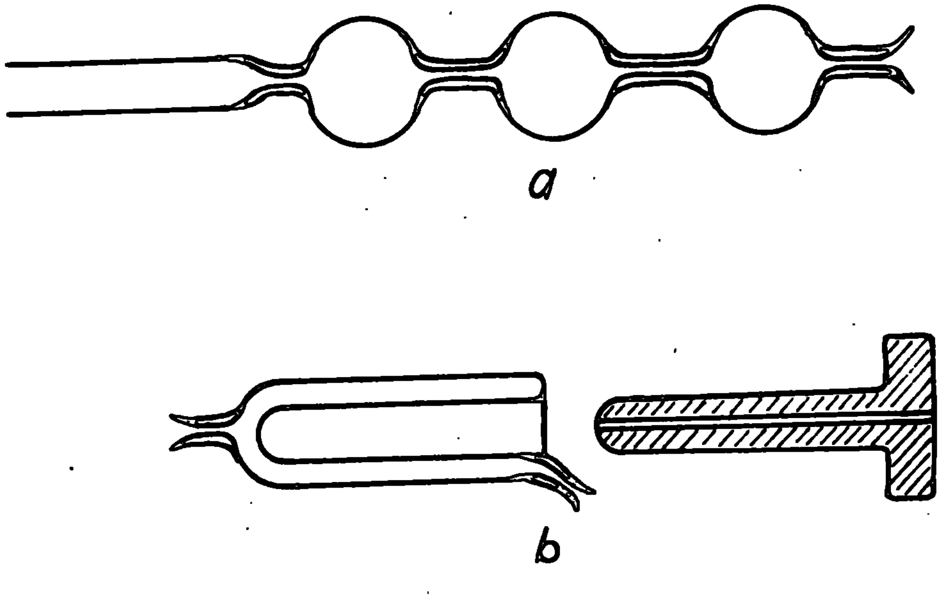


Fig. 11.

shield, and rested on the flattened top of the reaction chamber. The third, at the bottom of the opposite end, was shaped to fit over the iodide lead at that point. This shield served, to some extent, to concentrate the heat from the coil on to the unit.

Sodium Purification

When it was to be used for reactions on the test apparatus, the sodium was distilled directly into the chamber according to the following procedure: A piece of glass tubing was shaped, as illustrated in figure 11a, into a series of fairly thick-walled bulbs separated by "seal off" constrictions. The last constriction was sealed to the reaction chamber. At the other end about 6 cm. of the original tubing was left unaltered.

Lump sodium was cut into small pieces and melted under boiling toluene. This removed the outer "skin" of the sodium, and left it as fairly clean spheres. When the toluene had cooled it was poured off, the sodium was washed several times with small quantities of petroleum ether (low-boiling fraction), dried roughly with filter paper, and transferred to the open end of the glass side arm. This was then sealed off and pumped out.

The sodium was then gently heated with the hand torch, using a luminous gas flame. As it melted there was considerable evolution of gas. This probably came from traces of the various solvents which had been in contact with the sodium and had not been completely removed by the filter paper. This explanation was supported by the formation of black deposits, which could be carbon and other decomposition products, on the walls of the section into which the sodium was first introduced.

These deposits were visible before the development of the brown coloration referred to above, and were clearly distinguishable from it. When this initial heating was not carried out very gently the sodium was often forcibly ejected along the chain of bulbs into the sodium chamber. It was also necessary to take care that the constrictions ahead of the heated zone were not blocked by condensing sodium. As each bulb was cleared of sodium, it was sealed off and removed.

Since this was a very time consuming operation, alternative methods of distillation were tried. None was entirely satisfactory. Perhaps the best was to replace the chain of bulbs by a vertical pot. Near the bottom of this a side arm was attached, via a seal-off constriction, and arranged so that it sloped slightly down towards the pot. The sodium, cleaned as before, was placed in this side arm. When melted, it rolled down into the pot, and the side arm was removed. Distillation into the sodium chamber was carried out by electrical heating of the pot, which was sealed off and removed when sufficient quantity of sodium had been removed.

This process took place much more smoothly, but it took rather longer and it was still necessary to keep a constant watch on the constriction to make sure it did not become blocked. When this occurred, it was cleared by gentle heating with a fine gas flame.

When required for use in the beam apparatus, clean sodium was distilled into a slightly modified version of a device described by Sherwood (132). This consisted (fig.11b) of a small Dewar shaped vessel, approximately 4 cm. in length and 2 cm. outside diameter, to which two connecting tubes were attached, by means of seal off constrictions. One was attached to the end where the "nipple" is usually found on a Dewar flask, the other was attached to the rim of the Dewar seal.

A short length of duralumin rod was turned down on the lathe, first to a diameter which was just too large to fit in the well of the capsule, and then it was given a very slight taper. A "head" of rather larger diameter was left at the thicker end. This provided a cylindrical surface which could be held firmly in the lathe for the "finishing" operations, and also proved useful as a finger hold during the final manipulations in the laboratory. A hole was drilled down the centre to provide an exit path for water and carborundum during the grinding, and for air during subsequent evacuation. This tapered plug was then ground into the well of the capsule with fine carborundum until its tip just started to mark the bottom. The carborundum was then thoroughly washed out. If, on drying, the plug did not fit tightly into the well, a small amount was removed from its tip on the lathe.

The capsule was then attached to the auxiliary vacuum system (figs.13,22) by one lead, usually at the Dewar seal end, and to the other end was attached one or other of the sodium distillation systems already described. When sufficient sodium had collected in the capsule it was sealed off and stored for subsequent use.

When it was desired to start an experiment, the "sodium furnace" was heated. Because of its high expansion coefficient the duralumin usually succeeded in cracking the capsule at some temperature between 100 and 200°C., as intended. In trial experiments with empty capsules this worked very well, and the capsule was completely shattered. When it contained sodium, however (usually to not more than one third of its length), it did not shatter quite so well. The initial cracks appeared on the well at the expected temperature, but they did not spread very well to the outside. If the temperature was raised sufficiently, however, a strong resonance glow eventually filled the reaction chamber. One possible explanation for this is that these capsules had been too well annealed after manufacture. It had been found that a large number developed small cracks during the grinding process, and so they were annealed by electrical heating in an attempt to cut down the wastage of effort. It seems probable that a certain residual strain in the glass is desirable.

In the course of experiments on the main apparatus it was necessary to let the vacuum down every time a target was changed. Since contact with ordinary damp air would very quickly cause the cracks in the capsule to block up, "special" nitrogen, oxygen free, was always used to fill the apparatus to atmospheric pressure once the capsule had been broken. This was a slow process, but was well worth while in that it permitted the use of the one capsule for several runs.

Preparation and Storage of Alkyl Iodide Samples

A glass tap greased with silicone was the only means of isolating the storage section, which included the low temperature thermostat, from the rest of the source. Because the only pumping path was through the slit into the collimator chamber (see fig. 24), evacuation of the whole source section was a slow process, especially when glass blowing had recently been carried out.

It was therefore desirable to provide some arrangement whereby the alkyl iodide could be sealed on to the supply line, and kept isolated while the rest of the apparatus was being pumped down. A glass "break seal" was the most convenient

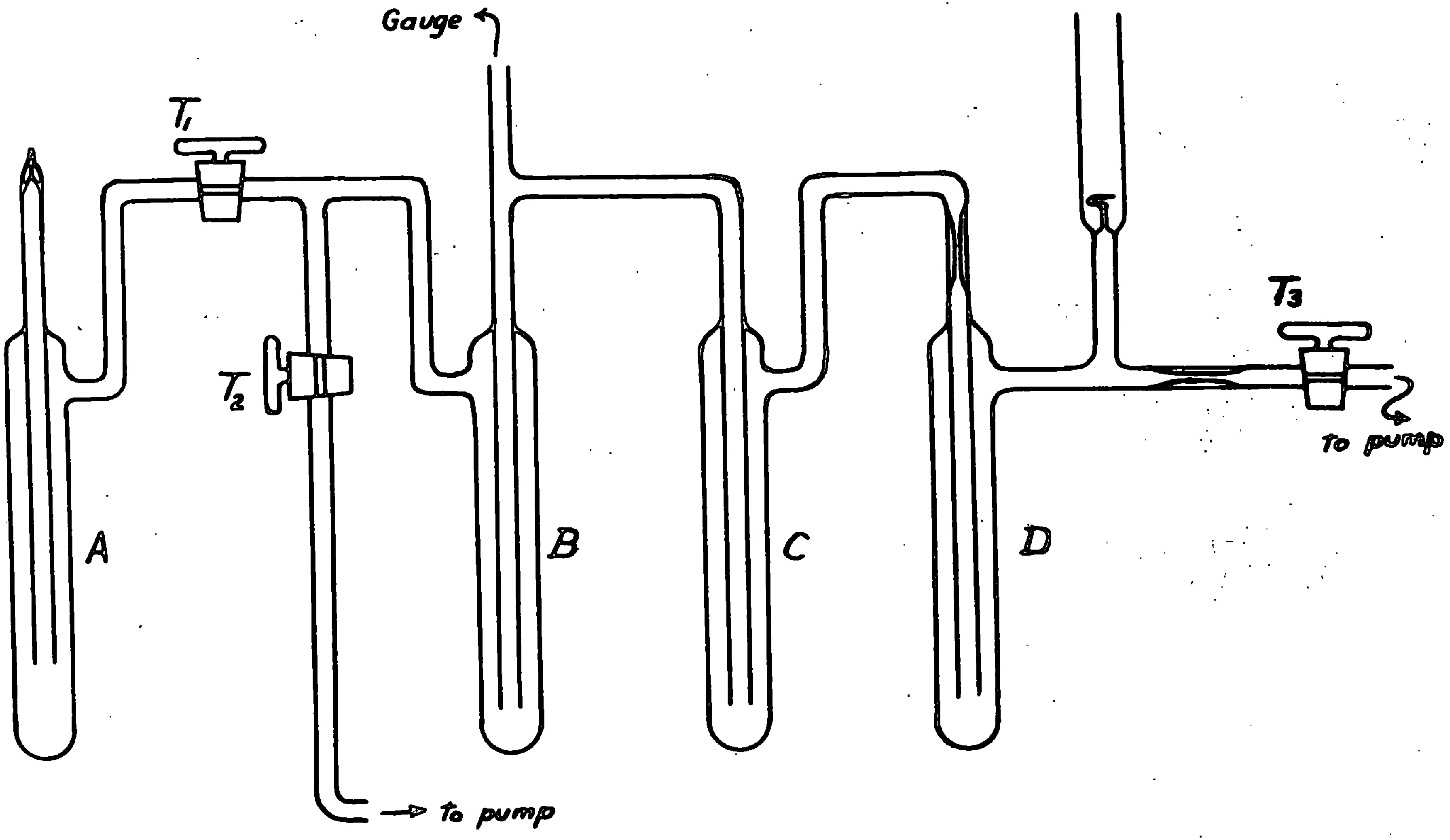


Fig. 12.

method of attaining this objective. Furthermore, the storage side of this seal should also be evacuated, so that no rush of air takes place when the iodide is admitted to the apparatus.

This was conveniently achieved on the auxiliary vacuum line. A series of traps (fig.12) was set up, with a connection at each end to the vacuum line, each connection containing a glass tap (T_2, T_3). These taps were lubricated with "sugar" grease in earlier operations, with silicone in later ones. Trap A was the storage vessel for the system, and was isolated from the rest by tap T_1, lubricated in the same manner as the others. Trap D was the final storage vessel. Attached to its side arm was a break-seal unit, and both tubes connecting it to the rest of the apparatus were provided with seal off constrictions. This vessel was sometimes of the type shown, and sometimes of the "well" type when the use of a pentane thermometer was intended (see fig.9). Some silver powder, to take up any free iodine formed, and some dehydrating agent, formerly calcium metal, later anhydrous magnesium sulphate, were placed in the bottom of each trap. It was found to be advisable to place some sharp bends between taps and traps when the latter dehydrating agent was used, as it is very finely divided and tends to fly about as the last traces of liquid evaporate from it. When a thermocouple gauge was available it attached in the position shown. As in all other operations, the "pump section" (fig.13) was separated from the "test section" by cooling the main trap with liquid nitrogen.

The methyl and ethyl iodide samples used in this work were obtained from Mr.H.C.Sutton, who had purified them by distillation when working in this laboratory. After purification they had been placed in blackened glass bottles and stored in a dark cupboard.

The liquid sample was introduced down the central tube of trap A by means of a funnel. This was then just frozen with liquid nitrogen, the tube was sealed, and the air pumped out. The sample was then outgassed by alternate freezing with T_1 open, warming with T_1 shut (c.f. p.85). Then trap B was cooled, and sufficient liquid for one charge was transferred from A. T_1 was subsequently kept shut. The sample was then transferred from trap to trap a number of times. Taps T_2 and T_3 were operated so that the direction of pumping was always the same as the direction of transfer. Thus there was always a trap at liquid nitrogen temperature between the liquid and the main trap. This process was continued until the McLeod gauge indicated that a satisfactory pressure ($< 10^{-5}$ mm.Hg.) had been attained. The liquid was then finally transferred to D, which was sealed off, removed, and stored.

This process was probably not really adequate to remove ethane (a possible decomposition product). For immediate purposes this was not, however, so very important, as long as oxygen was removed. For more recent samples of ethyl iodide, the method of continuous pumping at -95°C. (p.85) was employed. The low temperature thermostat would be well suited for such operations.

The free end of the break seal could then be attached to the source supply line on the main apparatus (fig. 26). Then, when the iodide was needed, the low temperature thermostat was adjusted and the septum broken with steel balls placed in a side arm in the line during assembly. During "shut down" periods the isolating tap was closed, and the liquid was returned to the original storage vessel, which was kept cool with liquid nitrogen.

CHAPTER IV. EXPERIMENTAL.

RADICAL DETECTION

In all molecular beam work great attention must be paid to the choice of detector, for, as has been shown in chapter II, the intensities encountered are small. A number of techniques has been used for this purpose, and the more recent ones are very satisfactory for most types of beam. None, however, with perhaps one exception, is suitable for the detection of a beam of radicals.

The manometric devices can be rejected immediately, for they can measure only the total intensity arising from all types of molecule. Even if carrier gas is not used, the radicals will be accompanied by their decomposition or reaction products. The concentrations of these can, in some circumstances, be considerably greater than the concentrations of the radicals themselves (61). Moreover, unless the conditions in the reaction chamber are chosen properly, there may also be present either the starting material itself or one of the products of its incomplete reaction (e.g. $PbMe_3$, $PbMe_2$, PbMe from the pyrolysis of $PbMe_4$ (61)). Thus, even if the methyls were deflected in an inhomogeneous field, the deflection could remain undetected by one of these devices because of the low proportion of radicals in the beam. Or, if some of the other constituents also possess a moment, the deflection of these could also mask the radical effect.

From these considerations it is apparent that the chosen detector must react strongly to radicals, and as little as possible to all other molecular types.

It may be possible, under some circumstances, to use a device which depends for its action on the relatively low ionisation potentials of the radicals (e.f. chapter I). Some such device may yet prove to be the best for quantitative radical beam intensity measurements.

The bolometric type of device, also, has been mentioned (see p. 13). It is understood that this method has been tried, and found to be insufficiently sensitive for the radical concentrations encountered (50 b). It might, however, be useful if more intense sources can be achieved.

When this investigation was being planned, it was considered that the best chance of success lay in the choice of a detector which relied on some specific chemical property of the radicals, with preference for a method which could eventually be made quantitative in its action. The first methods considered involved the application of their well-known property of attacking metallic mirrors. Such methods have two virtues for the present purpose. Firstly, they will detect nothing but radicals, and secondly, if a radioactive mirror is used, the sensitivity would seem to be governed

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ultimately by the specific activity, or isotopic purity, of the metallic deposit.

A numerical example is instructive.

In a calculation in chapter II (p. 37) it was estimated that the beam intensity at the detector might be of the order of 10^{14} molecule cm^{-2} sec^{-1} for a source pressure $p = 10^{-1}$ mm.Hg. The radical concentration in the source would probably amount to only one tenth of this under the most favourable conditions. Say $I_0 = 10^{13}$ molecule cm^{-2} sec^{-1}.

Suppose, now, the target to be a thin wire, 5 mm. long and 0.2 mm. diameter, and lying parallel to the slits. The surface presented to the beam will then be 10^{-3} cm^2. Thus the number of molecules arriving at this surface per second will be 10^{10} molecule sec^{-1}.

If the wire can be coated with isotopically pure RaE (^{210}Bi), the radicals would combine with this to form $BiMe_3$. Thus a beam of this intensity would be capable of removing 3.10^9 atoms of bismuth per second.

Now suppose the activity of the wire, immediately after it had been coated, was 4000 c/m. If we assume a counting efficiency of one in twelve (probably too high), this gives a figure of 800 disintegrations per second, $= dN/dt$ in the decay equation. $\frac{dN}{dt} = -\lambda N_0$, where N_0 is the number of atoms present at zero time $t=0$.

The half life, τ, of RaE is 5.0 day (133), i.e. $4.32.10^5$ sec. Thus, since λ, the decay constant, $= .693/\tau$, we obtain that

$$N_0 = 5.10^8 \text{ atoms (of Bi) on the wire.}$$

Thus a beam of the assumed intensity should be capable, under ideal conditions, of removing such a deposit in about 10^{-1} second, and not much longer than fifteen minutes should be taken to remove all this activity by a beam with an intensity as low as 10^9 molecule cm.$^{-2}$ sec.$^{-1}$.

It is not necessary that all the activity be removed. The radical beam intensity can equally well be estimated by following the decrease in activity over a period of time. This should make it possible to measure even smaller intensities, and the limit of detection could be lowered further still by the use of a more active target. Because of their high reactivity, the "background" concentration of scattered radicals should be negligible.

The detectable intensity thus calculated will be a lower limit, for it is not at all certain that the RaE coating will be absolutely uncontaminated by inactive bismuth, although it should be possible to make it substantially so.

This example illustrates one possible method of utilising the mirror technique for beam detection which has been considered. The major attraction of this method lay in the possibility of its use for plotting the beam peak-shape. If this proved feasible it would furnish a means of estimating the dipole moment by the standard procedure outlined in chapter II.

A detector arrangement designed for this purpose will be described in the next chapter. It consists of some means for traversing the fine wire across the beam in small steps, and an end-window counter placed inside the vacuum behind the wire, and perpendicular to the direction of the beam. It is clear that it is necessary to use a β or γ active isotope. If the wire is small enough its absorption of the β rays will be small . Thus it should not matter that the surface from which the activity is being removed is on the far side of the wire from the counter.

It is necessary, however, to ensure by previous experiment that sufficient activity can be deposited on such a wire, and that this activity can be removed by the action of radicals. Moreover the rate of removal must be proportional to the radical intensity. The desired relationship is of the form $dN/dt = -kI$, where k is a constant for the detector, N the number of detector atoms at time t and I the radical intensity. N may conveniently be represented by the measured activity of the detector, suitably corrected for the natural decay rate of the isotope used. In the following pages the measured activity at time t is represented by the symbol A, and B is used for the activity which the detector would have had if no removal by radicals had occurred. For any time t after the initial count $(A = A_0 \text{ at } t = 0)$, the ratio (B/A_0) % may be read off from a semi-log. plot of the decay curve calculated from the accepted figure for the half-life of the isotope (133). From this, t may be obtained, and the corrected activity is represented by the ratio (A/B) %.

Thus the detector will have the desired characteristics if a straight line is obtained when A/B is plotted as a function of t, for constant I, and if the slope is proportional to I. If these conditions are satisfied, it would be necessary to make two, or at most three, activity measurements for each setting of the wire as it is traversed across the beam. Then the slope of the A/B — t curve may be taken to represent the intensity, and may be plotted against the wire position to give the peak shape of the beam.

Another possible application of the mirror technique was also considered. In this, which bears a close resemblance to the original molecular beam target techniques, the active mirror is deposited on a flat surface which may be either metal or glass. This is then placed within the apparatus in the usual target position - i.e., perpendicular to the beam direction.

After it has been exposed to the beam for a time which it is estimated will be long enough for almost complete removal of the activity from the area impinged on by the beam, the plate is removed from the apparatus and an autoradiograph is prepared. In the ideal case, the result will be a "negative" image of the beam, with a minimum of blackening on the photographic plate where the radical intensity at the target was greatest. This method is, in the first instance, purely qualitative in nature, although it might prove possible to obtain at least semi-quantitative results with a microdensitometric scanning of the photographic image. It has the advantage in principle that it should be possible to form several images, slightly displaced from each other on the one target, before the photographic exposure. This is of importance when the apparatus has to be shut down, and air let in, each time a target is changed.

Should it happen, however, that surface migration takes place to any appreciable extent on the target at the temperature at which it is maintained, the method would be useless. This migration could be either of the original active deposit, of the radicals themselves, or of the partial products of the reaction. It would appear that migration of bismuth is not very great at room temperature. It might seem, however, that formation of the final products would involve a certain amount of migration at some stage of the reaction with the radicals. For this reason the method would require exhaustive testing before any confidence could be placed in the results it yielded.

In contrast with the wire method, an α-active isotope is to be preferred in this method, in order that the density distribution in the photograph may correspond as closely as possible to the intensity distribution in the beam (c.f. [illegible]). The most obvious choice for this purpose is the thoron active deposit.

Some preliminary experiments on both of these procedures are described in the following pages. Neither is, in its present form, entirely satisfactory.

Some experiments on the use of a molybdenum oxide deposit will also be described, and a report is also made of a single trial of a new method suggested by Mr.G.R.Martin.

If it should prove possible to make it sufficiently sensitive, this latter technique has interesting possibilities. It should be insensitive to the presence of traces of atmospheric oxygen - an advantage which is not shared by mirrors of lead or bismuth - and should be suitable for the wire technique.

Iodine reacts very rapidly with alkyl radicals ([illegible]), and is therefore a useful detector for them, particularly if a radioactive isotope (e.g. ^{131}I, τ = 8 day) is employed. However, because it is so volatile, it is not conveniently applicable to beam detection. Its use might be possible,

TABLE II

Radical	H^o_f, at 25°C, in Kcal/mole	ΔH, reaction Kcal/mole
	$R_{(g)} + AgI_{(s)} \rightarrow RI_{(g)} + Ag_{(s)}$	
CH_3	32.0 − 14.91 = 4.9 + 0	−12.19
C_2H_5	22.0 − 14.91 = −1 + 0	−8 (approx.)

The value for ethyl iodide is not certain, as only that for the liquid (−7.4 Kcal/mole) is listed in the literature (136, 137). From its heat of vaporisation at 72.3°C (7.15 Kcal/mole), and by analogy with methyl iodide, for which values for both states are listed, it is assumed that the value used is correct to within one or two kilocalories.

Closely agreeing values for methyl radical are given in refs. 2 (32.0 Kcal/mole, calculated) and 43 (32.5 Kcal/mole, from experiment). Those for ethyl differ rather more, being 25.2 Kcal/mole (ref.2, calculated) and approximately 22 Kcal/mole (ref.135, from experiment). The less favourable value is used here.

The other values were obtained from references 136 and 137.

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however, if it could be "fixed" by some means which would lower its effective vapour pressure without at the same time making it impossible for the radicals to react with it.

It is known that clean metallic silver is a very efficient method of removing elementary iodine from organic solvents, and it was considered likely that this could take place also from aqueous solutions. If it is assumed that the iodine deposits on the silver as AgI, a rough thermochemical calculation should indicate whether it could be removed by free radicals. Sufficient information is now available for the calculation of the heat of the reaction

$$R_{(g)} + AgI_{(s)} \longrightarrow RI_{(g)} + Ag_{(s)} \quad ,$$

where R is either ethyl or methyl.

The calculations are presented in table IX.

Thus it would seem that both radicals are likely to react with silver iodide. Of the two reactions, that of methyl is probably the more favourable.

BISMUTH TRACER TECHNIQUES

PRELIMINARY EXPERIMENTS WITH RaE

In most previous applications of the mirror technique the detector metal has been deposited on a glass or silica surface and has, moreover, been present in sufficient quantity to be readily visible. In the method now proposed the conditions are very different, as a further extension of the numerical example (p. 102) will show.

The total surface area of the wire is of the order of 3.10^{-2} cm.^{2}. On this there are 5.10^8 atoms of ^{210}Bi. Thus the area of surface "occupied" by each atom is 6.10^{-11} cm.^{2}, i.e. 6.10^5 A^2. The area covered by a single atom of neutral bismuth ($r = 1.46$ A) is 6.7 A^2. The smallest number of atoms needed to form a barely discernible trace in atomic beam experiments with metals (cf. 106) corresponds to a closely packed deposit of two atoms average thickness. The average inactive mirror used for radical detection will usually contain even more atoms per unit area.

It was necessary, therefore, to carry out some experiments to determine whether such a sparse deposit could, in fact, be removed from a metallic surface by radicals. At the same time this investigation was of value in that it provided an opportunity to gain some experience in the production of radicals as well as their detection, and also of general operating conditions, such as those required for the vacuum handling of organic vapours. It has already been shown in the previous chapter that special conditions arose in this last connection, for the conventional type of mercury cut-off control could not be used in the final arrangement.

Since ^{210}Bi was readily available from "stale" radon capsules, and inactive bismuth has often been used in the past for radical detection, it was decided to carry out the first experiments with this material. ^{210}Pb (RaD) is dissolved, with some ordinary lead chloride as carrier, in dilute (0.2%) hydrochloric acid. The daughter element ^{210}Bi will accumulate in this solution, and will have reached 75% of its maximum concentration within ten days of the purification of the lead. The isotope purity of this bismuth will depend only on the amount of bismuth impurity in the added lead carrier.

If a piece of clean nickel is then immersed in this solution, it has been found (133 p.218; 138 p.52) that a large proportion of the bismuth will deposit electrochemically on the nickel, whereas the lead is almost exclusively left in the solution. The presence of the carrier lead ensures that, if any of the lead is deposited, the amount of RaD will be relatively small.

Preparation of RaD Solution.

The source of RaD was two small glass capsules obtained from Woolwich which had, twelve months previously, contained 1020 mc and 980 mc of radon, respectively. They also contained some charcoal, and were about one third full of mercury. It was necessary to carry out a preliminary wet-way separation of the mercury from the lead, since mercury is said (139) to interfere with the anodic deposition of PbO_2. The procedure is further complicated by the necessity for dissolving the charcoal, and the glass itself, in order to ensure the highest possible activity in the final solution. It was found that a considerable proportion of the activity was retained by the glass if it were merely ground up and leached with a boiling mixture of concentrated nitric and perchloric acids.

