STUDIES IN THE PYROLYSIS OF METHYL IODIDE

Robert Bowser Cundall

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

1953

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STUDIES IN THE PYROLYSIS OF METHYL IODIDE WITH PARTICULAR REFERENCE TO THE TRANSITION FROM FIRST TO SECOND ORDER KINETIC BEHAVIOUR.

A Thesis presented by

ROBERT BOWSER CUNDALL, B.Sc.,

to the

UNIVERSITY OF ST. ANDREWS

in application for

the

DEGREE OF DOCTOR OF PHILOSOPHY

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DECLARATION

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

The investigations were carried out in the Chemical Research Laboratories of the United College, St. Andrews, under the direction of Dr. C. Horrex.

[redacted]

UNIVERSITY CAREER

I entered the United College of the University of St. Andrews in October, 1946 and graduated as a Bachelor of Science with First Class Honours in Chemistry in June, 1950.

The researches described in the present thesis were carried out in the United College under the direction of Dr. C. Horrex within the period September 1950 to February 1953.

CERTIFICATE

I hereby certify that Mr. R.B. Cundall, B.Sc., has spent nine terms at Research Work under my direction, that he has fulfilled the conditions of Ordinance No.16 (St. Andrews) and that he is qualified to submit the accompanying Thesis in application for the Degree of Doctor of Philosophy.

[redacted]

Director of Research.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Dr. C. Horrex for his invaluable assistance and advice in both the practical and theoretical aspects of this work. Also to Dr. C.B. Cowan and Mr. R.N. Pittilo for many helpful discussions.

The author also wishes to thank Professor J. Read, F.R.S., for the provision of facilities to carry out the present investigation and the University of St. Andrews for the award of a University Post-Graduate Scholarship.

CONTENTS

INTRODUCTION

The investigations recorded in this thesis arose from previous work of Lapage[1] and Butler and Polanyi[2] on the pyrolysis of methyl iodide. The latter work involved a limited study of methyl iodide, only five experiments being quoted, all at the same temperature, but by use of the equation for a unimolecular decomposition $k(\sec^{-1}) = 10^{13}\exp.(-E/RT)$ a value of E = 54 k.cal. was derived for the C-I bond energy. This value permitted a deduction of the C-H bond energy in methane which proved in agreement with later determinations by separate methods.

The experimental methods of Butler and Polanyi were critically examined by Moore[3] and the results of his investigations incorporated by Lapage in extensive investigations on the thermal decomposition of methyl iodide. She found that temperatures 100°C higher than those used by Butler and Polanyi were required to obtain the decompositions the latter quoted and the agreement of their deduced C-I bond energy with other work must be regarded therefore as fortuitous. Lapage concluded that the typical experimental conditions of Butler and Polanyi, (halide pressures 0.1 - 1 mm. in 3 - 5 mm. nitrogen as carrier gas), did not give first order kinetics for methyl iodide but that a transition from second to first order was evident. After varying the experimental conditions widely she selected a carrier gas pressure of 600 mm. of nitrogen, included a few millimetres partial pressure of toluene in order to remove methyl radicals and was able to obtain first order constants $k(\mathrm{sec}^{-1}) = 10^{13}\exp.(-54700/RT)$. This was considered to be the high pressure limiting rate for the reaction.

Although the evidence presented by Lapage covered a wide range of conditions and the conclusions seem most plausible there are some features which required more extensive investigation and it has been the aim of the present work to do this.

Two main points of interest have been taken up. The first is concerned with the essential problem attempted by Lapage - the selection of conditions of pyrolysis which permit the evaluation of an energy of activation for the unimolecular dissociation of methyl iodide. Lapage had to select conditions without having time to obtain all the desirable supporting evidence, and in particular the efficiency of suppression by toluene of the reverse reaction between methyl radicals and iodine molecules or atoms had to be dealt with in more detail. From this side of the problem there arises those general aspects of free radical chemistry and bond energy determinations which are dealt with in the survey of other relevant work which follows this introduction.

The second item of interest has been concerned with the pyrolysis at low pressures where the efficiency of various inert gases in producing activated methyl iodide molecules has been investigated. The transition from first to second order kinetics as the gas pressure is lowered has a considerable theoretical interest since simple and undoubted examples of this behaviour are rare. The general theory of such transitions however has been developed for over 20 years, following the initial suggestions of Lindemann[4]. In the last two years there has been a considerable rise in interest in the field of energy exchange between molecules and the effects on chemical kinetics which are dependent upon it.

Before detailing and discussing the experimental work done in the investigations of the author a survey is given in the following pages of important items of published work which are relevant to the above two topics.

BOND ENERGIES

General Importance. The provision of quantitative physical knowledge of reactions is one of the prime aims of chemistry. Possible chemical changes and conditions of equilibrium can be decided by using knowledge of heat capacities and thermochemical data, but thermodynamics is unable to predict the rate at which a reaction will occur or the mechanism it will follow. The problem of investigating the rates and mechanisms of chemical changes has proved much more difficult and has lent itself much less readily to the formulation of general laws.

It has been pointed out[5] that many gas phase reactions involve the making or breaking of bonds and this causes four main types of process to be of interest:-

(i) rupture of a bond in a stable molecule leading to the formation of atoms or radicals,

(ii) reactions between two atoms or radicals and molecules,

(iii) reactions between two atoms or radicals,

(iv) the decomposition of radicals.

For an understanding of such types of reaction a knowledge of the strength of chemical bonds is clearly essential.

<u>Definitions.</u> Clear definitions of the various connotations of bond energy are essential. Many workers have framed terminology and definitions but in this case we will use the designations of Evans and Szwarc[6].

(a) Bond Dissociation Energy - the endothermicity of the process in which a molecule dissociates into fragments produced by the rupture of one bond only

i.e. $R_1 - R_2 \longrightarrow R_1 + R_2 - D(R_1 - R_2)$k.cal/mole.

Accurately this process should take place in the gas phase at 0°K. and the molecule and radicals be in specified states.

(b) Average Bond Energy - the amount of work required for the rupture of the bond when the molecule swells infinitely without losing its original shape. This quantity if determinable would correspond approximately to the force between bonded atoms in the non-reacting molecules.

It is the bond dissociation energy which is of importance in chemical kinetics, but the distinction has to be made since in most cases the two quantities are not equal.

Methods of determining Bond Dissociation Energies[7].

The earliest estimates made by thermochemical methods gave average bond energies not bond dissociation energies. Essentially the method is exemplified by saying that the C-H bond strength in methane was given by Qa/4, where Qa is the heat of formation of methane from atoms. The values obtained were open to doubt due to uncertainty in the heat of reaction for

$$\text{C graphite} \longrightarrow \text{C gas}$$

essential for calculating Qa values. The C-H bond strength values were used to deduce C-X bond strengths in CH_3X derivatives. The question of the heat of sublimation of carbon is still a matter of dispute as is seen from the recent review by Springall[8].

Further the method ignores the probable influences of molecular environment on the strength of the bond.[9] In fact modern thermochemical data of high accuracy due to Rossini[10] definitely shows it to be in error in this matter. The following reactions:-

$$2CH_4 = C_2H_6 + H_2 \quad , \Delta H^\circ = 15,539 \text{ cals.}$$

and $$3C_2H_6 = 2C_3H_8 + H_2 \quad , \Delta H^\circ = 11,073 \text{ cals.}$$

do not have the same heats of reaction although the L.H.S. and R.H.S. of both equations differ by the same number of ruptured and formed bonds

i.e. two C-H bonds lost from the L.H.S. and one C-C one H-H made on R.H.S.

The difference in heats of reaction must arise from differences in the C-H and C-C bond strengths of the homologous paraffins. This fact could not have been proved but might have been inferred from the particularly simple series of reactions studied by Polanyi and collaborators[2] of the type Na + RX where the rate for a fixed X varied markedly with the nature of R.

All the methods used for determining bond dissociation energies depend on supplying energy to a molecule in some form or other. Methods which have been used include:-

(1) <u>Electron Impact</u>[11] - the energy of colliding produces a process $RX \longrightarrow R^+ + X + e$ which if the energy change in $R^+ \longrightarrow R$ is known will suffice to give the required $RX \longrightarrow R + X$ energy change.

Frequently the data are not easy to interpret.

(2) Photochemical[12] - the energy of a light quantum is used to produce a dissociation $RX \longrightarrow R + X$, and often one of the products is in an excited state. The difficulty of interpretation of the observed spectra limits the application of the method to the more simple molecules. Methods based on predissociation and photodecomposition have also been used.

(3) Thermal Methods.

(a) Equilibrium Method - depends on the production of a stable equilibrium $RX \rightleftharpoons R + X$ at various temperatures. Applications of the method have not been wide as free atoms or radicals frequently react with the parent molecule but it has been used for diatomic molecules and has been applied by White[13] for determining D(NC - CN).

(b) Kinetic Method - the essential principle of this method is the determination of the energy of activation for the process $RX \longrightarrow R + X$, assuming $R + X$ to be without activation energy i.e. $\Delta H_f = E_f$.

If the method is to be valid it is essential that the following conditions are satisfied:-

(i) the mechanism should be clearly established,

(ii) the rate determining step should be the bond dissociation which is under consideration,

(iii) side reactions should be suppressed as much as possible or their extent accurately assessed.

These conditions have not been satisfied in obtaining

Table I.

Iodide	Bond Dissociation Energy (R - I) k. cals/mole	
	Butler, Mandel, Polanyi,	Horrex, Szwarc[6], Gowenlock[7], Lapage.
Methyl	(54)	54.7
Ethyl	52.2	54 - 56
n-Propyl	50.0	-
iso-Propyl	46.1	-
n-Butyl	49.0	-
tert-Butyl	45.1	-
Acetyl	(50.7)	-
Acetonyl	45.0	-
Allyl	39.0	-
β-Chloroethyl	45.9	-
Dibromomethyl	41.4	-
Dichloromethyl	42.4	-
Diiodomethyl	(37.0)	-
Vinyl	55.0	-
Benzyl	43.7	(29.5)
Benzoyl	43.9	-
β-Phenylethyl	50.0	-
cycloHexyl	49.2	-
Phenyl	54.0	-

(To face page 8.)

much of the data and often pressure measurements alone have been used to follow the course of a reaction without even an accurate knowledge of the products. The development of experimental methods has concentrated on techniques to minimise side reactions of unknown character by conducting the reaction at low pressures of reactant and endeavouring to offer some easy and preferential reaction to the radicals.

The earliest work was that of Rice[14] who used metallic mirrors to remove the radicals. The method was susceptible to error due to failure to eliminate possible side reactions and the time lag before the produced radicals arrived at the mirror.

Polanyi[5, 15] and his collaborators endeavoured to work with iodides assuming that R- and -I did not interfere seriously through the medium of secondary reactions, provided the pressure of reaction was low. Their assumptions seem likely to be of variable validity and to depend very much on the compound.

The values they obtained are given in Table I.

An improvement on this was the technique of using toluene as carrier gas and radical acceptor, developed by Szwarc[18]. It depends upon the fact that benzyl radicals are thermally stable and unreactive as shown by the work of Horrex and Szwarc[16] on benzyl iodide and the low C-H bond dissociation energy of toluene[7]. If the formed radicals R react with toluene and produce benzyl radicals:-

$$C_6H_5.CH_3 + R = C_6H_5.CH_2 + RH,$$

the benzyl radicals survive the short time of heating, are removed intact from the reaction vessel and eventually dimerize outside the hot zone. It is essential to avoid formation of dibenzyl in the hot zone. Both back and chain reactions are prevented and the rate of decomposition measured by the rate of formation of R_1H, R_2H or dibenzyl.

Examples (i) the decomposition of benzyl bromide[19]

$$C_6H_5.CH_2Br = C_6H_5.CH_2 + Br$$

$$C_6H_5.CH_3 + Br = C_6H_5.CH_2 + HBr$$

The rate of reaction was measured by titration of the hydrogen bromide.

(ii) the decomposition of hydrazine[20]

$$N_2H_4 = 2NH_2$$

$$C_6H_5.CH_3 + NH_2 = C_6H_5.CH_2 + NH_3$$

In this case the formation of dibenzyl was used to measure the rate, since hydrazine also decomposes by a wall reaction to give ammonia.

For successful application it is necessary that the radical R is sufficiently reactive to attack the toluene before back or secondary reaction can occur. The technique is also unsuitable when the bond energy is stronger than the C-H bond dissociation energy in toluene, or when the measured bond strength is very weak.

The method is most suitable for benzyl derivatives $C_6H_5.CH_2 - R$ and has been used to determine the resonance energies of a number of radicals, e.g. $CH_2(CH_3)_2$[21].

In some cases the kinetics of decomposition are greatly simplified; the unimolecular fission of the bond is completely rate determining, and the resulting radicals do not initiate a chain reaction. Examples of such reactions are the pyrolysis of toluene (Szwarc)[22] which proceeds:-

$C_6H_5.CH_3 = C_6H_5.CH_2 + H$, (rate determining)

then $C_6H_5.CH_3 + H = C_6H_5.CH_2 + H_2$,

or $C_6H_5.CH_2 + H = C_6H_6 + CH_3$,

$CH_3 + C_6H_5.CH_3 = CH_4 + C_6H_5CH_2$,

$2C_6H_5.CH_2 = C_6H_5.CH_2.CH_2.C_6H_5$,

and pyrolysis of dibenzyl studied by Horrex and Miles[23]. They assumed that the first order reaction represented the following dissociation

$$C_6H_5.CH_2.CH_2.C_6H_5 = 2C_6H_5.CH_2.$$

A mechanism was suggested accounting for the products which were; toluene, stilbene, benzene and styrene.

Bond dissociation energies have been determined from studies on the thermal decomposition of nitroalkanes[24] where it has been shown that the dissociation of the $R - NO_2$ bond is the initial step.

While these methods endeavour to satisfy the conditions laid down above it is as well to consider what can happen when a simple reaction mechanism is not achieved.

SOME KINETIC FEATURES ARISING FROM FREE RADICAL MECHANISMS

The existence of free radicals was first shown by Paneth and Hofeditz[25] who demonstrated that free methyl radicals, formed by heating lead tetramethyl vapour, could be detected by their reaction with a metallic mirror deposited on the walls of a tube through which the carrier gas with radicals was flowing. Further work by Paneth et al. was followed up by Rice and collaborators[5,14], using a more refined but similar technique. The latter were led to the suggestion that thermal decompositions of organic compounds proceeded by free radical mechanisms.

Since then much confirmatory evidence for such mechanisms has been obtained. For example Frey[26] was able to start chains in butane at temperatures below its normal decomposition range by adding methyl radicals. Allen and Sickman[27] showed that the chain decomposition of acetaldehyde could be induced by methyl radicals from decomposing azomethane. Leermakers[28] produced a chain decomposition of methyl ether in the presence of photolysed acetone.

Other evidence is the inhibiting effect of nitric oxide[29] and propylene[30] on many decompositions where the radical reacts with nitric oxide or propylene rather than start a chain. The formation of dibenzyl when decompositions proceed in the presence of toluene is most feasibly explained by free radicals[31].

Eltenton[32] employed a mass-spectrometer to measure directly radical concentrations.

The Rice-Herzfeld theory[33] for thermal decompositions explained the following observations, (i) first order behaviour, and (ii) activation energies far lower than the strength of the broken bonds.

For example, the decomposition of a paraffin M_1

$$(1)\quad M_1 = R_1 + M_2$$

$$(2)\quad R_1 + M_1 = R_1H + R_2$$

$$(3)\quad R_2 = R_1 + M_3$$

$$(4)\quad R_1 + R_2 = M_4$$

Setting up equations giving the radical concentrations in the steady state

$$\frac{d}{dt}[R_1] = 0 = k_1[M_1] - k_2[R_1][M_1] + k_2[R_2] - k_4[R_1][R_2]$$

$$\frac{d}{dt}[R_2] = 0 = k_2[R_1][M_1] - k_3[R_2] - k_4[R_1][R_2]$$

$$\text{whence } [R_1] = \frac{k_1}{4k_2} \pm \sqrt{\left(\frac{k_1}{4k_2}\right)^2 + \frac{k_1k_3}{2k_2k_4}}$$

If it is assumed k_1 is small (i.e. the chains are long)

$$\text{then}\quad R_1 = \sqrt{\frac{k_1k_3}{2k_2k_4}}$$

$$\therefore \frac{d}{dt}[M_1] = k_1[M_1] + k_2[R_1][M_1]$$

$$= k_1[M_1]\left(1 + \sqrt{\frac{k_2k_3}{2k_1k_4}}\right)$$

$$= k_1[M_1]\sqrt{\frac{k_2k_3}{2k_1k_4}}$$

$$= [M_1]\sqrt{\frac{k_1k_2k_3}{2k_4}} \quad \text{(i.e. 1st. order)}$$

The temperature coefficient is given by

$$E_{\text{overall}} = 1/2(E_1 + E_2 + E_3 - E_4)$$

These results have shown that it is possible for a chain sequence to give first order behaviour. Such a scheme also gives measured activation values lower than actual bond energies and if present in whole or in part can invalidate bond energy determinations.

It is also obvious that the observed order depends on the chain ending reaction.

If it is assumed that it is $2R_1 = M_5$, by similar reasoning it is found that the order is 1.5.

If the chains terminate $2R_2 = M_6$ the order of the overall reaction will be 0.5.

It is still a matter of controversy as to whether reactions proceed entirely by a free radical mechanism. Hinshelwood[34] on the basis of the observed residual rate when nitric oxide is present assumes that a true molecular decomposition also occurs. Pease[35] has suggested that many thermal reactions interpreted as first order are better represented as 1.5 over the whole pressure range.

The importance of such reactions as the chain steps of the Rice-Herzfeld mechanism $R_1 + M_1$, and the efficiency of such reactions as $R + C_6H_5.CH_3$ or the back reaction such as R + I_2 depend on the magnitude of the pre-exponential factor and energy of activation for radical reactions. It appears well established that the activation energies of radical reactions are small. In the case of bimolecular reactions the pre-exponential factor is represented by PZ, where P is the probability of steric factor and is a measure of the deviation of the actual reaction from the ideal behaviour of the collision theory. The value of the P factor for radical reactions is at present a matter of dispute which experiment has not yet resolved. Evans and Szwarc[36] conclude that P factors for atomic reactions are greater than 0.1, whilst Bamford and Dewar[37] sweepingly generalize that radical reactions have P factors equal to 10^{-5} approximately.

The experimental evidence of Steacie and Trotman-Dickenson[38] Steacie and Marcus[39], Steacie and Miller[40], Noyes, Gomer and Dorfmann[41], and Dodds[42] for reactions of the type

$$CH_3 + RH = CH_4 + R$$

$$\text{and} \quad CH_3 + CH_3 = C_2H_6$$

favour steric factors of the order of 10^{-4} and lower. Szwarc and Roberts[43] conclude that the steric factor of the reaction $CH_3 + C_6H_5.CH_3$ is not less than 0.1. Gomer and Kistiakowsky[44] deduce a normal (1 - 0.1) steric factor through studying the photochemical dissociation of mercury dimethyl by a rotating sector method. Lucas and Rice[45] for methyl radicals and Ivin and Steacie[46] for ethyl radicals also favour high P values.

The problem has been tackled theoretically by Szwarc[47] and Hill[48] but the results cannot be said to offer any definite solution. Marcus and Rice[49] have shown in a examination of the recombination of methyl radicals and iodine atoms that the steric factor of recombination and the effect of pressure on the rate of decomposition depend on the nature of the activated complex. The need for more accurate experimental information is very apparent from the observed data. It does appear that the larger the radical the smaller the steric factor, information being derived mainly from polymerisation studies.

It is clear from the Rice-Herzfeld mechanism that the energy of activation of the primary dissociation could be found if all the steps in the reaction mechanism were firmly established and their separate activation energies known, together with the energy of activation for the overall reaction. This is seldom practicable but there is one well investigated case which has yielded a bond dissociation energy through a knowledge of all the kinetic steps.

For the photobromination of methane Kistiakowsky and van Artsdalen[50] put forward the following mechanism:-

$$Br_2 + h\nu = 2\,Br \qquad (1)$$

$$Br + CH_4 = CH_3 + HBr \qquad (2)$$

$$CH_3 + Br_2 = CH_3Br + Br \qquad (3)$$

$$CH_3 + HBr = CH_4 + Br \qquad (4)$$

$$Br + Br + M = Br_2 + M \qquad (5)$$

Reaction (2) is certainly rate determining and so the measured activation energy is considered to be that of (2)

$$E_2 = 17.8 \text{ k.cal.}$$

Since (4) is the reverse of (2),

$$CH_4 + Br = CH_3 + HBr - (17.8 - E_4)$$

$$HBr = H + Br - 85.8$$

$$\therefore \quad CH_4 = CH_3 + H \ -(103.6 - E_4)$$

Kistiakowsky et al. put $E_4 = 1.5 \pm 1$ k.cal. from the evidence of hydrogen bromide inhibition and from evidence by the photolysis of CH_3I - HBr mixtures. They deduced that :-

$D(CH_3H)$ in methane = 102 ± 1 (later revised to 101 k.cal./mole).

A similar investigation was made of the photobromination of ethane[51], although not with the same thoroughness as for methane. A similar mechanism was proposed and a C-H bond dissociation energy equal to 98 ± 2 deduced.

Extension of this work to other hydrocarbons[52] has not yielded such useful information on C-H bond dissociation energies.

One remaining pitfall is heterogeneous reaction. Surface effects are often important in the thermal decomposition of gases and tests for homogeneity by changing the surface-volume ratio are essential. In the case of complex reactions results are often ambiguous and the role of the surface difficult to assess. It is well known that the past history and condition of the walls of a reaction vessel may have an effect on pyrogenic decompositions. Rice and Herzfeld[53] have recently proposed a mechanism for chain reactions in which initiation occurs at the wall, the reaction chain goes out into the body of the gas and is eventually stopped at the surface.

Failure to investigate surface effects has often led to erroneous conclusions, as for example with the thermal decomposition of phosphine[54].

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DECOMPOSITION OF ORGANIC HALIDES

Much of the work on the decomposition of organic halides has not been of a character which yields activation energies for individual reaction steps, but since it is of interest to the present investigation and illustrates in various ways the phenomena discussed above, a survey of such work is made below.

Studies on the thermal and photochemical decomposition of organic halides have been considerable. The results are summarised for different halides, particularly with regard to types of mechanism.

Chlorides

Recently very extensive studies have been carried out by Barton and his co-workers. All the results may be grouped into three mechanisms:-

(i) heterogeneous decomposition on glass surfaces, e.g. tert-butyl chloride[55].

(ii) homogeneous first order unimolecular decompositions, e.g. ethyl chloride[56], 1.1 dichloroethane[56], tert-butyl chloride[56], isopropyl chloride[56], 2-chloropropane[57], 1:2-dichloropropane[57], 1:1:1 trichloroethane[58], n-propyl and n-butyl chlorides[59], 2:2 and 1:1 dichloropropane[60].

(iii) homogeneous first-order decomposition by radical chains, e.g. 1:2 dichloroethane[61], and 1:1:1 trichloroethane[58], 1:1:2:2 and 1:1:1:2 tetrachloroethane[62]. 1:4 dichlorobutane and 1:1:2 trichloroethane[63], 1:1 dichloropropane[60]. The chlorocompound decomposes by a radical mechanism so long as neither the compound itself nor the reaction products are inhibitors for chains.

In the case of the radical chain reactions an induction period is observed which apparently corresponds to the rupture of the molecule at the beginning of a chain sequence. The induction period has been treated by a Rice-Herzfeld mechanism[64]. The first order decompositions of ethyl chloride and 1:1 dichloroethane have been carefully examined and the results shown to be in close agreement with unimolecular theory[65]. The relationship between the Arrhenius parameters has also been discussed[60].

Barton et al.[66] have employed the pyrolysis of (-) menthyl chloride for stereochemical determinations.

Bromides

The kinetics of the decomposition of bromides have been more widely investigated than the chlorides. It appears that the pyrolysis of organic bromides occurs by 3 main processes

(i) a unimolecular split into hydrogen bromide and an olefine, e.g. the decomposition of tert-butyl bromide observed by Kistiakowsky and Stauffer[67].

(ii) the breaking of the C-Br bond leading to a Br atom which interacts further leading to the production of HBr and olefine by a non-chain mechanism, e.g. ethyl bromide studied by Daniels et al.

(iii) the Br atom may participate in the propagation of long chains such as that suggested by Meissner and Schumacher[68] for methyl bromide.

Ethyl bromide is the most intensively studied example but the reaction is still obscure. It was originally investigated by Lessig[69] and has been found to be sensitive to the presence of impurities. Vernon and Daniels[70] suggested it to be a true unimolecular reaction but later work by Fugassi and Daniels[71] made this appear doubtful. Daniels[72] in a summary of the work discusses the effect of the vessel wall on reproducibility and concluded that the decomposition is not a simple unimolecular reaction. Bromine accelerates the reaction in a manner proportional to $(Br_2)^{1/2}$. Roof and Daniels[73] have shown that ethyl bromide can sensitise the decomposition of acetaldehyde but photolysed acetone initiates no reaction in the presence of ethyl bromide. It is concluded that free radicals are produced by the decomposition of ethyl bromide but free radical chain processes are of little importance.

The most recent work on bromide decompositions has been done by Maccoll[74] et al. who have studied n-propyl bromide (mechanism ii), isopropyl bromide (mechanism i), allyl bromide (mechanism ii) amongst others. Szwarc has measured the C-Br bond dissociation energy of many alkyl and aryl bromides using the toluene carrier gas technique. He postulates the following mechanism:-

$$R - Br = R + Br \quad \text{(rate determining step)}$$

$$R + CH_3.C_6H_5 = R.H + CH_2.C_6H_5$$

$$Br + CH_3.C_6H_5 = C_6H_5.CH_2 + HBr \quad \text{(titrated)}.$$

Bromides so studied have included benzyl[19] and methyl bromides[75] along with many of their substituted derivatives[76].

Iodides

Organic iodide decompositions have been studied both thermally and photochemically. Polissar[77] studied the thermal decomposition of ethylene iodide in carbon tetrachloride. Lessig[69] investigated the thermal decomposition of some alkyl iodides in the gas phase by the static method. Ogg and his collaborators studied a whole series of alkyl iodides. Those studied were n-propyl iodide[78], n-butyl iodide[78], sec-butyl iodide[79], iso-butyl iodide[80], t-butyl iodide[81], ethylene iodide[82] and acetyl iodide[83]. Hydrogen iodide was formed in the case of the following, n-propyl, iso-propyl, n-butyl, sec-butyl and iso-butyl iodides. The rates of decomposition of n-propyl and iso-butyl iodides were increased by the initial addition of iodine, the rates of reaction being given by

$$\frac{d(RI)}{dt} = k(RI)(I_2)^{1/2}$$

In the case of the decomposition of sec-butyl iodide the reaction rate was given by

$$\frac{d(RI)}{dt} = k_1(RI) + k_2(RI)(I_2)^{1/2}$$

All this was done by the static method: tert-butyl iodide decomposition was found to be heterogeneous in clean vessels.

The reactions of methyl, ethyl and n-propyl iodides with hydrogen iodide were also studied by Ogg[84]. He showed that the reaction could be best represented by

$$\frac{d(I_2)}{dt} = k_1(RI)(HI)+k_2 \frac{(RI)(HI)}{(HI)+(I_2)}$$

A falling off of k_2 with pressure was observed and explained on the collision theories of unimolecular reactions.

It was suggested that the following mechanism with the given activation energies explained the experimental results.

$$RI + HI = RH + I_2 + 16 \text{ k.cals.} \quad (\text{accounts for } k_1)$$

$$\left.\begin{array}{lll} RI & = & R + I - 43 \text{ k.cals.} \\ R + HI & = & RH + I + 24 \text{ k.cals.} \\ R + I_2 & = & RI + I + 8\text{k.cals.} \\ 2I + M & = & I_2 + M \end{array}\right\} \text{accounts for } k_2$$

The $D(CH_3 - I)$ value of 43 k.cals. cited by Ogg is now definitely regarded as being too low.

Butler and Polanyi[2], and Butler, Mandel and Polanyi[15] investigated the pyrolysis of iodides by a flow technique. As previously mentioned the advantages of the method were

(a) small partial pressure of reactant,

(b) total decomposition limited to very small percentages, by means of which it was hoped to reduce considerably the amounts of secondary reaction. They claimed also, that the brief duration of the reaction suppressed secondary reaction, but collision theory calculations show that this will only be true if steric factors of the order of 10^{-4} apply to the radical reactions.

Since the C-I bond is the weakest, the formation of iodine was attributed to

$$RI = R + I.$$

When HI was formed, they explained it by an alternative unimolecular decomposition such as

$$C_2H_5I = C_2H_4 + HI$$

The iodine must result from $I + I = I_2$ either by a three body collision, or on the walls of the reaction vessel.

If this is the only reaction removing iodine atoms

$$R + I = RI$$

$$R + I_2 = RI + I$$

can be neglected, and if R is removed without initiating a chain reaction then the rate of iodine formation measures the rate of initial decomposition. Butler and Polanyi tried to obtain evidence for back reaction by

a) adding mercury vapour and nitric oxide - Hg vapour had no effect on the ethyl iodide decomposition and NO only doubled the rate,

b) agreement of activation energies derived from the rate constant and that calculated assuming a frequency factor of 10^{13} sec^{-1}.

On the basis of these two arguments they concluded that the rate of formation of iodine molecules approximated closely to the rate of dissociation of R - I. They were aware of the crude nature of this approximation and calculated the activation energies from $k_{uni} = 10^{13} e^{-E/RT}$, since they did not consider the activation energies derived from the temperature coefficient sufficiently reliable.

The reaction R + I = RI which is most probably bimolecular would be faster than I + I which requires a third body, and the chance of recombination is increased by

$$R + I_2 = RI + I$$

Butler and Polanyi accumulated evidence to show that in the cases of ethyl iodide, propyl iodide and n-butyl iodide back reaction was negligible. It appeared therefore that back reaction was prevented by the removal of the organic radicals.

Possible reactions by which radicals may be removed are

$$R + R = RR$$

$$\text{or} \quad R + R = RH + \text{olefine}$$

and $R + RI = RH + R^1$ where R^1 is of the type $-CH_2I$. The first cannot be more efficient than $R + I$ or $R + I_2$ and so $R + RI$ appears the more likely owing to the higher concentration of RI.

Evidence for the types of reaction involved may be obtained from the photochemical investigations of West and Ginsburg[65], West and Schlessinger[66], and Bates and Spence[67] on methyl iodide. They showed that at room temperature the quantum yield was very low due presumably to the efficiency of the back reaction. West and Schlessinger proposed the following mechanism

$$CH_3I + h\nu = CH_3 + I \quad (1)$$

$$CH_3 + I = CH_3I \quad (2)$$

$$CH_3 + CH_3I = CH_4 + CH_2I \quad (3)$$

$$CH_2I + I = CH_2I_2 \quad (4)$$

$$CH_2I + CH_3 = C_2H_5I \quad (5)$$

$$CH_2 + CH_3I = CH_2I_2 + CH_3 \quad (6)$$

$$CH_2I_2 + h\nu = CH_2 + I_2 \quad (7)$$

$$2\,CH_2 = C_2H_4 \qquad (8)$$

$$CH_2 + CH_3I = C_2H_5I \qquad (9)$$

$$CH_3 + CH_3 = C_2H_6 \qquad (10)$$

$$I + I + M = I_2 + M \qquad (11)$$

It was assumed that reaction (2) was highly efficient whilst (3), (4) and (6) accounted for the products. If silver was added to the system the quantum yield rose to nearly unity, practically all the iodine appearing as silver iodide.

Bates and Spence attach some importance to the reaction

$$CH_3 + I_2 = CH_3I + I \qquad (12)$$

Support for this was obtained by Iredale[88] investigating the reaction in the presence of nitric oxide, the rate being increased twelve times. Anderson and Kistiakowsky[80] investigated the photolysis of CH_3I, HBr and I_2 mixtures, but the large excess of iodine undoubtedly favoured (12).

Jungers and Yeddanapalli[89] investigated the sensitisation of ethylene polymerisation by a series of alkyl iodides. An increase in effectiveness was found in the order Me, Et. nPr, iso Pr. This is presumably due to a decrease in the same order of the efficiency of the reaction $R + I = RI$, probably on steric grounds.

Williams and Ogg[90] studied the photolysis of methyl iodide in the presence of hydrogen halides. They assumed the main back reaction to be :-

$$CH_3 + I_2 = CH_3I + I$$

CH_3 + I being neglected. Schultz and Taylor[191] have studied the photolysis of methyl iodide and explain their results by assuming that methane is formed by the attack of hot methyl radicals on methyl iodide molecules, and ethane from the association of methyl radicals which have lost their excess of kinetic energy. Studying the effect of carbon dioxide on the relative amounts of product they concluded that CO_2 is 67% as effective as methyl iodide in cooling a hot methyl radical. Dacey[92] has shown that the photolysis of trifluoromethyl iodide has a very low quantum yield proceeding

$$CF_3I + h\nu = CF_3 + I$$

$$CF_3 + I = CF_3I$$

$$CF_3 + I_2 = CF_3I + I$$

Nitric oxide and silver increase the yield by preventing the reverse reaction. The activation energies of the radical reactions must be low and of the order of 1 k.cal. Benson[93] has studied the nature of recombination processes and shown that they have a negative temperature coefficient so chain lengths will be longer and radical-molecule reactions more likely in pyrolytic reactions than in photolysis systems.

It is assumed that the mechanism of the pyrolysis of iodides follows

$$RI = R + I$$

$$R + RI = RH + R^1$$

$$R^1 = \text{olefine} + I$$

$$I + I(+ M) = I_2.$$

The third reaction is plausible as the C-I bond dissociation energy in the radical R^1 is considerably lower than D(R - I). This yields a first order scheme in which the iodine formation measures the rate of initial dissociation. Szwarc[7] suggests n-propyl and n-butyl iodide approximate to this scheme. Ethyl iodide was found by Gowenlock[17] to behave similarly, but in addition there was a hydrogen iodide forming reaction. Butler, Mandel and Polanyi[15] had found that hydrogen iodide was formed in the pyrolysis of ethyl, n- propyl (I_2:HI ≈ 1:1) but in the case of iso-propyl, n-butyl, cyclohexyl, and β-phenylethyl iodides, HI was the chief product. As pointed out by Szwarc[7] many of the pyrolyses are very much more complicated than first thought and it has proved impossible to elucidate many of the details of these reactions.

Reinvestigation of the pyrolysis of benzyl iodide by Horrex and Szwarc[16] led to postulation of the following mechanism:-

$$C_6H_5.CH_2I \longrightarrow C_6H_5.CH_2 + I$$? $\rightleftharpoons$

$$I + I \longrightarrow I_2$$

$$2\ C_6H_5.CH_2 \rightleftharpoons C_6H_5.CH_2.CH_2.C_6H_5$$? $\longrightarrow$

The benzyl radicals were unreactive and not removed by the reaction R + RI = RH + R_1 and therefore the system approached an equilibrium state for R_1 I and I_2.

The dimerization of benzyl radicals ~~being~~ was the rate determining step. This scheme represents only a first approximation to the actual decomposition of benzyl iodide. Other evidence has confirmed the stability of benzyl radicals; they are even unaffected by oxygen.

The pyrolysis of allyl iodide was studied by Shaw and Szwarc[94] using a static system. The following scheme represented a first approximation to the kinetics of decomposition

$$CH_2 = CH.CH_2I \rightarrow CH_2 = CH.CH_2 + I$$

$$I + I = I_2$$

$$CH_2 = CH.CH_2 + CH_2 = CH.CH_2I \rightarrow \text{biallyl} + I.$$

……

UNIMOLECULAR PROCESSES.

Experimental and theoretical investigations on first order reactions have been extensive but even today the position is far from being satisfactory. At one time it appeared that first order reactions were unknown but examples were eventually found. They were explained on the basis of the now obsolete radiation hypothesis since it was argued that activation by collision was impossible. The energy chain theory of Christiansen and Kramers[95] was rejected because of observations on the effect of inert gases, and the endothermocity of some reactions which could not be plausibly explained.

An explanation using collision theory was put forward independently by Lindemann[4] and Christiansen[96] in which it was assumed that the energy obtained by collision was distributed amongst a number of internal degrees of freedom. If such energy exceeded a critical amount there was a certain probability of decomposition. It was also assumed that complete energy redistribution occurs in a collision. The theory was further developed by Fowler and Rideal[97], and Hinshelwood[98]. It appears that the maximum rate of a unimolecular reaction should be given by $k = Ze^{-E/RT}$ whereas observed rates were faster by several powers of ten. This was due to the fact that use of the factor $e^{-E/RT}$ involves energy changes for only two square terms. The difficulty was resolved by suggesting that for the complex molecules involved in unimolecular processes n square terms can contribute to energy of activation[99] . To a first approximation the rate of reaction is given by :-

$$k = Z \frac{(E/RT)^{n/2 - 1}}{\underline{|(n/2 - 1)}} e^{-E/RT}$$

This is applicable only when there is equilibrium between normal and activated molecules.

The Lindemann idea may be developed:-

$$\begin{tikzcd} A + A \arrow[r, shift left, "k_1"] & A^{\ddagger} + A \arrow[l, shift left, "k_1^1"] \arrow[d, "k_2"] \\ & \text{Products} \end{tikzcd}$$

where $A^{\ddagger}$ is the activated molecule, i.e. a molecule possessing energy in excess of that required for reaction.

In the stationary state

$$-\frac{dC_A}{dt} = kC_A = \frac{k_1 k_2 C_A^2}{k_1^1 C_A + k_2}$$

if C_A is large then $k_1^1 C_A \gg k_2$

$$\text{and} -\frac{dC_A}{dt} = \frac{k_1 k_2}{k_1^1} C_A$$

i.e. the reaction is kinetically first order.

But if C_A is small, $k_1^1 C_A \ll k_2$

$$\text{then} -\frac{dC_A}{dt} = k_1 C_A^2$$

i.e. the reaction is second order.

It is seen that the order increases gradually from 1st to 2nd order as the pressure decreases as represented in figure 1.

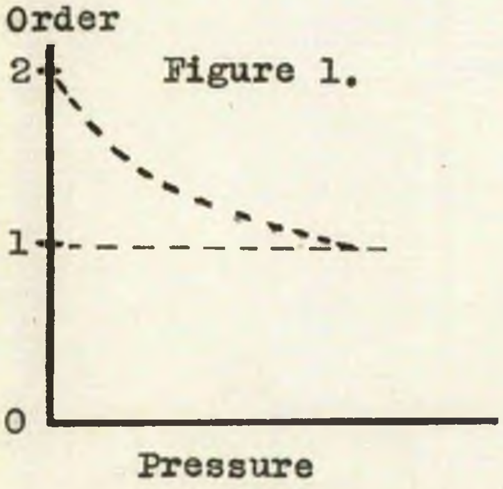

Figure 1.

It may also be deduced that

$$\frac{1}{k_{uni}} = \frac{k_1^1}{k_1 k_2} = \frac{1}{k_1 C_A}$$

i.e. assuming constancy of k_1, k_1^1 and k_2 a plot of $1/k_{uni}$ against $1/p$ should be linear.

The first order gas reactions discovered were later treated as radical chain reactions. More recently the apparent first order behaviour decompositions have been examined by Pease[35] who suggests that the experimental orders are better represented as 1.5. Hinshelwood[34] does not concur with this sweeping generalization.

The decomposition of nitrogen pentoxide exhibited first order characteristics even down to the lowest pressures. The failure to observe a falling off in rate was explained by assuming a dubious molecular diameter and the maximum possible degrees of freedom. The early extensive investigations are reviewed by Daniels[100]. Recently the reaction appears to have been satisfactorily explained by Ogg[101] and the extensive and accurate kinetic researches of H.S. Johnston[102] and his collaborators have found evidence of a Lindemann behaviour in some of the participating reactions.

Most of the theoretical aspects of unimolecular processes were founded on the decompositions of ethers and azocompounds[103]. Pease[35] questions the interpretation of the data and stresses the fact that many of the reactions are more complex than originally assumed e.g. azomethane decompositions.

When the Lindemann theory in the simple form deduced above was applied to experimental data, instead of obtaining a known plot of $1/k_{uni}$ against $1/p$ a curve as shown in figure 2, was found.

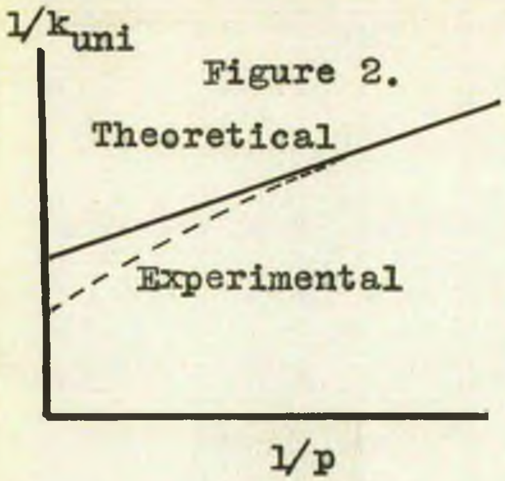
Figure 2.

This was explained by making the very reasonable assumption that k_2 the rate constant for

activated molecules $\longrightarrow$ products

depends on the energy the activated molecules have in excess of the minimum. This theory was developed by O.K. Rice and Ramsperger[104], and also by Kassel[105]. In spite of the more reasonable assumptions, these theories have the disadvantage that their mathematical expressions are complex, involving graphical integrations for attempts at numerical manipulation.

More refinements have been made by consideration of the following steps

$$A \overset{I}{\rightleftharpoons} \underset{\text{energised molecule}}{A} \overset{II}{\rightleftharpoons} \underset{\text{activated molecule}}{A} \xrightarrow{III} \text{Products}$$

of which steps II or III may be rate determining. Evans and Rushbrooke[106] have shown, that, provided the hypothesis of Rice, Ramsperger and Kassel is assumed, the rate constant is of the form $10^{13}e^{-E/RT}$ for both possibilities and hence the distinction is not useful. D.D. Eley[107] has suggested that a distinction might be made by determining the sign of temperature coefficient of the activation energy.

