AN INVESTIGATION OF THE KINETICS OF THE DECOMPOSITION OF METHYL IODIDE WITH PARTICULAR REFERENCE TO THE DETERMINATION OF THE CARBON-IODINE BOND ENERGY

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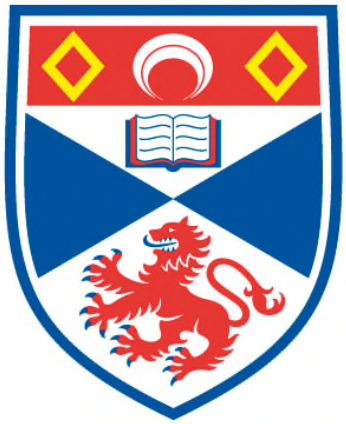
A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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AN INVESTIGATION OF THE KINETICS OF THE DECOMPOSITION OF METHYL IODIDE WITH PARTICULAR REFERENCE TO THE DETERMINATION OF THE CARBON-IODINE BOND ENERGY.

A Thesis presented by

RUTH LAPAGE, B.Sc., M.Sc.

to the

UNIVERSITY OF ST. ANDREWS

in application for

the Degree of

DOCTOR OF PHILOSOPHY

May 1950.

Ms 1058

DECLARATION

I hereby declare that the following Thesis is a record of experiments carried out by me, that the Thesis is my own composition and has not previously been presented for a Higher Degree.

The investigation was carried out in the Chemical Research Laboratory, United College, St. Andrews, under the direction of C. Horrex M.Sc.Ph.D.

CERTIFICATE

I hereby certify that Miss Ruth Lapage B.Sc. M.Sc. has spent nine terms at Research work in the Chemical Research Laboratory of United College, that she has fulfilled the conditions of Ordinance No. 16 (St Andrews), and that she is qualified to submit the accompanying Thesis for the Degree of Ph. D.

University Career and Research Experience

I entered the University of Toronto in October 1943 and on returning to England in 1944 I transferred to the University of Manchester where I graduated as a Bachelor of Science in December 1945. I accepted a Department of Scientific and Industrial Research Assistantship at Sheffield in May 1946 where I began work on the pyrolytic decomposition of iodides under Dr.C.Horrex. For a thesis on this work I was granted the degree of Master of Science by Manchester University in September 1947. I was accepted as a Research Student for the degree of Doctor of Philosophy by the University of St.Andrews in October 1947 and was awarded a Department of Scientific and Industrial Research Maintenance Grant. I continued the investigation of the pyrolysis of methyl iodide, which is the subject of this thesis, under Dr.C. Horrex.

ACKNOWLEDGEMENTS

The author wishes to thank Dr C. Horrex for invaluable assistance and advice in both the practical and theoretical aspects of this work and Mr. C. B. Cowan for many helpful discussions.

The author also wishes to thank the Department of Scientific and Industrial Research and the University of St. Andrews for maintenance grants made during the execution of the work.

Contents

Introduction

In recent years a great deal of attention has been paid to the determination of chemical bond energies. This has been due to a variety of factors, but one important reason has been the development during the last twenty years of ideas about the detailed molecular interactions which take place during the process of chemical change. Since chemical change involves the making and breaking of bonds, either as separate or simultaneous processes, it is clear that progress from qualitative to quantitative explanations of chemical interactions will be greatly assisted by more precise knowledge of the strength of the links in the individual molecules.

The early tables of bond energies (of Pauling[1]) laid more emphasis on the approximate constancy of the values for any bond in various molecules than on variation from the mean. Chemical intuition on the other hand, would suggest that the difference in the reactivity of say $CH_3.CH_2.Cl$ and $CH_3.COCl$ might be due chiefly to some difference in the strength of the C-Cl links. More recent work substantiates this and has provided evidence from various sources to show how bond energies for certain links depend on their molecular environment. In the following pages a survey is given of the methods which have been employed for this purpose and some of the results achieved.

Definition of Bond Energy and Bond Energy Terms

The literature contains the term "bond energy" used in senses which are not quite equivalent. In this work the definition given by Butler and Polanyi[2] will be used. Thus the bond energy is the energy absorbed when a gaseous compound is decomposed, by the breaking of that bond, into two unexcited radicals or atoms.

Another usage is that bond energies are quantities which may be assigned so that their sum for any one molecule gives its heat of formation from the separated atoms. Butler and Polanyi call this the bond energy term.

It is obvious from the preceding definition that in the case of such molecules as H_2O or CH_4 the use of bond energy terms assumes that the same amount of energy is associated with each bond. The breaking of only one linkage may involve energies of reorganisation in the radicals formed and this means the two quantities bond energy and bond energy term are unlikely to be equal. There is distinct evidence for differences and, as one example, the case of the mercuric halide, which has been discussed recently by Skinner[3], can be quoted. It has been found that

$$HgCl_2 \rightarrow HgCl + Cl \qquad -80.5 \text{ K.cals}$$

while

$$HgCl \rightarrow Hg + Cl \qquad -24 \text{ K.cals}$$

The very accurate thermochemical data of Rossini[4] can also be used to demonstrate the fallacy of this assumption. Thus if ΔH is the heat of formation of the gas Rossini gives

Gas	ΔH K.cals
CH_4	-17.89
C_2H_6	-20.24
C_3H_8	-24.82

If we consider the two reactions

$$2\,CH_4 \rightarrow C_2H_6 + H_2 \qquad (1)$$

$$3\,C_2H_6 \rightarrow 2\,C_3H_8 + H_2 \qquad (2)$$

We find (1) is endothermic to the extent of 2(17.89) - 20.24 = 15.54 kals whilst (2) is endothermic to the extent of 3(20.24) - 2(24.82) = 11.08 kals. The right hand side of each equation contains one C-C bond and one H-H bond which replace two C-H bonds in the left hand side. Thus from the point of view of bond breaking and reformation these two reactions are precisely the same and yet the heat effect is not identical. It is impossible from such data however to specify whether the variation was in the C-H or C-C strengths.

The determination of absolute values of bond energy terms is also complicated, in the case of organic compounds by uncertainty as to the value of the heat of sublimation of carbon. This quantity is needed in order to derive from Q (heat of formation of a compound from its elements in their standard states) the heat of formation from atoms. Since this uncertainty underlies the values of bond energy terms and impedes correlation with bond energies the various views which have been expressed are listed below.

Heat of Sublimation of Carbon (L)

The main values which have been proposed for L are 125, 135, 156 and 170 kals.

The value of 125 kals is strongly supported by Long and Norrish[5] who also point out that many of the differences in value arise from an insufficient consideration of the state of the gaseous carbon atom, they regard the dissociation as

$$C_{diamond} = C_{gaseous}\ (^3P) - L_1 \qquad 1$$

$$C_{diamond} = C_{gaseous}\ (^5S) - L_2 \qquad 2$$

$$(^5S)\ C = (^3P)\ C + L_2 - L_1 \qquad 3$$

Since tetravelent carbon is in the ^5S state they consider L_2 to be the important quantity in calculating bond energy terms in hydrocarbons, and suggest values of $L_1 = 125$ kals and $L_2 = 190 \mp 10$ kals.

The value for $L_2 - L_1$ has been put at 100 kals by Bacher and Goudsmit[6] but Ufford[7] has placed it at 73 kals which is in agreement with Long's value of 65 ± 10 kals.

Thus as Long and Norrish point out any value for L_1 above 125 kals would give a very high value for L_2 and correspondingly higher values for the bond energies of hydrocarbons than comparison with other data warrants.

Several authors[8] have attempted to find the value of L_1 from a consideration of the energy of dissociation of carbon monoxide, determined spectroscopically, but the results are very ambiguous and vary between 74 kals and 170 kals. Marshall and Norton[9] have studied the rate of sublimation of carbon and obtained a value of 170 kals. This method is open to error since carbon is in the ^5S state in the solid and it cannot be assumed that the gaseous carbon is produced directly in the ^3P state thus any dynamic method of this sort may give a value of L_2 or at any rate a lower limit to it. The dissociation of cyanogen into CN radicals together with its heat of formation and that of the CN radical could give a value of L_1 but the experimental data is very varied and Springall uses it to support a value of $L_1 = 170$ and Long[5b] for $L_1 = 125$.

Brewer[10] and his co-workers have studied the vapour pressure of carbon under equilibrium conditions, and after making due allowance for C_2 gas derive a value of $L_1 = 170$ kals and regard all previous lower estimates obtained from

earlier vapour pressure work to be liable to considerable experimental error particularly in the measurement of temperature but Long[5c] considers their results to be based on several unjustifiable assumptions. Gordy[11] from a consideration of the relationship between bond energy and bond length finds a value between 150 and 190 kals for L_2 but the method is not sufficiently refined to distinguish between these values.

If the bond energy term of methane were known it would be possible to calculate L_2 from the following

$CH_4 = {}^{C}_{graphite} + 2H_2$		-17.87 kals
$2H_2 = 4H$		-208.2 kals
${}^{C}_{graphite} = ({}^5S)\ C$		$-L_2$ kals
$CH_4 = ({}^5S)\ C + 4H$		$-L_2 + 226.1$ kals

and if the various bond energies in methane were known then from

$$CH_4 = ({}^3P)\ C + 4H \qquad -(a + b + c + d)$$

where a b c and d are the energies of removal of successive H atoms - and the relationship

$$({}^5S)\ C = ({}^3P)\ C \qquad +L_2 - L_1$$

it would be possible to determine L_1.

Gero and Valatin[12] adduce evidence from the spectroscopic study of CO by Gero and Schmid[13] for L_2 = 170 kals, L_1 = 73 kals and a = 100.7 kals, b = 97.36 kals, c = d = 97.02 kals. The value of a is in very good agreement with that of Van Artsdalen and Kistiakowsky[14] which is obtained from kinetic considerations of the photobromination of methane. Herzberg[15], however, from a spectroscopic investigation of the CH radical gives a value of

80 kals for d, Gero regards the CH_2 and CH radicals as still containing carbon in the tetravalent state which seems most unlikely.

Baughan[16] used data calculated by Voge[17] giving a = 113 kals b = 94 kals c = 92 kals to support a value of L_4 = 170 kals, Voge[18] has however recalculated his values in the light of more recent data to give a = 101 kals b = 90 kals and c = d = 80 kals which is in agreement with a value of L_4 = 120-140 kals.

The data on this problem is, as can be seen from the above, of a very conflicting nature and the evidence for either value of L remains incomplete. However, in the normal processes of chemical reactions where few links are broken and formed the Butler and Polanyi definition of bond energy is very much more relevant even if the determinations of the value in a particular case may prove more difficult. It is apparent that the bond energy of a link defined as its dissociation heat means that the value is peculiar to a given molecule and the radicals formed by the dissociation, since the latter may be stabilised by resonance.

Methods of Determining Bond Energies

Several methods of determining bond energies have been developed. They can be divided into two main categories - physical and chemical.

Physical methods involve breaking of the bond by supplying energy either photochemically or by bombardment with electrons of controlled velocity. Chemical methods include the consideration of heats of reactions, equilibrium constants and the velocity of reactions either separately or in conjunction with one another.

Electron Impact Methods

Franck and Hertz[21] first showed that electrons must have a minimum velocity before they will ionize a gas, which depends on the nature of the gas. Smith[22] studied the ionisation of methane in this manner. The electrons from a hot filament are accelerated through an electric field and enter the ionisation chamber. The products, which are numerous, are differentiated by use of a positive ray analysis. The appearance potential of the ions is determined by the change in current through the plate to which the electrons and ions proceed.

That is to say, the energy of the reaction:-

$$RH \rightarrow R^+ + H + e^- \qquad (1)$$

is measured and if the energy of:-

$$R \rightarrow R^+ + e^- \qquad (2)$$

is known then the value of:-

$$RH \rightarrow R + H \qquad (3)$$

can be determined.

Stevenson[23] has obtained the following values by these means:-

CH_3-H = 101 $\mp$ 4.5 kals C_2H_5-H = 96.5 $\pm$ 4.5 kals

CH_3-CH_3 = 92,6 $\mp$ 9 kals C_2H_5-C_2H_5 = 77.6 $\pm$ 9 kals

he has also studied some higher hydrocarbons and some chlorides. Results obtained in this way are open to considerable doubt. In the case of diatomic molecules it is assumed that the products are formed in their ground states. If they possess excitational energy this must also be subtracted from the energy of reaction (1) and in most cases it is very

difficult to estimate such energy accurately. In the case of polyatomic molecules there are additional uncertainties due to the vibrational energy of the ion and, if more than two fragments results, due to unknown electronic vibrational and kinetic energies of the products as well as their states of aggregation. Thus such a method can only lead to an upper limit to the bond energy.

Spectroscopic Methods

When the vibrational energy of a diatomic molecule is increased the amplitude of the vibration increases until at a definite energy, corresponding to dissociation, it becomes infinite. When the absorption band spectrum of such a molecule is observed the vibrational bands are found to converge until continuous absorption is found at the dissociation limit. The energy of dissociation, E, can then be found from

$$E = hc/\lambda$$

h = Planck's constant. c = wavelength of light and λ = wavelength of the convergence limit. This method was developed by Franck[24] and has been applied to many diatomic molecules. The band spectrum of polyatomic molecules is in general too complex for any decisive interpretation.

In many cases the higher vibrational bands cannot be observed and extrapolation to the convergence limit is necessary. Birge[25] and Birge and Sponer[26] have suggested various methods of extrapolation to determine E. The simplest method is to plot the known vibrational energy intervals against the vibrational quantum number and extrapolate the curve to zero interval. The area under the curve then represents the dissociation energy.

Some molecules, such as Cl_2 and O_2, display bands corresponding to transitions from the lower vibrational levels of the electronic ground states to vibrational levels of an excited electronic state, such bands converge to the dissociation limit of the excited molecule and are followed by a continuous absorption corresponding to photo-dissociation. By observing this limit a value for the dissociation energy of the excited state can be determined, if the energy state of the dissociated atoms can be found a value for normal dissociation can then be derived.

In some cases the upper electronic state is unstable and the absorption spectrum is continuous. The long wavelength limit of such absorption will then correspond to a value for the dissociation energy, but an accurate value cannot, in general, be determined from such a spectrum.

The phenomenon of predissociation was originally used to determine bond energies by Henri.[27] In some cases the sharp lines in a band, due to the rotational fine structure become diffuse and then end abruptly. This occurs when the energy of the molecule exceeds that required for dissociation and a radiationless transition to the dissociated state is possible. The most frequent cause of pre-dissociation is overlapping of a discrete part of a stable excited electronic state and a dissociation continuum of another electronic state.

Equilibrium Method

The temperature coefficient of the equilibrium constant of a reaction is related to the heat of the reaction, Q, in the following manner.

$$\frac{d\,(\log_e K_e)}{dt} = \frac{-Q_2}{RT^2}$$

when K_e = equilibrium constant, T = absolute temperature, R = gas constant.

White[28] has studied the dissociation of cyanagen in this fashion. He determined the absolute absorption coefficient of CN in order to have quantitative measure for the concentration of CN radical whenever its absorption was observed, this together with the temperature and the partial pressure of cyanagen gives a value of the dissociation energy directly. From these determinations he obtains a value of 146 ± 4 kals for the dissociation energy. Earlier work by Kistiakowsky and Gershinowitz[29] gave a value of 77 kcals but in this case the resolving power of the spectrograph was low and the effect of pressure in broadening the absorption bands was ignored. This method is however of only very limited applicability.

Method Based on Studies in Chemical Kinetics

This method rests on the hypothesis that certain chemical reactions proceed by a rate-determining first step which consists in the breaking of one bond in a molecule. The essence of a variety of considerations (summarized recently by Williams and Singer[30]) on such unimolecular decompositions is that the energy of activation of the reaction has to accumulate in the one oscillator which then breaks. For such a case the rate constant K is given by

$$K = 10^{13} e^{-E/RT}$$

and E can be interpreted as the limiting vibrational energy of the bond.

The conception that the energy of activation of a unimolecular decomposition could be taken as the bond energy was used by Rice[31] and collaborators

in a series of studies in which emphasis was also laid on the subsequent reactions of the radicals or atoms produced by the initial decomposition. Rice showed how the further reactions of the radicals could lead by a simple series of steps to an explanation of the variety of products usually found in thermal decomposition reactions and postulated that whilst the activation energies of these secondary reactions were low they were not necessarily zero. Since only the overall activation energy is determined experimentally care must be exercised in interpreting the data.

The scheme suggested by Rice for the decomposition of propane may be regarded as typical of a hydrocarbon decomposition. In this Rice has assumed the primary decomposition into radicals could be followed by reaction of the latter with surrounding molecules, further decomposition on some form of recombination after diffusion to the wall. The proposed steps were

$$CH_3CH_2CH_3 \rightarrow CH_3 + CH_3CH_2 \qquad (a)$$

$$C_2H_5 \rightarrow C_2H_4 + H \qquad (a_1)$$

$$CH_3CH_2CH_3 + R \rightarrow RH + CH_3CH_2CH_2 \qquad (b)$$

$$CH_3CH_2CH_2 \rightarrow C_2H_4 + CH_3 \qquad (c)$$

$$CH_3CH_2CH_3 + R \rightarrow RH + CH_3CHCH_3 \qquad (d)$$

$$CH_3CHCH_3 \rightarrow CH_3CH = CH_2 + H \qquad (e)$$

where R is a CH_3 radical or an H atom.

Rice has assumed in order to account for the reaction products that the n-propyl radical will give a CH_3 radical and the iso-propyl radical an H atom. He also assumes that whilst reactions (c) and (e) occur quite readily such reactions as:-

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$$R + CH_3CH_2CH_3 \rightarrow RCH_3 + CH_2CH_3$$

do not easily occur from steric considerations. He estimated, from the relative number of primary and secondary bonds and their relative strengths of binding, that (c) : (e) as 6:4 and hence that the production of C_2H_4 to that of C_2H_6 is 6:4 which is in accordance with experimental results.

By plotting the logarithm of k, the velocity of the reaction, against I/T°A the activation energy of the overall reaction may be obtained from the slope of the resulting line, this, together with a knowledge of the activation energies of the secondary reactions gives a value for the energy of the primary break.

For example, taking the following as a general case for the decomposition of a paraffin M_1 :-

$$M_1 \rightarrow R_1 + R_2 \qquad (1)$$

$$R_1 + M_1 \rightarrow R_1H + R_3 \qquad (2)$$

$$R_3 \rightarrow R_1 + M_3 \qquad (3)$$

$$R_1 + R_3 \rightarrow M_4 \qquad (4)$$

from derivations of the concentration of the intermediate products and using the usual ideas of stationary states of the chain propagating entities we obtain:-

$$-\frac{d[M_1]}{dt} = \left(\frac{5}{4} k_1 + \frac{k_1^2}{16} + \sqrt{\frac{k_1 k_2 k_3}{2k_4}} \right) [M_1]$$

and if k is assumed to be small this reduces to:-

$$\frac{d[M_1]}{dt} = \sqrt{\frac{k_1 k_2 k_3}{2k_4}} \; [M_1]$$

and if E is the overall activation energy then:-

$$E = \frac{1}{2}(E_1 + E_2 + E_3 - E_4)$$

This shows that the measured activation energy of a reaction can be very much less than the energy required for the primary break. Moreover these mechanisms offer an explanation for the observed first order behaviour of many of these reactions although the reactions themselves are complex. If we postulate that the chain breaking mechanism is:-

$$2R_1 \rightarrow M$$

then by the previous method of calculation we obtain an order of 1.5 for the reaction velocity; if we had assumed chain breaking by:-

$$2R_3 \rightarrow M$$

an order of 0.5 is obtained. Thus we see that the relative rates of formation and removal of R_1 and R_3 will govern the apparent order of the reaction and these in turn depend on the ratio of E_2 to E_3. These considerations have been extended by Goldfinger to the case of third body recombination of the radicals and to cases with added inhibitors.

If the third body is the parent molecule a first order behaviour results; if the third body is nitric oxide or some other added substance an order of 1.5 is obtained.

Rice and his co-workers have extended these considerations to compounds containing oxygen and nitrogen. They have also been applied by many workers to problems concerning polymerisation reactions.

Confirmatory evidence for the possibility of these free radical reactions at lower temperatures was given by Frey[32] who started reactions in butane, below the temperature for normal decomposition, by the introduction of methyl radicals. Later work has shown many instances of such radical induced decompositions and polymerisations, for instance that of Allen and Sickman[33] and of Leermakers.[34] Other evidence was afforded by the observed inhibition of some reactions by the addition of nitric oxide and propylene, due probably to the radical reacting with these inhibitors rather than starting a chain.

The chain length of a reaction can be determined from the relative rates of such inhibited and uninhibited reactions. In the main, such chain lengths seem rather short for a chain of the Rice type, if nitric oxide is assumed to stop the chain completely. This suggests that possible the reactions may proceed partly by a few long chains and partly by molecular reactions or free mechanisms that do not involve chains.

The main difficulty in applying this method is that a knowledge of the mechanism must be obtained, also a good many assumptions often have to be made regarding the activation energies of many of the intermediate reactions. Rice and Rice and Johnston measured the decomposition into free radicals directly by observing the rate of removal of standard metallic mirrors by the radicals as they left the furnace. The products were identified chiefly by their alkyl mercuric bromides. If the pressure was sufficiently low (1-2 mms.) the percentage decomposition was a measure of the radical concentration and so the velocity constant could be calculated.

Eltenton[35] has developed a method in which radicals can be detected in reactions proceeding at higher pressures. He withdrew a portion of the

reacting system through a pinhole leak into a mass spectrometer and since the ionisation potential of free radicals is lower that the appearance potential of the radical ion from the parent molecule, it is possible to select a value of the electron accelerating voltage so that only the radicals are detected. In this way changes in radical concentration can be followed very quickly. So far he has only studied the thermal decomposition of various hydrocarbons in a general way. A major difficulty lies in the interpretation of the positive result for certain masses. For example in the decomposition of ethane, where ethylene is an end product, it cannot be definitely assumed that the mass 29 is due to the ethyl radical as the ionisation potential of ethylene is only two volts above that of the ethyl radical and the isotope C^{13} in ethylene would be sufficient to account for the amount of mass 29 observed. At lower pressures the amount of mass 29 observed is three times that which could be ascribed to ethylene. Similarly in the case of the decomposition of lead tetramethyl in oxygen it cannot definitely be said whether mass 30 should be regarded as due to formaldehyde or ethane, in this case he ascribes it to formaldehyde since when nitrogen is used instead of oxygen there is very little of mass 30 formed.

Another difficulty is the interpretation of a negative result, for example neither vinyl radicals in the decomposition of propylene

$$C_3H_6 \rightarrow CH_3 + C_2H_3$$

or H-atoms in the decomposition of ethane could be detected presumably due to their quick recombination and great reactivity. In the case of H-atoms Eltenton suggests the use of tantalum for parts of the apparatus as it does

not catalyse the recombination of H-atoms. Despite these initial difficulties the method seems to have considerable possibilities. Eltenton has also applied it to the study of low pressure flames.

Without giving further details of reaction schemes which have been proposed for various compounds we can summarize the advantages and disadvantages of the chemical kinetic method for bond energy determination in the following way.

There is a great deal of evidence that the initial step in pyrolytic and photochemical decomposition involves the rupture of one bond but subsequent reaction may seriously limit the accuracy of equating an experimental activation energy with the strength of the bond. In order to have no ambiguity it would be necessary to determine radical concentration before further reactions took place. As this is very difficult it is most desirable that the possible reactions be limited by choice of conditions so that the occurrence of a particular reaction will then be a significant measure of the extent of formation of the initial radical. But it is very desirable that all the products of the reaction are known in order to check this point. Unfortunately much of the data of chemical kinetics has used the concentration of one product as a measure of reaction rate, or even used the rate of change in pressure, without due regard to the reaction complexities.

The most favourable conditions for deducing bond energies would be when only small percentage decompositions are permitted, thus limiting, as far as possible, secondary reactions to those between radicals and the parent molecule, also using low partial pressures of the reactant gives the radicals a greater chance of disappearing at the walls.

Butler and Polanyi[2] stated and adapted these conditions for organic iodides and also specified short times of reaction. This last condition seems unnecessary as the lowest practicable period is of the order of 0.1 sec. and many collisions can occur in such a period at feasible pressures.

Derivation of One Bond Energy from Another Using Thermochemical Data

As Baughan and Polanyi[36] first pointed out, if we know one bond energy R-X it is possible to assess another bond energy R-Y provided we know the heat of substitution of the reaction

$$RY + X \rightarrow RX + Y + Q_s \text{ kcals}$$

from thermochemical heats of formation.

Thus

$$Q_s = Q_f\,(RX) - Q_f\,(RY) + Q_f\,(Y) - Q_f\,(X)$$

where the terms in Q_f are the heats of formation of gaseous RX, RY, Y and X from elements in their standard states and $D(R\text{-}Y) = D(R\text{-}X) - Q_s$ kals.

Another way is to use the following equations

$$D(R\text{-}X) = Q_f\,(RX) - Q_f\,(R) - Q_f\,(X) \qquad (1)$$

$$D(R\text{-}Y) = Q_f\,(RY) - Q_f\,(R) - Q_f\,(Y) \qquad (2)$$

from a value of D(R-X) a value for Q_f (R) can be determined which can then be substituted in equation 2 to obtain a value for D(R-Y). Roberts and Skinner[38] have applied this method to organic compounds very extensively. They used certain well established C-H bond energies as a starting point, and the best available thermochemical data to derive bond energies for a wide selection of C-C, C-H, C-OH, $C\text{-}NH_2$, C-Cl, C-Br and C-I bonds.

Applications of these Methods to the Alkyl Iodides

Neither the electron impact nor the equilibrium methods have been

applied to any of the alkyl iodides.

Spectroscopic Applications

Iredale[39] found that the alkyl halides all displayed a continuous spectrum. For methyl iodide in the liquid phase he found a long wave length limit to the continuum at 3950 A and in the gaseous phase at 3300 A. Hubumato[40] studied a great many organic halides. In all the iodides he observed two or three continua, which may correspond to the production of slightly excited alkyl radicals. He found that the long wave length of these continua increased asymptotically with the halide pressure. He and Herzberg and Scheibe[41] have suggested that the halide decomposes into a free radical and a halide atom in the $2^2P_{\frac{1}{2}}$ state. This could be proved either by chemical reaction (see Kato[42]) or by observing the characteristic frequency of the transition of the halide from $2^2P_{\frac{1}{2}}$ to the unexcited $2^2P_{\frac{3}{2}}$ state, which would be in the far infra-red.

Porret and Goodeve[43] found that for methyl iodide the long wave length limit depended not only on the halide pressure but also on the length of the absorption tube and so point out the impossibility of deriving an accurate value for the dissociation energy from the spectrum.

Chemical Kinetic Applications

The criteria mentioned before (Page 16) for a correct estimation have not been satisfied in many of the earlier studies of the reactions of the halides. For instance, Ogg[44] in a study of pyrolysis of the alkyl iodides used the pressure change as a measure of the rate of reaction, in the case of the reaction of the alkyl iodides with hydrogen iodide he estimated the amount of iodine formed colorimetrically.

Lessig[45] and Polissar[46] have studied the static thermal decomposition of the alkyl halides, the latter determined the reaction velocity by titrating the iodine formed; in both cases, however, the percentage decomposition was high and any secondary reactions would play an important part.

A very extensive study of the static photolysis of methyl iodide has been carried out by West and Schlessinger.[47] They determined the products of the reaction after separating them by fractional distillation at low temperatures, the iodine formed being estimated colorimetrically.

On the basis of the observed products (chiefly CH_4, C_2H_6, C_2H_4 and CH_2I_2). They propose the following mechanism.

$CH_3I + h\nu$	→	$CH_3 + I$	(1)
$CH_3 + I$	→	CH_3I	(2)
$CH_3 + CH_3I$	→	$CH_4 + CH_2I$	(3)
$CH_2I + I$	→	CH_2I_2	(4)
$CH_2I + CH_3$	→	C_2H_5I	(4a)
$CH_2I + CH_3I$	→	$CH_2I_2 + CH_3$	(5)
$CH_2I_2 + h\nu$	→	$CH_2 + I_2$	(6)
$2CH_2$	→	C_2H_4	(7)
$CH_2 + CH_3I$	→	C_2H_5I	(8)
$CH_3 + CH_3$	→	C_2H_6	(9)
$I + I + M$	→	$I_2 + M$	(10)

The quantum yield was found to be very low due, presumably, to the high efficiency of reaction (2), whereas reactions (3), (4) and (5) were responsible for the bulk of the products. The efficacy of (2) was supported

by the results obtained when silver was added to the reaction. In that case the quantum yield rose to about one and all the iodine formed appeared as AgI. Moreover Bates and Spence[48] found the addition of hydrogen had no effect which means reaction (2) is faster than

$$CH_3 + H \rightarrow CH_4$$

An alternative to reaction 2 is

$$CH_3 + I_2 \rightarrow CH_3I + I \qquad (11)$$

This has been supported by Iredale[49] from a consideration of the reaction in the presence of nitric oxide and by Andersen and Kistrakowsky[50], who investigated the photolysis of mixtures of CH_3I, HBr and I_2. In this latter case, however, a large excess of I_2 was present which might be expected to favour (11). It was suggested that (2) and (11) occur at almost every collision.

The technique developed by Rice was extended by Butler, Mandel and Polanyi[2, 51] to the thermal decomposition of organic iodides at low pressures. The progress of the reaction was measured by collection and titration of the iodine formed. They interpreted their data in terms of the first order constant (k); from the temperature variation of k or from the equation

$$k = 10^{13} e^{-E/RT}$$

they deduced a value for the activation energy of the decomposition which they associated with the energy required to break the R-I bond. Their work aimed at a broad survey with the object of seeing if bond energies derived in this way agreed with other data and ordinary expectations. This proved, in general, to be the case but later and more detailed studies of particular iodides have shown that the kinetics of the reactions were not as simple as

they assumed. Their work suggested however, that the C-I bond energy could vary between 39 kcals and 55 kcals.

Application of Thermochemical Data

Skinner and Roberts[38] applying the method previously described obtain values for several iodides where the appropriate data was available. Their results show the same trends with structure as Butler and Polanyi[2] found. In a later study Skinner[52] has obtained very accurate values for the C-I bond in methyl and ethyl iodides. An accurate value for the heat of formation of CH_3I was determined from a measurement of the heat of hydrolysis of cadmium dimethyl in water and in dilute sulphuric acid, the heat of reaction of cadmium dimethyl and iodine in ethereal solutions and other established thermochemical data. This together with the dissociation energy of 102.0 kcals for the C-H bond in methane gives a value for the C-I bond in methyl iodide.

A table of the various results obtained by Butler and Polanyi,[2,51] Horrex,[53] Gowenlock and Szwarc[54] and Skinner[38] are given below.

Table I

Iodide	Butler Mandel Polanyi kcals	Horrex Szwarc Gowenlock	Skinner	
Methyl	(54)		55.0	54.8
Ethyl	52.2	54-56	52.8	52.8
n-Propyl	50			
Iso-Propyl	46.1			
Butyl	49			

Table I (Contd)

Iodide	Butler Mandel Polanyi kcals	Horrex Szwarc Gowenlock	Skinner
Tert-Butyl	45.1		45.0
Allyl	39.0		34.4
Benzyl	43.7	(29.5)	36.5
Vinyl	55.0		
Acetonyl	45.0		46.0
Acetyl	(50.7)		
Benzayl	43.9		
Cyclohexyl	49.2		
β-phenyl ethyl	50.0		
Dichlormethyl	42.0		
Dibromomethyl	41.4		
Diiodomethyl	(37)		
β-chloroethyl	45.9		

The Effect of Structure on Bond Energy

Since many compounds containing the same characteristic link have been found to vary widely in reactivity (see Hammett[55]) which in turn depends on the energy required to break the link in question, it is clear that a relationship between reactivity and bond energy may be assumed.