The procedure used was as follows:

1. The capsules were ground to a fine powder in a mortar, and washed into a small beaker. The grinding was carried out in a "perspex" dust box.

2. Concentrated nitric acid, and some concentrated perchloric acid, were added, and the solution was simmered for several days until all the charcoal had disappeared.

3. About 50 mg. Analar quality lead nitrate was then added and, after some further heating, the solution was diluted and filtered. The filtrate was set aside, after first evaporating it to a small volume.

4. The powdered glass, which was still very active, was transferred to a platinum crucible, solid ammonium fluoride was added, and the crucible was heated, gently at first, until all the ammonium fluoride had sublimed. This process was carried out three times.

5. The residue was then fumed to dryness several times with concentrated perchloric acid to ensure complete removal of fluoride, a crystal of lead nitrate was added, and the material was transferred to a silica evaporating dish. It was then fumed to dryness several times with concentrated nitric acid, and finally dissolved in a small quantity of water.

6. The two fractions (3 and 5) were then transferred to a centrifuge tube, and the lead precipitated with a few drops of dilute sulphuric acid. This was centrifuged immediately and the mother-liquor drained off. By this means most of the mercury was separated from the lead.

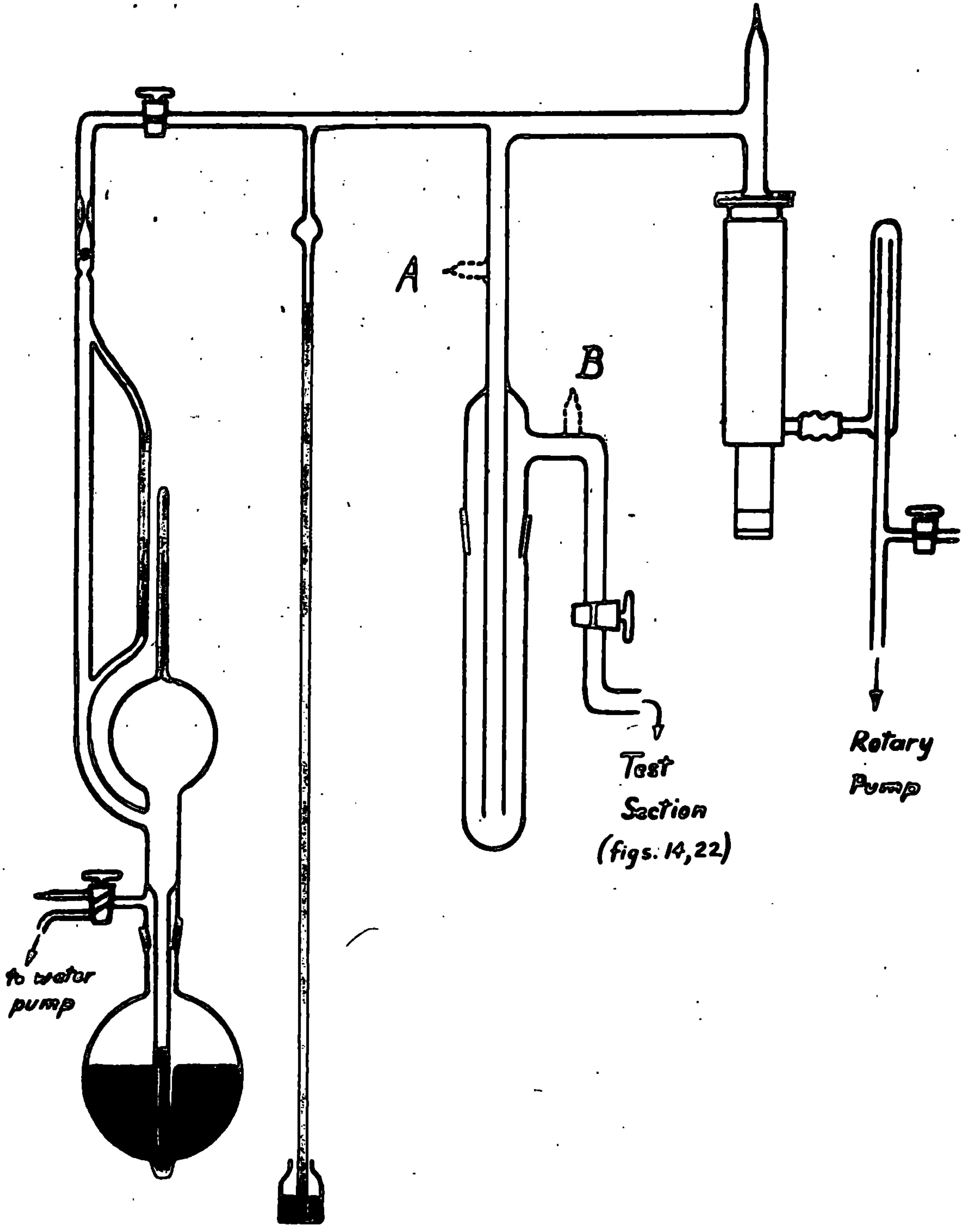


Fig. 13.

7. The lead sulphate, after washing, was dissolved in a strong acid solution of ammonium nitrate formed by mixing concentrated ammonium hydroxide with excess of concentrated nitric acid. Solution was rather slow. At this stage a test was made, with a clean copper rod, for the presence of mercury.

8. The concentration was then adjusted to give a 15% nitric acid solution, and the lead was collected on a platinum strip by electrolytic deposition as PbO_2. (2 V, about 0.2 amp. cf. ref. 139).

9. This deposit was dissolved in dilute nitric acid by the addition of a few drops of hydrogen peroxide solution. The resulting solution was evaporated to dryness, and converted to chloride by repeated evaporation to dryness of 5N hydrochloric acid.

10. Finally, sufficient 0.2% hydrochloric acid was added to dissolve the lead chloride, and the solution was divided into three portions, which were stored in glass containers.

Since each run usually lasted at least three to four days, it was therefore possible, by using each solution in rotation, to ensure that sufficient time was allowed for the RaE to accumulate before it was needed again.

Apparatus.

The vacuum was produced by means of a small electrically heated all-metal mercury diffusion pump (Edwards Type 3), backed by an Edwards "Speedivac" single stage rotary pump. The pump and gauge section, which was separated from the experimental section by the main trap is illustrated in figure 13. This section was subsequently transferred to the new laboratory, and used on the auxiliary or test, apparatus. The vacuum jackets of the low temperature thermostats were connected to this pumping system at A.

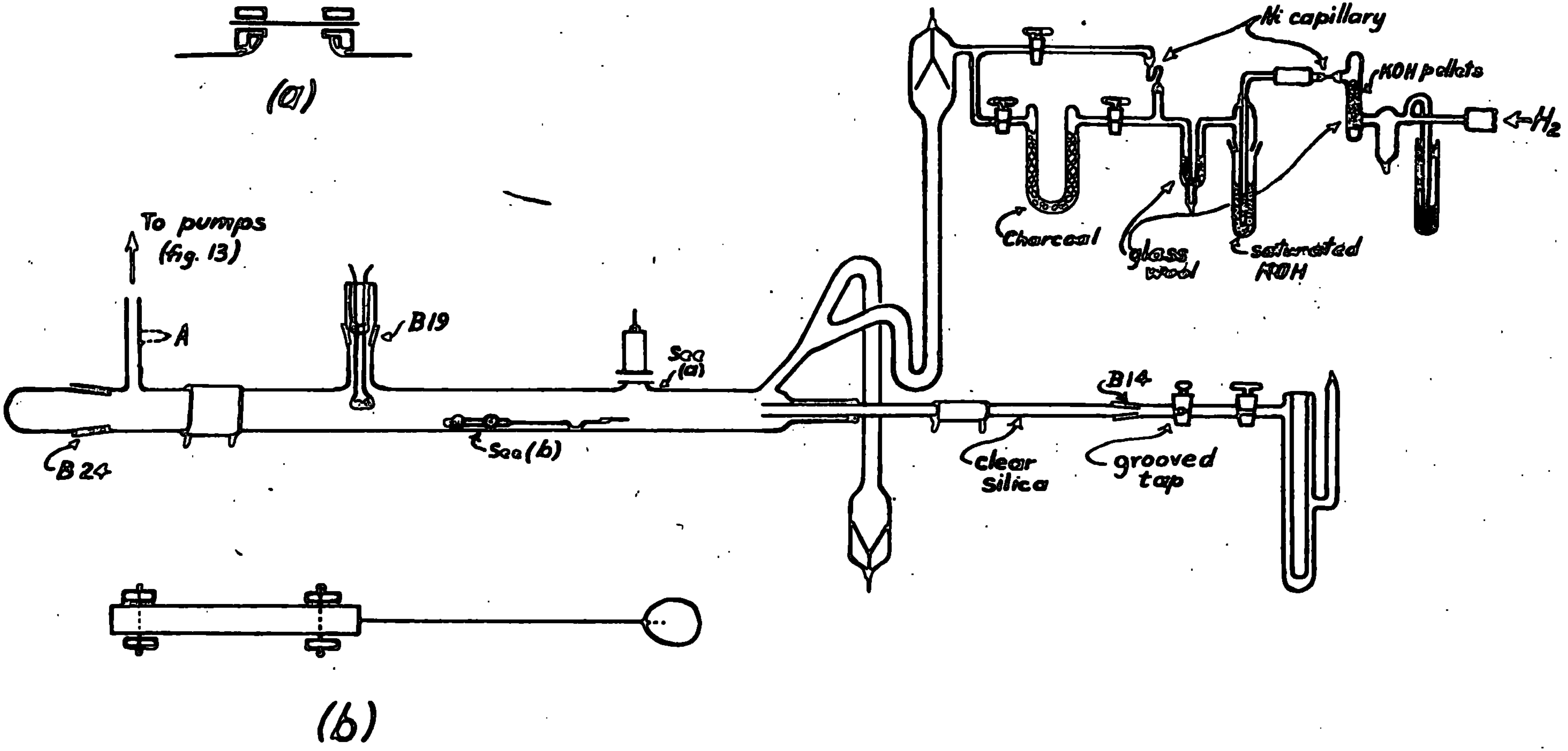

(a)
Ni capillary
KOH pellets
H_2
Charcoal
glass wool
saturated KOH
To pumps (fig. 13)
A
B19
Sca (a)
B24
Sca (b)
B14
clear silica
grooved tap
(b)

Fig. 14.

The apparatus used for the first experiments is illustrated in figure 14.

The main section consisted of a long straight tube, about 25 mm. bore and 1 metre long. The small electric heater (<u>the reducing furnace</u>) next to the pumping lead was formed by winding nichrome tape over asbestos paper on to a cylindrical brass former. Its resistance was 22 Ω .

The central B19 side arm held the small nickel spiral used for collecting the RaE from the solution. The activity could then be evaporated on to a metal foil placed underneath the spiral. Copper connections were provided between the spiral and tungsten seal. This permitted adjustment of the position of the spiral in the tube, while at the same time being sufficiently rigid to ensure that the setting, once made, would not suffer any unintentional alteration. The external leads were again copper. All metal connections were made by silver soldering the ends of the wires into nickel sleeves. The external well was filled with soft wax to give mechanical protection to the seals. A piece of mica was placed around the spiral in such a way that it protected as much as possible of the surroundings from contamination when the spiral was heated. In this way the background count was kept down to some extent.

An end-window counter (made by G.E.Co.) was mounted over the mica window which was further along the tube. The mica, thickness 17 mg. cm.$^{-2}$, was supported by a circular brass platform which fitted over a "blown out" section of the tube. The rim of this "blow out" was ground flat. "Sucking in" of the mica was inhibited by placing over it a brass guard ring (see inset a, fig. 14). The whole assembly was held together and rendered vacuum tight by means of Apiezon W ("black") wax. Provision was made for building a "castle" of lead bricks round the counter and this section of the tube.

To this end of the tube was attached a tube of narrower bore, into which the silica pyrolysis tube just fitted. This also was sealed in with black wax, and was fitted with a small heater - the pyrolysis furnace - narrower in diameter than the reducing furnace, but of similar construction.

Temperature measurmments on both furnaces were carried out with a narrow gauge chromel-alumel thermocouple, connected through copper leads to a micro-ammeter. Junctions were effected by means of silver solder. The arrangement was roughly calibrated against a mercury-quartz thermometer.

The source of lead tetraethyl is shown attached. The initial method of pressure control, by means of a scored tap, was described in chapter III.

To the other side arm on the long tube, near the silica tube, was attached the hydrogen line. This incorporated a discharge tube with conical aluminium electrodes for the production of hydrogen atoms, a charcoal trap which could be immersed in liquid nitrogen if pure hydrogen was required, and a system of taps, pinched nickel capillary leaks, bubbler, and blow-off tube, to control the flow rate. Cylinder hydrogen was used as a source of supply.

Subsequently, when a satisfactory thermocouple gauge had been built, it was attached to the pumping lead at A. This gauge was in use during the sodium flame runs (6 - 14) with methyl radicals. For these latter experiments the silica tube was removed, and the first type of reaction chamber (fig. 10a) was sealed on in its place. A well type reservoir, similar to that shown in figures 9 and 14, was again used. This time it was isolated by just one tap, and lubricated with "sugar" grease.

In most of this series of preliminary runs the pressure was governed by a rough temperature control exercised by attempting to keep the reservoir at approximately the same height above a small quantity of liquid nitrogen in the bottom of a Dewar flask. In one or two of the later runs (13 - 14) the methyl iodide temperature was controlled by immersion in an acetone-solid carbon dioxide bath. The control methods described in the last chapter were not developed until some time later.

Detector Preparation.

The choice of the metal to be used as the support for the RaE is governed, in the first place, by two considerations.

Firstly, the radicals must be able to remove the deposit from this support. Secondly, it is preferable to deposit the activity directly on to the wire, for it would seem unlikely that a sufficiently high activity could be transferred from, say, a nickel wire to some other fine wire by vacuum evaporation. This transference is, in general, only practicable when the receiving surface is large, although a technique has been proposed (140) in a recent publication which might be adapted for the transfer to smaller surfaces. Alternatively, it should be possible to deposit RaE on to any metal by an electrolytic method, provided that none of the many interfering ions are present. This would be most suitably performed by the electrolysis of a carrier free solution of pure RaE. A method for the preparation of such a solution has recently been published (141). However, the whole procedure, starting from the RaD solution, would have to be carried out each time a target was required.

Nickel is the most obvious choice in the first place, as has already been indicated. But should it prove difficult to remove the activity from it, platinum could be used. A method has been published (142) by which bismuth and polonium can be collected on a platinum surface which has been saturated with hydrogen.

Since, therefore, it may have proved necessary to try a number of metals as support for the RaE, the apparatus had to be arranged, as described, so that this could be done. Foils were used, for it is easier to evaporate a useful activity on to a large surface, and, besides, a variety of metal foils was available in the laboratory.

The design of the apparatus required that the foil could be moved from place to place along the main tube between successive operations. This was achieved by means of the little mild steel "trolley" illustrated in figure 14, inset *b*. The foil was silver soldered to a length of 0.5 mm. tungsten wire, bent as shown. This bend served to support the foil at a fixed distance from the walls of the tube, and hence from the counter when measurements were being taken. It was necessary that the supporting wire should be thin, so that the area exposed to the evaporating RaE should be small compared with the area of the foil, and long to ensure that little activity was received on the trolley. The length was also arranged so that the trolley projected from the lead castle. This permitted the adjustment of the foil without the necessity for removing the castle. The trolley was moved from outside the tube by means of a small permanent magnet. The position of the foil under the counter was defined by a scratch mark on the tube.

The sequence of operations was as follows:

With the apparatus evacuated, a stream of hydrogen was pumped by way of the liquid nitrogen cooled charcoal trap, and sufficient current was passed through the nickel spiral to [illegible] it to a red heat. This ensured a clean surface. The spiral was then removed from the apparatus and placed in one of the RaD solutions. The silver-soldered joints proved to be a great disadvantage at this stage, for it seemed to be very difficult to remove the last traces of flux from them. Interaction of the flux with the lead eventually produced a deposit at the bottom of the solution, and this had the effect of reducing the amount of available RaD in the solution. Thus the solutions had to be re-treated from time to time. Spot-welding, rather than silver soldering, of the wires would eliminate this difficulty.

The rate of deposition depends, for a small area of nickel and a large volume of solution, on the rate of diffusion of the RaD to the surface. Immersion for periods as long as half an hour without stirring was found, however, to give adequate activity. The spiral was then withdrawn, washed with water and alcohol, dried with a current of warm filtered air, and its activity was checked by placing it momentarily near a counter. It was preferable that the activity should, at this stage, be sufficient to "jam" the scaler, i.e. > [illegible]00c/m, when the wire was several centimeters from the counter window.

The spiral was then replaced in the apparatus, the trolley with its attached foil was inserted through the B 24 joint, and pumping was re-started. The foil was then maintained at about 500 to 550°C, by means of the reducing furnace.

stream of purified hydrogen for at least half an hour. It was then moved into position under the mica window, and the background count was recorded as the last of the hydrogen was being pumped away.

The foil was then moved back to a position directly under the spiral, which was electrically heated to a dull red for a maximum of about 6 minutes. The "background" was again counted, the foil was returned to its position under the counter, and the experimental run was begun.

In the last two runs (13 and 14) with this apparatus, the foil was replaced by a loop of nickel wire. The RaE was then deposited directly on the loop, and the procedure was modified accordingly.

Testing Procedure.

Two sets of experiments were carried out with this arrangement.

The results of three of the first set (runs 2, 3, 5), using ethyl radicals from lead tetraethyl, are shown in figures 15, 16, 17. The annotations indicate the operations which were carried out during these runs. Times were taken from the laboratory clock. Each deposit was used until the activity became too low (~ 1000 to 2000 c/m) for convenient measurement with short counting times. One or two minute counts were preferred, with the proviso that a 1% statistical accuracy (10,000 total counts) was aimed at. The results so obtained were corrected for the "normal" decay according to the procedure set out on page 105, and plotted as shown. No correction was made for counting losses at high counting rates. The usual counting arrangement was used, but one or two minor variations in procedure should be noted.

It was shown that movement of the trolley, for the purpose of taking frequent background counts, was not desirable as it was very difficult to replace it in exactly the same position each time. These slightly differing positions showed up as excessive deviations of the recorded count from the value to be expected from the "normal" decay rate. Since, in these early experiments, the control over radical intensity was not good, it was decided to neglect the background count in the calculation of the results. That this makes comparatively little difference, particularly at high counting rates, can be seen in figure 15, where the broken line was calculated after first correcting the activities with reference to a background count taken at the end of the run. The background at any given time was calculated from the observed figure by assuming that it arose, for the most part, from RaE contamination on the inside glass walls, and applying the 5 day half life correction. In all other curves, where the background has been neglected, the percentage drop in activity will appear to be slightly less than it really is.

It was found, also, that the starting voltage of these commercially made counter tubes had a very high temperature coefficient, being upwards of 80 v for a 5° (C) rise in room temperature. A standard source superposed on the foil activity would be of little value because of the large counting losses at high rates of count. It was therefore assumed that the counting rate at a given position on the "plateau", relative to the starting voltage, would be reproducible from day to day within a sufficient degree of accuracy. Before each count, therefore, the counter voltage was found for which the counting rate was approximately half the "plateau" counting rate, and the measurements taken at a setting exactly 100 v higher than this. This procedure was possible because the "plateau" extended over some 250 v, and the operating voltage was thus well away from the ends of the plateau. This "half counts" voltage was chosen in preference to the starting voltage, for the counter characteristic curve changes very rapidly in this region, and the reference point was thus more closely defined. When this technique was used, it was found that individual measurements remained within the expected statistical error unless some other, chemical, effect was occurring.

The sequence of operations was decided during the course of the experiments, and was altered periodically in order to check on the possible causes of the phenomena observed. The result of the possible operations on the decay rate, when lead tetraethyl is being used, should be as follows:

1. "Normal" 5 day half life when the vacuum system is shut down. If appreciable amounts of RaD are collected, this should not be so.
2. Again, normal half life on continuous pumping, with the reservoir tap shut, whether the pyrolysis furnace is hot or cold.
3. Continuous pumping, reservoir tap open, pyrolysis furnace cold - still no effect.
4. As in 3, but pyrolysis furnace on - linear drop in activity, with slope dependent on radical concentration.

However, it is well known (cf. 41) that traces of oxygen inhibit the removal of lead or bismuth by radicals. The standard technique for overcoming this, when the mirror is deposited on the walls of a tube, is to move the mirror up and down the tube a few times by gently warming it in a stream of pure hydrogen gas. Although this is not possible when the "mirror" is deposited on a wire or foil, it is said that hydrogen atoms from a discharge are equally effective. The discharge tube shown in figure 14 was installed for this purpose. Finally, therefore, it was necessary to investigate

5. The effect of discharge alone on the activity should not be large, but it might facilitate the removal of the activity by radicals.

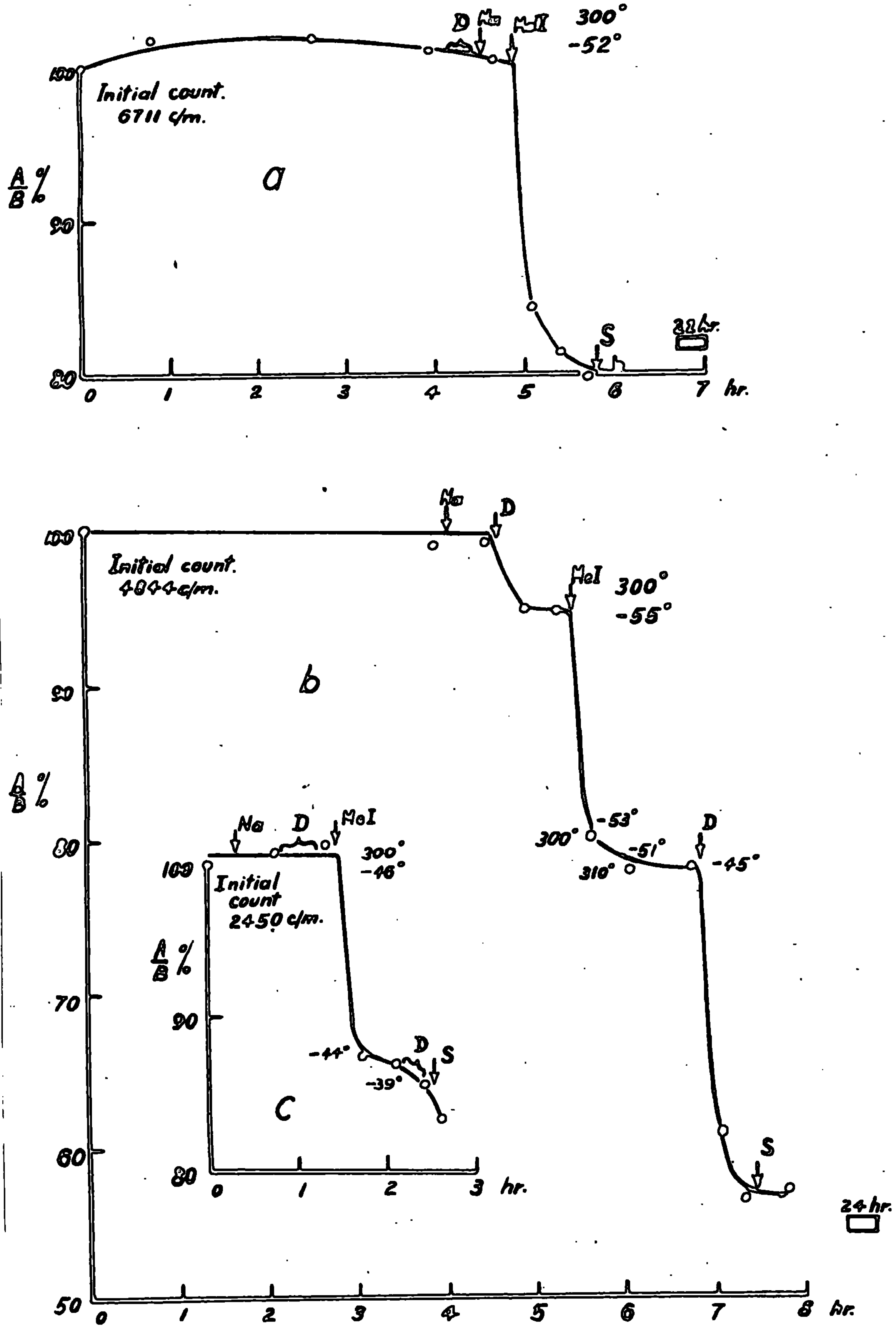

D
Na
MeI
300°
-52°
100
Initial count.
6711 c/m.
A/B %
a
90
S
22 hr.
80
0
1
2
3
4
5
6
7
hr.
Na
D
Initial count.
4044 c/m.
MeI
300°
-55°
b
90
A/B %
-53°
300°
-51°
310°
D
-45°
80
70
60
S
24 hr.
50
0
1
2
3
4
5
6
7
8
hr.
Na
D
MeI
300°
-46°
100
Initial count
2450 c/m.
A/B %
90
-44°
D
S
-39°
C
80
0
1
2
3
hr.

Fig. 19.