Long calculations have been made by Barrer[108] on step II, but apart from confirming that the greatest probability of decomposition comes from molecules which initially possess large amounts of energy the results are of little practical value.

Although the mathematical extensions mentioned above are more logically satisfying than the original Lindemann hypothesis and its treatment by Hinshelwood it has to be admitted that, until very recently at any rate, experimental data ~~was~~ were decidedly lacking and even now ~~is~~ are inadequate. Pease[35] in 1939 concluded that the isomerisation of cyclopropane to propylene[109] was the only reaction to which the theory of unimolecular reactions could be applied. Corner and Pease[110] in a reinvestigation of the reaction suggested that their observations could equally well be explained by a radical mechanism. Trotman-Dickenson[111] et al. find the reaction to be truly quasi-unimolecular and in close agreement with the Kassel theory. Howlett[65] has found that the decomposition of ethyl chloride and 1:1 dichloroethane exhibit the behaviour required by such a theory. These reactions do not involve radicals.

H.S. Johnston has shown that nitrous oxide[112] and nitrogen pentoxide decompositions[102] show unimolecular behaviour when the complicated kinetics are disentangled and freed from the effects of heterogeneity. The decomposition of nitric acid vapour[113] has been shown to be a unimolecular process, the first order rate constant for the reaction $HNO_3 \longrightarrow HO + NO_2$ falling off below one atmosphere pressure.

An earlier example, is the decomposition of F_2O_2[114] which could well be a chain reaction yet it has not been so discussed.

Theoretical calculations of first order rate constants have been made by many workers. Although the actual values obtained are of little practical value the models and postulated processes are instructive.

The form of the rate equation for unimolecular reactions, is $k = Ae^{-E/RT}$ where $A = 10^{13}$ and can be accounted for by the so-called absolute reaction rate theory[115] which amounts to a statistical treatment of the case of a molecule attaining and passing through an activated state

$$A \rightleftharpoons \underset{\substack{\text{activated}\\\text{complex}}}{A^{\ddagger}} \longrightarrow \text{Products}$$

The reaction is first order in spite of the fact that two molecules in collision are required for activation due to the fact that the activated state consists of a single molecule $A^{\ddagger}$ and not a double molecule $A_2^{\ddagger}$. The rate of reaction can be calculated from a knowledge of partition functions. Evans and Rushbrooke[106] deduced that the transition state theory and the kinetic theory of Kassel both give the same form for the rate equation if allowance is made for the fact that molecular vibrations are not harmonic, assumed as an approximation by Kassel. A neat and original treatment of unimolecular processes on the absolute rate theory has been given by Szwarc[7].

Slater[116] has devised a method of calculating first order rate constants based on the assumption that when the extension of a bond exceeds a critical amount dissociation occurs. The rate is calculated by finding the frequency with which normal vibrations of the molecule combine to make the bond extension greater than the critical amount. Pelzer[117] much earlier used a similar but less general treatment. Polanyi and Wigner[118] first tackled this problem by assuming that energy fluctuated in the molecule in elastic waves, transformation occurring by interference causing the disturbance to exceed a critical value. All these theories have required that the pre-exponential factor should be of the order of molecular vibrations, i.e. 10^{13}. Recently Slater[119] has made a considerable advance in producing a theory by which it is possible to define precisely the number of effective oscillators given a knowledge of the structure of the molecule. Its application to the cyclopropane case[111] gives a high degree of accuracy in agreement with observation.

Fugassi and Warrick[120] have endeavoured to correlate activation energy and vibration frequency of the dissociating bond. The data lends support to the views of Slater. A recent paper by Benson[13,121] examines the implications of Slater's theory. He suggests that the Lindemann hypothesis can only be verified experimentally by studies on polyatomic molecules with 3, 4, 5 or at the most 6 atoms. Nitrous oxide kinetics as analysed by Johnston[112] is consistent with the Slater theory.

Quantum mechanics have been used to explain unimolecular processes from analogies with other physical phenomena; non-classical escape through an energy barrier analogous to radioactivity[122] and an Auger effect analogous to predissociation[123]. It is assumed in the established kinetic theories that activated molecules are in equilibrium with normal molecules. Theoretical attempts have been made which are not dependent on this assumption. Kramers[124] used an analogy to Brownian particles escaping by diffusion over an energy barrier. Zwolinski and Eyring[125] consider a chemical reaction to be represented by transitions between a number of quantum states. Both theories suggest little error is introduced in the equilibrium hypothesis.

On the other hand, Hirschfelder[126], considering that activation can only be attained by single quantum steps, suggests that there is some discrepancy. The equilibrium hypothesis remains far more useful in spite of its logical inferiority.

The kinetics of certain cis-trans isomerizations exhibit certain unusual characteristics e.g. the isomerization of dimethyl maleate studied by Kistiakowsky and Nelles[127], where a falling off in rate was found and a high pressure rate constant given by $k_1 = 1.3 \times 10^5 e^{-26.5/RT}$. These are explained in terms of the transmission coefficient and quantum mechanics of energy barriers (Glasstone, Laidler and Eyring[115]).

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ENERGY TRANSFERENCE AND THE EFFECT OF INERT GASES

In homogeneous unimolecular reactions activation occurs as result of collisions and consequently understanding of the mechanism of this exchange is important. In fact the influence of an inert gas on a quasi-unimolecular reaction in the region where the Maxwell-Boltzmann quota is not maintained is one of the most reliable tests for Lindemann theory behaviour. The method may not be completely reliable since the added gas may be having a blanketing effect which prevents chain propagating radicals reaching and ending their lives on the wall. The added gas may restore a unimolecular reaction to its limiting rate but cannot exceed it.

The sources of information on energy transference in collision processes and the results obtained will now be briefly described.

(i) Spectroscopy

It is a well known fact that abnormal molecular rotation is exceptional and so it is inferred that vibration is more important in representing activation energy. It is also found that it rarely happens that as a result of collision energy accumulates in one degree of freedom. So translational energy only activates a chemical reaction if the molecule reacts without many intervening collisions. Abnormally high amounts of vibrational and rotational energy tend to be dissipated rapidly on collision. Roessler[128] studied spectroscopically iodine vapour in the presence of added gases. Results showed that transfer occurred in every case and the probability depended in a complex manner on the molecular weight of colliding gas. Similar results were obtained by Rieke[129] with HgH and N_2. Other studies on fluorescence have given information on vibrational energy transfers but the method is far from simple and the high quanta exchanged do not quite correspond to chemical energy changes. Observations have also been carried out on electric discharges.

(ii) Sound Dispersion

The phenomenon of sound dispersion was discovered by Pierce[130] who used a piezo-quartz oscillator to measure the velocity of sound. Dispersion involves a dependence of the velocity of sound on the frequency as shown in figure 3. Dispersion is observed almost exclusively above the audible range. This behaviour was explained by Herzfeld and Rice[131] as being due to the fact that vibrations are slow at picking up the energy

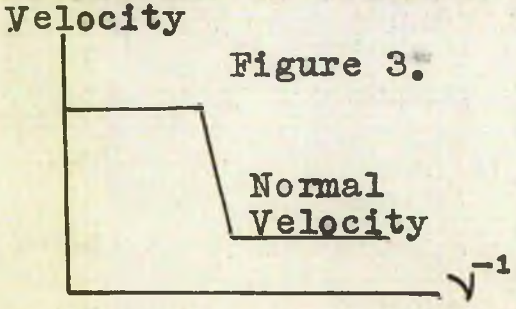


Figure 3.

Table II.

Added Gas ↓	Cl_2	N_2O	CO_2
N_2	0.88	-	-
A	1.11	-	1.0
He	33.3	3.3	33.3
D_2	-	12.5	-
H_2	50.0	9.1	125.0
CO	107.0	1.6	-
CH_4	200.0	6.7	25.0
HCl	200.0	-	500.0
NH_3	-	12.5	-
H_2O	-	-	2000.0

(To face page 39)

which would correspond to equilibrium and that above a certain frequency the energy changes are too fast to allow energy to enter vibrational degrees of freedom. Foreign gases have a varied influence in preventing dispersion which is regarded as a measure of their efficiency in transferring energy. Kneser[132] developed the method of calculating the average number of collisions required to produce an energy interchange between vibrational and other degrees of freedom. Knudsen[133] found that the critical frequency is very sensitive to the presence of impurities e.g. H_2O. A systematic investigation was carried out by Eucken and his collaborators[134] who succeeded in establishing general rules. A table of relative efficiencies of gases in transferring energy is given in Table II; it is derived from dispersion of sound data for chlorine, nitrous oxide and carbon dioxide.

No simple relationship with molecular weight is apparent but it is seen that gases with which reaction is possible are more efficient than in cases where the molecule is physically similar but reaction is not possible, e.g. N_2 and CO and Cl_2. This was pointed out by Eucken and Becker[135]. Franck and Eucken[136] point out that the mechanical picture fails and an electronic effect similar to the beginning of chemical reaction is necessary. Eyring, Gershinowitz and Sun[137] have discussed the problem in terms of potential energy surfaces.

Chemically sound dispersion provides more useful information than spectroscopy since electronic excitation and large ~~high~~ quanta are not involved. It is the energy range just exceeding the thermal average which is important in chemical activation. Dispersion indicates that the persistence of energy is for collisions of the order of thousands compared with spectroscopic evidence for very short activated life-times.

Lambert et al.[138] have investigated supersonic dispersion in organic vapours with the aim of finding if excitation of intramolecular vibration of more than one mode is possible and how much the relative ease of excitation varies. Such distinct regions were found and attempts made to relate the different activating molecules with the complex products obtained by thermal decomposition. Acetaldehyde was investigated and evidence for dimerization found.

(iii) Chemical

Information on transference of energy may be obtained from considerations of two types of reactions.

(a) Association Reactions. When two atoms combine it is essential for stabilization that some of the vibrational energy is removed as kinetic, or other, energy by collision with another atom or molecule.

Most of the data obtained has been for reactions involving halogen atoms. Hilferding and Steiner[139] investigated hydrogen bromide formation reaction from hydrogen and bromine and obtained data on the reaction $\frac{d(Hal_2)}{dt} = k_1[Hal]^2[x]$.

Rabinowitch and Wood[140] made a very careful investigation of the kinetics of the recombination of bromine and iodine atoms. The gases used as third bodies were helium, argon, nitrogen, oxygen, methane, carbon dioxide and benzene. At low pressures the reaction was heterogeneous, but at higher pressures the wall effect decreased due to increased probability of triple collisions. It was found that the velocity of recombination of iodine atoms is 2 or 3 times greater than that of bromine atoms with the same third body. Analysis of the results has indicated that the dependence on the nature of the gas is a matter of diffusion and recombination efficiency. The order of efficiency in promoting recombination is:-

H_e, A, H_2 N_2 O_2, CH_4 CO_2, C_6H_6.

Monatomic gases are least efficient and more degrees of freedom make energy transfer easier. Increasing molecular size also increases efficiency. Calculation from the data showed that for iodine, one double collision in 530 is a recombining one in helium, and 1 in 50 in carbon dioxide at atmospheric pressure ~~for iodine~~. For bromine one collision in 1100 is a recombining one in helium, and 1 in 175 in carbon dioxide at atmospheric pressure. The reliability of this work is testified by the fact that later studies[141] on the I + I → I_2 reaction have almost exactly born out the figures obtained by Rabinowitch and Wood.

E. Rabinowitch[142] has given the results (see Table III) for $k_1 . 10^{-15}$ (conc. in mol. cm.$^{-3}$) derived from

$$\frac{d(Hal_2)}{dt} = k_1 [Hal.]^2 [X]$$

Table III.

Gas	Hilferding and Steiner	Rabinowitch for Br_2	and I_2
He	0.47	1.35	3.2
Ar	0.11	2.2	6.9
H_2	1.25	3.9	7.1
N_2	0.82	4.6	14.2
O_2	-	6.9	19.0
CH_4	-	6.4	22.0
CO_2	-	9.8	33.0
C_6H_6	-	-	182
Br_2	2.6	-	-
HBr	2.1	-	-
HCl	4.9	-	-

Recent data ~~is~~ are ~~that~~ those of Christie, Norrish and Porter[143] who used the flash photolysis technique which has the advantage of eliminating heterogeneity and uncertainties in the mechanism. They investigated the recombination of iodine atoms in the presence of rare gases. Some attention is paid to the theoretical interpretation of termolecular processes and it is concluded that simple

Table IV

Recent Determinations of Relative Efficiencies of Gases in catalysing the Recombination of Iodine Atoms

Results expressed as velocity constant for recombination.10^{32} (mol.$^{-2}$ cm.^{6} sec.$^{-1}$).

Gas	Russell, Simons.	Christie, Norrish, Porter.	Rabinowitch, Wood.
He	0.94	1.73	1.8
Ne	1.00	1.86	-
A	2.00	2.42	3.6
Kr	-	3.41	-
X	-	3.44	-
H_2	2.63	-	4.0
N_2	2.49	-	6.6
O_2	3.69	-	10.5
CO_2	7.44	-	18
CH_4	4.90	-	12
C_6H_6	48	-	100
$C_6H_5.CH_3$	116	-	-
C_2H_5I	138	-	-

(To face page 43)

kinetic theory is inadequate, some special treatment of the nature and duration being essential. Russell and Simons[144] have also studied I + I + M using a photometric method for measuring the effect of many third bodies. Their results are extensive and in agreement with those of Rabinowitch and Wood. They suggest that the varying effects are due to the nature of the perturbing field (van der Waals type) of the molecule. In support of this is the near linear relationship between log k (k is the rate constant for 2I + M) and the boiling point or critical temperature. Marshall and Davidson[144] have studied the recombination of iodine atoms using a similar technique.

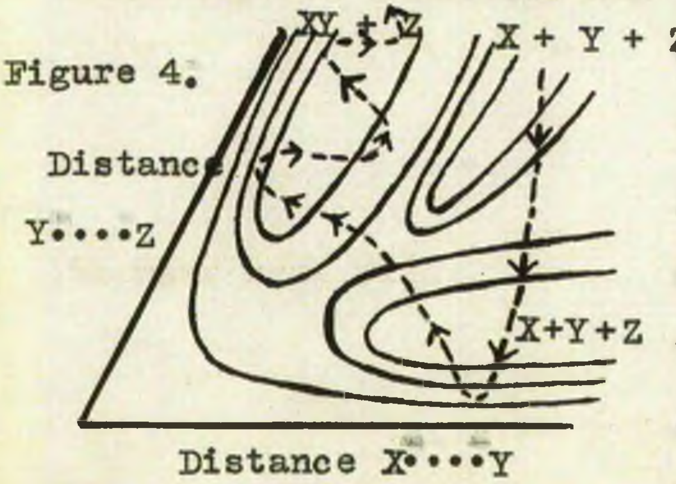
Other workers have obtained data of a more limited kind. Schweitzer and von Artsdalen[52] who investigated the bromination of neopentane found that neopentane is some 174 times more efficient as third body for

$$2\ Br + M = Br_2 + M$$

than hydrogen. The proposed mechanism for the reaction has been a subject of dispute.

Recombination reactions may be treated by the construction of potential-energy surfaces which illustrate the conversion of translational energy to vibrational energy (figure 3). Eyring, Gershinowitz and Sun[137] considered the

Figure 4.



H•••H•••H reaction by this method. Careri[145] and O.K. Rice[146] have lately discussed the theory of atomic recombination.

The potential energy surface represents the parallelism of the recombination reaction with the conversion of kinetic to vibrational energy which occurs in unimolecular processes.

(b) Unimolecular reactions. The pressure at which a reaction changes from first to second order depends upon how frequently collisions are required to maintain a sufficient supply of activated or highly vibrating molecules. Hinshelwood[147] in studies on aldehydes&ethers showed that the falling off was strongly dependent on the presence of inert gases. Nitrogen and helium had little effect but hydrogen was particularly effective. These reactions are not now regarded as being examples of unimolecular processes but the effect of hydrogen is still obscure.

The number of reactions which have been studied is small and many of these are not regarded as being true examples of unimolecular processes. Nevertheless the effects of inert gases are difficult to explain otherwise.

Volmer et al.[148] studied the decomposition of nitrous oxide. They found that the decomposition behaved as predicted by the Kassel theory although due to the simplicity of the molecule the plot $1/k_{uni}$ - $1/p$ was practically linear. The effects of different added gases were measured and the relative and absolute collisional efficiencies calculated from comparisens of the rate with and without added gases. Later work has shown the reaction to be more complex, but recently H.S. Johnston[112] has shown that if heterogeneous reaction is eliminated, the results show that the reaction is simply a unimolecular process. He finds that the Hinshelwood theory is invalid, but the rate constants are in harmony with the Rice-Ramsperger formulation.

The thermal decomposition of fluorine monoxide was studied by Koblitz and Schumacher[149]. In this case the reaction was held to be in the second order region throughout the experimentally investigated range. The effects of different added gases ~~being~~ were calculated from the equation

$$-\frac{d[F_2O]}{dt} = \frac{dp}{dt} = k_1[F_2O] + k_2[F_2O][O_2] + k_3 \cdots\cdots$$

The k values observed were compared with those calculated from collision theory, the deviation providing a measure of the relative efficiencies of energy transfer. There are indications of a chain however and the data ~~is~~ are ambiguous.

The thermal decomposition of azomethane[103] has been important in the development of unimolecular rate theory and used by Rice and Sickman[150] for studies on the effect of added gases. The relative efficiencies were calculated from measured pressures and the rate constants for pure reactant using

$$p_{effective} = p_{reactant} + \lambda p_{inert}$$

where λ is relative efficiency.

The curve of log k - $\log_p$ agreed closely with the Rice-Ramsperger theory. Rice and Sickman used pressure as a measure of the extent of reaction assuming that it took place

$$CH_3.N = N.CH_3 = C_2H_6 + N_2.$$

Later work by Riblett and Rubin[151] and also Taylor and John[152] has shown that a complex mixture of products are obtained and that the reaction has a far more complex mechanism than imagined.

Frisch and Schumacher[153] found that the fluorine dioxide (F_2O_2) decomposition followed a unimolecular law, agreement between theoretical (Kassels theory) and observed values for a plot of log k - log p being very close. The influence of added gases was studied and the relative efficiencies calculated. This work has been rather overlooked in the literature and has apparently never been reinvestigated.

Schumacher and Sprenger[154] found a falling off in rate with pressure in the decomposition of nitryl chloride. The following gases chlorine, hydrogen, nitrogen and carbon dioxide were added. All had much the same effect. This reaction is suspect, even the composition of the reactant has been disputed.

Heckert and Mack[155] decomposed ethylene oxide alone and in the presence of added gases but the nature of the

Table V

Relative Efficiencies of Gases in Transferring Energy in Unimolecular Decompositions

The measured efficiencies are compared with the efficiency of the decomposing molecule itself.

Added gas	F_2O 250°C	N_2O 653°	Azomethane 310°	F_2O_2 -37°	CH_2 CH_2-CH_2	N_2O_5
He	0.4	0.66	0.07	0.07	0.048	-
Ne	-	0.47	-	-	-	-
A	0.82	0.20	-	0.40	0.070	0.14
Kr	-	0.18	-	-	-	-
X	-	0.16	-	-	-	-
N_2	1.01	0.24	0.21	0.21	-	0.070
O_2	1.13	0.23	-	1.2	-	-
CO	-	-	0.13	-	0.84	-
CO_2	-	1.32	0.25	0.45	-	0.40
CH_4	-	-	0.20	-	0.24	-
NO	-	-	-	-	-	0.30
H_2O	-	1.5	0.46	-	0.74	-
Propylene	-	-	-	-	1.0	-
$C_6H_5CH_3$	-	-	-	-	1.10	-
D_2	-	-	0.46	-	-	-
H_2	-	-	-	-	0.12	-

(To face page 47)

reaction is unknown.

Recently Johnston[109] has studied the effect of added gases on the nitrogen pentoxide decomposition. A careful kinetic analysis has been made; limiting low concentration rate constants have been found for the reaction

$$N_2O_5 + M \longrightarrow NO_2 + NO_3 + M$$

in the presence of different foreign gases. These provide a direct comparison of the relative efficiencies of various gases in activating the reactant molecule and some information about the form of the deactivational rate functions.

In Table V results for some of the reactions are presented.

As mentioned earlier the effect of added gases may be used as a test for a true unimolecular reaction. Corner and Pease[110] added different gases to the decomposing cyclopropane system but the results were not conclusive and did not distinguish between the radical-chain and rearrangement mechanisms. Experiments with added n-butane indicated a radical reaction but the results may have no direct bearing on the usual reaction. Pritchard, Sowden and Trotman-Dickenson[111] have shown that reaction to be a molecular rearrangement and observed the effect of additives. It appears that the efficiency of energy transfer is greater the more complex the colliding molecules. Another example is provided by the investigation[65] of the decomposition of ethyl chloride and 1:1 dichloroethane, where it was found that the addition of hydrogen chloride restored the rate below the critical pressure to the limiting rate.

The results show that there appears little relationship between the results obtained from different sources. In spite of this much theoretical work has been done but the mathematical difficulties have proved formidable. The persistence of energy in a molecule varies from periods sufficient for thousands of collisions in sound dispersion examples to the time needed for a collision for loss as fluorescence energy. It is an assumption of the unimolecular rate theories that complete loss of energy occurs on collision. This has been discussed by Kassel[156] who has pointed out the final expressions are much the same even if only one fifth of energy is lost in ten successive collisions. Zener[157] and Rice[158] have treated the problem using an idealized system the basis of which is the head-on collision of a simple particle with an oscillator fixed in space. They conclude that the nature of the molecule's force field decides the ease of transfer of vibrational energy. The role played by resonance is obscure; Patat and Bartholemé[159] conclude that identical molecules prove very effective in unimolecular and recombination reactions where resonance aids vibration-vibration changes, but is ineffective for vibration-translation changes such as occur in the dispersion of sound. On the other hand Zener believes that resonance transfer is of very small magnitude. Massey[160] has recently reviewed physical theory on this matter but the results quoted do not provide much useful information from the chemical aspect. Earlier reviews of collision processes and the relationship to chemical activation have been presented by Oldenburg and Frost[161] and by Patat[162].

APPARATUS AND EXPERIMENTAL TECHNIQUE

All the experiments were carried out using a flow system with continuous circulation of the carrier gas. Two sets of conditions were employed:-

(i) high pressure experiments with 150-600 mm. of nitrogen as carrier gas,

(ii) low pressure experiments with 1.5 - 15 mm. of different gases.

The following is a general account of the apparatus and technique, modifications for particular purposes being described later in the section dealing with the results.

The Vacuum Line. The apparatus was evacuated by means of a mercury diffusion pump backed by a rotary oil pump. A pressure of 10^{-6} mm. of mercury was normally attainable, the actual pressure being read on a single McLeod gauge

The Circulation Pump. For work at high pressures a pump illustrated in figure 5 was constructed. Drayton flexible

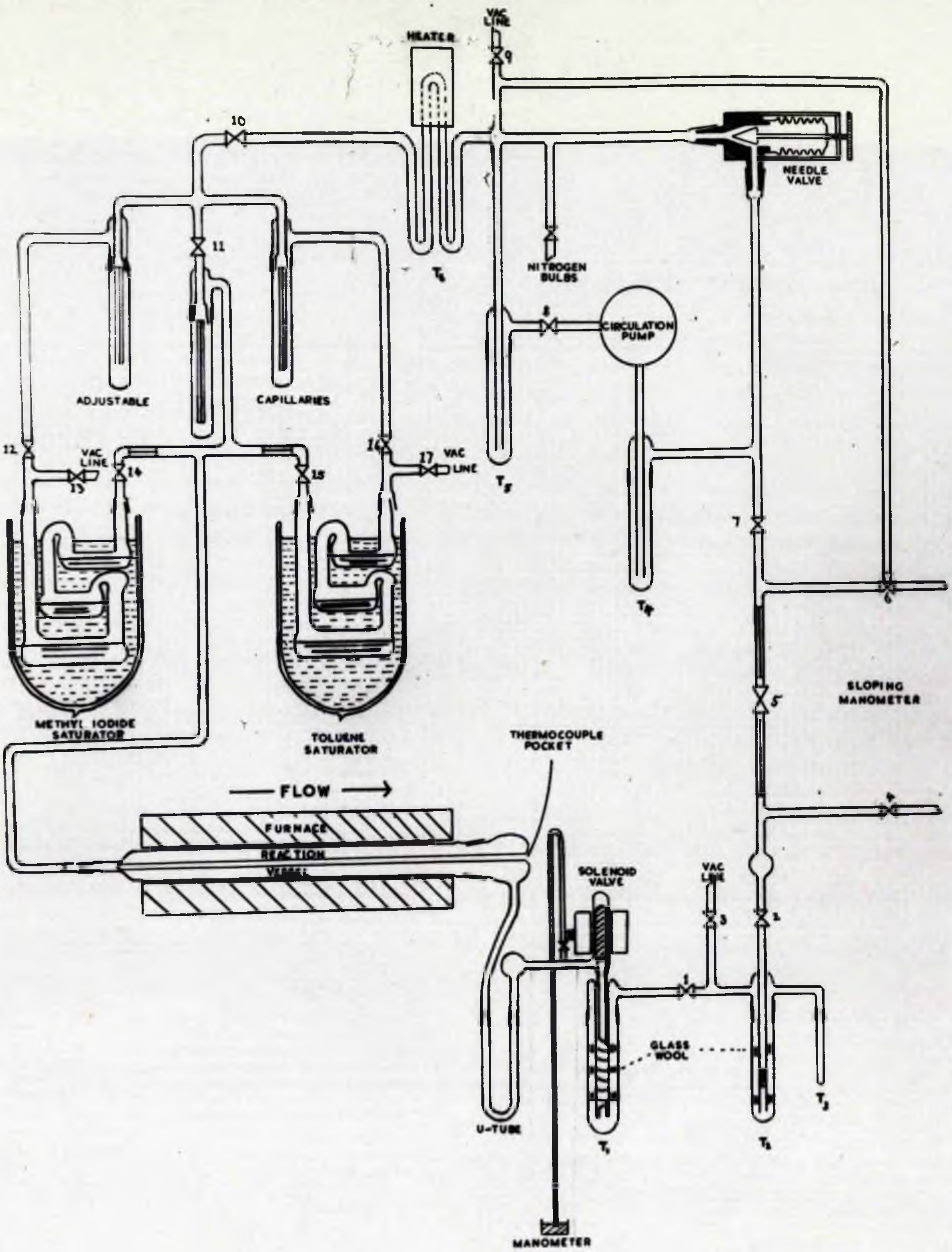


FIGURE I.

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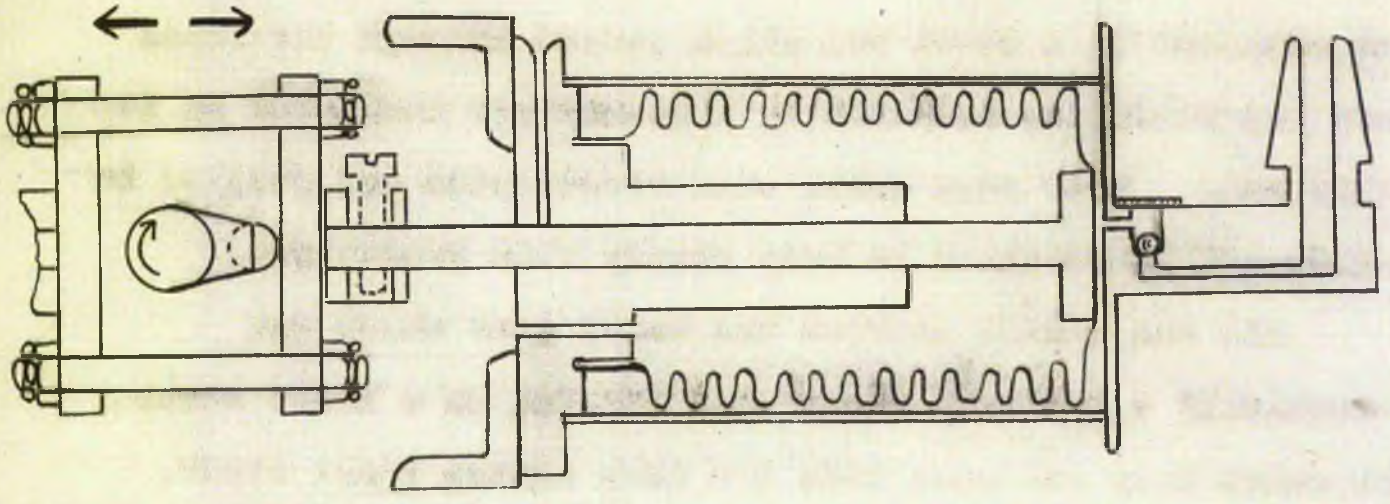
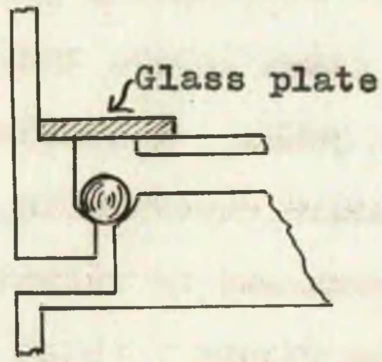


Cross section of pump unit with inlet valve.

Figure 5 (a)



Cross section of outlet valve.

Figure 5 (b)

(To face page 50.)

brass bellows were fixed to a brass base and enclosed by a brass tube and end plate. The inside head of the bellows was attached to a steel rod which passed through the brass base and which was actuated by a crankshaft mechanism at its other end. Four such units were constructed and coupled in pairs. This resulted in very steady flow conditions.

The end plates carried the valve gear which was essentially a 1/8 inch steel ball bearing on a brass seat. The valve body was made from 1/2 inch square brass stock. Glass plates were sealed over the holes with picein allowing the ball bearings to be easily cleaned or replaced. Except for the valves which were brazed all the metal joints were soft soldered. Small magnets were used to lift the bearings during evacuation of the pump unit which was made vacuum tight.

The rate of flow of circulating gas was adjusted by means of a needle valve fixed across the inlet and outlet tubes of the circulation pump. A similar flow adjustment was used in the low pressure experiments.

(All the description may be related to the diagrams of the complete apparatus in figure I (high pressure) and figure II (low pressure)).

At low presures the gas was circulated by a mercury pump (with three jets in parallel) heated by Wood's metal bath. This bath was maintained at a fixed temperature (±1°C) by means of a Sunvic energy regulator. Moore[3] demonstrated that the optimum performance of such a pump was dependent both on the bath temperature and also on the pressure. The pump was

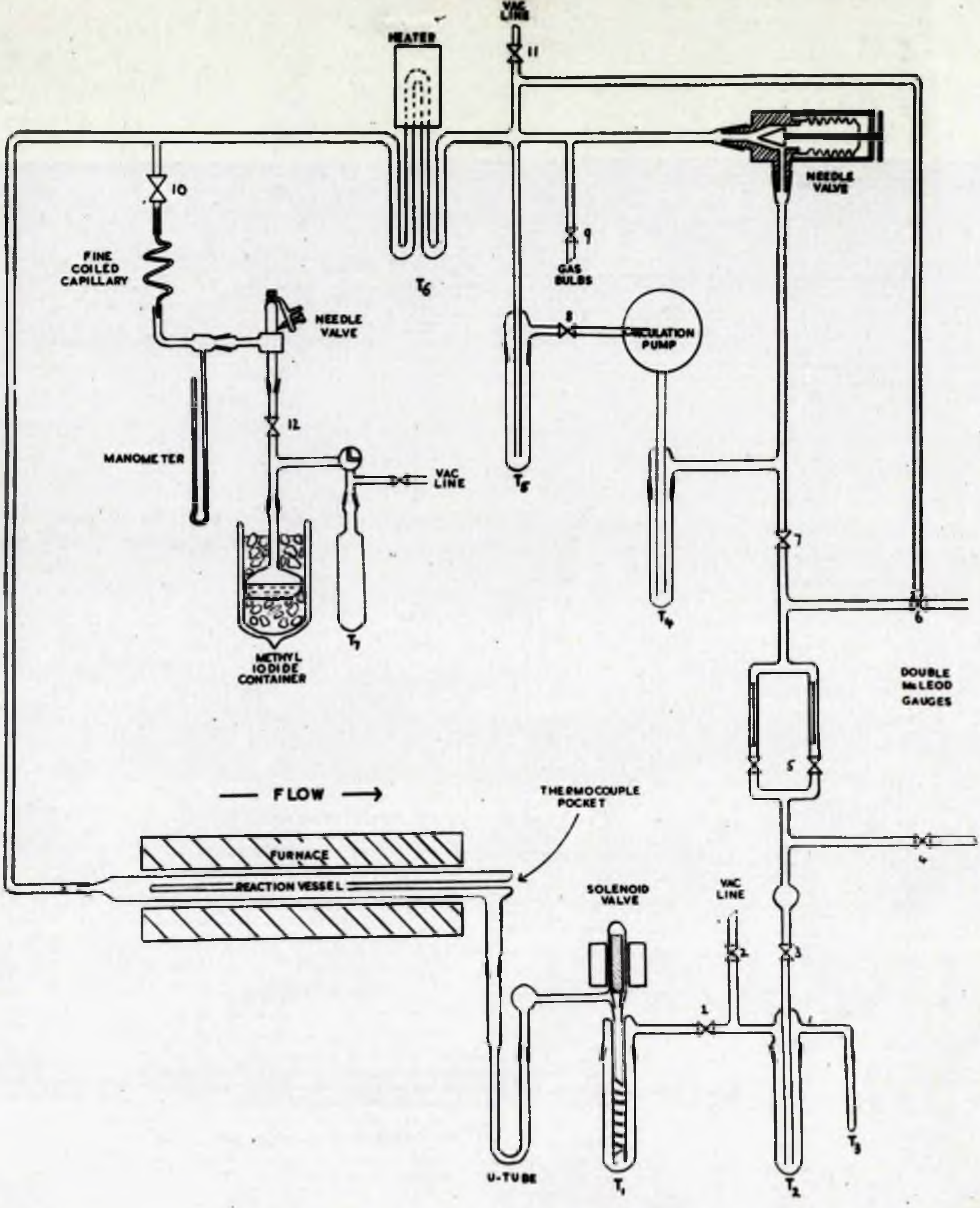


FIGURE II.

(To face page 51)

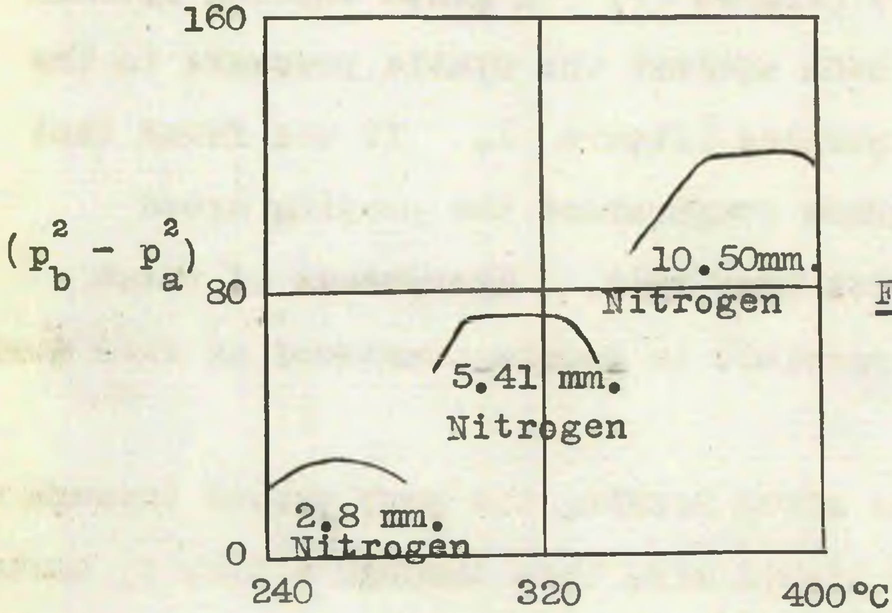


Figure 6.

Variation of flow rate with bath temperature.

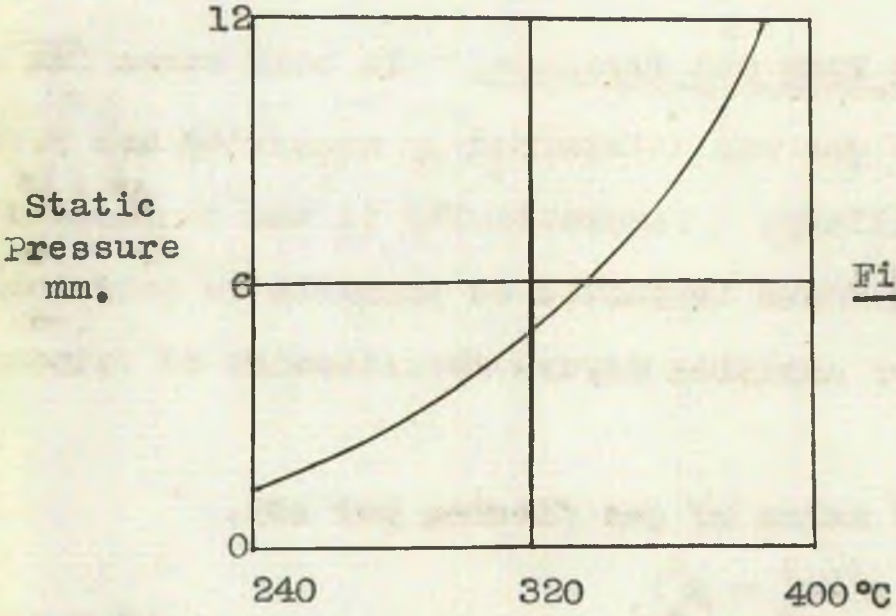


Figure 7.

Bath temperature for optimum pump performance at various pressures of nitrogen.

(To face page 51.)

therefore calibrated by plotting ($p_b^2 - p_a^2$), a quantity proportional to the rate of flow of gas (where p_b and p_a are the pressures before and after the capillary), against the bath temperature (figure 6). A graph showing optimum temperature of the bath against the static pressure in the apparatus was also plotted (figure 7). It was found that above a certain minimum temperature the pumping speed remained constant over some 25°C. Observance of these conditions made it possible to ensure constancy of flow during an experiment.

The carrier gas after leaving the pump passed through a trap T_5 immersed in liquid air, then through a trap T_6 heated at the top to 300°C and cooled below in liquid air to ensure complete removal of mercury vapour. The gas stream then passed through a jet to prevent back diffusion from the reaction vessel.

Measurement of Gas Flow and Pressure. In both cases the rate of flow of carrier gas was determined by measuring the pressure drop across a capillary. Theoretically if the dimensions of the capillary were known it should be possible to calculate the rate of flow by applying Meyers modification of Poiseuilles Law.

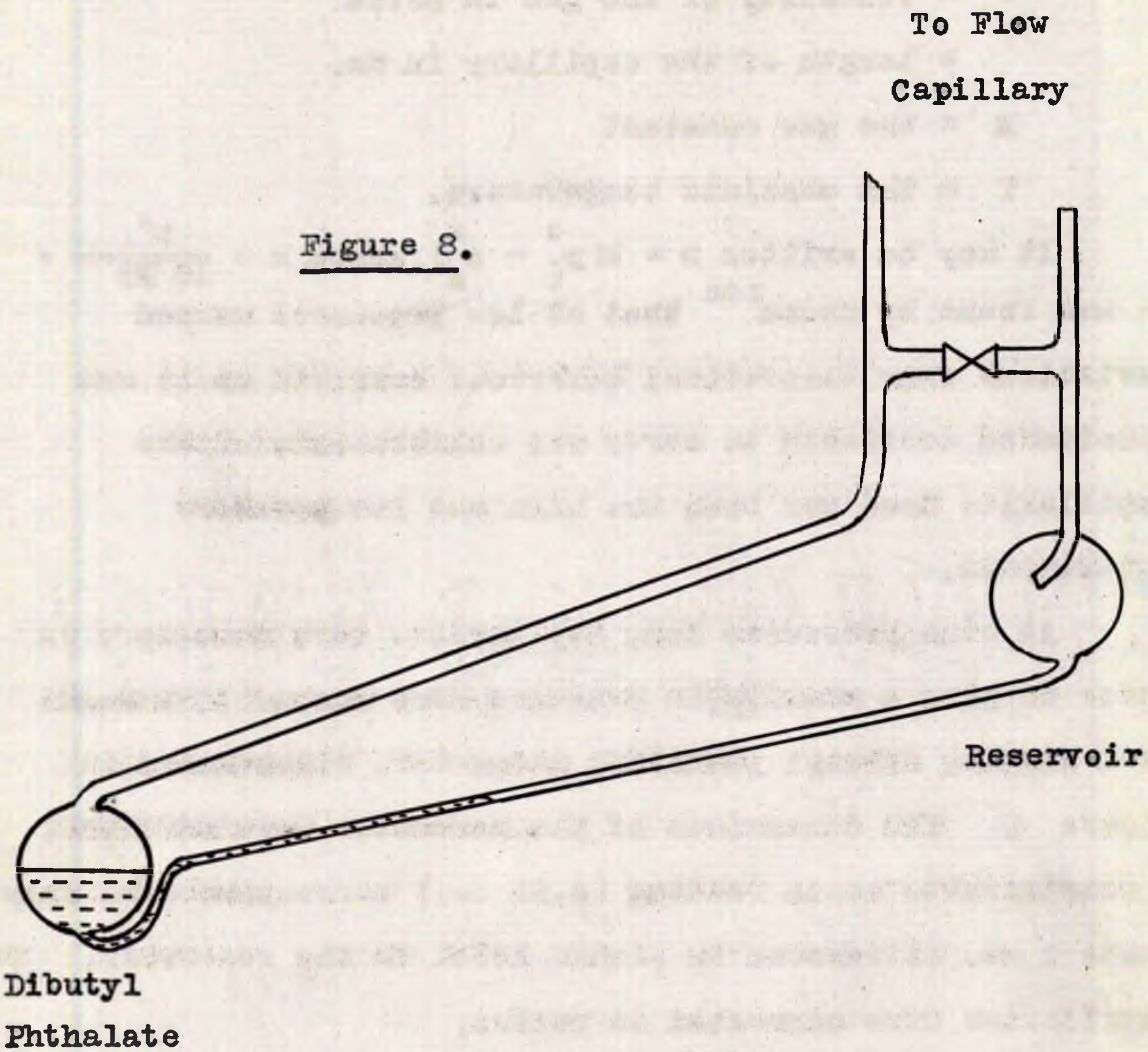
The number of moles of gas flowing per sec.

$$n = \frac{\pi r^4 (p_b^2 - p_a^2)}{16(RT\eta}$$

where r = radius of the capillary in cm.

p_b = the pressure before the capillary in dynes/cm.^{2}

Figure 8.