The preceding table demonstrates very clearly that the bond energy of the C-I bond is very dependent on the compound in which it is found. The work of Polanyi[56] and collaborators on the reaction between sodium and the

various organic halides further supports the previous table. The following activation energies were found by Polanyi for the reaction

$$Na + RCl \rightarrow NaCl + R$$

where R is an organic halide

Table II

R	Activation Energy kcals
Methyl	10.0
Ethyl	9.4
n-Propyl	9.2
Iso-Propyl	8.6
n-Butyl	8.6
sec-Butyl	8.4
ter-Butyl	7.8
Vinyl	10.4
Allyl	6.0
Benzyl	2.9
Phenyl	10.4
Acetyl	5.0
Benzoyl	0
Acetonyl	2.0

57

Evans and Polanyi from a consideration of the potential energy diagram for the approach of the sodium atom to the chloride and passage through a transition state

Na ----- R ------ Cl

showed that the relationship between the difference in bond energy (ΔH) and the difference in activation energy (ΔE) should be of the form

$$\Delta E = \alpha \Delta H$$

if the changes are solely due to alterations in R. Butler and Polanyi[2] calculated a value of $\alpha = 0.27$ which agrees with the experimental value of 0.28 obtained by plotting the value of the activation energies for the reaction with sodium against the bond energies for the iodides.

Many other workers have found variations in bond energy in other types of links. For example Ziegler[58] determined the bond energy of the C-C bond in several aryl substituted ethanes by an equilibrium method and obtained values ranging from 19.0 kcals to 30.0 kcals. Similar variations in the C-C bond were found by Conant[59] and Keevil[60] in the case of the dixauthyl compounds.

Many workers have found a progressive weakening of the C-H bond in the sequence primary, secondary, tertiary. For example Steiner[61], in a study of the substitution of chlorine in hydrocarbons obtains a decrease of 1.1 - 1.3 kcals and 1.7 kcals in the C-H bond energies for the change to secondary and tertiary respectively which agrees with Rice's values of 1.2 kcals and 1.8 kcals for these changes. The general trends in the activation energies with sodium suggest that variations in the C-halide bonds are produced in the following way.

(1) Weakening of Bond due to:-

a) The change from primary to secondary to tertiary halide.

b) An aromatic group on the C-atom.

c) The introduction of a β double bond.

d) An increase in the number of halogen bonds on the carbon atom.

e) Lengthening of the carbon chain

f) Progressive change from chloride to bromide to iodide.

(2) Strengthening the bond is caused by:-

a) The introduction of an α - double bond.

b) When the carbon atom is part of an aromatic ring.

(3) Branching of the chain some distance from the C-atom has little effect.

Theoretical Explanations of these Variations as Applied to Halides

The energy of a bond must depend on a variety of factors the chief of which are the extent of resonance involving the bond, the existence of angular strain in the molecule, polarity of the bond and the energy of reorganisation of the radicals formed when the bond is broken.

Walsh[62] has recently stressed the effect of polarity, together with the effect of the extent of valency hybridization in the arbitals of the carbon bonding electrons. Since the electronegativity of the carbon atom, with respect to the bond, depends on the amount of S character in the carbon valency, the effect of hybridization and of polarity are basically two ways of expressing the same thing.

Furthermore Walsh has been concerned mainly with the quantity we have called "bond energy term" rather than dissociation energies and some of his conceptions appear rather difficult to translate into quantitative terms at present.

Pauling and Wheland[63] have suggested that these variations can be explained by considering that there is resonance within the radicals which

gives the radical extra stability. This has been extended by Baughan, Evans and Polanyi[64] to a consideration of the possible resonance between a covalent and ionic bond and the effect of stabilizing resonance in the ion, radical or whole molecule.

They regard every bond as having three components, the covalent state and the two ionic states $R^+ - Hal^-$ and $R^- - Hal^+$ which can each be defined by an energy which is a function of interatomic distance. The $R^- - Hal^+$ state is so far above the other two that for practical purposes the ground state can be regarded as a resonance hybrid of the other two alone.

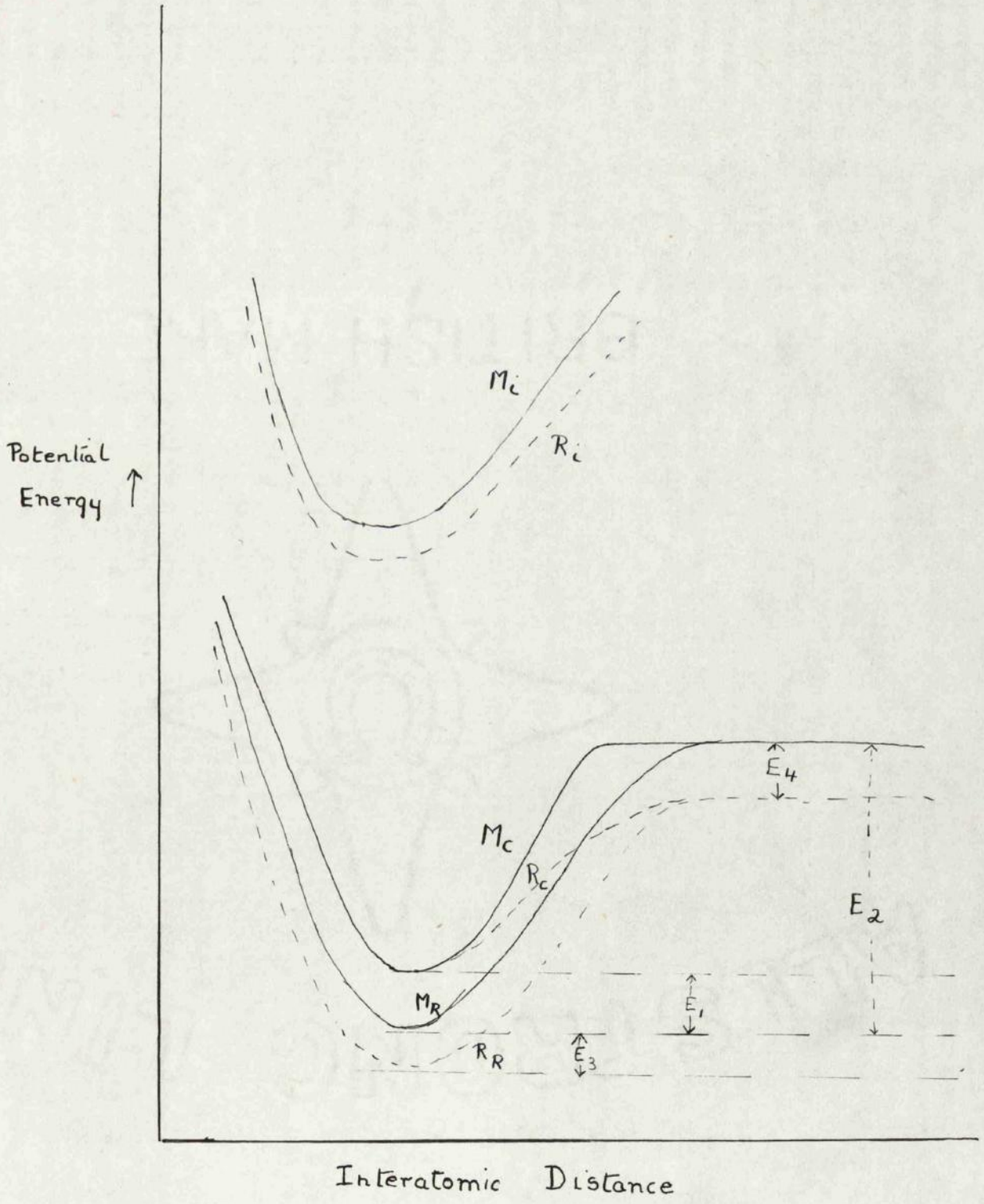
The influence of resonance can best be shown by consideration of potential energy curves. If we take a methyl halide as the standard of reference, since it has no possible resonance except that between the ionic and covalent state, we can represent these two states on a potential energy diagram by the curves M_i and M_c (Fig.1). The ground state of the molecule will be below the covalent curve by an amount depending on the energy of separation and the interaction between the two states (neglecting zero point energy). This interaction has a resonance energy E, and results in a bond energy of E_2. When resonance is possible in only the covalent molecule, as for instance in vinyl halide between the forms

$$CH_2 = CH - I \quad \text{and} \quad -CH_2 - CH = I^+$$

The ground state energy will be decreased and the strength of the bond increased, (see Tables I and II). Moreover, Hugill, Coop and Sutton[65] found that the bond length was smaller in vinyl iodide than in methyl iodide.

When resonance can occur in both the ion and the radical interaction

FIGURE 1


Potential Energy
M_i
R_i
M_c
R_c
M_R
R_R
E_4
E_2
E_1
E_3
Interatomic Distance

between the two curves R_i and R_c would occur (Fig.1) with a consequent lowering of the ground state. Thus the bond energy would become

$$E = E_2 - (E_4 - E_3)$$

where E_2 = methyl halide bond energy

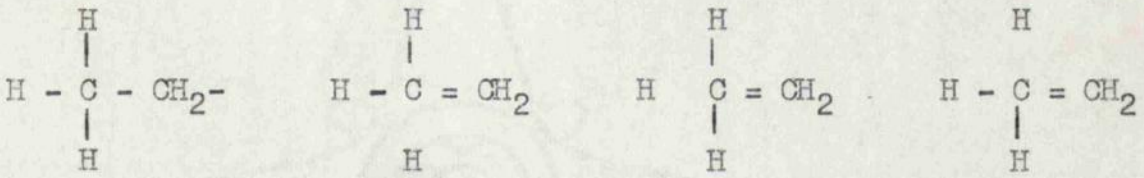
E_4 = Resonance energy of radical R

and E_3 = Difference in resonance energy between CH Halide and R Halide.

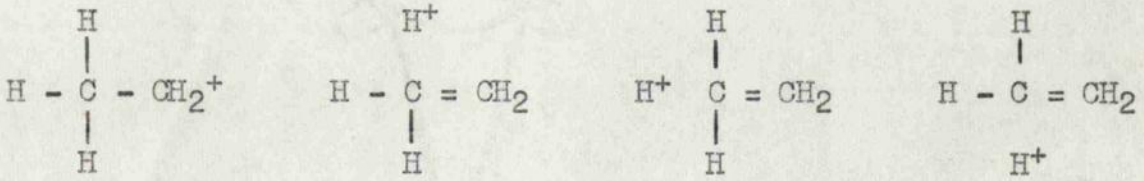
Baughan, Evans and Polanyi[64] and Butler and Polanyi[2] have used known forms of resonance to explain the differences obtained in tables I and II.

Alkyl Halides

Wheland[66] has suggested the following resonance possibilities in the radical



which can also occur in the ion thus

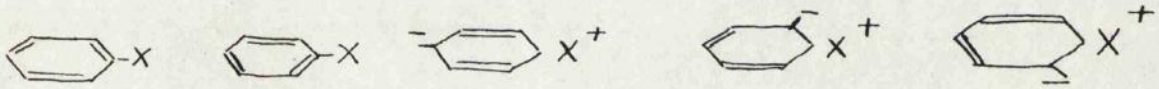


but cannot in the covalent state. These considerations were extended by Baughan Evans and Polanyi to longer hydrocarbon radicals.

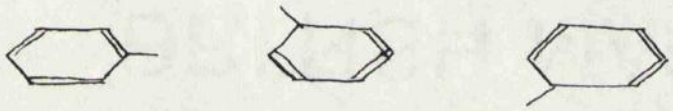
They explain the decreases in bond energy in the sequence methyl → tert-Butyl as a balance of the two opposing factors (E_4 and E_3) the increasing radical resonance which tends to weaken the bond and the increasing interation of the ionic and covalent states.which tends to strengthen the bond.

Phenyl Halide

This is a similar case to that of allyl halide since the covalent molecule can resonate between the five structures

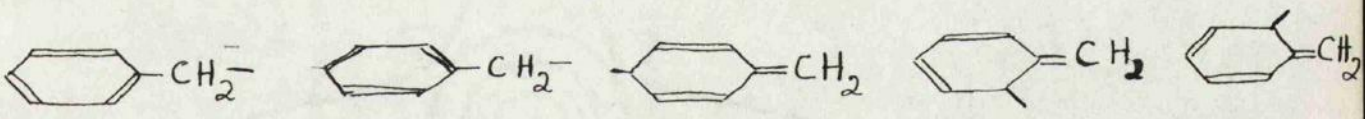


whereas the radical can only resonate between the structures:-



Benzyl Halide

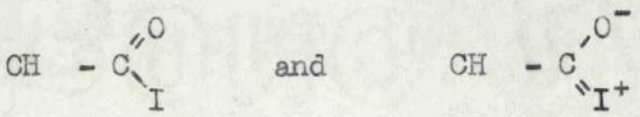
In this case the bond energy is found to be much reduced as might be expected from the radical resonance possibilities of



whilst the ion can resonate between three possible structures and the covalent molecule only between the two Kekulé forms.

Acetyl and Halide Substituted Methyl Halides

The case of Acetyl halide at first appears anomalous since the covalent molecule can resonate between the two structures



and there should be strengthening of the bond. Polanyi explains the observed weakening (Table I) by regarding the resonance effect as offset by the withdrawal of electrons from the bond by the electronegative oxygen atom. This

is supported by the observed weakening in the case of the di-chloro, di-bromo and di-iodo methyl iodide though one would expect the chlorine substitution to cause a greater reduction in bond energy than the iodine. However, the data is not of sufficient accuracy for great emphasis to be laid on such small variations and only general trends can be considered.

Walsh,[62] in his considerations, has regarded the polarity of the bond as proportional to the ionization potential of the non-bonding electrons in the molecule; where bond energy data is not available he considers variations in bond length to correspond to changes in bond energies. The relationship he derives can be best shown in the case of carbonyl compounds.

Molecule	I.P. volts	C-O Bond Length A	C-O Bond Energy kals	% Polarity
CO	14.55	1.128	211	1
CO_2	13.73	1.15	~202	9
COS	~12	1.16	~199	13
Glyoxal	~11.4	1.20	~186	29
CHO	10.83	1.21	~190	35
CH_3CHO	10.18	1.22	~184	42
C_2O	~11.4	1.20		

He regards the changes in polarity to be caused by change in the electronegativity of the other atoms or groups attached to the carbon atom. In the case of the halides the data is not sufficiently extensive for any definite conclusions to be drawn, though Price and Stevenson and Hipple[67] have found a decrease in ionization potential down the series methyl, ethyl, i-propyl to

t-butyl chloride which agrees with the decrease in bond energies found by Butler and Polanyi.

Previous Determinations of the C-I Bond in Methyl Iodide

One of the first estimates was made by Ogg and Polanyi[68] who, from a consideration of the heats of ionization of, and negative ion substitution in alkyl halides obtained a value of 44 kals. Ogg[69] derived a value of 43 kals from the heat of reaction of methyl iodide with hydrogen iodide.

Iredale[70] obtained the two values of 50 k.cals and 54 k.cals from the absorption spectrum in the liquid and gas phase respectively but as has been mentioned, Porret and Goodeve[71] have shown that an accurate value cannot be found in this way.

Skinner,[72] from thermochemical considerations incorporating a value of 102 kals for the C-H bond, derived values of 55.0 kals and later 54.8 kals.

Several estimates of the energy have been made by consideration of data on other C-I bonds and the observed effect of structure; thus Butler and Polanyi[2] estimate a value of 54 kals from their other pyrolytic data. Iredale[70] considers it likely that the CH_3 radical can be regarded as similar to that of the fluorine atom, and so reaches a value of approximately 52 kals from the following data

Bond	I-I	I-Br	I-Cl	I-CH_3
D k.cals	36	46	50	(52)

which he finds to be in agreement with his value of 52 k.cals derived from the data on Raman spectra of Dadien and Kohlrausch.[72]

The Present Investigation

The work of Butler and Polanyi[2] on the pyrolysis of organic iodides contained only a very cursory investigation of methyl iodide; their data consists of five experiments, all at the same temperature from which they concluded that reproducible results were not given. As a preliminary to more detailed work on the decomposition of the halides the experimental arrangements of Butler and Polanyi were subjected to a critical investigation by Moore.[73] The modifications suggested by his work were embodied in an apparatus used by Szwarc[54] for benzyl iodide and by Gowenlock[53] for ethyl iodide and produced an increase in reproducibility.

The essential alterations were the maintenance of more constant flow rates, modification of the furnace design to obtain temperature uniformity, improved measurement of temperature and provision of sampling systems for triplicate analyses on each experiment.

All these improvements have been applied in the work described below together with experimental arrangements devised to suit the problems arising during the investigation.

Butler and Polanyi assumed the rate determining step of the pyrolytic decomposition of the iodides to be the breaking of the R-I bond. The results in the particular case of benzyl iodide do not support this hypothesis. The kinetic data obtained by Szwarc can be interpreted on the basis of the following reaction scheme:-

$$C_6H_5CH_2I \rightleftarrows C_6H_5CH_2- + I \quad (1)$$

$$I + I + M \rightleftarrows I_2 + M \quad (2)$$

$$2C_6H_5CH_2- \rightarrow C_6H_5CH_2-CH_2C_6H_5 \quad (3)$$

The rate determining step in the reaction sequence is reaction (3) and the extent of dissociation of benzyl iodide is progressively decreased as reaction proceeded due to the accumulation of iodine, some of which is in the atomic form (reaction (2)) and therefore has to be allowed for in the equilibrium (1). In this case the energy of activation is related to the heats of the reactions (1) and (2) in a simple way but the complexity revealed indicates the need to consider the influence of reactions following the primary break.

Gowenlock's work on ethyl iodide showed that the reaction is not of the first order and that the reaction scheme is probably more complicated but he had insufficient data to select the predominant reactions from a number of possibilities.

The present study of methyl iodide is an extension of work started at Sheffield University[76] on this compound which showed that the reaction is not of the first order. Various aspects of this earlier work will be considered in the appropriate sections below.

Apparatus and Experimental Technique

The apparatus (Fig.2) consisted of:-

1. A circulating system containing a circulating pump, mercury traps, a reaction vessel heated by an electric furnace, 3 sets of traps for collecting the products of the decomposition and capillaries for measuring the rate of

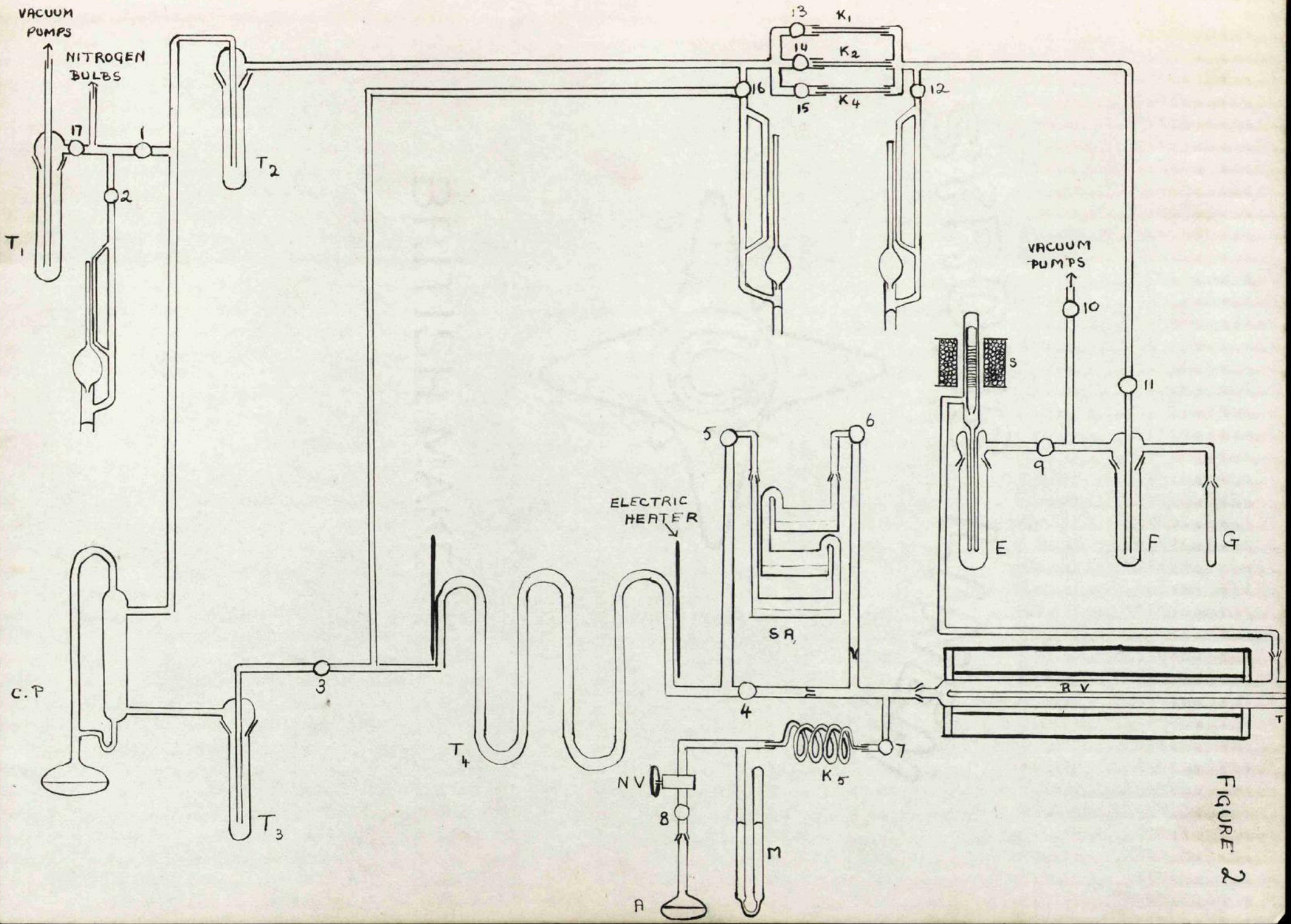

VACUUM PUMPS
NITROGEN BULBS
17
1
2
T1
T2
13
K1
14
K2
16
15
K4
12
VACUUM PUMPS
10
S
11
9
E
F
G
5
6
ELECTRIC HEATER
SA
C.P
3
4
RV
T
T4
7
K5
NV
8
M
A
T3

FIGURE 2

flow. The flow of gas could be directed through a saturator to pick up volatile liquids or solids.

2. A device for introducing the halide.

3. A vacuum line and storage bulbs for the carrier gases.

The Reaction Vessels

The reaction vessel in Fig.2 R.V. was made of silica and had a centrally placed thermocouple tube T.H. The diameter of the heated portion was 2.8 cms. the length was 60 cms and the volume 275 ccs. In later work at lower temperatures a pyrex vessel was used which had a diameter of 4.5 cms. and a volume of 385 ccs. In this case the thermocouple tube and exit end of the furnace could be removed by means of a ground glass joint so that tubes of known dimensions could be put in the reaction vessel to change the ratio of surface to volume by an accurately known amount.

The Furnace and Temperature Control and Measurement

The furnace consisted of a wrought iron tube, insulated with asbestos and alundum and wound with nichrome tape. The winding was closer at each end and there were also tappings along the winding so that by altering the voltage across the various portions of the tube a constant temperature, $\mp$ 3°C could be obtained along it. The tube was encased in an asbestos fibre casing and the ends plugged with asbestos. The temperature of the furnace was maintained constant to $\mp$ 2°C by manual control of a rheostat, as mains voltage variations were removed by a constant voltage transformer this proved satisfactory.

The temperature of the reaction vessel was measured by a Chromel Alumel thermocouple which was calibrated at various standard temperatures and the values for the electromotive force were plotted against the temperatures, see Table. The temperature of the reaction vessel for any particular E.M.F. was then read directly off the graph.

TABLE

	Temperature °C	E.M.F. in millivolts
Ice	0	0
M.p. Tin	231.9	9.25
M.p. Lead	327	13.31
M.p. Zinc	419	17.175
M.p. Antimony	630.5	26.15
M.p. Silver	960.5	39.76

The Circulation Pump

A mercury vapour pump (V.P.) was used to circulate the carrier gas. This pump was heated by a Woods metal bath which could be maintained at a constant temperature ∓ 1°C by means of a Sunvic energy regulator. Moore found that there was a definite temperature, dependent on the pressure, at which the pump gave optimum performance, In the case of the pump used here it was found that provided a certain minimum temperature was reached the pumping speed remained constant over some 20°C.

For later high pressure, 600 mms, experiments a different pump was used. At first a pulsating rubber diaphragm type of pump was used, but it was very difficult to ensure that this was completely airtight. Later a pump was made

out of four Drayton bellows, Fig. 7. The bellows were actuated by shafts attached to the inside of the head of the bellows and bearing against an eccentrically mounted ball race at the other end. The bellows moved up and down inside steel tubes and steel ball bearings on brass seats were used as valves. The whole system was made vacuum tight and could be made to pump up to 3 litres a minute depending on the extent of the throw of the bellows. A small magnet was used to lift the ball bearings in the valves during evacuation.

The carrier gas after leaving the pump passed through a trap T_3 immersed in liquid air and then through trap T_4, which was heated at the top to 300°C and cooled below in liquid air, to ensure the complete removal of all mercury vapour. The stream then passed through a jet to prevent back diffusion to the reaction vessel, the traps E and F for collecting the products and then through one of the capillaries K_1 K_2 or K_4.

Collection of the Products

The traps were arranged in a triple system so that three runs could be done consecutively without opening up the apparatus to the air. The delivery tube from the reaction vessel divided into three paths one of which is shown in Fig. 2 . The gas first passed through the all glass valve, V, consisting of a plunger with a piece of soft iron piceined inside it. The plunger could be raised or lowered into the ground glass joint by switching the current in the solenoid S on or off. The gas passed down the double walled tube, on the inner wall of which nichrome tape had been wound and which could be heated to prevent the products condensing on it. The gas then passed through trap E, tap 9 and trap F and tap 11 and was then joined by the other two parallel paths.

This part could be evacuated separately through tap 10. In the case of experiments with no carrier gas all the products were frozen out in trap E in liquid air so that first the iodine and then the methyl iodide could be titrated.

In the high pressure experiments it was found necessary to have both traps in liquid air to obtain complete removal of the products, it was also necessary to insert a tube wound with glass wool in a spiral, see Fig. 7 into trap F to ensure removal of all the products.

The Circulation Capillaries K_1 K_2 and K_3

These were also in a parallel system so that any one of the three may be used, thus enabling a change in flow rate to be easily effected. From Poiseuilles formula the rate of flow of a gas in moles per sec $= \frac{\pi r^4 (P_1^2 - P_2^2)}{16 L \eta R T}$

r = radius of the capillary in cms. determined by measuring the length and weight of a thread of mercury.

n = the viscosity of the gas in Poises. L = length of capillary (cms). T = Absolute temperature and R = the gas constant. P_1 and P_2 are the pressures on either side of the capillary in dynes/cm^2, and are determined from the double McLeod gauge readings.

Other work has shown that Poiseuille's formula is not always accurate for short capillaries, due probably to the end effect, the capillaries used were calibrated experimentally by determining the time taken for a known volume of air to pass through at a measured pressure. The difference between the calibrated rate of flow and that calculated from Poiseuille's formula was found to be negligible. The results obtained are shown graphically in

FIGURE 3

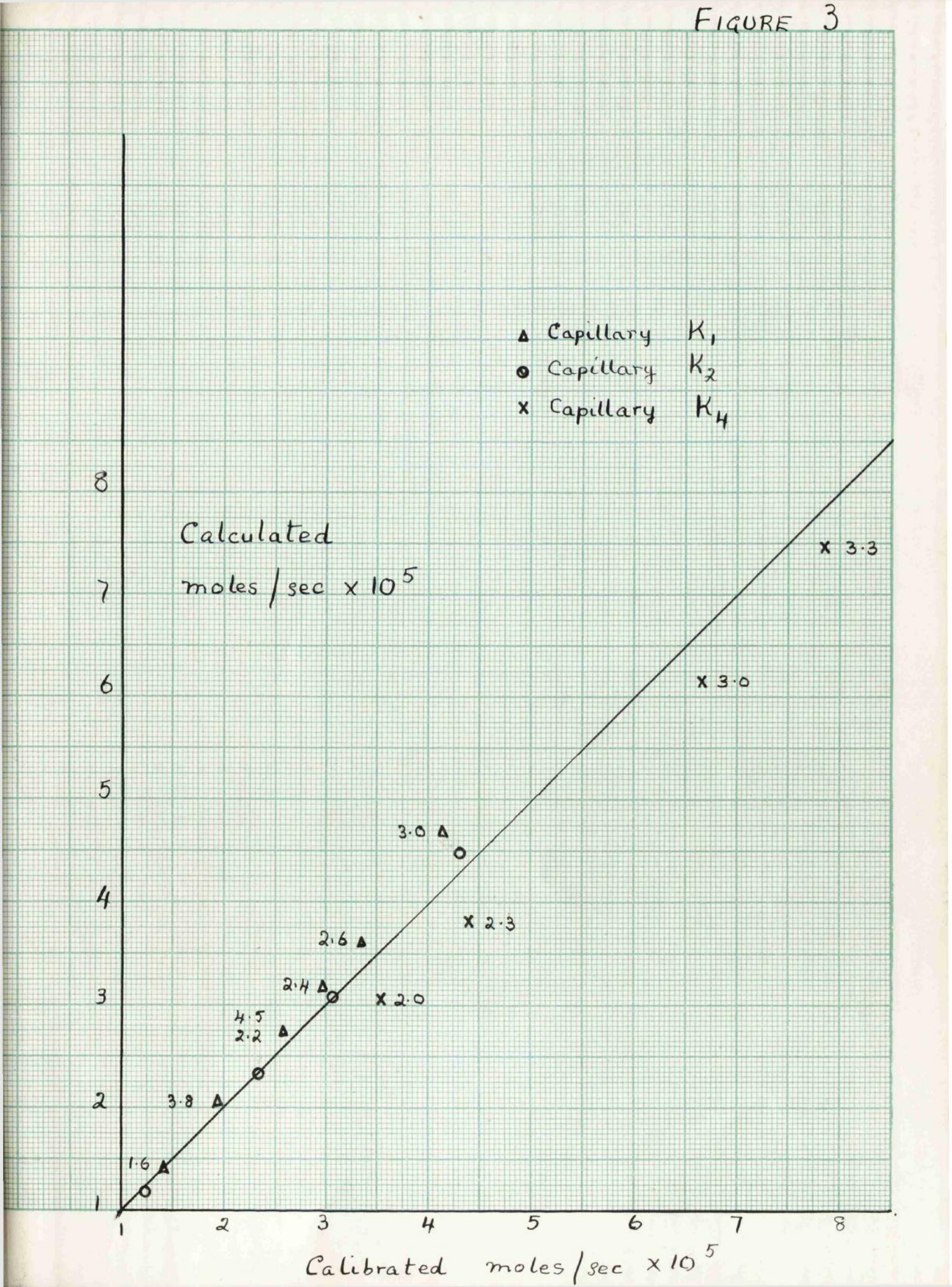

▲ Capillary K_1
● Capillary K_2
x Capillary K_4
Calculated
moles / sec x 10^5
Calibrated moles / sec x 10^5
1
2
3
4
5
6
7
8
1.6
3.8
4.5
2.2
2.4
2.6
3.0
x 2.0
x 2.3
x 3.0
x 3.3

Fig 3. The figures by the points correspond to the average pressure in mms. at which the calibration was made.