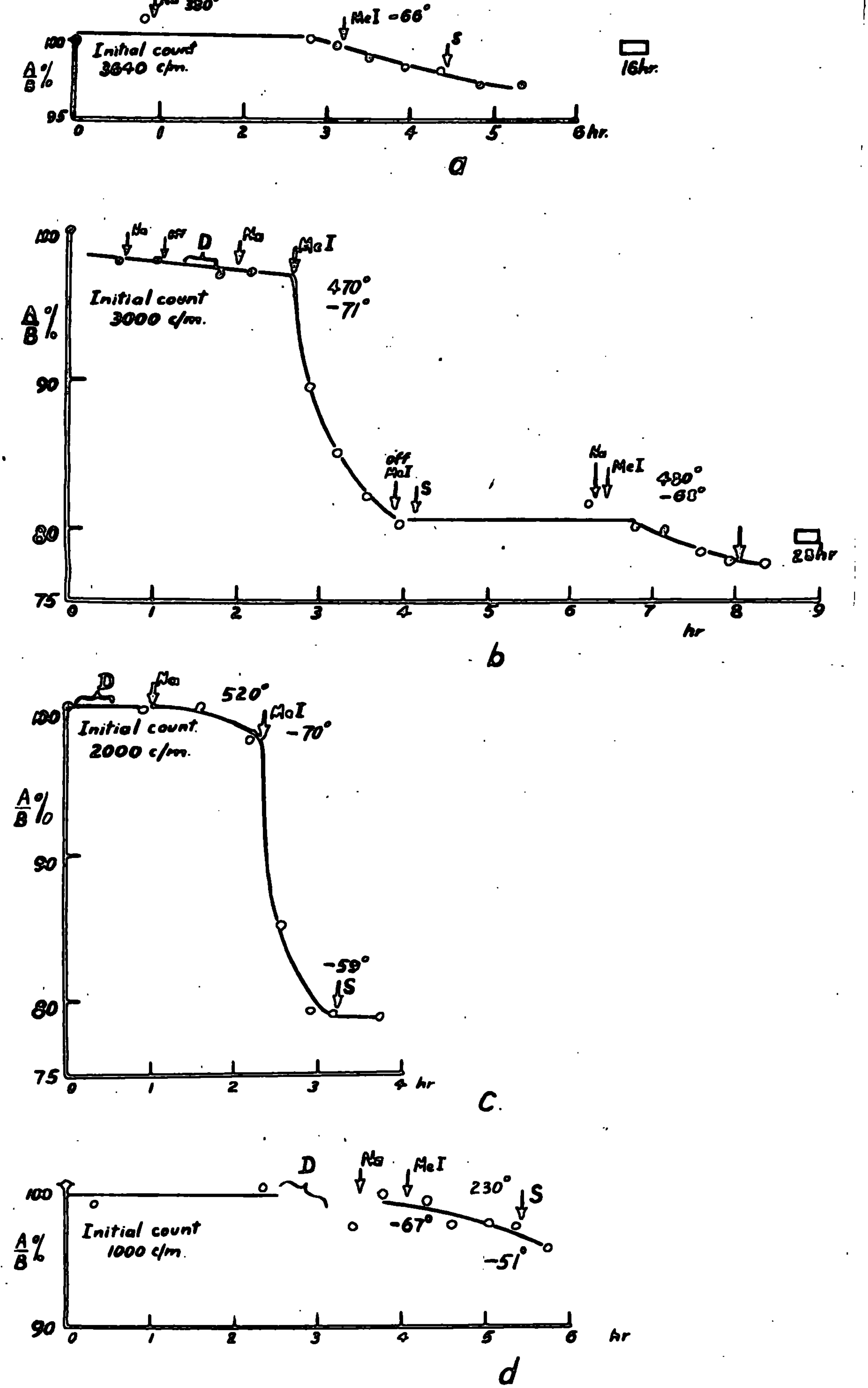

380°
MeI -66°
S
100
Initial count 3640 c/m.
A/B %
95
0
1
2
3
4
5
6 hr.
16 hr.
a
100
Na
off
D
Na
MeI
470°
-71°
Initial count 3000 c/m.
A/B %
90
off MeI
S
Na
MeI
480°
-68°
80
28 hr
75
0
1
2
3
4
5
6
7
8
9
hr
b
D
Na
520°
MeI
-70°
100
Initial count 2000 c/m.
A/B %
90
-59°
S
80
75
0
1
2
3
4 hr
c
D
Na
MeI
230°
S
100
-67°
Initial count 1000 c/m
A/B %
-51°
90
0
1
2
3
4
5
6
hr
d

Fig. 18.

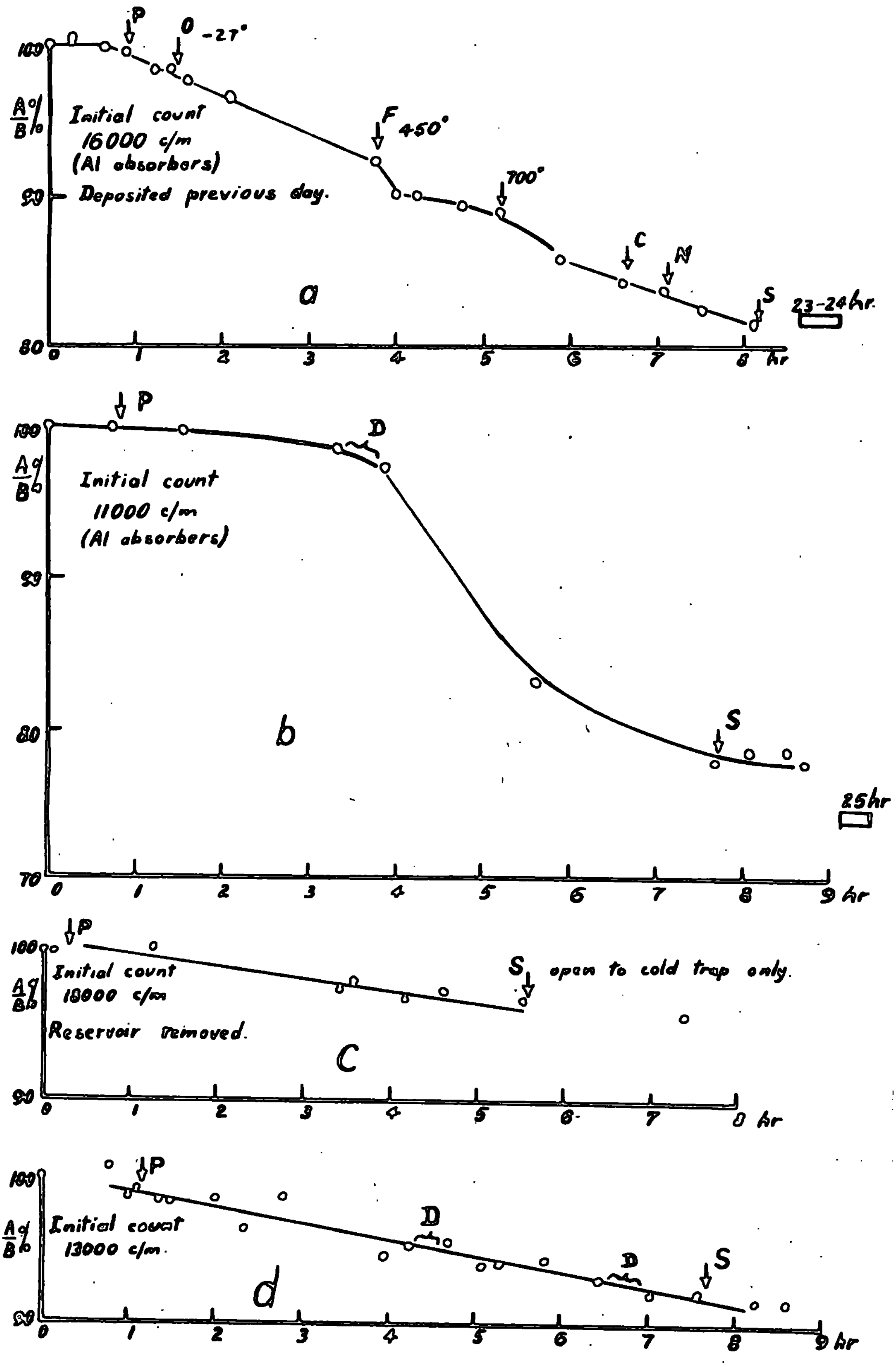

P
O -27°
F 450°
700°
C
N
S
23-24 hr.
A°/B%
Initial count 16000 c/m (Al absorbers) Deposited previous day.
a
100
90
80
0 1 2 3 4 5 6 7 8 hr
P
D
A%/B%
Initial count 11000 c/m (Al absorbers)
b
S
25 hr
100
90
80
70
0 1 2 3 4 5 6 7 8 9 hr
P
S
open to cold trap only.
A%/B%
Initial count 10000 c/m
Reservoir removed.
c
100
90
0 1 2 3 4 5 6 7 8 hr
P
D
D
S
A%/B%
Initial count 13000 c/m.
d
100
90
0 1 2 3 4 5 6 7 8 9 hr

Fig. 17.

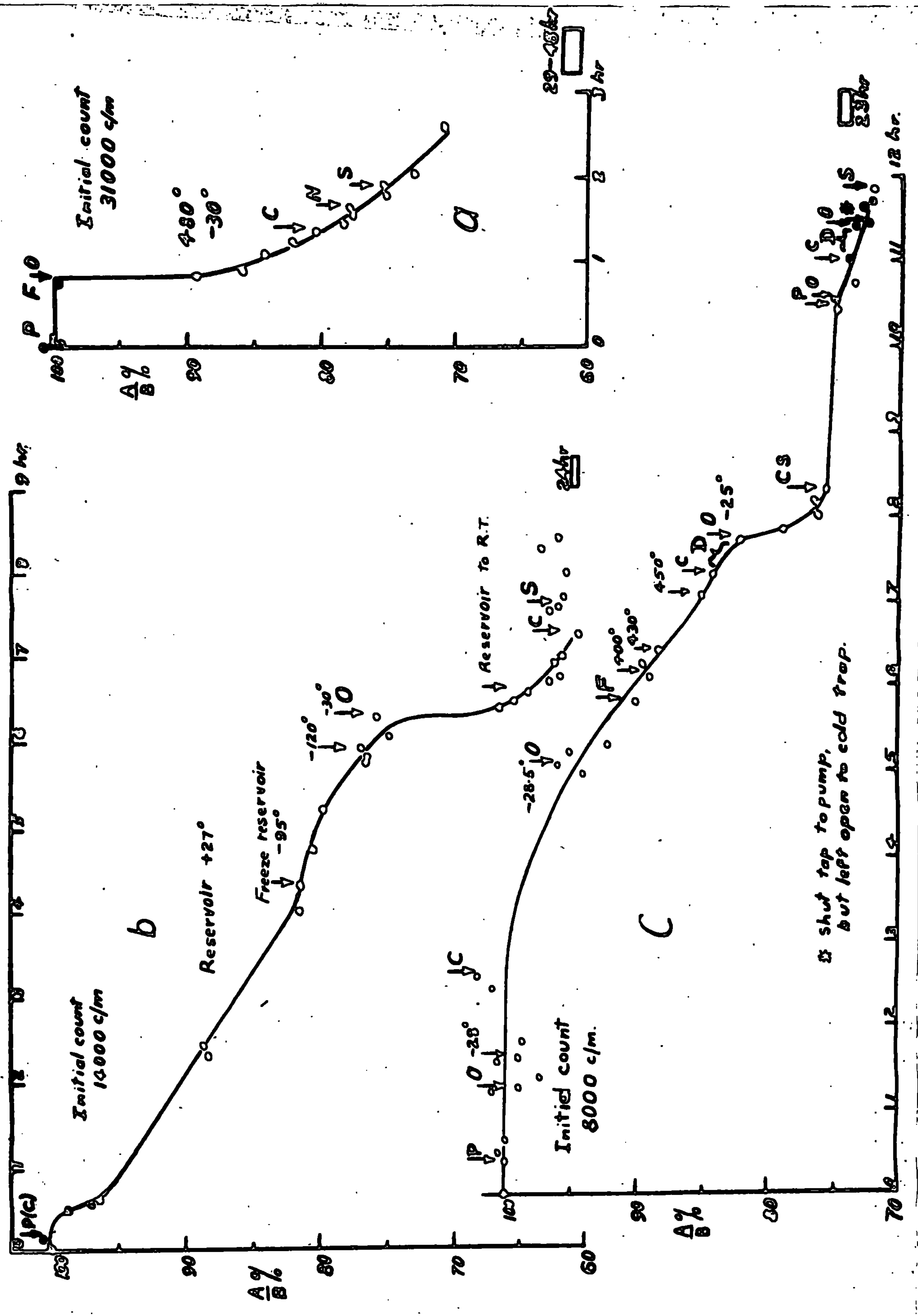

a
Initial count 31000 c/m
+80°
-30°
P
F
O
C
N
S
A%/B
100
90
80
70
60
0
1
2
3 hr
29-46 hr
b
Initial count 14000 c/m
Reservoir +27°
Freeze reservoir -95°
-120°
-30°
O
Reservoir to R.T.
C
S
P(C)
A%/B
100
90
80
70
60
10
11
12
13
14
15
16
17
18
19 hr
24 hr
c
Initial count 8000 c/m.
P
O -28°
C
-28.5° O
F
+100°
+130°
+50°
C
D
O
-25°
CS
P
O
C
D
O
S
* shut tap to pump, but left open to cold trap.
A%/B
100
90
80
70
10
11
12
13
14
15
16
17
18
19 hr
23 hr

Fig. 16.

KEY TO FIGS 15-19

A	air let in (to re-grease tap).
C	close reservoir tap.
D	discharge.
F	pyrolysis heater on.
N	" " off.
O	open reservoir tap.
P	Start pumping.
S	shut down (e.g. stop pumping)

Fig. 15 only.

✩	no lead deposited at heater to this point
⚄	moved foil, took background. Foil right up to hydrogen inlet for discharge, then replaced.

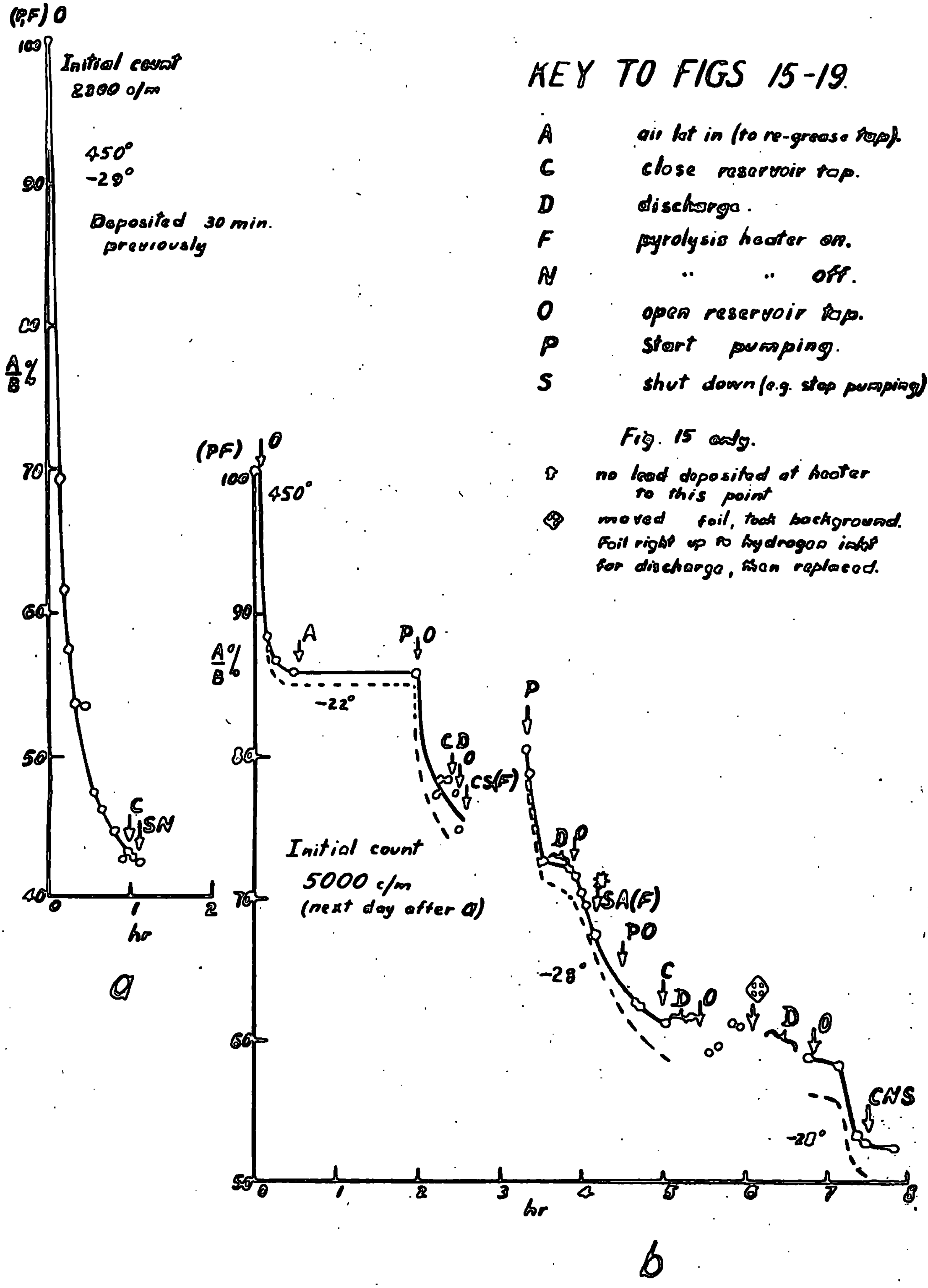


Fig. 15.

When it had been shown that ethyl radicals would remove at least some of the activity, and a possible explanation obtained for some other of the observed effects, the whole experimental section of the apparatus was taken down and thoroughly cleaned. After it had been re-assembled, pumping was continued for a period of two to three weeks before the second set of experiments was begun, (i.e. with methyl radicals produced by the sodium flame technique).

The combinations of operations investigated were similar to those outlined for lead tetramethyl. In some of the runs, particularly when tests were being made of the effect of the discharge on the activity (no radicals), the nickel grid was replaced by a platinum one. Figures 18 and 19 (runs 13 and 14) represent the results obtained for the action of methyls on RaD deposited on a loop of nickel wire.

Discussion.

Although they differ in detail in numerous respects, the curves shown in Figures 15 - 19 have one important feature in common. In most of the cases where a sharp initial drop was obtained - presumably by radical attack - only a portion of the activity was removed, and the sharp drop was followed by a "tailing off".

Thus, although there is some slight indication from the sodium flame results that the initial slope does depend on the methyl intensity, the other condition for the use of [illegible] method as a beam detector is not fulfilled, at any rate under the conditions which are obtained in these experiments. That is, dN/dt is not constant. Indeed, in some cases the "tailing off" occurred as the methyl iodide pressure was increasing.

In these experiments the conditions were continuously adjusted so that a slight haze was always visible in the reaction chamber when it was illuminated with a sodium vapour lamp. That is, the conditions were always of slight sodium excess. Since the capillary through which the sodium emerged tended to become blocked with sodium iodide deposit, the methyl iodide temperature, rather than the reaction temperature, should be taken as a rough indication of the relative radical intensities. Thus in figure 18, the radical intensity in curve a (-66°C) was probably greater than it was in curve b (-71°C). It should be noted that, at these temperatures, methyl iodide is solid. Thus the extrapolation procedure mentioned on page 71 can only give, at best, a very approximate idea of the probable vapour pressures. Bearing this in mind, the pressures at these two temperatures will be of the order of 2.1 and 1.4 mm.Hg. respectively. However, the pressures in the reaction chamber were sure to be much less than this, for the methyl iodide was pumped through some 14 cm. of capillary tubing with bore rather less than 1 mm. The thermocouple gauge indicated pressures of 10^{-3} mm.Hg.

There are a number of possible explanations of the "tailing off" process. Firstly, it may be that small traces of oxygen are in some way being continuously introduced into the system, and that this oxygen progressively reacts with the bismuth until the stage is reached when it is no longer possible for the radicals to react with it. If this is so, treatment with hydrogen should regenerate the surface, which would then be available for further reaction until it once more became oxygenated. Some of the results with methyls could be taken to support this explanation. No particular precautions were taken to ensure that completely clean sodium was transferred into the sodium chamber, and the methyl iodide was outgassed by the usual technique of freezing and pumping until no further bubbles were evolved on re-melting. This is usually taken to be sufficient, but the amount of RaE is so small that very slight traces of oxygen could cause the effect.

Curve a in figure 18 might indicate that the methyls remove the activity but only very slowly, when they are not preceded by hydrogen atom treatment. This is shown again in the latter part of curve b. On the other hand it can be seen (curves b and c) that previous discharge treatment results in a much sharper fall, whose slope also varies in the expected direction with methyl iodide temperature. The same effect can also be seen in figure 19. Moreover in 19b it can be seen that a second sharp drop is obtained when the discharge treatment is applied after the first "tail" has been reached. In this curve can also be seen an example of a phenomenon which sometimes occurred in the preceding runs with foils, whose results are not shown. Discharge treatment by itself can give rise to a drop in activity. This does not happen every time, and is usually not very large. It cannot be ascribed in all cases to the formation of radicals in the discharge, even though this explanation could be advanced for the last steep drop in 19b. In some of the earlier runs this effect was obtained before any methyl iodide had been introduced into the system. It may be that the discharge, whose conditions of hydrogen flow rate were not exactly reproducible, sometimes produced atoms in sufficient quantity to cause appreciable heating of the foil and thus evaporate the bismuth. It is said (ref. 41, p. 48) that this metal does not form a hydride by direct reaction with hydrogen atoms.

Evidence which appears to be in contradiction with this oxygen hypothesis is presented, however, by the curves from the lead tetraethyl experiments. In figures 15 and 16 a number of examples may be found of sharp drops which were not preceded by discharge treatment of the foil. Indeed, in 15b, the initial portion of the curve shows what occurred when an air leak developed in the reservoir tap. The curve did indeed flatten out, and only the normal decay occurred during the time when the whole system was at atmospheric pressure while the tap was re-greased. Immediately the vacuum was restored, however, and the lead tetraethyl was once more being pyrolysed, another sharp drop, although smaller, was obtained. This one occurrence by itself seems to cast considerable doubt on the validity of the oxygen hypothesis (cf., however, figure 17a).

Alternatively, this "tailing off" could be explained by assuming that, in addition to the volatile metal alkyls whose formation is responsible for the decrease in activity, some are formed which are relatively involatile and prevent any further reaction by "clogging" the surface. Discharge treatment could then perhaps generate sufficient heat to volatilise these compounds. This is quite feasible, particularly for methyls, for Paneth (19) has recorded that the compound $\left(Bi(CH_3)_2\right)_2$ has been isolated as a product of the reaction of methyls with a hot bismuth mirror. It is not inconceivable that small traces of this compound are formed on a mirror at room temperature. No similar compound seems to have been isolated in the case of ethyl radicals, although only a very small amount would be needed to explain the results. This explanation is very difficult to prove or disprove with the available data, although, once again, the initial portion of figure 15b is difficult to reconcile with it, unless the supposed involatile material is destroyed on contact with the air. If, however, the explanation is that involatile ethyl compounds are not formed, some other explanation for the "tailing" off must still be sought.

A third possible explanation is associated directly with the sparse distribution of the bismuth atoms on the surface. With the foils this is even greater than was indicated by the numerical illustration previously given in this chapter. The surface area of the foil was of the order of 1 cm.^{2}. Thus, even with a counting rate of 40,000 c/m, and a counting efficiency of only 1%, the area occupied by each bismuth atom turns out to be of the order of 2.10^5 Å^2. Even if this amount of activity were deposited on the loop (about .2 mm. diameter, 2 cm. length, i.e. surface area 0.13 cm.^{2}) the area per atom comes to about 3.10^4 Å^2. It is very likely that these atoms will not be uniformly spread out over the surface, but will coalesce to form small aggregates of varying size. The radicals, which are themselves not so very much bigger than the atoms, will strike the surface at random. Thus, unless some surface migration process takes place, only a proportion of the radicals will react with the detector, and as this is removed, the number of available reaction centres will decrease, with a consequent reduction of the rate of activity decrease. This hypothesis would give rise to an explanation of the form $dN/dt = -kIf(N)$ (cf. p. 104), where f(N) is the relationship between the number of RaE atoms on the surface (N) and the number of reaction centres. This would fit in with the shape of the curves quite well, provided that, in addition, it was postulated that a certain minimum size of aggregate of bismuth atoms is necessary before reaction can take place. Otherwise the curve should not completely "flatten out" until a large proportion of the activity was removed. Then discharge treatment could have the effect of redistributing the remaining atoms on the surface, and thus create fresh reaction centres.

This hypothesis by itself does not, however, account for the inference to be drawn from curve a, and the latter part of curve b, in figure 18 - that a discharge seems to be necessary before methyl radicals will cause a sharp drop in activity. None of these explanations accounts satisfactorily for the phenomena shown in figures 16 and 17 where, with comparatively low ethyl concentrations, a relatively steady, but slow decrease takes place over quite an extended period of pumping and even, in one instance, overnight when the pumps were shut off.

The possible causes of this low decrease require some further explanation. It occurred only during those early ethyl runs, and usually only when the long "test" chamber was being continuously pumped. As a general thing the last count at night, after the pumps had been turned off, and the first count next morning, before they were started again, gave evidence that only the "natural" rate of decay had taken place. Two separate factors gave rise to this phenomenon. Firstly, concentrated sulphuric acid had been applied to the walls of the discharge tube. Secondly, the taps shutting off the reservoir had been lubricated with Apiezon grease, which very rapidly absorbed an appreciable amount of lead tetraethyl, particularly when the reservoir had been left at room temperature. Thus, even when the tap was shut, the lead tetraethyl diffused through the grease in sufficient amount to give an appreciable concentration in the pumped chamber. This could then react with the acid (143), yielding lead sulphate and ethyl radicals.

In one small pool of the acid which had collected, indeed, a white crystalline solid was observed, and was shown to be lead sulphate. Thus, when the system was being pumped, the radicals were drawn over the foil and removed the activity. Under stationary conditions an equilibrium state was set up and most of the radicals were probably destroyed before reaching the foil. This, then, can account for curves 16b and c (run 3). However, before run 5 (fig.17) was carried out, the sulphuric acid had all been washed out, and the apparatus cleaned. The decrease still occurred (fig.17b). That this was in some way connected with the lead tetraethyl is shown by curves 17c and d. These show a slight, but nevertheless real, decrease even when the lead tetraethyl reservoir had been removed altogether, and the silica tube blanked off at its ground joint by means of a sealed off socket. Moreover, when the use of this substance was discontinued altogether, the apparatus was thoroughly cleaned and subjected to several weeks pumping. In subsequent runs it could be assumed that all traces of lead tetraethyl had been removed. The loss in activity then followed the natural decay curve unless methyl radicals were present.

It might seem then that the lead tetraethyl could react with the bismuth even when there was no apparent means of producing radicals from it. No further attempt was made to follow up this interesting side-line. It would be of interest to investigate, some time, whether this is, in fact, a real effect. For the immediate task it was taken to be the final argument in deciding to seek some other source of radicals.