High Pressure Sloping Manometer.

(To face page 52.)

p_a = pressure after the capillary in dynes/cm.^{2}

η = viscosity of the gas in poise

l = length of the capillary in cm.

R = the gas constant

T = the absolute temperature.

It may be written $n = k(p_b^2 - p_a^2)$ where $k = \dfrac{\pi r^4}{16 l R T \eta}$. It was found by Cowan[163] that at low pressures marked deviations from theoretical behaviour occurred, so it was considered desirable to carry out calibrations of the capillaries used for both the high and low pressure experiments.

At high pressures long capillaries were necessary in order to give a measurable pressure drop measured by means of a sloping dibutyl phthalate manometer, illustrated in figure 8. The dimensions of the manometer were such that a considerable scale reading (c.25 cm.) corresponded to only about 1 mm. difference in liquid level in the reservoir. Two capillaries were connected in series.

The calibration compared with the calculated result from the dimensions and summation using the formula $\frac{1}{K} = \frac{1}{K_1} + \frac{1}{K_2}$ for capillary constants of tubes in series, showed little difference so the calibrated values were accepted with assurance.

The method of calibrating was essentially the same both at high and low pressure, involving the pumping of a known

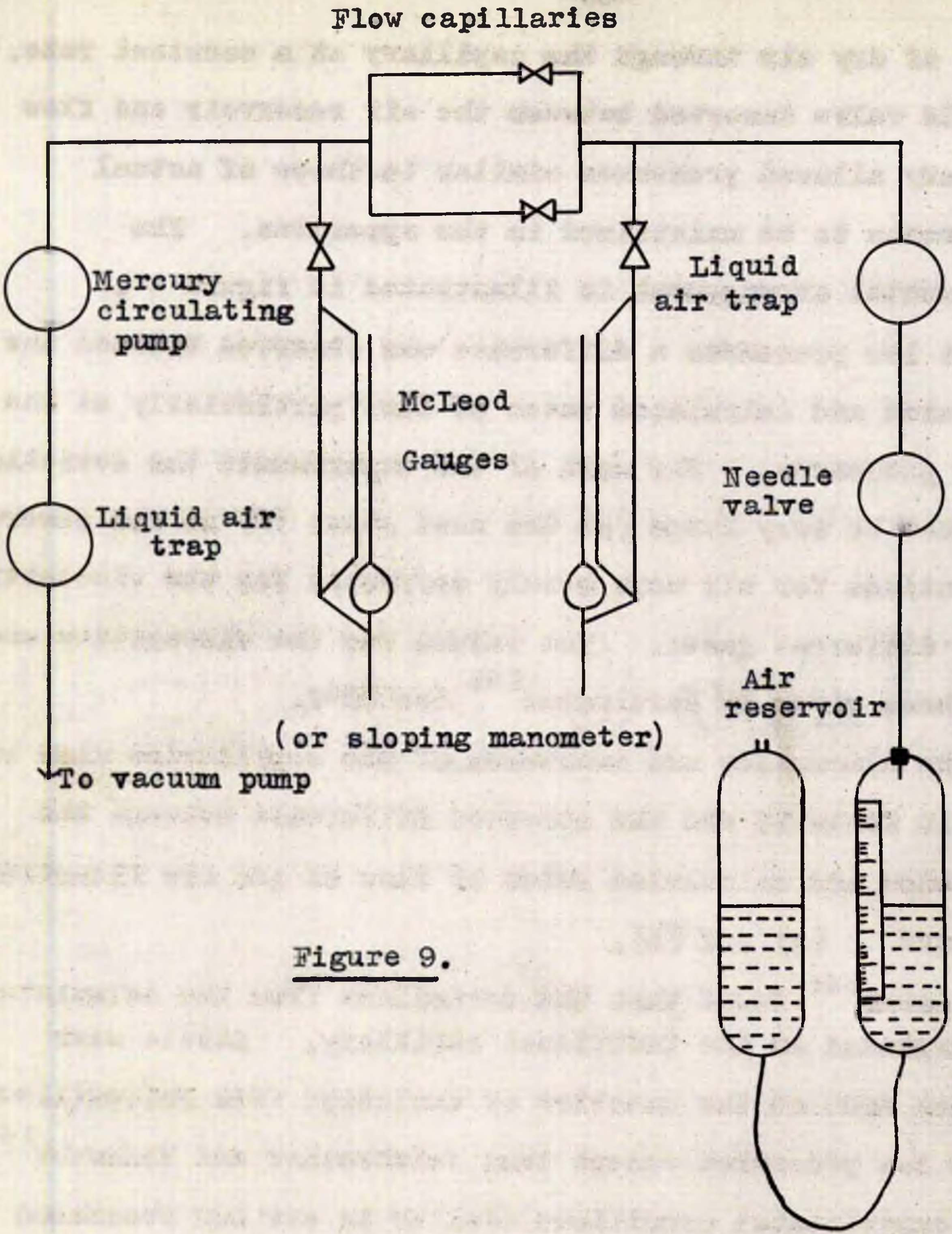


Figure 9.

Experimental arrangement for the calibration of the flow capillaries.

(To face page 53.)

volume of dry air through the capillary at a constant rate. A needle valve inserted between the air reservoir and flow capillary allowed pressures similar to those of actual experiments to be maintained in the apparatus. The experimental arrangement is illustrated in figure 9 .

At low pressures a difference was observed between the calibrated and calculated rates of flow,(particularly at the higher ~~pressures~~ values). For most of the experiments the deviations would not be very large (at the most about 7%) so the observed calibrations for air were merely corrected for the viscosities of the different gases. The values for the viscosities used were those given by Partington[164] for 20°C.

The dimensions and constants of the capillaries used are given in Table VI and the observed difference between the calibrated and calculated rates of flow of gas are illustrated in figure 10 (a) and (b).

Cowan[164] found that the deviations from the calculated rate depended on the individual capillary. Little work has been done on the question of deviation from Poiseuille's Law at low pressures, except that Fairbrother and Warhurst[165], under experimental conditions similar to our own, recommend insitu calibration.

At low pressures the pressures on each side of the capillary were measured by means of double McLeod gauges.

In order to determine the contact time it is necessary to know the average pressure in the furnace. At high pressures where the pressure drop along the tubes used was

Table VI

Details of the flow capillaries.

Capillary	Length cm	Radius cm	Capillary Constant (pressure in mm.)^2 moles N_2/sec 10
High pressure	-	-	6.320 (calibrated)
Low pressure			
(i)	14.30	0.1095	82.71 (calculated)
(ii)	7.975	0.1081	140.1 (calculated)

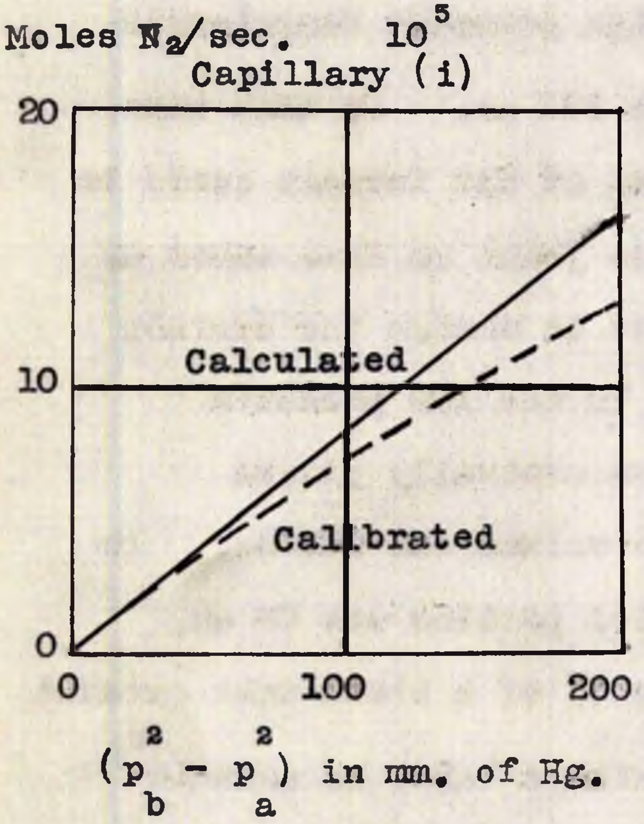


Figure 10 (a)

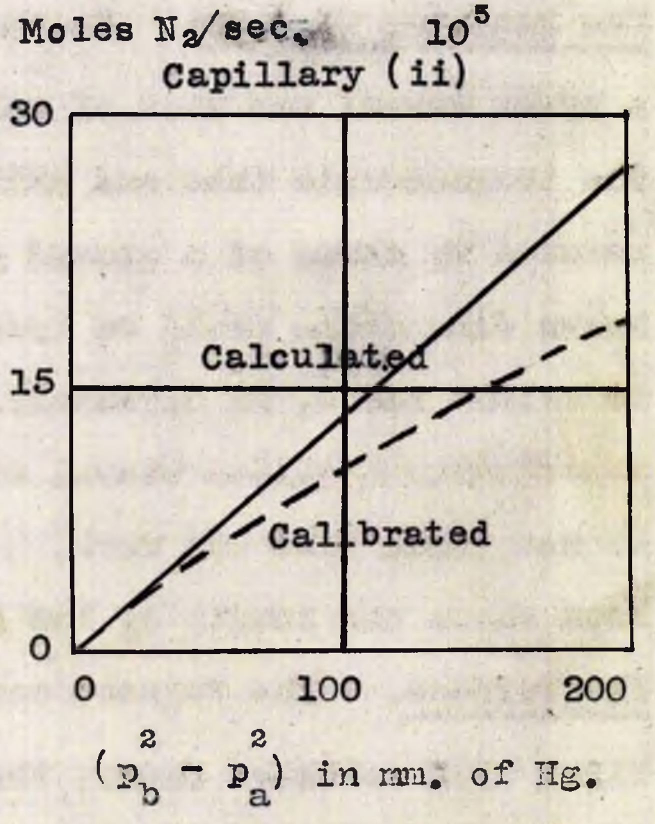


Figure 10 (b)

(To face page 54.)

negligible the furnace pressure was read directly from a mercury manometer at the exit end of the furnace. The average pressure in the furnace at low pressures was taken as that at the exit of the furnace plus one third of the difference between this and the pressure between traps T_5 and T_6 (figure II). One third and not half the difference was taken since the greatest pressure drop was at the jet before the furnace. Preliminary experiment showed that the pressure at the exit of the furnace was measurably the same as that immediately before the flow capillary. A two way tap was used so that the pressure immediately after the capillary, or the pressure between traps T_5 and T_6 could be measured.

The Reaction Vessels. In the high pressure experiments a pyrex vessel was used of volume 387 cc. 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 inserted to change the surface to volume ratio, if necessary. In the low pressure experiments a silica vessel with a centrally placed thermocouple tube was used. The volume was 265 cc. In both cases the length of the heated portion was 60 cm.

The Furnace. The furnace consisted of a steel tube covered first with asbestos paper, then with a layer of alundum cement and wound with nichrome tape. The winding was closer at the ends and six tappings made along it. Shunts

Table VII

Metal	Melting point °C	Measured E.M.F. mv.
Tin	231.9	9.40
Lead	327.4	13.33
Zinc	419.4	17.19
Antimony	630.5	26.18
Silver	960.5	39.65

(To face page 55.)

were connected across the tappings and varied so that in the working region the temperature was constant along the tube to ±1°C, except near the ends.

Temperature Control and Measurement. The temperature of the furnace was controlled and maintained constant within ±0.5° by means of a Variac transformer fed from the mains via a constant voltage transformer.

The temperature of the reaction vessel was measured by means of a chromel-alumel thermocouple calibrated at points given in Table VII. The E.M.F. was measured on a direct reading potentiometer and the results plotted against temperature. The results agreed with the literature data[166] within the limits of experimental error at high temperatures.

Collection of the Products. The traps were arranged in triplicate so that three experiments could be done without opening up the apparatus to the air. After leaving the reaction vessel the gas stream passed through a U-tube into one of three possible paths (only one is illustrated in the diagram) through an all glass valve consisting of a plunger with a piece of soft iron sealed inside it. The plungers were raised and lowered by means of a rheostat which controlled the current through the solenoids.

Each solenoid could be switched on or off independently of the others. The gas passed down a double walled tube with a nichrome tape heater in the interspace, which prevented products blocking the tube. The gas passed through the trap T_1, tap 1, trap T_2, and then rejoined the common line (CL). The system of traps T_2 and T_3 could be evacuated separately through tap 2. The uses of the traps and refrigerants depended on the nature of the particular experiments.

In the high pressure experiments it was necessary to have both traps T_1 and T_2 in liquid air to obtain complete removal of the products. It was also necessary to have the traps loosely packed with glass wool for the same reason.

A spare single trap was added to the apparatus so that if conditions were changed during a run the gas flow could be passed through it until steady conditions were attained. It was also useful before an actual experiment began for the same reason.

Introduction of Methyl Iodide and Toluene. A split-flow technique was used to introduce the methyl iodide and toluene into the apparatus at high pressures. This is illustrated in figure I. Three paths were available to the gas stream; (a) straight through to the furnace, (b) through the MeI saturator to the furnace, (c) through the toluene saturator. The partial pressure of halide and toluene depended on the amount of liquid picked up by the gas stream so adjustment of the flow through the three paths by use of suitable capillaries gave required values. Capillaries after the saturators prevented back diffusion.

In most experiments baths around the saturators were maintained at 0°C by immersing in melting ice, but in some experiments when the partial pressure of toluene was varied, baths at different temperatures were used. These were kept constant within ±0.2°C.

At low pressures the halide was injected into the gas stream by means of an injection unit shown in figure I. The methyl iodide was contained in a vessel A and the vapour passed through a coiled capillary into the apparatus. The fore-pressure was controlled by means of a needle valve and read off on a manometer. The methyl iodide container was immersed in melting ice.

The suitability of the capillary was checked by doing runs with a cold furnace and estimating the amount of halide that came over for different values of the pressure drop across the capillary. In the low pressure experiments the partial pressure was of the order of 0.1 mm.

Purification of Substances. The methyl iodide was a product of Whiffen. It was shaken with mercury, dried with calcium chloride and sodium sulphate, and twice distilled through a long Fenske column, the fraction boiling at 42.5°C being collected. It was stored in a dark bottle over a globule ~~by~~ of mercury. Further purification was carried out by distilling into the injector unit bulb cooled in liquid air from trap T, surrounded by acetone/CO_2. Exposure to light was avoided. The methyl iodide retained its absence

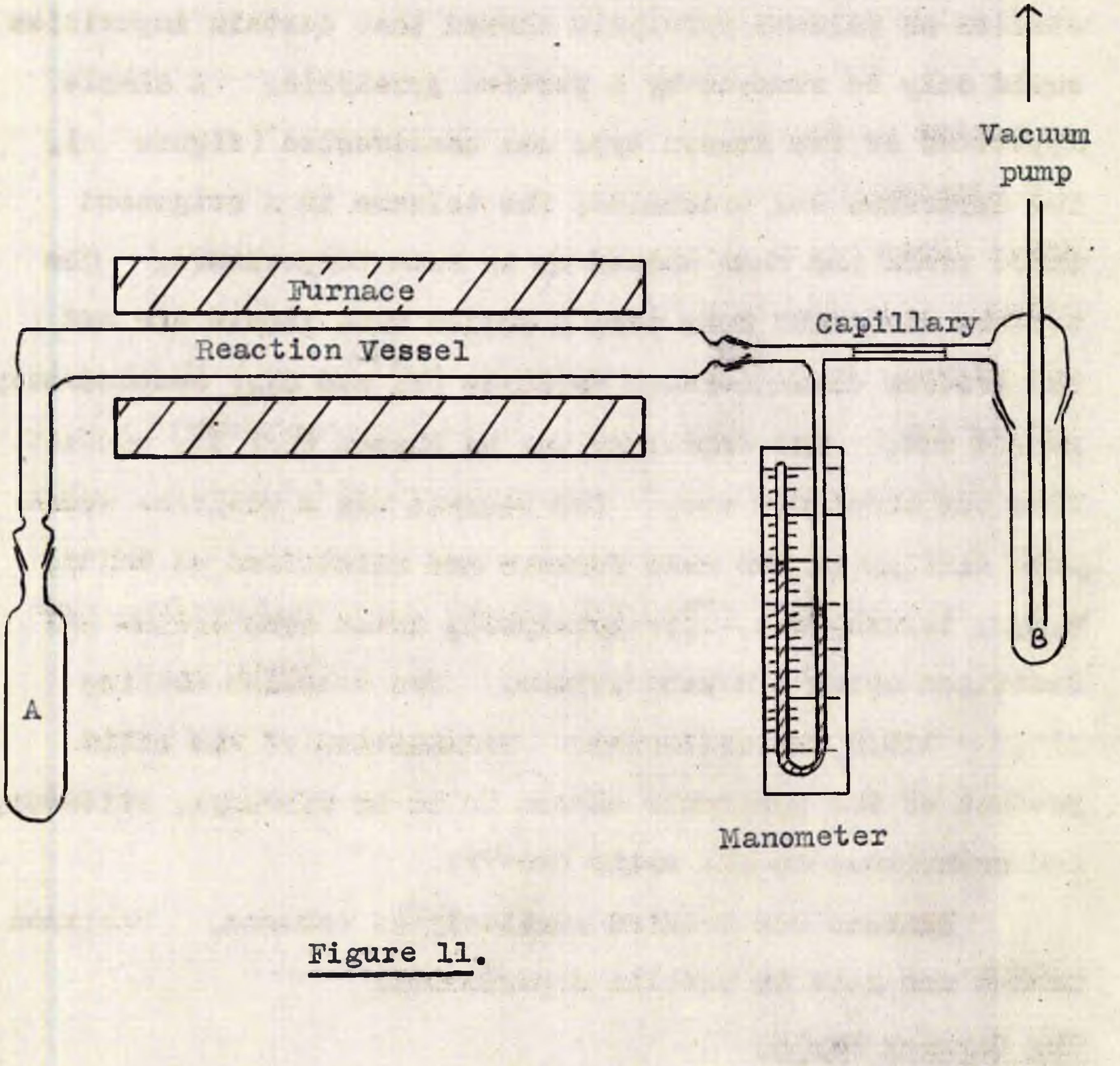


Figure 11.

(To face page 58.)

of colour for several weeks under these conditions.

When using toluene as a radical acceptor Lapage showed that consistent results were only obtained if the toluene had been previously pyrolysed. Szwarc[22] in studies on toluene pyrolysis showed that certain impurities could only be removed by a partial pyrolysis. A simple apparatus of the Szwarc type was constructed (figure 11). The apparatus was evacuated, the toluene in A outgassed three times and then warmed up to room temperature. The toluene distilled into trap B cooled with liquid air and the gaseous decomposition products (H_2 and CH_4) continuously pumped off. The capillary was so chosen that the contact time was about 0.2 sec. The furnace was a nichrome wound tube similar to the main furnace and maintained at 850°C. B.D.H. toluene was twice pyrolysed, dried over sodium and distilled using a Fenske column. The fraction boiling 110.7 - 110.9 was collected. Examination of the solid product of the pyrolysis showed it to be dibenzyl, stilbene, and anthracene in the ratio 380:7:1.

Benzene was treated similarly to toluene. Sublimed iodine was used in certain experiments.

The Carrier Gases.

(i) Nitrogen (B.O.C.) from a cylinder was purified by passing through a liquid air trap to remove condensible impurities, two sodium traps at 300°C to remove oxygen, a tube packed with glass wool to remove sodium oxide, and stored in large bulbs from which it could be admitted to the apparatus.

(ii) Argon (B.O.C.) was obtained from a cylinder and similarly treated.

(iii) Helium (B.O.C.) was similarly obtained and purified.

(iv) Neon and Krypton were spectrally pure specimens supplied by B.O.C. in soda glass vessels.

(v) Methane was obtained by treating methyl magnesium iodide with water. Pure reagents were used and the preparation carried out in vacuum using degassed reagents. The methane was allowed to rise up from a liquid air trap into a bulb.

(vi) Carbon monoxide was prepared by the action of concentrated sulphuric acid on 100% formic acid. The preparation was carried out in vacuum and the gas passed through traps packed with glass wool, soda-lime, and cooled by liquid air.

(vii) Nitric oxide was made by the action of 50% sulphuric acid on a saturated solution of equimolecular parts of potassium iodide and sodium nitrite. It was passed through towers containing concentrated sulphuric acid and concentrated potassium hydroxide. The gas was condensed in a liquid air trap, from which it was allowed to vapourise by using a bath at -80°C and recondensing in another liquid air trap. It was collected in an evacuated bulb by evaporation from a molten ligroin bath at -150°C.

A sodium trap was provided as a by-pass in the apparatus to remove, if necessary, traces of oxygen before an experiment.

Analysis of the Products. The products were collected in trap T_1 and washed out with methanol. The free iodine was titrated with sodium thiosulphate solution of suitable concentration (N/1000, N/100, or N/10) using a potentiometric method for determining the end point. The method used was similar to the very sensitive technique of Faulk and Bawden[167].

The amount of methyl iodide which passed over during a run was also determined by titration, the alcoholic solution being treated with bromine and crystalline sodium acetate. This oxidises the iodide to sodium iodate. Excess bromine was removed with formic acid, potassium iodide and hydrochloric acid added and the liberated iodine titrated with N/10 thiosulphate.

When analysis was made for hydrogen iodide, acetone/CO_2 was used to cool T_1 and liquid air trap T_2. The hydrogen iodide was condensed in T_2 and after the experiment was distilled into degassed methanol in T_3 by replacing the liquid air bath on T_2 by acetone/CO_2. The liquid air cooled methanol-hydrogen iodide mixture was allowed to melt, the hydrogen iodide passed into solution. It was refrozen, T_3 removed and water added. Potassium iodate and hydrochloric acid added and the liberated iodine titrated with thiosulphate. In some experiments, the solutions in water were titrated with N/100 caustic soda using bromophenol blue as indicator.

All analytical reagents were frequently standardised and the analytical procedures were checked for validity by making up known mixtures, e.g. in the benzyl iodide determinations.

Gas analyses were performed by use of a 60° mass-spectrometer of the Nier pattern. A gas handling unit with McLeod and bulbs manipulated the samples. Pure methane and ethane were used as reference compounds for the determinations.

Description of an Experiment. Before an experiment the apparatus was pumped out for two hours with the furnace hot and liquid air on traps T_4, T_5, and T_6. The halide was outgassed by freezing in liquid air, opening the appropriate taps and pumping out. The taps were then closed, the halide allowed to warm up whereupon any dissolved gas came out of solution. The halide was then refrozen and pumped. This was repeated three times The same procedure was carried out for toluene or other substance. The vacuum line taps were closed, carrier gas admitted to a suitable pressure and the circulating pump started. Liquid air was then put on the traps T_1 and T_2. When flow conditions were steady the halide injector taps were opened, in the case of low pressure experiments, and the halide fore pressure quickly adjusted to the desired value by means of the needle valve. The time was noted. When a sufficiency of iodine was deposited in one trap, the gas stream was changed to pass through another trap system by operation of the solenoid valves. A second experiment was then started and the time again noted. At the end of the third experiment, the halide injector taps were closed, the circulation continued for a few minutes and then stopped.

The collection and analysis of the products was carried out as described above.

In the case of low pressure experiments the furnace was allowed to cool before letting air into the apparatus. By this means the carbon coating on the furnace, essential for reproducibility, was not burnt off.

Calculation from the Results. Butler and Polanyi[2] assumed that the rate of decomposition followed an approximate first order law, the rate constants for iodine formation being calculated from the expression

$$k_{\text{uni}} = \frac{1}{t} \ln \frac{a}{a - x} \text{ sec}^{-1}$$

where t = contact time = $\dfrac{\text{volume of the reaction vessel in cc.}}{\text{rate of flow of gas in cc./sec.}}$

$$= \frac{\text{volume of vessel} \quad p \quad 273}{\text{average rate of flow in moles/sec.} \quad 22400 \quad T \quad 760}$$

where p = the average pressure in the reaction vessel in mm.

T = the absolute temperature in the reaction vessel

a = the total amount of halide passed in moles,

and x = the g atoms of iodine formed.

The percentage decomposition was calculated directly.

Most of the experimental results were expressed similarly. The partial pressures were calculated from the expression:-

$$\text{p.p.} = \frac{\text{moles of substance}}{\text{Total no. of moles passed}} \times \text{average pressure}$$

and the relationship

average pressure = the sum of the partial pressures of
(observed) all the substances.

EXPERIMENTAL RESULTS

As explained before the experiments on the kinetics of methyl iodide decomposition are subdivided into two groups dependent on the magnitude of the inert gas pressure.

HIGH PRESSURE EXPERIMENTS

Lapage in an attempt to find a method for obtaining an accurate value of the C-I bond dissociation energy, adopted the use of high inert gas pressure in order to reduce the amount of surface reaction, by allowing the methyl iodide molecules to make fewer collisions with the wall. The rate of reaction in the system 600 mm. of nitrogen and 1 - 2 mm. of methyl iodide was given by $k_2 = 10^{7.55} e^{-35,800/RT}$. The reaction being apparently first order and homogeneous within the limits of reproducibility which was poor. This unusual expression for the rate constant suggested that considerable reverse reaction existed. Nitric oxide had no effect on the reaction but in the presence of 1 - 2 mm. of toluene as radical acceptor the rate was first order and given by $k_1 = 10^{13.7} e^{-54,700/RT} \text{ sec}^{-1}$. The energy of activation is in good agreement with recent values for the C-I bond energy in methyl iodide and the frequency factor in line with theoretical expectations. It was felt however that a more detailed study of the possible variables was desirable to obtain more precise ideas of the kinetics involved. The results of such investigation are described below.

The first experiments were done in order to find if results in agreement with Lapage were obtained for the effect of temperature on the system, nitrogen (5 - 600 mm.) 1 - 2 mm. of methyl iodide and 2 - 3 mm. of toluene. The results obtained are given in Table VIII.

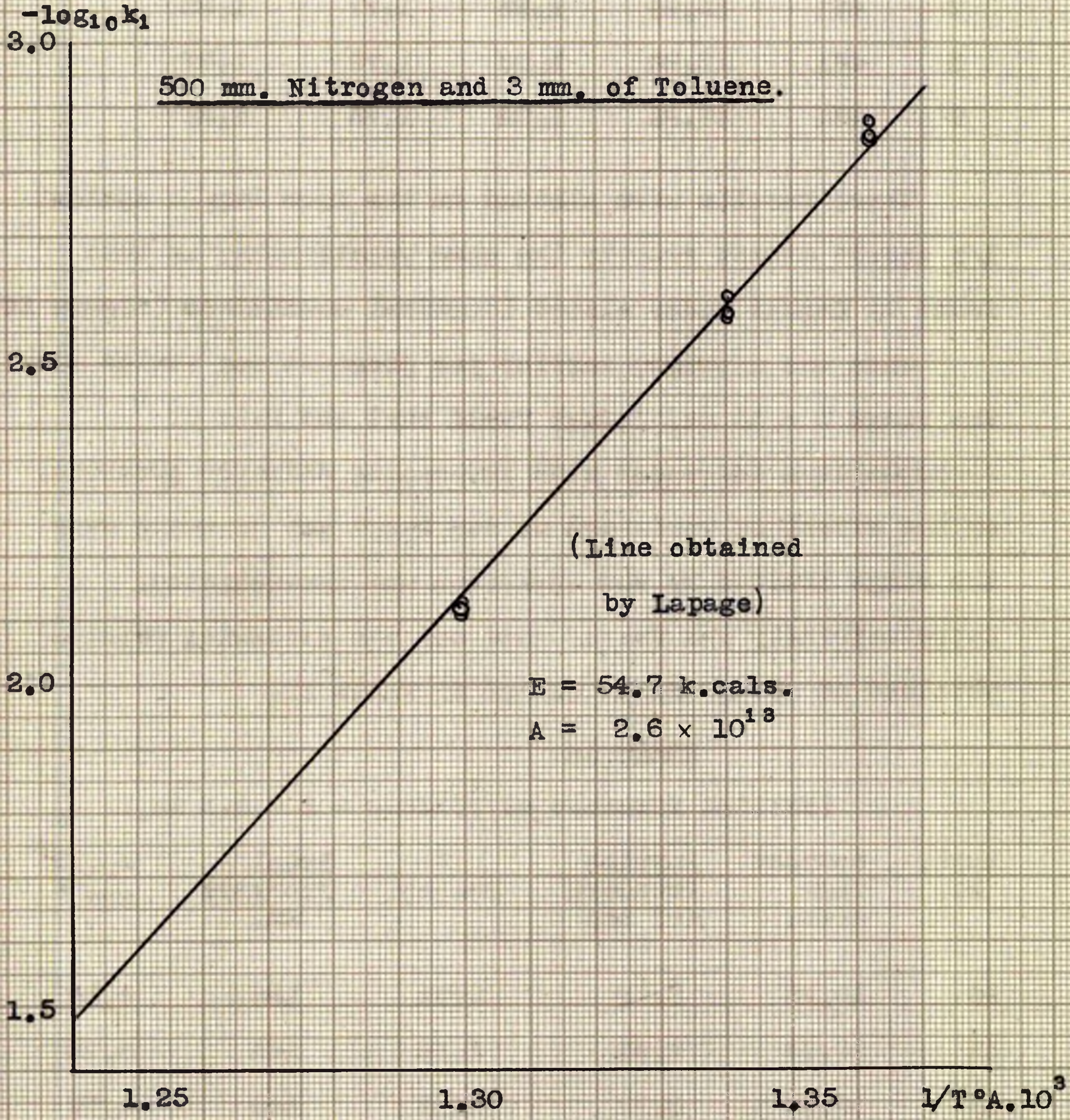
Table VIII

(Pressure of Nitrogen = 420 - 480 mm.)

(Partial Pressure of Toluene = 3 mm.)

Expt. No.	Temp. °C	Contact Time secs.	Partial Pressure MeI mm.	% Decomp.	$k_1 . 10^3$ sec^{-1}.
1	497	11.36	1.83	9.35	8.62
2	497	11.31	1.92	8.04	7.44
3	497	11.28	1.88	8.17	7.60
4	477	10.35	1.73	2.03	2.47

Figure 12.



500 mm. Nitrogen and 3 mm. of Toluene.

(Line obtained by Lapage)

E = 54.7 k.cals.

A = 2.6×10^{13}

(To face page 65).

5	477	10.35	1.93	2.02	2.65
6	477	10.35	1.93	2.02	2.66
7	461	13.29	1.23	1.77	1.33
8	461	13.29	1.26	1.76	1.32
9	461	13.33	1.22	1.73	1.30

These results when plotted in the form $\log_{10}k$ against 1/T showed almost exactly the same relationship as that found by Lapage under almost identical conditions (figure 12).

When the nitrogen carrier gas pressure was varied over the range 3 - 10 mm. Lapage found that the rate of decomposition increased with increasing nitrogen pressure, so the effect of variation of the inert gas pressure over the range limited by the apparatus was investigated. Reproducibility was fairly good and the following results obtained at 497°C are presented in Table IX.

<u>Table IX</u>

(Partial Pressure of Toluene = 3 - 3.5 mm.)

Expt. No.	Contact Time secs.	Partial Pressure MeI mm.	% Decomp.	Total Pressure mm.	$k_1 . 10^3$ $\sec^{-1}$
10	10.25	2.68	8.91	150	9.13
11	10.26	2.90	5.58	148	8.75
12	10.25	3.13	8.58	149	8.72
13	12.13	2.18	11.97	224	10.51
14	12.13	2.22	10.28	226	8.93
15	12.13	2.22	12.50	225	11.00
16	9.72	2.13	8.54	248	9.18

17	9.72	2.23	8.79	250	9.49
18	9.73	2.15	8.38	249	9.00
19	12.09	1.75	10.54	285	9.19
20	12.10	1.76	10.00	281	8.70
21	12.10	1.77	10.39	281	9.05
22	12.09	1.64	9.80	319	8.50
23	12.10	1.67	10.58	320	9.22
24	12.10	1.73	10.48	320	9.15
25	12.09	1.64	9.17	368	7.95
26	12.09	1.53	9.18	368	7.96
27	12.09	1.62	10.20	368	8.94
28	12.70	1.64	9.78	398	8.06
29	12.70	1.61	10.35	398	8.56
30	12.70	1.66	10.63	398	8.83
31	11.00	1.54	8.76	452	8.35
32	11.00	1.68	8.76	452	8.35
33	11.00	1.72	7.85	452	7.78
34	11.36	1.83	9.35	468	8.62
35	11.31	1.92	8.04	464	7.44
36	11.28	1.88	8.17	461	7.60
37	9.69	1.48	8.28	466	8.92
38	9.69	1.56	8.01	466	8.64
39	9.69	1.56	8.12	466	8.77
40	8.44	1.36	7.30	509	8.99
41	8.44	1.36	7.22	509	8.99
42	8.44	1.36	7.29	509	8.99

No significant trend or variation of the k_1 values accompanies the increasing nitrogen pressure. It was therefore concluded that the rate of reaction was independent of carrier gas pressure over the range 150 - 500 mm. The accompanying methyl iodide pressure variation appeared to have little or no effect either.

It was observed that a small amount of carbon was produced in the form of a slight brown deposit at the exit to the furnace. A crystalline deposit in the exit U-tube had a melting point of about 114°C, close to that of stilbene m.p. 118°C. Some benzyl iodide could be detected by its smell and also visually by the formation of small oily droplets during a long run involving a fairly high decomposition. Any attempt at estimation was impracticable. In one or two experiments analysis was made for hydrogen iodide but the amount detected was negligible.

Since the addition of toluene to the system had such a marked effect on the rate it was necessary to ascertain whether the limiting rate had been attained under the previous conditions (pp. toluene = 3 mm.). This was investigated by varying the partial pressure of toluene by surrounding the toluene saturator with baths at different temperatures. Ice and salt, melting ice and water were used. The actual partial pressures were determined by calibration experiments using the same conditions as for actual experiments except that the methyl iodide saturator was empty. The toluene was condensed in T_2, distilled into T_3 and the amount which had passed over in a given time determined by weighing. From these data the partial pressure could be calculated.

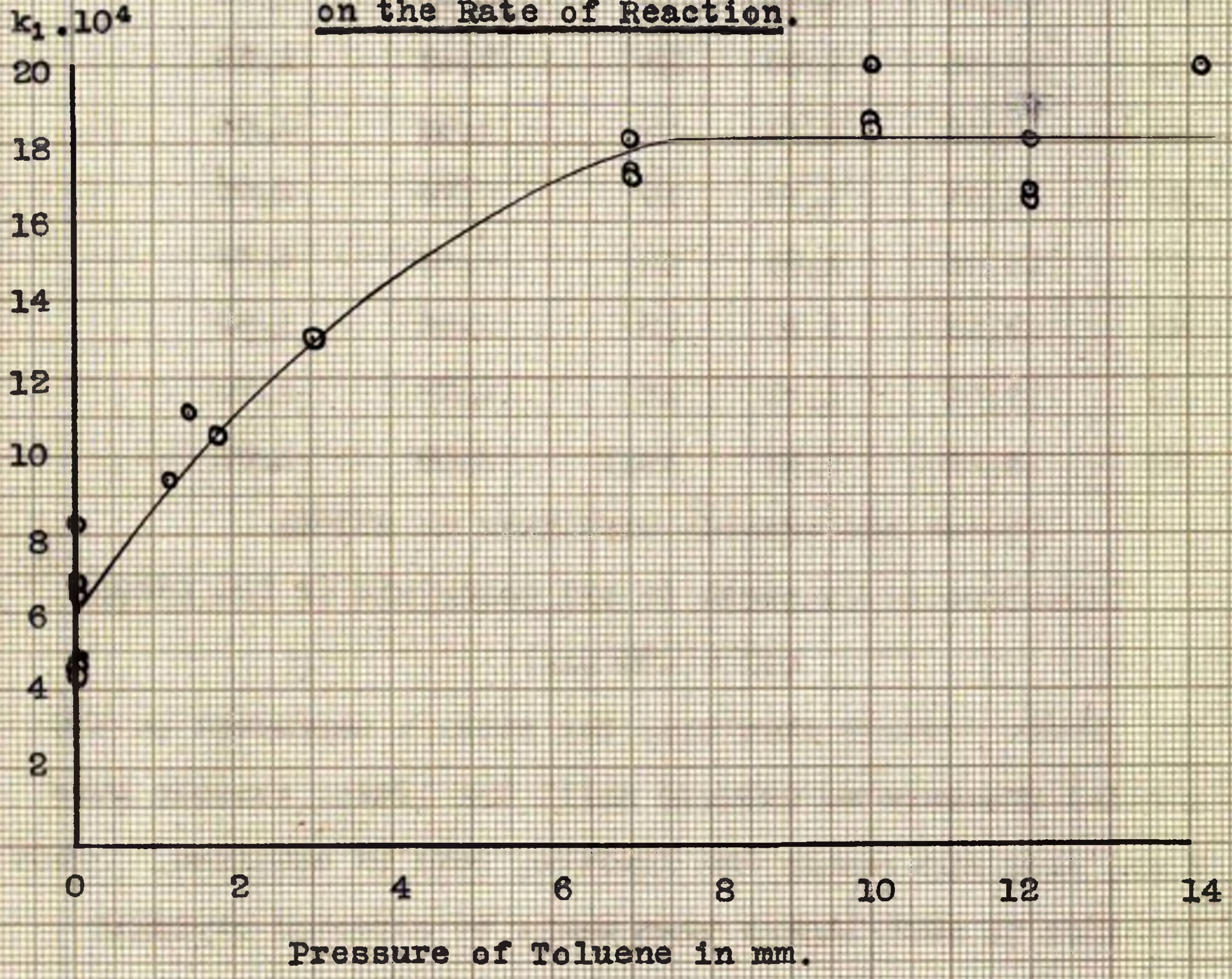
The results are listed below in Table X and in figure 13 the dependence of the rate constant k_1 on the toluene pressure is shown.

Table X

Expt. No.	Contact Time secs.	Partial Pressure MeI mm.	Partial Pressure Toluene mm.	% Decomp.	$k_1 . 10^3$ sec.$^{-1}$
43	9.03	1.46	3	10.80	12.7
44	9.04	1.48	3	11.54	13.6
45	9.02	1.53	3	12.02	14.1
46	9.03	1.48	7	19.40	23.8
47	9.04	1.48	7	19.54	24.0
48	9.02	1.55	7	19.56	24.1
		(All the above at 497°C)			
49	13.29	2.78	0	1.10	0.83
50	13.29	2.71	0	0.95	0.68
51	13.29	2.84	0	0.94	0.67
52	13.34	4.20	0	0.59	0.45
53	13.34	4.18	0	0.64	0.46
54	13.34	4.18	0	0.65	0.46
55	13.56	1.59	1.8	1.45	1.46
56	13.56	1.62	1.4	1.52	1.11
57	13.54	1.54	1.25	1.28	0.94

Figure 13.

Graph of the Effect of Toluene Pressure on the Rate of Reaction.



(To face page 69).

58	13.29	1.23	3	1.77	1.30
59	13.29	1.26	3	1.76	1.30
60	14.33	1.22	3	1.73	1.30
61	13.39	1.48	7	2.28	1.70
62	13.38	1.48	7	2.40	1.79
63	13.38	1.54	7	2.26	1.68
64	13.56	1.56	10	2.46	1.82
65	13.56	1.62	10	2.48	1.84
66	13.56	1.74	10	2.79	2.00
67	13.65	1.81	12	2.29	1.69
68	13.65	1.81	12	2.45	1.80
69	13.65	1.78	12	2.23	1.70
70	13.35	1.27	14.1	2.69	2.01

{these experiments performed at 461°C)

(Pressure of Nitrogen in all cases was of the order 440 - 480 mm.)

These results show that the rate is dependent on the partial pressure of toluene until the latter exceeds some 8 mm. when apparently the limiting rate is attained. This pressure is much higher than would be expected strongly suggesting that the reaction between toluene and methyl radicals does not occur at every collision.

It was also observed that the slight deposit of carbon which was formed during experiments with a partial pressure of toluene about 3 mm. disappeared at the higher partial pressures. This suggests that the carbon formation results from the decomposition of methyl radicals on the wall, not the gas phase. At the higher toluene pressures all the methyl radicals react with the radical acceptor, no reaction occurring at the wall and no other methyl radical reaction takes place. The effect of increasing toluene pressure is not an activating effect, such as is believed to occur in the lower pressure region since the rate appears independent of both methyl iodide and carrier gas pressures in the region 200 - 600 mm. of nitrogen. Incidentally the formation of stilbene and dibenzyl proves that the decomposition involves free radicals since neither of these substances was formed when toluene alone was passed through the hot furnace. The observed increase in rate in the presence of toluene, a known suppressor of chain reactions involving radicals, proves that the decomposition does not involve radical chains.

The Reverse Reactions of the Methyl Radical with Iodine

The low rate of decomposition for the methyl iodide and nitrogen system can only be explained as being due to a back reaction between the methyl radicals and iodine reforming methyl iodide. There are three possible mechanisms for the reverse reaction

$$CH_3 + I \longrightarrow CH_3I$$

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

$$CH_3 + I_2 \longrightarrow CH_3I + I.$$

To verify the correctness of this explanation and if possible to decide which of the above reactions is responsible

Figure 14.