Pressure Determination

The average pressure in the reaction vessel was also determined from the double McLeod gauge readings. When there was no carrier gas the pressure could not be read on the McLeod gauge since the methyl iodide vapour would condense and a spiral Bourdon gauge was used instead. One side of the gauge was connected to the reaction vessel and the other side to the vacuum line and to one of the double McLeod gauges. In order to amplify the deflection of the mirror on the end of the glass spiral, the reflection of an ordinary galvanometer lamp was allowed to fall on to a photocell which had been divided down the centre of its sensitive face. When the spot of light moved to one side a current passed from one half to the other and could be measured with a galvanometer. To measure the pressure in the reaction vessel the pressure in the outside of the spiral was adjusted until there was no deflection of the galvanometer and then read on the McLeod gauge. By this means a sensitivity of 5 cms. galvanometer deflection for 1 mm pressure difference was obtained. The Bourdon gauge was used to measure the pressure in the high pressure experiments as well, though in this case the equalizing pressure was read on a manometer.

Halide Introduction

The halide was contained in A. The rate of efflux of the halide was controlled by the needle valve N.V. and was measured by the drop in pressure across the capillary K. The fore pressure was read directly off the

manometer and the back pressure taken as the average pressure in the reaction vessel.

Tap 16 is a two way tap so that either the pressure immediately after the capillaries could be read or the pressure between traps 3 and 4. The average pressure was taken as that at the exit of the furnace plus one third of the difference between this and the pressure between traps 3 and 4. One third was taken rather than a half to allow for the fact that the major part of the pressure drop was found to be jet before the furnace.

The value of the capillary constant was determined experimentally by doing runs with the furnace cold and weighing the amount of halide that came over for different values of the pressure drop across the capillaries. In the case of a fine straight capillary a straight line relationship between the constant and pressure difference was obtained (Fig. 4). With a coiled capillary the relationship between the constant and the pressure drop was of the form shown in Fig. 5.

In the case of experiments performed without a carrier gas the arrangement shown diagrammatically in Fig. 6 was used. The rate of flow of the halide was controlled by closely fitting rods which could be moved along the tube by means of solenoids, and held in position against the gas flow by the same means. The amount of halide flowing through was determined by titration at the end of the experiment.

In the high pressure experiments the halide was put in the saturator S which was kept at 0°C. In order to obtain a partial pressure of approximately 1 mm. (vapour pressure of MeI at 0°C = 140 mms.) the carrier gas flow was

FIGURE 4

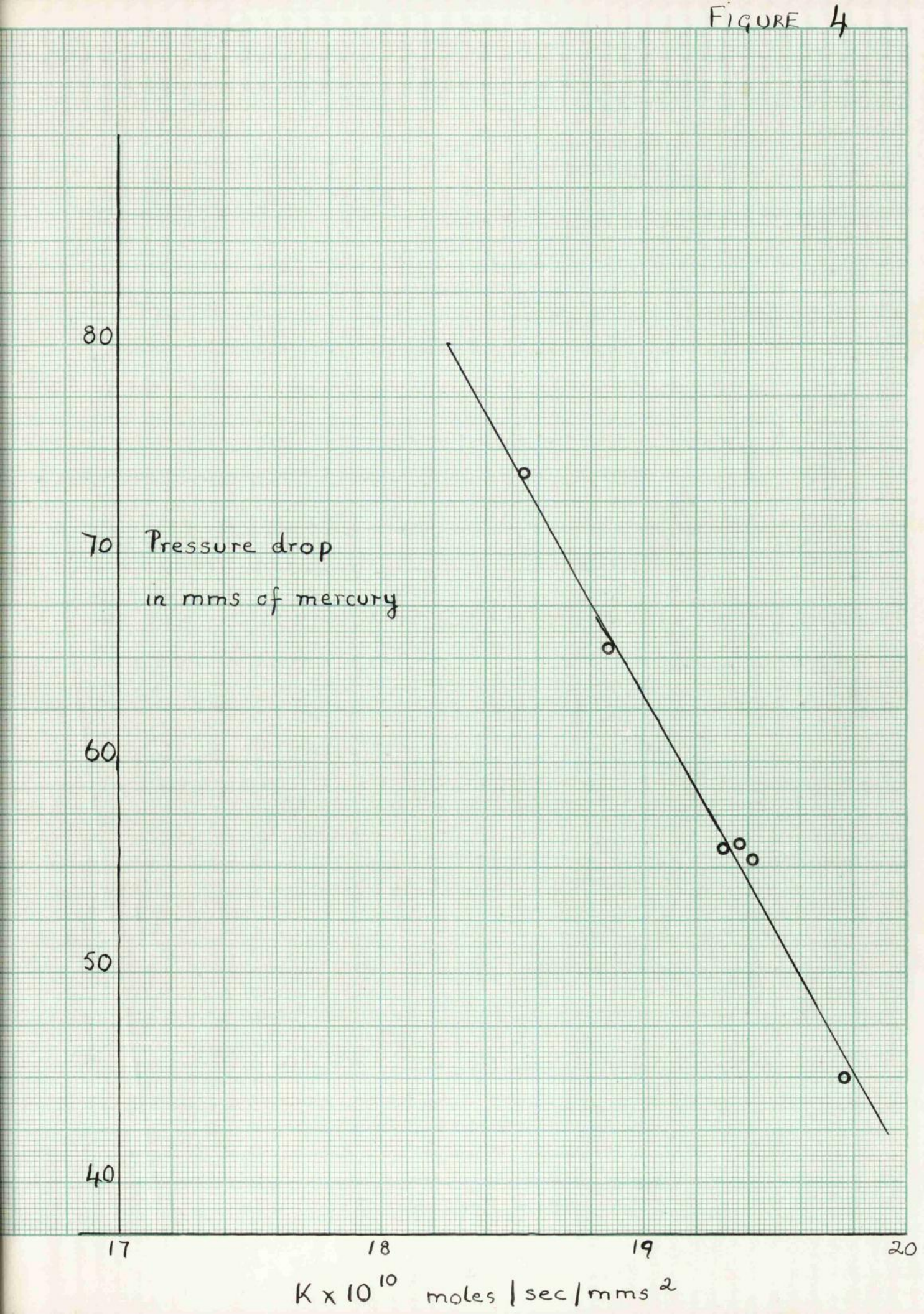

80
70
Pressure drop
in mms of mercury
60
50
40
17
18
19
20
K x 10^10 moles / sec / mms^2

FIGURE 5

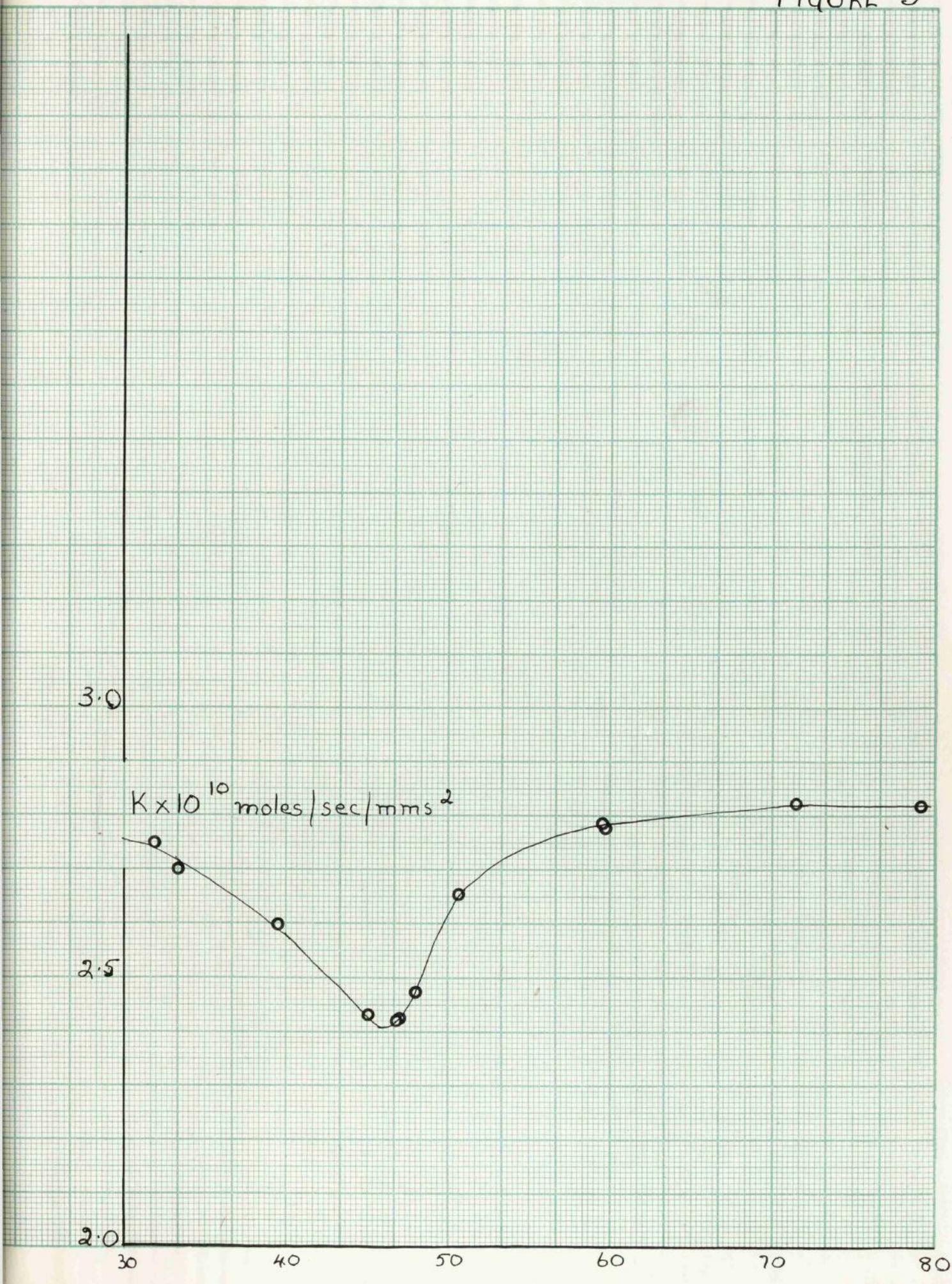

3·0
2·5
2·0
K x 10^10 moles/sec/mms^2
30
40
50
60
70
80
Pressure drop in mms of mercury.

FIGURE 6

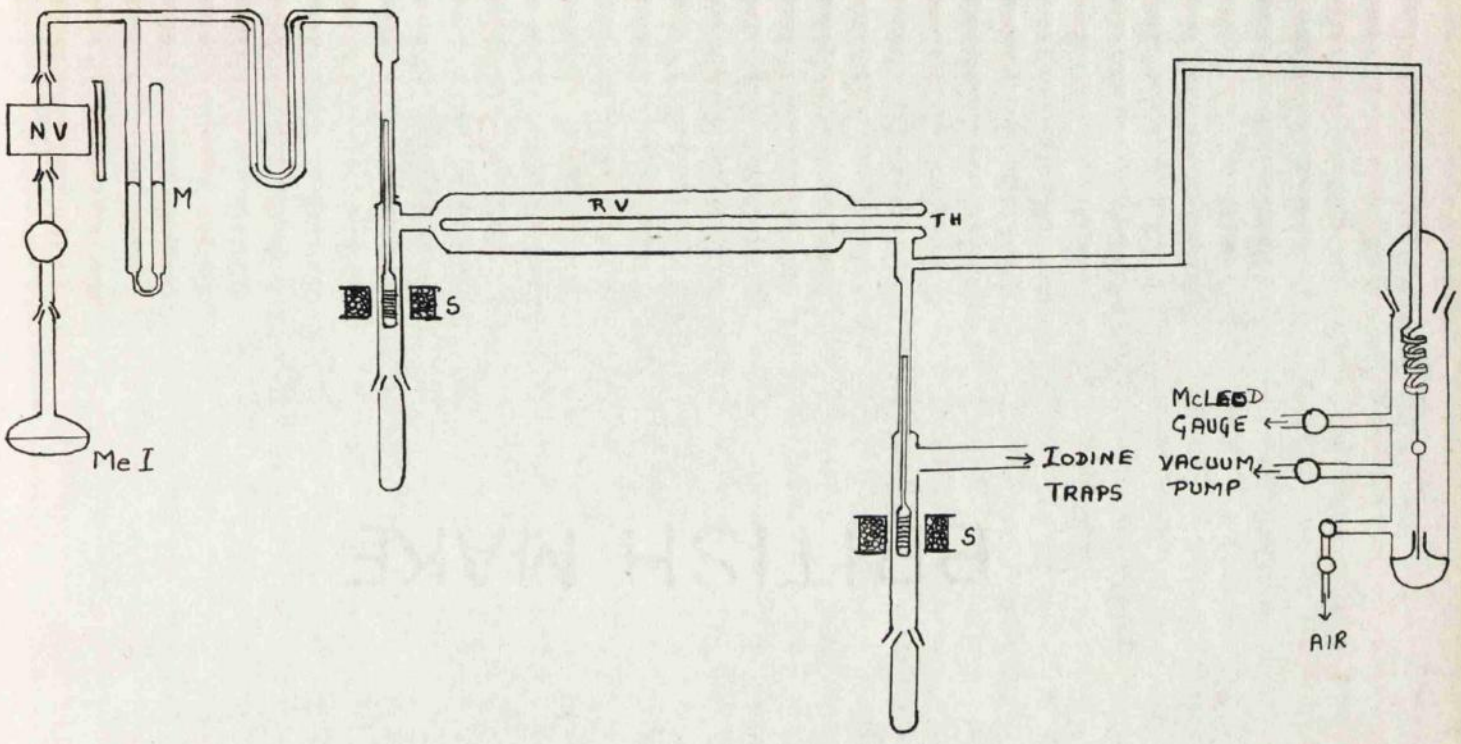
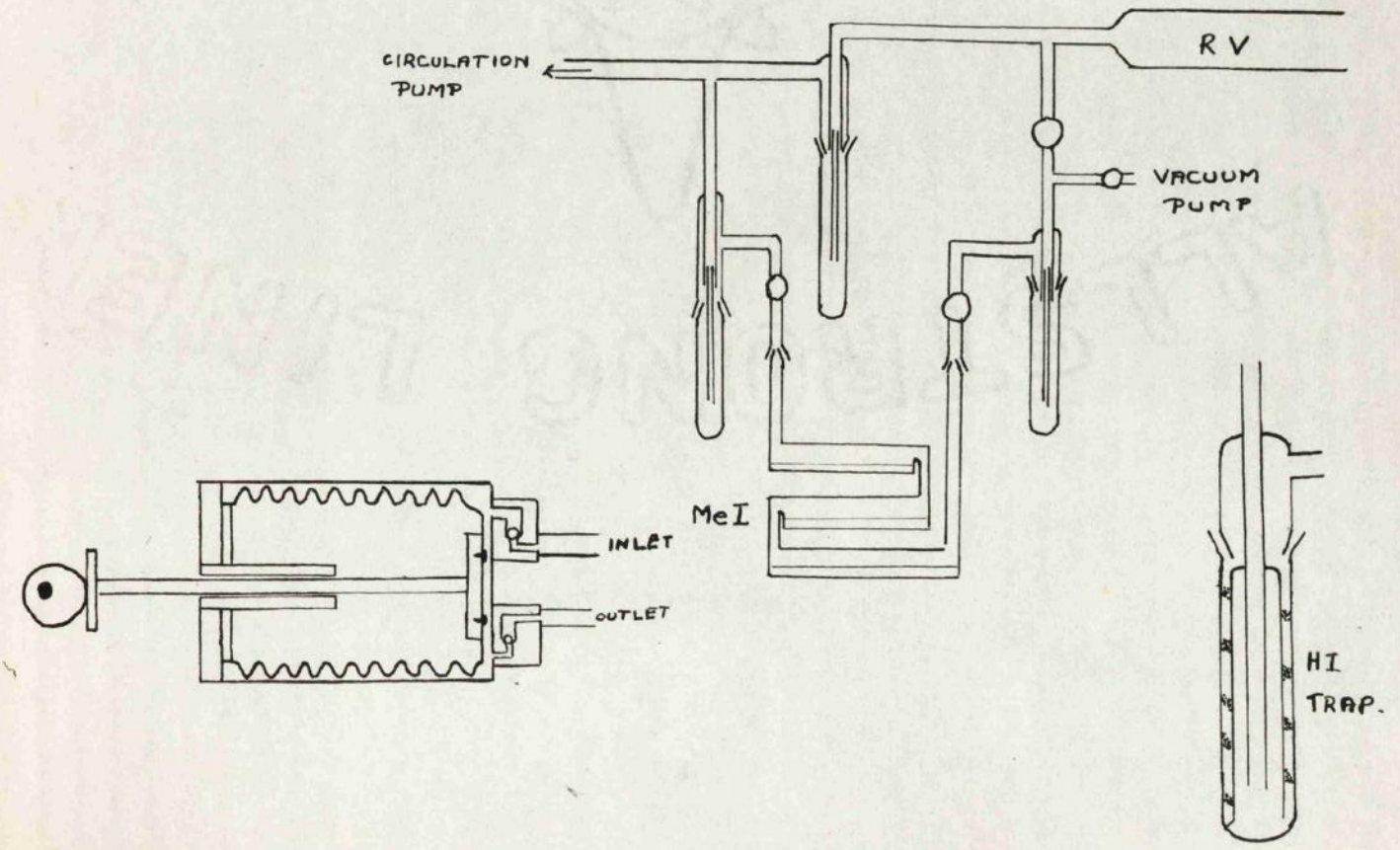


FIGURE 7



divided and the proportion passing over the halide controlled by capillaries (see Fig. 7). The partial pressure could be altered by changing these capillaries. The amount of halide passing was again determined by titration.

The Vacuum Line

The apparatus was evacuated by means of a mercury diffusion pump backed by a two-stage rotary oil pump. The pressure of the whole apparatus can be read on the single McLeod gauge. A pressure of 10^{-5} - 10^{-6} cms. Hg was obtainable.

The Carrier Gases

Nitrogen from a cylinder was purified by passage over sodium at approximately 300°C and through a trap at -180°C and was stored in three 3 litre bulbs.

Nitric oxide, used in conjunction with nitrogen in the high pressure experiments, was made by the action of 50% sulphuric acid on a solution of equimolecular proportions of potassium iodide and sodium nitrite. The gas was passed over concentrated sulphuric acid, soda lime, concentrated potassium hydroxide, calcium chloride and phosphorus pentoxide into an evacuated bulb. The gas was then further purified by freezing it in liquid air and pumping off any non-condensible gas, and then distilling it back to the flask at -80°C to remove any nitrogen peroxide.

Purification of Substances

The methyl iodide was a product of British Drug Houses Ltd. It was dried and fractionated through a long column, the fraction boiling between 42.3 - 42.6°C was collected.

The toluene used in later experiments was dried and fractionally distilled, the fraction boiling between 109° -110°C was collected. The results obtained with toluene purified in this manner were irreproducible, the work of Szwarc[74] on the pyrolysis of toluene has shown that certain of the impurities of toluene can only be removed by a partial pyrolysis of the toluene. A simple apparatus embodying the basic features of Szwarc's apparatus was set up (Fig. 8). After evacuation of the apparatus and outgassing the toluene three times, the toluene was allowed to reach room temperature when it distilled over into trap 1 which was immersed in liquid air the methane and hydrogen formed were pumped off continuously. The capillary at the exit of the furnace was of such a size that the toluene distilled over with a contact time of approximately 0.2 sec. The furnace was a silica tube heated by an iron tube wound with nichrome in a similar fashion to the main furnace. The furnace was maintained at 845°-855°C and the temperature was measured by a chromel alumel thermocouple placed in the furnace alongside the silica tube. Under such conditions Szwarc found that it was necessary to pyrolyse the toluene twice before consistent results were obtained, so the toluene was passed through the furnace twice and then fractionally distilled over sodium. Toluene prepared in this manner gave reproducible results when it was added to the carrier gas.

Estimation of Methane

The methane was estimated by combustion in the apparatus shown in Fig. 9. After a run all the gas, both nitrogen and methane, was extracted from the circulation system by means of the circulation pump and the Topler pump into

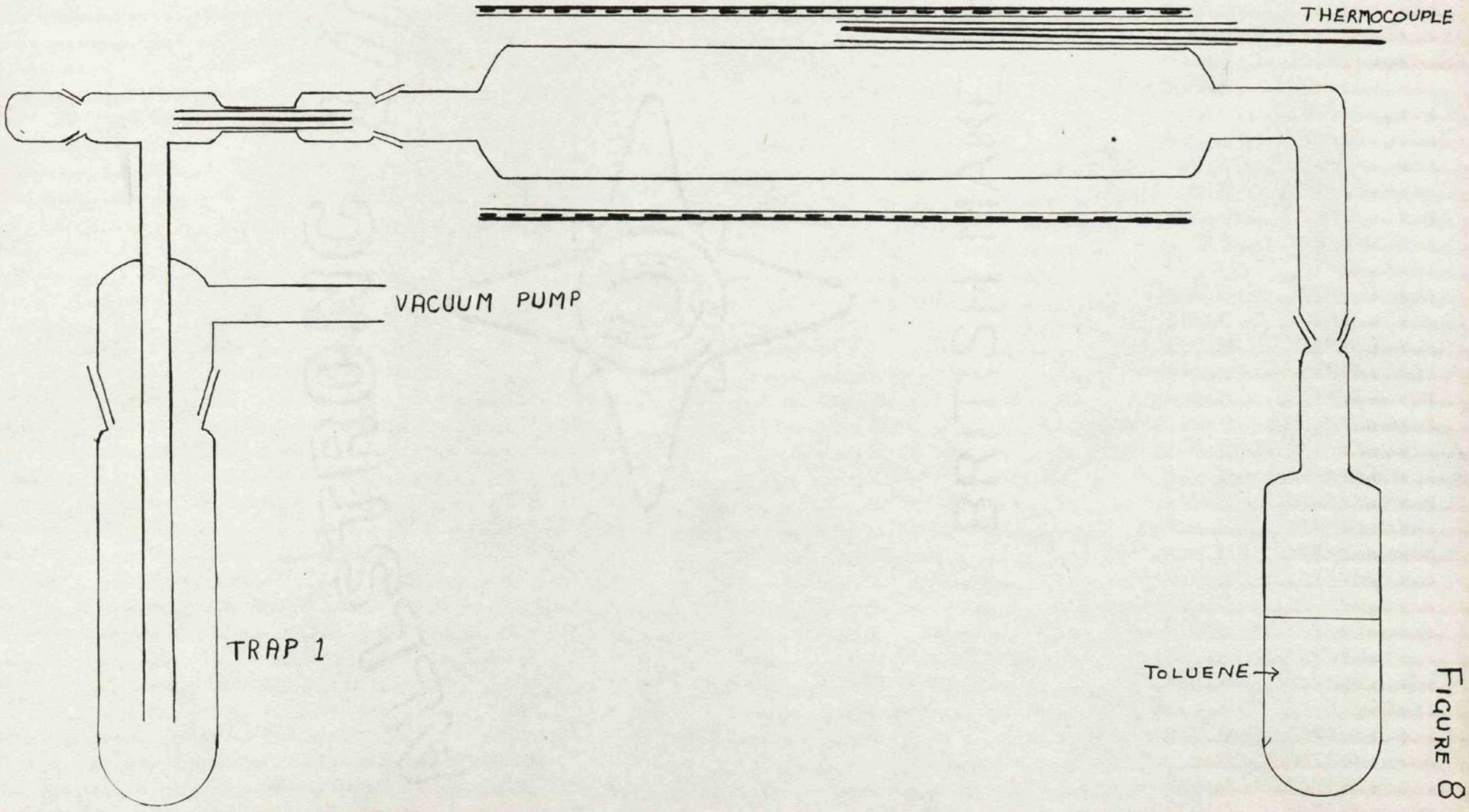


FIGURE 8

the combustion apparatus. Approximately three times as much oxygen as methane was admitted to the system and the resultant mixture was circulated over copper oxide at 300°-350°C by means of a small piston and valve with a soft iron core which was operated by an intermittently energised solenoid. When combustion of the methane was considered to be complete liquid air was put on the U-tube and the carbon dioxide formed during the combustion frozen out. The remaining nitrogen and oxygen were pumped out of the U-tube by means of the Topler pump. The amount of CO_2 was then measured by allowing it to evaporate into a known volume and measuring the pressure rise. The combustion was repeated until the amount of CO_2 became constant.

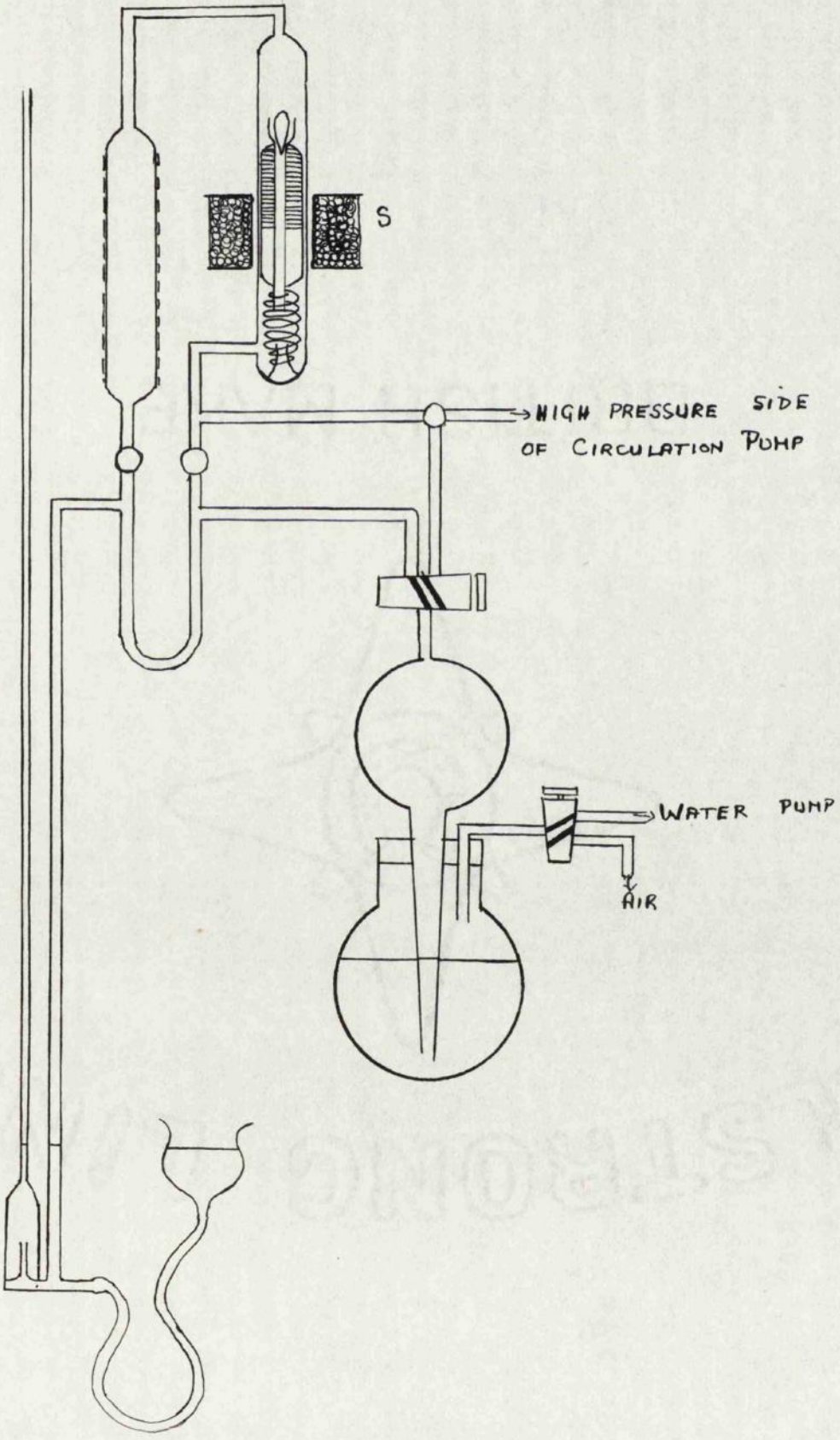
Estimation of Carbon formed on the Walls of the Reaction Vessel

The carbon formed on the walls of the reaction vessel was estimated by combustion. About 15 mms. of oxygen was admitted to the circulation system, after it had been evacuated of nitrogen and methane, and allowed to circulate through the furnace which was maintained at 700°-750°C. The carbon dioxide formed was frozen out in trap F immersed in liquid air. When combustion was thought to be complete the taps 9 and 11 were shut and the trap F evacuated, the carbon dioxide was then distilled into a tube of known volume and the amount formed was measured by determining the pressure rise when it evaporated into the known volume. As before the combustion was repeated until the amount of carbon dioxide was constant.

Description of an Experiment

Before an experiment the apparatus was subjected to a hard vacuum for one to two hours with the furnace hot and liquid air on traps T_1 T_2 T_3 and

FIGURE 9



T_4. The halide was outgassed by freezing it in liquid air in A and pumping out through tap 8, tap 8 was then closed and the halide allowed to warm up whereupon the air dissolved in the halide bubbled out. The halide was then refrozen and pumped out, this was repeated three or four times after which all the air had come out of solution. The halide was then allowed to warm up and A was immersed in ice and water.

In the high pressure experiments the halide and in some cases toluene were in the saturator S.A. and this was outgassed in a similar manner.

When a pressure of 10^{-5} cms. Hg had been obtained taps 1 and 10 were closed and the carrier gas was admitted to the desired pressure, this pressure was read accurately on one of the McLeod gauges. The Wood's metal bath was then put round the circulating pump and brought to an appropriate temperature. When the gas flow was steady, as indicated by the readings on the double McLeod gauge, liquid air was put on traps F and solid CO_2/acetone baths on traps E which had their heaters switched on. Two of the glass plungers were lowered into their seats so that all the gas stream passed through one trap E.

Taps 7 and 8 were now opened and the needle valve N.V. quickly adjusted so that the desired fore pressure was obtained. The time was noted. Readings of the double McLeod gauge with tap 16 turned both ways were taken at frequent intervals, the temperature of the reaction vessel was maintained constant (within $\mp$ 1°C) by adjustment of a rheostat and the fore pressure as read on the manometer M was also kept constant by use of the needle valve. The iodine formed in the reaction was condensed in trap E and the methyl iodide, toluene and hydrogen iodide and any other products formed were collected in trap F. Due to the formation of methane the pressure rose during a run and

formed a useful criterion of the amount of iodine formed. When sufficient iodine for estimation had been formed the next plunger was raised and the first one lowered, a second run thus being started the time being noted. At the end of the third run taps 7 and 8 were closed and the gas allowed to circulate for a few minutes, then the Wood's metal bath was removed from the pump and taps 9 and 11 closed.

The traps F and G were then evacuated and any hydrogen iodide, or in the high pressure experiments any methyl iodide and iodine that may have been carried over into trap F, distilled into trap G from which they could be washed out for titration.

Air was let into the rest of the apparatus, the three E traps were removed in turn and the iodine in them washed out with methyl alcohol. This was titrated against 0.01 N sodium thiosulphate, and the end point was determined potentiometrically. 10 millivolts were put across platinum electrodes and when all the iodine has reacted no current passed as measured on a galvanometer. The normality of the thiosulphate was determined by titration against standard potassium iodate with excess potassium iodide and hydrochloric acid.