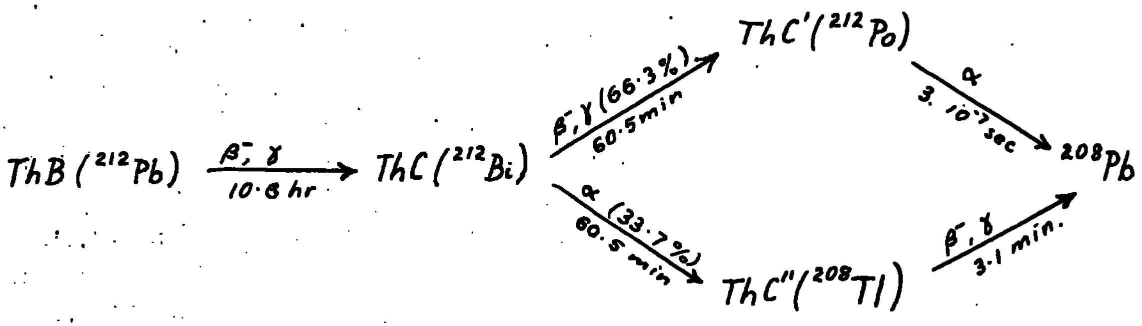
Although these results indicated that further development was needed before the "wire" form of detector could be accepted as satisfactory, it was considered that this development might possibly be fruitful. Attention was then turned to the construction of the beam apparatus, for it seemed that this would offer the best chance of obtaining a controlled variation of intensity which could be used to check whether the slope of the "decay" curve really depends on the radical intensity. In the design of this apparatus, therefore, provision was made for the introduction of hydrogen atoms into the target chamber, and for a device on which the wire could be mounted and traversed across the beam. Attention was also paid to the question of preparing samples of sodium and of alkyl iodide which were oxygen free.

AUTORADIOGRAPHIC TECHNIQUE

This technique has received comparatively little attention for, in addition to the doubts raised on page 106, the results discussed in the preceding section apply to this also. For this technique the most significant observation is that only a small proportion of the activity was removed before the rate of decrease "tailed off". Unless, therefore, the conditions could be arranged so that all the activity was removed by a sufficiently prolonged radical treatment, the technique would not be satisfactory. A reduction of even 30% in activity along a very narrow strip in an area of otherwise uniform activity would not yield a photograph of very great contrast, and the fine details of intensity variation would be difficult to pick out.

A few exploratory investigations were performed to find out something about the best conditions for obtaining a uniform deposit and a satisfactory photographic image at the end of an experiment, but no separate test was made of the ability of radicals to remove this deposit. A few runs were also carried out in the beam apparatus, to try out the operating procedure.

For the radioactive deposit it was decided to simplify procedure by using the whole of the active deposit from thoron (cf.133). This consists of a mixture of isotopes of lead, bismuth, polonium, and thallium. The first two are known to be attacked by radicals. It is possible that the other two will also be attacked, but this is not important because of their very short half lives. The decay scheme is



This deposit has the advantage that it omits the particles required for the production of a good autoradiograph and at the same time there is an adequate flux of β and γ radiation which permits a rough preliminary check on the deposited activity by means of an ordinary end window counter. This is very useful for the estimation of photographic exposure times. It has the disadvantage, however, that its half life is only 10.6 hr. Because of the required operating procedure the activity must still be sufficient to give a good photographic image at least 50 to 70 hours after the target has been removed from the emanating source, that is, for at least five to seven times its half life. Thus the initial activity must be of the order of 100 times the activity finally required for the autoradiograph. An activity of about 2,000 c/m when the target was about 1-1/4 cm. from the counter window gave a useable photographic density after two days exposure (cf.a.fig.21).

Small pieces of Ilford C2 Nuclear Research Plate were used. This type of emulsion has the advantage that it is sensitive to α-particles while being relatively insensitive to other types of radiation, including light. Thus advantage could be taken of the sharper resolution offered by α-autoradiographs (cf.134), and a fairly bright green safe-light (X-ray type) could be used. Because of the low penetration of these particles into the emulsion, only a short development time was necessary (maximum of 4 to 6 minutes at 18°C, cf. ref.134), using developer solution ID19. Because of the thickness of the emulsion, a relatively long fixing time, of at least 30 minutes agitation in IF2 solution, was required. The emulsion was then washed in running tap water for at least an hour, and stored vertically until dry. For these preliminary investigations no special precautions were taken to ensure that the target did not move on the emulsion during exposure. They were simply laid together and stored in a cardboard photographic plate box.

Two other conditions must be satisfied. Firstly, materials which can cause the <u>pseudophotographic</u> effect must be avoided (ref.134, p.9), even though it is said that this effect is not of particular importance when nuclear type plates are used. Hydrogen peroxide, which is said to be the cause of this production of an image in the absence of ionising radiations, is also said to cause a fading of the latent image in this type of emulsion. Lead, copper, [illegible], iron, silver, nickel, and cobalt are suitable materials. Possibility of corrosion makes iron, and even copper, if it is accidentally touched with the bare fingers, unsuitable. Lead is too soft. It was decided, therefore, to use nickel.

Secondly, the best resolution is obtained when the active surface has the largest possible area of contact with the emulsion. To a close approximation the central portion of a nuclear plate is of uniform thickness. Consequently, if the edge sections are rejected when the plate is cut up, it may be assumed that the emulsion surface is flat. It was therefore necessary to ensure that the target surface also was flat. This was done by lapping on a flat piece of plate glass, first with fine carborundum then with "Sira" abrasive. Sheets of nickel of suitable thickness were not available. Therefore the target (fig.20a) was made of copper sheet, which was lapped before nickel was plated on to it. Since the nickel was deposited on both sides of the copper base, the "bimetallic strip" action was minimised, and the target remained constantly flat over the whole range of room temperatures encountered.

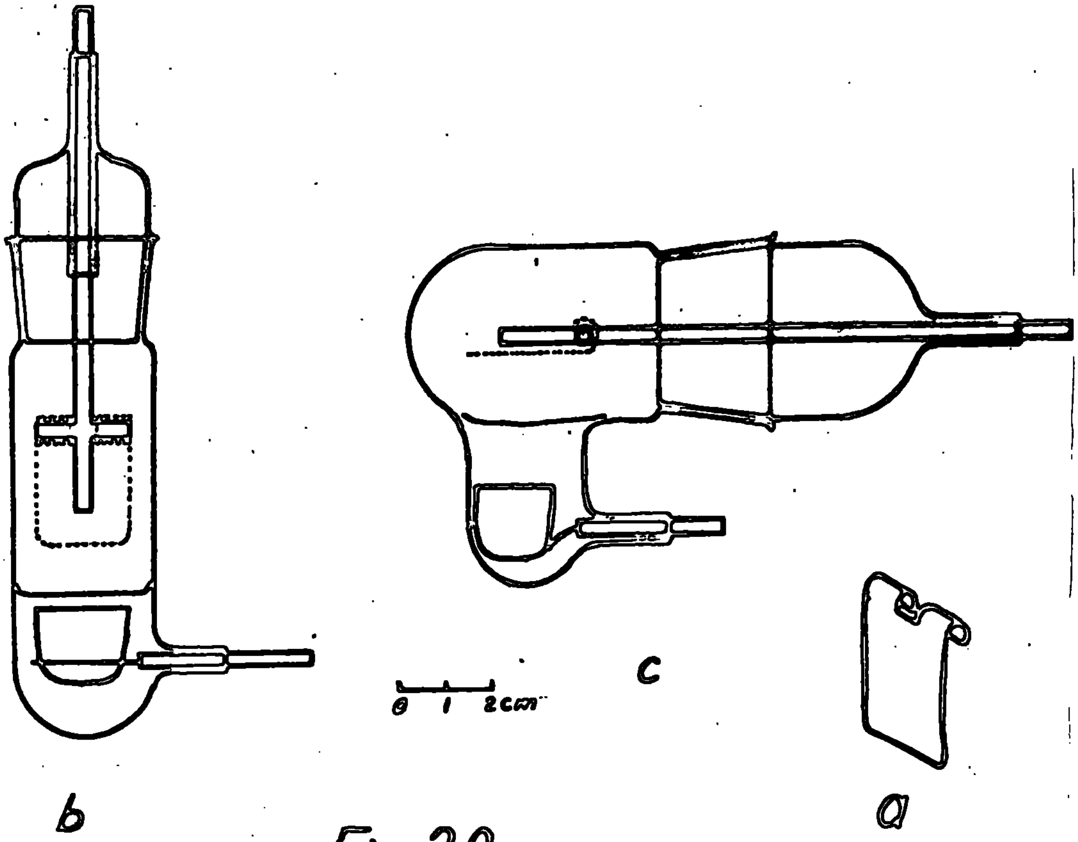
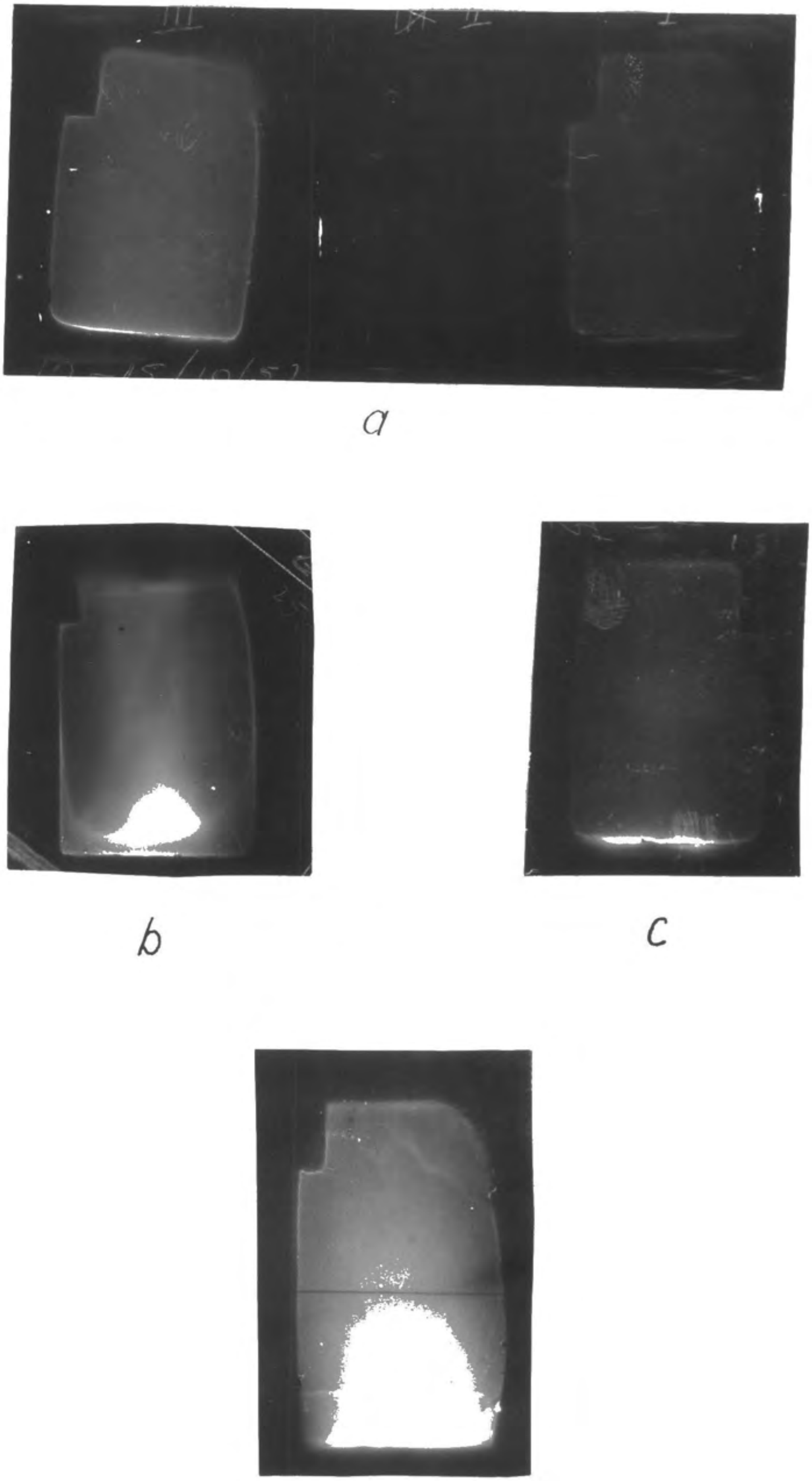


Fig.20.

Emanating Source.

A small amount of solution containing ferric iron and radiothorium dissolved in hydrochloric acid was available in the laboratory. On addition of dilute ammonium hydroxide, the ferric hydroxide carried down with it the radiothorium. This was filtered on a pad of filter paper pulp, washed, and pushed out, pad downwards, on to a small "dish" made from a piece of gold foil.

Two types of glass "emanating source chamber" were used (fig.20). Both were fitted with leads so that a potential difference could be applied between the gold dish and the target, if desired. The target lead, which served also as its support, was provided with a small cross bar which fitted into the curled "hook" on the top of the target. It was arranged so that the target could be put into place without the need for too much force, yet was held firmly once in place. This support was made from 1/8" brass welding rod, and was waxed into the narrow tube at the end of the ground glass cone. Connection was made to the gold dish by means of a "spring" of fine tungsten wire, silver soldered to another piece of welding rod. This rod was also waxed into its side arm. In both arrangements a single thickness of "Androx" toilet paper was placed over the gold dish to ensure that only gaseous molecules could reach the target. The ground joints were lightly greased with vaseline, to ensure that no appreciable



a

b

c

d

Fig. 21.

amount of thoron escaped into the atmosphere. At the same time this helped to preserve the ferric hydroxide in a damp condition, thus preventing it from "ageing" prematurely.

The first arrangement (fig.20b), with the target hanging vertically over the source, was fairly satisfactory as long as no potential was applied (fig.21d). Since an electric field caused all the activity to collect along the bottom edge (fig.21e), the second arrangement (fig.20c) was tried. This was only partially successful (fig.21b).

With the first, vertical, arrangement, a rough check was made of the effect of the applied voltage, and its sign, on the activity collected. The results are shown in table XXI, and are in qualitative accord with expectations.

TABLE XXI

Target	Volts on target	exposure t hrs.	min.	$\beta + \gamma$ activity c/m	background c/m	% of max. for $t = \infty$	c/m for $t = \infty$
XI	0	16	35	2793	17	66.5	4187
II	−130 to −150	17	35	9222	–	68.5	13450
I	+130 to +150	25	40	632	17	81.0	776

Each activity was measured by hanging the target in roughly the same position on a fixed support in front of a G.E.C. counter which was laid on its side on the bench. No lead shielding was employed. The percentages shown in the second last column were obtained graphically, assuming a 10.6 hr. half life. A rough check, over an eight hour period with target II indicated that this was correct.

These results indicate that the application of a negative potential to the target greatly increases the collecting efficiency. However, since this destroys the uniformity of the deposit (fig.21b and c), it is probably better to use a more active source with no field than to attempt to shape the target in an attempt to achieve a more uniform field distribution.

One other small point was investigated. In order to obtain some guide to the resolution attainable, a short length of fine nickel tape (cross section .03 x .005 mm.) was placed across a target prior to exposure over the emanating source, with no field. The tape was fixed in place with a touch of soft wax, applied to the back of the target. Prior to the photographic exposure, the wire was removed. Figure 21d indicates that little of the activity deposited under the wire, and that the resolution promised to be reasonably good, provided that the surface migration effect turned out to be not too large.

However, the preliminary experiments with RaE seemed to indicate that a reasonable proportion of the activity might be removed only by the application of repeated discharge treatments. Operational trials (see next chapter) with the beam apparatus indicated that this would be far from convenient, for a satisfactory beam is only to be achieved when a good vacuum ($\not>$ 10^{-6} mm.Hg.) is attained, and every hydrogen discharge destroys the vacuum. This takes at least 15 to 20 minutes to restore.

It was decided, therefore, to discard both of these radioactive methods for the time being, and to search for some alternative detector which does not need any "sensitising" treatment once it has been installed.

OTHER TECHNIQUES

AUXILIARY APPARATUS

At the close of the RaE experiments it became necessary to transfer the apparatus to another laboratory. In the course of the move it was re-designed so that it would take up less space, and at the same time be adaptable to a wider variety of purposes. All the subsequent tests were carried out with this system, which is referred to as the test or auxiliary vacuum line.

The pumping unit (fig.13) was as before, and the hydrogen line (fig.14) was much the same, with the exception that the charcoal trap was subsequently removed. The taps isolating it were, however, left in place, and a glass socket (B.14) was sealed to the tap on the discharge tube side. A needle valve could then be inserted in the hydrogen line if it was desired to control the flow rate when, for instance, vacuum gauges were to be calibrated.

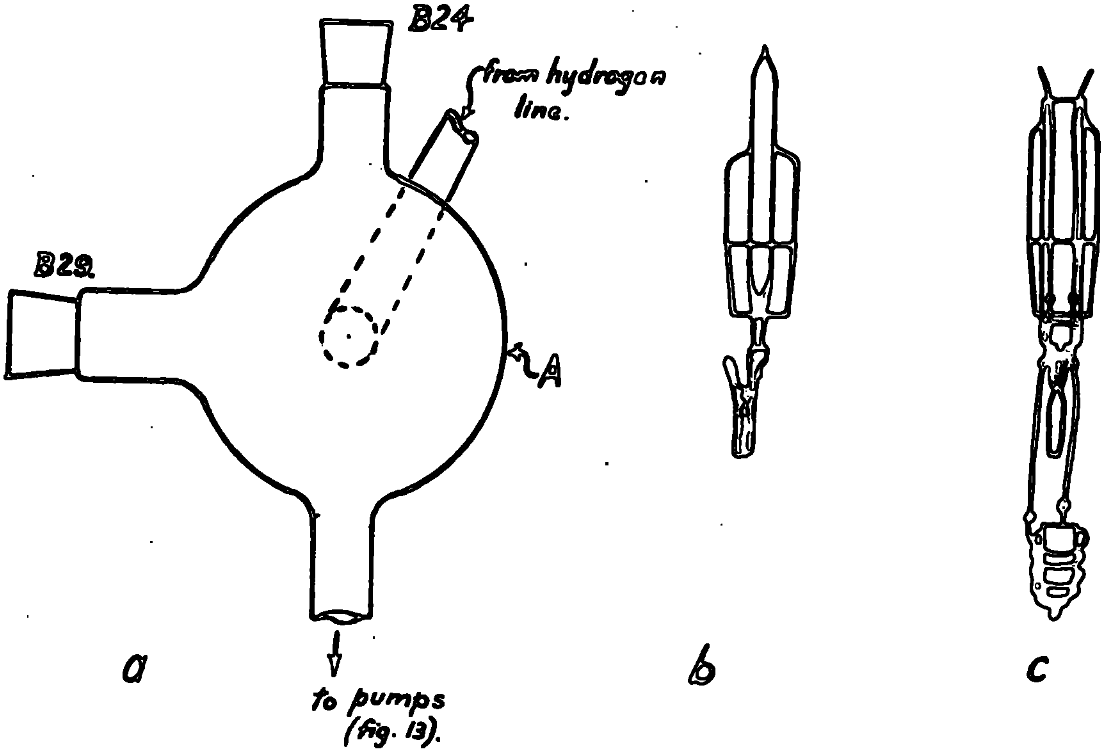


Fig. 22.

The new test section consisted of a glass bulb, of approximately 700 cc. capacity. It is shown in figure 22. Targets were inserted through the top B.24 socket, and were supported by a "crocodile" clip which was waxed to a glass rod sealed to the corresponding cone (fig.22b). The source of radicals was similar in construction to the source used in the beam apparatus (fig.10b). It was attached to the B.29 side arm by means of a B.14 - B.29 adaptor with an "extended" cone. Subsequently the B.14 joint was omitted. In its place a constriction of comparable dimensions was formed. This obviated the necessity for a greased joint so close to the heated zone. The alkyl iodide supply line was similar to that described for the main apparatus. The first model thermocouple gauge (p. 83) and the second model low temperature thermostat (p. 73) were used. Sodium was, however, distilled directly into the end of the sodium chamber. With this design the sodium tended to condense on the sides of the reaction chamber during the distillation. In order that the resonance light could be seen during the reaction, this film of sodium was moved to nearby glass surfaces by gentle heating with a small flame. During the reaction, the sodium was heated by a small electrical heater of conventional design (see p. 113). The reaction chamber was kept warm by a few turns of nichromewire in series with the sodium furnace. Taps and joints on this section were lubricated with silicone grease.

It was found to be desirable to make some provision for the "working" of the joints nearest to the reaction chamber. This was achieved by incorporating a glass spiral in the alkyl iodide supply line between the reaction chamber and the "buffer" bulb. After the radical source had been put in place the alkyl iodide line was sealed together with the spiral in slight compression so as to compensate for the tendency of the silicone to flow out of the joint. This spiral was shaped as a very flat double cone. This shape gave it more stability under compression than is possessed by the more usual helical form.

No one particular point was used for connection with the other arrangements used for special purposes, such as the preparation of alkyl iodide and sodium samples, or the calibration of the thermocouple gauge (chapter III). Point B (fig.13) and either of the two sockets (fig.22) were the points of attachment most frequently used. The choice was decided according to the other operations being carried out at the time.

In the first of these spherical test vessels a mica window, similar to that shown in figure 14, was provided at A (fig.22). This window was later omitted.

MOLYBDENUM OXIDE

Melville and Robb (48) have observed that radicals produce a blue coloration in molybdenum oxide. Since they claim that ethyl radicals are 0.38 times as effective as hydrogen atoms in this regard, it was considered that this might prove to be a useful qualitative detector. They give no figure for methyl radicals, but the indication from the present tests is that they are less effective. In agreement with these authors (48b, 49) it has been found that the sensitivity of this material as a detector does depend on its "previous history". The coloration, as with that produced by hydrogen atoms, does not persist on exposure to air (cf.114). The time taken for it to fade seems also to depend on the method of deposition of the oxide.

Initially, the deposit was formed in a very simple manner (cf.144). Some powdered molybdenum oxide in a silica crucible was heated with an oxy-gas flame to a temperature in excess of its melting point (795°C, ref.145). The surface to be coated, usually a piece of microscope slide, was held in the smoke of subliming oxide above the crucible until sufficient thickness of deposit was obtained. This deposit was rapidly turned blue by close proximity to the edge of the flame.

Subsequently a system of electrical heating was employed in an attempt to obtain a more uniform and coherent deposit. A length of "Kanthal" resistance wire was formed into a cup shaped spiral, whose diameter was adjusted so that it fitted closely round a small silica "test tube", of about 15 mm. bore and 2-1/2 cm. length. This contained the molybdenum oxide. This unit was suspended inside a cylindrical glass envelope with the top of the silica tube about 1 cm. below the rim of the envelope.

The intervening space was packed with pieces of asbestos. The heater wire was protected from the molybdenum oxide by means of a mica annulus which covered the entire space between the silica tube and the glass envelope. On top of this, wet asbestos pulp was built up to form a tight seal, leaving the orifice of the silica tube at the bottom of a shallow well. A rectangular hole was cut in another piece of mica, which served to support the microscope slide on top of this device, and at the same time to shut out stray air currents which would otherwise disturb the homogeneity of the deposit.

If the temperature of this arrangement was brought up gradually to a bright red heat (approx. 800-850°C), a coherent deposit formed on the glass slide without cracking it. If the slide was placed too close to the orifice, the resulting deposit was hard and almost clear, as though the oxide had condensed as a liquid, and subsequently crystallised. This was found to be unsuitable for detection purposes. Insufficient access of air, as with heating in vacuo, was found to result in the formation of the blue coloration. With this arrangement, however, the deposit was always white.

These deposits were shown to possess a greater sensitivity to radicals than that obtained by the original method, and the blue coloration was much more stable on exposure to the atmosphere. Although fading is appreciable after several months, little change was noticed in the space of a week. The contrast in light values

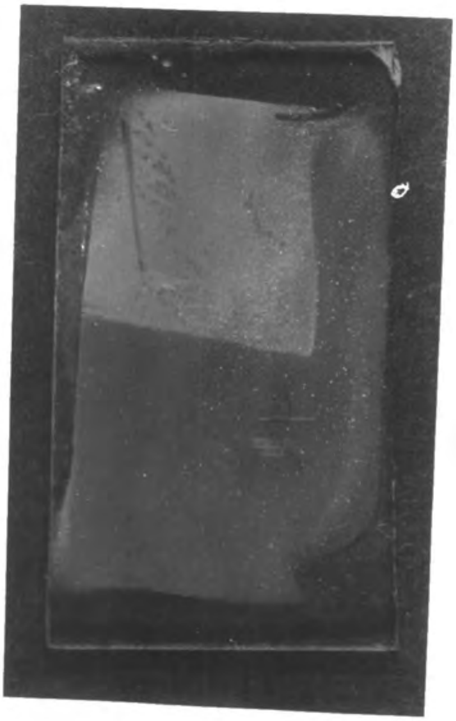


Fig. 23.

is not good, but it is possible to obtain photographic reproduction of the "radical blue", as shown in figure 23. The uniformity of deposition is much better than that obtained in the first method, although in this last respect there is still some room for improvement.

It was hoped that, if this deposit proved to be sufficiently uniform and sensitive, the beam could be detected as a visible trace. It is claimed (48) that every radical colliding with this material is captured by it. Therefore it would appear that, as long as the radicals continue to reach the target, it should only be a matter of time before a trace was produced by even a weak beam. This method could not very easily be made quantitative, but it could show qualitatively whether an inhomogeneity was producing a broadening of the beam.

Reaction with Ethyls.

For the preliminary tests one corner of the deposit was covered with another, smaller, piece of microscope slide. By this means it was possible to detect quite small changes in coloration.

Before setting up the sodium flame system, a preliminary trial was made by pyrolysing lead tetraethyl in a silica tube. This was waxed in to a B.29 cone, and attached to the test bulb. With the reservoir held at between -8 to -14°C, the thermocouple gauge registered pressures from 10^{-1} to 4.10^{-2} mm.Hg. The heated zone was maintained at 420°C, and the total distance from heater to target was 29 cm. Appreciable blueing was obtained within a few minutes, and steadily became more intense, although it was only a pale pastel shade, which faded rapidly on exposure to air.