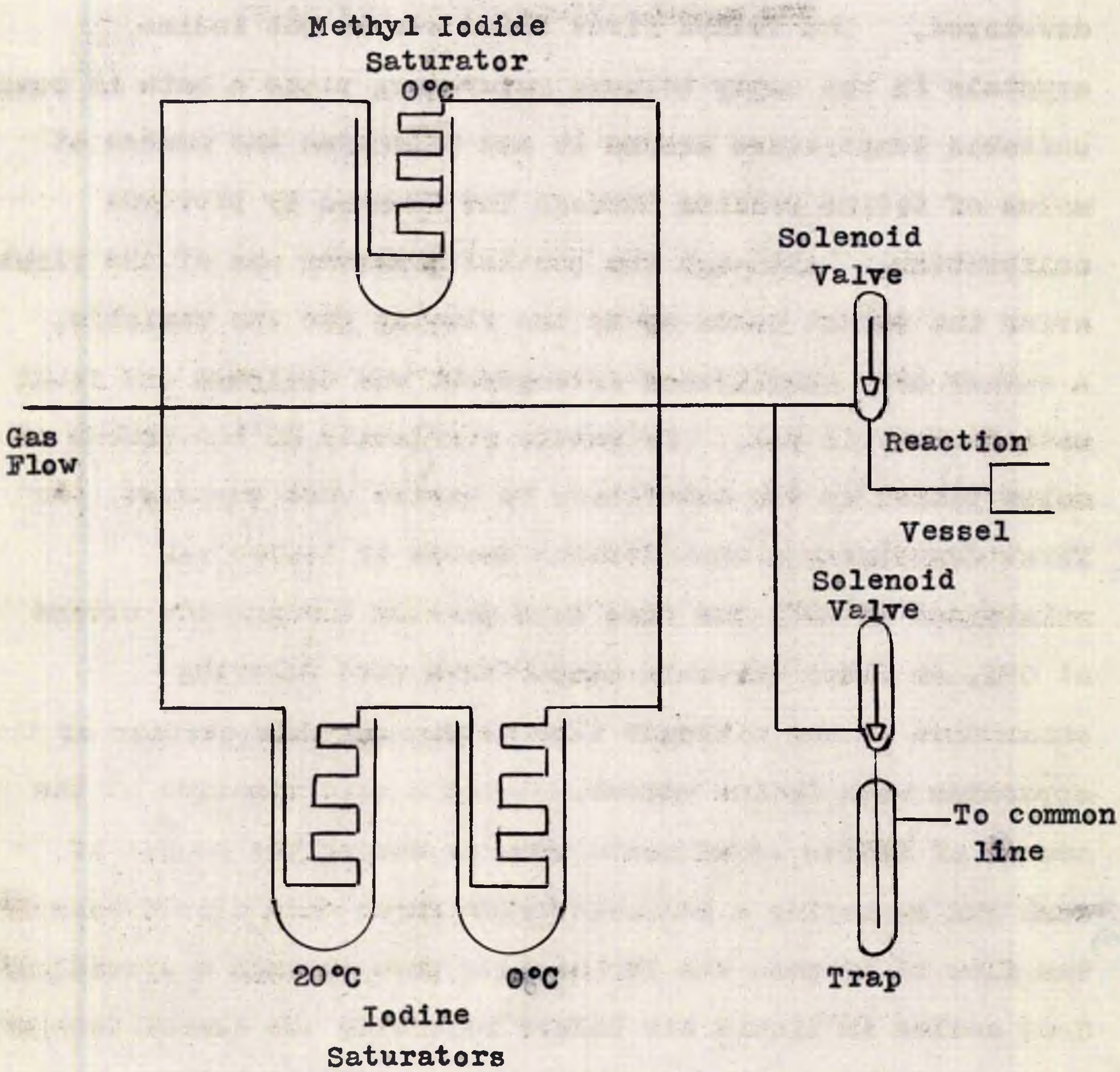


Diagram of Experimental Arrangement used for Experiments on the Effect of Added Iodime

(To face page 71).

an investigation of the effect of added iodine was carried out.

As a preliminary a method of iodine addition had to be developed. The method first tried was to put iodine crystals in the empty toluene saturator, place a bath at some suitable temperature around it and determine the number of moles of iodine passing through the furnace by previous calibration. Although the partial pressure was of the right order the amount taken up by the flowing gas was variable. A rather more complicated arrangement was designed and found satisfactory in use. To ensure regularity in the number of moles picked up two saturators in series were employed, the first containing a considerable amount of iodine was maintained at 20°C the flow then passing through the second at 0°C, or other suitable temperature thus ensuring saturation of the nitrogen flowing through this section of the apparatus with iodine vapour. Also a determination of the amount of iodine added could be made during the course of each run by having a solenoid valve which when closed caused the flow to by-pass the furnace and pass through a special trap cooled in liquid air before rejoining the common line. The essentials of this arrangement are illustrated diagrammatically in figure 14.

The first experiments were conducted at different temperatures.

Table XI

(Pressure of Nitrogen was 460 - 475 mm.)

(Toluene was absent in all these experiments)

Expt. No.	Temp. °C	Partial Pressure MeI mm.	g.moles I_2 added per sec. $\times 10^8$	Partial Pressure I_2 added mm	% Decomp.	Contact Time secs.
71	461	3.84	1.365	0.023	0.908	13.81
72	461	3.92	-	-	2.341	13.81
73	461	3.51	1.425	0.023	1.01	13.75
74	461	2.80	-	-	2.084	13.75
75	482	3.53	1.305	0.021	2.43	13.80
76	482	2.66	-	-	4.48	13.80
77	492	3.28	1.458	0.024	4.13	13.23
78	492	2.55	-	-	5.16	13.28
79	470	3.27	1.560	0.026	1.578	13.65
80	470	2.53	-	-	2.15	13.60
81	477	3.46	1.726	0.028	2.04	13.55
82	477	3.50	1.726	0.028	2.28	13.55
83	477	2.32	-	-	2.49	13.55
84	487	3.14	1.207	0.020	3.12	13.33
85	487	2.79	-	-	3.63	13.33

(The partial pressure of iodine is not the actual partial pressure in the furnace since dissociation occurs.)

These results definitely showed that the amount of decomposition was decreased by the addition of iodine.

In the next experiments different amounts of iodine were added to methyl iodide decomposing under approximately the same conditions. The results are recorded in Table XII.

Table XII

(Pressure of Nitrogen was 440 - 470 mm. in all the experiments)

(No Toluene was added)

(Temperature 461°C)

Expt. No.	Contact Time secs.	Partial Pressure MeI mm.	g.moles of I_2 added per sec. $\times 10^8$	Partial Pressure I_2 added mm.	% Decomp.
86	13.29	2.78	-	-	0.955
87	13.29	2.71	-	-	0.940
88	13.71	3.28	0.83	0.014	0.847
89	13.70	3.32	0.83	0.014	0.834
90	13.70	3.50	0.83	0.014	0.864
91	13.72	3.94	1.605	0.026	0.723
92	13.72	4.15	1.605	0.026	0.795
93	13.72	4.13	1.605	0.026	0.826
94	13.80	3.28	2.91	0.048	0.427
95	13.80	3.45	2.91	0.048	0.361
96	13.80	3.39	2.91	0.048	0.402
97	13.80	3.18	7.52	0.123	0.302
98	13.80	3.10	7.52	0.123	0.302
99	13.80	3.16	7.52	0.123	0.299
100	13.72	3.30	8.73	0.142	0.239
101	13.72	3.31	8.73	0.142	0.268

102	13.80	3.38.	9.88	0.162	0.221
103	13.80	3.42	9.88	0.162	0.179

Examination of the results shows that the amount of reaction became less as the iodine addition increased. This is what would be expected from a reverse reaction between iodine and methyl radicals.

Mass Spectrometric Estimation of the Gaseous Products

Previously no attempt had been made to examine the gaseous products of the reaction at high pressures, since in the presence of such a large excess of nitrogen chemical analysis would have presented a problem of some difficulty. A mass spectrometric technique was attempted at this stage.

Much experimental investigation and trial was required before a suitable method of product collection was developed. First, complete condensation of the carrier gas by means of a trap cooled by a Dewar flask containing liquid oxygen boiling under reduced pressure, followed by pumping away of the nitrogen was tried but the last stage proved difficult to accomplish. The methane was left condensed and then allowed to vapourise and the trap taken away from the apparatus for analysis. The ethane was allowed to rise from the product traps T_1 and T_2 by replacing the liquid air by a -80°C bath. The ethane was then removed from the apparatus to an evacuated bulb by means of a Toepler pump. The reproducibility of the results did not prove satisfactory.

Figure 15.

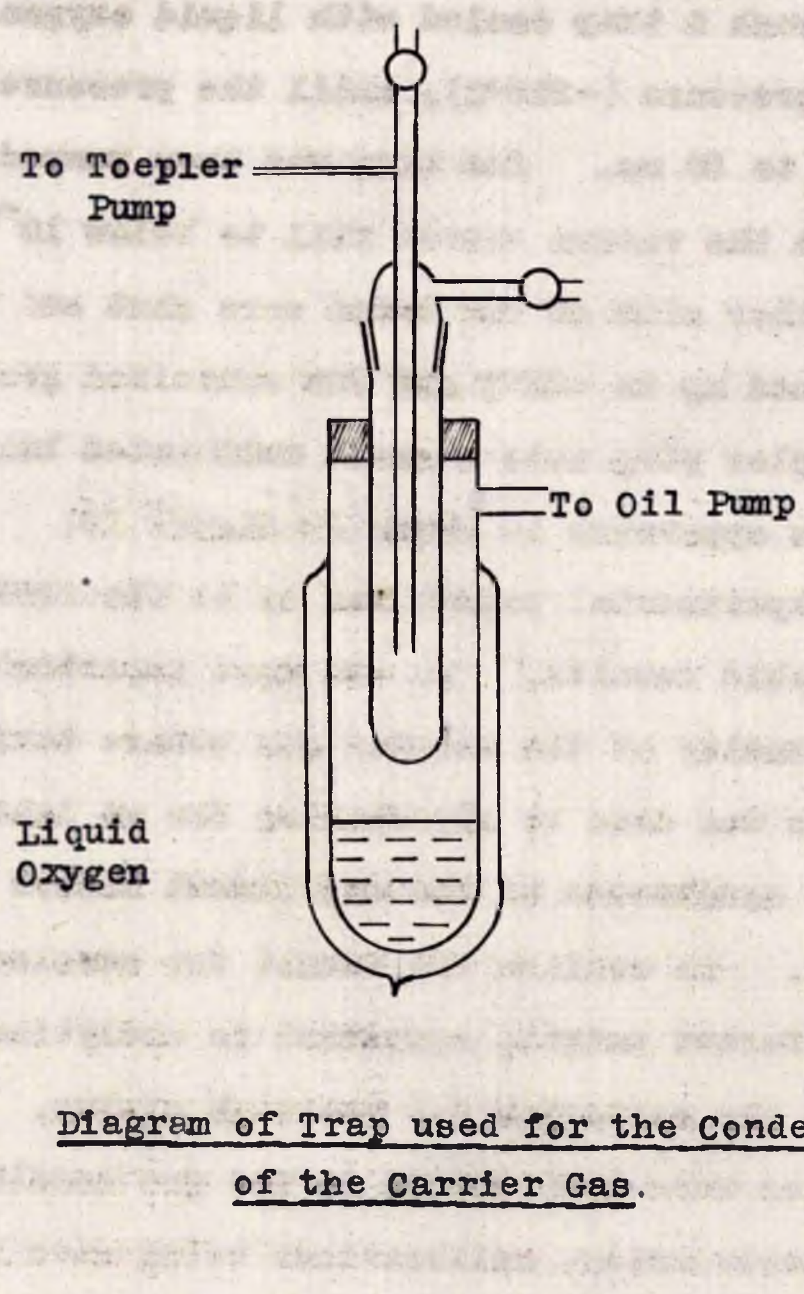


Diagram of Trap used for the Condensation of the Carrier Gas.

(To face page 75).

The method finally adopted was the following. A sample of the carrier gas was taken off in a small evacuated bulb and the gas analysed for the proportion of methane present. The product traps were then cooled to -80°C and the gas circulated through a trap cooled with liquid oxygen boiling under reduced pressure (-216°C), until the pressure in the apparatus fell to 50 mm. The trap was then pumped until the pressure in the vacuum system fell to below 10^{-4} mm. The taps on either side of the traps were shut and the condensate warmed up to -80°C and the contained gas taken out with a Toepler pump into a small calibrated bulb.. A diagram of this apparatus is shown in figure 15.

Certain experimental points had to be observed in order to obtain reliable results. It was most important to ensure complete homogeneity of the carrier gas before taking off the samples. This was done by circulating for at least one hour after the conclusion of the experiment before withdrawing the gas sample. To confirm the result two samples were usually taken from different points, agreement in analytical results being taken as the criterion for thorough mixing.

The samples were manipulated in the gas handling system of the mass spectrometer, calibrations being made for each sample using pure methane and ethane at suitable pressures.

Estimations were first carried out in experiments in which methyl iodide alone was decomposed in nitrogen. Since carbon was also formed on the walls of the reaction vessel it was decided to estimate the amount by combustion.

This was done by allowing the furnace to cool before admitting the air and collecting the products. The apparatus was then evacuated and the furnace heated to 550°C (just below the softening point of pyrex). Pure oxygen was then admitted and allowed to circulate through the apparatus and the liquid air trap for four hours. The apparatus was pumped out and the carbon dioxide formed, distilled into a small bulb with tap. The bulb cooled in liquid air was then attached to the gas handling unit of the mass spectrometer which was evacuated. The amount of carbon dioxide formed was determined by measurement of its pressure in an known volume at 0°C. The results of the analyses for a series of experiments are given in Table XIII.

Table XIII

(Pressure of Nitrogen in these experiments was in the range 450 - 470 mm.)

Expt. No.	Temp. °C	Amount of Iodine formed in g.atoms $\times 10^3$	g.moles of methane $\times 10^3$	g.moles of ethane $\times 10^6$	g.atoms of carbon $\times 10^4$	CH_4/I	I/C
104	497	2.70	2.14	1.08	-	.79	-
105	511	2.70	2.20	1.06	-	.82	-
106	511	3.00	2.32	0.98	-	.76	-
107	521	2.77	2.08	2.5	-	.75	-
108	511	2.53	2.10	-	3.93	.83	6.4
109	511	2.53	2.10	-	4.03	.83	6.3

These results show that the amount of ethane formed is very small (less than 1%) so if it is assumed that the only products are iodine, methane and carbon the stoichiometric equation must be:-

$$4CH_3I \longrightarrow C + 3CH_4 + 2I_2.$$

Examination of the data shows a small deviation from the CH_4/I ratio of 3/4 required, in some of the experiments in favour of methane. So some work was done in order to find other iodine containing products. No hydrogen iodide was found. Other possible products were ethylene iodide (formed by $2 - CH_3I \longrightarrow CH_2I.CH_2I$) and methylene iodide (formed by $CH_3I + CH_3I \longrightarrow CH_2 + CH_2I_2$). Cooling the exit U-tube with ice produced no crystalline deposit such as would be expected if ethylene iodide was formed (m.p.41°C). Approximate calculations from literature values of the vapour pressure showed that its deposition, if formed, would be certain.

In another experiment the products collected in the minimum quantity of methanol and shaken with two or three globules of mercury to remove free iodine. The mixture was filtered and evaporated to dryness. There was some mercuric iodide but not the slightest trace of any other substance could be detected, even when other solvents such as ether were tried. The detection of methylene iodide would be difficult, the use of ultra violet spectroscopy being complicated by the presence of iodine.

The high value for the I/C ratio (about 50% too high) may be due to inefficient collection of the carbon dioxide formed by combustion.

It appears that it may safely be concluded that the main reaction scheme is expressed by:-

$$4CH_3I \rightarrow C + 3CH_4 + 2I_2.$$

The deviations found are probably well within the limits of experimental error. A small amount of methane has been analysed in the presence of a much larger amount of nitrogen and interference in the ionisation of the methane probably occurs.

No appreciable amounts of hydrocarbons higher than ethane were found nor was there any detectable amount of hydrogen.

Gas analyses were also carried out for the reaction where methyl iodide was decomposed in the presence of toluene. Sufficient toluene was put into the system to attain the limiting rate (more than 7 mm.), as shown in previous experiments.

Experimentally the technique was exactly as that described previously the results are presented in Table XIV.

Table XIV

(Pressure of Nitrogen in the experiments was
470, 474 and 416).

(Toluene pressure 7 mm.)

(Partial pressure of methyl iodide 1.4 mm.)

Expt. No.	Temp. °C.	Amount of Iodine g.atoms. $\times 10^3$	g.moles of methane $\times 10^3$	g.moles of ethane $\times 10^6$	CH_4/I
110	490	2.73	4.21	0.96	1.54
111	483	2.04	3.75	5.7	1.87
112	483	1.75	2.46	1.5	1.58

If the reaction $CH_3 + C_6H_5CH_3$ captured all the radicals and all the iodine was recovered, then CH_4/I should equal unity. It is seen from the results that a considerable difference is found between the amount of iodine and methane necessitating the conclusion that some hitherto unforeseen reaction is taking place, probably one which removes iodine. The amounts of ethane formed are again very small (less than 1%). The poor concordance of the ethane analysis is due to the small percentage present causing large errors in the mass spectrometric results. In the following experiments determination of hydrogen iodide was made as described earlier (Table XV).

Table XV

(Pressure of Nitrogen 520 - 540 mm.)

(Partial pressure of Methyl Iodide 1.26 - 1.65 mm.)

(Partial pressure of Toluene 7 mm.)

Expt. No.	Temp. °C	Amount of Iodine g.atoms. $\times 10^3$	g.moles of methane $\times 10^3$	g.moles of hydrogen iodide $\times 10^4$
113	484	1.92	3.28	2.5

114	497	2.12	3.32	4.63
115	497	2.19	3.40	4.26
116	497	2.24	3.50	4.78

The hydrogen iodide found is less an amount than the difference between the amounts of methane and iodine formed, but it has been observed that benzyl iodide is also formed in the reaction. In fact Lapage in experiments at low pressures using toluene as radical acceptor found amounts of benzyl iodide up to 20% of the iodine formed.

Some experiments were done under the conditions originally used to measure the activation energy, i.e. 1 - 2 mm. of methyl iodide, 1 - 2 mm. of toluene and 600 mm. of nitrogen.

Table XVI

(Pressure of Nitrogen 600 - 605 mm.)

(Partial pressure of Toluene 2.3 mm.)

(Partial pressure of Methyl Iodide 1.2 - 1.9 mm.)

Expt. No.	Temp. °C	g.atoms of iodine $\times 10^5$	g.moles of Hydrogen Iodide $\times 10$	g.moles of methane $\times 10^4$
117	459	6.16	0	
118	459	6.62	0	3.62
119	459	6.22	0	
120	511	63.3	0	
121	511	57.2	0	33.9
122	511	49.0	0	

The analyses for methane are probably correct to only ±10% owing to the very small proportion present in the nitrogen, but it is clear that the iodine does not provide a completely accurate measure of the decomposition. In fact according to the above data the reaction is twice as fast as the iodine formation indicates. The failure to detect hydrogen iodide appears due to the difficulty of freezing out this comparatively volatile substance from the much larger amount of fast flowing gas. This was proved to be the case by taking off a sample of carrier gas and examining it by means of the mass spectrometer. Hydrogen iodide was found to be present by an examination of the 128 positive ion peak. The failure to detect hydrogen iodide in experiments 120 - 122, whereas it was found in previous experiments 113 - 116 may have been due to less efficient condensation or to the differing chemical conditions (2.3 mm. of toluene as opposed to 7 mm. in the previous experiments).

Reaction between Toluene and Iodine

The formation of benzyl iodide and hydrogen iodide must result from some reaction(s) involving some, or all of the following molecules or radicals, I_2, I, $C_6H_5CH_3$ or $C_6H_5CH_2$. The hydrogen iodide must arise from the toluene because a most searching examination both of the products and carrier gas did not reveal more than the smallest amount when methyl iodide was decomposed alone.

In order to obtain some insight into the problem experiments were performed to observe any effect that iodine might have on toluene. A search of literature showed that practically no study has been made of the reactions of iodine with hydrocarbons when substitution occurs as in RH + I_2 giving RI + HI. In Beilstein it is recorded that heating toluene and iodine together for a prolonged period gives hydrogen iodide and other products. In the present case the iodine was introduced as described previously and the toluene was contained in the other saturator.

It was at once evident that some reaction was occurring, a white crystalline deposit appeared at the exit to the furnace. This showed that the toluene must be attacked since toluene alone does not decompose under the conditions of the experiment. The deposit was scraped out of the exit U-tube, dissolved in alcohol and shaken with mercury to remove free iodine and filtered. Examination by ultra violet spectroscopy showed that it consisted largely of stilbene together with a small amount of dibenzyl. A melting point determination carried out on the original solid gave a value of 116° and when mixed with pure stilbene 117°. This is also proof that the chief product is stilbene. A Lassaigne test showed that no iodine containing solid compound was deposited. The condensed products were analysed for free iodine and hydrogen iodide as previously described. The total amount of iodine was then estimated by the bromine-acetate method. It was assumed that the balance was benzyl iodide. The technique of analysis was tested by estimations of synthetic mixtures of iodine, hydrogen iodide and benzyl iodide and found to be accurate. The only estimate of the iodine entering the system was from the addition of the hydrogen iodide, benzyl iodide and iodine figures at the end.

Table XVI gives the results obtained.

Table XVI

(By calibration the partial pressure of toluene was found to be 4 mm.)

(Pressure of Nitrogen 420 - 480 mm.)

Expt. No.	Temp. °C	g.atoms of total Iodine $\times 10^4$	g.moles of Iodide $\times 10^4$	g.moles of benzyl Iodide $\times 10^4$	g.atoms of Iodine $\times 10^5$	Contact Time secs.
123	511	4.83	1.95	2.88	1.94	13.00
124	511	4.92	1.89	2.90	1.3	13.00
125	511	4.95	2.09	2.68	1.85	13.00
126	511	4.83	2.45	2.10	2.76	13.00
127	511	5.42	3.54	1.62	2.58	13.00
128	511	5.62	3.05	2.13	2.58	13.00
129	509	7.35	3.27	3.88	1.97	13.03
130	509	7.00	4.17	2.68	1.46	13.03
131	509	7.80	4.26	2.35	1.94	13.03
132	513	4.60	2.27	1.85	4.78	12.88
133	513	4.57	2.42	1.73	4.23	12.88

134	513	4.52	2.08	1.98	4.83	12.88
135	433	2.42	-	1.56	8.59	14.37
136	433	3.74	-	1.59	21.5	14.37
137	433	6.42	-	2.23	41.9	14.37
138	459	3.14	-	1.89	12.5	13.86
139	459	4.75	-	2.98	17.7	13.86
140	459	7.47	-	2.65	48.2	13.86
141	452	1.75	-	1.11	6.38	13.97
142	452	3.98	-	1.21	21.7	13.97
143	452	5.00	-	1.79	32.1	13.97

In previous discussions it has been pointed out that hydrogen iodide proved difficult to freeze out, this was also found to be the case here(mass spectrometric examination of the gases). The mass spectrometer also showed that very little hydrogen and no volatile hydrocarbons were present. The amount of hydrogen iodide is therefore almost certainly formed in greater amounts than the titrations lead one to suppose. The actual amount condensed appears dependent on the efficiency of the glass wool packing in the traps. The amount of free iodine emerging from the furnace in all cases was low so that it appears that the reaction had gone a long way towards completion in even the lowest temperature runs.

The data obtained for the reaction between toluene and iodine indicate that the products are stilbene, benzyl iodide and hydrogen iodide. The amount of hydrogen iodide ~~being~~ was greater in quantity than the benzyl iodide.

This work concluded the study of methyl iodide decomposition in the presence of a high pressure of nitrogen. It has shown that the kinetics are much more complicated than at first appeared to be the case. Nevertheless it would appear that the investigation has provided an experimental basis for a reaction mechanism and an interpretation of the results obtained.

LOW PRESSURE INVESTIGATIONS

Lapage studied the reaction at pressures of nitrogen of 2 - 9 mm. and methyl iodide partial pressures of 0.2 - 1.3 mm. Some surface effect was found but the reaction was predominantly homogeneous. The activation energies determined from the first order rate constants were in the region 53 - 58 k/cals. The rate was increased by increasing methyl iodide concentration, the reaction being nearly second order at the lowest partial pressures, rising to nearer first order above 1 mm. The rate was also increased with nitrogen pressure. This dependence of the rate on concentration was discussed in terms of a Lindemann mechanism of collisional activation.

The following experiments were carried out in order to study the change more fully and in particular to employ it as a means of obtaining data on the efficiency of energy transfer between gas molecules during a collision.

Experiments were first of all carried out as part of a general study of the reaction with the prime aim of justifying the measurements to be used later, but also to verify and possibly improve upon the previous work.

Thirty preliminary experiments were done using nitrogen as carrier gas in order to study the technique. The results were not very reproducible even within three consecutive experiments; the following experiments in Table XVII are quoted as being typical.

Table XVII

Expt. No.	Temp. °C	Total Pressure mm.	Partial Pressure of MeI mm.	Contact Time secs.	% Decomp.	k_1 10^2 sec^{-1}
146	579	10.5	0.128	1.10	3.38	3.3
147	579	10.6	0.130	1.12	2.80	2.1
148	579	10.6	0.131	1.12	2.33	2.2
149	579	7.7	0.220	2.81	12.55	5.1
150	579	7.8	0.149	2.82	13.70	6.6
151	579	7.9	0.164	2.87	16.1	6.5
152	579	7.06	0.148	1.85	7.66	4.5
153	579	7.20	0.155	1.86	5.14	3.0
154	579	7.30	0.157	1.84	5.00	3.0
155	579	7.45	0.157	1.87	5.12	3.0

The agreement between different sets was poor and in consecutive experiments usually the first gave a particularly high value for the rate constant. Such behaviour was previously observed by Gowenlock with ethyl iodide. The carrier gas was circulated over sodium at 300° in the apparatus to remove traces of oxygen but no improvement occurred. The peculiar irregularity of the first experiment is strongly suggestive of some surface effect, made even more likely by the slight heterogeneity of the reaction and by the deposition of carbon on the walls of the reaction vessel during an experiment. It is a wellknown fact that many pyrogenic decompositions give abnormal results in clean vessels and conditioning by carbonisation of the surface is needed to obtain reproducibility. The effect is especially evident in the thermal decomposition of alkyl halides e.g. tert-butyl and tert-amyl chlorides[53], 1:1:1-trichloroethane,[58] and ethyl bromide.[72] In the light of these facts the reaction vessel was carbonised by performing several long decompositions. After this the furnace was never open to the air for the collection of the products until its temperature was below 200°C. A spare trap was used so that before the actual experiments some methyl iodide pyrolysis occurred in the vessel as a form of preparation.

The reproducibility was then markedly improved and all the experiments which follow were carried out in this manner.

Estimation of the Products of the Reaction

The products of the decomposition were examined carefully in a few experiments. The iodine was determined by titration asusual. The methane was measured by the pressure rise which occurred during long runs in conjunction with a volume calibration. Amounts of ethane and ethylene were measured by evacuating the apparatus and then replacing the liquid air around the products by a molten ligroin bath at -150°C. The amounts of C_2 hydrocarbons were measured by the pressure rise. Hydrogen iodide was determined as described above. Samples of the carrier gas were taken off from the apparatus in a small bulb and examined by the mass spectrometer; methane was the only gas found. The C_2 hydrocarbon fraction was taken off into a bulb by means of a Toepler pump and also examined. Only ethane could be found. The quantities found are listed in Table XVIII.

Table XVIII

Expt. No.	Temp. °C	g. atoms of Iodine $\times 10^4$	g. moles of Hydrogen Iodide $\times 10^5$	g. moles of methane $\times 10^4$	g. moles of ethane $\times 10^6$	CH_4/I
156	579	4.32	3.5	3.15	4.6	0.73
157	579	3.79	-	2.78	4.0	0.73
158	579	3.40	3.0	2.58	8.0	0.76
159	579	3.65	0.8	2.72	4.2	0.74
160	579	1.20	0.22	0.84	-	0.70

(Initial static pressures of Nitrogen 1.83, 1.82, 3.18, 4.07 and 2.75 mm.)

The results show that the amount of hydrogen iodide is small (this was repeated and confirmed with many other experiments) and there is no regularity in the amounts formed. Its presence in most experiments was neglected. The amount of ethane was also very small being of the order 2 - 3%. Estimation of the carbon formed was not attempted owing to the necessity of having the carbon deposit on the walls of the vessel for obtaining reproducibility.

The Dependence of the Rate of Decomposition on the Partial Pressure of Methyl Iodide

The pressure dependence of the rate of decomposition observed by Lapage appeared to be explained most satisfactorily by the classical theory of unimolecular reactions. An examination of the rate dependence on methyl iodide pressure at low values of the latter was carried out. The carrier gas pressure was kept constant for all the runs whilst the methyl iodide partial pressure was adjusted by manipulation of the needle valve of the injector unit. The carrier gas used was helium because of its assumed low activating efficiency. Results obtained are given in Table XIX.

Table XIX

Expt. No.	Temp. °C	Total Pressure mm.	Partial Pressure MeI mm.	% Decomp.	Contact Time	k_1 $10^3 sec^{-1}$
161	579	2.42	0.135	1.27	2.86	4.3
162	579	2.49	0.187	1.09	2.78	3.9
163	579	2.51	0.164	1.10	2.77	3.9
164	579	2.61	0.195	6.21	3.61	7.6
165	579	2.94	0.170	5.33	3.20	7.4
166	579	3.14	0.163	2.05	2.94	6.7
167	579	2.52	0.246	3.46	2.75	12.8

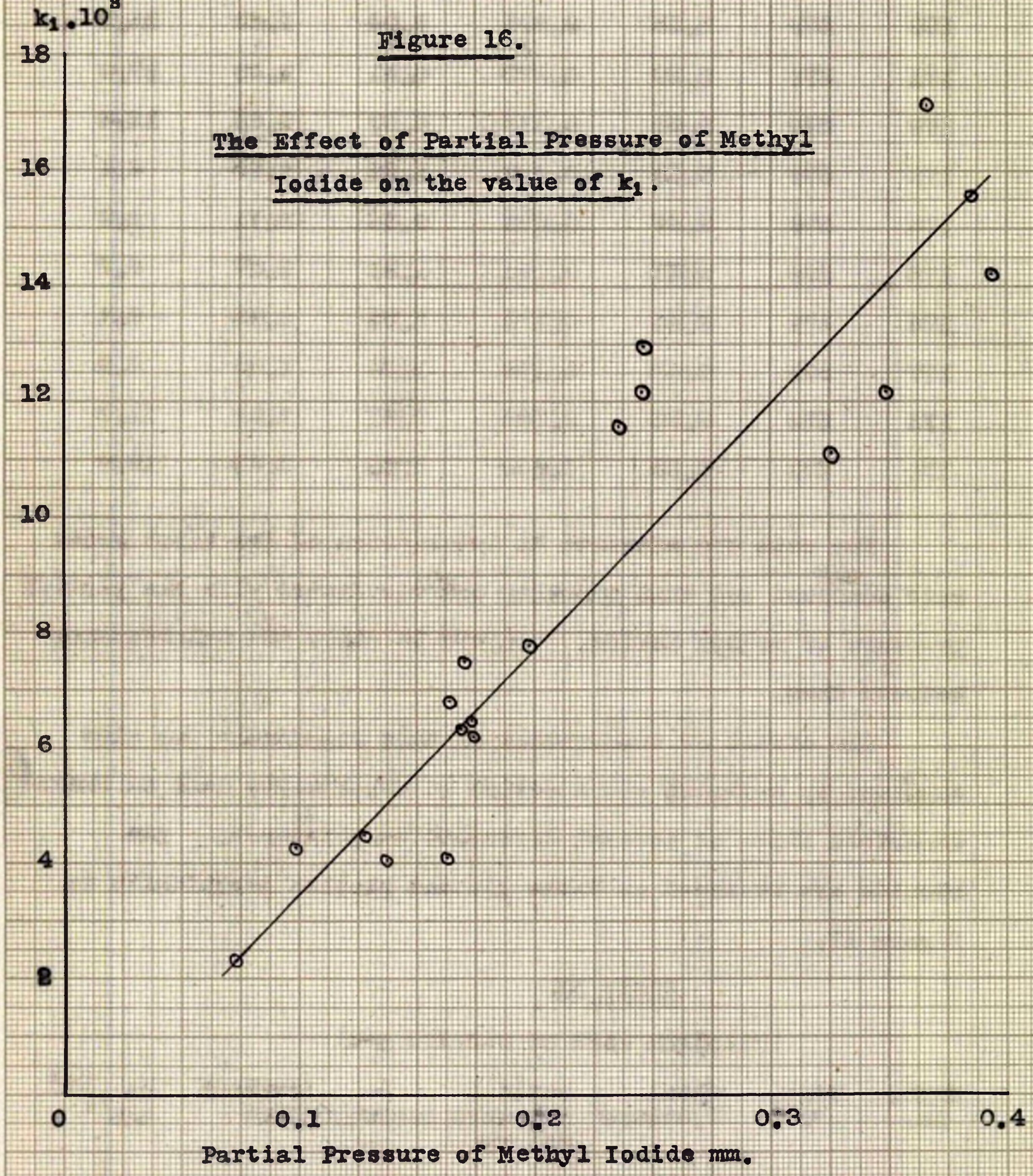


Figure 16.

The Effect of Partial Pressure of Methyl Iodide on the value of k_1.

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168	579	2.62	0.245	3.09	2.66	12.0
169	579	2.78	0.235	2.77	2.55	11.4
170	579	2.55	0.395	3.94	2.83	14.1
171	579	2.50	0.370	4.11	2.50	17.0
172	579	2.66	0.385	4.03	2.65	15.4
173	579	2.53	0.099	1.12	2.75	4.1
174	579	2.57	0.072	0.64	2.71	2.2
175	579	2.48	0.169	1.80	2.87	6.2
176	579	2.50	0.175	1.74	2.84	6.1
177	579	2.57	0.173	1.80	2.80	6.4
178	579	2.56	0.325	2.61	2.47	11.0
179	579	2.63	0.346	3.00	2.58	12.0

The rate was measured by calculation of the first order rate constant and this quantity was correlated with the partial pressure of methyl iodide. Figure 16 shows the relationship between them.

The effect of temperature on this dependence was also examined by carrying out a series of experiments such as those described above at several different temperatures. The results are recorded in Table XX, and plotted graphically in figure 17.

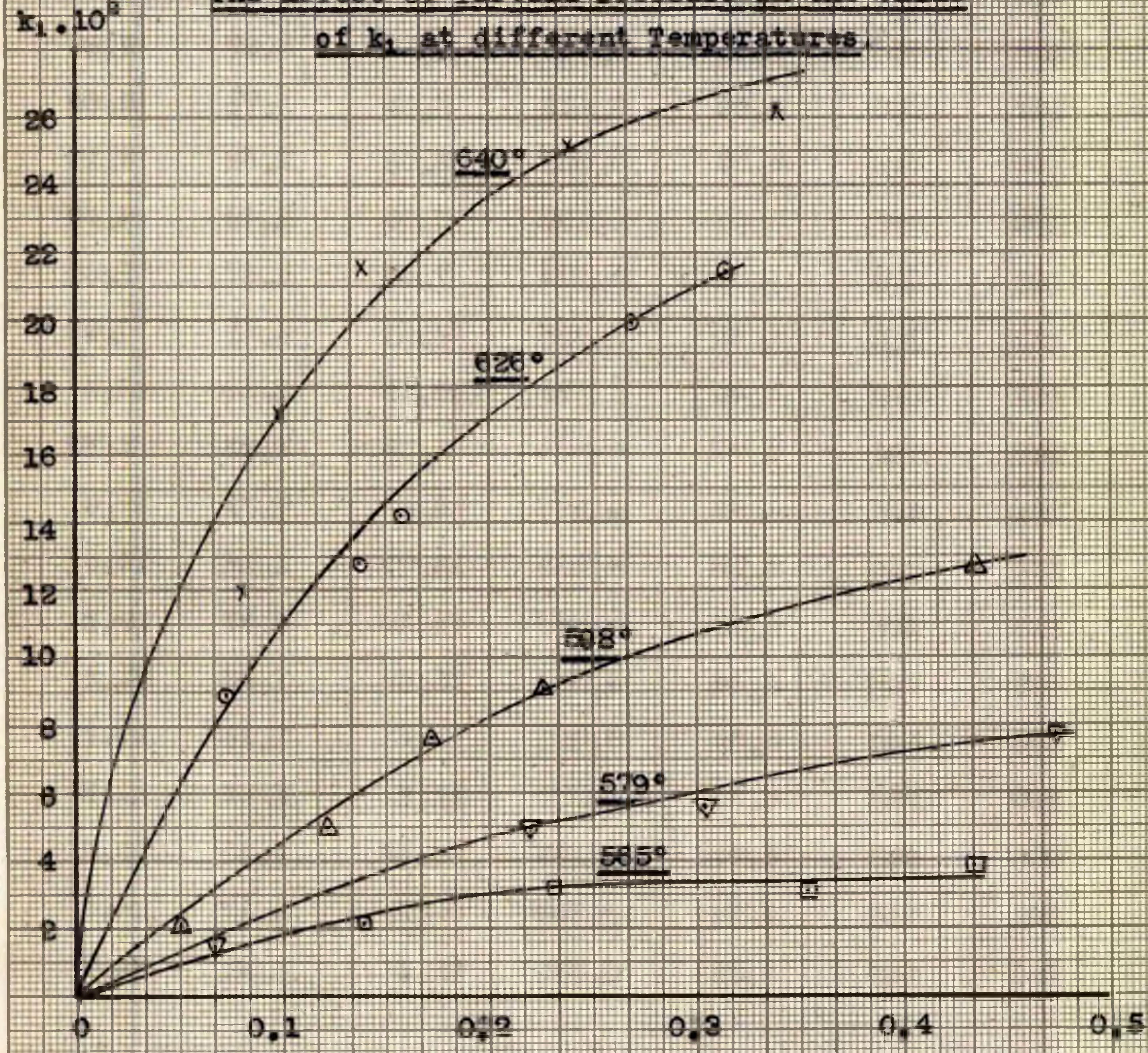
Table XX

(Nitrogen used as carrier gas)

Expt. No.	Temp. °C	Total Pressure mm	Partial Pressure MeI mm.	% Decomp.	Contact Time	k_1 10^2 sec^{-1}
180	579	4.12	0.065	4.03	1.98	2.1

Figure 17.

The Effect of Partial Pressure on the value of k_1 at different Temperatures.

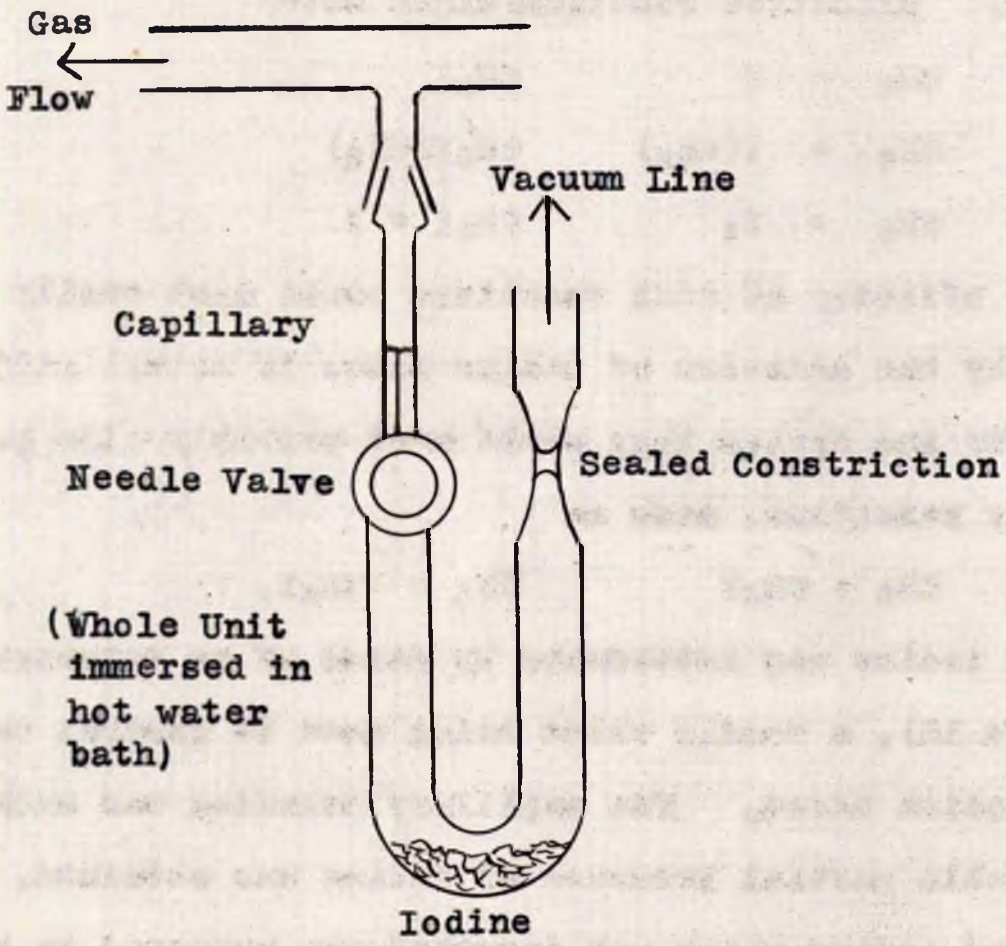


(To face page 91).