In the later experiments without a carrier gas and at very much higher pressures the methyl iodide passed during a run was also titrated since the amount passed could not be calculated. The methyl iodide, dissolved in methyl alcohol, was oxidised by bromine in the presence of water and sodium acetate to give the iodate, which, after removal of the excess bromine by formic acid was titrated against sodium thiosulphate using excess potassium iodide and mineral acid. (Pregl)[75].

$$CH_3I + Br_2 \rightarrow CH_3Br + IBr$$

$$IBr + 3H_2O + 2Br_2 \rightarrow HIO_3 + 5HBr$$

Calculation from the Results

Butler and Polanyi in the case of the other halides considered that the formation of iodine followed an approximate first order law, the first order constants for the rate of production of iodine being calculated from the expression

$$K_1 = \frac{1}{t} \log_e \frac{a}{a - x} \quad \text{sec}^{-1}$$

when t = contact time = $\frac{\text{volume of the reaction}}{\text{rate of flow of gas in ccs/sec}}$

$$t = \left[\frac{275 \times P \times 273}{\text{Circulation rate in moles/sec} \times 22400 \times T \times 760}\right]$$

where P was the average pressure in mm. Hg, T the absolute temperature in the reaction vessel and 275 ccs the volume of the reaction vessel.

a = the total amount of halide passed was found by multiplying the time of the experiment by the halide rate of flow. This latter was given by [Halide capillary constant x (Halide fore pressure^2 - Average pressure^2)]. The partial pressure of the halide was given by

$$\left[\frac{\text{Rate of flow of Halide}}{\text{Circulation Rate}} \times \text{average pressure}\right]$$

x = the gram atoms of iodine formed and is determined from the titrations.

The percentage decomposition was calculated directly from a and x.

The activation energy of the reaction was obtained directly from the slope of the graph of $\log_{10} k_1$ against $\frac{1}{T}$ or from the expression

$$k_1 = A\, e^{-Q/RT}$$

where A was 10^{+13}.

Experimental Results

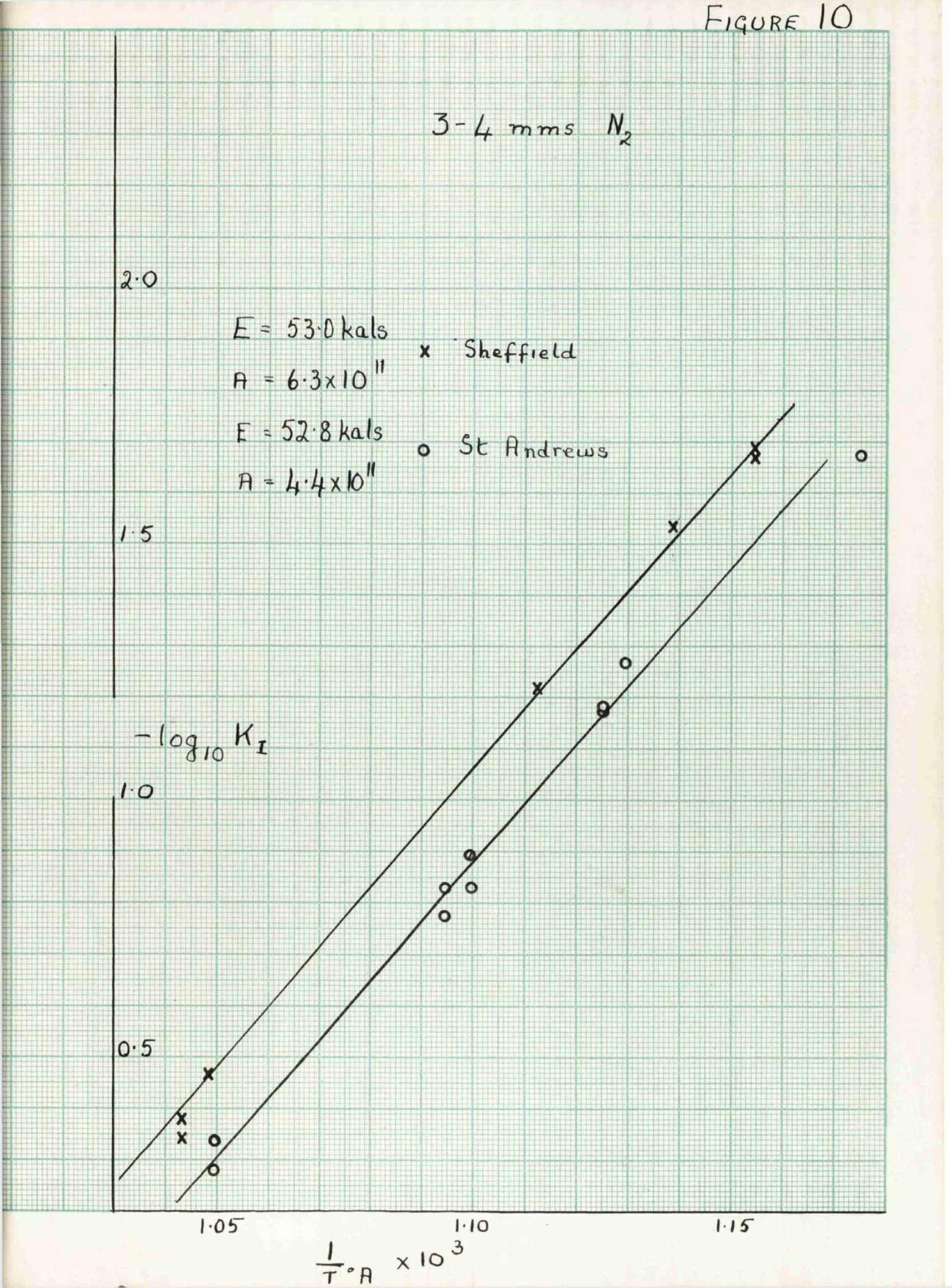
The work at Sheffield showed that the decomposition of methyl iodide did not follow the first order law exactly, but that the reaction was more nearly first order than any other. The present experiments were undertaken to try and elucidate the features shown previously and find conditions under which the reaction did obey the first order law.

After the apparatus had been reassembled several experiments were carried out to find whether the results were consistent with those obtained at Sheffield. In every case the value of the reaction velocity k_1 was found to be approximately 10% higher than at Sheffield. The variations in k_1 due to alteration in the partial pressure, contact time and average pressure remained as before. Also the plot of log k_1 against $1/T^{o}A$ gave the same slope as previously although the intercept was slightly different. (See Fig. 10 and Table III).

TABLE III

Expt: No.	Temp. °C	Partial Pressure mins	Contact Time Secs	% Decomposition	K_1
Sheffield					
172	593	.21	1.02	2.1	.020
171	593	.23	0.95	1.9	.021
168	681	.21	0.83	24.4	.33
169	686	.19	0.80	27.9	.41
163	663	.12	0.85	13.4	.17
138	626	.20	0.86	5.7	.067
137	606	.25	1.02	2.9	.029

FIGURE 10


3-4 mms N_2
2·0
$E = 53{\cdot}0$ kals
$A = 6{\cdot}3 \times 10^{11}$
× Sheffield
$E = 52{\cdot}8$ kals
$A = 4{\cdot}4 \times 10^{11}$
o St Andrews
1·5
$-\log_{10} K_I$
1·0
0·5
1·05
1·10
1·15
$\frac{1}{T} \cdot A \times 10^3$

St. Andrews

1	641	.31	1.11	19.3	.19
2	641	.27	.97	15.2	.17
4	638	.23	.93	13.0	.15
5	638	.22	.87	10.6	.13
7	613	.21	.87	4.6	.054
12	680	.22	.96	30.7	.46
13	680	.19	.86	36.4	.52
18	616	.27	.97	18.1	.20
19	616	.25	.99	17.1	.21
8	578	.21	1.06	2.2	.021
9	578	.37	1.03	2.6	.026
10	578	.83	0.96	3.5	.037

Before any mechanism for the reaction could be considered a greater knowledge of the products formed and their relative quantities was necessary. The work at Sheffield had shown that methane was formed, the ratio to iodine being approximately 0.7. No other product had been found either in the iodine or hydrogen iodide traps. However, when the furnace was packed with silica wool the reaction was found to be partly heterogeneous and the percentage decomposition rose to 50%. Under these conditions a considerable amount of carbon was deposited on the surface of the reaction vessel, in the earlier experiments the amount of carbon would have been of the order of 10^{-3}-10^{-4} gram-molecules and was probably burnt away when air was admitted to the furnace prior to titration.

The technique described above was used to determine the amounts of carbon and methane, the results obtained were as follows:-

TABLE IV

Methane

Partial Pressure	% Decomposition	CH_4 in Gm-Moles x 10^{-4}	I in Gm-Atoms x 10^{-4}	CH_4/I
.45 - .30	17	8.3	11.7	.73
.45 - .36	17	7.4	10.2	.73
.07 - .06	10	4.9	6.8	.72
.07 - .06	10	5.2	7.1	.72

Carbon

Partial Pressure	% Decomposition	C in Gm-Moles x 10^{-4}	I in Gm-Atoms x 10^{-4}	C/I
.4	15	10.9	37	.25
.4	15	10.0	40	.26
.4	15	4.3	16.3	.26
.4	15	4.9	18.6	.26

Packed Furnace

Carbon in Gm-Moles x 10^{-4}	Methane in Gm-Moles x 10^{-4}	Iodine in Gm-Atoms x 10^{-4}	Hydrogen Iodide in Gm-Moles x 10^{-4}	C : I : H
1.32	4.4	5.6		1 : 1 : 3.2
1.36	4.36	5.6		1 : 1 : 3.1
1.17	3.68	4.55	.5	.94 : 1 : 3.01
2.16	3.48	8.0	.85	.96 : 1 : 3.02

Thus we see that the products are the same whether the furnace is packed or not.

The overall reaction is evidently

$$4CH_3I \rightarrow 4I + 3CH_4 + C \qquad (1)$$

If the primary break is taken as:-

$$CH_3I \rightarrow CH_3- + I \qquad (2)$$

then the methyl radicals must either react with themselves or with the parent methyl iodide to give methane:-

$$-CH_3 + CH_3- \rightarrow CH_4 + -CH_2- \qquad (3)$$

or

$$CH_3I + CH_3- \rightarrow -CH_2I + CH_4 \qquad (4)$$

Bawn[77] has done a considerable amount of work on the reactions of methyl radicals using a sodium flame technique using an excess of sodium and considers the energy for reaction (4) to be too high to make it an important factor.

Surface Effects

Since the carbon was invariably found on the hot zone a closer examination of the surface effect was deemed necessary, moreover if the reaction is partly heterogeneous then the overall activation energy has little meaning unless the heats of adsorption and desorption are known.

The effect of surface was studied by packing the furnace with silica wool. The diameter and length of several strands of silica wool was measured and from their weight an average value for the surface per gram of silica wool was determined and used to calculate the surface increase for the addition of a known amount of wool.

The following results were obtained at 592°C :- (See Fig. 11).

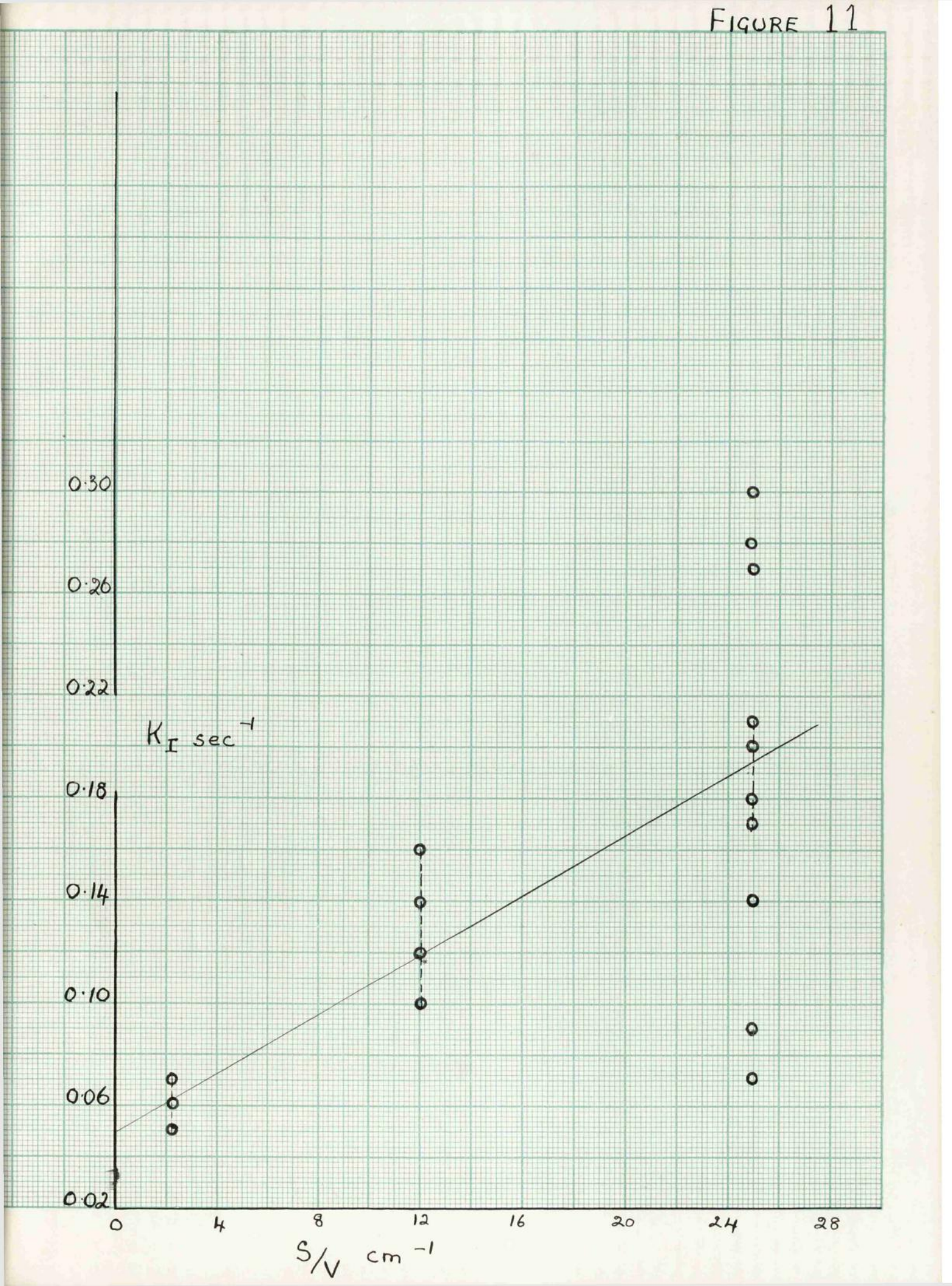
TABLE V

Expt: No.	S/V cm^{-1}	Partial Pressure mms	Contact Time sec.	% Decomposition	k_1
23	2.2	.30	1.0	6.7	.07
24	2.2	.29	.95	5.7	.06
25	2.2	.27	.90	4.3	.05
35	12.1	.34	1.2	12.7	.12
36	12.1	.30	1.0	16.0	.16
37	12.1	.33	1.1	10.0	.10
38	12.1	.30	1.1	14.5	.14
42	25	.35	1.1	7.2	.07
43	25	.32	.98	18.1	.18
44	25	.29	.91	23.6	.30
47	25	.30	1.0	19.2	.21
48	25	.28	.95	23.1	.28
49	25	.27	.90	23.8	.30
50	25	.34	1.1	17.3	.17
51	25	.31	1.0	15.4	.17
52	25	.29	.97	12.8	.14
53	25	.31	1.1	10.1	.09
54	25	.30	1.1	19.6	.20
55	25	.28	1.0	23.2	.27

Before experiments 50-52 methyl iodide was allowed to pass through the hot furnace for about 30 minutes to ensure a complete coating of carbon on the walls. In the case of experiments 42-44 and 53-55 the surface was entirely clean of carbon before the run was started.

It is clear from the preceding table that the results are far from reproducible and an accurate knowledge of the reaction in the presence of a large surface could only be obtained from a great deal more work. This object was not pursued as it had no direct bearing on the purpose of present work since the data indicated clearly the essential point that the surface

FIGURE 11



reaction, under the conditions used, was appreciable. The graph (Fig. 11) of K_I against S/V ratio shows however that the rates increased much less than proportionately with surface. It can be estimated that when $S/V = 0$ at this temperature of 592°C the reaction constant K_I would be 0.04 - 0.05 instead of 0.06 as observed in the particular reaction vessel used.

Higher Average Pressure and Partial Pressure

If as Table V indicates the reaction is a mixture of a heterogeneous and homogeneous reactions it is likely that the ratio of one to the other will be altered by variations in the conditions of the reaction.

At Sheffield it was observed that an alteration in partial pressure and average pressure had an effect shown graphically in Figs. 12 and 13. Thus the greater the partial pressure and the average pressure the more nearly first order behaviour is followed. Moreover at a greater average pressure it might be expected that the homogeneous reaction would be favoured as the methyl iodide will attain the temperature of the reaction vessel by collision with the molecules of nitrogen rather than the wall. Several experiments with an average pressure of 8-9 mms of nitrogen and 1-2 mms of methyl iodide were carried out. Some representative results obtained in these runs are listed below.

TABLE VI

Expt: No.	Temp. C	S/V cm^{-1}	Partial Pressure mms	Contact Time secs.	% Decomposition	K_1
56	546	25	2.1	.75	5.8	.078
57			1.9	.72	6.5	.093
58			1.7	.70	6.4	.095
60	534		.87	.93	4.4	.049
61			2.3	.75	5.2	.072

FIGURE 12

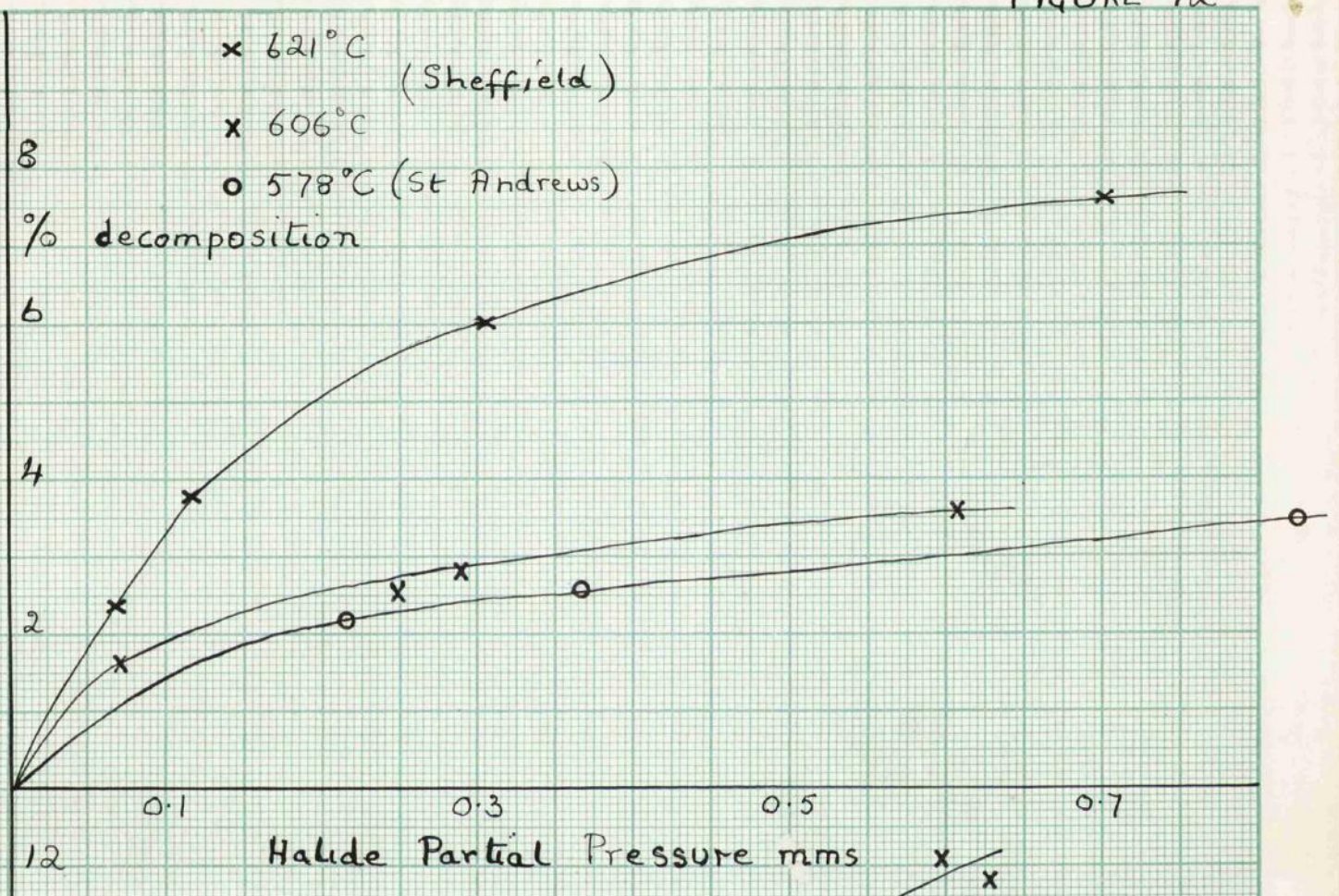


FIGURE 13

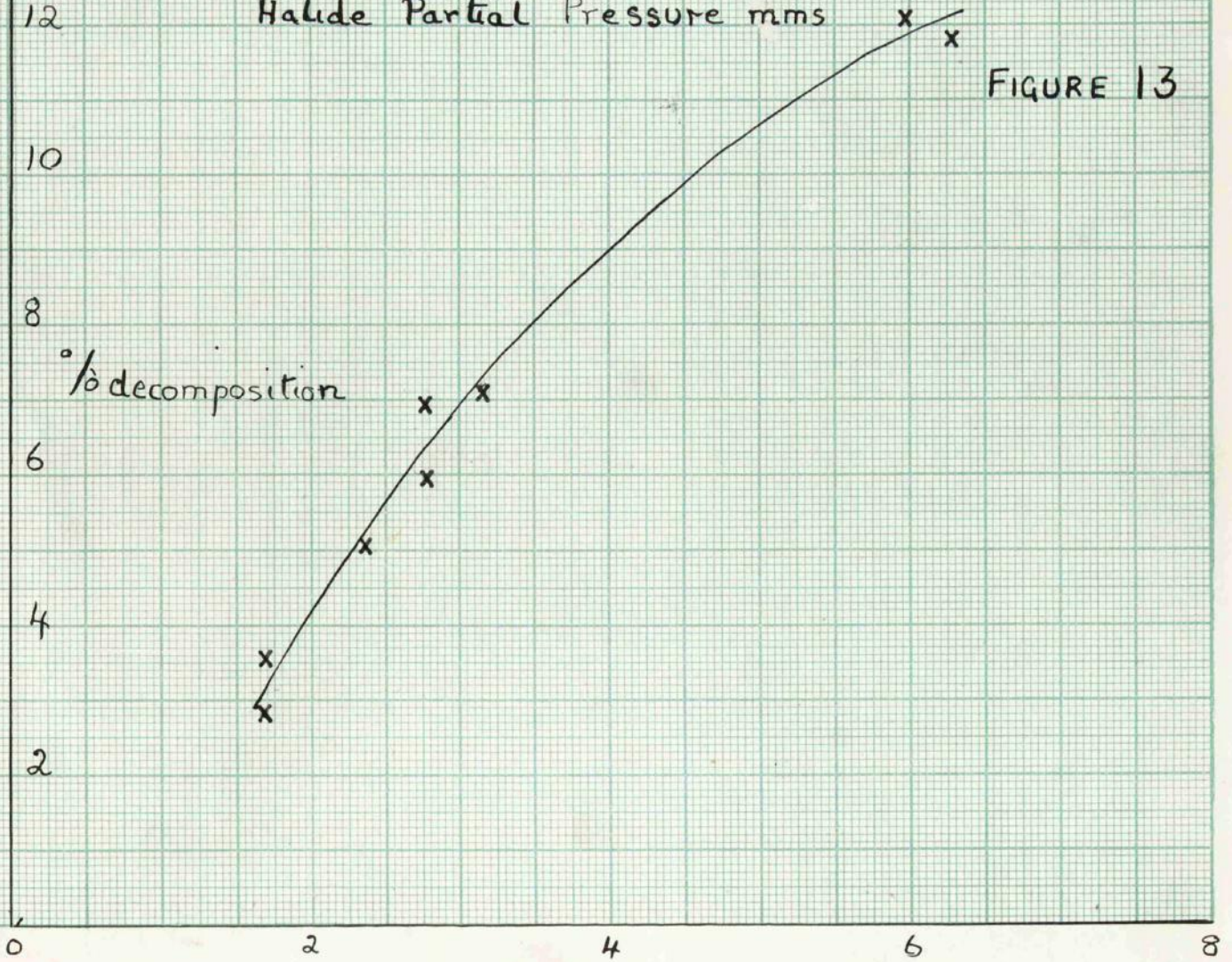
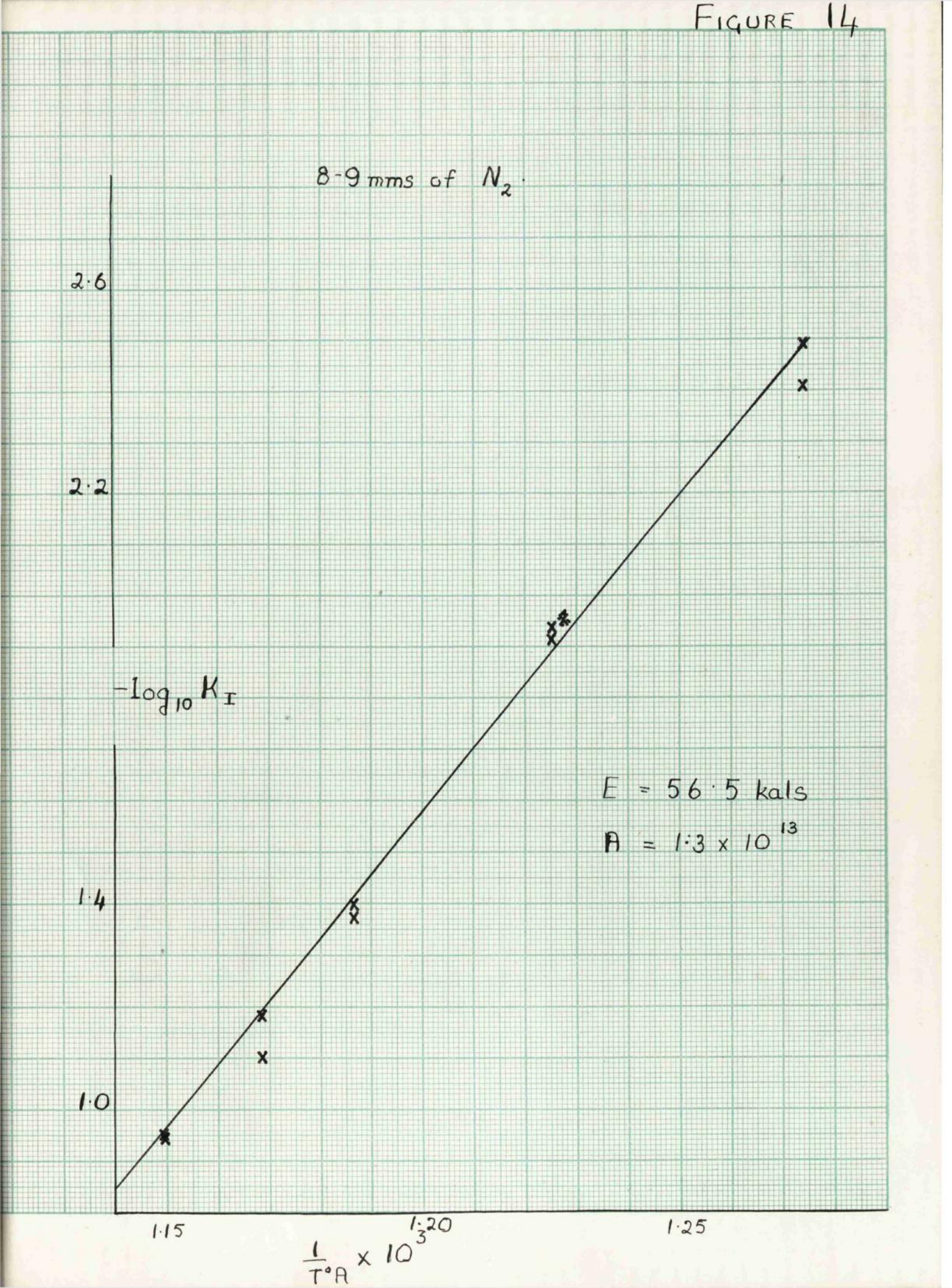


TABLE V (Continued)

Expr: No.	Temp. °C	S/V cm^{-1}	Partial Pressure mms	Contact Time secs.	% Decomposition	K_1
65	531	2.2	1.0	.5	1.2	.024
66			.98	.48	1.3	.026
69			1.3	.53	1.5	.029
70			1.3	.53	1.4	.027
71			1.9	.54	1.4	.027
72			1.8	.53	0.9	.018
75	531	2.2	2.5	.58	1.7	.029
76		2.2	2.4	.57	1.6	.029
80		2.2	3.3	.51	1.2	.024
81		2.2	3.3	.51	1.3	.025
83	552	2.2	1.1	.52	2.4	.048
88		2.2	3.3	.50	1.9	.039
99	543	2.2	1.4	.52	.58	.011
100		2.2	1.4	.52	.62	.012
105	542	2.2	1.6	.59	.63	.017
106		2.2	1.6	.59	.63	.017
107	570	2.2	1.1	.49	1.9	.040
109		2.2	1.1	.49	2.0	.042
110	583	2.2	1.1	.48	3.7	.079
111		2.2	1.1	.48	3.1	.065
114	597	2.2	1.1	.46	5.1	.112
115		2.2	1.1	.46	5.0	.111
123	512	2.2	1.1	.50	0.2	.004
124		2.2	1.1	.50	0.16	.003

From these results it is seen that packing the furnace has much the same effect as before so that the heterogeneous reaction has not been reduced to any extent. However the effect of variation in partial pressure has been greatly reduced, Experiments 65-81.

FIGURE 14


8-9 mms of N_2.
2·6
2·2
$-\log_{10} K_I$
1·4
1·0
$E = 56 \cdot 5$ kals
$A = 1 \cdot 3 \times 10^{13}$
1·15
1·20
1·25
$\frac{1}{T°A} \times 10^3$

If log k_1 is plotted against $1/T°A$, the slope gives a value of 57 kcals for the activation energy of the reaction (Fig. 14).

Since the results were not very reproducible even within three consecutive runs (e.g. 56-58, 60-61, 65-67), the rate of flow of the methyl iodide was tested to see whether it was constant and whether it agreed with the amount calculated from the capillary constant. The methyl iodide was collected in the hydrogen iodide trap and titrated in the manner described previously. The results obtained were as follows.

TABLE VII

Fore Pressure mms	Length of run secs.	Methyl Iodide in Gm-Mols Estimated x 10^3	Methyl Iodide in Gm-Mols Calculated x 10^3	Iodine in Gm-atoms x 10^5
86	360	5.16	5.08	
84	360	4.87	4.68	
83	360	4.18	4.16	
85	570	6.88		5.47
86	570	6.92		4.72
86	570	6.85		4.74

from which we see that the irreproducibility in rate of iodine formation does not arise from any variation in the halide rate of flow and that the estimated quantity of halide agrees with the calculated amount.

Experiments without a Carrier Gas

Since the existing circulation pump would not pump any higher pressures some experiments using no carrier gas were studied. The increased partial pressure of methyl iodide used, together with a slightly longer contact time than that used in previous work with a carrier gas meant that a lower temperature would yield sufficient iodine for titration and so a Pyrex reaction vessel was suitable.

The halide was introduced from the saturator and controlled in the fashion described previously (Page38). The pressure of the halide was approximately 4 mms and the contact time of the order of 1-2 secs. In preliminary experiments the pressure in the furnace was measured with a sloping mercury manometer, this was found to be unsatisfactory and a glass spiral capillary gauge was used, as described on Page 37. The effect of partial pressure in these experiments was found to be negligible as was the effect of contact time. The following runs were all performed at 499°C.