The trials with the sodium flame apparatus were carried out under conditions roughly comparable with those obtaining in the beam apparatus. The iodide supply line was, however, rather longer because of the spiral, and so it could be expected that the pressure drop from the "buffer" vessel (to which was attached the thermocouple gauge) to the reaction chamber would be greater on the test arrangement, particularly in those experiments which were conducted with no slit between the reaction zone and the target. Thus, although the ethyl iodide temperature was about the same ($\sim -72^\circ C \equiv 0.2$ mm.Hg. pressure), the sodium temperature needed was low ($\sim 250^\circ C \equiv 2.10^{-3}$ mm.Hg. pressure). Further, since the pumping system was not as efficient, the pressure in the target space was higher ($\sim 10^{-4}$ mm.Hg. on the McLeod gauge). As a consequence the mean free path would be shorter, and thus there was a greater probability that the radicals would be reacted before they reached the target. All of these factors would tend towards yielding a maximum estimate of the probable "appearance time" of a trace in the beam apparatus. As against this the distances from the tip of the ethyl iodide jet in the reaction zone to the target were 22 cm. in the test arrangement and 35 cm. in the beam apparatus. For those tests where a slit was waxed to the flat end of the B.29 extension, the slit to target distances were 10-1/2 cm. and 29 cm. (source slit) respectively.

This test slit was of very simple construction. A small disc was cut from duralumin sheet. Its diameter was just equal to the outside diameter of the glass extension piece. A slot, about 3 mm. x 2 mm., was cut in the centre of this, and over it were waxed two pieces of razor blade whose sharp edges formed the slit jaws. These were arranged by eye to be roughly parallel, and of the order of 0.1 mm. apart.

If the radical concentration deviates, as it surely will, from the inverse square law in the test arrangement, this deviation will have the effect of increasing the appearance time of the blue coloration.

Thus, on the assumption that the inverse square law holds for both the respective slit to target distances, it is estimated that the beam trace appearance time will be, at a maximum, seven times the appearance time for the blue coloration when the slit is in the test apparatus.

The appearance times recorded in the following pages are not to be relied on too closely, for the first visible sign of coloration is difficult to detect. A much greater number of trials would be required before the accumulation of experience made it possible to place any real confidence in the figures.

Melville and Robb used a photometric device for following the change, but this could only be applied with difficulty to the detection of a narrow streak of blue in a large expanse of unchanged white background, such as was expected to be the result with the beam. It was decided, therefore, to rely on visual observation for a beginning.

Despite these limitations, some interesting deductions were possible. As soon as the experiment with pyrolysed lead tetraethyl had confirmed that detection of ethyl radicals was possible with this technique, an unsuccessful attempt had been made to detect these radicals in the beam apparatus, both at the detector position and at a position just in front of the source slit, in the collimator chamber. Radicals were undoubtedly being formed in the source, for there was a heavy deposit of sodium iodide. Therefore it would seem that, either they were being destroyed before they passed through the slit (an eventuality which is not at all unlikely), or the detector might have been desensitised by oil vapour from the diffusion pump. Since, in the design of the baffles in the pump throats, high efficiency was sacrificed in the interests of high pumping speed, it was considered not at all unlikely that "hot" oil molecules were striking the target.

The first sodium flame experiments on the test apparatus suggested that this desensitisation could take place. In order that the sodium should be exposed to the air as little as possible, a target was placed in position before it was distilled. The reaction was then started, and the first faint coloration was noticed some 15 to 18 minutes after opening the ethyl iodide reservoir tap. The reaction was then stopped. After several hours further pumping, radicals were produced for a further half hour with only a slight intensification of the blue color. When the sodium had had time to cool, a fresh target was introduced. Under the same conditions this target showed some coloration within four minutes from the time of starting. After about 40 minutes treatment the blue coloration was considerably more intense than in the previous case. On exposure to air both targets faded overnight. Of the two, the color of the second was slightly more persistent.

The slit was then installed and the procedure repeated. The times were now about 40 minutes for the target which was in place during the sodium distillation, and about 14 minutes for the first signs of color in the next one.

An interpretation of this phenomenon may be offered after reference to the account of the sodium preparation procedure (p. 92). It was noted there that appreciable evolution of gas, and charring, was encountered when the sodium was heated in the first stage of the distillation. Some of the products of this reaction could well be adsorbed on the target as they are being pumped away, and thus affect the target sensitivity. For subsequent runs a fresh sodium sample was only introduced when the thickness of the sodium iodide deposit made it necessary to clean the reaction chamber. Admission of air to the cold sodium did not seem to have any great effect on the temperature at which the resonance appeared. This observation does not, of course, have any bearing on the occasions when a capsule is employed, for then the cracks from which the sodium emerges are much more easily blocked.

The target support in the test chamber was therefore modified so that an investigation could be made of the effect of silicone vapour on the target. In addition to the "crocodile" clip target holder, two tungsten leads were sealed into the central stem fitted to the B.24 glass cone (fig.22c). These leads supported a "Kanthal" spiral, similar to that employed for the molybdenum oxide furnace. A small amount of silicone pump oil was contained in a small glass vessel placed in the heater spiral. With the target supported vertically about one centimeter above the top of the spiral, varying amounts of the oil could be condensed on to it by controlling the duration and amount of heating prior to treatment with the radicals.

These and succeeding runs were carried out with targets deposited by electrical heating. An indication of the improved characteristics of this type of deposit was furnished by the first trial, with no slit, in which an appreciable coloration was obtained within two minutes of opening the ethyl iodide tap to the already heated sodium. The sodium temperature was slightly lower in this case (220°C $\equiv\ < 10^{-3}$ mm.Hg.) than previously, as also was the reservoir pressure (-76°C, thermocouple gauge, $\sim$ 0.1 mm.Hg). Furthermore, in the run immediately preceding the silicone tests it was noticed that, with the sodium at only 200°C, and the ethyl iodide tap closed, a distinct blue had developed in just over 35 minutes. This implied that sufficient ethyl iodide was diffusing through the silicone tap grease, which had not been renewed for some time. Whatever the origin of the iodide, the concentration of radicals can not have been greater than 10^{-3} mm.Hg., which was about the lowest pressure detectable by the thermocouple gauge. Further investigation of this was left until after the silicone tests, which were carried out with the ethyl iodide tap shut.

It was found that the silicone oil did not completely inhibit the coloration of the target under these particular conditions unless it was condensed in sufficient quantity to be readily visible. However, with amounts of heating found to be just insufficient to cause condensation of droplets, a distinct gradation of the color was observed up the target, from a very pale blue at the bottom to a deeper color at the top. In a run typical of these tests, the color first appeared, after about 20 minutes, on the upper portion of the target where, presumably, relatively little of the vapour had been adsorbed. On prolonged ethyl treatment the intensity gradually increased.

Thus it would appear that, to be quite certain that the target sensitivity is as great as possible, its surface must be protected from the oil vapour by an efficient baffle in the pump throat.

From a cursory examination of the blueing obtained by merely heating the sodium, it would appear that diffusion through the tap grease is not the only source of the ethyl iodide. It is to be presumed that the presence of this compound is necessary for the production of the blue coloration, which took place even when the reservoir tap was re-greased and the reservoir itself was kept cold with liquid nitrogen, not only during the run itself, but also at all other times. Warming up of the reservoir, however, cannot be entirely avoided, for very little of the coolant remained in the Dewar flask by morning, even when the level had been replenished just prior to departure the previous evening. That the "diffusion" effect may play some part in this effect is illustrated by the following appearance times:

1. Immediately after the tap was re-greased, a faint suggestion of coloration 17 minutes after starting to heat the sodium; a definite blue developed in about 24 minutes.
2. Eight days later, a blue developed in 12 minutes.
3. Three days after this again, a definite blue appeared in 10 minutes.

The sodium temperature in all three runs was 250°C.

At this stage the slit was replaced, fresh sodium was introduced, and the isolating tap was replaced by a new one. The sodium was pre-heated for about 30 minutes before the fresh target was introduced, and the ethyl iodide was kept cold, and not outgassed, during this time. Heating of the sodium then produced no coloration in 42 minutes.

Even after allowing for the presence of the slit, this might be taken to indicate that, although some of the ethyl iodide in the previous runs had diffused through the silicone tap grease, some must also have been adsorbed on the reaction chamber side of the tap. The most likely place is the small quantity of grease which always tends to accumulate after some time in the tap sidearms. This material is difficult to remove completely unless the tap is cut out of the apparatus. Adsorption of the iodide at some point nearer to the reaction vessel is not ruled out by these observations, but it is considered to be less likely.

Thus it would seem that, although the silicone grease is more resistant to these vapours than is Apiezon grease, it is advisable to take the precaution of keeping the reservoir as cold as possible at all times when it is not actually in use.

The two final runs in this series were carried out in order to gain some idea of the effect of the slit on the flow of radicals, and thus to estimate the exposure time probably required for detection of the beam with a molybdenum oxide target.

The ethyl iodide temperature lay in the range -72 to -76°C (.2 to .15 mm.Hg. pressure at liquid). The sodium temperature, 250°C (approximately 2.10^{-3} mm.Hg.) gave a slight excess of sodium in the reaction zone. A blue coloration was detected after 54 minutes.

With a fresh target, the corresponding time was 48 minutes, with the temperatures at -76°C and 250°C respectively.

Thus on the basis of the arguments presented above (p.145) a trace of the beam should be detectable after a maximum of seven hours running time.

OTHER TARGETS

Silver Iodide.

It has been demonstrated (p.108) that radioactive "silver iodide" might prove to be of use as a detector. An opportunity was therefore taken to compare this method with the molybdenum oxide during the course of the experiments just described.

A piece of silver foil was soldered, for convenience in handling, on to the top of a nickel counting tray. The silver was cleaned with metal polish, washed first with benzene, then acetone, and finally with alcohol which was burnt off. After this treatment, water spread readily over the surface. A solution of paraffin wax in petroleum ether was then prepared and painted on to the back and sides of the nickel tray, and also around the edge of the silver surface. Thus when this target was dipped into the solution, the silver was the only metal to come in contact with it.

An old solution containing ^{131}I as sodium iodide, allegedly "carrier free", was obtained from Mr.B.C.Purkayastha. From information supplied by him it was possible to calculate that 10 ml. of this solution should contain, at the time of this test, approximately 3800 c/m of ^{131}I, if it were all contained in a solid source placed on the top shelf in a "lead castle".

To 20 ml. of this solution (which was neutral to litmus) were added two drops of dilute sulphuric acid to liberate the iodine, and the silver disc was immersed, with occasional agitation, for 130 minutes. On removal it was washed with distilled water and acetone, and dried in a stream of filtered air.

Its activity was found to be

$A_0 = (1057.3 \pm 10.28) - (17.6 \pm 0.6) =$

1039.7 ± 10.3 (i.e. $\pm$ 0.99%) c/m.

That is, about 14% of the activity in the solution had been collected.

The target was placed in the test apparatus and, after evacuating, the sodium was heated to 250°C (no slit present) for 23 minutes with the ethyl iodide tap shut.

On removal from the apparatus, the activity $3\frac{1}{2}$ hours after the first count was found to be

$A_{3\frac{1}{2}} = (963.5 \pm 9.8) - (17.6 \pm 0.6) =$

945.9 ± 9.8 (i.e. $\pm 1.04\%$) c/m.

Thus the ratio $A_{3\frac{1}{2}} / A_0 = 91.0 \pm 1.4\%$.

The ethyl radicals had therefore removed 9% of the ^{131}I in 23 minutes. Since the half life is 8 days, there was no need to correct for the natural decay.

A molybdenum oxide target, treated an hour after the silver disc had been removed from the apparatus, gave a blue coloration in 10 minutes under the same conditions.

A calculation similar to that carried out for RaE (p. 109) would show that the area occupied by each iodine atom on the silver is almost as great. Further investigation might therefore show that the activity-time curve for this detector was similar to those obtained for RaE. In this connection it is of interest to note that the percentage reductions obtained for the two different detector elements are very similar in amount, although naturally the evidence with the iodide is much too meagre to draw any conclusions from this. The matter was not pursued, for the result was sufficient to indicate that the molybdenum oxide was, at the present stage, preferable for use as a qualitative indicator.

Tellurium.

Early workers with inactive mirrors (146) found that tellurium was a very suitable detector for it seemed to retain its activity towards radicals even when exposed periodically to the atmosphere. The possibility of using this element was, therefore, also considered. Some visible deposits of inactive tellurium were evaporated on to pieces of microscope slide by vacuum evaporation in the "test" bulb. This was simply done by replacing the silicone oil "cup" by a fresh one containing a small lump of the element. The glass "target" was introduced through the B.29 side arm, and was supported horizontally over the cup by means of a "crocodile clip".

When these deposits were tested with ethyl radicals, very little difference could be detected between the exposed surface and the corner protected by the glass cover.

Of the available active isotopes, it might be possible to try ^{129}Te, which has a half life of 32 days and emits measurable γ rays and some β rays, if it could be obtained in high isotopic purity.

METHYL RADICALS

Di-ter-butyl peroxide ($Bu^t_2\ O_2$).

An account of the short exploratory investigation into the pyrolysis of this compound has been left until the last, since molybdenum oxide was used as the detector. A resume of its possible advantages as a radical source, and the pyrolysis temperatures reported in the literature, was presented on p. 62

Modification of the test apparatus was simply achieved. The sodium reaction unit was replaced by a glass tube of about 2-1/2 cm. bore. One end was sealed to the same line which had been used for the ethyl iodide. The other was attached to the test bulb by means of the B.29 joint (fig.22a). This tube was heated with the old reducing furnace (p.113) which is 6·5 cm. long. No slit was used.

The available vapour pressure data are meagre. Boiling points at two pressures are given by Milas and Surgenor (120), who also list a melting point of -18°C. Widely diverging extrapolation formulae are given by Egerton, Emte, and Minkoff (147) on the one hand, and by Vaughan (148) on the other. These two sources of information list the melting point at -18 to -19.5°C, and -40°C, respectively. Vaughan's boiling point (110.0°C), however, agrees fairly well with that given in reference 120 (109-109.2°C at 760 mm.Hg.).

If Milas and Surgenor's two results are extrapolated, we obtain that the vapour pressure at the melting point, assuming this to be -18°C, is about 3-1/2 mm.Hg. Extrapolations to temperatures below the melting point can only be relied on to give even an approximation to the vapour pressure if the latent heat of fusion is small, and therefore such extrapolations can not be relied on to any great extent, as has already been mentioned in the discussion about methyl iodide pressures. However, the heat of fusion is usually low for organic compounds, and the extrapolation of the two figures of Milas and Surgenor was used as a rough guide. On this basis, a vapour pressure of 0.15 mm.Hg. could be expected at about -60°C. Of the two extrapolation formulae, that of Vaughan gave very much lower pressures, whereas the other gave pressures just a little higher.

The thermocouple gauge used in the present experiments (first model, calibrated with air only) is not particularly sensitive at pressures of this order. Nevertheless the readings it gave with ethyl iodide corresponded fairly closely with the pressures to be expected from the extrapolated vapour pressure curve, which, with this substance, is more reliable in that all experimental temperatures were above the melting point (cf. p.71). It is therefore of interest to observe that the vapour pressures indicated for $Bu^t_2O_2$ were only a little lower than the pressures deduced from the two points of Milas and Surgenor. Temperatures in the region of -60° gave vapour pressures of the order of 10^{-1} mm.Hg. This would seem to indicate that the heat of fusion is not very large. The results are not sufficiently accurate, however, for any firm conclusion to be drawn.

The results of these experiments are collected in table IV.

TABLE IV

Pyrolysis of Di-ter-butyl Peroxide

Effect on Molybdenum Oxide

$Bu^t_2 O_2$ temperature °C	Approx.press. T/C gauge mm.Hg.	Pyrolysis temperature °C	Comment and pyrolysis time
-59	.15	320	no coloration, 47 minutes
-51 to -48	.24 to .3	430	first sign of blue, 30 mins. pale blue, further 11 mins.
-55 to -50	.14 to .18	470	very pale blue, 69 minutes.
-53	.17	540	target two days old. first sign blue, 18 minutes.
-49	.2	540	good coloration, further 42 minutes.

From these results it is apparent that, when due allowance has been made for the differences in pressure, much higher pyrolysis temperatures are needed under these conditions than those usually quoted in the literature (cf. p. 63). At these pressures the mean free path is short compared with the length of the heated zone, and so most molecules passing through it must presumably have come to temperature equilibrium with the glass walls. Therefore it would seem that there is little advantage to be gained by using this material, as far as the low temperature requirement is concerned.

Even in the last run, the coloration was not nearly as intense as that produced by ethyls in the previous experiments, and, in general, the appearance times are considerably greater. It may be that a lower concentration of methyls contributes to this, but on the whole it would appear that methyls are not as effective as ethyls with this detector. Since the pyrolysis zone was of pyrex glass, it was not possible to use the higher temperatures quoted by Lossing and Tickner (60). It would be of interest to try this.

A few trials with targets several weeks old, some but not all of which had been used in the beam apparatus and may therefore have been contaminated with pump oil vapour, gave negative results under conditions where freshly prepared targets turned blue. This tends to suggest that "ageing" of the oxide deposit might take place in time, although this was not appreciable (last run in table IV) after only two days.

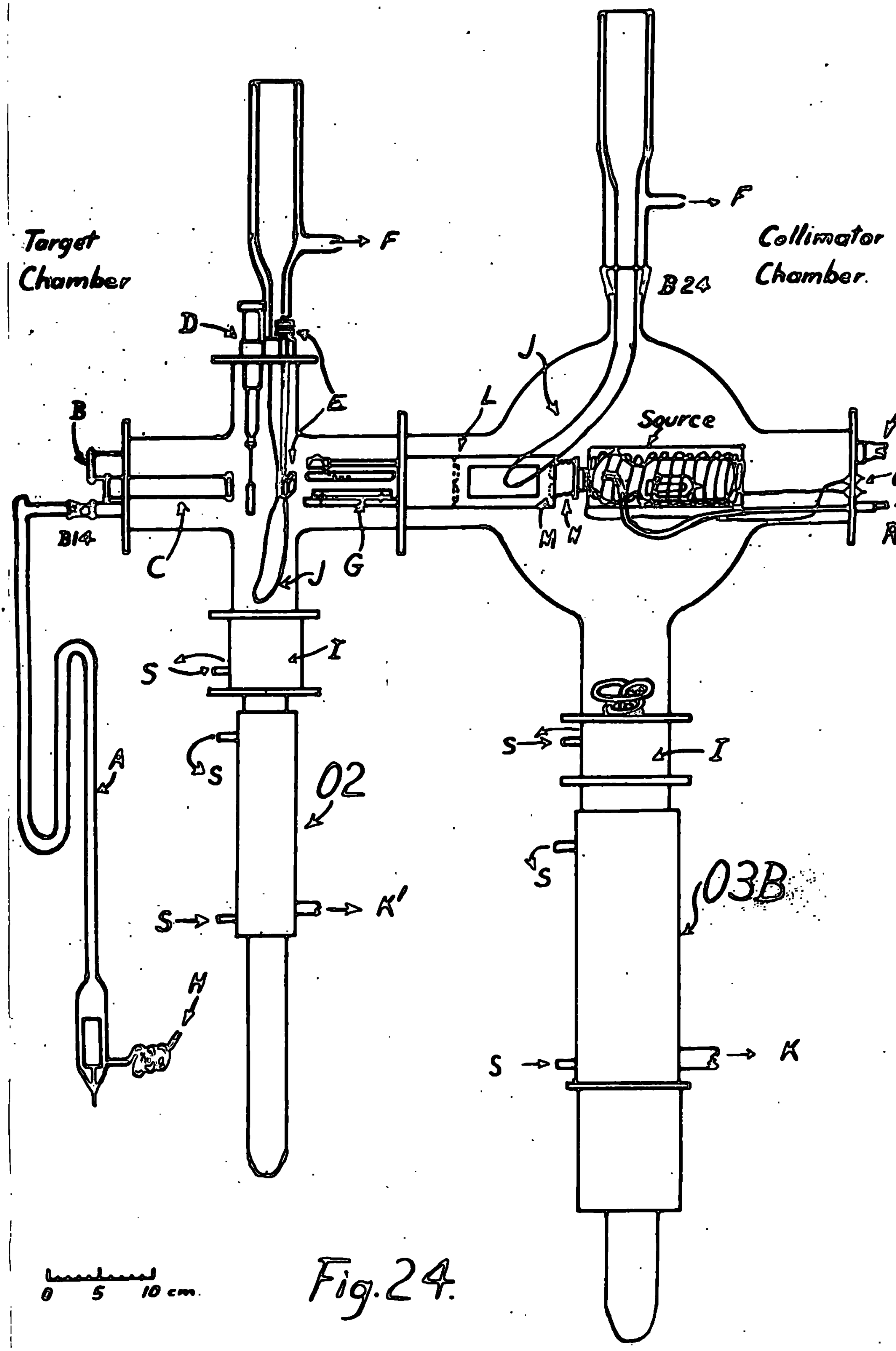

Target Chamber
Collimator Chamber
F
F
B24
D
E
J
J
L
Source
P
Q
R
B
B14
C
G
M
N
I
I
S
S
S
S
S
S
02
03B
A
H
K'
K
0 5 10 cm.

Fig. 24.

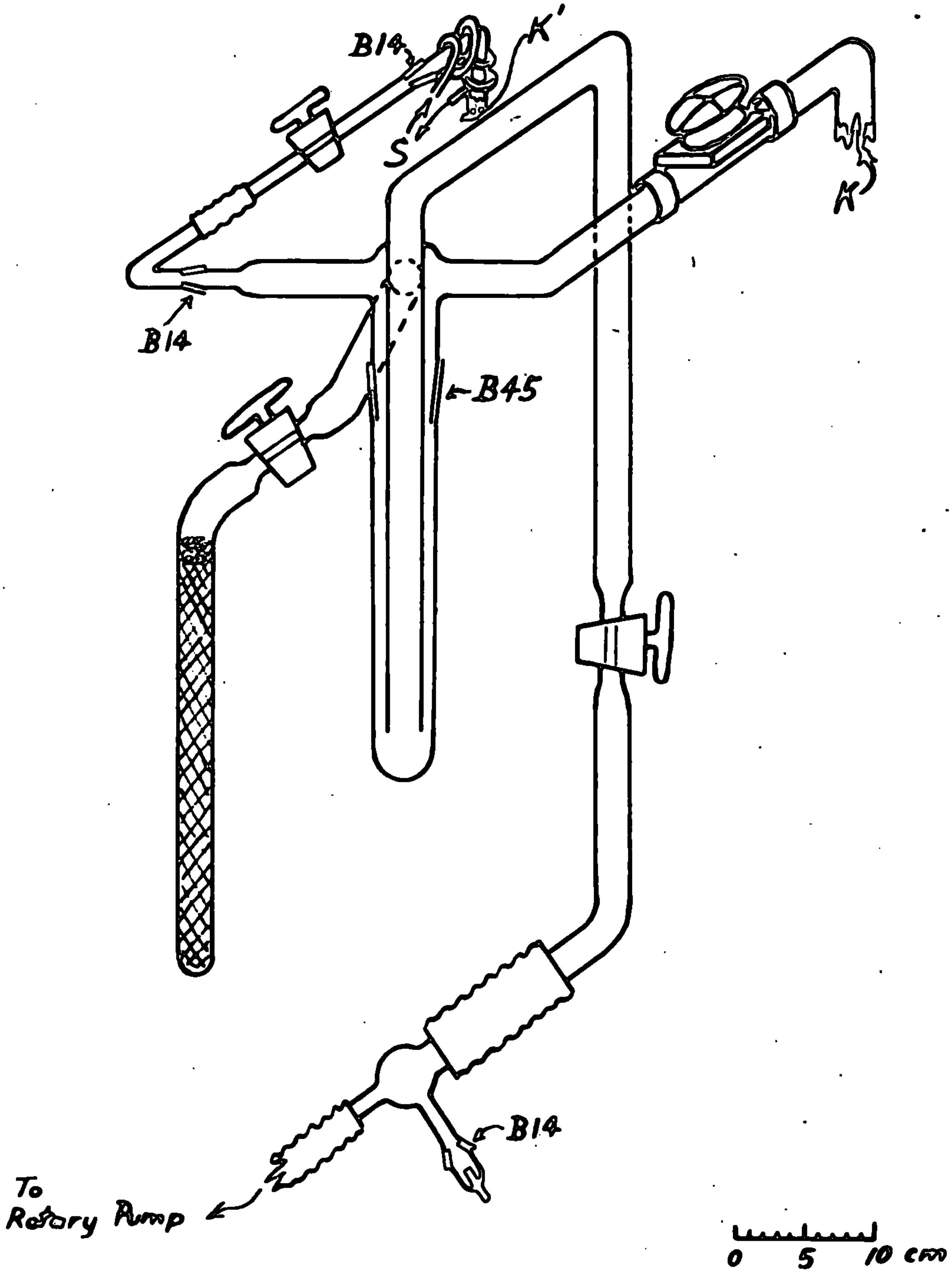
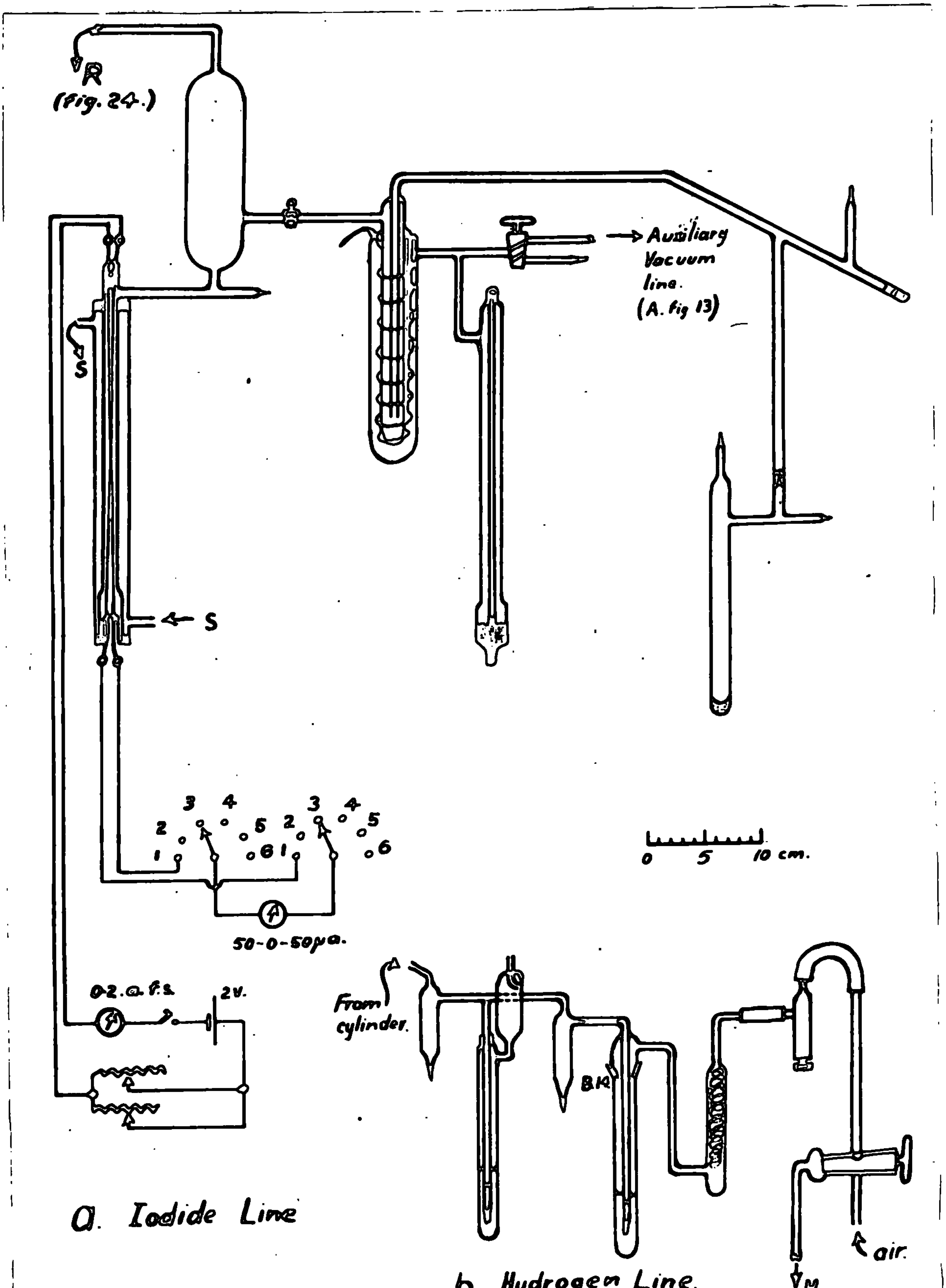


Fig. 25.



a. Iodide Line

b. Hydrogen Line.