181	579	4.19	0.221	8.14	1.77	4.78
182	579	4.32	0.303	9.09	1.73	5.5
183	579	4.62	0.473	12.89	1.78	7.7
184	565	4.12	0.135	4.94	2.46	2.05
185	565	4.28	0.232	5.95	1.89	3.24
186	565	4.41	0.351	5.12	1.87	2.86
187	565	4.63	0.432	3.58	1.71	3.62
188	598	4.36	0.068	2.09	1.52	2.10
189	598	4.43	0.120	7.09	1.49	4.90
190	598	4.54	0.174	7.40	1.47	7.66
191	598	4.75	0.225	8.51	1.41	8.95
192	598	4.44	0.432	10.15	1.43	12.5
193	626	4.22	0.074	9.16	1.43	8.70
194	626	4.53	0.137	16.5	1.39	12.9
195	626	4.18	0.156	16.65	1.28	14.2
196	626	4.86	0.267	23.13	1.33	19.8
197	626	4.84	0.313	23.99	1.28	21.3
198	640	4.56	0.099	15.6	1.33	17.1
199	640	4.64	0.077	11.2	1.32	11.8
200	640	4.91	0.137	24.46	1.30	21.6
201	640	5.34	0.238	22.2	1.17	24.9
202	640	5.08	0.340	22.9	1.21	25.9

If the reaction were of the first order the amount of decomposition should remain constant whatever the partial pressure, at one particular temperature. The experimental results clearly show that the reaction is not first order

Figure 18.



Injector Unit used for the Addition of Iodine in the Experiments at Low Pressures.

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under the examined conditions.

It will be shown later that an increase of inert gas pressure has the same effect. If the reaction were of the first order, inert gas pressure should have no effect.

The Possibility of Back Reaction

The possibility of back reaction taking place has to be examined. Effective reactionsmight be:-

$$CH_3 + I \longrightarrow CH_3I$$

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

and $$CH_3 + I_2 \longrightarrow CH_3I + I.$$

The efficacy of such reactions could most easily be studied by the addition of iodine since if methyl radicals were added to the system they would most probably also partake in secondary reactions, such as

$$CH_3 + CH_3I \longrightarrow CH_4 + {-CH_2I}.$$

The iodine was introduced by means of an injector unit,(figure 18), a needle valve being used to control the amount of iodine added. The capillary selected was such that a suitable partial pressure of iodine was obtained. The amount of iodine which was injected was measured by a calibration experiment performed during a run comprising a series of two experiments. The effect of the added iodine is shown in the following Table.

Table XXI

Expt. No.	Temp. °C	Contact Time secs.	Partial Pressure MeI mm.	g.atoms of Iodine formed per sec. $\times 10^8$	g.atoms of Iodine added per sec. $\times 10^8$	% Decomp.	Total Press. mm
203	579	1.72	0.145	1.60	-	3.80	3.80
204	579	1.68	0.146	1.55	6.01	3.60	3.89
205	579	1.63	0.099	0.76	-	2.54	4.05
206	579	1.59	0.096	0.75	6.07	2.48	4.12
207	579	1.91	0.159	1.81	-	4.36	3.3
208	579	1.87	0.157	1.80	6.20	4.30	3.5

The results show that there appears to be a slight depression of the rate of the reaction, but difficulties involved in the operation of the injector made quantitative conclusions uncertain. It appears definite however that there was no marked depression (or acceleration) of the reaction and that errors due to back reaction may be neglected.

Lapage investigated the effect of nitric oxide and toluene on the reaction. An acceleration resulted in both cases so the decomposition does not involve long radical chains. The effect of nitric oxide was investigated and is discussed later. The formation of dibenzyl with toluene is a proof of the fact that methyl radicals are involved in the decomposition mechanism.

The Effect of Foreign Gases

The data obtained above has shown that the overall reaction may be expressed as:-

$$4CH_3I = 3CH_4 + C + 2I_2.$$

The rate governing step is $CH_3I \longrightarrow CH_3 + I$, the reverse reaction being unimportant under the experimental conditions. The rate is clearly pressure dependent, increasing with pressure. Since the reaction does not involve chains, as shown by the effect of nitric oxide and toluene,this behaviour is most readily explained on the basis of the classical theory of unimolecular reactions. The best test of this is a study of the influence of different inert gases on the transition from first to second order with decreasing pressure. In the transition region one of the rate determining factors is the efficiency with which energy is obtained by the reacting species from collision in order that it may react. This clearly depends upon the ease with which energy is transferred from a molecule of inert gas to one of the reactant during a collision. Since the transfer process must depend on the nature of the inert gas molecule the form of transition must be different for different inert gases. Experimental investigation of the effect of different inert gases on the methyl iodide decomposition therefore served a dual purpose; (a) confirmation of the unimolecular mechanism used to explain the pressure dependence of the decomposition rate, and (b) the obtaining of data relative

Diagram of Gas Burette used for introducing the Carrier Gas

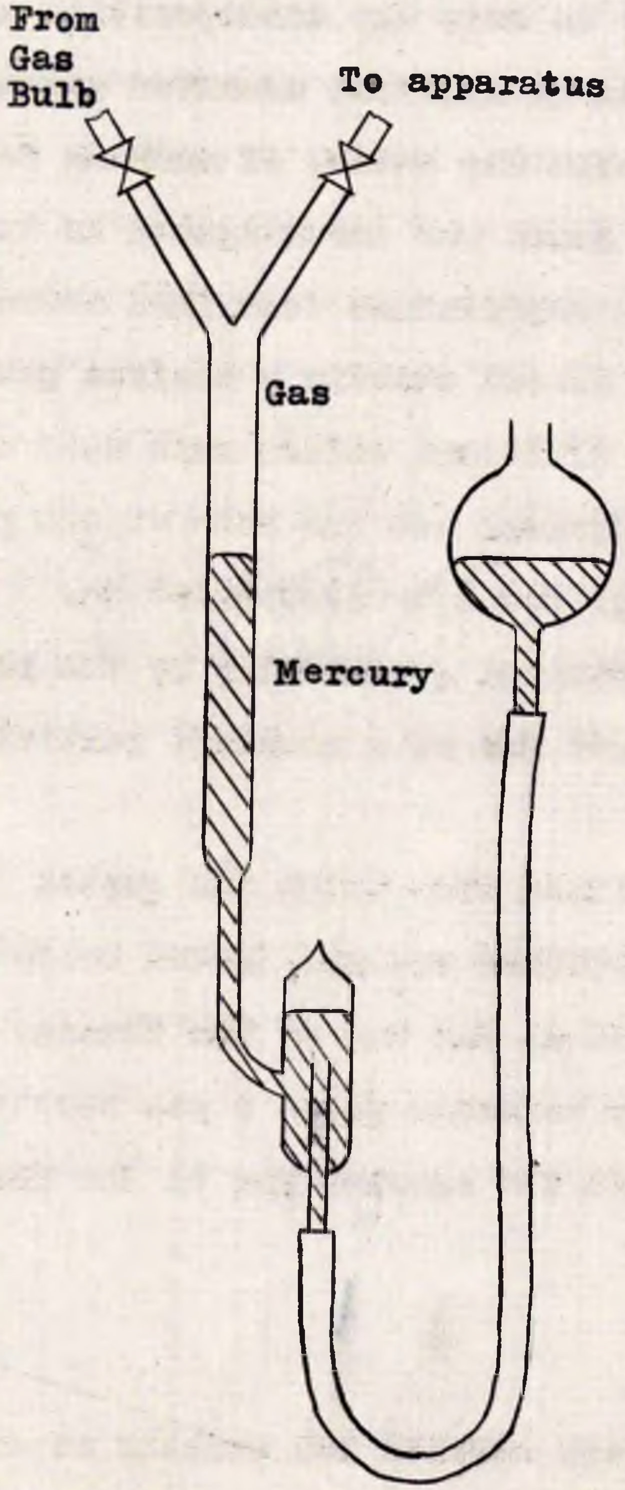


Figure 19.

(To face page 95).

efficiencies of energy transfer in molecular collisions.

In order to obtain the data under the best conditions it was decided (i) use as low a partial pressure of methyl iodide as possible in order that the predominant activating effect would be collisions between inert gas and methyl iodide molecules, and (ii) to keep the decomposition as low as practically possible to minimise unwanted secondary reactions, and (iii) minimise the amount of methane formed.

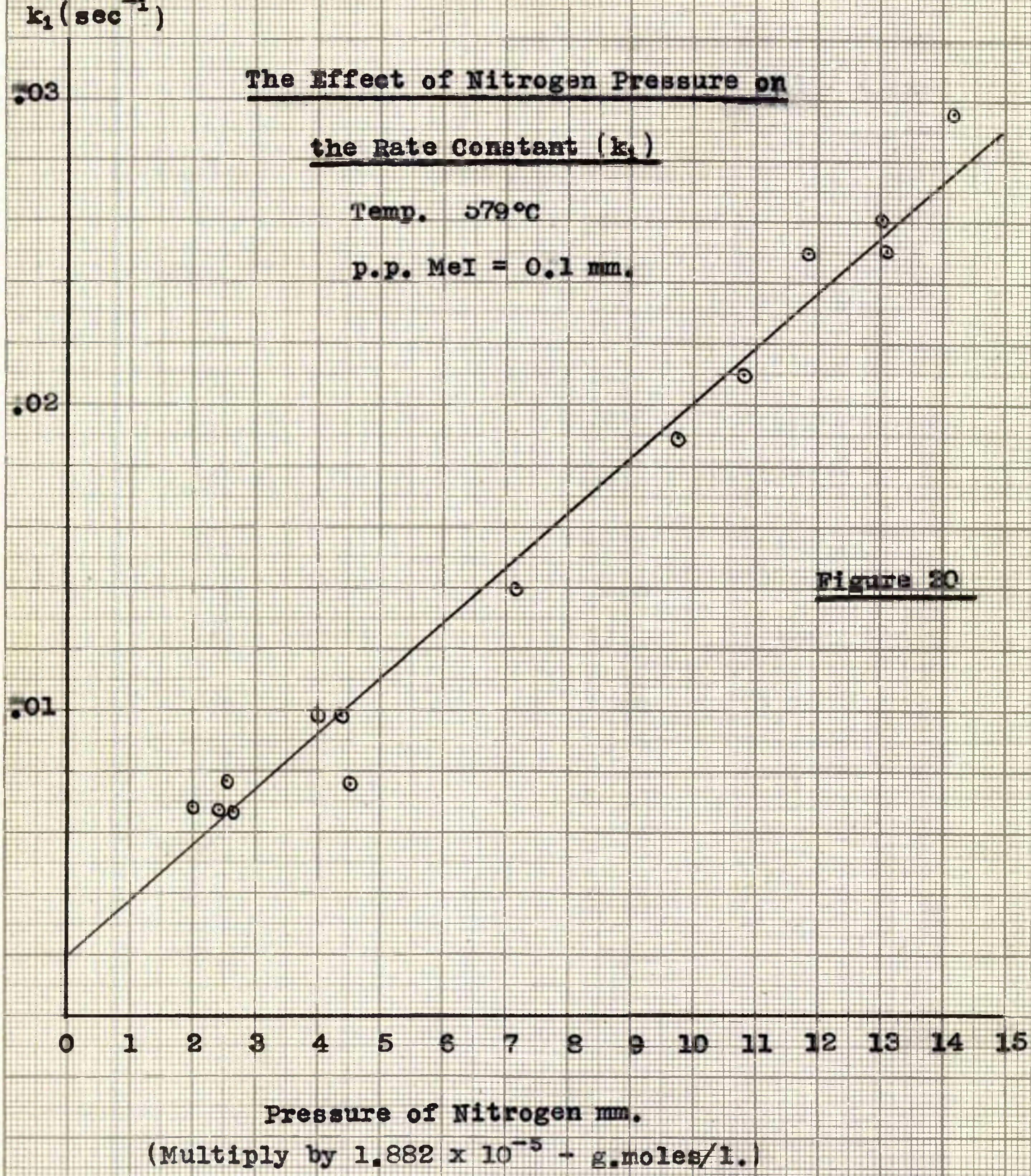
The effect of inert gases was investigated in exactly the same manner as for the experiments described above. Since it was difficult to obtain exactly a desired partial pressure of methyl iodide different values were used under almost identical flow conditions and the rate at the partial pressure selected (0.1 mm.) found by interpolation. The results obtained are illustrated graphically by the plots of k_1 against pressure of inert gas at a constant partial pressure of methyl iodide.

The experimental values from which the quoted interpolated values are obtained are not listed below but are given in full in the tables at the end of the thesis.

When using the more valuable gases a gas burette (Fig. 19) was used to admit the carrier gas to the desired pressure.

Nitrogen

The experiments were carried out exactly as described above.



The Effect of Nitrogen Pressure on the Rate Constant (k$_1$)

Temp. 579°C

p.p. MeI = 0.1 mm.

Figure 20

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Table XXII (See Figure 20)

Temperature 579°C.

Partial Pressure of methyl iodide 0.1 mm.

	Nitrogen Pressure mm.	k_1 (sec^{-1})
(i)	2.00	.0070
(ii)	2.56	.0079
(iii)	2.58	.0068
(iv)	2.70	.0068
(v)	4.02	.010
(vi)	4.44	.010
(vii)	4.61	.0076
(viii)	7.24	.0141
(ix)	9.77	.0190
(x)	10.8	.021
(xi)	11.78	.0250
(xii)	13.06	.0250
(xiii)	13.20	.0260
(xiv)	14.1	.0295

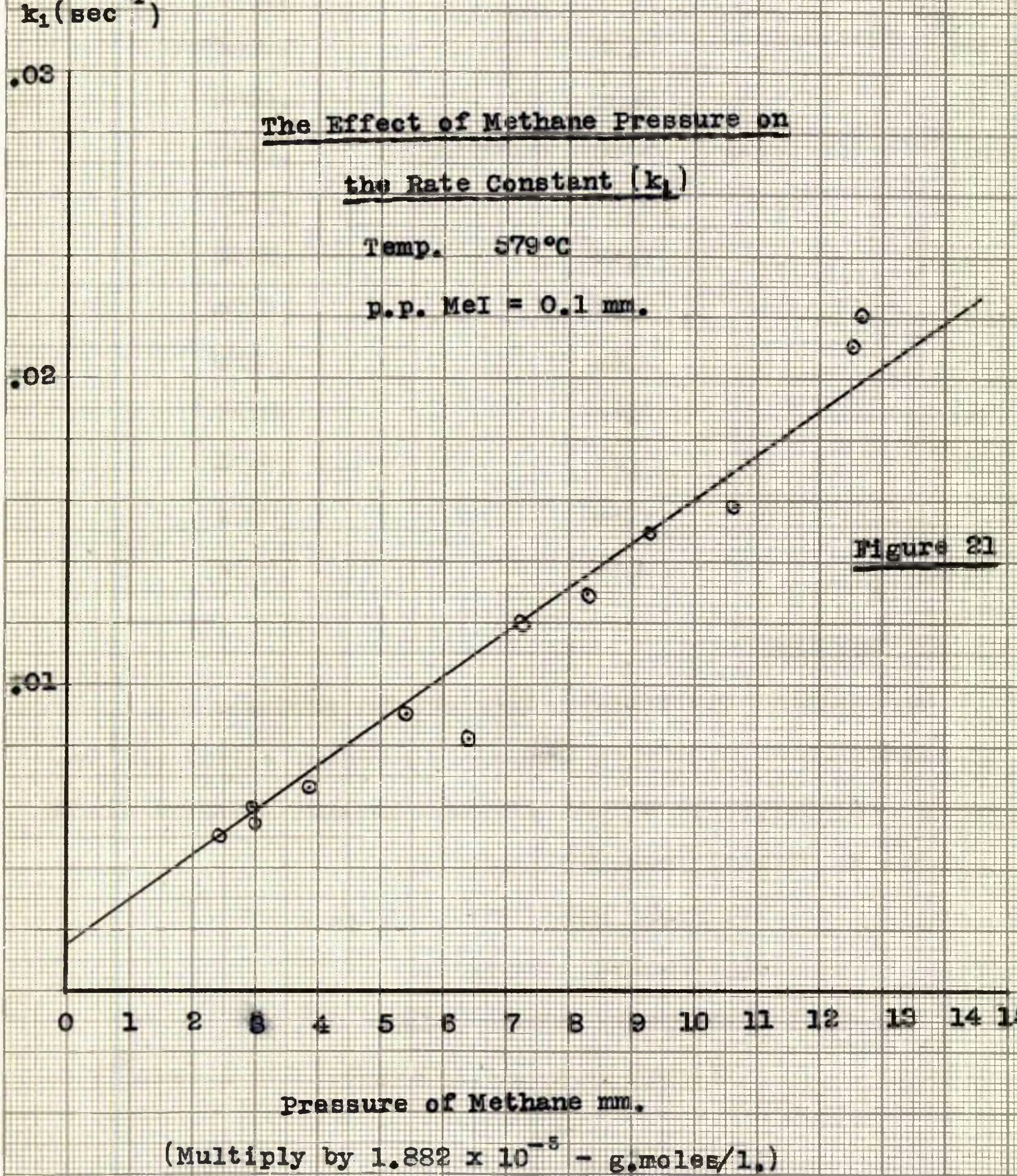
Methane

Table XXIII (See Figure 21)

Temperature 579°C

Partial Pressure of methyl iodide 0.1mm

	Methane Pressure mm.	k_1 (sec^{-1})
(i)	1.40	.0039



The Effect of Methane Pressure on the Rate Constant (k_1)

Temp. 579°C

p.p. MeI = 0.1 mm.

Figure 21

(To face page 97).

(ii)	2.51	.0050
(iii)	3.05	.0060
(iv)	3.06	.0055
(v)	3.95	.0076
(vi)	5.51	.0091
(vii)	6.5	.0084
(viii)	7.33	.0120
(ix)	8.35	.0130
(x)	9.28	.0150
(xi)	9.35	.0150
(xii)	10.57	.0159
(xiii)	12.45	.0210
(xiv)	12.50	.0220

Carbon Monoxide

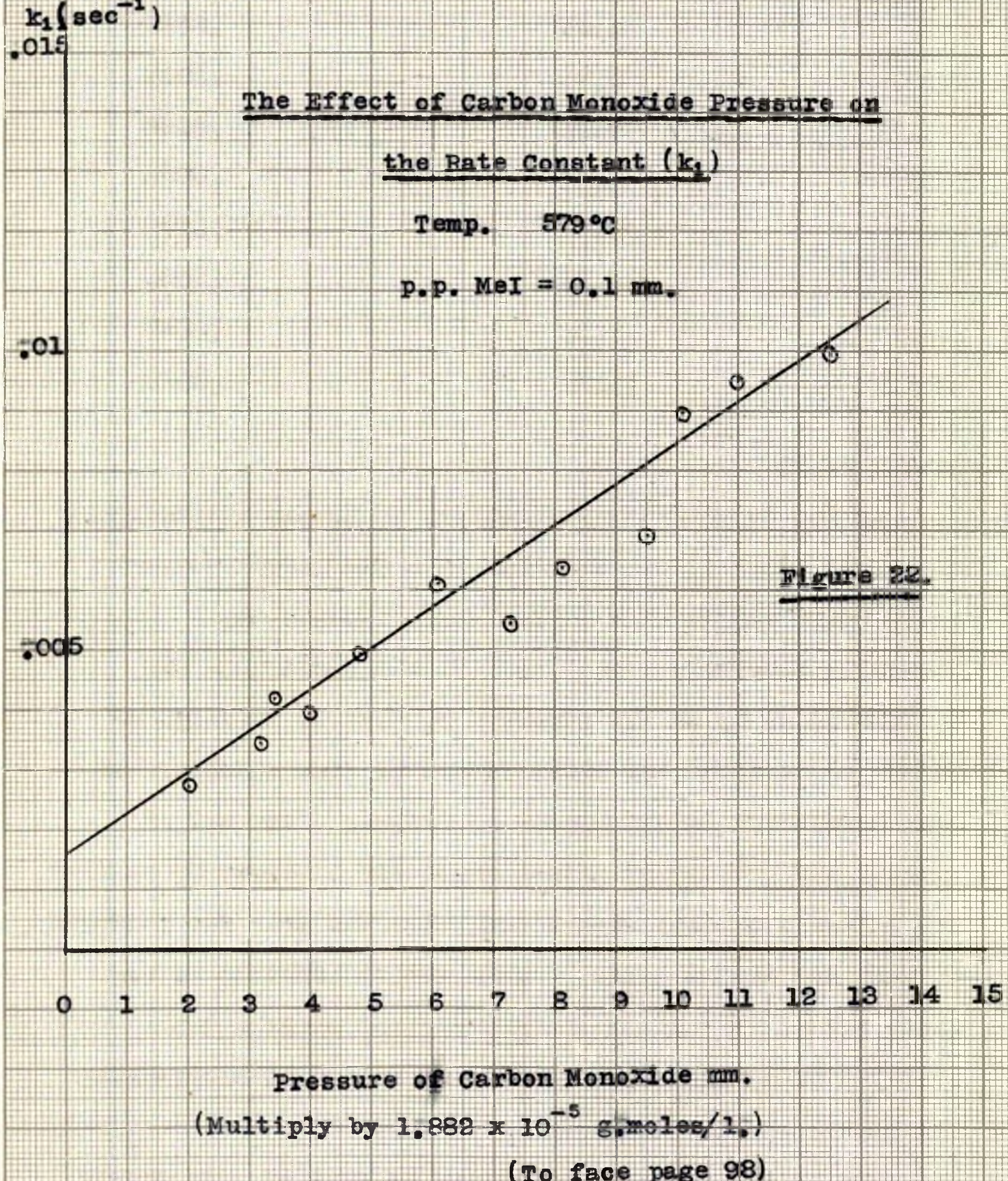
No reaction was detected between the products or intermediates (i.e. methyl radicals or iodine atoms) and the carbon monoxide. No marked pressure changes occurred during runs and no unusual products observed.

Table XXIV (See Figure 22).

Temperature 579°C

Partial Pressure of methyl iodide 0.1 mm.

	Carbon Monoxide Pressure mm.	k_1 (sec^{-1})
(i)	1.30	.0020
(ii)	2.10	.0028
(iii)	3.26	.0035



The Effect of Carbon Monoxide Pressure on the Rate Constant (k_1)

Temp. 579°C

p.p. MeI = 0.1 mm.

Figure 22.

(To face page 98)

(iv)	3.50	.0042
(v)	4.03	.0040
(vi)	4.92	.0050
(vii)	6.20	.0063
(viii)	7.42	.0055
(ix)	8.17	.0064
(x)	9.52	.0070
(xi)	10.15	.0090
(xii)	11.00	.0095
(xiii)	12.50	.0100

Nitric Oxide

In the original investigations of Lapage nitric oxide was added since it was expected that the methyl radical would react easily with it and thus suppress any occurring secondary reactions. It was found that the dependence of k_1 on the reaction conditions remained as before and methane was still formed in approximately the same proportion to the amount of iodine. The use of various proportions of nitric oxide and nitrogen as carrier gas showed a gradual change over from the rate for nitrogen to that for nitric oxide. This was in contrast to the usual effect in radical chain reactions where a small quantity of nitric oxide is very effective in suppressing the amount of the reaction.

The reason for the increasing in rate as more nitric oxide was added is readily explained on the collisional hypothesis used to explain the observation on methyl iodide decomposition, if it is certain that no chemical reaction was occurring. Experiments were carried out to investigate this. It was observed that no decrease or marked increase of carrier gas pressure took place during a run indicating that no reaction of large magnitude was occurring. A careful analytical investigation of the products was made to find possible compounds resulting from:-

$$CH_3 + NO \longrightarrow ?$$

Taylor and Bender[168] concluded from investigations on the pyrolysis of formaldoxime that the facts of nitric oxide inhibition where methyl radicals are involved could be explained by assuming $CH_3 + NO \longrightarrow CH_3NO \longrightarrow CH_2{:}NOH$.

The formaldoxime decomposes yielding cyanides, ammonia, etc. which have been detected by other investigators on nitric oxide inhibitions. This is supported by the work of Thompson and Meissner[169] on the absorption spectra of mixtures of nitric oxide and decomposing organic compounds.

Cyanides were tested for by making a solution of the products of a run strongly alkaline with caustic soda, adding freshly prepared ferrous sulphate solution, boiling, then acidifying with hydrochloric acid. No Prussian blue was formed and it was concluded that no cyanides were produced.

Nessler's reagent was used to detect the presence of ammonia. A negative result was obtained.

The Effect of Nitric Oxide Pressure on the Rate Constant (k_1)

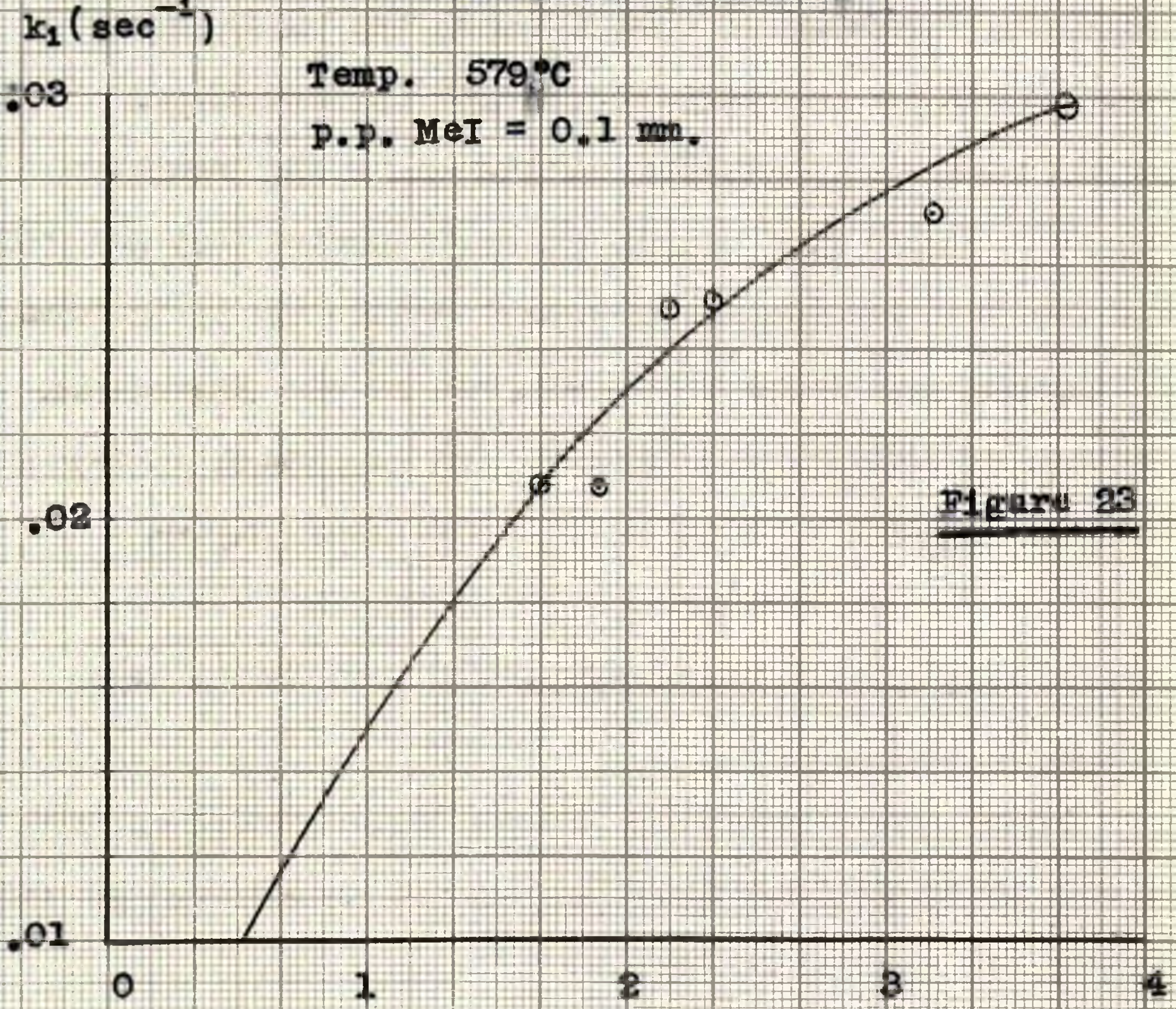


Figure 23

Pressure of Nitric Oxide mm.

(Multiply by 1.882×10^{-5} - g.moles/l.)

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From the above evidence it was concluded that under these experimental conditions no reaction was taking place between methyl radicals and nitric oxide. Reaction between methyl radicals and NO appears very dependent on the conditions. Forsyth[170] investigated the reaction by a Paneth technique and Steacie and his collaborators[171] have used his results in studies on the $CH_3 + CH_3$ reaction. Iredale[172] found that nitric oxide increased the quantum yield for the photolysis of methyl iodide up to 12 times.

Echols and Pease[173] in studies on the inhibition of butane decomposition, explain the transient inhibitory effect by suggesting that there is an equilibrium

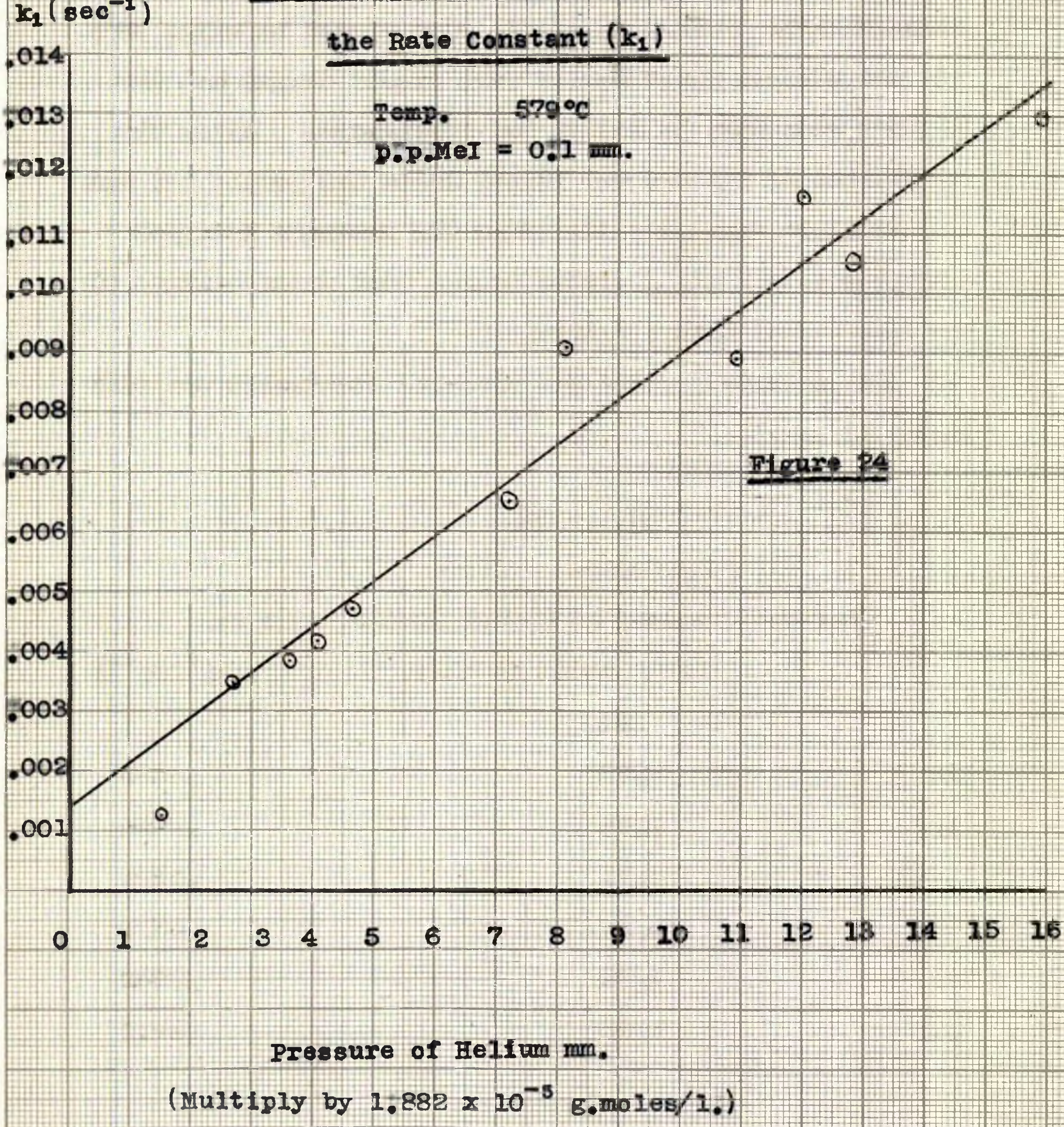
$$R + NO \rightleftharpoons RNO$$

which is only slowly established and then feeds back radicals to the system.

There is no evidence for any such effect in this case and it is assumed that the effect is similar to that observed for the other gases.

Recently Chilton and Gowenlock[174] published details of work on the interaction of nitric oxide with higher alkyl radicals, derived from the thermal decomposition of mercury alkyls, in a similar apparatus to that used in this case. These experiments however, were done at a lower temperature where nitric oxide appears to act in a more definite manner.

Some alteration in technique was necessary owing to the



The Effect of Helium Pressure on the Rate Constant (k_1)

Temp. 579°C

p.p.MeI = 0.1 mm.

Figure 24

(To face page 101).

low vapour pressure of nitric oxide at liquid oxygen temperatures. Traps T_5 and T_6 were cooled to minus 80°C and the product traps cooled with liquid oxygen but the heaters were kept on during the experiment. After the completion of the run the nitric oxide was pumped off and the products degassed, otherwise the nitrogen peroxide formed when air was admitted caused some decomposition of the unaffected methyl iodide.

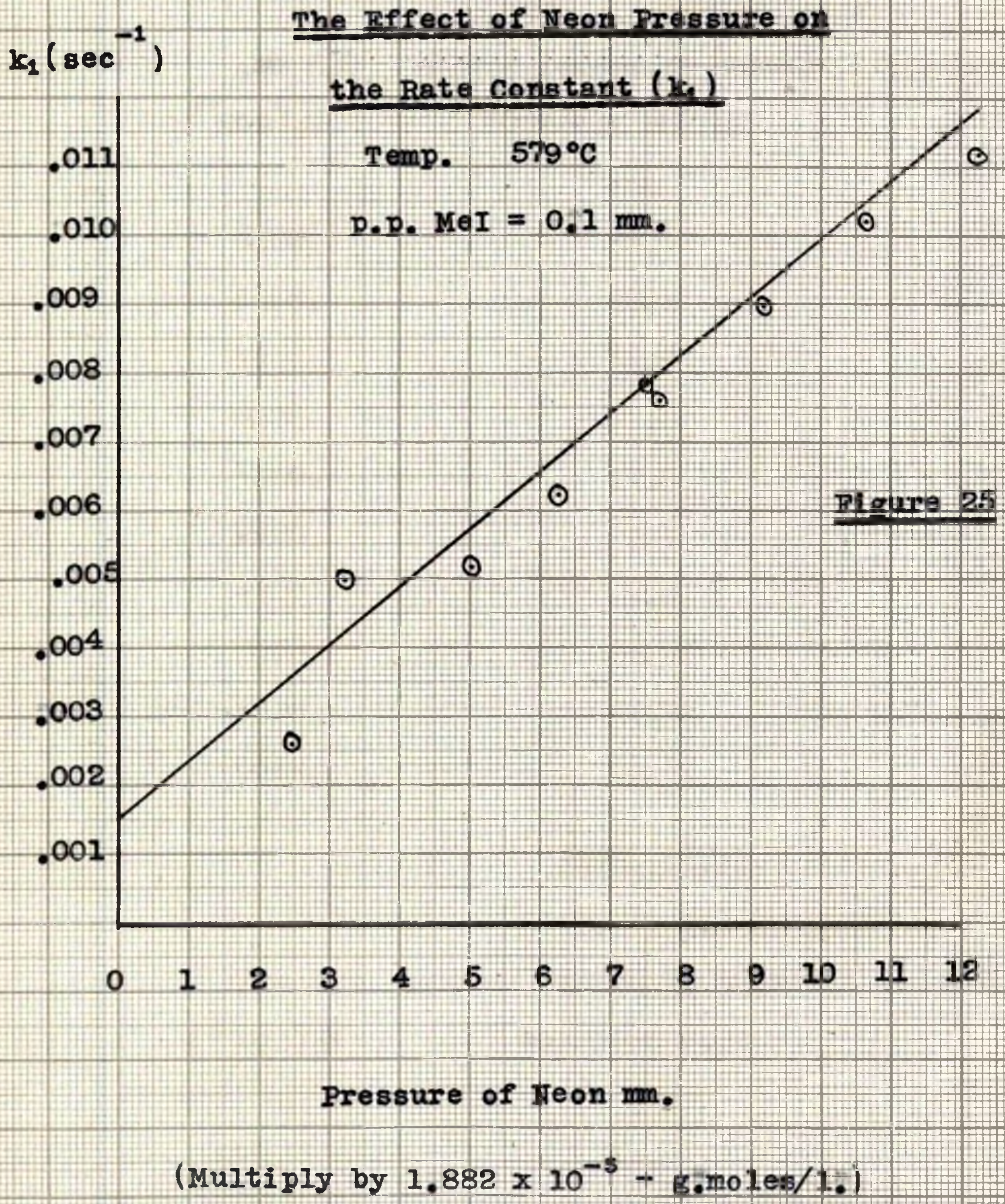
The maximum carrier gas pressure obtainable was only about 3.8 mm.

Table XXV (See Figure 23)

Temperature 579°C

Partial Pressure of methyl iodide 0.1 mm.

	Nitric Oxide Pressure mm.	k_1 (sec^{-1})
(i)	2.34	.0254
(ii)	1.91	.0208
(iii)	3.71	.0296
(iv)	3.18	.0272
(v)	2.16	.0252
(vi)	1.64	.0208



The Effect of Neon Pressure on the Rate Constant (k_1)

Figure 25

(To face page 102).

Helium

Table XXVI (See Figure 24)

Temperature 579°C

Partial Pressure of methyl iodide 0.1 mm.

	Helium Pressure mm.	k_1 (sec^{-1})
(i)	1.55	.0013
(ii)	2.72	.0035
(iii)	3.68	.0039
(iv)	4.10	.0042
(v)	4.73	.0047
(vi)	7.11	.0066
(vii)	8.10	.0089
(viii)	10.91	.0089
(ix)	12.00	.0116
(x)	16.00	.0130

Neon

Table XXVII (See Figure 25)

Temperature 579°C

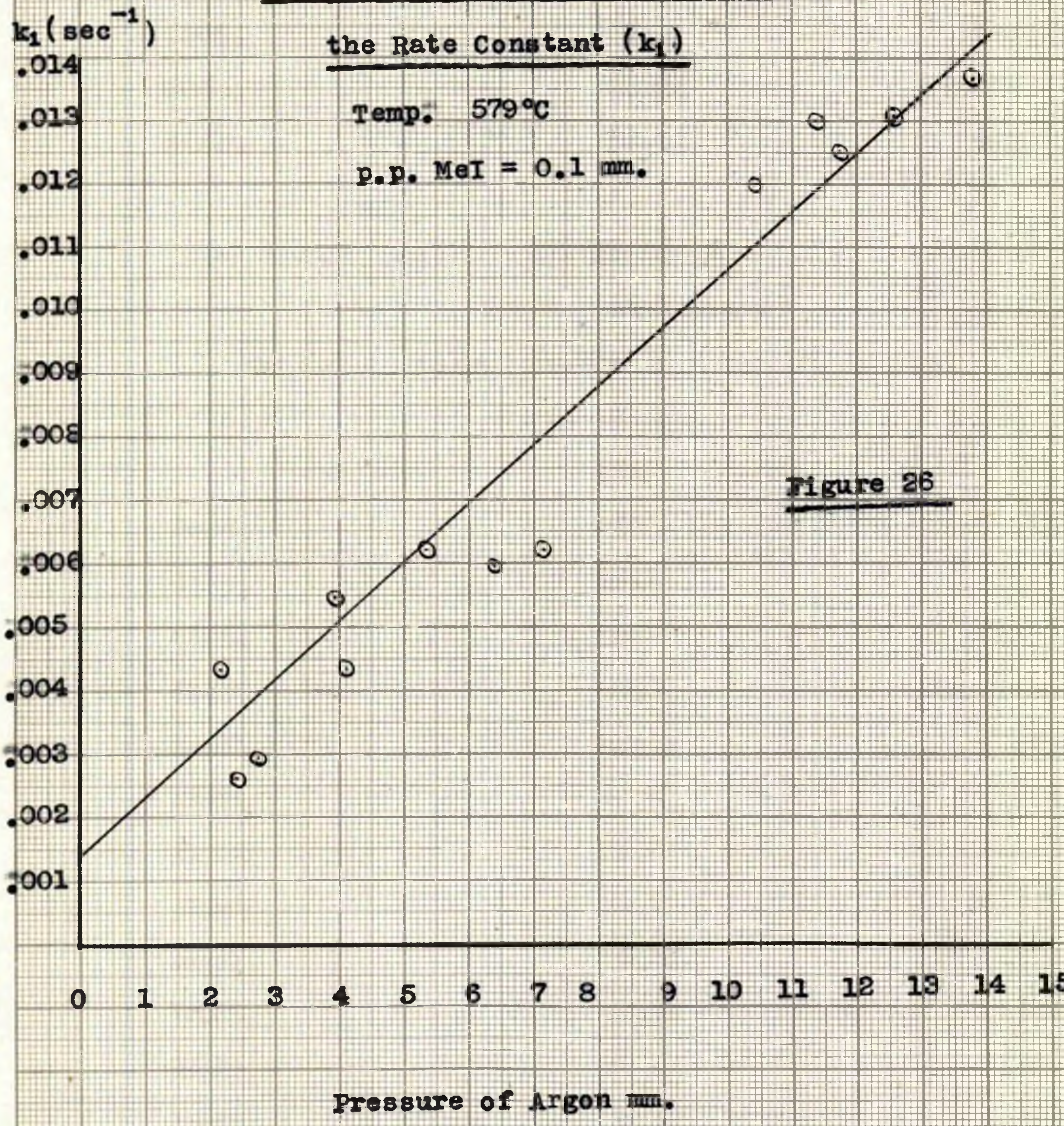
Partial Pressure of methyl iodide 0.1 mm.