TABLE VIII

Expt. No.	Contact Time secs.	Halide Pressure mms	% Decomposition	K_1 x 10^{+3}
149	1.8	4.15	.90	5.1
150	1.6	4.15	.86	5.3
151	1.6	4.20	.80	5.1
157	1.7	2.65	.82	4.8
158	1.6	2.65	.86	5.5
159	1.6	2.65	.86	5.5
155	1.8	7.0	1.03	5.7
156	1.9	7.0	1.01	5.3
161	1.2	7.1	.62	5.2
162	1.2	7.1	.62	5.1
164	4.5	7.0	2.1	4.7
165	4.2	7.0	2.0	4.8
167	2.3	11.2	1.23	5.5
168	2.2	11.2	1.15	5.4

The variation of k_1 with temperature was found to be as follows:-

TABLE IX

Expt. No.	Temp. °C	Halide Pressure mms	Contact Time secs.	% Decomposition	K_1 x 10^{+3}
172	517	4.0	1.6	1.5	9.3
171	517	4.0	1.6	1.45	9.0

FIGURE 15

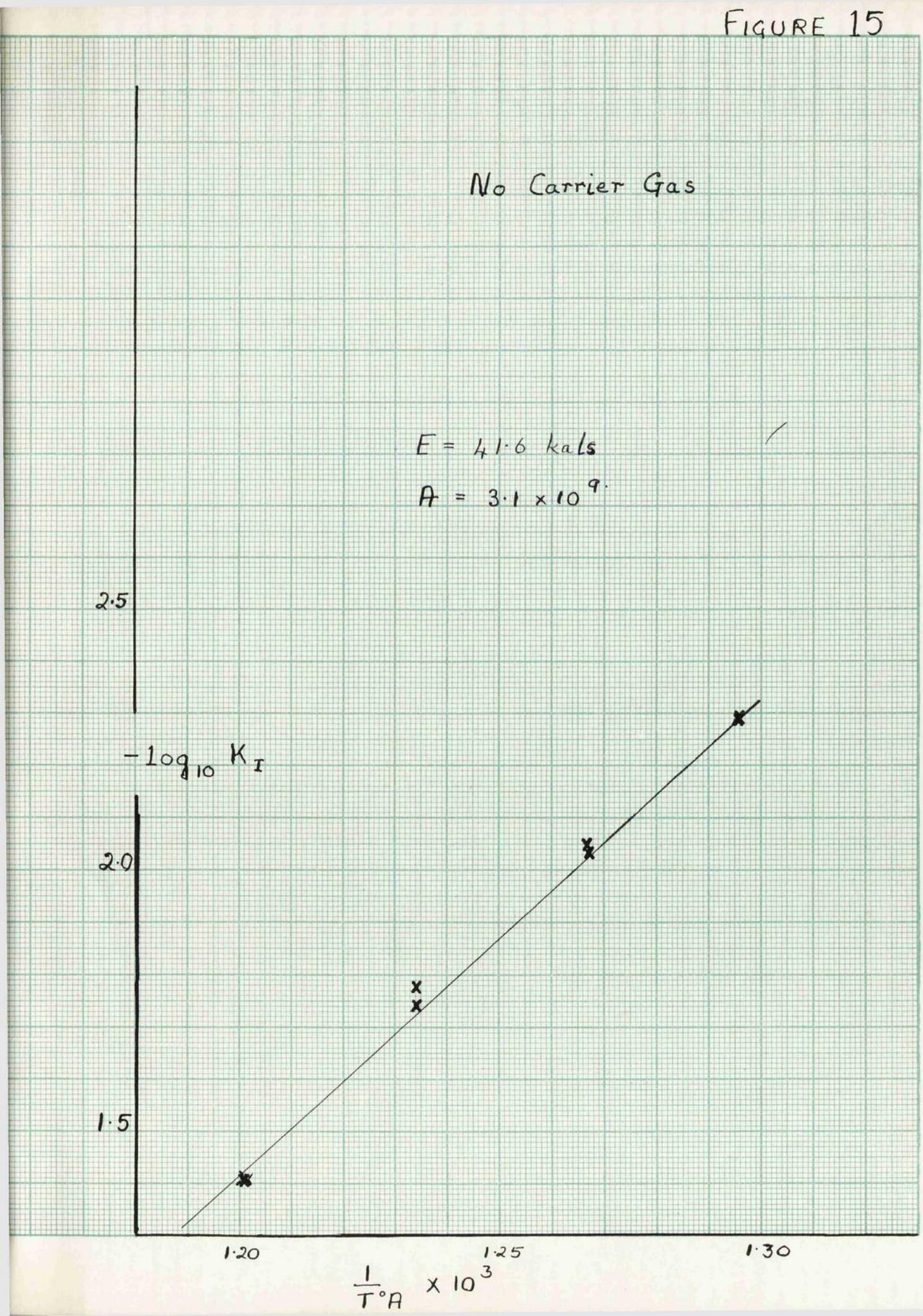

No Carrier Gas
E = 41·6 kals
A = 3·1 × 10^9
2·5
2·0
1·5
−log10 KI
1·20
1·25
1·30
1/T°A × 10^3

TABLE IX (Continued)

Expt: No.	Temp. °C	Halide Pressure mms	Contact Time secs.	% Decomposition	K_1 x 10^{+3}
174	538	4.2	1.6	2.72	16.8
175	538	4.2	1,5	2.70	18.2
177	560	4.1	1.6	6.01	40.1
178	560	4.1	1.5	5.74	39.8
179	499	4.2	1.6	.77	5.0
180		4.3	1.4	.74	5.2
181		4.3	1.4	.75	5.2

The activation energy derived from the slope of log k_1 against 1/T°A is 41.6kals this is lower than is to be expected for the C-I bond-strength in CH_3I and suggests either some form of chain reaction or a large amount of surface reaction, or both, to test the effects of surface the latter was increased from 474 cm^2 to approximately 2814 cm^2 by packing with pyrex glass wool with the following effect at 499°C.

TABLE X

Expt: No.	S/V	Halide Pressure mm	Contact Time secs.	% Decomposition	K_1 x 10^{+3}
181	1.9	4.2	1.6	.77	5.0
185	11.3	4.4	1.7	2.7	16.3
186		4.4	1.6	2.7	16.9
187		4.4	1.6	2.4	15.4
188		4.3	1.6	1.7	10.9
189		4.3	1.6	1.6	9.6
190		4.3	1.6	1.5	9.4
191		4.3	1.8	2.3	12.7
192		4.4	1.6	1.4	8.9
193		4.4	1.6	1.5	9.1
194		4.3	1.9	1.8	9.9
195		4.3	1.7	1.5	8.7

Before experiments 189 and 192 methyl iodide was passed through for 30 minutes to ensure a complete coating of carbon, as carbon was still deposited on the walls of the furnace. In this case the carbon coated surface seems to slow down the reaction to a slight extent. The increase of surface by 6 times therefore increases the decomposition rate by 2-3 times.

Methane was also formed and the amount was estimated by pumping it off and measuring its pressure in a known volume. The proportion of methane to iodide was nearly the same as before. The amount of CO_2 formed when the methane was burnt was equal to the amount of gas estimated before burning so all the non-condensible gas formed was CH_4.

Table II

Expt. No.	Methane in Gm.-Moles x 10^4	Iodine in Gm-atoms x 10^4	CH_4/I
201-203	14.1	20.4	0.69
204	3.64	5.17	0.70
205	3.07	4.69	0.65
206	3.09	4.40	0.70

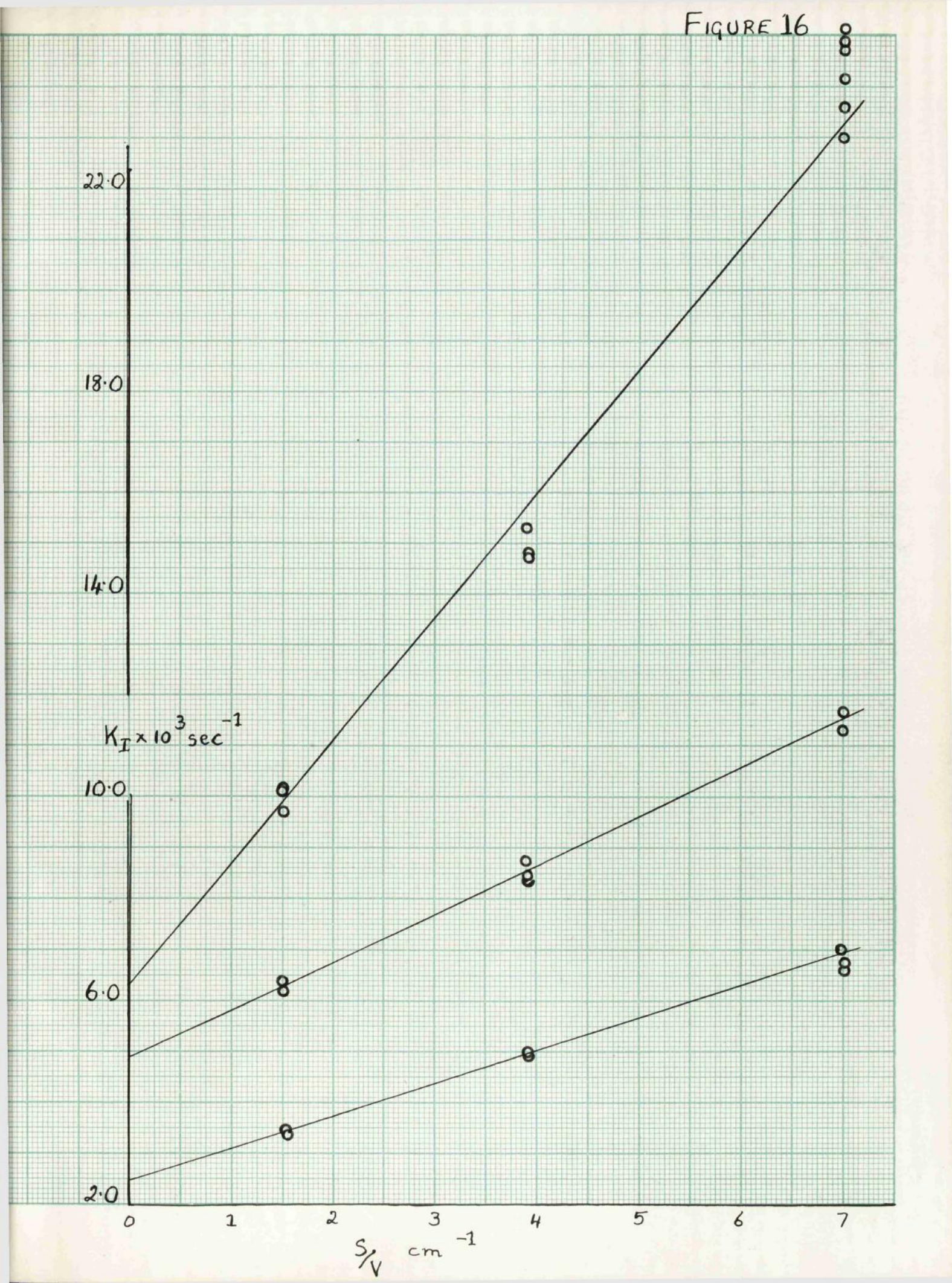
In order to study the effect of the surface/volume ratio on the reaction more closely a wider reaction vessel of pyrex was made, into which pyrex tubes could be inserted so that the exact variation in surface was known. The results obtained were as follows.

Table 12 and Figure 16

Expt: No.	S/V	Temp. °C	Halide Pressure mms.	Contact Time secs.	% Decomposition	K_I x 10^{+3}
196	1.5	502	4.1	2.2	.74	3.48
197			4.1	2.2	.76	3.45
198			4.1	2.2	.70	3.22
208	3.9		4.7	2.0	.98	4.82
209			4.7	2.0	.98	4.96
219	7.0		4.1	2.0	1.28	6.55
220			4.7	1.9	1.31	6.97
221			4.7	1.9	1.26	6.70
201	1.5	520	4.7	2.6	1.52	5.96
202			4.7	2.7	1.71	6.49
210	3.9		4.7	2.1	1.77	8.71
211			4.7	2.2	1.77	8.31
212			4.7	2.2	1.81	8.30
217	7.0		4.3	2.2	2.23	11.25
218			4.3	2.1	2.21	11.7
228	1.5	540	4.6	2.4	2.33	9.76
229			4.5	2.5	2.45	10.1
230			4.9	2.3	2.29	10.1
213	3.9	540	4.9	2.3	3.38	14.7
214			4.9	2.4	3.68	15.3
215			4.8	2.4	3.51	14.8
222	7.0		4.8	1.9	4.54	24.7
223			4.8	2.0	4.80	25.2
224			4.8	1.9	4.64	24.9
225			4.8	1.8	4.80	24.2
226			4.8	1.8	4.04	23.0
227			4.8	1.8	4.35	23.6

The data in Fig. 16 seem to indicate that when S/V = 0 there is a residual rate of reaction of some magnitude. For the reaction vessel used at 502°C the value of K_{Iv} x 10^3 was 3.4, without liners, which has to be compared with the extra-

FIGURE 16



polated value of 2.5 for S/V = 0, that is about 70% of the reaction is homogeneous under these conditions. The data in figure 16 can be expressed by the following equations:-

$$10^3 \times K_I = 2.5 + 0.62\,S/V \quad \text{at } 502^\circ C$$

$$10^3 \times K_I = 5.0 + 0.9\,S/V \quad \text{at } 520^\circ C$$

$$10^3 \times K_I = 6.5 + 2.4\,S/V \quad \text{at } 540^\circ C$$

We can analyse this data further if we consider the two reactions, one homogeneous and the other heterogeneous as occurring simultaneously. It is probable that the heterogeneous reaction is first order at these temperatures as the CH_3I is not likely to be strongly absorbed. In this case the composite K_I calculated is represented by

$$K_I = K_{homogeneous} + K_{heterogeneous} \times \left(S/V\right)$$

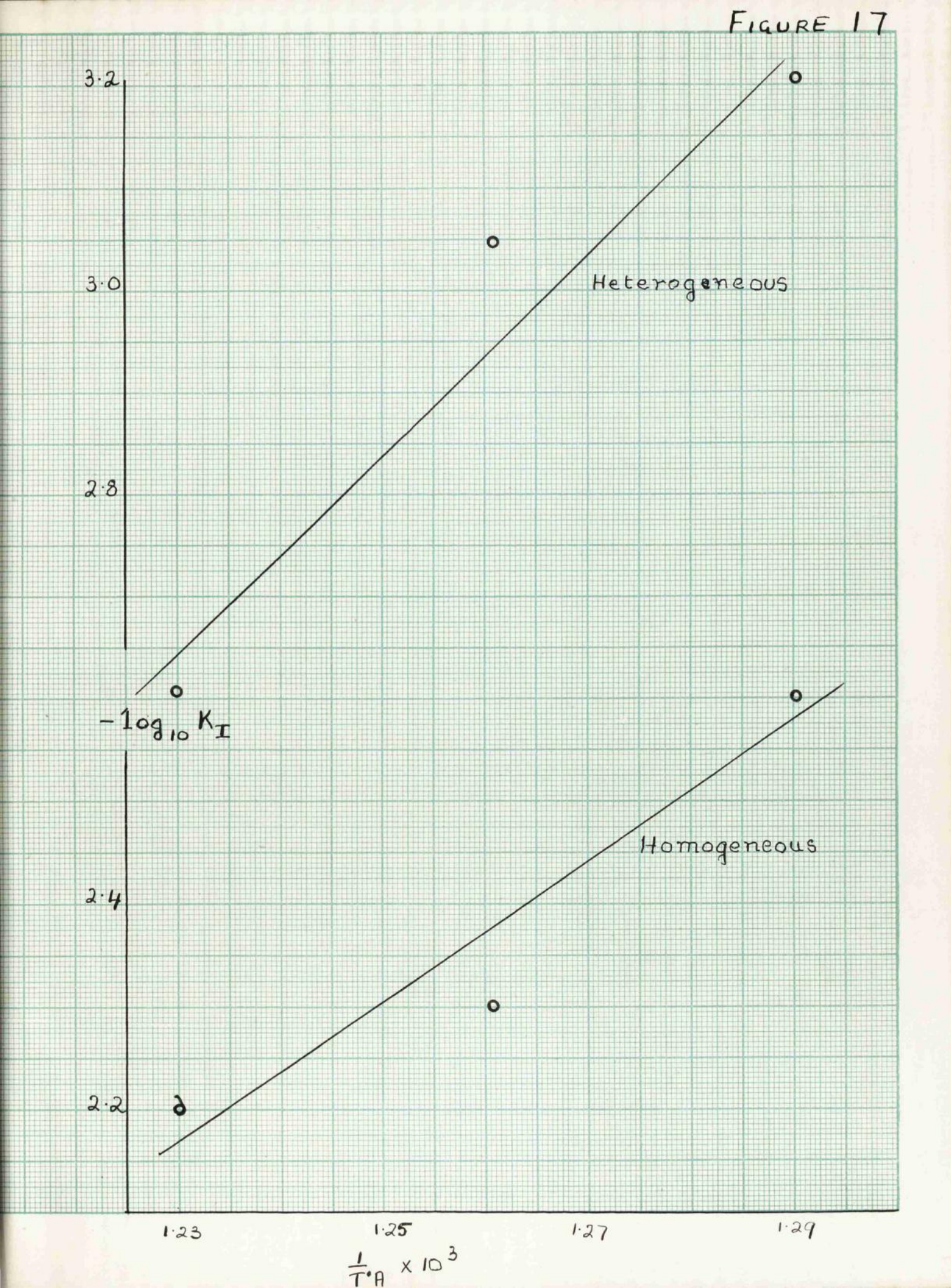
where $K_{heterogeneous}$ is the rate for the reaction per unit S/V. In Fig 17 the values for $K_{homogeneous}$ and $K_{heterogeneous}$ from the previous equations are plotted against $\frac{I}{T^\circ_A}$. The data are subject to considerable uncertainties and obtaining it was very laborious so that attempts to clarify the position further were not made. From Fig. 17 it is clear however that if two concurrent reactions are assumed then they proceed with very similar activation energies.

High Pressure Experiments

The only apparent way of reducing the proportion of the heterogeneous reaction appeared to be to increase the pressure of the carrier gas so that the methyl iodide would make fewer collisions with the wall.

The nitrogen pressure was therefore raised to approximately 600 mms and

FIGURE 17


3·2
3·0
2·8
2·4
2·2
Heterogeneous
Homogeneous
$-\log_{10} K_I$
1·23
1·25
1·27
1·29
$\frac{1}{T}$ · A × 10^3

the partial pressure of halide was of the order of 1-2 mms. The contact time was increased to 10 secs as, at these high pressures, the gas might not attain the temperature of the furnace in a shorter time. With the 10 secs. contact time, when the gas flow was started there was no detectable decrease in the temperature measured in the central thermocouple tube, so it was assumed that the gas was reaching the furnace temperature.

In the first experiments a rubber diaphragm pump was used to circulate the gas but it was very difficult to make this completely airtight, particularly when it was operating, so later a bellows pump, as described on Page 35 was employed. To measure the rate of flow a sloping paraffin manometer was used across two 150 cms. capillaries, after it had been found impossible to measure the pressure drop across any of the original capillaries at these rates of flow. The sensitivity of the manometer was 9 cms. for 1 mm. of mercury. The capillary constants were calculated from Poiseuilles formula for each capillary and summed together as for resistances

$$1/k = 1/k_1 + 1/k_2$$

to give the composite constant. Moreover it was discovered after several runs had been carried out that, at these high pressures, the products and methyl iodide were not being completely frozen out even with liquid air on both the "iodine and hydrogen iodide" traps. The hydrogen iodide traps were wound with glass wool so that the gas came into contact with the cold walls of the trap as much as possible (see Fig. 7). This proved effective in removing all the condensible compounds from the nitrogen stream.

The following results were all obtained after the above alterations and

modifications had been made. In the first experiments the effect of partial pressure and surface were studied at 487°C.

Table 13

Expt: No.	S/V	Partial Pressure mms.	Contact Time sec.	% Decomposition	K_I x 10^3
323	1.5	1.9	9.9	2.24	2.28
324		1.8	9.9	2.17	2.20
325		2.0	10.4	2.42	2.36
327		0.76	10.6	2.00	1.90
328		1.1	10.5	1.99	1.91
329		1.09	11.0	2.33	2.19
330		1.11	11.0	1.80	1.64
331		1.24	11.0	1.87	1.51
344		1.75	10.6	1.48	1.41
345		2.06	10.8	2.14	1.99
346		2.09	10.7	2.33	2.09
338	7.0	0.7	9.6	1.31	1.38
336		0.83	6.9	0.84	1.26
339		1.08	9.7	1.11	1.15
337		1.46	6.9	1.00	1.46
333		2.07	8.2	1.29	1.57
341		3.16	9.4	0.98	1.05
342		4.18	9.5	1.21	1.26

Thus we see that the reaction is of the first order and homogeneous within the limits of reproducibility which is poor.

The effect of temperature on k_1 was studied next the results obtained are listed below:-

Table 14 and Figure 18

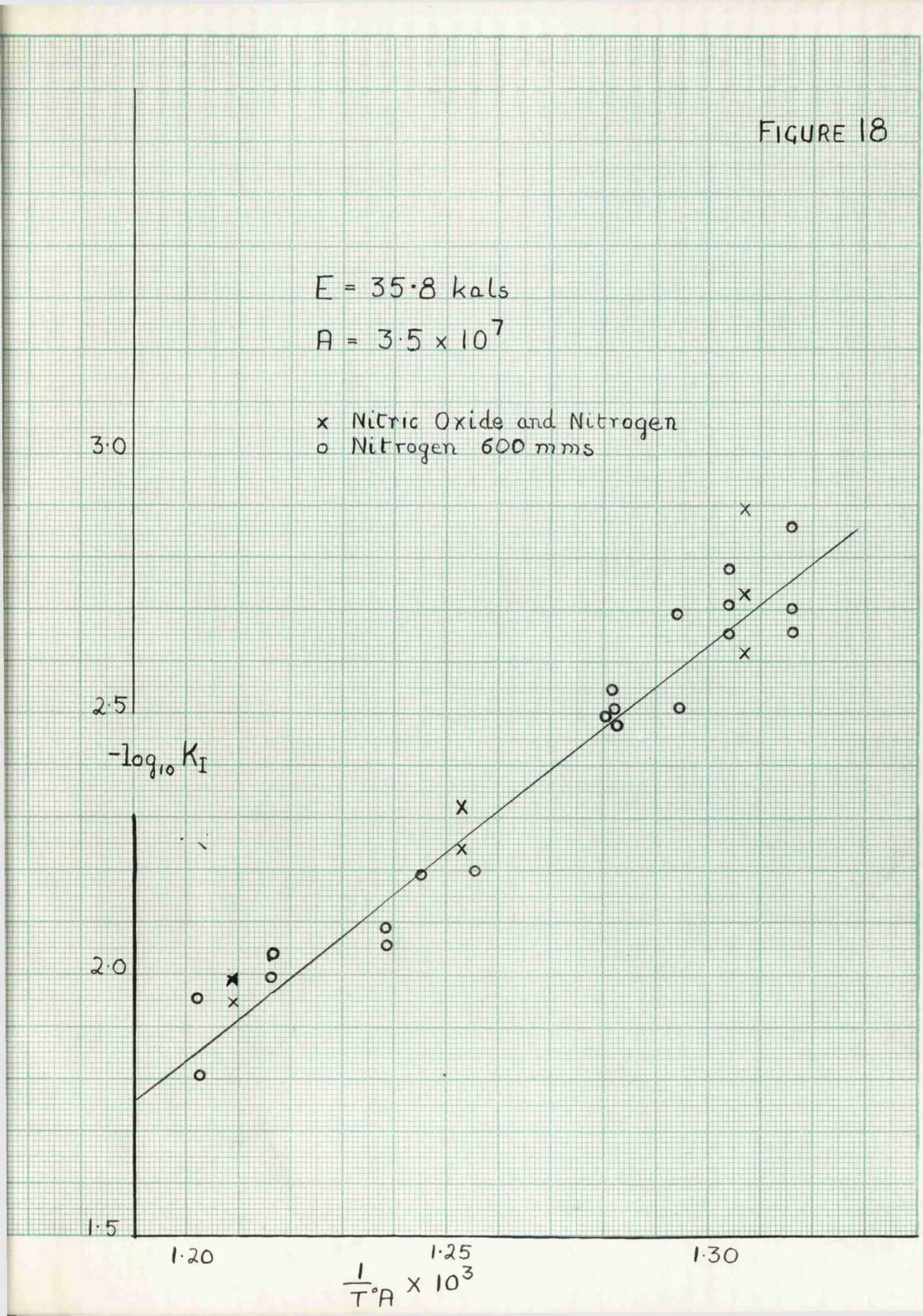
Expt. No.	Temp. °C	Partial Pressure mms.	Contact Time secs.	% Decomposition	k_1 x 10^3
344	487	1.75	10.6	1.48	1.41
345		2.06	10.8	2.14	1.99
346		2.09	10.7	2.33	2.21
365	494	1.14	10.6	1.76	1.68
366		1.09	11.0	2.15	1.97
367		1.00	10.6	2.33	2.22

Table 14 and Figure 18 (Contd.)

Expt: No.	Temp. C	Partial Pressure mms.	Contact Time secs.	% Decomposition	k_1 x 10^{+3}
360	500	1.14	10.2	3.09	3.09
357		0.93	10.2	2.02	2.07
350	507	1.36	10.4	2.91	2.85
351		2.05	10.8	3.53	3.34
352		2.11	10.3	3.15	3.11
353	508	1.78	10.3	3.27	3.22
356	524	1.09	9.8	5.99	6.32
354	530	1.37	10.3	6.43	6.45
358	535	1.24	10.0	8.47	8.87
359		1.18	10.1	8.03	8.31
361	549	1.24	10.1	8.96	9.25
362		1.25	10.2	9.76	10.1
363	559	1.18	9.81	14.4	15.8
364		1.23	9.90	11.1	11.9

The slope of log k_1 against $1/T°A$ gave an approximate activation energy of 35.8 kals see Figure 18 . The results are very irreproducible even within three consecutive runs, carbon was still deposited on the furnace walls but as the furnace was made of pyrex a temperature sufficiently high to burn the carbon in oxygen could not be attained. There was also a very slight pressure rise which was probably due to methane, though this effect was difficult to separate from the pressure rise due to the evaporation of the liquid air round the traps. The methane could not be estimated due to the very high proportion of nitrogen. A test for any ethane or ethylene produced and condensed by the liquid air in either the iodine or hydrogen iodide traps was made and proved negative. The two traps were immersed in solid CO_2/acetone baths so that any gas that evaporated could distil into a U-tube in liquid

FIGURE 18


E = 35·8 kals
A = 3·5 x 10^7
x Nitric Oxide and Nitrogen
o Nitrogen 600 mms
3·0
2·5
2·0
1·5
-log10 KI
1·20
1·25
1·30
1/T°A x 10^3

air which had a manometer attached. After 30 minutes the U-tube was separated from the rest of the apparatus and allowed to warm up to room temperature the pressure increase in a known volume was measured.

Gas in Gm-moles x 10^4	Iodine in GM-atoms x 10^4	Gas/I
.091	4.5	.02

which indicates a negligible amount of ethane or ethylene.

These experiments with high carrier gas pressure had produced conditions where a first order homogeneous reaction was achieved but were distinctly disappointing in respect of reproducibility. Moreover, the graph in Fig. 18 leaves no doubt that, in spite of the scatter of the points, the activation energy of the reaction was about 36 kals. This fact is quite at variance with any interpretation of the kinetics as being determined simply by the rupture of the C-I bond since this bond in methyl iodide is known to be far stronger than this value. Further discussion of this is left until later but since the high carrier gas pressures had minimized surface effects it was decided to make an attempt to improve reproducibility and reduce the likelihood of secondary reactions.

The carrier gas purification had been done in the usual way by passing nitrogen from a cylinder over hot sodium. As the possibility existed that at the higher pressures involved some oxygen might be present an extra heated sodium trap was put as a by-pass on the circulation system. Before an experiment the gas was circulated over this hot sodium. This extra purification was found to have no effect and the reproducibility was not improved.

The activation energy being much less than the order of magnitude of the C-I bond strength suggested the possibility of secondary reactions being prominent. Such reactions would be favoured by the higher carrier gas pressure hindering diffusion of the radicals to the walls or the carrier gas as a third body. Two methods suggested themselves for trial, the inhibition of the secondary reaction by removing the radicals by nitric oxide or alternatively to add a compound which would react readily with methyl radicals to leave a relatively stable and unreactive radical. Nitric oxide was therefore added to the carrier gas to a pressure of 3 mms (its vapour pressure over liquid air). This was found to have no effect as a comparison of the following results with Table 14 shows. The values of log k_1 are also plotted on Figure 18 for comparison with the results with nitrogen only.

Table 15

Expt. No.	Temp. °C	Partial Pressure mms	Contact Time secs.	% Decomposition	$k_1 \times 10^3$
374	492	1.05	10.8	2.60	2.44
375		1.05	10.7	2.01	1.89
376		1.12	10.8	1.36	1.26
368	525	1.49	10.3	5.72	5.72
369		1.28	10.1	4.74	4.81
370		1.30	9.9	4.65	4.82
371	553	1.28	9.9	9.49	10.1
372		1.10	10.1	10.7	11.2

Since nitric oxide did not alter the results the effect of adding toluene to the reaction was studied. At Sheffield it had been found that the addition of toluene to the carrier gas at low pressures caused a twofold increase in the rate of reaction. Szwarc[54] in his work on benzyl iodide showed that the

benzyl radical was very stable and only combined with each other to give dibenzyl, it was thought that the methyl radical might be fixed by reaction with the toluene to give methane and a benzyl radical which would then give dibenzyl.

The toluene, a B.D.H. product was dried and distilled, the fraction boiling between 109-110°C was collected and used. The toluene was then put into a saturator and picked up by the nitrogen carrier gas flowing over it. The saturator was immersed in a large beaker of water to eliminate large variations in vapour pressure due to fluctuations in the room temperature. The approximate partial pressure of the toluene was determined as in the case of the calibration of the halide capillary by allowing the gas to circulate over the toluene and weighing the amount of toluene passed over in a known time. The pressure was found to be 1-2 mms. The results obtained by this technique are listed below. Those in Table 16a were carried out with unpyrolysed toluene.

Table 16a

Expt. No.	Carrier Gas	Temp. °C	Contact Time sec.	Partial Pressure mms	% Decomposition	$k_I \times 10^3$
366	N_2	494	11.2	1.1	2.15	1.97
380	N_2 and	495	11.3	1.2	4.15	3.76
381	C_7H_8		11.1	1.3	4.09	3.74
382	N_2	516	10.2	1.1	16.3	17.3
383	and		10.4	1.1	18.0	19.0
384	C_7H_8		10.0	1.2	19.0	21.0
386	N_2	477	10.8	0.87	1.1	1.00
387	and		10.9	0.89	1.5	1.35
388	C_7H_8		10.8	1.10	0.71	0.67
393	N_2 and	501	10.4	0.55	5.5	4.30
394	C_7H_8		10.6	1.03	8.7	8.61

Szwarc in his study of the pyrolysis of toluene found that he only obtained reproducible results when he used toluene that had been previously pyrolysed twice. As described on Page 40 an apparatus embodying the main features of Szwarc's technique was set up and the toluene pyrolysed twice through it. This toluene when added to the carrier gas gave a much improved reproducibility as can be seen in Table 16b. These results are also graphed in Fig.19 and from the slope of the line we obtain a value of 54.7 kcals for the activation energy and a value of 2.6×10^{13} for the temperature independent factor. The effect of variation of contact time or partial pressure was found to be negligible as can be seen in experiments 421-422 and 425 and 432 in Table 16b.