Fig. 26.

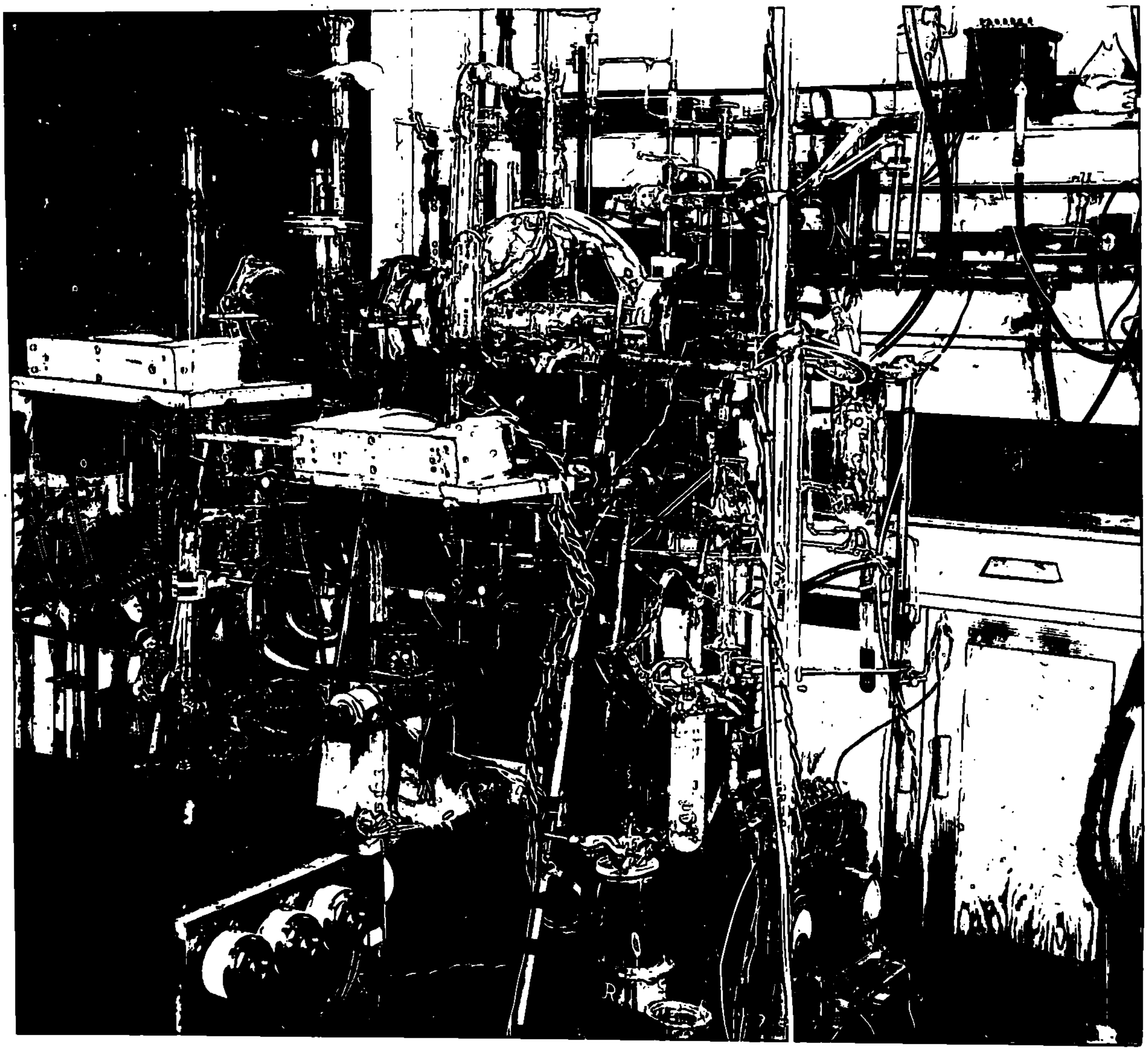


Fig. 27.

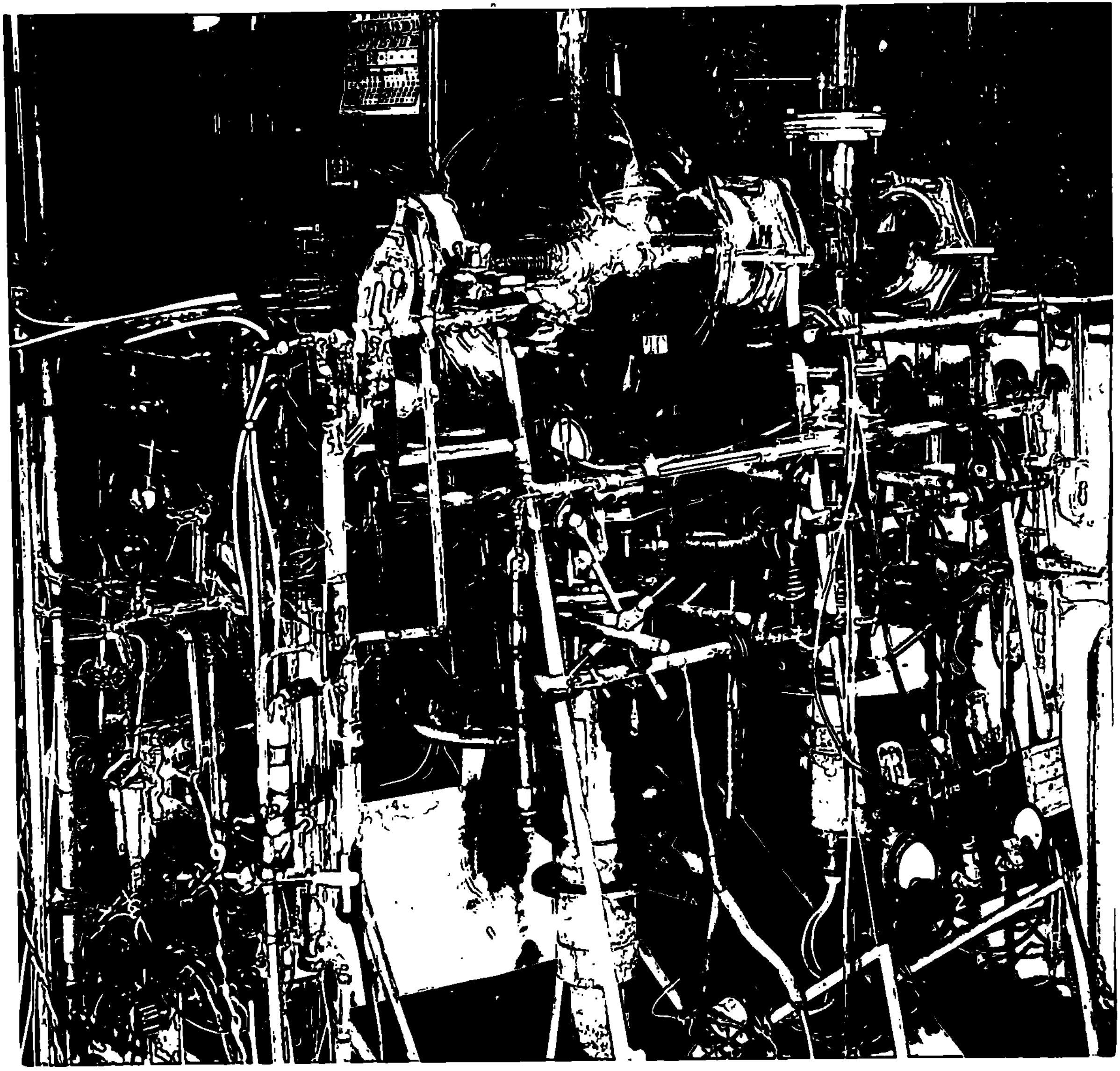


Fig. 28.

CHAPTER V. EXPERIMENTAL AND DISCUSSION

MOLECULAR BEAM

The conditions required for molecular beam production were reviewed in Chapter II, and summarised on page 58. Within these limits a wide variety of designs is possible, depending on the properties of the substance to be investigated. For a start, therefore, it was decided to base the design of the present apparatus on the arrangement used by Fraser and Jewott (53) for their measurements of the ionisation potential of free methyl.

Figure 24 is a drawing, approximately to scale, of the main vacuum chambers in which the beam was to be formed and detected. The "backing line", source supply, and "hydrogen line" are shown in figures 25 and 26. An idea of the general arrangement may be obtained from the photographs in figures 27 and 28.

During the course of the investigations with this equipment a number of inadequacies in design became apparent. Minor modifications were effected as they became necessary, and have been included in the description, which is of the apparatus as it was finally evolved. Alterations which would involve major changes were left, however, until sufficient experience had been accumulated in this technique to make a completely new design worth-while. The stage has now been reached where this is necessary, and suggestions for further developments will be found in the last section.

VACUUM SYSTEM

The maximum permissible pressure is governed by the condition that the mean free path of the "stray" molecules must be greater than the path length of the molecules in the beam. The source to collimator slit distance was just under 10 cm., and the distance from the collimator slit to the target was approximately 20 cm. The mean free path of the ammonia molecule is 5 cm. at 10^{-3} mm.Hg. (ref.149, p.113). If this is assumed, for the sake of argument, to be roughly comparable with free methyl, it may be deduced that the maximum permissible pressures will be of the order of 5.10^{-4} mm.Hg. in the collimator chamber and 2.10^{-4} mm.Hg. in the target chamber. The proportion of molecules scattered out of the beam at these pressures will, however, be high (c.f. p. 36). It is best, therefore, to demand pressures not greater than 10^{-4} mm.Hg. in the collimator chamber, and of the order of 10^{-6} mm.Hg., or better, in the target chamber.

These pressures must be maintained against a continuous flow of gas coming from the source, where the pressure is to be about 10^{-1} mm.Hg. If these conditions are to be attained, the outer envelope must be completely free of leaks, and a high pumping rate must be maintained.

Glass vessels fitted with "Pyrex Industrial Pipeline" connections were used for the two main chambers. This type of connection has the great advantage that it is sturdy at diameters much wider than are possible with the cone and socket type of joint. Also it requires a relatively small space for manipulation during assembly, and connections to metallic sections of the apparatus are achieved with a minimum of machining. Rubber "Pipeline" gaskets lightly greased with silicone high vacuum grease were found to be adequate. The target chamber was a crosspiece made from two 3 in. and two 2 in. connections. Its volume was approximately 1-1/2 litre. The collimator chamber was a 10 litre bulb, to which were attached three 3 in. connections and one B.24 socket. The end plates, through which connections to the inner parts of the apparatus were made, were 1/4 in. brass discs, with diameters 6 in. and 4-3/4 in. for the 3 in. and 2 in. connections, respectively. This large volume was chosen for the collimator chamber so that the heated source would not be too close to its walls, and also to minimise the effect on the pressure of any small inrush of gas. The wide connections made it possible to achieve one of the conditions for high pumping rates. That is the provision of short wide connections between the pump and the evacuated space.

Pumps

Since the impedance to gas flow of the slits is much greater than that of any other part of the system, the problem of calculating the necessary pumping speeds may be reduced to very simple proportions. The speed of an "ideal" aperture (S), which is independent of the magnitude of the pressure subject to the condition of molecular flow, may be defined as

$$S = a\sqrt{\frac{RT}{2\pi M}} \quad \text{cm.}^3 \text{ sec.}^{-1},$$

where a is the area of the aperture in cm.^{2}, M the molecular weight of the gas, T the absolute temperature, and R the gas constant (in dyne cm.$^{-2}$). Since the same restriction applies to the validity of this expression as applies to the formation of a beam, i.e. $\lambda \gg 2b$ (c.f. p. 56), it is assumed that it may be applied with sufficient accuracy to the source pressures which will be encountered in practice. The speed of a slit with finite thickness will be less than that given by this expression.

The quantity q of gas which passes through the slit from a region where the pressure is p_1 to a region where it is p_2 is given by $q = (p_1 - p_2)$ S, where p is expressed in mm.Hg.

A similar expression holds for the speed of the pump (S_p):- $p.S_p = q$, where p is the pressure at the pump head. For a system at equilibrium q will be constant throughout.

With the short, wide connections used, p may be taken as approximately equal to p_2.

$$\text{Thus } S_p = \frac{\Delta p}{p_2} S.$$

For deflection experiments, the slits must be as narrow as possible. The dimensions assumed in this calculation were, therefore, 3 mm. x 0.05 mm., i.e. $a = 1.5 \cdot 10^{-3}$ cm.^{2}. For air (or ethyl), $M = 29$.

Thus $S = 17.5$ cm.^{3} sec.$^{-1}$ at $T = 300°K$.

For source pressure $p_1 = 10^{-1}$ mm.Hg., and p_2 (collimator chamber) $= 10^{-4}$ mm.Hg., $\Delta p \approx 10^{-1}$ mm.Hg. Thus $S_p = 17.5$ lit.sec.$^{-1}$.

It would seem, then, that a "Metrovick" type 03B oil diffusion pump ($S_p = 30$ lit.sec.$^{-1}$) would be sufficient. Under the conditions stated, this pump would maintain a pressure $p_2 = \Delta p \frac{S}{30} \cdot 10^{-3} = 5.8 \cdot 10^{-5}$ mm.Hg. for ethyls or air. Since both S and S_p depend in the same way on M, this pressure should be independent of the molecular weight of the gas.

For a wider slit (0.1 mm. x 3 mm., $a = 3.10^{-3}$ cm.^{2}) this would not seem to be quite so satisfactory. The attainable pressure then is $1.2 \cdot 10^{-4}$ mm.Hg. However it must be remembered that the source slit was canal shaped.

This would tend towards improving the vacuum attained. Moreover, "cold fingers" (P, fig.24) were to be provided in each chamber. If the vapour pressure of the gas is negligible (say $< 10^{-7}$ mm.Hg.) at the temperature of this surface, it has a very high effective pumping speed (c.f. ref.103, p.21). The average area of liquid nitrogen cooled surface in the collimator chamber was of the order of $A = 90$ cm.^{2}. Thus, on the assumption that every molecule is condensed on its first impact, this surface by itself should be capable of maintaining a pressure (loc. cit.) of $\frac{p_1 a}{A} = 3.10^{-6}$ mm.Hg., even when the slit is 0.1 mm. wide.

Thus it was considered that the 03B pump and the cold surface could deal adequately with all gases, both condensible and non-condensible, which were likely to occur in the beam.

A similar calculation was made for the target chamber. For $a = 1.5 \,.\, 10^{-3}$ cm.^{2}, $p_2 = 10^{-4}$ mm.Hg., $p_3 = 10^{-6}$ mm.Hg., the pumping speed required was $S_p = 1.7$ lit.sec.$^{-1}$. Thus the "Metrovick" type 02 oil diffusion pump (7 lit.sec.$^{-1}$) was more than adequate, even without a cold surface. The calculated pressure given by this pump was 2.10^{-7} mm.Hg.

It was decided to use silicone pump oils (type 703) instead of the hydrocarbon oil recommended by the makers, since it is claimed that a lower ultimate vacuum is possible by its use. Also it is more resistant to decomposition if large quantities of air are accidentally admitted while the pumps are in operation.

A baffle unit (I. fig.24) was installed between each pump and the chamber it was to evacuate. This consisted of a water cooled conical copper spiral, soldered into the walls of a copper cylinder, of 3 in. diameter, fitted at each end with brass flanges. The coils of these spirals were arranged so that, as far as possible, the pump throat was prevented from "seeing" into the chamber. They were connected in series with the pump cooling jackets. The 02 pump baffle (not shown) was completely enclosed within its housing, and was expected to be rather more efficient in that a copper strip was soldered to it to make quite sure that pump oil must strike it. The 03B baffle was left as a simple spiral in the interests of high pumping rates.

All flange connections on the high vacuum side were bolted together. With the exception of the junctions between the baffle housings and the pumps, which had O-ring seals, the flat rubber "Pipeline" gaskets were used.

The two diffusion pumps were connected to a common backing line (fig.25) which was exhausted through a liquid air trap by a two-stage rotary pump (Edwards "Speedivac" type 3). Wide bore (3 cm.) glass tubing was used for connections on the 03B pump line.

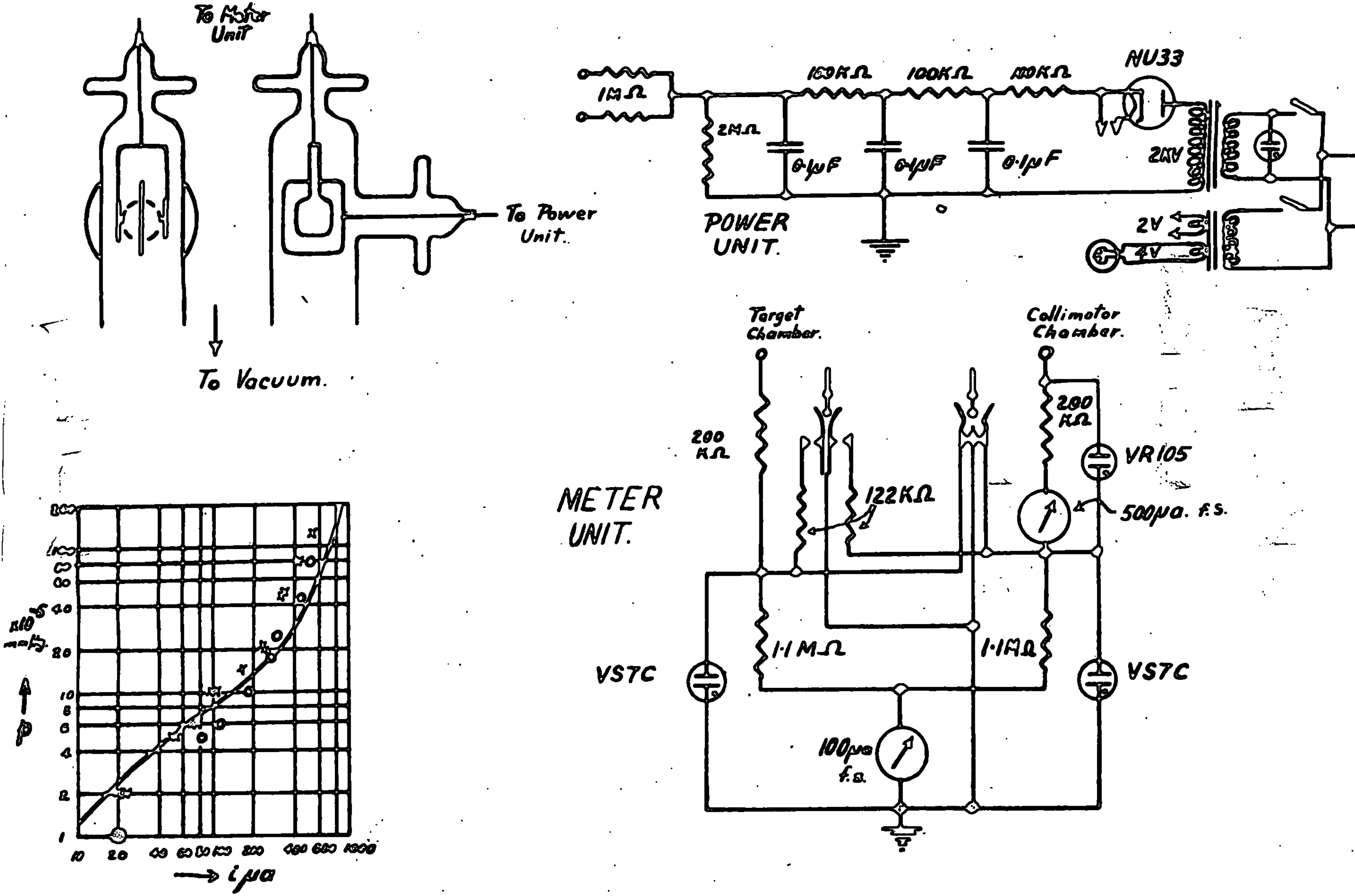

To Motor Unit
To Power Unit.
To Vacuum.
1MΩ
2MΩ
100KΩ
100KΩ
100KΩ
0·1μF
0·1μF
0·1μF
NU33
2KV
2V
4V
POWER UNIT.
Target Chamber.
Collimator Chamber.
200 KΩ
200 KΩ
122KΩ
VR105
500μa. f.s.
METER UNIT.
1·1MΩ
1·1MΩ
VS7C
VS7C
100μa f.s.
p
x10^-5 mm Hg
1
2
4
6
8
10
20
40
100
10
20
40
60
80
100
200
400
600
1000
i μa

Fig. 29.

The long tube (shown hatched) was filled with activated charcoal, and was also provided with a glass isolating tap. This tube, when cooled with liquid nitrogen, served as an adequate substitute for the backing pump when it was desired to continue pumping, with the reservoir shut off, overnight and at week-ends. It was necessary, however, to replenish the coolant at least once a day. Periodically the diffusion pumps were isolated from the backing line, and the charcoal was pumped out with the backing pump while maintained at 350 to 400°C. with a tube furnace. The temperature was measured by a chromel-alumel thermocouple connected to contacts 5 on the selector switch (fig.26a).

Pressure Measurement

Because of their simplicity and ease of operation it was decided to use Penning (150) gauges for pressure measurements in the two main chambers.

The anode was a ring of stout nickel wire. The cathodes were aluminium. During operation a brown deposit, which may be conducting, forms on the inner walls of the glass, which was therefore shaped as shown to inhibit the formation of a continuous layer between the electrodes.

The two gauges were run in parallel from a half-wave rectified power supply whose output was approximately 1800 V. (nominally 2 kV.). The circuits of this unit and the associated metering unit are shown in figure 29. The resistances placed in series with the meters were chosen so that the voltage drop for full scale meter deflection was just sufficient to cause the neon tube to strike. The 500 μA. meter was permanently in series with the collimator chamber gauge. Two switches were provided for the 100 μA. meter. One made it possible to measure the current flowing through either gauge on the more sensitive meter without interrupting the discharge, or to short the meter out altogether. The second switch, with its associated shunt resistors, was incorporated later to extend the range of both gauges to higher pressures. (The X 0.1 range.)

The magnet field, of about 2000 gauss parallel to the common axis of the electrodes, was obtained by the use of a magnetron magnet.

Since, in common with all vacuum gauges which involve the action of ions (149), these gauges have a "gettering" action, it is desirable that they should be connected to the vacuum by a short wide connection if they are to give a true reading. In the present arrangement the only available means of connection was through the ground joint (F, fig.24) on the "cold finger" jacket (see fig.27). This was not at all ideal, both because of the length of the connecting tube which was required, and because of the possibility that condensible material would not reach the gauge when the trap was filled with liquid nitrogen. This latter effect did not, however, appear to be appreciable if the level of coolant was maintained a few centimeters below the B24 ground joint on the top of the chamber. It was not considered advisable to make any attempt to shorten the connection by sealing another connection into the side of the main envelope.

Before they were finally installed in this position the gauges were roughly calibrated against the McLeod gauge on the test apparatus (point B, fig.13). The "gettering" action in a "static" vacuum (i.e. no continuous flow of gas) was very marked. In quite a short time the pressure was reduced to a "sticking vacuum" as measured on the McLeod (10^{-6} mm.Hg. or less). At pressures of this order the Penning gauge reading was in the range 1 to 5 μA. Therefore a needle valve was installed in the B.14 joint in the hydrogen line (see p.139), and a continuous flow of cylinder nitrogen was maintained through the test apparatus. By this method the points shown on the graph in figure 29 were obtained. The full line is the curve given in his paper by Penning (loc.cit.). It will be seen that each gauge differs slightly in its characteristics, but that these differences are relatively unimportant when an indication of the order of magnitude of the pressure is all that is required. This calibration was carried out before the (X 0.1) range was installed. It has since been found that saturation current for this arrangement is in the region of 600 to 650 μA. ($\sim$ 2 to 4 . 10^{-3} mm.Hg.).

Leaks

The apparatus was checked for leaks at each stage of its erection. Gross leaks were detected by the change in the color of a discharge, at backing pressures, when either coal gas or cotton wool soaked with acetone was applied at the position of the suspected leak. When no serious leaks were present, the backing pump could reduce the pressure from atmospheric to about 10^{-2} mm.Hg. (discharge almost completely disappeared) in less than 30 minutes. The hydrogen discharge tube (A, fig.24) was used for these tests. In the early stages a second small discharge tube, run from the "Ford" coil, was temporarily attached to the collimator tube by the B.19 joint (P) in the end plate. Although, for the most part, they were satisfactory, the rubber "Pipeline" gaskets needed replacing after a time for they tended to become deformed. Acetone was not used for leak testing on these. Suspect soldered joints in the end plates (usually soft soldered) were painted. This usually proved to be effective, except for the B.24 socket on the top plate of the target chamber (fig.24) to which was attached the "cold finger". When this was cooled the thermal stresses were too great for the solder. Apiezon Q compound proved to be an effective seal in this instance.