	Neon Pressure mm.	k_1 (sec^{-1})
(i)	2.48	.0027
(ii)	3.25	.0050
(iii)	5.00	.0052
(iv)	6.27	.0063
(v)	7.50	.0079

The Effect of Argon Pressure on the Rate Constant (k_1)

Temp. 579°C

p.p. MeI = 0.1 mm.



(Multiply by 1.882×10^{-5} - g.moles/l.)

Figure 26

(To face page 103).

(vi)	7.75	.0076
(vii)	9.10	.0090
(viii)	10.55	.0102
(ix)	12.33	.0112

Argon

Table XXVIII (See Figure 26)

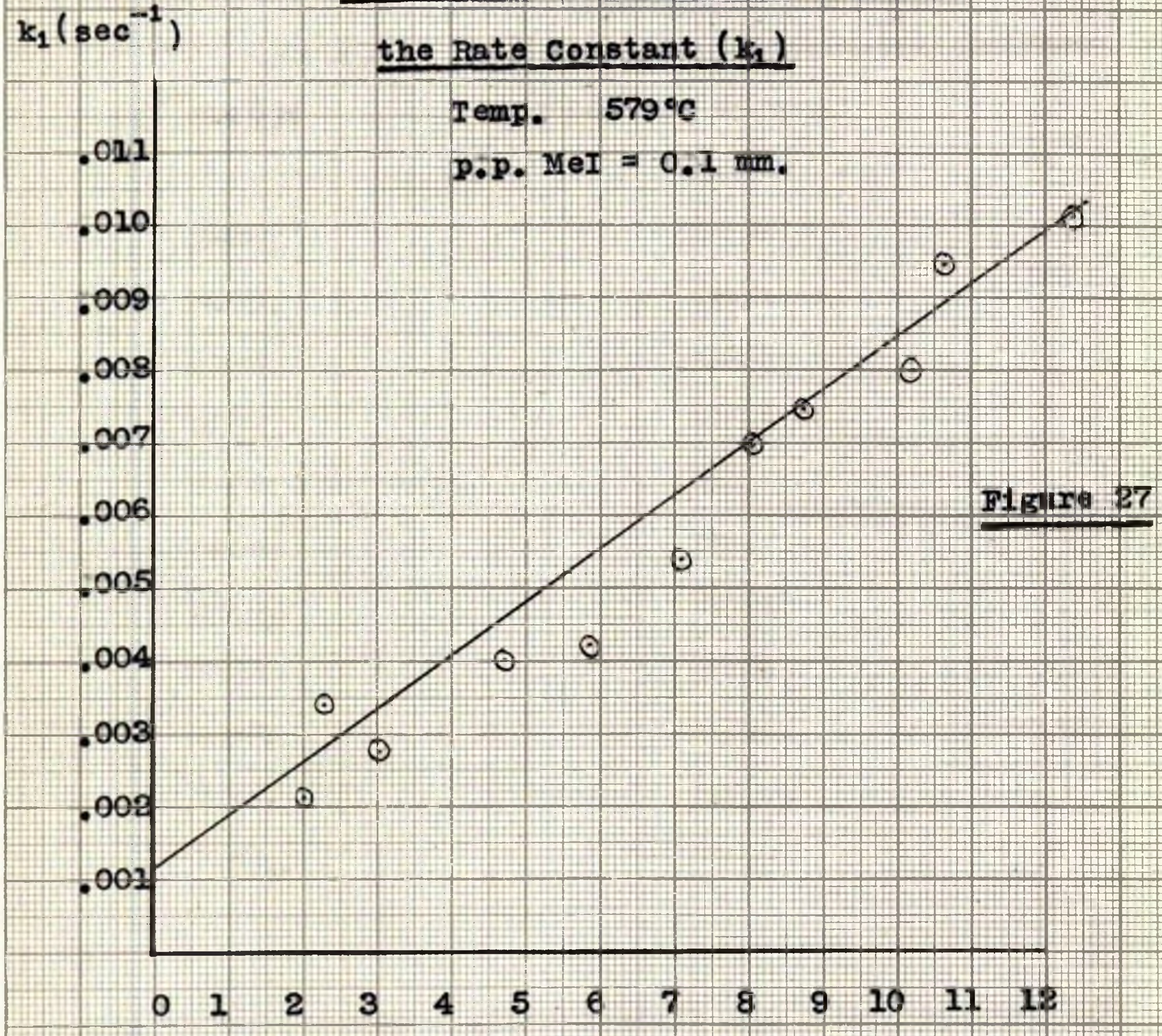
Temperature 579°C

Partial Pressure of methyl iodide 0.1 mm.

	Argon Pressure mm.	k_1 (sec^{-1})
(i)	2.26	.0043
(ii)	2.48	.0026
(iii)	2.83	.0030
(iv)	4.00	.0055
(v)	4.13	.0044
(vi)	5.44	.0062
(vii)	6.50	.0061
(viii)	7.35	.0063
(ix)	10.37	.0120
(x)	11.39	.0130
(xi)	11.71	.0125
(xii)	12.5	.0130
(xiii)	13.70	.0137

The Effect of Krypton Pressure on

the Rate Constant (k_1)



Temp. 579°C

p.p. MeI = 0.1 mm.

Figure 27

(Multiply by 1.882 x 10^{-5} - g.moles/l.)

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Krypton

Table XXIX

(See Figure 27)

Temperature 579°C

Partial Pressure of methyl iodide 0.1 mm.

	Krypton Pressure mm.	k_1 (sec^{-1})
(i)	2.05	.0021
(ii)	2.35	.0034
(iii)	3.09	.0028
(iv)	4.76	.0040
(v)	5.90	.0042
(vi)	7.10	.0054
(vii)	8.05	.0070
(viii)	8.75	.0075
(ix)	10.18	.0080
(x)	10.60	.0095
(xi)	12.30	.0102

Benzene

The decomposition was studied using a mixed carrier gas of benzene and nitrogen. The nitrogen was necessary to provide a means of measuring a rate of flow and the average pressure. The benzene, previously purified by pyrolysis and distillation, was injected into the system by means of the unit illustrated in figure 28. The partial pressure was varied by surrounding the bulb with baths at different temperatures. Tap grease on the two taps was replaced

Diagram of the Injector Unit for the Introduction of Benzene

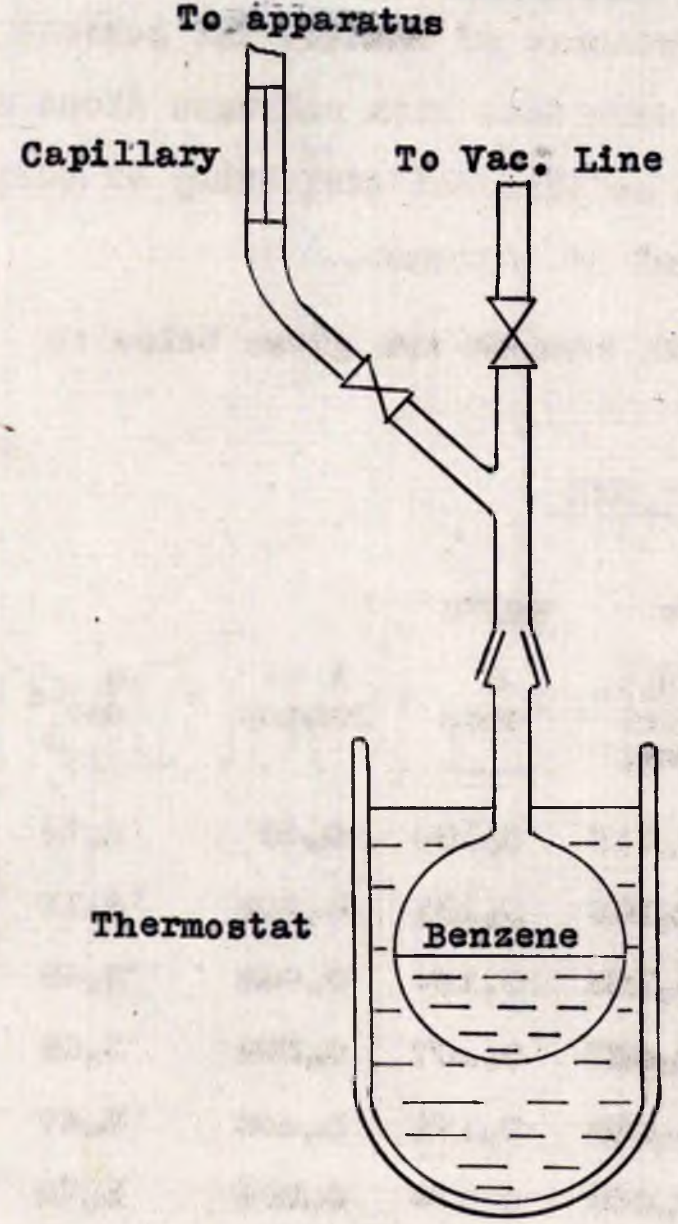

Figure 28

(To face page 105).

by suitable mixture of fluorinated hydrocarbons. The temperature of decomposition had to be raised since in experiments with a high pressure of benzene the contact time was small. Experiments were done with nitrogen alone as carrier in order that the collisional efficiency of benzene could be compared with that of nitrogen.

The data obtained with benzene are given below in Table XXX.

Table XXX

Temperature 625°C						
Expt	Aver. p.mm.	p.p. C_6H_6 mm.	p.p. MeI mm.	t secs	% Decomp	k_1 sec^{-1} 10^2
(i)	2.76	2.52	0.112	0.180	0.49	2.74
(ii)	2.82	2.52	0.163	0.181	0.909	5.11
(iii)	2.94	2.59	0.133	0.189	0.648	3.49
(iv)	3.08	2.82	0.057	0.207	0.524	3.09
(v)	2.58	2.38	0.089	0.172	0.458	2.67
(vi)	2.64	2.45	0.066	0.176	0.316	1.78
(vii)	2.66	2.43	0.105	0.174	0.507	1.91
(viii)	2.72	2.42	0.163	0.174	0.625	3.60
(ix)	2.54	2.28	0.162	0.163	0.387	2.40
(x)	2.68	2.43	0.108	0.175	0.529	3.02
(xi)	2.75	2.46	0.136	0.177	0.481	2.76
(xii)	2.72	2.53	0.040	0.182	0.261	1.47

The Effect of Benzene on the Rate Constant (k_1)

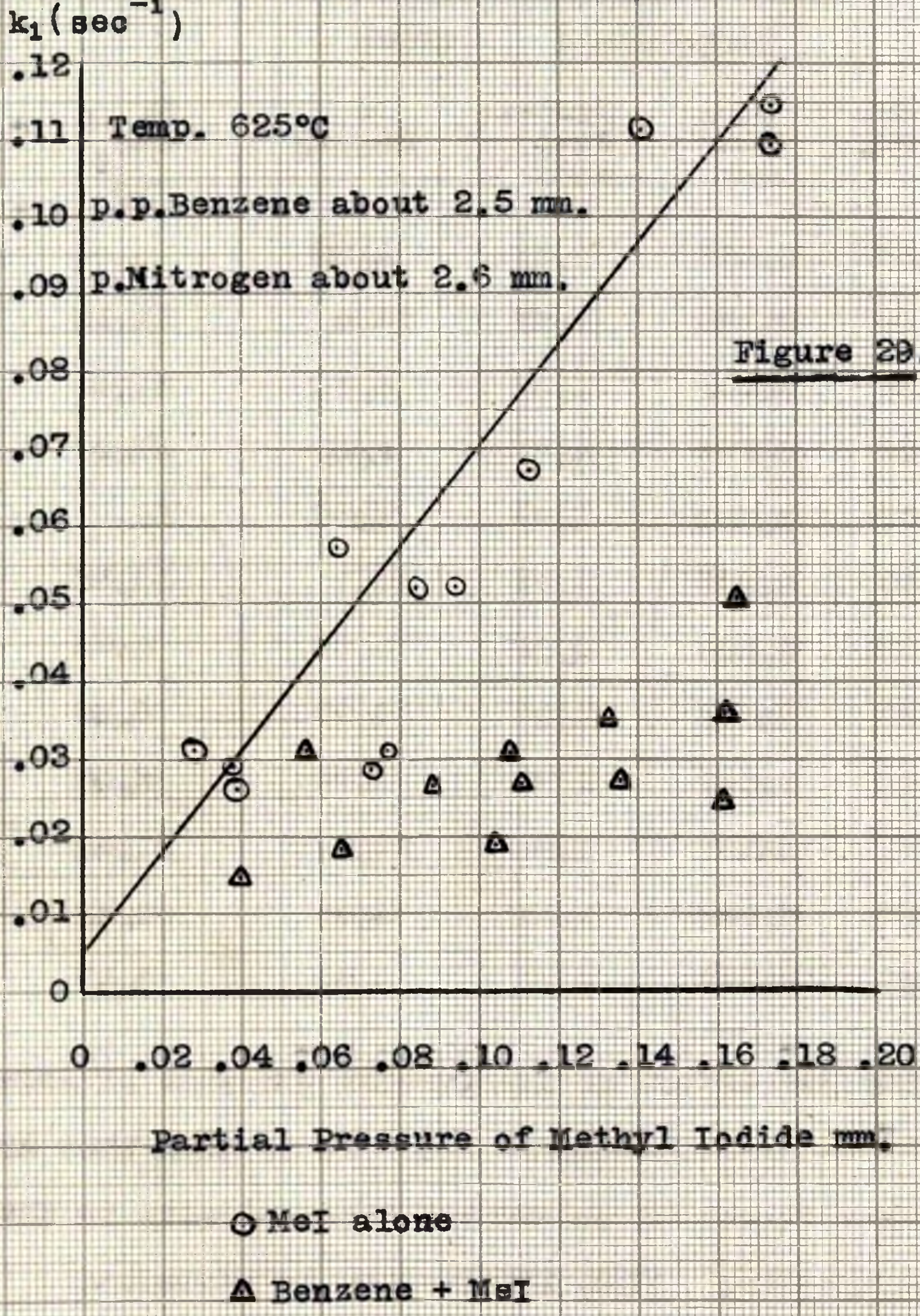

Figure 29.

(To face page 106)

Experiments with nitrogen at pressures comparable with those of benzene are given in Table XXXI.

Table XXXI

Temperature 625°C					
Expt	Aver. p.mm.	p.p. MeI mm.	Contact Time secs	% Decomp	k_1 sec^{-1} 10^2
(i)	2.62	0.113	1.51	9.68	6.74
(ii)	2.78	0.140	1.39	14.4	11.18
(iii)	2.83	0.029	1.40	4.34	31.4
(iv)	2.85	0.064	1.37	7.59	57.4
(v)	2.67	0.094	1.40	7.36	54.9
(vi)	2.80	0.167	1.38	14.1	10.98
(vii)	2.85	0.040	1.45	3.82	2.70
(viii)	2.75	0.067	1.44	4.02	2.86
(ix)	2.45	0.082	1.56	7.77	5.22
(x)	2.61	0.167	1.54	16.2	11.52
(xi)	2.55	0.040	1.55	4.40	2.89
(xii)	2.60	0.078	1.56	4.85	3.17

Plotting the effect of the partial pressure of methyl iodide on k_1 is shown in figure 29. It is seen that the usual pressure effect is eliminated substantially in the benzene experiments. This observation is discussed later.

DISCUSSION

Before dealing with the interpretation of the experimental results it is convenient to summarize by means of headings the aspects of methyl iodide decomposition which have been investigated.

High Pressure Experiments.

(i) The variation of log k_1 with temperature.

(ii) The effect of nitrogen pressure on the reaction rate.

(iii) The effect of toluene pressure on the decomposition.

(iv) The addition of iodine to the system:-

  (a) temperature varied, when the amount of iodine was constant,

  (b) iodine addition varied, when the temperature was constant.

(v) Gas analyses (a) for the CH_3I system alone and (b) for the $CH_3I + C_6H_5CH_3$ system.

(vi) The iodine and toluene reaction.

Low Pressure Experiments.

(i) Reproducibility of experiments.

(ii) Analysis of the products of reaction.

(iii) Effect of variation of the partial pressure of methyl iodide on the rate of reaction.

(iv) The effect of temperature on the rate of reaction.

(v) The effect of iodine addition on the decomposition.

(vi) The influence of different inert gases on the reaction rate.

High Pressure System Reaction Scheme

When methyl iodide was decomposed in the presence of toluene both methane and dibenzyl were formed, so the production of methyl radicals was proved. It is reasonable therefore to assume that the initial step in the decomposition is

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

The subsequent reactions of the methyl radicals depend on the conditions. In the presence of toluene, they react

$$CH_3 + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2.$$

When toluene is not present the overall reaction is given within the limits of experimental error by:-

$$4CH_3I \longrightarrow 3CH_4 + C + I_2.$$

The carbon formed being deposited on the hot portion of the reaction vessel walls, a fact which makes it almost certain that the formation of carbon does not occur in the gas phase.

Bawn[175] has discussed the fate of the methyl radicals in terms of a stepwise mechanism

$$CH_3 + CH_3 \longrightarrow CH_4 + CH_2$$
$$CH_3 + CH_2 \longrightarrow CH_4 + CH$$
$$CH_3 + CH \longrightarrow CH_4 + C.$$

In our system the conditions are not quite the same as in Bawn's work with methyl iodide and sodium and the radicals are unlikely to reach as high a concentration. Another possible scheme is

$$CH_3I \longrightarrow CH_3 + I$$

$$CH_3 + CH_3I \longrightarrow CH_2I + CH_4$$

$$- CH_2I \longrightarrow CH_2 + I$$

$$CH_2 + CH_3I \longrightarrow CH_4 + CHI$$

$$CHI \longrightarrow CH + I$$

$$CH + CH_3I \longrightarrow CH_4 + C + I.$$

This mechanism assumes that collisions between methyl iodide molecules and unstable intermediates are more frequent than between radicals and that such reactions are more probable unless there are large differences in activation energy. Products resulting from the dimerisation of radicals proved almost negligible in amount. Recently Bawn[176] has shown that the reaction $CH_3 + CH_3I$ is not easy. There remains the possibility that the reaction of the methyl radicals occurs on a surface:-

$$4CH_3 \longrightarrow 3CH_4 + C.$$

This would explain our observations on the deposition of carbon.

Bevington[177] has recently produced a method for studying inter-radical reactions using thermodynamic considerations, a discussion of which is given in an appendix. The essence of the procedure however is to discuss the two alternative reactions $2R- \longrightarrow M_1 + M_2$

(disproportionation) and 2R → R - R(combination) and use the free energy difference as a criterion of which is more probable. This free energy difference is really only the free energy change in the direct interconversion $R - R \longrightarrow M_1 + M_2$. Applied to the case of methyl radicals it shows that the system ($3CH_4 + C$) has a lower free energy than $2C_2H_6$. This suggests that disproportionation is more likely than dimerisation at our temperatures.

The small amount of ethane observed (1%) is in line with Bawn's results. He found that the ratio of CH_4/C_2H_6 produced, changed with rising temperature in favour of increased amounts of methane. By way of confirmation of this Ingold and Lossing[178] have shown that the $2CH_3 \rightarrow C_2H_6$ reaction has a negative temperature coefficient making the formation of ethane very much less likely at higher temperatures. This they explain as being due to changes in the nature of the van der Waals forces at the higher temperatures. Ingold and Lossing apparently noticed no carbon under the conditions they used but Eltenton[32] had to use non-catalytic surfaces in his apparatus to avoid decomposition producing free carbon.

There is also the possibility of other mechanisms for the decomposition;

$$CH_3 + CH_3I \longrightarrow CH_2I + CH_4$$

$$2CH_2I \longrightarrow C_2H_4I_2$$

or

$$CH_2I + CH_3I \longrightarrow CH_2I_2 + CH_3.$$

These reactions are unlikely for the reasons given above and there is no definite evidence for them although they may occur to a small extent.

The fate of the iodine atom also formed during the bond rupturing process must be considered.

The photochemical decomposition of methyl iodide has a low quantum yield which rises to almost unity if acceptors are provided for the methyl radicals or iodine atoms. This is no doubt due to the ready back reaction

$$CH_3 + I \longrightarrow CH_3I$$

$$\text{or} \quad CH_3 + I_2 \longrightarrow CH_3I + I.$$

Which of these is the more effective appears uncertain. The first would almost certainly require a third body.

The reaction $2I \rightleftharpoons I_2$ is of much importance in working out details of the reaction. The recombination of iodine atoms has been widely studied by many workers but the results of Rabinowitch and Wood[140] are largely substantiated. Their data showed that the maximum stationary concentration of iodine atoms that could be obtained was only about 10%. This was in the presence of 336 mm. of helium and the system was irradiated with a sufficient number of quanta to decompose all the molecules. At lower pressures heterogeneous combination reduces the concentration of iodine atoms, whilst at higher pressures homogeneous recombination is rapid. They also found that in the presence of nitrogen the rate constant for the rate of the recombination process ($-d\,I/dt = k[I]^2[N_2]$) was about 10^{-31} (concentration in molecules/cc).

In our system with about 500 mm. of nitrogen, 2 mm. of methyl iodide and about 10% decomposition in 10 secs, the rate of production of iodine atoms is about 7×10^{14} per cc. per sec.

The No. of atoms recombining per sec. $= 10^{-31} \times (0.2/760 \times 2.5 \times 10^{19})^2 \times (500/760 \times 2.5 \times 10^{19})$

$= 7.2 \times 10^{19}$.

It is seen from these approximate calculations that the rate of homogeneous recombination is 10^5 times faster than the rate of production of iodine atoms and a close approach to the equilibrium $2I \rightleftarrows I_2$ must result. Bodensteins'[179] data shows that some 10 - 20% of the iodine exists as atoms in the gas phase.

Radicals or atoms formed in the gas will undergo collisions in diffusing to the wall where in our case they undergo reaction. This is discussed in detail by Semenoff[180] but for our purposes the formula given by Bursian and Sorokin[181] is sufficiently accurate. This states that the average number of collisions made by a particle in diffusing to the wall $= n = 3/32\,(d^2/\lambda^2)$ where d = the diameter of the cylindrical vessel in cms. and λ = the mean free path of the molecule in cms.

The mean free path can be calculated from the following equation

$$= 1/\sqrt{2}\ \sigma^{2} m \qquad \frac{1}{\sqrt{2}\,\pi\sigma^{2} m}$$

where σ = molecular diameter

m = no. of molecules per cc.

For simplicity we may take σ as being the same for all molecules and equal to that for the nitrogen molecule (3.84×10^{-8} cm).

Then at 500 mm. pressure and 500°C

$$m = 1.00 \times 10^{19} \quad \text{molecules/cc}$$

$$= 1.47 \times 10^{-5} \qquad \sigma^{2} = 1.47 \times 10^{-15} \ ?$$

$$n = 2.94 \times 10^{9}.$$

The figure for n gives the total number of collisions of all kinds. The number of specific collisions such as $CH_3I - CH_3$ is in proportion to the relative concentrations.

The number of collisions with methyl iodide molecules a particle makes in diffusing to the wall in the system 448 mm. N_2 and 2 mm. MeI is given by $2/498 \times 2.94 \times 10^{9}$

449

$$= 1.17 \times 10^{7} \text{ collisions.}$$

Ignoring the steric factor for the moment, if we suppose that reaction occurs at a rate given by

$$\text{no. of collisions} \times e^{-E/RT}$$

then the reaction $CH_3 + CH_3I$ only occurs if the activation energy is less than 25 k.cals. Bawn[176] quotes 13 k.cals.

for this reaction in a reference to unpublished work.

Similarly we may consider the reactions of a methyl radical with atoms or molecules of iodine assuming that equilibration of iodine atoms takes place. For 500 mm. of nitrogen, 2 mm. of methyl iodide and 2% decomposition the number of $CH_3 + I$ collisions is about 234×10^4. The number of ternary collisions may be given approximately by

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

Under these conditions about 1 collision in a 1000 is a ternary one so the $CH_3 + I + N_2$ reaction is feasible. It is very unlikely that this reaction requires any activation energy. The number of collisions of methyl radicals with iodine molecules is about 10^5. The activation energy required to prevent the $CH_3 + I_2$ reaction would by similar reasoning need to be 18 k.cals. , a very high figure compared with generally accepted order of 1 k.cal.

The effect of steric factors has been neglected in the above discussion. The views expressed on the magnitude of the P factor are conflicting, some workers prefer $P \approx 1$, whilst others propose $P = 10^{-5} - 10^{-6}$. Taking the latter view, the evidence for which is growing (e.g. ref. [36-46]), and if we also assume that a methyl radical is destroyed at the wall we can equate the collisions it makes with methyl iodide molecules (1.17×10^7) to $e^{-E/RT}/10^{-5}$ to calculate the limiting value of E to prevent reaction. This would make any value greater than 7 - 8 k.cal. adequate to prevent reaction. Bawn's estimate of 13 k.cal. would mean that CH_3 and CH_3I would not react.

In the case of iodine molecules the calculation above shows that only about 10^5 collisions would be made and if the energy of activation had the value 1 k.cal., i.e. the $e^{-E/RT}$ factor equals $10^{-3\cdot 7}$, a steric factor smaller than 10^{-2} would prevent reaction. Experimentally reaction does occur as iodine inhibits the reaction at high pressures. There is not much data on the steric factor of radical reactions with simple molecules. Data for $CH_3 + H_2$[182] put the steric factor as 10^{-3}. A summary[183] shows the literature to be inconsistent and in one case, where methyl radicals were produced from acetaldehyde[191], the steric factor is nearly unity. From our results it would appear that if E is low P must be greater than 10^{-2} for the reaction with iodine.

Lapage[1] did calculations on the number of collisions particles made in diffusing to the wall but she took no account of the magnitude of P factors since the recent knowledge on these quantities was not then available to her.

Mechanism of the Decomposition in the Presence of much Nitrogen.

The experimental data obtained does allow us to suggest a mechanism which will, qualitatively at any rate, explain the observed reaction.

The experiments carried out with toluene appeared at first sight the easiest to explain but the effect of variation of toluene pressure and the reaction between toluene and iodine showed hitherto unsuspected complexity.

The following mechanism is proposed

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

$$CH_3 + I \longrightarrow CH_3I \qquad (2)$$

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

(2) and (3) are completely suppressed in the presence of sufficient toluene.

The methyl radicals react:-

$$CH_3 + C_6H_5CH_3 \longrightarrow C_6H_5CH_2 + CH_4 \qquad (4)$$

The benzyl radicals dimerise to give dibenzyl,

$$2C_6H_5CH_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (5)$$

which is subsequently attacked by either benzyl or methyl radicals to give stilbene. Attack by the methyl radical is the more likely on therma~~l~~o- chemical as well as steric grounds.

$$C_6H_5CH_2CH_2C_6H_5 + R \longrightarrow C_6H_5CHCH_2C_6H_5 + RH \qquad (6)$$

$$C_6H_5CHCH_2C_6H_5 \longrightarrow C_6H_5CH{:}CHC_6H_5 + H \qquad (7)$$

$$C_6H_5CHCH_2C_6H_5 + R \longrightarrow C_6H_5CH{:}CHC_6H_5 + RH \qquad (8)$$

Reactions (4) to (8) are necessary to account for the production of stilbene. In support of reactions (4) to (8) we may quote the low activation energy for reaction (4) obtained from the work of Taylor and Smith[184], Szwarc and Roberts[185], and Steacie and Trotman-Dickenson[186] (8.3 k.cal.).

Horrex and Miles[23] in studying the pyrolysis of dibenzyl showed that benzyl radicals in the presence of dibenzyl led to a series of reactions giving stilbene as the chief product.

The gas analysis experiments showed a difference between the amounts of iodine and methane (theoretically $CH_4/I = 1$). This was shown to be due to a reaction between toluene and iodine which appears to involve:-

$$I_2 \longrightarrow I + I \quad (9)$$

$$C_6H_5CH_3 + I \longrightarrow C_6H_5CH_2 + HI \quad (10)$$

$$C_6H_5CH_2 + I_2 \longrightarrow C_6H_5CH_2I + I \quad (11)$$

$$C_6H_5CH_2 + I \longrightarrow C_6H_5CH_2I \quad (12)$$

$$2C_6H_5CH_2 \longrightarrow \text{dibenzyl} \quad (5)$$

$$C_6H_5CH_2CH_2C_6H_5 + I \longrightarrow C_6H_5CHCH_2C_6H_5 + HI \quad (13)$$

Radicals (methyl or benzyl) may attack the hydrogen iodide:-

$$R + HI \longrightarrow RH + I \quad (14)$$

The iodination of toluene follows in reactions (10) and (11) a course analogous to the bromination kinetics studied by van Artsdalen and his collaborators[187]. There appear to be no previous studies on the iodination of hydrocarbons, which is surprising for as shown by simple thermochemistry the reaction is not unlikely in the case of toluene.

$$C_6H_5CH_2 - H + I \longrightarrow C_6H_5CH_2 + H - I$$

$$D = 77.5 \text{ k.cal./mole} \qquad D = 70 \text{ k.cal./mole.}$$

and also

$$C_6H_5CH_2 + I - I \longrightarrow C_6H_5CH_2 - I + I$$

$$D = 35 \text{ k.cal./mole} \qquad D = 37\text{-}40 \text{ k.cal./mole.}$$

In the system $CH_3I - C_6H_5CH_3$ the methyl radicals will react readily with the hydrogen iodide

$$CH_3 + HI \longrightarrow CH_4 + I \qquad (15)$$

which has a very low activation energy. This together with the practical difficulty mentioned earlier may explain the small amount of hydrogen iodide found.. The origin of the benzyl iodide produced is also explained.

In spite of these complications certain conclusions may be drawn about the $CH_3I \longrightarrow CH_3 + I$ reaction. The data shows it to be first order, the limiting rate having been attained. The fact that the rate (as measured by the iodine formation) is independent of the nitrogen and methyl iodide pressures demonstrates this.

The value of 54.7 k.cal./mole for the activation energy obtained by Lapage, and apparently confirmed by this work, was taken as being equal to the energy of dissociation of the C-I bond. This value is in close agreement with that estimated by Skinner[188] on thermochemical grounds. In spite of the complexity of the reaction the value may still be regarded as a fairly close approximation since the error in the rate as measured by the free iodine concentration was about 70% which would only result in about 1 k.cal. error in the activation energy. Also the CH_4/I ratio probably remains much the same over a small temperature range and the log k - 1/T slope is not appreciably different.

The experiments with 2 mm. of methyl iodide in 500 mm. of nitrogen were homogeneous even though carbon was deposited on the walls of the reaction vessel. The velocity constants were substantially less than the values obtained in the presence of added toluene (about five times at 461°C). The difference becomes greater at higher temperatures. In fact Lapage from her data calculated that $k_1 = 10^{7.55} . e^{-35.8/RT}$; the results of this work being in reasonably close agreement. The decrease in the value of k_1 suggests that some back reaction reforming methyl iodide takes place. Such a reaction becomes of greater importance with increasing decomposition since the amount of iodine in the system is then greater. This is the case and so explains the increased difference in rates for the $CH_3 - N_2$ and the $CH_3I - N_2 - C_6H_5CH_3$ systems with increasing temperature.

Confirmation is obtained from the experiments on the addition of iodine, the depression in the rate constant k_1 increasing as more iodine is added. The results in the case of experiments where a constant amount of iodine was added at different temperatures can also be interpreted on this basis.

Possible back reactions are :-

$CH_3 + I$ (+ third body)

and $CH_3 + I_2$.

Calculations have been made earlier on the likelihood of these reactions and it has to be concluded that a choice between these alternative methods of removing methyl radicals is difficult because either scheme can adequately explain the low rates of reaction. Both are feasible and it is most likely that both participate to some extent.

The possibility of the reaction

$$I + CH_3I \longrightarrow CH_3 + I_2$$

which is endothermic to the extent of 20 k.cal. has to be examined. It is necessary to consider both steric factors and the low collision number of such a bimolecular process at the pressures involved. The number of collisions a particle makes with methyl iodide molecules in diffusing to the wall is about 10^7 under the conditions we are considering. Assuming that the activation energy for such a reaction was 20 k.cal. then $e^{-\overset{\times 10^3}{20}/RT}$ is about 10^{-6}. A steric factor of reasonable size (10^{-2}) would be all that was required to make the process inefficient. Moreover, the endothermicity is merely the minimum activation energy, (i.e. $E \geq 20$), so the possibility of the $I + CH_3I$ reaction is not serious on these grounds.

Low Pressure Reaction Scheme

In the elucidation of a mechanism for the reaction at low pressures of carrier gas the chief fact that has to be explained is the dependence on the pressure of the reaction rate.

Lapage found that some degree of surface reaction was evident but the decomposition appeared predominantly homogeneous. The falling off in rate with decreasing pressure cannot be due to back reaction such as was postulated for the high pressure of nitrogen experiments, because as Lapage showed the low pressure experiments have an apparent activation energy of 53-58 k.cal. if calculated on a first order basis. The value of 36 k.cal. was obtained in the high pressure experiments in the absence of toluene. This suggests that the two observations do not have a common explanation.

The participation of methyl radicals was also proved by Lapage who showed that, in the presence of toluene, methane and dibenzyl were produced. The initial step is certainly

$$CH_3I \longrightarrow CH_3 + I.$$

As for the high pressure experiments carbon was deposited on the wall of the reaction vessel and the overall reaction was expressed by:-

$$4CH_3I \longrightarrow 3CH_4 + C + 2I_2$$

By similar reasoning to that used in the high pressure case it can be shown by a rough calculation that in a system of 4 mm. of nitrogen and 0.1 mm. of methyl iodide at 580°C that a methyl radical in diffusing to the wall makes 1.65×10^{5} collisions. If we postulate that a methyl radical can react with a molecule of methyl iodide an activation energy of 14 k.cal. will ensure reaction if the steric factor was of the order of unity. On the other hand it now appears that steric factors of the order $10^{-5} - 10^{-6}$ may be the rule and this combined with Bawn's postulation that the $CH_3 + CH_3I$ reaction may not be easy safely rule out further consideration of this reaction. The most likely fate of the methyl radicals is a wall reaction resulting in:-

$$4CH_3 \longrightarrow 3CH_4 + C.$$

The disproportionation of the methyl radical has been demonstrated as being more likely than combination at these temperatures. This is supported by the almost complete absence of ethane.

The slight surface effect found by Lapage may be due to a normal heterogeneous decomposition of the methyl iodide molecule, or it may have the effect of preferentially removing methyl radicals other than by $CH_3 + I$ etc. No heterogeneity was found at high pressures even though carbon was deposited on the wall of the reaction vessel. Greatly lowering the inert gas pressure did not result in an increase in rate (in fact the opposite was observed). Neither of these facts suggest that a true decomposition on the wall takes place to any extent.

The improvement in reproducibility resulting from a carbon coating on the wall may result from an elimination of some heterogeneous decomposition in an originally clean vessel.

The surface effect most probably arises from the preferential removal of the methyl radicals by the wall, a carbon coated wall more readily, or at least more uniformly, adsorbing impinging radicals.

The possibility of back reactions:-

$CH_3 + I$ (+ third body)

and $CH_3 + I_2$

must be considered.

The arguments presented earlier have shown that in the system there is practically an equilibrium $2I \rightleftharpoons I_2$ set up. The recombination of iodine atoms must take place mainly by combination at the wall, since ternary collisions only amount to about 1 in 5×10^6 under our conditions (4 mm.). This implies that if $CH_3 + I$ requires a third body it is not likely to be of importance for recombination. If it is assumed that about 10% of the iodine is in the form of atoms for the system 4 mm. of N_2, 0.1 mm. of CH_3I and 2% decomposition, the methyl radicals will make about 8 collisions with iodine atoms and 35 with iodine molecules in diffusing to the wall. If the CH_3 + I reaction did not require a third body the small number of collisions require that the activation energy should not be greater than 3.5 k.cal. for the reaction with iodine atoms and 6 k.cal. for the reaction with iodine molecules. The small values allowed are probably in excess of the activation energy actually required but if steric factors of the now accepted order (10^{-2} - 10^{-6}) are postulated then reaction is very unlikely before the radical reaches the wall. In support of the argument against appreciable recombination is the very slight retardation observed when iodine was added to the system. The recombination, such as it was must take place on the wall, or from methyl radicals which rebound without being adsorbed on the wall.

The I + CH_3I reaction need not be considered under the low pressure conditions for if the activation energy is 20 k.cal. or above the number of collisions is insufficient to allow any measurable reaction to occur.

Recently there has been some theoretical discussion of reactions of the type $A + B + M \longrightarrow C + M$ which have some relevance to our argument. Marcus and Rice[49] considered the CH_3 + I + M reaction and concluded that the steric factor for the recombination of free radicals and the effect of pressure on such recombination mutually depend on the nature of the activated complex. It is tentatively inferred that the collision efficiency for the recombination increases from about 0.001to 0.01 as the total pressure rises from 20 mm. to infinity. This conclusion was drawn from the postulated rigid complex, i.e. a complex in which some of the rotational degrees of freedom between the two radicals are frozen out. Such behaviour has been found by Kistiakowsky and Kirk Roberts[189] for the combination of methyl radicals in good agreement with Marcus's[190] mathematical prediction. Although such work is very largely theoretical it may be of help in understanding the differences between the kinetics at high and low pressures. The pressures for the changing rates predicted by Marcus and Rice are higher than those deduced from these experiments.

The kinetics of the reaction as developed above suggest that recombination is unimportant and that CH_3 + CH_3I reactions can be ruled out. The pressure dependence of the reaction can therefore only be explained as being quasi-unimolecular behaviour of the Lindemann-Hinshelwood hypothesis, the elementary theory of which has been developed in the introductory section.

Confirmation of this explanation has been obtained by observing the effect of different inert gases on the form of the k_1 - pressure relationship.

The Effect of Inert Gases

Lapage tested the validity of the quasi-unimolecular hypothesis by plotting $1/k_1$ against 1/(effective concentration) and obtained a fairly reasonable linear relationship such as simple theory would lead one to expect. The slope of such a plot should give the bimolecular rate constant for activation by collision between methyl iodide molecules and from which by use of the Hinshelwood expression

$$k = Z(E/RT)^{(n/2 - 1)} \quad \frac{1}{\underline{|n/2 - 1}} \; e^{-E/RT}$$

it is possible to calculate the number of vibrational degrees of freedom contributing to the activation of the molecule. Lapage performed such a calculation and obtained n = 18 for the number of contributing square terms, a value in agreement with the number of permissible vibrations calculated from the expression 3a - 6 for a non-linear polyatomic molecule with a atoms.

Such calculations and plots although satisfactory for confirming the general correctness of the theory are not suitable for detailed quantitative examination of the data because:-

(a) a mixture of gases is used in the system and the activation processes

$CH_3I + CH_3I$

and $CH_3I + X$ (inert gas)

have both to be considered. It is well known that the efficiency of transfer of energy on collision depends on the nature of the colliding molecules so instead of using the actual pressure it is necessary to use

$$p_{\text{effective}} = p_{\text{MeI}} + \lambda p_{\text{inert gas}},$$

where λ = the efficiency of the inert gas in activating molecules relative to methyl iodide. λ may only be found by picking out equal rate constants when the partial pressures are different. This is not satisfactory as the method is very susceptible to experimental error.

(b) the linearity of the $1/k_1 - 1/p$ plot assumes the simple theory of the Lindemann mechanism which, for reasons previously discussed (page 32), is hardly expected to be more than an approximation. In the case of a relatively simple molecule like methyl iodide the difference would not be expected to be very great however.

In order to measure the relative efficiencies of different gases in transferring energy some more suitable method must be used. Johnston[102] employed the following type of reasoning which is here applied to the methyl iodide case.

Consider the reactions

$$CH_3I + M \xrightarrow{k_{iM}} CH_3I_i^* + M$$

$$CH_3I_i^* + M \xrightarrow{k'_{iM}} CH_3I + M$$

$$CH_3I_i^* \xrightarrow{k_i^*} CH_3 + I$$

* indicates an excited molecule.

i refers to the particular energy state of the methyl iodide molecule above the critical energy required for decomposition.

M stands for any gas molecule capable of activating or deactivating methyl iodide. The subscript M is necessary for the rate constants because the activation and deactivation rates depend on the nature of the gas M as well as on its concentration.

Using reasoning similar to that presented for the simple theory (page 29) the first order rate constant is given by

$$k = \sum_i \frac{k_i^* \sum_M k_{iM}[M_M]}{\sum_M k'_{iM}[M_M] + k_i^*}$$

This equation shows that the concentrations of the gases in the reaction system appear in such a manner that only under special conditions will the different rate constants have a simple interpretation.

If however the foreign gas is in considerable excess and it is allowed to approach zero pressure useful information is obtainable, since it is only at low concentrations that the relative values of the rate constant give the different values of the activating efficiencies of inert gases.

At the low concentration limit

$$\sum_{M} k'_{iM} [M_M] \ll k_i^*$$

for all values of i, under which conditions the above equation reduces to

$$k^0 = [M_1] \sum_i k_{1i} + [M_2] \sum_i k_{2i} + \cdots\cdots + [M_M] \sum_i k_{Mi}$$

$$= k_1^0 [M_1] + k_2^0 [M_2] + \cdots\cdots\cdots + k_M^0 [M_M]$$

where k^0 is the observed first order rate constant when the conditions stated above are met.

k_1^0 is the second order rate constant for activation of the reactant by foreign gas M_1, etc.

For the case of methyl iodide in the presence of an inert gas in which the concentration of methyl iodide is held constant (0.1 mm. at 579°C), while the pressure of inert gas is varied, we have then

$$k^0 = k_1^0 [CH_3I] + k_2^0 [M]$$

when the limiting low concentration conditions apply.

This means that a plot of the first order rate constant against the concentration of inert gas (or pressure) is linear over short range, until the limiting conditions are no longer met when higher order terms must be added and the plot of $k_1 - [M]$ curves downwards.