Table 16b

Expt. No.	Temp. °C	Contact Time secs.	Partial Pressure mms.	% Decomposition	$k_1 \times 10^3$
420	463	8.8	0.61	1.03	1.18
421		14.7	1.28	1.72	1.18
418	464	10.9	0.89	1.67	1.54
416	472	10.8	.84	2.31	2.16
398	487	10.7	1.13	4.35	4.15
399		11.1	1.14	4.57	4.23
400		10.6	1.27	3.96	3.81
405		9.7	1.05	4.35	4.59
406		9.9	1.01	4.41	4.55
425	502	8.1	0.78	6.88	8.75
430	504	10.7	1.70	11.2	11.1
431		11.5	1.73	9.34	8.53
432		11.2	1.72	9.75	9.13
408	503	10.4	1.14	7.74	7.74
409		11.6	0.70	9.95	9.04

FIGURE 19

600 mms N_2 and 2mms C_7H_8

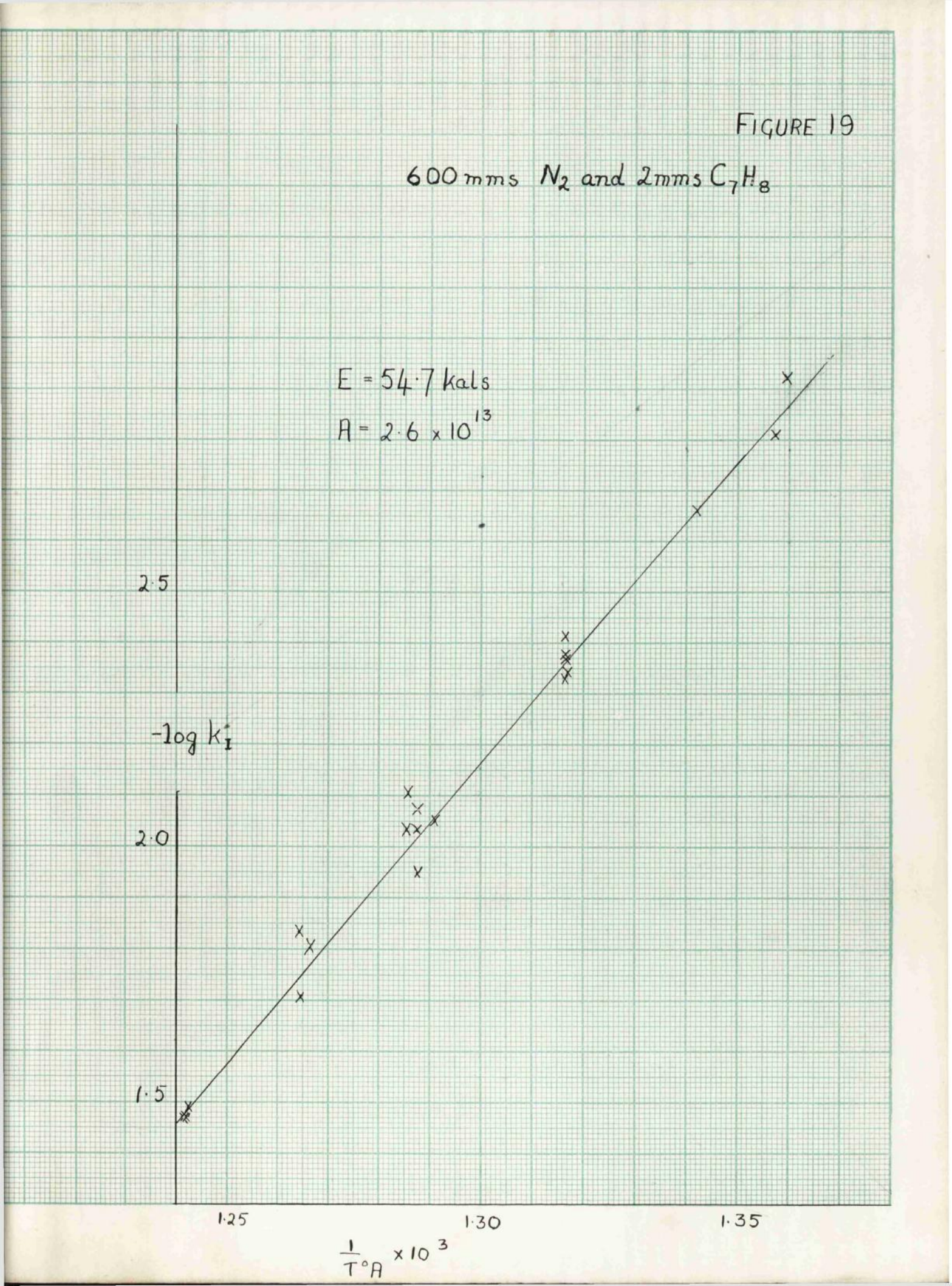


Table 16b (Continued)

Expt. No.	Temp. °C	Contact Time secs	Partial Pressure mms	% Decomposition	k_1 x 10^3
412	517	10.2	1.36	14.7	15.5
411	518	10.2	1.08	13.7	14.5
401		10.2	1.48	18.0	19.5
473	533	9.4	1.08	27.1	33.7
414		9.5	0.91	26.2	32.1
415		9.7	1.10	28.0	33.8

The chief product of the reaction other than iodine was stilbene, this was deposited on the walls of the tube at the exit of the reaction vessel. It was identified by scraping it off the sides of the tube and subliming it in vacuo. Three separate fractions were obtained by this method, the main fraction decolourized bromine water and was found to have a melting point of 119-123°C. The mixed melting point of this with stilbene was 119°-123°C and the melting point of the stilbene sample used was found to be 120-123°C therefore this main fraction was stilbene. A second fraction condensed out further from the source of heat, it was a very small amount and only sufficient for one melting point determination was obtained. This fraction was found to melt over a range, one part seeming to go at approximately 90°C and the whole was molten at 104°C. There was also a black carbonaceous deposit left after the distillation which could be heated to red heat without any further effect, this was also very small in quantity and was probably carbon formed in the furnace being carried through in the gas stream, which seems to indicate that in this case the carbon is not formed exclusively on the walls. The walls of the furnace were found to have only a very light carbon deposit, as compared

to previous experiments without toluene. The carbon could not be estimated as the reaction vessel was made of pyrex. However, the amount of stilbene found and the improved results indicated that the secondary reactions were no longer interfering with the rate of iodine production.

Discussion

The previous pages contain a description of the experimental work on the decomposition of methyl iodide in which the main alterations in technique have involved the carrier gas for the flow system. The most significant finding is that the apparent energy of activation could have values varying from 36 K.cals to 55 K.cals (approx.) depending on the technique which was used. Since the aim of the investigations was to obtain for the case of one typical halide a more complete understanding of the factors determining the energy of activation of its decomposition and its relation to bond strength considerable attention must be paid to this striking difference. Before discussing this in detail it is convenient to collect some general points.

Products and Possible Reaction Schemes

So far as was ascertained the overall products of the thermal decomposition for all conditions are given by the equation

$$4CH_3I \rightarrow 3CH_4 + C + 4I$$

and the rate of reaction was close to first order. The presence of the methyl radical was clearly shown by the formation of methane and the benzyl radical when the decomposition was carried out in the presence of toluene. As a result we can write the decomposition given above as

$$4CH_3I \rightarrow 4CH_3 + 4I \qquad (1)$$

for the first step and possible subsequent reactions by stepwise mechanisms discussed by Bawn[77]

$$CH_3- + CH_3- \rightarrow CH_4 + -CH_2- \qquad (2)$$
$$CH_3- + -CH_2- \rightarrow CH_4 + \gtrdot CH \qquad (3)$$
$$CH_3- + \gtrdot CH \rightarrow CH_4 + C \qquad (4)$$

or an overall $4CH_3 \rightarrow 3CH_4 + C$

In addition we have to consider the possibility that this reaction of methyl radicals occurs on a surface.

However in a system in which CH_3I is decomposing slowly the CH_3- radicals are unlikely to reach a high concentration and the case is not the same as Bawn's, (where CH_3I was not present), and a possible scheme seems to be

$$CH_3I \rightarrow CH_3 + I \qquad (5)$$

$$CH_3 + CH_3I \rightarrow -CH_2I + CH_4 \qquad (6)$$

$$-CH_2I \rightarrow -CH_2- + I \qquad (7)$$

$$-CH_2- + CH_3I \rightarrow CH_4 + -CHI- \qquad (8)$$

$$-CHI- \rightarrow \geqslant CH + I \qquad (9)$$

$$\geqslant CH + CH_3I \rightarrow CH_4 + C + I \qquad (10)$$

The basic assumption in this scheme is that collisions between CH_3I and unstable intermediates are more frequent than between radicals and unless great differences of activation energy intervene are inherently more probable. Products resulting from dimerisation of the radicals have not been found (C_2H_6, C_2H_4, C_2H_2) and this is in line with Bawn's results if due account is taken of the temperature of our experiments. For instance in the case of methyl radicals he found that the ratio of CH_4/C_2H_6 production changed with rising temperature in favour of increased amounts of CH_4. The log (CH_4/C_2H_6) was linear against $I/T^{\circ}K$ and an extrapolation to 500°C, (the temperature of the majority of experiments in the cases of no carrier gas and a high pressure of carrier gas), gives $CH_4/C_2H_6 = 93/1$. Since the amounts of

methane handled were of the order of 10^{-4} gm. moles a quantity of ethane of the order of 10^{-6} gm. moles would be outside the limits of easy detection, and is roughly the value obtained in the estimation with high carrier gas pressure described on Page 61.

As far as the schemes (1-4) and (5-10) are concerned there is no difference in the final result but the first scheme implies a primary rate of reaction four times as great as that in the second scheme where $3CH_3I$ molecules are decomposed by secondary steps after one CH_3I has decomposed in a primary step. Certain further considerations on these mechanisms are discussed in relation to the frequency of collisions and activation energies in later sections.

It is a well known feature of the photochemical decomposition of methyl iodide that the quantum yield is low and rises nearly to unity if acceptors are provided for the methyl radicals or iodine atoms. This has been explained on the grounds of a ready back reaction $CH_3 + I \rightarrow CH_3I$ (11) or $CH_3 + I_2 \rightarrow CH_3I + I$, (12) considerable differences of opinion having been expressed as to which reaction is the most effective. It is probable that the first would require the presence of a third body. From the point of view of the thermal decomposition these reactions have to be considered, and in addition the problem of the rate of $I + I \rightarrow I_2$ has to be dealt with since the extent of this conversion is relevant to the cases $(CH_3 + I)$ and $(CH_3 + I_2)$.

Under the experimental conditions investigated the existence of an effect of the surface area of the reaction vessel was observed for all cases

except where a high pressure of carrier gas was used. The surface of the reaction vessel can be the seat of a heterogeneous decomposition of CH_3I or the place at which radicals and atoms formed in the homogeneous phase end their existence. It is important to note however that the products were the same even when a large amount of packing was used, and at the present stage of the discussion specific steps occurring at the wall are not included in the above schemes.

Number of Collisions Made by a Particle in Diffusing to the Wall

Any radicals or atoms formed in the homogeneous gas phase will undergo collisions in diffusing to the wall which can be calculated by the formula given by Bursian and Sorokin[78]:-

$$\text{Average number of collisions} = n = \frac{3}{32}\frac{d^2}{\lambda^2}$$

where d = diameter of cylindrical vessel in cms. and λ = mean free path of the particle in cms. The mean free path can be calculated from the following equation:-

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 m}$$

where σ = molecular diameter and m = number of molecules per cc. To a first approximation we can take σ as being constant and equal to the value for N_2 molecule (3.84×10^{-8} cm.). If we consider a temperature of 800°A then at the following gas pressures we have the values of m, λ and n.

Pressure of N_2	4 mms. Hg	600 mms. Hg	
m	7.8×10^{16}	1.16×10^{19}	molecules/cc.
λ	1.90×10^{-3}	1.27×10^{-5}	cms.
n	1.75×10^{5}	3.94×10^{9}	collisions

These figures give the total number of collisions of all kinds, some of these are made with N_2, CH_3I and I_2 molecules, others with CH_3 radicals and I atoms in proportion to their concentrations.

In the cases where N_2 was used as a carrier the methyl iodide partial pressure can be taken as 1 mm. for purposes of calculation and this gives 4.4×10^4 and 6.57×10^6 collisions in the two cases (3 mm. N_2 + 1 mm. CH_3I). and (599 mms N_2 + 1 mm. CH_3I)
Under such circumstances the $e^{-E/RT}$ factor would just permit reaction to occur at 800°A if the value of the activation energy was 17,000 and 25,000 calories in the respective cases. Bawn has quoted a figure of 13 K.cals for the reaction $CH_3 + CH_3I$ in a reference to unpublished work.

The collisions with iodine atoms or molecules will be smaller in number since the fractional decomposition is small in the majority of cases. Taking a representative 2% decomposition in our above examples with 1 mm. CH_3I and 3 mms. N_2 we would have a diffusing methyl radical making 2% of $4.4 \times 10^4 = 880$ collisions with iodine if it stayed all as atoms and the reaction $I + I \leftrightarrow I_2$ did not occur. There are good grounds, see later sections, for supposing the iodine atoms are substantially equilibrated to molecules and some 10-20% remains in the form of atoms under the conditions employed. This would reduce the collisions of CH_3 with I atoms to 80-90 collisions before reaching the wall and with I_2 to around 400. With this small number of collisions the activation energies could not be greater than 7.0 - 8.0 K.cals (I atom case) or 9.6 K.cals (I_2 molecule case) for reaction to occur. The $CH_3 + I$ case is not likely to have any activation energy restriction but it may require the presence of a third body to take away the energy of combination. The

frequency of termolecular collisions at pressures as low as 4 mm. is small. The usual rough approximation is that the

$$\frac{\text{binary collision rate}}{\text{ternary collision rate}} = \frac{\text{mean free path}}{\text{diameter of binary complex}}$$

This gives for these conditions of 4 mm. N_2 $10^{-3}/10^{-8}$ or 10^5 to 1. This restriction would be severe and if a third body was required the CH_3 and I collisions would not be fruitful for recombination. There is not a firm value for the activation energy of the $CH_3 + I_2$ reaction in the literature but it is usually regarded as having a low value, probably less than 5 K.cal and it has been suggested to be as low as 1 K.cal.

These last considerations on the reactions of a methyl radical with atoms or molecules of iodine can be repeated for the case of 600 mm. N_2. Making the same assumptions of 1 mm. CH_3I and 2% decomposition we get 1.30×10^5 collision if all the iodine existed as atoms in the furnace and 1,300 - 2,600 if the more probable equilibration occurred. In the latter case also the collisions of a methyl radical with iodine molecules would number about 11,000. Of the collisions with iodine atoms about 1 in 1000 at this N_2 pressure would have a third body present also and in view of the calculation of binary collision frequency of $(CH_3 + I)$ the recombination reaction even as a three body mechanism may be feasible. If Rabinowitch and Wood's[79] data for iodine atom recombination is capable of extension to the case of $CH_3 + I$ then the case made out above is not as favourable as the actual state of affairs may be in reality. They found, for iodine atoms in N_2, that 7 out of every 1000 binary collisions were effective instead of the estimated 1 in

1000. If 11,000 collisions are made with iodine molecules the activation energy would need to be 14,800 calories to prevent reaction - a very unlikely figure.

Summarising the above conclusions we observe that in the case of 3 mms. N_2 and 1 mm. CH_3I the average methyl radical would be expected to react with methyl iodide molecules even if E_6 was as great as 17 K.cals, with iodine molecules if E_{12} was 9.6 K.cals, while in 600 mms. N_2 and 1 mm. CH_3I the upper limit of E_6 rises to 25.0 K.cals and of E_{12} to 15 K.cals.

The effect of any steric factor has been neglected in the above considerations, but such an effect is not very likely to be large. The views expressed in the literature on the size of the steric factor are somewhat conflicting. Steacie, Darwent and Trost[80] propose abnormally low steric factors (10^{-5} - 10^{-6}) for reactions of the type

$$CH_3 + RH \rightarrow CH_4 + R$$

but Evans and Szwarc[81] do not agree with this view and in the particular case of ethyl benzene derive a value of 10^{-2} from experimental work by Szwarc.[81a] They also adduce considerable evidence for a steric factor of about 10^{-1} for a considerable number of atom and molecule reactions.

The situation regarding reaction with iodine atoms turns on the third body restriction for removing the energy of combination. In connection with both iodine molecules and atoms it is clear that these products accumulate as reaction proceeds so that conditions change along the reaction furnace to a greater extent than is the case for collisions with CH_3I. In order to establish the proportion of iodine in the form of atoms and molecules some consideration is given below to the available evidence.

Combination of Iodine Atoms

The most relevant evidence in this matter is the experimental work of Rabinowitch and Wood[79] which was done at room temperature with iodine atoms produced by irradiation of iodine vapour. The dimensions of their vessel were 2 x 2 x 12 cm. so that the wall was slightly more accessible to diffusing atoms than in the present work. In their study of the recombination of atoms they found that in N_2 gas heterogeneous combination predominated at low pressures of nitrogen (0 - 60 mm.) and homogeneous combination by a three body mechanism predominated above about 100 mm. N_2. In a system containing about 10^{15} molecules/cc. of iodine and irradiated steadily so that 10^{15} quanta/cc. sec. are absorbed the recombination was so rapid with 336 mm. Helum as the inert gas that only 0.011×10^{15} molecules existed in the form of atoms in the stationary state. Helium showed a poorer capacity than N_2 as a third body and the particular pressure chosen for illustration provides a maximum in the stationary concentration of iodine atoms - at lower pressures heterogeneous combination reduces the value and at higher pressures homogeneous recombination.

Assuming the combination to be homogeneous and to have no energy of activation, [redacted] the rate constant they obtained with N_2 as inert gas (6.6×10^{-32} concentration in molecules per cc.) can be used as a first approximation at higher temperatures to calculate the number of atoms combining per cc. per sec. Assuming an initial concentration of 0.15 mm. iodine atoms.

No. of atoms combining $= 6.6 \times 10^{-32}\left(\frac{0.15}{760} \times 2.5 \times 10^{19}\right)^2\left(\frac{600}{760} \times 2.5 \times 10^{19}\right)$

$= 3.18 \times 10^{19}$ atoms per cc. per sec.

If the thermal decomposition was conducted with 1.5 mm. CH_3I and produced 10% decomposition in 10 secs. the rate of production of iodine atoms is only of the order 5×10^{14} per cc. per sec.

Thus in the presence of 600 mm. N_2 the rate of homogeneous combination must be very much faster than the rate of production of iodine atoms and a close approach to the equilibrium $2I \leftrightarrow I_2$ must result. As shown in Appendix I this equilibrium would mean 10-20% of the iodine as atoms in the gas phase.

Even at a pressure of 4 mm. N_2 the homogeneous recombination is $\frac{3.18 \times 10^{19}}{600/4}$ i.e. about 10^{17} molecules per cc. per second which remains higher than the rate of production in a pyrolysis experiment and would be outweighed by a faster heterogeneous combination rate at these low pressures.

Thus the general conclusion is that for the experimental conditions examined the equilibrium of iodine atoms and iodine molecules may be assumed in the reaction furnace.

Decomposition in About an Atmosphere of Nitrogen

(a) With added toluene

This was the last series of experiments to be done but it appears to be the simplest to interpret. The time available was too short to make a very extensive investigation of all the variables and establish the first order constants with great detail but, when using toluene purified by partial pyrolysis the reproducibility was much improved and the first order law appears

to be followed (Table 16b). The variation of the constants with temperature is well represented by the equation

$$k_1 = 2.6 \times 10^{13} e^{-54700/RT}$$

in which the frequency factor has the magnitude expected on theoretical grounds for a unimolecular decomposition and found to be the case for certain other decompositions. Moreover the energy of activation is in excellent agreement with the bond energy value for C-I in methyl iodide as determined by other methods, for example the value of 54.8 K.cals derived by Skinner[51]. If it is postulated that the primary step of dissociation into a methyl radical and iodine atom is followed by :-

$$CH_3 + CH_3C_6H_5 \rightarrow CH_4 + {}^{\cdot}CH_2C_6H_5 \qquad (1)$$

then the following reactions must occur

$$2\ C_6H_5CH_2{}^{\cdot} \longrightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (2)$$

$$C_6H_5CH_2CH_2C_6H_5 + R \longrightarrow C_6H_5CHCH_2C_6H_5 + RH \qquad (3)$$

$$C_6H_5CHCH_2C_6H_5 \longrightarrow C_6H_5CH{=}CHC_6H_5 + H \qquad (4)$$

$$\text{or } C_6H_5CHCH_2C_6H_5 + R \longrightarrow C_6H_5CH{=}CHC_6H_5 + RH \qquad (5)$$

in order to account for the observed production of stilbene. In this the radical R might be methyl or benzyl.

In support of this we can advance the following evidence. Taylor and Smith[82] found reaction (1) to have an activation energy of 5.6 K.cals, a value lower by 2.5 K.cals than the figure for reactions of methyl radicals with primary hydrogen

atoms in saturated paraffins. Horrex and Szwarc studied the pyrolysis of benzyl iodide andshowed the benzyl radical to have unusual stability and this suggested a trial of toluene as a radical acceptor. As has been previously mentioned, this was done in the work at Sheffield using a low pressure of nitrogen as a carrier gas for the methyl iodide but no great application of the technique was made at that time. Since then Szwarc has studied the pyrolysis of toluene and applied it as a radical acceptor. Horrex and Szwarc[54] in the pryolysis of benzyl iodide and Szwarc[74] in pyrolysing toluene found dibenzyl as the product from the benzyl radicals. This work was done at low pressures of carrier gas and no stilbene was detected. Horrex and Miles,[83] however, in studying the pyrolysis of dibenzyl showed that benzyl radicals in the presence of dibenzyl lead to a reaction giving stilbene as the chief product, and it seems that in the other experiments sufficient dimerisation of the radicals may not have occurred owing to the low ineert gas pressure. In 600 mms of nitrogen and with 10 secs contact time as in our experiments the conditions would favour dibenzyl formation more strongly than 2-10 mms of nitrogen and up to 1 sec contact time used by those not finding stilbene. The technical difficulties of estimating amounts of methane of 1 mm partial pressure of less in some 600 mms of nitrogen prevented a more complete assay of theproducts. It was clear, however, from the very small deposit of carbon formed during runs that

the usual method of disappearance of the methyl radicals was not being followed to any extent.

In adopting this interpretation of the results the rate of iodine formation is determined solely by the rate of dissociation of the methyl iodide and the activation energy of 54.7 K.cals can be taken as the C-I bond energy.

(b) Without added toluene.

The experiments with methyl iodide in about 600 mms of nitrogen were started in an attempt to favour a homogeneous reaction and minimise the effect of surface. That this proved successful is shown in Table 13 and not until the activation energy of 36 K.cals was found was it seen that an entirely new set of difficulties was presented in these conditions

In comparing these results with other data it is also important to note that the magnitude of the velocity constant is substantially less than the value obtained in the presence of added toluene. The value of the first order constant k_1 is about five times smaller at 800°A and ten times smaller at 870°A as can be seen from Table 17 where some comparative data are collected

Table 17

Values of k_1 taken from the graphs.

Gas Pressure in mms	$\frac{1}{T°A} \times 10^{+3}$		
	1.25	1.20	1.15
600 N_2 2 C_7H_8	0.028	0.11	0.40
600 N_2	0.0056	0.014	0.032
600 N_2 3 NO	The available data lie on the graph for 600 mms N_2		
3 N_2 0.3 CH_3I	0.0016	0.0089	0.025
3 N_2 1-1.3 CH_3I	0.0056	0.024	0.1
9 N_2 1-1.3 CH_3I	0.0066	0.027	0.11
3 NO 0.3 CH_3I	0.0044	0.020	0.1

This decrease in the value of k_1 suggests strongly that a back reaction reforming methyl iodide is taking place. Such a reaction will become of greater importance as the percentage decomposition increases since the iodine accumulates in the system. The reaction must presumably be homogeneous since increasing the surface by four times produced no acceleration. Moreover the calculations given previously would lead one to suppose that the collisions the average radical will make with possible reactants would be sufficient to ensure reaction on any reasonable estimates of activation energy. When we consider

which are the possible processes for reforming methyl iodide we have only CH_3 + I and a possible third body or $CH_3 + I_2$ to consider. The literature as has been noted, suggests the latter has a low activation energy and it would certainly be exothermic to the extent of 20 K.cals - the difference of the C-I and I-I bond energies. If this reaction is important it should imply that the reaction

$$I + CH_3I \longrightarrow CH_3 + I_2 \qquad (6)$$

would have an activation energy of the order of 20 K.cals. Allowing for the fact that at these temperatures iodine is to some extent dissociated we might have expected an acceleration of the decomposition by reaction (6) as there is a considerable change in the iodine concentration as the reaction proceeds. It can not be said that this was observed ; in the previous work at low pressures of nitrogen iodine was added to the carrier gas and a small degree of retardation was observed. The possibility remains of the CH_3 + I + third body being effective for recombination. As shown in the previous calculations a radical should make a three body collision with an iodine atom before reaching the wall.

If we take the results with toluene as indicating the maximum rate of production of methyl radicals then at 870°A the rate of recombination must be about 9/10 of the rate of formation. As a first approximation we can consider the

reaction as proceeding $CH_3I \rightleftharpoons CH_3 + I \rightleftharpoons I_2$

CH_3 ↓ reacting to give $C + CH_4$

Thus the rate of decomposition in this scheme is governed by the removal of the methyl radicals from the system. Such a removal could be by either of the reactions put forward previously - either they react with each other, at a rate determined by $(CH_3)^2$, or they react with methyl iodide; either method would provide an overall reaction of

$$CH_3 + 3CH_3I \longrightarrow 3CH_4 + C + 3I$$

i.e. an increase in the amount of iodine. This increase could not easily be disentangled from the loss consequent to the postulated back reaction.

If the rate of reaction $= \frac{d(CH_3)}{dt} = k^* (CH_3)^2$

and if $\frac{(CH_3)\ (I)}{(CH_3I)} = K$

then rate of reaction $= k^* K^2 \frac{(CH_3I)^2}{(I)^2}$

On the assumption that the equilibrium $2I \rightleftharpoons I_2$ is established, (as discussed previously) then for any given decomposition the amount of iodine atoms can be calculated from Bodenstein's data, see Appendix.

If a = gm-moles of CH_3I initially / litre

x = gm-moles of CH_3I decomposed/ℓ then we can write $\propto x$ = gm-atoms of I / litre

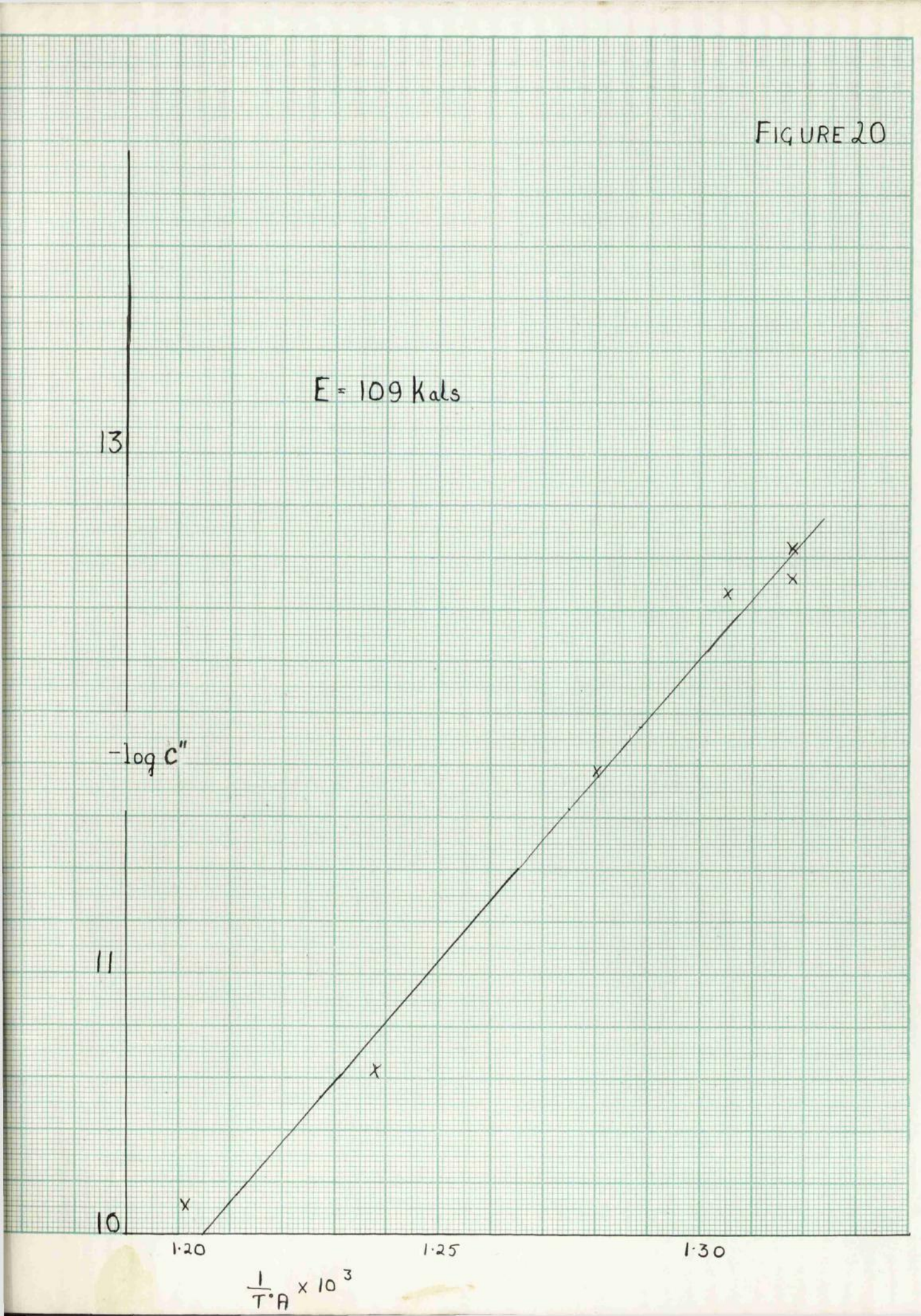
and $\frac{dx}{dt} = C'' \frac{(a-x)^2}{\propto^2 x^2}$

This can be integrated graphically most readily since α has a peculiar dependence on x. This has been done for several representative cases from the results of Table 14 and the Log C plotted against $1/T°A$ in Graph 20. The slope of the line corresponds to an apparent activation energy of 109K.cals. Since $C = k^* K^2$ this energy $E = E^* + 2\Delta H$ where ΔH is the heat for $CH_3I \rightleftarrows CH_3 + I$

Bawn[77] has assessed E^* for the disproportionation of methyl radicals as 8 K.cals, this would lead to $\Delta H = 50.5$ K.cals. This is undoubtedly low but the assumption of an initial equilibrium is only partly justified, but the treatment shows the order of result to be expected and probably shows the source of errror.