Because of the large surface area of metal exposed to the vacuum the time required to obtain a really good vacuum was rather long, particularly as "baking out" was not practicable. Careful polishing of the metal parts was found to be beneficial in this respect. A steady rate of fall in the Penning gauge reading from day to day, however slow, was taken to indicate that the system was leak-tight. The pressures finally obtained, after continuous pumping for 24 hours per day for several months, were around 3 to 4 μA. ($\sim 10^{-6}$ mm.Hg. or better) when the source reservoir was closed.

BEAM FORMATION

Slit System

It has been seen (Chap.II) that narrow slits which are not too long are required for success in deflection experiments. Maximum beam intensity can only be obtained if they are exactly parallel. This is most conveniently achieved by constructing the slit system as one rigid unit, with provision for its adjustment which can be carried out on the bench before it is installed in the apparatus. The alignment of the electric field unit with the slits is also of importance, for the "wire" must lie parallel, and very close, to the beam. Therefore this unit must also be rigidly attached to the slit mounting. For ease of alignment, and for flexibility in the control of experimental conditions, it is desirable that the width of each slit should be adjustable. In achieving this object it is important, however, to ensure that the two jaws of each slit remain parallel at all settings. A further

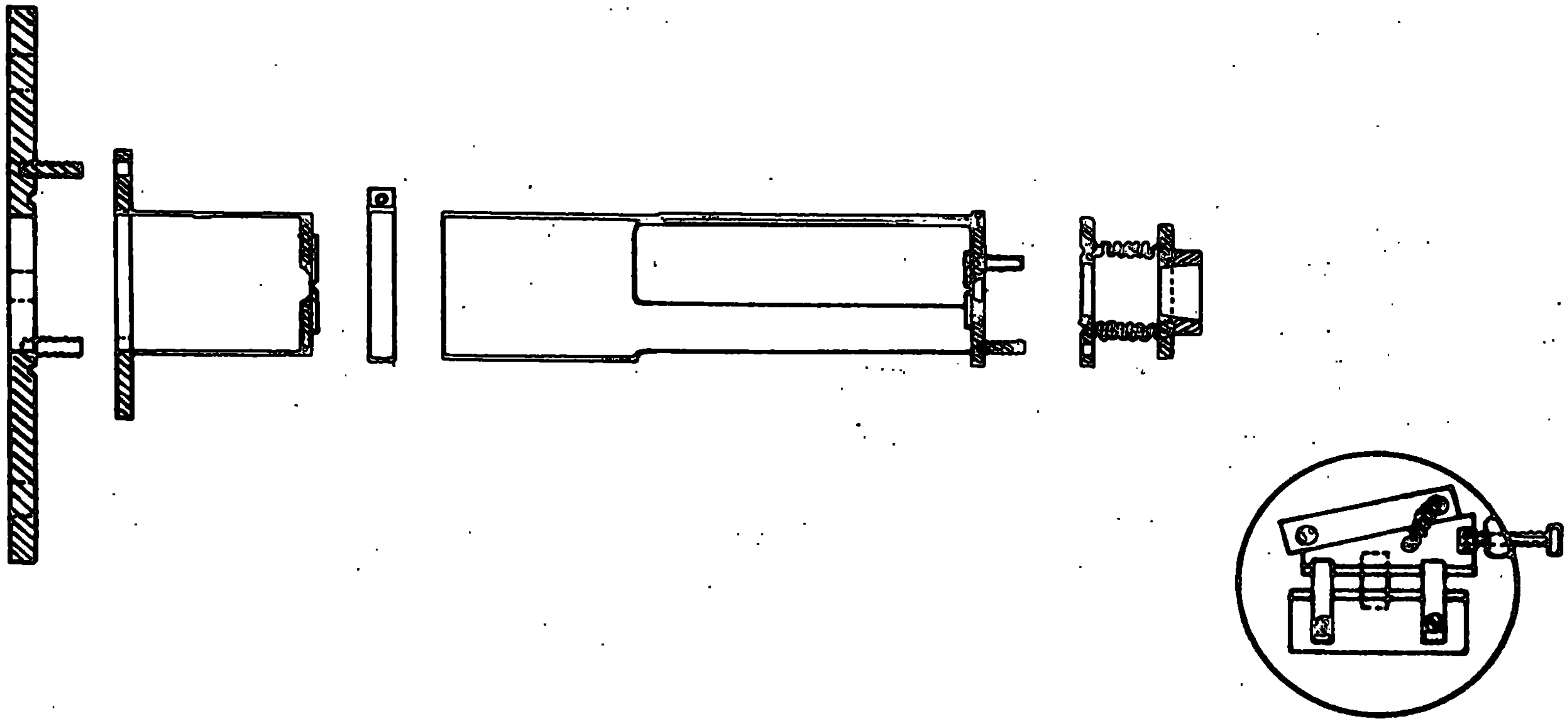


Fig. 30

desirable, but not necessary, feature would be a provision for altering the slit width from outside the apparatus without the necessity for disturbing the vacuum. Finally, if the calculated pump speeds are to be adequate, the slit apertures must be the predominant, if not the only means of communication between the three chambers of the system. With the slit jaws themselves, the best that can be done is to ensure that the leakage paths are as long as possible. Other parts of the mounting should be made vacuum tight.

The general arrangement of the system designed to satisfy these conditions is shown in figure 24, and figure 30 is a more detailed drawing. The slits, which were similar to each other in construction, were made by Sir Howard Grubb-Parsons Ltd. Standard stainless steel optical slit jaws were attached to a brass disc-shaped base plate. The slot in the plate, 3 mm. wide, defined the length of the slit. The bottom fixed jaw was held in place by two screws, which also held two small strips of spring steel whose function was to press the top, moveable jaw firmly against the base plate. The width of the slit was controlled by means of a small screw attached to the base plate. This pushed the top jaw along the fixed runner, attached to the base plate immediately above it, against the tension of the small helical spring in the top right hand corner. This spring also served to hold the top jaw firmly against the runner.

The collimator slit had bevelled jaws. Its base plate was "sweated" with soft solder into the end of a small well which was firmly screwed, by means of its flanged O-ring joint, to the 6 in. brass centre plate. The source slit jaws had flat edges, thus forming a "canal" of about 1 mm. depth. Although this increases the difficulties of alignment, it is of advantage in that it is said to reduce the total quantity of gas effusing through the slit without materially affecting the intensity in the beam (c.f. ref.103, p.17). Three small screws in the rim of this base plate fixed it to a brass tube which was a "telescopic" fit over the collimator slit well. This tube was slotted along the length of the well, and a small brass band, similar in construction to a small hose clip, clamped it firmly to the base of the well. The section of this tube between the two slits was cut away to allow the greatest possible flow of gas without, at the same time, reducing the rigidity. The three holes at the end of this tube, through which passed the source slit fixing screws, were slotted to allow the base plate to be rotated and tilted to the required setting. The brass connection to the glass reaction unit (see p. 89) consisted of a ground socket to fit the B.14 cone on the reaction chamber, a short metal bellows for flexibility, and an O-ring flange which was firmly screwed to the back of the slit base plate.

the apparatus, by trial and error, until the lead moved freely in the tube when the end plate was in position. It was then sealed to the control system, with the bellows in slight compression, and then the wax was applied.

The sodium heater current was lead in through the end plate by means of two small "Kovar" seal units, which were soldered in place (Q, fig.24). Two chromel-alumel thermocouples were provided. One was attached to the reaction chamber at its "waist", the other to the source slit base plate. These were brought out through four glass capillary side arms in the end of a B.19 cone (P), into which they were sealed with black wax (Apiezon W). They were connected to the microammeter (fig.26a) through connections 3 and 4 on the selector switch.

Alignment.

The slits were aligned, prior to assembly in the apparatus, by means of a vernier microscope with a cross-wire in its focal plane. It had an (X.7) eyepiece and a 3 in. objective, and its overall magnification was approximately (X.12). The slit widths were measured by substituting a small graduated graticule for the cross wire graticule. The graduations were calibrated against a steel rule whose accuracy was guaranteed to be within 1/10 mm. in 50 cm. overall length at 20°C.

The 6 in. centre plate, with the slit system attached, and the microscope were mounted on a stout duralumin base plate. The slit system was supported by the arrangement illustrated in

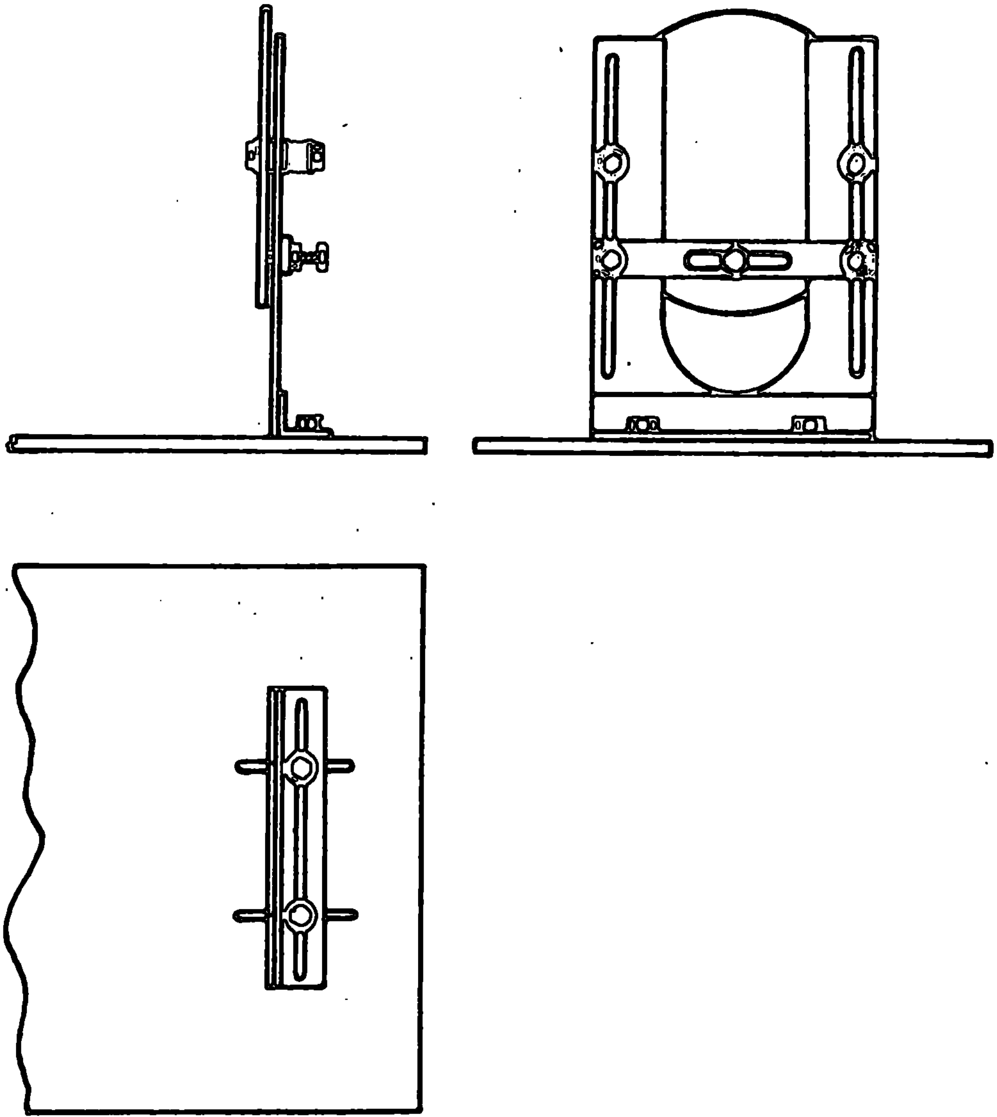


Fig. 31.

figure 31. The adjustment procedure was as follows:

The "travel" of the microscope was first made parallel to one edge of the base plate to better than $^1/256$ in. in 30 cm. This was checked by sighting the cross wire of the microscope, which was swung into a vertical position, on to a pre-determined graduation on an engineer's square which was set against the reference edge.

Small metal wedges were then adjusted under the base plate until the "bed" of the microscope carriage was horizontal when checked with a small spirit level in two directions mutually at right angles at each end of the "bed". The engineer's square was then again used while the bottom of the slit system support was adjusted perpendicular to the base plate reference edge. At the same time the microscope, now in a horizontal position parallel to the direction of travel, was focussed on to a spare brass disc supported in the mounting, to ensure that the vertical cross wire coincided approximately with the centre of the turning marks on the disc.

The slit system was then installed, and adjusted so that the tube joining the slits was horizontal, and the cross wires focussed on the slit. At the same time the centre plate should be vertical. The source slit was then removed, and the cross wire was focussed on the edge of the fixed jaw of the collimator slit, which was opened wide. At this stage the horizontal cross wire should be close to, and parallel to, the jaw edge, and the vertical wire should come in the centre of the slit. If this was not so, the system was re-adjusted until this was attained. The slit was then closed down, the cross wire was replaced with the graduated scale, and the slit width was measured. Visibility was improved by means of a small auxiliary light.

With the cross wire replaced, a further check ensured that it still retained its previous orientation with respect to the slit. The microscope was then withdrawn and the source slit was inserted. The distance between the slits was recorded. The source slit was then adjusted parallel to the cross wire, tilted until front and back edges of the fixed jaw were in line with the fixed jaw on the other slit (i.e. the same orientation to the cross wire), and screwed firmly into place. It was then closed down, and its width measured.

Next the iodide lead was adjusted. The central brass plate was laid flat on a retort stand base with the slits pointing upwards. The collimator chamber end plate was then clamped above it. A spirit level was used to check that both plates were horizontal, and three plumb lines were used to arrange them in the same relative orientation that they occupied when fixed on to the collimator chamber. The reaction unit, with only the bent part of its lead attached, was clamped in position, and the straight portion of the lead was inserted down the tube R (fig.24) and sealed on.

Assembly.

The supporting framework was constructed from lengths of 1/2 in. iron rod welded together and screwed to the floor. This is most clearly illustrated in fig.28. Two semi-circles of 3/4 in. hoop iron, padded with felt, supported the ends of the collimator chamber. This was clamped in position and it was rarely necessary to disturb it, or to disconnect it from the O3B pump. A third hoop iron support was provided for the further end of the target chamber. The attachment to the collimator chamber provided sufficient support at the other end. The diffusion pumps were normally supported by their connections to the chambers, although a system of rods and bosses was provided to support them during assembly, or at other times when it became necessary to disconnect them.

When the alignment had been completed, the reaction chamber was removed, and the slit assembly was inserted from the left hand side (fig.24) of the collimator chamber. The target chamber was then installed and bolted in place. The

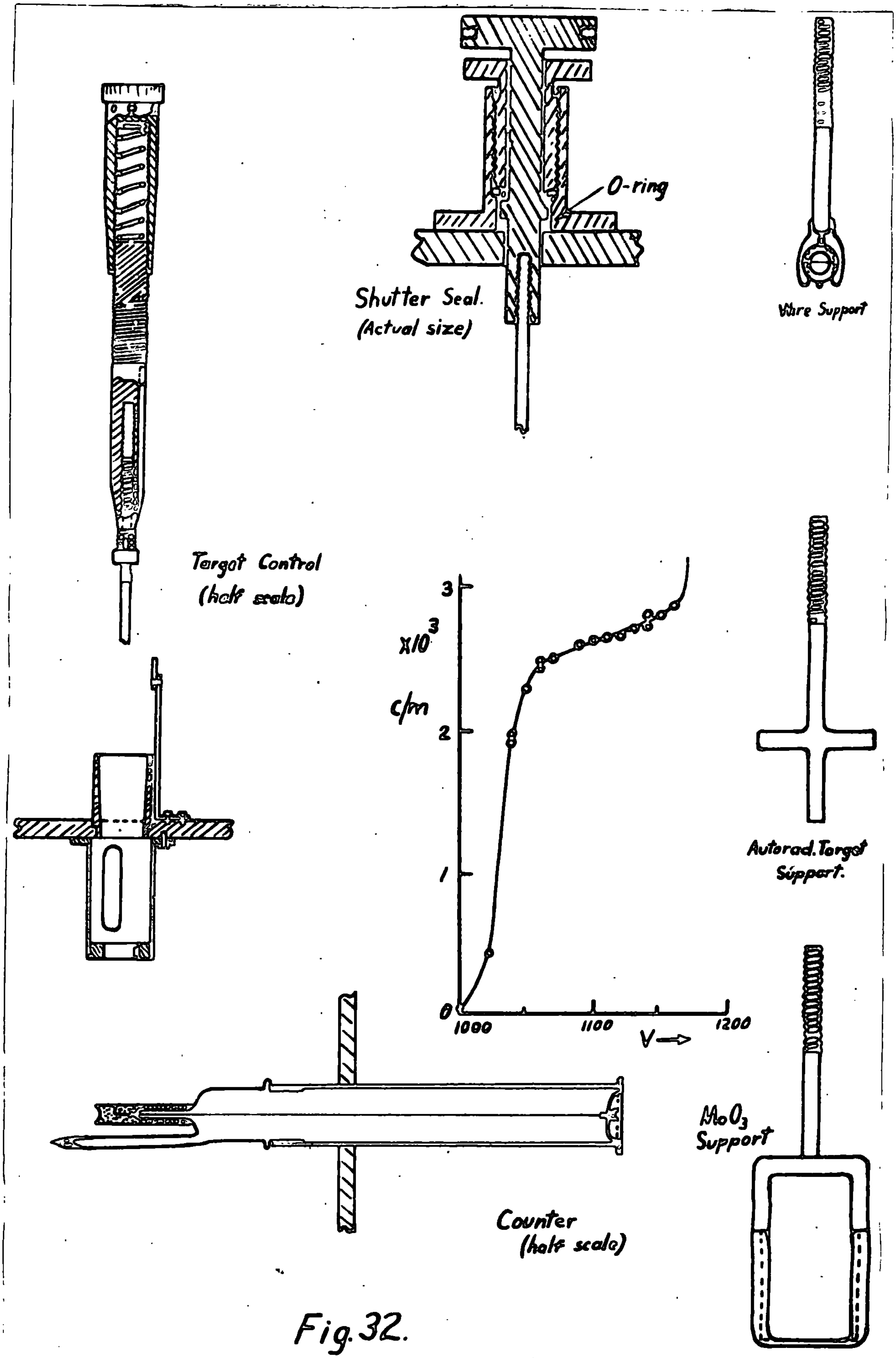
02B pump and baffle and the target chamber end plates were then attached, and the connections made to them. Next the reaction chamber, with its cone lightly greased with silicone, was inserted from the opposite end, and the end plate was carefully placed in position. The rest of the procedure has been described above (p. 176).

BEAM DETECTION

Since work on the design and construction of the beam apparatus was proceeding simultaneously with the experiments described in Chapters III and IV, the target system was designed so that it could be used for any of the detector methods envisaged. It consisted of three parts:- the counter for measuring the activity, if any, of the target (C, fig.24); the target mounting (D) which provided the means for moving the target, in a vertical direction, across the beam; and the discharge tube with its associated hydrogen line (A, fig.24, fig.26b), in case it was decided to use lead or bismuth isotopes, which need activating by hydrogen atoms (p. 122).

Counter.

The counter was of a conventional end-window pattern with some special features. The window was of copper foil (~ 23 mg.cm.$^{-2}$), soldered to the end of a brass tube which was sealed into the end plate with soft solder. The diameter of this tube was limited to 1.9 cm. because of the need to leave room for other attachments to the end plate, and its


Shutter Seal.
(Actual size)

Wire Support

Target Control
(half scale)

Autorad. Target
Support.

MoO_3
Support

Counter
(half scale)

Fig. 32.

length (13 cm.) was governed by the desire to have the window as close as possible to the target. The central wire was a piece of non-thoriated tungsten, 0.1 mm. diameter. The glass cap, through which the tungsten was sealed, was attached to the brass with black wax. A small brass cylinder was waxed over this seal to give it some protection, and was connected to the tungsten by a length of fine copper wire. To maintain the rigidity of the arrangement it was necessary to support the "free" end of the tungsten wire. This was done by fusing to it a small bead of silica which was supported in a phosphor bronze "stirrup". This stirrup rested in two small niches in the end of the counter immediately below the window. The soft solder ensured that this end was leak-tight. The counter was filled with 9 cm.Hg. of argon and 1 cm.Hg. of ethanol. The characteristic curve (fig.32) was not ideal, but was good enough for use. Standard counting equipment was used.

During the final experiments, when it was decided to concentrate on the molybdenum oxide target, the window and wire attachments were removed, and a small disc of flat glass was waxed to the outer end of the counter tube. This provided a clear view of the target.

Target Support.

The target control was similar in its action to a micrometer head. A detailed drawing of its construction is given in figure 32. The brass capstan head formed the cone of a B.19 ground joint. A graduated scale with 50 equal divisions was marked on its top circumference. Immediately below this, six tapped holes were provided for the insertion of a mild steel lever which was used for turning it. The central well, 1/2 in. diameter, was threaded with 40 turns per inch. Thus each scale division on the capstan head corresponded to 0.0127 mm. displacement of the target in a vertical direction.

The lower, non-threaded, section of the brass shaft which screwed into this well was provided with a slotted keyway. This engaged with a key in the housing which was screwed to the underside of the top plate. "Back-lash" in the thread was prevented by means of the compression spring in the well, above the shaft. This shaft was itself provided with a threaded well (6 B.A.) which held the target support. This thread provided an additional means of adjusting the distance of the target below the top plate when it was being set in position, and at the same time provided for the correct orientation of the target face about a vertical axis. A lock nut was provided to fix this position once the setting had been made.

Three different types of target support were provided each attached to a length of 6BA threaded rod which fitted into the bottom of the micrometer unit (see fig.32).

The first, for the wire, was a small hollow cylinder, mounted horizontally, and held in place by a brass "fork" which was pressed round it. The activated wire was waxed into two small grooves on the end of this cylinder. Two small posts were provided so that the wire could be adjusted parallel to the slits by rotation of the cylinder from outside the apparatus.

The second type of support, for the autoradiographic targets was cross shaped, similar to the support in the emanation collector (p. 136).

The third was a small brass frame, with slotted side pieces, which held the pieces of microscope slide on to which the molybdenum oxide had been deposited.

<u>Shutter.</u>

The third attachment to the target chamber top plate was provided for the shutter - a metal "gate" which could be interposed between the target and the beam. With this device the target could be protected during the starting up and closing down periods or while it was being reset to a new position. This made possible the estimation of the precise time of exposure to the beam. Since the preparation of conical ground joints involves much tedious grinding of the brass components, a simple type of seal, involving a greased O-ring, was tried as an alternative. No alteration of the Penning gauge reading was observable when this was rotated. It was therefore presumed to be satisfactory. The O-ring was kept in compression by means of the screwed insert which bore on the enlarged section of the central stem.

Hydrogen Line.

A glass tube, ending at the outside with a B.19 socket, was waxed into a brass tube which was soldered to the target chamber end plate. A slight expansion of the glass where it butted against the brass tube ensured a firm joint. The glass extended to the inner face of the end-plate. The B.19 cone attached to the centre of the discharge tube was of the extended type so that there was only a small possibility of the discharge or its products coming into contact with the wax seal, which made simple the removal of the end plate. The electrodes were aluminium cylinders closed at the bottom, and connection to them was made by tungsten seals through the glass. The discharge was produced by not more than 0.1 to 0.2 amp. at about 3 kV. A.C., supplied from a transformer run off the mains.

The hydrogen supply was controlled by the system shown in figure 26b. The bubbler and "blow off" units contained concentrated sulphuric acid. The brass needle valve had been constructed for some previous worker in this laboratory. Since it may at some stage have been contaminated with mercury, a piece of gold foil was placed in the tube between it and the two-way control tap. The small glass spiral (fig.24) was inserted to allow the discharge tube to be disconnected from the endplate without breaking the hydrogen line. Although, in the end, this line was not used for its original purpose, the discharge proved useful when leaks were being investigated, and the line was used for the admission of oxygen/nitrogen free (c.f. p.96).

DEFLECTION

As it has turned out, the electrostatic field unit which has been designed for the initial attempt to deflect the radical beam has not been required up to the present, for the attempts to detect the undeflected beam have not yet proved successful. The following is a description of this arrangement, which had been constructed and was ready for immediate use.

Although the condenser used by Scheffers (c.f. p.47) would seem to be the best for this purpose, it was decided that, since rather precise machining was needed for its satisfactory operation, the construction of a more adjustable device (fig.33) would be preferable for a beginning. The "wire" section consisted of a small blade, with a rounded upper edge, which was attached to a shelf by means of two identical lever systems. The shelf was to be fixed rigidly to the 6 in. centre plate which supported the slit system (see fig.24, G). Two pairs of small set screws, one pair for each of the lever systems, were provided. The two screws in each pair were mutually at right angles, and operated against the tension of a small spring.

With these it was possible to adjust the top edge of the blade so that it was exactly parallel to, and running just below, the central axis of the beam. Lock nuts were provided on the set screws to fix them firmly in position once the blade had been adjusted. This part was to have been at earth potential, since it was firmly attached to the slit system, which was earthed.

The "cylinder", to which the potential was to be applied, was to be a "flat" plate in the first place. It was given rounded edges, and the central portion on the top surface was hollowed out to reduce its weight. It was supported by a metal strip from a small bracket which was fixed to another bracket screwed to the centre plate by means of two lengths of silica tubing, which also provided the insulation (see fig.33). The tubing fitted into small brass tubes on the brackets, and was held in place by black wax. Holes were drilled in the flat front of the "high tension" bracket to permit the air inside the tubes to be pumped away.

The high tension lead was to be a long brass rod supported in the centre of a glass tube of the widest possible diameter (1 in.) which was waxed into the third brass tube (B, fig.24) on the target chamber end plate. By this arrangement it was hoped that the region of greatest inhomogeneity round the lead would be well away from the glass, and the danger of dielectric breakdown thereby diminished. The end of this brass lead, which was about 3/16 in. diameter, made "push" contact with the flat end of the plate supporting bracket by means of a small spring device shown in figure 33.