Inspection of the results obtained shows that very nearly linear plots were obtained for nitrogen, methane, carbon monoxide, helium, neon, argon and krypton.

The equation deduced above implies that for such graphs the slope for the linear region gives the second order rate constant for activation by the $CH_3I + M_{\text{inert gas}}$ process. The intercept of such graphs is equal to the rate constant for the $CH_3I + CH_3I$ reaction divided by the concentration of methyl iodide (which was the same for all the gases, 1.882×10^{-6} mol. l^{-1}).

The values for the slopes (l.mol.$^{-1}$ sec.$^{-1}$), intercepts (sec.$^{-1}$) and the second order rate constant for the $CH_3I + CH_3I$ reaction are given in Table XXXII. These values were deduced from figures 20,21,22,24,25,26 and 27.

Table XXXII

Temperature 579°C

Concentration of Methyl Iodide 1.882×10^{-6} mol. l^{-1}.

Gas	Slope l.mol.$^{-1}$ sec.$^{-1}$	Intercept sec.$^{-1}$	Intercept (conc.MeI)$^{-1}$ l.mol.$^{-1}$ sec.$^{-1}$
Nitrogen	95.6	0.0020	1060
Methane	77.5	0.0016	850
Carbon Monoxide	36.1	0.0016	850
Helium	39.8	0.0014	745
Neon	45.2	0.0015	797
Argon	48.9	0.0012	638
Krypton	38.8	0.0012	638
	Mean	0.0015	800

The Dependence of the limiting bimolecular rate constant on temperature

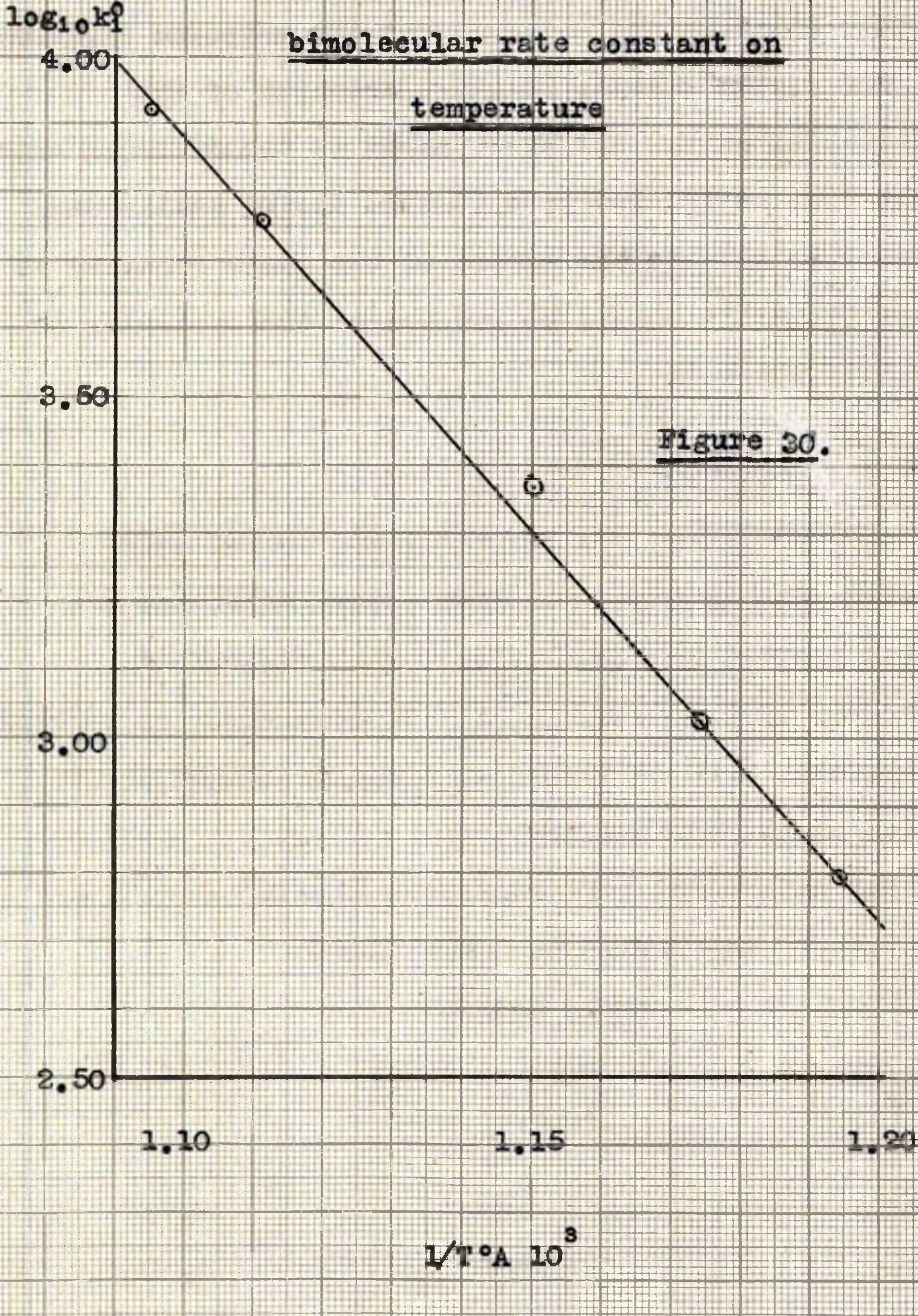

Figure 30.

(To face page 131)

The fact that within the limits of experimental error the intercepts are of the same order for all gases provides confirmatory evidence for the proposed explanation.

The slopes provide relative measures of the efficiencies of the different gases in transferring energy to and from methyl iodide molecules during collisions. In order to compare the effect of the gases relative to methyl iodide it should be sufficient theoretically to calculate the ratio

$$\frac{\text{slope}}{\text{intercept/conc.MeI}} .$$

Another method for obtaining the second order limiting rate constant for $CH_3I + CH_3I$ is to use the results plotted in figure 17. The temperature dependence of this reaction may be determined by plotting the limiting rate constant, as found by measuring the initial slope, against 1/T.

The determined initial slopes ($l.mol.^{-1}$ $sec.^{-1}$) and temperatures are listed in Table XXXIII.

Table XXXIII

Temperature °C	Initial Slope $l.mol.^{-1}$ $sec.^{-1}$ k_1^0	$\log_{10} k_1^0$
565	627	2.797
579	1062	3.026
598	2338	3.3689
626	5740	3.759
640	8510	3.930

From the slope of the plot of $\log_{10}k_1^0$ against $1/T$, figure 30, an activation energy of 54.4 k.cal./mole is obtained. This value is in good agreement with thermochemical estimates of the C-I bond dissociation energy for methyl iodide and also with the value deduced above from the kinetics of methyl iodide decomposition. It is also strong confirmatory evidence for the unimolecular behaviour of the decomposition reaction. Also from the graph a pre-exponential factor of about $10^{14.5}$ is found which means that the k_1^0 values are higher than those which would be expected if the constant k_1^0 equals $Ze^{-E/RT}$ where Z is of the order of $10^{11} - 10^{12}$ (the collision number). If we apply the Polanyi-Hinshelwood expression

$$k = Z(E/RT)^{n/2 - 1} \frac{1}{\underline{\left| n/2 - 1 \right.}} e^{-E/RT}$$

with $E = E_{exp.} + (n/2 - 1)RT$, we need to use n at its maximum value of about 18 for methyl iodide to accommodate the high k_1^0 values obtained experimentally. This is in agreement with the value obtained by Lapage from the slope of the $1/k_1$ against $1/p_{effective}$ graph.

From the graph in figure 30 the rate constant for the second order $CH_3I + CH_3I$ reaction at 579°C a value of 1060 was obtained compared with about 800 obtained by the intercept method. Since the experimental uncertainties are much the same for both methods we may take a mean value of 930. Using this value the relative efficiencies of the different gases in transferring energy to the methyl iodide molecule as measured by the rate constant for the various CH_3I + M processes are

CH_3I	N_2	CH_4	CO	He	Ne	A	Kr
1.0	0.13	0.083	0.038	0.043	0.049	0.053	0.041

The results for nitric oxide cannot be treated in the same manner as for the other gases since the $k_1 - P_{NO}$ plot is not linear, the nitric oxide apparently being an extremely efficient activating substance since no evidence for any chemical reaction involving nitric oxide could be found.

An approximate value for the relative efficiency was obtained by extrapolation to pass through the point 0.0018 on the k_1 axis and measurement of the initial slope. The determined value for the rate constant of the CH_3I + NO process was 744 which is an activating efficiency of 0.80 relative to methyl iodide.

The results obtained have shown that the polyatomic gases appear to be the most effective in activating methyl iodide molecules although none, with the exception of nitric oxide, compare in efficiency with methyl iodide itself. The low efficiency of carbon monoxide may be due to the reaction

$$CH_3 + CO \longrightarrow CH_3 \cdot CO$$

occurring which would prevent the methyl radical diffusing to the wall where it would end its life. This would make it possible for methyl iodide reforming reactions to occur. The inert gases are as expected comparatively inefficient.

The results on benzene are surprising for as the plot in figure 29 shows the effect of the partial pressure of methyl iodide on the rate appears to have been very substantially eliminated.

The contact times for the nitrogen andbenzene experiments were very different and it is possible that for times of about 0.2 sec. the period spent in the reaction vessel might not be enough for the reactant to reach the correct temperature. (Radiation, as in a vacuum, would give the thermocouple its reading). Lapage found that when contact times were very short the effective contact time was considerably less than the actual value.

On the other hand, if the temperature was reached. there seems no reason why the methyl iodide should not decompose. Benzene is known to be a very efficient third body for the recombination of atoms[114] so it may act in a similar fashion for the recombination of methyl radicals and iodine atoms. Rabinowitch and Wood suggested that a complex was formed between the benzene and the iodine atoms and that recombination took place

Graph of $1/k_1$ against $1/p_{effective}$.

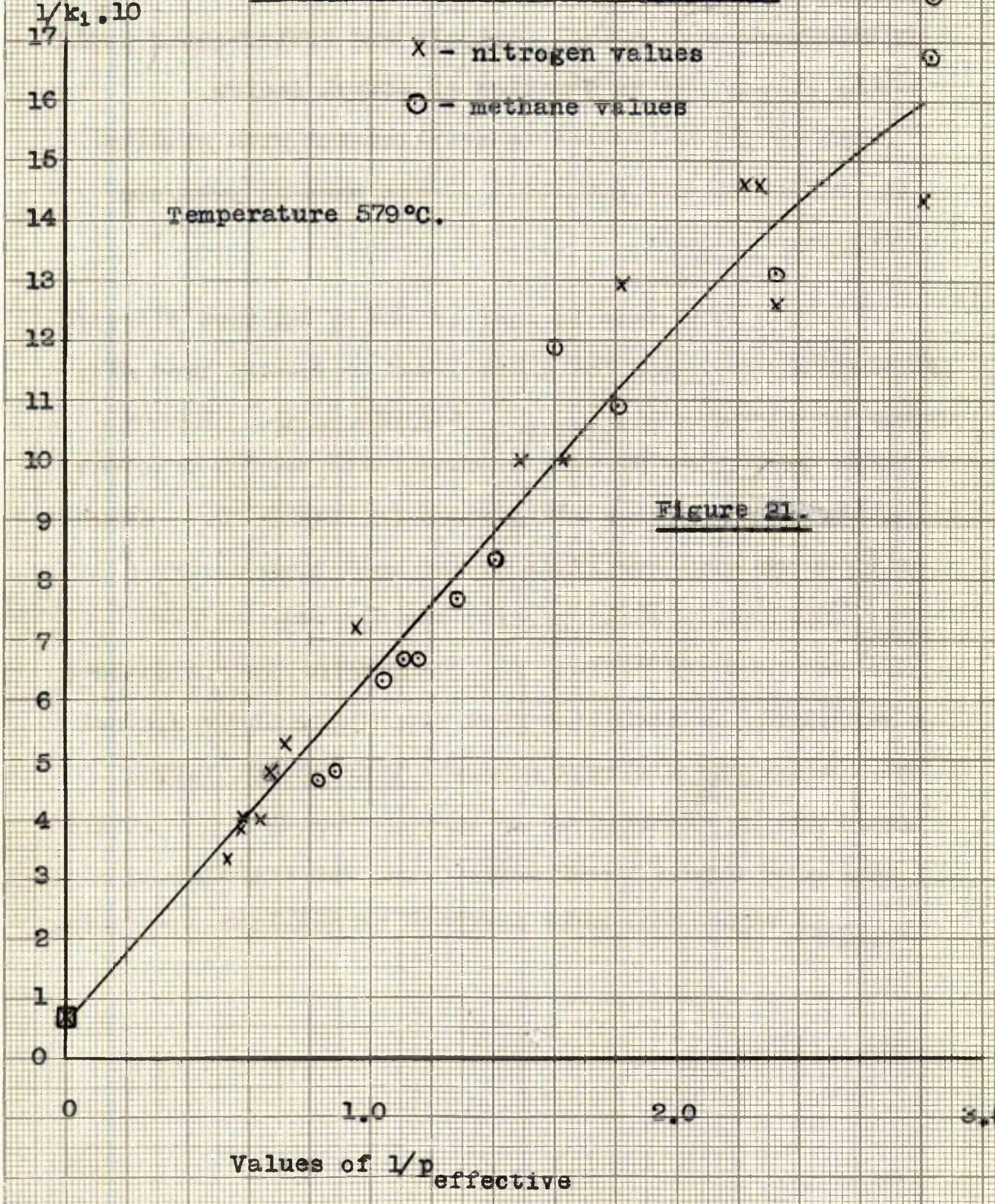

Figure 21.

(To face page 135)

$$C_6H_6 + I \longrightarrow C_6H_6.I$$

$$2C_6H_6I \longrightarrow 2C_6H_6 + I_2.$$

Such behaviour with methyl radicals and iodine atoms would strongly favour the reformation of methyl iodide.

Further investigation is still needed with studies on the effect of the variation of the partial pressure of benzene.

Attempts were made to find if the k_1 against pressure relationship followed the Hinshelwood or Kassel type of theory by plotting $1/p_{effective}$ against $1/k_1$. Values of these quantities for the decomposition in the presence of nitrogen and methane are plotted in figure 29. There appears to be some curvature of the plot such as the Kassel type theory would predict but the data do not appear sufficiently refined for quantitative discrimination. The curvature, or deviation from the simple theory is not large, indeed, for a simple molecule like methyl iodide it would not be expected to be large. Uncertainty within the limits of experimental error (e.g. the calculation of $p_{effective}$) might well make accurate conclusions uncertain.

SUMMARY AND CONCLUSIONS.

(1) The previous work of Lapage (Thesis, St. Andrews, 1950) on the decomposition of methyl iodide has been extended and confirmed in all essential detail. In particular attention has been paid to the transition from first order to second order kinetics as the total pressure of the reacting system is lowered and the activating efficiencies of different inert gases have been evaluated.

(2) It is concluded that the reaction mechanism shows the following features:-

(a) the primary step under all conditions is the dissociation into methyl radicals and iodine atoms.

High Pressure Experiments.

(b) It has been shown that increasing additions of toluene can result in the complete capture of the methyl radicals provided that its pressure is about 8 mm. and the inert gas pressure is about 600 mm. thereby impeding diffusion to the walls where destruction can otherwise occur by $4CH_3 \longrightarrow 3CH_4 + C$. (The toluene pressures used by Lapage tended to be rather low for the purpose).

(c) The reaction conducted in the above conditions with added toluene is faster than in its absence. This shows no chain reaction is involved but a recombination process of methyl radicals and iodine is occurring.

(d) The recombination reaction has been proved by the effect of increasing additions of iodine to the system, causing a decrease in rate. This point was not proved in previous work.

(e) During the investigations with added toluene it has been noted and proved by separate experiments that iodine and toluene react with the production of hydrogen iodide. It is suggested that this is due to $C_6H_5CH_3$ + I. Experiments on this aspect of the work involved mass spectrometric analysis of products.

(f) In the presence of sufficient toluene and with about 600 mm. of nitrogen the first order constant has a temperature dependence given by

$$\log k_1 = 13.7 - 54,700/2.303RT$$

in agreement with Lapage.

(g) A study has been made of the effect of nitrogen pressure on the rate of reaction in the range 100 - 600 mm. nitrogen. No effect was observed. Taken in conjunction with the conclusions detailed below, it is considered that this shows that the high pressure limiting rate of decomposition was attained in this region.

Low Pressure Experiments.

(a) The products of the reaction were shown to be carbon, methane and iodine, in agreement with the equation $4CH_3I \longrightarrow 3CH_4 + C + 2I_2$. Analyses were made by the mass spectrometer for ethane and it was shown to account for only 1% approximately of the products.

(b) Reproducibility of the experiments was enhanced by using a carbon coated vessel.

(c) At the low pressures used (4 mm. nitrogen and 0.1 mm. methyl iodide) with decompositions usually no greater than 3% iodine did not appear to inhibit the reaction. This was proved by direct additions.

(d) Extensive verification has been made of the fact that a decline in rate of reaction occurs as the pressures of nitrogen and methyl iodide are lowered below 10 mm. and 0.5 mm. respectively. This has been shown to occur over a wide range of temperatures and the first order behaviour changes to second order at lower pressures.

(e) The effect of the following gases has been investigated in order to confirm the theory of second order to first order transition for this reaction. All the data are in agreement with this view.

(f) Using a treatment analogous to that given by Johnston[102] the following efficiencies as activators have been deduced.

CH_3I 1, N_2 0.13, CH_4 0.083, CO 0.038, NO 0.80, He 0.043, Ne 0.049, A 0.053, Kr 0.041.

(g) The bimolecular constant for the reaction has been found at various temperatures and shown to be described by

$$\log k_2 = 14.5 - E/RT.2.303$$

$$(\mathrm{l.mol.}^{-1}\,\mathrm{sec.}^{-1}). \quad E = 54.4\ \mathrm{k.cal./mole.}$$

This value of E is in agreement with that derived from the high pressure first order constants.

(h) A discussion of the efficiencies of the inert gases has been given.

APPENDIX

The Dissociation of Iodine.

If x g.atoms of iodine are present in the reaction vessel and a fraction of these stay as atoms, then for

$$\begin{array}{cc} I_2 & I + I \\ 1 - \alpha & \alpha \quad \alpha \end{array}$$

$$K = \frac{[I]^2}{[I_2]} = \frac{\alpha^2 x^2}{(1-\alpha)x/2} \text{ or } K_p = \frac{\alpha^2 p_I^2}{(1-\alpha)p_I/2}$$

So
$$\log K_p = \log \frac{\alpha^2}{1-\alpha} + \log p_I + \log 2$$

Bodenstein[179] gave the following equation for the equilibrium constant for the dissociation of iodine

$$\log K_{p_{atms}} = -\frac{7550}{T} + 1.75 \log T - 4.09\ 10^{-4}\ T + 4.726\ 10^{-8}\ T^2 - 0.440$$

where T is the absolute temperature.

Using this formula, values of K_p were calculated and plotted against temperature so that the value of $\log K_p$ for any particular temperature could be found. Knowing $\log K_p$ at temperature T°A and the value of p_I, a value of $\log \frac{\alpha^2}{1-\alpha}$ could be derived and from a graph of $\log \frac{\alpha^2}{1-\alpha}$ against α a value for α obtained.

The more recent data of Perlman and Rollefson[141] are probably more accurate but for our purposes the difference between their results and Bodenstein's is unimportant.

Calculations such as outlined above were made to find the fraction of iodine atoms present in the reaction system under the conditions described in the Discussion.

Thermodynamics of Inter-Radical Reactions.

(A modified treatment of the method described by Bevington[177]).

Consider the possible reactions

$$4CH_3 \begin{array}{l} \xrightarrow{D} 3CH_4 + C \\ \xrightarrow[C]{} 2C_2H_6 \end{array}$$

Expressed thermodynamically

$$\text{(D)} \qquad \Delta G_D = (3G_{CH_4} + G_{Ce}) - 4G_{CH_3}$$

$$\text{(C)} \qquad \Delta G_C = 2G_{C_2H_6} - 4G_{CH_3}$$

$$\therefore \qquad G_C - G_D = \Delta G_R = \Delta G^0_R + RT \ln \frac{p_{C_2H_6}{}^2}{p_{CH_4}{}^3}$$

where ΔG_R is merely the free energy change for the reaction

$$3CH_4 + C \longrightarrow 2C_2H_6.$$

There is no term p_c because $G_{Ce} = G^0_C$, the standard state for the element.

Also $G^0_{Ce} = 0$ for this reason.

This gives

$$\Delta G_R = \Delta G^0_R + 4.57\ T \log \frac{p^2_{C_2H_6}}{p^3_{CH_4}}$$

In Bevington's rather involved method for the case of ethyl radicals he considers ΔS_{mixing} and also ΔS for a pressure change. The term

$$4.57\ T \log \frac{p^2_{C_2H_6}}{p^3_{CH_4}}$$

refers to all his corrections from standard entropies.

Data on the free energies of formation, ΔG_f, are required for CH_4 and C_2H_6.

The Amer. Inst. Petroleum Project No.44 data gives the ΔG_f values (in k.cal.) for various temperatures directly.

°K	CH_4	$3CH_4$	C_2H_6	$2C_2H_6$	$2C_2H_6 - 3CH_4$
298	-12.14	-36.42	-7.86	-15.72	20.7
400	-10.048	-30.15	-3.447	-6.89	23.26
500	-7.841	-23.523	+1.168	+2.336	25.86
600	-5.49	-16.5	5.97	11.94	28.44
700	-3.05	-9.15	10.90	21.8	30.95
800	-0.55	-1.65	15.92	31.84	32.49
900	+2.01	+6.03	21.00	42	36
1000	4.61	13.83	26.13	52.26	38.43
1100	7.22	21.66	31.28	62.56	40.90

These values are clearly all positive and large, i.e. the equilibrium constant derived from ΔG^0 favours methane and carbon in the equilibrium system at all temperatures.

Turning to the correction term 4.57 T log $\frac{p^2_{C_2H_6}}{p^3_{CH_4}}$ it is necessary to choose pressures.

If p_{CH_3} is 1 atm. and the volume constant

$$\text{then} \quad 4CH_3 \longrightarrow 2C_2H_6$$

$$1 \text{ atm.} \qquad 1/2 \text{ atm.}$$

$$\text{or} \quad 4CH_3 \longrightarrow 3CH_4 + C$$

$$1 \text{ atm.} \qquad 3/4 \text{ atm.}$$

or for $3CH_4 + C \longrightarrow C_2H_6$

$3/4$ atm. $1/2$ atm.

Under these conditions $\frac{4.57\,T}{1000} \log \frac{(1/2)^2}{(3/4)^3}$

$$= - \frac{1.03\,T}{1000} \text{ k.cal.}$$

For pressures near atmospheric this would be a negligible term.

For low pressures there will be a 10^{-6} term giving

$$4.57\,T \log \frac{(1/2)^2}{(3/4)^3} \quad \frac{1}{10^{-6}} = - \frac{6.18\,T}{1000} \text{ k.cal.}$$

This term cannot be sufficiently negative to outweigh the large positive ΔG^0.

These results also imply that at 300°K for

$3CH_4 + C \longrightarrow C_2H_6$

$$\log K_{eq} = - \frac{20.7 \times 1000}{4.57 \times 300} = - 15.1$$

$$\text{i.e.} K_{eq} = 10^{-15}$$

Which means that the proportions of

$CH_4 + C \longrightarrow C_2H_6$ at equilibrium.

This argument shows that CH_3 radicals ought to form $CH_4 + C$ as the thermodynamically most stable state and ethane is formed merely as being more stable than $2CH_3$. The chemical inertia (possibly catalytic wall reaction is required to overcome it) prevents the loss of hydrogen atoms from CH_3 to produce methane molecules.

It is also worthwhile to briefly work out the thermodynamics of

$$4CH_3I \longrightarrow 3CH_4 + C + I_2$$

for which the collected data are:-

ΔG_F^0 at 298°K

CH_3I = 5.3 k.cal. (Selected values - Thermodynamic Const. Nat.Bur.Std.Circ. No.500)

$4CH_3I$ = 21.2

$3CH_4$ = -36.42

$$4CH_3I \longrightarrow 3CH_4 + C + 2I_2$$

$$\Delta G^0 = -57.62$$

i.e. the reaction is very likely.

Considering

$$\Delta G_{reaction} = \Delta G_r^0 + RT \ln \frac{p_{CH_4}{}^3 \, p_{I_2}{}^2}{p^4{}_{CH_3I}} ,$$

the last term will be without effect for reasonable concentrations.

The following tables present a complete list of all the experiments referred to in the text. Qualitative and calibration experiments are not listed.

HIGH PRESSURE EXPERIMENTS.

Expt.	Temp °C	t secs	Aver p.mm	p.p. MeI mm	p.p. Tol mm	Time of Expt secs	% Decomp	$k_1 . 10^3$ sec^{-1}
1	497	11.36	468	1.83	3	2700	9.35	8.62
2	497	11.31	464	1.92	3	2700	8.04	7.44
3	497	11.28	461	1.88	3	2700	8.17	7.60
4	477	10.35	421	1.73	3	1500	2.03	2.47
5	477	10.35	421	1.93	3	1500	2.02	2.65
6	477	10.35	421	1.93	3	1500	2.02	2.65
7	461	13.29	473	1.23	3	1800	1.77	1.33
8	461	13.29	471	1.26	3	1800	1.76	1.32
9	461	13.33	470	1.22	3	1800	1.73	1.30
10	497	10.25	150	2.68	3	1800	8.91	9.13
11	497	10.26	148	2.90	3	1800	8.58	8.75
12	497	10.25	149	3.13	3	1800	8.53	8.72
13	497	12.13	224	2.18	3	2100	11.97	10.51
14	497	12.13	226	2.22	3	2100	10.28	8.93
15	497	12.13	225	2.22	3	2100	12.50	11.00
16	497	9.71	248	2.13	3	1800	8.54	9.18
17	497	9.72	250	2.13	3	1800	8.79	9.49
18	497	9.73	249	2.15	3	1800	8.38	9.00
19	497	12.09	285	1.75	3	1800	10.54	9.19
20	497	12.10	281	1.76	3	1800	10.00	8.70
21	497	12.10	281	1.77	3	1800	10.39	9.05
22	497	12.09	319	1.64	3	1800	9.80	8.50
23	497	12.10	320	1.67	3	1800	10.58	9.22
24	497	12.10	320	1.73	3	1800	10.48	9.15
25	497	12.08	368	1.64	3	1800	9.17	7.95
26	497	12.09	368	1.52	3	1800	9.18	7.96
27	497	12.09	368	1.62	3	1800	10.20	8.94
28	497	12.70	398	1.64	3	2700	9.78	8.06
29	497	12.70	398	1.61	3	2700	10.35	8.56
30	497	12.70	398	1.61	3	2700	10.63	8.83
31	497	11.00	452	1.54	3	2700	8.76	8.35
32	497	11.00	452	1.68	3	2700	8.76	8.35
33	497	11.00	452	1.72	3	2700	7.85	7.78
34	497	11.36	468	1.83	3	2700	9.35	8.62
35	497	11.31	464	1.92	3	2700	8.08	7.44
36	497	11.28	461	1.88	3	2700	8.17	7.60
37	497	9.69	466	1.48	3	1800	8.28	8.92
38	497	9.69	466	1.56	3	1800	8.01	8.64
39	497	9.69	466	1.56	3	1800	8.12	8.77

Expt	Temp °C	t secs	Aver. p.mm	p.p. MeI mm	p.p. Tol mm	Time of Expt secs	% Decomp	$k_1 . 10^{3}$ $\sec^{-1}$
40	497	8.44	509	1.36	3	1800	7.30	8.99
41	497	8.44	509	1.36	3	1800	7.22	8.99
42	497	8.44	509	1.36	3	1800	7.29	8.99
43	497	9.03	479	1.46	3	1500	10.80	12.7
44	497	9.04	477	1.48	3	1500	11.54	13.6
45	497	9.02	473	1.53	3	1500	12.02	14.1
46	497	9.03	482	1.48	7	1800	19.40	23.3
47	497	9.04	481	1.48	7	1800	19.54	24.0
48	497	9.02	480	1.55	7	1800	19.56	24.1
49	461	13.29	460	2.78	0	1800	1.10	0.83
50	461	13.29	457	2.71	0	1800	0.95	0.68
51	461	13.29	456	2.84	0	1800	0.94	0.67
52	461	13.34	460	4.20	0	1560	0.59	0.45
53	461	13.34	459	4.18	0	1560	0.64	0.46
54	461	13.34	459	4.18	0	1560	0.65	0.46
55	461	13.56	454	1.59	1.8	1260	1.45	1.06
56	461	13.56	455	1.62	1.44	1260	1.52	1.11
57	461	13.54	454	1.54	1.25	1260	1.28	0.94
58	461	13.29	473	1.23	3	1800	1.77	1.30
59	461	13.29	471	1.26	3	1800	1.76	1.30
60	461	13.33	470	1.22	3	1800	1.73	1.30
61	461	13.39	449	1.48	7	1500	2.28	1.70
62	461	13.38	442	1.48	7	1500	2.40	1.79
63	461	13.38	440	1.54	7	1500	2.26	1.68
64	461	13.56	464	1.56	10	1800	2.46	1.82
65	461	13.56	462	1.62	10	1800	2.48	1.84
66	461	13.56	462	1.74	10	1800	2.79	2.0
67	461	13.65	472	1.81	12	1500	2.28	1.69
68	461	13.65	472	1.84	12	1500	2.45	1.80
69	461	13.65	472	1.68	12	1500	2.23	1.70
70	461	13.35	461	1.27	14.1	1800	2.69	2.01

Expt	Temp °C	t secs	Aver. p.mm	p.p. MeI mm	g.m. I_2 added per sec 10^8	p.p. I_2 added	% Decomp	Time of Expt
71	461	13.81	471	3.84	1.365	0.023	0.908	2100
72	461	13.81	470	3.92	-	-	2.341	2100
73	461	13.75	468	3.51	1.425	0.023	1.01	2100
74	461	13.75	468	2.80	-	-	2.08	2100
75	482	13.80	437	3.53	1.305	0.021	2.43	2400
76	482	13.80	437	2.66	-	-	4.48	2400
77	492	13.23	475	3.28	1.458	0.024	4.13	2400
78	492	13.28	470	2.55	-	-	5.16	2400
79	470	13.65	475	3.27	1.560	0.026	1.578	2800
80	470	13.60	465	2.53	-	-	2.15	2800
81	477	13.55	462	3.46	1.726	0.028	2.04	1800
82	477	13.55	462	3.50	1.726	0.028	2.28	1800

Expt	Temp °C	t secs	Aver. p.mm.	p.p. MeI mm	g.m. I_2 added per sec 10^8	p.p. I_2 added	% Decomp	Time of Expt secs
83	477	13.55	460	2.32	-	-	2.49	1357
84	487	13.33	477	3.14	1.207	0.020	3.12	1800
85	487	13.33	476	2.79	-	-	3.63	1800
86	461	13.29	460	2.78	-	-	0.955	1800
87	461	13.29	457	2.71	-	-	0.940	1800
88	461	13.71	470	3.28	0.83	0.014	0.847	1800
89	461	13.70	467	3.32	0.83	0.014	0.834	1800
90	461	13.70	467	3.50	0.83	0.014	0.864	1800
91	461	13.72	469	3.94	1.605	0.026	0.723	1800
92	461	13.72	467	4.15	1.605	0.026	0.795	1800
93	461	13.72	467	4.13	1.605	0.026	0.826	1800
94	461	13.80	471	3.28	2.91	0.048	0.427	1800
95	461	13.80	471	3.45	2.91	0.048	0.361	1800
96	461	13.80	471	3.39	2.91	0.048	0.402	1800
97	461	13.80	452	3.18	7.52	0.123	0.302	1800
98	461	13.80	452	3.10	7.52	0.123	0.302	1800
99	461	13.80	451	3.16	7.52	0.123	0.299	1800
100	461	13.72	466	3.30	8.73	0.142	0.239	1500
101	461	13.72	463	3.31	8.73	0.142	0.268	1500
102	461	13.80	436	3.38	9.88	0.162	0.221	1800
103	461	13.80	437	3.42	9.88	0.162	0.179	1800

Expt	Temp °C	t secs	Aver. p.mm.	p.p. MeI mm	g. atoms I fmd 10^3	g.m. CH_4 10^8	g.m. C_2H_6 10^6	g. atoms C 10^4	Time of Expt secs
104	497	13.25	442	3.26	2.70	2.14	1.08	-	18000
105	511	13.20	479	2.82	2.70	2.20	1.06	-	19200
106	511	12.98	475	2.98	3.00	2.32	0.98	-	19320
107	521	12.86	452	3.00	2.77	2.08	2.5	-	16500
108	511	12.86	452	3.64	2.53	2.10	-	3.93	18000
109	511	13.04	451	3.07	2.53	2.10	-	4.03	18000
								p.p. Tol mm	
110	490	13.22	470	1.39	2.73	4.21	0.96	7	14400
111	483	13.55	474	1.38	2.04	3.75	5.7	7	14400
112	483	13.55	416	1.40	1.75	2.46	1.5	7	12900

Expt	Temp °C	t secs	Aver. p.mm.	p.p. MeI mm	g atoms I fmd 10^5	g.m. CH_4 10^5	g.m. HI 10^4	p.p. Tol mm	Time of Expt secs
113	484	13.58	535	1.65	1.92	3.23	2.5	7	10800
114	497	13.30	518	1.52	2.12	3.32	4.63	7	10800
115	497	13.35	537	1.40	2.19	3.40	4.26	7	10800
116	497	13.25	547	1.26	2.24	3.50	4.78	7	10800
117	459	12.95	602	2.01	0.0616	)	0	2.3	3600
118	459	13.00	601	1.59	0.0663	0.362	0	2.3	2700
119	459	13.00	594	1.52	0.0622	)	0	2.3	2700
120	511	13.09	609	1.93	0.633	)	0	2.3	1800
121	511	13.18	605	1.64	0.572	3.39	0	2.3	1800
122	511	13.12	607	1.24	0.490	)	0	2.3	1800

Expt	Temp °C	t secs	Aver. p.mm.	p.p. Tol mm	g.m. Free I 10^5	g.m. HI 10^4	g.m. Benzyl Iodide 10^4	Time of Expt
123	511	13.00	483	4.0	1.94	1.95	2.88	3600
124	511	13.00	483	4.0	1.30	1.89	2.68	3600
125	511	13.00	483	4.0	1.85	2.09	2.68	3600
126	511	13.00	450	4.0	2.76	2.45	2.10	5400
127	511	13.00	450	4.0	2.58	3.54	1.62	5400
128	511	13.00	450	4.0	2.58	3.05	2.13	5400
129	509	13.03	442	4.0	1.97	3.27	3.88	3600
130	509	13.03	442	4.0	1.46	4.17	2.68	3600
131	509	13.03	442	4.0	1.94	4.26	2.35	3600
132	513	12.88	418	4.0	4.78	2.27	1.85	3600
133	513	12.88	418	4.0	4.23	2.42	1.73	3600
134	513	12.88	418	4.0	4.83	2.08	1.98	3600
135	433	14.37	451	4.0	8.59	0	1.56	5400
136	433	14.37	444	4.0	21.5	0	1.59	3600
137	433	14.37	441	4.0	41.9	0	2.23	3600
138	459	13.86	445	4.0	12.5	0	1.89	3600
139	459	13.86	447	4.0	17.7	0	2.98	3600
140	459	13.86	449	4.0	48.2	0	2.65	3600
141	452	13.97	431	4.0	6.38	0	1.11	3600
142	452	13.97	431	4.0	21.7	0	1.21	3600
143	452	13.97	431	4.0	32.1	0	1.79	3600

For these experiments a pyrex reaction vessel of volume 380 cc was used. Surface/Volume ratio 1.5.

LOW PRESSURE EXPERIMENTS.