As indicated above extensive work to establish the kinetic order was not done in view of the evident difficulties of interpretation, but at the outset the fact that the % decomposition did not change for a sixfold variation in concentration of methyl iodide had seemed adequate grounds for assuming first order behaviour. It was unfortunate that these data were obtained at the lowest temperature where the final % decomposition was only 1-2 %, since the numerical values do not make distinction between $\frac{dx}{dt} = k_1(a-x)$ and $\frac{dx}{dt} = C''\frac{(a-x)^2}{\alpha^2 x^2}$ very easy in this range. Thus the values for k_1 for a series of experiments ranging from 0.76 mm CH_3I

FIGURE 20



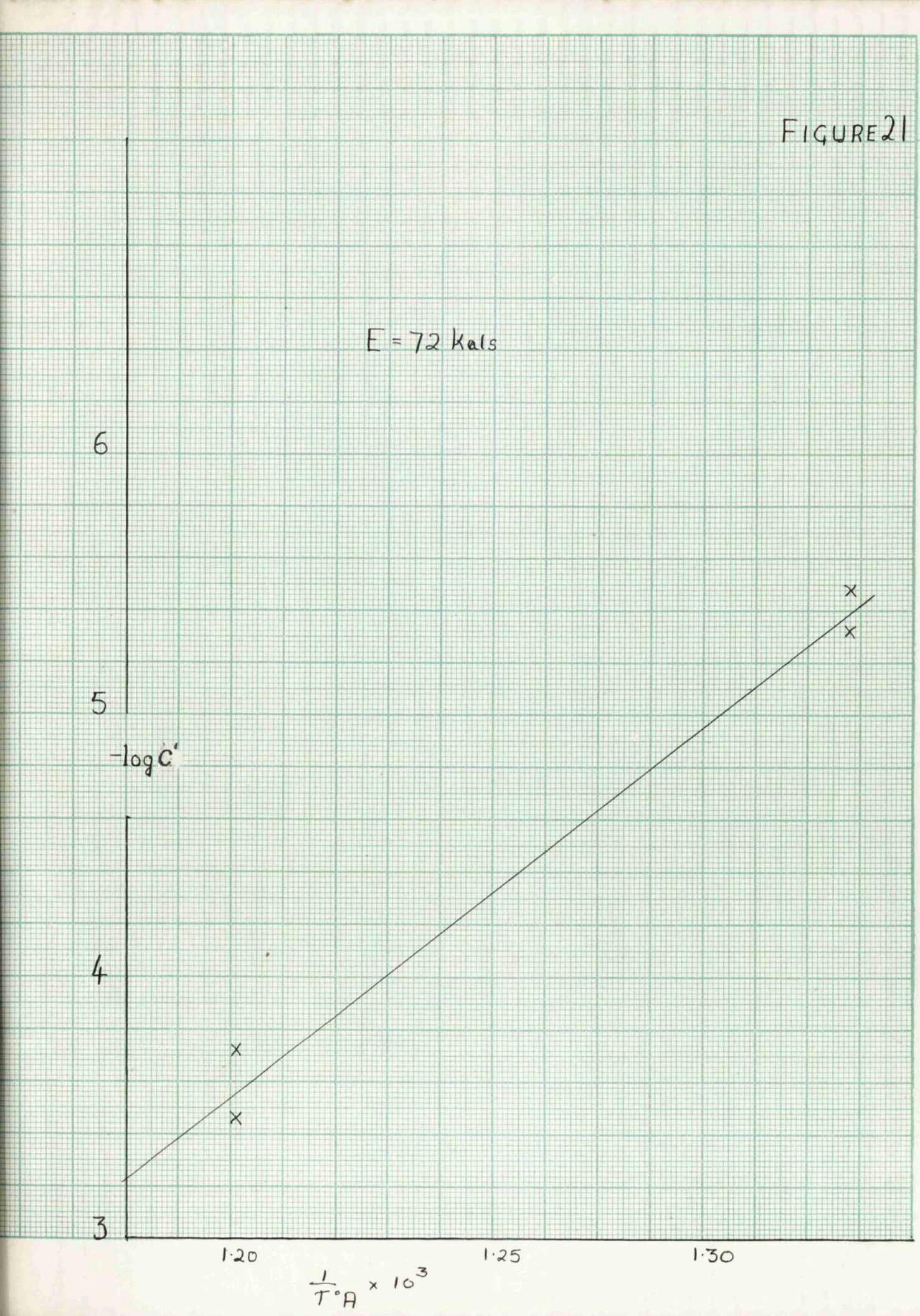
to 2.06 mm CH_3I gave values of k_1 varying from 1.4×10^{-3} to 2.3×10^{-3}. The values of C'' evaluated for these limits of the CH_3I range were 23.6×10^{-14} and 30.6×10^{-14}. It is clear that a firm distinction cannot be drawn from the existing data and a decision would require substantial experimentation with added iodine to demonstrate the equilibrium effect.

An alternative mode of removal of the methyl radicals from the proposed equilibrium would be reaction with methyl iodide in a scheme of reactions as discussed above. Such a scheme would give $\frac{dx}{dt} = k^\circ \underline{(CH_3)(CH_3I)} = k^\circ (\underline{CH_3I}) K \frac{(CH_3I)}{(I)}$

therefore $\frac{dx}{dt} = C' \frac{(a-x)^2}{\alpha x}$

This scheme seems more likely in view of the higher concentrati of methyl iodide but the activation energy of this step may well be higher. To test the equation and its consequences the value of C' was calculated for the two extremes of CH_3I pressure used previously. The results were 4.89×10^{-6} and 3.57×10^{-6}, again showing the insensitivity of the data to even a threefold variation in 'a'. The constant C' was also evaluated at the extremes of the temperature range and log C' plotted against 1/T°A in Figure 21. The activation energy in this case was approximately 72 K. cals, this energy is for $E^\circ + \Delta H$ where E° is the energy for $CH_3 + CH_3I$ and ΔH has the same meaning as before. If ΔH is taken as 55 K. cals it would

FIGURE 21



mean E° was of the order of 17 K.cals, and it has been shown in the earlier calculations that a methyl radical diffusing to the wall through 600 mms of nitrogen makes sufficient collisions with the methyl iodide to react under such conditions.

A choice between these alternative methods of removing the methyl radicals cannot be made on the basis of the existing data and approximations involved. Either scheme is sufficient to deal with the problem of the low apparent activation energy based on first order analysis and the fall in rate compared to the parallel experiments with added toluene.

(c) With added Nitric Oxide.

In the present work the addition of nitric oxide to the high pressure of nitrogen had no influence, the data falling in line with the rest and the activation energy being similar (Figure 18). The evidence in the literature[30] on the action of nitric oxide is mainly concerned with its action in chain reactions and even then is conflicting. Some reactions not inhibited by nitric oxide are inhibited by propylene, so that its value as a test for free radicals is not very clear.

At low total pressures, work done at Sheffield did show some effect. The percentage decomposition remained reasonably constant for partial pressures of methyl iodide above 0.15 mm of CH_3I when using nitric oxide instead of nitrogen as a carrier gas. The rate of decomposition rose about 2.5 times compared to the parallel nitrogen experiments and rose quite uniformly in 0-100% nitric

oxide in nitrogen mixtures. These facts could be explained by a Lindemann mechanism if we assume that the nitric oxide makes efficient energising collisions with methyl iodide. It is well known that the efficiencies for this purpose vary considerably. On any other basis it is difficult to present a precise interpretation. If the nitric oxide formed a complex with the free radical it could only increase the rate by protecting the radicals from reaction at the wall and permitting a bigger concentration of radicals to build up and so increase the iodine production by secondary reactions. This is however entirely without proof. The energy of activation rose to 60-65 K.cals and the frequency factor to 10^{14}-10^{15} when 3mms of nitric oxide were used as a carrier gas, and the possibility of a bimolecular oxidation proceeding at the same time as the first order decomposition should not be overlooked.

From the point of view of the present work this previous data throws little light on the nitric oxide problem. In fact the absence of any effect of nitric oxide at high pressures might well be passed over were it not for the previous results described above. The difference cannot be ascribed to a difference in the nitric oxide sample as the same bulb was used, having been brought from Sheffield.

Experiments with a Low Pressure of Carrier Gas.

These experiments were the starting point of this work since the technique arose out of Butler and Polanyi's original experiments. The work reported in earlier pages aimed at extending the knowledge acquired at Sheffield, and in the following discussion an attempt is made to consider the whole field of data. The salient features requiring explanation are more numerous than in the cases discussed above.

Some degree of surface reaction is evident but the reaction appears predominately homogeneous, (Figure 11). The % decomposition under given conditions of temperature and time of reaction rose considerably with increasing pressure of methyl iodide or nitrogen, (Figures 12 and 13). The rate constants calculated on a first order basis show the reaction under these conditions to be five times slower when the methyl iodide pressure was 1 mm and fifteen times slower with 0.3mms halide than the rate using 600 mms N_2 with added toluene. In this there is some resemblance to the case of 600 mms N_2 only but the temperature coefficients of these two cases differ markedly, since the low pressure experiments have an apparent activation energy of 53-58 K.cals if calculated on a first order basis as compared to the value of 36 K.cals obtained with high pressure nitrogen. Clearly this difference prohibits a common explanation for both cases.

It is known from the earlier work at Sheffield that added toluene speeded up the production of iodine at these low pressures by a factor of two but even in the presence of toluene the same type of variation of k_1 with increasing partial pressure of halide was observed (Figure 22). Since dibenzyl and stilbene were produced under these conditions it seems correct to regard the mechanism as involving free radicals.

As in the previous sections it is necessary to consider the fate of the methyl radical formed by the primary dissociation of the methyl iodide. From the point of view of relative concentrations the most likely reaction partner is methyl iodide and the possibilities can be listed below :-

$$CH_3 + 3CH_3I \longrightarrow 3CH_4 + C + 3I \quad \text{in a series of steps} \quad (1)$$

$$CH_3 + I + (N_2) \longrightarrow CH_3I + (N_2) \quad (2)$$

$$CH_3 + I_2 \longrightarrow CH_3I + I \quad (3)$$

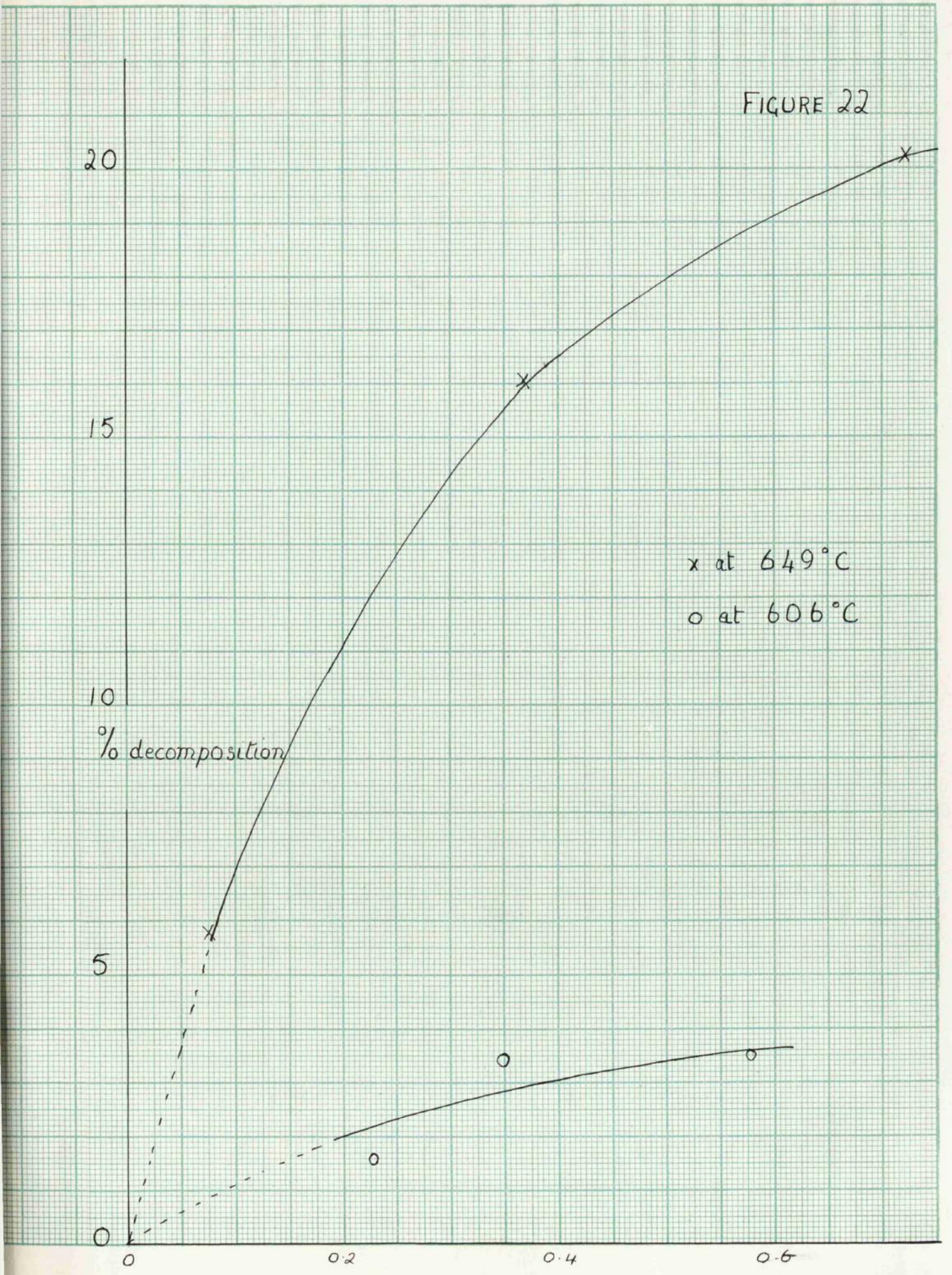
$$CH_3 + 3CH_3 \longrightarrow CH_4 + C \quad \text{in a series of steps} \quad (4)$$

Any of these reactions occurring on the wall (5)

The 3-4 mms of nitrogen used in these experiments will reduce the rate of (2) by 150-200 fold compared with the experiments at 600 mms, the calculations given earlier on the proportion of three body collisions suggest that the heterogeneous mechanisms of (5) would be more important than (2) at these pressures.

Reaction (4) involving the collision of two methyl radicals

FIGURE 22


20
15
10
5
0
% decomposition
x at 649°C
o at 606°C
0
0·2
0·4
0·6
Partial Pressure mms

cannot be very frequent as the radical concentration should be low, particularly if reaction at the wall is fairly rapid. As shown in the previous calculations the alteration from 600 mms pressure to 4 mms reduces the collisions made before reaching the wall by 22,500 times, $(600/4)^2$, and so increases the chances of (5) superseding (4). Paneth and Lautsch[84] found that methyl radicals had a longer life when the walls of the tube were hot and could make up to 1000 collisions with the wall before decomposing; however, this may not be very applicable in this case where the walls are coated with carbon formed during the reaction. Adsorption of methyl radicals and iodine atoms seems more likely in this case than on a clean glass surface.

It was shown in the previous calculations that the average number of collisions by the radical on the way to the wall were sufficient to ensure reaction with methyl iodide even if the activation energy of (1) were as high as 17 K.cals. Such a calculation is rather rough but it shows that there is a reasonable chance of removing the methyl radicals by this reaction. If this is the case the percentage decomposition would increase as the concentration of the methyl iodide increases. This suggests an explanation for the results of Figure 12, the interpretation being that over 1 mm halide pressure the capture of radicals is nearing completion and that at lower pressures

reaction (1) was less in evidence. This assumed that the radicals not reacting at 0.2 mms methyl iodide reached the wall and there reacted by a heterogeneous analogue of (4). If they recombined with iodine a greater decrease in % decomposition should follow. Such a scheme as this would lead to an asymptotic rise to a limiting percentage decomposition covering the range x% - 4x%. The data observed lie within these limits.

But the addition of toluene in some Sheffield experiments raised the percentage decomposition by a factor of about two. In view of the more recent experience with toluene as a radical acceptor, and the general agreement that the removal of one hydrogen atom from its side chain is a relatively easy process we would expect methyl radicals to react preferentially with toluene when it is present in equal concentration with methyl iodide. Certainly the behaviour in the high nitrogen pressure experiments suggests that this is the case. Moreover in the particular experiments we refer to, the production of carbon dropped and of methane rose, as if the methyl radicals formed methane and dibenzyl as postulated previously. If preferential capture of the methyl radicals did occur reaction (1) should be inhibited and a smaller percentage decomposition should result. It could be argued that not only is reaction (1) inhibited by prior removal of the radicals but that the same would apply to reaction (2) and (3) - the recombination reactions - and that

the overall result would be to raise the percentage decomposition But a fact which is more difficult to explain is that, in the presence of toluene, the percentage decomposition still rises when the partial pressure of the methyl iodide is increased (Figure 22). If preferential reaction with toluene was effective then this should not happen as a result of reaction(1).

The suggestion made above that reactions (2) or (3) could be substantially inhibited by the addition of toluene assumes that they exist in its absence. Arguments against (3) have been advanced earlier and against (2) there is the fact that at these pressures it could not occur by homogeneous three body collisions. Further evidence against the occurrence of reactions (2) and (3) is provided by a test made at Sheffield, of the effect of adding iodine to the carrier gas. The results obtained are reproduced below :-

Table 18

Temperature °C	Contact Time secs	Pressure of CH_3I mms	Pressure of added I_2 mms	% decomposition
649	1.02	0.17	0.06	10.85
649	0.90	0.17	—	12.4
626	0.98	0.17	0.059	3.85
626	0.94	0.22	—	4.5
635	0.95	0.17	0.059	6.4
635	0.86	0.18	—	8.0

The proportion of iodine added was such that the total iodine

present throughout the passage of the gas through the furnace was some 3-7 times the concentration reached at the exit of the furnace in the usual experiments. Calculation of the degree of dissociation of the iodine showed that the concentration of iodine atoms was over double that normally occurring in the usual experiments. In view of this the slight retardation observed argues strongly against any appreciable recombination at these low pressures. The only way to avoid such a conclusion is to postulate a wall saturated with iodine as an absorbed layer at very low partial pressures of iodine, and say that recombination occurred entirely on the walls of the vessel. This does not seem very plausible and does not fit in with the accelerating influence of an increased surface. Moreover if substantial recombination takes place on the walls at these low pressures then the rate of rection (1) must be governed by a rather high activation energy of an unusually high steric factor. There is the fact that the rate of decomposition at low pressure is much lower than at high pressure (Table 17) which calls for some explanation. To suggest a 5 to 15 fold decrease in rate is caused by a high rate of recombination at the wall increases the difficulty of interpreting the low pressure results and correlating them to the high pressure ones.

In looking for some other explanation of the results the graph of Figure 12 suggests the possibility that at low partial

pressures the reaction is bimolecular and changes over to unimolecular at higher methyl iodide pressures. This can be explained on the usual Lindemann-Hinshelwood[84] mechanism for the production of activated molecules by collision

$$A + A \underset{k_1}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_2} \text{Products}$$

with the appropriate rate constants as indicated. It is also necessary to consider the collisions between the inert gas and A and include the further scheme

$$A + X \underset{k_x'}{\overset{k_x}{\rightleftharpoons}} A^* + X$$

$$A^* \xrightarrow{k_2} \text{Products}$$

from this we have

$$\frac{dA^*}{dt} = k_1(A)^2 - k_1'(A^*)(A) + k_x(A)(X) - k_x'(A^*)(X) - k_2(A^*)$$

At the stationary state $\frac{dA^*}{dt} = 0$

$$\therefore \quad (A^*)\left[k_1'(A) + k_x'(X) + k_2\right] = k_1(A)^2 + k_x(A)(X)$$

$$\therefore \quad (A^*) = \frac{k_1(A)^2 + k_x(A)(X)}{k_1'(A) + k_x'(X) + k_2}$$

Rate of reaction $-\frac{dx}{dt} = k_{uni}(A) = k_2(A^*)$

$$\therefore \quad \frac{1}{k_{uni}} = \frac{1}{k_2} \cdot \frac{k_1'(A) + k_x'(X) + k_2}{k_1(A) + k_x(X)}$$

As it stands in this scheme A would be methyl iodide and X would be nitrogen in most cases. The scheme however, has too many constants in it for simple treatment unless a knowledge of k_{uni} - the experimental first order constant is available over wide ranges of independent variation of the concentrations of A and X. It is known that the efficiency of energy exchange

between molecules varies with the nature of the colliding particles and a simple approximation would be to put

$$\frac{k_x}{k_1} = \alpha = \frac{k'}{k'_1}$$

In this case the previous equation reduces to :-

$$\frac{1}{k_{uni}} = \frac{1}{k_2}\,\frac{k'_1\left[(A)+\alpha(X)\right]+k_2}{k_1\left[(A)+\alpha(X)\right]}$$

$$= \frac{k'_1}{k_2k_1} + \frac{1}{k_1\left[(A)+\alpha(X)\right]}$$

If we can assess a figure for α this equation can be applied to experimental data at a fixed temperature. The data from which graphs 12 and 13 are plotted give that at 649°C we have for 4.5 mms N_2 and 0.46 mms CH_3I, $k_{uni} = 0.18$ while for 6 mms N_2 and 0.18 mms CH_3I, $k_{uni} = 0.18$. We can therefore say

$$\frac{1}{0.46 + 4.5\alpha} = \frac{1}{0.18 + 6\alpha}$$

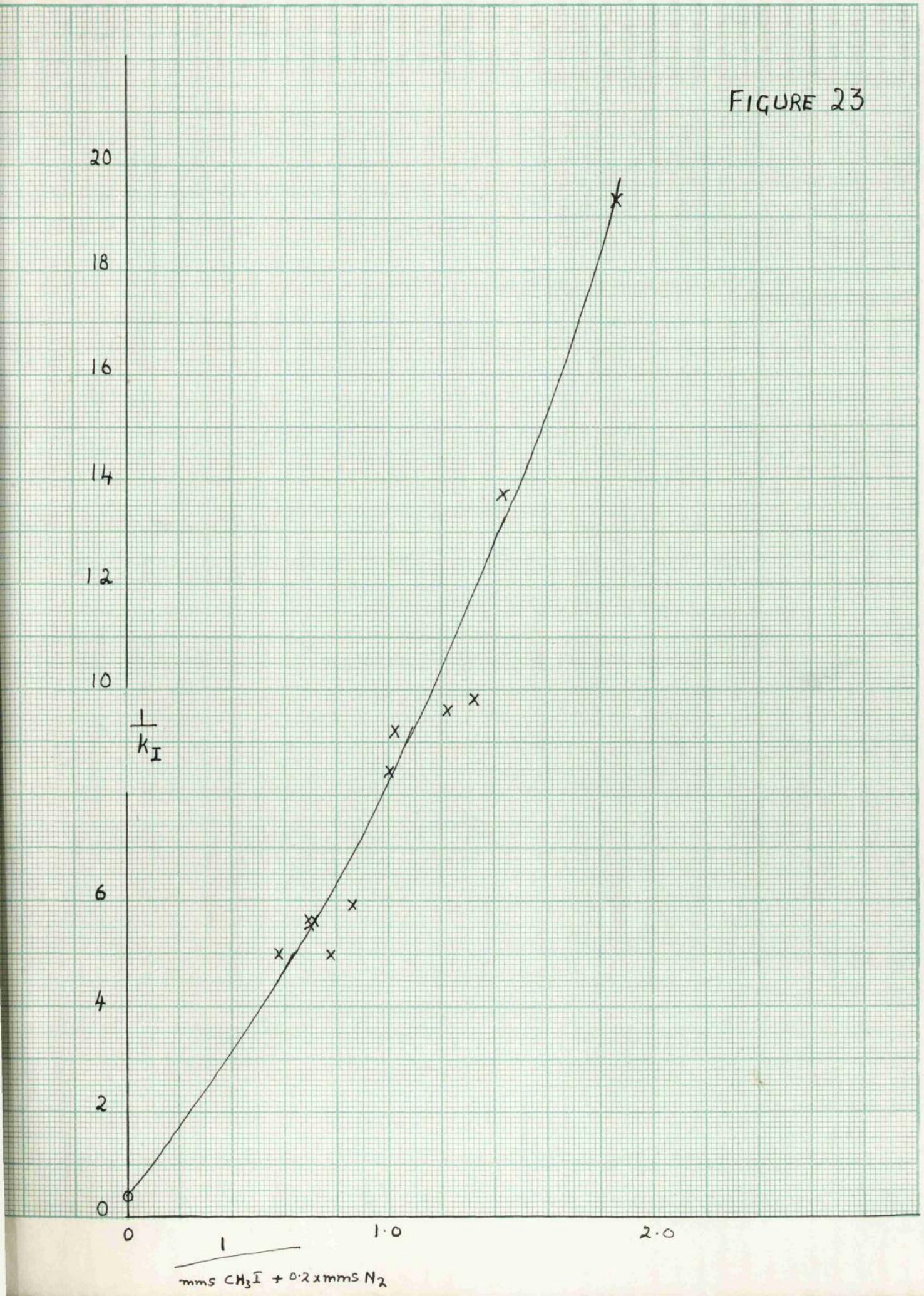
$$\therefore \quad \alpha = 0.2$$

This would mean that collision with nitrogen was only 1/5 as efficient as collisions with methyl iodide. Using this we can test the equation by plotting $1/k_{uni}$ against $\frac{1}{\text{mms}CH_3I + 0.2\ N_2}$ This has been done in figure 23.

The data at low pressure should give an intercept on the ordinate for the limiting high pressure value of $1/k_{uni}$. The value of 2.65 for k_{uni} at 649°C for a high pressure of nitrogen has been obtained by extrapolation in the equation

$$k_{uni} = 2.63 \times 10^{13}\ e^{-54700/RT}$$

FIGURE 23


20
18
16
14
12
10
$\frac{1}{k_I}$
6
4
2
0
0
1·0
2·0
$\frac{1}{\text{mms } CH_3I + 0{\cdot}2 \times \text{mms } N_2}$

The resulting graph is not quite linear but it is very much better than many cases examined in the past. It is doubtful in fact if there is any case of an indisputable check on this equation due to complications in the mechanisms of the reactions to which it has been applied. The range of the variables in this testtis considerable, and it must be emphasised that the highest values of $1/k_{uni}$, which lie somewhat off a linear plot refer to the lowest partial pressure of methyl iodide and are therefore not of the highest experimental accuracy. A further point is that a variation in the extent of reaction (1) will be more likely at these pressures and the resulting decrease in k_{uni} will enhance the value of $1/k_{uni}$. The graph is not very sensitive to values of α near 0.2 but with $\alpha = 0.1$ the curvature was very marked.

The slope of a linear plot should give $1/k_1$, the bimolecular constant for activation by collision of methyl iodide molecules. Taking from the graph $k_1 = 1/8$ and converting from the mms of Hg^{-1} in which the abscissa are plotted we get

$$k_1 = 57500/8 \approx 7 \times 10^3$$

with concentrations in moles/ litre. If we apply the usual Polanyi-Hinselwood[86] formula

$$k_1 = Z \left(\frac{E}{RT}\right)^{1/2n - 1} \frac{1}{\lfloor 1/2n - 1} e^{-E/RT}$$

with $E = E_{experimental} + (1/2n - 1)RT$

we can calculate the maximum rate of activation using n square terms. For a molecule containing five atoms we can take the permissible fundemental vibrations as equal to $[(3x5) - 6]$, hence giving 18 square terms . The second and third terms of the above expression for T = 922°A become $= \left(\frac{55000 + 14560}{1820}\right)^{8} \times \frac{1}{\lfloor 8} = 10^{8}$

so that k_1 now becomes approximately

$$k_1 = 10^{11 \text{ to } 12} \times 10^{8} \times 10^{-38/2.3} = 10^{2.5 \text{to} 3.5}$$

Thus to accomodate a k_1 as high as derived for the graph we need to set 'n' at its maximum value for methyl iodide.

The effect of increasing the nitrogen pressure is most readily understood in these terms. In Figure 13 it is difficult to see any sign of the percentage decomposition reaching a limiting value as the pressure of nitrogen is increased, even though the range is limited. If bimolecular activation were taking place this is what might be expected since as the pressure increased so would the rate of activation. The effect of toluene under the postulates of this second view point could be twofold. It will certainly act as a radical acceptor but it would also be very likely to act as a very efficient energy exchanger in the bimolecular activation of the methyl iodide. It is known for instance that benzene acts as a very efficient third body in halogen atom recombinations[79].

Experiments without a Carrier Gas.

Reproducibility was good in this series of experiments but the results seem to fall intermediately in interpretation to the cases discussed above. The partial pressure of methyl iodide used, 4 - 11 mms, would be expected to give a rather higher rate of decomposition to be in line with the previous discussion on the effect of total pressure. Judging by the data at 800°A (Table 17) the apparent first order constant lies mid-way between the low pressure and high pressure and toluene experiments. An extrapolated value of the first order constant at 649°C is not of much value for insertion in Figure 23 since the apparent activation energy is 41.6 K.cals and is consequently anomalous like the high pressure of nitrogen without toluene. An interpretation of this can be made on the same lines as previously, by postulating some degree of recombination and the need to remove the radicals from the system

$$CH_3I \rightleftharpoons CH_3 + I$$

It is clear however that the case is not the same as the experiments with 600 mms of nitrogen since some effect of the surface/volume ratio exists. The graph of the surface to volume ratio against k_1 shows that the heterogeneous reaction is a minor part of the whole and the analysis of the data in Figure 17 shows that the activation energies of the

homogeneous and heterogeneous reactions are of the same order. From this we might conclude that the primary rate determining step is the same in the packed and unpacked furnace and that the extent of surface alters the balance of the subsequent reactions.

Some calculations have been made using the scheme considered previously for 600 mms of nitrogen, that is

$$CH_3I \rightleftharpoons CH_3 + I \rightleftharpoons I_2$$
$$\downarrow CH_3I$$
$$CH_4 + C + I$$

The integration of the constant in the equation

$$\frac{dx}{dt} = C' \frac{(a-x)^2}{\alpha x}$$

has been done graphically as before (see Appendix) for the two extreme cases of experiments 149 and 167 where the halide pressure varied from 4 mms to 11 mms, the results are

Expt	mms CH_3I	% decomposition	k_1	C'
149	4.15	0.90	5.1×10^{-3}	4.89×10^{-6}
167	11.2	1.23	5.5×10^{-3}	4.1×10^{-6}

Thus although the values for k_1 are rather closer together no real distinction can be made between these radically different mechanisms.

It is of interest to note that the value of 42 K.cals obtained for the activation energy on a first order basis is close to that obtained by Ogg[44] for the value of the C-I bond

energy in methyl iodide; this value of 43 K.cals has now been discredited. He obtained it from a consideration of the reaction $CH_3I + HI \longrightarrow CH_4 + I_2$ under conditions where the production of iodine was considerable and concluded that the rate determining step was the decomposition of the methyl iodide. It is possible that inadequate allowance was made for any back reaction.

Surface Effects.

The part played by the surface in reactions involving free radicals and atoms is not easy to distinguish from a normal heterogeneous decomposition of the parent molecule. Undoubtedly surfaces assist the combination of free radicals and molecules but the present case illustrates some of the prevalent difficulties. If we assume that equal numbers of methyl radicals and iodine atoms impinge on the wall we have no real basis for assuming either

$$CH_3 + I \longrightarrow CH_3I \qquad (1)$$

or

$$4CH_3 \longrightarrow 3CH_4 + C \qquad (2)$$

or

$$I + I \longrightarrow I_2 \qquad (3)$$

as the preferred reaction. So far as we know (2) is irreversible and an equivalent amount of iodine is found. Reaction (3) can also be regarded somewhat similarily as the final stage in the overall decomposition but in this case it is not so crucial as (2) in that it might undergo reconversion to methyl iodide as a result of attack by a methyl radical.

Quite apart from this possibility of selective action by the surface the other way in which the surface can alter the balance of the secondary reactions can be seen in the following considerations. Consider the radicals to be diffusing from the reaction space to two parallel walls distance d apart ~~if we~~ and then insert between these walls an additional surface which because of its two sides exposes a surface equal to the original one. Then the actual collisions with the surface will be increased two times but also there will be a difference in the number of collisions that the average particle makes before reaching the surface. In the original conditions the distance the particle diffused was d/2 and the number of collisions was proportioal to $d^2/4$ whereas with the packing the number of collisions is reduced to a number proportional to $d^2/16$. Thus the collisions at the surface are doubled and the particle makes 1/4 of the previous collisione before reaching the wall.

Referring to the experimental data in the light of these considerations the rise in iodine production might be caused by (a) a genuine heterogeneous decomposition of methyl iodide on the wall or (b) a preferential action on the reactions by which methyl radicals are removed excluding recombination reactions. If (a) were the case then some effect of surface should have been observed with high pressures of nitrogen

although it would be reduced by the lesser accessibility of the surface. The reasons for introducing the higher pressure of nitrogen rested on the hope of some action of this kind. Thus (b) has some support both on these grounds and also on the approximate identity of the activation energy for the homogeneous and heterogeneous reactions.