All metal surfaces near the high tension components were rounded and polished to reduce the possibility of breakdown.

The high voltage was to be obtained from an old X-ray supply set which consisted of an oil-immersed voltage doubler valve rectifying unit, and its associated control unit which controlled the input to the main transformer by means of a system of selector switches connected to an autotransformer. As received, the set was said to deliver a range of five selected voltages between 60 and 100 kV. across the two output terminals, or between 30 and 50 kV. from one terminal to earth. This was modified by connecting a Variac and protecting fuse in the control unit output line, in such a position that the circuit breaker incorporated in this line came between the Variac and the main transformer. An A.C. volt meter, 250 V. full scale, was placed across the output of the Variac. In this way it was possible to obtain any voltage up to a maximum of 50 kV. This could be either positive or negative with respect to earth, depending on the choice of output terminal. A meter reading 5 kV. full scale was available, and this was used to obtain the beginning of a calibration curve, of A.C. volts input to the rectifier unit against kV. output. The straight line extrapolated from these readings passed through the expected point of 50 kV. output for 233 V. input. This input voltage had been measured, in checks on the control unit alone, as the maximum autotransformer output under the specified operating conditions.

This high tension was to be supplied to the lead on the apparatus through the circuit shown in figure 34. The two resistors were of the liquid type, made by Mr. D. Hall according to the directions of Gemant (151). Two flat platinum electrodes, perpendicular to the direction of current flow, were sealed into opposite ends of a glass tube. This contained a central side-arm for filling. After filling, this side arm was corked, and waxed over. The length of each resistor was 30 cm.

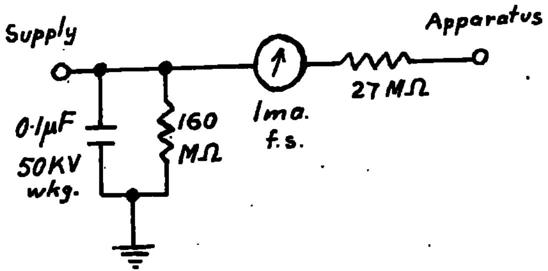


Fig. 34.

The "line" resistance, in a tube of cross sectional area of about 1 cm.^{2}, contained 22% ethanol and 25% phenol (by volume). The "bleeder" resistance, in a tube of cross sectional area 3.8 cm.^{2}, contained 11% ethanol and 25% phenol. Each solution contained 1% picric acid, and was made up to 100% by volume with benzene. It was found that care was needed to ensure that all components were dried before the solutions were made up. The resistance of each unit was calculated from the measured currents at a range of voltage drops from 1 to 5 kV. All connections were made with "co-axial" cable, with P.V.C. insulation. The resistors were mounted away from the wall, in a fume cupboard, on "tufnel" strips. This insulation was not adequate, however, at 30 kV.

OPERATIONAL TESTS

Pumps and Vacuum.

As each stage of construction was completed, the apparatus was continuously pumped for at least several days. A steady fall in the Penning gauge reading was taken to indicate that no leaks had developed (c.f. p. 172).

Further, it was possible to check that the pumps were able to deal with a continuous flow of gas as soon as the slit system had been installed. Air was used for this purpose, and the "cold fingers" were left at room temperature. The readings given by the two Penning gauges were observed for varying "source" pressures, as measured by the thermocouple gauge, at several different slit widths.

For this test the source consisted merely of a tube attached to the bellows behind the source slit. This was lead out through opening R (fig.24) and connected to a flask of 1 litre capacity to which was attached the thermocouple gauge (first model). Air was allowed to leak into this flask through a fine capillary, and its flow was controlled by a tap. The external slit controls (p. 175) were used. Tests carried out

TABLE V

Source		Collimator Chamber		Target Chamber		Comment
µA.	mm.Hg.	µA.	mm.Hg. x 10^5	µA.	mm.Hg.	
6	.5	81	6	14	$<10^{-5}$	slits almost closed. (~ 0.01 mm.)
7	.4	46	4	14	"	
8	.3	38	2½	16	"	
9	.2	32	2	16	"	
12	.1	22	1	16	"	
8	.3	69	5½	19	$<10^{-5}$	source slit. open 2/3 turn. (~ 0.04 mm. width) coll.slit. open ¼ turn. (~ 0.03 mm. width)
9	.2	75	6	18	"	
10	.15	64	5	19	"	
12	.1	49	4	18	"	
14	.07	37	2½	18	"	
17	.05	29	1.8	17	"	
21	.025	29	1.8	18	"	
7	.4	270	25	15	$<10^{-5}$	source slit open another ½ turn. (~ .07 mm.) coll.slit. open another ¼ turn. (~ .05 mm.)
8	.3	180	15	18	"	
9	.2	150	13	17	"	
10	.15	120	12	17	"	
11	.13	110	10	17	"	
12	.1	86	7	18	"	
13	.08	75	6	20	10^{-5}	

when the slits were being aligned showed that only a very approximate idea could be gained of the slit widths actually used in this series of tests.

The results, which are shown in Table V, indicate that the observed pressures agree fairly well with those to be expected from the pump speed calculations (p. 164). At this stage the target chamber had not been pumping for very long, and therefore the pressure was still rather high. The pressures obtained at this time for no gas flow were:- Collimator chamber, 4 to 5 μA. ($\sim 10^{-6}$ mm.Hg.); Target Chamber, 16 to 17 μA. ($< 10^{-5}$ mm.Hg.). After several months pumping, both gauges eventually gave readings of from 2 to 4 μA.

It was therefore assumed that the slits would be satisfactory, and that, with a condensible gas in the system and the "cold fingers" at liquid nitrogen temperature, the pressures would be sufficiently low for satisfactory beam production.

Choice of Ethyl Iodide.

All the subsequent tests were carried out with the reaction chamber in position, and ethyl iodide in the reservoir. This compound was used in these initial experiments in preference to methyl iodide for two major reasons.

Firstly, the most satisfactory radical detector of those tried was molybdenum oxide. Therefore, since this seemed to be more sensitive to ethyls than to methyls, a search for a beam of ethyl radicals would have more chance of success.

Secondly, the required source pressures were of the order of 0.1 to 1.0 mm.Hg. Ethyl iodide and methyl iodide have an equilibrium vapour pressure of 0.5 mm.Hg. at -63°C., and approximately -82°C., respectively. At these temperatures, methyl iodide (M.P. -64.4°C.) is solid, ethyl iodide (M.P. -105°C.) is still liquid. Therefore ethyl iodide is the more reliable for preliminary experiments on vapour pressure control.

Slit Alignment.

Before any attempt at radical production was made, the slit system was further tested by an attempt to form a beam of ethyl iodide. This was detected by a conventional condensation target.

A deposit of platinum, obtained by "burning in" several successive applications of "Liquid Bright Platinum" solution, was formed on the lower portion of the target chamber cold finger (c.f. ref.106). A thick layer (approx. 0.3 to 0.5 mm.) of copper was electrodeposited on this, and polished smooth with fine emery paper. A piece of silver foil was firmly attached with soft solder to a copper backing, and this composite plate was soft-soldered to the copper on the cold finger. In this way good thermal contact between the cold finger and the target was assured. The silver surface was given a high polish with metal polish, which was rubbed on in such a way that any faint scratch marks were perpendicular to the length of the expected trace.

The dimensions of the trace were calculated from the geometry of the apparatus. Although it meant placing a great deal of reliance on the collimator chamber cold finger, the slits were set wide (.10 mm.) for these exploratory experiments, so that a more readily visible trace could be obtained. The dimensions were:- both slits, 0.1 mm. x 3 mm.; distance between the slits, 8.41 cm.; collimator slit to target, 17.7 cm. Thus the "umbra" should be 0.1 mm. x 3 mm., and the limits of the "penumbra", 0.52 mm. x 14.9 mm. These figures assume that the pressures are so low that scattering is negligible.

The glass walls of the target chamber were streaky, were not uniform in thickness, and were of variable curvature, particularly in the region where it was desired to view the target. Consequently it was not at all easy to see the trace, and any "times of appearance" have very little significance since the deposit was probably very thick before it could be distinguished from the streaks in the glass with any degree of certainty. The observation of a trace was considered to be confirmed if the "trace" disappeared when the target was allowed to warm up to room temperature.

After some preliminary trials, in which it was thought that a trace was probably being obtained, and which confirmed

TABLE VI

Reservoir		Source T.C. gauge		Coll. Chamber Penning		Target Chamber Penning		Comment
°C.	equil. V.P. mm. Hg.	µA.	mm. Hg.	µA.	mm. Hg.	µA.	mm. Hg.	
-89	0.033	28	0.004	5		7	$<10^{-5}$	no coolant in cold fingers.
-67½	0.35	26.3	0.007	8		7	"	
-66	0.38	17.5	0.023	25	2.10^{-5}	7	"	
-63	0.50	12.7	0.05	47	4.10^{-5}	7	"	
-64	0.46	11	0.065	56	5.10^{-5}	3	"sticking"	coolant in target finger only.
-	-	9.3	0.09	88	7.10^{-5}	3	"	
-60	0.65	8.7	0.11	-	-	-	-	
-	-	19.3	0.02	44	4.10^{-5}	-	-	no coolant. target Penning disconnected.
-	-	13.2	0.04	74	6.10^{-5}	-	-	
-64	0.45	12.5	0.05	70	$5\frac{1}{2}.10^{-5}$	-	-	
-63	0.50	10.2	0.075	5	10^{-6}	-	-	coolant in both fingers.
-52	1.3	9	0.1	86	7.10^{-5}	8	$<10^{-5}$	Na heated no coolant.

that the target chamber pressure was never more than 7 µA. ($\sim 10^{-6}$ mm.Hg.) even when the cold finger was at room temperature, a final run was carried out with the Penning gauge disconnected from this chamber, and the connecting cone blanked off with a sealed off socket. Thus it was possible to swing the condensation target parallel to the chamber wall when it was desired to obtain a close look at the trace. This time it quite definitely appeared 50 minutes after liquid nitrogen had been placed in the trap. The source pressure was steadily increased from .08 to .13 mm.Hg. during this period. The trace was approximately of the expected size (1-1/2 cm. x 1/2 mm.), "thickest" in the middle and "tailing off" at the edges, and was, as far as could be judged, in line with the slits. It disappeared when the target was warmed up.

This, therefore, was taken to indicate that the slits were in reasonably good alignment and that, as far as beam production was concerned, the design was satisfactory.

At the same time some further information about the pressure relationships in the apparatus was obtained. Some sample figures are collected in Table VI. These illustrate very clearly the effect of the cold fingers on the chamber pressures, and the relationship between source pressure and collimator chamber pressure. Further, it is to be noticed that the reservoir pressure, as indicated by its temperature, is much higher than the pressure given by the thermocouple gauge (second model), which is situated nearer to the slit. This difference seems to be much greater than would be expected to occur as a result of the gas flow. However, there is another possible factor which must be considered. The reservoir thermocouple was situated in a well on the outside of the vessel, in the vacuum jacket, and near the heating wire. Thus the recorded temperature is likely to be higher than its true value for two reasons. Firstly, the liquid may well be cooled somewhat because evaporation is taking place from its surface, and secondly, the relatively poor conductivity of the glass may well result in an appreciable temperature difference between the liquid and the thermocouple.

The new model L.T. thermostat (c.f. p. 77) incorporated modifications which should overcome these objections.

Radical Beam.

Finally, a number of attempts were made to produce a beam of ethyl radicals and operational trials of the various possible detection methods were carried out.

Quite apart from the apparent non-linear decrease of activity with time (c.f. p.124), the wire and autoradiographic methods were shown to have severe practical disadvantages. Firstly, a fresh target is required for each experiment. Pumping must be stopped, and air at atmospheric pressure introduced each time a target is changed. Even when dry oxygen free nitrogen is introduced along the "hydrogen" line (fig.26b) during this process, a minimum of 8 to 10 hours (i.e. overnight) is required to restore the vacuum to a practicable level. Therefore it is highly desirable that the chosen detector should be capable of measuring the beam "profile" at least three to five times before a new one is required, so that alternate measurements, under otherwise constant conditions, can be made on the beam with and without the imposition of the electric field.

The experiments described in Chapter IV are not in disagreement with the previous workers with visible deposits, who claimed that hydrogen treatment of lead or bismuth is necessary before these metals are attacked by radicals. This is a further disadvantage in molecular beam work, for comparatively large quantities of hydrogen are needed to produce a discharge ($\sim 10^{-1}$ to 10^{-2} mm.Hg. at least), and the pumps take at least 15 to 20 minutes to restore the vacuum.

The wire technique has the further disadvantage that, if a reliable peak shape is to be obtained for the beam, the wire must be very nearly parallel to the slits. This can only be done, with an appreciable expenditure of time, by a careful optical re-alignment each time a fresh wire is mounted in its holder.

For these reasons it was decided that a relatively large area of molybdenum oxide deposit (approximately 2-1/2 cm. square) would, of the detectors tried, offer the best chance of success, provided that it could be protected from any possibility of contact with "hot" oil molecules from the pump. From ten to twelve parallel traces could, if required, be formed on the one target simply by rotating the capstan head on the target micrometer each time a fresh section of target was required.

A number of attempts were made to obtain a trace on this type of target, but without success. From the experiments on the test apparatus (p. 153), it was deduced that a detectable trace should have appeared in a maximum exposure time of 7 hours. An account is presented here of the last of these experiments which was carried out.

With the shutter closed, thus protecting the target from the beam, the following conditions were established, in the order indicated:

1. With the ethyl iodide tap closed, the target chamber pressure was 9 µA. ($\sim 6.10^{-6}$ mm.Hg.), and collimator chamber 3 µA. During this time the reservoir was brought up to the required temperature. ($\sim$ -61°C., i.e. $\sim$ 0.6 mm.Hg.)

2. The sodium (fresh capsule) was then heated, until a good resonance was visible ($\sim$ 290°C. at the "waist" of the reaction unit. The sodium was probably appreciably hotter than this).

3. The reservoir tap was then opened. With the reaction then proceeding, the pressures were 9 µA., target chamber;

66 μA., collimator chamber ($\sim 5.10^{-5}$ mm.Hg.); source, $\sim$ 0.15 mm.Hg.

4. Liquid nitrogen was then placed in the cold fingers. (Only a few centimeters height was maintained in the collimator chamber trap), and the beam shutter was opened.

During the following period of 7 hours, the conditions fluctuated between the limits:

Target chamber, 1-1/2 to 2-1/2 μA. ("sticking" vacuum)
Collimator chamber, 49 to 57 μA. (3 to 4 times 10^{-5} mm.Hg.)
Source pressure, 0.13 to 0.15 mm.Hg.
Reaction temperature, 280 to 290°C.

Conditions of sodium excess were continuously maintained. A very heavy deposit of sodium iodide formed in the reaction chamber. No sign of a trace could be observed.

In a previous experiment a sample of molybdenum oxide, deposited on a metal surface, was suspended on a length of stout wire which was sealed into one of the B.10 brass ground joints in the collimator chamber end plate which had been provided for the slit width controls. This "target" was arranged so that it could be moved into a position about half way directly between the two slits by rotation of the joint. At this position the intensity of molecules issuing from the source should have been $\left(\frac{26}{4}\right)^2$, i.e. at least thirty, times greater than the intensity at the target position. No blue coloration of this deposit was observable after 3-1/2 hours radical production.

It may be that, since the O3B pump baffle was not very efficient, this deposit had been de-sensitised by oil vapour. However, when these observations are considered in the light of the mass spectrometric results published by Lossing and Tickner (60, c.f. p.66 , this thesis), it is apparent that there is a much more fundamental cause of the failure to detect any radicals. In their apparatus, these authors made provision for separate pumping on the source side of the slit and found that, if the rate of pumping were too low, no radical products of the pyrolysis reaction were detected. They found, moreover, that the presence of a carrier gas was essential if a sufficiently high flow rate were to be maintained.

Fraser and Jewett (53) have published an account of an attempted production of a radical beam. Although they used a carrier gas, their experimental arrangement was in all other respects comparable with that described in this chapter. That is, they used a conventional molecular beam source (with no provision for its separate pumping). It is of interest that Hipple and Stevenson (61) have remarked that the proportion of radicals in Fraser's beam must have been very low. The attempts of Kistiakowsky's co-workers (50) have also been hampered by low radical concentrations in the beam.

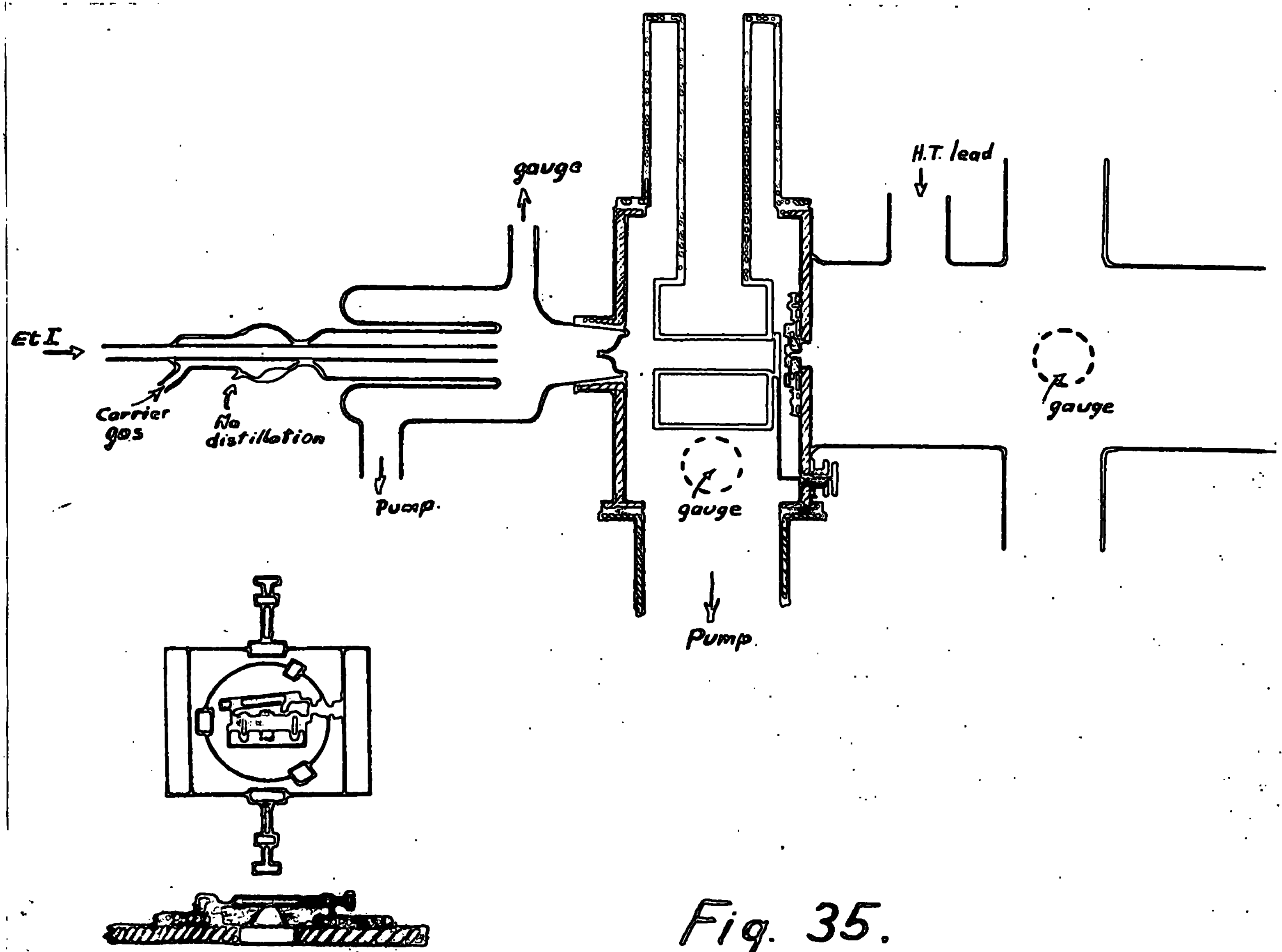

gauge
H.T. lead
Et I
Carrier gas
Na distillation
Pump.
gauge
gauge
Pump.

Fig. 35.

It has recently been learnt (152) that over the years, other (unpublished) attempts to produce a radical beam have been made by J.H.Simons and his co-workers, and by T.E.Phipps, working in the University of Illinois.

FUTURE DEVELOPMENTS

Although it is not absolutely certain, it is very likely that all these experiments have involved the use of a conventional molecular beam source. Since Lossing and Tickner were able to measure a beam of ionised radicals quite easily, it would seem that a source arrangement similar to theirs could be applied to the production of a beam of neutral radicals with some hope of success.

Since the present design, with the source completely inside the reaction chamber, makes extremely difficult the provision of both separate pumping and a supply of carrier gas over the sodium, a completely new design, of this half of the apparatus at least, is necessary.

Figure 35 is a section drawing which illustrates the lines along which the new design might be developed. The source should be outside the apparatus. This facilitates the connection of pumping and carrier gas leads, and at the same time permits the direct distillation of sodium into the sodium chamber, thus making the capsules unnecessary. The constriction between this space and the reaction chamber will help to inhibit the spread of the sodium deposit during the distillation. The space between the outer walls and the co-axial iodide lead at this constriction can be quite narrow, as the flow of carrier gas will help to inhibit the back diffusion of the iodide. The cylindrical symmetry makes more easy the provision of uniform heating. A conventional tube heater may be used for the sodium chamber, and an element cut from nichrome sheet, similar to that used by Lossing and Tickner (60), may be used to keep the reaction chamber warm. Observation of the sodium glow is possible through the clear space near the slit. It is recommended that the source slit itself be of glass, since most metals seem to be more efficient recombination catalysts than this material. Tho method for constructing a glass slit has been described by Wrede (114), Phipps & Taylor (153), and Johnson (144). The re-entrant mounting of the slit makes it possible to place it close to the position of maximum radical intensity. It will, however, be necessary to carry out some experiments to investigate whether it becomes blocked by sodium and sodium iodide deposits. The carrier gas should help in this respect. It if proves impossible to avoid this deposition, one of the pyrolysis production methods (p.61) must be given further consideration. The connection to the source pressure gauge is shown immediately adjacent to the reaction zone.

The illustration shows a ground joint connection to the collimator chamber. This permits adjustment of the slit to an approximately horizontal position before the glass connections are sealed on. It is desirable, however, to make provision for fixing the two sections firmly in place once the adjustment has been made. Black wax may be suitable, for it is likely that the liquid nitrogen cooled condenser will keep the whole collimator chamber fairly cool in this design.

It is suggested that the collimator chamber, and condenser, should be constructed of metal. The cylindrical bottom of the condenser, with its central canal to allow the passage of that part of the "pencil" required for the beam formation, should prove to be much more effective than the type used so far. In fact it should act as a "fore slit" (c.f. ref.103, p. 22).

The Penning gauge connection could be attached to the side of this chamber without much difficulty. It is also recommended that the shutter be introduced into this chamber, well away from any possibility of interference with the deflecting field. If it is placed between the condenser and the collimator slit the deflected molecules would quickly be condensed. The O-ring type of seal (fig.32) should suffice for its connection to the external control handle.

The metallic structure of this chamber should provide a sufficiently rigid mounting for the slits. It is desirable, however, to provide for the adjustment of the collimator slit both by rotation, and by its bodily movement in a vertical direction. This should take care of any possible variation in the construction of the glass source slit. Alignment in a horizontal direction (for horizontal slits) is not so critical. A possible method of achieving these adjustments is illustrated.

For immediate purposes, the target chamber cross-piece already in use could be employed, although two additional side arms would be of advantage - one for a short Penning gauge attachment, and another for a completely separate point of entry for the high tension lead. As a final aim, it is recommended that the use of rubber gaskets should be avoided where possible, for they tend to take a permanent "set" after a time, and are a possible source of sulphur which could be the explanation of the heavy brown coating observed to develop on copper surfaces exposed to the vacuum. A glass target chamber is desirable, for it offers at the same time good insulating properties and a convenient means of watching for the development of electrical breakdown when the high fields are employed.

The molybdenum oxide detector will probably suffice for the preliminary attempts to obtain a sufficiently intense beam of ethyls with this new apparatus. This detector has the advantage that, with a sufficiently long exposure, a trace should eventually form, and would be sufficiently stable for photographic reproduction. However it is desirable to aim eventually for a more quantitative type of detector. From the experiments described in Chapter IV it seems highly likely that isotopically pure radio-elements will prove to be unsatisfactory because of the sparse distribution of even a highly active deposit. Isotopic dilution should improve the "linearity" of the detector if this interpretation is correct but would, at the same time, reduce its sensitivity to a point where it may no longer be of advantage, for it would seem that dilution by a factor of about 10^5 is necessary (c.f. pp. 109, 128) to obtain a layer of one molecule average thickness, even when the deposit is formed on the very small surface of a thin wire.

It is the writer's opinion that the best type of detector would probably consist of an arrangement similar to the ionisation chamber of a mass spectrometer, followed by some very simple form of mass analyser. If this were placed behind a slit which could be traversed across the beam, the resulting beam peak shape could be plotted from the ionisation current arising from methyl ($^m/e = 15$) or ethyl ($^m/e = 29$) as required. The distance of traverse need not be more than a few tenths of a millimeter, and there would be no need to open the apparatus to the atmosphere at all, except when the source required cleaning.

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SUMMARY

This thesis presents an account of a number of experiments carried out during an investigation of the problem of estimating the dipole moment of free radicals by the molecular beam technique.

A number of possible detection methods was tried. Of these, a deposit of molybdenum oxide smoke was the most successful for the detection of ethyl radicals. The use of isotopically pure radioactive elements, although appearing to offer the possibility of high sensitivity, seems to be limited by the atomically sparse nature of the deposit.

A molecular beam apparatus was constructed which, although capable of producing beams of stable molecules, was no more successful for the production of a beam of radicals than the attempts of previous workers in this field.

In a recent paper, however, a new type of source has been described which made it possible to produce a good beam of radical ions in a mass spectrometer. This source differs from the conventional molecular beam source in that it is provided with a separate pumping lead. In this way a high rate of gas flow is maintained on the "high pressure" side of the source slit, with a consequent improvement in the concentration of radicals passing through the slit.

Suggestions are made for a new molecular beam apparatus, incorporating this type of source, which should make it possible to produce a satisfactory beam of radicals and thus to determine whether the free methyl possesses a dipole moment.

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