Expt	Temp °C	Aver p.mm	t secs	p.p. MeI mm	Time of Expt secs	% Decomp	k_1 $10^2 sec^{-1}$
146	579	10.5	1.10	0.128	1200	3.38	3.3
147	579	10.6	1.12	0.130	1200	2.80	2.1
148	579	10.6	1.12	0.131	1200	2.33	2.2
149	579	7.7	2.81	0.220	1200	12.55	5.1
150	579	7.8	2.82	0.149	1200	13.70	5.6
151	579	7.9	2.87	0.164	1200	16.1	6.5
152	579	7.05	1.85	0.148	1200	7.66	4.5
153	579	7.20	1.86	0.155	1200	5.14	3.0
154	579	7.30	1.84	0.157	1200	5.00	3.0
155	579	7.45	1.87	0.157	1200	5.12	3.0

(Experiments 146 - 160 carrier gas nitrogen)

Expt	Temp °C	Time of Expt	g.a. I 10^4	g.m. HI 10^5	g.m. CH_4 10^4	g.m. C_2H_6 10^6
156	579	1200	4.32	3.5	3.15	4.6
157	579	1200	3.79	-	2.78	4.0
158	579	1200	3.40	3.0	2.58	8.0
159	579	1200	3.65	0.8	2.72	4.2
160	579	1200	1.20	0.22	0.84	-

Expt	Temp °C	Aver. p.mm.	t secs	p.p. MeI mm	Time of Expt secs	% Decomp	k_1 $10^3 sec^{-1}$
161	579	2.42	2.86	0.135	1200	1.27	4.3
162	579	2.49	2.78	0.137	1200	1.09	3.9
163	579	2.52	2.77	0.164	1200	1.10	3.9
164	579	2.61	3.61	0.195	1200	6.21	7.6
165	579	2.94	3.20	0.170	1200	5.33	7.4
166	579	3.14	2.94	0.163	1200	2.05	6.7
167	579	2.51	2.75	0.246	1200	3.46	12.8
168	579	2.62	2.66	0.245	1200	3.09	12.0
169	579	2.78	2.55	0.235	1200	2.77	11.4
170	579	2.55	2.83	0.395	960	3.94	14.1
171	579	2.50	2.50	0.370	960	4.11	17.1
172	579	2.66	2.65	0.385	960	4.03	15.4
173	579	2.53	2.75	0.099	1500	1.12	4.1
174	579	2.57	2.71	0.072	1500	0.64	2.2
175	579	2.48	2.87	0.169	1200	1.80	6.2
176	579	2.50	2.84	0.175	1200	1.74	6.1
177	579	2.57	2.80	0.173	1200	1.80	6.4
178	579	2.56	2.47	0.325	1200	2.61	11.0

Expt	Temp °C	Aver. p.mm.	t secs	p.p. MeI mm	Time of Expt secs	% Decomp	k_1 10^3 sec^{-1}
179	579	2.63	2.58	0.346	1200	3.00	12.0

(Experiments 161 - 179 carrier gas helium)

Expt	Temp °C	Aver. p.mm.	t secs	p.p. MeI mm	Time of Expt secs	% Decomp	k_1 10^3 sec^{-1}
180	579	4.12	1.98	0.065	1800	4.03	21.0
181	579	4.19	1.77	0.221	1500	8.14	48.0
182	579	4.32	1.73	0.303	1500	9.09	55.0
183	579	4.62	1.78	0.473	1500	12.89	77.0
184	565	4.12	2.46	0.135	1800	4.94	20.0
185	565	4.28	1.89	0.232	1800	5.95	32.4
186	565	4.41	1.87	0.351	1800	5.12	28.6
187	565	4.63	1.71	0.432	1800	3.58	36.2
188	598	4.36	1.52	0.068	1260	2.09	21.0
189	598	4.43	1.49	0.120	1260	7.09	49.0
190	598	4.54	1.47	0.174	1260	7.40	76.6
191	598	4.75	1.41	0.225	1260	8.51	89.5
192	598	4.44	1.43	0.432	900	10.15	125
193	626	4.22	1.43	0.074	1260	9.16	87.0
194	626	4.53	1.39	0.137	1260	16.5	129
195	626	4.18	1.28	0.156	900	16.65	142
196	626	4.86	1.33	0.267	900	23.13	198
197	626	4.84	1.28	0.313	720	23.99	213
198	640	4.56	1.33	0.099	960	15.6	171
199	640	4.64	1.32	0.077	960	11.2	118
200	640	4.91	1.30	0.137	960	24.46	216
201	640	5.34	1.17	0.238	960	22.2	249
202	640	5.08	1.21	0.340	600	22.9	259

Expt	Temp °C	Aver. p.mm.	t secs	p.p. MeI mm	Time of Expt secs	g.a. I fmd per sec 10^8	g.a. I add. per sec 10^8	% Decomp
203	579	3.80	1.72	0.145	1500	1.60	-	3.80
204	579	3.89	1.68	0.146	1500	1.55	6.01	3.60
205	579	4.05	1.63	0.095	1500	0.76	-	2.54
206	579	4.12	1.59	0.096	1500	0.75	6.07	2.48
207	579	3.30	1.91	0.159	1500	1.81	-	4.36
208	579	3.50	1.87	0.157	1500	1.80	6.20	4.30

(Experiments 180 - 208 carrier gas nitrogen)

Experiments with Nitrogen (all at 579°C)

Expt	Aver. p.mm.	t secs	p.p. MeI mm.	Time of Expt secs	% Decomp	k_1 sec^{-1} 10^3
209	4.47	1.56	0.116	1200	1.98	12.7
210	4.57	1.55	0.116	1200	2.09	13.5
211	4.59	1.55	0.130	1200	2.45	16.0
212	11.78	0.938	0.110	1200	2.40	25.9
213	11.85	0.963	0.125	1260	2.51	26.4
214	12.00	0.972	0.131	1200	2.58	26.8
215	1.93	3.28	0.186	1200	8.56	26.4
216	2.11	2.94	0.183	1500	6.94	24.5
217	2.27	2.80	0.201	1500	8.05	29.8
218	14.05	1.225	0.162	1200	5.08	43.0
219	14.3	1.20	0.158	1200	4.89	47.0
220	14.35	1.26	0.170	1200	5.35	44.0
221	10.93	0.94	0.136	1200	2.48	26.0
222	11.00	0.91	0.129	1200	1.78	19.4
223	12.85	1.04	0.135	1020	3.47	34.1
224	13.16	0.985	0.127	930	2.98	30.8
225	13.48	0.965	0.110	930	2.62	27.6
226	2.63	2.45	0.108	1080	2.36	9.8
227	2.64	2.45	0.102	1080	1.87	7.9
228	2.72	2.35	0.106	1080	1.96	8.4
229	7.32	0.99	0.092	1200	1.23	12.3
230	7.31	0.97	0.085	1200	0.94	9.3
231	7.40	0.96	0.088	1200	0.99	10.8
232	4.60	1.44	0.098	1200	1.16	7.9
233	4.71	1.41	0.116	1200	1.14	8.2
234	4.82	1.38	0.102	1200	1.09	7.3
235	2.67	2.39	0.171	1260	8.15	35.3
236	2.86	2.20	0.160	1200	5.38	25.2
237	2.97	2.14	0.146	1200	4.03	22.0
238	2.61	2.40	0.163	1200	6.63	32.3
239	2.68	2.35	0.138	1200	4.76	20.8
240	2.75	2.28	0.144	1200	6.53	30.5
241	9.78	0.78	0.085	960	0.88	10.9
242	9.94	0.795	0.075	960	0.65	7.8
243	9.90	0.785	0.078	960	0.79	8.5
244	4.09	1.62	0.170	960	2.78	18.0
245	4.13	1.62	0.143	960	2.32	14.6
246	4.14	1.59	0.151	960	2.23	14.1
247	13.38	0.59	0.073	1020	0.80	13.4
248	13.3	0.54	0.057	1020	0.44	7.8
249	13.17	0.57	0.049	1020	0.48	8.1

Experiments with Methane (all at 579°C)

Expt	Aver. p.mm.	t secs	p.p. MeI mm.	Time of Expt secs.	% Decomp	k_1 sec^{-1} 10^3
250	1.32	2.75	0.099	2400	1.05	3.8
251	1.47	2.68	0.129	1860	1.60	5.8
252	1.58	2.68	0.103	1800	1.22	4.1
253	3.13	1.26	0.056	1440	0.63	4.5
254	3.14	1.22	0.076	1440	0.54	3.9
256	3.16	1.27	0.093	1440	0.66	5.2
257	3.05	1.30	0.073	1680	0.63	4.4
258	3.12	1.28	0.052	1680	0.35	3.0
259	3.16	1.25	0.115	1200	1.10	8.7
260	4.04	1.00	0.074	1800	0.51	4.8
261	4.09	0.99	0.059	1800	0.39	3.9
262	4.11	0.99	0.048	1800	0.28	2.9
263	6.49	0.945	0.047	1800	0.33	3.0
264	6.51	0.945	0.068	1800	0.48	5.0
265	6.57	0.940	0.083	1800	0.60	6.1
266	7.27	0.614	0.032	1800	0.40	6.2
267	7.33	0.593	0.048	1800	0.48	8.0
268	7.41	0.610	0.037	1800	0.41	6.2
269	5.50	0.801	0.043	1800	0.31	3.6
270	5.57	0.781	0.052	1800	0.33	3.7
271	5.60	0.774	0.061	1800	0.40	4.9
272	8.29	0.625	0.030	1800	0.31	6.1
273	8.31	0.629	0.041	1800	0.34	6.4
274	8.48	0.642	0.066	1800	0.74	10.4
275	10.49	0.578	0.037	1800	0.48	8.2
276	10.59	0.566	0.053	1320	0.48	8.4
277	10.67	0.568	0.064	1500	0.73	11.7
278	9.24	0.543	0.029	1500	0.248	3.5
279	9.28	0.542	0.043	1500	0.335	5.3
280	9.39	0.545	0.056	1500	0.48	8.7
281	12.25	0.492	0.029	1500	0.42	7.7
282	12.39	0.532	0.050	1320	0.62	13.3
283	12.59	0.503	0.058	1320	0.87	17.7
284	12.37	0.378	0.027	1440	0.21	5.0
285	12.43	0.358	0.043	1200	0.40	10.7
286	12.67	0.351	0.029	1200	0.20	5.4
287	2.57	1.56	0.063	1500	0.14	0.7
288	2.61	1.56	0.094	1380	0.76	4.9
289	2.63	1.54	0.093	1380	0.63	3.7
290	9.40	0.695	0.025	1200	0.67	9.6
291	9.38	0.685	0.059	1200	0.77	11.1
292	9.30	0.731	0.094	1200	0.98	13.6
293	9.35	0.741	0.132	1200	1.37	18.6

Experiments with Carbon Monoxide (all at 579°C)

Expt	Aver. p.mm.	t secs	p.p. MeI mm.	Time of Expt secs	% Decomp	k_1 sec^{-1} 10^3
294	9.67	0.795	0.048	1200	0.353	4.3
295	9.54	0.785	0.070	1200	0.378	4.9
296	9.61	0.778	0.090	1200	0.428	6.1
297	5.01	1.41	0.059	1200	0.417	2.7
298	5.00	1.42	0.098	1200	0.0680	5.0
299	5.05	1.42	0.088	1200	0.500	3.4
300	1.34	4.75	0.046	1380	0.403	0.8
301	1.40	4.55	0.152	1320	2.50	5.6
302	1.51	4.18	0.203	1320	3.15	7.6
303	2.11	3.02	0.158	1320	0.847	3.0
304	2.17	3.00	0.073	1320	0.24	0.9
305	2.26	2.86	0.150	1320	1.01	3.7
306	12.63	0.580	0.033	1320	0.204	3.3
307	12.55	0.578	0.063	1320	0.415	6.7
308	12.58	0.579	0.080	1320	0.491	8.2
309	11.02	0.647	0.046	1320	0.222	3.0
310	11.05	0.608	0.063	1320	0.358	6.3
311	11.10	0.602	0.092	1320	0.643	9.5
312	8.24	0.857	0.058	1320	0.218	2.2
313	8.28	0.852	0.094	1320	0.488	5.6
314	8.25	0.851	0.082	1320	0.364	4.5
315	4.15	1.55	0.056	1320	0.192	12.3
316	4.11	1.56	0.099	1320	0.483	3.1
317	4.15	1.54	0.108	1320	0.390	4.7
318	10.30	0.831	0.053	960	0.558	6.9
319	10.10	0.880	0.075	960	0.431	4.3
320	10.08	0.930	0.161	960	1.81	18.9
321	10.32	0.887	0.124	960	1.27	14.6
322	6.38	1.50	0.138	960	1.82	11.7
323	6.3	1.58	0.198	960	2.81	17.9
324	6.35	1.49	0.270	960	3.51	23.6
325	6.30	1.63	0.103	960	1.07	6.7
326	3.37	1.18	0.026	960	0.185	0.8
327	3.33	1.16	0.038	960	0.187	0.9
328	3.37	1.16	0.064	960	0.185	0.8
329	3.36	1.16	0.100	960	0.187	0.9
330	3.58	1.775	0.085	1500	0.56	3.2
331	3.58	1.775	0.068	1500	0.26	1.6
332	3.60	1.78	0.125	1500	1.14	6.1
333	7.43	0.970	0.060	1260	0.177	1.9
334	7.42	0.955	0.082	1260	0.371	3.8
335	7.52	0.955	0.100	1260	0.532	4.8

Experiments with Nitric Oxide (all at 579°C)

Expt	Aver. p, mm.	t secs	p.p. MeI mm.	Time of Expt secs	% Decomp	k_1 sec^{-1} 10^3
336	2.42	1.69	0.051	1680	2.09	12.6
337	2.43	1.69	0.070	1500	3.80	23.0
338	2.46	1.66	0.116	1320	4.27	26.3
339	1.93	2.12	0.076	1500	3.80	18.5
340	2.00	2.02	0.175	1260	5.14	26.2
341	2.12	1.92	0.114	1260	4.03	21.6
342	3.74	1.13	0.042	1260	1.12	9.7
343	3.87	1.09	0.060	1260	1.56	14.3
344	3.83	1.09	0.092	1260	3.02	28.0
345	3.27	1.36	0.046	1260	1.42	10.1
346	3.27	1.36	0.065	1260	2.45	18.1
347	3.31	1.35	0.098	1260	3.61	26.8
348	2.21	1.91	0.053	1440	4.3	23.0
349	2.24	1.91	0.086	1440	4.6	24.6
350	2.34	1.82	0.124	1440	5.77	33.0
351	1.70	2.36	0.054	1500	4.08	18.2
352	1.71	2.37	0.074	1500	4.1	18.2
353	1.81	2.37	0.146	1500	5.42	23.1

Experiments with Helium (all at 579°C)

Experiments 161 - 179 were done with helium as carrier gas.

Expt	Aver. p.p. mm.	t secs	p.p. MeI mm.	Time of Expt secs	% Decomp	k_1 sec^{-1} 10^3
357	4.77	1.48	0.248	1200	1.71	12.4
358	4.83	1.48	0.237	1200	1.71	12.3
359	4.88	1.48	0.260	1200	2.25	15.4
360	1.62	4.50	0.125	1200	1.46	3.3
361	1.62	4.40	0.157	1200	2.04	4.7
362	1.71	4.20	0.222	1200	3.94	9.5
363	12.83	0.762	0.095	1200	0.89	12.3
364	12.87	0.770	0.095	1200	0.89	12.1
365	12.92	0.802	0.106	1200	1.02	12.6
366	15.85	0.519	0.087	1200	0.57	11.4
367	16.08	0.499	0.086	1200	0.60	12.6
368	16.2	0.510	0.077	1200	0.53	10.9
369	8.1	0.965	0.082	1260	0.82	8.9
370	8.17	0.957	0.086	1260	0.73	8.2
371	8.00	0.969	0.087	1260	0.77	8.2

Expt	Aver. p.mm.	t secs	p.p. MeI mm.	Time of Expt secs	% Decomp	k_1 sec^{-1} 10^3
372	8.25	1.28	0.087	960	1.14	9.0
373	8.24	1.28	0.073	960	0.99	7.8
374	8.32	1.36	0.072	960	1.05	7.8
375	7.01	2.95	0.034	1020	1.62	5.6
376	7.07	2.93	0.034	1020	1.65	5.7
377	7.33	2.95	0.034	1020	1.60	5.5
378	12.3	4.17	0.079	1200	3.13	7.9
379	12.93	3.96	0.075	1200	2.82	7.3
380	13.6	4.36	0.085	1200	3.50	8.3
381	3.73	1.87	0.148	1200	1.62	8.6
382	3.79	1.83	0.146	1200	1.74	8.9
383	3.79	1.87	0.148	1200	1.70	9.0
384	12.18	0.672	0.172	1200	1.32	19.9
385	12.18	0.660	0.174	1200	1.50	21.6
386	12.13	0.652	0.172	1200	1.33	20.5
387	10.94	0.730	0.075	1200	0.40	4.9
388	11.0	0.728	0.086	1200	0.46	6.1
389	11.07	0.720	0.106	1200	0.61	8.9
390	7.43	1.042	0.085	1200	0.44	4.3
391	7.61	1.020	0.113	1200	0.67	6.5
392	7.57	1.020	0.057	1200	0.33	3.3
393	4.18	1.66	0.084	1260	0.62	3.9
394	4.15	1.67	0.109	1260	0.74	4.6
395	4.18	1.65	0.055	1260	0.49	3.1

<u>**Experiments with Neon**</u> (all at 579°C)

Expt	Aver. p.mm.	t secs	p.p. MeI mm.	Time of Expt secs	% Decomp	k_1 sec^{-1} 10^3
396	5.15	2.18	0.177	1320	4.70	22.1
397	4.96	2.51	0.108	1320	1.59	6.5
398	5.00	2.55	0.220	1320	7.45	30.3
399	5.35	2.32	0.276	1320	8.45	38.0
400	3.30	3.52	0.080	2040	1.54	4.5
401	3.36	3.65	0.241	1260	9.12	26.8
402	3.44	3.54	0.156	1260	5.66	17.5
403	3.62	3.43	0.284	1260	11.50	35.8
404	6.32	1.92	0.098	1200	1.18	6.3
405	6.35	1.91	0.066	1200	0.82	4.5
406	6.39	1.87	0.152	1260	1.73	9.5
407	6.43	1.85	0.208	1200	3.61	20.0
408	7.82	1.66	0.127	1200	2.01	12.3
409	7.81	1.66	0.080	1200	1.57	6.8
410	8.00	1.61	0.157	1200	2.78	17.4
411	7.97	1.62	0.216	1200	3.36	21.1

Expt	Aver. p.mm.	t secs	p.p. MeI mm.	Time of Expt secs	% Decomp	k_1 sec^{-1} 10^3
412	9.37	1.39	0.160	1200	2.41	17.5
413	9.27	1.39	0.110	1200	1.36	10.0
414	9.23	1.40	0.247	1200	3.78	26.9
415	9.26	1.39	0.218	1200	3.49	25.6
416	12.54	1.21	0.193	1200	2.39	20.6
417	12.47	1.22	0.261	1200	2.81	24.3
418	12.46	1.24	0.120	1200	1.11	9.0
419	12.52	1.25	0.158	1200	1.88	15.5
420	2.52	4.54	0.148	960	2.23	5.1
421	2.57	4.48	0.092	960	0.99	2.1
422	2.68	4.31	0.266	960	6.85	16.4
423	2.79	4.14	0.201	960	4.26	10.3
424	10.72	1.16	0.179	960	1.76	15.4
425	10.75	1.16	0.228	960	3.04	26.6
426	10.76	1.16	0.352	1020	4.73	41.7
427	10.80	1.18	0.402	1020	7.03	61.8
428	7.68	2.10	0.161	960	3.95	19.2
429	7.61	2.25	0.187	960	4.82	22.0
430	7.81	2.14	0.256	960	7.38	35.8
431	7.85	2.14	0.410	960	8.22	39.9

<u>Experiments with Argon</u> (all at 579°C)

Expt	Aver. p.mm.	t secs	p.p. MeI mm.	Time of Expt secs	% Decomp	k_1 sec^{-1} 10^3
432	10.27	1.81	0.180	1200	2.69	15.2
433	10.42	1.82	0.184	1200	2.69	15.2
434	10.50	1.92	0.150	1260	2.82	15.0
435	2.47	3.28	0.370	1200	10.47	34.0
436	2.61	3.12	0.340	1200	9.67	32.5
437	2.64	3.15	0.330	1200	8.48	28.2
438	10.35	2.57	0.330	1200	7.27	29.3
439	10.63	2.45	0.373	1200	8.37	35.5
440	10.67	2.78	0.395	1200	8.26	31.0
441	3.91	3.45	0.422	1200	7.84	23.6
442	4.09	3.40	0.425	1200	8.45	26.2
443	4.31	3.28	0.417	1200	8.66	26.4
444	12.4	2.25	0.278	1200	7.52	35.2
445	12.6	2.39	0.314	1200	8.08	35.1
446	12.7	2.30	0.320	1200	7.98	36.0
447	2.79	3.45	0.182	1200	5.31	15.8
448	2.93	3.25	0.145	1200	4.18	12.2
449	3.06	3.13	0.192	1200	5.18	17.0

Expt	Aver. p.mm.	t secs	p.p. MeI mm.	Time of Expt secs	% Decomp	k_1 sec^{-1} 10^3
450	13.3	3.66	0.430	1200	17.95	54.0
451	13.73	3.38	0.415	1200	14.95	47.8
452	14.16	3.24	0.410	1200	15.76	45.7
453	6.2	2.09	0.257	1200	7.21	35.7
454	6.51	2.05	0.207	1200	6.08	31.3
455	6.85	2.10	0.215	1200	7.10	35.0
456	7.7	2.70	0.315	900	10.13	39.6
457	7.9	2.66	0.297	900	9.64	38.2
458	8.15	2.97	0.312	900	9.97	35.4
459	5.34	1.69	0.284	1200	3.98	23.7
460	5.41	2.93	0.180	1200	4.52	15.6
461	5.66	2.28	0.230	1200	4.26	18.3
462	6.44	1.58	0.151	1200	2.03	13.0
463	6.53	2.05	0.087	1200	0.87	4.6
464	6.85	1.70	0.086	1200	0.87	4.0
465	2.27	3.67	0.274	1200	10.56	30.5
466	2.36	4.21	0.176	1200	6.57	16.1
467	2.46	5.98	0.206	1200	14.78	27.2
468	11.43	0.959	0.091	1200	1.29	13.7
469	11.25	2.84	0.098	1200	3.98	14.3
470	11.74	1.14	0.068	1200	7.68	7.0
471	2.59	3.14	0.262	1200	10.52	35.7
472	2.83	2.83	0.208	1200	7.40	26.9
473	2.96	2.74	0.181	1200	5.66	21.2
474	2.62	3.10	0.201	1200	8.35	28.1
475	2.80	2.90	0.190	1200	5.39	19.2
476	2.95	2.72	0.179	1200	4.91	18.5
477	11.78	1.09	0.112	1020	1.49	13.9
478	11.83	1.06	0.131	1020	1.50	14.4
479	11.85	1.08	0.090	1020	0.33	8.6
480	7.36	1.24	0.090	1200	0.42	3.5
481	7.32	1.24	0.125	1080	0.87	7.3
482	7.36	1.26	0.098	1080	0.53	4.7
483	4.23	1.96	0.091	1200	0.42	2.8
484	4.23	1.96	0.121	1200	0.83	4.8
485	4.23	1.96	0.106	1200	0.82	4.4

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Experiments with Krypton (all at 579°C)

Expt	Aver. p.mm.	t secs	p.p. MeI mm.	Time of Expt secs	% Decomp	k_1 sec^{-1} 10^3
486	3.13	2.92	0.083	1560	0.45	1.6
487	3.13	2.92	0.042	1560	0.12	0.4
488	3.19	2.81	0.093	1560	0.65	2.4

Expt	Aver. p.mm.	t secs	p.p. MeI mm.	Time of Expt secs	% Decomp	k_1 sec^{-1} 10^3
489	3.23	2.83	0.089	1560	0.67	2.4
490	2.41	2.13	0.061	1020	0.10	0.4
491	2.41	2.27	0.044	1020	0.10	0.4
492	2.40	2.13	0.089	1020	0.60	2.9
493	2.49	2.17	0.125	1020	1.08	5.0
494	2.13	4.20	0.128	1200	1.28	3.1
495	2.22	4.30	0.195	1200	3.69	8.8
496	2.35	3.80	0.227	1200	4.91	13.1
497	2.52	3.52	0.284	1200	5.08	15.0
498	4.85	2.00	0.048	1200	0.09	4.8
499	4.82	2.07	0.084	1200	0.56	2.8
500	4.82	2.07	0.160	1200	1.54	7.6
501	4.87	2.08	0.251	1200	3.18	15.6
502	6.00	1.63	0.090	1200	0.52	2.4
503	6.00	1.63	0.103	1200	0.73	4.7
504	6.01	1.68	0.171	1200	1.44	8.8
505	6.02	1.70	0.227	1200	2.32	13.9
506	7.30	1.36	0.131	1200	0.85	6.9
507	7.20	1.41	0.102	1200	0.73	5.4
508	7.22	1.41	0.189	1200	1.17	8.4
509	7.33	1.39	0.228	1200	2.16	15.8
510	8.25	1.28	0.118	1200	1.12	8.8
511	8.18	1.28	0.136	1200	1.59	11.7
512	8.19	1.33	0.177	1200	1.68	12.9
513	8.23	1.33	0.231	1200	2.32	17.6
514	8.92	1.56	0.171	1260	2.15	14.0
515	8.83	1.52	0.211	1260	3.30	22.1
516	8.93	1.70	0.335	1380	7.05	43.0
517	9.10	1.62	0.340	1260	6.90	44.0
518	10.20	1.30	0.136	1200	1.35	10.6
519	10.23	1.28	0.165	1200	1.65	13.0
520	10.41	1.25	0.203	1200	2.78	22.7
521	10.48	1.26	0.247	1200	3.85	31.2
522	10.75	1.40	0.174	1080	2.14	22.4
523	10.75	1.41	0.229	1140	4.69	34.5
524	10.77	1.38	0.286	1080	5.34	40.3
525	10.93	1.39	0.330	1080	6.92	49.0
526	12.25	1.31	0.180	1020	3.01	23.9
527	12.20	1.33	0.211	1140	3.77	29.0
528	12.45	1.24	0.250	1020	3.75	30.8
529	12.68	1.20	0.287	900	4.68	40.1

Experiments with Benzene (all at 625°C)

Expt	Aver. p.mm.	p.p. C_6H_6 mm.	p.p. MeI mm.	Time of Expt secs	t secs	% Decomp	k_1 sec^{-1} 10^2
530	2.76	2.52	0.112	960	0.180	0.49	2.74
531	2.82	2.52	0.163	960	0.181	0.909	5.11
532	2.94	2.59	0.133	960	0.189	0.648	3.49
533	3.08	2.82	0.057	960	0.207	0.524	3.09
534	2.58	2.38	0.089	960	0.172	0.458	2.67
535	2.64	2.45	0.066	960	0.176	0.316	1.78
536	2.66	2.43	0.105	960	0.174	0.506	1.91
537	2.72	2.42	0.163	960	0.174	0.625	3.60
538	2.54	2.28	0.162	960	0.163	0.387	2.40
539	2.68	2.43	0.108	960	0.175	0.529	3.02
540	2.75	2.46	0.136	960	0.177	0.481	2.76
541	2.72	2.53	0.040	960	0.182	0.261	1.47

Comparable experiments with nitrogen (also at 625°C)

Expt	Aver. p.mm.	t secs	p.p. MeI mm.	Time of Expt secs	% Decomp	k_1 sec^{-1} 10^2
542	2.62	1.51	0.113	1320	9.68	6.74
543	2.78	1.39	0.140	1020	14.4	11.18
544	2.83	1.40	0.029	1080	4.34	3.14
545	2.85	1.37	0.064	1020	7.59	5.74
546	2.67	1.40	0.094	1080	7.36	5.49
547	2.80	1.38	0.167	1080	14.1	11.0
548	2.85	1.45	0.040	1320	3.82	2.70
549	2.75	1.44	0.067	840	4.02	2.86
550	2.45	1.56	0.082	1020	7.77	5.22
551	2.61	1.54	0.167	1020	16.2	11.52
552	2.55	1.55	0.040	1020	4.40	2.89
553	2.60	1.56	0.078	1020	4.85	3.17

For these experiments a silica reaction vessel of volume of 265 c.c. was used.

REFERENCES

1. Lapage..................M.Sc. Thesis - Manchester
Ph.D. Thesis - St. Andrews

2. Butler and Polanyi......Trans. Far. Soc.,39,19,(1943)

3. Moore...................M.Sc. Thesis - Manchester

4. Lindemann...............Trans. Far. Soc.,17,598,(1922)

5. Rice and Rice...........Aliphatic Free Radicals - Baltimore (1935)

6. Evans and Szwarc........J. Chem. Phys.,18,618,(1950)

7. Szwarc..................Chemical Reviews,47,75,(1950)

8. Springall...............Research, 3,260,(1950)

9. Baughan,Evans and Polanyi.........Trans. Far. Soc.,37,377,(1941)

10. Rossini.................J.Res.Nat.Bur.Stand.,13,21,(1934)

11. Stevenson...............J. Chem. Phys. 10,291,(1942)

Hipple and Stevenson....Phys. Rev., 63,621,(1943)

12. Herzberg................Molecular Spectra and Molecular Structure,I: Diatomic Molecules (Prentice-Hall, New York, 1939)

Gaydon..................Dissociation Energies and Spectra of Diatomic Molecules. (Chapman and Hall, 1947)

13. White...................J. Chem. Phys., 8,79,479,(1940)

14. Rice and Johnston.......J. Amer. Chem. Soc.,56,214,(1934)

Rice and Dooley.........J. Amer. Chem. Soc.,55,4245,(1933)

Rice and Dooley.........J. Amer. Chem. Soc.,56,2747,(1934)

Rice,Johnston and Evering...........J. Amer. Chem. Soc.,54,3529,(1932) Rice and Rodowskas....J. Amer. Chem. Soc.,57,350,(1935)

15. Butler,Mandel and
Polanyi........Trans. Far. Soc.,41,298,(1945)

16. Horrex and Szwarc.....Unpublished data.

17. Gowenlock.............M.Sc. Thesis - Manchester

18. Szwarc................Proc. Roy. Soc.,A270,5,(1951)

19. Szwarc and Ghosh......J. Chem. Phys.,17,744,(1949)

Szwarc,Ghosh and
Sehon.........J. Chem. Phys.,18,1142,(1950)

20. Szwarc................Proc. Roy. Soc.,A198,285,(1949)

21. Leigh and Szwarc......Discuss. Far. Soc.,10,336,(1951)

22. Szwarc................J. Chem. Phys.,16,128,(1948)

23. Horrex and Miles......Discuss. Far. Soc.,10,187,(1951)

24. Cottrell,Graham and
Reid.......Trans. Far. Soc.,47,269,(1951)

Hillenbrand and
Kilpatrick.........J. Chem. Phys.,19,381,(1951)

25. Paneth and Hofeditz...Ber., 62,1335,(1929)

26. Frey..................Ind. Eng. Chem.,26,198,(1934)

27. Allen and Sickmann....J. Amer. Chem. Soc.,56,1251,(1934)

28. Leermakers............J. Amer. Chem. Soc.,55,3499,(1933)

29. Hinshelwood...........Kinetics of Chem. Change,Oxford (1940)

Smith and Hinshelwood.Proc. Roy. Soc.,A180,237,(1942)

30. Rice and Polly........J. Chem. Phys.,6,273,(1938)

31. Szwarc................Trans. Far. Soc.,47,269,(1951)

32. Eltenton..............J. Chem. Phys.,10,403,(1942)

Eltenton..............J. Chem. Phys.,12,469,(1944) Eltenton................J. Chem. Phys.,15,455,(1947)

33. Rice and Herzfeld.......J. Amer. Chem. Soc.,56,284,(1934)

Rice and Herzfeld.......J. Amer. Chem. Soc.,56,1311,(1934)

Rice and Herzfeld.......J. Amer. Chem. Soc.,56,2747,(1934)

34. Hinshelwood.............Pres. Address: J. Chem. Soc., 531, (1951)

35. Pease...................J. Chem. Phys.,7,749,(1939)

Pease...................Equilibrium and Kinetics of Gas Reactions: Princeton Univ. Press, (1942).

36. Evans and Szwarc........Trans. Far. Soc.,45,940,(1949)

37. Bamford and Dewar.......Nature, 163,256,(1945)

38. Steacie and Trotman-Dickenson......J. Amer. Chem. Soc.,72,2310,(1950)

39. Steacie and Marcus......Z. Naturforsch, 49,332,(1949)

40. Steacie and Miller......J. Chem. Phys., 19,73,(1951)

41. Dorfmann and Noyes......J. Amer. Chem. Soc.,70,587,(1948)

Gomer and Noyes.........J. Amer. Chem. Soc.,71,3390,(1949)

Gomer...................J. Amer. Chem. Soc.,72,201,(1950)

Gomer...................J. Amer. Chem. Soc.,18,998,(1950)

42. Dodds...................J. Chem. Phys., 17,234,(1949)

43. Szwarc and Roberts......Trans. Far. Soc.,46,625,(1950)

44. Gomer and Kistiakowsky.......J. Chem. Phys.,19,85,(1951)

45. Lucas and Rice..........J. Chem. Phys.,18,993,(1950)

46. Ivin and Steacie........Proc. Roy. Soc.,A208,25,(1951)

47. Szwarc..................J. Phys. Coll. Chem.,55,939,(1951)

48. Hill......................J. Chem. Phys., 17, 303, (1949)

49. Marcus and Rice..........J. Phys. Coll. Chem., 55, 894, (1951)

50. Andersen, Kistiakowsky and van Artsdalen.......J. Chem. Phys., 10, 305, (1942)

van Artsdalen............J. Chem. Phys., 10, 653, (1942)

Andersen and Kistiakowsky........J. Chem. Phys., 11, 6, (1943)

Kistiakowsky and van Artsdalen........J. Chem. Phys., 12, 469, (1943)

51. Andersen and van Artsdalen..........J. Chem. Phys., 12, 479, (1944)

52. Swergler, Scheraga, and van Artsdalen..........J. Chem. Phys., 19, 135, (1951)

53. Rice and Herzfeld.......J. Phys. Coll. Chem., 55, 975, (1951)

54. Trautz and Bhardarkar...Z. anorg. Chem., 106, 95, (1919)

Hinshelwood and Topley..J. Chem. Soc., 125, 393, (1924)

55. Barton and Onyon........Trans. Far. Soc., 4~~6~~5, 725, (1949)

Brearly, Kistiakowsky and Stauffer..........J. Amer. Chem. Soc., 58, 43, (1936)

56. Barton and Howlett......J. Chem. Soc., 155, 165, (195~~0~~) 49.

57. Barton and Head.........Trans. Far. Soc., 46, 114, (1950)

58. Barton and Onyon........J. Amer. Chem. Soc., 72, 988, (1950)

59. Barton, Head and Williams.............J. Chem. Soc., 2039, (1951)

60. Howlett.................J. Chem. Soc., 4487, (1952)

Howlett.................J. Chem. Soc., 945, (1953)

61. Howlett.................J. Chem. Soc., 155, (1949)

Howlett.................Trans. Far. Soc. 48, 25, (1952)

62. Barton and Howlett......J. Chem. Soc., 2033, (1950)

63. Williams.................J. Chem. Soc.,113, (1953)

64. Howlett.................Trans. Far. Soc.,48,35,(1952)

65. Howlett.................Nature, 170,168,(1952)

Howlett.................J. Chem. Soc., 3695, (1952)

66. Barton,Head and Williams..............J. Chem. Soc., 453, (1952)

67. Kistiakowsky and Stauffer.............J. Amer. Chem. Soc.,59,165,(1937)

68. Meissner and Schumacher.Z. phys. Chem.,185,435,(1940)

69. Lessig..................J. Phys. Chem.,36,2325,(1932)

70. Vernon and Daniels......J. Amer. Chem. Soc.,55,922,(1933)

71. Fugassi and Daniels.....J. Amer. Chem. Soc.,60,771,(1938)

72. Daniels and Veltmann....J. Chem. Phys.,7,756,(1939)

Daniels.................J. Amer. Chem. Soc.,72,424,(1950)

73. Roof and Daniels........J. Amer. Chem. Soc.,62,2912,(1940)

Roof....................J. Amer. Chem. Soc.,66,358,(1944)

74. Maccoll.................J. Chem. Phys.,17,1350,(1949)

Agius and Maccoll.......J. Chem. Phys.,18,158,(1950)

Maccoll and Thomas......J. Chem. Phys.,19,977,(1951)

Green,Harden,Maccoll and Thomas.............J. Chem. Phys.,21,178,(1953)

75. Sehon and Szwarc........Proc. Roy. Soc.,A209,110,(1951)

76. Leigh,Sehon and Szwarc..Proc. Roy. Soc.,A209 (1951)

77. Polissar................J. Amer. Chem. Soc.,52,956,(1930)

78. Jones and Ogg...........J. Amer. Chem. Soc.,59,1931,(1937)

79. Ogg.....................J. Amer. Chem. Soc.,61,1946,(1939)

80. Jones and Ogg.............J. Amer. Chem. Soc., 59, 1939, (1937)

Jones.....................J. Amer. Chem. Soc., 60, 1877, (1938)

81. Jones and Ogg.............J. Amer. Chem. Soc., 59, 1943, (1937)

82. Ogg.......................J. Amer. Chem. Soc., 58, 607, (1936)

83. Jones.....................J. Amer. Chem. Soc., 61, 1946, (1939)

84. Ogg.......................J. Amer. Chem. Soc., 56, 526, (1934)

Newton....................J. Chem. Phys., 18, 797, (1950)

85. West and Ginsburg.........J. Amer. Chem. Soc., 56, 2626, (1934)

86. West and Schlessinger....J. Amer. Chem. Soc., 60, 961, (1938)

87. Bates and Spence.........J. Amer. Chem. Soc., 53, 1689, (1931)

Bates and Spence.........Trans. Far. Soc., 27, 468, (1931)

88. Iredale..................Trans. Far. Soc., 35, 450, (1938)

89. Jungers and Yeddanapalli.Trans. Far. Soc., 36, 483, (1940)

90. Williams and Ogg.........J. Chem. Phys., 15, 696, (1947)

91. Schultz and Taylor.......J. Chem. Phys., 18, 194, (1950)

92. Dacey....................Discuss. Far. Soc., 14, 84, (1953)

93. Benson...................J. Chem. Phys., 20, 1064, (1952)

94. Shaw.....................Thesis - Manchester

95. Christiansen and Kramers.Z. phys. Chem., 104, 451, (1923)

96. Christiansen.............Proc. Camb. Phil. Soc., 23, 438, (1926)

97. Fowler and Rideal........Proc. Roy. Soc., A113, 570, (1927)

98. Hinshelwood.............Proc. Roy. Soc.,A113,230,(1926)

99. Hinshelwood.............Kinetics of Chemical Change in
Gaseous Systems. Oxford (1933)

100. Daniels................Chemical Kinetics. Ithaca (1938)

101. Ogg....................J. Chem. Phys.,18,572,(1950)

102. Mills and Johnston......J. Amer. Chem. Soc.,73,938,(1951)

Johnston................J. Amer. Chem. Soc.,73,4542(1951)

Johnston and Perrine....J. Amer. Chem. Soc.,73,4782(1951)

Johnston and Crosby.....J. Chem. Phys.,19,799,(1951)

Johnston................J. Chem. Phys.,20,1103,(1952)

Johnston................J. Amer. Chem. Soc.,75,1567(1953)

103. Ramsperger.............Chemical Reviews,10,27,(1939)

104. Rice and Ramsperger.....J. Amer. Chem. Soc.,49,1617(1927)

105. Kassel..................J. Phys. Chem.,32,225,1065(1928)

Kassel..................Kinetics of Homogeneous Gas
Reactions. Chem.Cat.Co.,(1932)

106. Evans and Rushbrooke...Trans. Far. Soc.,41,621,(1945)

107. Eley....................Trans. Far. Soc.,39,168,(1943)

108. Barrer..................Trans. Far. Soc.,44,398,(1948)

109. Chambers and
Kistiakowsky.....J. Amer. Chem. Soc.,56,399,(1934)

110. Corner and Pease.......J. Amer. Chem. Soc.,67,2067,(1945)

111. Pritchard,Sowden and
Trotman-Dickenson.Proc. Roy. Soc.,A217,563,(1953)

112. Johnston...............J. Chem. Phys.,19,663,(1951)

113. Johnston,Foering and
Thompson..........J. Phys. Coll.Chem.,57,390,(1953)

114. Frisch and Schumacher...Z. phys. Chem.,34,322,(1936)

115. Glasstone,Laidler and Eyring.......Theory of Rate Processes,McGraw Hill, (1941)

116. Slater..................Proc. Camb. Phil. Soc.,35,56,(1939)

Slater..................Nature, 159,264,(1947)

Slater..................Proc. Roy. Soc.,160,576,(1947)

117. Pelzer..................Z. Elektrochem.,39,608,(1933)

Pelzer..................Nature, 160,576,(1947)

118. Polanyi and Wigner......Z. phys. Chem., 139,439,(1928)

119. Slater..................in course of publication.

120. Fugassi and Warrick.....J. Phys. Chem.,46,630,(1942)

121. Benson and Axworthy.....J. Chem. Phys.,21,428,(1953)

122. Bourgin.................Proc. Nat. Acad. Sci.,15,357,(1927)

123. Roginsky and Rosenkewitsch......Z. phys. Chem.,10,47,(1936)

124. Kramers.................Physica, 7,284,(1940)

125. Zwolinski and Eyring....J. Amer. Chem. Soc.,69,2702,(1947)

126. Hirschfelder............J. Chem. Phys.,16,22,(1948)

127. Kistiakowsky and Nelles.J. Amer. Chem. Soc.,54,2208,(1932)

128. Roessler................Z. phys. 96,251,(1935)

129. Rieke...................J. Chem. Phys.,4,513,(1936)

130. Pierce..................Proc. Amer. Acad. Arts. Sci.,60,271,(1923)

131. Herzfeld and Rice.......Phys. Rev. 31, 691, (1928)

132. Kneser..................Ann. Physik.,11,777,(1931)

Kneser..................Phys. Rev.,43,1051,(1933)

133. Knudsen.................Phys. Rev.,37,1699,(1931)

Knudsen.................Phys. Rev.,43,1051,(1933)

134. Eucken..................Oester. Chem. Zeit.,38,162,(1935)

135. Eucken and Becker.......Z. phys. Chem.,27,235,(1934)

136. Franck and Eucken.......Z. phys. Chem.,20,460,(1933)

137. Eyring,Gershinowitz and
Sun.........J. Chem. Phys.,3,786,(1935)

138. Alexander and Lambert...Proc. Roy. Soc.,A179,499,(1941)

Lambert and Rowlinson...Proc. Roy. Soc.,A204,424,(1950)

139. Hilferding and Steiner..Z. phys. Chem.,B20,399,(1935)

140. Rabinowitch and Wood....Trans. Far. Soc.,32,907,(1936)

141. Rabinowitch and Wood....J. Chem. Phys.,4,497,(1936)

141. Perlman and Rollefson...J. Chem. Phys.,9,362,(1941)

Norrish and Porter......Nature, 164, 658,(1949)

142. Rabinowitch.............Z.phys. Chem. B33,275,(1936)

143. Christie,Norrish and
Porter.......Proc. Roy. Soc.,A216,152,(1953)

144. Russell and Simons......Proc. Roy. Soc.,A217,271,(1953)

Marshall and Davidson...J. Chem. Phys.,21,659,(1953)

145. Careri..................J. Chem. Phys.,21,749,(1953)

146. Rice....................J. Chem. Phys.,21,750,(1953)

147. Hinshelwood and
Thompson.........Proc. Roy. Soc.,A113,221,(1926)

Hinshelwood and Askey...Proc. Roy. Soc.,A116,163,(1927)

Hinshelwood.............Proc. Roy. Soc.,A114,84,(1927)

148. Volmer and Froehlich............Z.physik Chem.,B19,85 (1932)

Volmer and Froehlich............Z.physik Chem.,B19,87 (1932)

Volmer and Bogdan...............Z.physik Chem.,B21,257, (1933)

Volmer and Briske...............Z.physik Chem.,B25,81, (1934)

149. Koblitz and Schumacher..........Z.physik Chem.,B25,283 (1934)

150. Rice and Sickman.................J.Chem.Phys.,4, 242,608, (1936)

151. Riblett and Rubin...............J.Amer.Chem.Soc.,59, 1537 (1937)

152. Taylor and Jahn..................J.Chem.Phys.,7,470, (1939)

153. Frisch and Schumacher...........Z.physik Chem.,B37,18 (1937)

154. Schumacher and Sprenger.........Z.physik Chem.,B12,115 (1931)

155. Heckert and Mack................J.Amer.Chem.Soc.,51,2706 (1929)

156. Kassel..........................Chem.Rev.,10,11,(1932)

157. Zener...........................Phys.Rev.,37,556,(1931)

158. Rice............................J.Amer.Chem.Soc.,54,4558 (1932)

Rice............................Chem.Rev.,10,125,(1932)

159. Patat and Bartholeme............Z.physik Chem.,B22,396, (1936)

160. Massey..........................Rep.Prog.Physics,12,248, (1948-9)

161. Oldenburg and Frost............Chem.Rev.,20,99,(1937)

162. Patat.........................Z.Elektrochem.,42,265,
(1936)

163. Cowan.........................Ph.D. Thesis,St.Andrews,
(1950)

164. Partington....................An Advanced Treatise on
Phys.Chem.,Vol.I,
Longmans, (1948)

165. Fairbrother and Warhurst......Trans.Far.Soc.,31,987,
(1935)

166. Roeser,Dahl and Gowens.........Bur.Stds.Jour.Res.,14,
239, (1935)

167. Faulk and Bawden...............J.Amer.Chem.Soc., 2045,
(1926)

168. Taylor and Bender..............J.Chem.Phys.,9,761,(1941)

169. Thompson and Meissner..........Nature, 139,1018,(1937)

170. Forsyth........................Trans.Far.Soc.,37,312,(19

171. Durham and Steacie.............J.Chem.Phys.,20,582,(1952

(Also Miller and Steacie)......J.Chem.Phys.,19,73,(1951)

172. Iredale........................Trans.Far.Soc.,35,458,
(1939)

173. Echols and Pease...............J.Amer.Chem.Soc.,61.,1024
(1939)

174. Chilton and Gowenlock..........Nature, 172,73,(1953)

175. Bawn and Tipper................Far.Soc.Disc.,2,108,(1948

176. Bawn...........................Disc.Far.Soc.,14,120,(195

177. Bevington......................Trans.Far.Soc.,48,1045,
(1953)

178. Ingold and Lossing.............J.Chem.Phys.,21,1135,(195

179. Bodenstein.....................Z.Elektrochem.,22,338,
(1916)

180. Semenoff....................Chemical Kinetics and Chain Reactions, Oxford,(1935)

181. Bursian and Sorokin.......Z.phys.Chem.,B12,247,(1931)

182. Majury and Steacie........Disc.F.Soc.,14,47,(1953)

183. Trotman-Dickenson.........Quart.Rev.,VII,198,(1953)

184. Smith and Taylor..........J.Chem.Phys.,7,390,(1939)

Smith and Taylor..........J.Chem.Phys.,8,583,(1940)

185. Szwarc and Roberts........Trans.Far.Soc.,46,625,(1950)

186. Steacie and Trotman-Dickenson .....J.Chem.Phys.,19,169,(1951)

187. Anderson,Scheraga,and van Artsdalen.....J.Chem.Phys.,21,1258,(1953)

188. Roberts and Skinner.......Trans.Far.Soc.,45,339,(1949)

189. Kistiakowsky and Kirk Roberts.....unpublished

190. Marcus.....................J.Chem.Phys.,20,352,359,364,(1952)

191. Davison and Burton........J.Amer.Chem.Soc.,74,2307,(1952