It would be expected that when a surface accelerates a reaction by facilitating the removal of radicals that lowering the pressure of the inert gas would increase the rate of reaction. In fact the opposite was the case and the possible reasons for the effect of ingreased pressure have been discussed above.

In the literature various cases where a carbon coating on the walls of the reaction vessel was found to have an effect have been reported. The data is not very consistent, for example Daniels and Veltmann[87] in studying the decomposition of ethyl bromide and Barton and Onyon[88] in studying the decomposition of t-butyl chloride both found that the results were more reproducible in a carbon coated furnace and that such a coating reduced the reaction rate. But whilst in the former case only some two or three runs were required to produce sufficient carbon for reproducibility in the latter case some thirty runs were needed to get a good result.

In the case of methyl iodide the deposition of carbon is

an integral part of the reaction which means that the surface is being continually renewed and there would be little point in precoating the surface as it could not be maintained stable. Moreover, in this case the effect of the carbon seems to be catalytic although it does produce more reproducible results.

Conclusions

(1) In the decomposition of methyl iodide you get a primary dissociation into a free methyl radical and iodine atom; there is, however, no chain reaction leading to decomposition as the fastest rate occurs in the presence of toluene as radical acceptor.

(2) The rate of reaction in the system, 600 mm. nitrogen, 1-2 mm. toluene, and about 1 mm. CH_3I was given by $k_I = 10^{13.7} e^{\frac{-54,700}{RT}}$. This energy of activation is in good agreement with recent values for the C-I bond energy in methyl iodide and the frequency factor is in line with theoretical expectations.

(3) In the above conditions, but with the radical acceptor omitted, the use of first order calculations would lead to a rate constant = $10^{7.55} e^{\frac{-35,800}{RT}}$. It is suggested that to explain the reduced rate compared with (2) that a considerable reverse reaction exists CH_3I (+ N_2) $\rightleftarrows$ CH_3 + I (+ N_2) and that the frequency of removal of methyl radicals becomes important. First order constants, although apparently valid, would not be sufficiently sensitive to detect the error and the mechanism - would give reasonable values for the energies of activation involved.

No surface effect exists in (2) or (3). Nitric oxide additions were without effect in (3).

(4) At pressures of nitrogen of 2-9 mm. and methyl iodide partial pressures of 0.2-1.3 mm. additional reaction features are in evidence. Some surface effect is shown but the reaction is predominantly homogeneous. The activation energies determined from first order rate constants are in the region

53-58. K.cals. Rates of reaction are much slower at the same temperature than in (2). They are increased by increasing the concentration of methyl iodide, behaviour being near second order at the lowest partial pressures, rising to nearer first order over 1 mm. The rate also increased with nitrogen pressure. A discussion of possible secondary reactions and the usual Lindemann mechanism have been applied to the problem. It is considered the latter offers the simplest explanation of the broad features of the data on comparative rates under conditions (2) and all the variations tried in (4).

(5) It is probable that in low and high pressure experiments the energy of activation is for the same process - the dissociation of the C-I link, but in view of the dependence of rate constants on conditions at low total pressures the Butler - Polanyi technique for methyl iodide is not very satisfactory.

APPENDIX

Calculation of Constants from $\frac{dx}{dt} = k \frac{(a-x)^2}{\propto x}$ etc:.

The method of calculation of the constants for the reaction schemes

a) $CH_3I \rightleftharpoons CH_3 + I \rightleftharpoons I_2$ (1)

$CH_3 + CH_3I \rightarrow CH_4 + C + I$

b) $CH_3I \rightleftharpoons CH_3 + I \rightleftharpoons I_2$ (2)

$CH_3 + CH_3 \rightarrow CH_4 + C$

requires a) $-\frac{d(CH_3)}{dt} = k' (CH_3) (CH_3I)$ (3)

b) $-\frac{d(CH_3)}{dt} = k'' (CH_3)^2$ (4)

in both cases it is postulated that

$$\frac{(CH_3)(I)}{(CH_3I)} = K \quad (5)$$

and that $$\frac{(I)^2}{(I_2)} = K_{I_2} \quad (6)$$

Therefore we have

a) $-\frac{d(CH_3)}{dt} = k' K \frac{(CH_3I)^2}{(I)}$ or $-\frac{dx}{dt} = C' \frac{(a-x)^2}{\propto x}$ (7)

b) $-\frac{d(CH_3)}{dt} = k'' K^2 \frac{(CH_3I)^2}{(I)^3}$ or $-\frac{dx}{dt} = C'' \frac{(a-x)^2}{\propto^2 x^2}$ (8)

In these equations $\propto x$ is the gm-atoms/litre of iodine assuming equilibration of the iodine atoms formed during

the decomposition, so that:-

$$\frac{\alpha^2 x^2}{(1-\alpha)x} = K_{I_2} \quad \text{or} \quad \frac{\alpha^2 P_I^2}{(1-\alpha)\frac{P_I}{2}} = K_p \qquad (9)$$

where P_I is the pressure in atmospheres of the iodine if it were all present as atoms. Equation (9) can be written:-

$$\log K_p = \log \frac{\alpha^2}{(1-\alpha)} + \log P_I + \log 2 \qquad (10)$$

and for a particular value of P_I and a particular temperature we can find the value of α by use of equation (10) and Bodenstein's formula:-

$$\log K_p = -\frac{7550}{T} + 1.75 \log T - 4.09 \times 10^{-4} T + 4.726 \times 10^{-4} T^2 - 0.440 \qquad (11)$$

where T is in °A.

Certain values of $\log K_p$ were calculated and plotted against temperature so that a value of $\log K_p$ for any particular temperature could be obtained.

Temp °A	800	850	900	950
$\log K_p$	-5.096	-4.514	-3.990	-3.527

Knowing $\log K_p$ at temperature T°A and the value of P_I for a particular experiment a value of $\log \frac{\alpha^2}{(1-\alpha)}$ could be derived from equation (10). By use of a graph of $\log \frac{\alpha^2}{(1-\alpha)}$ against α a value for α was obtained.

Cases (a) and (b) can be written:-

(a) $$\int_0^x \frac{\alpha x}{(a-x)^2}\, dx = C' \int_0^t dt \qquad (b) \int_0^x \frac{\alpha^2 x^2}{(a-x)^2} dx = C'' \int_0^t dt$$

In order to integrate (a) a graph of $\left[\frac{\alpha x}{(a-x)^2}\right]$ against x was prepared for values of x from zero to the value at the end of the particular experiment and the area under the curve found. This divided by t gives C'. The case

of (b) is treated similarly.

A detailed example is given below.

This graphical method is necessary as the dependence of α on x is complicated and the integrated form quite unsuitable for computations.

Expt. 345 Temp. 487°C ≡ 760°K $\therefore \frac{1}{T°K} = 1.3175 \times 10^{-3}$ mm. $CH_3I = 2.06$

% decomposition = 2.14

P_I at exit of furnace $= \frac{2.06}{760} \times \frac{2.14}{100}$ atms. $= 5.8 \times 10^{-5}$ atms.

$\log P_I = 5.763 = -4.237$

At 760°K $\log K_p$ (atms.) for Iodine = -5.70

$\therefore -5.70 = \log \frac{\alpha^2}{1-\alpha} - 4.237 + 0.3010$

$\log \left(\frac{\alpha^2}{1-\alpha}\right) = -1.764$ $\qquad \therefore \alpha = 0.13$

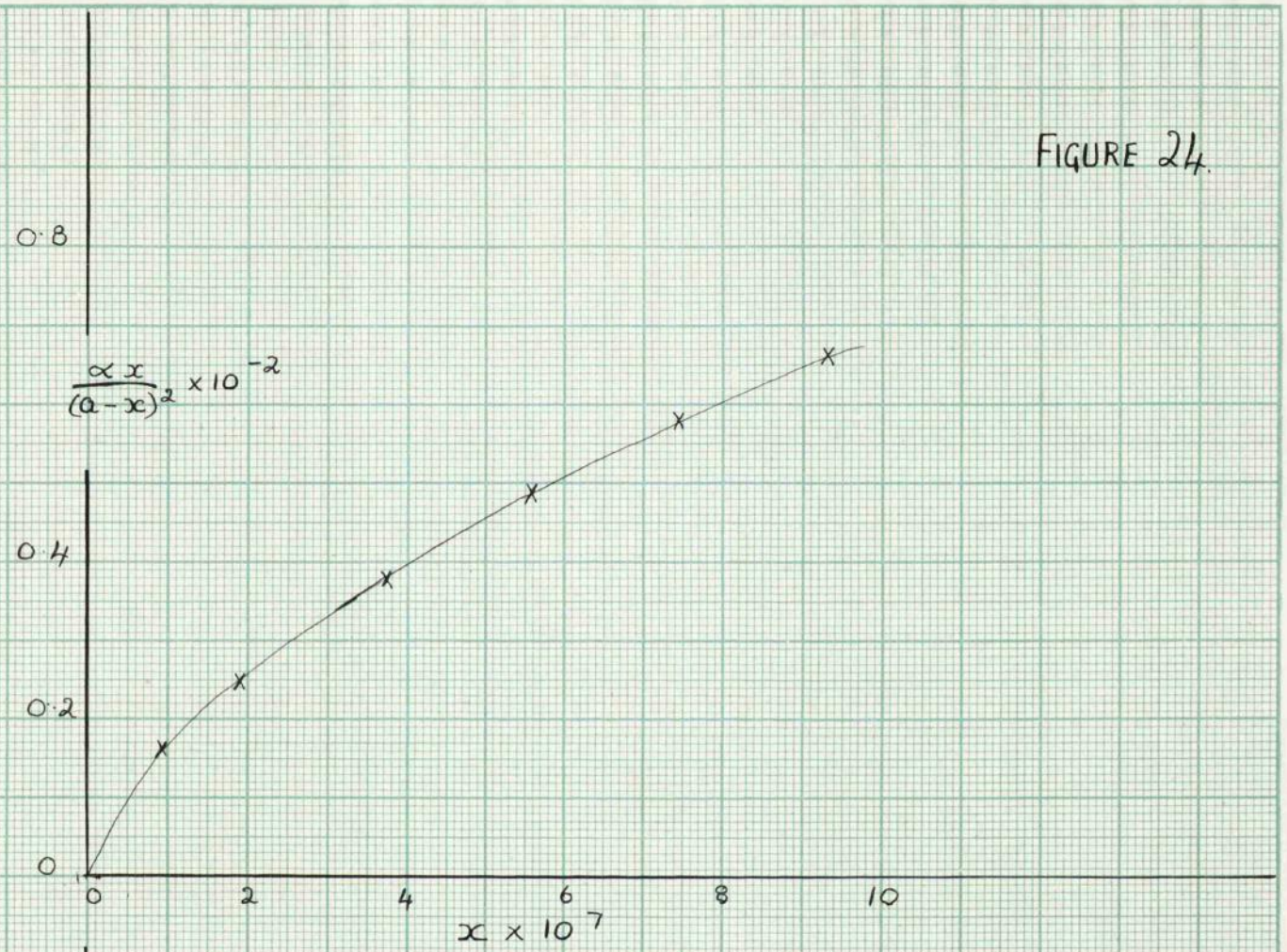
"a" moles/l CH_3I for this experiment

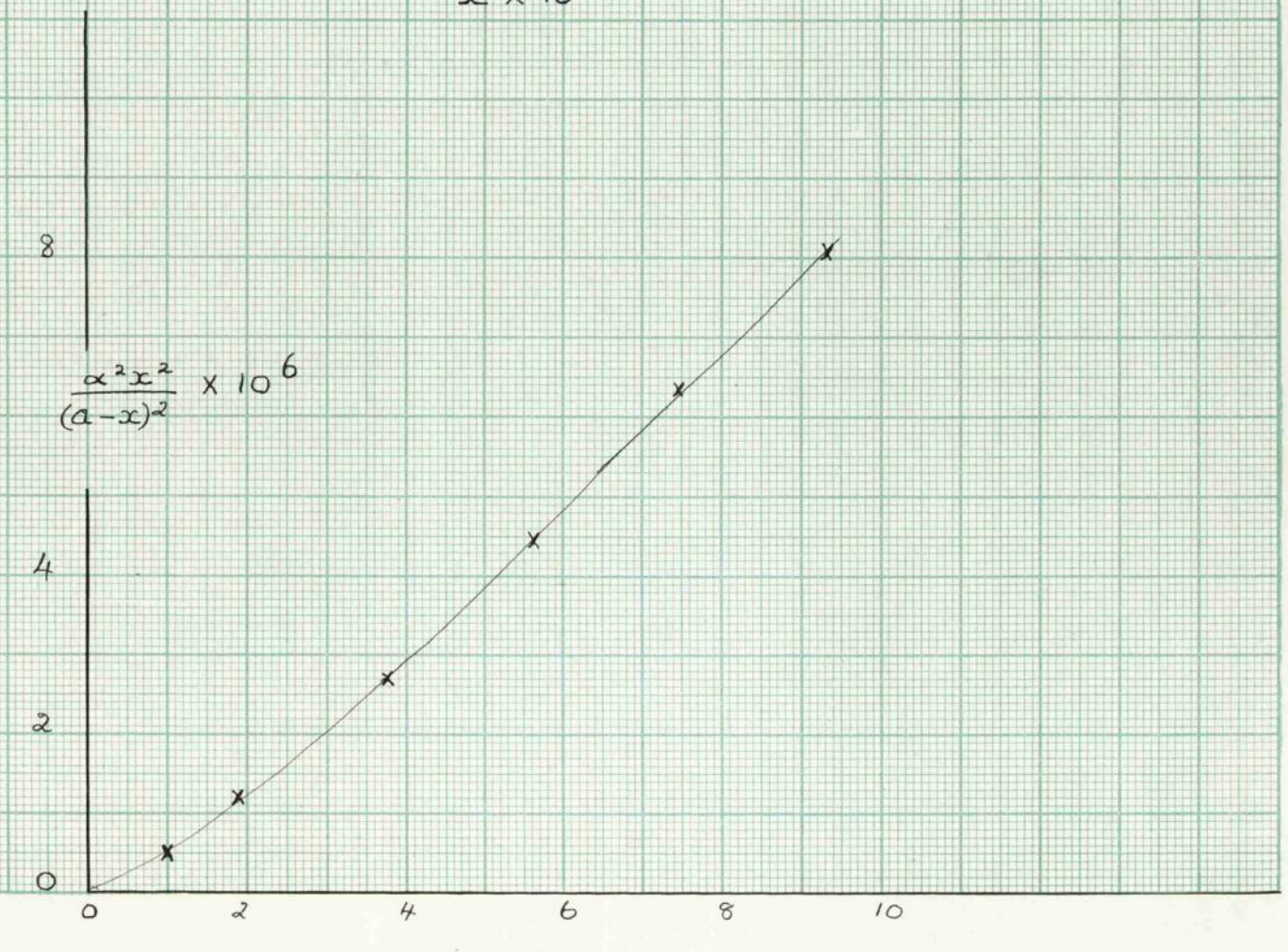
$= \frac{2.06}{760} \times \frac{273}{22.4 \times 760} = 4.35 \times 10^{-5}$ moles/l

Iodine Pressure	$\log\left(\frac{\alpha^2}{1-\alpha}\right)$	α	$\frac{x}{\left(\frac{a\ z\%}{100}\right)}$	$(a-x)^2$	αx	$\left(\frac{\alpha x}{a-x}\right)^2$	$\frac{\alpha^2 x^2}{(a-x)^2}$
P final	-1.764	0.13	9.31×10^{-7}	18.15×10^{-10}	1.21×10^{-7}	0.667×10^{2}	$8.05 \times 10^{-}$
0.8 P_I final	-1.668	0.145	7.45	18.4	1.08	0.587	6.35
0.6 "	-1.554	0.162	5.59	18.5	0.907	0.490	4.45
0.4 "	-1.36	0.19	3.73	18.6	0.709	0.381	2.70
0.2 "	-1.064	0.255	1.86	18.8	0.474	0.252	1.20
0.1 "	-0.764	0.34	0.93	18.9	0.316	0.167	0.529

The data of the 4th column is graphed against that in the last two columns in Fig. 24 A and B. The area under each curve was found by the usual

FIGURE 24.


0·8
0·4
0·2
0
$\frac{\alpha x}{(a-x)^2} \times 10^{-2}$
0
2
4
6
8
10
$x \times 10^7$


8
4
2
0
$\frac{\alpha^2 x^2}{(a-x)^2} \times 10^6$
0
2
4
6
8
10
$x \times 10^7$

methods of dividing it up for suitable x intervals and treating each section as a simple geometrical figure. The area under Fig. 24 A is $\int_0^x \frac{\alpha x}{(a-x)} 2\, dx$ and since this is C′t and t = 10.8 the value of C′ = 3.57×10^{-6} sec^{-1}. Similarly from Fig. 24 B. C″ = 3.06×10^{-13} mols. l^{-1} sec^{-1}.

This method has been applied to relevant experiments and results derived are quoted below.

Expt. No.	°K	C′	C″
		sec^{-1}	mol. l^{-1} sec^{-1}
345	760	3.57×10^{-6}	3.06×10^{-13}
358	808		2.34×10^{-11}
366	767		3.46×10^{-13}
353	781		1.605×10^{-12}
364	832	1.87×10^{-4}	7.8×10^{-11}
363	832	3.37×10^{-4}	1.81×10^{-10}
327	760	4.89×10^{-6}	2.36×10^{-13}
149	772	4.89×10^{-6}	4.46×10^{-13}
167	772	4.1×10^{-6}	8.27×10^{-13}
177	833	2.36×10^{-4}	
174	811	5.36×10^{-5}	

The following tables are a complete list of all the experiments referred to in the text from which further calculations can be made

Experiments with a low pressure of nitrogen.

Expt No	Temp °C	Contact Time secs	Average Pressure mms	Partial Pressure of HeI mms	S/V	Time of run (secs)	% decomposition	k_1
1	641	1.11	3.4	0.30	2.2	720	19.3	0.19
2	641	0.97	3.8	0.27		720	15.2	0.17
4	638	0.93	4.0	0.23		900	13.0	0.15
5	638	0.87	4.3	0.21		900	10.6	0.13
7	613	0.87	4.5	0.21		1200	4.6	0.054
8	578	1.06	3.8	0.21		2700	2.2	0.021
9	578	1.03	4.0	0.36		900	2.6	0.026
10	578	0.96	3.2	0.83		360	3.5	0.037
12	680	0.96	3.7	0.22		600	35.7	0.46
13	680	0.86	4.2	0.19		480	36.4	0.52
18	616	1.02	3.8	0.27		900	6.5	0.065
19	616	0.97	4.0	0.25		900	6.3	0.067
23	592	1.00	3.9	0.30		1505	6.7	0.070
24	592	0.95	4.2	0.29		1550	5.7	0.062
25	592	0.90	4.4	0.27		1530	4.3	0.048
35	592	1.20	3.4	0.34	12.1	600	12.7	0.12
36	592	1.00	3.8	0.30		600	16.0	0.16
37	592	1.20	3.4	0.33		540	10.0	0.10
38	592	1.00	3.7	0.30		540	14.5	0.14
42	592	1.10	3.9	0.35	25.0	420	7.2	0.07
43	592	1.00	4.2	0.32		360	18.1	0.18
44	592	0.91	4.5	0.29		360	23.6	0.30
47	592	1.00	4.0	0.30		360	19.2	0.21
48	592	0.95	4.4	0.28		360	23.1	0.28
49	592	0.90	4.8	0.27		360	23.8	0.30
50	592	1.10	3.7	0.34		360	17.3	0.17
51	592	1.00	4.0	0.31		360	1544	0.16
52	592	0.97	4.3	0.29		360	12.8	0.14
53	592	1.1	3.7	0.31		360	10.1	0.09
54	592	1.1	3.9	0.30		480	19.6	0.24
55	592	0.99	4.2	0.28		360	23.2	0.27
56	548	0.75	3.9	0.12		300	5.8	0.079
57	546	0.72	4.3	1.91		240	6.5	0.093
58	546	0.70	4.6	1.74		300	6.4	0.095
60	534	0.93	5.0	0.87		510	4.4	0.049
61	534	0.75	5.7	2.35		300	5.15	0.072

Expt: No:	Temp: °C	Contact Time secs	Average Pressure mms	Partial Pressure of MeI mms	S/V	Time of run (secs)	% decomposition	k_1
65	531	0.49	9.1	1.00	2.2	780	1.18	0.024
66	531	0.48	9.3	0.98		780	1.27	0.026
69	531	0.53	9.3	1.33		360	1.54	0.029
70	531	0153	9.4	1.33		360	1.42	0.027
71	531	0.54	8.8	1.89		300	1.43	0.027
72	531	0.53	9.0	1.79		310	0.93	0.018
75	531	0.58	8.8	2.50		310	1.68	0.029
76	531	0.57	9.2	2.35		290	1.62	0.028
80	531	0.51	8.0	3.30		360	1.20	0.024
81	531	0.51	8.1	3.33		360	1.25	0.024
83	552	0.52	8.7	1.12		360	2.4	0.048
88	552	0.50	8.1	3.26		300Ø	1.94	0.039
99	543	0.52	8.2	1.41		375	0.58	0.011
100	543	0.52	8.2	1.41		360	0.63	0.012
105	542	0.59	7.5	1.64		570	0.63	0.017
106	542	0.59	7.5	1.64		570	0.63	0.017
107	542	0.49	8.7	1.11		360	1.93	0.040
109	570	0.49	8.7	1.11		360	2.03	0.042
110	583	0.48	8.7	1.10		360	3.71	0.079
111	583	0.48	8.8	1.07		360	3.09	0.065
114	597	0.46	9.0	1.10		300	5.06	0.11
115	597	0.46	9.1	1.10		300	5.01	0.11
123	512	0.50	8.7	1.10		900	0.20	0.004
124	512	0.50	8.8	1.10		900	0.16	0.003

Experiments without a carrier gas.

Expt: No:	Temp °C	Contact Time secs	MeI passed in (gm-mols x 10^{-3})	Pressure of MeI mms	S/V	Time of run secs	% decomposition	k_1
149	499	1.78	7.3	4.1	1.9	600	0.90	0.005
150	499	1.64	7.8	4.1		600	0.86	0.005
151	499	1.59	8.3	4.2		600	0.80	0.0053
155	499	1.83	10.8	7.0		540	1.03	0.0057
156	499	1.90	10.4	7.0		540	1.01	0.0053
157	499	1.71	7.3	2.65		900	0.82	0.0048
158	499	1.57	6.7	2.65		900	0.86	0.0055
159	499	1.59	6.8	2.65		900	0.86	0.0055
161	499	1.21	11.1	7.1		360	0.62	0.0052
162	499	1.21	11.1	7.1		360	0.62	0.0052
164	499	4.50	4.9	7.0		600	2.10	0.0047
165	499	4.20	5.2	7.0		600	2.00	0.0048
167	499	2.29	7.9	11.2		310	1.23	0.0055
168	499	2.16	7.9	11.2		290	1.15	0.0053
171	517	1.63	3.8	4.0		300	1.45	0.0090
172	517	1.64	3.8	4.0		300	1.49	0.0093

Expt: No:	Temp °C	Contact Time Secs	MeI passed in (gm-mols x 10^{-3})	Pressure of MeI mms	S/V	Time of run secs	% decomposition	k_1
174	538	1.64	3.8	4.2	1.9	300	2.72	0.017
175	531	1.50	4.2	4.2		300	2.70	0.018
176	560	1.52	3.9	4.1		300	5.68	0.038
177	560	1.55	3.9	4.1		300	6.01	0.040
178	560	1.49	4.0	4.1		300	5.74	0.040
179	499	1.55	8.7	4.2		600	0.77	0.0050
180	499	1.43	9.5	4.2		600	0.74	0.0052
181	499	1.44	9.4	4.3		600	0.75	0.0052
185	499	1.68	8.2	4.4	11.3	600	2.69	0.016
186	499	1.62	8.6	4.4		600	2.69	0.017
187	499	1.60	8.6	4.4		600	2.43	0.015
188	499	1.60	4.2	4.3		300	1.73	0.011
189	499	1.58	4.3	4.3		300	1.58	0.0096
190	499	1.60	4.2	4.3		300	1.49	0.0094
191	499	1.79	3.8	4.3		300	2.26	0.013
192	499	1.59	4.3	4.4		300	1.40	0.0089
193	499	1.63	4.2	4.4		300	1.45	0.0091
194	499	1.87	3.6	4.3		300	1.80	0.0098
195	499	1.74	3.9	4.3		300	1.49	0.0087
196	502	2.15	7.3	4.1	1.5	480	0.74	0.0035
197	502	2.23	7.0	4.1		480	0.76	0.0035
198	502	2.17	7.2	4.1		480	0.70	0.0032
201	520	2.55	6.0	4.7		420	1.52	0.0060
202	520	2.66	5.8	4.7		420	1.71	0.0065
208	502	2.03	6.8	4.7	3.9	420	0.98	0.0048
209	502	1.98	7.0	4.7		420	0.98	0.0050
210	520	2.05	5.7	4.7		360	1.77	0.0087
211	520	2.15	5.9	4.7		390	1.77	0.0083
212	520	2.15	5.9	4.7		390	1.81	0.0083
213	540	2.34	4.2	4.9		300	3.38	0.015
214	540	2.45	4.0	4.9		300	3.68	0.015
215	540	2.41	4.6	4.9		330	3.51	0.015
217	520	2.15	4.2	4.3	7.0	300	2.23	0.011
218	520	2.09	4.3	4.3		300	2.21	0.012
219	502	1.97	3.6	4.1		3000	1.28	0.0066
220	502	1.90	4.2	4.7		300	1.31	0.0070
221	502	1.90	422	4.7		300	1.26	0.0067
222	540	1.88	4.2	4.8		300	4.54	0.025
223	540	1.95	4.0	4.8		300	4.80	0.035
224	540	1.91	4.1	4.8		300	4.64	0.025
225	540	1.81	3.4	4.8		240	4.30	0.025
226	540	1.80	2.6	4.8		180	4.04	0.023
227	540	1.83	3.3	4.8		240	4.35	0.024
228	540	2.40	4.4	4.6	1.5	300	2.33	0.0098
229	540	2.49	4.1	4.5		300	2.45	0.010
230	540	2.29	4.9	4.9		300	2.29	0.010

Experiments with a high pressure of nitrogen

Expt: No	Temp: °C	Contact Time secs	Total Pressure mms	Partial Pressure of MeI mms	S/V	Time of run secs	% decomposition	k_1
323	487	9.94	599	1.86	1.5	1800	2.24	0.0023
324		9.96	599	1.81		1800	2.17	0.0022
325		10.4	599	2.04		1800	2.42	0.0024
327		10.6	578	0.76		2400	2.00	0.0019
328		10.5	578	1.12		2400	1.99	0.0019
329		11.0	629	1.09		900	2.33	0.0022
330		11.0	629	1.11		900	1.80	0.0016
331		11.0	619	1.24		1800	1.87	0.0015
333		8.22	573	2.07	7.0	1200	1.29	0.0016
336		6.88	687	0.83		2400	0.84	0.0013
337		6.88	687	1.46		2400	1.00	0.0015
338		9.60	640	0.70		2400	1.31	0.0014
339		9.71	640	1.08		2400	1.11	0.0012
341		9.40	600	3.16		1200	0.98	0.0011
342		9.51	600	4.18		1200	1.21	0.0013
344		10.6	600	1.75	1.5	1800	1.48	0.0014
345		10.8	600	2.06		1980	2.14	0.0020
346		10.7	600	2.09		1800	2.33	0.0021
350	507	10.4	593	1.36		1200	2.91	0.0028
351	507	10.8	593	2.05		1200	3.53	0.0033
352	507	10.3	593	2.11		1200	3.15	0.0031
353	508	10.3	641	1.78		1200	3.27	0.0032
354	530	10.3	641	1.37		960	6.43	0.0064
524	524	9.8	585	0.59		1200	3.35	0.0035
356	524	9.8	585	1.09		1200	5.99	0.0063
357	500	10.2	585	0.93		1800	2.02	0.0021
358	535	10.0	491	1.24		1200	8.47	0.0089
359	535	10.1	491	1.18		1200	8.03	0.0083
360	500	10.2	491	1.14		1800	3.09	0.0031
361	549	10.1	580	1.24		900	8.96	0.0093
362	549	10.2	580	1.25		900	9.76	0.010
363	559	9.8	541	1.18		600	14.4	0.016
364	559	9.9	541	1.23		600	11.1	0.012
365	494	10.6	643	1.14		1800	1.76	0.0017
366	494	11.0	643	1.09		1800	2.15	0.0020
367	494	10.6	643	1.00		1800	2.33	0.0022
368	525	10.3	657	1.49		1275	5.72	0.0057
369	525	10.1	657	1.28		1200	4.74	0.0048
370	525	9.9	657	1.30		1200	4.65	0.0048
371	553	9.9	571	1.28		900	9.49	0.010
372	553	10.1	571	1.10		900	10.7	0.011
374	492	10.8	575	1.05		1800	2.60	0.0024
375	492	10.7	575	1.05		1830	2.01	0.0019
376	492	10.8	575	1.12		1800	1.36	0.0013

Experimentswith high pressure nitrogen and 1-2 mms toluene

Expt: No	Temp: °C	Contact Time secs	Total Pressure mms	Partial Pressure of MeI mms	S/V	Time of run secs	% decomposition	K_1
380	495	11.3	583	1.2	1.5	900	4.15	0.0038
381	495	11.1	583	1.3		900	4.09	0.0037
382	516	10.2	572	1.1		900	16.3	0.017
382	516	10.4	572	1.1		900	18.0	0.019
384	516	10.0	572	1.2		900	19.0	0.021
385	480	10.7	531	1.1		1800	3.78	0.0036
386	477	10.8	626	0.87		1800	1.08	0.0010
387	477	10.9	626	0.89		1800	1.47	0.0014
388	477	10.8	626	1.1		1800	0.71	0.0007
393	501	10.4	565	0.55		960	5.5	0.0043
394	501	10.6	565	1.03		960	8.7	0.0086
399	487	10.2	620	1.14		1800	4.57	0.0042
400	487	10.6	620	1.27		1940	3.96	0.0038
401	518	11.1	578	1.48		900	18.0	0.019
405	487	9.7	528	1.05		1800	4.35	0.0046
406	487	9.9	528	1.01		1800	4.41	0.0046
408	503	10.4	568	1.14		900	7.74	0.0077
409	503	11.6	568	0.70		900	9.95	0.0090
410	519	9.6	564	1.08		900	18.4	0.021
411	519	10.2	564	1.08		900	13.7	0.015
412	517	10.2	564	1.36		900	14.7	0.016
413	533	9.4	533	1.08		600	27.1	0.034
414	533	9.5	533	0.91		660	26.2	0.032
415	533	9.7	533	1.10		600	28.0	0.034
416	472	10.8	487	0.84		2700	2.31	0.0022
418	464	10.9	487	0.89		2700	1.67	0.0015
420	463	8.8	627	0.61		2580	1.03	0.0012
421	463	14.7	627	1.28		2700	1.72	0.0012
425	502	8.1	563	0.78		960	6.88	0.0087
430	504	11.7	599	1.70		1260	11.2	0.011
431	504	11.5	599	1.73		900	9.34	0.0085
432	504	11.3	599	1.72		1260	9.75	0.0091

Volume of the Furnace

Volume = 275 ccs for Expts: 1 to 124

Volume = 252 ccs for Expts: 124 to 195

Volume = 385 ccs for S/V = 1.5

Volume = 340 ccs for S/V = 3.9

Volume = 276 ccs for S/V = 7.0

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